COAGULANT DIPPING OF NATURAL RUBBER LATEX

by

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ABSTRACT

A detailed study has been made of the coagulant dipping of natural rubber latex using calcium chloride as the coagulant. The primary object of the investigation was to deepen understanding of the kinetics and the mechanisms of deposition.

Results are given for the effect of variables such as solids content, latex viscosity, added fatty-acid soaps, amount of calcium on the former, added non-ionic surfactants and latex pH upon the thickness-time relationship in the coagulant dipping process. All, except the initial amount of calcium on the former, were found to have little effect upon the wet thickness-time relationship. The relationship between the wet deposit thickness and the square root of the dwell time was found to be linear.

An investigation has also been made into the fate of the calcium ions during the dipping process. It was found that the deposition of rubber on the former involves reaction between the cations of the coagulant and the adsorbed anions which stabilise the latex. Fatty-acid anions and other unknown anions were found to react with the calcium ions.

The process was found to be diffusion-controlled. The diffusion coefficient of calcium ions in the latex gel was calculated to be approximately 1.4 x 10^{-6}cm^{2} sec^{-1}. However, the assumptions made in deriving this value are such that it should be viewed with suspicion until confirmed by further experimentation and analysis.

It postulated that the mechanisms of deposition involve dehydration of the latex particles, neutralisation of the fatty-acid anions adsorbed on the latex particles and there is some evidence for compression of the double layers.

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CHAPTER 1

INTRODUCTION

1.1 Defination of a latex

A latex may be defined as a stable dispersion of a polymeric substance in an essentially aqueous medium. It is therefore essentially a two-phase system, consisting of a disperse phase and a dispersion medium. The disperse phase consists of small particles of a polymeric substance, often spherical in shape, and less than 5 μm in diameter. The dispersion medium, or aqueous phase as it is sometimes called, is a very dilute aqueous solution which can vary in chemical composition from one latex to another.

1.2 Stability of a latex

The stability of a polymer latex may be divided into two distinct aspects: (1) mechanical stability, (2) chemical stability. The mechanical stability of a latex is usually defined as the resistance to those mechanical influences which increase the number and violence of the collisions between particles and as a consequence tend to coagulate the latex. The chemical stability of a latex is more relevant to the present work and therefore will be considered further.

By the term ' chemical stability ' is meant the ability of the latex to resist the effects of chemical destabilising agencies. For most anionic latices, such agencies include strong acids, metallic ions, polymer-miscible organic solvents and cationic surface active-agents. Divalent metallic ions destabilise anionic latices quite effectively. The type of reaction which may occur between the divalent metallic ions and the adsorbed stabilisers present on the latex particles is thought to be

$$M^{2+} + 2RCOO^- \longrightarrow (RCOO)_2M$$

This reaction is envisaged as occurring at the surface of the particles. Insoluble, un-ionised metallic soap is formed at the interface. This reduces the charge on the particle and may cause collapse of the double layer and hydration layer.

1.3 Theory of latex stability

The stability of lyophobic sols is believed to arise principally from the balance between two types of forces acting between the particles:

(1) attractive forces, of which those known collectively as the ' Van der Waals' forces are the most important;

(2) repulsive forces of various kinds, arising from, for examples, electrostatic and steric interactions.

1.3.1 Attractive forces

The attractive potential energy, V_A, between two spherical colloidal particles arising from the ' Van der Waals ' attractive forces is,

$$V_A = -\frac{A}{6}\left[\frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln\frac{R^2 - 4a^2}{R^2}\right] \quad \ldots\ldots\ldots (1.1)$$

where A is the effective Hamaker constant for the material, a is the radius of the particles and R is the distance between the centre of the spheres. V_A is negligible when the separation is large compared to the radius of the particle. When the separation of the particles is small compared to the radius of the particles, the equation reduces to approximately,

$$V_A = -\frac{Aa}{12H_o} \quad \text{....................} \quad (1.2)$$

where $H_o = R - 2a$

1.3.2 Repulsive forces

There are at least four proposed mechanisms by which stability may be imparted to a colloid such as latex. These are, respectively,

(a) electrostatic stabilisation,

(b) steric stabilisation,

(c) solvation stabilisation,

(d) depletion stabilisation.

(a) Electrostatic stabilisation

The concept of electrostatic stabilisation was first introduced by Helmholtz[1] and later modified by Gouy[2], Chapman[3] and Stern[4]. The stabilisation is due to the presence of bound charge at the particle surface that leads to the formation of a diffuse counterion cloud in the dispersion medium. The potential in the diffuse double layer decreases exponentially with distance away from the surface of the particle.

The equation for the change of potential, Ψ, with distance, x, across a diffuse double layer is

$$\Psi = \Psi_o \left(\exp^{-Kx} \right) \quad \text{.................} \quad (1.3)$$

where $$K = \sqrt{\frac{4\Pi}{D} \cdot \frac{e^2}{kT} \sum Z_i^2 \left(C_i \right)_o} \quad \text{............} \quad (1.3a)$$

and D is the dielectric constant of the dispersion medium, e is the electronic charge, T is the obsolute temperature, Z_i is the valency of ion i including sign and $(C_i)_o$ is bulk concentration of ion i. Equation (1.3) is valid only when $\frac{Z_i e \psi}{kT} << 1$. This means that the energy required to move an ion from the bulk of the solution up to the interface is very small compared to kT, the thermal energy per ion.

It is seen from Equation (1.3) that when x = 1/K, ψ is approximately $\frac{1}{3}\psi_o$. K is therefore a measure of the rapidity with which ψ decreases; the greater the value of K the more rapid the decrease of potential and the more " compressed " is the double layer. Further, it is seen in Equation (1.3a) that the thickness of the double layer (1/K)

(i) increases with increasing dielectric constant (D),

(ii) decreases with increasing ionic strength $(C_i)_o$

(iii) decreases with the valency of the counter ion (Z_i)

The repulsive potential energy, V_R, for a limiting situation of two large and equal spheres of relatively low potential is

$$V_R = \tfrac{1}{2} Da\, \psi_o^2 \ln\left[1 + \exp(-KH_o)\right] \quad \text{...........} \quad (1.4)$$

The total potential energy, V_T, in the DVLO theory[5,6] is therefore the sum of the attractive potential energy, V_A, and the repulsion potential energy, V_R, i.e.

$$V_T = V_A + V_R \quad \text{........................} \quad (1.5)$$

The form of potential energy curves for two particles as calculated from Equation (1.5) is shown in Figure 1.1. The hump in the resultant curve represents a maximum potential energy barrier (V_{max}) over which two particles have to pass if they are to attain the coagulated state. If the height of this hump is large, then a high repulsive energy barrier must be overcome before the particles can get close enough to form

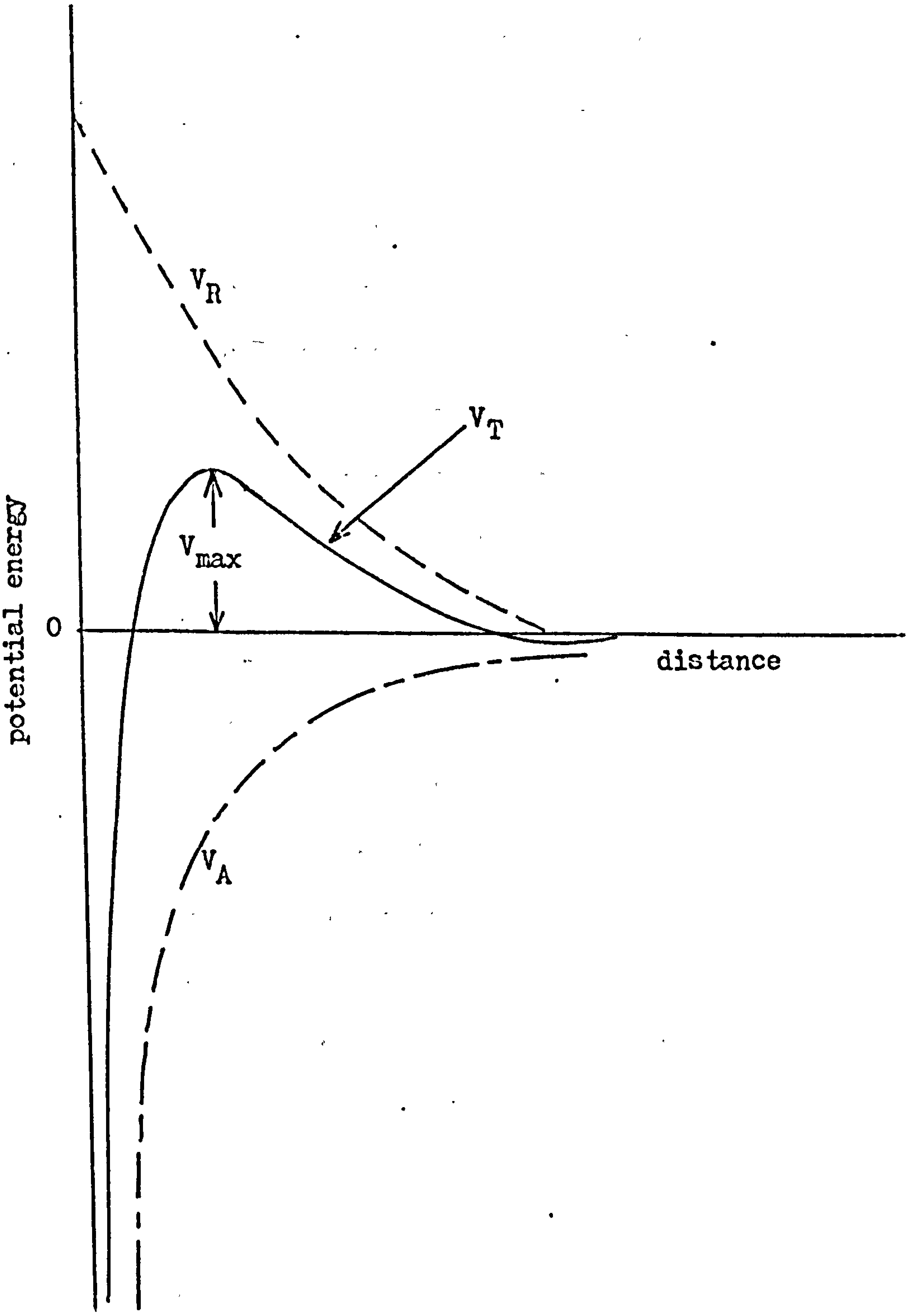


Figure 1.1. Potential energy of interaction against distance for interaction between two charged particles.

coagulum in the deep " well ".

(b) Steric stabilisation

The term steric stabilisation was first adopted by Heller and Pugh[7] for a theory which describes the effect of adsorption of non-ionic surfactants and macromolecules at the surface of colloid particles upon the ability of the particles to approach one another closely. The stabilisation effect arises from (a) excess osmotic pressure in the interaction zone between two approaching particles[8] and / or (b) from elastic compression of the adsorbed layer[9].

The first mechanism (a) is probable when the concentration of the adsorption layer is low. Thus, when two spherical colloidal particles approach each other to a distance of separation less than twice the thickness of the adsorption layers, mixing of the two adsorption layers will take place. This in turn will result in displacement of some of the solvent from the adsorption layers giving rise to a net increase in the free energy of the system. If the resultant " steric " repulsive energy between the particles is larger than the Van der Waals attraction between the two particles, a stable dispersion will result.

The second mechanism (b) is probable when the concentration of the adsorption layer is high. When two spherical colloidal particles with dense adsorbed layers approach each other to a distance of separation less than twice the thickness of the adsorption layer, the particles will undergo a pseudoelastic collision. The polymeric layer will therefore be compressed with the exclusion of solvent from the adsorption layers. Such a compression would reduce the number of possible configurations of each polymeric molecule and cause a decrease in entropy. This leads to an increase in the free energy of the system and therefore to repulsion.

(c) Solvation stabilisation

In this theory, it has been postulated that a layer of water, several molecules thick, could be " bound " at the interface, thereby promoting colloid stability by a mechanical " buffer " action during colisions of the particles. The water molecules are believed to be bonded to the adsorbed layer on the particle surface through hydrogen bonding.

(d) Depletion stabilisation

Depletion stabilisation was first proposed by Napper[10]. In contrast to steric stabilisation, where adsorbed or attached polymer is responsible for the repulsion between colloidal particles, stability in this case is imparted by the free polymer in solution. The depletion is envisaged as resulting from the exclusion of those polymer molecules with conformations that would cross the interface between the particles and the dispersion medium.

1.4 Nature of natural rubber latex

Ammonia-preserved natural rubber latex is essentially a two phase system consisting of a disperse phase and a dispersion medium. The disperse phase consists of small particles which are made up of long polymer molecules with molecular weight of the order 2×10^6 . The molecule is predominantly cis-1,4- polyisoprene. The rubber particles are polydisperse, their sizes varying between wide limits. A range of 0.02 to 2 μm is typical. The rubber particles are stabilised by fatty-acid anions and proteinate anions. The aqueous phase is essentially water. Dissolved in it are ions such as low-molecular-weight acids such as fatty acids, amino acids and inorganic acids.

1.5 Stability and destabilisation of natural rubber latex

The stability of natural rubber latex has two quite distinct aspects[11]:

(i) the tendency or otherwise for an individual particle to undergo changes by interaction with the aqueous phase, generally confined to hydrolysis of the non-rubber constituents on the surface of the rubber particles; and

(ii) the interaction which may occur between the particles themselves. This is the more important aspect and will be considered further.

Strictly speaking, latices are thermodynamically unstable. This is so because coalescence brings about a reduction in the specific surface area of the system and therefore in the interfacial free energy per unit volume of the disperse phase. However, for practical purposes, a latex is regarded as stable if the process of coalescence occurs only very slowly, say, over a period of months or years. Thus, a stable latex may be defined as one in which no aggregation or coalescence of the rubber particles occurs under the conditions studied[12].

The stability of natural rubber latex has been attributed to three important and interrelated factors[11], namely:

(a) the presence upon the particles surfaces of structures or interfacial films causing reduction of the free energy associated with the interface which separates the rubber particles and the serum;

(b) the presence of electric charges upon the surface of each particle that leads to the formation of a diffuse counterion cloud in the dispersion medium. This results in a repulsive force between the particles (see Section 1.3.2).

(c) the presence around the particles of a layer of tightly-bound water molecules which acts as a mechanical barrier.

These three factors arise principally as a result of the adsorption of surface-active substances (mainly fatty-acid soaps and protein) from the aqueous phase. Adsorption processes are almost invariably accompanied by a reduction in interfacial free energy. Since both adsorbed soaps and proteins are ionised in alkaline medium, they confer electric charges upon the surfaces of the rubber particles. Also, because of the hydrophilic nature of part of these molecules, they adsorb water molecules to form a sheath of bound water surrounding the rubber particles.

Of these three factors, the first can do no more than mitigate the tendency to thermodynamic instability. Although, interfacial free energies may be reduced, they always remain positive, and can never be reversed in sign. Reduction in interfacial free energy does not therefore make coalescence energetically unfavourable; it merely makes it less favourable than would otherwise have been the case.

The second factor, namely the acquisition of electric charges, constitutes a positive deterrent to coalescence (see Section 1.3.2). With regard to the third factor, the extent to which hydration occurs is unknown. However, it is believed to depend very much upon the nature of the soap-protein film which is adsorbed at the particle interface. It is generally assumed that the coagulation of natural rubber latex by solvents, such as acetone and alcohol, is partly brought about by dehydration of the interfacial soap-protein film.

By destabilisation is meant any process which destabilises a latex to such an extent that the particles coalesce in large numbers. Destabilisation or coacervation may be occur in three distinct forms, depending upon the nature of the product which is formed, namely, gelation when a continuous uniform gel is obtained; coagulation when lumps of coagulum are formed; and flocculation when a mass of small flocs is obtained.

Probably the most common way in which the destabilisation of natural rubber latex can be brought about is by using direct coacervants which reduce the electrical charges which surround the rubber particles. These coacervants include those substances which bring about an immediate and evident destabilisation as soon as they are added to the latex. Examples of such substances are strong acids, metallic salts, etc.

1.6 Latex dipping

1.6.1 Background of dipping processes

The object of all dipping methods is to shape the rubber phase and to give these shaped masses the desired qualities. In essence, the dipping process consists of the immersion of a former into a suitably compounded latex, followed by slow withdrawal in such a way as to leave a uniform deposit of latex on the former. The process is completed by drying, leaching and, if necessary, vulcanising the deposit. However, despite its long-established practice, there are many aspects of the dipping processes which are still not well-characterised and understood.

Natural rubber latex was used in the late thirties primarily to replace solutions of rubber in organic solvents, thus avoiding the cost involved in preparing the solutions, and also the fire and toxicity risks. However, the presence of water and the relative instability of the latex created new problems. Shortly after the end of World War 1, the appearance on the market of adequately-preserved natural rubber latex concentrates of uniformly high quality was a most important factor in promoting the development of this process. When a changeover to latex was made, it was found that not only had the products vastly superior physical properties, but also that these properties were retained much better during ageing.

The work of rubber chemists and technologists over the past 40 years or so has revealed many factors influencing the thickness of the deposit obtained by the dipping process, but unfortunately few investigations have been undertaken with a view to deepening understanding of the mechanism of the process.

Despite the lack of fundamental investigations, the manufacture of dipped rubber articles from latex is practised in virtually every country of the world. The latex dipping industry accounts for an annual consumption of about 170,000 tonnes of latex[13]. The range of products made by the dipping processes includes rubber gloves of all kinds, meteorological balloons, teats and soothers, bladders, catheters and other surgical devices, condoms, finger cots, rubber tubings, toys and toy moulds. Furthermore, some types of dipped products, such as rubber gloves and condoms, are usually produced in very large number using highly-automated production lines.

Three principal methods of dipping are in commercial use, namely, straight, coagulant and heat-sensitised dipping. Of the three methods, the straight and coagulant dipping methods have been studied in the investigation and described in this thesis, and they will be discussed further.

1.6.2 Straight dipping

Straight dipping is the first recorded and the simplest of all the dipping processes. It consists of immersing a former into a latex compound, followed by slow withdrawal and finally by drying the wet latex deposit. The operation can be repeated several times until the desired thickness of deposit is obtained. The thickness of the deposit obtained in a single dip depends upon many factors, including the total solids content and the viscosity of the latex mix, the speed of withdrawal of the former, the temperature of the latex and the former, and the flow of the latex upon the surface of the former[14-17]. For a given latex compound, the thickness of the deposit is approximately proportional to the number of dips[18]. Usually, the thickness of the deposit is approximately 0.05 mm per dip[13]. The process is mainly used for the production of thin-walled articles such as condoms.

1.6.3 Dry-coagulant dipping

Dry-coagulant dipping is probably the most widely-used method in the dipping industry. The former is first immersed in the coagulant solution (e.g., calcium chloride in a mixture of water and industrial methylated spirit). After withdrawal of the former from the solution, the solvent is allowed to evaporate, leaving either a very viscous concentrated solution or a dry deposit of calcium chloride. This is the origin of the term ' dry-coagulant ' dipping. The coated former is then immersed in the latex and allowed to dwell for a predetermined time. In this time, the coagulant migrates from the former into the latex and brings about destabilisation of the latex particles adjacent to the former and in the zone of activity of the diffusing ions. Local diminution of the concentration of the latex is said to be compensated by the diffusion of the rubber particles in the inverse direction[17]. The speed of this gelation process is therefore a balance of these two opposing rates of diffusion.

The thickness of the deposit obtained in a single coagulant dip may in principle depends upon many other factors in addition to those mentioned in Section 1.6.2. These other factors include the concentration and type of added surfactants, the pH of the latex, the dwell time, and the concentration and type of other compounding ingredients present in the latex mix[19-21]. The thickness of the deposit obtained in one dip typically varies from 0.2 to 0.8 mm[13]. The process is suitable for the production of rubber articles such as gloves and balloons.

1.7 Scope of present work

Many workers have studied the coagulant dipping process, especially the relationship between deposit thickness and time of dwell (see Section 3.3). However, there is considerable disagreement concerning the kinetics of deposition, and very little detailed understanding of the mechanism of deposition.

The major aim of this project was to study in a more systematic way those factors which affect the kinetics and mechanism of deposition. Consequently, one aspect of this work will deal with the distribution of calcium ions within the gel and on the former. The effects of syneresis, dehydration and coalescence of the gel are all thought to be important, and have therefore been investigated. The results have been compared with those of other workers, and where appropriate new hyphotheses are proposed and tested.

A secondary aim of this project was to investigate those factors which affect the physical properties of the wet gels which are obtained by coagulant dipping.

CHAPTER 2

CHANGES IN CHEMICAL COMPOSITION DURING AMMONIATION AND STORAGE OF NATURAL RUBBER LATEX

2.1 Sources of natural rubber latex

Natural rubber latices are produced in nature by various species of plants, including Hevea brasiliensis and guayule. Guayule[1] is a greyish-green or silvery-leafed shrub weighing approximately 0.5 to 1.0 kilogram. The standing height is less than 1.0 metre. The natural habitat of the plant is the semi-arid region of northern Mexico and the southwestern portion of the United States of America. Hevea brasiliensis[2] is a tree which has a fully grown height in the range 15 to 18 metres. The Hevea tree grows well under typical tropical conditions, in regions such as tropical America, tropical Africa, India, Sri Lanka and the tropical Far East. For a variety of reasons, the only species of tree which has been fully exploited commercially is Hevea brasiliensis. The latex is obtained by tapping or puncturing the bark of the Hevea tree, and allowing the latex to flow into a collecting device.

The latex which exudes from the tree is a thin and whitish fluid of density between 975 and 980 kgm^{-2}, pH from 6.5 to 7.0, and surface free energy from 40 to 45 ergs cm^{-2} (0.04 to 0.045 Jm^{-2})[3]. Its viscosity is variable. The latex particles exhibit Brownian movement. The larger particle in fresh Hevea latex move at speeds of about 1 mm per minute (12 microns per second).[4]

2.2 Composition of fresh natural rubber latex

Freshly-tapped natural rubber latex, being a natural product, shows considerable variations in composition and colloidal properties mainly attributable to genetical and enviromental factors. A typical composition for fresh natural rubber latex is as follows[5]:

	%
total solids content	36
dry rubber content	33
proteinaceous substances	1 - 1.5
resinuous substances	1 - 2.5
ash	up to 1
carbohydrates	1
water	ad.100

These substances are contained in three principal phases; the rubber particles, which account for some 35% of the latex by weight; the aqueous phase, which is approximately 55% by weight of the whole; and the lutoid or viscoid phase, which accounts for most of the remaining 10%. There are also many minor phases present; one of these minor phases is known as the Frey-Wyssling particles. Distributed between these phases, and present in relatively small amounts,are a large number of non-rubber constituents, e.g., proteins, lipids, quebrachitol and inorganic salts. These substances have been described in detail by various authors[5 - 8].

The differences in the composition of natural rubber latex from different sources partly accounts for the batch-to-batch variability of this material. This variability can be minimised by careful clonal selection or by blending batches from different sources.

2.3 Effect of ammoniation of natural rubber latex

Freshly-tapped natural rubber latex coagulates within a few hours of leaving the tree, often developing a bad odour. Thus, preservation is necessary in order to prevent coagulation and putrefaction.

When ammonia is added as preservative to freshly-tapped natural rubber latex, the chemical composition of ammonia-preserved latex after storage differs somewhat from that of the fresh unammoniated latex, quite apart from the presence of the ammonia itself[9,10]. On ammoniation, the lutoids and Frey-Wyssling particles dissolve in the serum. Most of the other particulate phases except the rubber particles also dissolve.

A more important effect of ammonia is that it promotes the hydrolysis of proteins and phospholipids. The former are degraded to polypeptides and amino acids; the latter are hydrolysed to various substances such as glycerol, fatty-acid anions, phosphate anions and organic bases. The liberated fatty-acid anions are adsorbed at the particle interfaces as ammonium salts, and thus enhance the colloid stability of the latex. This is why the stability of ammonia-preserved latex tends initially to increase during storage.

The extent of the changes in the composition brought about by hydrolysis depends upon the concentration of ammonia, and the time, temperature and conditions of storage[9 - 18]. In general, the quantities of both proteins and resinuous substances tend to fall, and are replaced by the ions noted above.

Thus, ammoniation is accompanied by considerable changes in the composition of the latex. Ammonia-preserved latex is a predominantly two-phase system, comprising rubber particles and serum only. The particles themselves are stabilised by fatty-acid anions and proteinate ions, instead of by the latter only, as is the case with fresh latex.

The proteins are important as steric stabilisers as well as ionic stabilisers. Steric stabilisation is probably very important for fresh latex, and is probably also of considerable importance in ammonia-preserved natural rubber latex. This accounts for some of the observed differences in colloidal behaviour between fresh and ammonia-preserved latex.

2.4 Effect of storage upon colloid stability of ammonia-preserved natural rubber latex

The anions of the so-called volatile fatty acids (formic, acetic and propionic) are formed by the action of micro-organisms (notably bacteria) upon certain of the carbohydrates dissolved in the serum. Ammonia and other bactericidal preservatives retard the formation of these anions. Thus it is that the VFA content (expressed as VFA Number) of an ammonia-preserved latex (ca. 0.02) gives a measure of the extent of micro-organic activity which has occurred during the time since the latex exuded from the tree.

The volatile fatty acids are present in ammonia-preserved latex as their ammonium salts. The principal effect of these salts is to reduce the mechanical and chemical stabilities of the latex. A similar effect is observed when ammonium acetate is added. The mechanism of both effects is probably that the increase in the ionic strength of the aqueous phase causes a compression of the electrical double layer which is associated with the rubber-serum interface. This subsequently allows the two particles to come closer together before any significant overlap of the counterion clouds take place. As the attractive force between particles increase as the distance of separation between the particles decreases, therefore the latex will flocculate more quickly.

The mechanical and chemical stability of ammonia-preserved latex which has been stored for any length of time is thus a product of several factors, the most important of which are VFA formation, which tends to reduce the stability, and lipid hydrolysis to give long-chain fatty-acid anions, which tends to enhance the stability. The final stability is largely determined by the balance between these two. It is significant that latex which has been stored under nominally air-free conditions which prevail in an almost full sealed container suffers a progressive reduction in stability, whereas the stability of latex which has been stored under aerobic conditions in half-full containers increases markedly and passes through a maximum. These observations are to be interpreted in the light of the fact that reducing conditions favour the formation of the anions of the volatile fatty acids.

2.5 Type of natural rubber latex used for dipping

In many industrial latex processes (e.g., dipping, casting and moulding), it is required that a strong continuous gel is rapidly formed almost immediately the latex is destabilised. Futhermore, the latex must have a reasonably high solids content in order to avoid excessive shrinkage of the gelled product, have a relatively low viscosity for processing, and must be stable during compounding operations.

Until about 20 years ago, rubber articles, such as gloves, were made exclusively from natural rubber latex. Natural rubber latex has good film-forming characteristics and has the high wet-gel strength which is necessary to withstand mechanical manipulation. It forms a smooth continuous film on drying, and its vulcanisates have high strength and elasticity. However, synthetic latices (based on polychloroprene and acrylonitrile-butadiene polymers) are now being used to replace natural rubber latex for products which require special properties such as resistence to hydrocarbon oils and other chemicals.

Centrifuged natural rubber latex concentrates are the most commonly used types of concentrate for dipping. Creamed and evaporated latices are not often used because they are somewhat more expensive and offer no special technical advantage over the centrifuged latices. High-ammonia (HA) centrifuged concentrate and low-ammonia concentrates preserved with zinc oxide and tetramethylthiuram sulphide (LA - TZ) are particularly recommended for use in dipping. Both latices can be used for all types of products.

For light-coloured products, e.g., babies' teats, low-ammonia latex preserved with boric acid (LA - BA) may be preferred since it has a slightly lighter colour than most other centrifuged latices. However, the use of boric acid is forbidden in some countries. Double-centrifuged latex has a lower colour still, because of its low non-rubber solids content; it is particularly useful where light colour and high electrical resistance are required in the product.

Prevulcanised latices are widely used in dipping processes. They are prepared by heating a stabilised latex with dispersions of sulphur, zinc oxide and an ultra-fast accelerator at temperatures of approximately 70°C for about two hours. The principal reason for prevulcanising natural rubber latex to be used in dipping processes is convenience - it is easier to vulcanise the latex in bulk than to vulcanise innumerable latex films. The resultant latex is similar to the unvulcanised latex except that the particles comprise vulcanised natural rubber. In order to optimise physical properties, it is customary to prevulcanise only partially, and then complete the vulcanisation after dipping and drying.

CHAPTER 3

LITERATURE SURVEY

3.1 Factors affecting thickness of deposit obtained by straight dipping

The formation of a rubber film by gelation and by drying of natural and synthetic latices has been investigated by many workers[1-26] Considerable progress has been made towards explaining the mechanisms by which films are formed by the two processes, and also towards understanding those factors which affect the formation of the film.

It is well known that the thickness of deposit obtained by straight dipping depends upon many factors. These factors include the total solids content and viscosity of the latex, the speed of withdrawal of the former, the temperature of the former and the latex, the number of dips, the flow of the latex upon the surface of the former, and, to a lesser extent, the rotations or other mechanical manipulations which prevent the liquid latex from dripping off the former before gelation or drying has occurred.

Klein[27] has shown that the thickness of deposit obtained in a single straight dip increases with increase in the total solids content (TSC) of natural rubber latex. The function is not linear, the thickness of deposit increasing substantially at above 50% TSC. In contrast, Gortons' data show a linear relationship between the thickness of a straight dip deposit and the TSC in the range 50 to 60% for three different compounds of natural rubber latex[28]. However, by extraploting these points to zero thickness, the lines cut the TSC axis at surprisingly high values (between 42 to 48% TSC). The apparently linear relationship appears to be the result of only considering a narrow range of TSC. The results shown by Klein[27] indicate that, in reality, the curve between 50 to 60% TSC only approximates to a straight line.

Gorton[28] has also shown that the relationship between the straight dip deposit thickness and the latex compound viscosity is given by

$$\theta_s = a_1 + k_1 \log_{10} \eta_{60} \qquad \ldots\ldots\ldots \qquad 3.1$$

where θ_s is the straight dip deposit thickness, a_1 and k_1 are constants, and η_{60} is the apparent (Brookfield) viscosity measured at 60 rpm.. Futhermore , it was shown that such a relationship holds for viscosities measured at other rates of shear.

Rhodes[29] and Vershaar[30] have shown that, by increasing the TSC of the latex, the viscosity of the latex increases, slowly at first and substantially at above 50% TSC. Hence, it is not clear from their results whether a thicker deposit is the consequence of increased TSC or of increased viscosity or of both since both workers have made no attempt to control the other of these two factors.

Another factor which has been found to influence the thickness of a straight dip deposit is the alkalinity of the latex[27]. The thickness of the deposit increases with decreasing alkalinity, becoming marked at very low alkalinities. The addition of casein or ammonium sulphate to the latex is also shown to give thicker deposits. In each case, Klein[27] attributed the thicker deposits to increase of the viscosity of the latex. However, no attempt was made to investigate the relationship between the deposit thickness and the viscosity of the latex.

The time of immersion has no effect upon the thickness of deposit obtained by a straight dip. The number of dips can, however, increase the thickness of deposit substantially. It has been stated that, for a given latex compound, the thickness of the deposit is approximately proportional to the number of dips[31].

3.2 Factors affecting thickness of deposit obtained by coagulant dipping

3.2.1 Introduction

It is generally accepted that the formation of rubber films by the coagulant-dipping processes is based principally upon the diffusion of the coagulating ions from the former into the latex. This brings about destabilisation of the latex particles adjacent to the former through the removal of charges which surround the particles. Further, it has been observed that other processes may be involved besides the diffusion of ions and the neutralisation of charges, such as, syneresis, dehydration and perhaps compression of the electrical double layers. The significance of these processes in bringing about the deposition of the latex particles on the former is still obscure.

The thickness of the deposit obtained in a single coagulant dip depends in principle upon many other factors in addition to those discussed in Section 3.1. These other factors include the concentration and type of added surfactants, the pH of the latex, the modulus of the contained polymer, the dwell time, and the concentration and type of other compounding ingredients present in the latex compound. The effect of some of these factors is discussed below.

3.2.2 Effect of coagulant

Martinon[32] has found that the thickness of deposit obtained by coagulant dipping depends upon the types and concentrations of the coagulants. The rate of deposition varied with the type of coagulants in the order:

calcium chloride > calcium acetate > zinc acetate.

It was also found that the higher the concentration of the coagulant, the thicker was the deposit obtained on the former. Similar results have been obtained by several other workers[33-36]. According to Hu and Huang[33], the effect of type of coagulants on the deposit thickness was in the order:

calcium chloride > calcium nitrate > calcium acetate >
barium chloride > barium acetate.

Gorton[34] has shown that calcium nitrate is a more effective coagulant than cyclohexylamine acetate of similar concentration.

Thorsrud[35] attempted to study separately the effect of the cation and the anion of a salt. The anions were investigated in the form of soluble ammonium salts. Since, the ammonium salts posses no coagulant power, they were added directly to the natural rubber latex compound. A straight dip into the latex compound gave an estimate of the effectiveness of the anions. The results are summarised in Table 3.1. Furthermore, it was also found that these salts, when added in concentrations higher than 3% based upon the rubber, generally induce coagulation, though not immediately. Whereas the anions were evaluated for their effect upon certain characteristics of dipped product obtained by straight dipping, the cations were evaluated as coagulants on the former. They were used in the form of salts of strong acids or in the form of the acetate. In choosing these salts, consideration was given to their coagulant power, their solubility in ordinary solvents, and their commercial importance. Table 3.2 summarises the effect of several bivalent cations upon certain characteristics of dipped product obtained by coagulant dipping. These results indicate qualitatively that both the anions

Table 3.1 Effect of anions upon certain characteristics of dipped product obtained by straight dipping[35]

anions	concentration on rubber, %	thickening effect	characteristics of dipped product	
			wetting	film
-	- control	-	good	uniform
bromide	0.5 - 1.0 - 3.0	average	good	uniform
chloride	0.5 - 1.5 - 3.0	average	good	uniform
nitrate	0.5 - 1.0 - 2.0	great	good	fairly uniform
sulfate	0.5 - 1.0 - 2.0	great	fairly good	fairly uniform
acetate	0.5 - 1.0 - 2.0	fairly great	fairly good	average
formate	0.5 - 2.0 - 4.0	fairly great	fairly good	fairly uniform
salicylate	0.5 - 2.0 - 4.0	weak	fairly good	fairly uniform
benzoate	0.5 - 1.5 - 3.5	weak	good	uniform

and cations probably have an effect upon the deposit thickness and the quality of the deposit.

Martner[36] has found that calcium chloride has certain advantages as regards both the rate of film formation and the uniformity of the films, but that calcium nitrate was the most suitable coagulant when other factors were considered, e.g., the ageing behaviour of the dried films. Martner also found that magnesium nitrate gave thinner deposits than did calcium nitrate. He suggested that the rate of film

Table 3.2 Effect of bivalent cations upon certain characteristics of dipped product obtained by coagulant dipping [35]

bivalent cations	coagulating power	characteristics of dipped product	
		wetting	film
Ba^{2+} (acetate)	excellent	good	uniform
Ca^{2+} (bromide)	excellent	excellent	uniform
Ca^{2+} (acetate)	excellent	good	uniform, rather hard
Ca^{2+} (chloride)	very good	excellent	uniform
Mg^{2+} (chloride)	very good	excellent	uniform
Ba^{2+} (chloride)	good	good	uniform
Ba^{2+} (nitrate)	good	average	irregular
Sn^{2+} (bromide)	fairly good	good	uniform
Zn^{2+} (nitrate)	fairly good	good	uniform
Zn^{2+} (acetate)	fair	fairly good	fairly uniform
Sn^{2+} (chloride)	weak	good	uniformly coloured
Zn^{2+} (chloride)	poor	good	fairly uniform
Zn^{2+} (sulfate)	poor	good	fairly regular, hard

formation depends hardly at all upon the speed with which the electrolyte diffuses into the dipping compound, but mainly depends upon the solubility of the salts formed by the electrolyte and the anionic surfactants in the latex; the calcium salts being generally less soluble than magnesium salts.

3.2.3 Effect of latex particle size and structure

Medalia[37] has observed that, if the latex has a very fine particle size, a very thin film may be deposited initially which resists further penetration by calcium nitrate and so prevents the formation of deposits of reasonable thickness. The rate of deposition was increased by the addition of non-ionic surface-active agents such as an alkyl phenoxypolyoxyethylene ethanol (Igepal CA - 633). However, it was found that addition of these surface-active agents to a latex of large particle size, which is capable of depositing a good film in their absence, results in weakening of the deposited film. In contrast, it has been reported that film formation from SBR latices is rapid compared to that from other latices because of the relatively small particles which they contain[38].

Storage or ageing substantially affects the properties not only of the latex as a colloidal system but also, in some cases, of the actual polymer[39, 40]. Shepelev et al.[40] have found that, during the ageing of polychloroprene latex, there is a reduction in alkalinity as a result of the evolution of hydrogen chloride from the polymer. In addition, there was a fall in surface tension, an increase in the degree of soap saturation of the particle surface, and an acceleration of coagulant deposition. It was also found that, during the ageing of polychloroprene latex, aggregation of the particles occurs[41].

Aggregation or enlargement of particles accelerates ionic deposition[42,43]. This later observation has been confirmed by several other workers[37,40,44].

According to Shepelev et al.[40], a latex gel with aggregated particles apparently has a looser structure and therefore allows more calcium to diffuse through the gel. Moreover, the reduction in the specific surface area, and in the fraction of the surface not covered with protective substances, greatly reduces the number of places where rubber-to-rubber contact may occur. Another important effect is probably that, with aggregation of the particles, some of the protective substances become trapped within the aggregates and do not react with the coagulant during deposition. This was confirmed by the reduction in calcium equivalent previously observed when polychloroprene latex was aged[45].

3.2.4 Effect of soaps

It is known that the addition of small quantities of soaps to natural rubber latex will substantially increase the mechanical and chemical stabilities of the latex[46 - 52]. The effectiveness of a soap in stabilising the latex depends in general upon the amount added, the type, and also the length of the hydrocarbon chain length of the soap. Similar, but less dramatic effects have been observed when these soaps are added into latex which is then subjected to destabilisation by dipping using calcium as the coagulant[53 - 55].

Gouw[53] found that latices stabilised with potassium oleate and with ethylene oxide-fatty alcohol condensate (Vulcastab LW) gave thinner deposits, whereas latices destabilised by adding ammonium acetate gave thicker deposits. Similar results were obtained by Teoh[54] and by Mortimer[55]. Cockbain et al.[56] have reported that 0.8% of a non-ionic stabiliser (Nonaryl 930) reduced the weight of the dry rubber deposit obtained by coagulant dipping by a factor of approximately 12. It has been postulated that the effectiveness of the non-ionic stabilisers in reducing deposition is a result of the ability of the strongly hydrated groups to retain the water surrounding the latex particles.

3.2.5 Effect of total solids content and viscosity of latex

Two other important factors which can influence the rate of deposition of latex by coagulant dipping are the total solids content and viscosity of the latex[28,34,37,44,57]. Medalia[37] has observed that a weak wet film may be obtained if the latex is too dilute. Likewise, in the case of a butadiene-based copolymer latex, if the latex is of high concentrations (50 to 60% TSC) but is viscous, a soft, incompletely coagulated film may also be obtained. In contrast, Medalia[37] has found that good films can be obtained from natural rubber latex over a range of TSC (40 to 62%). These general observations are consistent with several other findings of certain other workers[44,57].

Stewart[44] has also shown that there was no apparent effect upon film thickness when the TSC's of polychloroprene latices were varied between 65 and 45%. However, at TSC's of 30% and below, it was found that the rate of film formation increased with decreasing TSC. Also, the films obtained were very soft and spongy and exhibited a very large degree of shrinkage on drying.

Sandomirskii et al.[57] have shown that the dependence of the amount of deposition upon the viscosity of natural and synthetic latices is in all cases satisfactorily described by the empirical equation:

$$\nu = A/\eta^{b} \qquad \ldots\ldots\ldots\ldots \qquad 3.2$$

where ν is the volume of the gel, η is the viscosity of the latex, and A and b are constants. For the natural rubber latex and the polychloroprene latices, $b \simeq 0.5$ and for the butadiene-styrene latex, $b \simeq 0.25$. The constant A was found to be different for all the latices investigated.

3.2.6 Effect of cross-linking of latex particles

The degree of vulcanisation of natural rubber latex particles has been found to have no significant effect upon the rate of deposition in coagulant-dipping processes[58]. It was concluded that the rate of deposition depends upon the colloidal properties only, and is therefore not affected by the intraglobular structure. However, it must be noted that the deposit-time curves, with only one exception, showed an increase in deposit thickness as the degree of vulcanisation was increased.

In contrast, Shepelev et al.[40] and Stewart[44] have found that cross-linking of the polymer and the reduced flexibility of its molecules impede coalescence of polychloroprene particles into a coherent gel. This results in acceleration in the rate of deposition since a less coherent gel allows more calcium to diffuse through the gel.

3.3 Thickness-time relationships in coagulant-dipping processes

3.3.1 Introduction

The aspect of the dipping process which has received most attention has been the relationship between the deposit thickness and the dwell time[28,33,34,44,53,54,55,57,58]. A wide range of natural and synthetic latices, and also several different dipping techniques, have been used in these experimental studies. A consequence of this is that diverse mathematical relationships have been proposed to describe the deposit thickness-time relationship, and conflicting theories have been proposed to explain the coagulant-dipping behaviour of the different systems.

The mathematical equations which have been proposed to describe the dry deposit thickness-time relationship include those summarised below:

(a) Gorton[28,34]

$$\theta = a + kt^{\frac{1}{2}} \log_{10}\eta \quad \ldots\ldots\ldots\ldots\ldots \tag{3.3}$$

(b) Hu You-Mo[33,58]

$$q = kt^{n} \quad \ldots\ldots\ldots\ldots\ldots \tag{3.4}$$

$$q = 0.0107\, t^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots \tag{3.4a}$$

$$q = q_{\infty} \frac{kt}{1 + kt} \quad \ldots\ldots\ldots\ldots\ldots \tag{3.5}$$

(c) Gouw[53]

$$\theta = \theta_{\infty} (1 - e^{-kt}) \quad \ldots\ldots\ldots\ldots\ldots \tag{3.6}$$

$$\theta = a - k \log C_m (1 - e^{kt}) \quad \ldots\ldots \tag{3.7}$$

(d) Teoh[54]

$$\theta = \theta_{\infty} (1 - e^{-kt}) \quad \ldots\ldots\ldots\ldots\ldots \tag{3.8}$$

$$\theta = \theta_{\infty} \tanh kt \quad \ldots\ldots\ldots\ldots\ldots \tag{3.9}$$

$$\theta = \theta_{\infty} (2/\pi) \tan^{-1} kt \quad \ldots\ldots\ldots\ldots\ldots \tag{3.10}$$

$$\theta = \theta_{\infty} \operatorname{erf} (kt) \quad \ldots\ldots\ldots\ldots\ldots \tag{3.11}$$

$$\theta = \theta_{\infty} (1 - e^{-k\sqrt{t}}) \quad \ldots\ldots\ldots\ldots\ldots \tag{3.12}$$

(e) Mortimer[55]

$$\theta = \theta_\infty (1 - e^{-kt^n}) \qquad \text{.................3.13}$$

$$\theta = \theta_\infty' (1 - e^{-k'\sqrt{t}}) + \theta_\infty'' (1 - e^{-k''\sqrt{t}}) \qquad \text{........3.14}$$

(f) Sandomirskii and Korsunskii[57]

$$\gamma q^2 = 2 DC_o a_R t = kt \qquad \text{....................3.15}$$

$$q = k' t^y \qquad \text{....................3.16}$$

where $y = (1 - \beta) /2$ and $k' = (2DB\, a_R \cdot \frac{1}{\gamma})^{\frac{1}{2}}$

$$\log q = \log k' + y \log t \qquad \text{....................3.16b}$$

$$C_R = Bt^{-\beta} \qquad \text{.....................3.17}$$

(g) Stewart[44]

$$0 = 2\alpha (Dt)^{\frac{1}{2}} \Big\{ 1 - Am \exp (\alpha^2/2) \Gamma(2m) x\, t^{2m}$$

$$W_{(\frac{1}{4} - 2m,\ \frac{1}{4})}(\alpha^2) / (0.26) (2m + \tfrac{1}{2})\alpha^{\frac{1}{2}} \Big\} \qquad \text{........3.18}$$

where W denotes the Whittaker function and α satisfies the equations:

$$\alpha \exp (\alpha^2) \operatorname{erf} (\alpha) = (0.26) C/ b\pi^{\frac{1}{2}} \qquad \text{........3.18a}$$

$$G = 1/ \operatorname{erf} (\alpha) \qquad \text{.....................3.18b}$$

$$\text{and} \quad A = 2.22 \Big\{ \Big[\tau \sin m\pi / 8Er_1 \Big] \Big[\Gamma(m) \Gamma(2m)/ \Gamma(3m) \Big] \Big\}$$

$$\text{.....................3.18c}$$

where $\Gamma(m)$ denotes the gamma function of m, τ is the polymer/interfacial tension, r, is the radius of curventure when two latex particles come into contact and begins to coalesce, and m, E are constants.

In these equations, the following symbols are defined as indicated:

θ = thickness of dry deposit,

a, k, n, A = constants,

t = dwell time,

q = weight of deposit,

q_{∞} = limiting weight of deposit,

θ_{∞} = limiting deposit thickness,

C_m = chemical stability of latex,

η = viscosity of latex,

$\frac{1}{\gamma}$ = a coefficient which relates the amount of coagulant diffused into the latex to the amount of rubber deposited,

D = diffusion coefficient of coagulant ions in the coalescing latex film,

C_0 = initial concentration of coagulant on the former,

C_R = concentration of coagulant ions at the gel-latex interface,

C = concentration of calcium ions in a coagulant solution (assume to be constant).

a_R = concentration of rubber in the gel,

$2b$ = quantity of soap per unit volume of latex in a closed packed structure, and

B, β = constants.

Equations (a) to (e) were derived from general mathematical consideration and by fitting mathematical expressions to the experimental data. The significance and validity of these relationships are discussed in Section 3.3.2. Equations (f) and (g) were derived from more fundamental considerations. Factors which would be expected to affect deposit thickness, e.g., diffusion coefficient for calcium ions, have been used to derived the relationships, and these have been tested experimentally. These relationships thus provide some insight into the mechanism of gelation in the coagulant-dipping process. These equations will be further discussed in Section 3.3.3.

3.3.2 Relationships derived from general mathematical considerations and empirical curve fittings

Gorton[28,34] has studied the effect of the viscosity of latex upon the deposit thickness obtained by coagulant dipping. The dependence of deposit thickness with time of dwell (up to 5 minutes) is given in Equation 3.3. The total deposit thickness is directly proportional to the logarithm of the viscosity of the latex compound and to the square root of the dwell time. The constants were said to be dependent upon the latex compound and other conditions involved. In contrast, Sandomirskii and Korsunskii[57] have found that the volume of deposit obtained at a given time of dwell is inversely proportional to the viscosity of latex as indicated in Equation 3.2. Since both workers brought about the change of viscosity by dilution, they had inadvertantly investigated the effect of two different variables simultaneously, i.e., latex viscosity and total solids content. It seems probable that these relationships are not valid for other latex compounds, and therefore appear to have little fundamental significance.

Gorton and Iyer[34] have also observed that, as the deposit is formed, three effects hinder its growth, namely:

(i) release of serum and subsequent dilution of the coagulant on the former;

(ii) increase in the thickness through which the coagulant ions have to diffuse in order to reach the deposit-latex compound interface; and

(iii) the passage of serum towards the former to assist the initial dissolution of coagulant.

It has also been said that the thickness of rubber deposit obtained is directly proportional to the total solids content of the latex compound, which in turn is directly related to the pore size of the coagulum through which the coagulant ions have to pass. Diminution of pore size as a consequence of syneresis and the presence of water-soluble thickening agents such as carboxymethyl celluloses were also said to reduce the rate of diffusion and therefore the rate of deposition of latex particles.

Hu and Huang[33,58] have studied the deposit thickness-time relationship for natural rubber latex using different types and concentrations of coagulant and dwell times up to 50 minutes. From the experimental data obtained, the whole course of the coagulant deposition was expressed by an empirical equation of the type given in Equation 3.4 and 3.5. In addition, Hu[58] has also shown that the kinetics of coagulant deposition from vulcanised natural rubber latex is similar to that from the unvulcanised latex, and is expressed by the following equation,

$$q = 0.0107\,t^{\frac{1}{3}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.4a$$

where q is the amount of deposit, t is the deposition time.

Gouw[53] has investigated the deposit thickness-time relationship for uncompounded natural rubber latex concentrate using a mixture of calcium chloride and calcium nitrate solution in industrial methylated spirit as the coagulant. Ammonium acetate was added to the latex to reduce colloidal stability, and Vulcastab LW and potassium oleate were added to increase stability. The total solids content of each of the latices was adjusted to ca. 59% by adding distilled water. The results showed that the more stable latices gave thinner deposits, and vice versa. Using these experimental data, Gouw concluded that Equation 3.3 proposed by Gorton[28,34] is only valid for $t \leq 9$ minutes. Subsequently, Equations 3.6 and 3.7 were proposed. Equation 3.7 was an extension of equation 3.6 in which it was shown that

$$\theta_{\infty} = a - k \log C_m \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.6a$$

where C_m is the measured chemical stability of the latex, and a and k are constants which depend upon the latex as well as upon the method used to determine the chemical stability of the latex.

Teoh[54] has proposed the series of Equations 3.8 to 3.12. All these equations predict a typical deposit thickness-time relationship involving a high rate of deposition initially which subsequently reduces until a limiting thickness is obtained. Using Gouw's experimental data, Teoh tested Equations 3.8 to 3.11 and found that they did not fit the data well especially at longer dwell times ($t > 10$ minutes). However, Equation 3.12 fitted the experimental data reasonably well irrespective of the stabiliser content. Further, it was also found that the value of θ_∞ depends upon the stabiliser content, while that of k is independent of the stabiliser content. It follows that the deposit thickness-time relationship at a given level of stabiliser content will be characterised by the values of θ_∞ and k.

Teoh[54] argued that, in order to understand the significance of θ_∞, it is essential to understand the principles which underlie the coagulant dipping process. It was suggested that the calcium ions diffuse from the surface of the former, and eventually come into contact with the latex particles. They then reacts directly with the stabilising caboxylate ions thereby forming insoluble, unhydrated, and unionised soap. The deposition of the latex particles is a result of the removal of the electrical double layers which surround the particles and also of the loss of any hydration layers. Since θ_∞ is the limiting thickness of the film, it was taken as a measure of the total number of latex particles per unit surface area of the former capable of being destabilised by the calcium ions. As the surface density of calcium ions on the former was kept constant, the total number of latex particles deposited per unit surface area would depend upon the average number of stabiliser molecules per latex particle. Based on these assumptions, Teoh derived a mathematical equation relating θ_∞ to stabiliser content, namely

$$\theta_\infty = \frac{2VX}{N_0 + k_1W} \qquad \text{........................} \quad 3.12a$$

where V is the average volume per latex particle, X is the number of calcium ions per unit surface area of the former, N_0 is the initial number of carboxylate ions per latex particle (before the addition of soap),k_1 is a constant, and W is the total weight of soap added.

Since, N_o was approximately nine times as large as kW^* (where $W = W^*$ at 100% surface coverage), therefore, for the range of soap added in his experiment, a plot of θ_∞ versus W should approximate to a straight line. Experimentally, it was found that a plot of θ_∞ versus W was linear when the particle surface was incompletely saturated with soap. Above 100% surface coverage with soap, it was found that the deviation from linearity was found to be very much greater than that predicted from Equation 3.12a. It was then suggested that, after 100% soap coverage, the calcium ions appear to react preferentially with the carboxylate ions on the latex particles, as the graph begins to level out very fast immediately after 100% soap coverage. Similarly, a plot of $1/\theta_\infty$ versus W showed a negative deviation from a straight line prior to 100% soap coverage. A modified equation was proposed for the case where the soap coverage was less than 100%, i.e.

$$\frac{1}{\theta_\infty} = \frac{3k_1W_s}{6VX} + \frac{N_o - 2k_1W^*}{6VX} \qquad \ldots\ldots\ldots\ldots\ldots \quad 3.12b$$

where W_s is the weight of 10% potassium oleate solution added per 100g of latex solid, and W^* is the weight of a 10% potassium oleate solution added per 100g of latex at 100% soap coverage. It was shown that Equation 3.12b fits very well with the experimental results.

As for the significance of k in Equation 3.12, it is evident that k controls the rate at which θ approaches θ_∞ . The larger the value of k, the sooner θ approaches θ_∞, and vice versa. When θ approaches θ_∞, it was assumed that virtually all the calcium ions had been consumed, and that therefore k is related to the rate of removal of calcium ions. Since deposition probably proceeds by a mechanism which involves the diffusion of coagulant ions followed by chemical reaction between the coagulant and the stabiliser on the latex particles, it was then argued that k must be a function of the diffusion coefficient (D) of the calcium ions through the serum and the rate coefficient for the reaction between calcium ions and carboxylate ions (k'), i.e.

$$k = f(D, k') \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3.12c$$

It was shown that the values of k' were almost constant whatever the added soap concentration. Therefore, it indicates that k depends only on D, i.e.

$$k = k'f(D) \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 3.12d$$

A model based on simple diffusion theory was found to be inadequate to describe the mechanism involved in coagulant dipping. Differential equations based on a more elaborate models involving chemical reaction were also proposed. However, Teoh has made no attempt to solve these equations because of their complexity.

Finally, Teoh concluded that Equation 3.12 can be used to describe the relationship between the deposit thickness and dwell times in natural rubber latex coagualant dipping. However, minor deviations from the equation seem to occur at very long dwell times. The value of θ_∞ decreases sharply with increasing stabiliser content (i.e., slightly before approaching 100% surface coverage). The equation does not hold for the coagulant dipping of polychloroprene latex.

Mortimer[55] proposed Equation 3.13 to rectify some of the deviations observed by Teoh, together with a new one, Equation 3.14, to describe the coagulant dipping of polychloroprene latex. These proposed equations also do not appear to have any general applicability.

3.3.3 Relationships derived from more fundamental considerations

It is important to note that virtually all the proposed Equations 3.1 to 3.14 are based upon general mathematical consideration and empirical curve fitting. It is therefore not surprising that these equations generally fail to fit other experimental data, and also that they fail to give an insight into the mechanism of film formation on the former. However, in the equations proposed by Sandomirskii et al (f) and Stewart (g) an attempt has been made to derive equations which contain parameters which are known to affect the deposit thickness.

Unfortunately, the papers of Sandomirskii et al[57,59,60], are difficult to understand. This may be partly because of translation problems. Also, the concepts and arguments sometimes conflict with Western ideas of colloid chemistry. The present author has therefore tried to summarise Sandomirskii findings but cannot be sure that his interpretation is correct.

In deducing Equation 3.15, Sandomirskii et al[57] assumed that, in the course of deposition, the value of C_R (the concentration of calcium chloride at the latex-gel interface) remained constant. However, later it was realised that this assumption is incorrect. This can be seen from Figure 3.1, where the experimental data are clearly not described by the proposed Equation 3.15. Further studies by Sandomirskii[59] have suggested that the amount of free salt at the surface of the gel, which is in contact with the latex and determines the growth of gel, decreases continuously. To a first approximation, the change in the amount of salt with time is given by Equation 3.17.

Sandomirskii et al[57] changed Equation 3.16 to its logarithmic form, i.e.

$$\log q = \log k' + y \log t \quad \text{....................} 3.16b$$

where k' and $y = (1 - \beta)/2$, are constants, and $0 \leqslant y < 0.5$. It was shown that Equation 3.16b satisfactorily described the course of deposition, (Figure 3.2). The calculated constant y has the following values: Qualitex, 0.35; latex L - 4 and B - S latex, 0.40. It was stated that the bend in the curve in Figure 3.2 for B - S latex corresponds to the termination of deposition.

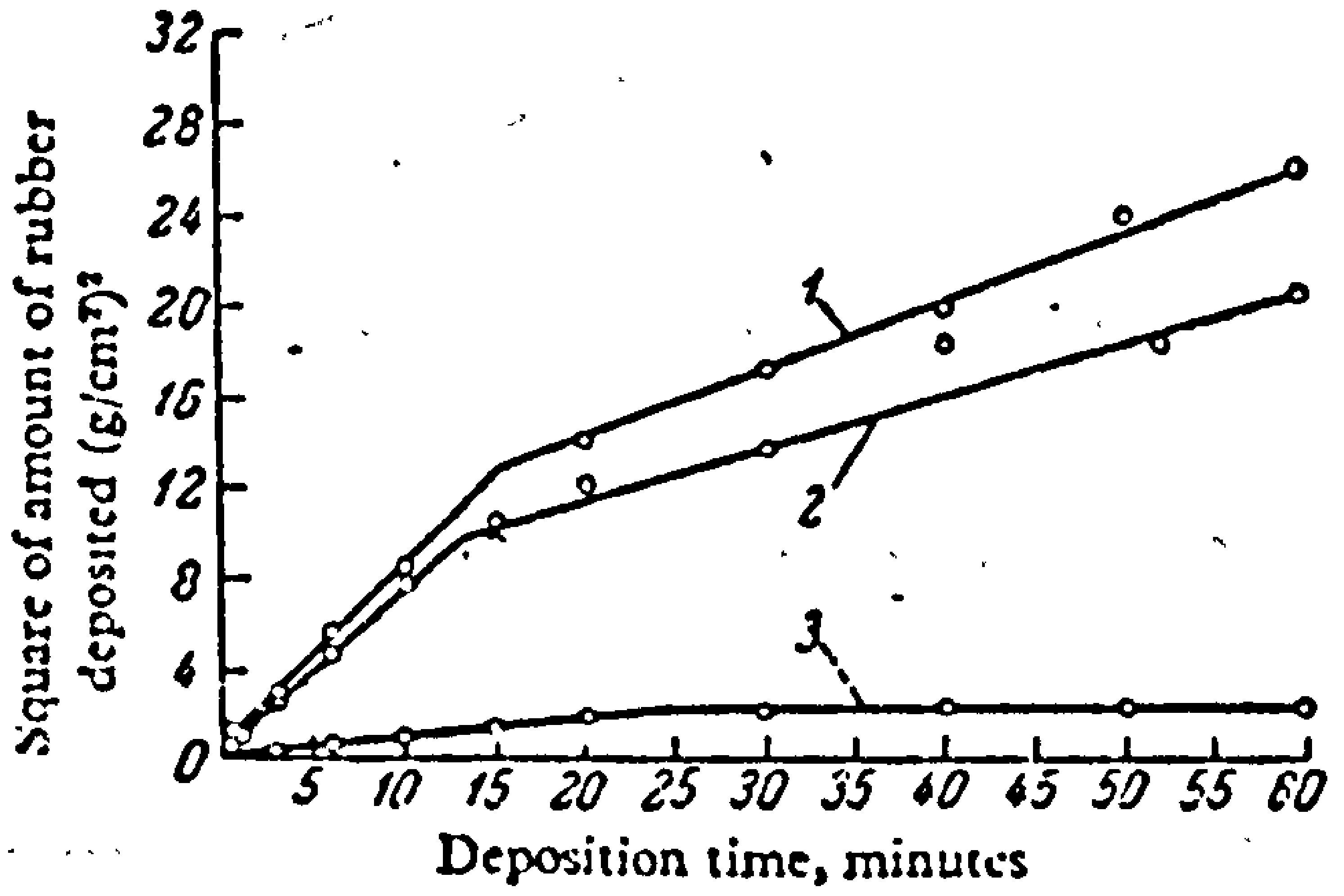


FIG 3.1-*Course of ionic deposition according to equation* (1) : 1, *Qualitex*; 2, *latex L-4*; 3, *butadiene-styrene* (50:50) *latex*. Ref.(57)

In deducing Equation 3.15, Sandomirskii et al[57] also assumed that the rate of deposition of rubber is directly proportional to the number of calcium ions which have diffused into the latex, and that the number of these ions is directly proportional to the initial concentration of salt on the former. As is indicated by Equation 3.15, the amount of salt which actually causes growth of the gel is related to its initial concentration in a way which is complex and has not been accurately established. Furthermore, it was found that the coefficient $1/\gamma$ depends to a considerable extent upon the deposition time.

