CROATICA CHEMICA ACTA CCACAA 53 (2) 167—181 (1980)

CCA-1198

YU ISSN 0011-1643
UDC 541.18:541.124/128
Conference Paper

Non-Equilibrium Surface Forces

S. S. Dukhin

The Institute of Colloid and Water Chemistry of the Academy of Sciences of the Ukrainian SSR Kiev, USSR

Received November 22, 1979

A theory of the non-equilibrium double layer and of non-equilibrium surface forces is presented. Departures from the equilibrium state in the double layer are observed whenever there is flow in this structure. In the theory only external field influences are treated. Dipolophoresis and diffusiophoresis are defined, and conditions for a steady-state are described. Application of the theory in interpreting phenomena of electrocoagulation, electrofiltration, bubble flotation, and electrodeposition of polymers is briefly discussed.

The non-equilibrium surface forces relate to the non-equilibrium double layer (DL) in the same way as the equilibrium surface forces (described by the theory of DLVO) to the equilibrium DL. The review deals with the forces conditioned by the non-equilibrium DL, which is caused by the electric current, liquid flow and phase developments. The theory of the reversible and the irreversible electrocoagulation is based upon the non-equilibrium surface forces. The DL polarized by the liquid flow could influence the particles deposition during flotation and filtration. Here new electrokinetic phenomena are important — the dipolophoresis and the diffusiophoresis which appear due to a spatial non- uniformity of the electric field and the electrolyte concentration macrogradient. Similar conditions are brough about by the phase developments (dissolving, crystallization in the electrolytes). This also provides the non-equilibrium surface forces which are important for the fabrication of latex films by the so-called method of ionic deposition.

The three branches of colloid science — the theory of the double electric layer[1], the electro-kinetics phenomena[2] and the electric surface forces (electrostatic component of the surface forces within the DLVO theory[3,4] have always been developed in close connection with each other.

The idealized conception of strict equilibrium of DL with the interaction of the particles (coagulation) or the particles with stretched surfaces (adagulation) is one of the factors which make the DLVO theory much simpler.

In many cases this idealization proves helpful. Though, since 1959[5] we have been indentifying the number of colloid-electrochemical processes which arise within the non-equilibrium DL. And the new effects estranged from

---

* Based on an invited lecture presented at the 5th »Ruđer Bošković« Institute's International Summer Conference *Chemistry of Solid/Liquid Interfaces*, Cavtat/Dubrovnik, Croatia, Yugoslavia, June 1979.

the DLVO theory appear provided there is an account of non-equilibrium state of DL.

We call additional types of the surface forces caused by the DL deviation from its aquilibrium state, non-equilibrium surface forces. Therefore, the non-equilibrium surface forces relate to the non-equilibrium DL in the same way like the equilibrium ones of the DLVO theory relate to the equilibrium DL.

The electric double layer leaves its equilibrium state for the non-equilibrium one under any effect which causes flow in the DL. If these effects are steady, the resulting flows of ions reach a steady state. In this case, instead of the condition of equality of ion flow to zero, typical of an equilibrium layer $j^{\pm} = 0$, the condition of equality of the divergence of flows to zero is satisfied $\mathrm{div}_s\, j^{\pm} = 0$[2].

The Brownian movement of a colloid particle is accompanied by the flow of liquid relative to its surface, which also carries away the ions of the diffuse part of the DL. It disturbs, of course, the equilibrium structure. Thus, the double layer of the colloid particles will deviate from the equilibrium state even in the absence of outer macroscopic effects. In this review however, we consider the deviation of the DL from the equilibrium state under outer effects.

In order to illustrate the qualitative distinction between the non-equilibrium and the equilibrium DL, we shall investigate a special case of the polarization of the DL of a spherical particle by an external stationary field. Under the external electrical field effects there appear a tangential flows of ions of the diffuse layer which redistributes them over the surface: the DL is being deformed and polarized diverting from the initially spherically symmetrical structure. The tangentaial flows of the DL ions are being locked through the electrolyte volume. The stationary ion exchange between the DL and adjacent electrolyte volume is potentiated only by the occurence of a spatial current distribution and an electric field which is beyond the limits of the double layer and maintains high values in the region with the linear dimensions of which are almost of the size of the particle $2\,a$.

The electric field beyond the limits of the DL may be called a long-range field as distinct from a short-range field of the equilibrium DL localized inside it if its thickness $\varkappa^{-1}$ is much less than a, i. e. when the condition

$$\varkappa a \gg 1 \tag{1}$$

is satisfied. The stationary tangential current of the ions of the diffuse layer is maintained owing to the charge supply from the volume to the left hemisphere and their discharge into the volume from the right hemisphere. Correspondingly, the intensity lines of a long-range electric field arising near one hemispherical surface run into the volume and approach the other hemisphere from the volume where the electric field outlets are distributed. Thus, the qualitative distinction between the non-equilibrium and equilibrium DL is antisymmetry of the spatial structure instead of spherical symmetry, and the presence of a long-range field together with a short-range field and the dipole moment.

