

# STABILITY AND ELECTROPHORETIC DEPOSITION OF SUSPENSIONS IN NON-AQUEOUS MEDIA

BY H. KOELMANS AND J. TH. G. OVERBEEK

Philips Research Laboratories, Eindhoven, Holland  
van't Hoff Laboratory, University of Utrecht, Holland

Received 21st June, 1954

The stability of suspensions in solvents of very low polarity is treated in part 1 of this paper. Theoretical considerations lead to the conclusion, that quite modest electric charges and  $\zeta$ -potentials are sufficient to stabilize suspensions of coarse particles ( $> 1\mu$ ) whereas hardly any stabilization can be expected from adsorbed layers of non-ionized long-chain molecules.

Experiments on the settling times of suspensions of a number of solids in xylene confirm that only ionized surface-active substances give rise to stability. Long-chain compounds that do not increase the conductance of the xylene, do not give rise to a sufficient  $\zeta$ -potential of the particles and do not improve the stability very much.

In part 2 the electro-deposition from suspensions in *polar* organic media is investigated. It is shown that the particles are accumulated near the electrode by the applied field, but that the formation of an *adhering* deposit is caused by flocculation introduced by the electrolyte formed by the electrode reaction.

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The combination of electric double-layer repulsion together with attraction of London-van der Waals nature allows a quantitative description<sup>1</sup> of the stability of aqueous colloidal systems. Changing from water to a non-aqueous solvent usually means a lowering of the dielectric constant  $\epsilon$ , bringing about a decrease in the dissociating power of the medium, thus limiting the formation of a sufficient charge on the particles.

This does not seem to be a serious disadvantage for systems in liquids of medium  $\epsilon$  like the lower alcohols and acetone. Merely by grinding the solid phase together with the medium, stable suspensions may be prepared,<sup>2</sup> which show electrokinesis and can be flocculated with electrolytes in a similar way to aqueous suspensions. The properties of these suspensions in relation to electrophoretic deposition will be discussed in part 2 of this paper. The same grinding technique applied to non-polar solvents results always in flocculated suspensions. This poor dispersion is often greatly improved when a surface-active stabilizer is added.

In part 1 of this paper special attention is given to the factors governing the stability of suspensions in solvents of low polarity.

## 1. THE STABILITY OF SUSPENSIONS IN NON-POLAR MEDIA

Recently two different views on the problem have been published. Van der Minne and Hermanic<sup>3</sup> measured electrophoresis of suspensions in benzene and found a good correlation between stability and electrophoretic velocity with a critical  $\zeta$ -potential of about 25 mV. They consequently attributed stability to the existence of an electric double layer. On the other hand, Mackor and van der Waals<sup>4</sup> explained the stabilization of carbon black in heptane by non-ionic chain-molecules as observed by van der Waarden,<sup>5, 6</sup> as caused by a repulsion of entropic nature, viz. steric hindrance of adsorbed chains. Before giving our own experiments we want to discuss these two concepts on the basis of the Verwey and Overbeek stability theory.

## ELECTRIC DOUBLE LAYER

As ionic concentrations in xylene (for convenience we will refer to this liquid) are always low, ionic double layers are very diffuse. At an ionic concentration of  $10^{-11}$  N, which is of the order of magnitude observed, the Debye length,  $1/\kappa$ , in xylene is about  $16 \mu$ . The capacity of a double layer is therefore very low, and only very little charge is needed to obtain appreciable surface potentials.

In analyzing whether the corresponding free energy can provide the potential barrier of about  $15 kT$  required for stability,<sup>7</sup> we may, at the low ionic concentrations involved, roughly describe repulsion with the Coulomb law.

$$V_R = \zeta^2 e r^2 / R, \quad (1)$$

where  $r$  is the radius of the particles considered as spheres and  $R$  the distance between their centres.

In contrast to aqueous systems where, as a result of the screening effect of the counter ions, the decay is much steeper, the repulsive potential decays slowly ( $R^{-1}$ ) with distance.

When the repulsion (eqn. (1)) is combined with the van der Waals attraction according to Hamaker,<sup>8</sup> the curve for the particle interaction plotted against the distance shows a maximum,  $V_{\max}$ . The height of the maximum is not very sensitive to the choice of the van der Waals constant  $a$  as a consequence of the slow decay of the repulsion. Table 1 gives values for  $V_{\max}$  calculated for  $a = 10^{-12}$  ergs, and expressed in units of  $kT$  at room temperature ( $4 \times 10^{-14}$  ergs).

TABLE 1.—MAXIMAL REPULSION AS A FUNCTION OF PARTICLE SIZE AND SURFACE POTENTIAL

| $\zeta$<br>mV | $r = 10^{-4}$ cm | $V_{\max}/kT$<br>$r = 10^{-5}$ cm | $r = 10^{-6}$ cm |
|---------------|------------------|-----------------------------------|------------------|
| 25            | 13               | —                                 | —                |
| 35            | 26               | 1                                 | —                |
| 50            | 62               | 4                                 | —                |
| 75            | 152              | 11                                | —                |
| 100           | 286              | 20                                | 1                |
| 150           | 662              | 54                                | 4                |

It appears that in spite of the low free energy of the double layer, particles of  $1 \mu$  and coarser can be stabilized by  $\zeta$ -potentials of the order of magnitude observed by van der Minne and Hermanie.<sup>3</sup> This must be ascribed to the fact that in the region where attraction gives no appreciable contribution the repulsion is still important. The low total repulsion which already threatens the stability of small particle systems ( $r < 10^{-6}$ ) in water, makes stabilization by electric charges for small particles in xylene completely impossible.

