Thermodynamic Interpretation of the Capacity Factor

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Key Words

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Summary

The thermodynamic description of the capacity factor (k'), the most widely used retention parameter, is presented. The connection of the thermodynamic adsorption equilibrium constant (K) and the retention parameters are shown. Methods for dead volume determination are described. A general thermodynamic approach of the chromatographic processes is described.

Introduction

Practically all relationships described up to now in liquid chromatography have connected the capacity factor (k') with the parameters of the system or the molecular characteristics of the solutes [1]. It had been shown that there is a linear relationship between ln k' and the number of carbon atoms in a homologous series and also between ln k' and the logarithm of the concentration of the mobile phase components [2, 3].

The capacity factor is the ratio of the adjusted retention volume to the void volume of the system and it can be interpreted as the ratio of the time the investigated compound is spending on the surface to the time it is spending in the mobile phase:

$$k' = \frac{V_R - V_0}{V_0} = \frac{t_R - t_0}{t_0} \quad (1)$$

The thermodynamic interpretation of this relationship is usually based on the distribution description of adsorption phenomena.

Scott and Kucera [4] suggested the connection of k' with the distribution constant, K_d, in the form of

$$k' = K_d V_s / V_0$$

where V_s is the volume of the adsorption layer and V_0 is the dead volume. Then it follows from eq. (1) that

$$V_R = V_0 + K_d V_s \quad (2)$$

The distribution constant as the equilibrium constant of the surface exchange reaction meets the Arrhenius equation:

$$\ln K_d = A \exp(-E/RT) \quad (3)$$

where E is the Gibbs free energy of molecule transfer in liquid chromatography from solution to the surface. In the first approximation it is the sum of the adsorption energies of structural fragments of a molecule. For a homologous series it will be

$$\Delta G = \Delta G_0 + n\Delta G_i \quad (4)$$

where ΔG_0 is the adsorption energy of the first member of a homologous series, G_i is the adsorption energy for one CH_2-group and n is the number of incremental CH_2 groups. From eqs. (3) and (4) we can see the linear dependence of ln K_d from n and we get the linear dependence ln k' vs. n from the equation $k' = \phi K_d$ where $\phi = V_s/V_0$ [4].

Systematic deviations from these dependencies are mentioned in the literature [5]. However, in those cases main attention was paid on the method of dead volume determination. We can change the form of the ln k' vs. n relationship by changing the value of the dead volume, and we can bring it closer to linear. The method of dead volume calculation was suggested on the basis of assuming that the ln k' vs. n relationship is linear (linearization of homologous series [6]).

The main disadvantage of the thermodynamic interpretation of k' is that it can be negative [7, 8] when $V_R < V_0$). As a rule, the authors explain this by errors in the dead volume determination. Only Knox [7] has shown that, in principle, it is possible, e.g., in exclusion chromatography.

In this report we will show the theoretical analysis of the connection of the capacity factor with the thermodynamic parameters of adsorption systems.

Theory

The basis of adsorption chromatography is the theory of adsorption from solutions. There are two approaches to the description of adsorption processes: 1) the excess values

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method, suggested 110 years ago by Gibbs and 2) the whole content method. The latter requires to introduce the adsorption phase in which the surface concentration of the components was determined. The excess method describes the solution over the adsorbent surface as one phase and does not require a separate adsorption layer. The detailed description of these methods has been published [9, 10].

It is important for us that the solution over the adsorbent used in the excess method is one unity, whereas in the whole content method that solution is devided into two parts one of which is the adsorption phase (s), and the other the volume phase (l).

Methodologically the thermodynamic description of the chromatographic process on the basis of the distribution theory is the same as the description of adsorption on the basis of the whole content method.

In the description of an adsorption system it is usually assumed that:

1. the excess adsorption of the pure component is equal to zero;
2. the adsorption system is in equilibrium or the changes of the Gibbs free energy equal zero;
3. in the description of the adsorption relationships the model of adsorption layer must be used (e.g., the model of monolayer adsorption or the model of a layer with finite thickness).

In the whole content method the last conditions is necessary but in the excess method it cannot be used.

The equality of the chemical potentials of the components in the volume and adsorption layers follows from the condition of adsorption equilibrium:

$$\mu_i^l = \mu_i^s, \quad \mu_i = \mu_i^0 + RT \ln (x_i \gamma_i) \tag{5}$$

where x_i is the mole fraction, μ_i is the chemical potential and γ_i is the activity coefficient of component i; superscripts s and l refer to the adsorption and volume phase respectively, and superscript 0 refers to standard conditions.

From eq. (5) the relationship connecting the concentration of all components may be derived:

$$K = \frac{x_1^s x_2^l}{x_1^l x_2^s} \frac{\gamma_1^s \gamma_2^l}{\gamma_1^l \gamma_2^s} = \exp. \frac{\Sigma(\mu_i^{\phi,s} - \mu_i^{\phi,l})}{RT} \tag{6}$$

where K is the adsorption equilibrium constant, x is the concentration and γ is the activity coefficient of the individual components, on the surface (s) and in the solution (l); superscript 0 again indicates the respective standard conditions.

