MUTUAL ANTAGONISM IN A 1–1 PLUS 2–1 ELECTROLYTE MIXTURE

AN EXACT SOLUTION OF THE POISSON–BOLTZMANN EQUATION

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Summary

The stability properties of two charged plate-like parallel colloidal particles immersed in an aqueous solution containing a 1–1 plus 2–1 electrolyte mixture is considered where the first-mentioned ion is the coagulating one. It is found that the relation between the coagulating concentrations of the two binary electrolytes is such as to predict a very weak mutual antagonism, even in the absence of a Stern inner region, when the plate potentials are above 250 mV at 25°C.

I. Introduction

Some colloidal systems can become unstable on addition of a sufficient amount of an inorganic electrolyte. When such a system is suspended in water it is called a hydrophobic sol since, on addition of the electrolyte, the particles of the sol crowd together forming a large loose cluster which eventually settles on the bottom. This phenomenon is referred to as flocculation or coagulation. In the present work we are only concerned with the coagulation of two parallel plate-like particles of infinite extent and so the stability of the sol depends on the electrical interactions of the two electric double layers at the plate surfaces, which provide a repulsive force, and on the van der Waals–London dispersion forces, which Hamaker (1937) proved to be an attraction inversely proportional to the fourth power of the plate separation. A study of these types of stability problems lead Derjaguin and Landau (1941) and Verwey and Overbeek (1948) to a criterion for the stability of binary electrolytes in an aqueous medium. This theory will subsequently be referred to as the DLVO theory of colloid stability.

Now most colloidal systems contain a mixture of electrolytes and, since even a small amount of an electrolyte component can have an appreciable effect on the stability of the solution, the extension to electrolyte mixtures is of considerable importance. In a recently published review article Levine, Mingins, and Bell (1967) have discussed the phenomenon of coagulation of two binary electrolytes in a hydrophobic colloid. They indicated that the coagulating concentrations of such mixtures can be divided into four distinct types, the behaviour of which are shown in Figure 1. Curve 1 is the simplest in that it shows a linear relation indicating the additivity of the coagulation action of the two electrolyte components. In this case the electrolytes behave independently in so far as the stability is concerned. On the other hand, the further possibilities are superadditivity (curve 2), sensitization (curve 3), and mutual antagonism (curve 4). A common feature of the first three effects is that less electrolyte of one type is required when electrolyte of the second type is present, and this is predicted by the classical DLVO stability theory. According to

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Glazman (1963), the phenomenon of mutual antagonism in the coagulation of a hydrophobic sol is a very complex matter having more than one source. Among possible factors are, for example, ion pairing as discussed by Levine and Bell (1965), the effect of the activity coefficient of counter-ions in the dispersion medium (see Kruyt 1935; Vester 1935), and the discrete-ion effect for adsorbed counter-ions as discussed by Levine and Bell (1965).

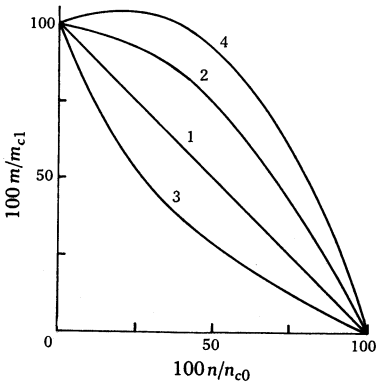

Fig. 1.—Typical coagulation curves in an electrolyte mixture showing the relation between the coagulating concentrations of 2–1 and 1–1 electrolytes added to a hydrophobic sol. The 100% mark for the 2–1 and 1–1 electrolytes are the molecular densities m_{c1} and n_{c0} for which there is coagulation of pure electrolyte. The curves are schematic and show:
1, additivity
2, superadditivity
3, sensitization
4, mutual antagonism

