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Abstract

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ON THE COAGULATING ACTION OF MIXTURES OF ELECTROLYTES ON LYOPHOBIC SOLS. THE INFLUENCE OF COUNTERION ADSORPTION

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The present communication, unlike the preceding ones ([1], [2]), in which highly charged sols were considered, is devoted to elucidating the influence of adsorption phenomena on the regularities of coagulation of lyophobic colloids by mixtures of electrolytes. In this work we investigate one of the limiting cases of coagulation: when, as a result of adsorption of counterions, the potential of the colloidal particles is lowered so strongly that the expression for the stability criterion of weakly charged sols ([3]) becomes applicable,

$$\psi_a^2/\varkappa \gg a_1 = \text{const.} \tag{1}$$

Here $\varkappa$ is the reciprocal thickness of the ionic atmosphere in the solution; ψ_a is regarded by us as the potential at the boundary of the adsorption layer of the colloidal particles.

To simplify the calculations, a number of assumptions is introduced:

1. The particle concentration of the colloidal system is assumed to be so small that the additional adsorption of potential-determining ions, occurring upon introduction into the sol of indifferent electrolytes ([4]), practically does not change their concentration in the solution. Owing to this, upon addition of coagulating electrolytes the value of the potential ψ_0 at the surface of the disperse phase remains constant.
2. It is assumed that adsorption of ions of the coagulating electrolytes obeys the simplest Langmuir equation

$$\Gamma_i' = \Gamma_\infty \frac{C_i'/b_i}{1 + \sum_{i=1}^{n} C_i'/b_i}, \tag{2}$$

where Γ_i' is the adsorption of the i-th ion from a mixture of electrolytes*; C_i' is the concentration of the i-th ion in the solution; b_i and Γ_∞ are constants of the

Langmuir equation.

Further, only adsorption of counterions is taken into account, and adsorption of indifferent ions bearing the same sign of charge as the colloidal particles is disregarded ([5], [6]).

3. As a first approximation it is postulated that the potential ψ_a at the boundary of the adsorption layer varies linearly with the magnitude of adsorption of the coagulating ions of the electrolyte Γ,

$$\psi_a = \psi_0 - k\Gamma z, \tag{3}$$

* Here and below, all quantities marked with a prime refer to the case when coagulation is effected by a mixture of electrolytes; absence of primes corresponds to coagulation by individual electrolytes.

where z is the valence of the counterions and k is a constant at the given ionic strength of the solution.

Denoting the densities of the electric charges, in electronic units (after addition of the coagulating electrolyte to the sol), at the boundary of the adsorption layer and, respectively, on the surface of the disperse phase by Q_a and Q_0, we can obviously write the equality

$$Q_a = Q_0 - \Gamma z. \tag{4}$$

If one takes into account that, at $\Gamma z = Q_0$, $\psi_a = 0$, then, using formulas (3) and (4), it is easy to obtain the expression

$$Q_a/Q_0 = \psi_a/\psi_0. \tag{5}$$

It follows from this that relation (3) is equivalent to the assumption of an insignificant influence of counterion adsorption on the value of the capacitance of the electrical double layer as a whole.

Since the capacitance of the double layer is inversely proportional to its thickness, or to the radius of the ionic atmosphere ($1/\chi$), which, in turn, is inversely proportional to the square root of the ionic strength of the solution J [7], then

$$Q_0/\psi_0 = Q_a/\psi_a = \alpha J^{1/2}, \tag{6}$$

where α is a certain constant.

In the case of coagulation of a sol by a mixture of two electrolytes, combining equality (1) with expressions (4) and (6) gives

$$\alpha\psi_0(J_c')^{1/2} - \alpha a^{1/2}(J_c')^{3/4} = \Gamma_{1c}' z_1 + \Gamma_{2c}' z_2, \tag{7}$$

where the subscript c, here and below, denotes the "critical" values of the corresponding quantities.

It is useful to transform the equation obtained somewhat. To this end, let us write equality (7) for each of the electrolytes under consideration separately and determine the values of the constants $\alpha a^{1/2}$ and $\alpha\psi_0$. Substituting the expressions found into equation (7), we obtain

$$\begin{aligned} &\frac{(J_{1c}/J_{2c})^{3/4} - (\Gamma_{1c}z_1)/(\Gamma_{2c}z_2)}{(J_{1c}/J_{2c})^{3/4} - (J_{1c}/J_{2c})^{1/2}}\,(J_c'/J_{2c})^{1/2} \\ -&\frac{(J_{1c}/J_{2c})^{1/2} - (\Gamma_{1c}z_1)/(\Gamma_{2c}z_2)}{(J_{1c}/J_{2c})^{3/4} - (J_{1c}/J_{2c})^{1/2}}\,(J_c'/J_{2c})^{3/4} = \frac{\Gamma_{1c}'z_1 - \Gamma_{2c}'z_2}{\Gamma_{2c}z_2}. \end{aligned} \tag{8}$$

Already in this form, equation (8) can be used to calculate the curve of the coagulating action of a mixture of two electrolytes, if the coagulating concentrations of each of the individual electrolytes and the adsorbabilities (i.e., the constants b_i in the Langmuir equation) of both coagulating ions are known. It must be noted, however, that the general character of the regularities of the coagulating action of electrolyte mixtures can also be established without resorting to a complete calculation of the curve. For this it is sufficient to determine the values of the quantities

$$\Phi = \lim_{C_1'=0} (dC_2')/(dC_1'),$$

$$F = \lim_{C_2'=0} (dC_2')/(dC_1'),$$

which characterize the course of the curve at its ends.

