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Abstract

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ON ION ANTAGONISM IN THE COAGULATION OF LYOPHOBIC SOLS BY ELECTROLYTES

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In our preceding work (1) it was shown theoretically that, in the coagulation of lyophobic sols by a mixture of two symmetrical electrolytes of the type 1—1 + 2—2, an effect of synergism should be observed over almost the entire range of their concentrations. At the same time, the supposition was expressed that in the case of other combinations of electrolytes the results of the calculation might prove to be quite different; in particular, for example, when such a mixture of electrolytes is added to a colloidal solution in which the side ion of the first component of the pair (possessing a weaker coagulating action) is multivalent, the possibility is not excluded of even the opposite effect—antagonism.

The present investigation was undertaken in order to verify the correctness of the indicated assumption. We carried out calculations analogous to the preceding ones (1), extending them to the case of coagulation of a sol by a mixture of electrolytes of the type 1_2—2+2—2 (here the first ion of each of the electrolytes is assumed to be the coagulating ion, and the second to be charged with the same sign as the colloidal particles).

Let a unit volume of solution contain n_1 positive ions and $2n_1$ negative ions of the first electrolyte, with charges respectively equal to $2ez$ and ez. Let, in addition, the solution contain a further n_2 positive and negative ions of the second electrolyte, each possessing charges of $2ez$. We shall assume, as in work (1), that the colloidal particles of the sol under consideration, whose stability is being investigated here, are sufficiently large (in comparison with the effective dimensions of the ionic atmosphere), and that two particles interacting with one another may be approximately represented in the form of infinite parallel planes. We denote the distance between these planes by h, and the electrostatic potential at an arbitrary point of the solution volume by Ψ. To determine Ψ, the equation is

$$\frac{d^2\Psi}{dx^2} = \frac{8\pi e}{\varepsilon}\left[n_1 \exp\left(\frac{ez\Psi}{\theta}\right) - n_1 \exp\left(\frac{2ez\Psi}{\theta}\right) + 2n_2 \operatorname{sh}\left(\frac{2ez\Psi}{\theta}\right)\right], \qquad (1)$$

analogous to equations (1) and (2) of work (^{1}). Here the previous notation is retained: e is the elementary charge, z is the smallest valency of the ions in the given mixture, ε is the dielectric constant of the solution, and $\theta = kT$.

The first integral of equation (1) determines the square of the field strength. Repeating the considerations and transformations given in work (^{1}), we write the expressions for the distance h and for the force P, acting on a unit surface of the plates, in the form

$$h = \sqrt{\frac{\varepsilon\theta}{2\pi e^2}} \int_{u_0}^{\infty} \frac{du}{\left[n_1\left(2u^3 - 2u^2 u_0 - u^2 u_0^{-2} + 1\right) + n_2\left(u^4 - u^2 u_0^2 - u^2 u_0^{-2} + 1\right)\right]^{1/2}}, \tag{2}$$

$$P = \theta\left[n_1\left(2e^{u_0} + e^{-u_0}\right) + 3n_2\left(\operatorname{ch} u_0 - 1\right)\right]. \tag{3}$$

For convenience, in expressions (2) and (3), instead of Ψ the dimensionless potential $u = \exp(ez\Psi/\theta)$ has been introduced. It is assumed that at the surface of the plates (at $x = \pm h/2$) the potential is positive and equal to u_1, while in the plane of symmetry ($x = 0$) it is equal to u_0. As before (^{1}), it is assumed that the sol is highly charged and, consequently, $u_1 \gg 1$. This justifies the infinite value of the upper limit of integral (2).