Although it is widely assumed that mutual antagonism cannot be explained by the DLVO theory alone, Glazman, Dykman, and Strel'tova (1958), Barboi (1965), and the present paper use this theory to show that weak antagonism can occur at high plate potentials. According to Barboi (1965) simple additivity should occur in electrolyte mixtures when the plate potential is below about 70–100 mV at 25°C. Jones (1966) found this conclusion to be correct for a 1–1 plus 2–2 electrolyte mixture, although the experiments of Lepin and Bromberg (1939) exhibited antagonism for such mixtures. The difference between these two results can be explained in terms of the discrete-ion effect associated with the electric double layer at the surface of the electrolyte. This phenomenon is discussed at length by Levine and Suddaby (1951, 1952) and Levine and Bell (1960, 1963, 1965). Hence, it is the potential at, what is referred to as, the outer Helmholtz plane rather than the potential at the plate surface that is relevant to the stability of the sol. The effects of this innermost Stern Layer will be neglected in the present paper, for its inclusion leads to much complication and it would have the effect of increasing the potential at which mutual antagonism first appears.

One of the many difficulties of the theory is associated with the type of mathematical approximations used to calculate the free energy of the colloidal system. Thus, expansions for the free energy as found by Levine and co-workers are based on the assumption that either the plate potential is high or the plate separation is small compared with the plate thickness. Jones (1966) showed that the high potential approximation is not satisfactory for a pure 1–1 plus 2–1 electrolyte mixture for, although the first term in the series predicts mutual antagonism effects, the second term in the series does not. This is not surprising because of the extremely weak antagonism that exists at infinite plate potential (see Fig. 2). It is the purpose of this paper to find an exact solution of the problem that is valid at high and infinite plate potentials.

II. Potential Distribution

The determination of the electrical forces between two parallel plate colloidal particles of infinite extent and immersed in an aqueous electrolyte requires a theory of the electric double layer at the plane surfaces. The earliest theory of such a layer was developed by Gouy (1910, 1917) and Chapman (1913) but was for a single plane interface. In the case under consideration here there exists two such double layers that interact and influence each other to a larger or smaller extent depending on the plate separation. In the present problem it will be assumed that the two plates are positively charged to a potential Ψ_0 and that they are of infinite thickness at a separation $2h$. The ions in the diffuse layer adjacent to the interfaces will be treated as point charges immersed in a continuous, homogeneous medium characterized only by its dielectric constant ϵ.

We shall suppose that the medium between the plates contains n_i^0 ions of species i ($i = 1, 2, 3, \ldots$) per unit volume in the bulk of the electrolyte solution (i.e. n_i^0 is the number of ions of type i corresponding to zero potential). Then, if the valency of the ions of type i is denoted by z_i, its charge is $z_i e$, where e is the magnitude of the electronic charge, and the condition of electrical neutrality becomes

$$e \sum_{(i)} n_i^0 z_i = 0 . \tag{1}$$

Now at any point in the diffuse layer near the plates the mean volume density of ions of type i is given by the Boltzmann equation

$$n_i = n_i^0 \exp(-z_i e\Psi/kT) , \tag{2}$$

where Ψ is the mean electrostatic potential at the point in question, k is the Boltzmann constant, and T is the absolute temperature.

The one-dimensional Poisson equation can now be written in the form

$$\mathrm{d}^2\Psi/\mathrm{d}x^2 = -4\pi\rho(x)/\epsilon , \tag{3}$$

where $\rho(x)$ is the charge per unit volume residing in the electrolyte of dielectric constant ϵ and $\Psi = \Psi(x)$ is the potential distribution at distance x ($|x| \leqslant h$) measured from the median plane at right angles to the two plates, whose separation is $2h$. It follows from equations (2) and (3) that, for a mixture of 1–1 and 2–1 valency types where the divalent ion has charge opposite to that at the surface of the plates,

$$\begin{aligned} \rho(x) &= e \sum_i n_i z_i \\ &= en\{\exp(-e\Psi/kT) - \exp(e\Psi/kT)\} + 2em\{\exp(-e\Psi/kT) - \exp(2e\Psi/kT)\} , \end{aligned} \tag{4}$$

where n and m are the densities of the dissociated molecules in the 1–1 and 2–1 electrolytes respectively. This equation forms the basis of the Gouy–Chapman theory of the electric double layer. The "thickness" of this layer is usually represented by the Debye–Hückel length $1/K$, where

$$K = (4\pi e^2/\epsilon kT) \sum_{(i)} n_i^0 z_i^2 = (8\pi e^2/\epsilon kT)(n+3m) \tag{5}$$

in the case under consideration.

