Solvent Concentration Dependence of Solute Distribution Coefficient

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A simple method for modeling the solvent concentration dependence of solute distribution coefficient is described. Ideal and modified distribution models are proposed based on the mechanism of multicomponent competitive adsorption and the theory of solvent association. The system cresol-methanol/water-β-CD-silica is tested using the models, which compared with other experimental results show that the ideal distribution model fails at higher water concentrations and that the modified model can describe well the observed solute distribution behavior over the entire concentration range. The relative impact of nonideal factors in the adsorbed phase and the solvent association in the mobile phase on the distribution dependence shows that the limitation of the ideal model at higher water concentrations results mainly from uneven saturation capacities of the solute and solvent components for the system studied here.

Introduction

The use of mixed solvents in liquid chromatography has attracted a good deal of attention, largely because it affords a convenient way to control solvent "strength," thereby allowing a degree of control of selectivity especially useful for "difficult" separation. Snyder (1968) was the first to propose the theoretical concepts underlying the use of mixed solvent in liquid chromatography, introducing the displacement model to describe the competitive character of component adsorption and to provide a theoretical basis for liquid chromatography with mixed mobile phases. Based on the displacement model, some solute distribution models incorporating the nonideal behavior in the mobile and stationary phases have been proposed (Soczewiński, 1969; Jaroninec et al., 1979; Snyder, 1983). The equilibrium solute distribution can also be described by the statistical thermodynamics (Boehm and Martire, 1980; Borówko, 1984). Although the theory incorporates many factors determining solute distribution, it is not very convenient for practical applications.

A chromatographic separation process is governed by the distribution of solutes between the stationary (adsorbed) and mobile phases. The equilibrium distribution is characterized by the distribution coefficient. In this study, a simple approach is described to model the solvent concentration dependence of the solute distribution coefficient. An ideal distribution model is proposed on the basis of the classical multicomponent Langmuir isotherm to approximately describe the solute distribution behavior between two phases. In order to include the effects of the deviation from ideality in both adsorbed and mobile phases on the solute distribution dependence, the ideal model is modified based on the consideration of the adsorption kinetics and the solvent association theory. The resulted models are tested and discussed in relation to an experimental liquid chromatographic study in which cresol isomers are distributed between a bonded β-cyclodextrin-silica stationary phase and a mobile phase consisting of methanol and water. Finally, the relative impact of the nonideality in the adsorbed phase and the solvent association in the mobile phase on modeling the solute distribution behavior is examined.

Ideal Distribution Model

In a liquid system there is always competition between solvent and solute for the adsorption sites. With a pure solvent this does not complicate the interpretation of chromatographic data since the distribution coefficient remains constant. However, with a mixed solvent the degree of competition varies with solvent concentration. To a faint approximation the competitive adsorption of solute and solvent can be described by the classical multicomponent Langmuir isotherm:

$$q_i = \frac{a_i c_i}{1 + \sum_{j=0}^{n} b_j c_j} \tag{1}$$

where q_i and c_i are the concentrations of component i in the adsorbed and mobile phases, respectively.

Let us consider a system in which there is one solute, designated by subscript 0, and n solvent components, designated by subscripts 1, 2. . .n, respectively. In the Henry region in which $b_0 c_0 \ll 1.0$, the representation of the solute adsorption equilibria can be simplified as follows:

$$q_0 = \frac{a_0}{1 + \sum_{j=1}^{n} b_j c_j} c_0 \tag{2}$$

Hence, the dependence of the solute equilibrium distribution coefficient or the pseudo-Henry constant can be described by:

$$K = \frac{a_0}{1 + \sum_{j=1}^{n} b_j c_j} \tag{3}$$

where c_j, in this study, is considered as the initial concentration of solvent component j.

Let us consider the ideal distribution model for binary solvent system. Considering the linear relation between the initial concentrations of solvent components 1 and 2 at a given solvent composition, Eq. 3 can be written as:

$$K = \frac{a'_0}{1 + b'_1 c_1} \tag{4}$$

which can be rearranged to the following linear form:

$$\frac{1}{K} = \frac{1}{a'_0} + \frac{b'_1}{a'_0} c_1 \tag{5}$$

Modification of the Ideal Distribution Model

Extension to the system with the nonideality induced in the adsorbed phase

For a multicomponent adsorption system dealing with the uneven saturation capacities of components, the multicomponent Langmuir isotherm is thermodynamically incorrect (Ruthven, 1984), and hence the ideal distribution model of Eq. 3 may not be used to represent the distribution dependence over a wider solvent concentration range.