On this basis three large branches of colloid science — the theory of the double layer[1], electrokinetic phenomena[2] and the theory of colloid stability[3,4] — are being transformed or supplemented by new branches. For instance, instead of electrokinetic phenomena, a considerably wider sphere of phenomena

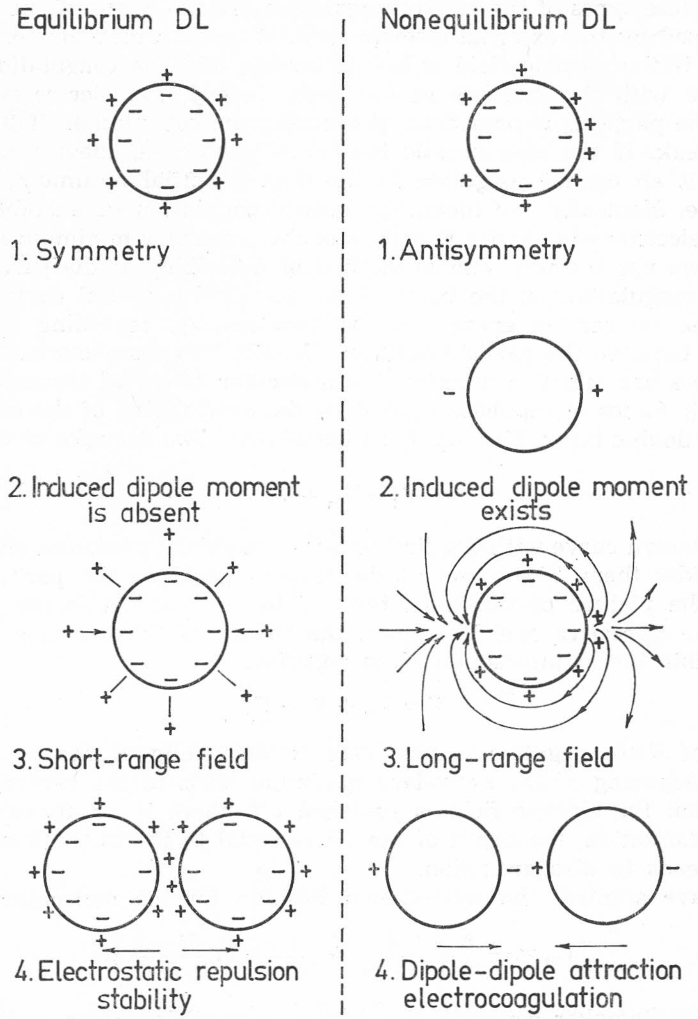


Figure 1. The qualitative distinction of the equilibrium and nonequilibrium double layers.

is being revealed which may be characterized as the new electrokinetic phenomena[6].

Coagulation is usually a result of a reagent addition to a solution. This addition can be brought about by electric current. The aluminium electrode dissolves and produces coagulating ions. This type of coagulation can be called the electrochemical coagulation. There is also the electrocoagulation provided by the external electric field effect on the charged particle without changing of the electrolyte content. Hence, the electrocoagulation is a reagentless method of the destruction of colloid stability. The electrocoagulation could be reversible or irreversible. The electrocoagulation is reversible if the aggregates formed by the electric field, disintegrate on switching off the field. If the aggregates do not disintegrate, the electrocoagulation is irreversible.

Both these types of the electrocoagulation are the result of the DL polarization caused by the external electric field. It is clear that the coagulation is reversible if the electric field is not to strong; and the coagulation becomes irreversible with the increase of the field. Indeed, the electrostatic barrier between the particles is preserved, preventing the coagulation, if the external field is weak. If the electrostatic barrier is preserved, the particles cannot overcome it an cannot coagulate in the first potential minimum, nearest to the surface. Naturally, we mean the electrocoagulation of a stable solution, when the electrostatic barrier is high, and the secondary minimum is not deep.

Here we use the well known method of describing of the particles interaction by coagulation on the basis of the so-called potential curve. It characterizes the interaction energy as the function V_Σ, regarding the shortest distance h between the particle surfaces. Usually two components of the interaction forces are taken in account: the molecular forces of attraction and the electrostatic forces of repulsion caused by the overlapping of the diffuse parts of particle double layer. The superposition of these two energies as the distance function

$$V_\Sigma = V_\mathrm{m} + V_\mathrm{i} \tag{2}$$

gives the known curve with the first and the secondary minimum and a barrier which divides them. The effect of the external field on the particles contributes to the picture of the third type of the interaction forces. This third force is the attractive one. Therefore, the energy of the particles non-equilibrium double layers interaction V_p is negative.

$$V = V_\mathrm{m} + V_\mathrm{i} + V_\mathrm{p} \tag{3}$$

Addition of these negative values leads to deepening of the secondary pit.

The deepening of the secondary minimum leads to the reversible coagulation. When the electric field is switched off, there is no attraction due to the DL polarization, the depth of the pit is equal to the initially small value, and this leads to disaggregation.

We have applied[7] the well-known formula for the molecular attraction

$$V_\mathrm{m} = -\frac{A}{2}\left(\frac{2}{S^2-4} + \frac{2}{S^2} + \ln\frac{S^2-4}{S^2}\right) \tag{4}$$

where A — Hamaker constant, S — h/a, a — particle radius and more specialized but effective one for the electrostatic repulsion[8]

$$V_\mathrm{i} = 16\,\varepsilon\left(\frac{kT}{e}\right)^2 \mathrm{th}\,\frac{\tilde{\psi}_\mathrm{d}}{2}\,\exp\left[-\frac{\varkappa a\,(S-2)}{S}\right] \tag{5}$$

where ε — dielectric constant, k — Boltzmann constant, T — absolute temperature, e — electron charge value, $\tilde{\psi}_\mathrm{d} = e\,\psi_\mathrm{d}/kT$. This formula is valid for any value Stern potential $\tilde{\psi}_\mathrm{d}$ and the value $\varkappa a$ is more than 1 but only for a weak overlapping of the double layers $\varkappa h > 2/3$. The formula is in a good accordance with the other formulas which describe the electrostatic repulsion of the identical spherical particles.

