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## Mechanisms of electrolyte (coagulant) dipping for thin nitrile gloves

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Two mechanisms for film deposition during the electrolyte dipping process are examined. The conventional, widely accepted, mechanism proposes that electrolyte on a former, immersed in latex compound for a controlled dwell time, diffuses into the compound and a wet gel coagulates on the former where the electrolyte concentration is above the critical coagulation value. An alternative mechanism proposes that deposition occurs *via* particle movement towards the former, driven by diffusiophoresis. The two mechanisms are examined using dipping nitrile latex compound and various mono and divalent cation electrolytes. The similarity of the total solids content (TSC) of the deposit on the former to that of the compound, the coagulated nature of the deposit and the success, at short dwell times, of a diffusion-coagulation model show that diffusion and coagulation operates exclusively for the divalent cations. For the monovalent cation electrolytes, this mechanism is also dominant, but the TSC of the deposits suggests that diffusiophoresis also plays a small part in the deposition process. A model for the two mechanisms acting together was devised and applied to deposition given by three monovalent electrolytes. This gave deposit TSCs that agreed with the diffusiophoretic prediction and was independent of dwell time. Quantitatively, the calculated amounts of deposit agreed reasonably well with experiment. The model therefore provides some support for diffusiophoresis affecting deposition for monovalent electrolytes. The reason(s) for the different diffusiophoresis behaviour of the monovalent and divalent electrolytes is suggested to be due to the much lower critical coagulation concentration for the divalent cations.

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### 1. Introduction

Thin elastomeric gloves are items of personal protective equipment that are essential in many occupations. Their value in the health and care sector was amply demonstrated during the viral pandemic of the early 2020s.

Most thin gloves are made from an aqueous polymer dispersion, often called a latex, using a dipping process. In brief, the process is to dip a hand-shaped mould (former) into an electrolyte solution, followed by oven drying. This coated former is then dipped into the polymer dispersion for a controlled period, known as the dwell time, during which a polymer deposit accumulates on the former surface. Drying of this deposit, often termed the wet gel, produces an elastomeric film that is peeled from the former to yield the glove product.

Since electrolyte dipping was developed in the early 1930s, relatively few attempts have been made to devise a quantitative model for the deposition of wet gel onto the former.<sup>1–5</sup> The first

of these was made by Sandomirsky *et al.* in 1954,<sup>1</sup> proposing that electrolyte diffuses from the former surface into the latex compound and causes the polymer particles to coagulate and deposit at a rate proportional to the rate of salt diffusion. Using Fick's first law, the authors showed that the square of the amount of rubber deposited was proportional to the duration of the dwell time. Their experimental results showed the same relationship, which was taken as a confirmation of the diffusion proposal. This general mechanism is referred to here in the abbreviated form DC.

In 1961, Derjaguin<sup>2</sup> proposed an alternative deposition mechanism in order to explain the increased polymer particle concentrations in the wet gel reported by Sandomirsky *et al.* This mechanism was diffusiophoresis,<sup>6–8</sup> the movement of colloidal particles caused by the presence of a solute concentration gradient. Here this is abbreviated to DP.

Over the ~70 years since those early papers, no other mechanisms have been proposed to explain deposition by electrolyte dipping. The DC mechanism has been assumed almost without question by the glove dipping community and the diffusiophoresis idea ignored. However, a recent paper by Williams *et al.*,<sup>5</sup> discussing latex gelation by electrolyte, considered the role of DP, but concluded that their results were

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unable either to demonstrate or refute the role of diffusiophoresis in the electrolyte gelation process.

The overall purpose of this paper is to examine, both theoretically and experimentally, the part that these two mechanisms play in electrolyte dipping of polymer dispersions.

## 1.1 Initial considerations

**1.1.1 Diffusiophoresis.** The case for diffusiophoresis as the sole or main mechanism for deposition, depends on there being a significant increase in the concentration of polymer particles in the wet gel compared to the host latex. Experimentally, we know that the latex used in the present work gives a fluid compound at 40% solids content, so in the absence of coagulation, it is highly likely that the particle concentration achieved by diffusiophoresis would need to be greater than this to give some form of wet gel. It could be argued that, in order to constitute a deposit, the particle volume concentration should approach that of close packing, about 64 vol%. Note that nitrile polymer has a density close to  $1 \text{ g ml}^{-1}$ , so the percentage solids content by weight equals the percentage volume fraction.

The Sandomirsky *et al.* work cited by Derjaguin mainly used compounds of natural rubber having TSCs in the range 20 to 50%, although most results were from 30% TSC compound. The coagulant was calcium chloride dissolved in a methanol-acetone mixture. Wet gel TSC was determined by cutting a piece of the gel of known dimensions from the former and, unusually, measuring its moisture content using the Dean and Stark method. Dwell times of 2 to 180 min were used. As will be seen, the methods used in the present study differ from these significantly. Summarising the results of Sandomirsky *et al.*, the measured TSCs of the wet gels reported were all about 20% greater than those of the host compounds. By contrast, in our own (mostly unpublished) work with nitrile latex and calcium nitrate electrolyte,<sup>4,9</sup> the measurement of the polymer concentration of very many wet gel samples has failed to show anything other than a TSC that is within a few percent of the host latex. We have found similar results for other latex systems, including natural rubber.

Qualitatively, in the laboratory, the wet gel is always observed to be a coherent film with sufficient strength to support its own weight when being handled. The wet gel can be leached by immersion in water, and indeed is always leached in industrial dipping, without the wet gel disintegrating or redispersing, demonstrating that the polymer particles in the wet gel have coalesced irreversibly, *i.e.* they have coagulated. This can be seen even at compound solids contents as low as 10%.

These observations are sufficient to reject diffusiophoresis as the sole or main deposition mechanism in the nitrile – calcium nitrate system. Additionally, the clearly coagulated nature of fresh wet gel lends qualitative support to the DC mechanism. However, it is acknowledged that the conditions for diffusiophoresis do exist during electrolyte dipping, so the possibility that it affects wet gel deposition alongside diffusion-coagulation must be considered.

**1.1.2 Diffusion-coagulation.** If the DC mechanism is accepted as the main mechanism, then the immediate question raised is whether the complex fluid flows accompanying the dipping process interfere with the diffusion of the coagulating ions. In practice it is observed that films made by coagulant dipping are uniform, apart from a slight thickness gradient in the vertical direction, suggesting that advection is not dominant. This flow question was considered explicitly in our previous publication,<sup>10</sup> where it was shown theoretically and experimentally that for calcium nitrate (by far the most commonly used electrolyte), former movement relative to the compound does not affect wet gel deposition. The reason is the low critical coagulation concentration of this electrolyte, so that most of its diffusion transport occurs through the wet gel and is therefore protected from advective flows. Interestingly, if a monovalent coagulant were to be used, it is possible that an effect from flow might be observed since its critical coagulation concentration is far higher. However, such systems are not used industrially and this situation has minimal practical importance. The negligible effect of former movement with calcium nitrate is confirmed by observation of industrial dipping, where billions of gloves are made annually. The process is continuous, not only involving former movement in the vertical direction, but at the same time with rapid horizontal movement of the electrolyte-coated formers through the latex compound. The gloves have a generally uniform thickness, readily and reproducibly controlled by electrolyte quantity and latex compound concentration, something that would not be possible if fluid flows had a significant effect. This finding is useful, since fluid flow effects need not be included when considering the deposition mechanisms.

