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Abstract

Full Text

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ON THE INFLUENCE OF ELECTROMAGNETIC RETARDATION OF MOLECULAR ATTRACTION ON THE COAGULATING CONCENTRATIONS OF ELECTROLYTES

The theoretical justification of the well-known Schulze–Hardy rule, first given in work (^{1}), leads for the coagulating concentration γ of a symmetric electrolyte to the equation

$$\frac{1}{\gamma n_1} = C_1^2 \frac{A^2 e^6 z_1^6}{\varepsilon^3 \theta^5}. \tag{1}$$

Here $\theta = kT$; k is the Boltzmann constant; T is the absolute temperature; γ is the concentration in moles per cubic centimeter; n_1 is the number of anions (or cations) in an electrolyte molecule—the “dissociation number”; ε is the dielectric permittivity of the solution; A is the van der Waals interaction constant; C_1 is a certain constant, the same for all binary electrolytes. Formula (1) was obtained for the interaction of two plane plates or (for another value of C_1) for two spherical particles satisfying the condition $\varkappa r \gg 1$ (here $\varkappa$ is the reciprocal Debye length, and r is the radius of curvature of the particle).

In deriving this relation it was assumed that the van der Waals interaction of plane plates is determined by the law

$$Q = -\frac{A}{6\pi H^3}, \tag{2}$$

where H is the distance between the plates.

According to formula (1), the coagulating concentration of the electrolyte is inversely proportional to the 6th power of the ion valence. This law has been repeatedly confirmed experimentally.

However, formula (2) is not of a general character, since it is based on the assumption that the distance between the bodies is such that the effects of electromagnetic retardation, considered for the first time in (^{2}), may be neglected. The latter means that relation (2) is valid only in the case where the distances between the bodies are substantially smaller than the wavelength of electromagnetic waves characteristic of the interaction of bodies of the given nature. In the opposite case the law (^{2,3}) is valid:

$$Q = -\frac{\beta}{H^4}. \tag{3}$$

Since relation (1) is essentially based on formula (2), it must have definite limits of applicability. Therefore let us derive an analogue of relation (1), assuming, for generality, an arbitrary law of van der Waals interaction for plane plates.

Let

$$Q = -\frac{A\alpha(H)}{H^3}, \tag{4}$$

where $\alpha(H)$ is a certain function of H, whose form for the time being need not be specified. Assuming, following (^{1}), that the condition for the onset of rapid coagulation is the disappearance of the force barrier, and completely reproducing the scheme for deriving relation (1) (see (^{1})), we obtain, as the coagulation condition, the equation

$$\frac{\partial \ln[P\alpha(H)]}{\partial \ln H} = -3. \tag{5}$$

Here P is the force of electrostatic repulsion.

Recalling that, as shown in (^{1}),

$$P = 4\gamma n\theta\left(\frac{1}{k^2} - 1\right), \qquad \frac{\chi H}{2} = kK(k),$$

where $K(k)$ is the complete elliptic integral of the first kind with modulus k; $k = 1/\operatorname{ch} z\eta_1/2$; η_1 is the minimum value of the dimensionless electrostatic potential in the plane of symmetry between the plates ($\eta_1 = e\Psi_1/\theta$), we obtain from (5)

$$\frac{d\ln\left[\left(\frac{1}{k^2} - 1\right)\alpha(kK(k))\right]}{dk} \Bigg/ \frac{d\ln kK(k)}{dk} = -3. \tag{6}$$

As it should, equation (6) reduces to the corresponding equation of work (^{1}) if $\alpha(H)$ is identically equal to unity. In the case where the critical distance H_c, at which coagulation occurs,* is so large that the law of van der Waals interaction has the form of equation (3) (and, consequently, $\alpha(H) \sim 1/H$), specialization of relation (6) leads to the formula

$$\frac{1}{\gamma n_1} = C_1' \frac{B}{\varepsilon^2} \frac{e^4 z^4}{\theta^3}. \tag{7}$$

Thus, allowance for electromagnetic retardation leads to the coagulating concentration being inversely proportional not to the 6th, but to the 4th power of the ion valency. The same law is obtained if the condition for the onset of coagulation is taken to be the vanishing of the potential barrier rather than of the force barrier. The law also remains unchanged in passing from plates to spherical particles satisfying the condition $\chi r \gg 1$.

It should be noted that, since the value of k at the critical point does not depend on the valency of the ions (see ([1])), it follows immediately from the relation $\chi H_c/2 = kK(k)$ that the critical distance H_c, at which the force barrier disappears, increases sharply with the valency of the electrolyte. Indeed, since in calculating χ we must substitute the coagulating concentration, then irrespective of whether the law determined by relation (1) or by relation (7) holds, the value of χ corresponding to the coagulating concentration decreases with increasing valency. Since the product χH_c does not depend on valency, the value of H_c increases. Calculations show that, for 4–6-valent ions, the values of H_c approach, in order of magnitude, 10^3 Å. In such systems the manifestation of retardation effects is entirely possible, as is especially clear from direct measurements of molecular interaction at such distances by B. V. Derjaguin and I. I. Abrikosova ([4]).

However, experiment ([5]) reveals the directly opposite effect: for multivalent cations the coagulating concentration is inversely proportional to a **higher** than 6th (approximately 8th) power of the valency. This can apparently be explained by the fact that highly charged cations, being strongly adsorbed, lower the particle potential so much that calculations which assume this potential to be infinite become inapplicable and the coagulating concentration is additionally reduced.

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* By this distance is meant the separation of the surfaces corresponding to the potential barrier near its disappearance.

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