We can now integrate equation (3) but before doing so it is convenient to introduce the parameters

$$\theta = Kx, \qquad y = \exp(-e\Psi/kT), \qquad y_0 = \exp(-e\Psi_0/kT), \qquad y_m = \exp(-e\Psi_m/kT),$$

where Ψ_m is the potential at the median plane. The first integral may then be expressed in the form

$$dy/d\theta = -Q(y), \tag{6}$$

where

$$Q(y) = (y_m - y)^{\frac{1}{2}}[c/3y_m + \{(1-c)/y_m + c/3y_m^2\}y - (1-\tfrac{1}{3}c)y^2]^{\frac{1}{2}} \tag{7}$$

and

$$c = 3m/(n+3m),$$

c being a measure of the relative concentrations and having the value 0 for a pure 1–1 electrolyte and the value 1 for a pure 2–1 electrolyte. Now

$$Q^2(0) = \tfrac{1}{3}c \geqslant 0 \qquad \text{and} \qquad Q^2(1) = \tfrac{1}{3}(1-y_m^{-2})\{(3-c)y_m + c\} \leqslant 0,$$

so that $Q(y)$ has three real zeros y_m, p_1, and p_2 which must satisfy the inequalities

$$p_2 < 0 < y_0 \leqslant y \leqslant y_m < 1 < p_1.$$

In fact

$$\left.\begin{matrix} p_1 \\ p_2 \end{matrix}\right\} = \frac{3(1-c)y_m + c \pm [\{3(1-c)y_m + c\}^2 + 4c(3-c)y_m^3]^{\frac{1}{2}}}{2(3-c)y_m^2},$$

where the positive sign corresponds to p_1 and the negative sign to p_2. Finally we can integrate (6) to obtain

$$Kh = \int_{y_0}^{y_m} dy/Q(y). \tag{8}$$

This last equation is an expression for the potential at the median plane and may be written in terms of Legendre elliptic integrals of the first kind. Thus, if we make the substitutions

$$k_1 = \{(y_m - p_2)/(p_1 - p_2)\}^{\frac{1}{2}} \qquad \text{and} \qquad \sin\phi = \{(y - p_2)/(y_m - p_2)\}^{\frac{1}{2}}, \tag{9}$$

equation (8) becomes

$$Kh = 2\Delta F(\phi_0, k_1)\{(p_1 - p_2)(1-\tfrac{1}{3}c)\}^{-\frac{1}{2}},$$

with

$$\sin\phi_0 = \{(y_0 - p_2)/(y_m - p_2)\}^{\frac{1}{2}} \tag{10}$$

and

$$\Delta F(\phi, k) \equiv F(\tfrac{1}{2}\pi, k) - F(\phi, k),$$

where $F(\phi, k)$ is the elliptic integral of the first kind as defined in Byrd and Friedman (1954).

In the case of a pure 1–1 electrolyte ($c = 0$) this reduces to

$$Kh = 2y_m^{\frac{1}{2}}\Delta F(\phi_0, y_m),$$

a result obtained by Langmuir (1938). On the other hand, for a pure 2–1 electrolyte ($c = 1$)

$$Kh = \{6/(p_1 - p_2)\}^{\frac{1}{2}}\Delta F(\phi_0, y_m),$$

in agreement with Corkill and Rosenhead (1939) and Levine and Suddaby (1951).

III. General Expression For Interaction Energy

The classical electrostatic energy per unit area of the two plates is, according to Böttcher (1952), given by

$$E_e(h) = (\epsilon/4\pi)\int_0^h (\mathrm{d}\Psi/\mathrm{d}x)^2\,\mathrm{d}x,$$

which on applying equations (6) and (7) leads to

$$E_e(h) = (\epsilon K/4\pi)(kT/e)^2\int_{y_0}^{y_m} Q(y)/y^2\,\mathrm{d}y. \tag{11}$$

