

## The Effect of Electrical Forces on the Stability of Colloidal Sols

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attempt to evaluate  $n$ , it is convenient to assume  $A_i$  to be given by Eq. (7), and calculate  $A_s/A_i$ . This quantity is given as a function of  $r^2$  in Fig. 6 as is also  $(A_s/A_i)^2$ . From these curves it is easy to evaluate  $V_s$ , which turns out to be 35 cc. This corresponds to a radius of 1.06 cm, as compared to the value of  $s_0$  of 0.75 cm.

At 300° the value of  $V_s$  may be taken as the same.  $D$ , of course, will be larger. The experiments indicate essentially the same value of  $\tau_0$ , but on account of the appreciable value of  $k_i$  in this case,  $\tau$  will be smaller, and this will be almost sufficient to offset the increase in  $D$ .  $D\tau$  will thus be sufficiently close, so that it is not worthwhile to make a separate calculation for 300°.

The value of  $V_s$  is, of course, extremely rough, but it may be remarked that the curves in Fig. 6 look very reasonable. The calculation of the concentration of radicals at the center of the cell should be fairly reliable, and it fits in well with the other points. By comparison of the area under the curve for  $A_s/A_i$  with that under the broken lines (which indicate the extent of the beam) it is observed

that Eq. (14) does not hold exactly, since the right-hand side appears to be about 10 percent larger than the left-hand side. This is undoubtedly due to the approximate integration used to obtain Eqs. (11) and (12). In obtaining Eq. (11) we overestimated the amount of diffusion, because the true contribution of the integration with respect to  $y$  goes to zero for  $x < r - (s_0^2 - Dt)^{1/2}$  faster than it goes to 1 for  $x > r - (s_0^2 - Dt)^{1/2}$ . Also, setting  $t = \tau$  in the argument of the probability function in Eq. (11) in order to get Eq. (12) was probably an overestimate for the average of  $t$ , and would result in an overestimate of  $A_s$ . It is difficult to say off-hand, whether these errors would more than compensate the underestimation of the amount of diffusion arising from the assumption that  $\tau$  is constant throughout the volume. The discrepancy between the right- and left-hand sides of Eq. (14) is in the direction to be expected from a decrease in  $\tau$  as the radical gets outside the illuminated cylinder; that it is not more than 10 percent suggests that the errors in integration have not overcompensated the error due to calling  $\tau$  constant.

## The Effect of Electrical Forces on the Stability of Colloidal Sols

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It is assumed that the stabilizing potential in a sol is not the potential at a distance  $l$  from the surface of the particle, ( $\zeta$ ), but the potential at a distance  $\lambda$ , ( $\lambda$ ).  $l$  is the distance from the solid surface at which a maximum in the potential energy curve determines the rate of coagulation, and  $\lambda$  is a constant for a given sol in states of equal stability. The quantities  $l$  and  $\lambda$  are evaluated from experimental data.

THE original concept of the relation of the  $\zeta$  potential to the stability of a slightly hydrated sol was that in the stable sol the  $\zeta$  potential of the particles was sufficiently high to prevent the close approach and adhesion of the particles. The addition of salt to the sol was supposed to lower the  $\zeta$  potential to the critical potential, ( $\zeta^*$ ), and at this point coagulation of the sol would begin. It was assumed, at least by implication, that  $\zeta^*$  was a constant for each sol.

However, it was soon demonstrated by data such as that of Ghosh,<sup>1</sup> which is given in Table I, that  $\zeta^*$  was not a constant for a given sol, but in general was higher for salts having higher flocculation values. It was even observed by Kruyt and van der Willigen<sup>2</sup> that the addition of KCl

or  $K_4Fe(CN)_6$  to an arsenous sulfide sol caused the  $\zeta$  potential to *increase* until  $\zeta^*$  was reached and coagulation began.