## STERIC HINDRANCE OF ADSORBED CHAINS

Repulsion by steric hindrance of adsorbed chains is only present when the adsorbed chains of two neighbouring particles interact. This means that at a distance more than twice the stabilizer length only van der Waals' attraction is present. The depth of the resulting minimum of energy at a distance of  $40 \text{ \AA}$ , for different values of  $r$  and  $a$  is given in table 2.

TABLE 2.—VAN DER WAALS' ATTRACTION BETWEEN SPHERES AT A DISTANCE OF  $40 \text{ \AA}$  BETWEEN THE SURFACES

| $a$        | $r = 10^{-4}$ cm | $V_{\min}/kT$<br>$r = 10^{-5}$ cm | $r = 10^{-6}$ cm |
|------------|------------------|-----------------------------------|------------------|
| $10^{-12}$ | 510.0            | 42.0                              | 1.2              |
| $10^{-13}$ | 51.0             | 4.2                               | 0.1              |
| $10^{-14}$ | 5.1              | 0.4                               | 0.01             |

As there is no reason to assume the van der Waals constant in xylene to be greatly different from that in water ( $a \approx 10^{-12}$ ) the figures of table 2 show that adsorbed chains cannot prevent flocculation, unless the stabilizer length is comparable with the particle size.

Summarizing the results, we may distinguish the four cases of table 3.

TABLE 3

| particle size | stabilizing mechanism | stability |
|---------------|-----------------------|-----------|
| 1 large       | ionic double layer    | stable    |
| 2 large       | steric hindrance      | flocc.    |
| 3 small       | steric hindrance      | stable    |
| 4 small       | ionic double layer    | flocc.    |

## EXPERIMENTAL

Our experiments, having been performed with relatively coarse particles, only give evidence about points 1 and 2 of table 3. Particles of different substances were prepared by grinding combined with gravity fractionation so as to give an average size of  $1 \mu$ . Substances used were  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{HgS}$ ,  $\text{BaSO}_4$ ,  $\text{CaCO}_3$ ,  $\text{SiO}_2$  (quartz),  $\text{TiO}_2$  (rutile), C (graphite), Se (metal). Suspensions were prepared by mixing the powders with xylene, care being taken to avoid moisture and (undesired) surface-active substances.

*Stability* was evaluated by measuring settling times in glass-stoppered graduated cylinders. At both ends of the stability scale there is some arbitrariness in noting the point of complete sedimentation. As in general great differences in stability were involved, the latter was not serious in our experiments.

*Electrophoresis* was measured in the cylindrical microcell according to the technique described by van der Minne and Hermanic.<sup>3</sup>

In the *adsorption experiments* the concentrations of stabilizer before and after addition of the powder were determined by titration (lower fatty acids) or by spreading on a Langmuir trough.

*Conductivity* down to  $10^{-14} \Omega^{-1} \text{cm}^{-1}$  was measured by a simple d.c. method using a Jones-type<sup>12</sup> cell with a constant of 0.0684 and a Philips d.c. electronic voltmeter G.M. 6010.

## STABILIZATION EXPERIMENTS

*Classification into ionic and non-ionic stabilizers.*—The criterion whether the stabilizers used were of ionic or non-ionic nature in xylene, was based on conductivity measurements. It is seen from table 4 that there is rather a sharp distinction between stabilizers increasing

TABLE 4.—SPECIFIC CONDUCTIVITY  $\kappa$  OF IONIC AND NON-IONIC STABILIZERS IN XYLENE

|           | stabilizer                            | conc.<br>mmoles/l. | $\kappa$<br>$\text{ohm}^{-1} \text{cm}^{-1}$ |
|-----------|---------------------------------------|--------------------|--|
| xylene    | no stabilizer                         |                    | $< 10^{-14}$                                 |
| non-ionic | oleic acid                            | 10                 | $5.0 \times 10^{-14}$                        |
|           | stearic acid                          | 10                 | $3.0 \times 10^{-14}$                        |
|           | stearyl alcohol                       | 10                 | $1.0 \times 10^{-14}$                        |
| ionic     | Cu oleate                             | 10                 | $4.7 \times 10^{-10}$                        |
|           | Aerosol OT*                           | 10                 | $2.0 \times 10^{-10}$                        |
|           | tri- <i>iso</i> -amyl-amm.<br>picrate | 10                 | $2.4 \times 10^{-10}$                        |
|           | Ca di- <i>isopropyl</i><br>salicylate | 10                 | $3.0 \times 10^{-10}$                        |
|           | Span 80 †                             | 10                 | $2.3 \times 10^{-10}$                        |
|           | Span 40 †                             | 10                 | $6.1 \times 10^{-10}$                        |

\* Aerosol OT = Na dioctylsulphosuccinate.

