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NEAR-WALL FIELD-FLOW FRACTIONATION

APPLICATION OF SURFACE FORCES AND TRANSVERSAL VOLTAGE TO FRACTIONATION IN LAMINAR FLOW

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SUMMARY

A theoretical analysis is presented of the motion and spreading of a probe containing particles in a transversal potential field. This arises in the vicinity of the flat channel walls as a laminar flow of carrier fluid moves in the channel. Parameters that characterize the process of fractionation in such a system and a system upon application of a transversal voltage were calculated. It is shown that the transversal electric field increases the fractionation efficiency. Also near-wall interactions can affect the process of electric field-flow fractionation.

Many articles have been devoted to the problems of particle fractionation in a stream of eluent with a transversal force acting on the interface between the solid and liquid phase. Capillary hydrodynamic chromatography[1], energy-barrier chromatography[2,3] and adsortion chromatography on glasses[4] are in a state of development. In the papers cited, the interaction of the separating particles in the vicinity of the capillary walls or near the surface of the beads of the column packing, and the changes in particle concentration across the flow in this field, are discussed.

Considering this kind of interaction, we can divide the potentials of the near-wall forces into three major groups.

(1) The repulsive near-wall potential. This is realized when the near-wall interaction energy has its greatest value on the wall, as is the case in capillary hydrodynamic chromatography of particles with sizes much smaller than the size of the cross-section channel.

(2) The attractive potential. This is realized when the potential energy minimum is positioned near the wall, or has its lowest value on the wall. This is almost the case in adsorption chromatography on glasses.

(3) The attractive potential with a potential barrier. This is different from case 2 in that the maximum in the profile depends on the potential energy. It is positioned such that the potential well near the wall is separated from the channel volume by the potential barrier. The possible application of this potential energy profile has been investigated in papers on energy-barrier chromatography.

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The above-mentioned techniques, at least their capillary variants, are based on a principle which is similar to that of field-flow fractionation[5]. The only difference is that the transversal force, initiating the particle redistribution, does not affect the whole cross-section of channel with the laminar flow, but only the near-wall region. This allows us to analyze the principal variants of the near-surface forces by the methods used for the description of field-flow processes[5–7]. In this paper a flat channel design is tested. In eqns. 1–4, x is a coordinate across the channel. It is calculated from the symmetry plane, $\varepsilon(x) = W(x)/kT$, where $W(x)$ is the interaction potential and kT the thermal energy. A bar indicates the averaging for the cross-section channel.

For the average velocity of a zone, $\bar{u}_1$, and for the effective dispersion coefficient, D_{eff}, the following expressions are valid

$$\bar{u}_1 = \overline{u(x)\,\mathrm{e}^{-\varepsilon(x)}} \tag{1}$$

$$D_{\mathrm{eff}} = \overline{\xi(x)\,u(x)} \tag{2}$$

where $\xi(x)$ is the solution of

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}x}\right)\xi = \frac{\mathrm{e}^{-\varepsilon(x)}}{Dh\,\overline{\mathrm{e}^{-\varepsilon(x)}}}\left[\bar{u}_1 - u(x)\right] \tag{3}$$

under the boundary conditions

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}x}\right)\xi = 0; \qquad x = \pm h \tag{4}$$

$$u(x) = u_0\left(1 - \frac{x^2}{h^2}\right) \tag{5}$$

u_0 is the maximal flow velocity and h is the half-width of the channel.

The expressions for $\bar{u}_1$ and D_{eff} include

$$\overline{\mathrm{e}^{-\varepsilon(x)}} = \frac{1}{h}\int_0^h \mathrm{e}^{-\varepsilon(x)}\,\mathrm{d}x \tag{6}$$

The integrating limits in eqn. 6 are the result of the symmetry of the problem. The whole integration domain can be divided into two parts: the near-wall region having a size of $\approx h^*$, where the transversal force is acting, and the region having a size of $h - h^*$, where that force is absent

$$\overline{\mathrm{e}^{-\varepsilon(x)}} = \frac{1}{h}\left[\int_{h-h*}^{h} \mathrm{e}^{-\varepsilon(x)}\,\mathrm{d}x + h - h^*\right] = \frac{h - h^*}{h}(1 + \beta) \tag{7}$$

where

$$\beta = \frac{\int\limits_{h-h*}^{h} e^{-\varepsilon(x)}\,dx}{h - h^*} \tag{8}$$