Sandomirskii[59] have also stated that the " calcium equivalent " depends neither upon the time of deposition nor upon the initial

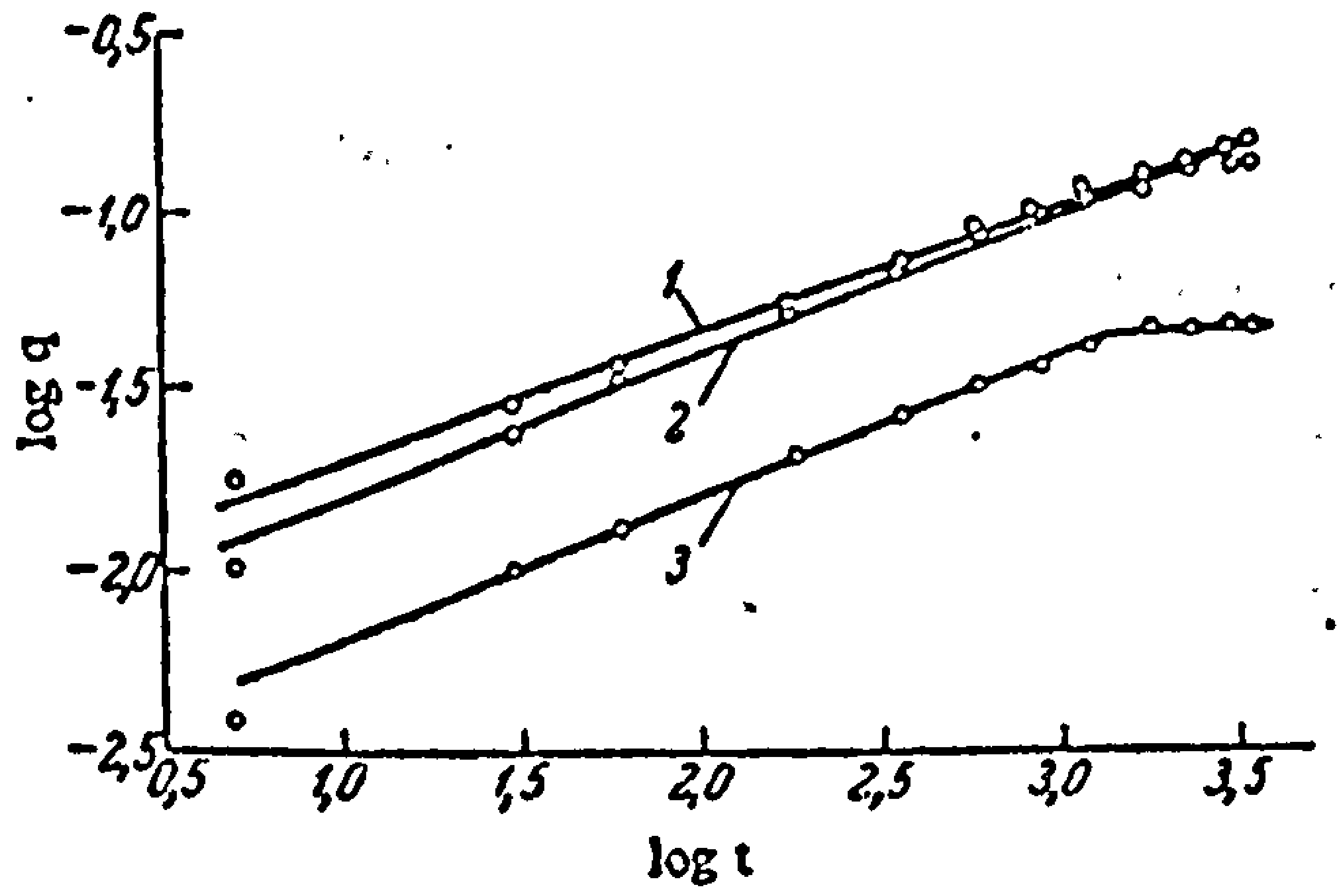


FIG.3.2-*Course of ionic deposition according to equation* (2) : 1, *Qualitex* ; 2, *latex L-4* ; 3, *butadiene-styrene* (50:50) *latex.*

Ref.(57)

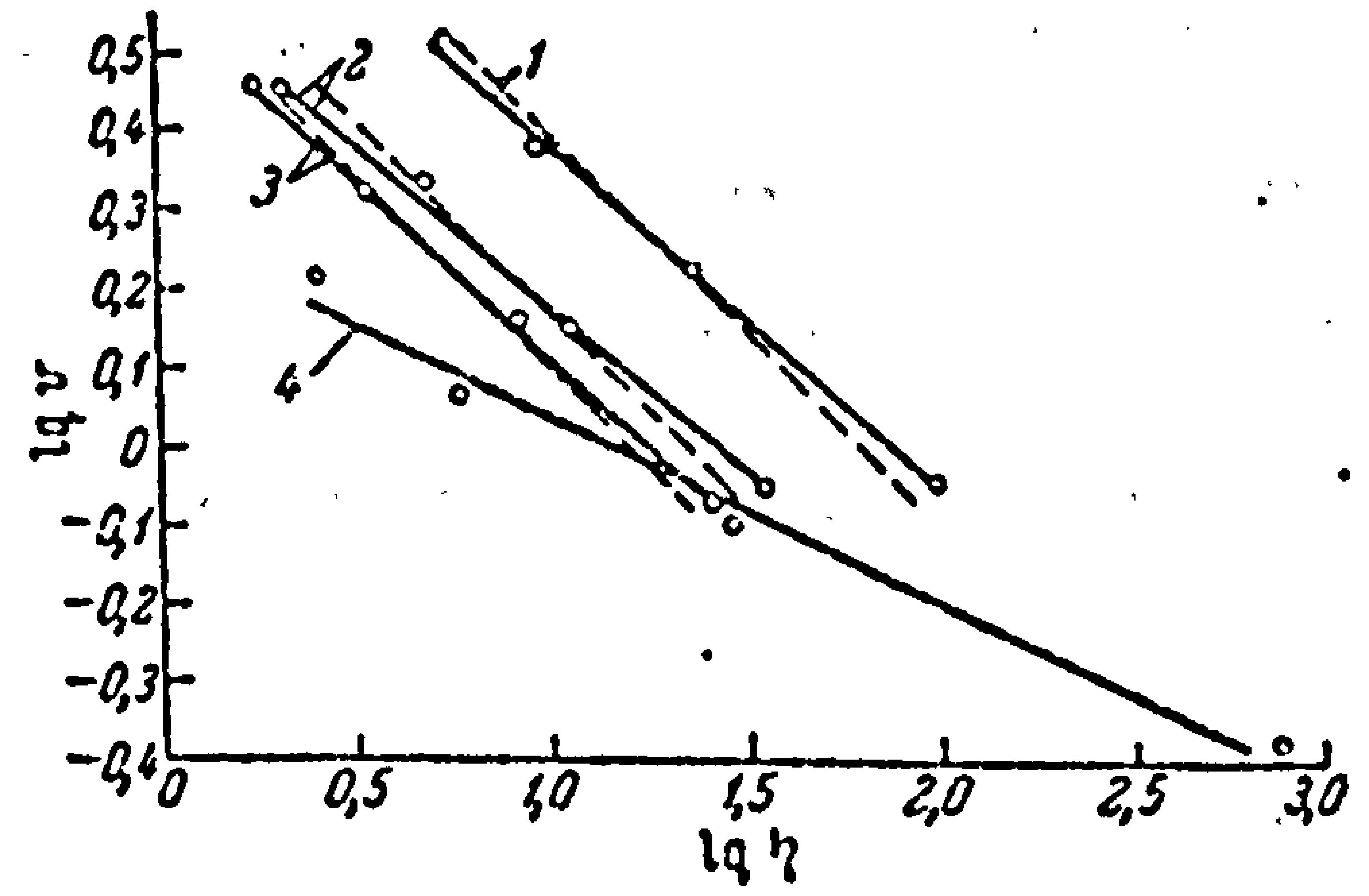


FIG.3.3-*Effect of the viscosity of the latex on the rate of ionic deposition (deposition time 5 minutes)* : ——— *experimental data* ; - - - - *calculated data.*
1—*Qualitex* ; 2—*latex L-4* ; 3—*latex L-7* ; 4—*butadiene-styrene* (50:50) *latex.* Ref.(57)

concentration of salt on the former (the calcium equivalent is the moles of calcium which reacts with a specified weight of latex). Consequently, the coefficient $1/\gamma$ should be proportional to the calcium equivalent of the given latex. Accordingly, these observations support the basic premise made in deducing Equations 3.15 and 3.16, namely, that the ionic deposition of rubber latex is a diffusion-controlled process. Sandomirskii et al. confirmed this by investigating the dependence of the rate of deposition upon the viscosity of the latex.

By substituiting in Equation 3.15 the value of the diffusion coefficient, $D = kT / 6\Pi r\eta$, according to the Stokes-Einstein equation, Sandomirskii et al. obtained the expression,

$$q^2 = 2\beta atykT / 6\,\Pi r\eta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.15a$$

if the time of deposition is constant, then

$$q = A / \sqrt{\eta} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 3.2$$

Experimental results for Qualitex, L - 4 and L - 7 showed that the dependence was close to the theoretical prediction (Figure 3.3). However, in the case of the B - S latex, the effect of viscosity was not so pronounced; the causes of this anomoly were not clear. However, it is said that the specific action of the glycerin, which was used to dilute and vary the viscosity of the latex, may have contributed to this anomoly.

Concerning the formation of the gel itself, Sandomirskii et al.[57] assumed that during deposition slow destabilisation of particles is caused by the gradual diffusion of cations from the surface of the former into the latex. This does not, however, explain why gel formation occurs at the very beginning of the deposition, that is, when the former together with concentrated coagulant comes into direct contact with the latex. It was therefore postulated that, in the initial stages, it was coagulation rather than gelation that took place, coagulation being much more spontaneous than gelation. This hypothesis was confirmed by the results for the dependence of the concentration of the gel upon the concentration of latex (Figure 3.4). The gel formed during the first 5 seconds had a considerably higher concentration than that which formed subsequently. The fall in the concentration of the gel was also noticeable during even longer deposition times (Figure 3.5). After the formation of the first layer of deposit, further diffusion of the electrolyte was already occurring through this layer because of the concentration gradient, but considerably more slowly[60], and subsquently resulting in the formation of a less coherent and looser gel.

As shown in Figure 3.4, as the concentration of the latex increases, the difference in concentration between gels obtained after different deposition times is reduced. Eventually these gel concentrations coincided on reaching a latex concentration of ca. 67%. This almost corresponds to dense packing of monodispersed spheres (74%), suggesting that the concentration of the deposit may depend only slightly upon the total solids content of the latex at high TSC. Hence, Sandomirskii et al. argued that this dependence is considerably less marked, (Figure 3.5), because an increase in the TSC of the latex makes it much more likely that a diffusing ion will collide with a rubber particle. Therefore, with latex of very high TSC, the gel concentration will probably be equal to that of the deposit obtained under the same conditions, and will not depend upon the deposition time.

It has also been noticed that, as the TSC of the latex

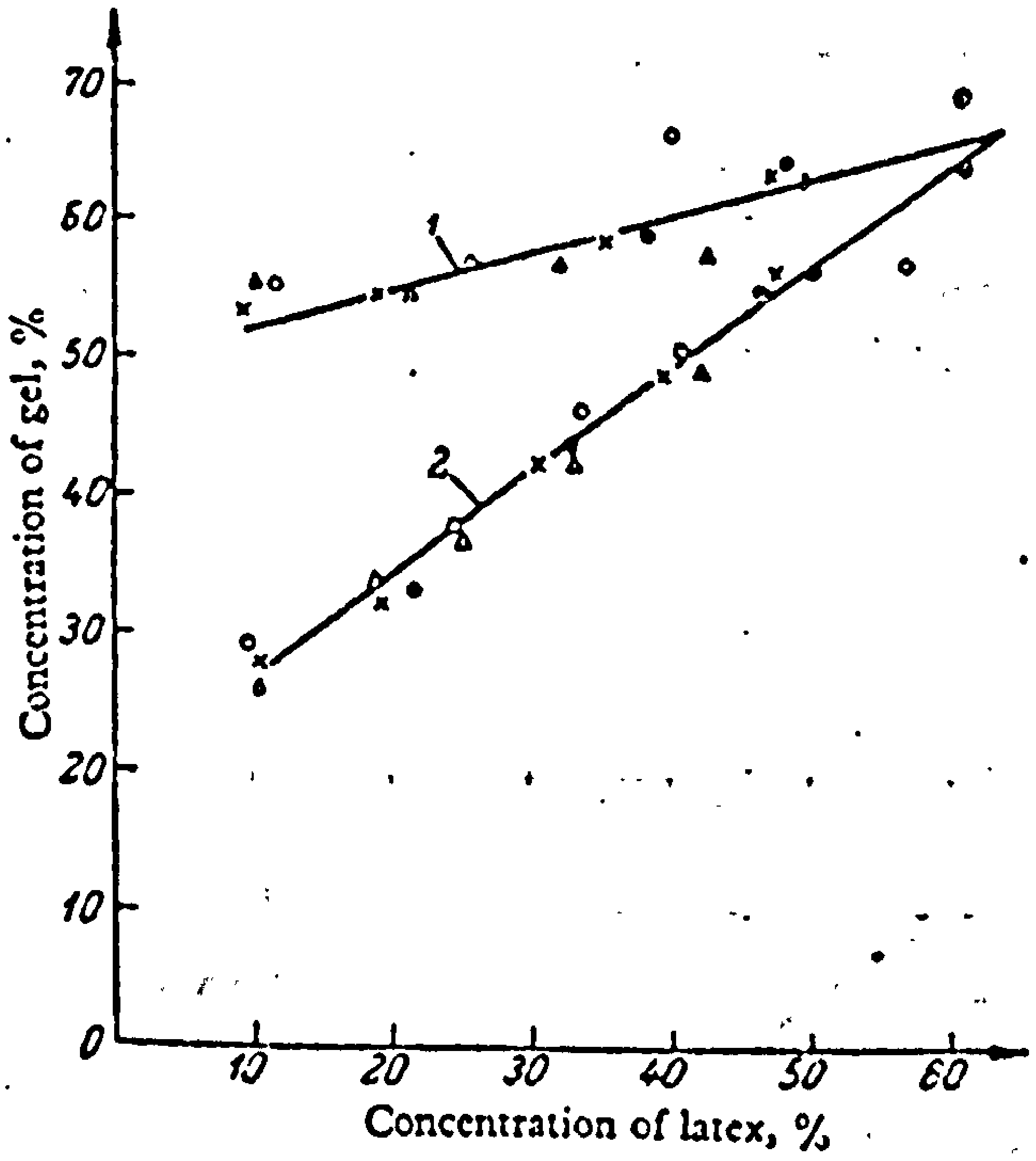


FIG.3.4—*Effect of the concentration of the latex and the deposition time on the concentration of the gel formed.* ●—*Qualitex*; X—*latex L-4*; Δ—*latex L-7*; o—*butadiene-styrene* (50:50) *latex*; 1—*time of deposition 5 seconds*; 2—*time of deposition 5 minutes.*

Ref.(57)

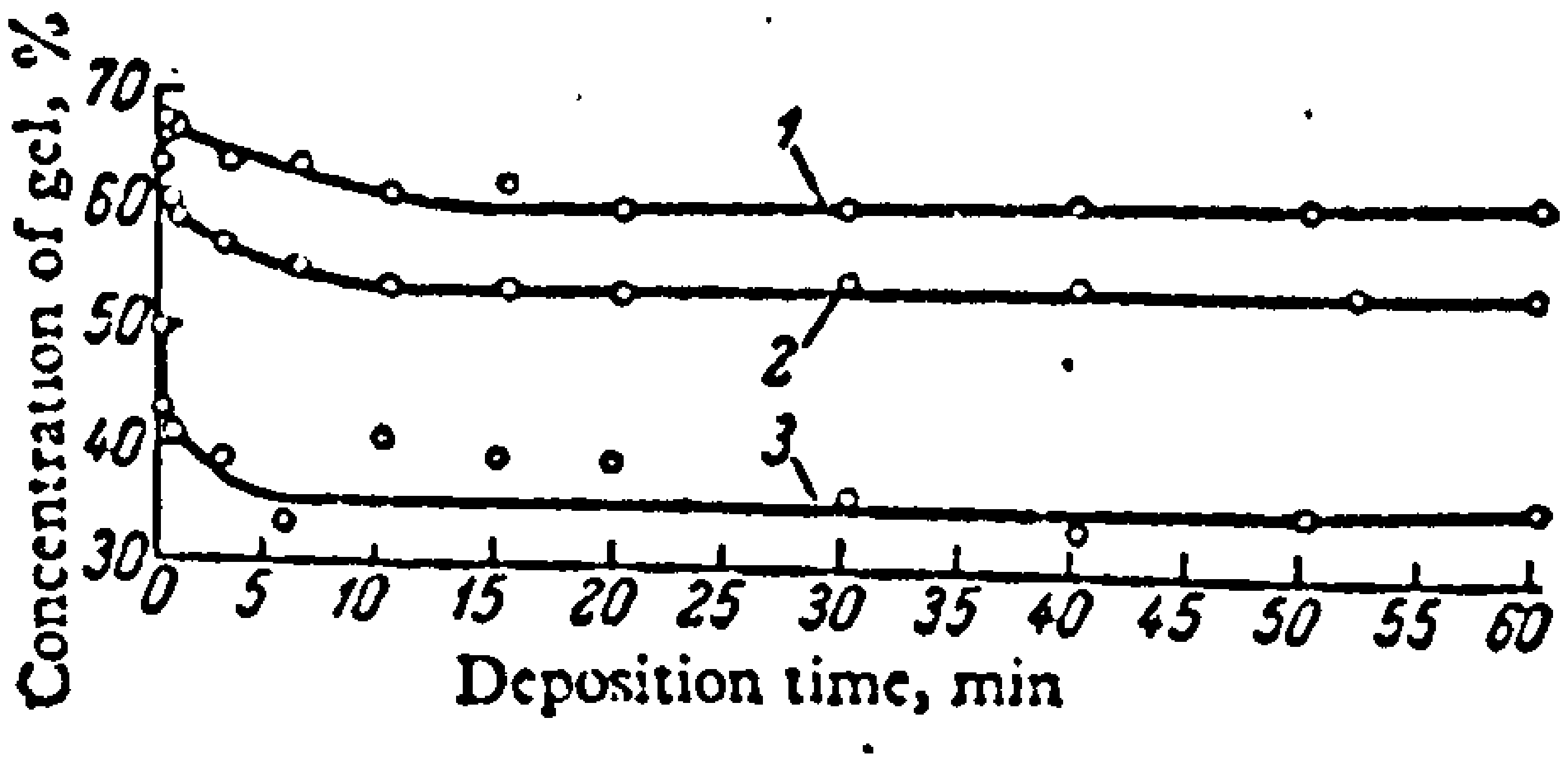


FIG.3.5—*Effect of the deposition time on the concentration of the gel*: 1—*Qualitex*; 2—*latex L-4*; 3—*butadiene-styrene latex.*

Ref.(57)

is increased, the concentration of protective substances also increases, as a result of which a greater number of electrolyte ions are needed to neutralise them. Consequently, the rate of deposition of a wet gel ($gcm^{-2}s^{-1}$) from concentrated latices should be reduced. However, a higher rate of deposition was generally observed the higher the concentration of the latex. As predicted, the amount of rubber deposited decreased with increasing level of soap (Figure 3.6).

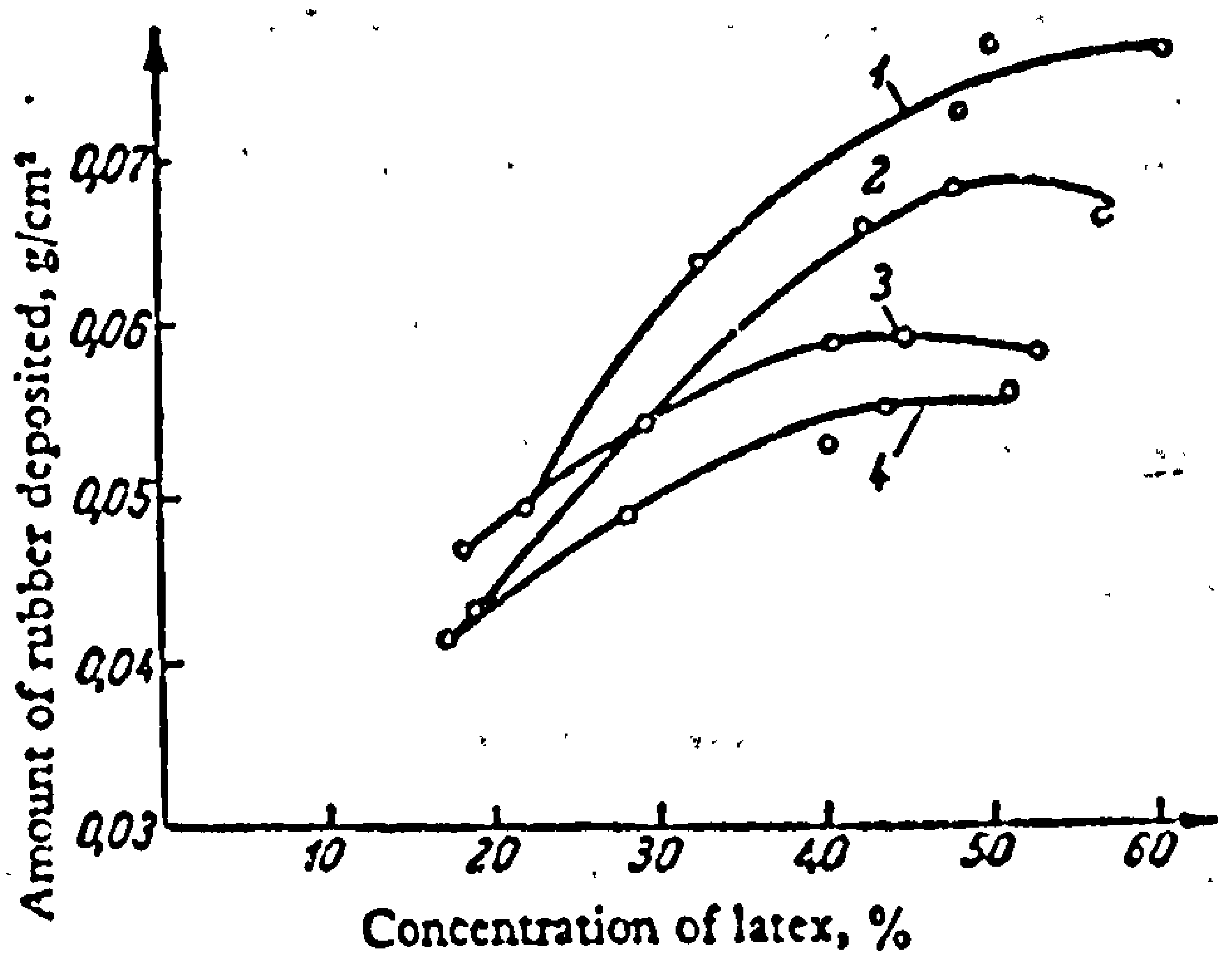


FIG.3.6–*Effect of potassium oleate on the rate of ionic deposition from Qualitex : 1, initial latex; 2, 1.75% of potassium oleate; 3, 4% of potassium oleate; 4, 6% of potassium oleate.*

Ref.(57)

Sandomirskii et al.[57] found that strongly stabilised latices behave somewhat differently. An example of such a latex is SBR which contains excess stabiliser. It is said that, when a sufficient additional amount of the protective substance was introduced into the latex, the rate of deposition increased. This is because the protective substance in the serum combines with a considerable portion of the electrolyte which has diffused into the latex. Accordingly, the firm gel structure which normally causes the rate of deposition to decrease is not formed. Unfortunately, as stated earlier, the present author has found it difficult to follow these arguments put forward by Sandomirskii and his coworker. However, two factors seem to be important, namely:

(i) excess soap requires more calcium and therefore slows down the rate of deposition;

(ii) some mechanisms speed up deposition when excess soap is present; it is unclear from his paper what these mechanisms are.

Probably the most versatile and satisfactory equation is that given by Stewart[44]. This equation was developed on the basis of a mathematical model which predicts the rate at which bivalent cations diffuse through a coalescing latex film. Also considered in the model are important variables such as the TSC of the latex, the quantity of the original emulsifier in the latex, the coagulant concentration, the pH of the latex, the type of added surfactants, and the type of contained polymer.

In general, the theory seems to predict correctly the effects that these various factors have upon the relative rates of deposition when polychloroprene latices come into contact with the coagulant. Thus it was found that, between 65 and 45% TSC, the TSC had no apparent effect upon film thickness, since the quantity of soap per unit volume of gel in a close-packed gel structure is not changed by dilution of of the latex.In this case, film formation is controlled solely by the diffusion rate of calcium ions through the coagulated film.

At TSC's below 30%, it was found that the rate of film formation increased with decreasing solids content. This surprising result was attributed to the formation of a very soft and loose deposit compared with the approximately closed-packed structure which forms with a high solids latex. It was argued that this open structure then allows calcium ions to diffuse much more rapidly through the deposit, and hence a higher rate of deposition is achieved. The theory, however, assumes that, immediately upon coagulation, the latex particles become arranged in a close-packed structure.

The theory predicts that changing the coagulant concentration from 1.34 M to 0.67 M or to 2.01 M would cause changes in the rate of film formation of about - 18% and + 12% respectively. Experimentally, the changes were found to be - 14% and + 9% respectively. Stewart thought the differences were the consequence of concentration-dependence of the diffusion coefficient; in the theory, the diffusion coefficient is assumed to be independent of concentration of coagulant.

An exceptional case also arises when a large quantity of surfactant is present in excess of the amount required completely to cover the surface of the latex particles. It would be expected that the added surfactant would cause a slight decrease in the rate of film formation as the diffusing calcium ions precipitate. However, there was actually observed an increase of more than 50%. The increase was said to be the result of hinderance of coalescence by the excess precipitated soap in the aqueous phase of the latex. A similar effect was observed when certain surfactants other than sodium rosinate were added to the polychloroprene latices.

Changes in the pH of the latex should quantitatively have the same effect as changes in the amount of surfactant present in the latex. However, Stewart found that the issue was complicated by the fact that, above a pH 11.0, calcium hydroxide precipitates together with calcium rosinate. Consequently, this reduces the diffusion of calcium ions through the film, and hence the deposition rate is markedly decreased. On the other hand, at a pH below 10.0, the rosin acid which is now present acts to destabilise partially the latex thus encouraging coalescence. Therefore, since less calcium rosinate now precipitates, the rate of film formation increases. Stewart suggested that it would require a modification of the theory in order to be able to predict quantitatively the effect of pH changes upon deposition rate.

Figure 3.7 shows the experimental results for the latices of polymers having a very broad range of viscoelastic behaviour from " high gel " (polymer A) to a very soft "gel " (polymer D). From these results it appears that the higher is the relaxation modulus of the latex particle, as expressed by E and m, the greater is the rate of deposition. This is what would be expected, since a low relaxation modulus corresponds to an increased tendency to flow, encouraging the the particles to coalesce rapidly. As the latex particles coalesce, there is a decrease in the cross-sectional area of serum through which the calcium ions diffuse. For soft polymers such as polymer D, an almost impermeable rubber barrier is eventually set up.

From the first term on the right side of Equation 3.18, it would be predicted that, for the diffusion of calcium ions through a close-packed assembly of non-deformable spheres, the boundary of the gel or precipitated calcium soap, θ, should follow the expression,

$$\theta = 2\alpha (Dt)^{\frac{1}{2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad 3.19$$

where $\alpha e^{\alpha^2} \mathrm{erf}(\alpha) = 0.26c / b\pi^{\frac{1}{2}}$ 3.19a

and $D = D_0 / \tau \quad (\tau = 1.26)$ 3.19b

Equation 3.19a takes into account the fact that the volume fraction of serum through which the calcium ions diffuse is 0.26, while Equation 3.19b, accounts for the additional distance that the unprecipitated calcium ions must travel in order to pass around the rubber spheres. Equation 3.19 then represents the greatest film thickness that one can expect to obtain when a high solids latex containing non-deformable particles comes into contact with a coagulant. Any coalescence of the latex particles will cause a reduced film thickness. The straight line in Figure 3.7 then gives the theoretical maximum film thickness for deposition from a latex of non-deformable spheres with concentrations of soap and coagulant as shown. It is seen that the latex containing a highly-gelled (and therefore non-deformable) rubber, obeys the theoretical prediction surprisingly well.

Finally, it must be emphasised that this theory, in its original form, may not be able to predict correctly the behaviour during an actual coagulant dipping process. This is because, in an actual coagulant dipping process, the coagulant concentration on the former decreases with time. Stewart deliberately maintained the coagulant concentration on the former constant in order to simplify the interpretation of the results.

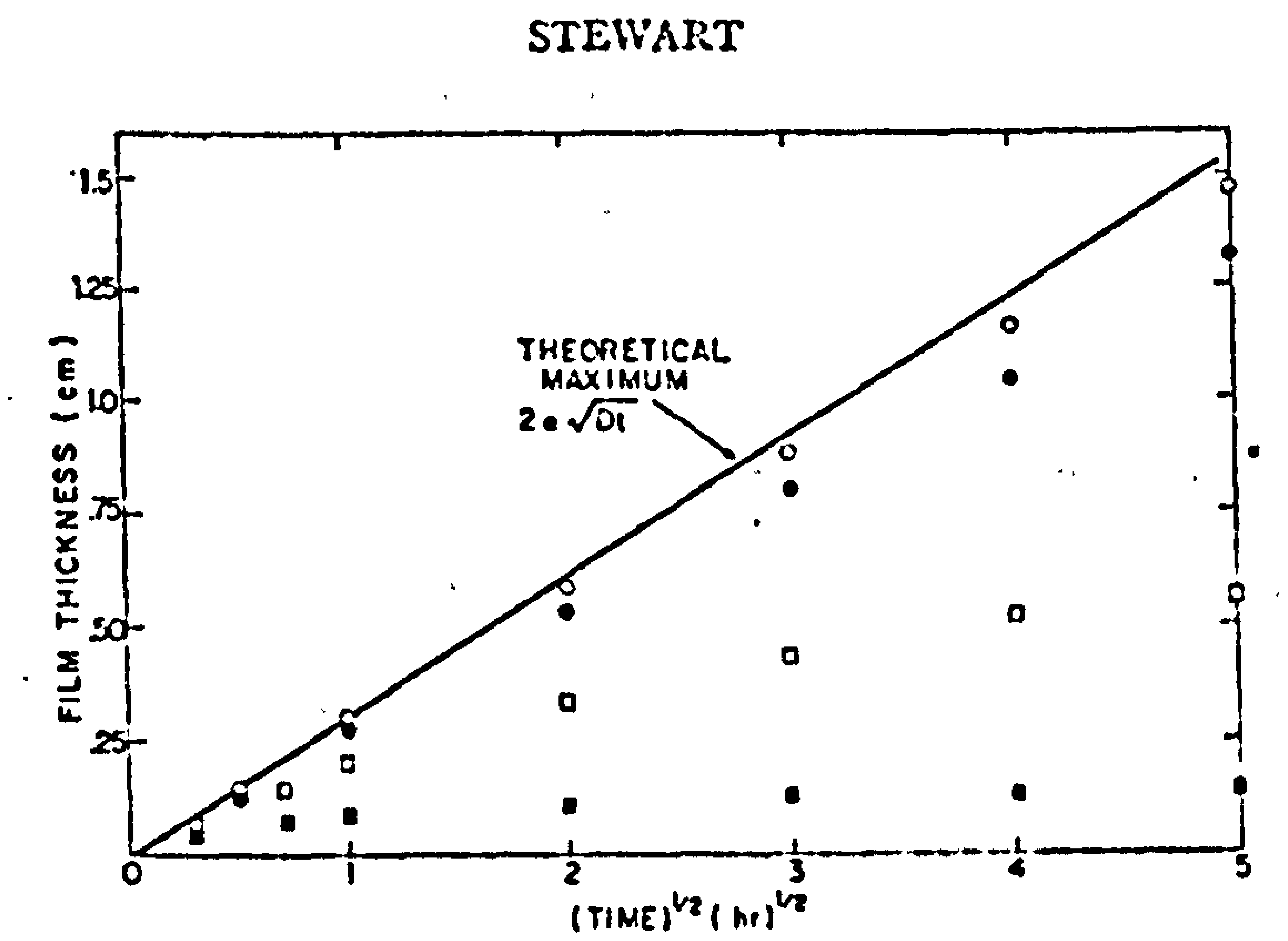


Fig.3.7. Film thickness as a function of (time)$^{1/2}$ for polychloroprene latices with a = 1.34 M; 2b = 0.118 M. (○) Polymer A; (●) polymer B; (□) polymer C; (■) polymer D.

Ref.(44)

3.4 Syneresis

In the gelation process, the rubber particles coalesce and produce a network structure of rubber filaments which enclose the serum. After gelation, these filaments may continue to contract spontaneouly such that the serum contained between them is squeezed out into the surrounding medium. This process of spontaneous contraction of the wet gel and expulsion of the serum is known as " syneresis ".

Syneresis is a recognised phenomenon in the latex-dipping industry and is important in that it determines the strength of the wet gel at the various stages of production of the article. The contraction of the wet gel results in an increase in its strength[37,61,62]. This is important from the technological point of view, because after dipping the wet gel is subjected to stretching and other mechanical manipulations. In addition, syneresis promotes the rapid drying of the wet gel because salts and other soluble materials are expelled with the serum because they are dissolved in it. During the dipping process, syneresis also has an influence upon the rate of deposition of the rubber particles on the former.

Despite the industrial importance of syneresis, very little has been published on this topic. Futhermore, the small amount of literature which has been published is confusing and often conflicting. This is partly because there has been no agreed standard definition of syneresis or the method of determining the rate of syneresis of a latex gel. In many cases, the process of syneresis is often confused with evaporation or leaching. A further complication is that syneresis may occur inwards towards the former and / or outwards away from the former. Generally the rate of syneresis is determined by measuring the total solids content of the wet gel as a function of time.

Russian papers on this subject often confuse syneresis with extraction and drying[40,61-67]. For example, Savinkova et al.[61] have shown that the medium in which syneresis occurs has a considerable effect upon the course of the process, (Figure 3.8). It is seen that syneresis generally occurred very rapidly during the first 2 to 3 hours, and then slowed down considerably. The results also showed that syneresis occurred more slowly in air than in water. This agrees well with the observations made by Voyutskii et al.[63] and by Sandomirskii[66]. Syneresis was also found to occur faster in hot water than in cold water. It was suggested that the heat from the hot water assits the mutual adhesion of the rubber particles, and hence syneresis. Syneresis occurred rapidly in xylitan, triethanolamine and ethly alcohol, apparently because of the dehydrating action of these compounds. Triethanolamine acted particularly strongly in the case of the natural rubber latex gel. Also, syneresis occurred much more slowly in a solution of caustic soda than in water. This was said to be a consequence of the peptising action of the hydroxyl ions.

Voyutskii et al.[63] have found that the greater is the amount of stabiliser in the latex, the slower is the rate of syneresis of the gel. It was also shown that the rate of syneresis decreased linearly with increasing degree of coverage of the surface of the latex particles with stabiliser.

According to Lazareva et al.[64], the rate of syneresis of latex gels in water at 60°C decreased with increasing time of maturation of the latex mix. They have suggested that this was a consequence of the formation of crosslinks within the latex particles during maturation. Crosslinking of latex particles was said to reduce the mutual adhesion of the rubber particles and hence syneresis.

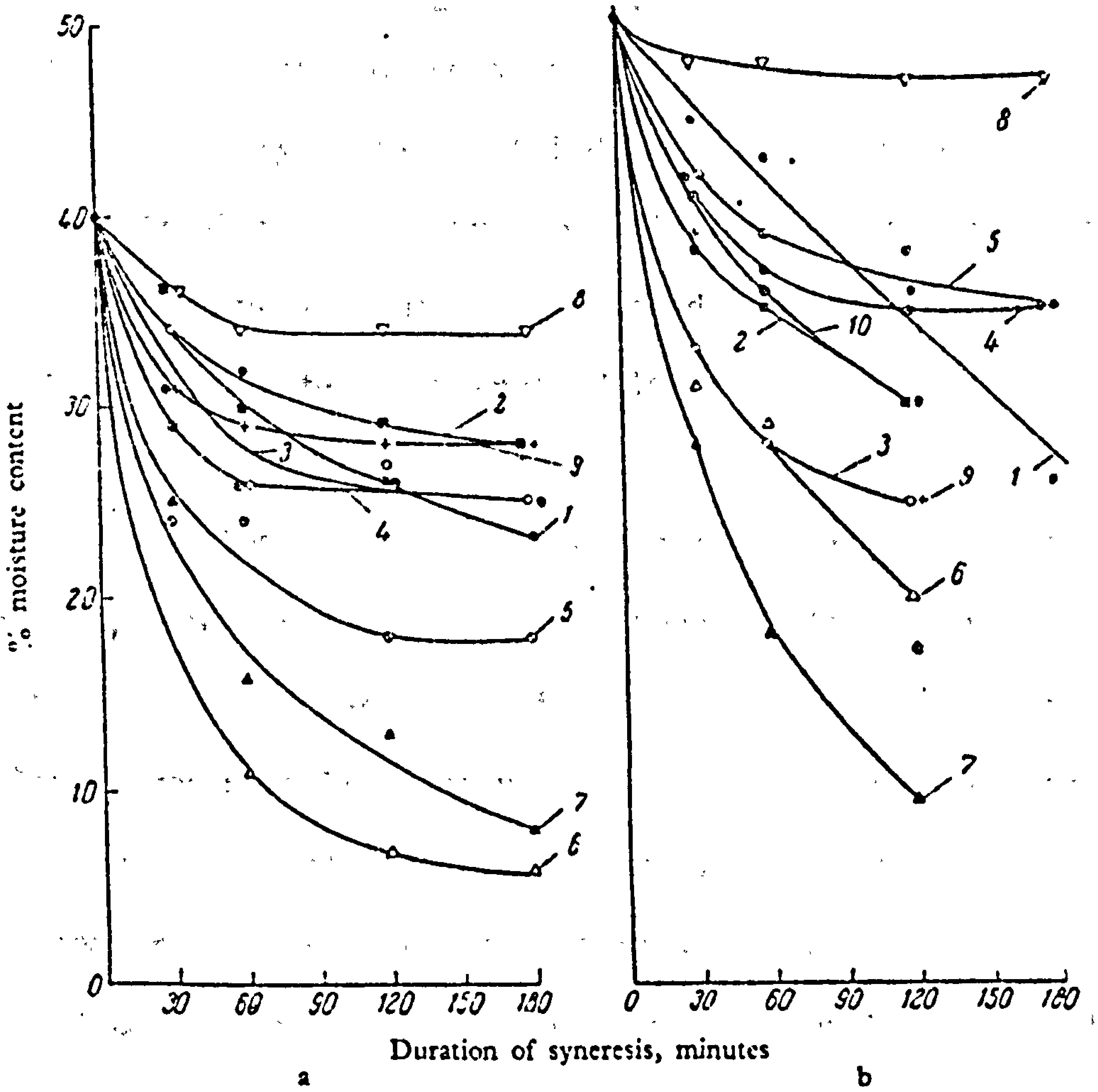


FIG. 3.8 *Syneresis of gels prepared from : (a) Qualitex and (b) synthetic polychloroprene latex in various media : 1—air ; 2—tap water ; 3—hot water (50 - 60 C) ; 4—a 10% solution of acetic acid ; 5—a 2% solution of hydrochloric acid ; 6—triethanolamine (50° - 60°C) ; 7—xylitan (50° - 60°C) ; 8—a 10% solution of caustic soda (50° - 60 C) ; 9—a 10% solution of barium chloride ; 10—ethyl alcohol.*

Ref.(61)

As has been stated earlier, the Russian works reported here have confused the spontaneous contraction of the gels with the processes of extraction and drying. As a consequence, very little understanding has been achieved of the kinetics and mechanism of the syneresis of latex gels.

3.5 Mechanical properties of wet latex gels

A knowledge of the mechanical properties of the rubber deposit both in its wet and dry state is of industrial importance. The wet gel formed in industrial processes must be able to sustain a certain amount of mechanical handling without being damaged or distorted.

The term " wet-gel strength " is often used to denote the tensile strength of the freshly-set latex film. It is well-known that the tensile properties of wet gels are far inferior to those of the dried product, often by a factor of one hundred. The inherent weakness of the wet gel imposes a severe limitation not only upon the applicability of many latex processes but also upon the possibility of measuring the tensile properties of the gel. Hitherto, there has been no adequate method of measuring these properties simply because the deposit is so weak that it cannot readily be removed from the surface on which it is deposited.

Two major methods have been reported for the measurement of the wet-gel strength of latex deposits. The first, developed by Medalia et al.[37], is the so-called " paper-dip " method. An absorbent paper of low wet strength, impregnated with calcium nitrate, is dipped into the latex to produce a latex deposit on both sides of the paper. The strip of paper, which may be of dumbbell shape, is dipped into the latex for 30 seconds and then removed together with the adhering wet gel. The film is rinsed in water before measuring its tensile properties.

Unfortunately, the paper-dip method does not simulate closely the conditions under which wet gels are produced in industrial latex coagulant-dipping processes, since the tissue paper and the serum are sandwiched between the two layers of the deposit. The effect of these composite structures upon the test-piece, and hence upon the wet-gel strength of the film, is not obvious. Despite this, the paper-dip method is the most widely-reported method in the literature.

The second method was developed by Golberg et al.[68]. The wet-gel deposit is mounted on a special device which produces two-dimensional deformation of the gel on inflation. The pressure require to inflate the gel is measured by a U-tube manometer. The stress is calculated from the following relationships:

$$\sigma = \frac{P\,{}^{3}R_o}{10^4\,2\theta_o} \quad \text{..........................} \quad 3.20$$

$$\lambda = \sqrt[3]{\frac{V_\tau}{V_o}} \quad \text{..........................} \quad 3.21$$

where σ is the stress in two-dimensional deformation calculated on the actual cross-sectional area; P is the air pressure in the inflated gel; R_o is the radius of the inflated sphere prior to deformation; θ_o is the thickness of the uninflated gel; λ is the elongation (strain) ratio in two-dimensional deformation; V_τ is the volume of air in the inflated gel; and V_o is the volume of air in the inflated gel prior to deformation. This method has not been widely used, presumably because it is difficult to prepare the test-piece and also to measure all the quantities in the above equations.

It has been reported that the wet-gel strengths of deposits are affected by the degree of ageing or storage of the latex[40,62,69], the concentrations and types of added soaps[36,40,63,66,67], the degree of prevulcanisation of the latex particles[36,37,58,64], the molecular structure of the contained polymer[36,37], the nature of the compounding ingredients, the dilution of the latices, and the degree of drying of the deposit[37]. It has also been found that the wet-gel strength of the deposit is very dependent upon the nature and temperature of the aqueous medium in which the wet gel was immersed during syneresis[40,61,62].

Medalia et al.[37] have shown that the wet-gel strengths of natural rubber latex gels are superior to those from latices of the butadiene-based copolymers, and that the Neoprene Types 571 and 735 are intermediate between these two extremes. The wet-gel strength of the gel from Neoprene Type 572 is slightly higher than that of the gel from natural rubber latex. Medalia et al. attributed the higher wet-gel strength of gel from Neoprene Type 572 to the higher crystallinity of the polymers. It was also found that the wet-gel strength of natural rubber latex gel is about 7% of that of the dry film. For the butadiene-based copolymers and nitriles, the fraction is about 12%.

The tensile strength and elongation at break of wet gels prepared from prevulcanised natural rubber latex have been found to decrease with increasing degree of vulcanisation[37]. The reason given for this observation was that, as the rubber within each polymer particle becomes more crosslinked, so the interparticle adhesion decreases. In contrast, Hu You-Mo[58] has found that the tensile strength of the wet gels initially increases as prevulcanisation progresses; however, he agrees that it subsequently decreases. This phenomenon was explained as arising from a balance of two factors, namely, the interdiffusion of chain segments in coalesced particles and the re-distribution of crosslinks within these coalesced particles. However, a critical analysis of the results by the present author shows that several other factors were not taken into consideration when the conclusions were drawn. These factors include the thickness of the deposit, the change in the latex gel properties during heating, the presence of calcium ions in the gel, and the extent of syneresis.

Shepelev et al.[40] have found that the ageing of polychloroprene latex reduces the wet-gel strength and the elongation at break of the gel. The reduction in the strength and elongation at break of the gel was attributed to the formation of crosslinks of the polymer molecules, such crosslinking reducing flexibility and impeding coalescence of the particles into a strong gel.

Figure 3.9 shows the effect of syneresis upon the strength of wet gels from various latices[61]. The gel initially has little strength, but as syneresis progresses the wet-gel strength increases considerably, especially if the medium is xylitan or hot water.

The curves in Figure 3.10 show the strengths of the same gels as functions of moisture content[61]. The gel strength at any given moisture content was greatest when syneresis was conducted in hot water. The latter was said to assist the removal of the adsorbed stabilisers and thus speeds up the adhesion of individual globules.

Voyutskii et al.[63] have shown that the tensile strength and elongation at break of the wet gels decrease with increasing stabiliser content. This was explained as being a consequence of the increase in the degree of coverage of the particle surface by the stabiliser and also of the increase in the moisture content of the gel. It was also reported that the wet gels obtained from latices containing ammonium

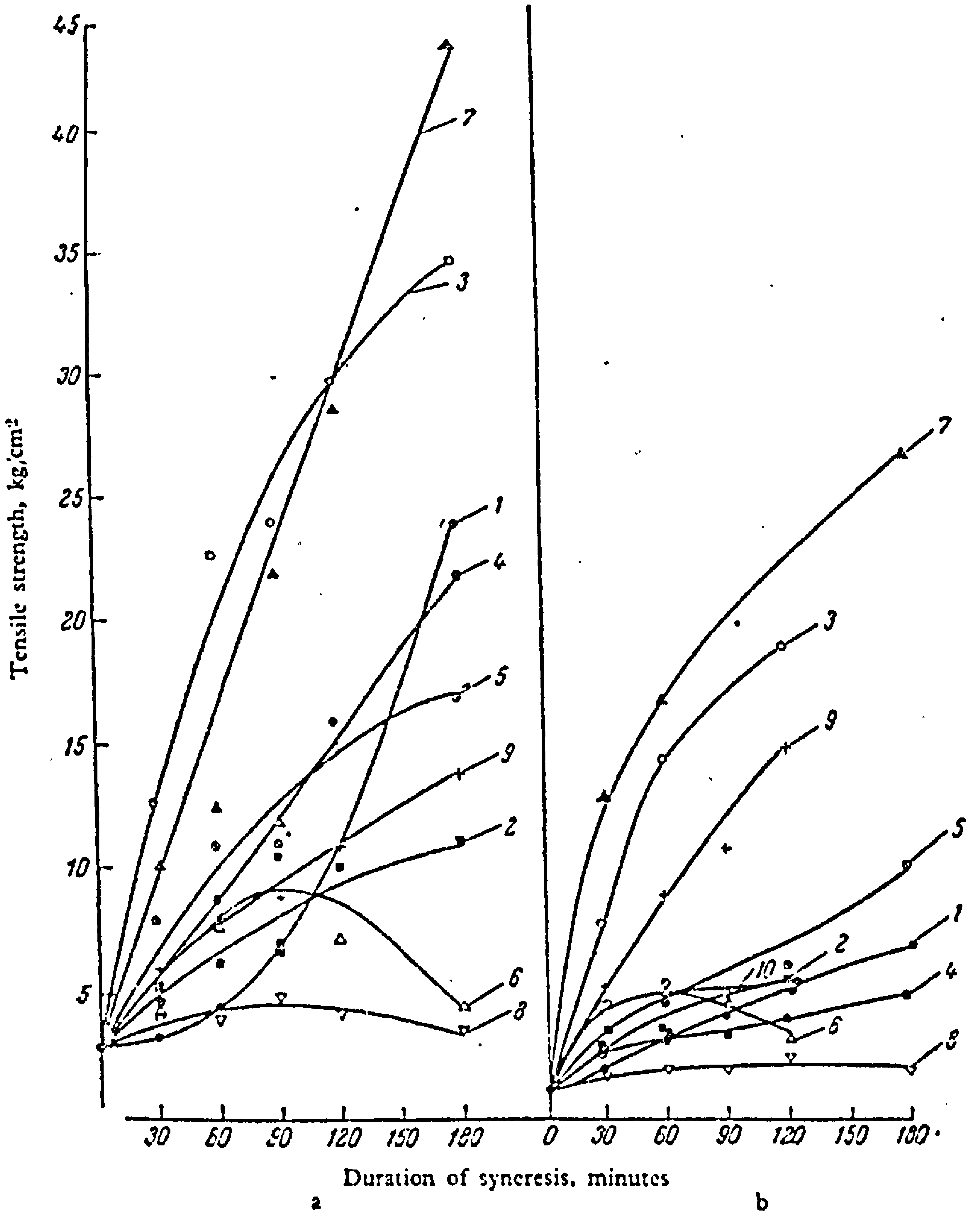


Fig. 3.9 ·*Tensile strength of moist gels from (a) Qualitex and (b) synthetic polychloroprene latex, subjected to syneresis in various media in relation to the duration of the process.*

ref.(61)

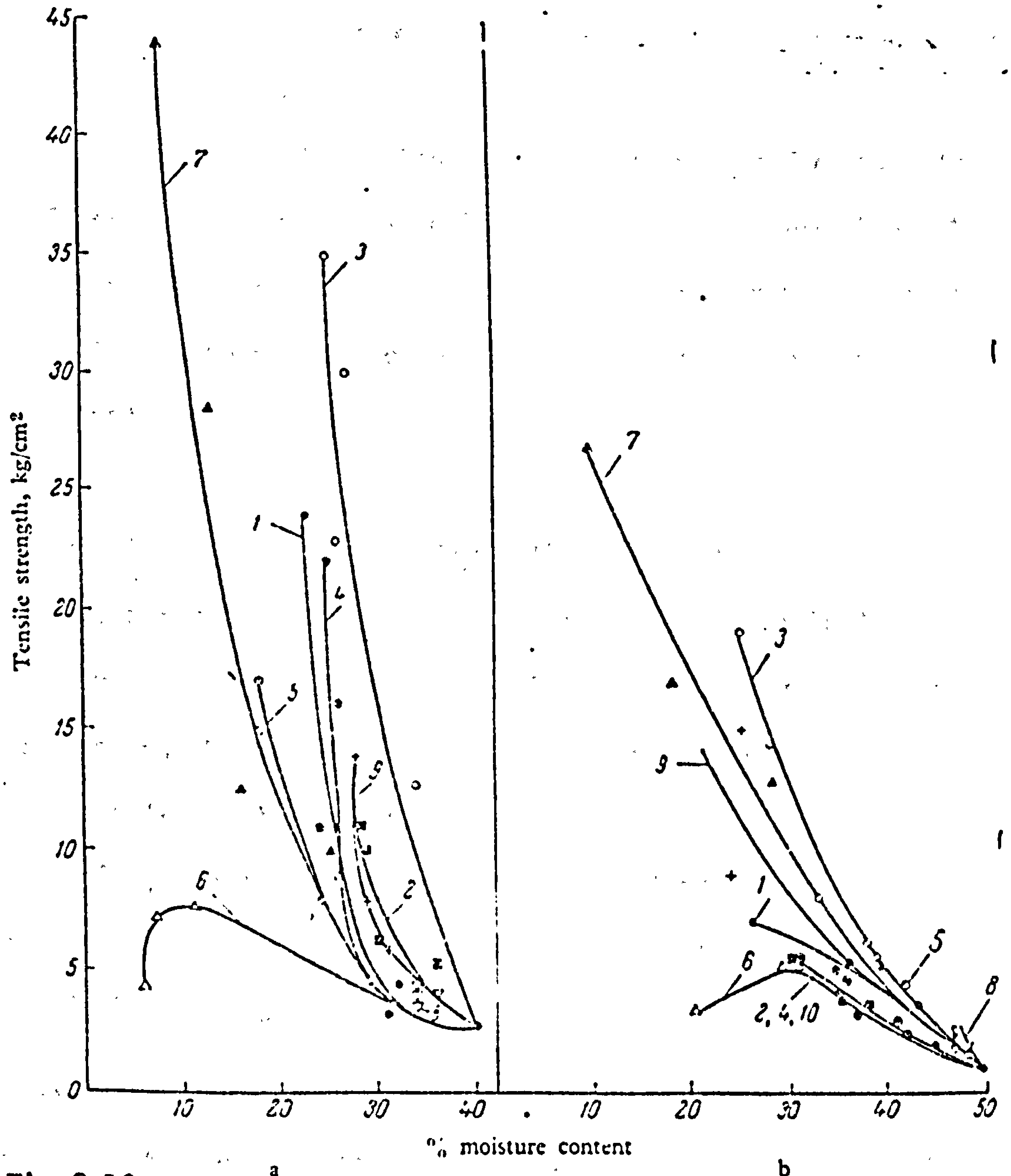


Fig 3.10 *The tensile strength of moist gels from (a) Qualitex and (b) synthetic polychloroprene latex subjected to syneresis in various media in relation to moisture content of the gel.*

ref.(61)

fatty acid salts as stabiliser had relatively high tensile strengths and moduli but low elongations at break compared to those from latices containing a sulphonate (Nekal) as stabiliser. It has also been found that the addition of a non-ionic soap such as an alkyl phenoxypolyoxyethylene ethanol (Igepal CA - 633) to a latex of large particle size results in weakening of the wet gel[37].

Most of the publications reviewed above merely state the effect of certain important variables upon the gel properties. The reasons for and mechanisms underlying the observations are hardly discussed. It has therefore to be concluded that the subject is but poorly understood at present.

3.6 Mechanical properties of dry rubber deposit

Much has been published concerning the mechanical properties of the dry rubber deposits which have been obtained by the coagulant-dipping process. The mechanical properties of dry deposits have been found to be affected by the type and concentration of coagulant used [32,33,35,70-74], the types and concentration of added soap[37,63,75-77], the pH of the latex[78,79], the degree of prevulcanisation of the latex [36,37,58,80-83], the type of contained polymer[36,37,84,85], the degree of shrinkage upon drying or stretching[37,85], the degree of maturation[64], the ageing or storage of the latex[40,86], and the thickness of the deposit[62,87]. Much of the above work is not strictly related to this study, and therefore only the more relevant work will be discussed further.

Thorsrud[35] has made systematic studies of the influence of salts upon the properties of dry deposits obtained by dipping. He found that the tensile strength of the deposits is considerably reduced, especially by salts of bivalent cations. On the other hand, the tensile strength is only slightly affected by ammonium salts. The results generally agreed with those of other workers[32,33,35,70-74]. The deposit used in the above work had been leached, but nothing was said about the effectiveness of leaching.

The dependence of the tensile strength of dipped latex film upon its thickness was such that it was found to pass through a maximum at a thickness of approximately 0.2 mm[62,87]. The reason for this was said to be traces of koalin which had been added to the coagulant; these caused micro-defects in the deposit and weakened the cross-section of the specimen, particularly for thinner deposits. However, it was found that the elongation at break was virtually independent of the thickness of the film.

The effect of increasing the degree of soap coverage of the particle surfaces of polychloroprene latex upon the mechanical properties of the gel obtained by coagulant dipping has also been reported[63]. It was found that the tensile strength and elongation at break decreased substantially while the modulus decreased only slightly.

3.7 Structure of gel

No published reports have been found concerning the internal structures of wet gels. However, electron microscopy has been used to study the surfaces of gels after partial or complete drying has occurred [88-90].

Guzman[91] has attempted to develop a simplified mathematical model which would give some representation of the structure of the gel in relation to its strength. Unfortunately, the model was not able to predict the experimental results with any degree of success.

CHAPTER 4

MATERIALS AND EXPERIMENTAL PROCEDURES

4.1 Materials

4.1.1 Natural rubber latex

The latex used in this work was ' Qualitex ', a high-ammonia centrifuged natural rubber latex concentrate supplied by LRC Products Ltd.. The properties of this latex are shown in Table 4.1. The determination of these properties was made in duplicate and the average values are recorded. The total solids content and dry rubber content were determined by the procedures specified in BS 1672 : 1972, alkalinity by the procedure specified in BS 1672 : Part 1 : 1950, and mechanical stability, KOH number and VFA number by the procedures specified in BS 1672 : Part 2 : 1954.

Table 4.1

Properties of ' Qualitex ' latex used in this investigation

total solids content, %	61.1
dry rubber content, %	59.6
alkalinity, g ammonia per 100 g water	1.59
mechanical stability time, secs.	945
potassium hydroxide number (KOH No.)	0.65
volatile fatty acid number (VFA No.)	0.14
pH	10.52

4.1.2 Potassium fatty-acid soaps

The following fatty-acid soaps were used, the numbers in parentheses indicating the number of carbon atoms present in the alkyl chain of the soap: laurate (11), myristate (13), palmitate (15), and stearate (17). These soaps were prepared from the corresponding free acids (specially-pure grades supplied by B.D.H. Chemicals Ltd.) by neutralisation with a 10 % aqueous solution of analar potassium hydroxide. The final soap solutions were either of 10 % or 5% concentration. The pH was adjusted to between 9.5 - 10.0 in order to suppress the hydrolysis of the soap to the acid soap or free fatty acid. The less soluble palmitate and stearate soaps were prepared as 5% aqueous solution, and were warmed before use to 50°C to ensure complete dissolution of the soap.

4.1.3 Ethylene oxide-fatty alcohol condensates

The condensates used in this work were of the form $RO\ (\ CH_2CH_2O\ )_i\ H$, where R was approximately equivalent to $C_{17}H_{35}$, and the average value of i varied from 6 to 60. These condensates were supplied by ABM Chemicals Ltd. and have the properties shown in Table 4.2. The condensates, prepared as 10 % aqueous solutions, were used without further purification.

Table 4.2

Properties of ethylene oxide-fatty alcohol condensates

commercial designation	mole ratio ethylene oxide to hydrophobic moiety	HLB value	appearance of 10% aqueous solution at room temperature
Texafor A6	6	10.4	thick white paste
Texafor A10	10	12.9	slightly cloudy soln.
Texafor A14	14	14.4	clear viscous soln.
Texafor A1	24	16.3	clear viscous soln.
Texafor A30	30	16.9	clear viscous soln.
Texafor A45	45	17.8	clear viscous soln.
Texafor A60	60	18.3	clear viscous soln.

4.1.4 Thickening agents

The thickening agents used were methyl cellulose M2500 and methyl cellulose M450 supplied by British Celanese Ltd. The number following the letter M represents the viscosity in centipoise of a 2% aqueous solution of the substance at 20°C. Solutions were prepared by dissolving the powdered methyl cellulose in distilled water to form a free-flowing 5% solution.

4.1.5 Coagulant

The coagulant used was anhydrous calcium chloride supplied by Anglia Chemicals Ltd.. The coagulant was made up into solutions of different concentrations as shown in Table 4.3. In each case, the ratio of calcium chloride to water was 0.59 : 1. A small amount (0.1%) of cetyl trimethyl ammonium bromide (CTAB) was added to assist in the wetting out of the former.

Table 4.3

Composition of coagulant solutions

(figures in the table are parts by weight)

composition	coagulant solution number				
	C15	C20	C25	C30	C35
$CaCl_2$	15	20	25	30	35
H_2O	25.2	33.6	42	50.4	58.8
IMS	59.8	46.4	33	19.6	6.2
CTAB (10% soln.)	1.0	1.0	1.0	1.0	1.0
solution concentration, %	15	20	25	30	35

4.1.6 Ammonium caseinate

This was prepared by dissolving the casein in 0.6% ammonia solution to form a pale brownish 5% solution. Heat was applied gently to help dissolve the casein.

4.1.7 Ammonium acetate

This was prepared from pure acetic acid by nuetralisation with a 25% ammonia solution to form a 10% solution.

4.1.8 Ammonium sulphate

This was prepared from pure concentrated sulphuric acid by nuetralisation with a 25% ammonia solution to form a 10% solution.

4.1.9 Other materials

All other materials used in this work were of analytical reagent grades wherever possible.

4.2 Determination of latex pH

In all pH measurements, a Philip digital pH meter, model PW 9409 was used. The pH meter was calibrated before use, and all measurements were made at room temperature.

4.3 Determination of latex viscosity

The viscosity of the latex compounds was determined at room temperature using the Haake Rotovisko viscometer (a concentric cyclinder viscosmeter). The latex compound, approximately 40g weight, was contained in a concentric cyclindrical cup and its viscosity determined from the torque which developed between the cyclindrical cup and the rotated cyclindrical bob. A range of shear rates were used in order to accommodate the wide range of viscosities of the latex compounds used.

4.4 Dipping procedure

4.4.1 Preparation of latex compounds

The requisite weight of the compounding ingredient was added to the latex with gentle stirring. The latex compound was then diluted to the required total solids content and allowed to mature for at least two days at 25±1°C. Thus, some apportunity was given for adsorption equilibrium with the compounding ingredients to be approached. The latex was strained through cheese cloth, and the pH and viscosity determined. Any air bubbles formed on the surface of the latex were removed with filter paper.

4.4.2 Formers

The formers were glass plates of dimensions approximately 10 x 1.7 x 0.38 cm and 10 x 3 x 0.38 cm. The rate of deposition of rubber was found to be independent of the size and shape of the glass formers used in this work. The formers were cleaned thoroughly with soap solution, then washed with distilled water and dried in an oven at 70°C.

4.4.3 Dipping

The dipping experiments were carried out using a ' Cotswold ' hydraulic dipping machine. The speeds of immersion and withdrawal of the former were 80 and 48 cm per minute respectively. The former(s) remained stationary and the latex moved vertically upwards on immersion and downwards on withdrawal. Several formers could be dipped simultanenously. The advantages of such an arrangement are:

(i) it allowed more process variables to be investigated;

(ii) it gave good discrimination between such variables at any given dwell time.

Preliminary work showed that the method of preparing the coagulant -coated former affected the rate of deposition of rubber on the former. To eliminate such variation, the following procedure was adopted: The former at a temperature ca. 70°C was first immersed into the coagulant solution to a depth of approximately 9.0 cm and withdrawn. Excess coagulant solution was allowed to drip off and the volatile solvent was allowed to evaporate (assisted by the heat of the former) leaving a very viscous layer of coagulant on the former.

The temperature of the former was allowed to drop to near room temperature; this occured about 2 - 3 minutes after withdrawal from the coagulant solution. The former was then immersed into the latex and allowed to dwell for a predetermined time. The former was withdrawn, excess latex was allowed to drip off, the former was inverted, and the product dried in an oven at 70°C for a period of up to 3 hours depending upon the thickness of the deposit. The dry deposit was dusted with talc in order to prevent the rubber surfaces from sticking, stripped off gently from the former and retained for further evaluation.

4.5 Measurement of deposit thickness

The thickness of the deposit was determined using a Mercer gauge type 57. Five measurements, taken at regular intervals from the top to the bottom of the deposit of each surface, were recorded and the arithmetic mean taken as an estimate of the thickness of the dry deposit.

4.6 Measurement of deposit weight

The weight of the deposit was determined using an analytical balance having an accuracy of ± 0.0001g.

4.7 Measurement of total solids content of wet gel

The deposit was dried and the TSC calculated as follows:

$$\text{TSC of wet gel} = \frac{\text{dry weight of gel}}{\text{wet weight of gel}} \times 100\ \%$$

4.8 Measurement of syneresis

Gelation is usually accompanied by a spontaneous contraction of the gel, during which a volume of serum is exuded equivalent to the extent of contraction. As a consequence, the total solids of gel also changes. This secondary process is known as ' syneresis '. Syneresis can take place inwards towards the former and outwards away from the former. In practice, syneresis can be followed by either measuring the weight of the latex gel or the weight of the serum exuded out from the gel. Various methods of determining syneresis inwards and outwards have been attempted in this work. The two techniques that yielded the most satisfactory results are described below.

4.8.1 Syneresis outwards

A former was dipped into the latex as described in Section 4.4.3 for the requisite time of dwell. It was then withdrawn from the latex and, together with the wet deposit, placed in an enclosed bottle to prevent evaporation. It was removed from the bottle periodically, the outer surface of the gel was blotted to remove any exuded serum, and the whole was weighed. Any loss of weight as time elapsed indicated syneresis outwards.

4.8.2 Syneresis inwards

In this case, the wet gel was stripped from the former and excess serum on both the inner and outer surface was removed before weighing. The gel was stored in an enclosed bottle to prevent evaporation. The results obtained, in conjunction with those from section 4.8.1 above, enabled the rate of syneresis and the change in total solids of gel to be calculated.

