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Non-equilibrium Surface Forces and Hydrodynamics of Thin Films*

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The notion »non-equilibrium surface forces« is advanced for the application in a number of cases of colloid stability and transport phenomena. The idealized concept of full equilibrium in the double layer, as used in the DLVO theory is shown to be too simple to describe the stability of a colloid particle not in equilibrium with the surrounding medium. Cases are described where surface forces are stipulated by adsorption layer effects, controlled by diffusion, such as flotation, crystal growth, hydrodynamic transport, and in describing the stability of living cells in suspension.

1. INTRODUCTION

The notion »non-equilibrium surface forces« appeared[1–3] at the study of coagulation processes in the systems, being further from equilibrium, than at traditional consideration of stability problem. If the particle is not in equilibrium with the medium, then qualitatively new mechanisms of stability and coagulation emerge.

Idealized concept of full equilibrium in double layer (DL) makes DLVO theory more simple.[4–5] This idealization is true in many cases. However since 1960 we have pointed out a number of non-eguilibrium colloid-electrochemical processes leading to new effects.

Another type of forces, which emerges because of DL deviation of equilibrium, we call non-equilibrium surface forces. Therefore, non-equilibrium surface forces are attributed to non-equilibrium DL, as well as equilibrium ones to equilibrium DL. If all the effects are stationary, the forces are also stationary. And there is one condition that divergence of ion flow equals to zero, instead of zero ion flow in equilibrium case.

Surface forces are stipulated not only by double electric layer. Adsorption layer concept has a more general character. That is why more general notion »non-equilibrium surface forces« should be associated with non-equilibrium adsorption layer effect on coagulation and adagulation. For example,

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non-equilibrium adsorption layer of non-ionogenic surfactant affect coagulation of bubble and emulsion drops.[1,6] That is why non-equilibrium surface forces may be caused by transport both of ions, and surfactant molecules.

The transport of dissolved substance may be stipulated by different factors and correspodingly non-equilibrium forces emerge under different conditions. Double electric layer deviation from equilibrium emerges under the influence of external electric layer and these non-equilibrium forces were considered by us earlier.[3] The deviation of double electric or adsorption layers from equilibrium also emerges under the influence of predetermined from outside concentration gradient. Non-equilibrium surface forces are considered in this paper. In the vicinity of mobile interfaces (bubbles, drops) non-equilibrium surface forces emerge as a sequence of surfactant adsorption layer destortion under liquid flow influence. Heterogeneous ion transport may cause non-equilibrium surface forces. In this respect non-equilibrium surface forces have been regarded earlier, emerging from phase transformation, e. g. at crystal growth or dissolution.[6] Heterogeneous transport variety has been in the focus of attention in recent years, which accompanies exchange processes in biological cell. Biological aspect of non-equilibrium surface forces will be considered in this paper too.

When creating quantitative theory of non-equilibrium surface forces there appears the necessity to describe space distribution of concentration of diffusing ions and molecules. In the first approximation the given particle may be regarded as being under homogeneous diffuse field effect, fully characterized by gradient concentration value, depending only on the shortest distance h between particle surfaces. The condition of this approximation is

$$h > a \tag{1}$$

where a is radius of the smallest particle. In this limiting case it is possible to describe rather universally non-equilibrium surface forces. Diffusiophoresis is the base of it.[7,8] It is particle movement under the effect of concentration gradient of dissolved substance.

Analytical description of non-equilibrium surface forces turns out to be possible at the condition being contrary to the condition (1).

$$h \ll a \tag{2}$$

At this condition the problem of non-equilibrium surface forces comes to the dynamics of thin liquid layer between the surfaces of interacting particles.[9] Concentration change along this layer results in tangential flow. Liquid flowing out of the layer favours coagulation and flowing into it favours system stability.

2. DIFFUSIOPHORESIS AND CAPILLARY OSMOSIS

Diffusiophoresis in electrolyte is simple, if diffusion coefficients of $D^{\pm}$ ions of binary electrolyte are not equal.[2] There is no electric current at stationary and quasistationary conditions and in the absence of outer field and electrodes supplying and removing the charges. When assuming contrary conditions, we come to a contradiction, as at the above mentioned conditions charge transfer leads to charge growth of the opposite sign in the areas

between which current lines are distributed. This charge growth is accompanied by electric growth induced by them, what contradicts the accepted condition of stationarity of the system.

