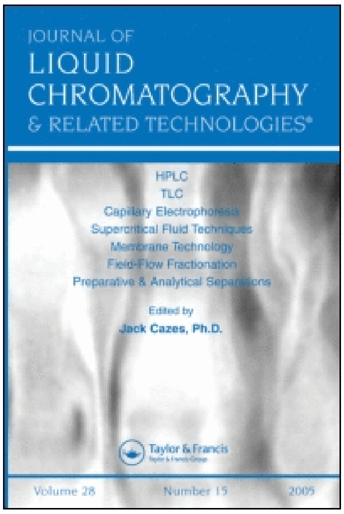

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SURFACE PHENOMENA IN SEDIMENTATION FFF

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ABSTRACT

The influence of the surface phenomena on the particle sedimentation in Sedimentation FFF is examined theoretically. It is shown that the tangential transport of surfactant in the particle surface layer, where the surfactant species are accumulated, causes the tangential concentration gradient of the surfactant, and the additional diffusiosmotic flow of the carrier liquid, which may decrease the particle sedimentation velocity. As numerical evaluations show, this change of sedimentation velocity may reach from ten to twenty percent for the particles being the typical objects of sedimentation FFF if surface potential well near the particle surface is deep (about 5-10 kT) and wide (about 10^{-6} cm) enough.

INTRODUCTION

Field-flow fractionation (FFF) presents the unique method, where quasi-equilibrium physicochemical parameters of the analyzed objects (particles, droplets or macromolecules) can be derived from the dynamic experiment, where these objects are driven by a liquid flow and certain transverse force (Ref. 1).

These quasi-equilibrium parameters are available in FFF experiments due to Boltzmannian transverse distribution of the analyzed objects in the FFF channel. Since these parameters are just quasi-equilibrium, but not thermodynamically equilibrium ones, they should be derived theoretically using kinetic approaches and methods of non-equilibrium thermodynamics. If the values of b and D are derived or measured, where b is the generalized mobility of a particle, a droplet or a macromolecule (the velocity in the unit gradient of the transverse potential), D is the particle diffusion coefficient, it is possible to obtain the transverse Peclet number

$$\mathrm{Pe} = \frac{\mathrm{bW}}{\mathrm{D}} \tag{1}$$

where W is the half of the potential drop across the FFF channel (we assume that the transverse particle velocity is constant over the FFF channel). Just the transverse Peclet number defines the retention of the FFF process Ret, and the width of the layer near a channel wall, where particles are accumulated. If transverse Peclet number is large enough, we can write (Ref. 1)

$$\mathrm{Ret} = \frac{\mathrm{Pe}}{3} \tag{2}$$

One can predict the parameter Pe, which defines the FFF behavior of the considered particles, by the procedure involving the measurement of the diffusion coefficient D or the derivation from Stokes expression (for the spherical particles,

$$\mathrm{D} = \frac{\mathrm{kT}}{6\pi\eta\mathrm{R}} \tag{3}$$

where η is the dynamic viscosity of a liquid, and R is the particle radius), by derivation the b value, and measurement or calculation of the transverse potential drop. The way considered above seems to be more complicated, but, in contrast to a more simple conventional way, it allows to take into account the contributions into the particle movement, which may be important. To demonstrate this, let us consider the sedimentation of particles, which is the basis of Sedimentation FFF. In this case, the common way to derive the transverse Peclet number Pe is the substitution of the gravity or sedimentation force acting on the particle

$$\mathrm{F} = \Delta\rho\upsilon\mathrm{G} \tag{4}$$

where $\Delta\rho$ is the density difference between the particle and the carrier liquid, υ is the particle volume and G is the acceleration of the centrifugal or gravity force, into the standard expression for the transverse Peclet number

$$\mathrm{Pe} = \frac{\mathrm{F} \cdot \mathrm{l}}{\mathrm{kT}} \tag{5}$$

where *l* is the half-width of the FFF channel. For the large particles, this way of consideration sometimes seems to be true. However, for the small particles being the objects of Sedimentation FFF (SdFFF), this approach may fail, since it does not take into account phenomena occurring in the surface layer of the particle. For example, in electrolytes, a so-called sedimentation electrostatic potential arises as a consequence of these surface phenomena (Ref. 2). This macroscopic sedimentation potential may change significantly the particle movement, and it is measurable even when the particles are so large as 0.6 mm diameter with the surface layer being about 0.1 micron thin.

