

Physico-chemical aspects of liquid chromatography

Yu.V.Kazakevitch*, O.G.Larionov, Yu.A.Eltekov

Institute of Physical Chemistry of the Academy of Sciences
 of the USSR, Leninski prosp., 31, Moscow, USSR

ABSTRACT

Connection between liquid chromatography retention parameters and the adsorption equilibrium constant is discussed. The methods of dead volume determinations are considered and also the dependence of retention volumes on the eluent composition and surface chemistry of adsorbent are described.

THEORY

The criterion of equilibrium in the adsorption thermodynamics is the equality of the Gibbs energy change to zero

$$(dG) = 0 \quad (1)$$

or the equality of chemical potentials of the solution components in volume and adsorption solutions

$$m_1^l = m_1^s \quad (2)$$

Chemical potentials of solution components may be written in form:

$$m_1 = m_1^0 + RT \ln(x_1 y_1) \quad (3)$$

From equation (2) it follows that:

$$\frac{x_1^s y_1^s}{x_1^l y_1^l} = \exp\left(\frac{m_1^{0s} - m_1^{0l}}{RT}\right) \quad (4)$$

After dividing such an equation for component 1 by a similar equation for component 2 we obtain:

$$K = \frac{x_1^s x_2^l}{x_1^l x_2^s} \left(\frac{y_1^s y_2^l}{y_1^l y_2^s} \right) \quad (5)$$

Equation (5) is valid for the case of molecule size equality of solution components. This equation describes an adsorption isotherm of solutions. From eqn. (5) we can derive an equation for x_1^s i.e. an isotherm of the whole content and also Gibbs excess adsorption isotherm as the difference $x_1^s - x_1^l = \Gamma$

$$\Gamma = \frac{(K-1) x (1 - x)}{1 + (K - 1) x} \quad (6)$$

This is so called excess adsorption isotherm, which value may be both greater or less than zero. It is essential that if the compounds under investigation interact with the surface weaker than the solvent, then their excess adsorption is negative.

The adsorption phenomena in chromatography occur under dynamic conditions. M.S.Tswett was the first who discover the connection of adsorption phenomena with the speed of the component moving through column.

NOTATION

<p>m - chemical potentials of solution components (dG/dx_1); G - Gibbs free energy; K - adsorption equilibrium constant; y - activity coefficient; Γ - Gibbs excess adsorption; V_0 - dead volume of chromatographic column; c - concentration (mole/l) x - mole fraction of solution component;</p>	<p>S - adsorbent surface area; V_a - volume of adsorption layer; w - eluent flow rate; V_r - retention volume; k' - capacity factor; subscript 1 - i-th solution component; superscripts l and s - related to volume and surface solution;</p>
---	---

Mathematical description of that was suggested by Whilson [1] and DeVault [2]

$$u_c = \frac{w}{V_0' + S' \left(\frac{d\Gamma}{dc} \right)_c} \quad (7)$$

The above equation is fundamental for the material balance in the adsorbent layer with thickness dx where w is the flow rate of eluent, V_0' and S' are the internal pore volume and the surface of the adsorbent per unit length of column, $d\Gamma/dc$ is the derivative of adsorption isotherm, u_c is the linear velocity of the concentration zone.

Principally in this equation we can use the derivative both as the excess adsorption isotherm and as the isotherm of the whole content. Only the values of V_0' will differ. This parameter has the same meaning as the system volume in the static adsorption investigations.

The principal difference of these two approaches (on the basis of excess adsorption, and on the basis of whole content) is that in the first case we have to take into account the volume of adsorbed layer in the system volume, but in the second case we must divide the system in two parts - the bulk solution and the surface adsorption solution. Obviously, the volume of the later will depend on the properties of the molecules under investigation.

Equation (7) gives the dependence of chromatographic peak shape on the shape of the adsorption isotherm, and also the dependence of the retention of the peak maxima on the concentration of the solution in maxima.

The retention volume of compounds is connected with u_c as follows:

$$V_R = \frac{L}{u_c} w \quad (8)$$

$$\text{combining equations (7) and (8) we get: } V_R = V_0 + S \left(\frac{d\Gamma}{dc} \right)_c \quad (9)$$

This equation connects the retention volume with the adsorption isotherm.