It has been known that the well-known multicomponent Langmuir isotherm can be derived by the following kinetic equation:

$$\frac{\partial q_i}{\partial t} = k_{ai} c_i \left(q^{\infty} - \sum_{j=0}^{n} q_j \right) - k_{di} q_i \tag{6}$$

which is based on the assumption that the binding kinetics is of second order and the disassociation first order. This assumes that the adsorbed phase is ideal, that is, the interactions between the adsorbed molecules in the adsorbed phase are negligible and the components are of the same saturation capacities. This equation has been applied to affinity adsorption, ion exchange, and other adsorption systems (Hiester and Vermeulen, 1952; Chase, 1984; Arve and Liapis, 1987).

It is known that Eq. 6, which stems from the rate equation in terms of the density of the component deposited on the adsorbent surface (Whitham, 1974), holds only when monolayer adsorption occurs on homogeneous surface and the adsorbed phase behaves ideally or only when the adsorbate densities on solid surface are strictly additive in multicomponent system. For the nonideal adsorbed phase induced by the different molecular sizes of adsorbed components and the lateral adsorbate-adsorbate interaction in the adsorbed phase, the densities of adsorbates become of nonadditivity. Based on the assumption of the monolayer adsorption, the mixed density, ρ_{mi}, of adsorbates corresponding to the adsorption sites for component i may be considered as a linear function of the densities of each adsorbate, and hence Eq. 6 can be modified as (Lin et al., 1989; Gu et al., 1991):

$$\frac{\partial q_i}{\partial t} = k_{ai} c_i \left(q_i^{\infty} - \sum_{j=0}^{n} \alpha_{ij} q_j \right) - k_{di} q_i \tag{7}$$

where k_{ai} and k_{di} are constants of adsorption and desorption rates for component i, respectively. The coefficient α_{ij}, which accounts for the influence of the deviation from ideality due to mixing in the adsorbed phase on the adsorption rate of each component, depends on the molecular sizes of the adsorbed components and the interaction strength between these molecules.

When the adsorption equilibrium is reached, Eq. 7 can be rearranged and expressed in the following matrix form:

$$[q] = ([B] + [I])^{-1} [A] \tag{8}$$

where

$[I]$ is a unit matrix, $A_i = k_{ai} c_i q_i^{\infty} / k_{di}$ and $B_{ij} = k_{ai} c_i \alpha_{ij} / k_{di}$

Equation 8 is a general representation for multicomponent equilibria incorporating the nonideal factors in the adsorbed phase. Note that if $\alpha_{ij} = 1$ and $q_i^{\infty} = \text{constant}$, Eq. 8 becomes identical to the classical multicomponent Langmuir isotherm.

Based on the general multicomponent equilibria model, let us consider the solvent concentration dependence of the distribution coefficient for a system in which there is one solute, designated by subscript 0, and two solvent components, designated by subscripts 1 and 2, respectively. For simplicity, we assume that the influence of the interaction of components in the adsorbed phase on the adsorption rate of each component is attributed to that of solute component interaction on the adsorption rate of the solvent components, and that the component saturation capacities differ from each other, that is:

$$\begin{gathered} \alpha_{ij} \neq 1 \quad (i = 1,2 \quad j = 0) \\ \alpha_{ij} = 1 \quad (\text{else}) \\ q_i^{\infty} \neq \text{constant} \quad (i = 1,2) \end{gathered} \tag{9}$$

then Eq. 8 becomes:

$$q_0=\frac{a_0c_0+a_1c_0c_1+a_2c_0c_2}{1+b_0c_0+b_1c_1+b_2c_2+b_{01}c_0c_1+b_{02}c_0c_2} \tag{10}$$

where

$a_0=b_0q_0^{\infty}$, $a_1=b_0b_1(q_0^{\infty}-q_1^{\infty})$, $a_2=b_0b_2(q_0^{\infty}-q_2^{\infty})$,

