

LYOPHOBIC SOL STABILITY IN MIXED MEDIA

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Abstract—This paper discusses certain features of the stability of lyophobic colloids against aggregation in mixtures of water and other water soluble substances. These latter substances affect the stability by their influence on the dielectric constant of the medium, on the dispersion force and on the composition of the electrical double layer. In order to assess the relative significance of the last mentioned factor, stability studies have been made in conjunction with double layer measurements. Examples are given, which have been obtained with AgI-sols in mixed solvents, leading to some general remarks on the future development of stability theory.

INTRODUCTION. LITERATURE

The effect of additives on the stability of hydrophobic sols and suspensions is a matter of considerable practical and theoretical interest. The practical interest derives from the frequent occurrence, in real systems, of admixtures, possibly deliberately formed, and from the possibility of linking stability in aqueous solvents to that in non-aqueous media for additives which can be mixed with water in all proportions. The theoretical interest stems, generally speaking, from the possibility of testing stability theories by changing important interaction variables and comparing observed changes in stability with theoretical predictions.

More specifically, all the following physical quantities are expected to change if a water-soluble substance is added to a hydrophobic sol or suspension:

- (i) The relative dielectric constant ϵ of the medium;
- (ii) the effective Hamaker constant $A_{1(2)}$;
- (iii) the viscosity η of the medium;
- (iv) the composition of the electrical double layer around the colloids.

Factors (i-iii) are essentially *solvent* properties, whereas (iv) is typically an *interfacial* property. Alternatively, distinction can be made between static properties (i) (ii) and (iv) vs kinetic properties (iii): a change of η affects the *kinetics* of coagulation but not the interaction force.

One of the difficulties in conducting research into effects on the medium is that it is hard to find an additive that varies only one of the variables mentioned. Extremely surface-active substances are perhaps an exception in that they adsorb so strongly that factor (iv) is already dramatically changed at negligible bulk concentrations, so that ϵ and η are virtually unaltered and the Van der Waals attraction is entirely accounted for by the Vold-effect.¹² However, in this paper we want to emphasize the effects of changes in the solvent composition, hence such strongly adsorbing surfactants are excluded from our considerations.

Looking through the literature on the subject matter, one soon concludes that comprehensive studies, encompassing all four variables simultaneously, are virtually non-existent. Information on the influence of additives on *some* of these variables is available, but because of the incompleteness of the data, the conclusions have only very limited validity. For example, Prasad and Ghosh, in a long series of papers³ studied the effect of urea, glucose, ethanol and other additives on the stability of ferric oxide-

and manganous oxide-sols. They could not interpret their results quantitatively because no simultaneous double layer studies were carried out. This work also suffered from the lack of control of pH (H^+ and OH^- are the potential-determining ions for these oxides) and from the use of a relatively arbitrary stability criterion. Mukherjee and Chatterjee⁴ studied the influence of alcoholic additives on the ζ -potential of glass and silver iodide. This could have been a very useful attempt to deal with factor (iv), but as neither pH nor pI were controlled, the outcome was meaningless.

Krahtovil *et al.*⁵ studied the stability of silver bromide sols in mixed media. One of their conclusions was that there is an effect due to the *nature* of the additive, in that the stability was not solely a function of ϵ but depended also on the chemical composition of the admixture used to obtain this value of ϵ . As different additives have different adsorbing powers and hence influence the diffuse double layer potential ψ_d in different ways, this result points also to the necessity of considering the double layer composition. A similar remark can be made with respect to a subsequent paper on the stability of silver bromide sols in mixtures of water and methylpropionamide or N,N-dimethylformamide.⁶ It is likely that the modification of the inner part of the double layer by the additive is also one of the reasons why Nand and Ghosh⁷ found that the stability of positively charged ferric oxide-sol depended less strongly on ϵ than predicted by the DLVO-theory.^{8,9}

The dielectric constant of the medium occurs also in the Bjerrum distance of ion association.¹⁰ The Yugoslavian School of colloid science has used this feature to describe counterion association with the colloid surface.¹¹ Consequently, this model encompasses only the effect of the additive on the inner part of the double layer, the Stern-layer.

It is concluded that a more systematic treatment of the effect of the medium is needed.