In order to express this in terms of the elliptic integrals we shall integrate (11) by parts and then make the transformations (9) and (10). It follows that

$$E_e(h) = (\epsilon K/4\pi)(kT/e)^2\{Q(y_0)/y_0 + \tfrac{1}{2}(3-c)I_1 - a_2 I_2 + \tfrac{1}{2}(1-c)I_3\},$$

where

$$a_2 = (1-y_0^{-1})^2\{(1-\tfrac{1}{3}c)y_m + \tfrac{1}{3}c\} + 2 - c > 0,$$

$$I_1 = \int_{y_0}^{y_m} y/Q(y)\,\mathrm{d}y$$

$$= 2p_1\{(p_1-p_2)(1-\tfrac{1}{3}c)\}^{-\frac{1}{2}}\Delta F(\phi_0, k_1) - 2\{(p_1-p_2)/(1-\tfrac{1}{3}c)\}^{\frac{1}{2}}\Delta E(\phi_0, k_1),$$

$$I_2 = \int_{y_0}^{y_m} \mathrm{d}y/Q(y) = \{(p_1-p_2)(1-\tfrac{1}{3}c)\}^{-\frac{1}{2}}\Delta F(\phi_0, k_1),$$

and

$$I_3 = \int_{y_0}^{y_m} \mathrm{d}y/yQ(y) = (2/p_2)\{(p_1-p_2)(1-\tfrac{1}{3}c)\}^{-\frac{1}{2}}\Delta\Pi(\phi_0, s, k_1),$$

with $E(\phi, k)$ and $\Pi(\phi, s, k)$ the Legendre elliptic integrals as defined by Byrd and Friedman (1954),

$$\Delta E(\phi, k) = E(\tfrac{1}{2}\pi, k) - E(\phi, k), \qquad \Delta\Pi(\phi, s, k) = \Pi(\tfrac{1}{2}\pi, s, k) - \Pi(\phi, s, k),$$

and

$$s = (p_2 - y_m)/p_2 > 1 \qquad \text{as} \qquad p_2 < 0.$$

Combining the above equations, we obtain

$$E_e(h) = (\epsilon K/4\pi)(kT/e)^2\{Q(y_0)/y_0 - 3w\,\Delta E(\phi_0, k_1)\} + \{(3-c)p_1 - 2a_2\}w^{-1}\Delta F(\phi_0, k_1)$$
$$+ (1-c)(p_2 w)^{-1}\Delta\Pi(\phi_0, s, k_1),$$

where

$$w = (p_1-p_2)(1-\tfrac{1}{3}c)^{\frac{1}{2}}. \tag{12}$$

When we take the limit as $h \to \infty$, $y_m \to 1$ and hence equation (7) becomes

$$Q(y) \to (1-y)f(y) \qquad \text{with} \qquad f(y) = \{\tfrac{1}{3}c + (1-\tfrac{1}{3}c)y\}^{\frac{1}{2}}.$$

The electrostatic energy corresponding to infinite plate separation then becomes

$$E_e(\infty) = (\epsilon K/4\pi)(kT/e)^2\int_{y_0}^{1}\{(1-y)/y^2\}f(y)\,\mathrm{d}y$$

$$= (\epsilon K/4\pi)(kT/e)^2\{-3 + (2+1/y_0)f(y_0) - G\}, \tag{13}$$

where

$$G = \tfrac{1}{2}(1-c)(\tfrac{1}{3}c)^{-\frac{1}{2}}\log\left(\frac{\{1+(\frac{1}{3}c)^{\frac{1}{2}}\}\{f(y_0)-(\frac{1}{3}c)^{\frac{1}{2}}\}}{\{1-(\frac{1}{3}c)^{\frac{1}{2}}\}\{f(y_0)+(\frac{1}{3}c)^{\frac{1}{2}}\}}\right). \tag{14}$$

Again considering the limiting cases, we have for a pure 1–1 electrolyte

$$E_e(\infty) = (\epsilon K/4\pi)(kT/e)^2 2\{y_0^{\frac{1}{2}} + y_0^{-\frac{1}{2}} - 2\}, \tag{15}$$

which is in agreement with the formula of Levine and Suddaby (1951); while for a pure 2–1 electrolyte we have

$$E_e(\infty) = (\epsilon K/4\pi)(kT/e)^2[\{(1+2y_0)^3/3y_0^2\}^{\frac{1}{2}} - 3],$$

which agrees with Levine and Suddaby (1952). Each of these equations is used in the following work.