In this paper, the DC and DP mechanisms are investigated quantitatively through experiment and modelling. The key measurements are the mass of wet gel deposited and the particle concentration in the wet gel as functions of dwell time. The experiments use a standard nitrile latex, with variations being made to the electrolyte. Three different calcium salts are compared and the effect of changing the electrolyte to a monovalent type is also investigated.

## 2. Materials

### 2.1 Latexes

The latex used in all the experiments was a commercial carboxylated nitrile latex (XNBR), supplied by Synthomer Sdn. Bhd. XNBR is a copolymer of butadiene, acrylonitrile and carboxylic acid monomer. The polymer composition was about 30 wt% of acrylonitrile and about 5% of acid monomer and contained synthetic anionic surfactant. The average particle diameter of the latex, obtained from dynamic light scattering, was 160 nm.

### 2.2 Zinc oxide

Zinc oxide was supplied by Aquaspersions Ltd, Halifax, UK, as a 50 wt% dispersion in water.



### 2.3 Latex compounds

In common commercial practice, nitrile latex is compounded with sulphur, accelerators, zinc oxide, defoamers/antifoam, antioxidant and pigments/fillers. The compound is also adjusted to the required pH and total solids content. To reduce the experimental complications that might arise when using dispersed, insoluble components, a simplified compound recipe was used in the present experimental work. The compound consisted of latex, zinc oxide (1 part per hundred dry rubber), de-ionised water to 20% total solids content and with pH adjusted to 9.3 through the addition of potassium hydroxide. At this pH, the carboxylic acid and surfactant gave the polymer particles a negative charge. It has previously been reported<sup>11</sup> that zinc oxide dissolves in XNBR wet latex through the formation of the zinc carboxylate salt and this can have an important influence on both the compound and dried film properties. Since zinc oxide dissolves, the nitrile compounds used here presented no separation problems.

### 2.4 Laboratory dipping apparatus

Laboratory dipping was carried out with a simple apparatus that used compressed air to lower and raise a former into and out of the latex compound. This operation was controlled by a manual switch and the dwell time was measured with a stopwatch. Formers were attached to the apparatus with a magnet to facilitate easy mounting and removal. A photograph of the apparatus is given as Fig. 1a.

### 2.5 Stainless steel formers

The formers were made of stainless steel. They were cylindrical and hollow with a hemispherical end. The cylinder and hemisphere diameter was 42 mm. The formers were conditioned by repeated dipping and cleaning with scouring powder and pads, to give a surface that the electrolyte solution wetted well. Scouring powder with water was also used to clean the former surface after each use.

### 2.6 Glass plate formers

A modified “dipping” method, described below, was used where greater amounts of electrolyte were required. Plates measuring 52 × 110 mm were made from 6 mm frosted glass. A bead of silicone was applied around the edge of one face of each plate to retain liquid in a well-defined area. Electrolyte solution and latex compound were applied to this area as needed, with the plate resting on a level surface. The plates were cleaned after each use as for the stainless-steel formers.

## 3. Methods

### 3.1 Critical coagulation concentration (ccc)

It is well-known that an electrostatically stabilised colloidal dispersion can be coagulated by contact with an electrolyte above a certain concentration, the critical coagulation concentration (ccc). This is often in a fairly narrow concentration range. For the present work, the critical coagulation concentration for a particular electrolyte with the 20% latex compound was measured by adding about 0.2 g of the compound to about 10 ml of electrolyte solution. This was done for a series of electrolyte concentrations, observing after 5 minutes whether there were signs of latex coagulation such as turbidity or coagulum. Small, 100 mol m<sup>-3</sup> increments in electrolyte concentration were used to determine the ccc. It was found that the onset of coagulation was more difficult to observe for the monovalent salts, manifesting as a change in turbidity rather than visible flocs.

### 3.2 Electrolyte pick-up

The amount of electrolyte applied to the steel formers by dipping was measured by weighing the electrolyte solution container before and after dipping and withdrawing four clean formers. Knowing the former dimensions, the dip length and the solution concentration, the amount of electrolyte deposited per unit area by a single dip was calculated.

The amount of electrolyte applied to the glass plates was measured directly by weighing the required amount of a solution of known concentration and ensuring an even coverage.

### 3.3 Laboratory dipping

The method was gravimetric, generally the same as previously described.<sup>4</sup> The stainless-steel former was heated to about 90 °C and dipped into the electrolyte solution (ambient temperature, about 20 °C), for 5 seconds, although separate testing showed that the pick-up did not depend on dwell time. The amount of solution in the container was controlled so that a consistent dip length was obtained. This was measured to be 57 mm. The coated former was placed in a laboratory oven for drying at 120 °C for 10 minutes, then transferred into a refrigerator for 25–30 minutes to bring it to 20 °C.

The former was then dipped into the latex compound using the apparatus described above. The amount of compound in the container was controlled by weighing, so that a dip length

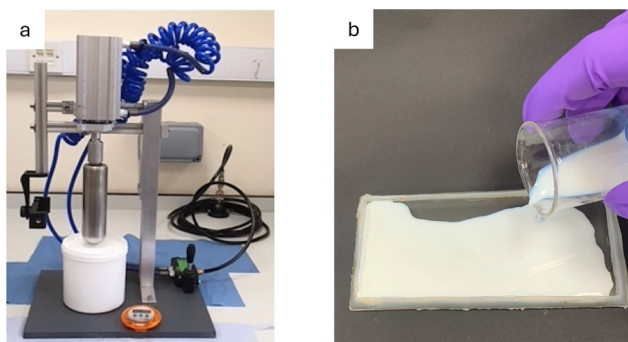


Fig. 1 (a) Photograph of the apparatus for conventional laboratory dipping, with stainless steel former attached. (b) Photograph of the horizontal plate method. Latex compound being poured onto a walled plate previously coated with a weighed amount of electrolyte.



of 55 mm was always achieved. After the desired dwell time and withdrawal, the wet gel was immediately removed from the former and transferred into a pre-weighed foil dish and the dish with wet gel weighed. The wet gel in the dish was oven dried at 120 °C, to constant mass. By this procedure the masses of wet gel and dry film could be obtained and therefore the total solids content (TSC) of the wet gel. Dwell times between 2 and 1200 seconds were used in this study. Each experiment was carried out at least in duplicate, more often with 4 repeats, and the average taken.

The masses of wet gel and dry film were converted to average thickness, knowing the former dimensions, dip length and polymer density. The density of the dry, compounded XNBR polymer was measured to be 1.02 g ml<sup>-1</sup> which, for the calculations, was taken to be 1 g ml<sup>-1</sup>. The experimental masses were corrected for the presence of calcium nitrate, assuming it was located within the film for all dwell times.

It is suggested that this gravimetric method yields a more accurate estimate of the average film thickness than direct measurement for the very soft, low solids content wet gel samples investigated here.

It will have been noted that these experiments were carried out at 20 °C, which is significantly lower than the temperatures commonly used in industrial dipping. However, the use of higher temperatures would introduce experimental difficulties in obtaining accurate masses because of evaporation.