It is easy to calculate the interaction of the particle polarized by the external field, if the distance between the particles is greater than their sizes.

In this case only the dipole — dipole attraction could be accounted. If the condition

$$h \geqslant a \tag{6}$$

is not satisfied, i. e. there is a small distance between the particles, one should consider the multipoles also (quadrupoles and so on).

The induced dipole moment completely characterizes the DL polarization only when the external field is uniform. The effect of a non-uniform field on the particle brings about not only dipoles but the multipoles too. The electric field of a dipole is non-uniform. Its value in the volume where the neighbouring particles are localized grows with the decrease of the distance between the particles. This non-uniform field can be as great as the external one. Consequently the particles are polarized together which results in the formation of multipole.

Since the calculation of depth of the potential pit is the most important, the condition (6) should be observed for $h_{\min}$ which is the distance between the particles equal to that of the secondary energetic minimum from the particle surface. The thicker are particles DL the overlapping of which makes the approach impossible, the greater is $h_{\min}$; $h_{\min}$ is proportionate to $\varkappa^{-1}$. At the fixed value a the increase $\varkappa^{-1}$ violates the condition (1), the decrease of $\varkappa^{-1}$ violates the condition

$$h_{\min} \geqslant a \tag{7}$$

It appeared after the calculations that (1) and (7) are compatible at $\varkappa a$ — 20—30. For these values $\varkappa a$ it is enough to consider the dipole — dipole interaction only. As is known, the interaction force of non-uniform electric field and dipole is expressed by

$$\mathbf{F} = (\mathbf{d}\,\nabla)\,\mathbf{E} \tag{8}$$

The value of dipole moment **d** is determined by the deformation of the DL diffuse part[2]. The effect of the field **E** on the DL diffuse part causes the force which is partly transferred to the particle and partly to the medium[7].

If the condition (1) is observed, the field effect on the DL diffuse part is almost completely transferred to the particle, and (8) is roughly valid.

The field of neighbouring dipole should be introduced into (8) as the external field in order to describe the dipole — dipole attraction. That's why F is proportional to the square of dipole. On the basis of the formulas for induced dipole[2] the formula (8) in case of the interaction of the identical spherical particles with the centre lines parallel to the field is reduced[7] to

$$F = 12\,\varepsilon\,B^2\,a^6/(2\,a + h) \tag{9}$$

in which

$$B = \frac{1}{2} - \frac{3}{2}\;\frac{Rel}{1 + Rel} \tag{10}$$

$$Rel = \varkappa^{\sigma}/ka \tag{11}$$

$\varkappa^{\sigma}$ and k are the surface specific and volumetric conductivities. Rel and $\varkappa^{\sigma}$ can be expressed by the dimensionless values of $\overline{\psi}_{\mathrm{d}}$, $\overline{\zeta}$, $\varkappa a$.

$$Rel = [\exp(\overline{\psi}_{\mathrm{d}}/2) + 3\,m\,\exp(\overline{\zeta}/2)]/\varkappa\,a \tag{12}$$

The formula for B (10) shows the dependence of the values and the direction of dipole moment on the DL parameters, because

$$d = E\,a^3\,B \tag{13}$$

when $Rel = Rel_{\mathrm{iso}} = 1/2$ there is no induced dipole, this condition has been called isopolarized. With $Rel < Rel_{\mathrm{iso}}$ dipole is oriented against the field, at $Rel > Rel_{\mathrm{iso}}$ along the field.

The standard equation

$$V_{\mathrm{E}} = \int_{\infty}^{h} F(h)\,\mathrm{d}H = 4\,\varepsilon\,E^2\,B^2\,a^3/S^3 \tag{14}$$

provides the energy of attraction.

The electrocoagulation is usually investigated in the alternating field, for it is impossible to avoid the complicated effect of electrophoresis in the direct field. If the frequency is high enough

$$\omega > D/a^2 \tag{15}$$

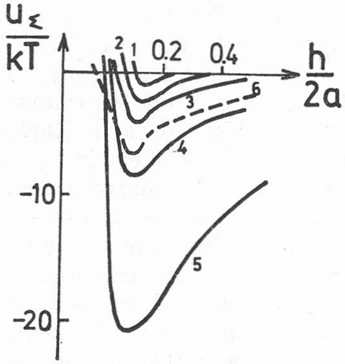
the tangential currents of the DL ions do not form the concentration drop beyond the DL[2,9]. These drops appear with the low frequencies which do not satisfy the condition (15). The concentration drops change the value of the tangential currents of the ions and, accordingly, effect the value of dipole moment. The latter has different expressions, regarding the fact whether the frequencies are low or high[9]. That's why (10) is of no use with the low frequencies.