BASIC CONSIDERATIONS

As the starting point for a more fundamental discussion of medium effects it is expedient to use the following equation for the critical concentration (c_c) of coagulation by electrolytes,

$$c_c = \text{const.} \frac{\epsilon^3 [\tanh(z e \psi_d / 4kT)]^4}{A_{1(2)}^2 z^6} \quad (1)$$

This equation follows from the DLVO theory.¹² It holds true for flat or spherical double layers, assuming that at $c = c_c$ the maximum in the potential energy of interaction vs distance curve is zero. For flat and spherical double layers, the constant in (1) has a different value. $A_{1(2)}$ is the effective Hamaker constant of particle 1 in medium 2. In the numerator we have written ψ_d for the interaction potential because, in the underlying picture, only the overlap of the diffuse parts of the double layers contributes to stability. ψ_d is the potential of the outer Helmholtz plane (OHP). It is lower than the inner Helmholtz plane (IHP) potential ψ_s , and under conditions of coagulation it is very much lower than the surface potential ψ_0 . For practical purposes ψ_d may be replaced by the electrokinetic or ζ -potential.

Although (1) requires modification if more sophisticated interaction models are chosen, it is useful in pointing out certain basic features. Upon the addition of a solute, c_c is bound to vary because of variations of ϵ , ψ_d and $A_{1(2)}$, i.e. factors (i), (iv) and (ii) respectively of the previous section. Since (1) is not a rate equation, it does not contain the viscosity coefficient.

The direct effect of ϵ is very strong. It stems from the occurrence of ϵ in the Poisson equation and ultimately reflects the extent of screening of the surface charge.

How strongly the effective Hamaker constant varies with composition depends on the nature of the additive. According to the classical ("microscopic") theory

$$A_{1(2)} = (\sqrt{A_{11}} - \sqrt{A_{22}})^2 \quad (2)$$

where A_{11} is the Hamaker constant for the attraction between particles 1 in vacuum and A_{22} that for the solvent.¹³ The extent of change of $A_{1(2)}$ upon alteration of the solvent properties depends on the extent of change of A_{22} and on the difference between A_{11} and A_{22} . For water, A_{22} is probably of the order of 5×10^{-20} J,^{14,15} and not too different from A_{22} for organic liquids. For most metals and inorganic substances, A_{11} is considerably higher, and certainly large in comparison with the variation in A_{22} . Consequently, for sols of these substances the medium effect on $A_{1(2)}$ is only minor. However, for organic sols (e.g. emulsions) the difference between A_{11} and the variation in A_{22} tends to be smaller. Hence, for such systems the variability of $A_{1(2)}$ is a factor that requires due attention. For reference purposes, tables of Hamaker constants are available in literature.^{16,17}

If for the solvent mixture dispersion data $\epsilon''_2(\omega)$ become available over the entire relevant composition and frequency ranges, effective Hamaker constants can also be evaluated according to the macroscopic theory.^{18,19} Strictly speaking, according to the macroscopic theory Hamaker constants are no longer constant but are somewhat dependent on distance. However, in the case of unretarded attractive forces (that is the case to which eqn (1) applies) the relation between $A_{1(2)}$ and the two imaginary dielectric constants $\epsilon''_1(\omega)$ and $\epsilon''_2(\omega)$ reads to good approximation,

$$A_{1(2)} = \frac{3h}{8\pi^2} \int_0^\infty \frac{[\epsilon_1(i\xi) - \epsilon_2(i\xi)]^2}{[\epsilon_1(i\xi) + \epsilon_2(i\xi)]^2} d\xi, \quad (3)$$

with

$$\epsilon(i\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega. \quad (4)$$

In (3), h is Planck's constant. Equation (4) is the so-called Kramers-Kronig equation, altering the complex dielectric

permittivity as a function of a real frequency ω into a real dielectric permittivity as a function of an imaginary frequency $i\xi$. At present, there is not enough experimental material available to check the conclusions about the influence of additives on $A_{1(2)}$ arrived at above using the microscopic theory. No drastically different outcome is expected since usually the results given by the two approaches tend to differ by not more than some tenths of a per cent. For a recent discussion on the macroscopic theory and its application, see.²⁰