We shall assume for simplification that the ideal adsorption system consists of molecules of the same size. In this case the excess adsorption can be written as a difference of component concentration in the surface and volume solutions. Therefore the excess Gibbs adsorption energy, Γ_i, is:

$$\Gamma_i = x_i^s - x_i^l \tag{7}$$

and the equation for the excess adsorption isotherm will be

$$\Gamma_i = \frac{(K-1)\, x_1 (1 - x_1)}{1 + (K-1)\, x_1} \tag{8}$$

Although the equation was derived using the monolayer model, only the equilibrium concentrations of the investigated component are used in eq. (8).

It can be seen from eq. (8) that due to weak interaction of the investigated compound with the surface ($K < 1$) the adsorption isotherm may be negative. Physically it seems as displacement of these molecules from the adsorption region.

Up to now we have considered the static adsorption process. Now we shall deal with the dynamic case. The connection of the velocity of the concentration zone in a chromatographic column with the adsorption isotherm was suggested by De Vault [11] and Wilson [12] in the form:

$$u = \frac{F}{V_0' + S' \dfrac{d\Gamma}{dc}} \tag{9}$$

where F is the flow rate of the mobile phase, V_0' and S' are the volume of the mobile phase and the surface area of the adsorbent per unit column length respectively, u is the linear velocity of the concentration zone in the chromatographic column and c represents concentration. From eq. (9) the dependence of the retention volume from the derivative of the adsorption isotherm can be derived:

$$V_R = V_0 + S \left(\frac{d\Gamma}{dc}\right) \tag{10}$$

Note, that the coefficients at the derivative and free part depend on the interpretation of the adsorption value. If we use the excess values then by analogy with the static adsorption V_0 will be the whole volume of the liquid phase in the column. However, if we use the whole content isotherm than V_0 will be the volume of mobile phase in the column without the adsorption layer volume. Hence, in the latter case the volume or the thickness of the adsorption layer must be determined. However, obviously, this will be depend on the surface chemistry, structure and properties of the investigated molecules.

From eqs. (10) and (1) we can get:

$$k' = \frac{V_R - V_0}{V_0} = \frac{S}{V_0} \left(\frac{d\Gamma}{dc}\right) \tag{11}$$

As we have seen earlier, the excess adsorption isotherm may be negative, hence, its derivative may also be negative (assumming that $\Gamma = 0$ for $x = 0$). Then k' may be negative. In the case when the eluent interacts more stronger with the adsorbent surface it will displace the investigated molecules from the adsorption layer. Consequently, the retention volume of this compound will be less than V_0. This can be seen, for example, for uric acid from acetonitrile/water on a reversed-phase adsorbent and also for other systems [8].

In order to connect k' from eq. (11) with the adsorption equilibrium constant (K) let us differentiate the equation describing the adsorption isotherm [eq. (8)] and combine it with eq. (11):

$$\frac{d\Gamma}{dc} = (K-1) \frac{(1-x)^2 - K x^2}{[1 + (K-1)\, x]^2} \frac{dx}{dc} \tag{12}$$

Hence

$$k' = \frac{S\,(K-1)}{V_0}\left\{\frac{(1-x)^2 - K\,x^2}{[1+(K-1)\,x]^2}\right\}\frac{dx}{dc} \qquad (13)$$

In elution liquid chromatography we use very small concentrations. Therefore, $x \to 0$ and thus,

$$k' = \frac{S}{V_0}(K-1)\,f \qquad (14)$$

where

$$f = [1+(K-1)\,x]^2$$

i.e., the expression in the denominator on the R.H.S. of eq. (12) which is equal to unity at $x \to 0$, or

$$K = k'\frac{V_0}{S} + 1 \qquad (15)$$

It can be seen from eq. (15) that k' may be negative, as a consequence of eq. (11) for negative slope of an excess adsorption isotherm of the investigated compound, but k' cannot be smaller then $-V_s/V_0$.

Eqs. (14 and (15) show the connection of the chromatographic retention parameter, k', with the thermodynamic equilibrium constant, K.

Let us now consider how the weak nonlinearity of the ln k' vs. n relationship and the negative values of k' can be explained on the basis of the suggested theory.

If the molecules of a compound do not interact with the adsorbent surface (more precisely: are strongly repelled from the surface) than these molecules do not penetrate into the adsorption layer and the retention of this compound can be expressed as $V_R = V_0 - V_s$. For this limiting case

$$k' = \frac{(V_0 - V_s) - V_0}{V_0} = -\frac{V_s}{V_0} \qquad (16)$$

It follows from eq. (15) that the adsorption equilibrium constant for this compound is equal to zero. In this way the existence of negative values of k' are explained by the suggested theory.

