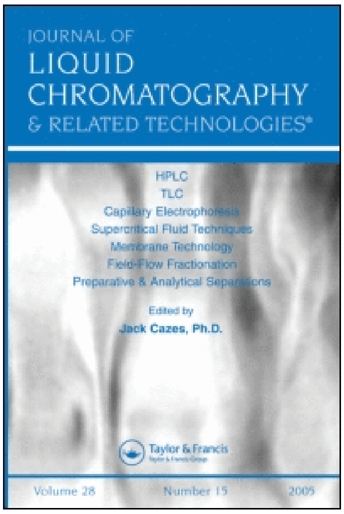

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ON THE MIGRATION OF THE MOBILE PHASE IN A THIN SORPTION LAYER

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The principles of impregnation of porous media with liquids are important for many technological processes, but their greatest significance is for development of the theory of thin-layer chromatography (TLC) methods. The velocity of migration of the mobile phase in the sorption layer of a chromatographic plate and the ratio of the volume of the stationary phase to that of the mobile phase, V_s/V_m, determine the time of separation and the deviation of the observed values for the relative migration distances of substance zones, R_f, from their factual values.

To determine the migration velocity of the mobile phase front and the separation time in linear TLC, use is made of the well-known relations [1,2]

$$dZ_f/dt=0.5K/Z_f \qquad (1)$$

and

$$Z^2_f=Kt \qquad (2)$$

where K is the mobile-phase front velocity constant, Z_f is the distance traveled by the solvent front for time t. To apply Eqs. (1) and (2), one should be aware of the numerical values of the velocity constants for selected "sorption layer - mobile phase" systems.

It has been noticed [3,4] that the velocity constant K in Eqs. (1) and (2) is not constant in fact and depends on the distance traveled by the mobile phase front. For example, H.Halpaap and J.Ripphahn [3] have reported the observed values of the velocity coefficients K_e for solvents normally used as mobile phases. The values of the front velocity coefficients have been shown for fixed Z_f values. Analysis shows the general tendency of the velocity coefficients to grow with Z_f. The velocity coefficients K_e have been presented [4] as a function of time for a high-boiling mobile phase (n-hexadecanol) at temperatures ranging from 80 to 180 C. The velocity coefficients appreciably rise at high temperatures. The curve $K_e = f(t)$ has been shown [4] to have two discernible intervals: the interval of the fast growth of the velocity coefficient with time and the slow-change interval.

The data published so far say nothing of the principles governing the behavior of the observed values of the front velocity coefficients K_e, nor do they give any idea of their relation to the velocity constants K in Eqs. (1), (2).

In order to find the dependence $K_e = f(Z_f, K)$, we studied experimentally the observed front velocity coefficient as a function of Z_f for a number of mobile phases. In measuring the characteristic curves, we used a horizontal unsaturated chamber (CAMAG) and HPTLC silica gel chromatographic plates (Merck). The results are shown in Fig.1.

The general features of the dependences of the front velocity coefficients K_e on Z_f conform to the data already published. As can be seen from Fig.1, the velocity coefficient K_e grows with Z_f.