Schilov and Estrela-Lopis[10,11] developed the diagram — analytic method of the estimation of the multipole polarized interaction. This method permits to calculate the interaction of the same and different spherical particles within the doublet oriented along the field vector. Since the solution results in a row, it has been compared with the precise solution of Krasny-Ergen[12]. The latter, however, does not consider the DL effect upon the particle dipole moment. So the multipole theory[10,11] is much more general than the work of Krasny-Ergen[12] which again is more strict in the case of the non-charged particles. The comparative calculations showed that the relative error of the multipole theory is less than 1% if the gap h_{min} between the particle surfaces equals to 0.1 of the diameter of the particles $2\,d$. The lesser is h_{min}, the greater is the error and vice versa. The error of the dipole approximation is less than 4% with $h/2\,a = 0.1$ and less that 1% with $h = 2\,a$. Since accordingly to (13) and (10) with $Rell \gg Rel_{\mathrm{iso}}$ dipole is greater than in the case of weakly-charged particles, the importance of the multipoles falls with the decrease of Rel.

The above mentioned maximum errors of the multipole and the dipole theories which correspond to $Rel > Rel_{\mathrm{iso}}$ diminish with the decrease of Rel.

The qualitative results (the dependences on dimensionless parameters) of the dipole and the multipole theories coincide, and can be determined by the consideration of (9), (10), (12). Here are the results of the more precise theory.

The greater is E, the deeper is the potential pit (Figure 2). There is the minimum of the polarized interaction in the isopolarized condition (Figure 3). The increase of the particle charge with $Rel > Rel_{\mathrm{iso}}$ causes the decrease of



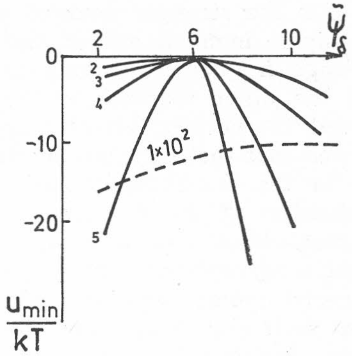
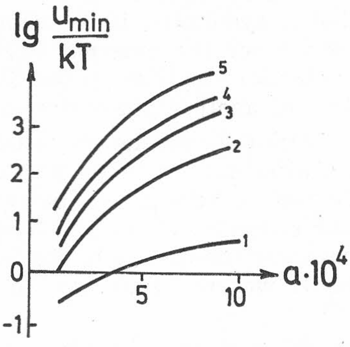


Figure 2. The potential energy of the colloid particles interaction versus distance h between their surfaces by $a = 10^{-4}$ cm, $\Psi_d = 10$, $\varkappa a = 30$. Curves 1, 2, 3, 4, 5 correspond values of electric field $E = 0, 20, 40, 60, 100$ V/cm respectively. Curve 6 correspond values $\Psi_d = 2$, $E = 100$ V/cm.

Figure 3. The bond energy of the particle doublet versus their Stern potential Ψ_d by $a = 10^{-4}$ cm, $\varkappa a = 30$. Curves 1, 2, 3, 4, 5 correspond values of $E = 0, 40, 60, 100, 200$ V/cm.



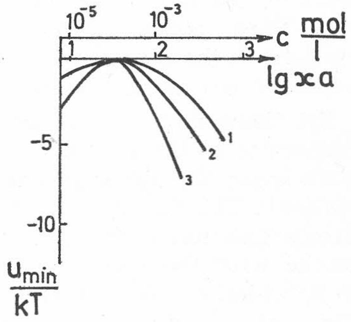


Figure 4. The bond energy of the particle doublet $U_{\min}$ versus their radius a by $\varkappa a = 30$, $\Psi_d = 5$. Curves 1, 2, 3, 4, 5 correspond values $E = 0, 20, 60, 80, 100$ V/cm.

Figure 5. The bond energy of the particle doublet versus electrolyte concentration c by $a = 10^{-6}$ m, $\Psi_d = 6$. Curves 1, 2, 3, correspond values $E = 0, 60, 100$ V/cm.

the stability of suspension (Figure 3), which is opposite to the classic coagulation in the abscence of the external filed. Therefore, the reagentless electrocoagulation is effective when the reagent coagulation is hampered. Figure 4 shows that the energy of the particle doublet is highly dependable upon their size, especially if $V_p > V_i + V_m$. Therefore, the enlargement of aggregates during the electrocoagulation is like an avalanche, more intense than during the reagent coagulation, when the energy of the bond is almost proportionate to the first degree of the particles. The application of the comparatively low fields provides the same bond energy as that caused by the considerable change of electrolyte concentration (Figure 5). Thus, with $E = 60$ V/cm and $C = 10^{-5}$ mol/dm^3 the energy of the bond is the same as that without the field at the concentration icreased by more than an order of magnitude. This makes possible to calculate the optimum complex conditions of the suspensions aggregation. These conditions should include both the reagent coagulation and the electrocoagulation.

For the strongly charged particles ($Rel > Rel_{iso}$) there is a decrease in the dipole moment and in the electrocoagulation while the transition from the high frequencies (satisfying condition (15)) to the low frequencies. These and the other features of the electrocoagulatin have been experimentally proved in work[13]. But the experimental work of Usiarov and Kaplan[14,15] showed that the aggregation minimum takes place at the isoelectric point and not in the isopolarized condition. This contradicted the above mantioned mechanism of the electrocoagulation. The statement has been provided by the microscopic calculation of the growing number of the monodisperse latex particle aggregates, suspended in the thin water film on an underlay. At the isoelectric point particles could stick to the underlayer and correspondingly loose their ability to aggregate. This may be misinterpreted as the minimum of the electrocoagulation. That's why the ultramicroscopic way of the electrocoagulation kinetics research (in the volume of suspension) should be recommended.