We have to pointed out that the above equations were derived for quasiequilibrium conditions, i.e. when in the column the adsorption equilibrium is performed in every moment of time.

CONNECTION OF THE EQUILIBRIUM CONSTANT WITH RETENTION

Let us consider the simplest form of an adsorption isotherm (equation (6), write its derivative and introduce it into eqn. (9)

$$\frac{d\Gamma}{dx} = (K - 1) \frac{(1 - x)^2 - Kx^2}{[1 - (K - 1)x]^2} \quad (10)$$

obviously if $x = 0$ then $d\Gamma/dx = K - 1$

$$\text{hence } V_R = V_0 + V_a(K - 1) \quad (11)$$

or

$$k' = (V_R - V_0)/V_0 = V_a/V_0(K - 1) \quad (12)$$

Therefore

$$K = k'V_0/V_a + 1 = k'V_0w/S + 1 \quad (13)$$

the limit of possible negative values of k' will be

$$V_R = V_0 - V_a \text{ --- } k' = -V_0/V_a \text{ --- } K = 0 \quad (14)$$

The adsorption equilibrium constant may be written as the constant of surface exchange reaction or in the form

$$\frac{x_1^s x_2^l}{x_1^l x_2^s} f = K = \exp \left(\frac{m_{01}^s - m_{01}^l - m_{02}^s + m_{02}^l}{RT} \right) = \exp \left(\frac{G}{RT} \right) \quad (15)$$

Let us consider now the chromatographic retention of the members of homologous series. Suppose their planar orientation is on the surface. Then the difference of adsorption energy of neighbor members will be equal to the adsorption energy of one CH_2 -group in the absence of solvation, association and intramolecular interaction effects. In this case the additivity of adsorption energy occurs

$$\ln K = A E_0 + n_1 E_1 \quad (16)$$

combining eqn.'s (13) and (16): $\ln K = \ln(V_0/V_a k' + 1) = a + nb$ (17)

Now consider capacity factor, k' : $\ln K = \ln(V_0/V_a k' + 1) = a + nb$ (18)

for the lowest members of the homologous series, k' values are low and digit one under the \ln -function plays a valuable role. For the higher members of the homologous series we can approximately write:

$$\ln\left(\frac{V_0}{V_a} k' + 1\right) = \ln \frac{V_0}{V_a} + \ln k' \quad (19)$$

or $\ln k' = a' + nb$ (20)

Such equations are very often mentioned in published articles.

The higher members of the homologous series have more conformational degrees of freedom and form intermolecular connections, as for example oxyethylated phenols, but it occurs only for $n \geq 6$. The deviations for the lower homologous series members are now explained by insufficient accuracy in V_0 determination, because at low retention values the influence of V_0 determination error increases.

The problem of dead volume determination is not as easy as one can think. For example, for the system acetonitrile-water-Separon-C18 practically all the known methods gave the dead volume value for one column (100*3 mm) not less than 1.03 ml, but compounds like 4,6-dioxypyrimidine or uric acid had noticeably less retention volumes, and consequently their values of k' were less than zero. However, it does not correspond to the opinion that $\ln k'$ is the energetic parameter of a chromatographic system. This opinion is based on the well known equation offered by Sckott and Kucera [3]

$$k' = V_0/V_a K_i \quad (21)$$

where K_i is the coefficient of distribution of substances between the volume and the adsorption phases. In case of such approach it is impossible to compare different chromatographic systems and retention of different compounds in one system, as in this case the adsorption volume is specific for each compound.

If we consider equation (9), we see that $V_R = V_0$ only if $d\Gamma/dc = 0$, i.e. the interaction of adsorbate molecules with the surface is the same as that of eluent molecules.

Let us discuss further the methods which are used for the dead volume determination.

1. Retention of unadsorbing component.
2. Retention of eluent component.

If the eluent consists of two components, it is clear that the adsorption of one component by another occurs, and the retention of one component obeys equation (7) and depends on the eluent composition.

3. Weighing method.

This method must give accurate results but it is rather complicated experimentally.

4. The linearisation of homologous series.

This method is based upon the proportion of linearity of $\ln k'$ on n , but as we have already shown, it is not absolutely true.