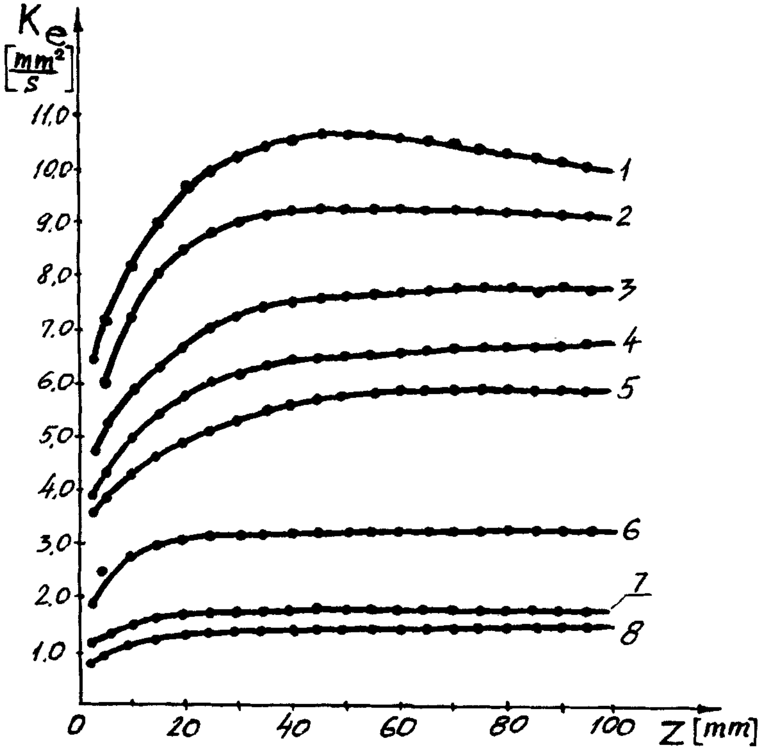

Fig. 1. Dependences of the observed front velocity coefficients K_e on the distance covered by the front for the following mobile phases: (1) diethyl ether; (2) hexane, (3) heptane ;(4) benzene; (5) methanol; (6) carbon tetrachloride; (7) tridecane; (8) isopropyl alcohol.

The variation in K_e can be attributed to several causes. First, at zero time (at $Z_f=0$), Eq. (1) yields the infinite migration velocity of the mobile phase, which contradicts reality. The discrepancy is due to the fact that Eqs. (1), (2) were derived within the linear porous layer model, which represents the porous layer as a bunch of crooked capillaries having effective diameter d_c. The derivation of Eqs. (1), (2) did not take into account the influence of local hydraulic resistances in the layer, while in reality part of the capillary pressure in the layer is consumed to impart a kinetic energy to the liquid, to form the laminar flow condition, and to overcome the local resistances (as abrupt narrowing, abrupt widening, flow turns). It is the strong influence of local resistances that is responsible for the sharp change in K_e at the initial interval reported in Ref.[4]. Indeed, with rising temperature the viscosity of the mobile phase decreases, while the Reynolds number increases.

Secondly, the proportion of mobile phase in a real porous layer is not constant and depends on the coordinate z. Since the real layer includes capillaries of various diameters, the mobile phase fills up the capillaries of small diameter first, because of the greater capillary rarefaction therein, whereas the major part of the liquid enters the layer through the grosser channels, which possess smaller hydraulic resistance. This accelerates the front migration.

Thirdly, the mobile phase near its front seems to be stretched out very much by capillary forces, which causes its intense evaporation. The vapor of the mobile phase scatters partly by diffusion over the layer and condenses on the surface not yet wetted, thereby accelerating the front migration. The remaining solvent vapor goes beyond the layer into the room of the separation chamber, which brings about a decrease in the front velocity coefficient, K_e.

The contribution of the above factors is not the same in different time intervals. The first factor predominates chiefly at small Z_f values and less so at intermediate and great Z_f values. The second factor, which affects the observed value of the velocity coefficient K_e, forms the mobile-phase concentration profile within the wetted portion of the layer as early as in the first impregnation stages and keeps on acting later. Experimental data on the mobile-phase concentration profiles in the layers of chromatographic plates have been reported in Refs [2,4-9].

The contribution of the third factor is proportional to time and becomes the most pronounced at great Z_f values. This conclusion is illustrated by the experimental dependence $K_e = f(Z_f)$ for diethyl ether shown in Fig.1.

The pressure of the saturated vapor of diethyl ether at 20 C is 59.88 kPa. Therefore ether readily evaporates into the atmosphere of the unsaturated separation chamber. As Z_f rises, the rate of flow of the mobile phase into the layer diminishes, while the mass of the mobile phase evaporating out of the layer per time unit remains virtually constant. If one managed to have the layer impregnated up to much higher Z_f values, then, at a distance $Z_{f\,max}$ around 0.3 m, the velocity of the mobile phase front would approach zero. At actual Z_f values, however, the third factor only lessens the K_e values to some extent.

Since the local resistances of the sorption layer strongly influence the observed values of the front velocity coefficient K_e, we try to take them into account first.