The work[16] was the launching pad for the development of the theory of the irreversible electrocoagulation. In order to ease the calculations the attention was focused on the case of flat-parallel gap between the two thin charged plates. The distribution of the potential is symmetric if the charges (or the Stern potentials) are equal. The imposition of the external field is equivalent to the change of the charge or the potential of plates, so the Stern potential of one of the plates increase while that of another plates decrease*.

Yet there may be the same asymmetric distribution of the potential in the abscence of the external field and with the differently charged particles, i. e. we mean the situation analysed in the Derjagin theory of the heterocoagulation[18]. This theory can be the basis for the criterium of the irreversible electrocoagulation, because all we need is to associate the change of the Stern potential with the value of the external field. It was but that item in the work[16], which has been corrected in the work[17].

The irreversible electrocoagulation makes difficult the regeneration of electric filtres. The reversible electrocoagulation is more suitable for the ele-

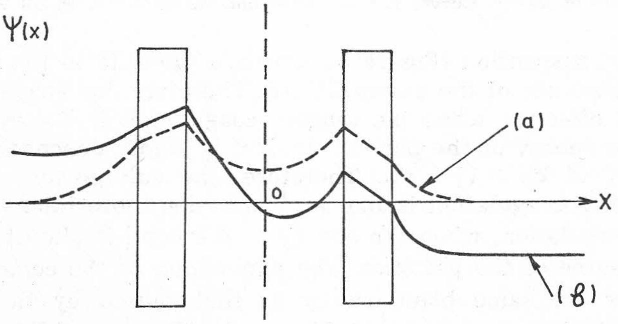


Figure 6. Illustration of the mechanism of the irreversible electrocoagulation. The electric potential distribution in absence of the external electric field and its change under influence of the external electric field.

---

* Here we take into account the fact that the reorganization of the DL diffuse parts is very quick, and all the stable changes in the system may be neglected at that time. Particularly, the charge of the plate changes very slowly and may be considered as stable.

ctrofiltration[19], because the after-voltage deposit disintegrates, and the electric filtre becomes clean. There is the simplest electrofiltration during the dispersion flow in the flatparallel gap between membranes. The colloid particles are moved electrophoretically towards one of the membranes and form a deposit on its surface due to a transverse electric field. The firmness of the deposit depends upon the electrocoagulation. Experiments proved[20] that there may be an analogous effect within the weak fields, if the intermembrane space is filled with granulated ionite. The deposit is formed in the narrow spot of the gap, for there are two effects of field strengthening in it[21]. If the electroconductivity of ionite K_i is much greater than that of electrolyte K, the electric field inside ionite is much lesser than a medium field E. This helps to consider the surface of an ionite granula in the first approximation as the isopotential one. Then it is easy to estimate[21]

$$E_{\max} = E\, 2\, a/h_{\min} \tag{16}$$

in which $E_{\max}$ is the field in the narrow gap with the width $h_{\min}$. As it is known, the concentration of electrolyte c is lower for one or two orders near the interface ionite-electrolyte, if the current reaches its maximum. That means the electric field increases to almost the same level, for $Ec = EK = I$, and electric current I does not change by the section of a diffusion lay. A large value of the electric field can be provided at but the point where it is necessary for the electrocoagulation and the deposit formation.

The electrofiltration is less intensive when the granulas or the fibres between the membranes are not conductive[22]. The electrofiltration in this case is conditioned by the interaction of electrophoresis and dipolophoresis[26] which is a new electrokinetic phenomenon.

Dielectrophoresis was known before, i. e. the motion of non-charged particles in the spatially non-uniform field, caused by the effect on the induced dipole moment of a particle. It is differently directed depending upon the value of $\varepsilon_i/\varepsilon_e$ in comparison with the unity (ε_i, ε_e are the dielectric constants of a particle and a medium). But the colloid particles are usually charged and with the condition $\varkappa a > 1$ the direction and the value of their dipole moment is determined by Rel, and not by $\varepsilon_i/\varepsilon_e$. Thus, dipolophoresis is caused by the double layer polarization (in contrast to dielectrophoresis).

Another new electrokinetic phenomenon called diffusiophoresis is also connected with the non-equilibrium surface forces[23,6].

Diffusiophoresis is caused by the DL polarization due to the electrolyte concentration drop. The externally imposed concentration macrogradient determines the difference in ion concentration of the volume adjacent to the outer boundary of the DL. Since local equilibrium is retained between two regions, the DL rearranges in accordance with the ion concentration distribution along its outer boundary. In the DL polarized in this way there arises the tangential component of the electric field, which sets the DL and the particle into motion. It can be shown that the particle moves towards the electrolyte concentration rise irrespectively of the sign of the ζ-potential. It may be assumed that the concentration falls from the left to the right and $\tilde{\psi}_d < 0$ (Figure 7) and that the Stern potential grows by its absolute value (Figure 6). The conclusion is that the field of the polarized DL E^* is directed from the left to the right, because the Stern potential reduces in the same direction. But since diffusio-