The parameter β is the ratio of the number of particles in the near-wall region to the number of particles in the region where the transversal force is absent. In calculating the average peak velocity, $\bar{u}_1$, the integrating domain can be divided into two parts as in eqn. 7:

$$\bar{u}_1 = \frac{1}{(h - h^*)(1 + \beta)}\left[\int\limits_{h-h*}^{h} e^{-\varepsilon(x)}\,u(x)\,dx + \int\limits_{0}^{h-h*} u(x)\,dx\right] \tag{9}$$

The relative contribution of the first integral within the square brackets is $\approx h^*/(H - h^*)$, since in the near-wall region $u(x) \approx (h^*/h)u_0$, and away from it, the contribution is $\approx u_0$. Usually, the transversal size of the capillary is $h \approx 10^{-2}$ cm, and the size of the near-wall region is $h^* \gtrsim 10^{-5}$ cm. Therefore, this contribution becomes appreciable only at $\beta \geqslant 10^2$. In the case of repulsive potentials, $\beta \ll 1$. Under these conditions, the average velocity of the peak must be higher than the average flow velocity, u, as a result of the particle repulsion from the near-wall region, where the flow velocities are small. However, the relative difference between these velocities is $\approx 10^{-3}$. Neglecting the contribution of the first integral within the square brackets of eqn. 9, and substituting the upper limit of integration in the second integral for h, we obtain

$$\bar{u}_1 = \frac{\bar{u}}{1 + \beta} = \frac{2\,u_0}{3\,(1 + \beta)} \tag{10}$$

where

$$\beta = \frac{1}{h}\int\limits_{h-h*}^{h} e^{-\varepsilon(x)}\,dx \tag{11}$$

The repulsive near-wall potential effect on the average velocity of the peak is widely used in capillary hydrodynamic chromatography. However, the small range of peak velocity variations upon interaction with the repulsive near-wall potential is often the reason for the low efficiency of a separation. Therefore, the application of attractive potentials is considered more advantageous.

Expression 10 for the average flow velocity is in agreement with the known expression of capillary hydrodynamic chromatography. This is related to the fact that, neglecting the flow velocities in the near-wall region, we consider it a stationary phase.

Eqn. 3 can be rewritten in the form:

$$\frac{d}{dx}\left(\frac{d}{dx} + \frac{d\varepsilon}{dx}\right)\xi = \frac{u_0\,e^{-\varepsilon(x)}}{Dh\,(1 + \beta)}\left[\frac{2}{3\,(1 + \beta)} - 1 + \frac{x^2}{h^2}\right] \tag{12}$$

The value of β in eqn. 12 and henceforth is defined by eqn. 11. The symmetry problem allows the boundary conditions for eqn. 12 to be presented in the form:

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}x}\right)\xi = 0; \qquad x = 0, h \tag{13}$$

Integrating eqn. 12 with respect to x yields:

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}x}\right)\xi = \frac{u_0}{Dh\,(1+\beta)}\int\limits_0^x \mathrm{e}^{-\varepsilon(x')}\left[\frac{2}{3\,(1+\beta)} - 1 + \frac{(x')^2}{h^2}\right]\mathrm{d}x' \tag{14}$$

The right-hand side of eqn. 14 can be presented differently in various domains:

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} + \frac{\mathrm{d}\varepsilon}{\mathrm{d}x}\right)\xi = \frac{u_0}{Dh\,(1+\beta)}$$

$$\begin{cases} \dfrac{2}{3\,(1+\beta)}\displaystyle\int\limits_{h-h*}^{x} \mathrm{e}^{-\varepsilon(x')}\,\mathrm{d}x'; & \text{for } h - h^* < x \leq h \\ -\dfrac{1+3\beta}{3\,(1+\beta)}\cdot x + \dfrac{x^3}{3\,h^2} + \dfrac{2\,\beta h}{3\,(1+\beta)}; & \text{for } 0 \leq x \leqslant h - h^* \end{cases} \tag{15}$$

As shown above, the contribution of the near-wall region to $\xi(x)$ can be neglected, because of the low flow velocities in this region and its small dimensions. Outside the near-wall region we obtain the equation

$$\frac{\mathrm{d}\xi}{\mathrm{d}x} = \frac{1}{Dh\,(1+\beta)}\int^x [\bar{u}_1 - u(x)]\,\mathrm{d}x \tag{16}$$

with a boundary condition of:

$$\frac{\mathrm{d}\xi}{\mathrm{d}x} = \frac{\bar{u}_1\beta}{D(1+\beta)}; \qquad x = h \tag{17}$$

