

Fundamental Study on Thin Layer Chromatography

I. Solvent Strength of Mixture for Polymeric Samples

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The validity of Snyder's solvent strength of mixed solvents was fully discussed in an adsorption case where a sample molecule displaces some number of solvent molecules while the one-to-one molecular displacement reaction takes place among component solvents. The theoretical foundation was given to Snyder's assumption of the equal molecular size to the sample and solvent molecule in the derivation of the solvent strength of the mixed solvent. Thus Snyder's treatments on adsorption chromatography of polymer molecules are supplementally justified through the discussions presented in this report.

KEY WORDS: Adsorption chromatography/ Solvent strength/ Macro-molecules.

INTRODUCTION

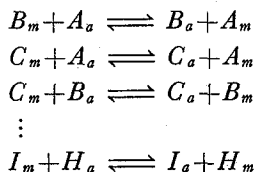
In the study on liquid-solid chromatography (LSC), Snyder has made an extensive effort to develop the theory for the retention mechanism¹⁾. One of the important results given by him and his coworkers is the method to estimate the solvent strength for a mixed solvent¹⁻⁶⁾. It has been also demonstrated^{7,8)} that his method is capable to rederive the same relationships found on the basis of somewhat different models by Soczewinski^{9,10)} and Scot and Kucera^{11,12)}. Snyder has derived the solvent strength of the mixture by assuming the equal molecular size of component solvents. A sample molecule is also assumed to have the same molecular size as solvent, though the sample molecule is considered to displace generally some number of solvent molecules on the adsorbent surface. This assumption has not been rigorously discussed by Snyder¹⁾, and thus it is suggested sometimes that Snyder's method can hold only in the limiting case of the competitive adsorption among the molecules having the same molecular size⁸⁾. Discussion will be focused on the adequacy of applying Snyder's treatment to adsorption chromatography of polymer molecules.

DERIVATION OF SOLVENT STRENGTH OF MIXTURES

Following Snyder and his coworkers^{1,9)}, we assume that all adsorption sites on the surface of adsorbent are physically equivalent and the adsorbates always compose a monolayer on it. Further, it is assumed that there are no interactions between adjacent adsorbed molecules. We consider the displacement reaction of one-to-one molecule among solvents A, B, ..., and I in the multi-component mixture. That is,

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one solvent molecule in the mobile phase reacts to displace the other solvent molecule adsorbed on the adsorbent surface. These are¹⁻³⁾



where subscriptions m and a denote the relevant solvent molecule being in the mobile and adsorbed phase, respectively. The thermodynamic equilibrium constant $K_{x,y}$ is expressed for the individual reactions as follows^{1,3)}

$$K_{x,y} = \frac{(\gamma_x)_a (\gamma_y)_m}{(\gamma_x)_m (\gamma_y)_a} \quad (1)$$

($x, y = A, B, \dots, H$ and $I, x \neq y$)

where (γ_x) and (γ_y) are the activities of the component x and y , respectively. When we assume that these activities are given in terms of the mole fractions of the individual components in the mobile phase, M_x and M_y , and in the adsorbed phase, θ_x and θ_y , respectively, then eq. (1) will be rewritten as:^{1,3)}

$$K_{x,y} = \frac{\theta_x M_y}{M_x \theta_y} \quad (1-a)$$

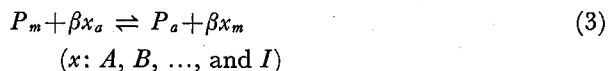
We introduce the dimensionless molar adsorption energy, E , of each component in the expression $K_{x,y}$, according to Snyder:^{1,3)}

$$K_{x,y} = 10^{E_x - E_y} \quad (2)$$

Since the adsorption energy is respectively divided in two terms; an activity parameter of adsorbent, α , and the standard adsorption energy E^0 at α being unity, eq. (2) reduces to¹⁾

$$K_{x,y} = 10^{\alpha(E_x^0 - E_y^0)} \quad (2-a)$$

We consider the adsorption of a sample molecule P which displaces β molecules of solvents on average. Polymer molecules are supposed to take this type of adsorption, when a polymer chain contacts to the adsorbent surface through several segments. Each segment is assumed to have the same dimension as solvent and the interaction between them is neglected. Adsorption of a polymer molecule will take place by equilibrating with β molecules of the solvent mixture of which composition is given in terms of the mole fractions of the component solvents in the adsorbed phase. The site of each adsorbed solvent is not fixed, so that the thermodynamic equilibrium condition should be taken into account for the displacement reaction between the polymer molecule and each solvent species:



The equilibrium constant $K^*_{P,x}$ is thus given as:

$$K^*_{P,x} = \frac{\theta_P (M_x)^\beta}{M_P (\theta_x)^\beta} \quad (4)$$

where θ_P and M_P are the mole fractions of polymer sample P in the adsorbed and mobile phase, respectively. Eq. (4) is given in terms of adsorption energies as¹⁾:

$$K^*_{P,x} = 10^{E_P - \beta E_x} \quad (5)$$

The adsorption equilibrium constant $K^*_{P-\overline{AB\dots I}}$ of polymer sample P in the multi-component mixture treated as a single solvent is defined as:

$$\begin{aligned} K^*_{P-\overline{AB\dots I}} &= \frac{\theta_P (M_A + M_B + \dots + M_I)^\beta}{M_P (\theta_A + \theta_B + \dots + \theta_I)^\beta} \\ &= 10^{E_P - E^*_{\overline{AB\dots I}}} \end{aligned} \quad (6)$$

where $E^*_{\overline{AB\dots I}}$ is the adsorption energy or solvent strength of the multi-component mixture corresponding to the displacement reaction of one polymer molecule. The sums of mole fraction of all components in the mobile phase may satisfy the equation:

$$M_P + \sum_{x=A}^I M_x = 1 \quad (7)$$

We, however, consider that the total coverage on the area of adsorbent surface should be expressed in terms of the mole fraction θ_s of the adsorbed segments in stead of θ_P , that is:

$$\theta_s + \sum_{x=A}^I \theta_x = 1 \quad (8)$$

θ_s may be approximated as $\beta\theta_P$ when the concentration of the adsorbed polymer segments is very small compared to that of the total adsorbed solvents. Thus, eq. (8) is also expressed as:

$$\beta\theta_P + \sum_{x=A}^I \theta_x = 1 \quad (9)$$

By using this relation, we can rewrite $K^*_{P-\overline{AB\dots I}}$ in the following form:

$$K^*_{P-\overline{AB\dots I}} = \frac{\theta_P (1 - M_P)^\beta}{M_P (1 - \beta\theta_P)^\beta} \quad (10)$$

A linear isotherm condition is satisfied for the adsorption of the sample P when both values of $(1 - M_P)^\beta$ and $(1 - \beta\theta_P)^\beta$ can be approximated as unity. Following our experience in adsorption TLC that polymer samples migrate without any detectable concentration dependency at a sufficiently lower sample load, we may assume the linear isotherm for the sample adsorption as a first approximation for such a system. $K^*_{P-\overline{AB\dots I}}$ is then written as:

$$K^*_{P-\overline{AB\dots I}} = \theta_P / M_P \quad (11)$$

The successive argument is based on this assumption of the linear isotherm adsorption. Combining eqs. (4) and (11), the ratio of the adsorption equilibrium constant is given in terms of the adsorption energies (see eqs. (5) and (6)) as:

$$K^*_{P-\overline{AB\dots I}}/K^*_{P,A} = 10^{E_P - E^*_{\overline{AB\dots I}}}/10^{E_P - \beta E_A} \\ = (\theta_A/M_A)^\beta \quad (12)$$

or

$$E^*_{\overline{AB\dots I}} = \beta[E_A - \log(\theta_A/M_A)] \\ = \beta E_{\overline{AB\dots I}} \quad (13)$$

where

$$E_{\overline{AB\dots I}} = E_A - \log(\theta_A/M_A) \quad (14)$$

$E_{\overline{AB\dots I}}$ corresponds to the value of the solvent strength when the sample molecule displaces one solvent molecule, i.e., $\beta=1$. Eq. (14) also corresponds to the formula derived recently by Snyder and Glajch⁹⁾.

The value of (θ_A/M_A) can be given in an appropriate form for respective cases of solvent mixtures. Binary mixture of A and B , for example, eq. (1-a) provides the following relation:

$$K_{B,A} = \frac{(1-\theta_A)M_A}{(1-M_A)\theta_A} \quad (15)$$

Here we took into account the following conditions:

$$M_A + M_B = 1, \quad \theta_A + \theta_B = 1$$

because both values of M_P and $\beta\theta_P$ are negligibly small compared to unity under usual experimental conditions. From eq. (15), we have

$$\left(\frac{\theta_A}{M_A}\right)_{Bi} = \frac{1}{M_A + (1-M_A)K_{B,A}} \quad (16)$$

Similarly, for the ternary mixture of A , B and C , the following relation is derived by using $K_{B,A}$, $K_{C,A}$ and $K_{C,B}$, provided that the sums of mole fractions of these solvents in the mobile and adsorbed phase are equal to one respectively:

$$\left(\frac{\theta_A}{M_A}\right)_{Ter} = \frac{1}{M_A + M_B K_{B,A} + M_C K_{C,A}} \quad (17)$$