The effect of additives on ψ_d is the compounded result of a number of processes occurring at the particle-solution interface. Actually, a great deal of the stability problem is centred around the assessment of ψ_d . In eqn (1), ψ_d virtually occurs to the fourth power because under ordinary conditions of flocculation $ze\psi_d/4kT < 1$. Hence, the hyperbolic tangent may to a very good approximation be replaced by the first term of its series expansion ($\tanh x \sim x$). It follows that instead of (1), may be written,

$$c_c = \text{const}' \frac{\epsilon^3 \psi_d^4}{A_{1(2)}^2 z^2}. \quad (5)$$

The strong sensitivity of stability towards ψ_d , together with the fact that ψ_d cannot independently be measured indicates that a major part of the problem really lies here. The magnitude of ψ_d is affected by adsorbing additives for the following reasons.

(i) Upon adsorption the point of zero charge (p.z.c.) shifts. The consequence is a shift of ψ_0 at constant activity of the potential-determining electrolyte. The shift of ψ_0 induces a concomitant shift of ψ_d .

(ii) Due to adsorption, the Stern-layer capacitance $\epsilon_s \epsilon_0 / d$ changes, or, in other words, at given ψ_0 there is a variation of the surface charge σ_0 and hence in the sum of the Stern-charge σ_s and the diffuse charge σ_d . Generally this leads also to an alteration of ψ_d .

(iii) Adsorption of foreign molecules in the Stern-layer alters the amount of specifically adsorbed counterions and hence at given σ_0 the distribution of charge over the Stern-layer and the diffuse layer is altered. This again leads to a change of ψ_d .

To sum up, even in the relatively simple interaction picture leading to eqn (1), the effect of additives is a multiparameter feature, and interpreting simple double-logarithmic plots of c_c as a function of ϵ can never serve as a serious basis for testing this aspect of the DLVO-theory.

Before proceeding to the interpretation of some of the experiments it is appropriate to make a few notes in connection with the picture developed above.

(1) Equation (1) seems to predict a proportionality between c_c and z^{-6} . This has led to much discussion in literature on the so-called Schulze-Hardy rule, invoking the argument that Schulze and Hardy found the inverse sixth power law, and that the validity of this law was in support of the DLVO-theory. It is now known that these arguments are incorrect. Basically, the theory predicts an inverse quadratic relationship (see eqn 5), but since specific adsorption tends to increase with z , in practice a higher power must be expected, although general rules cannot be given. In connection with our theme it can be noted that the functionality of z probably depends on the nature of the additive, on which the amount of specific adsorption also depends. Moreover, it must be said that in their papers Schulze²¹ and Hardy²² did not mention the sixth power law, they merely observed a very strong dependence of the coagulation concentration on the counterion valency.

(2) Equation (1) is based on a relatively simple double-layer picture and numerous improvements have been proposed in the literature, e.g. by accounting more explicitly for the sphericity of the colloid particles. These improvements, dealing with the diffuse double-layer part only, usually lead again to the factor $\epsilon^3/A_{i(2)}^2$. They are relatively uninteresting for our purpose since the screening in bulk phases is already properly understood. This is also supported by negative adsorption measurements, corroborating the Gouy-Chapman distribution in non-aqueous solvents.²³ One of the major improvements in interaction theory involving the non-diffuse part of the double layer is that it takes into account that the repulsive and attractive free energies, G_R and G_A respectively, do not operate over the same distance. G_A acts from surface to surface, but G_R covers only the diffuse parts of the double layers, which is shorter by 2Δ , where Δ is (almost) identical to the Stern-layer thickness. The introduction of this difference leads to a factor $\exp(2\kappa\Delta)$ in c_c where κ is the reciprocal Debye length. For our purpose it is important to realize that Δ depends on the nature of the additive; there is also a minor effect of ϵ on κ . Upon addition of the additive, Δ may undergo a systematic variation, reflecting the amount of additive adsorbed.^{24,25}