† Span 80 and 40 = sorbitan mono-oleate and -palmitate respectively. The origin of the ions in xylene solutions of Span 40 and 80 is not wholly clear. As the conductivity decreased rather sharply after repeated recrystallization from methanol, it may be due to impurities in these commercial products.

the conductivity of the xylene to about  $10^{-10} \Omega^{-1} \text{cm}^{-1}$  and others that do not bring the conductivity much above  $10^{-14} \Omega^{-1} \text{cm}^{-1}$ . It seems justified to consider the first group as ionic and the second as non-ionic.

*Stabilization with non-ionic detergents.*—A number of powders, viz.,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , C,  $\text{TiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{BaSO}_4$ , Se and HgS in xylene were stabilized with acids of varying chain length. The acids used were oleic, stearic, myristic, capric, caprylic, caproic and benzoic acid.

In general, the effect of the acids on stability was small. The suspension, which settled in less than 1 min in the absence of acid, now settled in a few minutes to 1 h, whereas more complete dispersion of the powder resulted in settling times of a day and more.

Exceptions to this behaviour were  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  suspensions, where sedimentation times up to several hours were observed. Prolonged heating of the powders at  $1200^\circ \text{C}$ , however, greatly reduced the settling time, suggesting that the stronger stabilization in suspensions of unheated powders is due to chemical reaction. The latter is supported by the fact that the stability increased gradually during several hours after preparation of the suspensions.

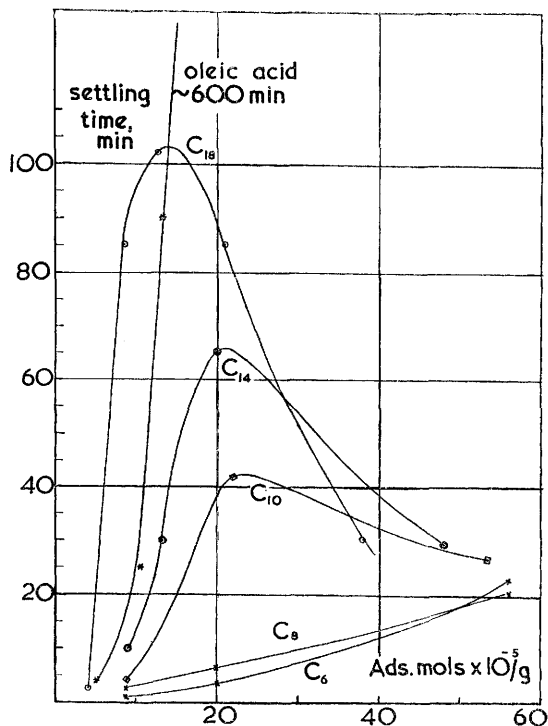


FIG. 1.—The settling time of  $\text{Fe}_2\text{O}_3$  in xylene, stabilized with fatty acids, as a function of adsorption.  $\text{C}_{18}$ ,  $\text{C}_{14}$ ,  $\text{C}_{10}$ ,  $\text{C}_8$ ,  $\text{C}_6$  represent stearic, myristic, capric, caprylic and caproic acid.

Fig. 1 gives the settling time in minutes as a function of adsorption for (unheated)  $\text{Fe}_2\text{O}_3$  in xylene with fatty acids. The effect of oleic acid is greatest, a result which was also found in other suspensions. In agreement with the results of Reh binder<sup>9</sup> the stabilization increases in the series of normal fatty acids. In contrast with the results with oleic acid, the higher normal fatty acids show a maximum stabilization. Analogous results were also found for  $\text{Al}_2\text{O}_3$  in xylene.

The stabilizing properties of fatty alcohols were still poorer than those of the corresponding acids. Table 5 shows that the effect again becomes smaller with decreasing length of the stabilizer molecule.

*Stabilization with ionic detergents.*—When an ionic stabilizer (cf. table 4) was added to  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{BaSO}_4$  and  $\text{SiO}_2$  in xylene, the suspensions in general did not settle

completely in several days. The sedimentation times did not differ much from that of a stable suspension of the same powder in water or a suitable organic solvent of a higher dielectric constant than xylene.

Complete stability could also be obtained in suspensions stabilized with fatty acids when 2 to 4 % of methanol was added to the suspension. Measurements showed that this addition increased the conductivity of the suspension by about a factor  $10^4$ . The influence of the length and nature of the fatty acid then disappeared; all suspensions showed settling times of several days, which is in agreement with complete dispersion.

TABLE 5.—STABILIZATION OF  $\text{Fe}_2\text{O}_3$  IN XYLENE WITH FATTY ALCOHOLS

| stabilizer       | conc.<br>(mmoles/l.) | settling time<br>(min) |
|------------------|----------------------|------------------------|
| blank            | —                    | 0.5                    |
| stearyl alcohol  | 10                   | 20.0                   |
| myristyl alcohol | 10                   | 10.0                   |
| lauryl alcohol   | 10                   | 6.0                    |
| capryl alcohol   | 10                   | 4.0                    |

#### ELECTROPHORESIS MEASUREMENTS

*The relationship between electrophoresis and stability.*—The work of van der Minne and Hermanic shows that in order to avoid an overshadowing of electrophoresis (proportional to the field strength  $E$ ) by electrostatic phenomena (proportional to  $E^2$ ) low field strength and perfect insulation are essential. The electrophoresis cell developed by these authors enabled us to measure electrophoresis in suspensions with a conductivity as low as  $10^{-11}$  ohm $^{-1}$  cm $^{-1}$ .