### 3.4 Horizontal glass plate test

As will be detailed later, dipping according to the process above, when using a saturated sodium chloride solution as the electrolyte, failed to produce a coherent polymer film on the former. This was due to insufficient sodium chloride being deposited on the former. It was therefore decided to devise a former-type process that would provide a measured quantity of electrolyte in a greater amount than is possible by dipping.

This new method was also gravimetric, with the same main aim of determining the wet gel thickness and TSC as functions of dwell time. The formers were the glass plates described above, at ambient temperature and placed horizontally on a level support. The required amount of electrolyte solution was weighed onto the plate and spread to the walls. The mass was then checked by re-weighing and this figure used to calculate the coagulant coverage. The plate and contents were placed for 10 minutes in a laboratory oven set at 120 °C. After cooling to ambient temperature, a separately weighed amount of the latex compound was poured onto the electrolyte. The amount of compound used was in excess of the amount that would be coagulated, determined by preliminary experiments. Typically, the mass of compound added was between 10 and 20 g. A photograph of this stage in the procedure is given as Fig. 1b.

The compound was left in contact with the electrolyte for the desired dwell time, after which the remaining liquid was removed by pouring from one corner of the plate. Normally this separation of compound from the coagulated wet gel was straightforward and equivalent to withdrawing a coated former from compound in the standard dipping process.

The plate with wet gel was then placed in the laboratory oven at 120 °C, until it was at constant mass, usually about 20 minutes.

Weighing at the appropriate stages of this test procedure enabled the amounts of electrolyte, wet gel, dried film and wet gel TSC to be determined. Wet gel and dry film masses were converted into average thicknesses using the plate dimensions. Each test was done at least in duplicate and the average taken. In this method, unlike that using steel formers, the electrolyte mass is allowed for as part of the weighing protocol.

Overall, this method is similar to casting a polymer film from latex, except that the plate substrate is covered with a known amount of electrolyte and the plate and contents are weighed at several stages of the process.

## 4. Models

### 4.1 The diffusion-coagulation model

As mentioned above, the relatively simple, commonly accepted DC mechanism for coagulant dipping is driven by electrolyte diffusing from the former surface. As the electrolyte concentration reaches the ccc, the latex particles coagulate forming the wet gel. The locus of coagulation therefore moves away from the former at the electrolyte diffusion velocity.

We previously proposed a quantitative diffusion-coagulation model to calculate wet gel growth with time,<sup>4</sup> the details are summarised in Appendix 1. The model is fairly simple and contains only three parameters, for which values are readily measurable or available in the literature. The basic model assumes a constant concentration of coagulant on the former face, implying an infinite amount is available. The model was found to predict the experimental results well for short dwell times but depart significantly thereafter, as will be seen in the Results & discussion section. Three possible explanations were given for this disparity:

- In reality, only a limited amount of electrolyte is present. The limited electrolyte question was addressed by calculating the dwell time at which the electrolyte on the former was depleted, then carrying out a numerical solution of the diffusion equation with the boundary condition of a constant electrolyte concentration at the former surface being replaced by one of zero electrolyte flux. This gave a better fit to the experimental results, but a significant difference still remained.
- Calcium ions may react with surfactant present in the latex. Reaction kinetics could be devised that provided a good fit to experiment, but there was no separate justification for the kinetics.
- The flux of calcium ions through the wet gel is reduced as latex particles wet sinter and the tortuosity of the ion path increases. It was concluded that the estimated tortuosity increase was inadequate to explain the experimental results

The diffusion equation for the case of a limited source can also be solved analytically, as pointed out by Williams *et al.*<sup>5</sup> Details are provided in Appendix 2. This is faster and more convenient than our previous numerical method and gives



identical results, so the analytical method is employed in the present work.

## 4.2 The diffusiophoresis model

Diffusiophoresis is the transport of colloidal particles driven by a concentration gradient of solute, without the application of any outside force.<sup>2,6,12</sup> The solute can be an electrolyte or non-electrolyte. With a non-electrolyte, the concentration gradient gives rise to an entropic driving force leading to particle movement. If the solute is an electrolyte, an additional electrophoretic effect can occur. If the cations and anions diffuse at different rates, an electric field is induced which causes movement of any dispersed charged particles. In the case of electrolyte dipping, these are the negatively charged latex particles.

The physics of diffusiophoresis is complex and has been considered for a variety of symmetric monovalent electrolytes (*i.e.* where the cation and anion have the same single valence). Details of the mathematics of diffusiophoresis are given in Appendix 3.

The mathematical treatment has limitations, including the assumption of symmetric electrolytes in dilute solution, something that isn't appropriate for the usual conditions for dipping. However, the model provides a general, qualitative conclusion that the direction of the DP velocity is strongly influenced by the sign of the diffusiophoretic coefficient of the electrolyte ( $\beta$ ), and the zeta potential of the particles ( $\zeta$ ). With calcium nitrate as the electrolyte (negative  $\beta$ ) and nitrile latex particles (negative  $\zeta$ ), DP theory predicts movement of the negatively charged latex particles to greater electrolyte concentration – that is, towards the former, as would be necessary for a particle deposit to occur.

## 4.3 Combination of diffusion-coagulation and diffusiophoresis models

The situation of having diffusion-coagulation and diffusiophoresis acting simultaneously during electrolyte dipping is shown in Fig. 2.

The coagulating front moves away from the former, reaching a distance  $x$  at dwell time  $t$ , according to eqn (A1.6) and (A2.5) for the unlimited and limited electrolyte cases respectively. Simultaneously, in the liquid latex compound, at distances greater than  $x$ , the electrolyte concentration is below the critical concentration for coagulation and the electrolyte has a concentration gradient that can induce latex particle movement by diffusiophoresis. This movement is shown towards the former in Fig. 2, but its magnitude and direction depend on the electrolyte and latex being used as described above.

The two movements have a velocity,  $U_{dc}$  for the coagulating front and  $U_{dp}$  for the particle movement. The net result of the movements is that at the point of coagulation, the TSC of the compound will be affected by diffusiophoresis.

Appendix 3 shows the derivations of equations for velocities  $U_{dc}$ ,  $U_{dp}$  at the wet gel face. It can be seen that both  $U_{dc}$  and  $U_{dp}$  depend on  $1/\sqrt{t}$ .

Also derived is an equation for  $\phi_g$ , the polymer content of the wet gel modified by the diffusiophoretic movement of the

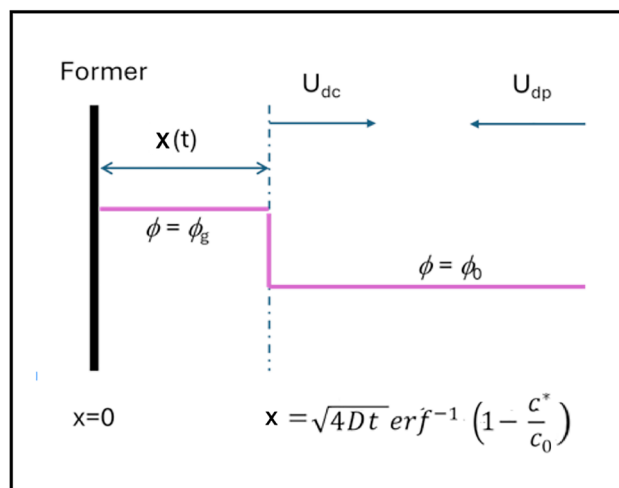


Fig. 2 Diagram of the wet gel after time  $t$ . The wet gel front is at position  $x$  according to the DC equation shown. At distances from the former greater than  $x$ , the volume fraction of polymer is that of the host latex  $\phi_0$ . The polymer fraction within the wet gel is  $\phi_g$ , which may differ from  $\phi_0$  because of latex particle movement caused by diffusiophoresis.

latex particles. Because this expression contains the ratio  $U_{dc}/U_{dp}$ ,  $\phi_g$  is independent of dwell time.