(3) The issue of interaction at constant charge or at constant potential²⁶ is of relevance for our subject matter. The basic question is: to what extent do the various parts of the double layer relax during particle encounter? It is generally accepted that the surface charge does not adapt itself fast enough to the variation dictated by equilibrium conditions during the approach of a second particle, but remains virtually constant during a Brownian encounter. On the other hand, the diffuse part of the double layer has a very short time of relaxation. Hence, it may be taken to be continuously in equilibrium during the penetration of the double layer by an approaching particle. In the author's opinion, the major problem is the relaxation of the Stern-layer. Very little information is available on this and systematic studies of relaxation processes in non-diffuse double layers are highly desirable. In the next section a suggestion will be made for dealing with this problem in real systems. The specific relevance for the subject matter of the effect of additives is that, if upon particle encounter, desorption of nonaqueous molecules from the surfaces occurs, this would lead to another contribution to the free energy of interaction.²⁷

(4) If the dielectric constant of the solvent becomes much lower than that of water it is especially necessary to pay due attention to the possibility of ion association. Because of association the valency z of the ionic species can be reduced, with an ensuing pronounced effect on c_c because of the quadratic relationship (5).

(5) In cases where no double layer data are available it is customary to replace ψ_d by ζ . This procedure is probably justified but it is not without complications. In the first place the calculation of ζ from mobilities²⁸ requires knowledge of conductivity data in the medium under consideration and it works only for special geometries. Secondly, the relation between ψ_d and ζ is by no means established. The collected evidence of the last decade points towards little difference between ζ and ψ_d in water but the corresponding information in mixed media is scarce. Much work remains to be done in this area.

(6) Finally it must be pointed out that the coagulation concentration, c_c , is not the most adequate measure of stability since it is based on a rather arbitrary interaction criterion. Experience has shown that for a given sol the

measured value of c_c can vary as much as 30% depending on the method of measurement. Measuring the rate of flocculation over a wide range of electrolyte concentrations around the coagulation concentration is preferable, even if this involves the introduction of kinetic considerations. Direct particle counting²⁹ is the best technique of assessing the extent of aggregation, but if the required apparatus is not available, turbidimetric measurement after rapid mixing of sol and electrolyte (e.g. in a stopped flow spectrophotometer) is an acceptable second choice.

SOME EXPERIMENTS WITH SILVER IODIDE SOLS

Silver iodide (AgI) sols in mixed media is one of the few systems for which the information on double layer composition and sol stability is fairly complete. Some properties in water-butanol (BuOH) and in water-ethylene glycol (EG) will be discussed below. The major difference between BuOH and EG is that BuOH has a limited solubility in water, whereas EG can be mixed with water in all proportions. The consequence is that BuOH exerts its influence almost solely through its adsorption on the particles whereas EG affects stability both by adsorption and by altering ϵ .

Double layer studies on AgI in the presence of BuOH and EG can be found in literature.^{30,31} Stability studies in water-BuOH mixtures are also available.²⁴ Below, some major conclusions of this work are discussed together with hitherto unpublished stability work in EG-water mixtures³² with the purpose of illustrating some of the issues of the preceding section.

In Figs. 1 and 2 the surface charge σ_0 as a function of pAg is given for silver iodide in water-BuOH and water-EG mixtures, respectively. The graphs apply to 10^{-1} M KNO_3 solutions which is close to the coagulation concentration.

Qualitatively, the two sets of curves are very similar. In both cases it is observed that:

- (i) the slopes of the curves decrease with increasing content of the organic admixture;
- (ii) for different concentrations of the organic substance all curves pass through a common intersection point;
- (iii) the point of zero charge (p.z.c.) shifts to the left, i.e. towards the positive side, with increasing concentration of the added compound.

All these observations reflect processes occurring in the

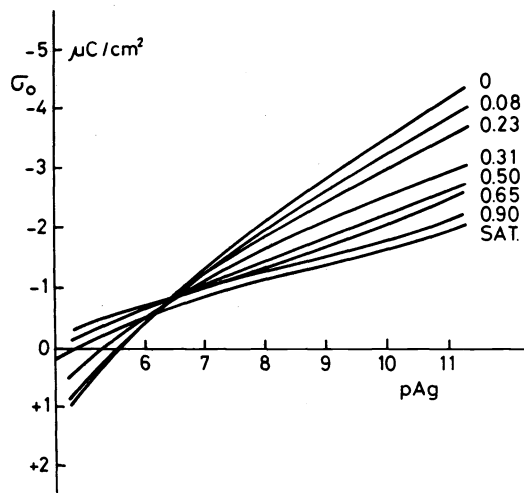


Fig. 1. Double layer on silver iodide in water-butanol mixtures. The butanol concentration (M) is indicated. Electrolyte: 10^{-1} M KNO_3 , temp 20°C .