Thus, to have the complete picture of the particle sedimentation, one should derive the particle mobility taking into account the phenomena near the particle surface.

The aim of this paper is to carry out the quantitative examination of the particle sedimentation using the hydrodynamic approach to surface phenomena, and to evaluate the effect of surface phenomena on the particle sedimentation.

HOW SURFACE PHENOMENA CAN AFFECT THE PARTICLE MOVEMENT

As the actual theory shows, the "surface-driven" movement may be caused by the flow of a carrier liquid in the surface layer, where the surfactant ions or (and) molecules are accumulated due to action of the surface potential. To simplify the further consideration, we will examine the surface accumulation of the single sort of surfactant species and neglect the effects due to electric fields generated by the concentration gradients in electrolytes. It should be possible, when the contribution of the electrostatic interactions to the value of the surface potential is small enough. The surfactant accumulation leads to the increase of the osmotic pressure in the surface layer. If the gradient of such an osmotic pressure arises, it causes a liquid flow in the surface layer. This "slipping" flow in a surface layer can cause either phoretic (surface-driven) movement of a particle or the osmotic flow of a liquid, when the particle together with its solid surface is fixed. Gradients of the osmotic pressure in the particle surface layer may be due to the macroscopic gradients of surfactant concentration or temperature, which can be predetermined by the "boundary conditions" in the FFF channel. If the particle movement is due to the "body" force like to the centrifugal one, a gradient of the osmotic pressure also may arise in its movement. This may be caused by the transport of surfactant molecules or ions along the particle surface, which should be compensated by the exchange of these molecules or ions between the surface layer and the outer liquid. As a consequence, the longitudinal gradient of the concentration may arise, which leads to the osmotic pressure gradient, and, in turn, to the "slipping" of the liquid in the surface layer.

The above discussed mechanism may add the surface-driven movement to the "body-driven" sedimentation movement of the particle. This longitudinal concentration gradient in the surface layer, due to compensating surfactant fluxes is known as the main reason of so-called "concentration polarization" (Ref. 3) in electrophoresis, where these phenomena are shown to be the reason for the measurable changes in the electrophoretic properties of particles. Though in electrolytes, the main reason of a liquid slipping in the surface layer is the effect of electric force on the non-compensated electric charge in the diffusive electric double layer, a diffusio-osmotic slipping flow also arises there, which may contribute to the particle movement.

FLOW VELOCITY PROFILE IN THE SURFACE LAYER

The theory of the surface phenomena is based on the Navier-Stokes equations for the liquid in the surface layer (Ref. 4)

$$\eta \frac{\partial^2 u_z}{\partial y^2} = \frac{\partial p_o}{\partial z} + \frac{\partial p_{osm}}{\partial z} \tag{7}$$

where $u_z(y)$ is the tangential flow velocity profile in the surface layer at the distance y from the particle surface, p_0 is the pressure excess due to sedimentation movement of particle and the corresponding hydrodynamic viscous stresses, p_{osm} is the osmotic pressure, and z is the longitudinal coordinate on the particle surface. For a spherical particle,

$$z = R \cdot \vartheta \tag{8}$$

where ϑ is the angle between the direction of the vector $\vec{F}$ given by Expression 5 and the radius vector $\vec{r}$.