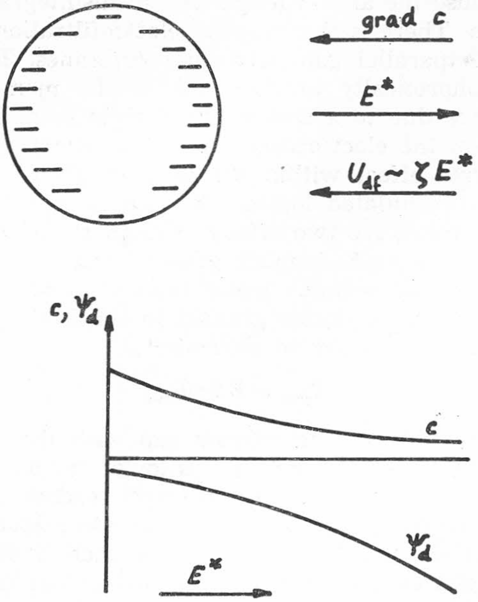


Figure 7. Illustration of the mechanism of the diffusiophoresis.

phoresis is effected by E^* field effect on the DL, and $\psi_d < 0$ in this case, the vector of the rate of diffusiophoresis V_d coincides with the concentration gradient. If we analyse the case $\zeta > 0$ in the same way we would see the vector E^* has also changed its direction, so the vector of the diffusiophoresis rate would be directed similar to the concentration gradient. The diffusiophoresis rate equation derived on the basis of the quantative approach shows this regularity[6,2]:

$$V_{df} = \frac{\varepsilon \zeta^2}{32 \pi \eta c_o} \text{grad } c \tag{17}$$

The liquid flow can deform the DL of a body (e. g. a bubble of a gas during flotation or a ionite granula during filtration) larger then the particles of the liquid flow. This causes the electroneutral thick electrodiffuse layer near the surface[24,25]. There is a deposition of the particles when the flow comes through the thick electrodiffuse layer and then through a thin zone of action of the surface equilibrium forces[24,25].

Therefore the non-equilibrium electric surface forces are in connection with the deformation of the DL of the body (which leads to the electrodiffuse layer formation) as well as with the deformation of the DL of the particle (which is the basis of the dipolophoresis and the diffusiophoresis). Since there are non-uniform electric field and the concentration drops in the convective electrodiffuse layer, the transport of the particles through that layer is effected by the diffusiophoresis and the dipolophoresis. Recently the effect of the equilibrium surface forces on the particle capture from the flow (whether by the granulas of filtre or by flotation) has been studied by many of the experts.

In 1960 Derjagin and Dukhin[24] substantiated the importance of the heterocoagulation and the non-equilibrium surface forces for the elementary act of flotation. At present the importance of the heterocoagulation for the smaller particle flotation is proved. Yet there is a lack of experimental data on the nature of the non-equilibrium surface force action.

During the flotation of a bubble its upper part is stretched, its lower part is contracted. New sections of the surface are filled with the adsorbed substance. This substance is desorbed when the surface contracts. The adsorption $\Gamma(\Theta)$ is lower on the upper part of a floating bubble compared with the value Γ_0 on the fixed surface. This provides continuous surfactant supply from the volume to the stretching surface. On the contrary, the adsorption $\Gamma(\Theta)$ is greater on the lower part of the bubble than Γ_0 which provides the surfactant desorption. The adsorption $\Gamma(\Theta)$ eventually increases along the bubble surface motion, i. e. from the upper pole $\Theta = 0$ to the lower one $\Theta = \pi$.

The surfactant transport described above is caused by the diffusion or by the formation of the diffuse boundary layer. Its thickness δ is much smaller than the radius of the bubble R:

$$\delta \approx R \cdot Pe^{-1/2} \tag{18}$$

in which the Pecklet criterium $Pe = Re\ \nu/D$, $Re = RU/\nu$ is the Reynolds criterium, U is the rate of the bubble, ν is the kinetic viscosity, and D is the diffusion coefficient.

The approximate equilibrium of every section of the surface (its electroneutrality, for example) is the characteristic feature of the thin DL deformation. The value of the adsorption also changes alongside the moving surface of a bubble. The same happens to the diffuse layer concentration. Therefore, the DL modification alongside the bubble surface is in good accordance with the change of the surface charge and electrolyte concentration. But its spatial structure on each section is described within the framework of the equilibrium DL theory. This makes possible to analyse the heterocoagulation on the basis of the DLVO theory. However, the deformation of the DL brings about new phenomena. As is known the diffusion in electrolyte usually causes the electric field — diffusion — electric phenomena. The vectors of the electric field E coincide with those of the concentration gradient — grad c. The electric field is expressed by the local value of the concentration gradient[2,27] in the case of binar electrolyte:

$$E_D = \frac{D^+ - D^-}{Z^+ D^+ + Z^- D^-} \; \frac{RT}{F} \; \frac{\text{grad}\, c}{C} \tag{19}$$

where $D^\pm$, $Z^\pm$ are the diffusion coefficients and the valency of anions and cations, F is the Faraday number.

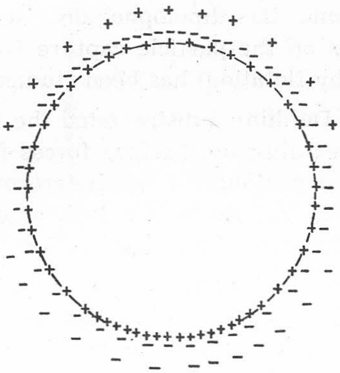


Figure 8. Diagram illustrating the charge distribution in the secondary electric double layer.