The absence of electric current and stationary condition are ensured by stationary electric field, causing such charge flow, which compensates charge flow, caused by different diffuse flows of ions. A simple formula of electric field of diffusion origin can be drawn from this:

$$\vec{E} = \frac{kT}{e} \frac{D^+ - D^-}{z^+ D^+ + z^- D^-} \frac{\text{grad } c}{c_o} \tag{2.1}$$

where $z^{\pm}$ is ion valency, $c = c^+/z^+ = c^-/z^-$. The possibility to express the distribution of cations $c^+(r)$ and anions $c^-(r)$ concentration by one and the same $c(r)$ function appears because of electric neutrality of electrolyte in every point of space

$$z^+ c^+(r) - z^- c^-(r) \equiv 0 \tag{2.2}$$

Therefore, even in the absence of outer electric field electrophoretic particle transport is possible under the effect of electric field of diffusive origin. If we express electrophoresis rate μ_{ef} by electric field with the help of Smoluchowski formula and then if we use the formula (2.1), we shall obtain:

$$\mu_{ef} = \frac{\varepsilon \zeta}{4 \pi \eta} v_o \frac{\text{grad } c(r)}{c_o} \tag{2.3}$$

where

$$v_o = \frac{D^+ - D^-}{D^+ + D^-} \frac{kT}{e}$$

k is Bolzmann constant, T — absolute temperature, e — electron charge. As the transport, according (2.3), is caused by concentration gradient, it is quite natural to use such term as diffusiophoresis. Diffusiophoresis, i. e. disperse particle motion under the effect of gradient of electrolyte concentration also emerges at $D^+ = D^-$. In this case capillary osmosis slipping (a new electrokinetic feature) causes diffusiophoresis. If electroosmosis slipping is a liquid flow in diffuse double layer effected by tangential component of electric field (in the absence of gradient concentration), then capillary osmosis is a liquid flow within DL effected by tangential component of gradient concentration (in the absence of gradient of electric potential).

The theory of capillary osmosis slipping[7] is based on concentrational polarization of thin double layer, i. e. at the condition

$$\varkappa a \gg 1 \tag{2.4}$$

where $\varkappa^{-1}$ — diffuse layer thickness. At this condition equilibrium between it and attached volume of electrolyte is maintained for each DL section. When electrolyte concentration is changing along outer DL boundary, caused by concentration gradient, diffuse layer thickness is also changing, as well as Stern potential and excess pressure inside DL. Therefore, pressure change along DL is caused by the change of concentraions. In its turn, such pressure change along DL causes tangential liquid flow, proportional to the concentration gradient. Flow rate near the surface equals to zero because of liquid

»no-slipping«. It increases from the surface because of DL polarization achieving its maximum at the outer boundary, which characterizes the rate of capillary osmosis slipping. It can be expressed by the following formula being (2.4) proportional to the meaning of concentration gradient near outer boundary of the given DL section and in case of binary uni-univalent electrolyte:

$$\frac{\varepsilon \zeta^2}{32 \pi \eta} \operatorname{grad} c \tag{2.5}$$

As electroosmosis slipping along particle surface induces its movement in opposite direction (electrophoresis), similarly to that capillary osmosis slipping induces particle movement in the opposite direction being effected by gradient concentrations (diffusiophoresis). Here is a formula, which unites electric field effect (2.1) and capillary osmosis slipping at diffusiophoresis:

$$V = 2K \frac{\operatorname{grad} c}{c_0} \tag{2.6}$$

where

$$2K = mD \left(\frac{D^+ - D^-}{z^+ D^+ + z^- D^-} \tilde{\xi} + \frac{\tilde{\xi}^2}{8} \right), \qquad m = \frac{\varepsilon}{4 \pi \eta D} \left(\frac{kT}{e} \right)^2 \tag{2.7}$$

3. DIFFUSIOPHORETIC FORCES IN ELEMENTARY ACT OF FLOTATION

During flotation the upper part of bubble surface is stretching, and the lower one is contracting. New surface sections are filled by adsorbed substances. These portions of adsorbed substance are desorbed at surface contraction. Adsorption is low on the stretching section of the surface to compare with that of non-changing one. This causes continuous substance supply to stretching surface. And, otherwise, adsorption is high on low surface and ensures desorption. Thus adsorption continuously increases with angle grow.

The described tr[illegible]sport is ensured by diffusion and by diffusion layer formation. Its thickness is much less than bubble radius R

$$\delta \sim R \cdot Pe^{-1/2} \tag{3.1}$$

where Pe is Peclét number, Re — Reynolds number, v — the rate of bubble buoying to the surface, η — kinematic viscosity, D diffusion coefficient.