4.9 Measurement of wet-gel strength of deposits

For this purpose, the wet-gel deposits were obtained by the procedure described in Section 4.4.3. The gel was carefully removed from the former, and placed on a plastic sheet in a closed container saturated with water. The gel was removed from the container after a predetermined time and dumbbell test-pieces were cut from it using a standard cutter. The remainder of the sheet was placed back into the container and its thickness and gel concentration determined at a later time. The dumbbell test-piece was immediately subjected to tension on the Instron machine at room temperature. The tensile strength was measured at a standard rate of jaw separation of 500 cm per minute. The determinations were carried out in duplicate on dumbbell test-pieces cut from the same piece of gel at 40 minutes and 4 hours after dwell respectively, and the tensile strengths were calculated.

4.10 Determination of concentration of calcium ions in gels by atomic absorption spectroscopy

4.10.1 Theory of atomic absorption spectroscopy

The atomic absorption spectroscopy is usually used to detect very small concentrations (i.e. parts per million) of metal ions. The principle of the method is based upon the characteristic absorption of electromagnetic radiation by atoms. The solution containing the metal atom to be analysed is first aspirated into a hot flame. Within the flame is produced a gaseous solution or plasma containing a significant concentration of elementary particles. The flame here serves the same purpose as a cell or cuvette in an ordinary spectrophotometer, i.e., the flame can be considered to be a dilute gaseous solution of the atomized sample held in place by the aspirator- burner. Radiation from a suitable source is passed through the atomized sample and into the slit of a spectrophotometer. The absorption spectrum of an atomized element consists of a relatively limited number of discrete lines at wavelengths which are characteristic of the element. The concentration of metal atoms can be determined by measuring the intensity of the absorption spectrum under controlled conditions.

A Pye Unicam SP 2900 atomic absorption spectrophotometer was used in the present work.

4.10.2 Setting of instrument

The atomic absorption spectrophotometer was set up as follows: Fuel (air/acetylene): 20 - 25; burner height: 9.0; lamp current: 5.0 mA; principal line: 422.67 nm; furnance temperature: maximum ash 1100°C, atomize 2850°C. The instrument was calibrated with standard calcium chloride solutions (0 - 5 ppm). The same batch of deionised water was used for the blank and for the preparation of the samples. The calibration curve obtained by determining the absorbance of the standard solutions is shown in Figure 4.1. The calibration curve was used to read off the concentration of solution corresponding to the measured value of absorbance.

4.10.3 Distribution of calcium during dipping process

During the deposition of rubber at the former surface, the calcium chloride coagulant diffuses into the latex and causes gelation. Consequently, the concentration and distribution of the calcium ions change with the time of dwell. In order to investigate the fate of these cations as the deposit builds up, it was necessary to determine the quantity of calcium in each of the regions shown in Figure 4.2. The calcium in each of these regions was collected and analysed for calcium content using an atomic adsorption spectrophotometer described above.

The procedures used to collect the calcium from the various

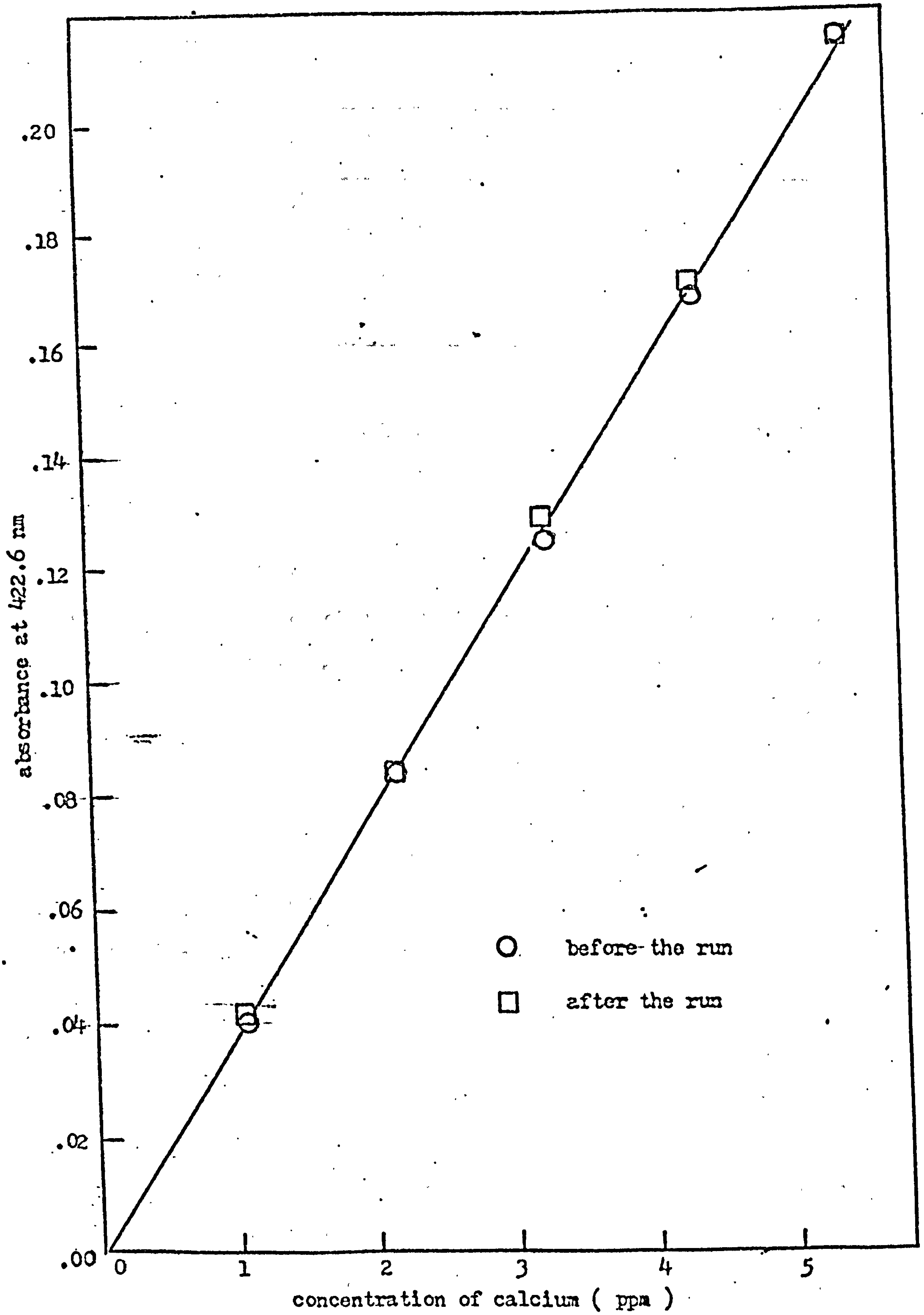


Figure 4.1. Calibration curve for calcium using standard calcium chloride solutions.

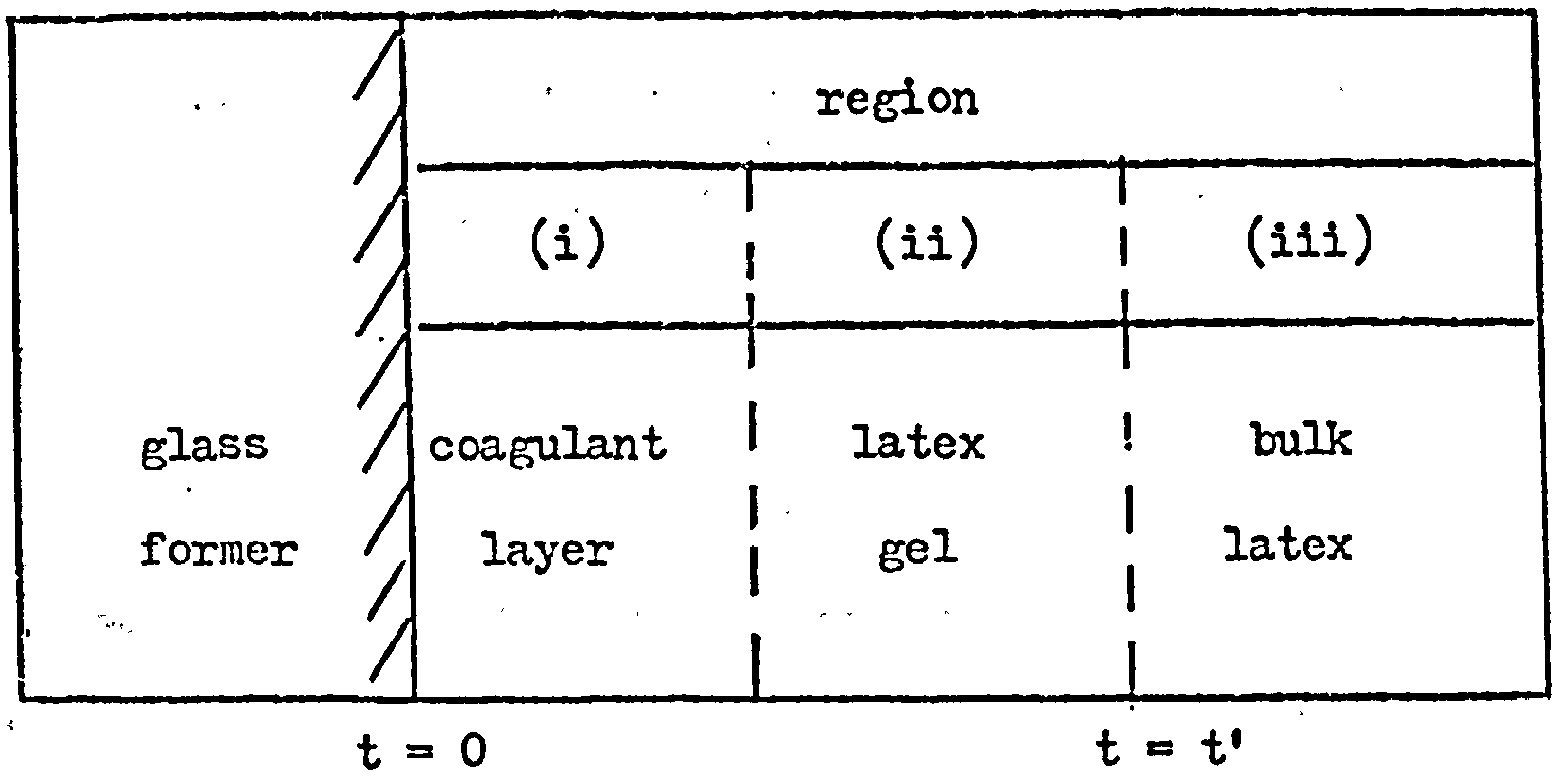


Figure 4.2. Regions in which calcium may be found during the deposition of rubber on the former.

regions were as follows;

Region (i) - (a) The calcium initially on the former was obtained as described in Section 4.4.3. It was collected by washing it from the former and dissolving it in deionised water.

(b) The calcium trapped between the former and the gel was collected by removing the gel from the former, and washing the surfaces of the former and the gel with deionised water.

Region (ii)- (a) The soluble calcium trapped in the interstices of the gel was collected by leaching the gel in deionised water at room temperature. For this purpose, the gel was leached for at least two days to ensure that all the soluble calcium in the gel was collected.

(b) The insoluble calcium left after leaching the gel was collected by ashing the deposit, dissolving the ash in dilute hydrochloric acid, and diluting with deionised water.

Region (iii) The calcium in the latex (approximately 60 g) before and after the dipping was collected by ashing the wet latex ($\sim$5 g) and dissolving the residue as described above.

4.10.4 Spatial distribution of calcium in region (ii)

The above determinations do not provide any indication of the spatial distribution of soluble and insoluble calcium within the gel. An attempt to determine the spatial distribution of calcium was made by freezing and sectioning the gel using a Base-Sledge microtome. Using this method, the amounts and concentrations of calcium in different slices of the gel were determined. Also, the total solid contents of successive slices of the gel were determined.

(a) Base-Sledge microtome

The MSE Base-Sledge microtome used in this work is shown in Figure 4.3. The MSE-Pelcool Freezing Stage, measuring 37 mm x 37 mm, was attached to the ball and socket clamp on the microtome and was connected to a Pelcool System power supply unit, through which the operating temperature could be continously varied and accurately controlled. With cooling water at + 15°C the operating plate will provide temperatures down to - 30°C. The microtome knife used in this work was a MSE No. 9051 W (240 mm,wedge-shaped). It was made of steel with special physical qualities. The knife was clamped at both ends from separately adjustable supports on opposite sides of the microtome, as shown in the photograph. The knife's cutting angle can be adjusted between 5 to 20° by swivelling the knife clamp on the knife block. The section thickness can be adjusted in steps of 1 μ within a range from 1 μ to 20 μ.

(b) Experimental procedure

A freshly formed gel was removed from the former and a specimen (ca. 19 mm diameter) was cut from it using a punch cutter. The specimen was stuck onto the operating plate using a paper gum. The temperature setting was 70 (ca. → 10°C). Before cutting was started, the specimen was roughly adjusted in height by rotating the micrometer screw with the hand crank. The cut was performed by horizontal sliding of the object carriage. A section of approximately 0.01 mm was cut through the gel. Each section was carefully removed and placed in an enclosed bottle for further evaluations.

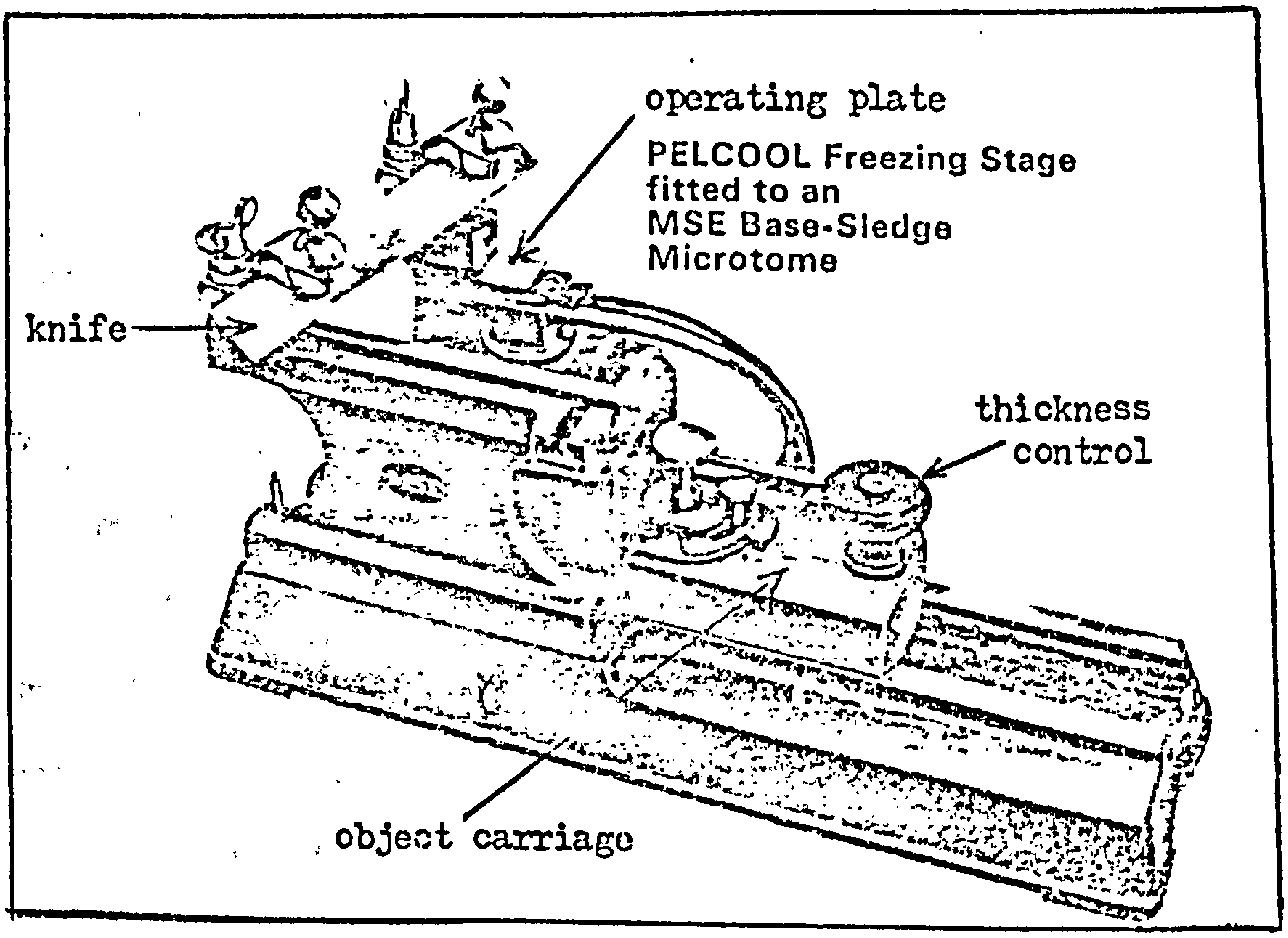


Figure 4.3. MSE Base-Sledge Microtome

4.11 Conductimetric titration

Natural rubber latex contains many anions, and it is uncertain which of these react with the calcium ions. Therefore, a series of experiments were carried out in which a calcium chloride solution was titrated against latex and also against solutions of the principal anions present in the latex. The concentrations of the anions were made approximately the same as those believed to be present in the latex. The equivalent points were determined conductimetrically using a cell of cell-constant 1.32 and a Wheatstone Bridge. In some cases, the titration was carried out in duplicate. The reproducibility was ± 1 %

4.12 Measurement of calcium diffusion in soap solution

In the dipping process, it is impossible to follow visually the movement of the gel/latex boundary, since both latex and gel are white and opaque. Therefore, a model system was developed in which calcium chloride was allowed to diffuse into a soap solution. The precipitation of the white calcium salt in the clear solution enabled the movement of the boundary to be followed, and hence the diffusion behaviour of calcium ions could be studied.

The apparatus used for this aspect of the investigation is shown in Figure 4.4. It consisted of a thick-walled glass tube of internal diameter 0.32 cm and length approximately 30 cm. A cylindrical container was fitted at both ends of the tube by means of a rubber bung. The assembly was placed on a horizontal table. A predetermined concentration of soap solution was placed into one of the containers and allowed to flow in the tube until it reached the far end. The other container was then filled with the coagulant solution, which then penetrated into the tube. The development of precipitate was followed by means of a vernier travelling microscope. The distance travelled and the time taken were recorded.

The procedure used in the calculation of the diffusion coefficient for calcium ions in soap solution is described in Chapter 7, Section 7.3.3.

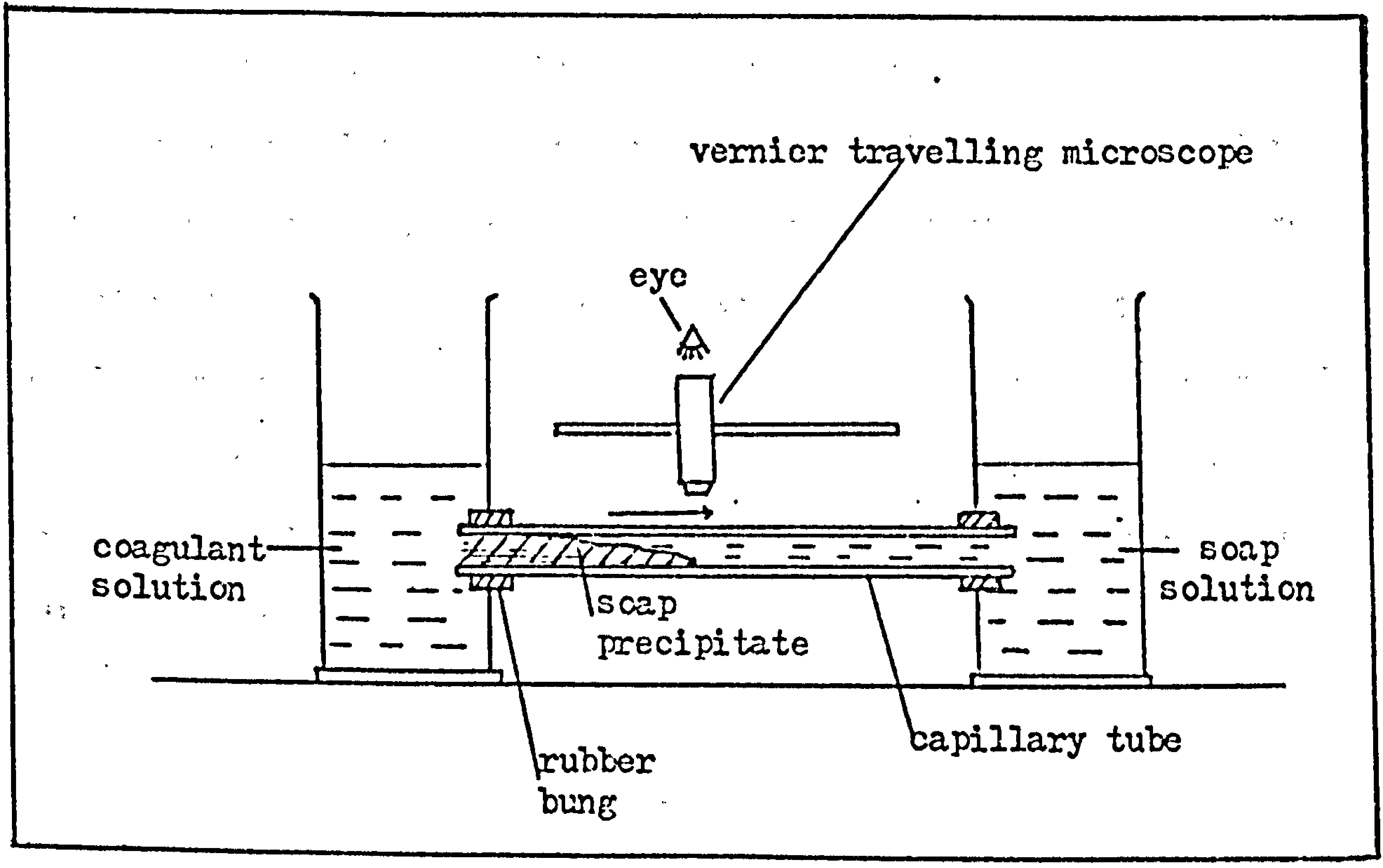


Figure 4.4. Diagram of apparatus used for studying calcium diffusion in soap solution.

CHAPTER 5

RESULTS FOR EFFECTS OF SELECTED PROCESS VARIABLES UPON DEPOSIT THICKNESS

5.1 Effect of total solids content of latex upon deposit thickness

5.1.1 Effect of TSC upon latex properties

The total solids content (TSC) was varied from 60 to 10% by diluting the latex with distilled water. The pH and viscosity of the latex after dilution and maturation were determined, but no further adjustments were made. The results for the effect of TSC upon pH and viscosity of the latex are shown in Table 5.1. The pH dropped approximately linearly with dilution from 10.52 to 10.11 over this range of dilution. The viscosity dropped very rapidly at first, but less rapidly below about 50% TSC. These results are in general agreement with published results[1,2].

Table 5.1

Effect of TSC upon pH and viscosity of latex

latex properties	TSC of latex, %							
	60	55	50	45	40	30	20	10
pH	10.52	10.45	10.43	10.40	10.38	10.32	10.22	10.11
viscosity (cps)	93.5	31.5	17.9	12.3	8.8	5.4	3.3	2.2

5.1.2 Effect of TSC upon straight-dip deposit thickness (θ_s)

Results for the effect of the TSC of latex upon the straight-dip deposit thickness (θ_s) are shown in Figure 5.1. The relationship between the TSC and θ_s is linear up to 50% TSC, but as the TSC increases above 50%, θ_s increases non-linearly. Theoretically, the curve should pass through the origin. The intercept that appears on the θ_s-axis is probably a consequence of error in the measurement of the very thin rubber deposits. Also, it must be noted that the talc applied on the surface of the deposit before the measurement may cause slight apparent increase in the measured thickness.

The curve in Figure 5.1 shows that θ_s is directly proportional to TSC up to 50% TSC. This suggests that the weight of latex picked up by the former is relatively constant at these low viscosities (2.2 to 17.9 cps.). However, as the TSC increases above 50%, θ_s increases non-linearly. This implies that the weight of latex picked up by the former also increases, presumably as a result of the sharp increase in viscosity (17.9 to 93.5 cps.) in this narrow TSC range.

In contrast, Gorton[3] has found a linear relationship between θ_s and TSC over the range 50% to 60% for three latex compounds. However, by plotting his data and extrapolating to zero thickness, the lines cut the TSC axis at surprisingly high values (between 42 to 48%). The results shown in Figure 5.1. indicate that, in reality, the curve only approximates to a straight line in the range 50% to 60% TSC. The results obtained by Klein[4] also indicate that the relationship is non-linear.

Gorton[3] has also shown that the relationship between θ_s and the latex compound viscosity is given by

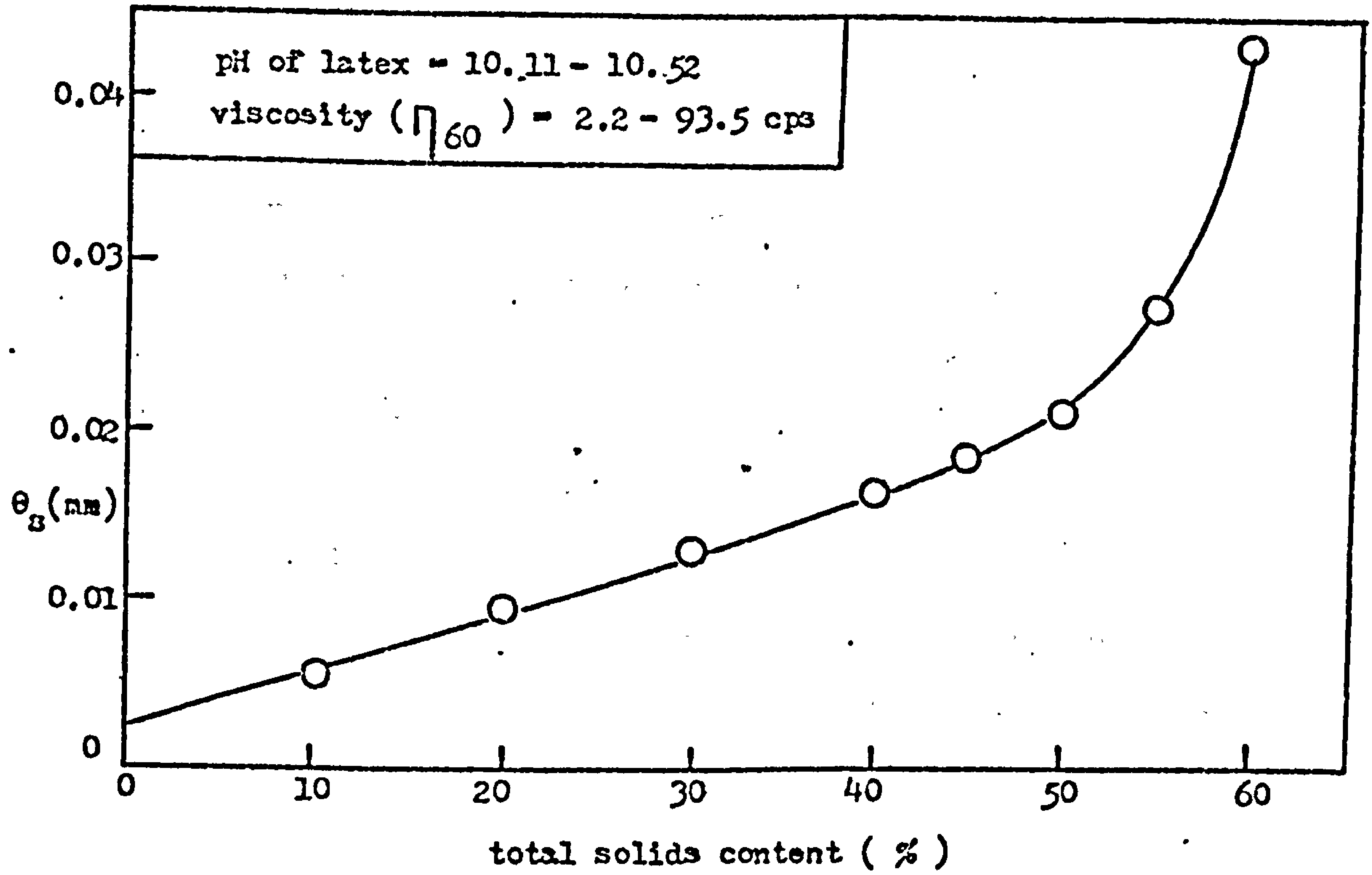


Figure 5.1. Effect of total solids content of latex upon straight-dip deposit thickness (θ_s)

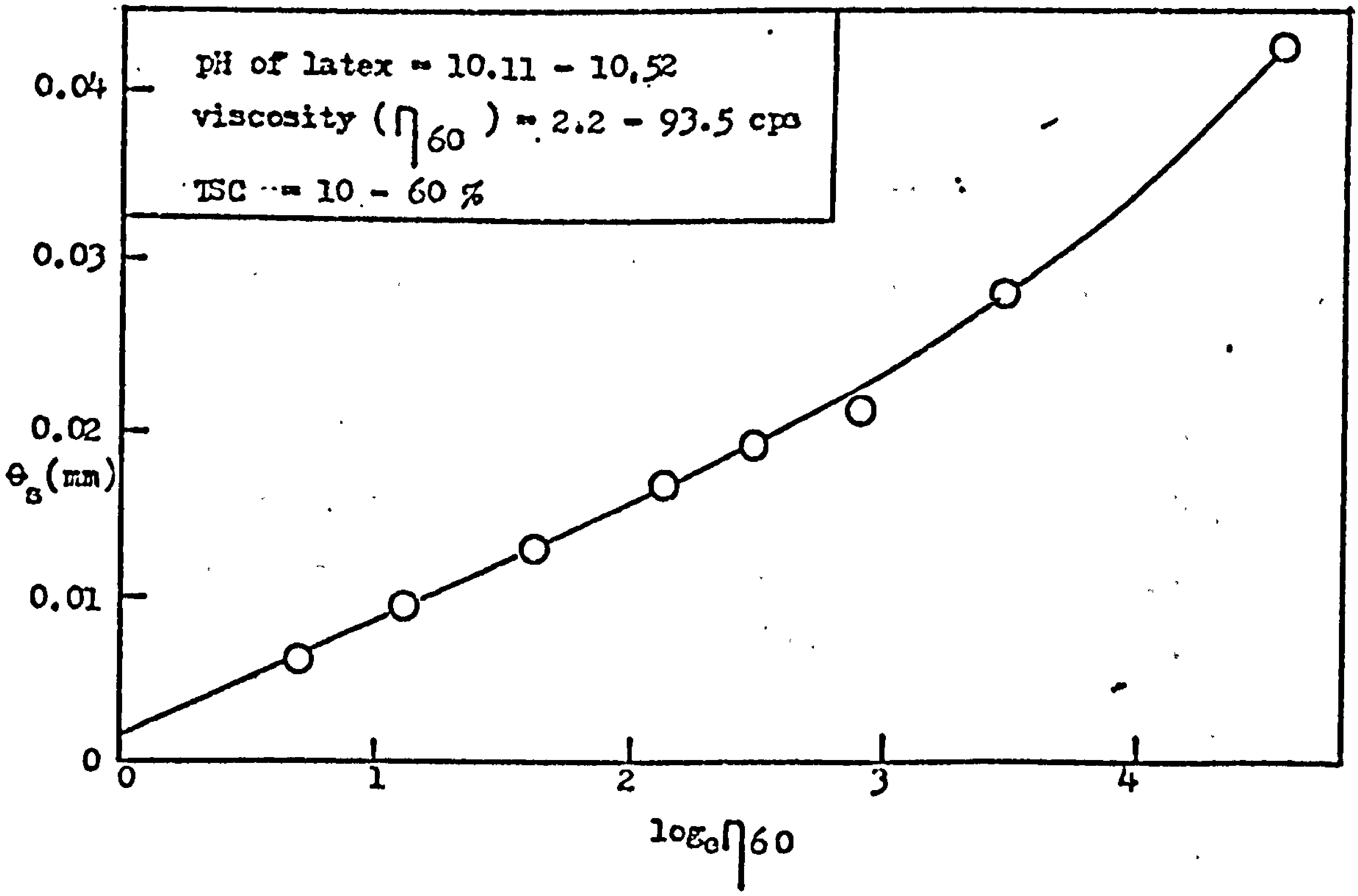


Figure 5.2. Relationship between straight-dip deposit thickness (θ_s) and logarithm of latex viscosity (η_{60})

$$\theta_s = a + k \log_{10}\eta_{60} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.1)$$

where a and k are constants, and η_{60} is the viscosity of latex compound measured on a Brookfield viscometer at 60 rpm. The results obtained in this work are shown in Figure 5.2; they do not support the linear relationship given above. The relationship between θ_s and $\ln\eta$ deviates from linearity, especially at higher viscosities or TSC. This is also found to be true when the viscosity of the latex was varied by adding thickening agents (see Section 5.2.2). As seen in Figure 5.10, it is unlikely that all latices will have identical flow behaviour at all shear rates. This may account for the deviation seen in Figures 5.2 and 5.13 .

5.1.3 Effect of TSC upon coagulant-dip deposit thickness (θ_c)

Typical relationships between the coagualnt-dip deposit thickness (θ_c) and the dwell time (t) for natural rubber latices of different TSC's and viscosities are shown in Figure 5.3. θ_c was calculated from

$$\theta_c = \theta_T - \theta_s \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.2)$$

where θ_T is the total dip deposit thickness. The straight-dip contribution to deposit thickness is present whenever a former is withdrawn from the latex; hence it must be substracted from θ_T to give the contribution to the deposit thickness from coagulant dipping. Because of practical difficulties, it was not possible to obtain θ_s directly; it was obtained separately by dipping a former, with no coagualant on it, into the appropriate latex as described earlier. . In adopting this procedure, it is inevitably assumed that θ_s is

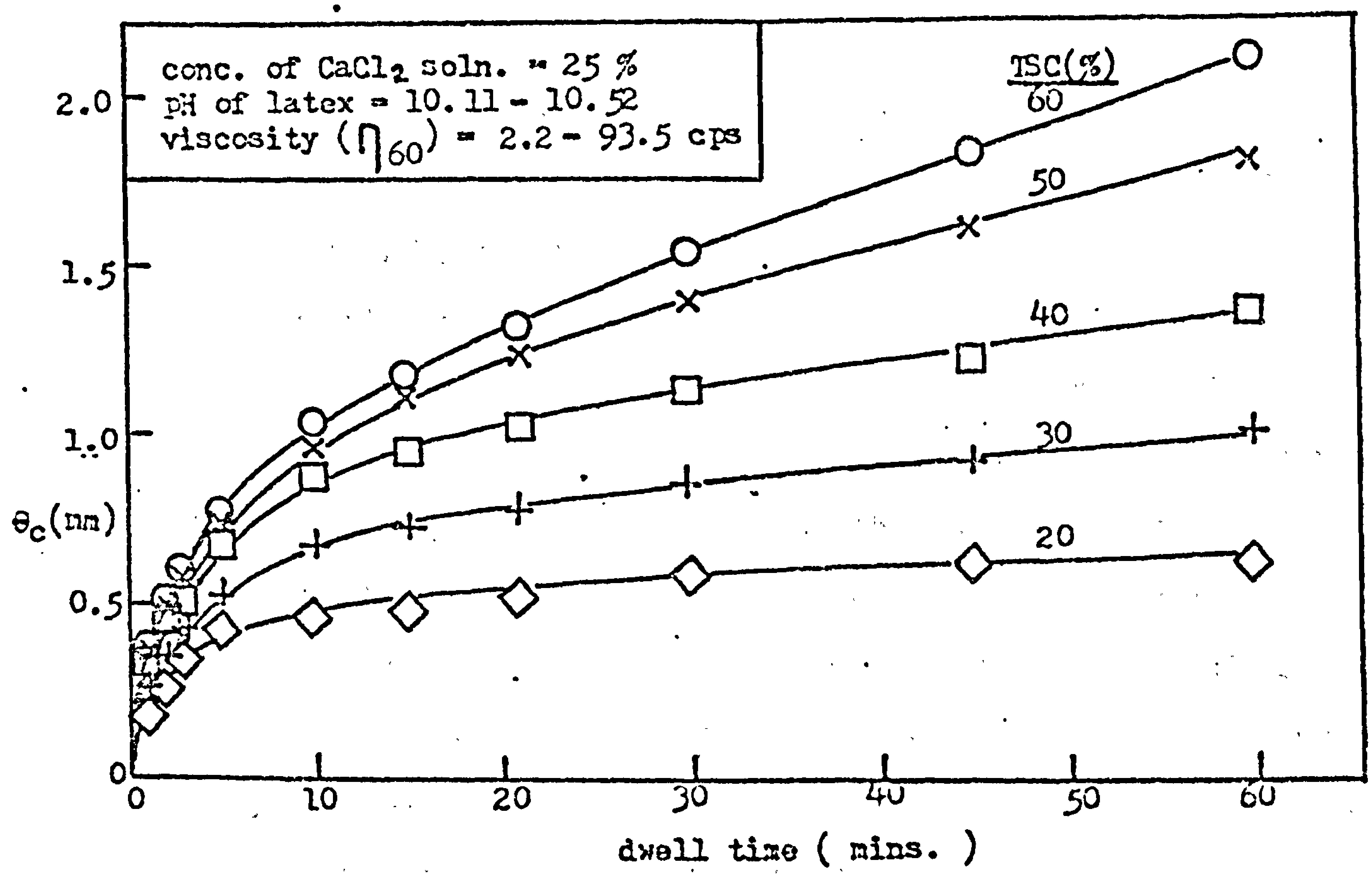


Figure 5.3. Coagulant-dip deposit thickness (θ_c) - time relationship, showing the effect of varying total solids content of latex.

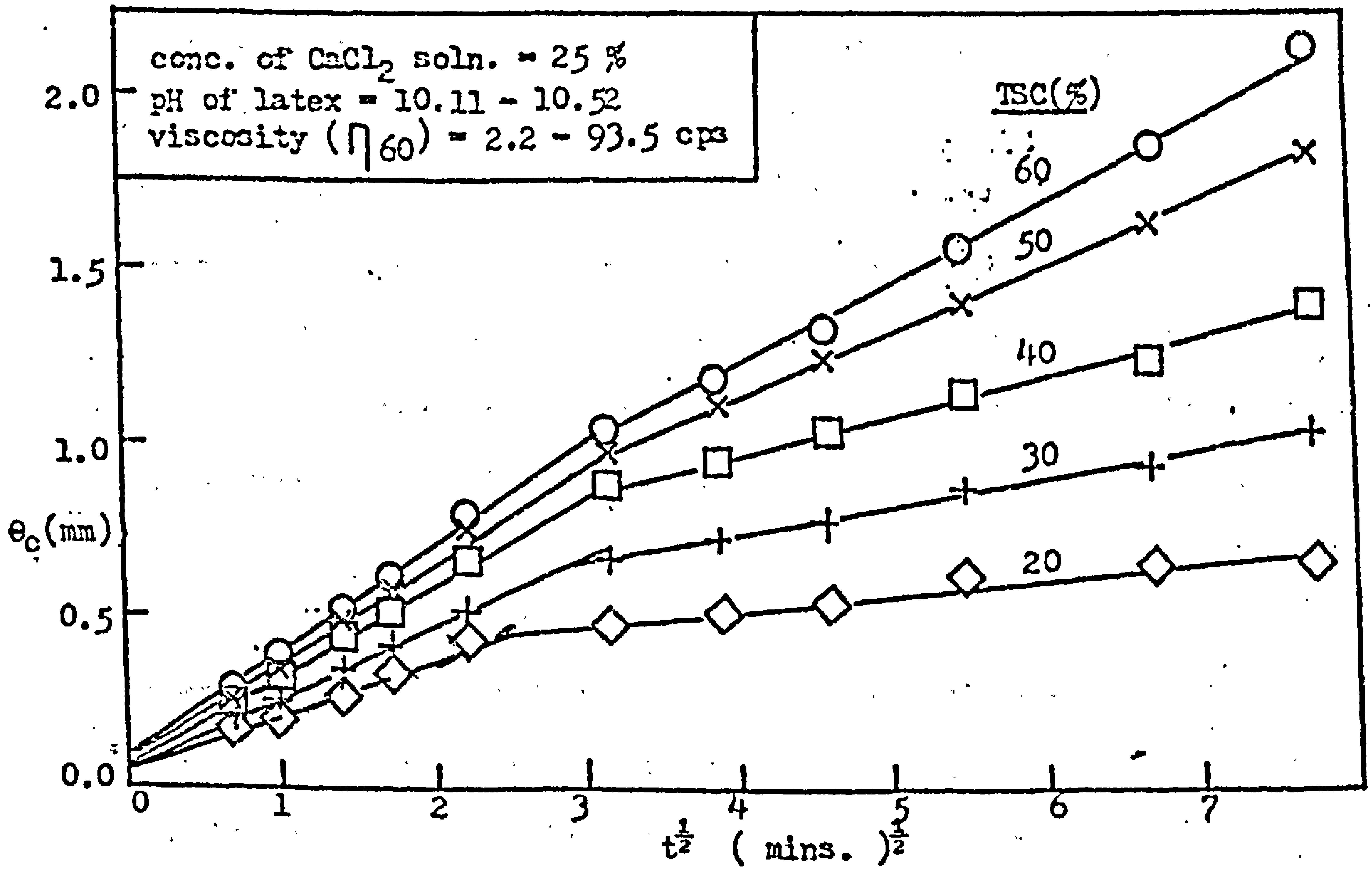


Figure 5.4. Coagulant-dip deposit thickness (θ_c) versus the square root of dwell time for latices of different total solids content.

independent of the coagulant and the time of dwell, and is equal to θ_s obtained from the same latex by straight dipping.

It has been found that θ_T is generally very much larger than θ_s . Hence, θ_c is not greatly affected by small errors in θ_s which may result from the assumptions made above. However, at short dwell times, θ_T is relatively small, and therefore a small difference in θ_s will have a far greater effect upon the value of θ_c. Furthermore, at short dwell times the concentration of the coagulant on the former is high (see Figure 7.8). This may influence the viscosity of the latex adjacent to the former, and therefore the values of θ_s and θ_c

It is seen in Figure 5.3 that the initial rate of deposition is high, and that deposition slows down as the time of dwell increases. The rate of deposition depends,amongst other things, upon the TSC and / or viscosity of the latex. These observations are in general agreement with those made by other workers[3-11].

As expected, reduction of the TSC of the latex leads to a reduction of the dry-coagulant dip deposit thickness obtained after a given time of dwell. However, appreciable deposit thicknesses are obtained even when the TSC of the latex is reduced to 20%. This observation is consistent with the assumption commonly made that the formation of gelled deposits in coagulant dipping processes is a result of chemical interaction between the coagulant and the latex stabilisers. The presence of insoluble calcium in the gel, shown in Figure 7.9, supports this assumption.

Several workers[3-11] have suggested that the deposition of rubber particles on the former is a diffusion-controlled process. Hence, the data in Figure 5.3 are presented as θ_c versus $t^{\frac{1}{2}}$ in Figure 5.4. The results plotted in this way support the view that the deposition of rubber particles on the former is indeed a diffusion-controlled process. However, two distinct mechanisms seem to be operative, one being dominant at short dwell times and the other at long dwell times. At short dwell times the rate of deposition is high, and at long dwell times the rate of deposition is slightly lower. However, subsequent work (see Section 5.1.4) has shown that the discontinuity revealed by Figure 5.4 may be an artifact of the experimental procedure.

Teoh[8] and Mortimer[9] have attempted to evaluate the significance of the slope of plots of θ_c versus $t^{\frac{1}{2}}$ using a natural rubber latex of fixed TSC and varied stabiliser content. According to Teoh, the slope is a function of the diffusion coefficient (D) of calcium ions only, and is independent of the stabiliser content. The results obtained in this work on the addition of soap and the reduction of pH (see Sections 5.3 and 5.4 respectively) appear to support Teoh's finding in that the slope is virtually independent of the stabiliser content within the range studied.

5.1.4 Explanation of discontinuity in θ_c versus $t^{\frac{1}{2}}$ curves

The normal method of determining θ_c was to withdraw the former from the latex bath and allow excess latex to drip off before drying the deposit. This was the method which was used up to this point in the investigation. However, a second method gave interesting results which are significant in that they provide an explanation of the discontinuity in the θ_c versus $t^{\frac{1}{2}}$ curves which had been obtained hitherto.

In the second method, the whole deposit (i.e., deposit plus drips) was collected after withdrawal and then weighed. It should be pointed out that the experiment was such that the drips from the former did not flow back into the latex bath. As a check, the weight of the latex in the bath before and after dipping was also determined. Figure 5.5 shows the relationship between the weight of latex on the former and the square root of the dwell time. The difference between line A and line B is that B refers to the weight on the former determined after allowing excess latex to flow off the former whereas A refers to the weight of latex removed from the latex bath. It is seen that no excess latex flowed off the former up to $t \simeq 10$ minute. When $t > 10$ minutes, the amount of excess latex that flowed off the former increased with increasing dwell time. The data for weight of latex removed from the bath by the former (line A) now lie approximately on a single straight line. The shaded region represents the weight of latex which ran back into the latex bath under the normal conditions of dipping and determining θ_c.

Examination of the latex which ran off the former has shown it to be of higher viscosity than the bulk of the latex, and to contain agglomerates of particles. It appears to be latex which is just on the point of gelling under the influence of calcium ions; but before gelation can take place, it runs off the former. It is concluded that the deposit which forms after long dwell times consists of two distinct regions:

(i) an inner region, which comprises a strong coherent latex gel; and

(ii) an outer region, which comprises ungelled but rather viscous latex, the viscosity being sufficiently high for the layer to be withdrawn with the former, but not sufficiently high to prevent the latex from flowing off the former subsequently.

It should be noted that it was not always possible to obtain

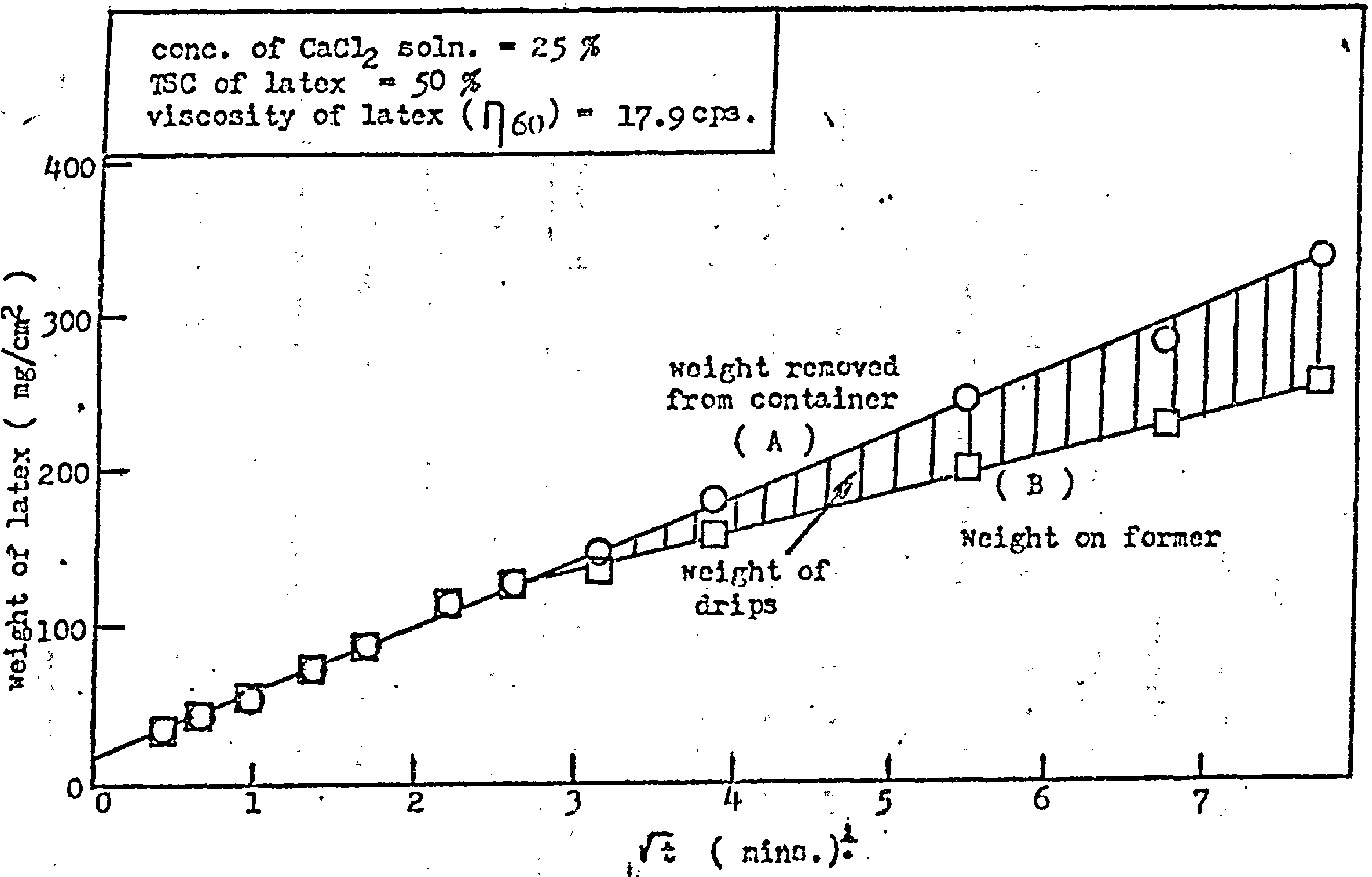


Figure 5.5. Relationship between the wet weight deposit and square root of dwell time (see text for significance of lines (A) and (B).

reproducible results for the weight of the latex which flowed off the former after withdrawal. Indeed, in some cases the latex merely flowed down to the bottom of the former where it remained as a large ' blob ', gelation having occurred before the latex could flow off. These observations confirm that the outer layer of the deposit which forms after long dwell times is in a critical condition of incipient gelation. The results obtained for the distribution of soluble and insoluble calcium within the latex deposit, as revealed by assays on microtomed slices, shown subsequently in Figure 7.12, clearly provide an explanation for the reluctance of the outer layers of the deposit to gel properly at long dwell times. It was also observed that the weight of latex which would flow off the former after withdrawal is sensitive to the temperature of the room in which the dipping experiment was carried out. Normally, an increase in temperature reduced the weight of latex which would flow off the former after withdrawal.

5.1.5 Effect of TSC upon thickness of wet-gel deposit (θ_c')

Since the process of deposition is concerned with the rate of diffusion of calcium ions through the wet latex gel, it is more appropriate to consider the thickness of the wet-gel deposit, θ_c' rather than the dry deposit thickness, θ_c. θ_c' was estimated as follows:

$$\theta_c' = \theta_c \times \frac{100}{(\mathrm{TSC})_L} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.3)$$

where $(\mathrm{TSC})_L$ is the total solids content of the bulk of the latex. Therefore θ_c' gives an estimate of where the boundary between gelled and non-gelled latex is in the liquid latex at any particular time. Hence, a plot of θ_c' versus $t^{\frac{1}{2}}$, given in Figure 5.6, gives an

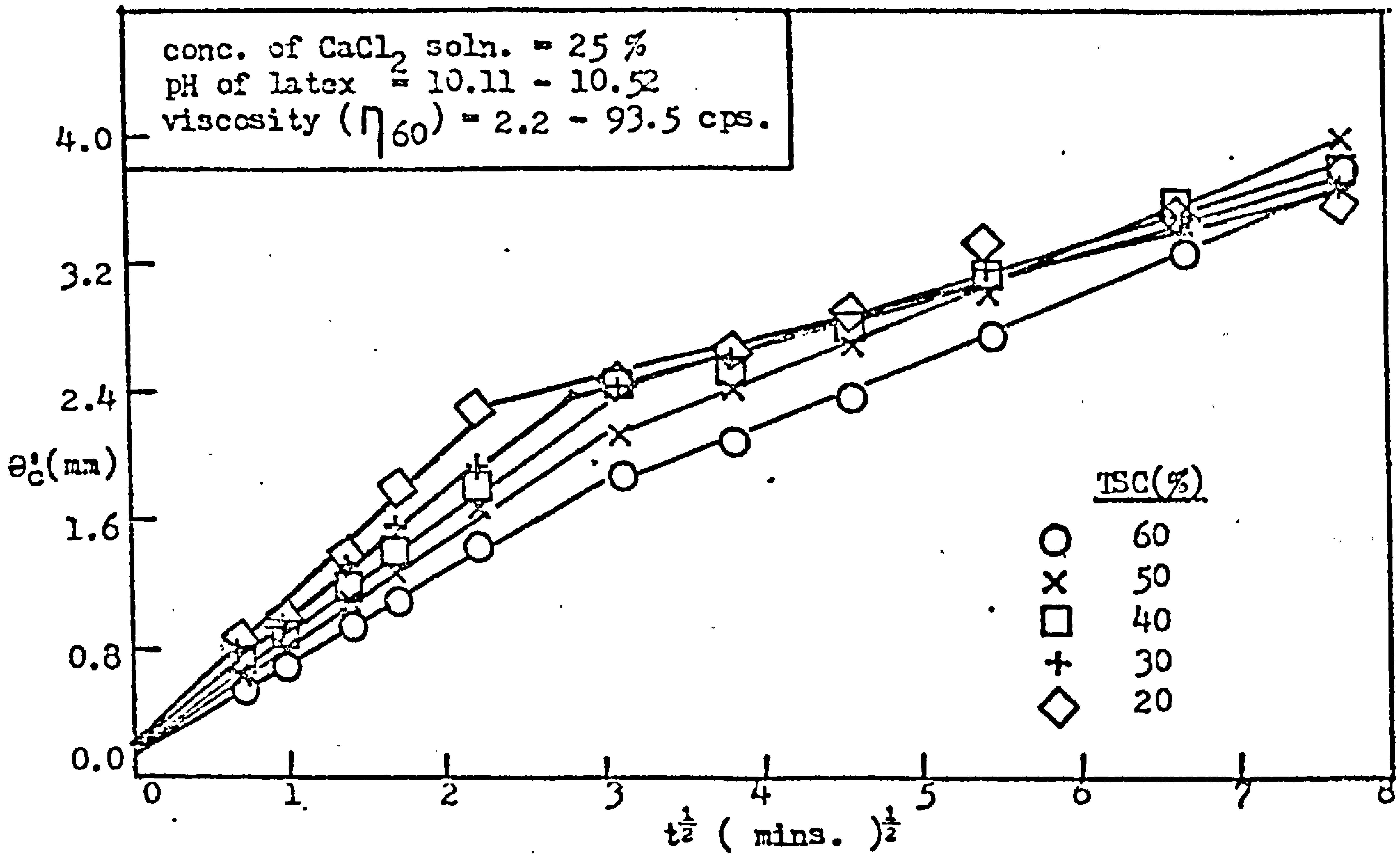


Figure 5.6. Wet coagulant deposit thickness (θ_c') versus square root of dwell time for latices of different total solids content.

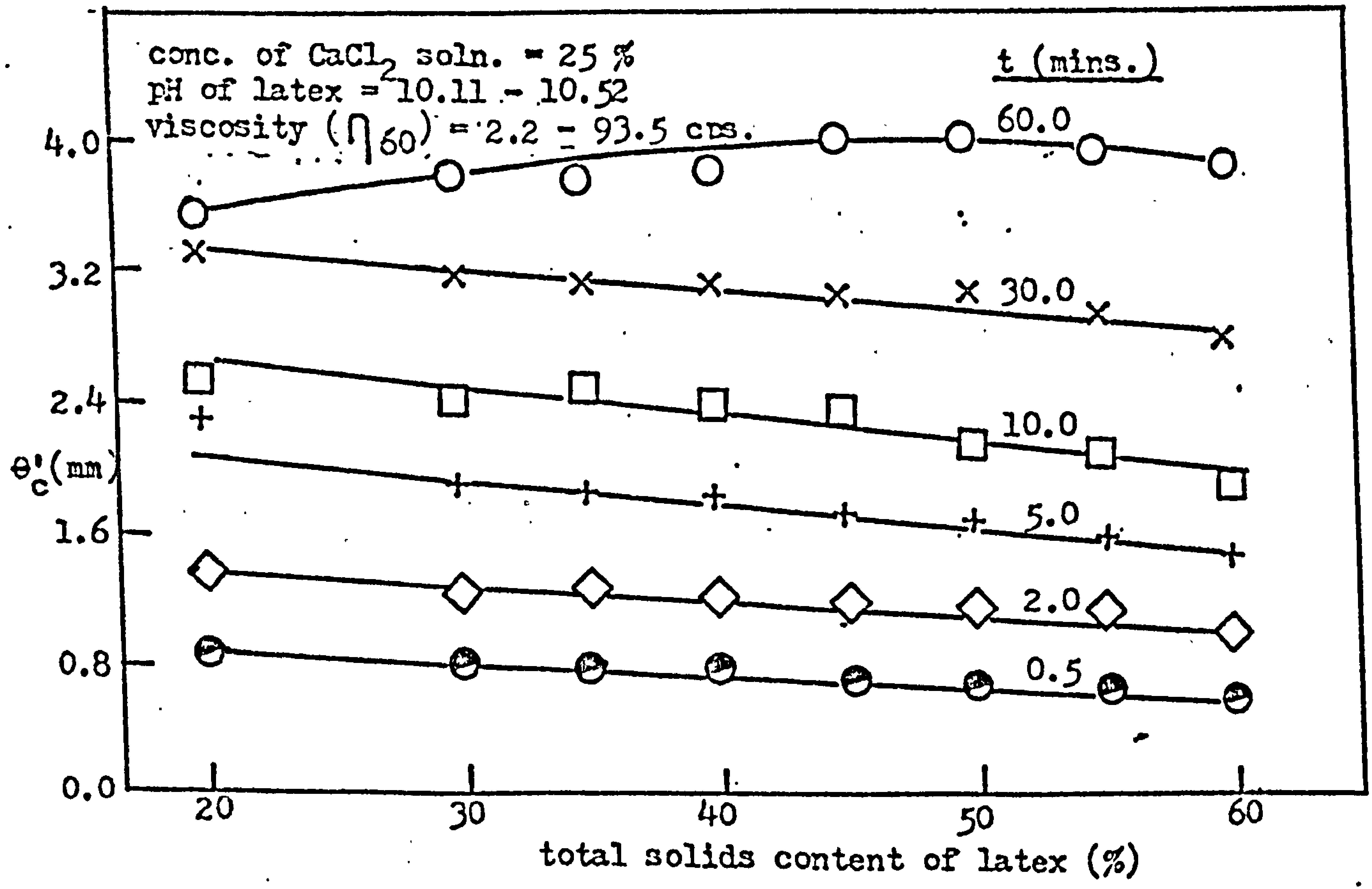


Figure 5.7. Effect of total solids content of latex upon wet coagulant deposit thickness (θ_c').

indication of the rate at which calcium ions diffuse through the wet-gel deposit. It is seen that, ~~at low TSC~~, the initial rate of diffusion of calcium ions is greater.the lower ~~greater~~ the TSC of the latex. However, the rates of diffusion at longer times ($t > 10$ minutes) are less differentiated, partly because of the soft nature of the wet-gel deposit obtained, which tends to drip off the former as described in the previous section.

A plot of θ_c' for fixed values of t versus TSC (Figure 5.7) shows that θ_c' decreases with increasing TSC. Four possible reasons to account the reduction in θ_c' with increasing TSC are as follows:

(i) The quantity of soap per unit volume of latex increases with increasing TSC. Therefore it might be expected that more calcium ions would be required to effect nuetralisation. This is not thought to be a likely explanation, because the level of soap has been found to have very little effect upon deposit thickness (see Section 5.3).

(ii) The viscosity of the latex increases with increasing TSC, and this might be expected to hinder diffusion of the calcium ions. An experiment was carried out to investigate the effect upon θ_c' of varying the TSC independently of the viscosity. Methyl cellulose was added to latices of different TSC's to bring them to approximately the same viscosity. The effect of TSC at approximately constant viscosity upon θ_c' at constant t is shown in Figure 5.8. It can be seen that there is little change compared with Figure 5.7. It was therefore concluded that differences in viscosity were not the cause of the decrease in θ_c' with increasing TSC. This matter will be discussed in more detailed in the next section.

(iii) The higher the TSC of the latex gel, the longer would be the diffusion path of the calcium ions. This has been referred to as the ' tortuosity factor ' by Stewart[11]. He postulated that, when the particles in a latex gel are closely packed together, the calcium ions will be constrained to diffuse along more tortuous paths rather than when the particles in the gel are less closely packed. This is because the calcium ions are quite reasonably assumed to be incapable of diffusing through the rubber particles, and are therefore confined to the channels of aqueous phase which exist between the rubber particles. In effect, the diffusion of the calcium ions outwards from the former surface is impeded by the presence of the rubber particles. The results shown in Figure 5.7 are certainly consistent with this interpretation, but nevertheless it is thought that this explanation is also invalid (see further below).

(iv) The method of calculating θ_c' is incorrect, and thus the values of θ_c' in Figures 5.6 to 5.8 are not a correct representation of the distance that the calcium ions have diffused. It is now thought that the position of the plane which defines the limit reached by the diffusing calcium ions is as discussed below.