Consequently, $E_{\overline{AB}}$, and $E_{\overline{ABC}}$ are given for the binary mixture (with eqs. (2), (14) and (16)) and for the ternary mixture (with eqs. (2), (14) and (17)), respectively as:

$$E_{\overline{AB}} = E_A + \log(M_B 10^{E_B - E_A} + 1 - M_B) \quad (18)$$

and

$$E_{\overline{ABC}} = E_A + \log(M_A + M_B 10^{E_B - E_A} + M_C 10^{E_C - E_A}) \quad (19)$$

Generally, the solvent strength of a multi-component mixture may be expressed for the displacement reaction of one-to-one molecule as:

$$E_{\overline{AB\dots I}} = E_A + \log(M_A + M_B 10^{E_B - E_A} + \dots + M_I 10^{E_I - E_A}) \quad (20)$$

Eq. (20) reduces to Snyder's equation given for the binary mixture of A and B . Here the solvent strength of the mixture per unit area of the standard activity surface ($\alpha=1$), ϵ^0_{AB} , is¹⁾

$$\varepsilon^0_{AB} = \varepsilon^0_A + (1/an_b) \log [M_B 10^{\alpha n_b (\varepsilon^0_B - \varepsilon^0_A)} + 1 - M_B] \quad (21)$$

where ε^0_A and ε^0_B are the solvent strength per unit area of pure solvent A and B , respectively, at the standard activity of adsorbent; n_b denotes the area of the adsorbed solvent A or B . Since the quantities of $an_b\varepsilon^0_B$ and $an_b\varepsilon^0_A$ in eq. (21) are supposed to correspond respectively to E_B and E_A in eq. (18), eq. (21) is the equivalent to eq. (18) and $an_b\varepsilon^0_{AB}$ should be equal to $E_{\overline{AB}}$.

From eq. (13), the approximated equilibrium constant for a polymer sample is rewritten as

$$\begin{aligned} \log K^*_{P-\overline{AB}\cdots I} &= E_P - \beta E_{\overline{AB}\cdots I} \\ &= \alpha(E^0_P - \beta E^0_{\overline{AB}\cdots I}) \end{aligned} \quad (22)$$

where E^0_P and $E^0_{\overline{AB}\cdots I}$ are the adsorption energies at the standard activity of adsorbent ($\alpha=1$). This relation may be understood intuitively by considering that the adsorption of one polymer molecule is equilibrated with β molecules of the solvent mixture having the solvent strength given as $E_{\overline{AB}\cdots I}$. Snyder has introduced the following relation for the adsorption of a sample having a molecular size larger than solvents¹⁾:

$$\log K_{th} = \alpha(S^0 - A_s\varepsilon^0) \quad (23)$$

where K_{th} is the equilibrium constant and corresponds to $K^*_{P-\overline{AB}\cdots I}$ for the multi-component mixture; S^0 is the adsorption energy of the sample and equivalent by definition to E^0_P in our notation while A_s denotes the area required for the adsorption of the sample molecule. Snyder proposed to use ε^0_{AB} defined by eq. (21) for a binary solvent mixture in the place of ε^0 in eq. (23). When both solvent A and B have the equal molecular size n_b , $n_b\varepsilon^0_{AB}$ and A_s/n_b yield E^0_{AB} and β , respectively. Consequently, eq. (23) becomes equivalent to eq. (22) derived as a first approximation, suggesting that the assumption of the equal molecular size for all molecules concerned is indispensable in Snyder's derivation of ε^0_{AB} . That is, eq. (23) is correct with respect to ε^0 only when ε^0_{AB} or $\varepsilon^0_{AB\cdots I}$ is derived on the basis of the one-to-one displacement reaction between a sample and solvent molecule.

Provided that $K^*_{P-\overline{AB}\cdots I}$ is given by (θ_P/M_P) , we may show the following relation as a result of summation of $\theta_P(M_x)^\beta/M_P$ given by eq. (4):

$$K^*_{P-\overline{AB}\cdots I} = \frac{(\theta_A)^\beta K^*_{P,A} + (\theta_B)^\beta K^*_{P,B} + \dots + (\theta_I)^\beta K^*_{P,I}}{(M_A)^\beta + (M_B)^\beta + \dots + (M_I)^\beta} \quad (24)$$

When β is unity, eq. (24) yields the following equation:

$$(K^*_{P-\overline{AB}\cdots I})_{\beta=1} = \sum_{x=A}^I \theta_x K_{P-x} \quad (25)$$

The result recovers the additivity of the equilibrium constants with the mole fractions of adsorbed solvents, which consists a basic assumption by Snyder.^{1,3)} But eq. (25) is valid only in the case of the sample displacing one solvent molecule.