## 5. Results and discussion

### 5.1 20% nitrile compound with calcium nitrate

We have previously reported the build-up of wet gel with dwell time for 20% nitrile latex, dipped using 20% aqueous calcium nitrate as electrolyte.<sup>4</sup> This is the standard system used in our studies and was used to validate the new glass plate method.

The plot of wet gel thickness *vs.* dwell time for this system, dipped with the steel formers, is shown as the black circles in Fig. 3. These data combine previous and additional results.

The plot shows that wet gel accumulation on the former is rapid at dwell times up to about 60 s, then slows and plateaus after about 450 s. Note that there is not an obvious delay in the start of the accumulation, suggesting that the dissolution of the electrolyte is rapid. Note also that the results become more scattered at longer dwell times, where the quality and uniformity of the wet gel deteriorate.

The present study introduced the horizontal glass plate test as described in the Experimental section above. The results from this test, with the same latex and electrolyte, are also shown in Fig. 3 for comparison with the results using the stainless-steel former.

The results from the two methods agree well, with the error bars overlapping throughout the range of dwell times. However, the glass plate method consistently produced a slightly greater wet gel thickness over the range 90 to 1200 s dwell. It is suggested that the difference was caused by particle coalescence in the wet state (wet sintering). This leads to shrinkage of the wet gel and serum expulsion, sometimes called syneresis, which increases with time. In the standard dipping method, clear serum is often visible on the former when removing the



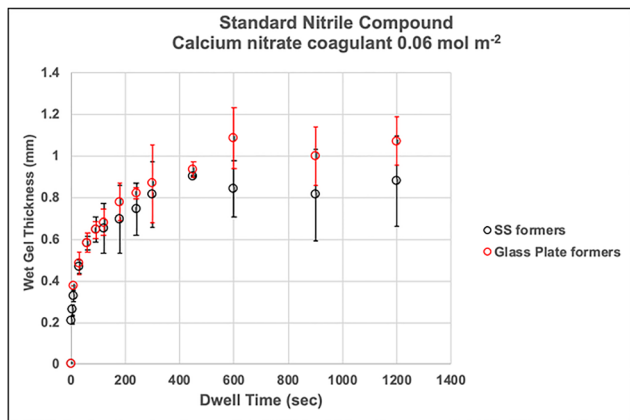


Fig. 3 Wet gel thickness vs. dwell time for 20% nitrile compound and 20% calcium nitrate electrolyte. Results from former dipping compared with glass plate method.

wet gel for weighing, so is not included in the wet gel mass. In the glass plate method, the wet gel is not removed, so a greater mass is recorded.

The TSC results for the wet gel deposits obtained by each method are presented in Fig. 4(a). Results for the first 60 s of immersion using steel formers are shown more clearly in Fig. 4(b). It can be seen that up to about 60 s, the wet gel TSCs are within 0.5% of the TSC of the host latex compound, suggesting any effect from diffusiophoresis was insignificant. Over the range of dwell times used, TSCs increased, with a greater increase seen for the steel formers, consistent with the effect of particle coalescence and syneresis described above.

These results provide confirmation for the assertion made in the Introduction, that the DP model cannot be the main mechanism for wet gel deposition.

The limited electrolyte DC model (Appendix 2, eqn (A2.4)) was applied to the same latex–electrolyte system using the parameters shown in Table 2. The result, compared to the experimental data, is shown in Fig. 5(a).

This figure shows clearly the discrepancy between experiment and the limited electrolyte model described in the Models

section above. This discrepancy has been noted in our earlier study<sup>4</sup> and its cause is still under investigation. Note that in practice, the dwell time used in making thin gloves is usually 30 s or less, where the model predicts wet gel accumulation accurately.

Using greater coverage of calcium nitrate on the stainless-steel formers, the effect on wet gel thickness is seen in Fig. 5(b) and (c). As expected, higher coagulant loadings produce greater wet gel thicknesses, with the limited salt model perhaps giving a very slightly better fit to experiment than at lower loadings.

## 5.2 20% nitrile compound with alternative calcium salts

To investigate the DP model, calcium chloride and calcium acetate were separately used as electrolytes with the same 20% nitrile latex compound. Qualitatively, the changes in the anion would be expected to affect the velocity of diffusiophoresis and therefore any deposit caused by the DP mechanism. The diffusion coefficients for nitrate, chloride and acetate ions are all greater than that for calcium ions,<sup>13</sup> suggesting that diffusiophoresis-induced particle movement would be towards the former with all these electrolytes, but perhaps at a lower velocity with the acetate.

Fig. 6 and 7 compare the wet gel build-up and TSC given by these electrolytes. All produced similar deposition results, suggesting that diffusiophoresis was only playing a negligible part in the wet gel deposition. The similarity of the results supports the DC mechanism, in which the diffusion of the coagulating calcium cation is expected to be a key factor. The combined DC–DP model was not attempted for calcium salts because of the inability to calculate the diffusiophoretic parameter,  $\beta$ , for divalent electrolytes.

## 5.3 20% nitrile compound with sodium chloride coagulant

The experiments described above focused mainly on calcium nitrate as the electrolyte, since it is by far the most commonly used material in commercial thin glove dipping. However, when considering the mechanisms of coagulant dipping, the behaviour of alternative electrolytes, for example those with a

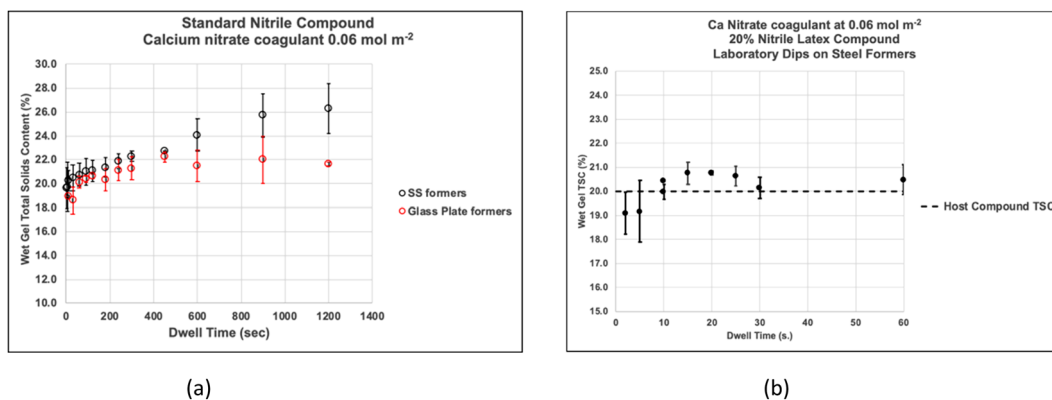


Fig. 4 (a) Wet gel TSC vs. dwell time for 20% nitrile compound and  $0.06 \text{ mol m}^{-2}$  calcium nitrate electrolyte. The two dipping methods compared. (b) Wet gel TSC data for dwell times up to 60 s.



