

INFLUENCE OF ADSORPTION ON THE PROPERTIES OF
DISPERSION IN UNDISSOCIATED SOLUTIONS

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The thermodynamic functions of dispersion in nonelectrolyte solutions are calculated, taking account of the sorption of solute molecules at the particle surfaces; the influence of this effect on the behavior of dispersion is discussed.

The importance of investigating the equilibrium properties of phases and components of finely disperse suspensions and colloids arises, in particular, in that the character of their dependence on the physicochemical parameters may influence the course of various non-equilibrium processes there. For example, the hydraulic characteristics – and hence the effective rheological parameters – of disperse flows depend strongly on the distribution of suspended particles, which is established as a result of competition between the action of some regular forces leading to migration of the particles and the development of inhomogeneity and the influence of gradient diffusion of the particles, leading to smoothing of this inhomogeneity [1].

Diffusional effects may be described by introducing a special thermodynamic force acting on the particles, proportional to the gradient of their chemical potential [1, 2]. Therefore, change in this gradient leads to restructuring of the particle-concentration field and hence to change in hydraulic characteristics of the disperse flow. This is associated with the possibility [1] of active intervention in such flows by introducing surfactants, polymers, and so on in the liquid phase.

In the present work, the problem is considered for the situation in which the liquid phase of the dispersion is a dilute solution of a single undissociated material which is capable of adsorption. The particles are assumed to be identical spheres; their volume concentration in the mixture may be large, so that the steric interaction due to excluded-volume effects are important. In addition, molecular surface interaction between particles is possible, usually leading to mutual attraction.

Consider a system consisting of n_p spheres of radius a and volume $v_p = (4\pi/3)a^3$; n_0 solvent molecules of volume v_0 ; and n molecules of some material (volume v) distributed between the solution and the surface phase, corresponding to an adsorptional layer at the particles (n_s and n_a molecules, respectively; $n_s + n_a = n$). Without loss of generality, n may be understood to be the number of particles and molecules in unit volume of the mixture. Obviously

$$\rho = v_p n_p + v n_a, \quad 1 - \rho = v_0 n_0 + v n_s \approx v_0 n_0 \quad (1)$$

(the approximate equality is for a dilute solution).

Suppose that the surface concentration of the possible adsorption sites, assumed to be identical for the sake of simplicity, is Γ ; then the total number of such sites per unit volume is

$$N = 4\pi a^2 n_p \Gamma = 3\Gamma \rho / a. \quad (2)$$

Taking account of the multiplicity of methods of distributing the adsorbed molecules over the accessible sites, the following expression may be written for the state function of the system

$$Z = Z|_{n_a=0} \frac{N!}{n_a! (N - n_a)!} (z_a)^{n_a},$$

where the first factor on the right-hand side corresponds to the same system without adsorptional layers, and z_a is the state function for one adsorbed molecule. Hence, for the free Helmholtz energy of the system, using the Stirling formula

$$F = -kT \ln Z = -kT \ln Z|_{n_a=0} - kT n_a \ln z_a - kT [N \ln N - n_a \ln n_a - (N - n_a) \ln (N - n_a)]. \quad (3)$$

Since, by hypothesis, the volume of the system is unchanged on adsorption of some of the solute molecules, the chemical potentials of the components of the system in isothermal conditions are equal to the partial derivatives of F with respect to the corresponding n . Taking account of Eqs. (2), it follows from Eq. (3) that

$$\begin{aligned} \mu_p &= \mu_p|_{n_a=0} + 4\pi a^2 \Gamma kT \ln \frac{N - n_a}{N}, \\ \mu_0 &= \mu_0|_{n_a=0}, \quad \mu_s = \mu_s|_{n_a=0}, \\ \mu_a &= -kT \ln z_a + kT \ln \frac{n_a}{N - n_a} \end{aligned} \quad (4)$$

(on differentiation, the relation $n_s + n_a = n$ is ultimately not imposed).

To determine the first terms on the right-hand side in Eq. (4), it is simplest to consider the dispersion of n_p particles in solution with a relative concentration n_s/n_0 using the method of [1]. If there is no molecular attraction of the particles, i.e., only excluded-volume effects are present, this problem was actually solved in [1] on the basis of a semiempirical equation of state of a dense gas of rigid spheres in the form proposed in [3, 4]

$$P = P^*(\rho) = \frac{\rho}{v_p} \frac{1 + \rho + \rho^2 - \rho^3}{(1 - \rho)^3} kT.$$

The attraction of the particles may in principle be taken into account using the well-known Braut method, considering the equation of state

$$P = P^*(\rho) - A\rho^2,$$

where A is a parameter characterizing the intensity of attraction, which may be expressed as some integral of the interaction potential and the binary correlation function for rigid spheres [4]. The calculation of the thermodynamic Gibbs potential of the system in this case is completely analogous to that in [1]; for the situation in which the effective attraction is due to the dipole interaction between the particles, see [5].