Nearly all modern attempts to interpret the significance of electrostatic forces in colloidal sols involve the use of the Debye-Hückel theory. The approximations involved in this theory introduce quantitative errors into calculations re-

TABLE I. Data of Ghosh (reference 1) for isostable states of the arsenous sulfide sol. (Coagulation time = 25–30 min.)

Salt	$C \times 10^3$ of moles +ion/l	$\zeta^*$ mv	$\lambda^* (= \psi_{l+16})$ mv
KNO <sub>3</sub>	70	45.8	10.8
KCl	68	43.2	10.4
MgCl <sub>2</sub>	1.02	15.0	10.6
SrCl <sub>2</sub>	0.98	14.6	10.6
BaCl <sub>2</sub>	0.92	14.2	10.2
AlCl <sub>3</sub>	0.3	15.1	11.2
Th(NO <sub>3</sub> ) <sub>4</sub>	0.125	13.9	10.6

<sup>1</sup> B. N. Ghosh, J. Chem. Soc. p. 2693 (1929).

<sup>2</sup> H. R. Kruyt and P. C. Van der Willigen, Zeits. f. physik. Chemie **130**, 170 (1927).

ferring to such systems. This is particularly true at higher salt concentrations and in the immediate neighborhood of a charged wall.

A recent survey of the role of electrical forces in colloidal systems is given in an impressive collection of papers by leading authorities.<sup>3</sup> Therefore it is not the purpose of the present paper to give a detailed discussion of any phase of the problem, but rather to show as briefly as possible how the application of a relation derived in a recent paper<sup>4</sup> leads to the almost quantitative explanation of anomalous experimental data of long standing.

This relation,

$$\ln \tanh (Z' \epsilon \psi / 4 k T) = \ln \tanh (Z' \epsilon \psi_0 / 4 k T) - \kappa X \quad (1)$$

involves the assumption that the thickness of the ion atmosphere is much less than the radius of curvature of the surface, but does not involve the Debye-Hückel approximations. It should therefore be most accurate at higher concentrations where  $1/\kappa$  is small, and should be applicable near the charged surface. This is, of course, the region of greatest importance from the standpoint of the surface properties of the system.

Substituting numerical values into Eq. (1) for water solutions at 25° and changing to common logarithms,

$$\log \tanh (9.75 Z' \psi) = \log \tanh (9.75 Z' \psi_0) - 0.142 Z' C^{\frac{1}{2}} X. \quad (2)$$

$Z'$  is the valence, and  $C$  the concentration in gram moles per liter, of the ion having the opposite sign of charge to the wall.  $\psi^0$  is the surface potential of the wall and  $\psi$  the potential in the solution at a distance  $X$  from the  $\psi^0$  plane. Potentials are in volts and distance in angstrom units. It was assumed that the electrokinetic potential ( $\zeta$ ) is the potential at the distance  $X = t$  and therefore,

$$\log \tanh (9.75 Z' \zeta) = \log \tanh (9.75 Z' \psi_0) - 0.142 Z' C^{\frac{1}{2}} t. \quad (3)$$

The exact physical significance of  $t$  is open to question. It was assumed that it represents the thickness of the immobilized liquid layer at the solid wall. Bikerman<sup>5</sup> on the other hand, has

<sup>3</sup> Trans. Faraday Soc. **36**, 1-322 (1940).

<sup>4</sup> W. G. Eversole and P. H. Lahr, J. Chem. Phys. **9**, 530 (1941).