The field applied never exceeded 100 V/cm. Comparison of table 6, columns 7 and 8, where the results are listed for suspensions stabilized with ionic detergents\* shows, that in agreement with the measurements of van der Minne and Hermanic, a close relationship between stability and electrophoresis exists. As the thickness of the double layer in our suspensions was always larger than the particle size,  $\zeta$ -potentials have been calculated from Hückel's equation

$$\zeta = 6\pi\eta V/\epsilon. \quad (2)$$

TABLE 6.—THE CORRELATION BETWEEN STABILITY AND ELECTROPHORESIS FOR SUSPENSIONS IN XYLENE

| powder                  | stabilizer                                    | conc.<br>mmoles/l. | vol. %<br>of polar<br>liquid added     | $s$              | charge | sed. time,<br>h | $V_{el}$<br>$\mu$ /sec per<br>V/cm | $\zeta$<br>mV |
|-------------------------|---|--------------------|--|------------------|--------|-----------------|------------------------------------|---------------|
| $\text{Fe}_2\text{O}_3$ | Cu oleate                                     | 5                  | no                                     | 2.3              | +      | >24             | 0.110                              | 53            |
| "                       | oleic acid                                    | 10                 | 2.25 % $\text{CH}_3\text{OH}$          | 2.6†             | +      | >24             | 0.145                              | 62            |
| "                       | stearic acid                                  | 15                 | "                                      | 2.6              | +      | >24             | 0.165                              | 70            |
| "                       | caproic acid                                  | 15                 | "                                      | 2.6              | +      | >24             | 0.150                              | 65            |
| "                       | oleic acid                                    | 15                 | 2.75 % $\text{C}_2\text{H}_5\text{OH}$ | 2.6 <sup>5</sup> | +      | 15              | 0.08                               | 31            |
| "                       | stearic acid                                  | 15                 | "                                      | 2.6 <sup>5</sup> | +      | 2               | 0.05                               | 20            |
| "                       | tri- <i>iso</i> -amyl-<br>ammonium<br>picrate | 10                 | no                                     | 2.3              | no     | 0.03            | no                                 | no            |
| "                       | Aerosol OT                                    | 10                 | no                                     | 2.3              | +      | >24             | 0.143                              | 68            |
| $\text{BaSO}_4$         | Span 80                                       | 10                 | no                                     | 2.3              | +      | >24             | 0.126                              | 60            |
| $\text{Al}_2\text{O}_3$ | Aerosol OT                                    | 10                 | no                                     | 2.3              | +      | >24             | 0.147                              | 71            |
| "                       | Span 40                                       | 10                 | no                                     | 2.3              | +      | 5               | 0.071                              | 33            |
| "                       | oleic acid                                    | 10                 | 2.25 % $\text{CH}_3\text{OH}$          | 2.6              | +      | >24             | 0.103                              | 43            |
| "                       | stearic acid                                  | 10                 | "                                      | 2.6              | +      | >24             | 0.110                              | 48            |

† The  $\epsilon$ -values in the cases where alcohol was added, were taken from literature.

A critical  $\zeta$ -potential of about 30 mV is found, in agreement with the results of table 1 for particles of  $1 \mu$ .

\* As might be expected from their low conductivity, the suspensions stabilized with non-ionic detergents only showed electrostatic phenomena.

*The relationship between adsorption and stability.*—The adsorption isotherm of Aerosol OT on  $\text{Fe}_2\text{O}_3$  in xylene is given in fig. 2. For each experimental point of the isotherm, stability and electrophoresis of the corresponding suspensions were determined. Owing to the low conductivity no electrophoresis could be measured at the lowest point of the curve. Fig. 2 shows that both stability and electrophoresis increase with increasing adsorption, and remain approximately constant when adsorption is maximal. Analogous

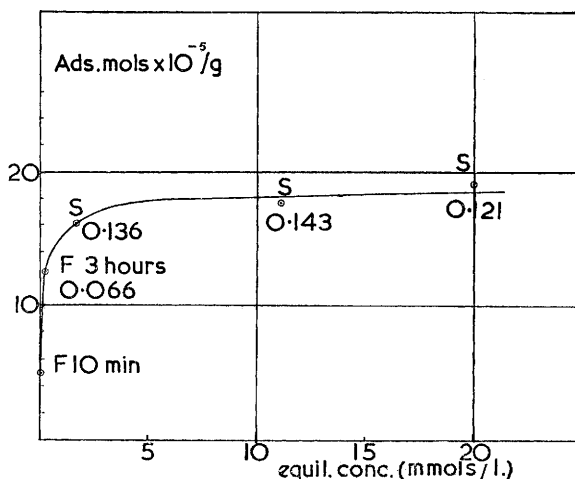


FIG. 2.—Adsorption isotherm of Aerosol OT on  $\text{Fe}_2\text{O}_3$  in xylene. For each point of the curve, stability and electrophoretic mobility of the corresponding suspensions are given.  $S$  = stable;  $F$  = flocculated.