According to Levine (1951) and Levine and Bell (1960), the free energy associated with the electric double layers of the two plates can be expressed by the equation

$$F(h) = -E_e(h) - 2\int_0^h P - P_0 \, dx, \tag{16}$$

where $P-P_0$ is the difference in the ideal (osmotic) pressures due to the thermal motion of the ions at any point x in the diffuse layers and hence

$$P - P_0 = kT(n+m) - kT(n^0 - m^0), \tag{17}$$

where n^0 and m^0 are the densities of the dissociated molecules corresponding to zero potential. Now, since the field at the median plane is zero, the double layer force of repulsion per unit area can be expressed in the form

$$P_e(h) = -\tfrac{1}{2}(\partial F/\partial h)_{\Psi_0} = kT(n+m-n^{(m)}-m^{(m)}), \tag{18}$$

where the derivative with respect to h is taken at constant plate potential Ψ_0 and $n^{(m)}$ and $m^{(m)}$ are the molecular densities at the median plane $x = 0$. The first form was derived by Verwey and Overbeek (1948) and the second independently by Frumkin and Gorodetskaja (1938) and Langmuir (1938). From the Boltzmann equation and (16), (17), and (18) it now follows that

$$F(h) = -2E_e(h) - 2hP_e(h),$$

and the double layer pressure is

$$P_e(h) = kT\{n(y_m + 1/y_m - 2) + m(1/y_m^2 + 2y_m - 3)\}.$$

The interaction energy is therefore

$$I(h) = F(h) - F(\infty) = -2E_e(h) - 2hP_e(h) + 2E_e(\infty),$$

because $hP_e(h) \to 0$ as $h \to 0$.

In the DLVO theory of colloidal stability we must take into account the van der Waals attraction between the plates as well. If the thickness of the plates is large compared with h, the energy of attraction per unit area takes the particularly simple form

$$W(h) = -A/48\pi h^2,$$

where the constant A depends on the material of the plates and on the dispersion

medium in which the plates are immersed. The derivation of this result is to be found in Derjaguin and Landau (1941) and Verwey and Overbeek (1948). Following these authors we find that the resultant interaction energy per unit area of the two plates is

$$U(h) = F(h) + W(h) - F(\infty).$$

IV. Coagulation Conditions

In the DLVO theory the limit of stability of a colloid is assumed to be reached when the force of repulsion just exceeds the van der Waals attractive forces between the plates and this leads to the coagulation conditions

$$\partial U(h)/\partial h = 0 \qquad \text{and} \qquad \partial^2 U(h)/\partial h^2 = 0.$$

However, it is felt that the criterion of a zero potential barrier between the plates describes the threshold of rapid coagulation and this criterion will be used here. Thus, the coagulation conditions are

$$U(h) = 0 \qquad \text{and} \qquad \partial U(h)/\partial h = 0.$$

Since the double layer force of repulsion per unit area is given by equation (18), it appears that the second coagulation condition may be written in the form

$$P_e(h) = A/48\pi h^3$$

while the first becomes

$$-W(h) = hP_e(h) = I(h) = -2E_e(h) - 2hP_e(h) + 2E_e(\infty),$$

that is,

$$3hP_e(h) = -2E_e(h) + 2E_e(\infty).$$

If we introduce the Debye–Hückel parameter and use equation (18) then the coagulation conditions take on the form

$$K = (6\epsilon/A)(kT/e)^2(Kh)^3 a(y_m, c), \tag{19a}$$

where

$$a(y_m, c) = (1-c)(y_m + y_m^{-1} - 2) + \tfrac{1}{3}c(y_m^{-2} + 2y_m - 3); \tag{19b}$$

and

$$3Kha(y_m, c) + 4(\epsilon K/4\pi)(kT/e)^2 h(y_0, y_m, c) = 0, \tag{20a}$$

where

$$E_e(h) - E_e(\infty) = (\epsilon K/4\pi)(kT/e)^2 h(y_0, y_m, c). \tag{20b}$$

The second of these conditions (20) leads to a determination of the potential Ψ_m at the median plane, while the first condition (19) gives the values of the concentrations m and n corresponding to coagulation at a given y_0.