Within diffusion layer electric field appears as a result of DL deformation and slight deviation from electroneutrality. Vector lines E_0 are similar to grad c and emerge on the outer face of quasiequilibrium DL and are orientated perpendiculary to the surface. As positive charges are the sources of electric field, and negative ones are outlets it should be concluded, that the charges of the opposite sign are distributed in diffuse and diffusional layer. This system of charges should be called secondary double layer, which by a number of orders of magnitude thicker than that of equilibrium one. That is why particle transport to the surface is mostly governed by diffusional field, diffusiophoresis.[10] Samygin, studying sedimentation of galenite particles on moving bubble surface, discovered that particles of $a < a_{cr}$ dimension do not reach its surface. Diffusiophoresis exceeds the rate of sedimentation.

The higher is the concentration of electrolyte, the weaker are the forces — a_{cr} drop proves it.

In the absence of dynamic adsorption layer particle sedimentation on the buoying surface of a bubble[11] is carried out thanks to radial component $V_r(r, \Theta)$ (r, Θ-spheric system of coordinates with the starting point in bubble centre) of hydrodynamic field of the bubble and final particle dimensions. As $V_r(r_o, \Theta)$ decreases when approaching bubble surface, diffusiophoresis may effect sedimentation, if its rate V_{dr} at the nearest possible distance between particle and bubble $R + a$ exceeds radial component of hydrodynamic rate

$$V_{dr}(R + a, \Theta) > V_r(R + a, \Theta) \tag{3.2}$$

where R is bubble radius.

Besides, diffusiophoresis effect may turn to be insignificant, if particle transport is sufficiently effective thanks to their Brownian motion. The less is the coefficient of Brownian diffusion, the thinner is diffusion layer δ_β, through wich the particles are transported because of Brownian diffusion. If diffusiophoretic rate is directed from bubble surface on its upper part ($m > 0$) and the condition is carried out

$$|2K| \frac{\Gamma_o}{c_o} \gg d_o + \frac{\gamma d_o^2}{\eta R} \qquad (Re \ll 1) \tag{3.3}$$

or

$$|2K| \frac{\Gamma_o}{c_o} \gg d_o + \frac{\gamma}{\eta} \frac{d_o^2}{\delta} \qquad (Re \gg 1) \tag{3.4}$$

diffusiophoresis will almost prevent sedimentation on the surface of the buoying bubble. Here Γ_o/c_o is surface activity of iongen surfactant, Γ_o — adsorption, γ — the degree of retardation by adsorption layer: η — water viscosity,

$$d_o = \max(\delta_\beta, a) \tag{3.5}$$

These results were obtained on the basis of quantitative consideration of particle trajectories, deposed on bubble surface taking into account both the effect of hydrodynamic field and diffusiophoresis.[12]

Diffusiophoresis enables flotation, if $2K < 0$. The rate of particle depo sition on the bubble is expressed by formula[12]

$$E_d = 4\sqrt{\frac{2|m|}{Pe}} \tag{3.6}$$

4. DIFFUSIOPHORETIC FORCES IN BIOLOGICAL SUSPENSIONS

Radius of diffusiophoretic forces effect is by a number of orders of magnitude greater, than that of equilibrium ones. That is why when the researches of living cells[13] gave the possibility to obtain long-range forces in mixtures of cells and solid particles[14], it was natural to attribute them to diffusiophoresis. Then the data[16] were obtained in favour of electromagnetic nature of long-range forces between living cells. But this does not exclude the role of diffusiophoresis in other cell systems.

Ion transport through cellular membrane at exchange processes, which enable vital activity of the cell, is accompanied by the formation of diffusion--electric field in the neighbourhood of the cell and it induces mutual electrodiffusiophoresis of cells. If the distance between the cells is rather long, it is possible to use superposition of their spheric fields. If the cells of one kind are considerably greater than the cells of the other kind and are characterized by intensive exchange processes, the cells of this kind repel intensively other cells, so that free zone appears around them — a halo. Effective halo radius is determined by counteraction of two factors: diffusiophoretic repulsion enables halo growth, and Brownian motion enables halo reduction. Stationary state of halo is described by the condition of diffusiophoretic and Brownian flow compensation.

