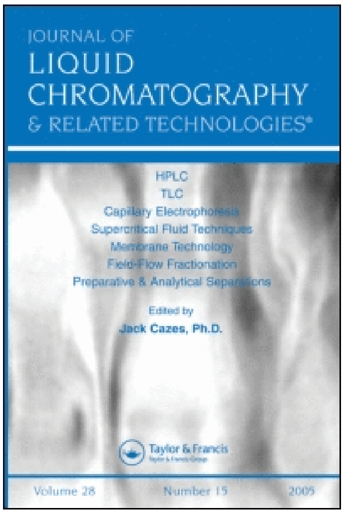

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ON CONSTRUCTING A QUANTITATIVE THEORY OF OPEN CAPILLARY CHROMATOGRAPHY

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Summary.

Electric double layers which occur at the conductive surface-electrolytic solution interface may be used as virtual stationary phases for separating macromolecules. The quantitative estimations of the efficiency of separation processes based on the features of double layers are essentially dependent not only on the values of pH, the characteristic size of a column or granules and the flow rate, but also on the externally applied potential and the current in the circuit. The specific models advanced herein are illustrated by analytical formulae which determine the effect of an increase of the field and hence the very process of separating macromolecules as that of proteins, depending on the characteristic size thereof, the space between the electrodes and the current in the circuit. The theoretical description needs no phenomenological coefficient as in theory advanced by K.Li and makes it possible to determine the conditions for open capillary chromatography more specifically, according to any advanced aim.

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The effects of an electric double layer appreciable in understanding the mechanism of separation processes by liquid chromatography have recently become the subject matter of a number of publications. The present analytical technique of separating proteins, ferments and other charged macromolecules incorporates a variety of procedures (such as electrophoresis, affine chromatography, isoelectric focusing etc.). At the same time, the use of properties of an electric double layer occurring at the interface of phases exhibites some advantages clearly disclosed in [1]. In addition, a practical use has been recently gained by methods which may be referred to open capillary chromatography, differing only in the treatment of substantial quantities of liquids. Thus, as shown in [2-4], the mechanisms of sorptive purification of blood with the use of activated carbon, which have gained a wide acceptance in clinical medicine, and the mechanisms of electrofiltration for water cleaning may also be explained by similar effects of a double layer increase in external electric fields. As a result of the practical use of such separation processes it is extremely necessary to obtain a quantitative estimation of the virtual stationary phase associated with double layers [1] under special conditions. However, such estimations are lacking in literature, since even the infrequent theoretical investigations in this direction lead to formulae with indefinitely and problematically defined parameters [1, 3] which naturally involves some difficulties in using these formulae. We guess that any of the theories should be brought up to such analytical expressions which might be easily calculated with the aim of testing the same, and the main thing here is to determine the conditions suitable for performing open capillary chromatography and detect specific macromolecules. In some instances, such a program may be realized.

The theory of open capillary chromatography disclosed in [1] is based on the effect of a double layer as a virtual stationary phase for separating charged macromolecules. The author of the above-mentioned article has managed to determine the confinement Re /the designations hereinafter referred to are given by the author [1] / as a function of a certain dimensionless parameter λ for the most real situation in the form of

$$Re = 4/\lambda \qquad (1)$$

$$\lambda = (z e \alpha V \kappa R)/(6\pi \mathcal{D} \eta \rho) \qquad (2)$$

where $\mathcal{D}$ is the diffusion coefficient of macromolecules to be separated, z is the number of charges per each of them, e is the elementary charge of an electron, R and ρ are the radii of a metal capillary and a macromolecule whose form is taken, for simplicity, as spherical, respectively, η is viscosity of a dispersion medium, κ is the Debye screening radius. All the values are generally known. However, it is not a simple matter to determine the parameter of α which to a great extent controls the original separation effect according to the relationship proposed in [1] :

$$\Phi = \alpha V, \qquad (3)$$

where Φ is the potential of the outer Helmholtz plane for simplicity designated as ζ -potential, V is the external voltage. The parameter α is not quite definite in [1] and this presents some difficulties in using the theory of open capillary chromatography for practical calculations.