The condition of the transverse hydrostatic equilibrium in the surface layer leads to the equation[4]

$$\frac{\partial p_o}{\partial z} + \frac{\partial p_{osm}}{\partial z} + c(y,z)\frac{\partial \Phi}{\partial y} = 0 \qquad (9)$$

where $c(y, z)$ is the surfactant concentration in the surface layer. On the outer surface of the surface layer, the surfactant concentration is designated as

$$c_{0S}(y,z) \qquad (10)$$

which may differ from the surfactant concentration in a liquid far from the particle c_o due to concentration polarization. Usually, one assumes that the surfactant concentration distribution in the surface layer is the Boltzmannian one

$$c(y,z) = c_{os}(y,z)e^{-\frac{\Phi(y)}{kT}} \qquad (11)$$

which allows to solve Eqn. 9 and write its solution, the pressure distribution in the surface layer, as

$$p = p_o + kTc_{os}\left(e^{-\frac{\Phi}{kT}} - 1\right) \qquad (12)$$

Let us discuss the boundary conditions to Eqn. 7. The first one is obvious:

$$u_Z = 0 \qquad \text{at } y = 0 \qquad (13)$$

and expresses the absence of any liquid slipping on the particle surface.

The second boundary condition is more complicated and corresponds to the transformation of the flow profile in the surface layer into the flow profile known from the Stokes problem concerning the flow around a sphere at low Reynolds numbers.[2]

Such a transformation should occur outside the surface layer, but at distance $y << R$ from the particle surface. According to (Ref. 2), the external flow profile and the pressure excess can be written as

$$u_r^e = \left(\frac{a}{r} + \frac{b}{r^3} + U\right)\cos\vartheta \tag{14}$$

$$u_\vartheta^e = \left(-U - \frac{a}{2r} + \frac{b}{2r^3}\right)\sin\vartheta \tag{15}$$

$$p_o = \frac{A \cdot \cos\vartheta}{r^2} \tag{16}$$

where u_r^e and u_ϑ^e are the radial and tangential flow velocity; accordingly, U is the velocity of the particle movement to be determined, a, b and A are the constants of the boundary problem, which also should be determined using the "external" boundary conditions near the particle surface, but outside the surface layer. The second boundary condition to Eqn. 7 can be written as

$$\frac{\partial u_z}{\partial y}\bigg| = \frac{\partial u_\vartheta^e}{\partial r}\bigg|_{r=R} \tag{17}$$

Using Expression 15, the latter equation can be formulated as

$$\frac{\partial u_z}{\partial y}\bigg|_{y=\infty} = \frac{\sin\vartheta}{2R}\left(\frac{a}{R} - \frac{3b}{R^3}\right) \tag{18}$$

Now, using boundary conditions given by Expressions 13 and 18, Expression 12 for the osmotic pressure, presenting the outer pressure in the surface layer as

$$p_o = \frac{A\sin\vartheta}{R^2},$$

and neglecting the terms containing the second power of y and the higher powers in this series, we have from Eqn. 7

$$u_z(y,z) \approx \frac{kT}{\eta}\frac{\partial c_{os}}{\partial z}\int_0^y dy \int_\infty^{y'} dy' \left[e^{-\frac{\Phi(y'')}{kT}} - 1\right] - \sin\vartheta\left(\frac{a}{R} - \frac{3b}{R^3}\right)\frac{y}{2R} \tag{19}$$

Outside the surface layer, where Expression 19 should transform into Expression 15, it can be written as

$$u_\vartheta^e = \frac{kT}{\eta \cdot R}\frac{\partial c_{os}(R,\vartheta)}{\partial \vartheta}\int_0^\infty dy\int_\infty^y dy'\left[e^{-\frac{\Phi(y')}{kT}}-1\right]-\sin\vartheta\left(\frac{a}{R}-\frac{3b}{R^3}\right)\frac{y}{2R} \tag{20}$$

which allows to write the boundary conditions to the external Stokes problem as

$$u_r^e(r=R)=0 \tag{21}$$

$$u_\vartheta^e(r=R)=u_s \tag{22}$$

where

$$u_S = \frac{kT}{\eta \cdot R}\frac{\partial c_{os}(R,\vartheta)}{\partial \vartheta}\int_0^\infty dy\int_\infty^y dy'\left[e^{-\frac{\Phi(y')}{kT}}-1\right] \tag{23}$$

is the "slipping" flow velocity in the surface layer.

Expressions 21-23 allow us to determine the constants *a* and *b* from Expressions 14 and 15 (constant *A* is unimportant) and to define the force of the hydrodynamic friction acting on the particle, which moves with the velocity U[5]

$$F_{\text{friction}} = -4\pi\eta a \tag{24}$$

To derive the friction force, one should have the surfactant concentration distribution outside the surface layer.