Golovanov[13] experimentally proved that at the introduction of concentrated solutions of inorganic electrolytes such as 15% natrium chloride solution in biological cell suspensions (e. g. blood) around some cells (tumour cells, leucocytes) haloes are formed (Figure 1), i. e. round free zones are free from

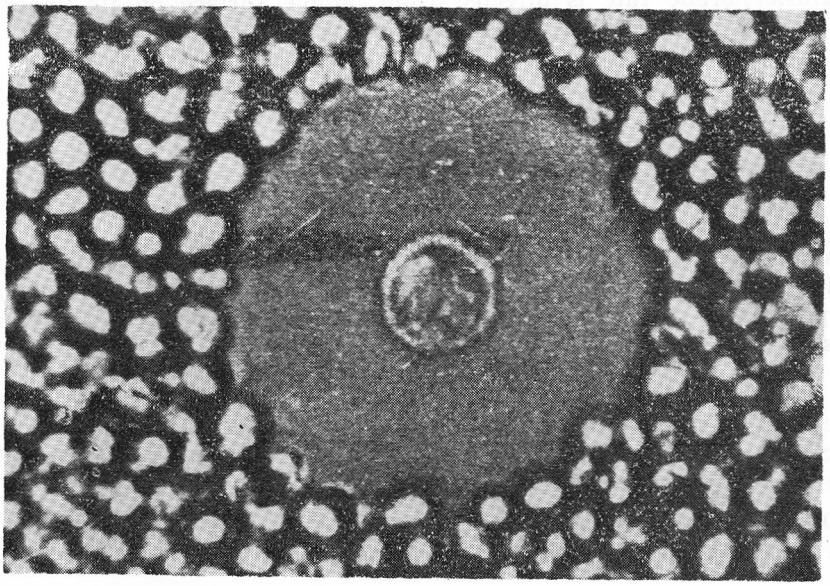

Figure 1. Halo.[13] The haloforming cell is in the center. The free zone around it. The red cells are distributed around the free zone.

background cells (red cells, yeast cells, colloid particle carcasses). In the medium of red cells haloes are formed during 5—10 minutes as a result of the observed background cells movement from the central haloforming cell (HFC) for the distance of 100 μ and more. Haloes in the medium of particle carcasses are formed during 2—4 seconds and achieve the thickness of 10 μ. Haloes are formed around tumour cells (sarcoma, leucose), leucocytes of blood, blust cells, lymphoid tissue.

Ion transport through biological cell membrane has quasistationary character as relaxation time of diffusiophoretic processes in small area with

dimension of 10 μ is not substantial. It is possible only when the cell is electroneutral and its charge does not increase and consequently the density of electric current equals to zero. The last condition is satisfied at ion diffusion flows, which appear only because of diffusion potential. It is natural to assume that membrane permeability for ions of type is the same for any part of its surface, which will be approximately considered as spherical one with radius. In such a case ion flow distribution in the vicinity of cell is also characterized by spherical symmetry. These flows for binary electrolyte are composed of electromigrational diffuse components

$$j_e^{\pm} = D^{\pm}\left(\mp \frac{F z^{\pm}}{R T} c^{\pm} \cdot \frac{\partial \varphi}{\partial r} - \frac{\partial c^{\pm}}{\partial r}\right)$$

where $c^{\pm}$, $D^{\pm}$ are concentrations and diffusion coefficients of cations and anions, R — universal gas constant, T — absolute temperature, F — Faraday constant. If current density equals to zero, flows $j^{\pm}$ are directed in one side and equal to each other: $j^{+} = j^{-} = j$. From this condition it is possible to express electric potential gradient in terms of concentration gradient and then to exclude potential gradient from $j^{\pm}$ expressions. As a result we express electrolyte flow $j(r)$ through spherical surface of any radius r using concentration gradient.

$$j(r) = j^{+} + j^{-} = -2 D_e \frac{\partial c}{\partial r} \tag{4.1}$$

where

$$D_e = \frac{D^{+} D^{-} (z^{+} + z^{-})}{z^{+} D^{+} + z^{-} D^{-}}$$

In stationary conditions the same quantity of ions (as well as through membrane) is transported through each cross-section, i. e.

$$4 \pi r^2 j(r) = 4 \pi R^2 j_m \tag{4.2}$$

where j_m– ion flow through membrane. Having substituted (4.2) in (4.1), we obtain

$$\frac{\partial c}{\partial r} = -\frac{1}{D_e} \frac{R^2}{r^2} \frac{j_m}{2} \tag{4.3}$$