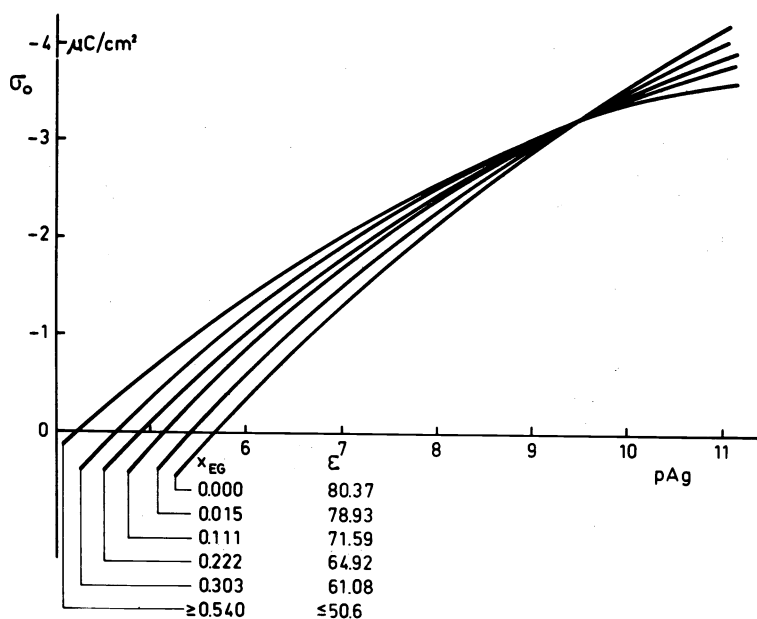


Fig. 2. Double layer on silver iodide in water-ethylene glycol mixtures. The mole fraction x_{EG} of the ethylene glycol and the relative dielectric constant ϵ of the medium are indicated. Electrolyte: 10^{-1} M KNO_3 , temp $20^\circ C$.

non-diffuse part of the double layer, since in 10^{-1} M carrier electrolyte the diffuse contribution is negligible. The following interpretation has been offered for these features.^{30,31}

The decrease of the slope is, except for a constant, identical to a decrease of the differential double layer capacitance $C = d\sigma_0/d\psi_0$ because by virtue of Nernst's law,

$$d\psi_0 = -2.3 \frac{RT}{F} dpAg. \quad (6)$$

This capacitance decrease can have three causes: a lowering of the relative dielectric constant ϵ_s in the Stern-layer, an increase of the thickness of this layer, or desorption of specifically adsorbed counterions by the organic molecule.²⁴ Without further information it is not possible to decide which causes are the most important in a particular case.

The common intersection point can be shown to be the pAg—or, for that matter, the σ_0 value—where the adsorption of the organic substance is a maximum.

The shift of the p.z.c. reflects the replacement of water dipoles (originally preferentially with their negative sides towards the surface) by BuOH or EG dipoles (both with their hydrocarbon moiety towards the surface).

Quantitatively, some differences between BuOH and EG can be observed. Generally speaking, BuOH is more surface active because of its lesser solubility, so that, at given solution concentration, it produces more drastic alterations of σ_0 than EG does. (In a saturated solution of BuOH, its mole fraction is only about 0.02.) For EG above $x_{EG} = 0.54$, addition of EG has no further effect on the Stern-layer, although the dielectric constant of the medium can be reduced still further. In other words, here we have conditions where it is essentially the medium effect that is important. On the other hand, with BuOH it is almost solely the surface properties that are affected. There are also quantitative differences between the greatest attainable p.z.c. shift and between the locations of the common

intersection points. We shall not discuss them here, they reflect the mode of adsorption of the organic substance.³¹⁻³⁵ Neither shall we pay attention to differences between the shapes of the σ_0 vs pAg curves.