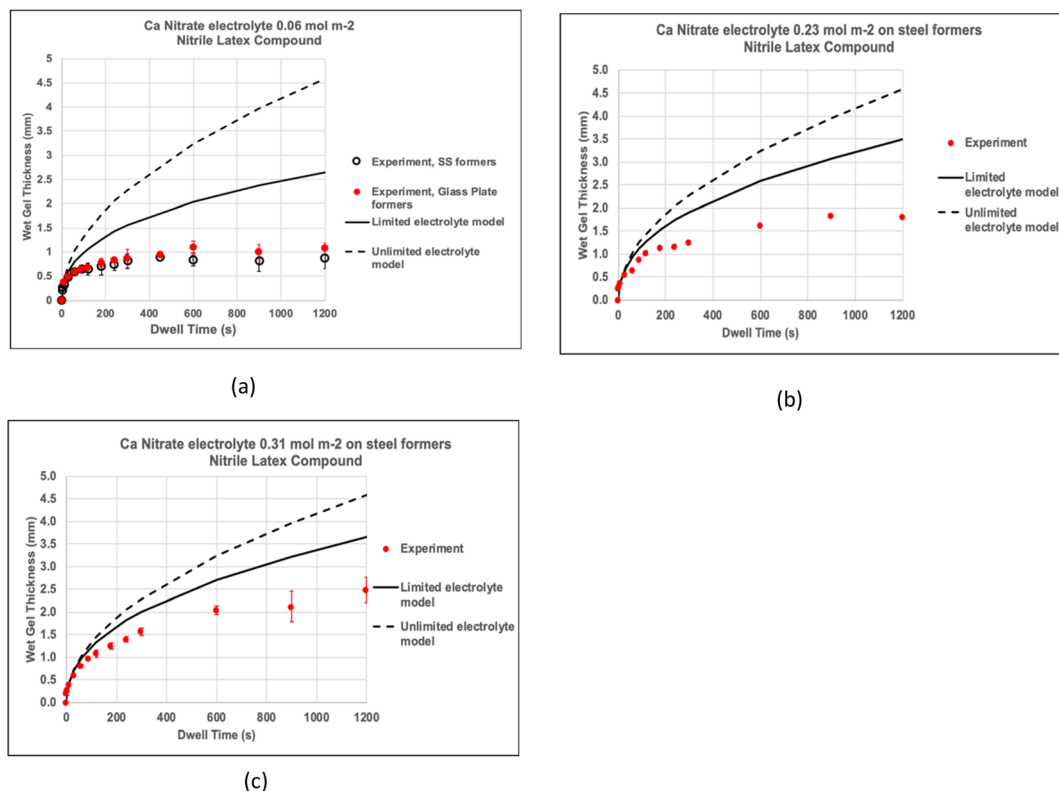


Fig. 5 (a) Wet gel thickness vs. dwell time for 20% nitrile compound and calcium nitrate electrolyte at 0.06 mol m<sup>-2</sup> compared to the unlimited and limited electrolyte DC models. (b) and (c) wet gel thickness plots as for (a), but at two increased loadings of Ca nitrate. Stainless steel formers.

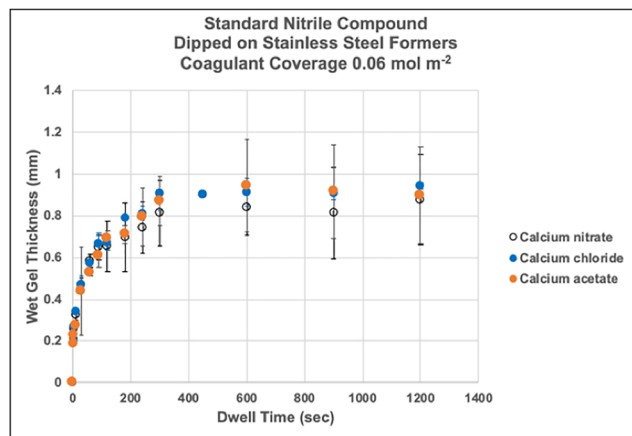


Fig. 6 Wet gel thickness vs. dwell time for 20% nitrile compound, with three different calcium salts as the electrolyte.

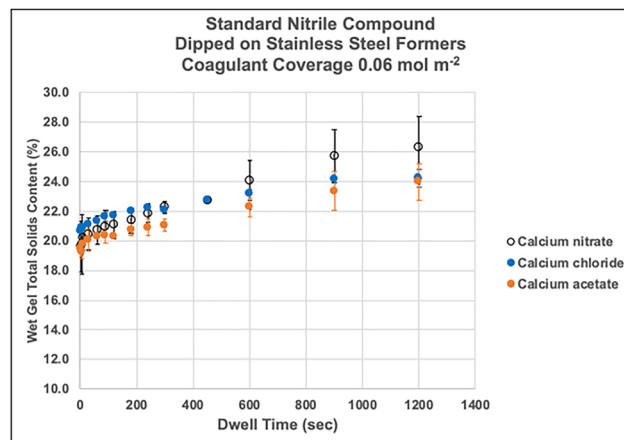


Fig. 7 Wet gel TSC vs. dwell time for 20% nitrile compound with three different calcium salts as the electrolyte.

monovalent cation, is of interest. An obvious candidate for study is sodium chloride, which is low cost, of low toxicity and good water solubility.

The first experiment with sodium chloride attempted laboratory dipping with the standard 20% nitrile compound, using the stainless-steel formers. A 26.5 wt% saturated solution of sodium chloride was applied to the formers by dipping. The coagulant dry coverage on the former was measured to be

0.18 mol m<sup>-2</sup> (10.5 g m<sup>-2</sup>), unaffected by dwell time in the coagulant. The dried deposit was observed to be a large number of small crystals. Dipping the coated former into the nitrile compound showed some evidence of a small amount of wet gel, but this appeared to be associated with the crystals and was not a coherent film. As it was not possible to remove the wet gel deposit for weighing, it was concluded that standard dipping would not yield results with sodium chloride.



The failure to produce a useful amount of wet gel can be explained by the DC limited electrolyte model. This predicts a low thickness (0.06 mm) deposit, because of the high critical coagulation concentration of sodium chloride with the nitrile latex and is clearly one of the reasons why sodium chloride is not used in commercial dipping.

The model also suggests that an increased coverage of sodium chloride should produce larger deposits. This was explored using the glass plate test to obtain deposition data with three coverage levels of sodium chloride.

#### 5.4 Wet gel deposition using the glass plate method and sodium chloride

Fig. 8 shows the wet gel thickness as a function of dwell times for NaCl coverages of 0.06, 0.92 and 2.3 mol m<sup>-2</sup>, together with the predictions of the limited electrolyte model.