Stationary diffusion equation, Laplace equation should be solved

$$\Delta c = 0 \tag{4.4}$$

in combination with boundary condition (4.3) and the condition on long distance from the cell

$$c/_{r \to \infty} = c_o \tag{4.5}$$

Then the solution is obtained

$$\frac{c(r)}{c_o} = 1 + \frac{\Delta c}{c_o} \frac{R}{r} \tag{4.6}$$

where concentration drop is

$$\Delta c = R j_m / D_e \tag{4.7}$$

Golovanov's experiments were carried out with an addition of electrolyte to biological suspension, also containing large and small particles. Stationary concentration distribution $c(r)$ was formed there after diffusion exchange in a certain time τ_D. The time of diffusion front movement at the distance of l equals to l^2/D_e according to Einstein equation. As it is seen from equation (4.6), the distance, where concentration changes considerably, equals to R. That is why

$$\tau_D \sim R^2/D_e$$

If we assume that $R \sim 10\,\mu = 10^{-3}$ s M, $D_e \sim 10^{-5}$ s M^2, then we shall obtain $\tau_D \sim 0.1$ s. Meanwhile observations showed that the halo of small particles was formed around large cells in several seconds. This means that cell diffusiophoresis rate is lower than ion diffusion rate. That is why invisible electrolyte concentration distribution is formed rather quickly and only after that small cells are redistributed under the effect of this almost stationary ion distribution during considerably longer period of time. If diffusiophoresis rate had been much higher than the average rate of Brownian movement of cells, small cells would be removed from the central large cell moving strictly along radial trajectories. Chaotic movement will overlap this ordered movement of cells. As small cell become more distant the acting concentration gradient of electrolyte decreases, therefore the rate of diffusiophoresis falls.

As the concentration of small cells in the area of halo is much less than the mean concentration of cells at long distance from central large cell, Brownian diffusion of cells emerges from their high concentration area into low one, i. e. in halo area. Therefore diffusiophoresis removes small cells from central large cell, Brownian diffusion counteracts it, bringing them back in halo. The observed stationary cell distribution on halo boundary is determined by the condition of compensation opposite to these directed flows and may be described by a special formula.

For the estimation of distances, where haloforming cell can repulse small ones, let us make an expression for the flow of the latter ones in spherical symmetric field of haloforming cell:

$$j_s = 4\pi r^2 \left(-D_\beta \frac{\partial n}{\partial r} + 2Kn \frac{\partial \ln c}{\partial r} \right) \tag{4.8}$$

where $n(r)$ — is unknown concentration distribution of Brownian particles, characterized by Brownian diffuse coefficient D_β. The condition of stationary halo existence is written as follows

$$j_s = 0 \tag{4.9}$$

Integrating equation (4.8) at the condition of (4.9) and condition of (4.5) and

$$n/_{r\to\infty} = n_o \tag{4.10}$$

where n_o is the concentration of particles at long distances from haloforming cell, we shall obtain[17]

$$n(r) = n_o \left(\frac{c}{c_o} \right)^{-2K/D_\beta} \tag{4.11}$$

We express the coefficient of Brownian diffusion of small cells (red cells, in particular) by coefficient of ion diffusion D_e:

$$D_\beta = D_e \frac{r_o}{R} \tag{4.12}$$

where r_o is ion radius, R — red cell radius. Then we shall obtain a convenient estimation

$$\frac{2K}{D_\beta} \simeq 3m\zeta_e^2 \beta \frac{R}{r_o}, \qquad \beta = \frac{D^+ - D^-}{D^+ + D^-} \tag{4.13}$$

where e index is related with red cell. Uniting the formulae (4.11) and (4.6), we shall take into account the condition (4.14)

$$\frac{\Delta c}{C_o} \frac{R}{r} \ll 1 \tag{4.14}$$

$$\frac{2K}{D_\beta} \gg 1 \tag{4.15}$$

and we shall use the well-known definition of e — number

$$e = \lim_{n\to\infty} (1 + 1/n)^n$$

Then

$$\frac{n(r)}{n_o} = \left(1 + \frac{\Delta c}{c_o} \frac{R}{r}\right)^{-2K/D_\beta} e^{-\mu R/r} \tag{4.16}$$

where

$$\mu = \frac{2K}{D_\beta} \frac{\Delta c}{c_o} = 3m\beta\zeta_e \frac{R}{r} \frac{\Delta c}{c_o} \gg 1 \tag{4.17}$$

Evidently, equation (4.17) is the condition of halo formation, as according to (4.16), at this condition red cell concentration is much lower in a certain vicinity of leucocyte (large cell) than that at considerably lower distances from it.