CONCENTRATION POLARIZATION OF THE MOVING PARTICLE

As Expressions 22 and 23 show, the surface phenomena may effect the sedimentation of a particle only in the case when the tangential surfactant concentration gradient exists on the particle surface. To estimate this possibility, we should have the equation for the surfactant concentration.

If the sedimentation velocity is constant and slow enough (in FFF it is about 10^{-4} cm/s), we can write the stationary convection-diffusion equation for the surfactant concentration in the form

$$\text{div grad } c_{os} = 0 \tag{25}$$

and assume that the solution of Eqn. 25 may be written in "dipole" form[3]

$$c_{os} = \frac{M_c}{r^2}\cos\vartheta + c_o \tag{26}$$

where M_c is the concentration "dipole moment" of the particle, which will be defined below. Eqn. 25 is valid outside the surface layer, but the more general equation

$$\text{div } \vec{j} = 0 \tag{27}$$

for the stationary surfactant flux $\vec{j}$ should be valid anywhere.

If the surface layer, where the surfactant molecules or ions are accumulated, is thin enough, i.e., its width is significantly smaller than the particle radius, Eqn. 27 can be reformulated as[2]

$$\vec{j}_n = -\,\text{div}_s\, \vec{j}_s \tag{28}$$

where

$$\vec{j}_n = -D_s \frac{\partial c_{os}}{\partial r}\bigg|_{r=R} \tag{29}$$

is the external surfactant flux on the particle surface, D_s is the diffusion coefficient of the surfactant, and

$$\vec{j}_s = \int_0^{\infty} \left[c_o u_z(y,z) - D_s \frac{\partial c_{os}}{\partial z}\bigg|_{r=R} \right] \left[e^{-\frac{\Phi(y)}{kT}} - 1 \right] dy \tag{30}$$

is the total excess of the surfactant transport in the particle surface layer. Operator div_s in the thin surface layer can be written as

$$\mathrm{div}_s = \frac{\partial}{\partial z}.$$

Writing Eqn. 30, we assume that the tangential concentration gradient in the surface layer is too weak to cause the concentration changes comparable to c_o. Also, Expression 11 is taken into account. Using Expressions 19, 26, 29, and 30, Expression 28 can be written as

$$\frac{2M_c}{R^3} = \int_0^\infty \frac{c_0 kT}{\eta D_s}\frac{M_c}{R^4}\left[e^{-\frac{\Phi(y)}{kT}} - 1\right]\int_0^y dy' \int_\infty^{y'} dy'' \left[e^{-\frac{\Phi(y'')}{kT}} - 1\right] dy +$$
$$+\frac{c_0}{2D}\int_0^\infty \left(\frac{a}{R} - \frac{3b}{R^3}\right)\frac{y}{R}\left[e^{-\frac{\Phi(y)}{kT}} - 1\right]dy - \frac{M_c}{R^4}\int_0^\infty \left(e^{-\frac{\Phi(y)}{kT}} - 1\right)dy \qquad (31)$$

Using Eqn. 31, we can obtain the concentration dipole moment M_c. However, to finish the derivations, a simplification is necessary. The most interesting situation is that, where the surface potential well is deep enough, because the concentration polarization should be the most significant due to the intensive transport of the surfactant highly accumulated in such a well. In this case, we can assume that

$$e^{-\frac{\Phi}{kT}} >> 1 \qquad (32)$$

and present the surface potential (in kT units) as

$$\frac{\Phi}{kT} \approx -\varepsilon_0\left(1 - \frac{y}{h}\right) \qquad (33)$$

where ε_o is the depth of the surface potential well, and h is the characteristic width of this well.