Solving this equation and calculating D_{eff} from eqn. 2, we obtain:

$$D_{\mathrm{eff}} = \frac{8\,u_0^2h^2}{945\,D}\cdot\frac{14 + 43\,\beta}{14\,(1+\beta)^2} \tag{18}$$

Using eqns. 10 and 18, we can obtain an expression for the plate height:

$$H = \frac{2\,D_{\mathrm{eff}}}{\bar{u}_1} = \frac{24\,u_0h^2}{945\,D}\cdot\frac{14 + 43\,\beta}{14\,(1+\beta)} \tag{19}$$

At $\beta \gtrsim 10$ from eqn. 19, we have the asymptotic value (43/14) H_0 where $H_0 = 24\, u_0 h^2/945\, D$ is the value of H at $\beta = 0$. To calculate β, it is necessary to define more scrupulously the form of the dependence $\varepsilon(x)$. If the near-wall potential is related to the double-layer field, it can be assumed, as in ref. 5, that

$$\varepsilon(x) \approx \varepsilon_0^* \left(1 + \frac{x - h}{\delta}\right) \tag{20}$$

where δ is the electric double layer thickness, and $\varepsilon_0^* = q\zeta/kT$. Here, q is the effective charge of the particle, and ζ is the electric surface potential, which in the approximation considered can be treated as the electrokinetic potential, though it might be much greater. With eqn. 20, the following expression can be obtained:

$$\beta = \frac{e^{\varepsilon_0^*}}{h} \int\limits_0^{\infty} e^{-\varepsilon_0^* \frac{x}{\delta}}\, dx = \frac{\delta e^{\varepsilon_0^*}}{\varepsilon_0^* h} \tag{21}$$

At concentrations of singly or doubly charged ions in the electrolyte solution $\approx 10^{-8}$ mol/cm^3, $\delta \approx 10^{-5}$ cm, *i.e.*, $\delta/h \approx 10^{-3}$. The value of ζ is usually 10–100 mV. For particles carrying $\approx$ 10 electron charges, at room temperature under these conditions, $\varepsilon_0^* \approx 10$. This means that, under such conditions, $\beta \approx 10$ can be obtained for particles resembling protein macromolecules. To obtain these values of β, the material for the capillary walls, the pH and the ionic strength of the eluent must be chosen.

If other interactions contribute to the near-wall potential, then the $\varepsilon(x)$ dependence might have minima and maxima[2]. According to eqn. 11, only the behaviour of the $\varepsilon(x)$ dependence near the minimum (or minima, if there are many of them) affects the value of β. Thus, the dependence $\varepsilon(x)$ in the integral calculation can be substituted for

$$\varepsilon(x) \approx \varepsilon_0^* \left[\left(\frac{x - x_0}{h^*}\right)^2 - 1\right] \tag{22}$$

where x_0 is the position of the minimum of $\varepsilon(x)$. From eqns. 22 and 11 we obtain:

$$\beta = \frac{h^*}{h} \sqrt{\frac{\pi}{\varepsilon_0^*}}\, e^{\varepsilon_0^*} \tag{23}$$

Eqn. 23 shows that at the same values of h, h^* or δ, ε_0^*, the value of β, defined by this expression is somewhat greater than the value of β in the case considered earlier (eqn. 21). This can be attributed to the effective sizes of the potential wall region, which have different dependences on ε_0^*. In the first case, this size is $\approx h^*/\varepsilon_0^*$, and in the second case, $\approx h^*/\sqrt{\varepsilon_0^*}$. In other words, the effective size in the parabolic well, similar to the layer depth of the stationary phase in capillary chromatography, is somewhat greater.

If there are several minima of $\varepsilon(x)$ then β is defined by the summation of expressions 21 or 23.

In refs. 2 and 3 great importance was attached to the existence of a potential barrier, *i.e.*, to the maximum in the curve $\varepsilon(x)$. However, from the above considerations, the presence of this barrier, under characteristic capillary conditions, practically does not affect the β value, *i.e.*, the average peak velocity. Thus, potential barrier capillary chromatography seems to be potential well chromatography. The potential barrier can substantially increase the time of establishment of equilibrium across the channel. In this situation, separation is possible according to the duration of equilibrium, which determines whether or not particles of the same kind can manage to rearrange themselves across the channel.