Special experimental methodology[18] has been elaborated to examine this mechanism of halo formation. In the thin film of liquid, brought on glass plate, disperse particles are suspended, particularly quartz micron particles. Capillary, soldered from one side, is filled with electrolyte solution. When dipping the open end of capillary in the film, the ions start to diffuse from the capillary into the film. Consequently, there appears spherical symmetrical diffusion-electric field, which effects quartz particles. Radially-symmetrical particle movement was observed and its rate was identified in time and distance from the centre of capillary. The agreement of these dependences with the above theory improved after consideration of capillary-osmotic and electroosmotic slipping, originating on glass-water interface and ζ-potential of particle dependence on salt concentration.

Experimental dependence of the average time of halo formation and its value on salt concentration was observed. It conforms to the theory. This is caused by two factors, depending on concentrations, i. e. the dependence of

diffusion-electric field prevails at low concentrations and is the cause of intensification of halo formation as concentration grows. ζ-potential decreases at high concentrations leads to the weakening of effect.

High stability of living cell suspensions is often observed, as well as stability loss by dead cells. This regularity may be stipulated by diffusion-electric fields of cells, appearing at ion transport through cell membrane at exchange processes, which keep up vital activities of the cell. The cessation of exchange processes after cell »death« and disappearance of its diffusion-electric field often lead to the fusion of cells, if stability factors, described by the theory of DLVO, for the given type of cells and in these conditions effect weakly.

As in the theory of slow coagulation, we shall consider Brownian diffusion of identical spherical particles at their simultaneous interaction, which is stipulated by diffusion-electric fields of cells in the considered system.

For the estimation of the energy barrier of repulsion forces we shall use the expression for particle flow, caused by mutual effect of Brownian diffusion and diffusiophoresis.

There is $j_\beta = \text{Const}$ at stationary conditions. For its determination it is necessary to integrate equation (4.8), taking in account the condition of approaching cell fusion, which is written in the same way as in the theory of slow coagulation

$$n_i'_{r=2R} = 0 \tag{4.18}$$

where R is cell radius.

The second boundary condition is given for infinity (4.10).

Equation (4.8) is similar to kinetic equation of slow coagulation. As the theory of slow coagulation, this paper considers the process of overcoming the barrier by Brownian particles. The only difference is the physical nature of barrier. According to DLVO theory the barrier appears as a result of overlapping of double electric layers of both particles.

The barrier caused by diffusiophoretic repulsion, but full analogy in mathematical aspect, may become more important for a living cell. The equation of slow coagulation kinetics differs only by coefficient shape before n in the second term of the right side of equation (4.8). Quantitative relationship between both mechanisms is expressed by relation

$$2K' \frac{d \ln c}{d r} \rightleftarrows - \frac{D_\beta}{k T} \frac{d V}{d r} \tag{4.19}$$

where $V(r)$ is potential energy of particle interaction.

Integrating (4.19) in the range from $2R$ to ∞, we shall obtain the value of diffusiophoretic barrier, expressed in kT units

$$\frac{V_{df}(2R)}{k T} = - \frac{2K'}{D_\beta} \ln \frac{c(2R)}{c_o} \approx \frac{\mu}{2}$$

The identity of equations and boundary conditions of slow coagulation theory in colloids and biocolloids, as well as the condition of correspondence

(4.19) enable to use integration result, first done by Fuks[19] for aerosols and by Derjaguin[20] for colloids. Substituting (4.19), we shall obtain:[21]

$$j_s = -\frac{4\pi D_\beta n_o}{\int\limits_{2R}^{\infty} \frac{dr}{r^2}\left(\exp \int\limits_{\infty}^{r} \frac{1}{kT}\frac{dV}{dr}\right)dr} = -\frac{4\pi D_\beta R n_o}{W} \tag{4.20}$$

where W is the factor of coagulation retardation. In this case

$$W = \int\limits_{2}^{\infty}\left[\frac{c(s)}{c_o}\right] - \frac{2K}{D_\beta}\frac{ds}{s^2} \tag{4.21}$$

where $s = r/R$, c_o is electrolyte concentration being far from the cell.

At high positive values of μ, corresponding to diffusiophoretic repulsion, integral (4.22) approximately equals to:

$$W = \frac{1}{\mu} e^{\mu/2} \tag{4.23}$$

as it follows from this formula, considerable stabilizing effect of diffusiophoresis is possible (at high μ). There is some information about biological system,[21] in which high value μ is realized, i. e. growing the biomass of *Candida boidimi* yeast.