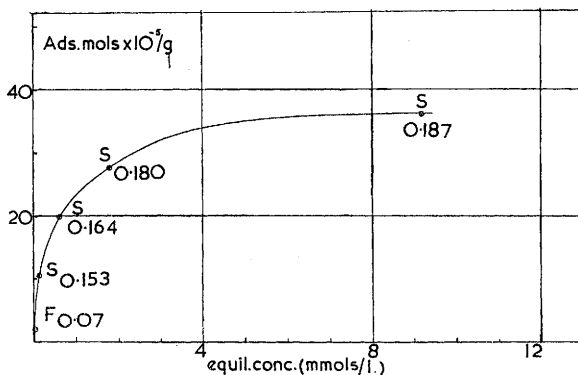


FIG. 3.—Adsorption isotherm of oleic acid on  $\text{Fe}_2\text{O}_3$  in xylene + 3.75%  $\text{CH}_3\text{OH}$ . For each point of the curve, stability and electrophoretic mobility of the corresponding suspensions are given.  $S$  = stable;  $F$  = flocculated.

experiments were carried out for a suspension of  $\text{Fe}_2\text{O}_3$  in xylene containing 3.75% of methanol, with oleic acid as a stabilizer. As the methanol itself greatly contributes to the conductivity, electrophoresis measurements in this case could be extended to low equilibrium concentrations of the stabilizer. Again (fig. 3) adsorption runs parallel with stability and electrophoresis.

## DISCUSSION

In agreement with the results of table 3 the experiments with suspensions show that stability is only obtained when an electrical double layer is formed on the particles. The primary demands for an electric charge are adsorption and

dissociation of the stabilizer. In the second place the polarity of the ions must differ enough to give preferential adsorption of one type of ion. This condition will in general be fulfilled when the stabilizer consists of a large organic and a small inorganic ion, the small polar ion being preferentially adsorbed by the polar surface. In confirmation of this view all suspensions of table 6, except the suspension with tri-*iso*-amyl ammonium picrate, where both ions are large, showed a positive charge.

In agreement with the figures of table 2 suspensions of large particles with non-ionic detergents are never truly stable. The slight stabilization observed increases with increasing chain length. The longer chains evidently keep the particles farther separated and make the energy trough less deep. As it is difficult to free oleic acid from molecules of higher molecular weight the greater effect of this acid in comparison to the normal fatty acids may be due to impurities. The stronger stabilization with fatty acids in the case of reactive powders is easily explained by ionization of the soap formed.

The maxima in the stability curves of fig. 1 might be due to a weak attraction between the aliphatic chains. This would lead to adsorption of a second layer of fatty acid molecules pointing with their polar heads to the medium, and to a slightly deeper minimum in the energy against distance curves. Support for this point of view is found in the work of Hirst and Lancaster,<sup>10</sup> who found partial desorption of normal fatty acids from powders in benzene not much above room temperature, and further by the fact that the maxima in the stability curves disappeared when the suspensions were heated to 60° C.

As we worked exclusively with rather coarse suspensions the predictions above for small particles cannot be verified from our experiments. The work of van der Waarden<sup>11</sup> shows that stability in this case can indeed be obtained with non-ionic stabilizers.

In order to complete the experimental check of table 3 it would be necessary to show that ionic stabilizers (with a short chain) fail to make a small particle system stable.

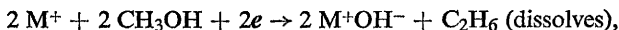
## 2. ELECTROPHORETIC DEPOSITION

Hamaker and Verwey<sup>1, 2</sup> consider the deposition of particles from a stable non-aqueous suspension by means of electrophoresis to be a close analogue to sedimentation. They assume that the accumulation of particles under influence of the applied electric field leads to sufficient pressure on the innermost layers of particles to overcome the double-layer repulsion and to lead to an adhering deposit.

It is shown in the following sections that by the electrolysis accompanying electrophoresis, sufficient electrolyte may be formed at the electrode to cause flocculation of the particles. The critical time  $t^*$  observed in electro-deposition, should therefore be interpreted as the time required to build up a critical electrolyte concentration rather than a critical particle accumulation.

### THEORY

Considering the deposition of a positively charged suspension in methanol, the cathode reaction might be



where  $M^+$  is the cation of the electrolyte in the methanol. A fraction of the  $OH^-$  ions generated at the cathode is transported away by the electric current. The net production of  $M^+OH^-$  at the cathode is thus  $t_M$  equivalents for every faraday passing,  $t_M$  being the transport number of the  $M$  ions. By diffusion,  $M^+OH^-$  is carried into the solution. By solving<sup>4, 5</sup> the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (3)$$

for the appropriate boundary conditions, the concentration of  $M^+OH^-$  can be

calculated as a function of time and place. The concentration at the electrode ( $c_{\text{electr}}$ ) is found to be

$$c_{\text{electr}} = c_0 + \frac{2}{\sqrt{\pi}} \frac{It_M}{SF} \left( \frac{t}{D} \right)^{\frac{1}{2}}, \quad (4)$$

where

$c_0$  = initial electrolyte concentration,

$I$  = current in A,

$t_M$  = transport number of  $M^+$ ,

$F$  = faraday,

$S$  = area of the electrode,

$D$  = diffusion constant of  $M^+OH^-$ ,

$t$  = deposition time.