The attractive potential of eqn. 20 is realized in adsorption chromatography on glasses for the isolation of viruses from protein mixtures. Here, $\varepsilon_0^* \approx 10^2$–$10^3$ and β is $\approx 10^5$–10^6 so that the viruses are practically resting on the glass surface. In order to elute them from the column, the eluent pH is adjusted so that the attraction of particles is substituted for the repulsion. The alternative is particle fractionation in the attractive potential with $\beta \approx 1$–10, values which can easily be obtained by adjusting the pH and ionic strength of the eluent. This would make it possible to avoid particle coagulation near their isoelectric points when the pH is adjusted, and it would be useful primarily for analytical purposes.

A study of the motion in a sample consisting of particles of the same kind might be valuable in investigations of reversible adsorption (adsorption of latex particles on a wall of the same or similar material), namely adagulation.

Although our experiments do not allow us to distinguish between the near-wall potentials of eqns. 20 and 22, they do define the order of magnitude of ε_0^*. More detailed information can be obtained through a study of the dependences of β on pH, ionic strength of the eluent, the concentration of other particles, etc.

It is seen from eqns. 19 and 20 that, over the whole range of variations, the plate height changes on the whole by a factor of as much as ≈ 4. With $u_0 \approx 10^{-2}$ cm/s, $h \approx 10^{-2}$ cm and $D \approx 10^{-7}$–10^{-6} cm^2/s, $H \approx 0.1$–1 cm. This is a rather large value, though of the same order as those used in capillary hydrodynamic chromatography. The joint effect of the near-wall potential and the "spatial" voltage difference applied across the channel is of great interest. This combination of electric field and near-wall potential chromatography should diminish the plate height substantially, and increase the separation efficiency.

The particles in the transversal field are concentrated in the thin layer in the vicinity of the capillary wall. This results in a diminishing of the flow-velocity interval. As a result of the decrease in the effective (for the particles) capillary width and the range of velocities of the flow which causes spreading of the sample, the hydrodynamic spreading of the peak must also diminish.

Particle separation in a laminar flow and in a transversal electric field is well known as electropolarized chromatography or electric field-flow fractionation (EFFF)[8–11]. In a number of experiments with EFFF some deviations from the theoretically predicted data were observed. Thus, there are at least two arguments in favour of an investigation of the coupled effect of the near-wall forces and the transversal electric field on the chromatographic efficiency, using the near-wall forces, and an attempt to explain these deviations of the experimental data from the theoretic ones of EFFF.

As previously, we shall assume that the outlet curve is of the Gaussian type, and its form is defined by the parameters $\bar{u}_1$, the average peak velocity and D_{eff}, the effective dispersion coefficient. In the electric transversal field the potential includes the potential of the near-wall forces, $W_s(x)$, and the electrostatic potential, $W_v(x)$. In the near-wall region with the near-surface forces applied, $W_s(x) \gg W_v(x)$, and without them, $W_s(x) \ll W_v(x)$.

While estimating, $\overline{e^{-\varepsilon(x)}}$, it is possible, as above (eqns. 7 and 9), to divide the whole integration domain into two parts:

$$\overline{e^{-\varepsilon(x)}} = \frac{1}{h}\left[\int_{h-h*}^{h} e^{-\varepsilon_s(x)}\,dx + \int_{0}^{h-h*} e^{-\varepsilon_v(x)}\,dx\right] \tag{24}$$

Here, $\varepsilon_s(x) = W_s/kT$ and $\varepsilon_v = -\varepsilon_0 x/h$, where $\varepsilon_0 = bU/D$, b is the electrophoretic particle mobility, U is is half the voltage across the channel. The result is:

$$\overline{e^{-\varepsilon(x)}} = \frac{1 + \varepsilon_0\beta}{\varepsilon_0} \tag{25}$$

In calculations of the average sample velocity, it is possible to neglect the particle motion along the capillary in the near-wall region as well. At $\varepsilon_0 \approx 10$–100, which are relatively easily obtained values for macromolecules, we can assume that the flow velocity in the near-wall region varies linearly with respect to the distance across the channel. Taking due account of these simplifications, we can obtain an expression for the average flow velocity:

$$\bar{u}_1 = \frac{2\,u_0}{\varepsilon_0\,(1 + \varepsilon_0\beta)} \tag{26}$$

From eqn. 3, we can obtain an equation for ξ function, neglecting the contribution of the near-wall domain in $\xi(x)$

$$\left(\frac{d}{dx} + \frac{d\varepsilon_v}{dx}\right)\xi = \frac{2\,u_0\varepsilon_0}{Dh\,(1 + \varepsilon_0\beta)}\int^{x}\left[\frac{1}{\varepsilon_0\,(1 + \varepsilon_0\beta)} - \frac{x'}{h}\right] e^{\varepsilon_0 \frac{x'}{h}}\,dx' \tag{27}$$

with the boundary condition:

$$\left(\frac{d}{dx} + \frac{d\varepsilon_v}{dx}\right)\xi = \frac{\varepsilon_0\beta\bar{u}_1}{D\,(1 + \varepsilon_0\beta)}; \qquad x = h \tag{28}$$