Eq.(1) can be derived from the Poiseuille equation [10], which gives the following front velocity constant

$$K = \frac{d_c \cdot \sigma \cdot \cos\theta \cdot \varepsilon}{4 \cdot \mu \cdot \omega^2 \cdot g \cdot (\varepsilon + \varepsilon_p)}, \quad [m^2/s] \tag{3}$$

where d_c is the equivalent diameter of capillaries [m], σ, the surface tension [N/m], θ, the angle of contact, μ, dynamic viscosity [Pa·s], ω, the crookedness of channels, ε the porousness of the layer (the porosity component defined through the volume of intergranular channels in the layer), ε_p, the porosity of the layer defined through the volume of pores in the sorbent grains, $\varepsilon+\varepsilon_p$, the total porosity of the layer, $y=(V_{\blacksquare}-V_{\blacksquare 0})/V_{\blacksquare}=(\varepsilon+\varepsilon_p-\varepsilon_{\blacksquare 0})/(\varepsilon+\varepsilon_p)$ is the fraction of the solvent-vapor-free porosity of the layer, $V_{\blacksquare}$, the total free volume of the layer ($V_{\blacksquare}/V=\varepsilon+\varepsilon_p$), $V_{\blacksquare 0}$ and $\varepsilon_{\blacksquare 0}$ are the absolute and relative volumes of the layer filled with condensed vapor of the solvent provided that the layer has been preliminarily vapor-loaded.

Eq.(3) will be used later on. As of now, let us derive an expression that would be similar to Eq.(1) except that it would take into account local resistances. For this purpose we can use the Hagen-Poisseuille law [11], which states that the laminar flow of a liquid with viscosity μ through a cylindrical capillary tube with diameter d_c and length l is described by the equation

$$\frac{8\beta\rho}{\pi^2 d_c^4}\cdot Q^2 + \frac{128\mu l}{\pi d_c^4} Q - \Delta p = 0 \tag{4}$$

where ΔP is the loss in pressure over the length l [Pa], Q, the flow rate of the liquid [m^3/s], ρ, the density of the liquid [kg/m^3], β, a coefficient describing the influence of local resistances.

Considering the pressure difference as determined by capillary forces only and taking into account Jurin's law $\Delta P=(4\sigma\cos\theta)/d$, we have

$$\frac{\pi d_c^4}{128\mu l}\cdot\frac{8\beta\rho}{\pi^2 d^4} Q^2 + Q - \frac{4\sigma\cos\theta}{d}\cdot\frac{\pi d_c^4}{128\mu l} = 0$$

Hence, we readily find the rate of flow:

$$Q = \frac{-1 + \sqrt{1 + 4\cdot\frac{\beta\rho}{16\mu\cdot l}\cdot\frac{\sigma\cos\theta\cdot d_c^3}{32\mu\cdot l}}}{\frac{\beta\cdot\rho}{8\pi\mu l}}$$

Recalling that $l=wZ_f$, $dl/dt=w(dZ_f/dt)$, and $dl/dt=Q/(\pi d_c^2/4)$, we obtain

$$\frac{dZ_f}{dt} = \frac{1}{T}\left(\sqrt{Z_f^2+a_1} - Z_f\right) \tag{5}$$

where $T=\frac{d_c^2\beta\cdot\rho}{32\mu}\cdot\psi\cdot\frac{\varepsilon+\varepsilon_p}{\varepsilon}$ is a time constant reflecting the relation between the pressure losses due to friction and those due to local resistances [c], $a_1=\frac{d_c^3\beta\rho\sigma\cos\theta}{128\mu^2\omega^2}$ =TK with K being the front velocity constant from Eq.(3).

Eq.(5) is similar to Eq.(1) but it allows for local resistances. The value of the dimensionless coefficient can be taken equal to $4\cdot10^6$ for HPTLC plates manufactured by Merck. Thus, Eq.(5) allows the front velocity to be calculated for any Z_f values. In particular, at Z_f approaching zero we have

$$\lim_{Z_f\to 0}(dZ_f/dt) = \sqrt{K/T} \tag{6}$$

Consequently, the local resistances of the porous layer confine the maximum velocity of migration of the mobile phase by the limit $\sqrt{K/T}$.