Omitting the details of the calculations, the result is

$$\begin{aligned} \mu_p|_{n_a=0} &= \mu_p^\circ + kT \left[\ln \rho - \rho + \rho \frac{8 - 5\rho}{(1 - \rho)^2} - \alpha\rho(2 - \rho) \right], \\ \mu_0|_{n_a=0} &= f_0 - kT \frac{v_0}{v_p} \rho \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1 - \rho)^3} - \alpha\rho \right], \\ \mu_s|_{n_a=0} &= f_s - kT \frac{v}{v_p} \rho \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1 - \rho)^3} - \alpha\rho \right], \end{aligned} \quad (5)$$

where $\alpha = v_p A/kT$ is a new dimensionless parameter characterizing the interparticle attraction. For a dilute solution, taking into account that $n_0 = v_0^{-1}(1 - \rho)$, it follows that

$$\begin{aligned} f_0 &= \mu_0^\circ - kT(n_s/n_0) = \mu_0^\circ - kT v_0 c_s, \\ f_s &= \psi(T) + kT \ln(n_s/n_0) = \psi(T) + kT \ln(v_0 c_s), \end{aligned} \quad (6)$$

where $\psi(T)$ is practically independent of the pressure, according to the theory of solutions [6]; $c_s = (1 - \rho)^{-1} n_s$ plays the role of the numerical concentration of the solution; μ_0° corresponds to pure solvent and μ_p° to the particle material.

To determine the degree of filling of the adsorptional layers $\tau = n_a/N$, the free energy in Eq. (3) must be a minimum with respect to change in the degree of adsorption $v = n_a/n$ under the condition that $n_s + n_a = n$. Hence

$$\ln \frac{\tau}{1-\tau} - \ln z_a - \frac{1}{kT} \mu_s|_{n_a=0} = 0,$$

which expresses the equality of the chemical potentials of the solute molecules in the solution and in the surface phase, from which, taking account of Eqs. (5) and (6) and the notation $\chi(T) = -kT \ln z_a$, the equation of the adsorption isotherm corresponding in fact to Langmuir theory follows

$$\frac{\tau}{1-\tau} = v_0 c_s \exp \left\{ \frac{U}{kT} - \frac{v}{v_p} \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1-\rho)^3} - \alpha \rho \right] \right\}, \quad (7)$$

where $U = \psi - \chi$ is the energy of specific adsorption. It is evident from Eq. (7) that increase in particle concentration in the system leads to weakening of the equilibrium adsorption of the molecules at small α , as for the adsorption of ions from electrolyte solutions [7]. At large α , some intensification of adsorption is seen. However, in view of the presence of a small factor in the exponential, it follows from Eq. (7) that these effects are very weak. Note that these discussions take absolutely no account of the possible dependence of α on the degree of filling of the adsorptional layers; construction of the corresponding theory is very complex.

The final expressions for the chemical potentials following from Eqs. (4)-(6) are

$$\frac{\mu_p}{kT} = \frac{\mu_p^0}{kT} + \ln \rho - \rho + \rho \frac{8-5\rho}{(1-\rho)^2} - \alpha \rho (2-\rho) + 4\pi a^2 \Gamma \ln(1-\tau), \quad (8)$$

$$\frac{\mu_0}{kT} = \frac{\mu_0^0}{kT} - v_0 c_s - \frac{v_0}{v_p} \rho \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1-\rho)^3} - \alpha \rho \right],$$

$$\frac{\mu}{kT} = \frac{\psi}{kT} + \ln(v_0 c_s) - \frac{v}{v_p} \rho \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1-\rho)^3} - \alpha \rho \right]$$

where the last formula corresponds to solute molecules, regardless of the phase in which they are found. Using Eq. (8), all the other thermodynamic functions of the given system may be found by the usual rules.

The results obtained offer the possibility of determining all the standard characteristics of the concentrated colloidal solution: osmotic pressure, temperature and pressure shifts, and phase transitions of liquid phase due to the presence of particles, the equilibrium conditions of colloids in different liquids, etc. This leads to the corresponding generalization of the distribution laws - van't Hoff, Raoult, Henry, and cryoscopic [6]. For example, consider the equilibrium of colloidal solutions of the same particles with concentrations ρ_1 and ρ_2 separated by a barrier which is only permeable to these particles. Equating the chemical potentials of the solvent and solute on both sides of the barrier, it is found that

$$c_{s2} - c_{s1} = c_{s1} [\exp(\sigma v/v_p) - 1] \approx \sigma c_{s1} (v/v_p),$$

$$p_2 - p_1 \approx \sigma (1 + v c_{s1}) (kT/v_p), \quad (9)$$

$$\sigma = \rho_2 \left[\frac{1 + \rho_2 + \rho_2^2 - \rho_2^3}{(1-\rho_2)^3} - \alpha \rho_2 \right] - \rho_1 \left[\frac{1 + \rho_1 + \rho_1^2 - \rho_1^3}{(1-\rho_1)^3} - \alpha \rho_1 \right],$$

determining, in particular, the osmotic pressure of the colloidal solution. Analogously, it is simple to consider the equilibrium in the presence of a barrier permeable only to the solvent.