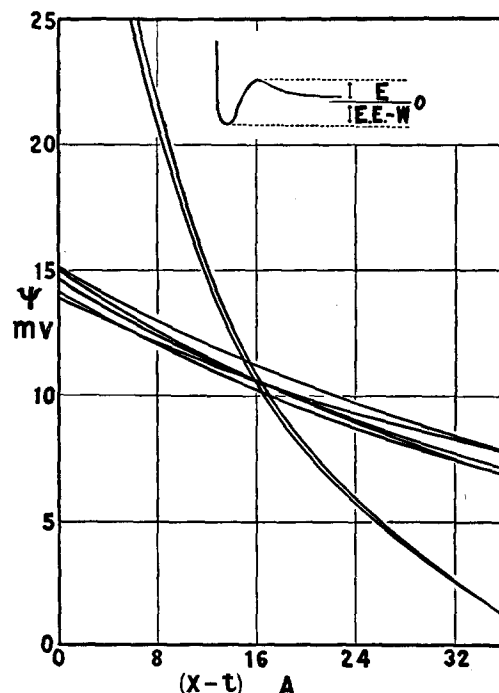


FIG. 1. Potential curves for isostable states of an  $\text{As}_2\text{S}_3$  sol.

maintained that  $t$  measures a fictitious thickness. He holds that roughness of the solid surface rather than rigidity in the liquid structure gives rise to the immobilization of the liquid. In support of the original assumption, it has been demonstrated<sup>6</sup> that the value of  $t$  varies significantly for different salt solutions using the same solid wall. It seems impossible to reach a final decision on this question at the present time. However, for the discussion which follows, it will be sufficient to point out that if suitable constant values are assigned to  $\psi_0$  and  $t$ , Eq. (2) expresses quantitatively the observed dependence of  $\zeta$  on  $C$  in many cases.

Eliminating  $\psi_0$  by subtracting Eq. (3) from Eq. (2),

$$\log \tanh (9.75 Z' \psi) = \log \tanh (9.75 Z' \zeta) - 0.142 Z' C^{\frac{1}{2}} (X - t). \quad (4)$$

Equation (4) expresses  $\psi$  as a function of the distance,  $(X - t)$ , from the  $\zeta$  potential plane, in terms of  $\zeta$  and  $C$ , both of which are measurable quantities. Each pair of experimental values of

<sup>5</sup> J. J. Bikerman, J. Chem. Phys. **9**, 880 (1941).

<sup>6</sup> W. G. Eversole and W. W. Boardman, J. Chem. Phys. **9**, 798 (1941).

$\zeta$  and  $C$  defines one of the family of potential curves represented by the equation.

In order to compare the effects of different salts on the stability of a given sol the particular pair of values must be chosen for each salt to correspond to states of equal stability of the sol (isostable states).

Data of Ghosh<sup>1</sup> for isostable states of an arsenous sulfide sol are given in the first three columns of Table I. The concentration  $C^*$  for each salt has a value such that coagulation of the sol occurred in from 25 to 30 minutes after the addition of the salt.  $\zeta^*$  is the critical  $\zeta$  potential of the particles corresponding to this degree of stability of the sol.

Using the  $C^*$  and  $\zeta^*$  values of Table I in Eq. (4), the potential curves shown in Fig. 1 have been calculated for the different salts. The salts corresponding to the different curves can be determined from the intercepts on the axis of ordinates by reference to Table I. It will be observed that the range of  $\psi$  values for the different salts is a minimum at  $X-t \doteq 16A$ . In fact the potential curves for three of the salts intersect in the immediate vicinity of the point, 16A, 10.6 mv, and the curves for the other four salts pass near this point on as many sides. Thus it is possible to eliminate the variation of the stabilizing potential for isostable states of the sol by postulating that the stabilizing potential is not the potential in the  $t$  plane ( $\zeta$ ) but the potential in the  $l$  plane ( $\lambda$ ), where in this case  $l = t + 16A$  and the value of the critical  $\lambda$  potential ( $\lambda^*$ ) is  $10.7 \pm 0.5$  mv. The  $\lambda^*$  values for the different salts are given in the last column of Table I.

The quantity  $l$  may be considered as the distance from the  $\psi^0$  plane at which there is a maximum in the potential energy curve which characterizes the approach of two particles, or a distance slightly greater than one-half the distance of closest approach of the two surfaces.