The physicochemical nature of these parameters will be discussed below. As the numerical evaluations show, the assumption given by Expression 32 is valid at

$$\varepsilon_0 \geq 5. \qquad (34)$$

Using the approximation given by Expression 33 and Expression 4 for the surfactant specie with radius d, we have from Expression 31

$$M_c = \frac{3\pi\eta\left(\frac{a}{R}-\frac{3b}{R^3}\right)c_o R^3 \cdot h \cdot d \cdot \mathrm{Rel}}{kT \cdot \varepsilon_0 \left(2+\mathrm{Rel}+\frac{3\pi}{\varepsilon_0}c_o dhR \cdot \mathrm{Rel}^2\right)} \tag{35}$$

where criterion *Rel* is introduced

$$\mathrm{Rel} = \frac{he^{\varepsilon_0}}{\varepsilon_0 R} \tag{36}$$

which characterizes the concentration polarization degree. Using Expressions 23, 24 and 35, we can express the slipping velocity as

$$u_s = \frac{3\pi c_0 dh^2 \cdot \mathrm{Rel}^2\left(\frac{a}{R}-\frac{3b}{R^3}\right)}{\varepsilon_0^2\left[2+\mathrm{Rel}++3\pi c_0 d\frac{h}{\varepsilon_0}R \cdot \mathrm{Rel}^2\right]} \tag{37}$$

As Expression 37 shows, the slipping velocity is small at $\mathrm{Rel} \ll 1$, and it reaches saturation at

$$\mathrm{Rel} \gg \left(3\pi c_0 d\frac{h}{\varepsilon_0}R\right)^{-1} \tag{38}$$

This saturation value is

$$u_s^{\max} = \left(\frac{a}{R}-\frac{3b}{R^3}\right)\frac{h}{\varepsilon_0 R} \tag{39}$$

The general expression for the slipping velocity can be written compactly as

$$u_s = \left(\frac{a}{R}-\frac{3b}{R^3}\right)\frac{h}{\varepsilon_0 R}f(\delta,\varphi,\mathrm{Rel}) \tag{40}$$

where

$$\varphi = \tilde{n}_0 \frac{3\pi d^3}{4} \tag{41}$$

is the volume fraction of the surfactant, and

$$\delta = \frac{hR}{\varepsilon_0 d^2} \tag{42}$$

is the reduced parameter characterizing the relationship between the parameters of the surface potential well ($\frac{h}{\varepsilon_0}$), the particle (R) and the surfactant specie (*d*).

Here,

$$f(\delta, \varphi, \mathrm{Rel}) = \frac{4\varphi \cdot \delta \cdot \mathrm{Rel}^2}{2 + \mathrm{Rel} + 4\varphi \cdot \delta \cdot \mathrm{Rel}^2} \tag{43}$$

is the function characterizing the concentration polarization in the sedimentation process. This function ranges from zero (at $Rel = 0$) to unity (at very large *Rel* values, where Expression 38 is valid). Using Expressions 40-42, and boundary conditions given by Expressions 21 and 22, we have for the constant *a* defining the particle sedimentation velocity

$$a = -\frac{3}{2} UR \frac{1 + \frac{h}{\varepsilon_0 R} f}{1 + 2\frac{h}{\varepsilon_0 R} f} \tag{44}$$

Taking into account the assumptions about the thin surface layer, the deep surface potential well, and Expression 42, the value of parameter $\frac{hf}{\varepsilon_o R}$ can not be larger than unity. The analysis of the Expressions 32 and 33 shows that the width of the layer, where surfactant species are accumulated, is about $\frac{h}{\varepsilon_0}$ Thus, considering the realistic potential wells with $h \leq R$, we should evaluate the parameter $\frac{h}{\varepsilon_0 R} f$ as $\frac{h}{\varepsilon_0 R} f \leq \frac{1}{\varepsilon_0}$.

For this reason, we can approximate 44 as

$$a \approx -\frac{3}{2}UR\left(1-\frac{h}{\varepsilon_0 R}f\right) \tag{45}$$

Using Expressions 24 and 45, we can write the expression for the particle sedimentation velocity as

$$U = U_0\left(1-\frac{h}{\varepsilon_0 R}f\right) \tag{46}$$

where

$$U_0 = \frac{F}{6\pi\eta R}$$

is the classic value of the sedimentation velocity. Since the maximum value of the parameter f is unity (see Expression 42), the maximum relative change of the particle sedimentation velocity at very large criterion *Rel* values (See Expression 38) is

$$\frac{U-U_0}{U_0} = -\frac{h}{\varepsilon_0 R} \tag{47}$$

Let us note that the change of the particle velocity predicted by Expression 47 is not linked strictly to the sedimentation, but may be observed in any particle movement where the Stokes flow profile arises around the particle. For example, Expression 47 should be valid for the particle movement in Flow FFF.