It is more convenient to differentiate equation (8) if, using formulas (1), (4), and (6), it is reduced to the form

$$\frac{1}{1-K_{2c}}\left(\frac{J_c'}{J_{2c}'}\right)^{1/2} - \frac{K_{2c}}{1-K_{2c}}\left(\frac{J_c'}{J_{2c}'}\right)^{3/4} - \frac{\Gamma_{1c}'z_1 + \Gamma_{2c}'z_2}{\Gamma_{2c}z_2}, \tag{9}$$

where $K = \psi_a/\psi_0$.

In differentiating equation (9) it should be borne in mind that the coagulating concentration of the electrolyte is related to the adsorbability of the counterion by the relation

$$\frac{(1-K_{1c})K_{1c}^2}{\Gamma_{1c}z_1} = \frac{(1-K_{2c})K_{2c}^2}{\Gamma_{2c}z_2} = \text{const}, \tag{10}$$

which is obtained by combining equality (1), represented in the form $\psi_a^2 = \text{const} \cdot {J'}^{1/2}$, with expressions (4) and (6). Without giving here the rather cumbersome formulas for the limits of the derivatives of Φ and F, we note only one very essential circumstance. The indicated expressions contain, as variables, only the quantities K_1, K_2, z_1, and z_2. Thus, by assigning various values of the potential drop in the adsorption layer for each of the electrolytes separately, it appears possible to calculate the values of the limits of the derivatives of Φ and F. Calculations carried out in this way showed that the derived equation reflects all the types of regularities of coagulation of lyophobic sols by mixtures of electrolytes usually observed experimentally—antagonism, superadditivity, and synergism.

To carry out a complete calculation of the entire curve of the coagulating action of a mixture of two electrolytes, it is necessary to have data on the numerical values of the four variables entering the corresponding equation. Of these, however—in view of relation (10)—only three quantities can be assigned arbitrarily. The numerical value of the constant in formula (10) can be estimated on the basis of the following considerations.

The numerator of the left-hand side of this equality has a maximum at the value $K = 2/3$. Assuming that among electrolytes with monovalent coagulating ions there must necessarily be one that will satisfy the condition $K = 2/3$, we find that in this case

$$\text{const} = \frac{4/27}{\Gamma}.$$

If we investigate only such coagulation phenomena in which, in the critical state of the sol, the filling of the surface of the colloidal particle by counterions is limited by the condition

$$\Gamma \leqslant \frac{1}{2}\Gamma_\infty, \tag{11}$$

then we obtain

$$\text{const} \cdot \Gamma_\infty = \gamma \geqslant \frac{8}{27}. \tag{12}$$

It is easy to verify that condition (11) corresponds to coagulation that occurs when, in the process of adding electrolyte to the sol, the value of the potential of the colloidal particles decreases to some (critical) value depending on the

Fig. 1. Change in the potential of a colloidal particle as a function of the concentration of electrolyte in solution (the scale along the abscissa axis, beginning with the value equal to unity, is reduced by a factor of 100)

Figure 1: Fig. 1. Change in the potential of a colloidal particle as a function of the concentration of electrolyte in solution (the scale along the abscissa axis, beginning with the value equal to unity, is reduced by a factor of 100)

ionic strength of the solution. Indeed, from relations (4) and (6) one obtains the formula

$$\psi_a = \psi_0 \left(1 - \frac{\Gamma z}{\beta {J'}^{1/2}}\right), \tag{13}$$

expressing the dependence of the potential at the boundary of the adsorption layer on the electrolyte concentration in the solution. Analysis of this equation shows that,

that the curve $\psi_a = f(C)$ passes through a minimum, whose position corresponds to the electrolyte concentration $C = b$ (Fig. 1). Consequently, restriction (11) means that in the present work we investigate coagulation only in the region of the descending branch of the curve in Fig. 1—at electrolyte concentrations $C < b$.

In view of the fact that the value γ, as is clear from expression (10), does not depend on the nature of the electrolyte, inequality (12) remains valid for any electrolytes. All calculations of the curves of the coagulating action of various electrolyte mixtures were carried out by us at the value $\gamma = 8/27$, since for $\gamma > 8/27$ the regularities of coagulation remain qualitatively unchanged.

Fig. 1. Change in the potential of a colloidal particle as a function of the concentration of electrolyte in solution (the scale along the abscissa axis, beginning with the value equal to unity, is reduced by a factor of 100)

As a result of the calculations performed, it was established that positive deviations from additivity of the coagulating action (antagonism or superadditivity) should occur in those cases when the critical values of the ionic strength of the solution for each of the electrolytes taken separately differ substantially from one another; as these differences increase, the tendency toward a transition from superadditivity to antagonism increases. Synergism can be observed only on the condition that the potential of the colloidal particles is sufficiently small not only in the critical state, but also in the initial state of the sol. It is especially necessary to note that antagonism in the coagulation of lyophobic sols proves possible even in the case when one of the counterions of the electrolytes added to the colloidal solution is not adsorbed at all. It is quite obvious that here the phenomenon of antagonism is no longer connected with the mutual suppression of adsorption of the coagulating ions; it is probably due to the fact that, upon addition of electrolytes to the sol, along with adsorption of counterions, there also occurs, as is known (^{4}), an additional adsorption of ions determining the potential of the colloidal particles.

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