TABLE II. Data of Powis (reference 8) for isostable states of an  $As_2S_3$  sol. (Coagulation time = 5 hr.)

Salt	$C^* \times 10^3$ of moles +ion/l	$\zeta^*$ mv	$\lambda^*$ mv
KCl	40	44	22.5
BaCl <sub>2</sub>	0.5	26	22.1
AlCl <sub>3</sub>	0.5	25	22.8
$l-t = 9.6A$		$t_{\max} = 13.8A$	

Data are not at hand to calculate the value of  $l$  for the arsenous sulfide surface. However, by substituting  $\psi = \infty$  in Eq. (4) and solving for  $(X-t)$ , the maximum possible value of  $t$  consistent with these data is obtained, since the value of  $t$  must be such that  $\psi^0$  will be finite for all salts. For  $KNO_3$ ,  $t_{\max} = 10A$ , while larger values are obtained for the other salts. Therefore it may be assumed that the value of  $l$  is between 16 and 26A. The location ( $l$ ) of the maximum in the potential energy curve is defined by the point at which the surface forces of adhesion become equal to the electrical forces of repulsion.

The reason for the existence of a potential energy maximum at such a distance is obscure. However, evidence based on direct measurements<sup>7</sup> indicates that the distance of closest approach of two quartz surfaces in water and dilute solutions may be even greater than 100A. In general, available evidence pertaining to the state of a thin water film between solid surfaces is limited in amount and is inconclusive. Under such conditions, one is forced to infer a potential energy relation from the observed behavior of the physical system. This has been done, and the potential energy curve for the arsenous sulfide sol is represented diagrammatically in Fig. 1.

On the basis of the argument presented here, a broad qualitative picture of the energy relations in sols becomes evident. The work of adhesion ( $W$ ) is opposed by kinetic energy (K.E.) which is a function of temperature, and by electrical energy (E.E.) which is a function of the potential at one-half the distance of closest approach of two surfaces. The stability ( $S$ ) of a sol is measured by  $S = K.E. + E.E. - W$ . The condition for a stable sol is  $S > 0$ , and for an unstable sol  $S < 0$ . In all isothermal, isostable states of a sol, K.E. and  $S$  are constant and therefore E.E. is constant (unless the added salts affect the value of  $W$ ). If  $W < K.E.$  the sol will be typically emulsoid in behavior and will be stable even at the isoelectric point. The condition,  $S = 0$  is defined by the minimum E.E. at which spontaneous peptization of the coagulated sol can occur.

A second, and perhaps more practical, criterion of isostable states of a given sol is the rate (or

<sup>7</sup> W. G. Eversole and P. H. Lahr, J. Chem. Phys. 9, 686 (1941).

time) of coagulation ( $S < 0$ ). From the standpoint of the kinetics of the coagulation, it may be considered that there is a potential barrier of Coulomb forces, the height ( $E$ ) being a function of  $\lambda$ , which opposes the approach of two particles within the range of the surface forces of adhesion. The velocity constant for the coagulation process is then proportional to  $\exp(-E/kT)$ . If  $E$  is of the order of magnitude of  $kT$ , the rate of coagulation should be sensitively dependent on the value of  $\lambda$ , so that isostable states of a sol, ( $S < 0$ ), can be defined accurately in terms of equal rates (or times) of coagulation.

This view is confirmed by a comparison of the results of Ghosh<sup>1</sup> with those of Powis.<sup>8</sup> Data of Powis<sup>8</sup> given in Table II have been treated in the same way as those of Ghosh.<sup>1</sup> The value of  $\lambda^*$  is about twice as large as that obtained from the data of Ghosh. This is accounted for by the slower rate of coagulation used by Powis in defining his isostable states. The smaller value of  $l-t$  (9.6Å) can be largely accounted for by the larger value of  $t_{\max}$  (13.8Å), giving a value of  $l_{\max} = 23.4\text{Å}$  as compared with  $l_{\max} = 26\text{Å}$  obtained from the data of Ghosh. This may perhaps be taken as evidence in support of the view of Bikerman<sup>5</sup> in regard to the significance of  $t$ .