Reasonably good agreement was found between the experimental and model wet gel thicknesses for all amounts of NaCl. For the two larger amounts at dwell times longer than 300 s, the experimental WG thicknesses are slightly greater than the model prediction. This may be a result of an underestimate of the value of  $c^*$ , which is difficult to measure for monovalent salts.

Clearly, for longer dwell times, NaCl gives wet gel deposition much closer to the limited electrolyte DC model than the calcium salts.

#### 5.5 Wet gel deposition using other monovalent electrolytes

Two more monovalent electrolytes were selected for testing by the glass plate method. These were potassium chloride and potassium acetate. As pointed out by Williams *et al.*,<sup>5</sup> these should induce different diffusiophoretic particle movements with negatively charged particles. For these tests, it was decided to use 0.92 mol m<sup>-2</sup> electrolyte coverage to compare with the NaCl results.

The wet gel thickness results for KCl, shown in Fig. 9, agree well with the limited electrolyte model throughout the dwell time range. For potassium acetate, also Fig. 9, the model followed the experimental results moderately well, but with the experimental film thicknesses consistently smaller than predicted by the DC limited electrolyte model.

Overall, for the three monovalent electrolytes, the wet gel build-up results match the predictions of the DC limited electrolyte model, certainly better than found for calcium salts at longer dwell times. This is further support for DC as the main mechanism for deposition.

It should be mentioned that the quality of the wet gel produced by the monovalent electrolytes was not as coherent as those from the calcium salts. In addition, the critical coagulation concentrations  $c^*$  were not as easy to identify and the model is quite sensitive to this parameter. This should be borne in mind when comparing the model and experimental results. Note also that any effect of diffusiophoresis will not be apparent in the wet gel mass and thickness results, because of the polymer density being very close to that of water.

#### 5.6 Wet gel total solids content for the monovalent electrolytes

For all three electrolytes, the measured wet gel TSCs were close to that of the host latex, generally within 3%, once again supporting the dominance of DC. The experimentally measured values for TSC are shown in Fig. 10. However, within that TSC range there were consistent differences between the electrolytes, with the TSC values being in the order NaCl > KCl > K acetate.

The DC and DP combination model described in Appendices 3 and 4 was used to calculate TSCs for the wet gels produced by the three monovalent electrolytes. The appropriate parameter values shown in Table 1 were used. For mathematical simplicity, the electrolyte concentration profile was that for the unlimited amount on the former. The predictions are also shown in Fig. 10.

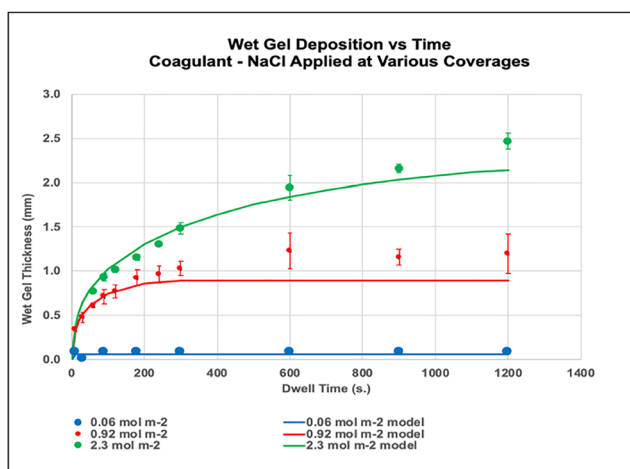


Fig. 8 The effect of increasing NaCl coverage on wet gel thickness, glass plate test. Limited electrolyte DC model predictions are included for comparison.

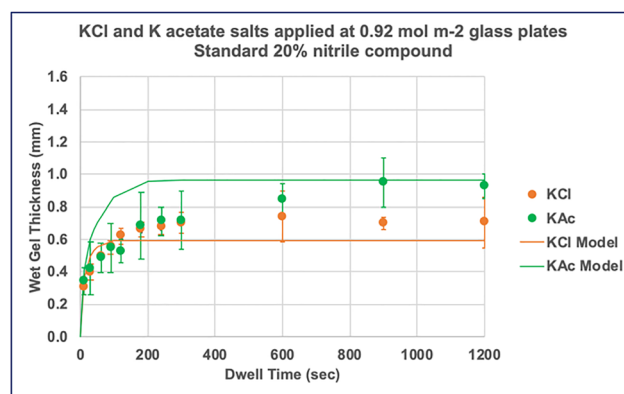


Fig. 9 Wet gel deposition for potassium chloride and potassium acetate compared to limited electrolyte models.



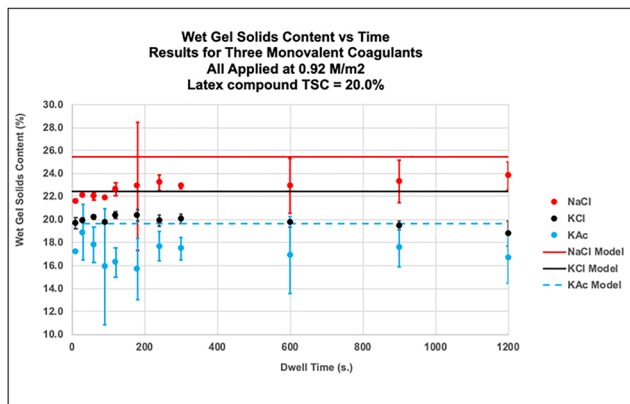


Fig. 10 Wet gel TSC vs. dwell time for monovalent electrolytes, NaCl, KCl and K acetate, compared to the values generated by the combined DC and DP model.

Table 1 Values of parameters used to estimate the diffusiophoretic and diffusional velocities

Symbol	Meaning	Value	Units
$\epsilon$	Permittivity of medium	$80 \times 8.854 \times 10^{-12}$	$\text{m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$
$\eta$	Solvent viscosity	$10^{-3}$	$\text{N s m}^{-2}$
$kT$	Thermal energy	$300 \times 1.38 \times 10^{-23}$	$\text{m}^2 \text{kg s}^{-2}$
$e$	Charge on electron	$1.6 \times 10^{-19}$	C
$\zeta$	Zeta potential on particles	$-50 \times 10^{-3}$	V
$\beta$	Diffusiophoretic coeff.		
	Na chloride	-0.207	
	K chloride	-0.019	—
	K acetate	+0.205	
$D$	Cation diffusion coefficient		
	Ca nitrate	$7.92 \times 10^{-10}$	$\text{m}^2 \text{s}^{-1}$
	Na chloride	$1.33 \times 10^{-9}$	

The model predicts that the TSC of the wet gel will remain constant with dwell time and this is seen in the experimental results for monovalent electrolytes. The additional effect of wet sintering giving a slight TSC increase with dwell time is seen with the calcium salts, but not with the monovalent salts. This difference is not considered in this paper. Quantitatively, the combined DC–DP model predicted the TSCs in the same order as the experimental results. The difference in TSC between model and experiment was about 2% for each electrolyte, which is a reasonable agreement considering the simplifications made in the model. The biggest uncertainty within the model concerns the value for the zeta potential in eqn (A3.4). We have measured the value using a few mM NaCl as background electrolyte and obtained a value of  $-50$  mV, which we use for the calculations. The actual background electrolyte in the 20% compounded latex is unknown and this may explain the overestimate of the effect of diffusiophoresis in Fig. 10. The overall consistent trend in effect of electrolyte and the measured increase in TSC provides some support for diffusiophoresis affecting deposition slightly for monovalent electrolytes.