The mobile-phase flux function can be obtained by separating the variables and integrating the expression from 0 to Z_f and from 0 to t:

$$\frac{1}{K}\int_0^{Z_f}\sqrt{Z_f^2+a_1}\cdot dZ_f + \frac{1}{K}\int_0^{Z_f}Z_f\,dZ_f = \int_0^t dt$$

Upon integration we have

$$t = \frac{1}{2K}\left[z_f\sqrt{z_f^2+a_1} + a_1 \ln\left(z_f + \sqrt{z_f^2+a_1}\right) - a_1 \ln a_1 + z_f^2 \right] \tag{7}$$

Eq.(7) is much more accurate than the equation relating the migration distance of the mobile phase front to the duration of the migration.

The observed values of the front velocity coefficient K_e can be found from the expression

$$K_e = \frac{z_f^2}{t} = \frac{2Kz_f^2}{z_f\cdot\sqrt{z_f^2+a_1} + a_1 \ln\left(z_f + \sqrt{z_f^2+a_1}\right) - a_1 \ln a_1 + z_f^2} \tag{8}$$

The calculated and experimental K_e values for octane as the mobile phase are shown in Fig.2.

We chose octane as the mobile phase here in order to make the error introduced by the third factor minimal. Indeeed, the pressure of octane vapor at 20 C is as low as 1.39 kPa, so the evaporation of octane into the gas volume of the chamber will be negligible. Fig.2 shows the observed front velocity coefficient to vary from zero at $Z_f=0$ to K at $Z_f>>1$. It is difficult to experimentally measure the K_e value at $Z_f<10$ mm with a sufficient accuracy, so two points, at $Z_f=3$mm and $Z_f=5$mm, lie aside from the dashed line which continues the experimental curve.

A comparison of the calculation with experimental results exhibits a discrepancy within a relative error of about 16%. This error can be attributed in part to lack of precision in the measurement of the equivalent diameter of capillaries, d_c, which, in reality, is somewhat greater. On the other hand, a

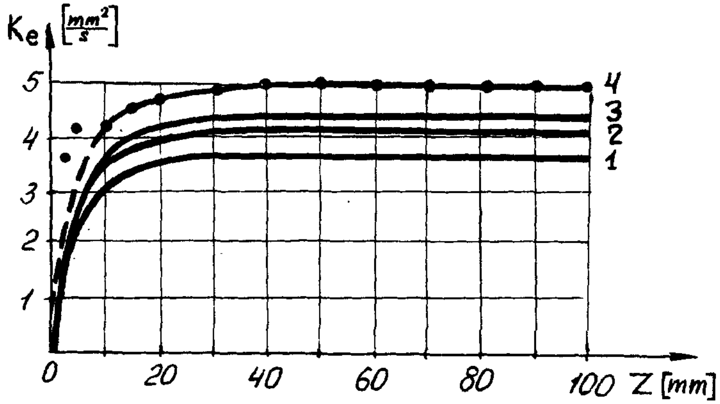

Fig.2. Calculated and measured values of Mobile phase is octane, HPTLC chromatographic plates are by Merck. 1,2,3, K_e values calculated at temperatures $t_1 = 10$ C, $t_2 = 20$ C, $t_3 = 25$ C ($\beta = 4\ 10^6$, $\dot{d}_c = 1.9\ 10^6$ m, $\varphi = 1$, $\varepsilon = \varepsilon_p = 0.4$); 4, experimental K_e values measured at 20 C.

considerable part of the error is associated with the second of the above factors, i.e., the gradient of the concentration of mobile phase along the wetted portion of the coat.

Let us consider the effect of the second factor on the observed front velocity coefficient K_e. Eq.(8) implies that at great Z_f values the coefficient K_e approaches the velocity constant K. Instead, experiment shows that the limiting value for K_e is a different great quantity. This maximum K_e value, which is to be established in practice, will be referred to as K_s. Thus, K_s is the actual velocity constant, which must be incorporated into Eqs (5), (7), (8) for the error due to the effect of the second factor to be eliminated.