To determine V_0 exactly we can use equation (9), for the conditions $d\Gamma/dc = 0$, we get $V_0 = V_R$. It can be done if the excess adsorption isotherm of the substance is known. But if it is not known, it is possible to measure it with the help of the disturbance method. The rate of motion of disturbance peak is determined by equation (7). After measuring such disturbances for different equilibrium concentrations for all concentration range we obtain a curve. After integrating equation (9) from 0 to 1 we get:

$$\int_0^1 \frac{1}{V} dx = \int_0^1 \left[\frac{1}{V_0} + \frac{V}{V_0} \frac{d\Gamma}{dx} \right] dx \quad (22)$$

Taking into account that $\Gamma = 0$ at $x = 0$ and $x = 1$, we get $V_R = V_0$, i.e. for the obtained dependence the average integrated value is the value of the system dead volume.

Let us consider now the influence of the eluent composition on the retention of substances. There are many descriptions of the retention dependences on eluent composition

$$k' = a + bx + cx^2, \quad (23)$$

$$\ln k' = a' + b'x + c'x^2, \quad (24)$$

$$\ln k' = a'' + b'' \ln x. \quad (25)$$

Frequently mentioned in different articles dependences of $\ln K'$ on $\ln C$ can be simply explained for medium range of eluent concentrations. As it was shown, the composition of the acetonitrile-water system adsorption layer in the range of concentrations from 20 to 60 % is constant. Let one of the components (ACN) be adsorptionally active, and the second one be a solvent, then we can derive:

$$x_a^s + nB^l \rightleftharpoons x^l + nB^s \quad (26)$$

$$K = \frac{x^s [B^l]^n}{x^l [B^s]^n} \quad (27)$$

$$\ln K = \ln K_1 + n \ln [B^s] + n \ln [B^l] \quad (28)$$

$$K' = V_0/V_a K_1 \quad (29)$$

$$\ln K' = A - n \ln C \quad (30)$$

thus, we have obtained linear dependence. It is clear that out of the chosen range this correspondence is not true.

From the equality of the system components chemical potentials we obtain:

$$K = \frac{x_a^s x_1^l x_2^l}{x_a^l x_1^s x_2^s} f \quad (31)$$

In the elutive chromatography negligibly small quantities of substances are usually introduced, hence

$$\lim_{x^l \rightarrow 0} (x^s/x^l) = K_1 + 1 \quad (32)$$

then we can write $x_1 + x_2 = 1$ (33)

or
$$K = f(K_1 - 1) \frac{x_1^l(1 - x_1^l)}{x_1^s(1 - x_1^s)} \quad (34)$$

a two-component eluent can be considered as a two-component adsorption system at first approach

$$x^s = \frac{K_1 x^l}{1 + (K_1 - 1) x^l} \quad (35)$$

hence
$$K = f(K_1 - 1) \frac{[1 + (K_1 - 1) x^l]^2}{K_1} \quad (36)$$

$$K = \frac{f(K_1 - 1)}{K_1} [1 + 2(K_1 - 1)x^l + (K_1 - 1)^2 (x^l)^2] \quad (37)$$

The last equation shows the connection of the eluent composition with the adsorption equilibrium constant of the substance under investigation. To obtain the dependence of K' on x it is necessary to introduce equation (17). As you can see, the form of this equation is very near to that of eqn. (24).

In conclusion we have to mention that if an adsorption equilibrium constant (K) is used instead of the capacity factor (k'), the direct connection of the system with thermodynamic parameters through the equations for chemical potentials and Maxwell equations is obtained.

CONCLUSION

In conclusion we can say that the main result of this article is the connection of the chromatographic parameters (like k' , V_r and V_0) with the thermodynamic parameters of the same adsorption system. We suggest the methods for dead volume determination on the basis of thermodynamic theory (eqn. 22) and from the eqn. 18 it can be seen that earlier suggested methods are unusable.

REFERENCES

1. W.R.Whilson, *J. Amer. Chem. Soc.* **63**, 645 (1943).
2. D.Devault J. *Amer. Chem. Soc.* **62**, 1583 (1940).
3. R.P.W.Scott, P.Kucera, *J.Chromatog.*, **112**, 425 (1975).