The correct formula for calculating θ_c' should be as follows:

$$\theta_c' = \theta_c \times \frac{100}{(\text{TSC})_G} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.4)$$

where $(\text{TSC})_G$ is the total solids content of gel. It was initially thought that $(\text{TSC})_G = (\text{TSC})_L$, but subsequent work has shown this

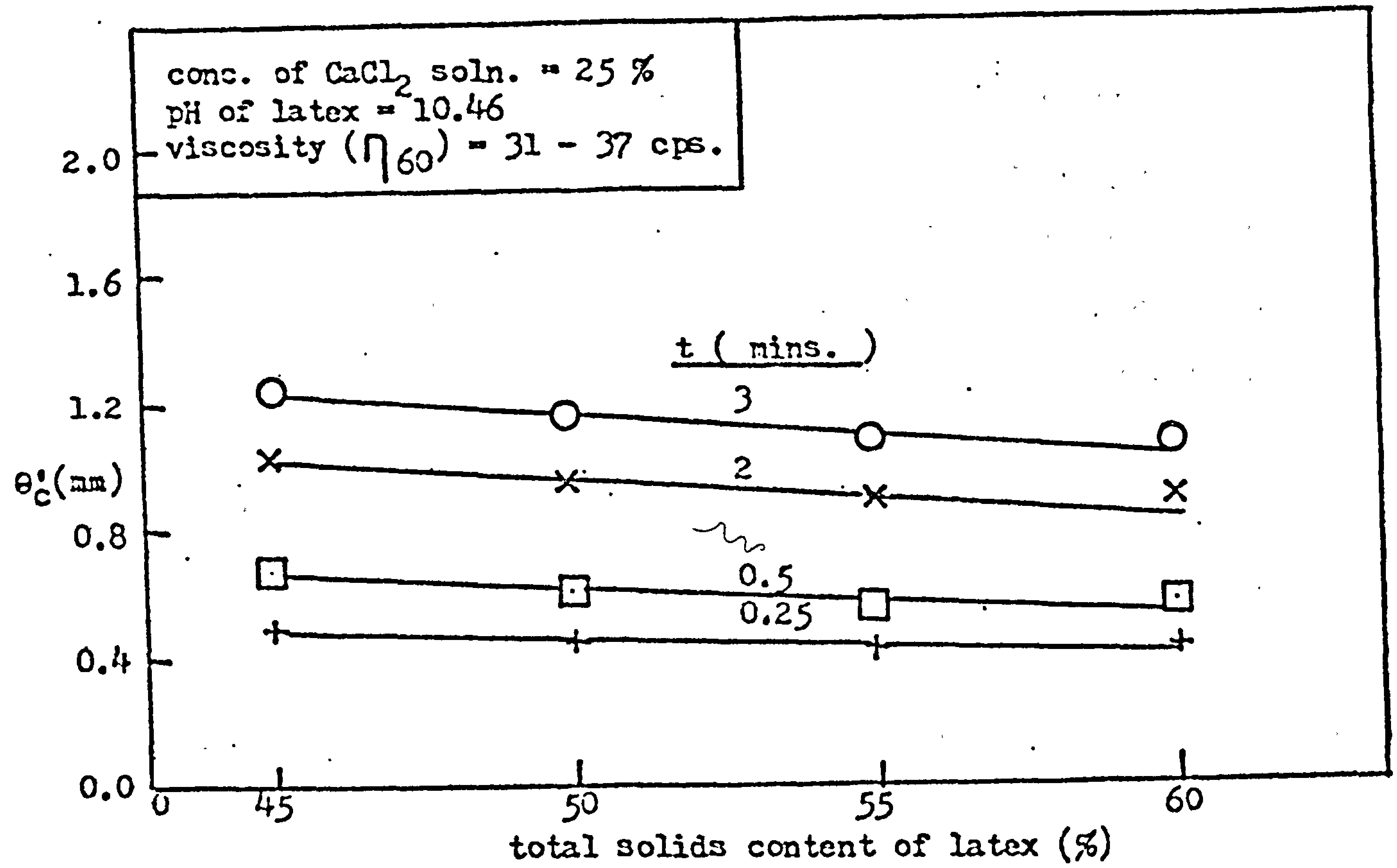


Figure 5.8. Effect of total solids content of latex of 'constant' viscosity upon wet coagulant dip deposit thickness (θ_c')

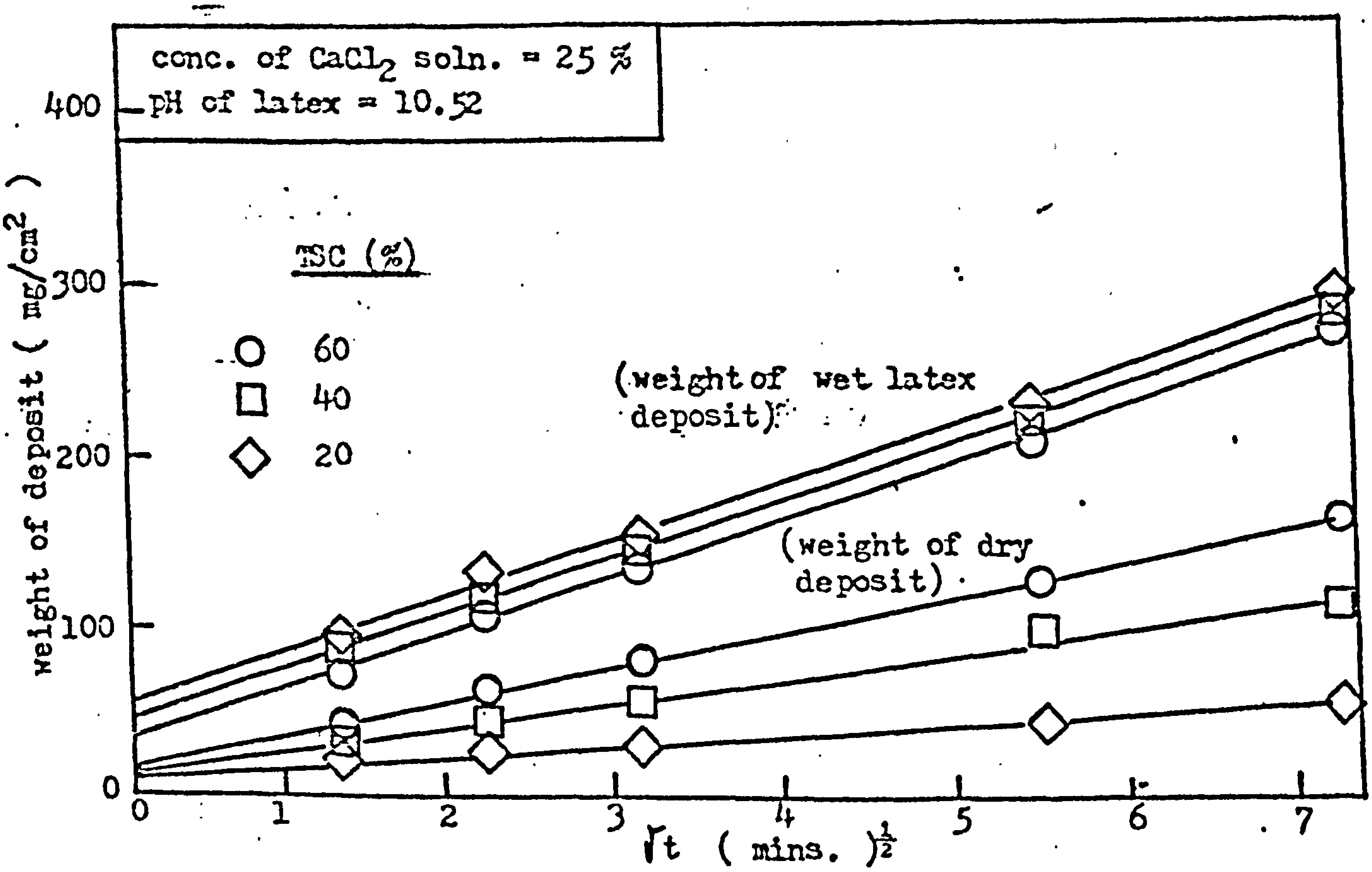


Figure 5.9. Relationship between weight of deposit and square root of dwell time. (The weight of the wet latex deposit is the weight pulled up on the former. The weight of dry deposit is the theoretical weight of deposit obtained if no latex is allowed to run off the former).

to be untrue (see Figure 5.9). Since, it is not always possible to measure (TSC $)_G$ accurately, a more precise way of estimating the distance travelled by the calcium ions is to determine the weight of latex picked up on the former as a function of $t^{\frac{1}{2}}$ (Figure 5.9). It is then seen that the wet weight of deposit is represented by a series of parallel lines. This suggests that the rate of diffusion is independent of the TSC of the latex, and also that there is apparently no tortuosity effect at high TSC.

It is not clear why the lines of Figure 5.9 do not superimpose. It is thought that this may arise (a) partly from differences in the densities of the latices, and (b) possibly from an initial dehydrating effect exerted by the calcium chloride layer on the former (see Figure 7.8).

5.1.6 Summary of results

It is clearly seen that the deposition process is diffusion-controlled. The rate of diffusion appears to be unaffected by varying the TSC of the latex, suggesting that the tortuosity effect proposed by Stewart[11] does not operate in this system. Although the rate of diffusion in the latices is approximately constant, the rate of deposition of rubber increases with increasing TSC. This is because the higher the TSC of the latex, the higher is the number of particles in a given volume of latex.

The shape of the curves for θ_c versus t depend very much upon the amount of latex which flows off the former, especially when $t > 10$ minutes dwell time. This may account to some extent for the multitude of mathematical relationships which has been derived from such curves, and why no single relationship will apply to all dipping systems.

5.2 Effect of thickening agents upon deposit thickness

5.2.1 Effect of thickening agents upon viscosity of latex

Two methyl cellulose thickening agents were used in this investigation, namely, Celacol M 450 and M 2500; the number following the letter M represents the viscosity in centipoise of a 2% solution of the substance at 20°C. The level of the thickening agents added to the latex were varied from 0 to 0.5% on the weight of the latex. The latex was diluted to 50% and 40% TSC respectively. The effect of the level of Celacol M 450 upon the viscosity of the latex at 50% TSC and at different rates of shear is shown in Figure 5.10. Similar trends were observed at 40% TSC, and also for the other grade of methyl cellulose investigated. The viscosity of the latex without the thickening agent is virtually independent of the shear rate. However, the apparent viscosity of thickened latex compound is dependent upon the shear rate; the lower the shear rate, the higher is the apparent viscosity of the latex compound. These pronounced rheological changes are probably caused by segments of the methyl cellulose molecules being anchored on to several latex particles simultaneously, thus forming a network structure. At higher rates of shear, this network structure is probably broken down to some extent; hence the fall in viscosity.

5.2.2 Effect of thickening agent upon θ_s

The effect of thickening agents on the straight dip deposit thickness, θ_s, is shown in Figure 5.11 for a latex compound of 50% TSC. Similar trends were observed for a latex compound of 40% TSC . In Figure 5.12, θ_s is plotted against viscosity for each of the latex compounds.

It is seen from Figure 5.11 that θ_s varies linearly with

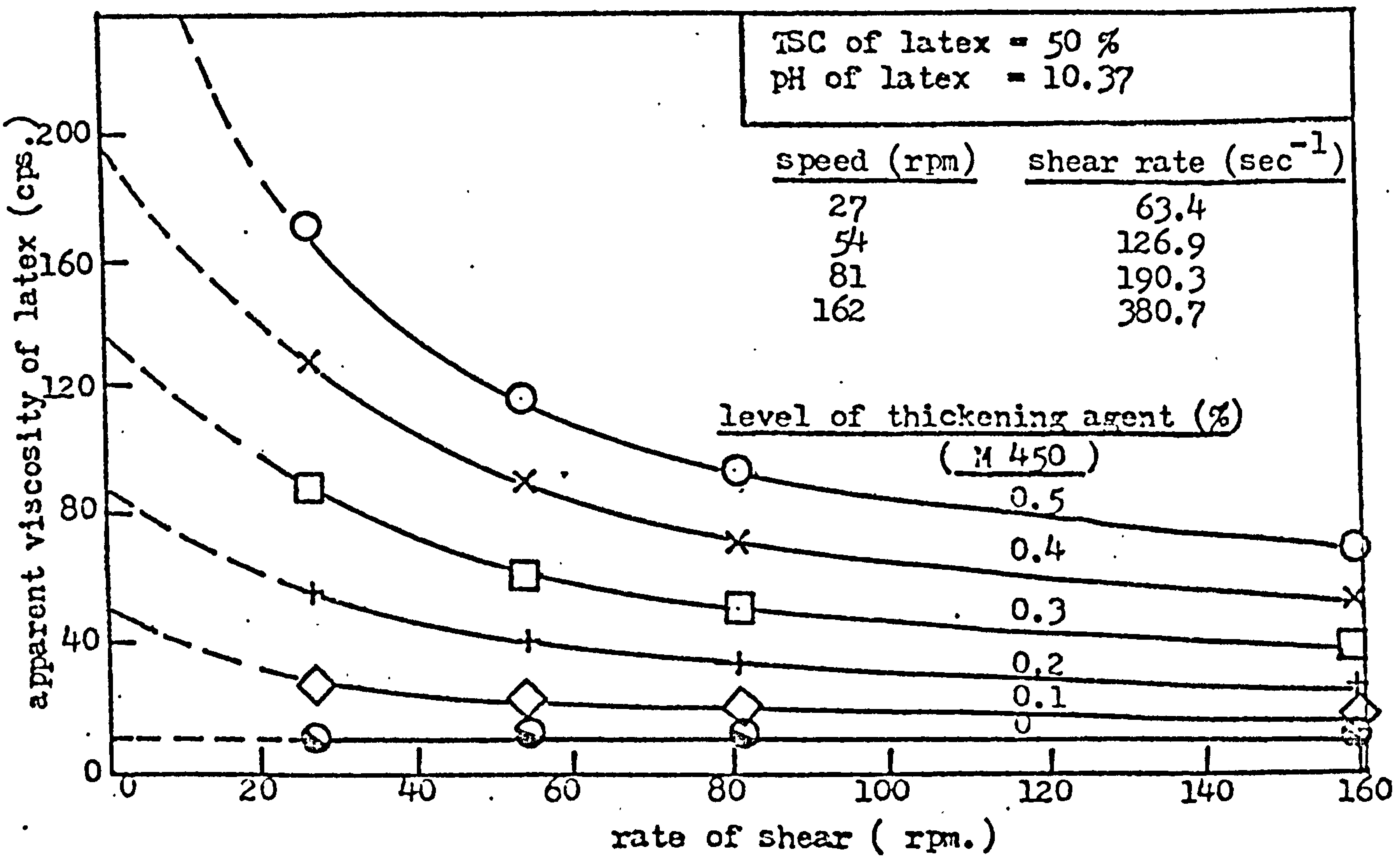


Figure 5.10. Effects of shear rate and level of thickening agent upon apparent viscosity of latex at fixed TSC.

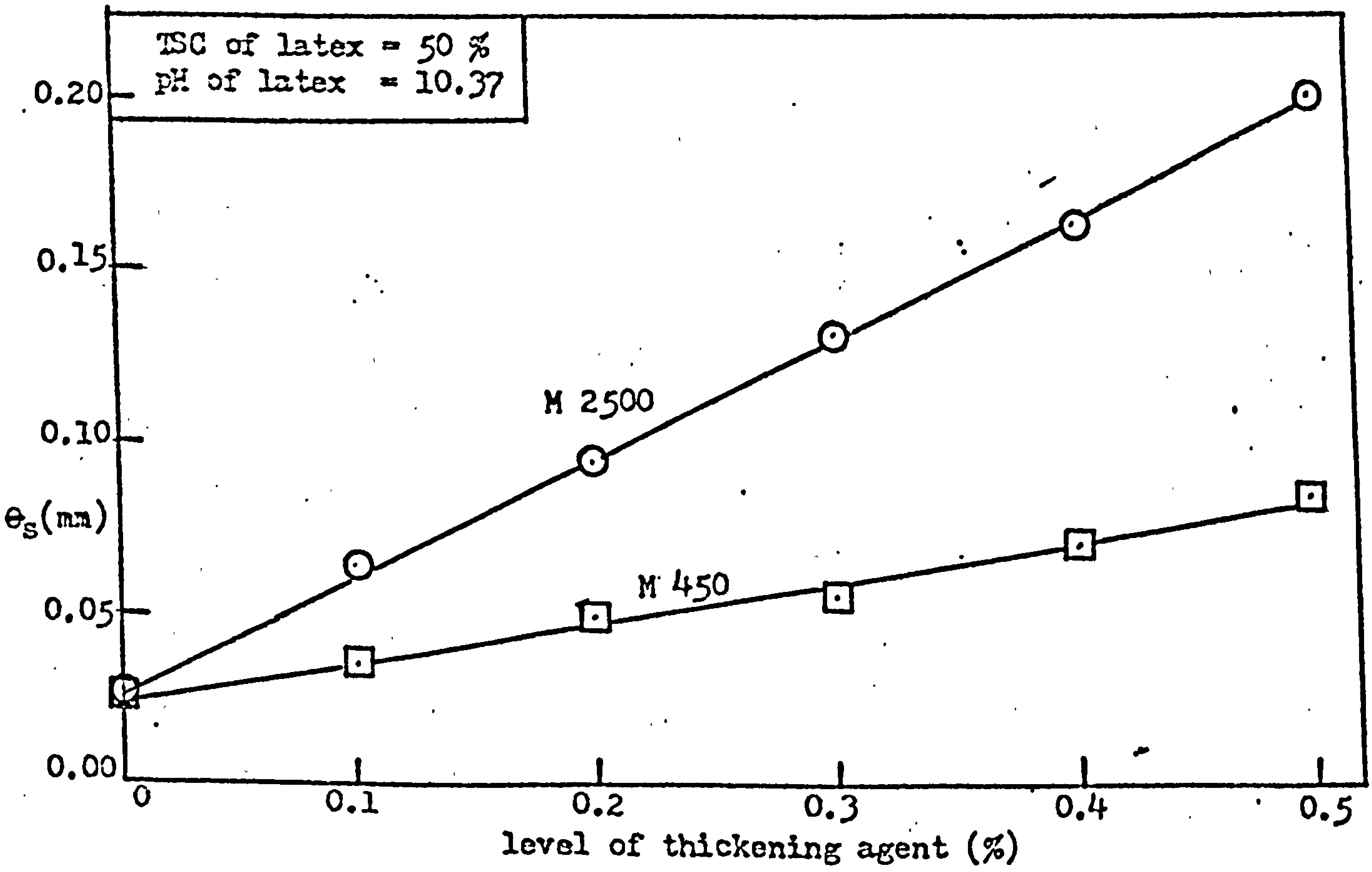


Figure 5.11. Effect of type and level of thickening agent upon straight-dip deposit thickness (θ_s)

the level of addition of thickening agents. However, θ_s varies non-linearly with the viscosity of the latex, as is evident from Figure 5.12. It is also seen that Celacol M 2500 is more effective in enhancing the thickness of deposit than is M 450 at any given concentration or viscosity. Similar behaviour was observed when the latex was diluted to 40% TSC.

The addition of the methyl celluloses increases the viscosity of the latices, and hence increases the weight of latices picked up on the former. At least three distinct mechanisms are possible to explain the increase in the viscosity of latices containing water-soluble hydrocolloids, namely:

(i) the hydrocolloid increases the viscosity of the aqueous phase;

(ii) the hydrocolloid becomes adsorbed on the polymer particles and thereby increases their effective hydrodynamic volume; and

(iii) the hydrocolloid becomes adsorbed on the polymer particles and thereby encourages interparticle bridging.

It was found that the level of M 2500 or M 450 added to the latex in this work would not markedly change the viscosity of the aqueous phase[12]. The second mechanism may offer some explanations for the increase in the viscosity of the latex. However, it is thought that the third mechanism offers the most likely explanation for the marked increase in the viscosity of the latex. The dependence of the apparent viscosity of the latex upon the shear rate, i.e., the lower the shear rate the higher is the apparent viscosity of the latex, is certainly seen to be consistent with the third mechanism. Kreider[13] and Brown[14] have also obtained similar results and suggested that these pronounced rheological

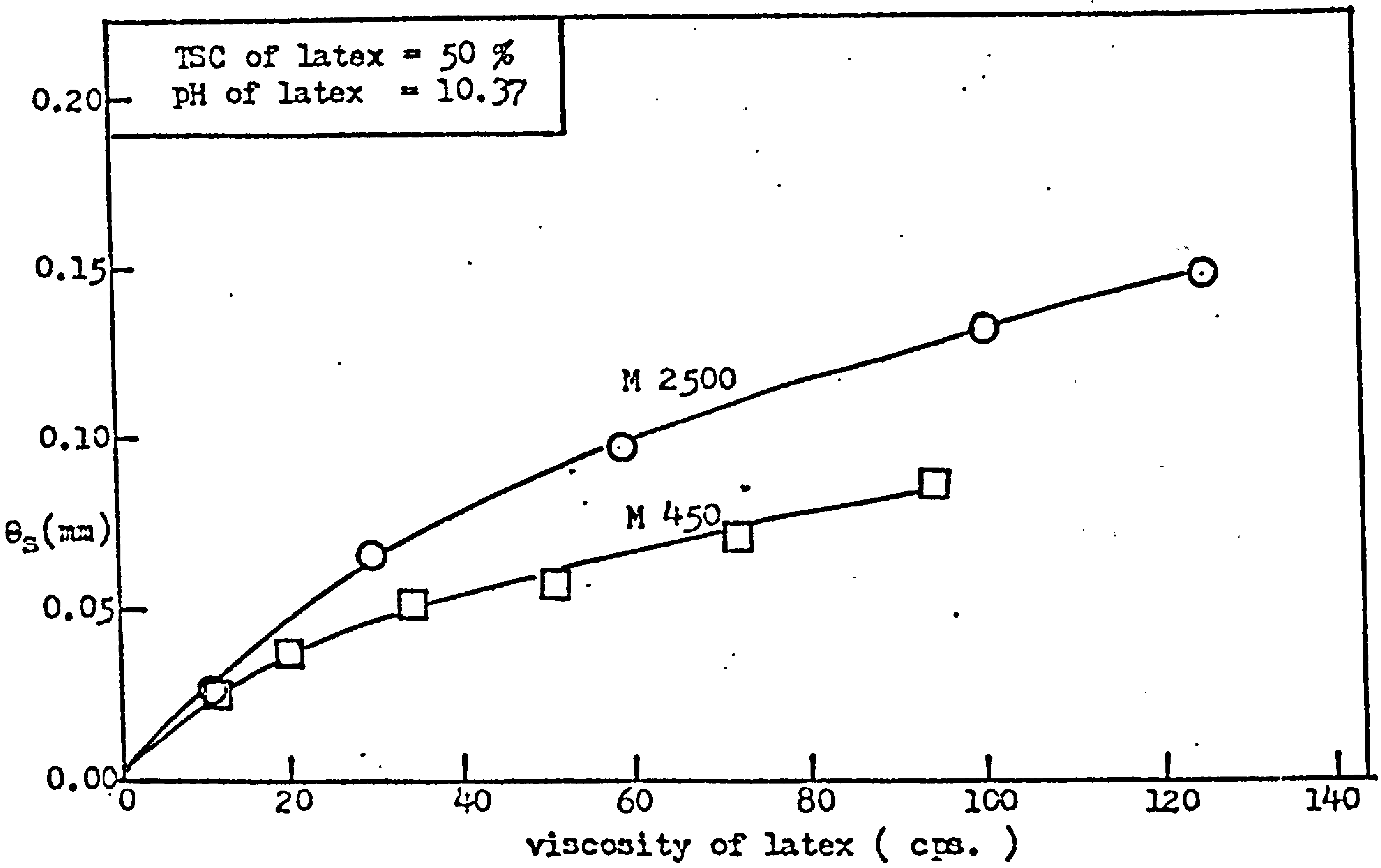


Figure 5.12. Effect of viscosity of latex on straight-dip deposit thickness (θ_s).

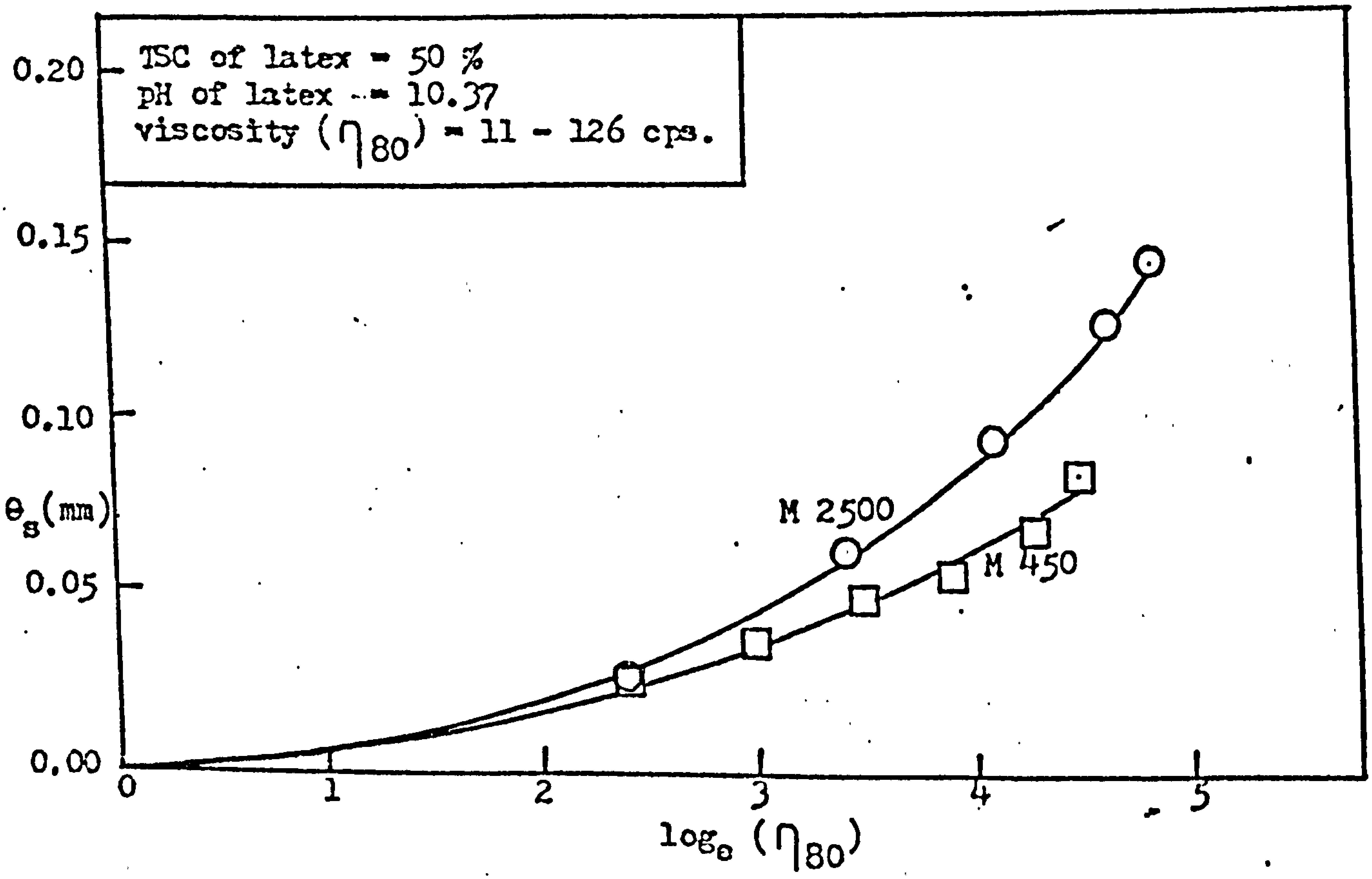


Figure 5.13. Relationship between straight-dip deposit thickness (θ_s) and logarithms of latex viscosity.

changes could only occur by segments of the hydrocolloid molecules being anchored on to several latex particles simultaneously, thus forming a network structure. At higher rates of shear, this network structure is probably broken down to some extent; hence the fall in viscosity. It is also seen from Figure 5.12 that methyl cellulose M 2500 gave thicker deposit than did M 450 at any given viscosity. Presumably, the observed difference arises from the different flow properties imparted by the methyl cellulose molecules of differing molecular weights.

Gorton[3] has reported that θ_s is proportional to $\log_{10}\eta$. This has not been found to be the case in this work (Figure 5.13) Presumably, the observed difference is a consequence of different flow properties imparted by the methyl cellulose molecules.

5.2.3 Effect of thickening agents upon θ_c

Figure 5.14 shows typical relationships between dry coagulant dip deposit thickness, θ_c and dwell time. The characteristics of the curves in the presence of Celacol M 2500 are almost similar to those of the curve obtained in its absence. A similar pattern is observed with the thickness-time relationship for a latex of 50% TSC in the presence of the Celacol M 450. However, on diluting the latex compounds to 40% TSC, the added methyl celluloses appears to have no discernible effect, as is demonstrated by the single curve shown in Figure 5.15. This is observed despite the fact that the latex compound viscosity varied from 5.0 to 70.4 cps.. The almost total lack of effect of methyl celluloses on θ_c is shown more clearly in Figures 5.16 and 5.17. The small change in θ_c with level of thickening agent is thought to arise from the method of calculation of θ from Equation 5.2, as is explained below.

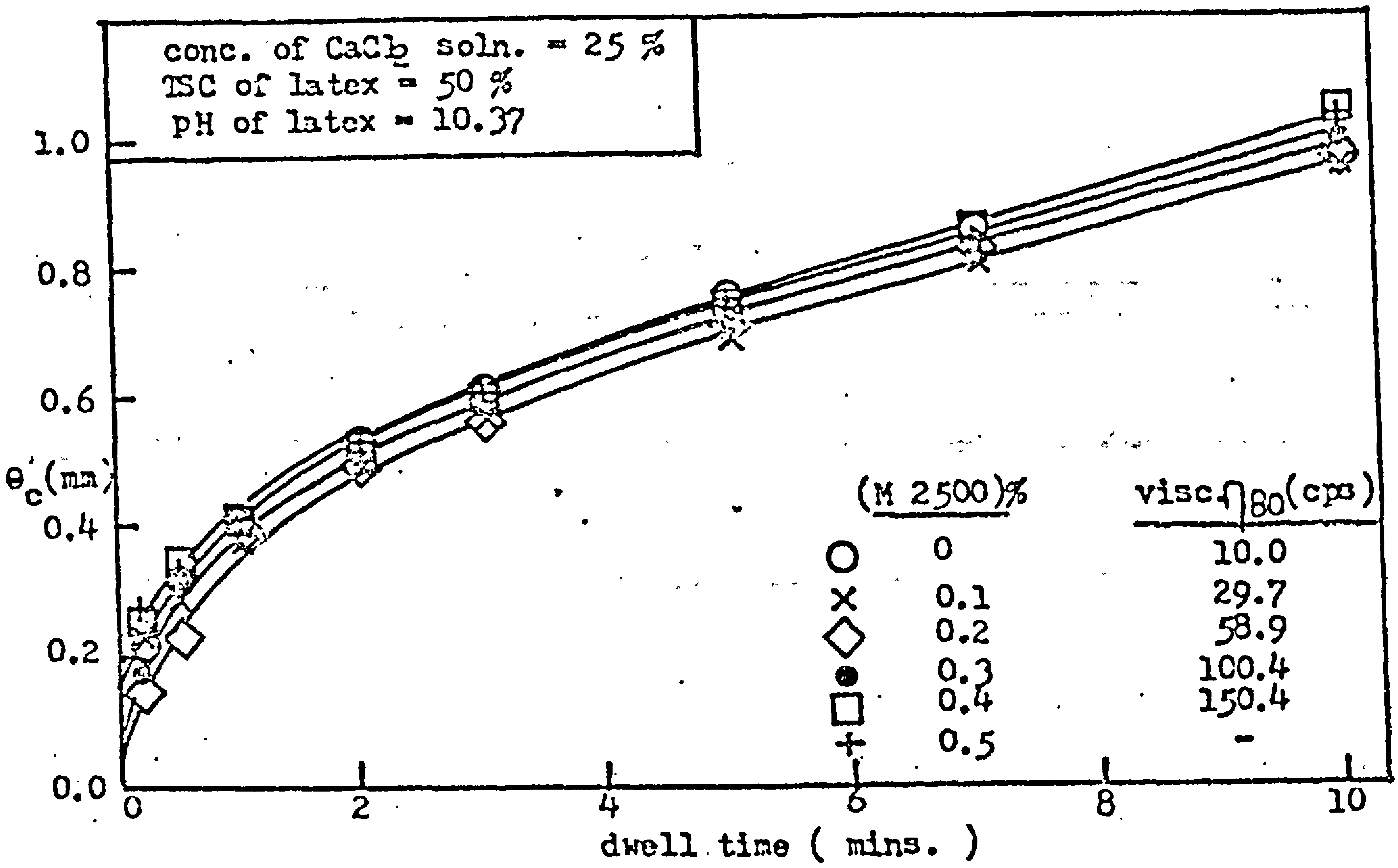


Figure 5.14. Dry coagulant deposit thickness-time relationship, showing the effect of added thickening agent.

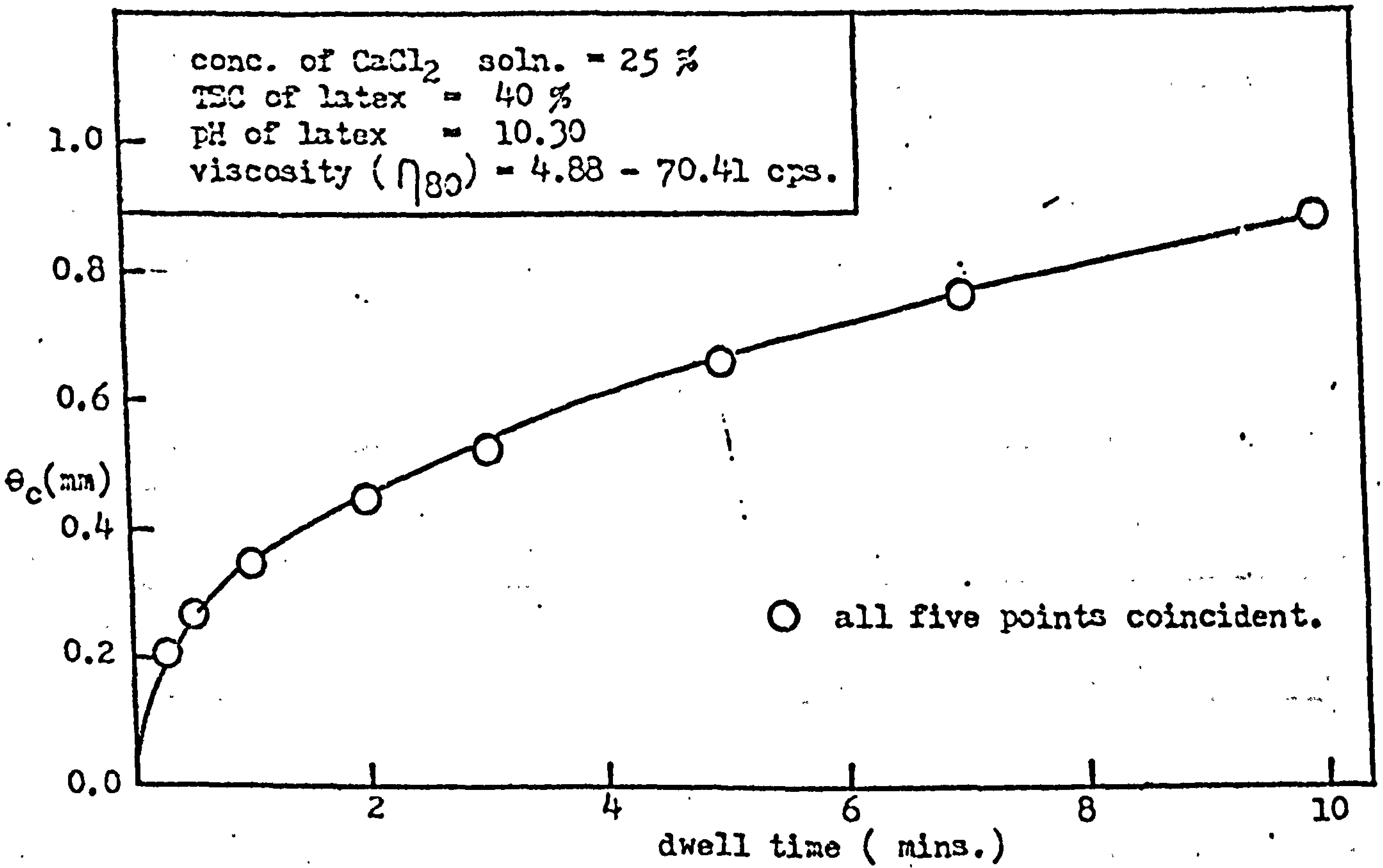


Figure 5.15. Dry coagulant deposit thickness-time relationship showing effect of added thickening agent.

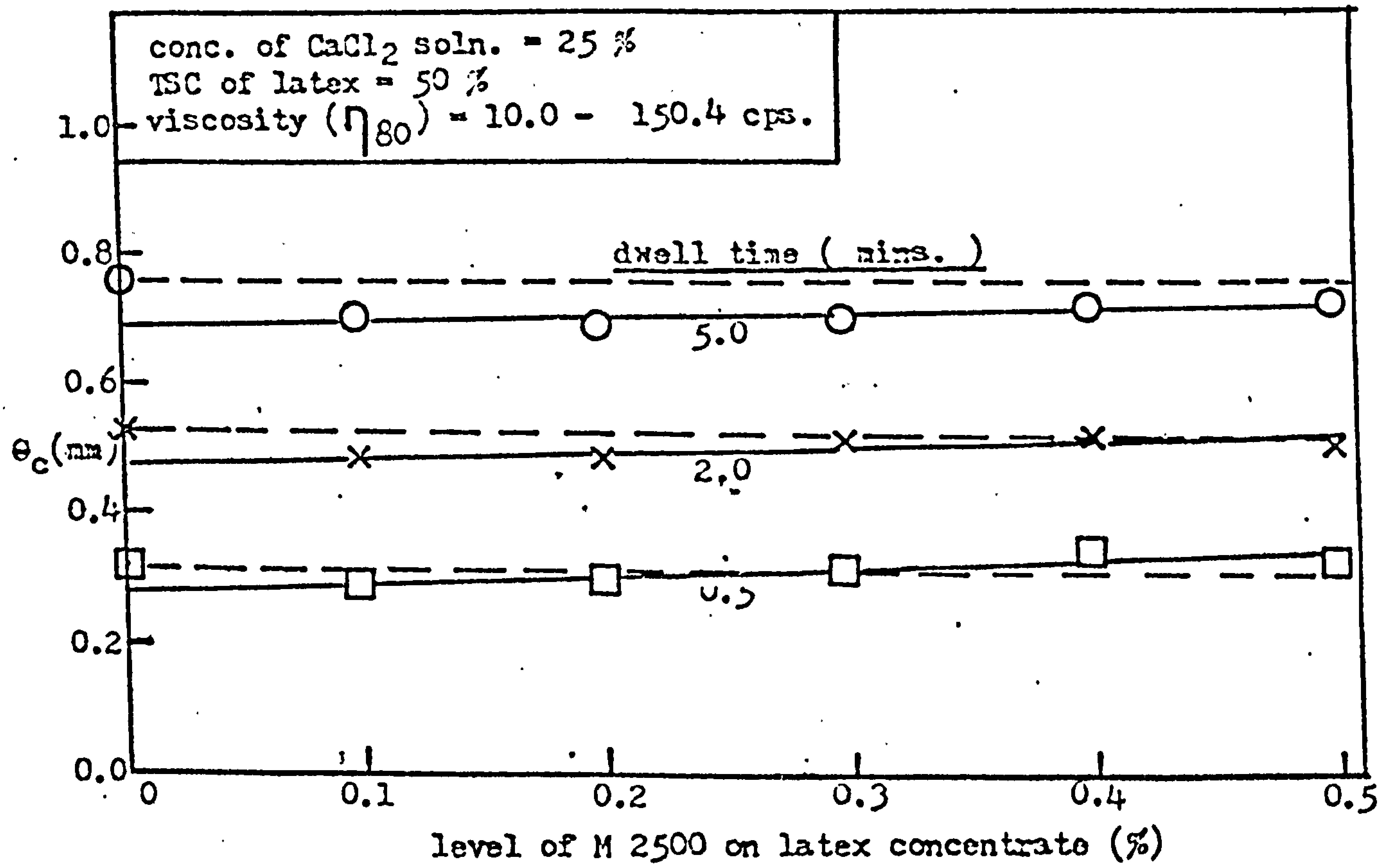


Figure 5.16. Effect of level of thickener upon dry coagulant deposit thickness (θ_c) obtained at various dwell times.

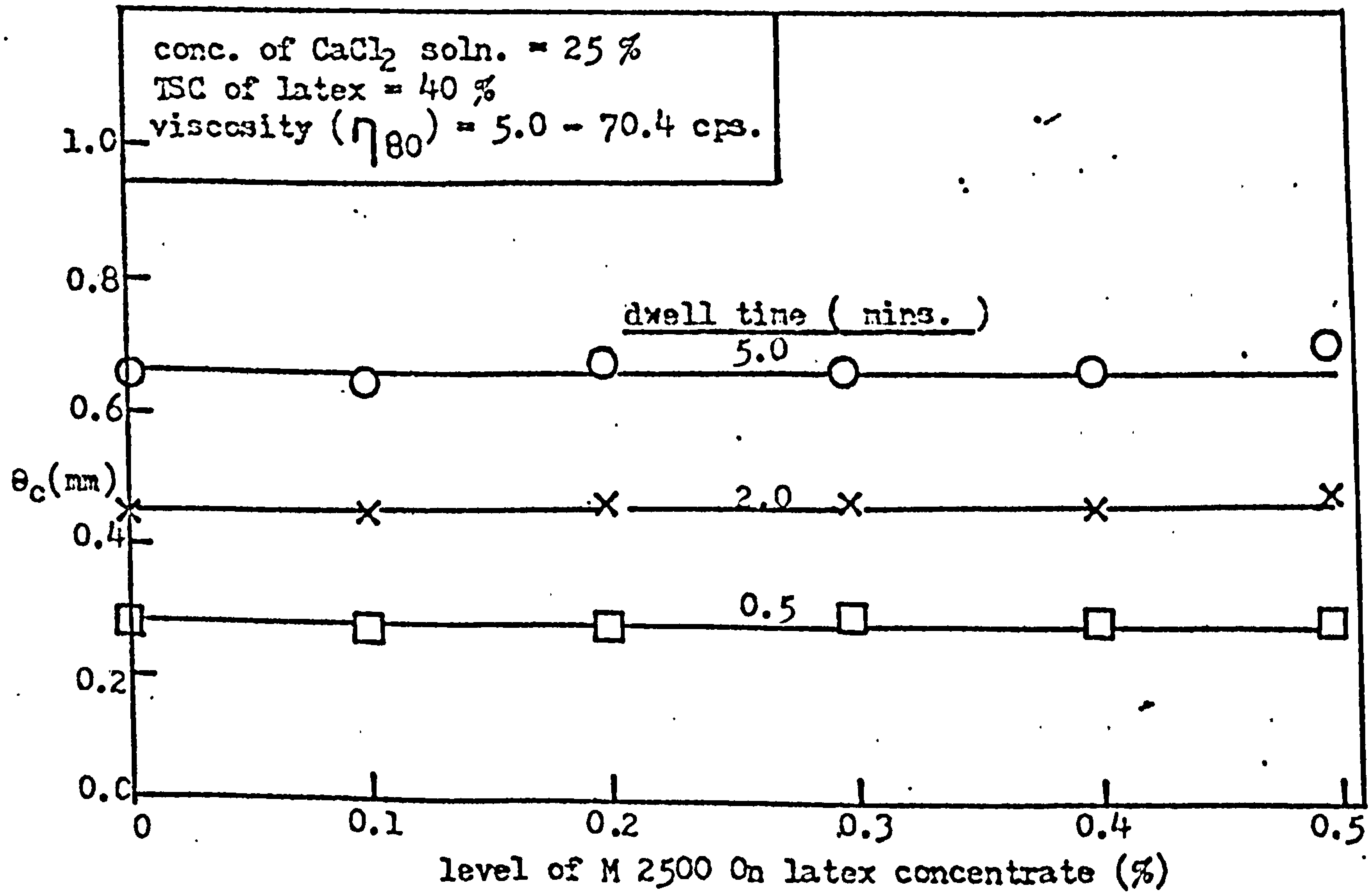


Figure 5.17. Effect of level of thickening agent upon dry coagulant deposit thickness (θ_c) obtained at various dwell times.

In view of the wide viscosity range of the latex compound used, it is possible that θ_s obtained with a coagulant dip may not be equal to that of θ_s obtained directly from a straight dip. In the former case, the straight-dip deposit is obtained in contact with the gel in which calcium ions are present and diffusing outwards. In the latter case, the straight-dip deposit is obtained in direct contact with the glass former, and consequently a greater flow of latex may be expected, especially for low-viscosity latex compounds, resulting in lower values of θ_s. Hence, θ_c calculated from Equation 5.2 using values of θ_s obtained from straight-dip thickness measurements may be over-estimated for viscous latex compounds. There is some evidence for this if plot of θ_c versus $t^{\frac{1}{2}}$ shown in Figure 5.18 is considered. It is seen that the intercept on the θ_c-axis increases with increasing level of thickening agent. It is thought that this difference is the increase in θ_s caused by the presence of the thickening agent. If this is so, then it appears that the viscosity of the latex, as modified by added methyl celluloses, has little effect upon θ_c.

The reason for the lack of effect of latex viscosity upon θ_c is thought to be as follows: When a gel is formed, the calcium ions diffuse through the capillaries of aqueous phase in the gel. The rate of diffusion is therefore controlled by the viscosity of the aqueous phase and not by the viscosity of the latex. The addition of thickening agents at the levels used in this work has a negligible effect upon the viscosity of the aqueous phase, although it does have a large effect upon the viscosity of the latex, possibly by interparticle bridging or some other mechanism[12,13]. Thus, since the viscosity of the aqueous phase remains substantially constant, the rate of diffusion of calcium ions is not affected appreciably by the presence of the

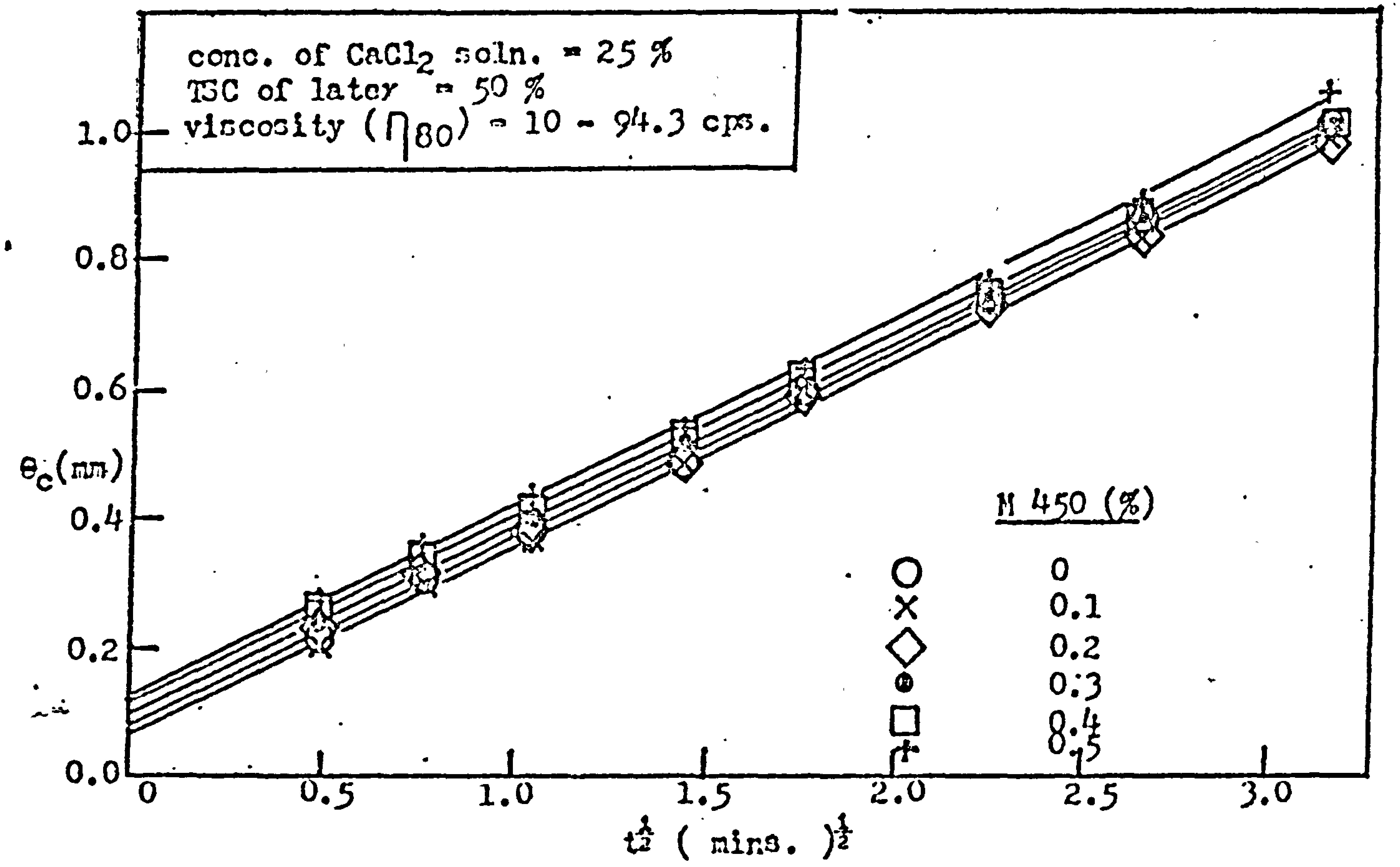


Figure 5.18. Dry coagulant deposit thickness versus the square root of dwell time for latices containing different level of added thickening agent.

thickening agents. Hence, the rate of deposition of rubber is not appreciably affected by the presence of the thickening agents.

5.3 Effect of surfactants upon θ_c

5.3.1 Effect of potassium fatty-acid soaps upon θ_c

The effect of potassium C_{12}- C_{18} fatty-acid soaps upon θ_s and θ_c were investigated. The level of soap added to the latex was varied from 0 to 1.0 parts by weight per 100 parts of latex solids. The total solids content was adjusted to 50%. The type and level of soap investigated had no effect upon θ_s. This was expected, since the soaps were found to have no effect upon the viscosity of the latex.

The effect of added soaps (laurate, myristate, palmitate and stearate) upon the relationship between θ_c and t is shown in Figure 5.19. The added soaps had only a slight effect upon θ_c. The effect upon θ_c was the same for all the soaps investigated. The characteristics of the curves in the presence of added soaps are similar to those of curves obtained in their absence. Similar observations have been reported by other workers[7-9].

The relationship between θ_c and $t^{\frac{1}{2}}$ for latices containing different types and levels of soap is shown in Figure 5.20. The results indicate that the levels and types of soap have virtually no effect upon the rate of diffusion of calcium ions in the latex gel deposit. Obvious mechanisms to explain the surprising lack of sensitivity of the thickness-time relationship to added fatty-acid soaps are as follows:

(i) The number of calcium-reactive anions in the latex is small compared to the number of calcium ions which are available

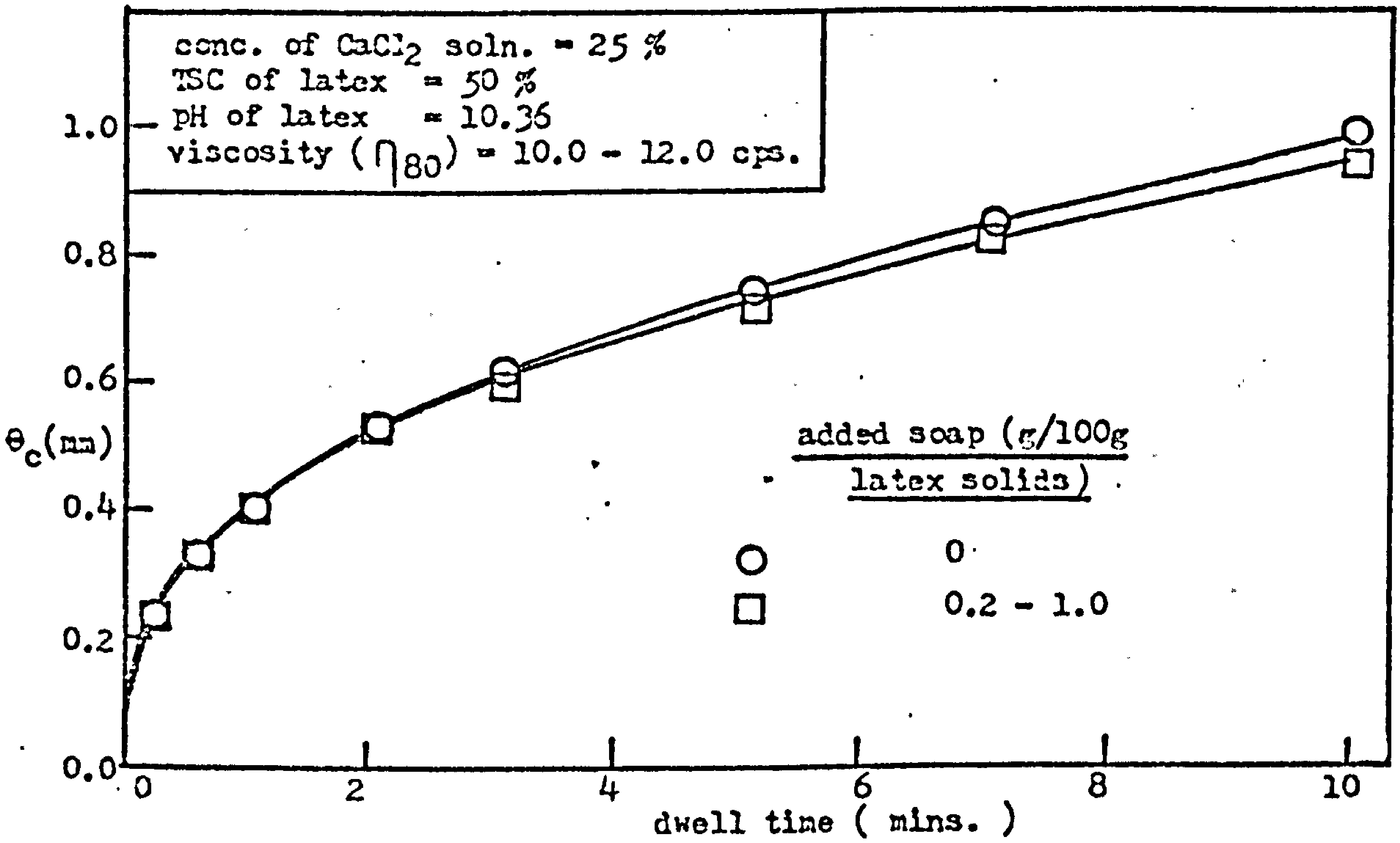


Figure 5.19. Dry coagulant deposit thickness-time relationship showing effect of added soap. The added soaps were potassium laurate, myristate, palmitate and stearate.

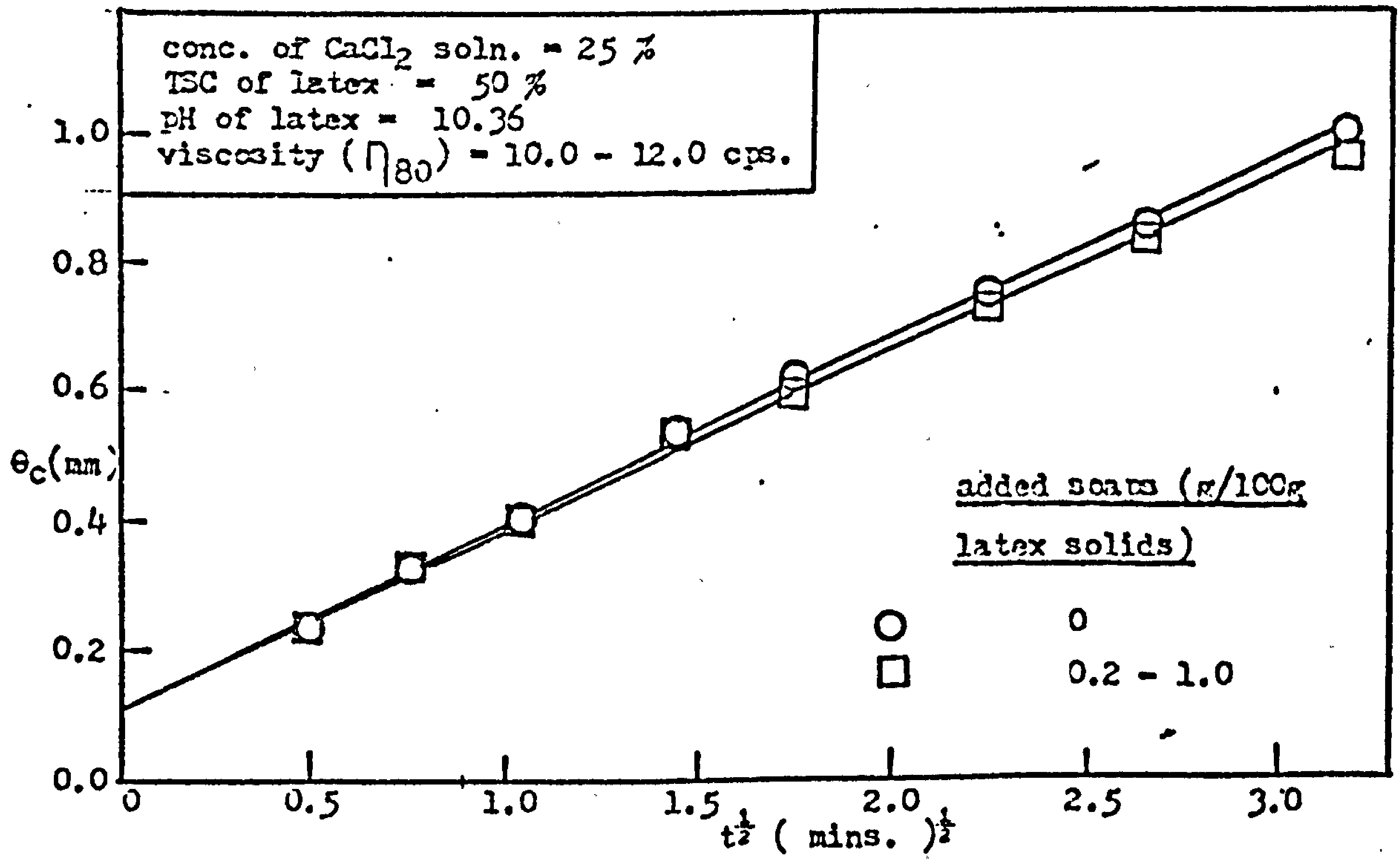


Figure 5.20. Dry coagulant deposit thickness versus square root of dwell time for different level of added soap. The added soaps were potassium laurate, myristate, palmitate and stearate.

for coagualtion, so that the addition of small amounts of fatty-acid soaps does not significantly alter the imbalance between calcium ions and calcium-reactive anions. ?

(ii) The principal species responsible for the colloid stability of the latex is not adsorbed higher fatty-acid anions but other species such as adsorbed proteins. If this were the case, then the level of added fatty-acid soap would have little effect upon the sensitivity to calcium ions.

(iii) The calcium chloride causes gelation solely by compression of the diffuse double layers which surround the rubber particles, rather than by reacting with adsorbed higher fatty-acid anions and proteins, i.e., the coagualting effect of the calcium chloride is non-specific rather than specific.

Reasonable calculations (see Section 8.2) show the first of these explanations to be implausible. Even at 10 minutes dwell time, the soap content within a gel only neutralises approximately 28% of the calcium present on the former, assuming that a 25% coagulant solution is used. The second explanation is inconsistent with the observation that, in respect of the effect of added fatty-acid soaps upon coagulant-dipping behaviour, synthetic latices stabilised exclusively with fatty-acid soaps behave similarly to natural rubber latex. The third explanation also appears to be implausible, partly because on general chemical grounds it is to be expected that the calcium ions will react with higher fatty-acid anions in the latex to form insoluble calcium soaps, and partly because the latex gels which form during coagulant dipping using calcium salts do not contain calcium in an insoluble form (see Section 7.2). Thus, the three suggestions above are not consistent with the observed results. It is likely that the mechanism of gelation is a combination of factors, namely compression of the diffuse double layers as in (iii) and neutralisation of the adsorbed higher fatty-acid anions and proteins. A more detailed discussion of these results will be given in Chapter 7 and 8.

5.3.2 Effect of ethylene oxide-fatty alcohol adducts upon θ_c

In these experiments, adducts of ethylene oxide and a given fatty alcohol of different molar ratios (n) of ethylene oxide to fatty alcohol were used. The values of n ranged from 6 to 60 (see Section 4.1.3). The level of ethoxylates added to the latex varied from 0 to 0.5 g per 100g latex solids. The type and level of ethoxylates investigated had no effect upon θ_s.

The effect of the addition of ethoxylate (n = 24) is shown in Figure 5.21. θ_c decreases slightly as the level of added ethoxylate increases, but above 5×10^{-4} moles per 100g latex solids, θ_c decreases rapidly to zero. Above this level, the deposit formed on the former was found to be too weak to adhere to the former when it was withdrawn, and the gel slipped off into the latex. It was also found that the dry deposit that remained on the former had cracked or broken surfaces; the higher the level of ethoxylate added, the greater was the number of cracks present.