The electric field should arise within the diffuse boundary layer, attached to dynamic adsorption layer of an ionogenic surfactant; the reason for that being the DL deformation and its negligible diversity from the electroneutrality.

The vectors of E_D like these of grad c originate (or terminate) by the external boundary of a quasiequilibrium DL and are oriented approximately towards normal of the surface. They terminate (or originate) at any point of the diffuse layer. Since positive charges are the sources of the electric field tension lines and negative charges are the outlets of them, it may be assumed that the charges of opposite sign (which compensate each other) are localised within the quasiequilibrium DL and the diffusion layer (Figure 8). These two layers are the integrity, the change of the charge of one layer causes the change of the charge of another layer. This system of the charges may be referred to as the secondary double layer. It is thicker than the equilibrium DL by some orders. That is why the particle precipitation on a bubble surface could be controlled, first, by the particle transport through the diffusion layer[5,24]. If the particle is smaller than δ, the problem tends to be much simpler, and the particle could be regarded as being affected by the uniform and diffusion fields. Consequently, the particle is affected by the electrophoresis and the diffusiophoresis[24]. Samygin[29], studying the precipitation inlfuenced by the weight of galenite particles onto the moving surface of a stabilized bubble, has discovered that the particle smaller than some critical value of a_{cr} does not reach the bubble surface. It has been established that with $a < a_{cr}$ the combined effect of the electro- and diffusiophoresis determines the repulsion forces of the particles which prevail the force of gravity. The higher is the electrolyte concentration, the weaker are these forces, — the fall of a_{cr} testifies to that.

A floating bubble diffusion layer is much thinner than described. This effect is valid only with the particles so small that they bring about the importance of a heat motion. The electro- and diffusiophoresis should be taken into account while describing the Broun diffusion of the submicron particles towards the moving surface of a bubble. The electrolyte concentration must be low. The concentration drop in the diffusion layer δ_c is very weak[30] with the steadiness of the bubble surface

$$\frac{\delta C}{C} \sim Pe^{2/3}/(\varkappa R)^2 \tag{20}$$

The mechanism of the non-equilibrium electric surface forces with $a > \delta$ could only be described, if the same ionogenic surfactant is sorbed on the surfaces of the bubble and the particle. This mechanism is in the relation with the desorption of a reagent from the particle surface, the diffusion through a film and the surface adsorption. The formation of a diffuse ion transport of an adsorbate is determined by the concentration drop of the reagent in the diffusion layer. The concentration drop spreads itself over the upper part of the bubble, and over the lower part too, with the condition $\Gamma_o/c_o \gg \delta$. The section on which the adsorption takes place acquires an extracharge. Its sign coincides with that of a quick — diffusing ion. The equal charge of the opposite sign appears on the section from which the reagent is desorbing. And as a result the electric field appear of 10^3 V/cm order.

The excess charges of the bubble are attached to the extra charges of the particle, so that the film becomes pressed as if by the surfaces of a condensator which leads to the film thinning. The non-equilibrium electric surface forces decrease in the presence of an indifferent electrolyte, provided its concentration is much higher than that of the ions forming the adsorption layer.

We think that the non-equilibrium surface forces of a diffuse nature expressed themselves in experiments done by Evers and Evans[32,33]. A thin layer of a soluble ionogenic surfactant had been spread over a small section of an inclined plane of a solid body. When the water was streaming down the slope, its thickness remained even except the section covered by the surfactant. The surfactant made the water surface got curved at the point of thinning, it was assumed that a considerable force had been applied to the water-to-air normal which should eventually compensate the capillar pressure. This effect is conditioned by the surfactant desorption, its diffusion to the water-air interface, and the adsorption on it.

The electrochemical processes and phase developments are always followed by the electrodiffusion layer formation. That's why they cause the dipolophoretic and the diffusiophoretic particle transport to the reagent surface.

The diffusiophoresis conditioned by the diffuse current of a dissolving salt, provides the deposition of latex particles onto a presalted surface during the fabrication of polymer films by ionic deposition[35,36].

REFERENCES

1. A. Sanfeld, *Introduction to the Thermo-dynamics of Charged and Polarized Layers,* Wiley-Intersience, New York 1979.
2. S. S. Dukhin and B. V. Derjaguin, *Electrokinetic Phenomena, Surface and Colloid Science,* E. Matijevich (Ed.), Wiley-Interscience, N-Y., Vol. **7**, 1974.
3. B. V. Derjaguin and L. D. Landau, *Acta Phys. Chem. USSR* **44** (1941) 633.
4. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids,* Elsevier, Amsterdam 1948.