## 6. Summary & conclusions

The only two mechanisms that have been proposed to explain the deposition of wet gel onto an electrolyte-coated former were investigated by experiment and models. The experiments were carried out with a commercial nitrile latex. The electrolytes investigated were three calcium salts; nitrate, chloride and acetate and three monovalent salts, sodium chloride, potassium chloride and potassium acetate.

The results presented here generally confirmed the diffusion and coagulation mechanism. The evidence found was:

- The quantitative agreement, for all six electrolytes tested, between the observed deposition and the results of a fairly straightforward model combining Fickian diffusion with the electrolyte concentration required for latex coagulation.
- The close similarity in deposition produced by the three calcium salts, consistent with deposition being related to diffusion of the cation.
- Observation of the coagulated nature of the wet gel and the close similarity of its TSC to that of the dipping compound.

The main difficulty at present with the DC model is that it fails to predict the experimental results obtained with calcium salts at longer dwell times. This discrepancy is under investigation and it is hoped that an explanation will be provided in the future.

Another finding that requires further study, is the TSC of the wet gel as dwell time increases. For both monovalent and divalent electrolytes at short dwell times, the wet gel TSC is close to that of the wet latex compound. This is compatible with the diffusion–coagulation mechanism, indicating rapid flocculation and coagulation at the critical electrolyte concentration, with little change in polymer particle spacing. The conditions at this point (the coagulation front) should be constant, regardless of dwell time and the quantity of wet gel deposited, so wet gel TSC should also be independent of dwell time. The results reported here show that this is indeed the case at all dwell times when monovalent electrolytes are used and also for divalent electrolytes at short dwell times ( $<60$  s). However, for the divalent electrolytes at longer dwell times, a steadily increasing wet gel TSC is observed. This is tentatively attributed to interfacial tension-driven polymer particle coalescence, often called wet-sintering. This will consolidate the wet gel, increasing its TSC. Wet sintering is also a potential explanation for the observed difference in TSC of the wet gel formed on the stainless steel formers compared to that from the horizontal glass plates, and for the reducing rate of wet gel deposition compared to the diffusion–coagulation model, that is often observed. Further work is needed to investigate the effects of wet sintering.

The second mechanism for deposition, diffusiophoresis, was also investigated. The indicator used for diffusiophoresis was the TSC of the wet gel deposit. As we reported previously and confirmed here, our experiments inevitably find that wet gel TSC is within a few percent of the latex compound that is being dipped. These results demonstrate that diffusiophoresis cannot be the sole or main deposition mechanism in the nitrile



latex/electrolyte systems investigated here. There is no reason to think that this finding would be different for other electrolyte dipping systems.

Although this conclusion also applied to the monovalent salts tested here, their wet gel TSC results showed small but interesting differences. Across the entire dwell time range used, the TSC produced with NaCl was slightly greater than that of the dipping compound, that from KCl was closely similar and that from K acetate was slightly lower. This is what might be expected if diffusiophoresis was causing a movement of latex particles in the region containing electrolyte at concentrations below the critical coagulation value  $c^*$ .

A model for the combined action of diffusion–coagulation and diffusiophoresis in electrolyte dipping was devised. This was reasonably successful in predicting wet gel TSCs.

To try to understand the possible difference with regard to diffusiophoresis between the calcium and monovalent salts, three key parameters in determining the magnitude of diffusiophoretic velocity, according to eqn (A3.1), were examined. Comments that can be made are:

(i) In eqn (A3.2), the diffusiophoretic flux is proportional to  $d \ln c/dx$  which is equal to  $1/c \, dc/dx$ .

It was found that the value of this term is greater for calcium nitrate than for sodium chloride, indicating a greater diffusiophoretic velocity for the calcium ions. The experimental evidence directly contradicts this prediction. A possible reason is that in eqn (A3.2) we assume the total salt concentration is only due to the calcium nitrate electrolyte and equal to  $c^*$ . There are other electrolytes in the system, KOH to regulate the pH and counterions from the surfactant. This is likely to be small compared to the ccc for the monovalent ions but far larger than  $c^*$  for calcium nitrate. Hence the magnitude of the  $1/c$  term is significantly reduced for calcium nitrate, reducing the diffusiophoretic flux, but not for sodium chloride.

(ii) The value of the zeta potential  $\zeta$  of the latex particles was measured from the latex dispersion. If, during dipping, the calcium ions are specifically adsorbing onto the surface of the latex particles then the surface potential will reduce, and this will reduce the magnitude of  $U_{dp}$ . The low value of the critical coagulation concentration  $c^*$  for calcium nitrate compared to the monovalent electrolytes is a possible indication of an interaction between the calcium ions and the latex particles. Strong evidence for this interaction (forming the calcium carboxylate salt) has recently been published.<sup>14</sup>

For the commercially important system of nitrile latex dipped using calcium nitrate as the coagulant, it was found that diffusion with coagulation was the mechanism of deposition, with no indication of an effect from diffusiophoresis. The deposition at short (<60 s) dwell times could be modelled successfully with a simple diffusion equation using only three easily and independently obtained parameters. However, we also note the significant slowdown in wet gel growth with this system at longer dwell times, not predicted by the diffusional model. We have speculated as to the reason for this slowdown but are yet to provide a definitive answer. The two explanations

currently under investigation are the specific adsorption of calcium ions into the carboxylate polymer effectively reducing the amount of electrolyte available for coagulation or wet sintering of polymer particles restricting the pathway for electrolyte diffusion through the wet gel.

Williams *et al.*<sup>5</sup> pointed out the values of diffusion coefficient in the literature are for infinitely dilute solutions and  $D$  would be smaller in more concentrated situations. Simply changing the value of  $D$  to a lower value in the limited electrolyte DC model does not improve its fit to experiment at longer dwell times and makes the fit worse at short dwell times. Of course, introducing a time-dependent value of  $D$  might be more successful, but more experimental work is needed to provide a basis for a suitable model calculation.

The success of the DC model in predicting the wet gel deposition at early dwell times with calcium nitrate as the electrolyte and throughout the dwell time range for the three monovalent electrolytes is surprising. This suggests that diffusion of the electrolyte through the wet gel is not as hindered as might be imagined. The fast initial deposition rate seen experimentally suggests that there is no significant delay in the action of electrolyte in the dissolution step.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

Data for this article, including an excel sheet with experimental data used to generate all the figures are available at the University of Cambridge data repository, Apollo at <https://doi.org/10.17863/CAM.124397>.

## Appendices

### Appendix 1

**The simple diffusion model.** The diffusion of electrolyte away from the former is described by Fick's law. The corresponding partial differential equation is

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad (\text{A1.1})$$

where  $t$  is time,  $x$  is distance (from the former) and  $D$  is the diffusion coefficient for the electrolyte cation.