$b_0=k_{a0}/k_{d0}$, $b_1=k_{a1}/k_{d1}$, $b_2=k_{a2}/k_{d2}$,

$b_{01}=b_0b_1(1-\alpha_{10})$, $b_{02}=b_0b_2(1-\alpha_{20})$

Considering that b_0c_0, $b_{01}c_0c_1$ and $b_{02}c_0c_2 \ll 1$ in the Henry region, so the solute distribution model accounting for the nonideality in the adsorbed phase for the binary solvent system can be expressed as:

$$K=\frac{a_0+a_1c_1+a_2c_2}{1+b_1c_1+b_2c_2} \tag{11}$$

It is obvious that if $q_0^{\infty}=q_1^{\infty}=q_2^{\infty}$, Eq. 11 becomes identical to the ideal distribution model.

For a binary solvent system Eq. 11 can also be simplified according to the relation between the initial concentrations c_1 and c_2:

$$K=\frac{a'_0+a'_1c_1}{1+b'_1c_1} \tag{12}$$

Similarly, the distribution model for ternary solvent system can be expressed by:

$$K=\frac{a_0+a_1c_1+a_2c_2+a_3c_3}{1+b_1c_1+b_2c_2+b_3c_3} \tag{13}$$

where

$a_0=b_0q_0^{\infty}$, $a_1=b_0b_1(q_0^{\infty}-q_1^{\infty})$, $a_2=b_0b_2(q_0^{\infty}-q_2^{\infty})$,

$a_3=b_0b_3(q_0^{\infty}-q_3^{\infty})$, $b_1=k_{a1}/k_{d1}$, $b_2=k_{a2}/k_{d2}$,

$b_3=k_{a3}/k_{d3}$

Further extension to solvent association system

If there is an association between the components of the mobile phase, the distribution of solute between the stationary and mobile phases will be influenced. We consider here a binary solvent mixture of A_1 and A_2. The association of species A_1 and A_2 proceeds by the following equilibrium reaction:

$$nA_1+mA_2 \rightleftharpoons PA_3 \tag{14}$$

The solvent association equilibrium constant, k, can be defined in terms of mole fraction, concentration, or volume fraction. In our study, the association equilibrium constant is based on the molar concentration and defined by the relation:

$$k=\frac{[c_3]^p}{[c_1]^n[c_2]^m} \tag{15}$$

where $[c_1]$, $[c_2]$ and $[c_3]$ are the molar concentrations of the components A_1, A_2 and A_3 in the mixed mobile phase, respectively, and can be expressed in terms of the initial concentrations, c_1 and c_2, of the solvent components:

$$[c_1]=c_1-\frac{n}{p}[c_3] \tag{16}$$

$$[c_2]=c_2-\frac{m}{p}[c_3] \tag{17}$$

Through Eqs. 15, 16 and 17, an equation relating the complex concentration to initial solvent concentrations is obtained:

$$[c_3]^p-k\left(c_1-\frac{n}{p}[c_3]\right)^n\left(c_2-\frac{m}{p}[c_3]\right)^m=0 \tag{18}$$

Now, we consider the simple situation $m=n=p=1$. Equation 18 is then reduced to:

$$[c_3]^2-\left(c_1+c_2+\frac{1}{k}\right)[c_3]+c_1c_2=0 \tag{19}$$

Considering that if c_1 or $c_2=0$, then $[c_3]=0$, we obtain:

$$[c_3]=\frac{1}{2}\left[c_1+c_2+\frac{1}{k}-\left(c_1+c_2+\frac{1}{k}\right)\sqrt{1-\frac{4c_1c_2}{\left(c_1+c_2+\frac{1}{k}\right)^2}}\right] \tag{20}$$

Hence, in a binary associated solvent system as described above, the modified solute distribution model expressed by Eq. 13 can be given by:

$$K=\frac{a_0+a_1[c_1]+a_2[c_2]+a_3[c_3]}{1+b_1[c_1]+b_2[c_2]+b_3[c_3]} \tag{21}$$