The effect of n was investigated at a constant level of added ethoxylates (3×10^{-4} moles per 100g latex solids). Figure 5.22 shows that θ_c is virtually independent of n at short dwell times (1 minute). At a dwell time of 5 minutes, there is a slight reduction of θ_c with increasing n. It was also observed that, as the values of n or the dwell time increased, the strength of the gel was reduced. (see Section 6.3.2)

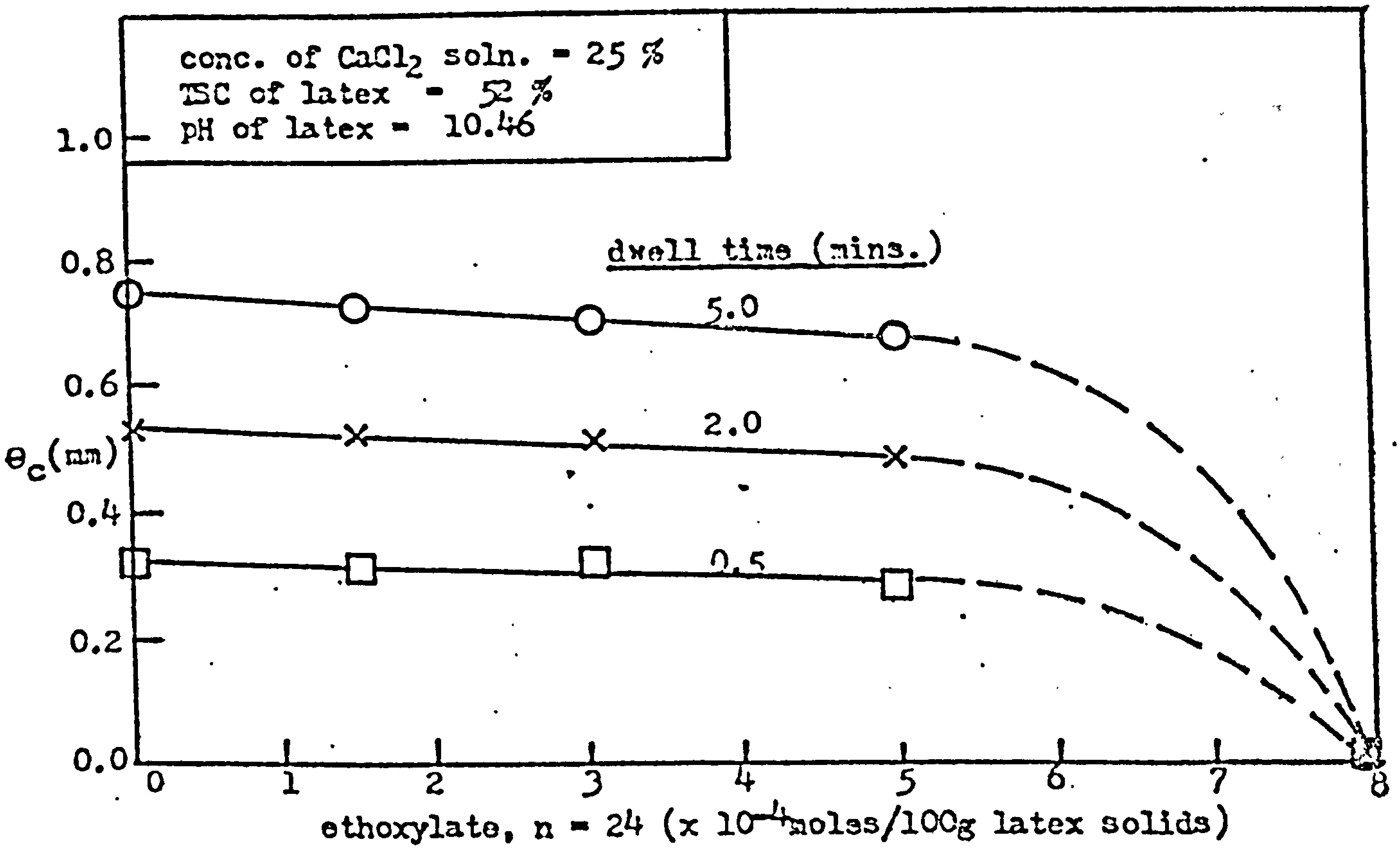


Figure 5.21. Effect of level of ethoxylate surfactant upon dry coagulant deposit thickness (θ_c) obtained at various dwell times.

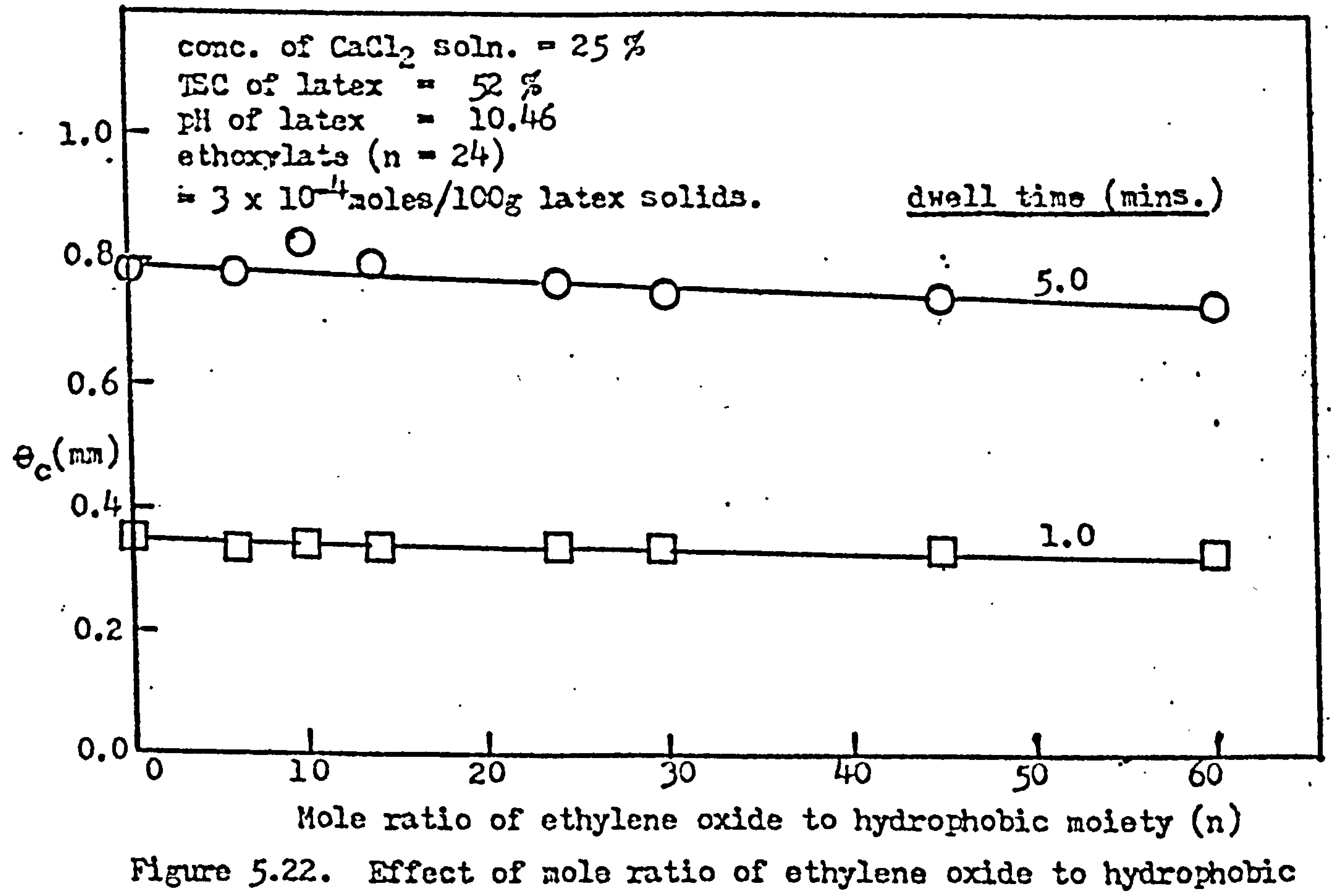


Figure 5.22. Effect of mole ratio of ethylene oxide to hydrophobic moiety upon dry coagulant deposit thickness (θ_c)

In all cases, the added ethoxylate had virtually no effect upon the thickness-time relationship. The fact that at higher level of addition the gel which formed was very soft and appeared to have insufficient mechanical strength to support its own weight suggests that the latex does gel at higher levels of addition. It also suggests that an increase in the degree of hydration, attributed to an increase in the bound water layers as the number of molecules of the ethoxylate adsorbed at the rubber-aqueous interface is increased, does not affect the rate of diffusion of calcium ions and the rate of deposition of rubber, but does affect particle coalescence, as indicated by the softer and less cohesive nature of the gels formed.

5.4 Effect of pH of latex upon θ_c

The pH of the latex was varied from 10.46 to 7.80 by adding an appropriate amount of a 10% formaldehyde solution. In each case, the TSC of the latex was adjusted to 48%. The viscosity of the latex was found to be virtually unaffected by pH change over the range pH 10.46 to 9.0. Below pH 8.5 the viscosity of the latex increased substantially, and at pH 7.81 the latex gelled completely after standing for about one week at room temperature.

The relationship between θ_c and $t^{\frac{1}{2}}$ for these latex compounds is shown in Figure 5.23. In each case, the relationship is linear, and is independent of pH except when the pH value falls below pH 8.95. Typical results for the effect of the pH of the latex upon θ_c are shown in Figure 5.24. The results show that θ_c is substantially constant between pH 9.0 to 10.5 at any given time of dwell (0 to 10 minutes). Between pH 8.5 to 7.8, there was a significant increase in θ_c. It was noted that θ_c also increased between this region.

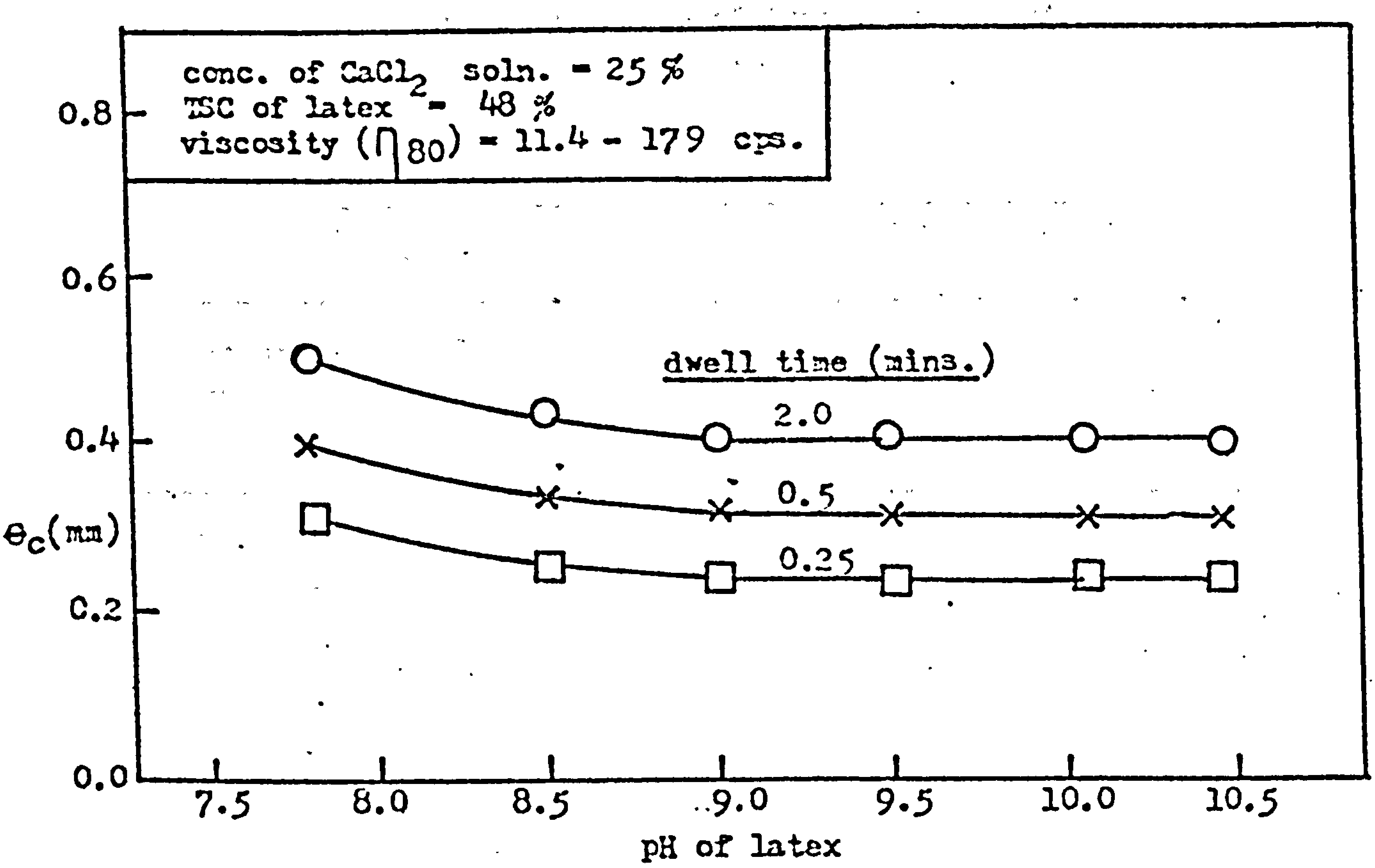


Figure 5.24. Effect of pH of latex upon dry coagulant deposit thickness (θ_c) at various dwell times.

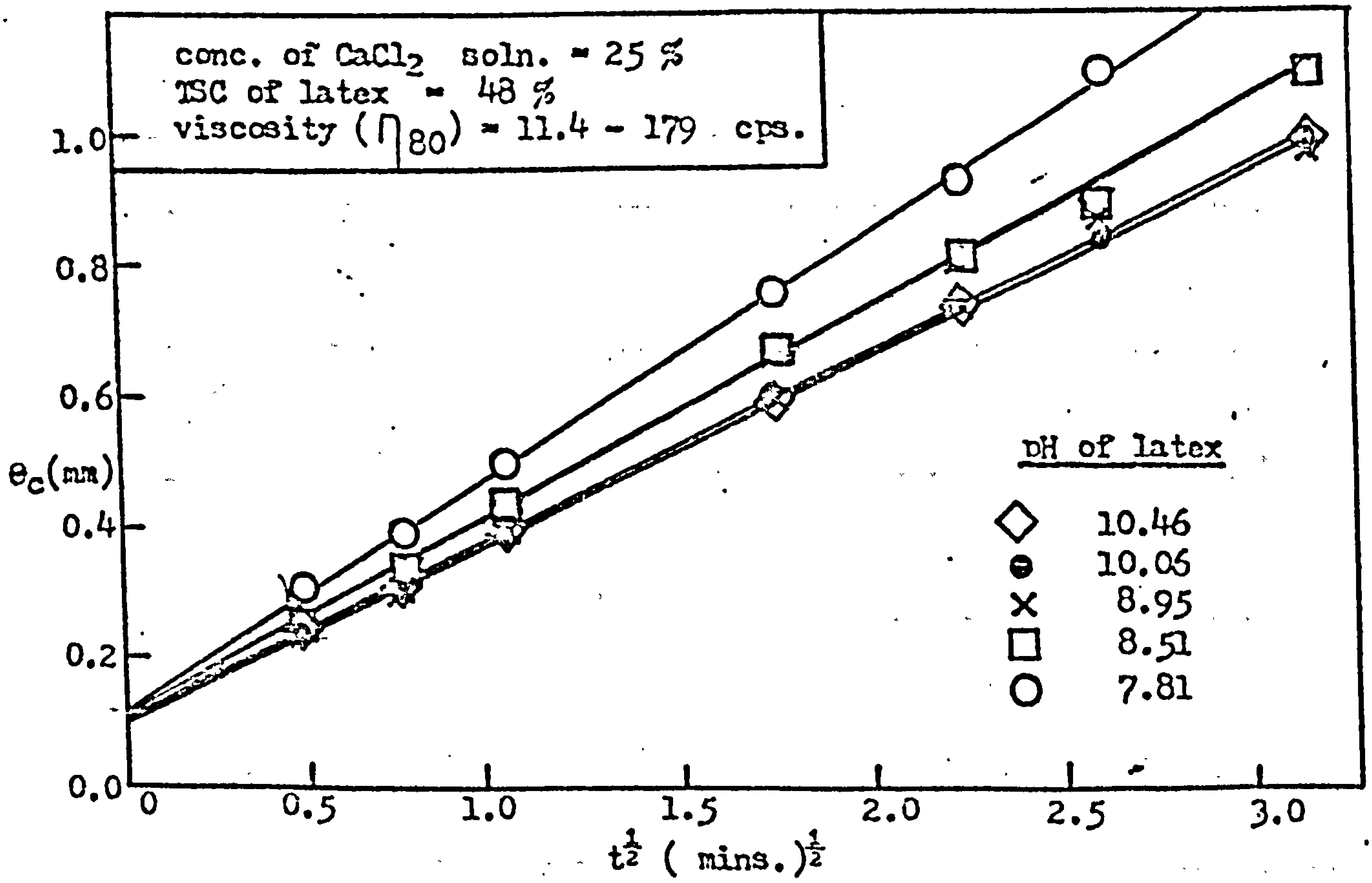


Figure 5.23. Dry coagulant deposit thickness versus square root of dwell time for latices having different pH values.

Table 5.1. Effect of pH upon degree of ionisation of stearic acid at 20°C (Turley(15) 1979)

pH	9.42	9.39	9.35	9.29	9.23	9.10
% ionisation	100	90	80	70	60	50
pH	8.97	8.81	8.61	8.35	7.55	
% ionisation	40	30	20	10	0	

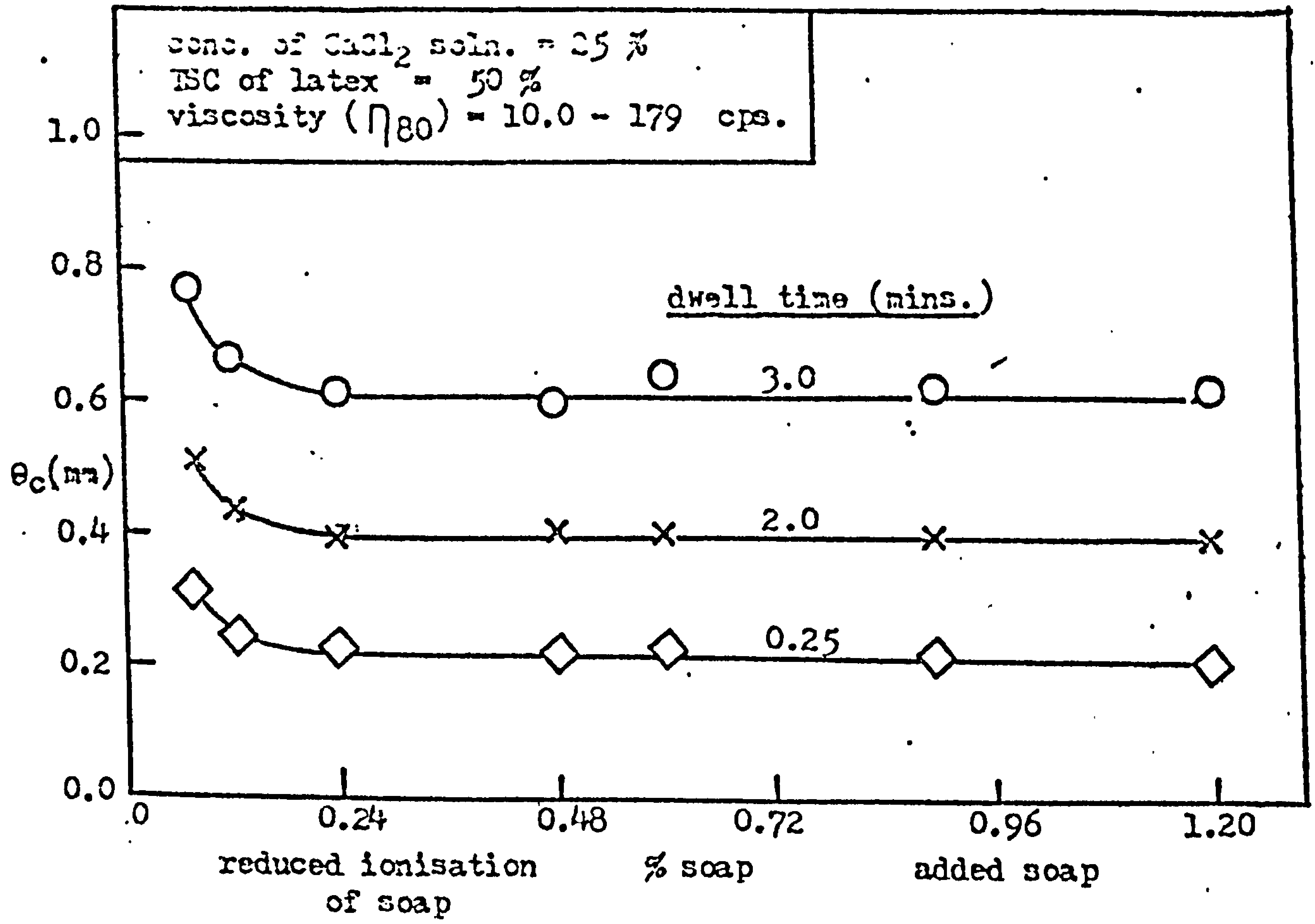


Figure 5.25. Effect of percentage soap ionised upon the dry coagulant dip deposit thickness (θ_c) at various dwell times.

Note: It is assumed that the latex contained 0.6 % indigenous soaps at pH of 10.4 (see Section 7.1.2.)

The effect of pH upon the degree of ionisation of stearic acid at 20°C has been calculated by Turley[15]. His conclusions are summarised in Table 5.1. Using these results, it is possible to estimate from the pH data the proportions of the soap present in the ionised form. The combination of these results with those for the effect of added soaps obtained earlier (see Section 5.3.1) is shown in Figure 5.25. For the purpose of relating the amounts of added soap to the amounts of indigenous soaps present in the ionised form at the various pH values, it was taken that the latex contained approximately 0.6% of fatty-acid soaps based upon the solids of the latex, and that these soaps were completely ionised at pH 10.4. This figure of 0.6% was found by titrating the latex with calcium chloride solution (see Section 7.1.2). It is seen that the relationship between θ_c and dwell time is remarkably insensitive to level of higher fatty-acid anions over a wide range. Since it has been found that the calcium ions react with the fatty-acid soaps to form insoluble salts, it is surprising that the level of soap does not affect θ_c. These results will be discussed further in Chapter 8.

5.5 Effect of concentration of coagualnt solution upon θ_c

The concentration of calcium chloride solution used in this investigation was varied from 15 to 35%. The compositions of the solutions are shown in Table 4.3, Section 4.1.5. The weight of calcium picked up per unit surface area of the former as determined by atomic absorption spectroscopy is shown in Figure 5.26.

The relationships between dry coagulant dip deposit thickness, θ_c, and the square root of the dwell time, shown in Figure 5.27, are linear except at low coagulant concentration and long dwell times.

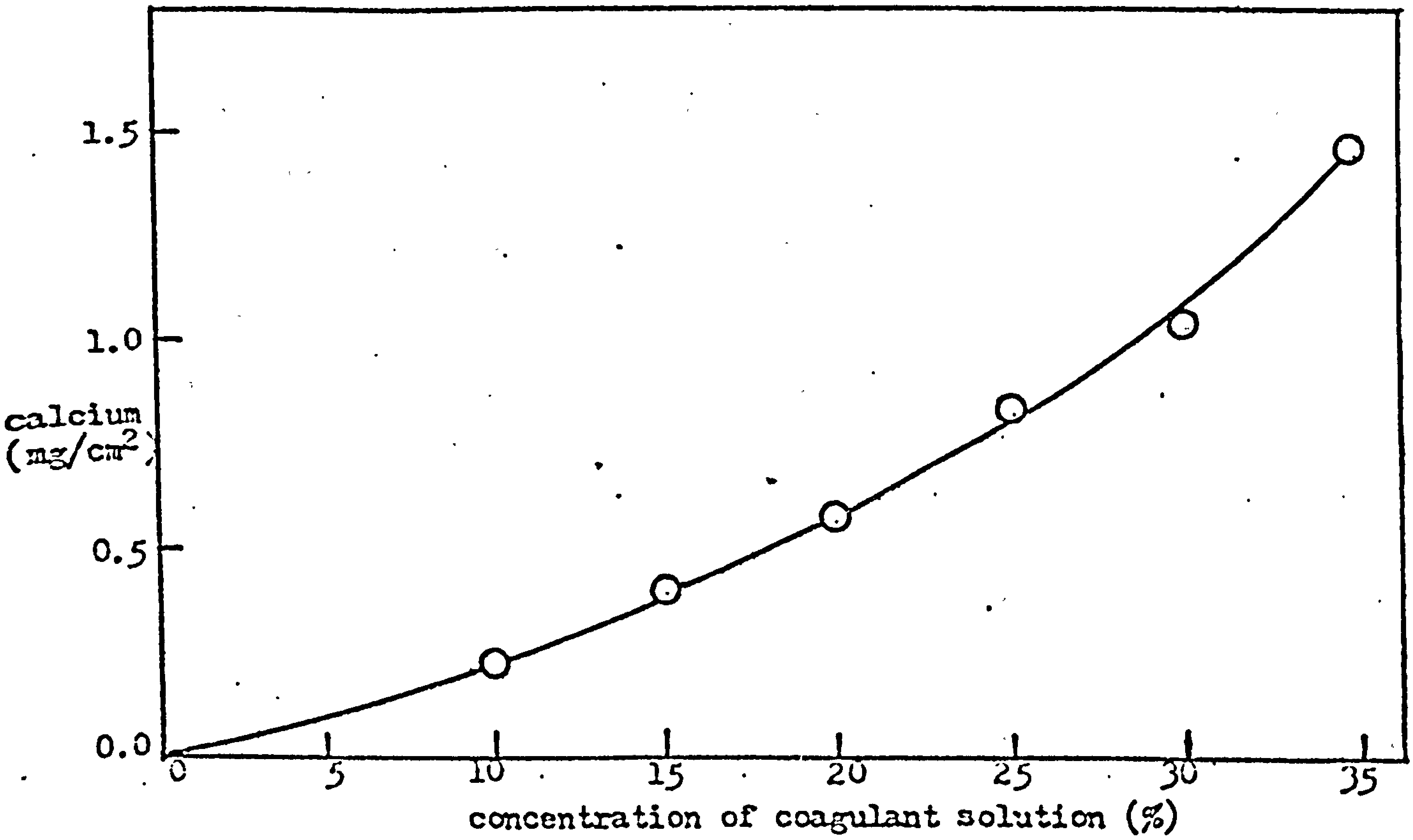


Figure 5.26. Amount of calcium pick-up per unit surface area of former as a function of concentration of coagulant solution.

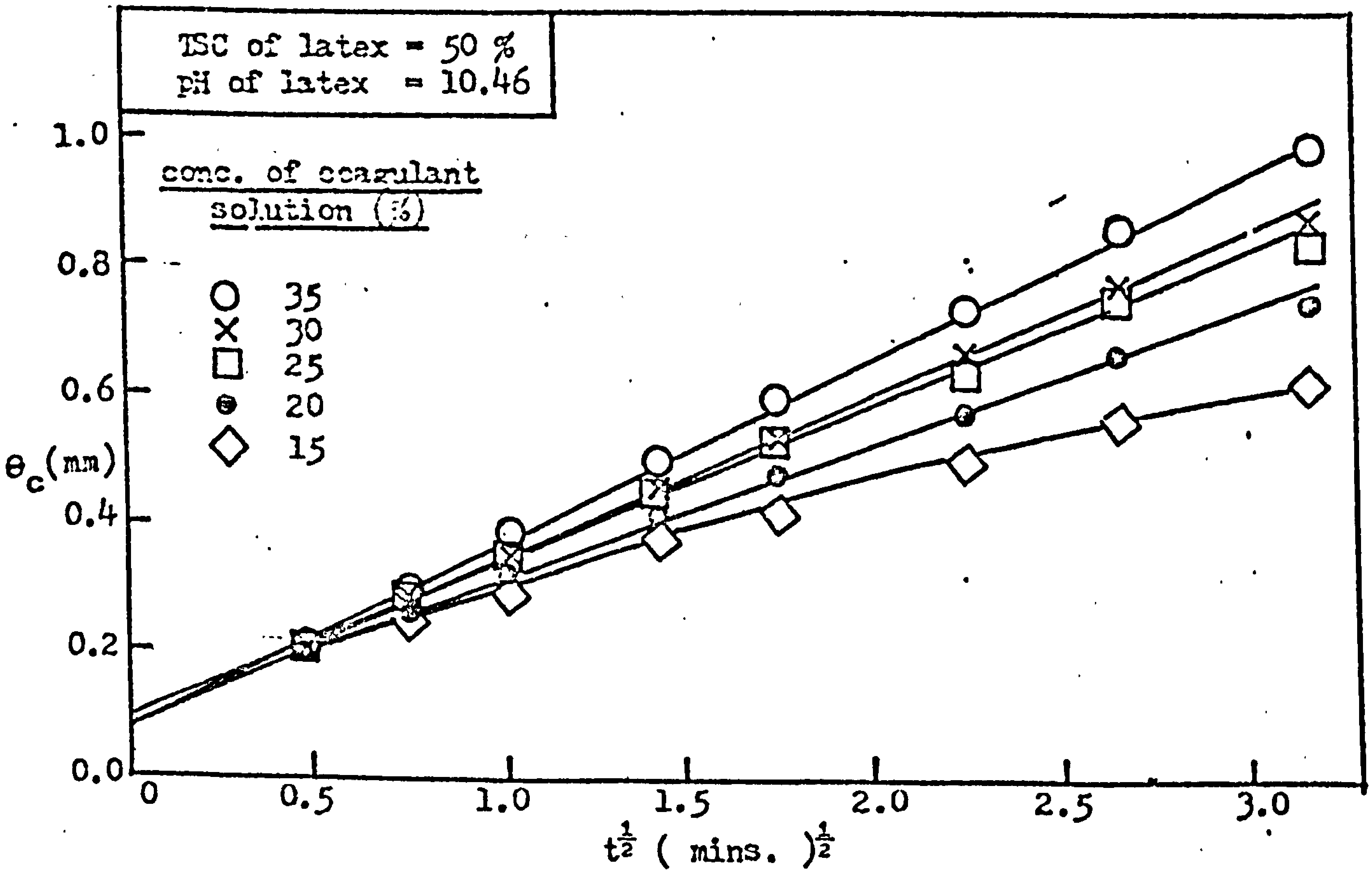


Figure 5.27. Relationship between dry coagulant deposit thickness and square root of dwell time for coagulant dipping using coagulant solution of various concentrations.

The amount of calcium on the former is thought to determine the concentration gradient of calcium in the latex gel, and hence the rate of diffusion of calcium ions and the rate of deposition of latex particles. As is evident from Figure 5.28, the value of θ_c obtained after a given time of dwell increases as the weight of calcium per unit surface area of the former is increased. The effect becomes more marked at the longer dwell times.

As expected, these results show that the amount of calcium which is present on the former has a significant effect upon the relationship between deposit thickness and dwell time. It has been found that water is exuded from the gel towards the former (see Section 6.1.2). This produces a calcium solution on the surface of the former, the concentration of which would be expected to depend upon the initial weight of calcium on the former; thus the greater the weight of calcium on the former, the greater the concentration of this solution. Presumably, the concentration of calcium solution on the former determines the concentration of calcium ions at the gel-latex interface, which in turn controls the growth of the gel[16]. This explains the nature of the curves shown in Figure 5.28. Again, this aspect of the investigation will be discussed more fully in Chapters 7and 8.

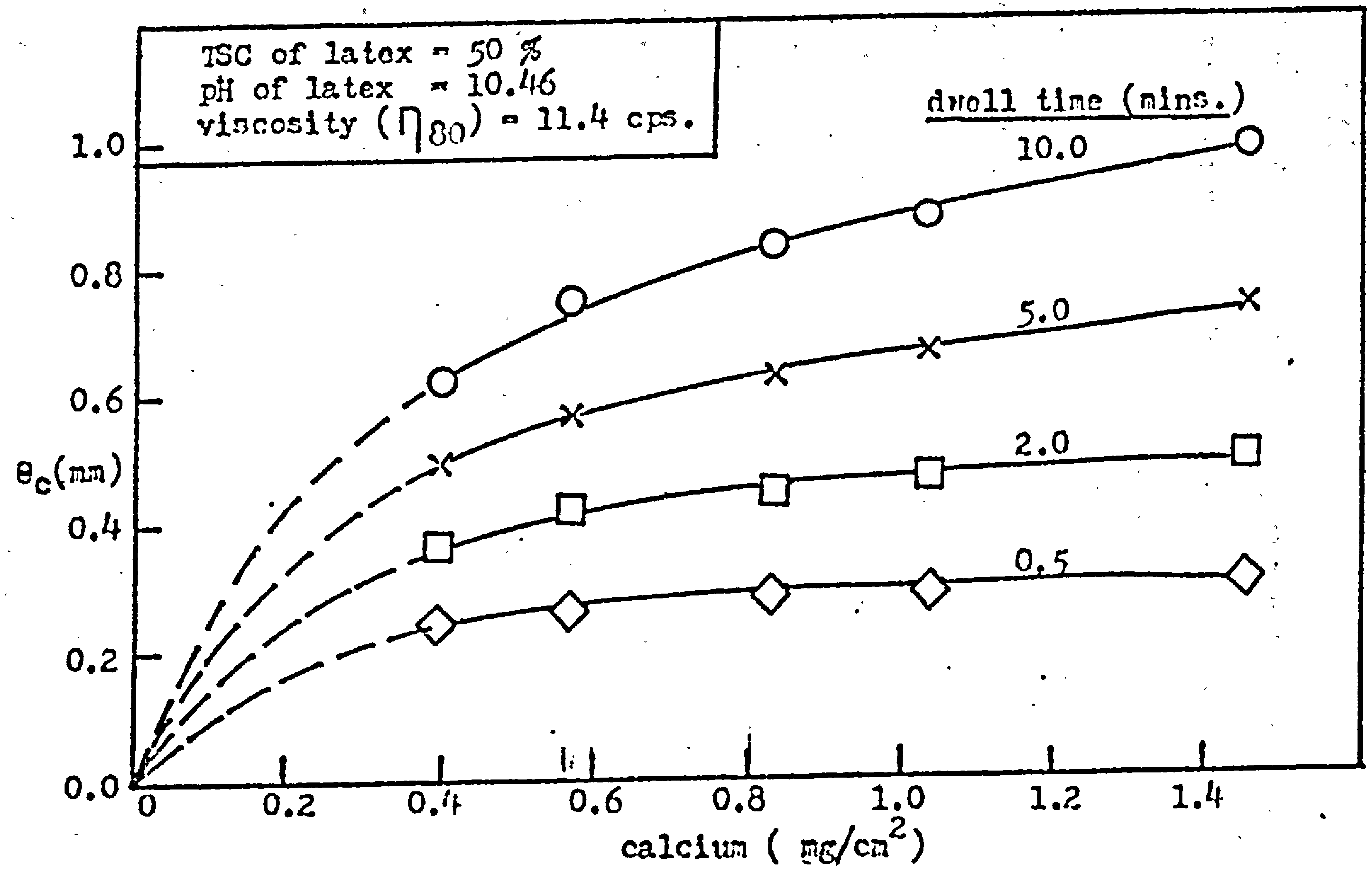


Figure 5.28. Effect of amount of calcium on the former on dry coagulant deposit thickness (θ_c) obtained at various time of dwells.

CHAPTER 6

RESULTS FOR SYNERESIS AND WET-GEL STRENGTH OF DEPOSITS

6.1 Syneresis of latex gels

After gelation or deposition, the gel sometimes continues spontaneously to contract such that the serum contained within the gel is squeezed out onto the surface. This process of spontaneous contraction of the gel and expulsion of the serum is known as " syneresis ". As a consequence, the total solids content (TSC) of the gel increases above that of the latex from which it was formed.

Much of the work reported in the literatures on syneresis is confusing because there has been little attempt to separate the processes of evaporation and dehydration of serum from the process of spontaneous syneresis[1-5]. In this work, an attempt has been made to eliminate the effects of evaporation. The results in Figure 6.1 show that the TSC of a gel left in air increases rapidly with time after removal from the latex (curves S1), while the TSC of a gel stored in a desiccator saturated with water vapour increases only very slightly (curve S2). Taken as an indication of syneresis, the results obtained in experiment S1 are quite misleading, because the water was lost as a consequence of evaporation rather than of syneresis alone. In order to study the syneresis of the gel, the effect of evaporation had therefore to be eliminated. This was achieved by placing the gel in an enclosed bottle, such that the serum squeezed onto the surface of the gel could be removed by blotting with paper, and the sample could be weighed without having to remove the gel from the bottle and expose it to evaporation in the open atmosphere (see Section 4.8).

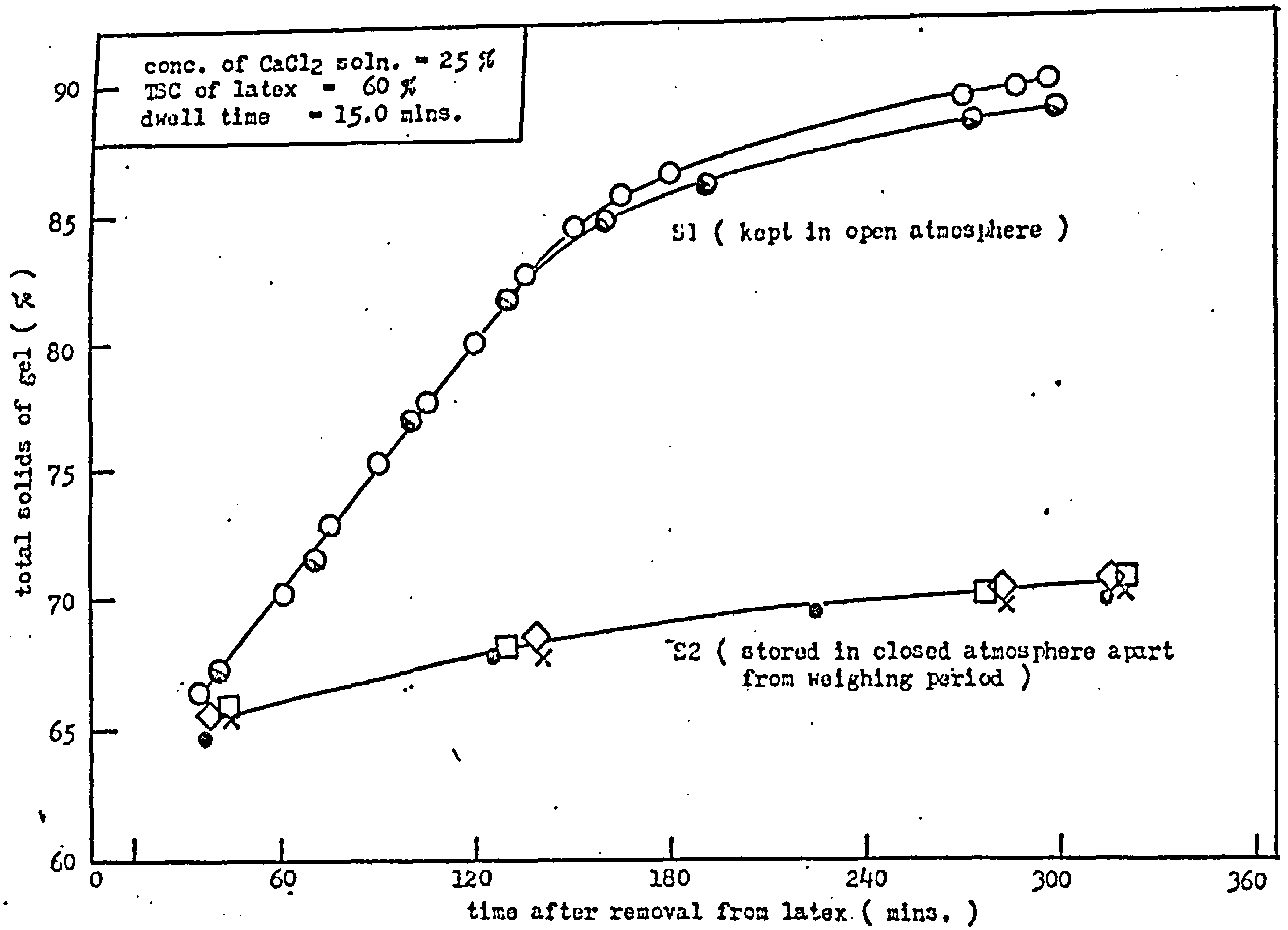


Figure 6.1. Total solids of gel as a function of time after removal from latex, showing effect of syneresis and evaporation.

The serum in a gel can be expelled to the outer surface or to the inner surface in contact with the former. The results described below were obtained in an attempt to differentiate between these two possibilities.

6.1.1 Syneresis outwards

In this experiment, the gel was allowed to remain on the former in an enclosed bottle. The outer surface of the gel was blotted to remove any exuded serum, and the whole was weighed at different time intervals after removal from the latex (0.25 to 5.0 minutes). The experiment was repeated for different dwell times.

The results shown in Figure 6.2 indicate that no serum is squeezed out to the outer surface of the gel over the time period investigated. Secondly, the apparent TSC of the gel was approximately the same as that of the latex. The total solids content calculated from this experiment is not the true TSC of the gel. It is the ratio

$$\frac{\text{weight of dry deposit}}{\text{weight of wet gel + coagulant solution on former}} \times 100$$

For this reason, it is referred to as the " apparent " TSC. Similar behaviour was observed for the other deposits obtained from latices of different TSC, as is shown in Figure 6.3. The dotted line represents the theoretical TSC of the gel on the assumption that its TSC was the same as that of the latex from which it was formed. The experimental values were somewhat higher because they included the weight of the coagulant on the former, which in this experiment was weighed together with the gel. The results clearly show that regardless of the time of dwell and the initial TSC of the latex, there is virtually no syneresis outwards.

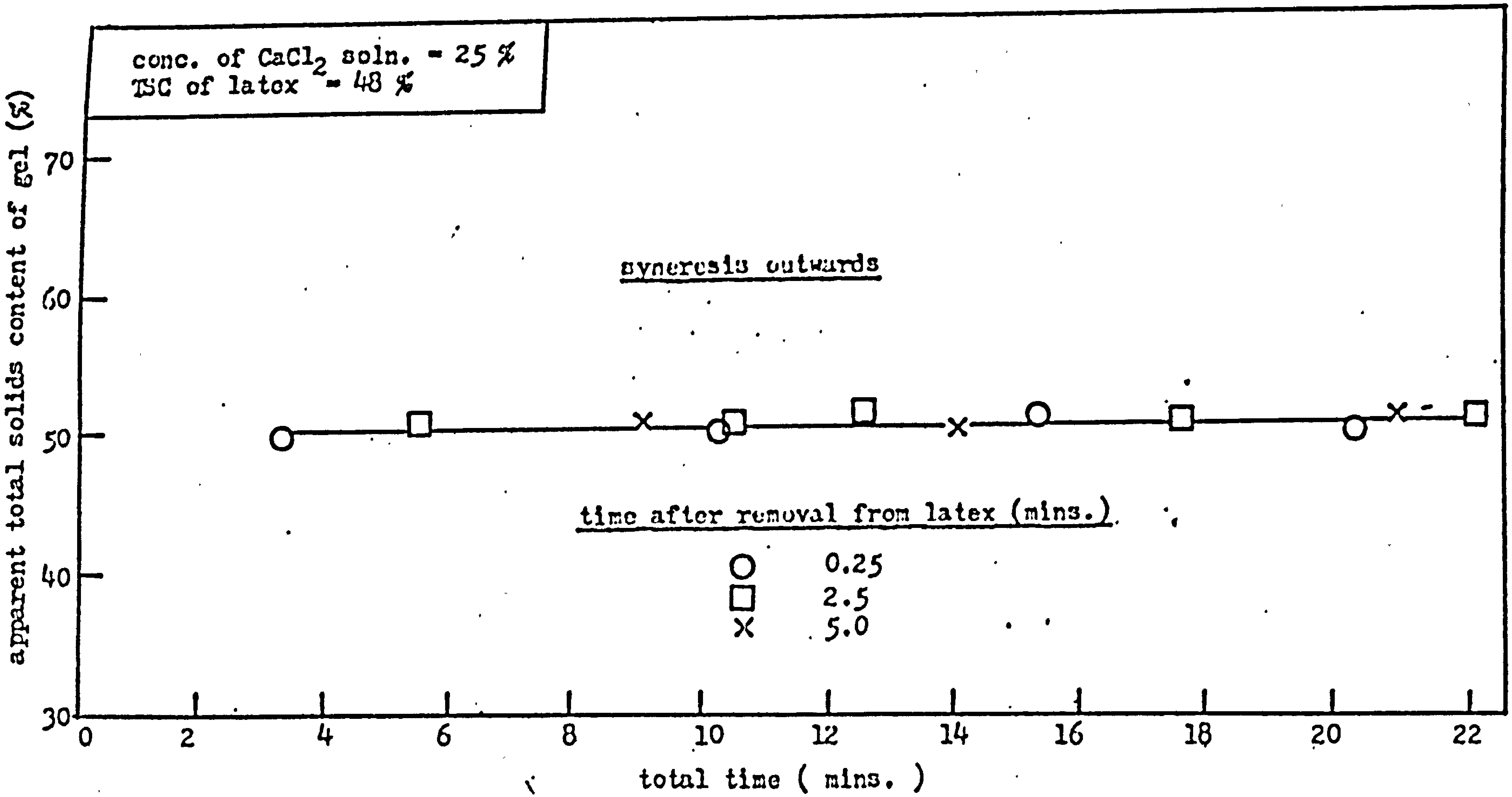


Figure 6.2. Apparent total solids content of gel as a function of total time. Total time (i.e. dwell time + time from withdrawal to weighing). The dwell times were 2, 5, 10 minutes.

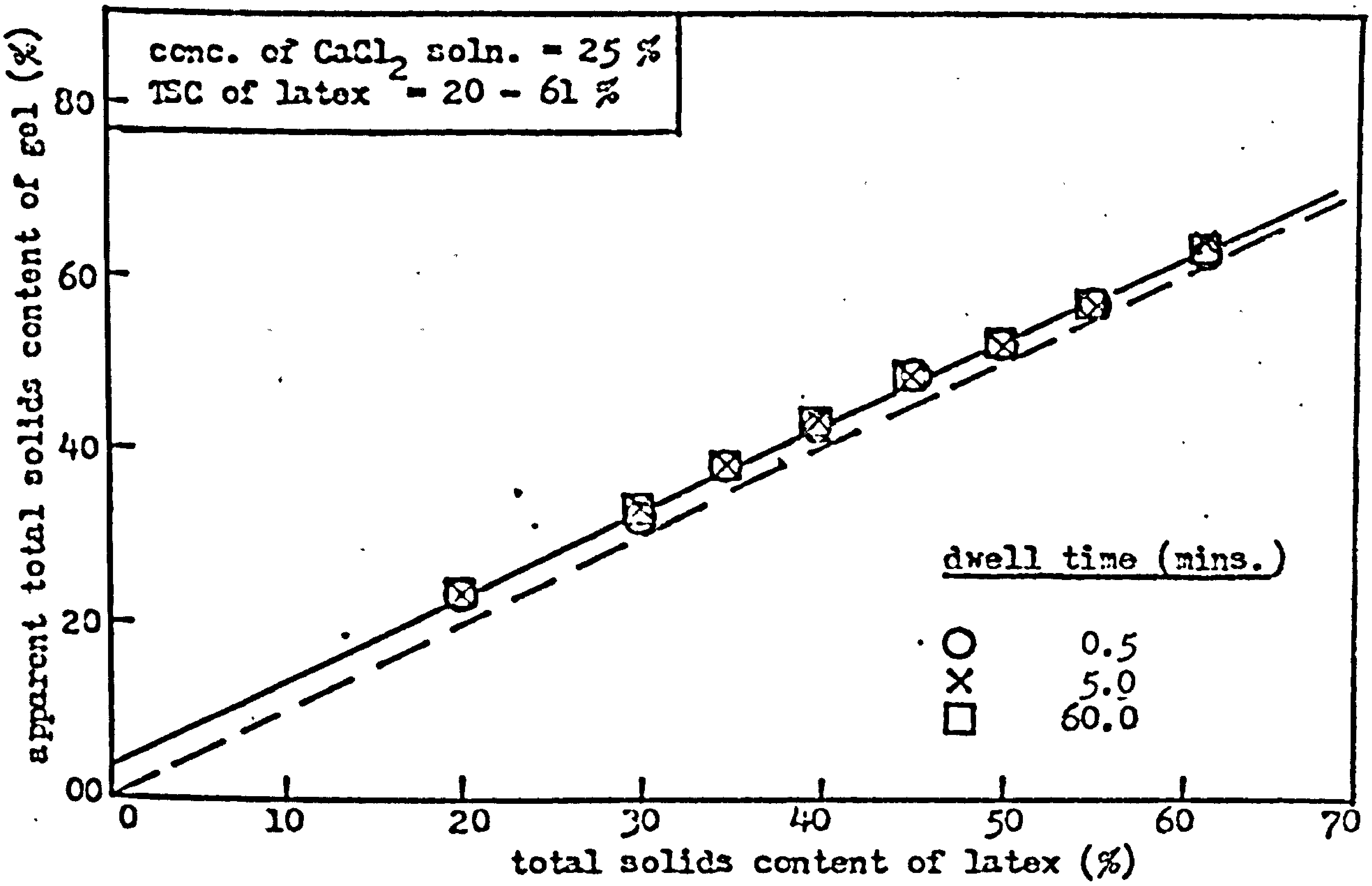


Figure 6.3. Apparent total solids content of gels obtained from latices of different total solids contents and various dwell times, showing effect of syneresis outwards.

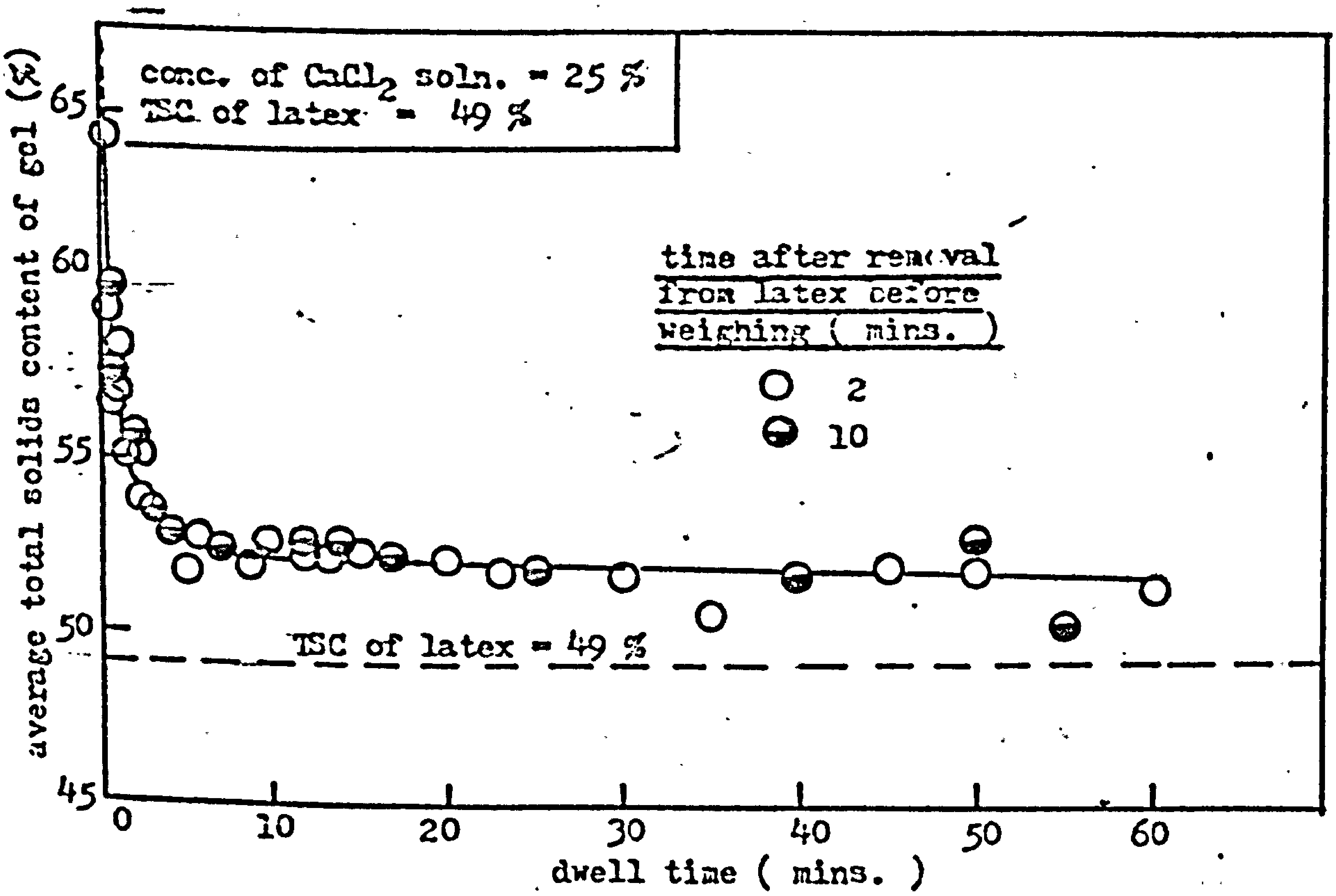


Figure 6.4. Total solids content of gel as a function of dwell time, showing effect of syneresis that occurs inwards during deposition.

6.1.2 Syneresis inwards

In this case, the gel deposit obtained was removed from the former and placed in an enclosed bottle. Exuded serum was removed by blotting with paper before weighing. The TSC of the gel was determined at different time intervals after removal from the latex (1 to 10 minutes). The experiment was repeated for different dwell times. The results are summarised in Figure 6.4. It must emphasised that the TSC referred to is the average TSC of the gel at that particular time of dwell; it is not the instantaneous TSC of a portion of the gel formed at any instant.

It is seen from Figure 6.4 that the TSC of the gel is greater than the TSC of the latex from which it was formed. Thus, syneresis occurs inwards. It is further seen that, within experimental error, very little change in the TSC of the gel occurs after removal from the latex. However, during the initial deposition, the TSC of the gel was very high but then gradually decreased as more deposit was formed, until , after about 5 minutes of dwell, the TSC of the gel remained approximately constant. This suggests that syneresis is rapid initially but subsequently slows down so that the TSC of the gel reaches equilibrium in about 5 minutes dwell time. It also suggests that syneresis occurs spontaneously during deposition, and then virtually stops after removal from the latex.

The relationship between the TSC of the latex and the TSCs of the gels obtained after 1.0, 3.0 and 5.0 minutes dwell time is shown in Figure 6.5. Similar patterns were found for other gels obtained from the latex containing added soaps. It is again apparent that the TSC of the gel is highest at short dwell times, and is directly related to the initial TSC of the latex. The TSC of the gel which has formed

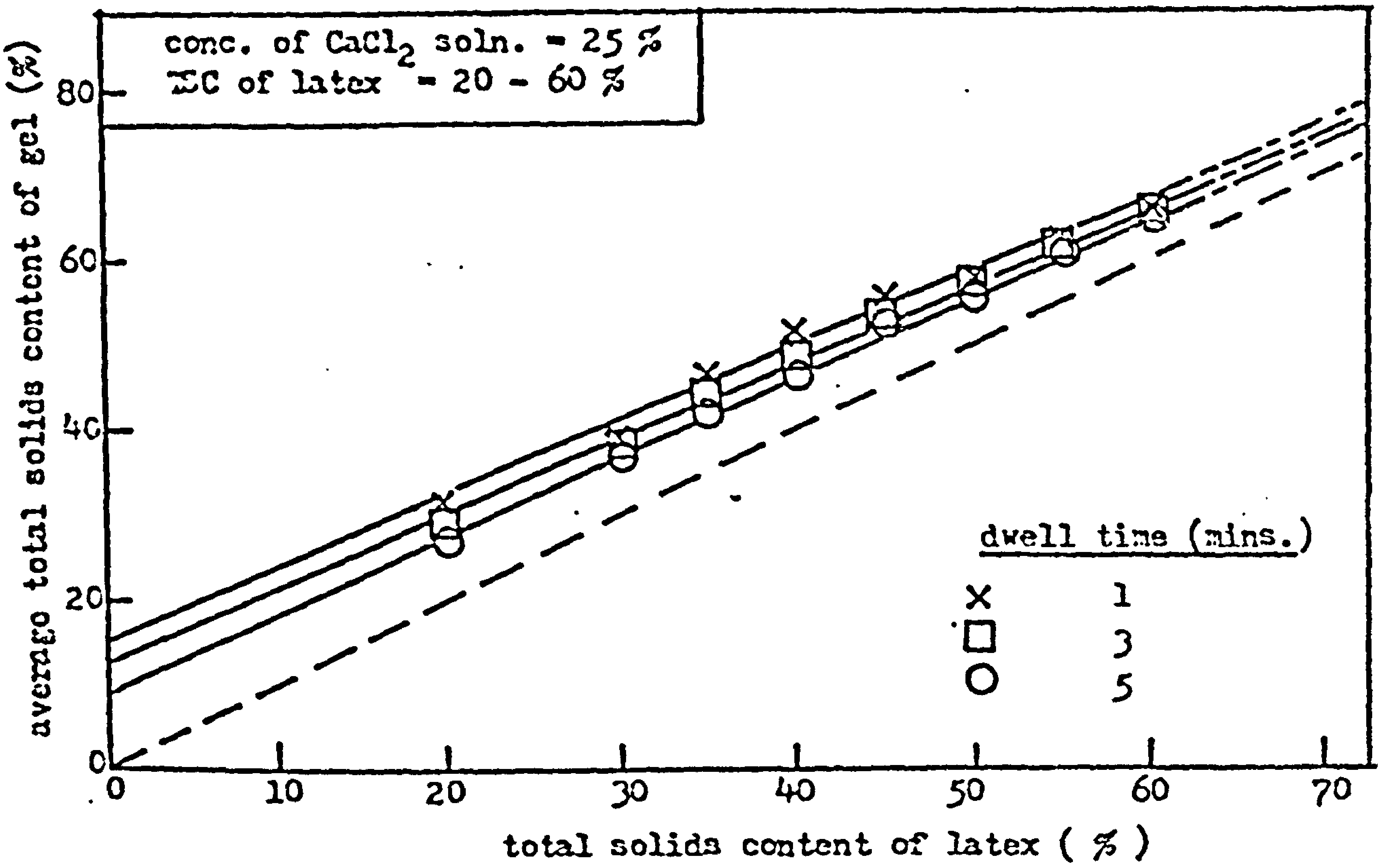


Figure 6.5. Total solids content of gel obtained from latices of different total solids content and after various dwell times, showing the effect of syneresis inwards. Each gel was weighed 2 minutes after removing the gel from the latex.

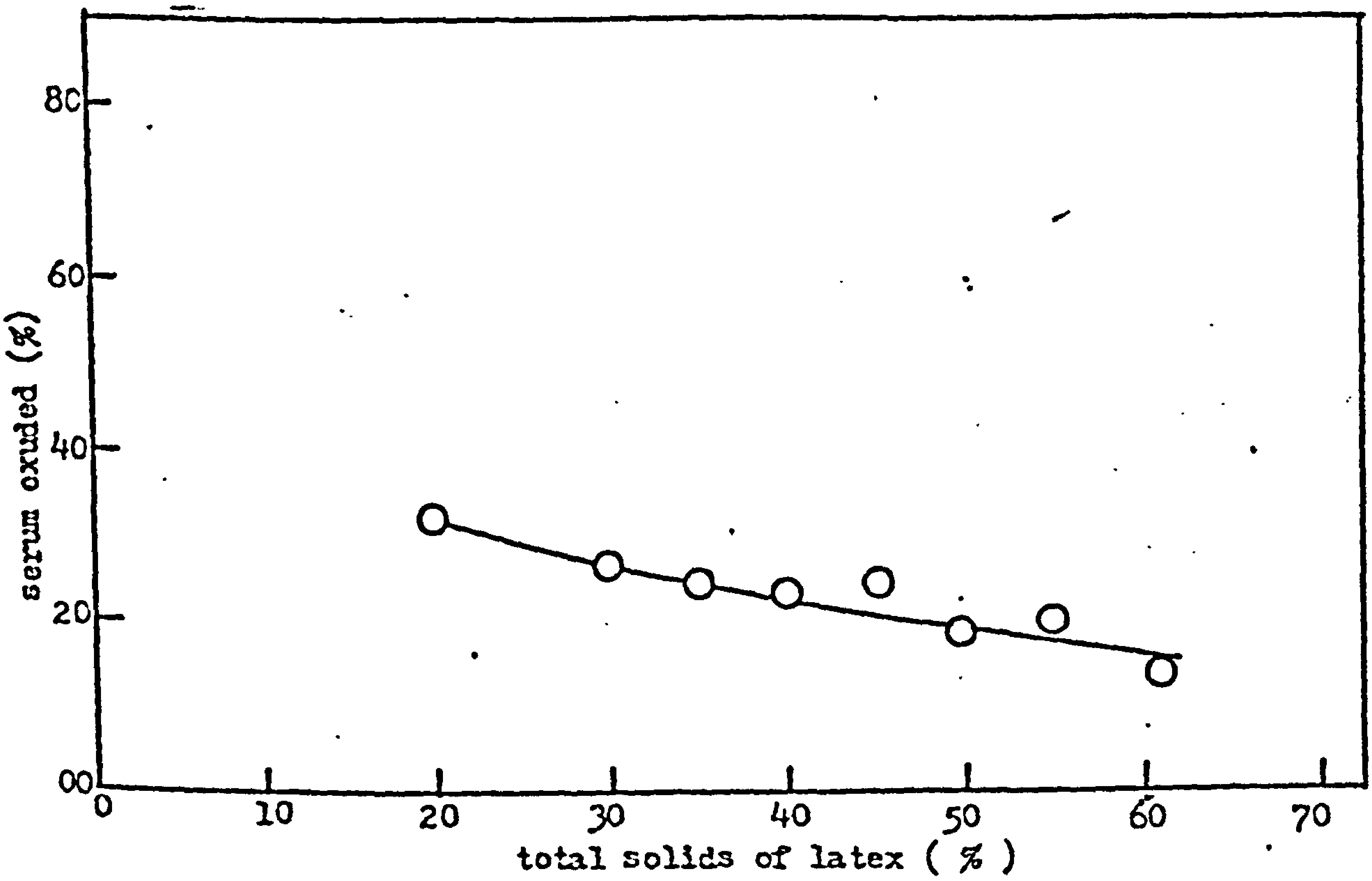


Figure 6.6. Volume percentage of serum exuded inwards towards the former at a specific time of dwell (5 minutes).

after any given time of dwell decreases with decreasing TSC of the latex. However, the volume of the serum exuded inwards towards the former increases with decreasing TSC of latex, (Figure 6.6).

In summary, the results show that the serum is exuded inwards, and that the TSC of the gel is greater than that of the latex from which it was formed. Thus, syneresis of the latex gels occurs inwards towards the former.

6.1.3 Syneresis during deposition

In the previous experiments, syneresis was measured after removing the former from the latex. An attempt was also made to measure directly the syneresis that occurs during the time that the deposit is forming. A former coated with coagulant salt was suspended from a balance arm, and then completely immersed into the latex. The apparent weight of the former and the deposit was recorded as a function of dwell time. The results are shown in Figure 6.7. The curves representing three repeated experiments (D1, D2 and D3), are all similar in shape although differing in detail. It is seen that the maxima in these curves occur at approximately 10 minutes dwell time. It is interesting to note that it was also seen earlier in Figure 5.4 that, when θ_c was plotted against $t^{\frac{1}{2}}$, there are two distinct lines intersecting at $t^{\frac{1}{2}} \simeq 3$. This is equivalent to a dwell time of approximately 10 minutes. It was postulated that after 10 minutes dwell time the latex gel was less coherent in the outer layers and flowed off the former when the former was withdrawn. However, the relevance of this to the shape of the curves in Figure 6.7 is not clear.