Now let us try to estimate an increase of the field of an elecric double layer more strictly. This is particularly necessary, since equation (3) is not suitable for estimating the size of area of the virtual stationary phase which increases when an external field is applied. The gain factor may be found through a simultaneous solution of the Nernst-Planck and Poisson equations. Here should be noted that the condition for an electric neutrality, which can substancially simplify such a set of equations, is unusable therewith. With the use of singular perturbation methods for a set of ordinary differential equations which disclose the passage of an electric current through a binary electrolytic solution[5] , it has been found that the effective thickness of the diffuse layer S_d depends on the value of the current j passing through the system according to the law

$$S_d \simeq \frac{1}{\kappa R \sqrt{\frac{2+j}{2}}} , \qquad (4)$$

the dimensionless current j being related to the dimensional density of the current J by the following relationship

$$j = \frac{2 J h}{N \mathcal{D}} , \qquad (5)$$

where h is the space between electrodes, $\mathcal{D}$ and N are diffusion coefficient and ion concentration, respectively. Reference [5] also deals with a model wherein the electrode surface is positively charged. Therefore, $j < 0$ and formula (4) has no sense when $j \simeq -2$ (limiting current). The last condition may be written as the following inequality defining the field of application:

$$\kappa h (2 + j) \gg 2 \qquad (6)$$

Formula (4) practically defines a thickening of the diffuse electric double layer by a factor of $\sqrt{\frac{2}{2+j}}$ as a result of a decrease in the electrolyte concentration in the vicinity of the electrode.

The effect of an increase of the virtual field may take place not only inside a metal capillary to capture macromolecules but also at an ion-exchange conductive membrane (ionite). These features are characteristic for activated carbons used, for example, as hemosorbents [2]. In this case the counter ions of ionite can move not from the membrane to the electrolyte but in the opposite direction. The charged macromolecules suspended in an electrolytic solution (with a fixed direction of the field), whose sign is coincident with that of counter ions of the membrane, will move in the same manner. In other words, here takes place the movement of particles onto the membrane surface. Therefore, we can make a conclusion that on the membrane surface close to which the effect of a field increase may be observed, there takes place a transportation of colloid particles whose sign of charge coincides with that of membrane counter ions and thus is opposite to the sign of the membrane charge. From this it follows that with an increase of the field, the first monolayer of particles on the membrane surface is formed as a result of different charges of particles and the membrane. An increase of the field is also necessary for forming polylayers of particles observed, for example, by means of chromatography.

To provide a maximum effect of the field increase and a formation of the virtual stationary phase it is necessary to use the densities of current which comply with the conditions:

$$\frac{2}{k\rho}\cdot\frac{\rho}{h} < 2 + \dot{j} < \frac{3\rho}{h} \qquad (7)$$

The field increase in the area of the n-monolayer of paticles may be expressed as

$$m_{n+1} = \frac{1}{2n+1}\cdot\frac{h}{\rho} \qquad (8)$$

Formulae (7) and (8) are substantially based on the model proposed in [5] . For other conditions for open capillary chromatography, the formular for an increase of the field may have peculiar analytical representations.

When $h = 10^{-2}$cm, according to formula (8), $\rho = 10^{-5}$cm and $m_2 \approx 300$. Any decrease in h intensifies the transportation of particles into the area of the field maximum, but as may be seen from (8) this is followed by a decrease in the effect of the field increase.

Thus, the thickness of an effective virtual stationary phase and the coefficient of a field increase for open capillary chromatography have been found. The described approach to the problem needs no special treatment of α included into the formula of [1] . The calculation of this parameter may be performed within the limits of the proposed model but it has not been given here.

The sedimentation (separation) of charged macromolecules may take place with an increase of the field and an elongation of electric double layers not only in a conductive (metal) capillary as has been shown by K.Li [1] but also in a packed bed of ionite or activated carbon granules. In this case the effect is dependent on the space between the two adjacent granules. An illustrative practical example of realizing such a situation is the method of hemocarboperfusion [2]. As has been recently revealed by experiments, the rate of soption (sedimentation) on the sorbents widely used in clinical practice depends to a great extent on the external potential of a certain polarity and magnitude which is applied to the system[6]. It is not difficult to note that under such conditions, which are generally speaking analogous to a chromatographical column, there also take place conditions similar to those disclosed in [1]. Under assumption of the same scheme in discussing and constructing quantitative formulae (likely to be permissable at this stage of investigations) the efficiency of the method is also dependent on the relationsip of type (1)-(8). However, the most significant for such models is the relationship between the conductivities of particles (granules) $æ'$ which should be much higher than those of substances $æ$ to be settled. The gain factor of the field may be calculated to a first approximation in considering a nonconductive medium with particles of an infinitely high conductivity (with an error of the order of $æ/æ'$) [2]. A more detailed similar investigation is given in [2].

Thus, a refinement of the conditions for an effective use of double layers as a virtual stationary phase for charged macromolecules, which is disclosed in this paper, makes it possible to relate the Li theoretical model [1] with the conditions of an experiment or a practical use thereof.

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