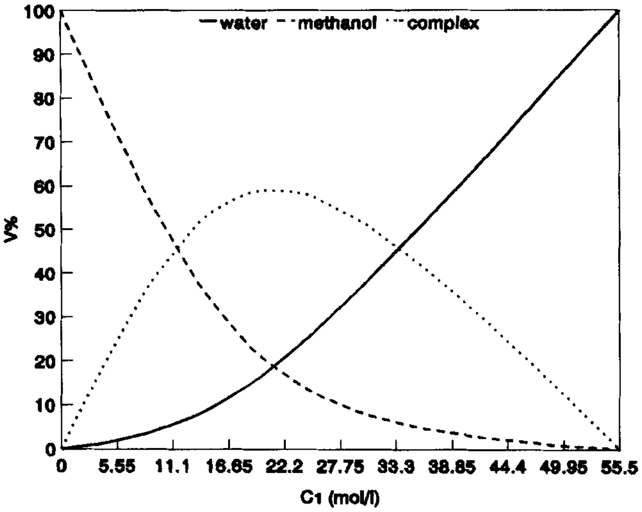

Figure 1. Volume fraction of water, methanol and methanol-water complex against initial concentration of water in the solvent mixture.

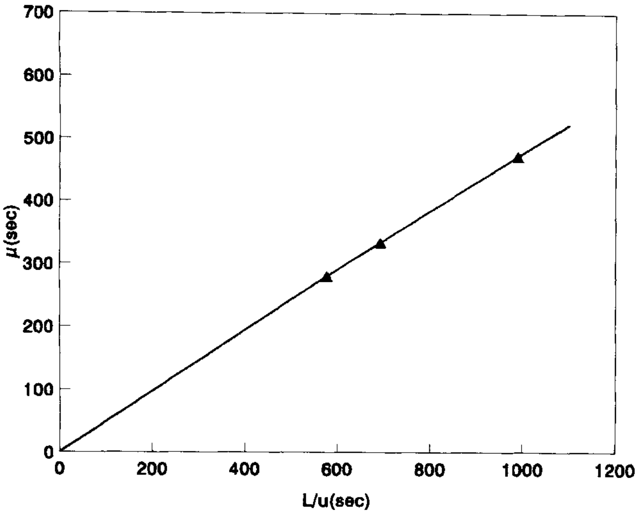

Figure 2. **μ vs. L/u for dextran 2,000,000.**

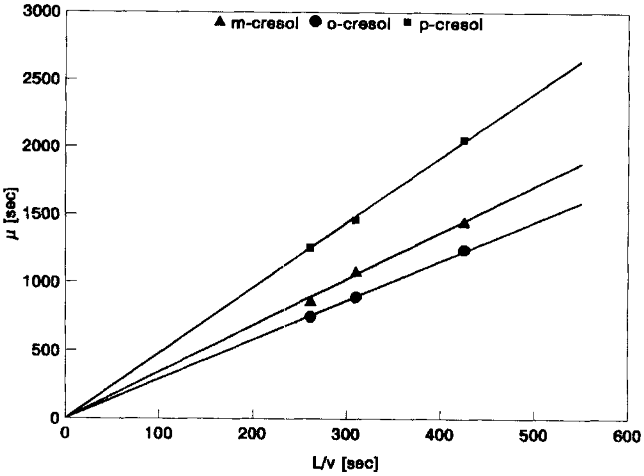

Figure 3. **μ vs. L/v for cresols at initial water concentration $c_1 = 44.4$ mol/L in the solvent mixture.**

Substitution of Eqs. 16 and 17 with $m = n = p = 1$ and $[c_3]$ given by Eq. 20 into Eq. 21 gives an expression relating the solute distribution coefficient to the initial solvent concentrations in a binary solvent system with association:

$$K = \frac{a'_0 + a'_1 c_1 + a'_2 c_2 + a'_3 [c_3]}{1 + b'_1 c_1 + b'_2 c_2 + b'_3 [c_3]} \tag{22}$$

For a binary solvent system, Eq. 22 can be reduced to:

$$K = \frac{a''_0 + a''_1 c_1 + a''_2 [c_3]}{1 + b''_1 c_1 + b''_2 [c_3]} \tag{23}$$

where $[c_3]$ is given by Eq. 20.