One of the difficulties associated with these formulae is that the electrostatic energies $E_e(h)$ and $E_e(\infty)$ each contain a term that behaves like $\{\frac{1}{2}(1-c)/\frac{1}{3}c\}\log y_0$ at high plate potential (i.e. at $y_0 = 0$) where mutual antagonism is most likely to occur. To overcome this difficulty we shall now develop a formula appropriate to infinite plate potential.

V. Expansions at High Plate Potential

From equations (12), (13), (14), and (20a) it follows that

$$h(y_0, y_m, c) = Q(y_0)/y_0 - 3w\Delta E(\phi_0, k_1) + \{(3-c)p_1 - 2a_2\}w^{-1}\Delta F(\phi_0, k_1) + \{(1-c)/wp_2\}\Delta\Pi(\phi_0, s, k_1) + 3 - (2+y_0^{-1})f(y_0) + G.$$

In order to find the solution corresponding to infinite plate potential, it is necessary to evaluate

$$\lim_{y_0 \to 0} h(y_0, y_m, c).$$

The proof of the existence of this limit is given in the next section. Since a considerable amount of algebra is required to obtain this limit only the result is given here.

To begin, we make the transformations

$$\operatorname{cosec}^2 B = (s^2 - k_1)/(s^2 - 1),$$

$$\sin^2\phi_1 = (1 - \sin^2\phi_0)/(1 - k_1^2 \sin^2\phi_0) \to \sin^2 B \quad \text{as} \quad y_0 \to 0,$$

and

$$k_1^* = (1 - k_1^2)^{\frac{1}{2}}.$$

Ultimately we find that, in the notation of Byrd and Friedman (1954),

$$\lim_{y_0 \to 0} h(y_0, y_m, c) = 3 - (3c)^{\frac{1}{2}} + (3c)^{\frac{1}{2}}/p_1 - 3wE(B, k_1) + \{(3-c)p_1 - 2a_2 + (1-c)/p_1\}F(B, k_1)\, w^{-1} - (1-c)(\tfrac{1}{3}c)^{-\frac{1}{2}} F(B, k_1)\, Z(B, k_1) + \tfrac{1}{2}(1-c)(\tfrac{1}{3}c)^{-\frac{1}{2}} \log\left(\frac{\{1 + (\frac{1}{3}c)^{\frac{1}{2}}\}^2 K(k_1) \sin 2\omega(B)}{\pi w (\frac{1}{3}c)^{\frac{1}{2}}}\right) + (1-c)(\tfrac{1}{3}c)^{-\frac{1}{2}} \sum_{i=1}^{\infty} \frac{\sin^2 2i\omega(B)}{i\{\exp(4iq) - 1\}}, \tag{21}$$

where

$$Z(B, k) = E(B, k) - E(k)\, F(B, k)/K(k), \tag{22}$$

$$\omega(B) = \pi F(B, k_1)/2K(k_1), \tag{23}$$

and

$$q = \pi K(k_1^*)/2K(k_1).$$

We are now in a position to calculate the coagulation relations corresponding to infinite plate potential. The results of this calculation are shown in Figure 2.

Equation (21) has also been used by Jones (1966), who developed the formula further by finding the term of order y_0. He showed that the extra term is such that it fails to predict the phenomenon of antagonism at high plate potentials. This is not surprising since the degree of mutual antagonism is extremely small at infinite potential. This type of expansion in terms of elliptic functions is quite a well-established technique and was developed in a series of papers by Levine and co-workers (Levine 1951; Levine and Suddaby 1951, 1952; Levine and Bell 1960, 1962, 1963, 1965) and by Barboi (1965). It has the advantage that tables of elliptic integrals may be used in the numerical work; however, with the advent of electronic

computers a more direct approach to the numerical work can be undertaken. With this fact in mind we shall use an alternative method that is valid at high and infinite plate potentials.