For the initial condition we take that the latex bath is initially devoid of electrolyte

$$t = 0 \quad c = 0 \quad (\text{A1.2})$$

The simple diffusion model assumes that the electrolyte at the former face dissolves in the solution giving a saturated solution (concentration  $c_0$ ) at that location, defined as  $x = 0$ . Hence the boundary conditions are:

$$x = 0 \quad c = c_0 \quad (\text{A1.3})$$



$$x \rightarrow \infty \quad c \rightarrow 0 \quad (\text{A1.4})$$

The solution to this model is the well-known error function

$$c = c_0 \left( 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right) \quad (\text{A1.5})$$

Eqn (A1.5) gives the concentration profile of the electrolyte cations with distance from the former at time  $t$ . By setting  $c$  to the critical coagulation concentration  $c^*$  and rearranging, an equation for the time  $t$  and distance ( $L(t)$ ) at which the electrolyte reaches  $c^*$  can be obtained:

$$x(t) = \sqrt{4Dt} \operatorname{erf}^{-1} \left( 1 - \frac{c^*}{c_0} \right) \quad (\text{A1.6})$$

$x(t)$  represents the position of the wet gel coagulating front as a function of time.

This basic equation assumes an infinite source of electrolyte on the former surface. It was not used in most calculations in this paper, the limited source electrolyte equation was preferred as a more realistic model (Appendix 2).

## Appendix 2

**The limited source electrolyte model.** This is a modification to the simple diffusional model, considering the limited amount of electrolyte that is applied to the former by dipping. For the limited electrolyte model there exists a time, defined as  $t_{\text{crit}}$  when all the electrolyte has diffused away from the former surface. At this point the boundary condition changes from a fixed value to a zero-flux condition. For  $t > t_{\text{crit}}$  the boundary conditions become

$$x = 0 \quad \frac{\partial c}{\partial x} = 0 \quad (\text{A2.1})$$

$$x \rightarrow \infty \quad c \rightarrow 0 \quad (\text{A2.2})$$

The value of  $t_{\text{crit}}$  can be found by integrating the diffusional solution and equating it to the loading of electrolyte on the former,  $c_{\text{load}}$ .

$$\int_0^\infty c_0 \left( 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt_{\text{crit}}}} \right) \right) dx = c_{\text{load}} \quad (\text{A2.3})$$

For times  $< t_{\text{crit}}$  we use eqn (A1.5), setting  $c = c^*$  to obtain the wet gel thickness,  $x$ , as a function of time. As time progresses the amount of coagulant which has diffused into the latex bath increases and at some point, the amount of coagulant on the former is depleted. This is given by solving eqn (A2.3) for  $t_{\text{crit}}$ .

For times greater than  $t_{\text{crit}}$  we previously proceeded numerically, solving eqn (A1.1) subject to boundary conditions (A2.1) and (A2.2). At each time step we evaluate the spatial position which corresponds to a coagulant concentration  $c^*$  and this provides the wet gel thickness.

Table 2 Parameters used in diffusion-coagulation calculations<sup>a</sup>

Electrolyte	Cation Diff. Coeff. ( $\text{m}^2 \text{s}^{-1}$ )	$c^*$ ( $\text{mol m}^{-3}$ )	Coverage on former ( $\text{mol m}^{-2}$ )
Calcium nitrate	$7.92 \times 10^{-10}$	5.4	0.06
Sodium chloride	$1.33 \times 10^{-9}$	500	0.06, 0.92, 2.3
Potassium chloride	$1.96 \times 10^{-9}$	780	0.92
Potassium acetate	$1.96 \times 10^{-9}$	460	0.92

<sup>a</sup> The diffusion coefficients are from ref. 13 and other data was measured by the authors.

As discussed by Williams *et al.*,<sup>5</sup> an analytical expression for the concentration profile is available:

$$c = \frac{N}{\sqrt{\pi Dt}} \exp \left( \frac{-x^2}{4Dt} \right) \quad (\text{A2.4})$$

where  $N$  is the quantity of the electrolyte on the former face (coverage,  $\text{mol m}^{-2}$ ) and the other symbols are as in Appendix 1.

As for the infinite electrolyte case, setting  $c = c^*$  and rearranging (A2.4), an equation is obtained that represents the position with time for the coagulating front:

$$x(t) = \sqrt{-4Dt \ln \left( \sqrt{\pi Dt} \frac{c^*}{N} \right)} \quad (\text{A2.5})$$

eqn (A2.5) is only valid up to the point (time and distance) at which the electrolyte is active (causing coagulation). It becomes meaningless when the electrolyte concentration everywhere on the curve falls below  $c^*$ . This equation was the basis of the limited electrolyte model data shown in this paper. The values of the parameters used are shown in Table 2.

## Appendix 3

### Combined diffusion-coagulation and diffusiophoresis models

*Velocity of the coagulating front.* For mathematical simplicity, the unlimited salt case is used. Eqn (A1.6) gives the position of the coagulating front as a function of time. The velocity of the front is given by the differential of (A1.6):

$$U_{\text{dc}} = dx/dt = \sqrt{\frac{D}{t}} \operatorname{erf}^{-1} \left( 1 - \frac{c^*}{c_0} \right) \quad (\text{A3.1})$$

The diffusiophoretic velocity is given by:<sup>8,15</sup>

$$U_{\text{dp}} = \frac{\varepsilon}{\eta} \left[ \frac{kT}{e} \beta \zeta + \frac{\zeta^2}{8} \right] \frac{d \ln c}{dx} \quad (\text{A3.2})$$

And at the wet gel face  $c = c^*$  and differentiating (A1.6) we obtain:

$$\frac{1}{c} \frac{dc}{dx} = \frac{c_0}{c^*} e^{-A^2} \frac{1}{2\sqrt{Dt}} \quad (\text{A3.3})$$

where  $A = \operatorname{erf}^{-1} \left( 1 - \frac{c^*}{c_0} \right)$ . Combining (A3.2) and (A3.3)



we obtain

$$U_{\text{dp}} = \frac{\varepsilon}{\eta} \left[ \frac{kT}{e} \beta \zeta + \frac{\zeta^2}{8} \right] \frac{c_0}{c^*} e^{-A^2} \frac{1}{2\sqrt{Dt}} \quad (\text{A3.4})$$

Examining the ratio  $U_{\text{dp}}/U_{\text{dc}}$  eliminates the time dependence. Using the estimated values in Table 1 for a solution for NaCl, we obtain  $U_{\text{dp}} = 0.33U_{\text{dc}}$ . Thus, we expect the coagulant diffusional mechanism to be more significant than the diffusiophoretic mechanism, although diffusiophoresis is expected to contribute.

#### Appendix 4

As shown in Fig. 2, the wet gel grows with time and the volume fraction of latex within the wet gel,  $\phi_{\text{g}}$  can be affected by particle diffusiophoresis.

A latex balance around the moving wet gel face provides

$$\phi_{\text{g}}U_{\text{dc}} = (U_{\text{dc}} + U_{\text{dp}})\phi_0 \quad (\text{A4.1})$$

and hence

$$\phi_{\text{g}} = \left( 1 + \frac{U_{\text{dp}}}{U_{\text{dc}}} \right) \phi_0 \quad (\text{A4.2})$$

This provides the expected result that in the absence of diffusiophoresis ( $U_{\text{dp}} = 0$ ) the wet gel TSC is the same as the bulk latex. In the case where  $U_{\text{dp}}$  is towards the former the TSC is above the bulk latex value and in the case where  $U_{\text{dp}}$  is away from the former, the wet gel TSC is below the bulk value.

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