We will find now the relation between the front velocity constant K determined by Eq.(3) and its actual value K_s. For this purpose we shall analyze experimental dependences of the occupied portion of the free volume in the sorption layer on the dimensionless coordinate, Z/Z_f [2,4-9]. The profile of the mobile-phase concentration is shown in Fig.(3). Near the mobile-phase front the relative coordinate Z/Z_f is equal to unity and the portion of the layer occupied by the mobile phase is equal to zero (a layer with no preliminary vapor loading, y=1).

At zero relative length (Z/Z_f=0) the portion of the layer occupied by the mobile phase is equal to unity, i.e., the entire free section of the sorption layer is filled up with solvent. All intermediate values of the concentration of mobile phase in the layer well conform to the expression

$$\frac{d\,(V_m/V_{fr})}{d(Z/Z_f)} = 1 - \left(\frac{Z}{Z_f}\right)^n, \tag{9}$$

where the exponent n is dependent on the properties of the sorption layer and of the mobile phase.

On separating the variables and integrating Eq.(9), we have

$$\frac{V_m}{V_{fr}} = \int_0^1 [1-\left(\frac{Z}{Z_f}\right)^n]\,d\left(\frac{Z}{Z_f}\right) = 1 - \frac{1}{n+1} = \frac{n}{n+1}, \tag{10}$$

where $1/(n+1) = \frac{\varepsilon_g}{\varepsilon+\varepsilon_n}$ is the portion of the layer occupied by gaseous phase, $n/(n+1) = \frac{\varepsilon+\varepsilon_n-\varepsilon_g}{\varepsilon+\varepsilon_n}$ is the portion of the wetted part of the layer occupied by mobile phase.

Thus, the exponent n has a clear physical meaning and can be found as the ratio of the volume occupied by the mobile phase in the sorption layer to that occupied by the gaseous phase:

$$n = V_m/V_{gf} = \varepsilon_m/\varepsilon_g \tag{11}$$

with ε_m and ε_g being the relative volumes of the wetted part of the sorption layer occupied by the mobile and gaseous phases.

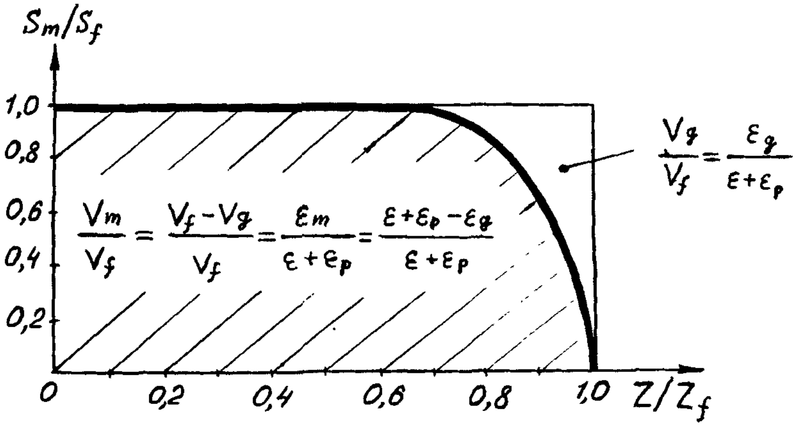

Fig.3. The portion of the free section of sorption layer occupied by mobile phase on dimensionless coordinates: S_m is the area occupied by the mobile phase, S_f, the area not occupied by solid phase, V_g and ε_g are the absolute and relative volumes of the wetted portion of the layer occupied by gaseous phase, V_f and $\varepsilon_f = \varepsilon + \varepsilon_p$, the absolute and relative volumes of the wetted portion not occupied by solid phase, Z is the current coordinate, Z_f, the coordinate of the mobile-phase front.

The exponent can be measured by the gravimetric method. For this purpose, one has to measure the mass of the dry chromatographic plate, m_d, the mass of the plate at its efficient saturation, m_{eff}, and the mass of the plate fully saturated with the mobile phase, m_f. According to Eq.(11), we obtain

$$n = (m_{eff} - m_d) / (m_f - m_{eff}) \tag{12}$$

Experimental data on the values of the exponent n show that it is independent of the values of the dimensionless coordinate Z/Z_f.