The assumption of undisturbed diffusion, on which eqn. (4) is based, becomes incorrect when  $t$  is great. There is evidence in the literature<sup>6, 7</sup> that in unstirred solutions the diffusion layer reaches to a depth of about  $500 \mu$ . As the average displacement  $(\bar{x}^2)^{\frac{1}{2}} = (2Dt)^{\frac{1}{2}}$ , ( $D$  being about  $10^{-5}$  cm<sup>2</sup>/sec for ordinary electrolytes) this means that eqn. (4) can be used safely up to  $t \approx 100$  sec.

It is generally observed that a critical time  $t^*$  has to elapse before the formation of an adhering deposit starts. Calculating the concentration at the electrode after the critical time with the aid of eqn. (4), values of the same order as the flocculation concentration are found.

In a positively charged suspension of  $MgCO_3$  in  $CH_3OH$ ,  $t^*$  was 20 sec for  $I = 1.55 \times 10^{-3}$  A and  $S = 1.26$  cm<sup>2</sup>. Taking  $t_M = 0.5$  and  $D = 10^{-5}$  cm<sup>2</sup>/sec, which are the values for KOH in methanol, we find

$$c_{\text{electr}} = 10 \text{ mmoles/l.}$$

The flocculation value with KOH for a concentrated suspension is

$$c_{\text{flocc}} = 6.0 \text{ mmoles/l.}$$

Applying an analogous calculation to a negatively charged suspension of  $SiO_2$  in acetone which is  $10^{-5}$  M in LiCl gives

$$c_{\text{electr}} = 4.2 \text{ mmoles/l. and } c_{\text{flocc}} = 4 \text{ to } 6 \text{ mmoles/l.}$$

The concentration built up by electrolysis is clearly of the same order as the flocculation concentration. A closer agreement cannot be expected because of the difficulty in determining the flocculation value under exactly the same conditions as prevail for the suspension near the electrode.

The following simple relations between the critical time and the conditions of electro-deposition are expected from eqn. (4)

$$t^* = pI^{-2} = qV^{-2}k^{-2},$$

where  $q$  and  $p$  are constants,  $V$  is the voltage applied and  $k$  the specific conductance of the suspension.

## EXPERIMENTAL

THE CRITICAL TIME  $t^*$ .—During electrophoresis the particles are accumulated at the electrode, but the deposit stays fluid as long as the double-layer repulsion between particles prevents actual contact. Consequently the yield  $Y$  will not only be dependent upon the time of electrophoresis but also on the time elapsed between the end of the electrophoresis and the moment of weighing, during which the non-solidified part of the layer can flow off. Fig. 4 illustrates this for  $MgCO_3$  in methanol. If the deposit is weighed continuously during deposition as has been done by Biguenet and Mano,<sup>8</sup> the yield is proportional to the time of electrophoresis and no critical time is found. If weighing is postponed until the fluid part of the layer has flowed off, which we found to be the case after a waiting period of 15 min ( $t_w = 15$ ), a  $Y$  against  $t$  curve of the type sketched in fig. 5 is found. Below  $t^*$ , no adherent deposit is found. At the critical time  $t^*$ , practically the whole deposit turns rigid within a few seconds.



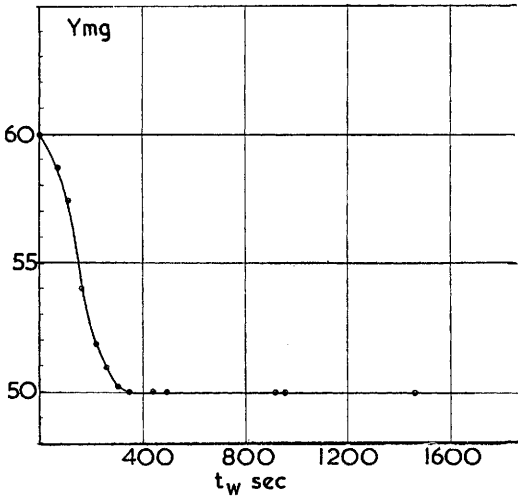


FIG. 4.—The weight of deposit as a function of the time between stopping electrophoresis and weighing the deposit for a  $MgCO_3 + CH_3OH$  suspension.

$V = 6 V$ ;  $C_{susp} = 8 \%$ .

FIG. 5.—The yield as a function of time of deposition at different waiting times ( $t_w$ ).