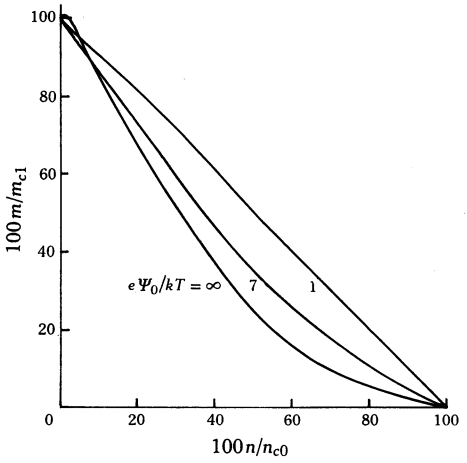

Fig. 2.—Coagulation curves for a 2–1 plus 1–1 electrolyte mixture in a hydrophobic sol at potentials $e\Psi_0/kT$ of 1, 7, and ∞. At infinite potential (∞) very weak antagonism occurs with a maximum at $m/m_{c1} = 1{\cdot}00015$, $n/n_{c0} = 0{\cdot}00181$; at intermediate potential (7) there is sensitization; at small potential (1) there is superadditivity.

VI. An Exact Solution at High Plate Potentials

The crux of the problem lies in the fact that the difference $E_e(h)-E_e(\infty)$ as defined by equations (11) and (13) has a singular point at $y_0 = 0$. To overcome this complication we can make use of the identity

$$\{Q(y)-(1-y)f(y)\}/y^2 = -(1-y_m^{-1})^2\{\tfrac{1}{3}c+(1-\tfrac{1}{3}c)y_m\}/\{Q(y)+(1-y)f(y)\},$$

so that

$$h(y_0, y_m, c) = -(1-y_m^{-1})^2\{\tfrac{1}{3}c+(1-\tfrac{1}{3}c)y_m\}\left(\int_{y_0}^{y_m}\frac{dy}{Q(y)+(1-y)f(y)}+\int_{y_m}^{1}\frac{(1-y)f(y)}{y^2}\,dy\right). \tag{24}$$

In this form both the integrals are well behaved at infinite plate potential but it is no longer possible to expand the integrals in terms of Legendre elliptic integrals.

If we now make use of the second coagulation condition given by (20) then we can find the potential at the median plane (given in terms of y_m) as a function of y_0 and c. This relationship is shown in Figure 3. Finally, the coagulation curve (Fig. 2) can be found by using the first coagulation condition (19) which can be more conveniently written in the forms

$$n = 3\epsilon^3(kT)^5(1-c)(Kh)^6\,a(y_m, c)/2\pi A^2e^6 \tag{25a}$$

or

$$m = 3\epsilon^3(kT)^5c(Kh)^6\,a(y_m, c)/2\pi A^2e^6\,. \tag{25b}$$

VII. Results

The computations are carried out in two stages. Firstly we solve equation (19a) for the potential at the median plane (i.e. for y_m) and we then use this value to calculate the densities of the dissociated molecules as given by (25a) and (25b).

As a check on the numerical work, the coagulation curve corresponding to infinite plate potential is obtained from the two sets of equations (24)–(25) and (20a). These methods give precisely the same result. On the other hand, at finite plate potentials, the author computed the gradient of the coagulation curves by the method of finite differences and compared this with an analytical expression found by a direct differentiation (the equations so found are extremely complicated and are not given here). The two methods agree and enable us to calculate the critical potential above which mutual antagonism occurs. One important point not mentioned so far is that equation (21) has an apparent singularity at $c = 0$ and thus it was found convenient to use equation (15) in the appropriate place. This intricate method of calculation was considered necessary in view of the very weak antagonism corresponding to infinite plate potential.

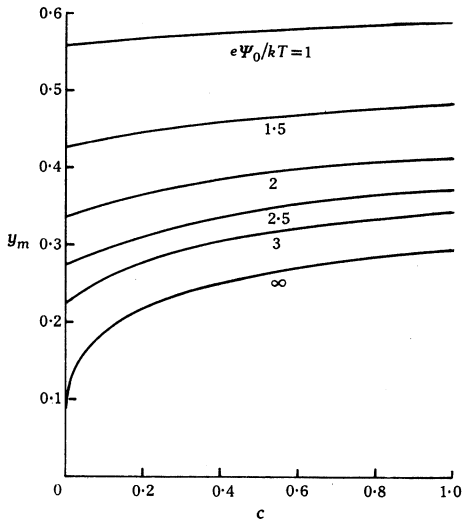

Fig. 3.—Variation in potential at the median plane, Ψ_m, given as a function of the coagulating concentrations. The curves show values of $y_m = \exp(-e\Psi_m/kT)$ versus $c = 3m/(n+3m)$ at plate potentials $e\Psi_0/kT$ of 1(0·5)3 and ∞.