It is thought that the change in the apparent weight shown in Figure 6.7 is related to density changes that occurred between the

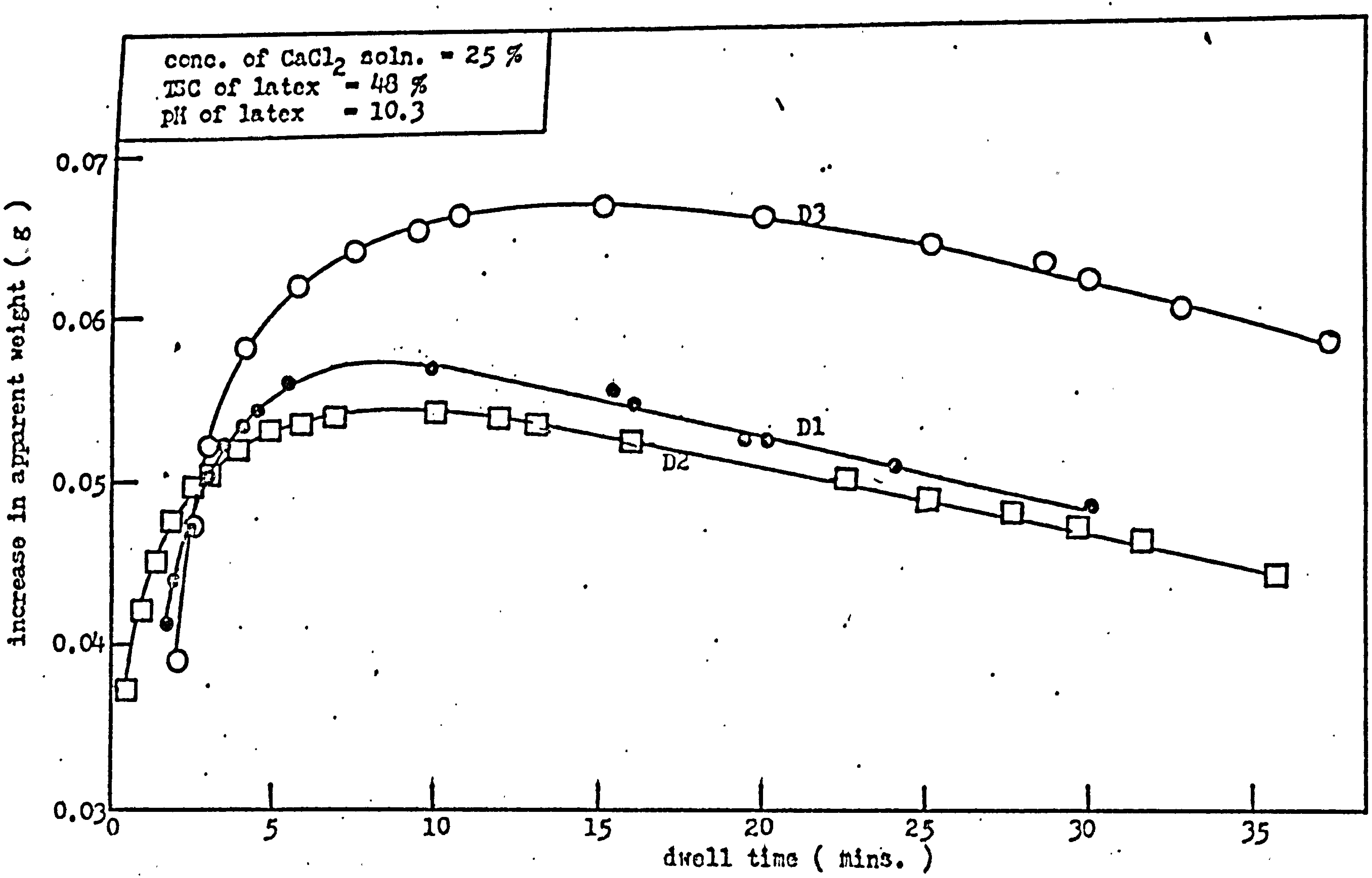


Figure 6.7. Apparent weight of deposit as a function of dwell time, showing effect of density change that occurs during deposition.

bulk latex and / or the deposit on the former. When the apparent weight is constant, the density of the deposit being formed at that instant of time should be equal to the density of the latex. However, when the apparent weight increases, the density of the deposit is possibly increasing and vice versa, since the density of the bulk latex is always constant. The change in density of the deposit may be the result of a change in the volume and / or composition of the deposit. The deposit is basically composed of two components, namely the rubber ($\rho_R = 0.92$) and the serum ($\rho_S = 1.02$). It was shown earlier that both the volume and the composition of the gel changed during deposition. However, it is not possible with the limited evidence available to draw any definite conclusions concerning the reason underlying the above observations.

6.1.4 Summary of results

The results shown in Figure 6.4 - 6.7 suggest that syneresis occurs during deposition, and that it occurs very rapidly. It reaches equilibrium in about 5 minutes dwell time. The amount of serum exuded depends upon both the dwell time and the TSC of the latex. Syneresis virtually ceases a short time after the gel has been removed from the latex. It is possible that the structure and composition of the gel are determined at the instant of formation of the gel, and do not change subsequently.

In industrial practice, syneresis is often seen to occur on both sides of the deposit. It has not been found to occur outwards in this investigation. It is possible that differences in the dipping procedures and the latex compounds used may have led to these conflicting observations. In this experiment, the temperature of the former was approximately room temperature, the depth of immersion was about 9 cm, and the dwell time ranged from 10 seconds to 60 minutes. In industrial practice, the temperature of the former is often high (60°C), the depth of immersion is often deeper depending upon the size and shape of the article. The latex is often prevulcanised. These differences in dipping procedures and latex compounding are thought to be important. For instance, heating increases the rate of syneresis, because increase in temperature assists the mutual coalescence of rubber particles[2]. The depth of immersion will give differences in hydrostatic pressure; the greater the depth, the greater the hydrostatic pressure exerted on the deposit. On withdrawal, the hydrostatic pressure is suddenly released, and this could cause syneresis to occur inwards and outwards. Gels obtained from prevulcanised latex compounds probably coalesce more slowly, with the result that syneresis is less rapid and continues for a longer period of time. Consequently, on withdrawal of a gel from an industrial latex compound, syneresis may possibly continue to occur on both sides of the deposit.

6.2 Total solids content of layers of gel

Syneresis is a dynamic and spontaneous process. During the formation of gel, the gel thickness builds up gradually with time of dwell (see Chapter 5). It is therefore expected that the TSC of successive layers of the gel will vary with time and thus thickness of deposit. An attempt has been made to (a) calculate and (b) measure experimentally the TSC of successive layers of the gel.

6.2.1 By calculation

The method of calculation described fully in Appendix 1 was used to calculate the TSC of successive layers within the gel. The method assumes that the composition of the gel remains constant once it is formed. The data for the average TSC of gel in Figure 6.8 were used to determine the TSC of successive layers of the gel. The calculated results are also summarised in Figure 6.8. It is seen that the TSC of successive layers of the gel decreases rapidly as the deposit builds up. On extrapolation to zero thickness, the curve cuts the axis at approximately 67% TSC of the gel (equivalent to 69% by volume). For a polydisperse system, the maximum volume packing fraction approaches 85%[6]. This suggests that the first layer of gel formed on the former is not packed to the maximum extent. Mc Geary[6] has stated that, in order to produce efficient packing, the following criteria are necessary:

(i) no plastic deformation should occur;

(ii) forces which tend to destroy systematic packing must be absent;

(iii) there should be at least a 7-fold difference between sphere diameters of the various individual components.

It is therefore not surprising that maximum packing is not achieved for latex particles within a gel, since there are at least three types of disrupture force acting, namely, electrostatic, steric and solvation forces. Futhermore, there is the mutual adhesion of particles that prevents any subsequent movement to produce more efficient packing. There may well be plastic deformation as well with a soft polymer such as natural rubber.

The rapid drop in the total solids content of the gel near the gel-latex interface suggests that the structure of the gel is becoming more open as the deposit builds up. The presence of the minimum trough shown in Figure 6.8. is possibly a consequence of experimental error or error in the assumptions made in the calculation.

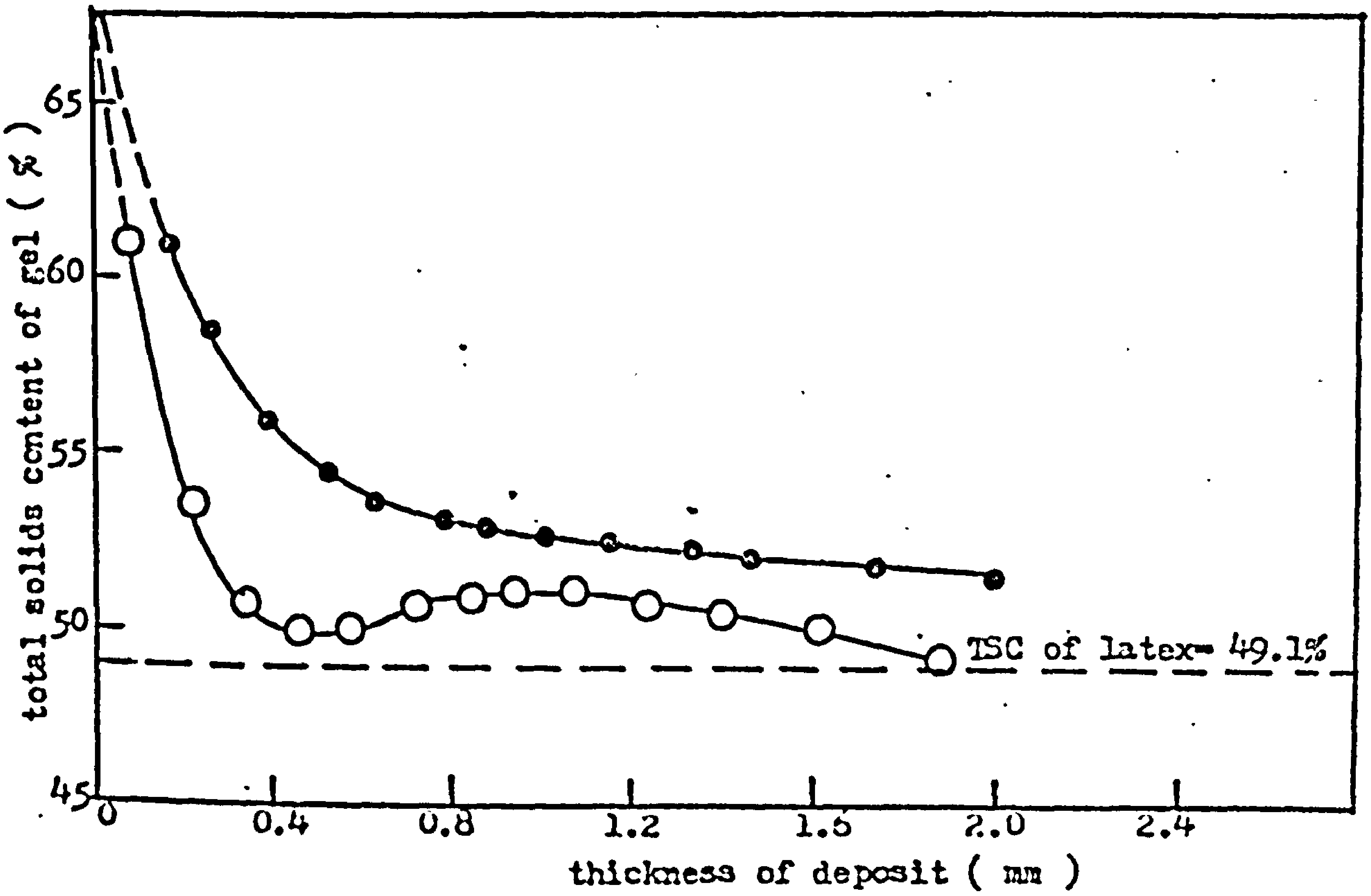


Figure 6.8. Total solids content of gel as function of deposit thickness.
● values of the average total solids of gel of thickness 0 - 2 mm.
○ values of the total solids content of successive strips of gel calculated from Equations 6.2 and 6.5 in Appendix 1.

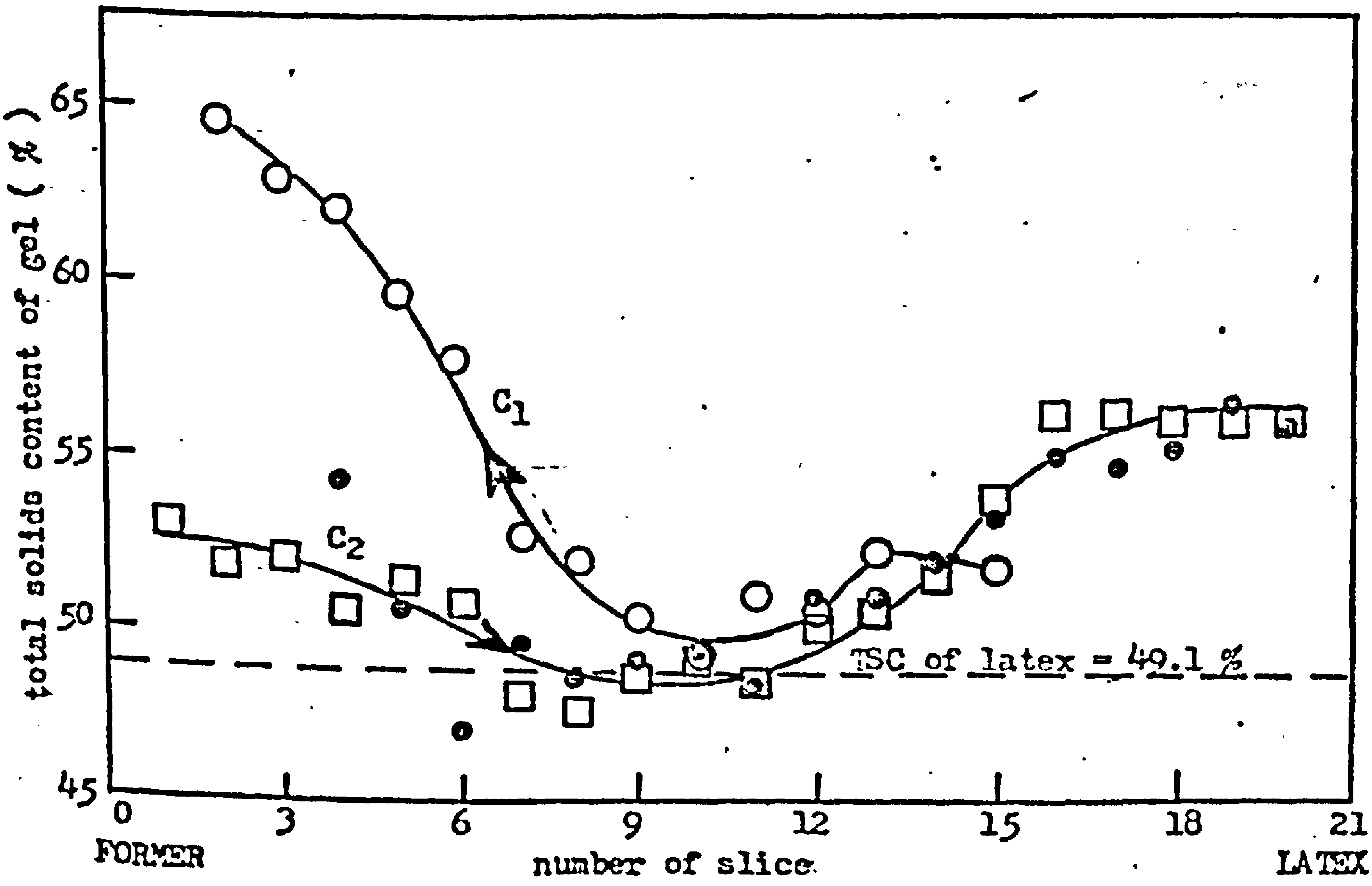


Figure 6.9. Total solids content of gel as function of number of slice. Each slice is approximately 0.01 mm thickness.

For example, one of the assumptions made is that the composition of the gel remains constant once it is formed. Although this may be true, it is not easily possible to verify it by experiment.

6.2.2 By experiment

An attempt was made to determine the TSC of successive layers of gel experimentally by freezing the gel and sectioning it with a microtome (see Section 4.10.4). In each case, the weight of the slice before and after drying was determined, and the TSC of each slice calculated.

The TSCs of successive layers of gel obtained after 60 minutes dwell time are shown in Figure 6.9. It is seen that two different curves are obtained. The first curve (C1) was obtained by freezing the gel from the outer surface to inner surface; the second curve (C2) was obtained by freezing from the inner surface to the outer surface. The curves are different because the freezing process altered the composition of the gel. This arises because of the volume change that occurred when the liquid aqueous phase was converted to the solid state. This method was therefore considered unsatisfactory as a mean of determining the TSCs of layers of gel. However, as will be described in Chapter 7, the microtome sectioning method has been used to obtain approximate estimates of concentrations of soluble and insoluble calcium within successive layers of the gel.

6.3 Wet-gel strength of deposits

The effects of TSC, pH and added soaps upon the wet-gel strength of deposits obtained by coagulant dipping were investigated. The strength of the gels obtained at 2 or 5 minutes dwell time was measured

40 minutes and 4 hours after withdrawal using an Instron tensile-testing machine (see Section 4.9). The test-pieces were used without leaching, in order to avoid further changes in the structure of the gel which might have occurred during the leaching process.

6.3.1 Effect of TSC of latex upon wet-gel strength of deposit

The effect of the TSC of the latex on the TSC of the gel is shown in Figure 6.10. The wet gels obtained after 2 minutes dwell time had higher ratios of rubber to serum than did those obtained after 5 minutes. Also, there is a linear relationship between the TSC of the gel and the TSC of the latex from which it was obtained. The lower is the TSC of the gel, the higher is the volume fraction of water in it, and therefore the more open is the structure of the gel.

Figure 6.11 shows that the tensile strength of the wet gel increases with increasing gel TSC. It is possible that the TSC of the gel indicates roughly the area of particle contacts within the gel; the higher is the TSC the higher is the number and area of particles in contact with each other. It is reasonable to suppose that the greater the number of interparticle contacts, the greater is the tensile strength.

It is also seen in Figure 6.11 that the tensile strength of the gel obtained after 2 minutes dwell time was found to be significantly greater than that of the gel obtained after 5 minutes dwell time at any given gel concentration. This suggests that the gels must have a different structure, and that this structure is important in determining the tensile strength of the gel. A similar trend was observed when the gel was tested 4 hours after withdrawal.

The actual TSC of the gel varies throughout its thickness (see Figures 6.8 and 6.9). The values used to construct Figures 6.10

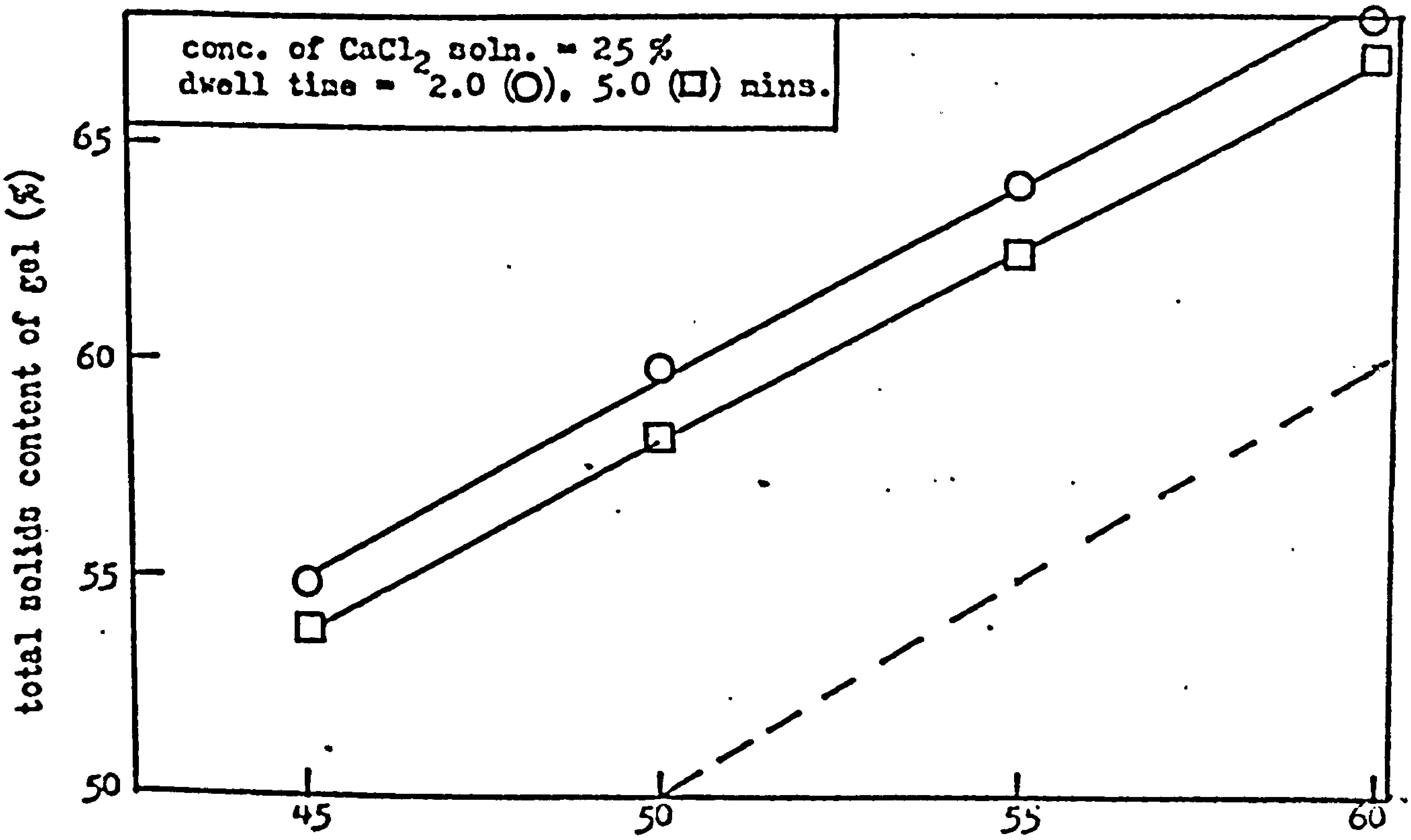


Figure 6.10. Total solids content of gels obtained from latices of different solids contents and at two different dwell time.

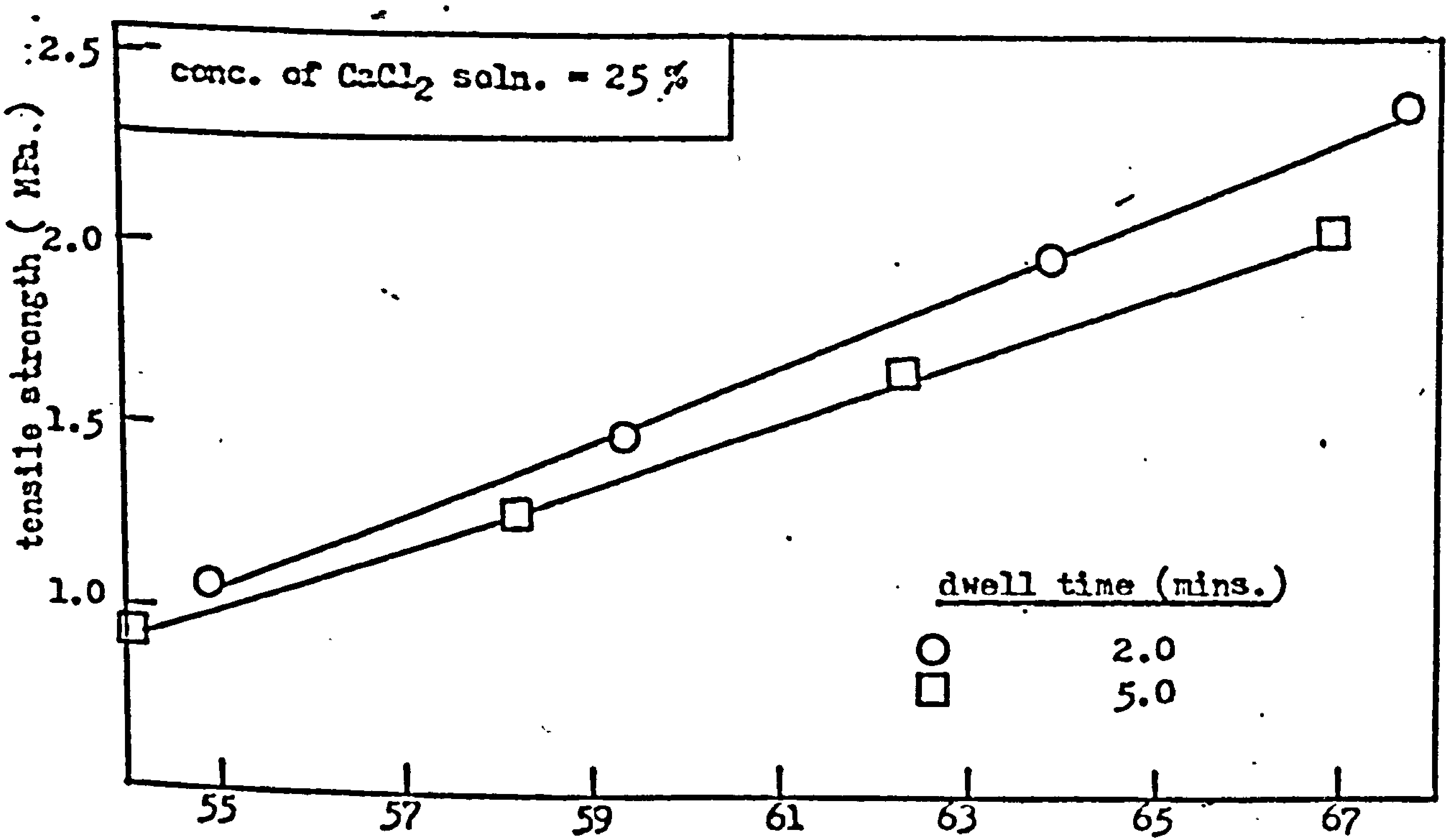


Figure 6.11. Relationship between wet-gel strength and total solids content of gel measured 40 minutes after dwell.

and 6.11 were average values of TSC for the gel. Thus, although two gels may have the same average TSC they are unlikely to have the same distribution of TSC throughout the thickness of the gels. Gels formed at shorter dwell times have a narrower range of TSC and this may be the reason for their significantly higher tensile strengths as compared to gels formed over longer dwell times.

Typical stress-strain curves for the gels referred to above are shown in Figures 6.12 and 6.13. Similar observations for natural rubber latex gels have been reported earlier[7]. These curves are also similar in shape to those for dry natural rubber latex films, except the former have lower tensile values. The tensile strength of the wet gel is approximately 10 % of that of the dry film.

6.3.2 Effect of pH and added soaps upon wet-gel strength of deposits

The results for the effect of pH upon the wet-gel strength of deposits obtained after 2 and 5 minutes dwell times are summarised in Figure 6.14. It is seen that lowering the pH of the latex increases the wet-gel strength of the deposit to a shallow optimum; thereafter the strength decreases slightly as the pH of the latex is further lowered. The wet-gel strength of the deposits obtained at 2 minutes dwell time was always higher than that obtained at 5 minutes, probably because the gel had higher TSC.

The effects of added potassium stearate and ethoxylate (n = 24) upon the wet-gel strength of the deposits are summarised in Figures 6.15 and 6.16 respectively. It is seen that in each case the wet-gel strength of the deposit increases with increasing concentration of soap to an optimum and thereafter decreases. As above, the wet-gel strength

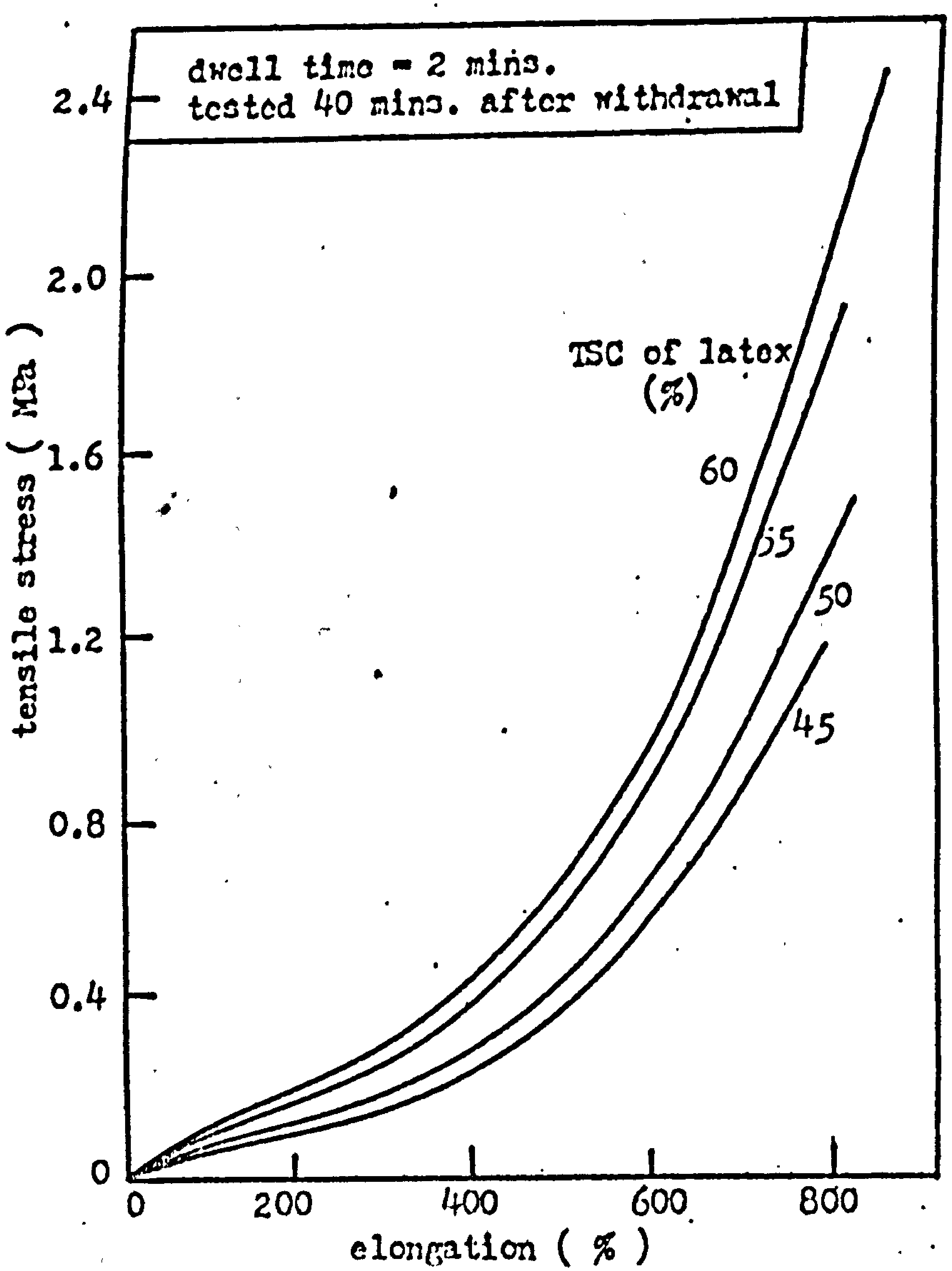


Figure 6.12. Stress-strain curves for natural rubber latex gels.

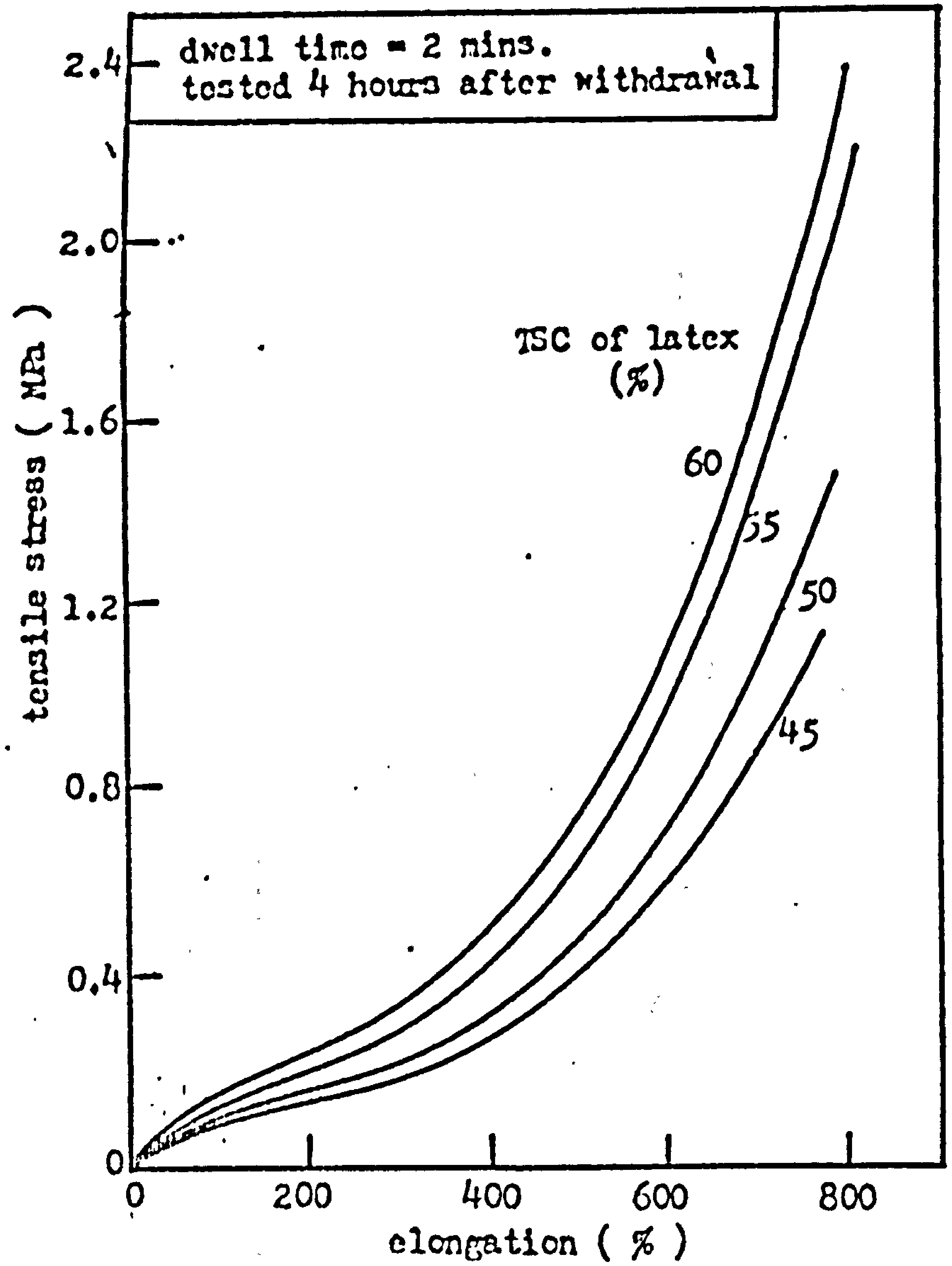


Figure 6.13. Stress-strain curves for natural rubber latex gels.

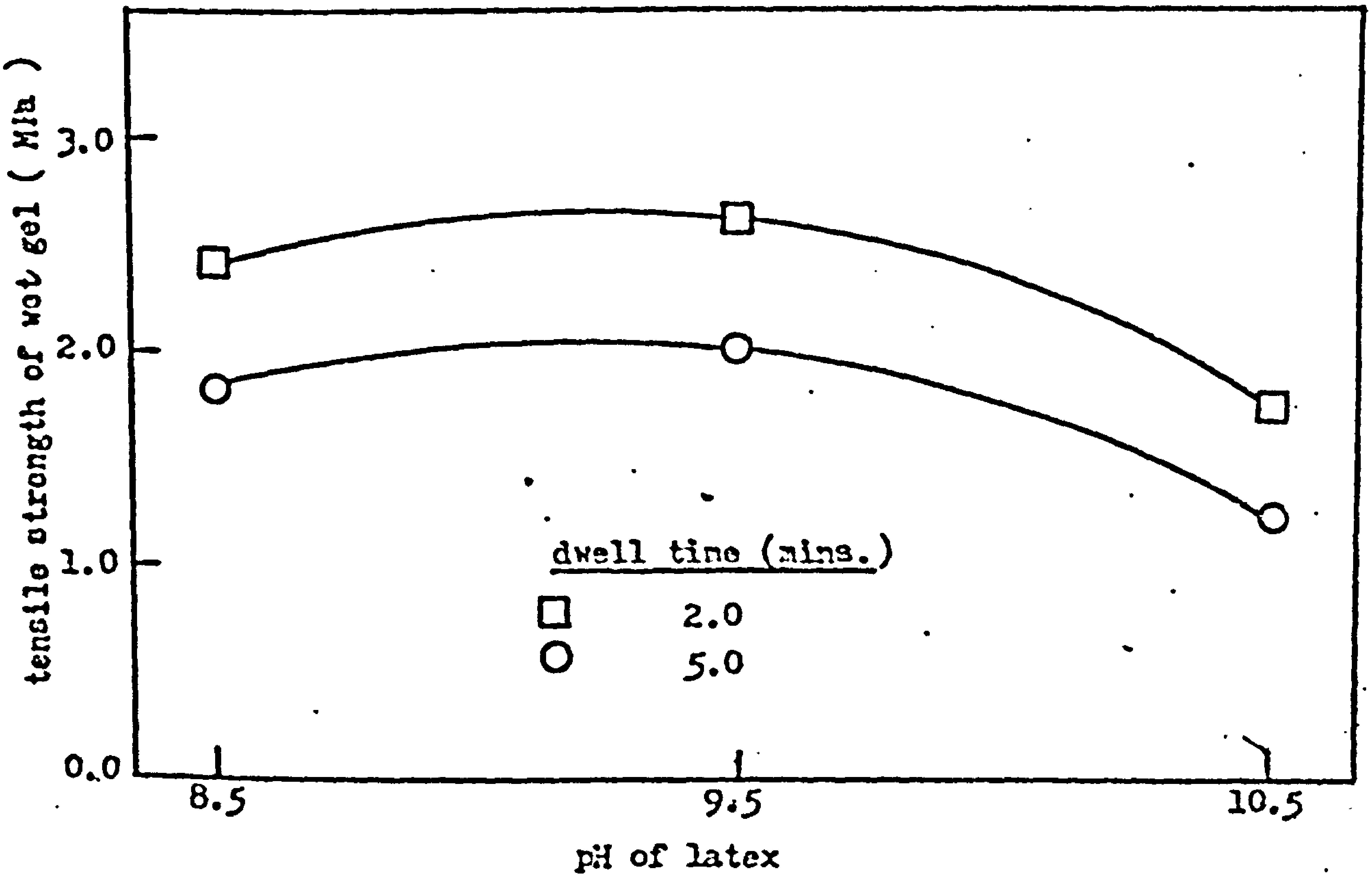


Figure 6.14. Effect of pH of latex upon wet-gel strength of deposit.

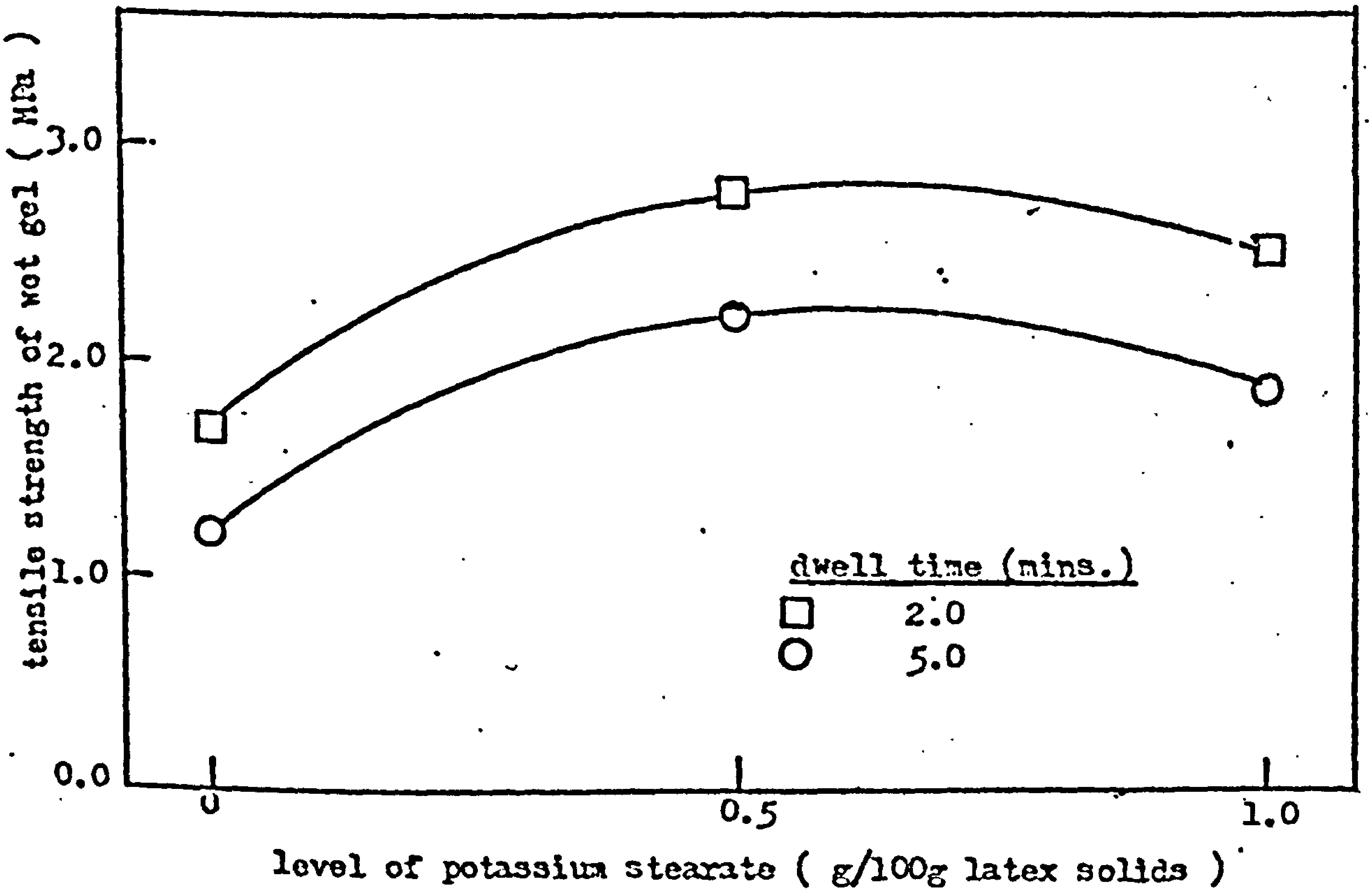


Figure 6.15. Effect of added soap upon wet-gel strength of deposit.

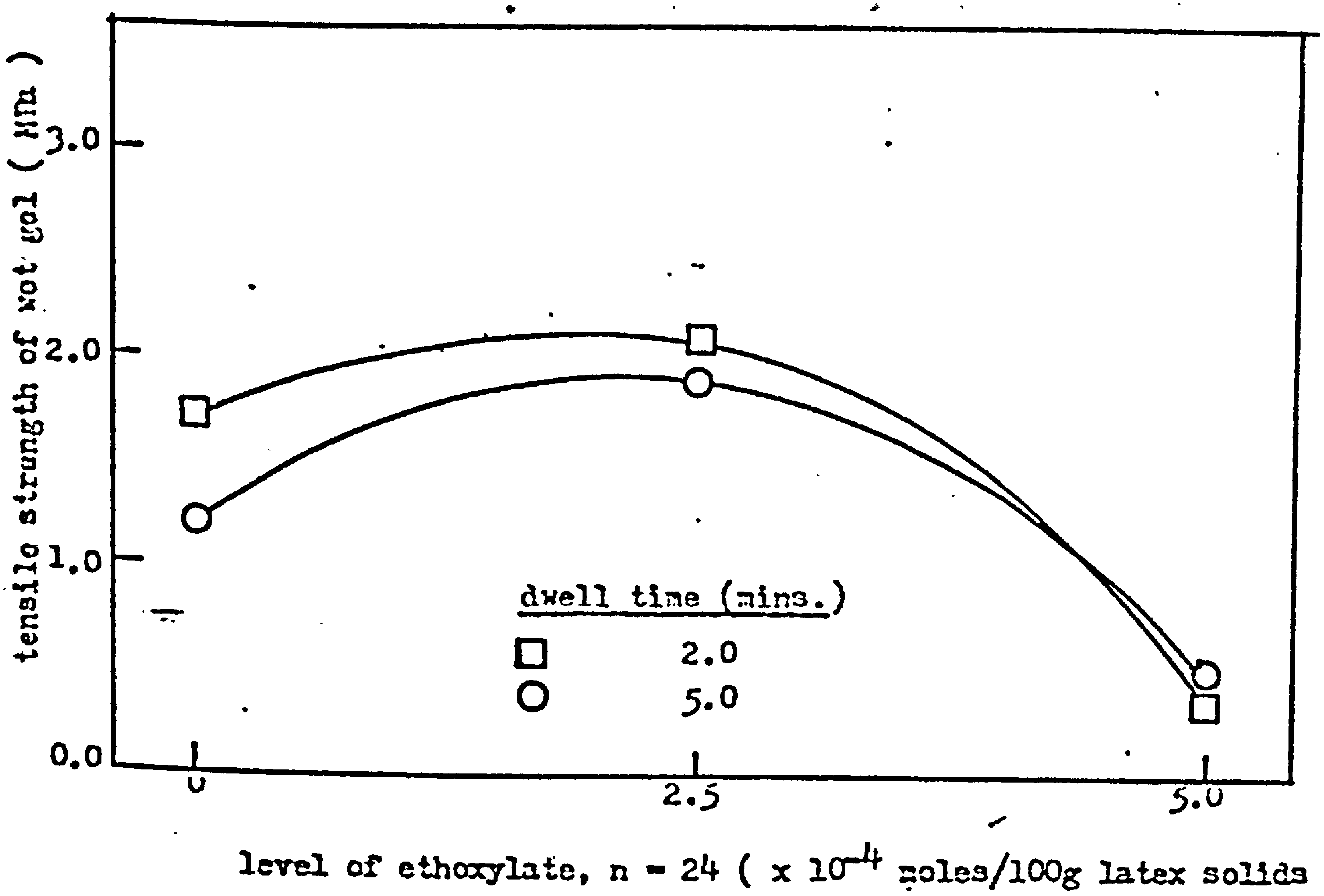


Figure 6.16. Effect of added surfactant upon the wet-gel strength of the deposit.

of the deposits obtained after 2 minutes dwell time was always greater than that obtained after 5 minutes dwell time.

The effects of pH and added soaps upon tensile strength are not attributable to changes in the TSC of the gels, since this was approximately constant for all the gels produced at a given dwell time. The most likely reason for the observed effects is thought to be that the absorbed soap molecules affect the ability of the latex particles to coalesce.

CHAPTER 7

RESULTS FOR CONDUCTIMETRIC TITRATION, CALCIUM DISTRIBUTION AND CALCIUM DIFFUSION IN SOAP SOLUTION

7.1 Conductimetric titration

The most probable cause of the gelation of natural rubber latex in the coagulant-dipping process is the reaction of calcium ions with the various anions in the latex, principally soap and protein anions. In order to confirm this possibility, a series of conductimetric titrations were carried out in which calcium chloride was titrated with the latex and with the principal ions that are thought to be present in the latex. These ions include fatty-acid soap anions, proteinate anions, sulphate anions and acetate anions. In this way, the indigenous ions in the latex which react with the calcium ions may be identified and their quantities may be estimated. Experimentally, it was found necessary to use calcium chloride solution of different concentrations to allow for the different solubilities of the various calcium salts. The concentrations most commonly used were:

(i) 20.1 mg calcium per ml (referred to as 'high' concentration);

(ii) 1.84 mg calcium per ml (referred to as 'low' concentration)

The above units of concentration have been used since they allow ready comparison with the data obtained in the dipping experiments (see Section 7.2). These concentrations were chosen since they are approximately the average concentrations of soluble calcium on the former at the two extreme dwell times (see Figure 7.8). The conductimetric titrations were carried out as described in Section 4.11. The results of these experiments are given in the subsequent sections below and are discussed more fully in Section 7.1.8.

7.1.1 Titration of soap solution with calcium chloride

The effect of addition of calcium chloride upon the conductance of a potassium laurate solution is shown in Figure 7.1 and summarised in Table 7.1. Calculations show that the calcium reacted is equivalent to 100.8 % of the potassium laurate. Therefore, within experimental error, the soap reacts stoichiometrically with calcium at 'low' concentration.

7.1.2 Titration of latex with calcium chloride

The effect of calcium chloride of 'low' concentration upon the conductance of the latex is shown in Figure 7.2. The results show a change in the slope of the conductance curve at a point which is equivalent to 0.39 mg calcium per g rubber.

When calcium chloride solutions of different concentrations are titrated against diluted latex, similar results are obtained to those shown in Figure 7.2. The results of these titrations are summarised in Table 7.2. The same data are presented in Figure 7.3 as the amount of calcium reacted (mg calcium per g rubber) as a function of the concentration of calcium in the aqueous phase of the latex mixture (mg per ml serum) at the end-point of the titration.

It is seen in Figure 7.3 that the amount of calcium reacted depends upon the concentration of calcium in the serum at concentrations up to 0.04 mg per ml serum, but is reasonably independent of concentration between 0.04 and 0.5 mg Ca ml^{-1}. It is thought that the plateau region represents the quantity of calcium (0.38 mg calcium per g rubber) needed to neutralise certain anions in the latex. The exact nature of these anions is uncertain. Therefore, for the purpose of the following discussion, they are referred to as Type X anions.

At lower concentrations of calcium in the latex mixture ($<$0.04

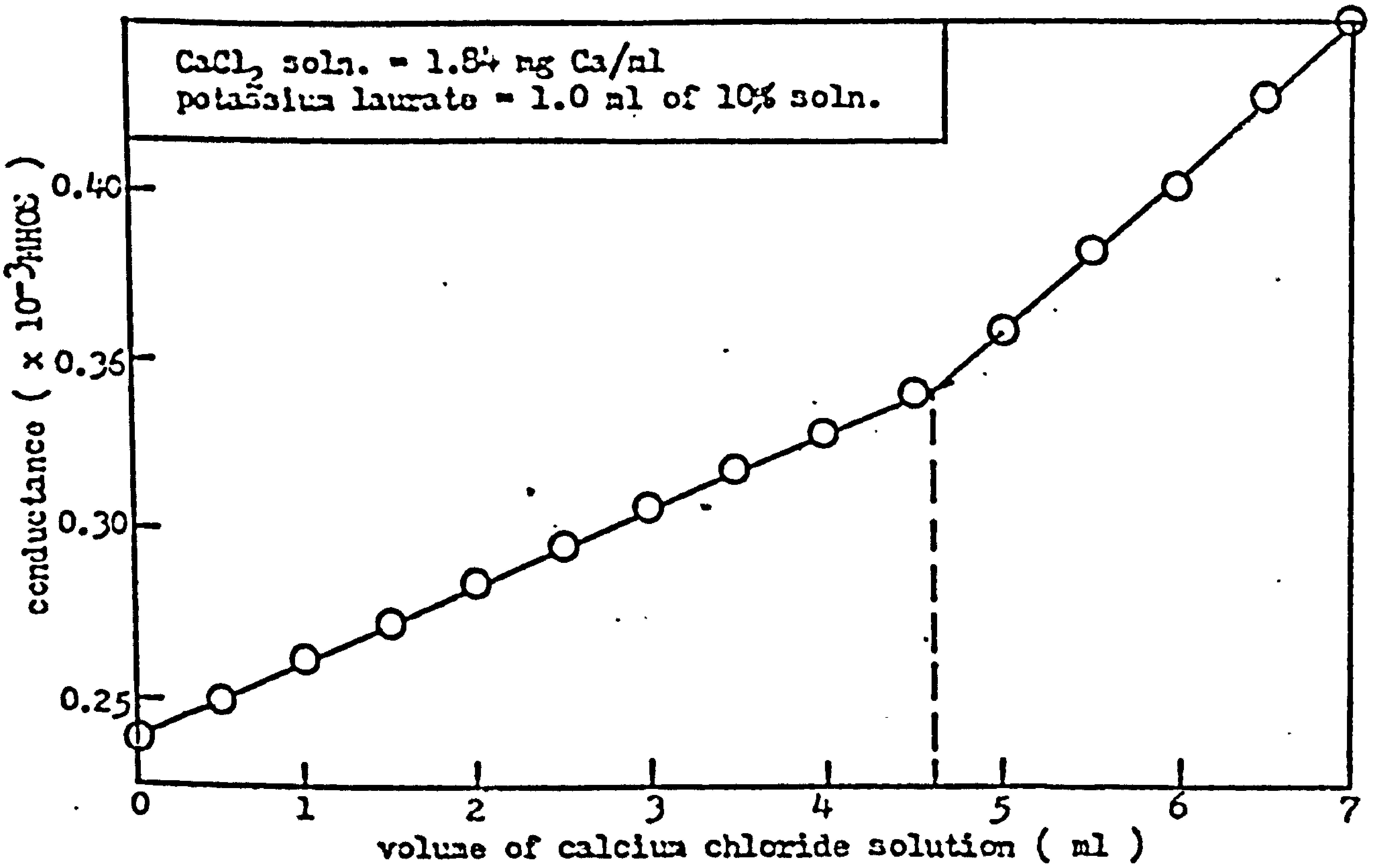


Figure 7.1. Conductimetric titration of soap solution with calcium chloride solution.

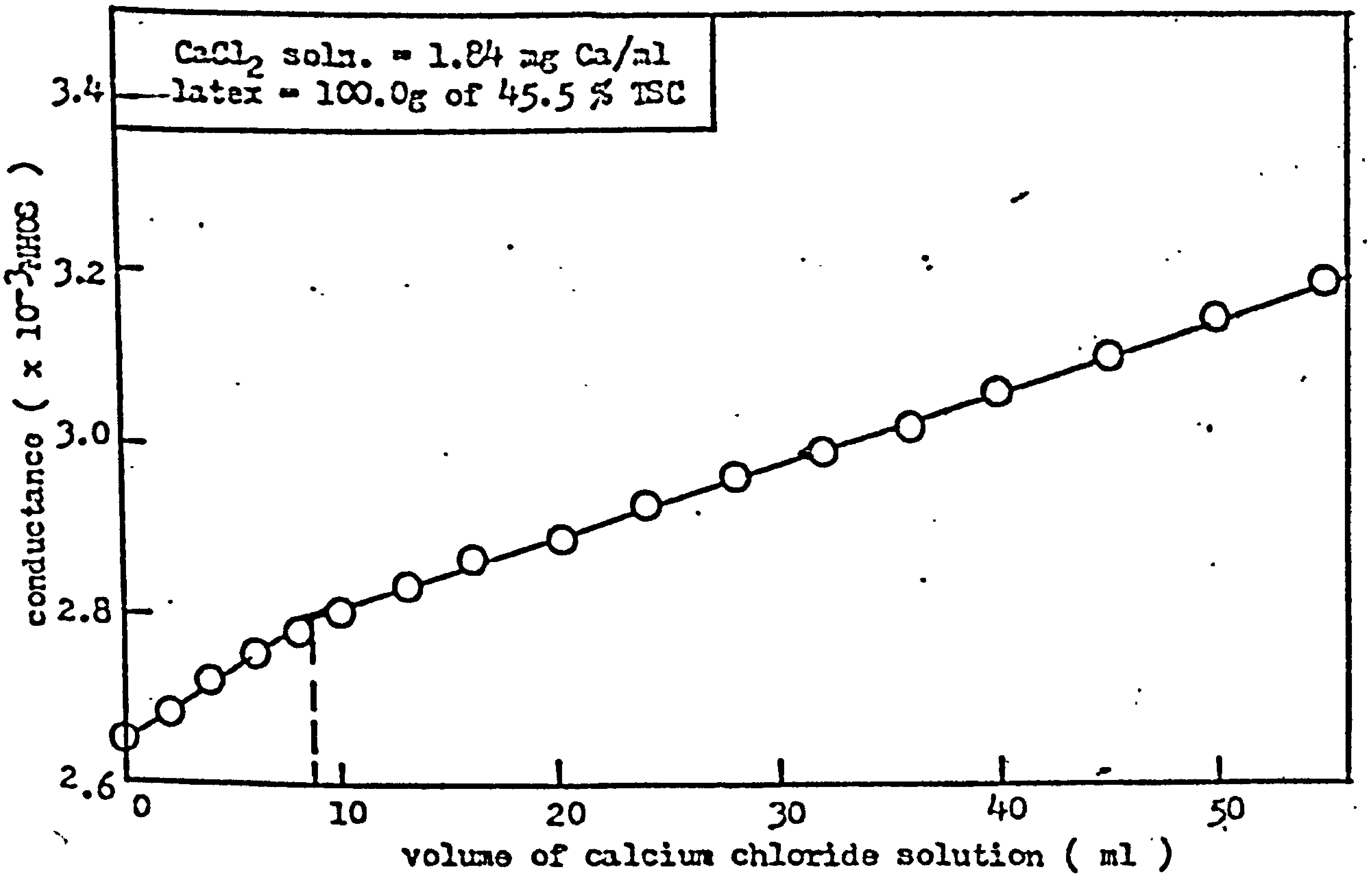


Figure 7.2. Conductimetric titration of latex with calcium chloride.

Table 7.1

Summary of results for conductimetric titration of selected ions with calcium chloride solution. The values in the Table are the concentrations at the end-point of the titration, or, in the cases when end-point was not observed, the concentration at the end of the titration

reactant / initial concentration	(%)	[reactant] (mole / 1)	[Ca] (mole / 1)	solubility product, S *	comments
potassium laurate	0.1	3.85×10^{-3}	1.94×10^{-4}	3.04×10^{-12}	Precipitation observed. $[Ca^{++}] / [laurate^{-}] = 0.5$, stoichiometric reaction $[Ca^{++}][laurate^{-}]^2 = 2.88 \times 10^{-9} = I$, $I > S$
ammonium sulphate	0.13	7.30×10^{-3}	1.31×10^{-2}	2.37×10^{-4}	No precipitation observed or expected. $[Ca^{++}][SO_4^{--}] = 9.56 \times 10^{-5}$, $I < S$
	1.0	6.50×10^{-2}	7.11×10^{-2}	2.37×10^{-4}	Precipitation observed. $[Ca^{++}]/[SO_4^{--}] = 1.09$ $[Ca^{++}][SO_4^{--}] = 4.62 \times 10^{-3}$, $I > S$, excess calcium required because of high solubility product.

* see Table 7.4

Table 7.1 (continued)

reactant / initial concentration	(%)	[reactant] (mole / 1)	[Ca] (mole / 1)	solubility product, S*	comments
casein	0.8	-	1.67×10^{-1}	-	No precipitate observed.
	2.71	-	6.83×10^{-2}	-	Precipitate observed. 117 mg calcium / g casein for neutralisation.
ammonium acetate	1.0	8.64×10^{-2}	1.67×10^{-1}	53	No precipitation observed. $[Ca^{++}][Ac^{-}]^2 = 1.24 \times 10^{-3}$, $I < S$
	2.0	1.73×10^{-1}	1.67×10^{-1}	53	No precipitation observed. $[Ca^{++}][Ac^{-}]^2 = 5.0 \times 10^{-3}$, $I < S$

* see table 7.4

Table 7.2

Results of conductimetric titration of latex with calcium chloride solutions of different concentrations. The values given in the table refer to the quantities or concentrations of ingredients at the end-point of the titration

calcium (mg)	rubber (g)	aqueous phase (ml)	[Ca] (mg/ml serum)	DRC (%)	calcium reacted (mg/g rubber)
1.38	9.8	93.2	0.015	9.5	0.14
2.39	9.6	95.6	0.025	9.1	0.25
2.76	9.8	93.2	0.030	9.5	0.28
3.13	9.8	93.6	0.033	9.5	0.32
3.50	9.6	94.2	0.037	9.2	0.36
3.68	9.6	94.4	0.039	9.3	0.38
5.80	19.3	87.0	0.067	18.2	0.30
6.36	19.3	87.5	0.071	18.1	0.33
7.75	19.6	84.6	0.091	18.8	0.39
16.93	45.5	63.7	0.266	41.7	0.37
17.67	45.5	64.1	0.276	41.5	0.39
36.56	85.8	66.0	0.554	56.5	0.43
42.17	85.8	64.4	0.617	55.6	0.49
45.58	85.8	68.7	0.663	55.5	0.53

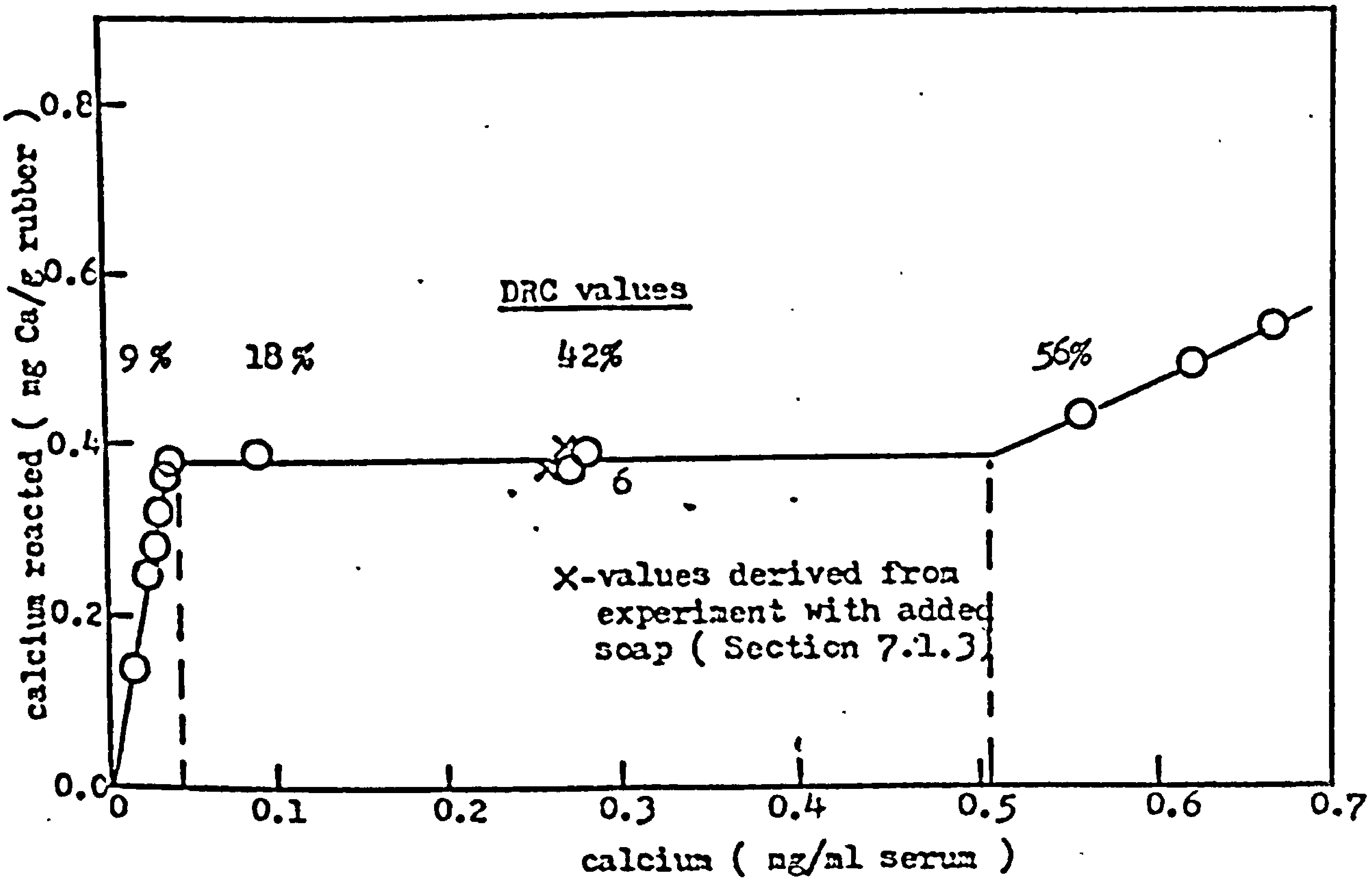


Figure 7.3. Relationship between the amount of calcium reacted and concentration of calcium in latex mixture at end-point of conductimetric titration.