To evaluate the possible changes in the particle movement due to surface phenomena, we should discuss the possible mechanisms of the surfactant accumulation within the surface potential well, the possible values of criterion *Rel*, and the possible values of the parameters φ and δ, which define the concentration dependencies of the surface effects in the sedimentation at the moderate values of criterion *Rel* and the conditions, where the saturation of the surface effects is reached.

DISCUSSION

Parameters of the Surface Potential Well

According to (Ref. 6), there are several main mechanisms to accumulate the ions or molecules near the surface:

a) dispersion or London - Van der Waals interaction with the potential

$$\Phi(y) = -A\frac{d^3}{y^3} \tag{48}$$

where A is Hamaker constant;

b) Coulomb electrostatic interaction in electrolytes with the potential

$$\Phi(y) = -q\zeta e^{-\frac{y}{\lambda}} \tag{49}$$

where q is the electric charge of the surfactant ion, ζ is the particle electrokinetic potential, and λ is the Debye length; and

c) the adsorption and structure forces, which have no analytical dependence of the surface potential on the distance, but have the parameters ε_o and h derived from the experimental data. These forces are due to structure changes in the surface layer and the correlation between different surfactant species.

Strictly, we can not examine the sedimentation in electrolytes due to the different nature of the slipping flow, which is discussed in introduction. But, in the cases, where electrical fields arising in the surface layer are too weak to contribute significantly to the liquid flow there, we can use Expressions 46 and 48 to analyze the surface phenomena in the particle sedimentation in electrolytes.

The results obtained should be valid, at least qualitatively. The data from (Ref. 6), concerning the surface potential well parameters ε_o and h, are collected in Table 1.

Table 1

Surface Potential Well Parameters

Surface Potential	Analytical Expressions for the $\Phi(y)$, ε_o and h			The Ranges of Values for Parameters ε_o and h	
	$\Phi(y)$	ε_o	h	ε_o	h
London - Van der Waals forces	$-A\frac{d^3}{y^3}$	$\frac{A}{kT}$	$\frac{d}{3}$	$5 \div 50$ *	$\approx 10^{-8}$ cm (low-molecular surfactant)
Coulomb electrostatic forces	$-q\xi e^{-\frac{y}{\lambda}}$	$\frac{q\xi}{kT}$	λ	$0 \div 10$	$10^{-7} \div 10^{-4}$ cm ** (aqueous electrolytes)
Adsorption forces	none	none	none	$0 \div 10$	$\approx 10^{-7}$ cm
Structural forces	none	none	none	$0 \div 10$	$\approx 10^{-5}$ cm

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* The maximum values of Hamaker constant are characteristic for metals and some hydrocarbons. ** The maximum value of the Debye length is reached in the pure water, where only H^+ and OH^- ions exist.

According to (Ref. 2), the size of particle being the objects of FFF are ranged from 10^{-6} cm to 10^{-4} cm. Thus, Expression 46 predicts the observable contribution of surface phenomena to the particles sedimentation for all the types of the surface interactions excepting the Van der Waals interaction. This kind of interaction can not provide the significant width of the surface potential well, if low-molecular surfactants are used. However, for the metals having the extremely high values of Hamaker constants, the saturation of the surface effects should occur at relatively low surfactant concentrations. Also, the contribution of surface phenomena should be especially high if polymer surfactants are used, since, in such a situation, parameter *h* should have a value comparable to the thickness of the cloud consisting of random-flight fragments of the polymer chains, which can be very large in comparison with the *h* value from Table 1.

As Expression 47 shows, the significant contribution of the surface phenomena to the sedimentation needs moderate values of the parameter ε_o defining the depth of the surface potential well.