The relation between double-layer data and stability is of special interest to our theme. BuOH and EG as additives influence the stability of AgI sols in a very different manner. This difference is clearly demonstrated in a plot of the coagulation concentration as a function of the composition of the medium. Figure 3 gives results of two series of experiments. In this figure, the composition axes are scaled so that comparison is facilitated. In both cases the c_c -values have been derived from rates of coagulation. The two sets of experiments were carried out with different batches of sols and using somewhat different equipment for mixing and measuring (Vitatron spectrophotometer for BuOH, Durum stopped-flow spectrophotometer for EG). It is generally known that under different conditions of measurement and with different sols the absolute values of the coagulation concentration can vary by various tens of per cents. The difference between the measuring points in pure water may be due to this. However, it is the trends of c_c with composition that count and here interesting differences manifest themselves that are obviously beyond experimental error.

For BuOH the curve has a maximum. Recalling that ϵ of the medium is hardly affected, this maximum suggests the occurrence of two opposing processes in the Stern-layer. The downward trend beyond the maximum is easily accounted for by the general decrease of total double-layer charge, at fixed pAg, as indicated in Fig. 1. The initial increase of c_c is more difficult to explain. The simultaneous increase of stability and decrease of surface charge are seemingly in conflict. In our opinion, the increase of c_c is attributable to desorption of specifically adsorbed ions from the Stern-layer. This would render the double layer relatively more diffuse and hence the sol more stable. The conclusion underlines that it is the charge- and potential distribution over the non-diffuse and diffuse double layer parts that counts for stability. The desorption feature could

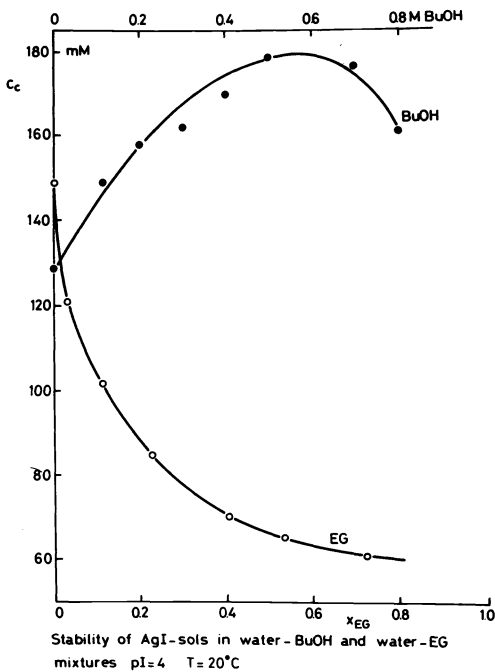


Fig. 3. Coagulation concentrations of AgI-sols for KNO_3 in water-butanol and water-ethylene glycol mixtures, calculated from rate of coagulation measurements temp 20°C .

only be discovered by combining data from entirely different sources (σ_0 and c_c data) measured under (almost) identical conditions.

As compared with BuOH, EG affects stability to a much greater extent through its influence on the medium. At least qualitatively the gradual decrease of c_c with increasing x_{EG} fits into the gradual lowering of ϵ upon increasing the bulk EG-content. However, this cannot be the entire story as Fig. 4 shows. Here, c_c is plotted as a function of ϵ . In media rich in water, the ϵ^3 -law (eqn 5) is corroborated but at higher EG concentrations c_c depends less strongly on ϵ . This does not mean that the DLVO-theory fails. It shows that there are other variations besides that of ϵ . For the water-EG mixture, $A_{1(2)}$ remains virtually constant over the entire x_{EG} range,³⁶ hence it is apparently ψ_d that changes. At first sight a variable ψ_d seems in conflict with the conclusion made in connection with Fig. 2 that for $x_{\text{EG}} \geq 0.54$, σ_0 is independent of x_{EG} . Even if one accepts that the distribution of the charge is more or less independent of x_{EG} (this is probably so for KNO_3),²⁵ ψ_d is a variable as can be shown by the following argument. The charge σ_d in the diffuse part of the double layer is related to ϵ and ψ_d . For a flat double layer and a symmetrical z - z electrolyte, this relation reads

$$\sigma_d = (8\pi n \epsilon_0 kT)^{1/2} \sinh\left(\frac{ze\psi_d}{2kT}\right) \quad (7)$$

where n is the salt concentration counted as the number of molecules per unit volume and ϵ_0 is the permittivity of free space. Corresponding equations for spherical double layers can be written. It follows from (7) that, at constant concentration and constant σ_d , ψ_d must increase if ϵ decreases. This explains why in the region of high x_{EG} c_c depends less strongly on ϵ than the third power. Actually, this argument applies also to the range of low x_{EG} , although there it is compounded by the variability of σ_0 and the