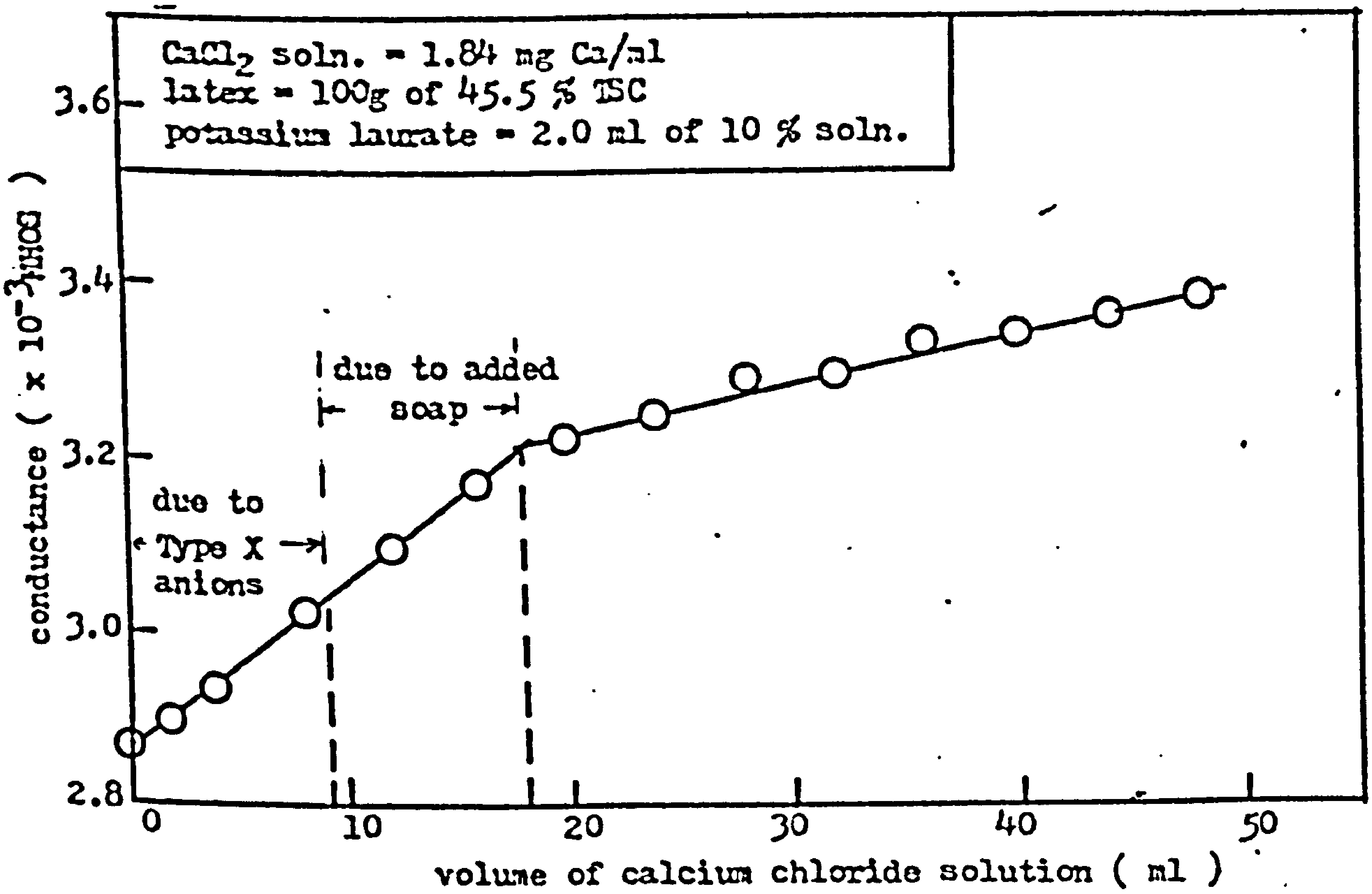


Figure 7.4. Conductimetric titration of latex containing added soap with calcium chloride.

mg calcium per ml serum), there are insufficient calcium ions to precipitate all the Type X anions. At the higher concentrations of calcium (>0.5 mg calcium per ml serum), there is possibility that anions other than Type X may be starting to precipitate. Unfortunately, it was not possible to obtain satisfactory results at higher concentrations of added calcium chloride solution, since the volume of titrant needed for neutralisation is very small. This leads to results which have increasingly greater experimental errors.

7.1.3 Titration of latex containing added soap with calcium chloride

The effect of calcium chloride of 'low' concentration upon the conductance of latex containing added soap (potassium laurate) is shown in Figure 7.4. The amount of calcium required to neutralise the anions was 0.76 mg calcium per g rubber. The added soap, which had already been shown to react stoichiometrically with calcium ions (see Section 7.1.1), required 0.37 mg calcium per g rubber for neutralisation. Presumably the Type X anions in the latex react with the remaining calcium, i.e., 0.76 - 0.37 = 0.39 mg calcium per g rubber. This is in agreement with the values obtained when the latex, without the added soap, was titrated against calcium chloride solutions of different concentrations (Figures 7.2 and 7.3). That there is a single point of intersection in Figure 7.4 is consistent with the view that the Type X anions in the latex may be indigenous soap anions. The nature of Type X anions will be discussed more fully in Section 7.1.8.

7.1.4 Titration of ammonium sulphate with calcium chloride

Calcium chloride of 'low' concentration was titrated against

0.13 % (9.8×10^{-3} moles per litre) ammonium sulphate solution. No inflexion point or precipitation was observed. The absence of reaction is a result of the relatively high solubility product of calcium sulphate (2.37×10^{-4})[1]. At first sight, it appears that the product of the concentrations of the two solutions is greater than the solubility product of calcium sulphate, and that therefore calcium sulphate should be precipitated. However, since the solutions are titrated against each other, both concentrations change during the titration. The concentration of sulphate ions in the mixture decreases and the concentration of calcium ions in the mixture increases with increasing additions of the calcium chloride solution. This is shown in Table 7.3. It is clear that the solubility product is never exceeded; therefore precipitation of calcium sulphate did not occur.

When 1.0 % (7.6×10^{-2} moles per litre) ammonium sulphate solution is titrated with calcium chloride solution of 'high' concentration (5.0×10^{-1} moles per litre), there is an inflexion point (Figure 7.5) and visible precipitation. At these higher concentrations, the calcium reacts approximately stoichiometrically with the ammonium sulphate (see Table 7.1); the discrepancy is attributed to the relatively high solubility of calcium sulphate in water. Although, the two lines drawn through the points have a distinct intersection point in Figure 7.5, the data clearly show a curve in this region. The exact position of the end-point is therefore in doubt.

7.1.5 Titration of casein with calcium chloride

Casein was used as a model for the protein present in the latex. When a 0.5 % casein solution is titrated with calcium chloride solution of 'low' concentration, there was no precipitate formed.

Table 7.3

Titration of 100 ml of 0.01 M (NH_4)$_2SO_4$ solution with $CaCl_2$ solution of 'low' concentration (4.6×10^{-2} mole l^{-1}) showing changes in concentration of Ca^{2+} and SO_4^{2-} and also changes in ionic products of calcium sulphate.

volume of $CaCl_2$ soln. (ml)	concentration of mixture		Ionic product, I =
	$[Ca^{2+}]$ $\times 10^{-3}$ mole l^{-1}	$[SO_4^{2-}]$ $\times 10^{-3}$ mole l^{-1}	$[Ca^{2+}][SO_4^{2-}]$ $\times 10^{-4}$
0	0	10.42	0
10	4.18	9.47	0.40
20	7.67	8.68	0.67
30	10.62	8.01	0.85
40	13.14	7.44	0.98
50	15.33	6.94	1.06
60	17.25	6.51	1.12
70	18.94	6.13	1.16
80	20.44	5.79	1.18
90	21.79	5.48	1.19
100	23.00	5.21	1.20

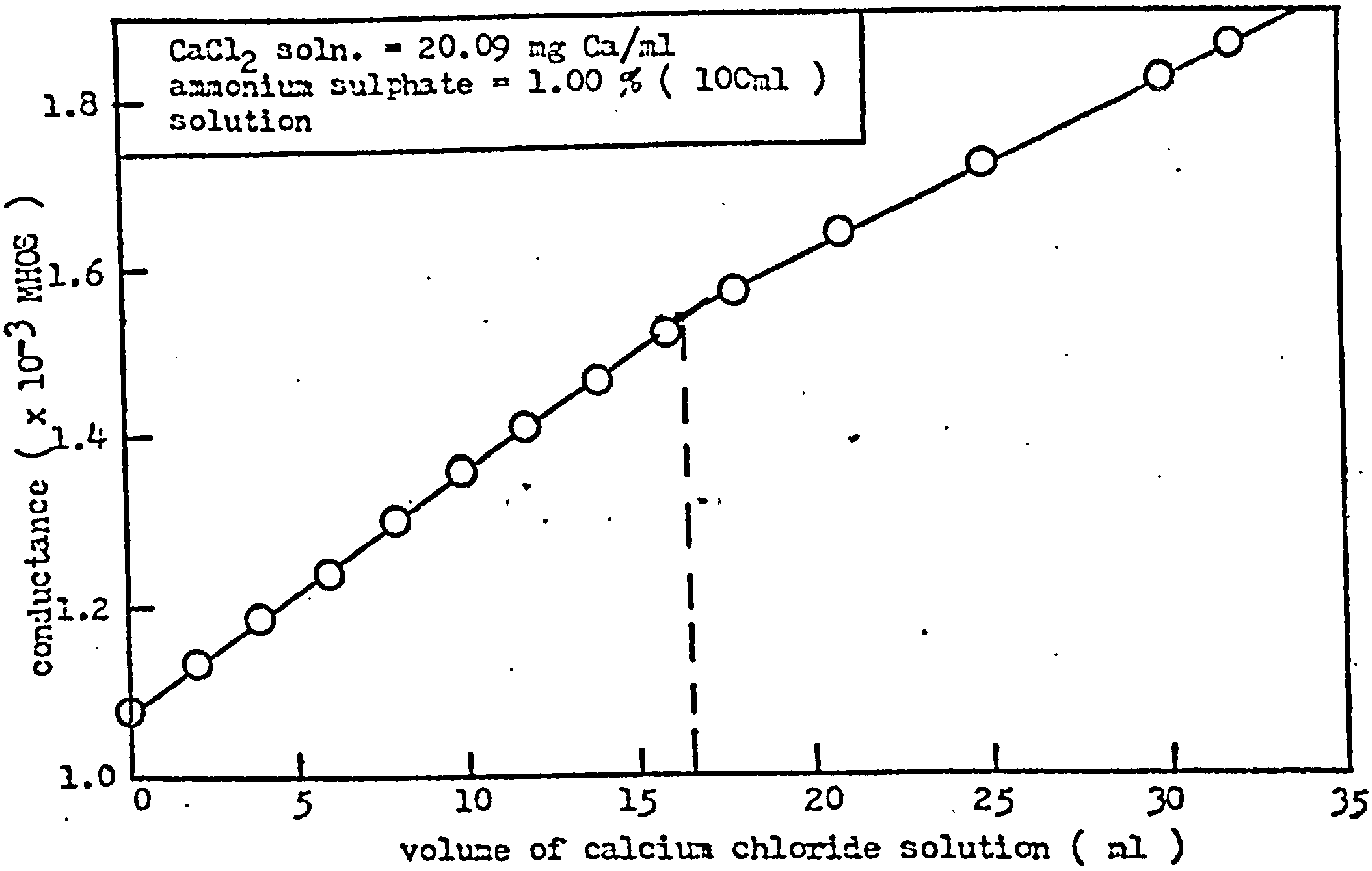


Figure 7.5. Conductimetric titration of ammonium sulphate solution with calcium chloride.

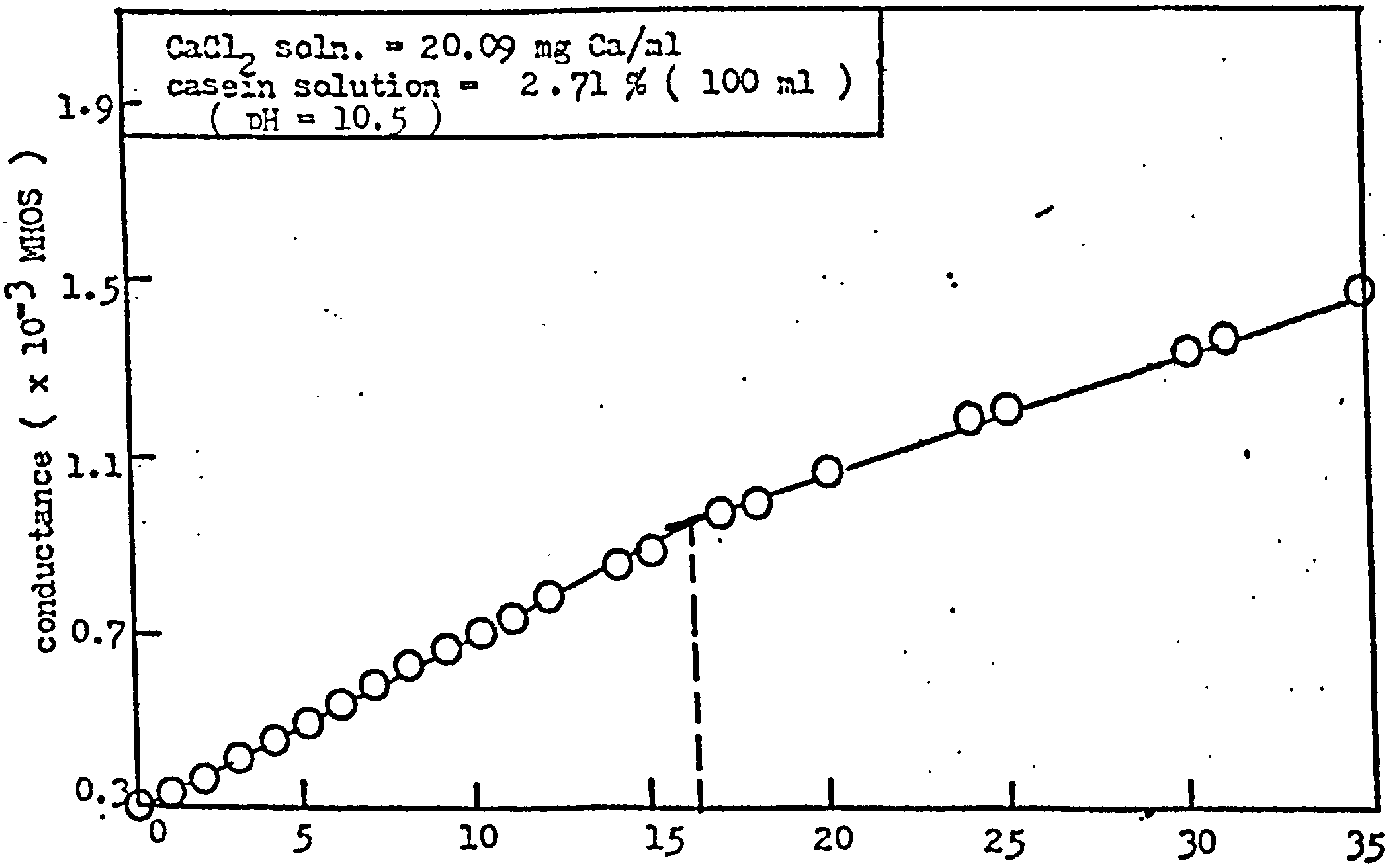


Figure 7.6. Conductimetric titration of ammonium caseinate solution with calcium chloride.

With calcium chloride solution of 'high' concentration and a 2.71 % solution of casein, the casein required 117.0 mg calcium per g casein for the attainment of the end-point (Figure 7.6). It is not known exactly how much indigenous protein is present in the latex or whether it reacts with calcium ions in a similar manner to casein. Thus, the above result is of little quantitative value. However, it does allow a rough estimate to be made of the possible quantity of calcium that is likely to react with the indigenous protein in the latex. The usual amount of protein present in natural rubber latex is ca. 1.0 % of the total solids[2]. If this amount is assumed to be as equally reactive as the casein, then it would require 1.17 mg calcium per g rubber.

7.1.6 Titration of ammonium acetate with calcium chloride

No reaction occurred even at 'high' concentration of calcium chloride solution (Table 7.1). This is not surprising since calcium acetate has a solubility of 347 g per litre at 20°C (cf. $CaSO_4\ 2H_2O$ of 0.64 g per litre).

7.1.7 An interpretation of the various conductimetric titration curves

The effect of the addition of calcium chloride solution upon the conductance of potassium laurate solution is shown in Figure 7.1. The shape of the curve can be explained by considering of the equation:

$$CaCl_2 + 2RCOOK \rightleftharpoons (RCOO)_2Ca\downarrow + 2KCl$$

The calcium ions precipitate the soap anions which are replaced by the chloride ions. The chloride ions have a higher conductance than the soap anions and therefore the conductance of the calcium chloride / soap mixture increases. When all the soap anions have reacted with the calcium ions, further addition of calcium chloride solution will not remove any additional calcium ions. Hence, the conductance increases much faster than when there is reaction between the calcium ions and the soap anions.

The shapes of the curves obtained for the titration of latex and other anions with the calcium chloride solutions differ from that for calcium chloride and soap solutions. It was found that, in each case, the conductance increases more slowly after passing the intersection point than that before passing this point. The reason for this is obscure, particularly for the titration of ammonium sulphate with calcium chloride solutions. The reaction,

$$CaCl_2 + (NH_4)_2SO_4 \rightleftharpoons CaSO_4\downarrow + 2NH_4Cl$$

would suggest that a similar curve to that in Figure 7.1 would be obtained. It has not been found possible to suggest satisfactory reasons to explain the unexpected shapes of the curves obtained in these experiments. Futher, it was also observed that the calcium ions formed precipitate with the sulphate anions similar to that of the soap anions, except that the calcium sulphate precipitate is very much more soluble than the calcium soap.

7.1.8 Discussion of results

It has been found that certain anions (referred to as 'Type X' anions) in the latex react with 0.38 mg calcium per g rubber. The exact nature of the Type X anions is unclear. Latex contains many anions, the most important in terms of concentration being sulphate, phosphate, citrate, malate, carbonate, acetate, proteinate and fatty-acid anions.

It is possible to eliminate some of these anions on the basis of the solubility products (S) of their calcium salts in water. The solubility products shown in Table 7.4 have been either taken from the literature or calculated from solubility data. The calculation below of S for calcium stearate illustrates the method of calculation.

<u>Calculation of S for calcium stearate</u>

Solubility of calcium stearate in water at 25°C = 0.04 g per litre[1]

$$\text{Therefore, molar concentration} = \frac{0.04}{606} \text{ mole per litre}$$

$$= 6.6 \times 10^{-5} \text{ mole per litre.}$$

$$\text{Now, } S = \left[Ca^{++}\right]\left[\text{stearate}^{-}\right]^2$$

$$= \left[6.6 \times 10^{-5}\right] \times \left[2 \times 6.6 \times 10^{-5}\right]^2$$

$$= \underline{1.15 \times 10^{-12}}$$

It is now necessary to calculate the concentration of calcium ions and the anions during the titration in order to determine whether or not the calcium salts will precipitate. For the purpose of these calculations, three concentrations of calcium during the titration have been chosen from Table 7.2, namely, 0.015, 0.276 and 0.663 mg per ml serum. These concentrations represent the lowest value, an intermediate value and the highest value respectively used in this work. The concentrations in mole per litre of aqueous phase are 3.75×10^{-4}, 6.90×10^{-3} and 1.66×10^{-2} respectively. In order to estimate the anion concentrations at these calcium concentrations, it has been assumed that it is equivalent to the Type X anion concentration of 0.38 mg calcium per g rubber. It is assumed that the Type X anions are univalent. It is thus likely that the anion concentration will be over-estimated. A more realistic

Table 7.4

Solubility product of various calcium salts

calcium salt	solubility(1) g/100 ml at 25°C	solubility product, S
acetate$^-$	37.4	53 (*)
citrate^{3-}	0.85	7.93×10^{-8} (*)
malate^{2-}	0.321	2.02×10^{-4} (*)
stearate$^-$	0.004	1.15×10^{-12} (*)
laurate$^-$	0.004	3.04×10^{-12} (*)
sulphate^{2-}	0.209	2.37×10^{-4} (*)
		1.95×10^{-4} (1)
carbonate^{2-}	0.00153	2.8×10^{-7} (*)
		8.7×10^{-7} (1)
phosphate^{3-}	0.18	1.45×10^{-3} (*)
phosphate^{3-}	0.002	1.2×10^{-19} (*)

(*) Calculated by author from solubility data.

approach is used in the later parts of this discussion.

If it is assumed that the calcium ions react with either A^-, B^{2-} or C^{3-}, then the ionic products (I) are:

For CaA_2, $I_A = [Ca^{2+}][A^-]^2$

For CaB , $I_B = [Ca^{2+}][B^{2-}]$

For Ca_3C_2, $I_C = [Ca^{2+}]^3[C^{3-}]^2$

The values of I at the different calcium ions concentration are given in Table 7.5. The method of calculating I is illustrated below:

Calculation of I of calcium salts at low calcium concentration

(0.015 mg calcium per ml serum or 3.75×10^{-4} moles per litre)

The assumed reactive anion concentration is equivalent to 0.38 mg calcium per g rubber or 0.95×10^{-5} mole calcium per g rubber. The amounts of rubber and serum present are 9.8 g and 93.2 ml respectively. Therefore, the anion concentration is equivalent to

$$\frac{0.95 \times 10^{-5} \times 9.8}{93.2} \times 1000 \text{ mole calcium per litre aqueous phase}$$

$$= 1.0 \times 10^{-3} \text{ mole calcium per litre.}$$

If, the latex anion is monovalent, then

$$[A^-] = 2 \times 1.0 \times 10^{-3} \text{ mole per litre}$$

$$\text{Therefore,} \quad I_A = [Ca^{2+}][A^-]^2$$

$$= (3.75 \times 10^{-4}) \times (2 \times 1.0 \times 10^{-3})^2$$

$$= \underline{1.5 \times 10^{-9}}$$

If, the latex anion is divalent, then

$$[B^{2-}] = 1 \times 10^{-3} \text{mole per litre}$$

$$\text{Therefore,} \quad I_B = [Ca^{2+}][B^{2-}]$$

Table 7.5

Theoretical ionic products (I) of calcium salts at different concentrations of calcium and rubber during conductimetric titrations. It is assumed that the anion concentration was = 0.38 mg Ca/g rubber

[Ca]	TSC of rubber (%)	weight of rubber (g)	Type X anion	I
0.015 (mg/ml serum) or 3.75×10^{-4} (moles/l)	9.5	9.8	A^-	1.50×10^{-9}
			B^{2-}	3.75×10^{-7}
			C^{3-}	2.35×10^{-17}
0.276 (mg/ml serum) or 6.90×10^{-3} (moles / l)	41.5	45.5	A^-	1.25×10^{-6}
			B^{2-}	4.65×10^{-5}
			C^{3-}	6.63×10^{-12}
0.663 (mg/ml serum) or 1.66×10^{-2} (moles/l)	55.5	85.8	A^-	0.94×10^{-5}
			B^{2-}	1.98×10^{-4}
			C^{3-}	2.88×10^{-10}

$$= (3.75 \times 10^{-4}) \times (1 \times 10^{-3})$$

$$= \underline{3.75 \times 10^{-7}}$$

If, the latex anion is a trivalent, then

$$[C^{3-}] = \frac{2}{3} \times 1.0 \times 10^{-3} \text{ moles per litre}$$

$$= 0.667 \times 10^{-3} \text{ moles per litre}$$

Therefore,

$$I_C = [Ca^{2+}]^3 \times [C^{3-}]^2$$

$$= (3.75 \times 10^{-4})^3 \times (0.667 \times 10^{-3})^2$$

$$= \underline{2.35 \times 10^{-17}}$$

In order for the calcium salts to precipitate during the titration, I must be greater than S. Comparison of Table 7.4 and 7.5 enable the following conclusions to be drawn:

(i) Calcium sulphate, malate, citrate and acetate will not precipitate at any value of added calcium concentration in the range studied.

(ii) Calcium stearate, laurate and presumably other calcium fatty-acid salts will precipitate at all values of calcium concentration.

(iii) The position with the calcium phosphates is unclear. The values of S have a wide range of values depending upon the type of phosphate present. Thus, calcium may or may not be precipitated with the phosphates.

(iv) In the case of the carbonate anion, it appears that it will precipitate at higher calcium concentrations.

Thus, the Type X anions can be fatty-acid anions, carbonate or phosphate only. It must be emphasised that the above deductions are based on the premise that each of the anions is the only one present as Type X anions in the latex. This is obviously incorrect since, it is known that all of these anions are present.

Since, calcium stearate has a lower value of S than does calcium carbonate (1.15×10^{-12} cf. 2.8×10^{-7}), it would be expected that the soap would be precipitated in preference to the carbonate. Thus, only when these soap molecules have reacted will the other principal anions react with the calcium ions. At this stage, the carbonate is not precipitated because the actual soluble calcium concentration is far lower than that assumed in the calculations of I. In fact, the soluble calcium concentration will be only 6.6×10^{-5} moles per litre. It thus seems reasonable to suppose that the Type X anions do not include carbonate.

Because of the uncertain nature of the phosphate present in the latex, it is assumed for the purpose of this discussion that the Type X anions do not contain phosphates. It is therefore assumed that the Type X are fatty-acid anions. Further evidence in support of this assumption is as follows:

(i) Calcium chloride reacts stoichiometrically with potassium laurate at approximately those concentrations used in the experiments when latex was titrated with calcium chloride solution (see Figure 7.1)

(ii) The addition of soap to the latex results in a titration curve (see Figure 7.4) which has a single intersection point.

(iii) The proteinate, sulphate and acetate were found not to precipitate in the concentration range represented by the plateau in Figure 7.3.

It is thus postulated that the predominant anions precipitated initially by the calcium are fatty-acid anions. It is possible that phosphate anions may also be precipitated.

7.2 Distribution of calcium during dipping process

The fate of the calcium ions during deposition was investigated using a latex of 50 % total solids content and a range of dwell times (0 to 60 minutes). The concentration of calcium chloride coagulant solution used in the investigation was 25 %, and this yielded a calcium layer on the former of 0.68 mg per cm^2. The regions investigated and the method used to determine the quantities of calcium in each of the regions are described in Section 4.10.

7.2.1 Calcium in bulk latex before and after dipping (region (iii))

The amount of calcium present in the bulk latex (approximately 60 g) before and after dipping the formers was found to be 0.054 and 0.046 mg per g rubber respectively. These values are the same within experimental error. The amount of calcium present in fresh latex range from 0.03 to 0.9 mg per g rubber[2].

Since, it was not possible to detect calcium diffusing from the former into the bulk of the latex, it was therefore assumed that such diffusion was negligibly small.

7.2.2 Calcium in serum trapped between former and gel (region (i))

The amount of calcium present in this region as a function of dwell time is shown in Figure 7.7. It is seen that the amount of calcium on the former (region (i)) decreases rapidly at first but more slowly as the time of dwell increases. The calcium ions diffuse from region (i) to region (ii) (the gel). As expected, the total amount of calcium present in regions (i) and (ii) is approximately equal to the initial amount of calcium present on the former, and is unaffected by the dwell time.

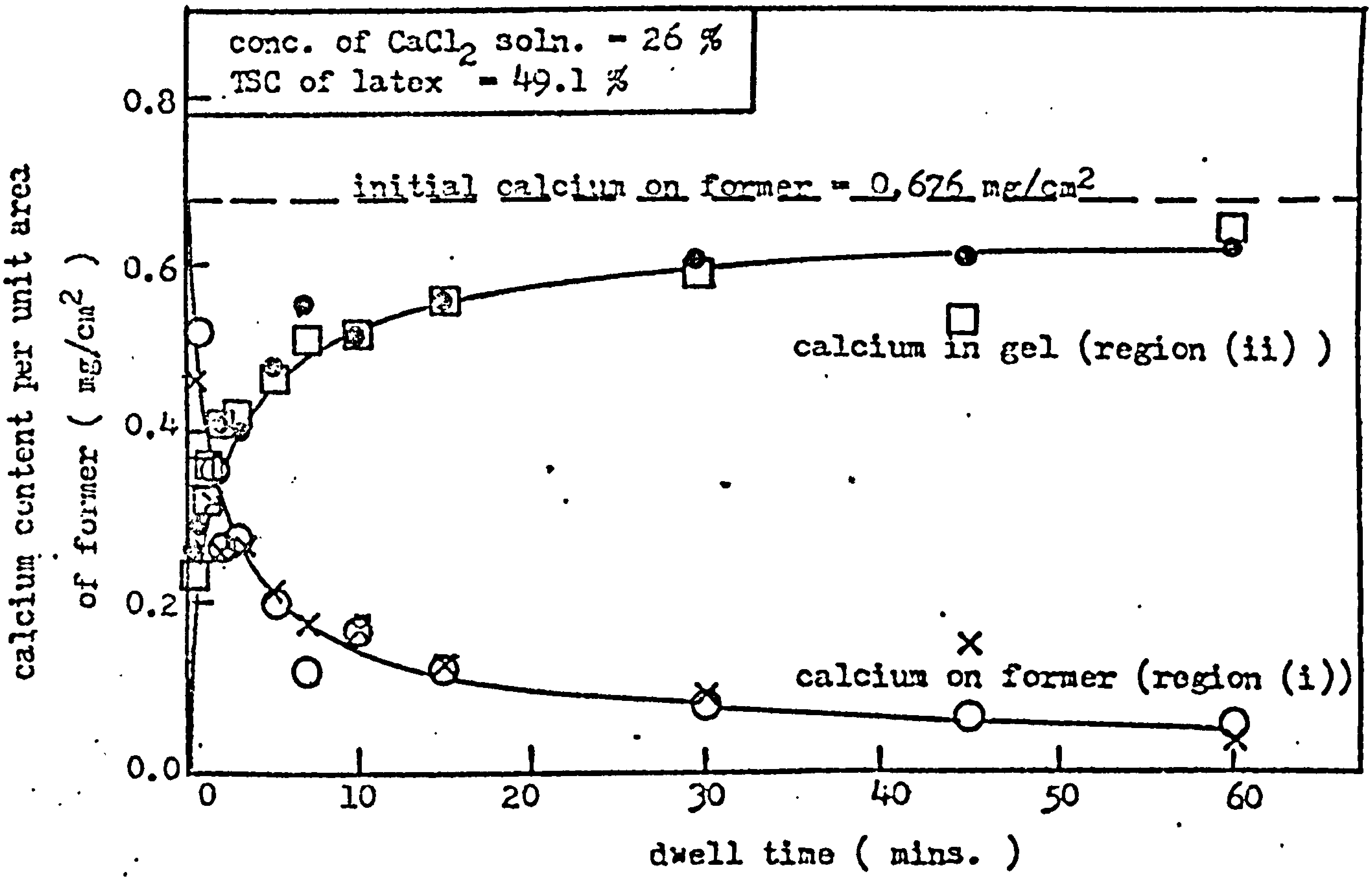


Figure 7.7. Distribution of calcium per unit surface area of former as a function of time of dwell. The experiment carried out in duplicate: First experiment ● and ○ second experiment □ and ×

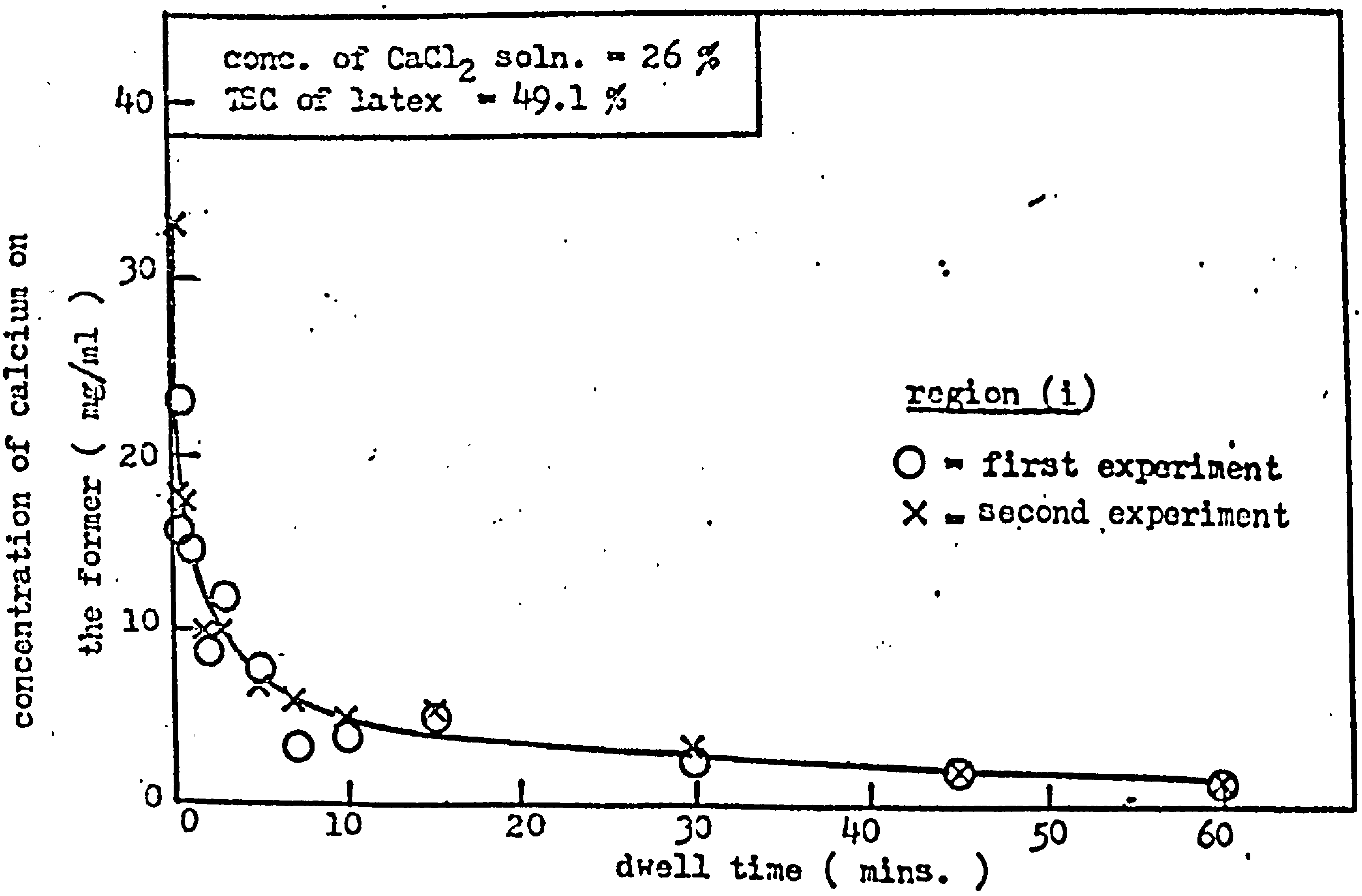


Figure 7.8. Concentration of calcium solution on the former as a function of time of dwell.

Figure 7.8 shows the actual solution concentration of calcium in region (i) as a function of dwell time. The concentration changes for two reasons:

(a) calcium ions diffuse outwards into the gel (region (ii));

(b) water is absorbed into this layer from the gel (the amount of water being calculated from the TSC of gel and compared with that in the bulk latex).

The initial rapid change in concentration of the calcium chloride in the first 10 seconds of dipping is caused by the dehydration of the latex. The slower changes (after approximately 5 minutes) in concentration are attributed to the diffusion of calcium ions from region (i) into region (ii). The surprising feature is that, despite the drastic changes in concentration of calcium on the former, the rate of diffusion varies linearly with $t^{\frac{1}{2}}$ (see Figure 5.9). This suggests that the concentration of calcium on the former, within the concentration range shown in Figure 7.8, is not the rate-determining concentration with respect to the diffusion of calcium ions through the latex. It also suggests that the diffusion coefficient (D) is independent of the concentration of calcium mentioned above. This will be further discussed in Chapter 8.

7.2.3 Calcium in gel (region (ii))

The calcium present in this region consists of soluble and insoluble calcium compounds. The soluble calcium compounds are expected to diffuse through the gel as long as a concentration gradient exists across the gel. On the other hand, the insoluble calcium compounds once formed will probably remained fixed in the gel.

Two distinctly different methods have been used to determine the concentrations of soluble and insoluble calcium within the gel. These are described further below:

(A) Method A for determining the distribution of calcium within the gel

In this method, gels were prepared at various dwell times ranging from 0.5 to 60 minutes. Each of the gels was then extracted, and the soluble and insoluble calcium contents determined as described in Section 4.10. The value obtained for each gel is therefore the average concentration throughout the thickness of the gel.

It is seen from Figure 7.9 and 7.10 that the concentration of soluble calcium in the gel decreases with increasing dwell time. It decreases rapidly during the first 10 minutes, but very much more slowly at longer times. The insoluble calcium, however, remains approximately constant in the time range investigated.

The insoluble calcium expressed in mg per g rubber obtained at various dwell times is summarised in Table 7.6. The results presented in this way give an estimate of the amounts of calcium that react with the soaps and other anions to bring about the destabilisation of the latex particles. It appears that, within the limitations of the experimental technique, the concentration of insoluble calcium remains relatively constant, and has an average value of about 0.72 mg calcium per g rubber.

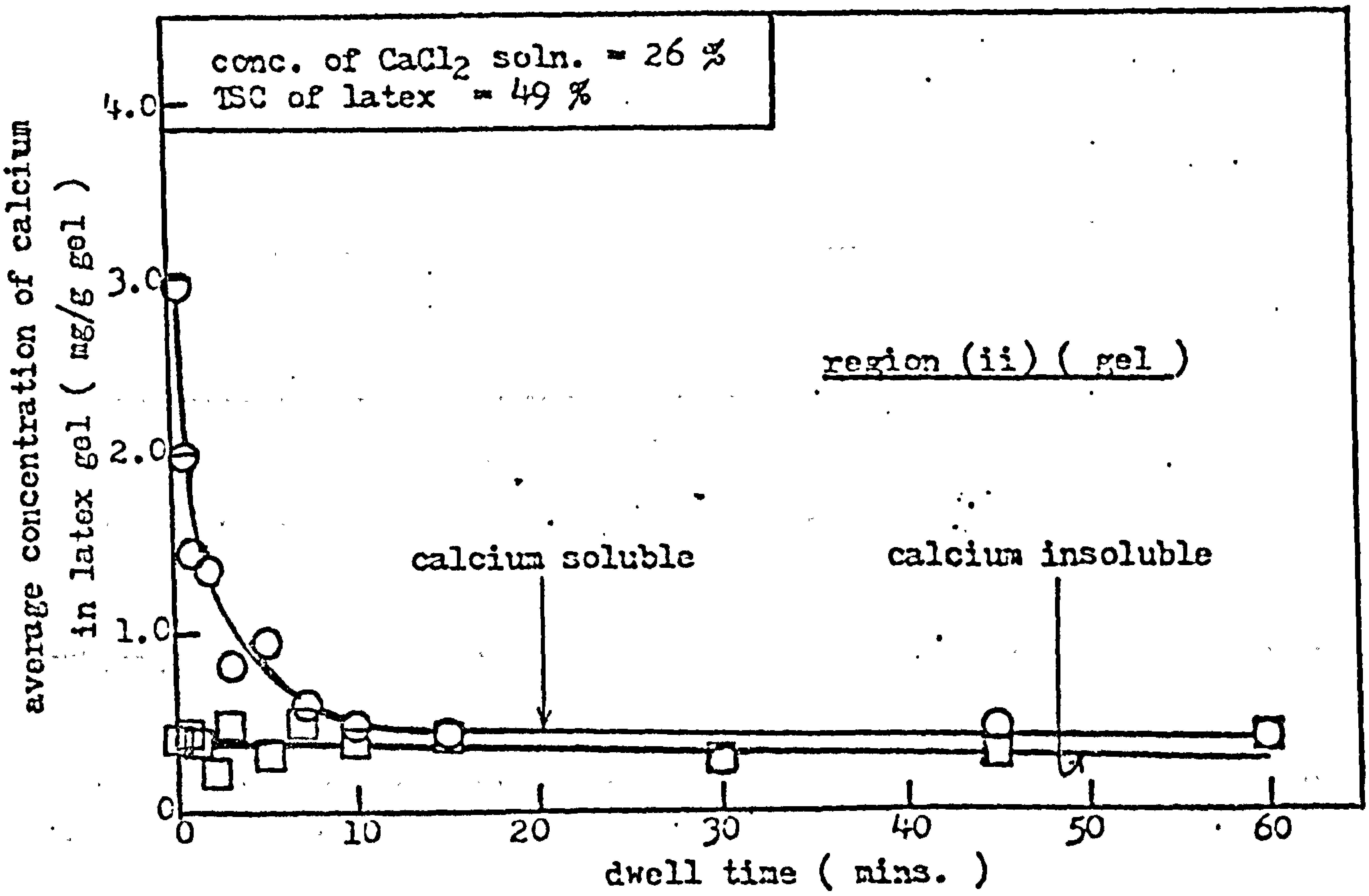


Figure 7.9. Average concentration of soluble and insoluble calcium in gel as a function of dwell time.

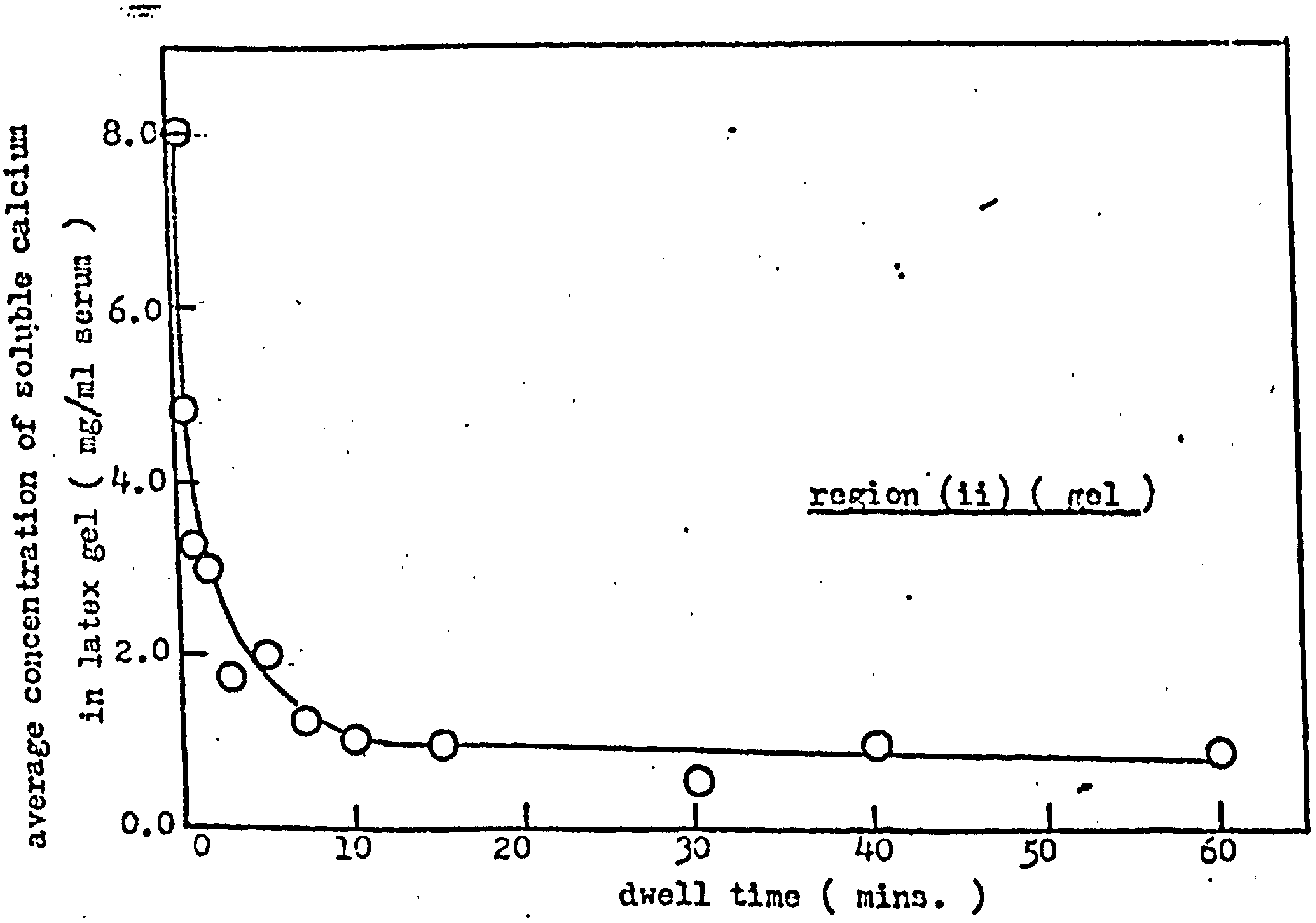


Figure 7.10. Average concentration of soluble calcium in latex gel as a function of dwell time.

Table 7.6

Insoluble calcium as a function of time of dwell (t)

t (mins.)	0.25	0.5	1	2	3	5
Ca (mg/gR)	0.64	0.70	0.65	0.37	0.94	0.60
t (mins.)	7	10	15	30	45	60
Ca (mg/gR)	0.97	0.83	0.87	0.53	0.62	0.83

The titration experiments (Section 7.1) have shown that the amount of calcium required to react with the soap alone in the latex is equal to 0.38 mg per g rubber. Clearly, this value for a given latex is independent of the dwell time. As seen in Table 7.6, the amount of calcium required to react with the soap and other anions present in the latex is approximately double this value. This suggests that the calcium has reacted with other anions such as, the proteinate, carbonate and sulphate under the conditions that prevail in the dipping process. This may be a result of the higher concentration of soluble calcium in the gel compared with those in the titration experiments (compare Figure 7.3 and Figure 7.10)

(B) Method B for determining the distribution of calcium within the gel

In this method, gels were produced at 60, 30 and 10 minutes dwell time respectively. The gels were frozen and sectioned using the procedure described in Section 4.10.4. Each layer (~0.1 mm thick) was then extracted and the soluble and insoluble calcium contents were determined.

The results presented in Figure 7.11 show that the concentration gradient of soluble calcium across the gel is approximately linear; the nature of the method, however, has resulted in a considerable degree of scatter in the results, especially at shorter dwell time. As expected, the concentration of soluble calcium in the gel is always highest at the surface near the former. It is also seen that the concentration of soluble calcium at any given plane in the gel appears to be higher the shorter the dwell time.

The results presented in Figure 7.12 give the amount of insoluble calcium present in each sectioned layer of the gel. The concentration of insoluble calcium is relatively constant up to a certain plane in the gel, and thereafter drops approximately linearly across the remaining thickness of the gel. The relatively constant sections (approximately equivalent to the first 10 minutes of the dwell time) appear to be independent of the dwell time, but the values thereafter are dependent upon the dwell time. The average amounts of insoluble calcium in the gels produced at 30 and 60 minutes dwell time are 0.68 and 0.76 mg calcium per g rubber respectively. This is in good agreement with the average value 0.72 mg calcium per g rubber calculated for gels as shown in Table 7.6.

The results summarised in Figure 7.12 clearly provide an explanation for the reluctance of the outer layers of the deposit to gel completely at long dwell times, ($t > 10$ minutes). It is suggested that many of the anions present in these outer layers remained ionised

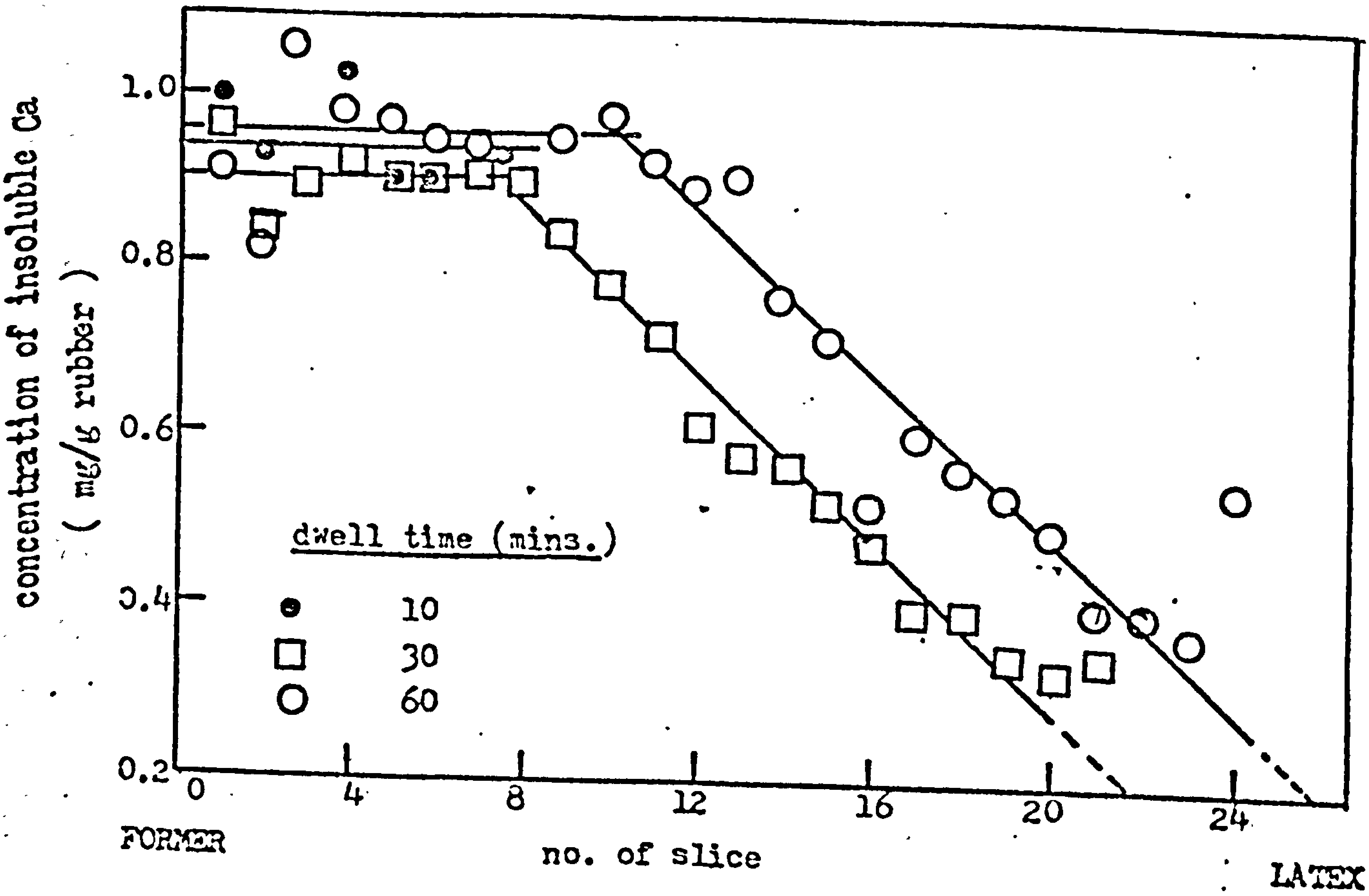


Figure 7.12. Distribution of insoluble calcium in gel obtained at different times of dwell.

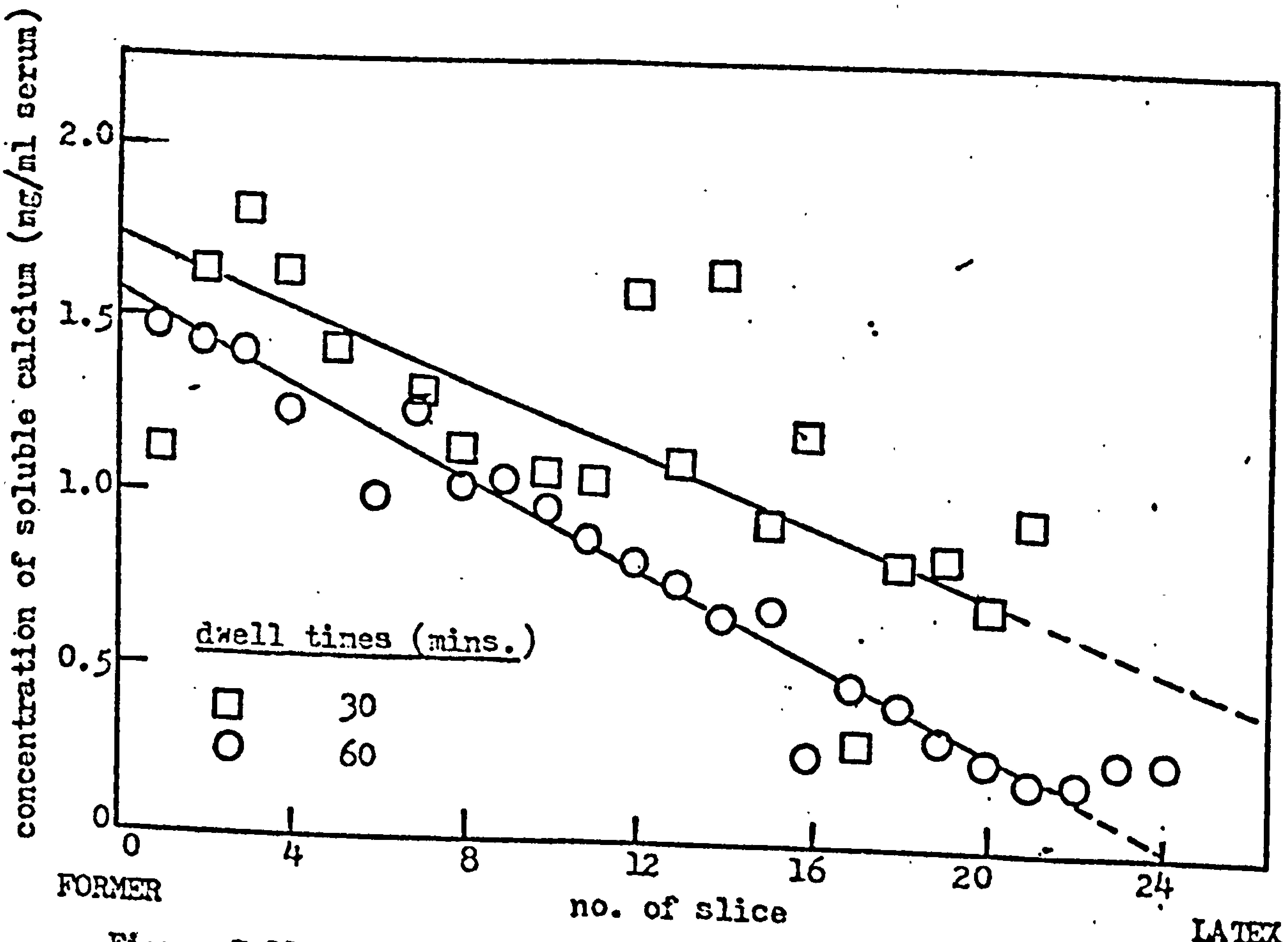


Figure 7.11. Distribution of soluble calcium concentration in gel obtained at different times of dwell.

and thus hindered the formation of a strong coherent gel. In the outermost layers, the amount of calcium reacted may only cause agglomeration of the particles. This would account for the viscous flow that has been observed to occur when the gel is withdrawn from the latex (see Figure 5.5). The further significance of these results will be discussed in more detail in Chapter 8.

7.3 Diffusion of calcium ions in soap solution

7.3.1 Distance-time relationship

The soap solution used in this investigation was a 1 % potassium laurate solution. It was thickened to approximately 12 cps with methyl cellulose (Celacol M 2500) in order to give an equivalent viscosity to that of a 50 % TSC latex. The calcium chloride coagulant was prepared as a 25 % solution. The experimental procedure for the measurement of diffusion of calcium ions in the soap solution is described in Section 4.12.

It was observed that, when the two solutions were brought into contact in the horizontal glass tube, immediate precipitation occurred to produce a white and distinct boundary between the two solutions. The white precipitate built up as interdiffusion took place between the two solutions. Since, the boundary only travelled in the direction towards the soap solution, it is assumed that the rate of diffusion of calcium ions is far greater than that of the soap anions. The two solutions were first allowed to reach an equilibrium level (2 to 3 minutes) before commencing measurements of the distance the front of the precipitate had travelled as a function of time. As a consequence, the distance-time scale recorded in this experiment is an arbitrary one. As the calcium laurate precipitated within the tube, the profile of the solid-liquid phase boundary was observed to change. This is shown diagramatically in Figure 7.13.

Figure 7.14 shows that the initial rate of precipitation is fast, but it slows down until a limiting distance is attained. When the distance travelled is plotted against $t^{\frac{1}{2}}$ (Figure 7.15), four straight lines of differing slopes are obtained.

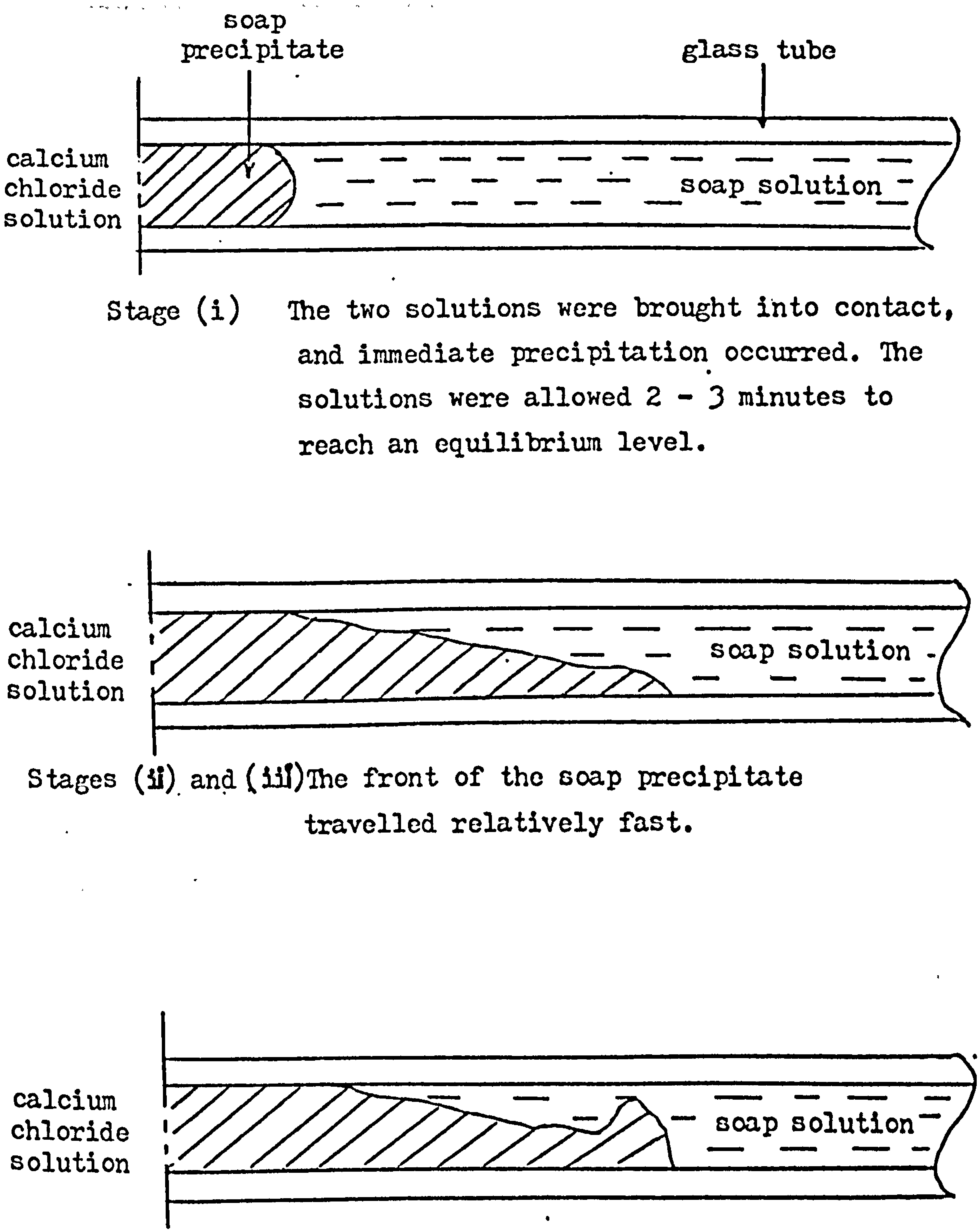
A possible reason for the front of the precipitate remaining stationary at long times is as follows: The concentration of calcium solution at the front is dependent upon the concentration gradient across the length of the precipitate. It can be imagined that, at longer times, this concentration may be very low. The concentration of soap at the front is, however, relatively high. Consequently, there is a greater rate of flow of soap to the left than of calcium chloride to the right. The resultant calcium laurate precipitates behind the front. This is clearly shown in stage (iv) in Figure 7.13, where a ' bump ' of precipitate built up just behind the front. This explains the approximately horizontal line D in Figure 7.15.