The derivative $\partial \mu_p / \partial \rho$ is now calculated taking account of Eqs. (7) and (8); simple transformations give

$$\frac{\partial \mu_p}{\partial \rho} = kT \left(1 + 4\pi a^2 \Gamma \frac{v}{v_p} \frac{x}{1+x} \frac{\rho}{1-\rho} \right) \times \quad (10)$$

$$\times \frac{d}{d\rho} \left[\ln \rho - \rho - \rho \frac{8-5\rho}{(1-\rho)^2} - \alpha \rho (2-\rho) \right],$$

$$x = v_0 c_s \exp \left(\frac{U}{kT} \right) \exp \left\{ - \frac{v}{v_p} \rho \left[\frac{1 + \rho + \rho^2 - \rho^3}{(1-\rho)^3} - \alpha \rho \right] \right\}.$$

The condition of thermodynamic stability of the colloidal solution demands that this derivative be positive [6]. It is readily evident from Eq. (10) that stability loss sets in when the total derivative with respect to ρ in Eq. (10) is zero. It is simple to show that this is possible when $\alpha \gtrsim 10.75$, i.e., with sufficiently strong attraction between the particles. Then the equation $\partial\mu_p/\partial\rho = 0$ has two roots ρ , depending on α . It also follows from Eq. (10) that the adsorption of the solute molecules has no influence on the loss of thermodynamic stability of the system, and hence on the onset of stratification of the colloid into two phases of different concentration (again, no account is taken here of the possible dependence of α on the state of the adsorbed layers at the particles).

The coefficient of gradient Brownian diffusion of the particles and the thermodynamic force tending to equalize the particle concentrations in the disperse flows are proportional to the derivative in Eq. (10). Therefore, it is clear that the influence of adsorption of material introduced in the flow may be significant if the degree of filling of surface layers of the particles is close to unity, which is quite possible with sufficiently high adsorptional energy U . Considering only this case, for the sake of simplicity, it is evident that the ratio of diffusion coefficients of the particles in the system in the presence and absence of adsorption may be written in the form

$$\frac{D}{D|_{\alpha=0}} \approx 1 + \frac{\kappa\rho}{1-\rho}, \quad \kappa = 4\pi a^2 \Gamma \frac{v}{v_p}. \quad (11)$$

Thus, the introduction of impurity capable of adsorption in a flow should lead to the intensification of diffusional processes and hence to weakening of the concentrational inhomogeneities in the flow. This effect is intensified with increase in concentration of the colloid. In order of magnitude, $\Gamma \sim \ell^2$ when $v_p = (4\pi/3)\ell^3$, i.e., $\tau \sim 4\pi\ell/a$. Hence it follows that the effect is very weak in the case of low-molecular impurities in systems with relatively large particles. However, it intensifies rapidly on passing to high-molecular impurities and finely disperse colloidal or micellar solution. If long-chain wetting materials and polymer additives are used, the given effect may be considerable in colloidal solutions with $a \sim 0.1-1 \mu\text{m}$.

Note that, in the simple theory here proposed, simple assumptions are made regarding the dilution of the molecular solution, the monodispersity and spherical form of the particles, the absence of a dependence of α on τ , the slight influence of adsorption and solvation of the particles on their size (allowing, in particular, the dependence of ρ on n_a in Eq. (1), which is important in calculating chemical potentials, to be neglected here), and so on. Therefore, the results obtained must be regarded as qualitative or approximate, in no sense exhausting the complexity of the given problem. However, they are adequate in the sense that they offer the possibility of suggesting promising directions for further investigation, including experimental.

NOTATION

a , particle radius; c , numerical concentration; D , diffusion coefficient; F , Helmholtz free energy; k , Boltzmann constant; N , number of adsorption sites; n , number of particles or molecules per unit volume; p , pressure; T , temperature; U , energy of adsorption; Z , z , state functions; α , parameter characterizing the attraction between particles; Γ , surface concentration of adsorption sites; μ , chemical potential; v , degree of adsorption; ρ , volume concentration of particles; τ , degree of filling of surface layers; χ , ψ , characteristic energies. Subscripts: p , particle; 0 , solvent molecule; s , a , solute molecule in solution and in adsorbed phase, respectively.

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