Application of the Distribution Model

Experimental model

Experiments to determine distribution coefficients were performed by injecting a small pulse of cresol into the mobile phase flowing through a packed column. The mobile phase used was a mixture of HPLC (high-performance liquid chromatography) grade methanol and deionized water in various proportions. A standard Pharmacia jacketed column, 0.65-cm ID and 30-cm height, was used in the experiments. 20 μm bonded β-CD-silica (Advanced Separation Technologies Inc., USA) was used as adsorbent in the column. The sample injection was performed with a Rheodyne Type 9125 injection valve fitted with a 10-μL sample loop. The response was detected by a Pharmacia Monitor UV-M detector. The linearity of the adsorption system was examined by repeating the experiments in which the concentration of the injection sample was varied. The column voidage was determined by injecting a pulse of dextran 2,000,000 into the mixed mobile phase.

Results and Discussion

Reportedly, there is a very strong association between methanol and water molecules as a result of hydrogen bonding so a mixture of methanol and water can actually be regarded as a ternary mixture consisting of water, methanol and the methanol-water complex. The determination of the ternary composition of the mixture of methanol and water has been carried

Table 1. Regressed Parameters of Distribution Equations for Cresols

Solute	Ideal Model (Eq. 5)		Modified Model (Eq. 23)		Modified Model (Eq. 12)	
m-cresol	a'_0	0.378	a''_0	0.378	a'_0	0.378
	b'_1	−0.0201	a''_1	0.0099	a'_1	0.0067
			a''_2	−0.0156	b'_1	−0.0182
			b''_1	−0.0177		
			b''_2	−0.0021		
o-cresol	a'_0	0.378	a''_0	0.378	a'_0	0.378
	b'_1	−0.0186	a''_1	0.0002	a'_1	0.0027
			a''_2	−0.0091	b'_1	−0.0180
			b''_1	−0.0178		
			b''_2	−0.0146		
p-cresol	a_0	0.388	a''_0	0.383	a'_0	0.380
	b'_1	−0.0214	a''_1	0.0125	a'_1	0.0111
			a''_2	−0.0141	b'_1	−0.0185
			b''_1	−0.0182		
			b''_2	−0.0040		

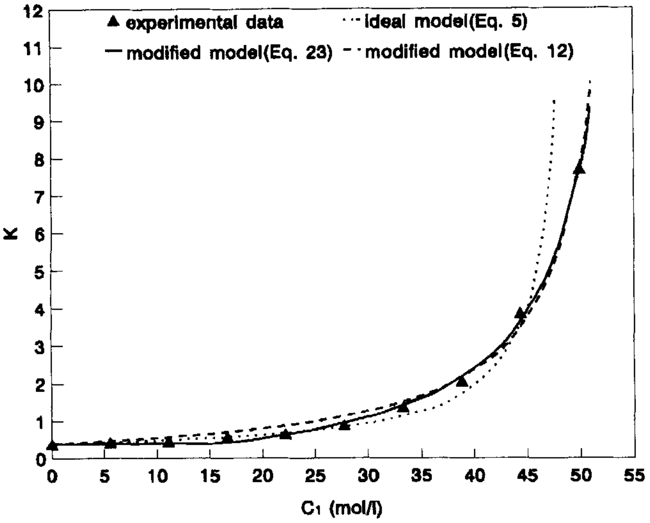

Figure 4. Calculated vs. experimental curves showing the dependence of distribution coefficient for *m*-cresol on solvent concentration.

out (Katz et al., 1986), and the composition plot is summarized in Figure 1. The experimental results demonstrate that the association between methanol and water proceeds in a reaction that 1 mol methanol and 1 mol water creates 1 mol of the methanol-water complex, and that the association equilibrium constant for the system is equal to 222.

The distribution coefficient K and the voidage of the packed column ϵ can be obtained from the first moment analysis of response peaks of adsorbates according to the following equation (Ruthven, 1984):

$$\mu=\frac{\int_0^\infty ctdt}{\int_0^\infty cdt}=\frac{L}{v}\left(1+\frac{1-\epsilon}{\epsilon}K\right) \tag{24}$$