If  $l=t$ ,  $\zeta$  and  $\lambda$  become identical and  $\zeta$  becomes a constant for a given sol in isostable states. This condition seems to be very nearly realized for the ferric oxide sol studied by Ghosh.<sup>1</sup> The values calculated from his data for this sol are,  $\lambda^* = 29.5 \pm 1.0$  mv,  $l-t = 1.5 \pm 0.25\text{Å}$ , and  $t_{\max} = 11\text{Å}$ . Thus a shorter distance of closest approach is indicated for this sol than for the  $\text{As}_2\text{S}_3$  sol, although  $t_{\max}$  is about the same.

Using the values of  $l-t$  and  $\lambda^*$  calculated from the data of Table I, it is possible to explain the behavior of the  $\zeta$  potential of the  $\text{As}_2\text{S}_3$  sol studied by Kruyt and Van der Willigen.<sup>2</sup> Introducing the values,  $X-t = 16$ ,  $\psi(=\lambda^*) = 0.0107$  v and  $Z' = 1$ , into Eq. (4) and rearranging

$$\log \tanh (9.75\zeta^*) = 9.0004 - 10 + 2.272C^{*1/2}. \quad (5)$$

This equation expresses the critical  $\zeta$  potential as a function of the flocculation value for salts of univalent precipitating ions. The values of  $\zeta^*$  calculated by means of this equation are plotted

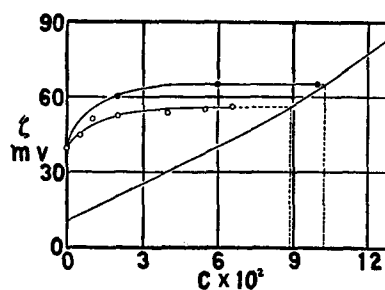


FIG. 2. Zeta-potential relations for an  $\text{As}_2\text{S}_3$  sol.

against the  $C^*$  values in Fig. 2. This curve divides the field into two areas. Above the curve, the coagulation time is greater than 30 minutes, while below is the region of rapid coagulation. Also plotted in Fig. 2 are the  $\zeta$  potentials calculated from the cataphoretic mobilities observed by Kruyt and Van der Willigen<sup>2</sup> for an arsenous sulfide sol at various concentrations of KCl (lower curve) and  $\text{K}_4\text{Fe}(\text{CN})_6$  (upper curve). The  $\zeta$  potentials were calculated by the classical formula using the factor  $4\pi$  and the viscosity and dielectric constant of pure water. Extrapolating the experimental curves to their intersection with the  $\zeta^*$  curve, the flocculation values (read from the graph) are 0.089 and 0.102 for KCl and  $\text{K}_4\text{Fe}(\text{CN})_6$ , respectively. The values reported by Kruyt and van der Willigen are 0.080 and 0.130. While the agreement is only semi-quantitative, the figure shows very clearly how it is possible for a stable  $\text{As}_2\text{S}_3$  sol to become unstable on the addition of a salt even if there is a pronounced increase in the  $\zeta$  potential. For multivalent precipitating ions, the increase in  $\zeta^*$  with  $C^*$  is much more rapid than with univalent ions, so that coagulation would occur at a low salt concentration even if there were a large increase in  $\zeta$  potential.

The mechanism suggested here involves surface forces of cohesion which are effective at somewhat greater distances than is ordinarily assumed. However, it is felt that the experimental evidence lends considerable support to the assumption of their existence. It seems probable that the application of Eq. (1) rather than the Debye-Hückel equation may lead to further progress in this important field, especially in the region immediately adjacent to the solid wall.

<sup>8</sup> F. Powis, J. Chem. Soc. 109, 734 (1916).