5. S. S. Dukhin, in: »*Research in Surface Forces*«, N. Y., 1963, Vol. **1**; S. S. Dukhin, in: *Issledowanija v oblasti poverhnostnih sil*, Isdatelstvo Akad. Nauk SSSR, Moscow 1961, p. 197.
6. S. S. Dukhin, in: *Uspekhi Kolloidnoj Chimij*, Nauka, Moscow, 1974 .
7. V. R. Estrela-Lopis, S. S. Dukhin, V. N. Shilov, *Kolloidn. Zh.* **36** (1974) 328.
8. S. S. Dukhin, B. V. Derjaguin, and N. M. Semenichin, *Dokl. Akad. Nauk SSSR* **192** (1970) 357.
9. S. S. Dukhin, V. N. Shilov, *Dielectric Phenomena and Double Layer in Disperse Systems and Polyelectrolytes*, Halsted Press., N. Y. 1974.
10. V. N. Shilov, V. R. Estrela-Lopis, in: B. V. Derjaguin (Ed.), *Poverhnostnie Sily v Tonkin Plenkah*, Nauka, Moscow 1979, p. 35.
11. V. R. Estrela-Lopis, *Dissertation*, Institute of Colloid and Water Chemistry, Kiev 1977.
12. V. N. Krasny-Ergen, *Ann. Physik* **27** (1936) 459.
13. V. N. Besryk et al., *Kolloidn. Zh.* **34** (1972) 165, 321.
14. F. S. Kaplan, *Dissertation*, Leningrad Technological Institute im. Lensoveta, Leningrad 1971.
15. O. G. Usiarov and F. S. Kaplan, in: collection »*Fiziko-khimicheskajo mekhanika i liofilnost dispersnych system*«, Naukova Dumka, Kiev 1978, p. 70.
16. V. R. Estrela-Lopis, S. S. Dukhin, and O. V. Smirnov, *Kolloidn. Zh.* **34** (1972) 306.
17. A. I. Gavriluk, N. V. Shilov, *Kolloidn. Zh.* **41** (1979), N 6.
18. B. V. Derjaguin, *Kolloidn. Zh.* **16** (1954) 425.
19. S. S. Dukhin, O. D. Kurilenko, and B. D. Grebenuk, *Kolloidn. Zh.* **37** (1975) 859.
20. S. S. Dukhin, V. D. Grebenuk, O. D. Kurilenko, and T. T. Sobolevskaja, *Kolloidn. Zh.* **37** (1975) 737.
21. S. S. Dukhin, V. L. Sigal, and L. N. Korneeva, *Elektronnaja obrabotka materialov* N6 (1977) 44.
22. S. S. Dukhin, V. D. Grebenuk, N. D. Strishak, and V. N. Shilov, *Kolloidn. Zh.* **39** (1977) 23.
23. B. V. Derjaguin and S. S. Dukhin, *Surface and Colloid Sci.* **7** (1974) 322.
24. B. V. Derjaguin and S. S. Dukhin, *Trans. Inst. Mining Met.* **70** (1961) 221.
25. B. V. Derjaguin, S. S. Dukhin, and V. A. Lisitchenko, *Zh. Fiz. Khim.* **33**, (1959) 2280; **34** (1960 324.
26. V. N. Shilov, V. R. Estrela-Lopis, in: B. V. Derjaguin, (Ed.), *Poverkhnosnye sily v tonkih plenkah i dispersnyh systemah*, Nauka, Moscow 1972, p. 214.
27. S. S. Dukhin and B. V. Derjaguin, *Electrophores*, Nauka, Moscow 1976.
28. S. S. Dukhin, *Zh. Fiz. Khim.* **34** (1960) 1052.
29. B. V. Derjaguin and V. D. Samigin, *Collection of works of Institute Gintsvetmet, Metallurgizdat*, **9** (1962) 240.
30. S. S. Dukhin and L. V. Bujkov, *Zh. Fiz. Khim.* **38** (1964) 3011.
31. S. S. Dukhin, *Dokl. Akad. Nauk SSSR* **130** (1960) 1928.
32. K. S. Sutherland and E. V. Work, *Printsipi Flotatsii*. Metallurgizdat, Moskva 1968.
33. L. P. Ewans and W. E. Ewers, *Recent developments in mineral dressing*, Institute of Mining and Metallurgy, London 1953, pp. 457--63. L. E. Ewans, *Ind. Eng. Chem.* **46** (1954) 2420.
34. S. S. Dukhin, *Kolloidn. Zh.* **23** (1961) 409.
35. B. V. Derjaguin, S. S. Dukhin, and A. A. Korotkova, *Kolloidn. Zh.* **23** (1961) 53.
36. B. V. Derjaguin, S. S. Dukhin, and A. A. Korotkova, *Kolloidn. Zh.* **15** (1978) 643.

SAŽETAK

Neravnotežne površinske sile

S. S. Duhin

Električki dvosloj dolazi u stanje neravnoteže pod utjecajem bilo kojeg efekta, koji uzrokuje električki ili hidrodinamički tok unutar te strukture. Sile koje uzrokuju odstupanje električkog dvosloja od ravnotežnog stanja nazivaju se neravnoteženim površinskim silama. U radu se teorijski obrađuju oni slučajevi, u kojima vanjska polja sila uzrokuju odstupanje dvosloja od stanja ravnoteže, a to su pojave dipoloforeze i difuzioforeze. Posebno se promatraju uvjeti za stacionarno stanje. Upućuje se i na primjenu teorije neravnotežnih sila u koloidnim sistemima i procesima kao što su elektrokoagulacija, elektrofiltracija, flotacija i elektrodepozicija polimera.

INSTITUT ZA KOLOIDNU KEMIJU I
KEMIJU VODE
UKRAJINSKA AKADEMIJA ZNANOSTI
KIJEV, SSSR

Prispjelo 22. studenog 1979.