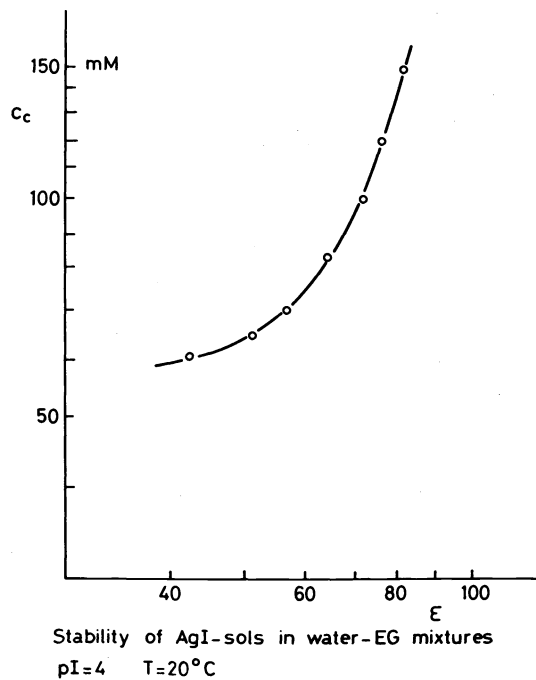


Fig. 4. Coagulation concentrations of AgI-sols for KNO_3 in water-ethylene glycol mixtures, plotted as a function of the bulk dielectric constant temp 20°C .

ensuing variability of σ_d . The two influences on ψ_d apparently compensate each other so that fortuitously the ϵ^3 power law applies. The conclusion is that the applicability of the ϵ^3 dependence in itself does not yet support the DLVO-theory, neither does its non-applicability disprove it.

Just as in the BuOH-case, the combined double-layer and stability data in water-EG mixtures can be advantageously utilized to obtain important information on the effect of EG on the composition of the Stern-layer.^{25,32} This has been done by considering not merely c_c -values but also the rates of coagulation over a wide range of salt concentrations. It was assumed that the Stern-layer did not relax during particle encounter ($\sigma_0 + \sigma_s$ constant if σ_s is the Stern-layer charge) but did come to equilibrium with the electrolyte during the time of mixing (10^{-3} s in aqueous solutions but longer in mixtures with EG because of the higher viscosity). Consequently, in the adsorption isotherm, $\sigma_s(c)$ for c the equilibrium electrolyte concentration had to be substituted. This procedure enabled the calculation of ψ_d as a function of c and x_{EG} , and from that the counterion adsorption isotherm could be established. It was found that for K^+ the degree of occupancy in the Stern-layer, measured as $\theta = \sigma_s/\sigma_0$, was almost independent of x_{EG} , and equal to 0.65–0.70, whereas for Ba^{2+} θ increased from ca. 0.85–0.95 for $x_{\text{EG}}=0$ to 1. The adsorption could be well described by a modified Langmuir equation (Stern-equation) with a specific free energy of adsorption of ca. $4kT$ for K^+ (independent of x_{EG}) and ca. 6 – $8kT$ for Ba^{2+} (increasing with x_{EG}).²⁵ All of this could be established without invoking electrokinetic data.

SOME GENERAL CONSEQUENCES

The procedure of combining double layer and stability data not only provides valuable information on the composition of the Stern-layer, it has also some bearing on

the directions in which future developments of stability studies are to be sought.

To that end it is necessary to assess the consequences of a compensation by up to 95% of the surface charge by specific adsorption in the Stern-layer. Less than 5% of the double-layer charge actually participates in interaction. A similar argument applies to the potential. For AgI sols, under conditions of coagulation, ψ_d is usually less than 10% of ψ_0 . The first general conclusion is obviously that the Stern-layer must be the main object of investigation. Endless improvements of the diffuse double layer theory cannot lead to significant progress.