The main idea of the suggested approach is in the interpretation of the dead volume. We state that its value is constand for any compound in the column and equals the whole volume of the mobile phase. However, if we use the approach of Scott and Kucera [4];

$$k' = K_d\,(V_s/V_l) \qquad (17)$$

where K_d is the distribution constant, then we must use a separate value of the dead volume for every solute.

The next task is the establishment of methods for measuring the dead volume.

The majority of the methods suggested in the literature was based on measuring the retention volumes of "nonretained" compounds [6, 13, 14]. However, actually, a "nonretained" compound must have $d\Gamma/dc = 0$, or it must have the same interaction with the surface as the eluent. Obviously, it is very hard to find such a compound. In reversed-phase chromatography often two or more components of the eluent are used for this purpose. For the proper determination of the dead volume by a marker-compound the independence of the marker's retention on the eluent composition is needed; however, this is impossible.

The moving of any molecule along the column is described by eq. (10) and depends on the derivative of the adsorption isotherm of the solute in that system.

It is clear that an universal method cannot be found for the dead volume determination without accounting for the adsorption isotherm.

On the basis of eq. (10) a very simple method can be suggested for dead volume determination.

We can measure the retention volume of the disturbance peak [7] of one eluent component for the whole concentration range as it was described by Riedo and Kováts [15]. Inserting the obtained V_R vs. x relationship into eq. (10) and integrating it in the whole range, we obtain

$$\int_0^1 [V_R(x) - V_0]\,dx = \int_0^1 \frac{d\Gamma}{dx}\,dx \qquad (18)$$

Since the excess adsorption of a pure component is equal to zero therefore, the right-hand-side of this equation is equal to zero. The left hand side may be transformed to the form of an integral average:

$$V_0 = \int_0^1 V_R(x)\,dx \qquad (19)$$

This represents a precise method for dead volume determination when we do not know the adsorption isotherm of the investigated compound; also, this method may be modified very simply to a method for the determination of the adsorption isotherm. If this isotherm is known we can measure the retention volume of the disturbance peak at the composition for which $d\Gamma/dc = 0$. This retention volume [from eq. (10)] will be equal to V_0.

The method for the determination of the dead volume by homologous series linearisation was based on the suggestion of a linear relationship between ln k' and n. As we have shown earlier the dependence of ln K and not of ln k' must be linear. Let us see what is the difference between these relationships. If

$$\ln K = a + bn \qquad (20)$$

then from eq. (15):

$$\ln k' = \ln \frac{V_s}{V_0}\exp.(a+bn) - 1 \qquad (21)$$

or

$$\ln k' = \ln (V_s/V_0) + \ln [\exp.(a+bn) - 1] \qquad (22)$$

The ratio V_s/V_0 is approximately equal to 10; thus, the adsorption equilibrium constant is ten times greater then k' [from eq. (15)]. Therefore, K will be greater then unity for compounds which have a positive interaction with the adsorbent surface. Thus, constants a and b will be greater then zero. In this case the right-hand side of eq. (17) is approximately linear at high values of n. For n in the range of 1 to 4 there is a slight deviation from linearity. This region is more sensitive for errors in dead volume determination.

This is the reason why scientists consider this nonlinearity as an experimental error in the dead volume values and suggest the method of linearisation of homologous series. However, in a more closer consideration [5] this method gives different results for various homologous series.

It mus be noted that the excess method of adsorption phenomena interpretation permits to abstract from the consideration of the processes which take place on the surface. We may consider the retention values only as functions of excess concentration changes in the solution. The general thermodynamic description of the various types of chromatographic methods including exclusion, ion-exchange and others is possible on the basis of this approach.

Actually, if the excess approach will be applied to exclusion chromatography then (from equation (10)) the excess adsorption isotherm will be represented by the dependence $\Gamma = f(M)$, where M is the molecular weight.

The nature of the process is not important in this case. It is only important that there is a concentration change in the solution and that this change depends on the molecular weight. Then, for every molecular weight there is a unique excess adsorption isotherm (generally speeking, negative).

Since in chromatography we use very low concentrations, therefore $d\Gamma/dc \rightarrow K_h$ (Henry constant) which is a function of the molecular weight. From eq. (10) we can obtain the dependence of V_R from the molecular weight. In this case the values of V_0 and S are the geometrical parameters of a column and an adsorbent.

In the derivation of equation (1) the ideality of the chromatographic system was assumed. All deviations form ideality (which are usually expressed as the activity coefficients) will be negligible.

In eqs. (9—15) we used the parameter S which connects with the model of the adsorption layer; in our case it is the monolayer model. However, the model of adsorption layer has an influence only on the coefficient in equation (15) but not on its form. The general view of this equation is reflecting the thermodynamic connection of the capacity factors with the of adsorption equilibrium constant.

Conclusions

The suggested approach to the interpretation of chromatographic retention is based on excess adsorption and it may be used to describe the chromatographic dependencies. This approach permits the explanation of experimental results which are not in agreement with earlier theories.

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