In the determination of n and m from equations (25a) and (25b) there is an unknown factor

$$d = 3\epsilon^3(kT)^5/2\pi A^2e^6 .$$

Thus, for a pure 1–1 electrolyte we may write

$$n = n_{c0} = da(y_m, 0)\,(Kh)^6 , \qquad \text{at} \quad c = 0 ,$$

while for a pure 2–1 electrolyte we may write

$$m = m_{c1} = da(y_m, 1)\,(Kh)^6 , \qquad \text{at} \quad c = 1 .$$

These data were used to draw the coagulation curves of Figure 2, which relate n/n_{c0} to m/m_{c1} at various plate potentials.

On examination of Table 1 it appears that, at infinite plate potential, the value of y_m at $c = 0$ is precisely the square of the value of y_m at $c = 1$. This is to be expected since there would be twice as much charge at the median plane for a pure

2–1 electrolyte as there would be for a pure 1–1 electrolyte. However, at finite potentials not all the negative ions are absorbed on the plate surface and this simple relation cannot hold.

The last column of Table 1 shows the variation in the gradient of the coagulation curve at $c = 1$ with plate potential. It is seen that the slope is small and positive for potentials above $5{\cdot}9140\,kT$ ($\simeq 250$ mV at 25°C) and hence that a very weak antagonism exists for these potentials.

TABLE 1

VALUES OF MOLECULAR CONCENTRATIONS AND GRADIENT OF COAGULATION CURVE AT $c = 1$ FOR A PURE 1–1 AND PURE 2–1 ELECTROLYTE AT VARIOUS PLATE POTENTIALS

The data show that a very weak antagonism, even in the absence of the Stern inner region, can occur at potentials above $5{\cdot}9140\,kT$

$e\Psi_m/kT$	y_m at $c = 0$	n_{c0}/d	y_m at $c = 1$	m_{c1}/d	$(n_{c0}/m_{c1})\mathrm{d}m/\mathrm{d}n$
∞	0·0870	176·3084	0·2949	2·5552	0·1634
7	0·1045	136·4571	0·2959	2·5354	0·0839
6·5	0·1095	127·0268	0·2965	2·5226	0·0520
6	0·1159	115·9305	0·2976	2·5016	0·0078
5·9140	0·1172	103·8758	0·2978	2·4974	0·0000
5·5	0·1242	103·1665	0·2992	2·4676	−0·0520
5	0·1350	88·8928	0·3020	2·4125	−0·1308
4·5	0·1491	73·4869	0·3064	2·3249	−0·2304
4	0·1678	57·5773	0·3136	2·1883	−0·3497
3·5	0·1927	42·0542	0·3251	1·9824	−0·4833
3	0·2265	27·9667	0·3432	1·6882	−0·6209
2·5	0·2729	16·3519	0·3716	1·3012	−0·7490
2	0·3378	7·9458	0·4155	0·8524	−0·8545
1·5	0·4294	2·9003	0·4836	0·4241	−0·9297
1	0·5597	0·6385	0·5892	0·1267	−0·9744

A further calculation shows that the gradient of the coagulation curve at $c = 0$ is less than -1 for potentials *below* about 135 mV at 25°C. It follows that there is sensitization for potentials in the range 135–250 mV and that for smaller potentials there is superadditivity. The predicted antagonism seems generally much weaker than that observed experimentally by Watelle-Marion (1960); nevertheless, the above analysis does show that a crude model which neglects the effects of the Stern inner region can exhibit mutual antagonism. This phenomenon is, therefore, a characteristic of the electrolyte mixture which is emphasized by the electric boundary layer.

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