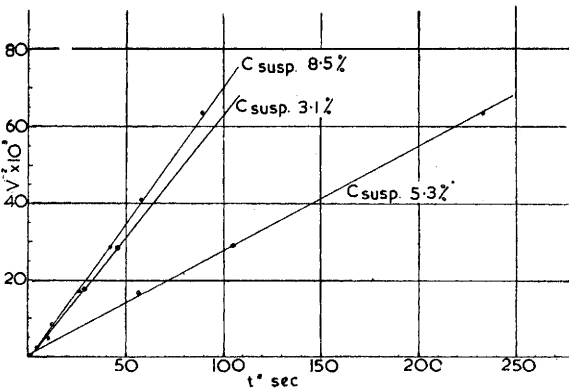
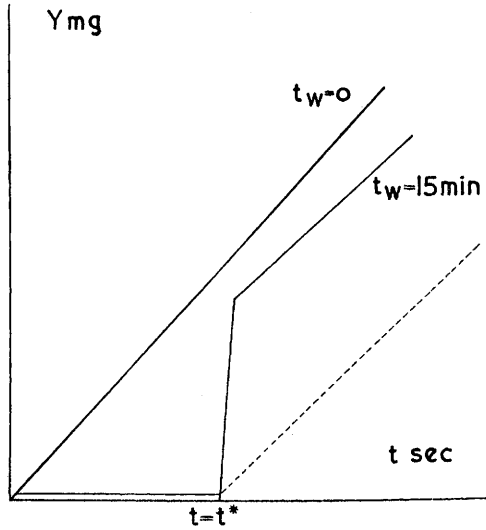


FIG. 6.—The dependence of the critical time on the voltage applied in  $MgCO_3 + CH_3OH$  suspensions.

FIG. 7.—The dependence of the critical time on the voltage applied in a  $\text{SiO}_2$  suspension in acetone ( $0.9 \times 10^{-4}$  N LiCl).

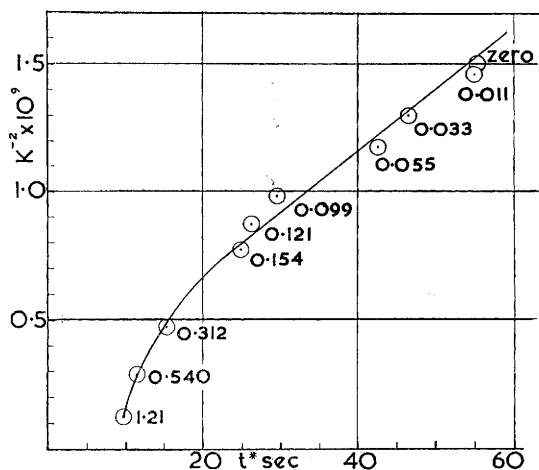
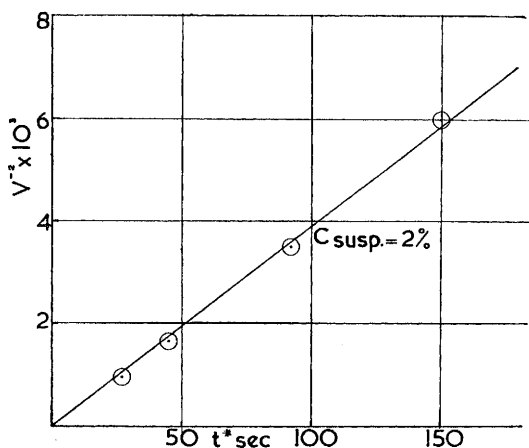
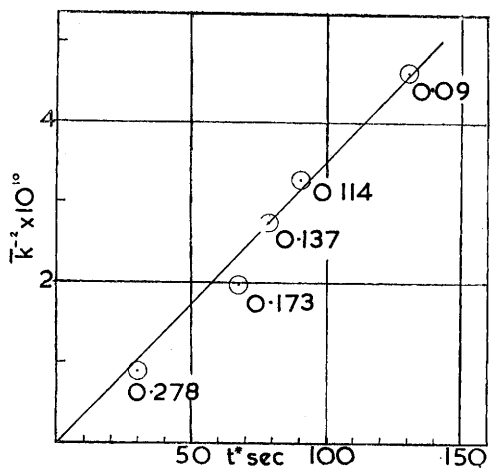


FIG. 8.—The dependence of the critical time on conductivity in a  $\text{MgCO}_3 + \text{CH}_3\text{OH}$  suspension. At each point the corresponding concentrations of added KI are given in mmoles/l.

$V = 7.2$  V;  $C_{\text{susp.}} = 7.4\%$ .

FIG. 9.—The dependence of the critical time on conductivity in a  $\text{SiO}_2 + \text{acetone}$  suspension. At each point the corresponding concentrations of added LiCl are given in mmoles/l.

$V = 7.0$  V;  $C_{\text{susp.}} = 2\%$ .



VARIATION OF  $t^*$  WITH APPLIED VOLTAGE.—The results for  $\text{MgCO}_3 + \text{CH}_3\text{OH}$  (at three suspension concentrations) and  $\text{SiO}_2 + \text{acetone}$  are given in fig. 6 and 7. The influence of the suspension concentration in fig. 6 which is quite non-systematic is evidently due to small variations in the electrolyte content between the different concentrations.

VARIATION OF  $t^*$  WITH CONDUCTIVITY.—The measurements for  $\text{MgCO}_3 + \text{CH}_3\text{OH}$  with KI as added electrolyte and  $\text{SiO}_2 + \text{acetone}$  with LiCl are given in fig. 8 and 9. Apart from the curvature in the lower part of fig. 8, for which no explanation has been found, the measurements confirm the proportionality of  $t^*$  with  $k^{-2}$ . In the  $\text{SiO}_2 + \text{acetone}$  curve no point is present for zero electrolyte concentration. The conductivity of the pure suspension was so low that even at 40 V applied voltage no adherent deposits were obtained. The additions of electrolyte, although they changed the conductivity considerably, had only a small influence on the electrophoretic velocity.