7.3.2 Summary of diffusion theory required for analysis of results

The usual equation for simple diffusion in one dimension is

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (7.1)$$

where C is the concentration of the diffusing substance at distance x and time t, and D is the diffusion coefficient, assuming that D is independent of C. If the diffusing substance reacts with a stationary phase during diffusion (as in diffusion with adsorption), then it is



Stage (i) The two solutions were brought into contact, and immediate precipitation occurred. The solutions were allowed 2 - 3 minutes to reach an equilibrium level.

Stages (ii) and (iii) The front of the soap precipitate travelled relatively fast.

Stage (iv) The front of the soap precipitate had virtually stop moving. A bump of precipitate was seen to build up behind the front.

Figure 7.13. Diagrams showing development of precipitated calcium laurate in horizontal tube at different stages of its formation.

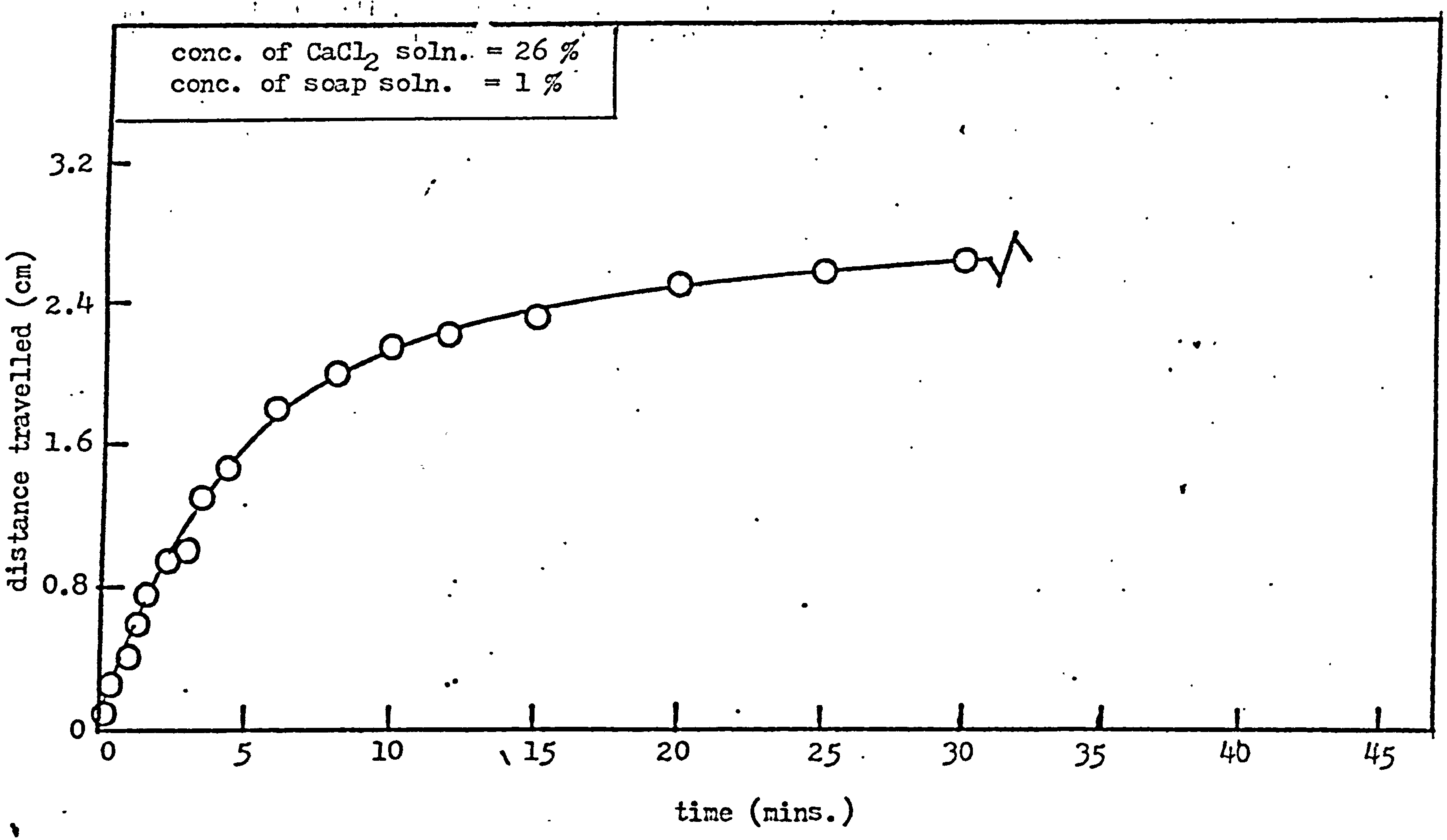


Figure 7.14. Relationship between distance of precipitate boundary and time.

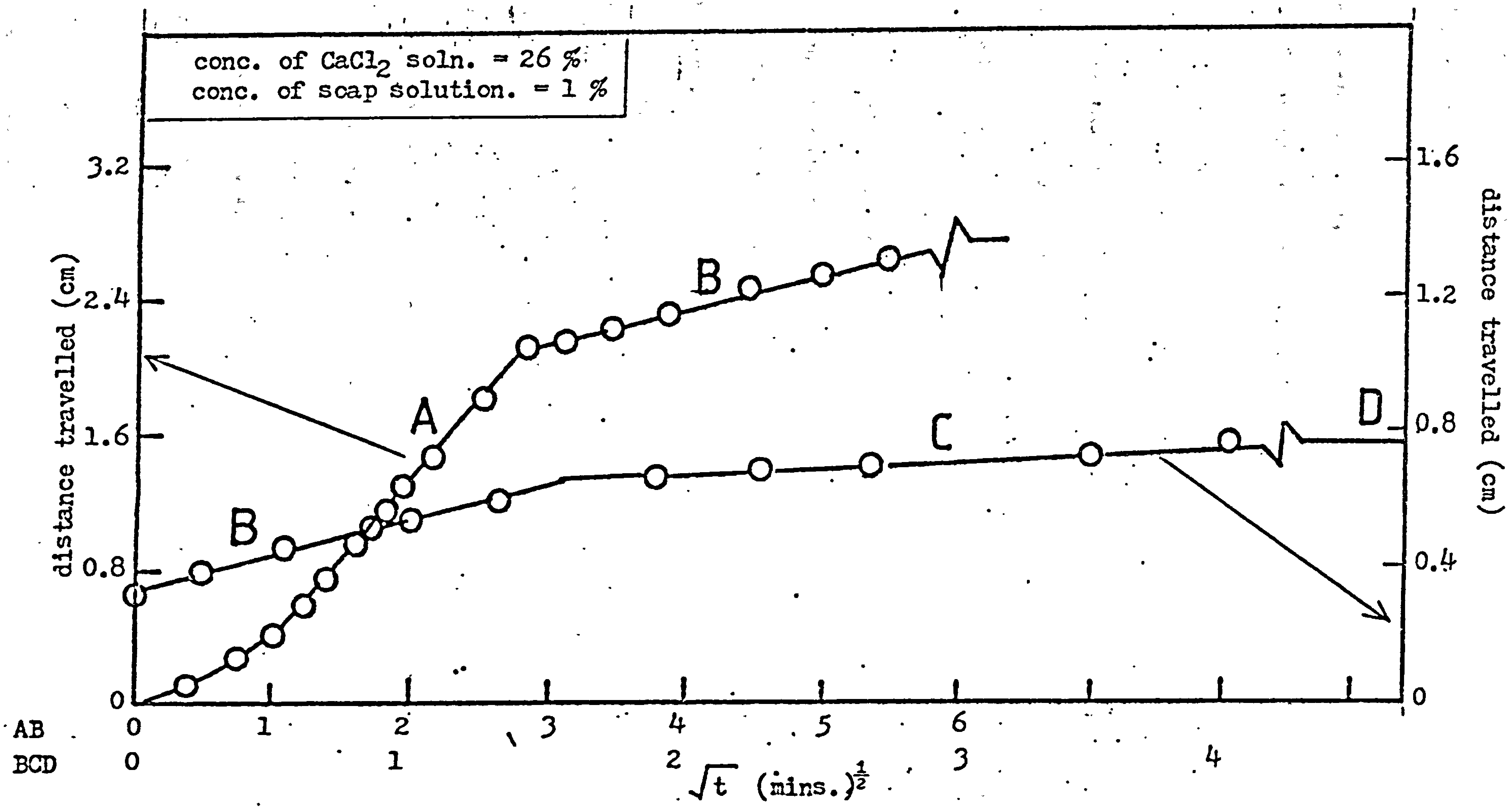


Figure 7.15. Relationship between distance of precipitate boundary and square root of time ($\sqrt{t}$).

necessary to modify D to $\frac{D}{R+1}$ where R is the proportionality constant in the equation,

$$S = RC \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.2)$$

S being the concentration of immobilised substance, and C the concentration of substance free to diffuse. Thus, Equation 7.1 becomes

$$\frac{\partial c}{\partial t} = \frac{D}{R+1}\left(\frac{\partial^2 c}{\partial x^2}\right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7.3)$$

Crank[3] states that this case can be considered as simple diffusion, but with a reduced diffusion coefficient. The effect of the chemical reaction is to slow down the diffusion process to a certain extent, since some of the diffusing substance becomes immobilised as diffusion proceeds. It is thought that this case may approximate that occurring during the coagulant -dipping process since the calcium ions become largely immobilised on the surface of the rubber particles which are ' fixed ' in the gel structure.

The theoretical considerations for the system in Section 7.3.1 are more complex, since both the calcium ions and the soap anions are free to diffuse in opposite directions. In addition, they react to form a precipitate. No satisfactory mathematical solution has been published for this case[3].

Because of the limited data available and the complexity of the system being studied, it was decided to apply the case of simple diffusion theory to the results in Section 7.3.1. The initial distribution of calcium for the case to be considered occupies an infinite region and an initial state such as that defined by $C = C_0$ at $x<0$ and $t = 0$; $C = 0$ at $x>0$ and $t = 0$. The concentration distribution for this case is shown schematically in Figure 7.16 and mathematically by Equation

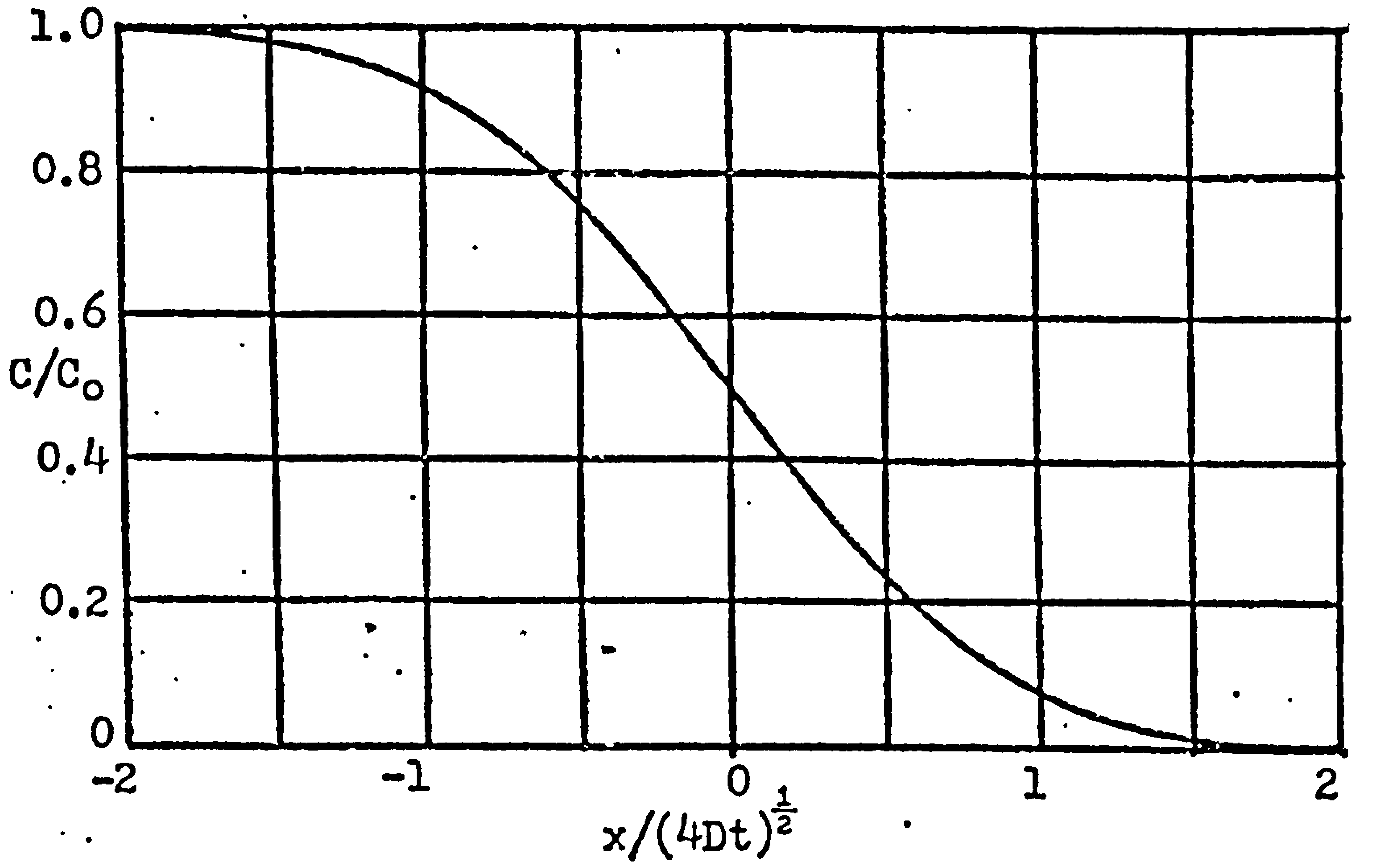


Figure 7.17. Concentration-distance curve for an extended source of infinite extent.

Ref.(3)

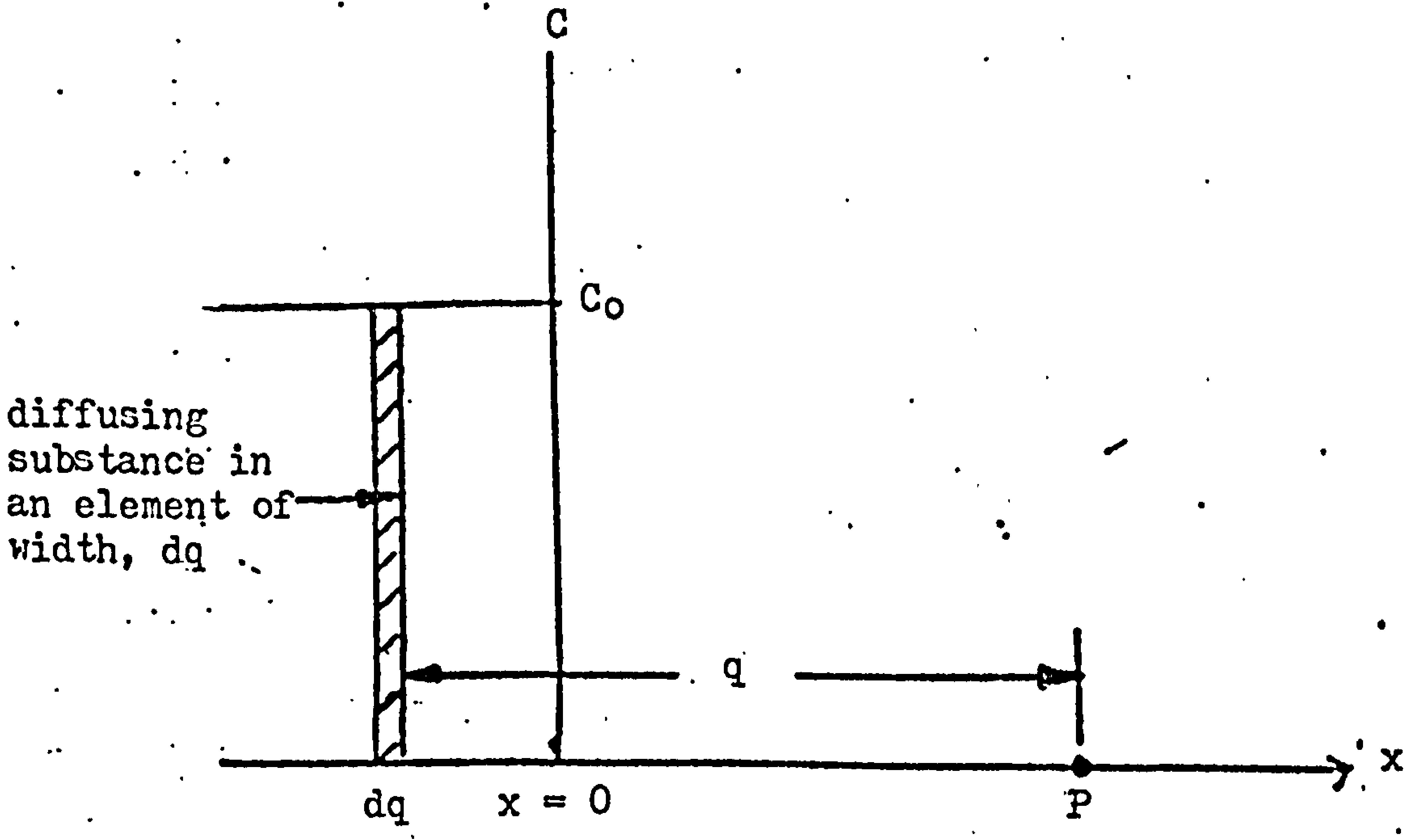


Figure 7.16. Extended initial distribution

7.1. The solution to equation 7.1 and with boundary conditions as defined above is shown in Figure 7.17. Hence, from Figure 7.17 if C/C_0 can be estimated, it is possible to read a value of $x/(4Dt)^{\frac{1}{2}}$ from the horizontal axis. Experimentally-determined values of $x/t^{\frac{1}{2}}$ then enable an estimate of the diffusion coefficient to be made.

7.3.3 Calculation of diffusion coefficient for diffusion of calcium ions in soap solution

The diffusion coefficient of calcium ions in soap solution was calculated as follows. Firstly, values of $x/t^{\frac{1}{2}}$ were calculated from Figure 7.15. It was then assumed that the concentration of calcium ions at the front of the precipitate was always very small compared with the initial concentration, C_0. Thus, C/C_0 is very small. From Figure 7.17 it is assumed that the value of $x/(4Dt)^{\frac{1}{2}}$ is 2 at low values of C/C_0. Substitution of the values for $x/t^{\frac{1}{2}}$ into this equation gives values for the diffusion coefficient as shown in Table 7.7.

It is seen that it is possible to calculate four values of diffusion coefficient from the data shown in Figure 7.15. Obviously, only one of the values represents the diffusion coefficient, D_S, for calcium ions in soap solution; the other three values must be artifacts of the experiment. In addition, it must be emphasised that all the values were obtained by making many assumptions, and may therefore be in considerable error.

The quoted diffusion coefficient, D, for calcium chloride of concentration 1.0 mole per litre at 25°C in water is $1.203 \times 10^{-5} cm^2 sec^{-1}$ (1). The diffusion coefficient, D_S, of calcium ions through a 0.118 M sodium rosinate solution was found to be $5.2 \times 10^{-7} cm^2 sec^{-1}$ (4). This was determined by dissolving the rosinate in a 2 % solution of 1000 cps

Table 7.7

Values of diffusion coefficient corresponding to the slopes A, B, C and D in Figure 7.15

slope, cm sec^{-1}	apparent diffusion coefficient, $cm^2 sec^{-1}$
A = 0.124	9.68×10^{-4}
B = 2.67×10^{-2}	4.46×10^{-5}
C = 4.30×10^{-3}	1.16×10^{-6}
D = 0	0

methyl cellulose and then drawing the viscous solution into capillary tubes. The tubes were placed into the 1.34 M calcium coagulant solution and the position of the precipitated calcium rosinate boundary was measured with time. D_s values of ± 5 % of the above value were obtained when the concentration of sodium rosinate was varied between the limits of 0.06 and 0.18 M, while the concentration of the coagulant solution was varied between 0.7 and 2.0 M[5]. According to Stewart[5], the constant value of D_s within these limited concentration ranges shows that this system is adequately described by the equations derived by Herman[5] for diffusion with precipitation into a medium which does not itself take part in the diffusion process.

The first two values in Table 7.7 are considerably higher than those reported for the diffusion coefficients for calcium ions in soap solution ($D_s = 5.2 \times 10^{-7}$ cm^2 sec^{-1}) or in water ($D = 1.203 \times 10^{-5}$

$cm^2 sec$). It is thought that these high values arise as a result of (a) the initial difference in the head of pressure between the two reacting solutions, and (b) a mass transfer of calcium ions into the soap solution as a result of osmotic pressure. Concerning (b), it may be that the precipitate which formed initially acted as a semi-permeable membrane, and since the concentration of calcium chloride solution was very high (25 %), it is possible that osmosis occurred. The fourth value (i.e., zero) is a consequence of the experimental observation that the precipitate of calcium laurate formed behind the precipitation front after diffusion has occurred for some time. This suggests that at this stage laurate ions are migrating towards the calcium solution at a greater rate than that at which the calcium are migrating towards the laurate solution (see Section 7.3.1). The third value 1.16×10^{-6} is approximately twice the reported value of 5.2×10^{-7} cm^2 sec^{-1} for the diffusion of calcium ions in a very viscous soap solution. The difference between the values of D_s obtained and reported is probably a result of the difference in the experimental conditions, such as the viscosity of soap solution (12 cps compared with 1000 cps). The diffusion of calcium ions in a very viscous soap solution is probably reduced to a certain extent compared to that in a relatively fluid soap solution.

The value 1.16×10^{-6} cm^2 sec^{-1} is a factor of ten lower than the reported value of D (1.203×10^{-5} cm^2 sec^{-1}) for the diffusion of calcium ions in water. If this value is correctly estimated, then clearly the effect of the reaction between the calcium ions and the soap is to slow down the overall process of diffusion by a factor of ten. The results of this sections are discussed more fully, together with the diffusion results obtained in the dipping process, in Chapter 8.

CHAPTER 8

FURTHER DISCUSSION OF RESULTS

8.1 Introduction

The purpose of this Chapter is to draw together the many results which have been presented in the previous Chapters, and thus obtain a greater understanding of the mechanisms of the coagulant-dipping process. The major findings reported in the previous chapters which will be discussed further can be summarised as follows;

(1) The calcium appears to react with certain anions in the latex, notably the fatty-acid anions, but the extent of reaction depends upon the concentration of reactive ions (Figure 7.3 and 7.12).

(2) The rate of deposition depends upon the initial concentration of calcium on the former (Figure 5.27).

(3) The rate of deposition appears to be diffusion-controlled, as evidence by the linear relationship between θ_c' and $t^{\frac{1}{2}}$ (Figure 5.9).

(4) The rate of diffusion, and hence the rate of deposition, is not affected by the large change in concentration of the calcium solution on the former during the dipping process (Figure 7.8).

(5) The rate of deposition is only slightly affected by added soaps, pH of latex (pH>8.5), and the viscosity of the latex (up to <u>ca</u>. 200 cps).

(6) The thickness of the wet-gel deposit is virtually independent of the TSC of the latex (Figure 5.9).

Some of the above finding are surprising and others appear to be contradictory. It is therefore necessary to consider these results further in order to obtain a deeper understanding of the process before any attempt can be made to postulate a coherent theory to account for the experimental observations. This further consideration of the results is given in the subsequent sections.

8.2 Fate of calcium ions

The results in Section 7.1 suggest that the soap anions precipitate as calcium salts even when the concentration of calcium ions in the latex is low. Further, it was deduced that the maximum amount of soap which reacted was equivalent to 0.38 mg calcium per g rubber. Assuming that the indigenous soap is stearic acid, then this corresponds to 0.57 g stearic acid per 100 g rubber. Values quoted for a typical natural rubber latex concentrate are of the order of 0.8 g fatty-acid soap per 100 g total solids[1]. Hence, the value suggested by this aspect of the investigation is not unreasonable.

In the actual coagulant-dipping process, it was found that anions other than the soap were also precipitated (Figure 7.12). The total amount of anions precipitated (approximately equivalent to 0.72 mg calcium per g rubber) was virtually independent of dwell time in the inner layers of the gel, but decreased almost to zero in the outer layers. From these observations, it is possible to estimate the proportion of the calcium originally on the former which had reacted with the anions present in the latex gel. For example, at 60 minutes dwell time, the weight of dry rubber deposited from 60 % TSC latex was 0.17 g per cm^2 (Figure 5.9). The average amount of calcium reacted was 0.72 mg per g rubber. Hence the total weight of calcium neutralised was 0.17 x

$0.72 = 0.12$ mg per cm^2. The original amount of calcium on the former was 0.68 mg/cm^2. Thus, $100 - \frac{0.68 - 0.12}{0.68} \times 100$ % , 17.6 %, of the calcium had reacted. The effect of added soap (potassium laurate) upon the ratio of calcium to reactive anions in the latex was estimated in a similar manner. Estimates of the percentages of calcium reacted at different times, and with the addition of soap, are summarised in Table 8.1.

It is seen that a high proportion of the calcium is still available to cause coagulation of the uncompounded latex, even after 60 minutes dwell time. This may, in part, explain the linearity of the θ_c' versus $t^{\frac{1}{2}}$ plots over this time period. With the added soap (2 parts per 100 parts by weight of latex solids), the amount of calcium available for coagulation is reduced considerably after any given time of dwell. However, the rate of deposition is only marginally affected by the addition of soap. This suggests that the rate of diffusion of the calcium ions is independent of the concentration of the calcium-reactive anions in the latex under the conditions used in these experiments.

In the dipping process, a maximum of 0.93 mg of calcium reacts with each gram of rubber deposited (see Figure 7.12). Approximately 0.38 mg of this appears to react with fatty-acid anions. The remaining calcium ($\sim$ 0.55 mg per g rubber) apparently reacts with other anions present in the latex, although the nature of these anions is not clear.

Table 8.1

Percentages calcium reacted at different dwell times (assumed 0.68 mg calcium per cm^2 of former).

	dwell time (mins.).	wt. of dry deposit $^{+}$ g cm^{-2}	wt. of calcium reacted mg cm^{-2}	calcium reacted %
	10	0.08	0.06	8.8
latex * (TSC = 60%)	30	0.13	0.09	13.2
contained 0.57 % of indigenous soap	60	0.17	0.12	17.6
latex ± +	1	0.035	0.08	11.8
added soap (2 pphr)	5	0.065	0.16	23.5
(TSC = 60%)	10	0.080	0.19	27.9

* approximate value deduced from Section 7.1

± theoretical value assuming all added and indigenous soaps are neutralised.

\+ values obtained from Figure 5.9.

8.3 Diffusion of calcium ions

8.3.1 Determination of diffusion coefficient of calcium ions during the dipping process

The results from the model studies on the diffusion of calcium ions in soap solution (see Section 7.3.3) indicate that the most likely value of the diffusion coefficient for calcium ions in soap solution, D_S, is 1.16×10^{-6} $cm^2 sec^{-1}$. However, it must be emphasised that many simplying assumptions were made in the theory in order to obtain this value. If the same assumptions are made, it is possible to calculate the diffusion coefficient for calcium ions in the latex gel, D_L, from the two different sets of data summarised in Figures 5.9 and 7.11.

(a) <u>Using the data shown in Figure 5.9</u>

The value of $x/t^{\frac{1}{2}}$ obtained from Figure 5.9 can be used to calculate D_L using the same technique and assumption that have been described in Section 7.3.2. It is noted that a conversion factor is required to change the units of x from mg cm^{-2} of deposit to mm thickness of deposit. It was found that 1.8 mg $cm^{-2}$of deposit was equivalent to 0.02 mm thickness. The value obtained, $D_L = 1.4 \times 10^{-6}$ cm^2 sec^{-1}, is in surprisingly good agreement with the result obtained for the diffusion of calcium ions in soap solution (i.e. $D_s = 1.16 \times 10^{-6}$ cm^2 sec^{-1}). With the limited amount of data available, it is not clear whether this agreement is fortuous or not.

(b) <u>Using the data shown in Figure 7.11</u>

From this graph, the value of the concentration of soluble calcium, C, at any distance, x, from the former at time, t, can be estimated. The value of C_0, the concentration of calcium (mg ml^{-1}) on the former at time t is obtained by extrapolating the line to $x = 0$. Hence the value of C/C_0 at any given distance and time can be calculated. Using these values in conjunction with Figure 7.17, values of $x/(4Dt)^{\frac{1}{2}}$, and hence of D_L, can be obtained. The values of D_L for t = 30 and 60 minutes as a function of x are shown in Figure 8.1. It is difficult to understand the significance of the change in D_L with distance. However, at the maximum value of x, i.e. at the gelation front, $D_L = 5.3 \times 10^{-7}$ and 1.4×10^{-6} cm^2 sec^{-1} at t = 60 and t = 30 minutes respectively. These values are in good agreement with the value of 1.4×10^{-6} cm^2 sec^{-1}obtained in (a) above.

8.3.2 Discussion of results

The values of the diffusion coefficients found for calcium ions in latex, D_L, and in soap solution, D_S, are in reasonable agreement and approximately ten times less than the diffusion coefficient, D, for calcium ions in water. There is some doubt about the validity of the calculated values; a very thorough investigation would be needed to evaluate correctly D_S and D_L (see Chapter 9).

However, assuming that the values are correct, it is possible to understand some of the surprising observations that have been made during the course of this investigation. Firstly, the rate of diffusion of calcium ions is independent of the presence or absence of latex particles (i.e. $D_S \propto D_L$). Thus explains why the TSC of the latex has virtually no effect upon the rate of diffusion of calcium ions through the latex gel (see Figure 5.9). It also lends confirmation to the earlier conclusion that there is no tortuosity factor. It is also apparent that the level of soap present in the latex will not significantly affect D_L . This observation is consistent with the results for the diffusion of calcium ions in soap solutions of different concentration which were reported to be approximately constant[2].

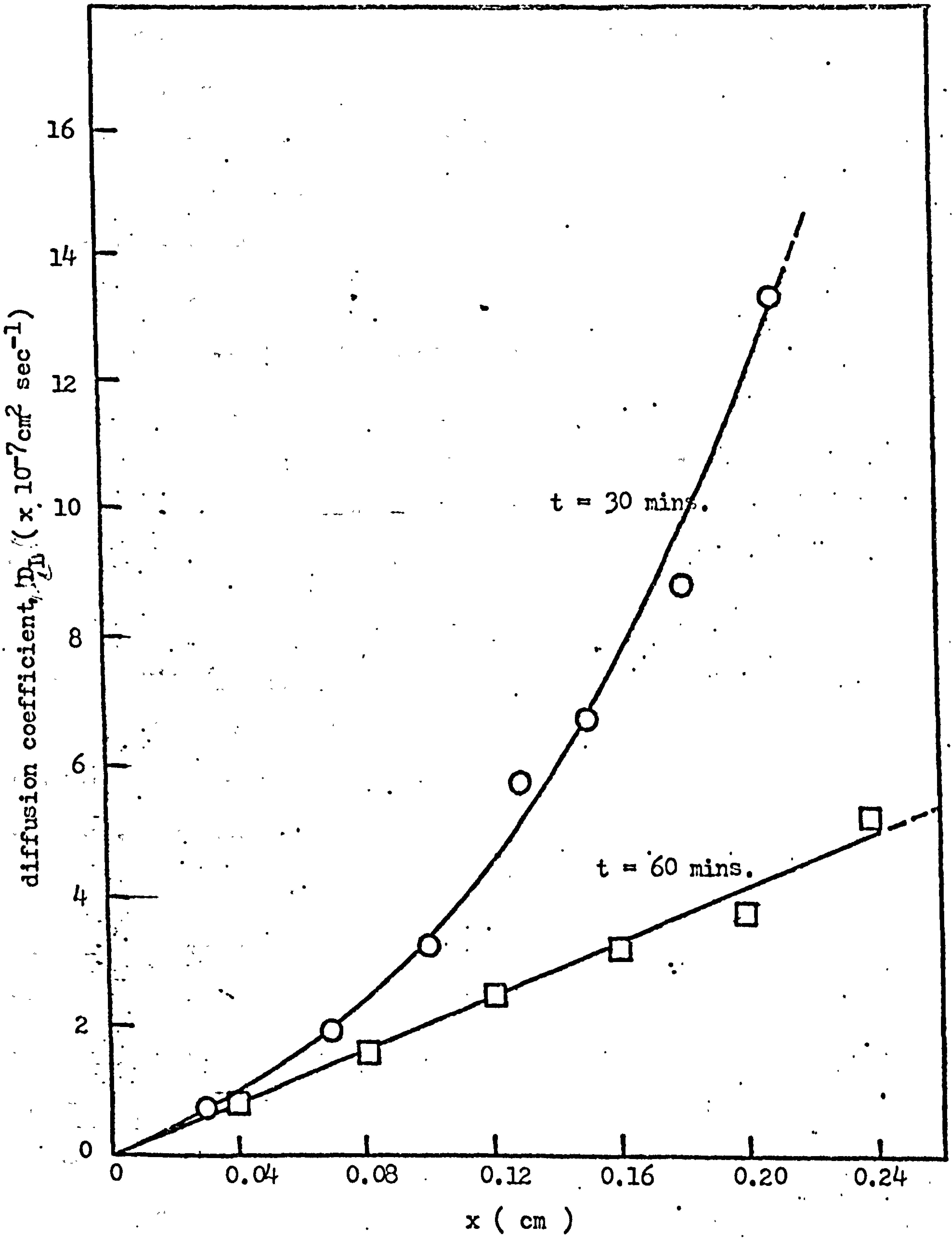


Figure 8.1. Relationship between D_L and thickness of deposit

8.4 Proposed mechanisms of deposition

The deposition of rubber on to the former involves one or more of the following mechanisms:

(i) initial dehydration of the latex by the calcium chloride on the former;

(ii) precipitation of the soap and other anions by the calcium ions;

(iii) compression of the electrical double layers surrounding the particles as a result of the increasing concentration of calcium and chloride ions, leading to agglomeration of the latex particles.

Each of these possible mechanisms will now be considered in some detail.

8.4.1 Dehydration of latex by calcium chloride

The immersion of a former coated with calcium chloride into the latex will be expected to cause an instantenous deposition of latex particles adjacent to the former by dehydration. In the process, the serum is drawn inwards towards the former by the hydroscopic calcium chloride to form a concentrated coagulant solution. As a consequence, there is a marked reduction in the concentration of the coagulant solution on the former (see Figure 7.8) and a marked increase in the total solids content of the gel nearest to the surface of the former (see Figures 6.4 and 6.8).

The concentration of calcium trapped between the former and the gel drops from approximately 20 % to 2.6 % in less than 10 seconds (see Figure 7.8). Thus, it is possible that within this very short time, the deposition may have been by dehydration rather than by precipitation of the higher fatty-acid soaps or by compression of the electrical double layer surrounding the particles. The dehydration theory is also consistent with the observation that the total solids contents of the gel adjacent to the former approaches that of a close-packed structure, and with the fact that calcium chloride is highly hydroscopic in nature. Further, it was found that a plot of θ_c versus $t^{\frac{1}{2}}$ does not pass through the origin (Figure 5.4). The intercept on the θ_c-axis strongly suggests that the initial deposition is by some mechanism other than precipitation of soaps through the diffusion of calcium ions, and this other mechanism could well be dehydration.

8.4.2 Precipitation of soaps by calcium ions

The reduction of the charges on the latex particles by chemical interaction between the calcium ions and the anions of the higher fatty-acid soap is a primary mechanism by which the latex becomes destabilised. The neutralisation of the charges occurs when the concentration of reactive ions in the latex exceeds the solubility product of the perspective calcium salts (see Table 7.4). This can only occur when calcium ions migrate away from the former into the latex. The precipitation of reactive anions in the latex is dependent upon the concentration of calcium ions, since the ion concentration of reactive anions in the latex is constant. The solubility product of the calcium salts of higher fatty-acid soaps is low compared to that of most other anions present in the latex. Therefore, the higher fatty-acid soap anions, which will be adsorbed at the rubber-aqueous phase interface and which play an important role in confering stability upon the latex initially, are preferentially precipitated compared to other anions such as the sulphate, citrate, etc. (see Section 7.1.8). At short dwell times ($t<20$ minutes), the higher fatty-acid soap anions present in the latex completely react with calcium ions to form insoluble salts (see Figure 7.12).

The rate of deposition of rubber on the former is a diffusion-controlled process (Figure 5.9). The diffusion coefficient of calcium ions with reaction is smaller than the corresponding diffusion coefficient of calcium ions in water. The rate of diffusion is dependent upon the initial amount of coagulant on the former.

The initial rate of deposition is fast (Figure 5.3). Clearly, this corresponds to the very high concentration of coagulant present initially on the former. The reduction in the concentration of the coagulant on the former as a result of dilution caused by dehydration and diffusion of calcium and chloride ions into the gel reduces the rate of deposition. The distance the cations travel through the gel is dependent upon the concentration of the coagulant in the gel. At long dwell times, the concentration of cations at the latex-gel interface is very low. Under, such conditions, the outer layers of the deposit consist of very viscous layers of latex which are in a critical condition of incipient gelation. This occurs when the concentration of soluble cations is very low and the concentration of reacted calcium is also very low (see Figures 7.11 and 7.12). In this situation, the outer layers of the gel readily flow off the former, and thus the relationship between the dry deposit thickness, θ_c, and $t^{\frac{1}{2}}$ forms two straight lines (see Figures 5.4 and 5.5).

8.4.3 Compression of electrical double layer surrounding the particles by calcium and chloride ions

The presence of calcium and chloride ions of high concentration in the gel will increase the ionic strength of the latex. The concentration of chloride ions is believed to be higher then that of the calcium ions because the chloride ions do not take part in the reaction to form insoluble salts. There will also be some liberation of soap counterions, e.g., K^+ or NH_4^+, which will further increase the ionic strength. The increase ionic strength reduces the thickness of the electrical double layer surround the particles, and the potential energy barrier between the latex particles. If the ionic strength is sufficiently high, it is possible that particle coalescence may occur without any chemical reaction taking place.

Gazeley[3] has postulated that this does in fact occur. Gazeley has reported results which differ somewhat from those obtained in this work. His results, together with the results from this work, are plotted in Figure 8.2. Gazeley's results show that, at low calcium levels, a greater weight of deposit is obtained than would be expected by mere precipitation of soap. Hence, he has postulated that gelation is primarily a consequence of compression of the electrical double layers, and not of reaction between calcium ions and latex anions. However, the levels of calcium on the former are very low, being approximately ten times less than those used in this work. The present author has attempted to repeat Gazeley's results for the pick-up of coagulant on the former. The results, shown in Figure 8.3, indicate much higher values of calcium pick-up. If Gazeley's results are replotted taking into account the higher values for the pick-up of calcium, then a curve is obtained which is very similar to that obtained in this work. There is thus some degree of doubt concerning Gazeley's postulate that deposition is a consequence of compression of the electrical double layer surrounding the particle, rather than of chemical reaction between the calcium ions and the latex anions. Further, the results of this work clearly show that the calcium ions do react with and precipitate soap. Although, Gazeleys' quoted concentrations

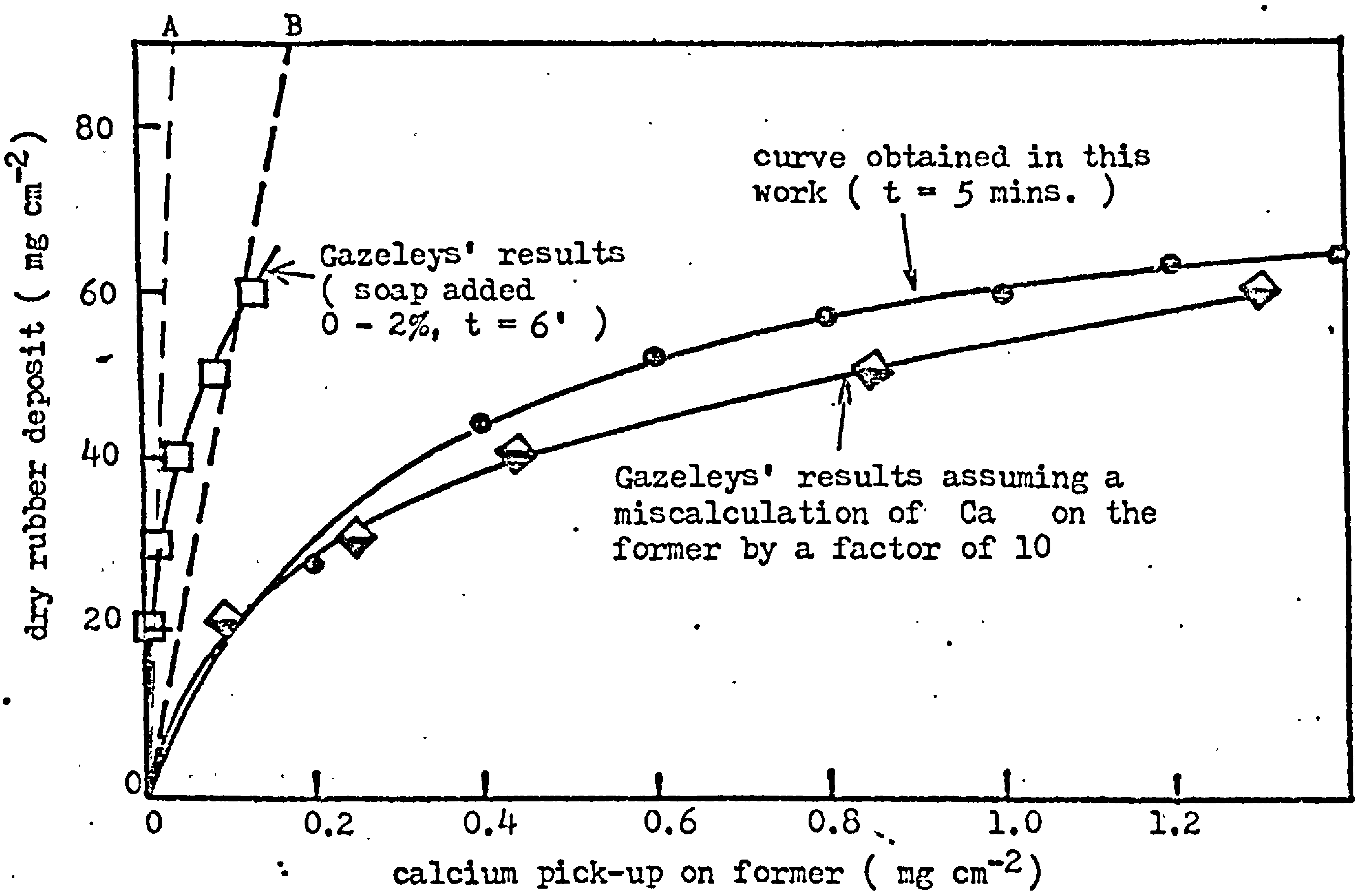


Figure 8.2. Dry rubber deposit versus calcium pick-up for a specific time of dwell. The dotted lines represent the maximum amount of rubber deposited if the deposit weight is dependent upon the reaction of soap with calcium. Line A represents no added soap; line B represents 2.4% added soap.

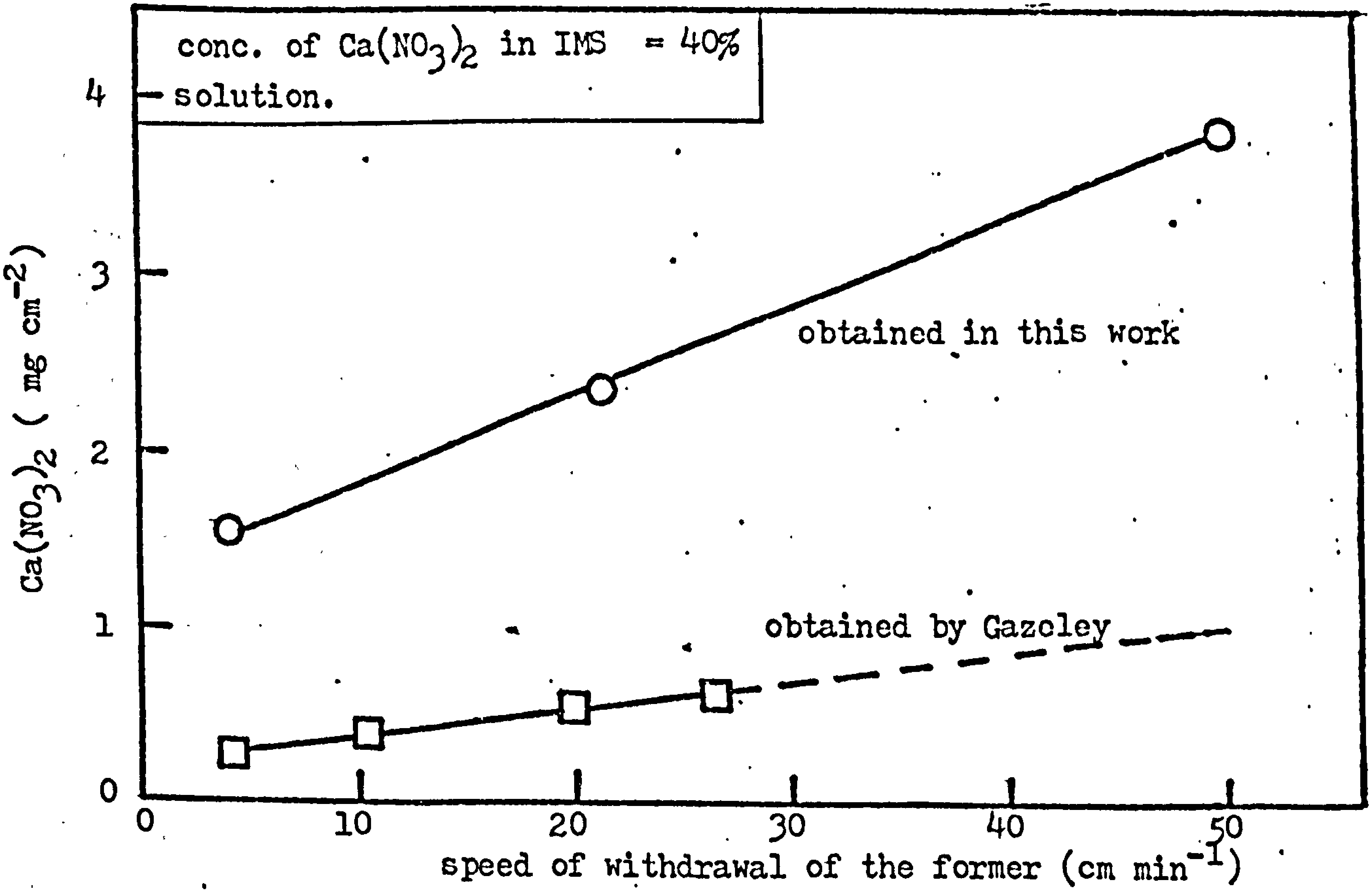


Figure 8.3. Calcium nitrate pick-up as a function of speed of withdrawal of the former.

of calcium on the former are low, the lowest level 0.025 mg per cm^2 is equivalent to a calcium concentration of 1×10^{-2} moles per litre if all the calcium dissolves in the serum in the gel. This would be sufficient to cause precipitation of some of the soaps. It is concluded that Gazeleys' results do not provide definite evidence for the importance of compression of the electrical double layer surrounding the particles. However, the results shown in Figure 7.12 suggest that the two outer layers of the gel do not need to have a high concentration of insoluble calcium in order to form a gel. It is therefore possible that the deposition may be partly caused by the compression of the electrical double layer by the calcium and chloride ions.

In addition, evidence that compression of the electrical double layer may be at least partly responsible for deposition comes from consideration of Figures 7.11 and 7.12. Calculations show that, in the outermost layer of the gel which formed at t = 60 minutes, the concentration of soluble calcium and indigenous soaps were 6.25×10^{-3} and 2.01×10^{-2} moles per litre respectively. Since the ionic product of calcium stearate is 1.01×10^{-5}, it would be predicted that it should precipitate. However, the results show that the soap does not precipitate in this outmost layer. This suggests that $I < S$, i.e., that $[6.25 \times 10^{-3}][\text{stearate}^-]^2 < 1.15 \times 10^{-12}$, i.e., that $[\text{stearate}^-]$ was less than 1.36×10^{-5} mole per litre. In practice, $[\text{stearate}^-] \cong 2.01 \times 10^{-2}$ mole per litre, which suggests that reaction would occur readily. The observation that no reaction occurred can be explained if the calcium only reacts with soluble stearate, i.e., it does not react with adsorbed stearate. This suggestion appears at first sight to be unlikely. However, if the experimentally derived values for soluble and insoluble calcium are correct, then this is one possible explanation.

The amount of soluble stearate is unknown and is difficult to estimate. It is known that the cmc of potassium stearate is 4.4×10^{-4} moles per litre in pure water at 50 - 60°C [4]. The effect of the presence of electrolytes often to reduce the cmc by a factor of ~ 10(5). Thus the latex it might be expected that the maximum concentration of stearate which is soluble will be ca. 4.4×10^{-5} moles per litre. However, since the latex is not saturated with soap, a lower figure than this is likely. Thus, it is possible that $[\text{stearate}^-]_{\text{soluble}}$ is less than 1.36×10^{-5} mole per litre, and hence that the stearate does not precipitate.

The above reasoning leads to the tentative postulate that the calcium ions only react with soluble anions. Closer consideration of Figures 7.11 and 7.12 shows that in the outer portion of the deposit ($\theta_c' > 2$ mm), the soap is not completely precipitated by calcium despite there being sufficient soluble calcium to bring this about. This leads naturally to the following extension of the postulate. Some calcium ions may react with soap anions in the aqueous phase. The reduction in concentration of ionised soap causes more soap to be desorbed. This in turn reacts in the aqueous phase. The rate of reaction is thus governed by the rate of desorption of soap anions from the rubber-aqueous phase interface into the aqueous medium. Further, if this is so, then it appears that reaction does not occur instantaneously because time is required for desorption.

It is further suggested that the unexpectedly high concentration of soluble calcium in the outer layers brings about loose particle aggregation but not complete agglomeration by compression of the electrical double layer. This would account for the viscous nature of the latex in the outer layers of the gel.

It must be emphasised that the above postulate is based upon a very limited amount of experimental information (i.e., the results summarised in Figures 7.11 and 7.12). In addition, the concentrations of soluble and insoluble calcium were obtained by freezing the gel, which is known to cause deformation and possibly flow of the serum during the freezing process. A considerable amount of additional work would be required before any firm postulate could be put forward.

CHAPTER 9

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 Summary and conclusions

This investigation has confirmed the generally-accepted view that the coagulant-dipping operation is a very complex process. The process is not easily amenable to experimental investigation, because it comprises several different aspects, such as diffusion, syneresis, precipitation of calcium ions, etc., all of which appear to be interrelated in a complicated manner.

The experimental problems are considerable, and the results obtained are in some cases difficult to analyse. For example, it would be very difficult to derive a diffusion equation which would satisfactorily represent the real situation in this case. The reasons for this are that not only is the concentration of calcium ions on the former changing with the time of dwell, but the calcium is being removed from solution by reaction with the stabilisers and other anions present in the latex. In addition, the instantaneous solids content of the gel changes with time of dwell, and serum flows towards the former. The flow path of the calcium ions is uncertain, since the structure of the gel is unknown. Since, the process is a dynamic one, it is not easy to stop the process and carry out an analysis at a fixed time with no further change occurring. The freezing of the gel followed by sectioning was an attempt to prevent continuation of the process, but even this led to experimental errors because of the increase in volume that occurs when the serum freezes. This results in distortion of the gel.

Despite all these practical and theoretical problems, considerable progress has been made towards an understanding of the mechanism whereby deposits form during latex·coagulant-dipping process. The major findings are summarised below:

(1) It was deduced from the conductimetric titration of latex with calcium chloride solution that the maximum amount of soap reacted is equilvalent to 0.38 mg calcium per g rubber. Assuming that the indigenous soap is stearic acid, then this value corresponds to 0.57 g of stearic acid per 100 g rubber.

(2) It was found that the mechanism of deposit formation involves reaction between the cations of the coagulant and the adsorbed anions which stabilise the latex. Anions other than fatty-acid anions also react with the calcium ions during the dipping process. Hence the process of deposit formation involves consumption of the coagulant as well as dilution of the coagulant. Consequently, the deposit thickness would certainly be expected to approach a finite limit at long dwell times, corresponding to complete consumption of the coagulant.

(3) The inner layers of the gel contain a constant amount of insoluble calcium (~0.93 mg per g rubber), but in the outer layers the amount of insoluble calcium continually decreases until in the outermost layer it is approximately zero. The rate of decrease of insoluble calcium and the position within the gel from which it decreases depend upon the time of dwell and the thickness of the gel. This explains the reluctance of the outer layers of the deposit to form a firm gel at long dwell times.

(4) The initial amount of calcium which is present on the former

has a significant effect upon the relationship between deposit thickness and dwell time. This is because the rate of diffusion of calcium, as determined by D_L, is dependent upon the initial concentration of calcium on the former, C_o.

(5) Reduction of the total solids content of the latex (60 to 20 %) leads to a reduction of the dry deposit thickness obtained after a given time of dwell. However, the wet deposit thickness remains approximately constant.

(6) Varying the viscosity of the latex by dilution with distilled water, or by the addition of methyl celluloses, has little effect upon the thickness-time relationship.

(7) The relationship between deposit thickness and dwell time is remarkably insensitive to the level of higher fatty-acid anions over quite a wide range. This is so despite the fact that the added soap does significantly alter the ratio of calcium ions to calcium-reactive anions.

(8) Despite the complexities of the process mentioned above, the wet deposit thickness could be satisfactorily described as a function of the square root of the dwell time. That the thickness-time relationship can be expressed in this way is consistent with the assumption commonly made that diffusion of the coagulant through the latex gel is an important aspect of the coagulant-dipping process.

(9) The diffusion of the calcium ions outwards from the surface of the former is retarded by chemical reaction between the diffusing ions and certain anions present in the latex ($D_L = 1.4 \times 10^{-6}$ cm^2 sec^{-1} compared with $D = 1.203 \times 10^{-5}$ cm^2 sec^{-1} for the diffusion of calcium ions in water).

(10) Syneresis only occurs inwards towards the former.

(11) The wet-gel strength of the deposit is lower than that of the dry deposit by a factor of ten, and depends upon the structure of the gel as well as upon its total solids content.

9.2 Suggestions for further work

This investigation of coagulant-dipping behaviour must be regarded as but a preliminary study of a very complex process. It has high-lighted some areas of study which are worthy of further and more extensive investigation. Suitable areas for further work are as follows:

(1) Calcium-reactive anions in NR latex

A more comprehensive study should be made to elucidate the nature of the calcium-reactive anions in NR latex, and the conditions under which they react with the calcium ions. It is envisaged that the work on conductimetric titrations might be extended to titration of the latex serum and solutions of different soaps and other anions not studied in this work. It would be necessary to determine the type and quantity of each anion present in the serum and adsorbed on the particles. Further, it would be essential to determine the solubility product of each species and the effect that a disperse phase has on this quantity. The use of coagulants containing other divalent cations, e.g., Mg^{2+}, Ba^{2+} and Zn^{2+}, would help to elucidate the importance of the solubility product for the rate of deposition and possibly the relative importance of compression of the electrical double layer surrounding the particles versus reaction with anions as the main cause of coalescence.

(2) Distribution of calcium within the gel

This factor has received only cursory study in this investigation. The work should be extended to study of the effect of concentration of added soap, TSC of latex and calcium pick-up on former upon the concentration of soluble and insoluble calcium in the gel.

(3) Diffusion studies

The experiments described in suggestion (2) above might throw further light on the diffusion behaviour of the system. However, studies on model systems would be necessary in order to clarify the process. For example, the rate of diffusion of calcium through a preformed gel (acting as a semi-permeable membrane) would enable the effects of coagulant concentration, gel structure and gel thickness to be evaluated. The calcium-impregnated gel could be sectioned in order to determine the concentration gradient of calcium in the gel in the absence of reaction.

(4) Model studies

A study based upon the use of model latices would be expected to give some simplification in the interpretation and analysis of the results. Investigation of the coagulant-dipping behaviour of well-characterised mono-disperse polyisoprene latices having a wide range of particle sizes, soap types and contents and modulus of the contained polymer should provide information concerning several of the most important aspects of the coagulant-dipping process. A fully defined dipping procedure, such as that adopted by Stewart[1], should enable predictions to be made of the rate of diffusion of calcium ions as reaction proceeds, and hence of the rate of deposition.

Appendix 1

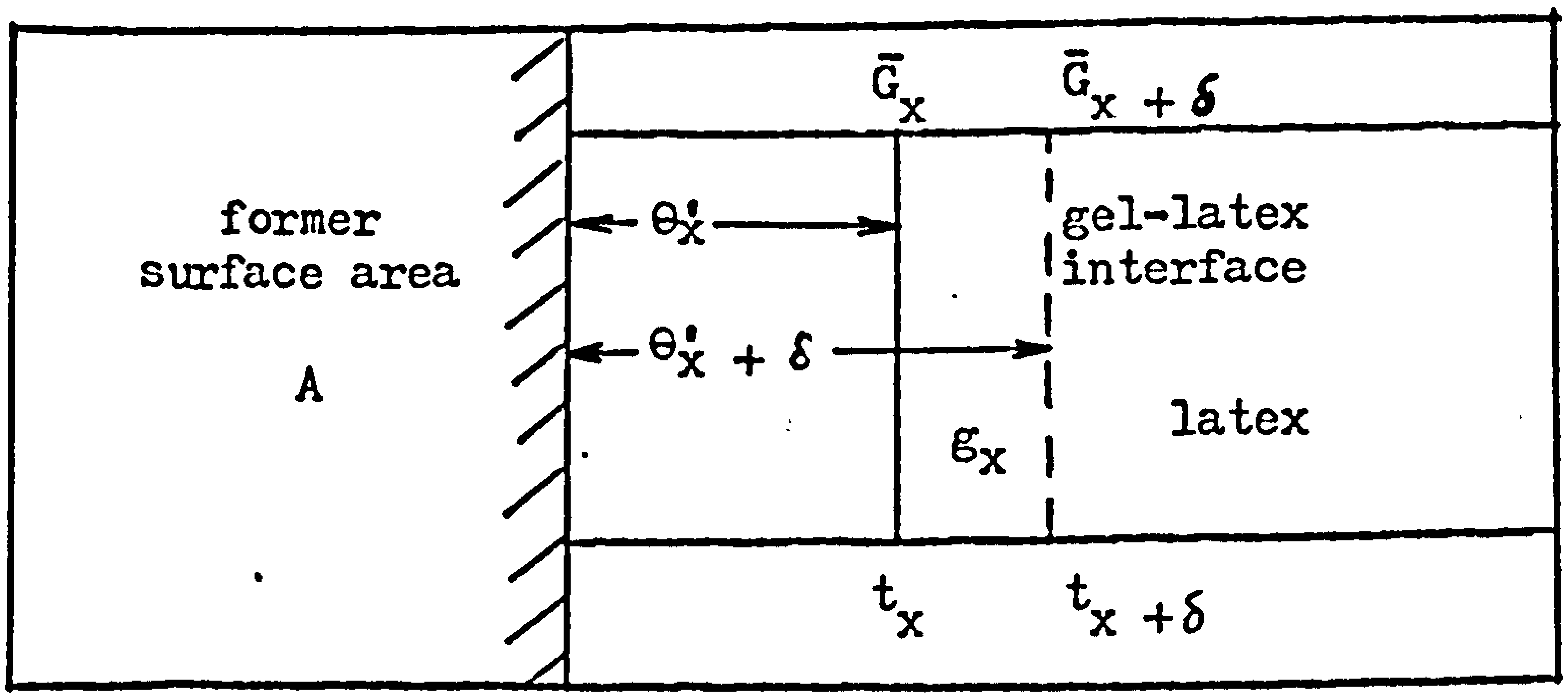


Figure 6.1A Diagramatic representation showing how total solids content of gel changes as gel-latex interface moves with increasing dwell time.

let the average total solids content of the gel at times t_x and $t_{x+\delta}$ be $\bar{G}_x$ and $\bar{G}_{x+\delta}$ respectively,

the total solids content of the gel in a small strip near the gel-latex interface be g_x,

the thickness of the wet gel at t_x and $t_{x+\delta}$ be θ'_x and $\theta'_{x+\delta}$ respectively.

It follows that

$$\bar{G}_x \cdot \theta'_x + g_x(\theta'_{x+\delta} - \theta'_x) = \bar{G}_{x+\delta} \cdot \theta'_{x+\delta} \quad \text{......(6.1)}$$

i.e.,
$$g_x = \frac{\bar{G}_{x+\delta} \cdot \theta'_{x+\delta} - \bar{G}_x \cdot \theta'_x}{\theta'_{x+\delta} - \theta'_x} \quad \text{..................(6.2)}$$

In this equation, $\bar{G}_x$ and $\bar{G}_{x+\delta}$ can be measured directly experimentally. The thickness of the wet-gel in this case was estimated as follows: Let the surface area of rubber deposited on the former be A.

The thickness of dry deposit at t_x is θ_x. Then if the density of dry rubber and gel composite at t_x are ρ_R and ρ_G respectively, we have that

$$\text{total solids content at } t_x = \frac{\text{weight of dry rubber}}{\text{weight of gel}} \times 100$$

$$\text{i.e.} \quad \bar{G}_x = \frac{\text{area x thickness of dry deposit x density of rubber}}{\text{area x thickness of gel x density of gel}} \times 100 \qquad \text{..................(6.3)}$$

$$= \frac{\theta_x \times \rho_R}{\theta'_x \times \rho_G} \times 100 \qquad \text{..................(6.4)}$$

$$\theta'_x = \theta_x \times \frac{\rho_R}{\rho_G} \times \frac{100}{x} \qquad \text{...................(6.5)}$$

It is assumed that ρ_G is proportional to the ratios of rubber to latex and their respective density. Using Equations (6.2) and (6.5), the total solids content of the gel in successive strips near the gel-latex interface could then be calculated.

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