Biochemical process intensity is limited, so that relative concentration drop is very small. That is why the condition (4.14) may be carried out only for sufficiently large particles. Their Brownian motion is weak, so that even weak diffusiophoresis noticeably effects coagulation.

That's why a rather interesting idea about diffusiophoresis effect on transport of macromolecules or colloid particles in the vicinity of biological cell is difficult for realization. It is quite possible that diffusiophoresis effects the interaction of cells and disperse particles of micron size. Serious difficulties arise at the development of theory.

5. DIFFUSIOPHORETIC INTERACTION IN THE PROCESS OF GROWING AND DISSOLVING OF IONIC MICROCRYSTALS

In contrast to biological systems relative drop of electrolyte concentration may be quite considerable in the processes of growing and dissolving of ionic microcrystals. The importance of diffusiophoresis for these systems had been pointed out earlier,[6] than that of biological suspensions. The theory elaborated for the later, may be also used for the estimation of diffusiophoretic interaction of growing or dissolving microcrystals. At the condition of (2.4), the rate of diffusiophoresis hardly depends on the particle form. As well as diffusion-electric field can hardly depend on its form at great distance from growing or dissolving crystal. Crystal sedimentation is more significant, than that of biological cells, which was not even taken into account.

Starting from a certain rather large size, which depends on the density of crystal substance, interaction becomes more complicated because of the rate differences of various size crystal sedimentation. It is possible to use formulae, obtained for spherical cells, for the crystal of smaller size, which can be hardly estimated at present. This is stipulated by diffusion-electric

field at great distances and the rate of diffusiophoresis depends weakly on crystal form.

As relatively great drop in the concentration of salts is also possible at the growth, at dissolving, μ criterion may achieve greater values even at submicron crystal dimensions. Nevertheless, μ criterion is small at early stages of homogeneous coagulation. It may be great and diffusiophoresis is considerable when the particles are of 10—100 nm. Quantitative theory for the group of microcrystals has been complicated by the necessity of combined consideration of diffusiophoresis effect on coagulation and in its turn, coagulation effect on the rate of crystallization and electrolyte concentration, on which diffusiophoresis depends on.

Diffusiophoresis may turn to be important for the purity of the growing crystals. It may prevent from dispersion impurities transport, when passing diffusion layer of the growing ionic macrocrystal.

6. COAGULATION AND HYDRODYNAMICS OF THIN FILMS

Surface forces effect on coagulation increases the particles approach each other. That's why the consideration of this coagulation stage is of utmost interest, at which liquid interlayer between particle surface is rather thin. The investigation of coagulation leads to this interlayer hydrodynamics, hindered by surface forces effect. They determine the distribution of tangential rate of liquid V_t along the surface

$$V_t = \beta \operatorname{grad} c \tag{6.1}$$

where β is the coefficient of proportionality.

The determination of rate and pressure distribution in the volume of a film is much easier, when using simplified equations of thin film hydrodynamics. For example, Stock's equation for the layer between two spheric particles is as follows:

$$\eta \frac{\partial z^2}{\partial V^2} = \frac{\partial P}{\partial \delta} \tag{6.2}$$

where cylindrical coordinates δ, z are introduced at the beginning, which is in the middle of interval between the centres of spheric particles. In these coordinates the equation of sphere surfaces reads

$$z = \pm f(\delta) = \pm \frac{h}{2} + \frac{\delta^2}{2a} \tag{6.3}$$

The condition of liquid incompressibility can be better expressed in integral form:

$$\int_{-f(\delta)}^{f(\delta)} v(\delta, z)\, dz = 0 \tag{6.4}$$

Equations (6.1), (6.3), (6.4) enable to calculate the distribution of motion and rate in the layer.