It is essential that not the entire range of possible concentrations n_1 and n_2 is of equal interest for our problem. In the preceding paper (^{1}) it was specially emphasized that, in the case of symmetrical electrolytes, only in the initial part of the curve $n_{2c} = n_{2c}(n_{1c})$ does there occur a certain excess over the straight line of additivity. It should be assumed that also in the case considered here of unsymmetrical electrolytes, the same initial part of the dependence curve $n_{2c} = n_{2c}(n_{1c})$ is of greatest interest. Therefore, in order to simplify the subsequent calculations, it is expedient from the outset to regard n_1 as an infinitely small parameter and, in the expansion in n_1, everywhere to retain only expressions linear with respect to it. In this approximation (with $f = n_1/n_2$) the right-hand side of formula (2) is represented by the difference of two integrals

$$h = \sqrt{\frac{\varepsilon\theta}{2\pi e^2 n_2}}\left[I_1 - \frac{f}{2} I_2\right], \tag{4}$$

where

$$I_1 = \int_{u_0}^{\infty} \frac{du}{(u^4 - u^2 u_0^2 - u^2 u_0^{-2} + 1)^{1/2}} = \frac{u_0}{u_0^2 + 1} K(k), \tag{5}$$

$$
\begin{aligned}
I_2 &= \int_{u_0}^{\infty} \frac{2u^3 - 2u^2u_0 - u^2u_0^{-2} + 1}{(u^4 - u^2u_0^2 - u^2u_0^{-2} + 1)^{3/2}}\, du \\
&= \frac{2u_0^4}{u_0^4 - 1}\left\{\frac{1}{u_0^2+1}F(\varphi,k) + \frac{1}{u_0^2-1}\left[E(\varphi,k) - 1\right]\right\} + \\
&\quad + \frac{u_0}{u_0^4-1}\left[\frac{u_0^4 - 2u_0^3 - 1}{2(u_0^2+1)}K(k) - \frac{u_0^4 - 2u_0^3 - 1}{2(u_0^2-1)}E(k) - \frac{2u_0}{u_0^4-1}\right].
\end{aligned}
\tag{6}
$$

Here $K(k)$ and $E(k)$ are complete elliptic integrals, respectively of the first and second kinds, and $F(\varphi,k)$ and $E(\varphi,k)$ are incomplete integrals of the first and second kinds. The argument φ and modulus k are determined by the relations

$$
\varphi = \operatorname{arc\,tg}\left(\frac{u_0^2+1}{u_0^2-1}\right)^{1/2}, \qquad k = \frac{2u_0}{u_0^2+1}. \tag{7}
$$

To determine the "critical" value h_c and, at the same time, the "critical" values of the concentrations n_{2c} and n_{1c}, we shall use the Derjaguin-Landau equation (^{2}), $(h/P)(dP/dh) = -3$, which in our case is conveniently written in the form

$$
h\frac{dP}{du_0} = -3P\frac{dh}{du_0}. \tag{8}
$$

Substituting expressions (2), (3) into equation (8) and taking (4)–(7) into account, we obtain an equation whose root directly determines the "critical" value of u_0. This equation has the form:

$$
\frac{3}{2}E(k) - K(k) = f\Phi(u_0), \tag{9}
$$

where $\Phi(u_0)$ is a function of u_0, not given here because of its cumbersome form. For $f = 0$, equation (9) becomes the well-known Derjaguin-Landau equation (2):

$$
\frac{3}{2}E(k) - K(k) = 0. \tag{10}
$$

The root of equation (10), k_0, is equal to 0.77394. According to formula (7), it corresponds to the value $u_{00} = 2.1103$.