DEPENDENCE OF $K^*_{P-\overline{AB}}$ ON SOLVENT COMPOSITION

We discuss here two relationships which have been presented to describe the dependence of an equilibrium constant (or a capacity factor) of a sample on a composition of binary mixtures.⁹⁻¹²⁾ According to Scott and Kucera,^{11,12)} the capacity factors in the binary mixture follow the relation:

$$\frac{1}{k_{AB}} = \frac{1}{k_A} + \left(\frac{1}{k_B} - \frac{1}{k_A} \right) M_B \quad (26)$$

where k_{AB} , k_A and k_B are the capacity factors obtained for the sample in the mixed solvent of A and B , pure solvent A and B , respectively. Narkiewicz *et al.*⁸⁾ have shown that eq. (26) can be derived from Snyder's equation (see eq. (25)) and the ratio of $(K^*_{P,A})_{\beta=1}$ to $(K^*_{P,B})_{\beta=1}$ given for the case of β being unity. These values k_{AB} , k_A and k_B are defined for retentions due only to the adsorption effect, corresponding to $(K^*_{P-\overline{AB}})_{\beta=1}$, $(K^*_{P,A})_{\beta=1}$ and $(K^*_{P,B})_{\beta=1}$, respectively. When the sample P displaces β molecules of the component solvent A and B , eq. (24) should be used in the place of eq. (25) if we follow Narkiewicz in his way of analysis. The ratio of $K^*_{P,A}$ to $K^*_{P,B}$ is given as:

$$K^*_{P,A}/K^*_{P,B} = (\theta_B M_A / \theta_A M_B)^\beta \quad (27)$$

$K^*_{P-\overline{AB}}$ for the binary mixture is calculated from eqs. (11) and (27) as (see Appendix):

$$\frac{1}{K^*_{P-\overline{AB}}} = \left\{ \left(\frac{1}{K^*_{P,A}} \right)^{1/\beta} + \left[\left(\frac{1}{K^*_{P,B}} \right)^{1/\beta} - \left(\frac{1}{K^*_{P,A}} \right)^{1/\beta} \right] M_B \right\}^\beta \quad (28)$$

Eq. (28) reduces to eq. (26) when β is equal to unity. When the solvent strength of B is much larger than that of A :

$$(K^*_{P,A})^{1/\beta} \gg (K^*_{P,B})^{1/\beta}$$

and if M_B is large enough to satisfy the following condition;

$$M_B (K^*_{P,A})^{1/\beta} \gg (K^*_{P,B})^{1/\beta}$$

then eq. (28) is approximated as:

$$\log (K^*_{P-\overline{AB}}) = \log (K^*_{P,B}) - \beta \log (M_B) \quad (29)$$

This equation is equivalent to that proposed by Soczewinski¹⁰⁾ who has also considered similar conditions as above in his derivation.

CONCLUSION

(1) Solvent strengths proposed by Snyder for binary¹⁾ and multi-component mixtures³⁾ are derived on the basis of competitive adsorption of the one-to-one molecular displacement reaction among all the components including the sample. Accordingly, it is proper to use the solvent strength in the place of ϵ^0 in eq. (23) when a sample molecule displaces a number of solvent molecules. However, in the case that the one-to-one displacement reaction is no longer assumed among the component solvents of the mixture, we cannot derive the solvent strength in an analytical form.

(2) For a polymer molecule having a high molecular weight, it depends largely on

the β value whether $K^*_{P-\overline{AB}\cdots I}$ is approximated by (θ_P/M_P) . In general, a part of the monomer units of a coiled polymer chain are adsorbed onto the adsorbent surface with some and the rest will form loops or bridges which extended into the mobile phase. Here it is known that the fraction of the adsorbed monomer units becomes small sharply with increasing the molecular weight.^{14,15} Thus, the linear isotherm condition could be fulfilled for the adsorption chromatography of polymer molecules. (3) Snyder's theory is incapable of providing Scott and Kucera's relation^{11,12}) when a sample molecule undergoes the displacement reaction with some number of solvent molecules, while Sozewinski's relation^{9,10}) can be derived under the specified conditions described above.

APPENDIX

The equilibrium constant for the binary mixture (see eq. (11)) is modified as:

$$\begin{aligned} K^*_{P-\overline{AB}} &= \frac{\theta_P (M_B)^\beta (\theta_B)^\beta}{M_P (\theta_P)^\beta (M_B)^\beta} \\ &= K^*_{P-B} (\theta_B)^\beta / (M_B)^\beta \end{aligned} \quad (i)$$

Provided that $(\theta_A + \theta_B)$ and $(M_A + M_B)$ can be approximated as unity, θ_B is calculated from eq. (27) as:

$$\theta_B = \frac{(K_{P,A})^{1/\beta} M_B}{(K_{P,B})^{1/\beta} (1 - M_B) + (K_{P,A})^{1/\beta} M_B} \quad (ii)$$

By introducing θ_B given in eq. (ii) into (i), we find eq. (28) in the text.

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