Stipulated by these fields effect, the analogue of diffusiophoretic force at short distances may be calculated with the help of formula for the forces,

effecting the sphere, which is flowed around by axisymmetric flow of viscous liquid at low Reynolds numbers

$$F = \int\int ds \left[\left(p + 2\eta \frac{\partial V r}{\partial r} \right) \cos\Theta - \eta \left(\frac{\partial V_\Theta}{\partial z} - \frac{V_\Theta}{r} \right) \sin\Theta \right]_{r=R} \tag{6.5}$$

Simplification of this formula (according to our task) is grounded in[21]

$$F \simeq \int\int ds\ p \cos\Theta \simeq 2\pi \int_0^R \delta\, d\,\delta\, p\,(\delta) \tag{6.6}$$

7. THE STABILITY OF LIVING CELLS SUSPENSION AND DIFFUSIOPHORESIS

The ideas cited in section 6 enable us to generalize the task, given in section 4 for the case of short distances between biological cells. For this purpose we find concentration distribution in the layer between the cells. Evidently, that in stationary conditions the equation must be carried out

$$2\pi\delta^2 j_m = -2\pi\delta D_e \int_{-f(\delta)}^{f(\delta)} \frac{\partial c}{\partial \delta}\, dz \tag{7.1}$$

In the thin part of interlayer derivative $\partial c/\partial \delta$ does not depend sufficiently on z. It enables to obtain the expression of this derivative from equation (7.1)

$$\frac{\partial c}{\partial \delta} = -\frac{j_m \delta}{2 D_e f(\delta)} \tag{7.2}$$

Giving concrete expression of boundary condition (6.1) on the basis of equation (7.2) and solving the equation (6.2) with the help of it, we shall obtain pressure distribution in the interlayer

$$p = -\frac{3}{4} \frac{2 K \eta j_m R}{c_o D_e f^2(\delta)} \tag{7.3}$$

Substituting this distribution in formula (6.6) after integration, we shall get the formula for diffusiophoretic potential (4.2)

$$\frac{V_{df}}{kT} \simeq \frac{\mu}{3} - \frac{\mu}{2} \ln M \tag{7.4}$$

where $M = h/a$.

According to formula (7.4) diffusiophoretic interaction decreases slower as the distance increases, than van der Waals one or ion-electrostatic one or ion-electrostatic one. That's why when calculating retardation factor, it is possible to take into account the effect of two latter factors with the help of M_{cr} parameters, assuming that at $M < M_{cr}$ the cells aggregate. And W is expressed by the following formula

$$W = \int_{M_{cr}}^{\infty} \frac{d\,M\,\beta\,(M)}{(M+2)^2}\ e^{V_{dt}/kt} \tag{7.5}$$

where $\beta\,(M) = 1 + 1/4\,M$ is dimensionless function, which takes into account the contribution of near hydrodynamic interaction in retardation factor of

coagulation. Using asymptotic formula (7.4), we shall estimate retardation factor contribution correct to the main term of $1/M_{cr}$, which gives in the interval of $M_{cr} < M < 1$

$$\int_{M_{cr}}^{1} dM \frac{\beta(M)}{(M+2^2)} \exp\left(\frac{\mu}{3} - \frac{\mu}{2}\ln M\right) \approx \frac{1}{8\mu} M_{zc}^{-\mu/2} e^{\mu/3} \qquad (7.6)$$

Comparing equations (4.23) and (7.6), and taking into consideration that $M_{cr} \ll 1$, we come to the conclusion:

1. The main effect of non-equilibrium surface forces is at short distances, in accordance with (1.2).
2. The theory of non-equilibrium surface forces of diffusion nature should be developed on the basis of thin film hydrodynamics.

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SAŽETAK

Neravnotežne površinske sile i hidrodinamika tankih filmova

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U radu se razmatra teorija neravnotežnih sila za slučaj kada koloidna čestica nije u ravnoteži s medijem. Taj koncept odstupa od idealnog slučaja pune ravnoteže u dvosloju na kojem se zasniva teorija DLVO (Derjagin-Landau-Verwey--Overbeek). Pojavu neravnotežnih uvjeta mogu uzrokovati vanjska električka polja, nametnuti koncentracijski gradijenti, adsorpcija na mobilnim granicama faza (na pr. mjehurići ili kapljice u flotaciji), heterogeni transport tijekom faznih transformacija ili npr. rasta kristala, te transport odnosno izmjena tvari u biološkim sustavima. U radu se sustavno razmatraju (1) difuzioforeza i kapilarna osmoza, (2) difuzioforetske sile u flotaciji, (3) difuzioforetske sile u biološkim suspenzijama, (4) difuzioforetska interakcija u rastu i otapanju ionskih mikrokristala, (5) koagulacija i hidrodinamika tankih filmova, te (6) stabilnost živih stanica u suspenzijama. Pokazano je da su efekti neravnotežnih površinskih sila značajni na malim udaljenostima, te da teorija tih sila može biti izvedena na osnovi hidrodinamike tankih filmova.