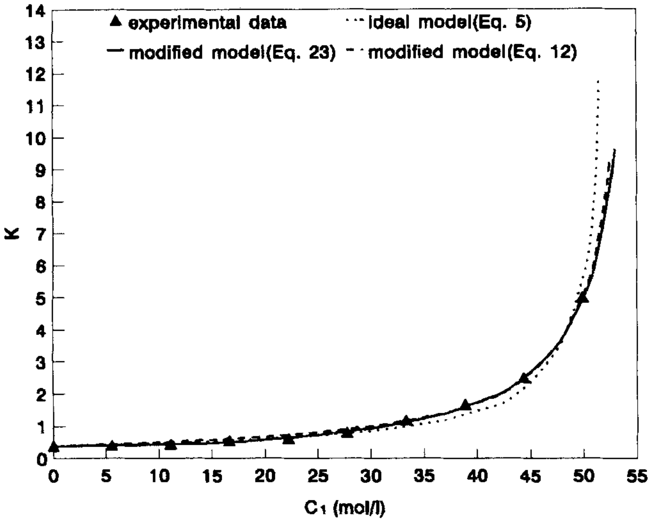

Figure 5. Calculated vs. experimental curves showing the dependence of distribution coefficient for *o*-cresol on solvent concentration.

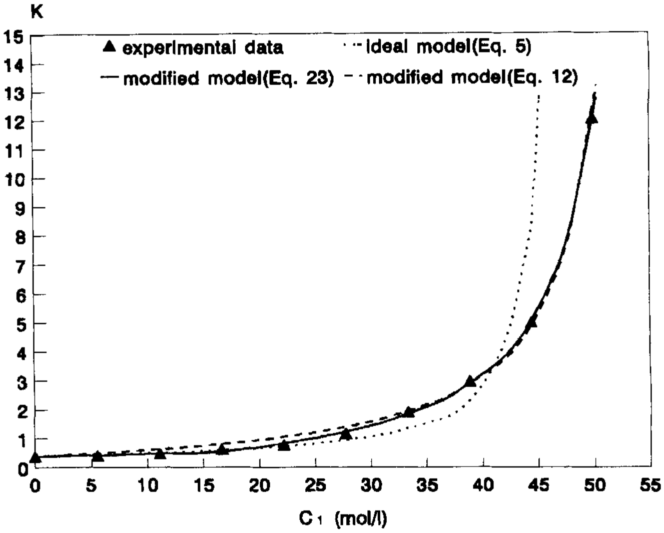

Figure 6. Calculated vs. experimental curves showing the dependence of distribution coefficient for *p*-cresol on solvent concentration.

The dextran 2,000,000 molecule is so large that it is effectively excluded from the pores of the adsorbent. For this species, Eq. 24 reduces to:

$$\mu=\frac{L}{u}\epsilon \tag{25}$$

The plot of μ against L/u for dextran 2,000,000 according to Eq. 25 is shown in Figure 2. The slope of the straight line yields $\epsilon=0.57$. Figure 3 shows a typical plot of μ against L/v for cresols at water concentration $c_1=44.4$ mol/L in the solvent mixture according to Eq. 24. The slopes of the linear plots of μ against L/v corresponding to different solvent concentrations yield a series of distribution coefficients.

The formulated ideal and modified models of Eqs. 5 and 23 are used in an attempt to match the experimental concentration dependence of the distribution coefficient for the present system. The parameters a_0' and a_0'' in the ideal and modified models are obtained from the experiments of solute distribution between two phases with pure methanol as mobile phase. The parameter b_1' in the ideal model is readily evaluated by fitting the experimental data to Eq. 5 using linear least-square method. To estimate the parameters a_1'', a_2'', b_1'' and b_2'' in the modified model, a standard nonlinear regression program of RNLIN from STAT/LIBRAY, IMSL, Inc. is used. The objective function is $\Sigma_{i=1}^{n}[K_i-f(c_i, \mathfrak{D})]^2$ where K_i is the value of

Table 2. Comparison of Deviations for Modified Models of Eqs. 23 and 12

Distribution Models	Solute	Dev. (%)
Modified Model (Eq. 23)	*m*-cresol	6.46
	o-cresol	2.87
	p-cresol	3.32
Modified Model (Eq. 12)	*m*-cresol	15.04
	o-cresol	7.34
	p-cresol	14.48

of distribution coefficient obtained experimentally, $f(c_i, \mathfrak{D})$ is the expression of the modified distribution model and $\mathfrak{D}$ is the vector of regression parameters. We hope further experiments of solute distribution with pure water as mobile phase can be done to obtain the parameter b_1'' so as to reduce the adjustable parameters. However, because of the solubility limitation of cresol in water or the relatively large distribution coefficient, no experimental data with pure water as mobile phase can be accurately obtained. This phenomenon suggests us the initial value of b_1'' may be approximately set to $-1/55.5$ by assuming $1 + b_1''c_1 \to 0$ (where $c_1 = 55.5$ mol/L). The values of the obtained parameters in the ideal and modified models, from which the distribution curves are calculated using Eqs. 5 and 23, are summarized in Table 1.