## DISCUSSION

Three different theories of electro-deposition have been advanced. In the first the electric field is supposed to overcome the repulsion between two particles. In the second, a cumulative influence is considered of several layers of particles pressing upon each other, causing the particles close to the electrode to adhere to it and to each other. The third theory postulated in this paper considers flocculation by electrolyte to be the final cause of formation of a deposit.

The fact that a critical time exists seems to rule out the first theory. Both the accumulation theory<sup>3</sup> and the flocculation theory demand that the critical time is inversely proportional to the voltage, but the influence of other variables is expected to be different as shown in the following table. The experiments described are in agreement with the flocculation theory, except for the concentration dependence shown in fig. 6. The critical time varies, however, erratically with concentration and this variation is probably more due to accidental variations in the conductance than to the concentration.

TABLE 7.—INFLUENCE OF DIFFERENT VARIABLES ON THE CRITICAL TIME

|                     | voltage  | conductance | electrophoretic mobility | suspension conc. |
|---------------------|----------|-------------|--------------------------|------------------|
| accumulative theory | $V^{-2}$ | independent | $u'$                     | $c^{-1}$         |
| flocculation theory | $V^{-2}$ | $k^{-2}$    | independent              | independent      |

The local increase in electrolyte concentration near the electrodes lowers the local field by a factor which may easily amount to 10 or more. This would make the accumulation mechanism still less probable. It is, however, conceivable that in other systems the products of the electrode reaction are weakly or not at all ionized. In such cases a decrease of the local electrolyte concentration would follow, coupled with an increase in the local field, the flocculation mechanism would be ruled out in favour of the accumulation mechanism.

An important factor in explaining why at  $t = t^*$  practically the whole layer turns rigid in a few seconds may be the following. When as a result of the flocculation mechanism the particles in the electrode area touch, part of the medium is squeezed, thereby bringing the electrolyte concentration in the adjacent layer, which is already high, to the flocculation value, etc. Owing to convection this mechanism might fail at the circumference of the layer, thus explaining why at  $t > t^*$  a small part of the layer still flows off. The part which flows off corresponds to a layer of about  $60 \mu$  the gradual divergence in fig. 3 being caused by the increasing radius of the coated electrode (a cylinder of 1 mm diam.).

The authors are indebted to Dr. E. J. W. Verwey, Director of the Philips Research Laboratories, for his permission to publish this paper; to Dr. J. L. van der Minne and Mr. P. H. J. Hermanie (Kon. Shell. Lab.) for their help in the construction and use of the electrophoresis cell, and to Mr. P. A. Boter for carrying out the adsorption measurements and most of the experiments on electrophoretic deposition.

## PART 1

- <sup>1</sup> Verwey and Overbeek, *Theory of the Stability of Lyophobic Colloids* (Amsterdam, 1948). *Colloid Science*, vol. 1, ed. by Kruyt (Amsterdam, 1952).
- <sup>2</sup> de Boer, Hamaker and Verwey, *Rec. trav. chim.*, 1939, **58**, 662.
- <sup>3</sup> van der Minne and Hermanie, *J. Colloid Sci.*, 1953, **8**, 38; 1952, **7**, 600.
- <sup>4</sup> Mackor and van der Waals, *J. Colloid Sci.*, 1952, **7**, 535.
- <sup>5</sup> van der Waarden, *J. Colloid Sci.*, 1950, **5**, 317.
- <sup>6</sup> van der Waarden, *J. Colloid Sci.*, 1951, **6**, 443.
- <sup>7</sup> ref. (1), p. 171. <sup>8</sup> Hamaker, *Physica*, 1937, **4**, 1058.
- <sup>9</sup> Rehbinder, Lagutkina and Wenström, *Z. physik. Chem. A*, 1930, **146**, 63.
- <sup>10</sup> Hirst and Lancaster, *Trans. Faraday Soc.*, 1951, **47**, 315.
- <sup>11</sup> ref. (5) and (6); cf. Mackor, *J. Colloid Sci.*, 1951, **6**, 492.
- <sup>12</sup> Jones and Bollinger, *J. Amer. Chem. Soc.*, 1931, **53**, 411.

## PART 2

- <sup>1</sup> Hamaker and Verwey, *Trans. Faraday Soc.*, 1940, **36**, 180.
  - <sup>2</sup> Hamaker, *Trans. Faraday Soc.*, 1940, **36**, 279.
  - <sup>3</sup> cf. also Hill, Lovering and Rees, *Trans. Faraday Soc.*, 1947, **43**, 407.
  - <sup>4</sup> Rosebrugh and Miller, *J. Physic. Chem.*, 1910, **14**, 816.
  - <sup>5</sup> Thomson and Cayley, *Quart. J. Math.*, 1857, **1**, 316.
  - <sup>6</sup> Nernst and Merriam, *Z. physik. Chem.*, 1905, **53**, 235.
  - <sup>7</sup> Agar, *Faraday Soc. Discussions*, 1947, 26.
  - <sup>8</sup> Biguenet and Mano, *Le Vide*, 1947, **2**, 291, 304.
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