On the other hand, the portion of the wetted part of the sorption layer occupied by gaseous phase can be defined through the expression

$$\frac{\varepsilon_g}{\varepsilon + \varepsilon_p} = \frac{1}{n+1} = \frac{\sqrt{K_s \cdot t} - \sqrt{K \cdot t}}{\sqrt{K_s \cdot t}} = 1 - \sqrt{\frac{K}{K_s}} \tag{13}$$

where K_s is the velocity coefficient at the efficient saturation of the layer with mobile phase, K is the front velocity constant defined by Eq.(3).

It follows from Eq.(13) that the velocity coefficient K_s and the velocity constant K are related by the expression

$$K_s = K \cdot \left(\frac{n+1}{n}\right)^2 = K \cdot \frac{1}{\left(1 - \frac{1}{n+1}\right)^2} \tag{14}$$

Eq.(14) can be rewritten as

$$n = \frac{\sqrt{K/K_s}}{1 - \sqrt{K/K_s}} = \frac{1}{1 - \sqrt{K/K_s}} \tag{15}$$

Taking into account Eqs (3) and (14), we can write Eq.(14) ultimately in the form

$$K_s = \frac{\sigma \cdot \cos\theta}{\mu} \quad \frac{d_e \ \varepsilon}{4\omega^2(\varepsilon + \varepsilon_p)} \cdot \left(\frac{\varepsilon + \varepsilon_p}{\varepsilon + \varepsilon_p - \varepsilon_g}\right)^2 = K/(1-C)^2 \tag{16}$$

with $C = \frac{1}{n+1} = \frac{\varepsilon_f}{\varepsilon + \varepsilon_p}$ being a constant.

Given Eq.(16), we can write Eqs (5), (7), and (8) as follows:

$$\frac{dz_f}{dt} = \frac{1}{T} \cdot \left(\sqrt{Z_f^2 + T \cdot \frac{K}{(1-C)^2}} - Z_f\right), \tag{17}$$

$$t = \frac{(1-C)^2}{2K} \cdot \Big[Z_f \cdot \sqrt{Z_f^2 + T \frac{K}{(1-C)^2}} + T \frac{K}{(1-C)^2} \cdot \ln\Big(Z_f + \sqrt{Z_f^2 + T \frac{K}{(1-C)}} \Big)\Big] \tag{18}$$

$$- T\frac{K}{(1-C)^2}\ln\Big[T\cdot\frac{K}{(1-C)^2}\Big]+Z_f^2\Big],$$

$$K_e=\frac{2\left[K/(1-C)^2\right]Z_f^2}{Z_f\cdot\sqrt{Z_f^2+T\frac{K}{(1-C)^2}}+T\frac{K}{(1-C)^2}\ln\Big(Z_f+\sqrt{Z_f^2+T\frac{K}{(1-C)^2}}\Big)-T\frac{K}{(1-C)^2}\cdot\ln\Big[T\cdot\frac{K}{(1-C)^2}\Big]+Z_f^2} \tag{19}$$

Introduction of an experimental correction represented as the factor $(1-C)^2$ into the front velocity constant makes it possible to perform practically precise calculations through use of Eqs (17)-(19), the accuracy of the calculated values of the parameters of migration of the mobile phase being determined for the most part by the accuracy of the initial data. Eqs (17)-(19) do not allow for the processes of evaporation of the mobile phase out of the sorption layer and hold only for those Z_f values where the observed velocity coefficient K_e does not diminish due to evaporation of the solvent as Z_f grows. Eq.(9) can be used for a more accurate calculation of the factual R_f values, because it contains information about the phase ratio V_s/V_m along the whole separation path from the start to Z_f.

Conclusions

Equations have been derived for the description of migration of the mobile phase front in linear TLC. The equations make allowance for the effect of local resistances (as narrowing, widening, bends of capillaries) and of the gradient of the proportion of the mobile phase in the coat of the chromatographic plate. The derived equations, which consider the above factors, quite well describe the experimentally observed dependences of the mobile-phase front velocity coefficient on the distance covered by the front on the plate.

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