Solving eqn. 27, and using eqn. 2, we obtain:

$$D_{\mathrm{eff}} = \frac{8\,u_0^2h^2}{D\varepsilon_0^4}\cdot\frac{2 + 3\,\varepsilon_0\beta}{2\,(1 + \varepsilon_0\beta)^2} \tag{29}$$

From eqns. 26 and 29 we can derive an expression for the plate height:

$$H = \frac{2\,D_{\mathrm{eff}}}{\bar{u}_1} = \frac{2 + 3\,\varepsilon_0\beta}{2\,(1 + \varepsilon_0\beta)} \cdot \frac{8\,u_0 h^2}{D\,\varepsilon_0^3} \tag{30}$$

In the interval of β, the plate height is within the limits of (1–1.5) H_0, where $H_0 = 8\,u_0h^2/D\,\varepsilon_0^3$ is the value of H at $\beta = 0$. The H_0 value corresponds to plate height in EFFF, where it amounts to 10^{-3}–10^{-2} cm. Thus, the applied transversal voltage can substantially diminish the value of H. Another way of achieving a more effective separation in the field of near-surface forces is to increase the "effective" value of β. From eqn. 25, the ratio of the number of particles in the near-wall region to the number of particles outside of this region, with the applied transversal voltage, is $\varepsilon_0\beta$. This means that, whenever the transversal voltage is not present, the "effective" value can be increased ε_0 times.

This might result in an increase in the fractional velocity difference and in a reduction in the separation time. In a number reports on EFFF, relatively small velocities of the sample motion were observed in comparison with the theoretical assumptions. Expression 26 also evidences a diminishing of the average sample velocity as compared to the classic expression:

$$\bar{u}_1 = 2\,u_0/\varepsilon_0 \tag{31}$$

Thought it is difficult to compare experimental data available in the literature and the dependence of $\bar{u}_1$ on the electric field strength given by eqn. 26, an evaluation of the order of magnitude of the relative variation of the average sample velocity resulting from near-wall interactions is of some interest. This can be done by use of eqn. 21. If $\delta \approx 10^{-5}$ cm, $h \approx 10^{-2}$ cm, $b \approx 10^{-4}$ cm^2/s · V, $D \approx 10^{-6}$ cm^2/s and $\zeta \approx 5 \cdot 10^{-2}$ V, then $\beta \approx 0.75$.

Values of the electrokinetic potentials, $\zeta \approx 10^{-1}$ V, are characteristic for a number of materials used for forming the channel in EFFF. For particles with $D \approx 5 \cdot 10^{-6}$ cm^2/s, other parameters being the same, we obtain $\beta \approx 0.015$. It is evident that in these cases deviations $\bar{u}_1$ (ε_0) from eqn. 31 will be observed at $\varepsilon_0 \approx 10$.

Therefore, the voltage applied across the capillary allows the separation in the field of near-surface forces to become more efficient, and an extension of the possible field of applications. One possible variant of this application may be the determination of minor values of the parameter β from the dependence of the average sample velocity on the transversal voltage. It is also necessary to take into account the interaction of separating particles with the field of the near-surface forces in EFFF experiments.

LIST OF SYMBOLS

b	electrophoretic mobility
h	halfwidth of channel
h^*	characteristic width of the near-wall region
k	Boltzmann constant
q	effective charge of particle
u	flow velocity
u_0	maximal flow velocity

$\bar{u}$	average flow velocity
$\bar{u}_1$	average velocity of zone
x	coordinate across the channel
D	diffusion ciefficient
D_{eff}	effective dispersion coefficient
H	plate height
T	temperature
U	half of transversal voltage
W	potential of transversal force
W_s	potential of the near-wall forces
W_v	potential of electrophoretic force
β	ratio of the number of particles in the near-wall region to the number of particles in the region where transversal force is absent
δ	electric double layer width
ε	potential of transversal force in kT units
ε_0	potential, corresponding to the half of transversal voltage in kT units
ε_0^*	depth of the near-wall potential well in kT units.
ε_v	electrostatic potential energy in kT units
ζ	electrokinetic potential
ξ	mathematical function, solution of eqn. 3

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