For f different from zero, the solution of equation (9) may be sought in the form

$$
u_0 = u_{00} + u_{01}. \tag{11}
$$

If (11) is substituted into equation (9) and it is taken into account that u_{00} satisfies equation (10), then (retaining only terms linear with respect to f), after simple transformations we obtain, for determining u_{01}, an equation of the form:

$$\left[-\frac{u_{00}^2-1}{2u_{00}(u_{00}^2+1)}K(k_0)+\frac{u_{00}^4-10u_{00}^2+1}{2u_{00}(u_{00}^4-1)}E(k_0)\right]u_{01}=f\Phi(u_{00}). \tag{12}$$

Hence it turns out that $u_{01} = 0.1379f$. Consequently, the full value of the root of equation (9), accurate to terms linear with respect to f, is equal to:

$$u_0 = 2.1103 + 0.1379f. \tag{13}$$

According to formulas (2) and (3), for u_0 equal to expression (13), the numerical values of the "critical" distance h_c and the "critical" force P_c are equal to:

$$h_c = \sqrt{\frac{\varepsilon\theta}{2\pi e^2 n_2}}(0.7540 - 0.1765f), \tag{14}$$

$$P_c = n_2\theta(2.678 + 1.998f). \tag{15}$$

If we now equate the repulsive force P_c to the force Q of mutual molecular attraction of flat colloidal particles located at a distance h_c from one another:

$$Q = \frac{\pi A}{6h_c^3}, \tag{16}$$

(A is the constant of molecular attraction), then, in the same way as in papers ([1,2]), we arrive at an equation of the form

$$\alpha + \beta f = B\sqrt{n_{2c}}, \tag{17}$$

from which it is easy to find the "critical" concentration n_{2c} of the second electrolyte. According to formulas (14)–(16), the constants entering into equation (17) have the following values:

$$\alpha = 1.148; \qquad \beta = 0.05053; \qquad B = \frac{\pi^2 A e^3}{3\varepsilon\theta^2}\sqrt{\frac{2\pi}{\varepsilon\theta}}. \tag{18}$$

Finally we find

$$n_{2c} = \frac{1}{B^2}(\alpha^2 + 2\alpha\beta f); \qquad n_{1c} = \frac{\alpha^2}{B^2}f. \tag{19}$$

At the point $n_{1c} = 0$, the derivative dn_{2c}/dn_{1c} is equal to:

$$\frac{dn_{2c}}{dn_{1c}} = \frac{2\beta}{\alpha} = 0.088. \tag{20}$$

The positive sign of the derivative dn_{2c}/dn_{1c} means that, upon coagulation of a sol by a mixture of two electrolytes of the type 1_2—2 + 2—2, the phenomenon of antagonism should be observed.

Thus, as the calculation shows, the regularities of coagulation of lyophobic sols by mixtures of electrolytes of the type 1—1 + 2—2 and, respectively, 1_2—2 + 2—2 are qualitatively opposite to one another: in the first case synergism is theoretically substantiated, while in the second the theory leads to a sharply pronounced antagonism.

The results obtained can be interpreted on the basis of Pauli' s ideas (^{3}) concerning the "discharge effect" of colloidal particles, which, as is known, is due to the electrostatic influence of the auxiliary ions of the coagulating electrolytes. At the same time, the calculation data are also qualitatively confirmed by some direct measurements carried out by us. Thus, for example, in studying the coagulation of a rosin hydrosol by a mixture of the electrolytes $KCl + MgSO_4$, a distinctly pronounced synergism was observed, and only in the very initial part of the curve (at low concentrations of KCl) was there a quite insignificant excess above the additivity straight line. On the contrary, in the case of coagulation of the same sol by a mixture of $K_2SO_4 + MgSO_4$, the phenomenon of antagonism was found, expressed to a fairly strong degree, and at all ratios of the indicated electrolytes the curve lay above the additivity straight line.

The whole body of literature material relating to the problem of coagulation of lyophobic sols by mixtures of electrolytes, as well as our own data on this question, indicate that the nature of antagonism is not the same in different cases. There apparently exist two types of antagonism in the coagulation of lyophobic colloids: 1) antagonism between coagulating ions, associated with competition for adsorption sites on the surface of colloidal particles, and 2) antagonism due to the mutual electrostatic influence of ions in the volume of the solution and in the electric field of the colloidal particles.

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Note: Figure translations are in progress. See original paper for figures.