If the assumption of no relaxation of the Stern-layer upon collision is correct (this still needs to be proved), the effective surface charge "seen" by interacting particles is identical to σ_d and of the order of a few tenths of $\mu\text{C cm}^{-2}$. One may wonder whether, for such a low charge, smeared-out double-layer models still apply. For $0.1 \mu\text{C cm}^{-2}$ the mutual distance between the charges is on the average of the order of 10^{-6} cm whereas the double layer thickness (taking the Debye length κ^{-1} as its yardstick) is about 10^{-7} cm, i.e. lower by an order of magnitude. The consequence is that interpretation must be sought in terms of discrete charge interaction theories, of which already some examples are available in literature (see e.g. Ref. 37). In addition it must not be overlooked that with bivalent counterions each monovalent surface charge, compensated by a bivalent counterion, actually counts as a positive site, so that the entire Stern-layer behaves as a mosaic-like charge array with only a slight net excess of negative charge.

The second consequence is that the assumption of homogeneity of the surface charge becomes questionable. Apart from any natural heterogeneity of the particle surface, thermal fluctuations could become important. Their relative magnitude can be estimated in the following way. The average number \bar{N}_i of a species i adsorbed per unit surface area follows from the grand canonical partition function Ξ of the adsorbate³⁸ as

$$\bar{N}_i = RT \left(\frac{\delta \ln \Xi}{\delta \mu_i} \right)_{\sigma_0, T} \quad (8)$$

where μ_i is its chemical potential. From this, the extent of fluctuation can be derived to be

$$\sigma_{N_i}^2 \equiv \bar{N}_i^2 - \bar{N}_i^2 = RT \left(\frac{\delta \bar{N}_i}{\delta \mu_i} \right)_T \quad (9)$$

In this equation $\bar{N}_i(\mu_i)$ is essentially the adsorption isotherm. Some model is required to evaluate Ξ and derive the precise functionality $\bar{N}_i(\mu_i)$ for the situation under consideration where an adsorption deficit is wanted (viz. \bar{N}_i must represent the average number of surface charges that is *not* compensated for by adsorption in the Stern-layer). Discussing orders of magnitude and assuming \bar{N}_i and μ_i to be roughly proportional one finds that the standard deviation σ_{N_i} is of the order of $\bar{N}_i^{1/2}$, μ_i being of the order of RT . Hence, the relative spread σ_{N_i}/\bar{N}_i is of the order of $\bar{N}_i^{-1/2}$. If the area of the particle that is effective in interaction is such that, say, some ten charges participate, the fluctuation of this charge is as high as ca. 30%. The consequence is that in fact one has to cope with a statistical average over individual pairs of *hetero*-interactions. In this context it is noted that a similar problem has already been dealt with by Levine.³⁹

A third general consequence is that a reappraisal is

wanted of the classical idea of interaction by ordinary, i.e. translatory, diffusion. If the interacting particles bear (during the time of encounter) non-relaxing mosaic-like potential fields, tangential approach without rotation of the particles does not automatically bring the double layers in the most favourable overlap position. However, such a position can be assumed by rotatory adjustment of the particles. The rate of rotatory displacement of a surface charge is of the same order of magnitude as that for translatory motion, as can be argued as follows.

For translatory diffusion of a spherical particle with radius a , during a time t , the mean square displacement is,

$$\overline{\Delta X^2} = \frac{kT}{3\pi\eta a} \cdot t \quad (10)$$

For rotatory diffusion the mean square of the angle of rotation $\overline{\Delta\phi^2}$ is, in radians

$$\overline{\Delta\phi^2} = \frac{kT}{4\pi\eta a^3} \cdot t \quad (11)$$

The distance ΔS of a point on the surface of this sphere traversed during t sec follows from $\Delta S = a\Delta\phi$ or

$$\overline{\Delta S^2} = a^2 \overline{\Delta\phi^2} \quad (12)$$

Hence we obtain for the ratio of rotatory and translatory displacement of a point charge on the surface of the particle

$$\frac{(\overline{\Delta S^2})^{1/2}}{(\overline{\Delta X^2})^{1/2}} = \left(\frac{3}{4} \right)^{1/2} = 0.866 \quad (13)$$

which is not far from unity. It means that rotation of colloid particles upon interaction deserves attention in the future development of the kinetics and hydrodynamics of particle aggregation, especially in those cases where the nature of the potential field around the particles promotes rotation at the expense of translation.

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