Table 2

Values of Criterion *Rel*

Depth of Surface Potential Well ε_o	**Particle Radius *R*** 10^{-6} **cm**	10^{-5} **cm**	10^{-4} **cm**
5	Rel = 30 (3)	Rel = 3 (0,3)	Rel = 0.3 (0,03)
7.5	Rel = 241 (24.1)	Rel = 24.1 (2.41)	Rel = 2.41 (0.24)
10	Rel = 2200 (220)	Rel = 220 (22)	Rel = 22 (2.2)

On the other hand, Expression 47 becomes valid at the values of criterion *Rel* large enough. Thus, we should estimate the possible values of criterion *Rel* to examine the role of the surface phenomena in the sedimentation.

The Values of Criterion *Rel*

As Table 1 shows, the typical values of parameter ε_o where the surface potential well is deep enough, are from about 5 to about 10. Moreover, the typical values of parameter h are ranged from about 10^{-7} cm to about 10^{-6} cm. The corresponding values of criterion *Rel* are collected in Table 2.

In Table 2, the upper *Rel* values present the case where $h \approx 10^{-6}$ cm, and the lower ones (in parentheses) are corresponding to $h \approx 10^{-7}$ cm. As data of Table 2 show, the most of the particles being the object of FFF should have an apparent degree of polarization at $\varepsilon_0 \geq 5$.

To finish these estimates, we should estimate the possible values of parameter δ and the volume fraction of surfactant φ. The latter one is estimated easily, because the molar concentration of surfactant usually is about $10^{-3} \div 10^{-2}$ m/L, i.e., the number of the surfactant species c_o is about $10^{18} \div 10^{19}$ per cubic centimeter. For the surfactant molecule radius $d = 3 \cdot 10^{-8}$ cm, using Expression 41, we have

$$\varphi \approx 10^{-4} \div 10^{-3} \qquad (50)$$

The values of parameter δ (Expression 42) at ε_o = 10 ranged from 10 (at h = 10^{-7} cm and R=10^{-6} cm) to 10^4 (at h=10^{-6} cm and R=10^{-4} cm). Thus, the condition of the saturation at the concentration polarization (Expression 38) may be fulfilled for the wide range of particles sizes if the surface potential well is deep enough. For example, using these evaluations, one can see that, at ε_o = 10 and h=10^{-6} cm, all the particles examined in Table 2 should be strongly polarized, and Expression 46 should describe adequately the contribution of the surface phenomena in the particle sedimentation. As Expression 47 shows for such particles, the relative decreasing of the sedimentation velocity due to concentration polarization should be about 0,1. For the smaller particles, where the saturation may be reached even at ε_0 = 5, this velocity change may reach up to 0,2. Such a change of the sedimentation velocity must be measurable in the real FFF conditions. Let us remember that, in experiments the standards often are used, which have size dispersion of about 2-3%, which gives the dispersion of about 4-6% of the peak maximum position.

The classical expression for the SdFFF retention gives the dependence of the retention on the particle radius as $\sim R^2$. The accounting of the surface phenomena gives more complicated dependence given by Expression 46 or 47, which should be not so steep. This difference can be useful in the determination of the role of surface phenomena in sedimentation. In electrolytes, where Debye length defines the width of the surface potential well and decreases with the concentration of the ionic surfactant as $c_0^{-\frac{1}{2}}$ (see, for example, Refs. 2 or 4), the increase of the sedimentation velocity with the surfactant concentration also may indicate the significant role of the surface phenomena. As Expression 43 and 46 show, at the moderate values of criterion *Rel*, the sedimentation velocity, that is, the retention of SdFFF, should depend on the surfactant concentration, besides the known concentration dependence of the liquid viscosity.

CONCLUSIONS

The most of the particles being the objects of SdFFF cause slipping flow within its surface layer, where surfactant species are accumulated, in the sedimentation. Due to this slipping flow, a concentration gradient of surfactant arises, which leads to additional diffusio-osmosis in the surface layer, which should compensate the convective surfactant transport. These surface phenomena can decrease the particle sedimentation velocity up to ten - twenty percent if the surface potential well is deep enough (*5 - 10 kT*). Similar changes may occur also in Flow FFF, where this surface slipping of the carrier liquid in the particle surface layer should have the same nature and properties.

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