Comparisons of the model results with the experimental data for each cresol are shown in Figures 4-6. It is seen that the ideal model permits a good agreement with the experimental data at lower water concentrations; as expected, however, the model results appear to scatter at higher water concentrations. The disagreement arises largely from the inadequacy of the ideal distribution model, which can seldom provide an adequate representation for solute distribution dependence over the entire concentration range due to the assumption that both the adsorbed and mobile phases are ideal. In order to obtain a good agreement between the model and experimental results some deviation from ideality must be accounted for. Obviously, as shown in Figures 4-6, a significant improvement of the performance of the modified model is obtained and the average relative deviations between the experimental data and the calculated values by the modified model of Eq. 23 for each cresol are less than 7%, as tabulated in Table 2, reflecting the validity of the modified distribution model of Eq. 23 and the reasonability of the assumptions made in the model.

In order to examine the relative impacts of the nonideality in the adsorbed phase and the solvent association in the mobile phase on the solvent concentration dependence of distribution coefficient, the modified model without the effect of association included, that is, Eq. 12, is applied. The obtaining of the value of a_0' and the setting of the initial value of b_0' are made in the same way as described above. The fitting of the experimental data with Eq. 12 is also performed by the nonlinear regression analysis. The obtained parameters are listed in Table 1. Figures 4-6 also show the dependence curves for cresols without considering solvent association in comparison with that including association. Interestingly, the distribution curve could also be fitted well by the nonassociation included model, especially in the range of $0 < c_1 < 11.1$ mol/L and 33.3 mol/L $< c_1 <$ 55.5 mol/L. The good agreement may be explained by the experimental observation shown in Figure 1. Note that the water concentration, c_1, or methanol concentration, c_2, is approximately equal to zero in the range of $0 < c_1 < 11.1$ mol/L or the range of 33.3 mol/L $< c_1 <$ 55.5 mol/L. In another words, in the two ranges $[c_3]$ can be approximately expressed as a linear function of c_1 or c_2 in terms of Eq. 20, and hence the nonassociation included model of Eq. 12 is of the almost identical form to the association included model of Eq. 23. When 11.1 mol/L $< c_1 <$ 33.3 mol/L, $[c_3]$ is no longer a linear function of c_1 or c_2 due to the existence of the ternary solvent mixture of methanol, water, and methanol-water complex; hence, the shape of the distribution curve should be affected by the solvent association. However, as can be observed from Figures 4-6, the included nonassociation model, in the range of 11.1 mol/L $< c_1 <$ 33.3 mol/L, shows only a slightly smaller difference in modeling the distribution dependence compared to the modified model including solvent association. The comparison of the average relative deviations between experimental data and the calculated values by Eqs. 23 and 12 for each cresol are tabulated in Table 2. The very small effect of solvent association on the shape of distribution curves indicated that the deviation from ideality is resulted mainly from the nonideality in the adsorbed phase. It follows from Eqs. 11 and 13 that the uneven saturation capacities of the solute and solvent components are the factors which make the ideal model fail. For a given mixed solvent, the larger the saturation capacity of solute, the larger the deviation from the ideality for the distribution model.

Much attention has been attracted to study the systems with uneven saturation capacities (Ruthven, 1984; Huang and Guichon, 1989; Fallah et al., 1990; Gu et al., 1991). It has been known that the uneven saturation capacities can be caused by physical and chemical reasons such as size exclusion and adsorption mechanism. Some reasons for the uneven saturation capacities of components in the reversed phase system have been analyzed and reviewed by Cox and Snyder (1989). In the studied system, the occurrence of uneven saturation capacities may be attributed to the difference in the adsorption mechanism for solute and solvent components. The occupancy by the guest molecules of solute (cresol) probably occur within the hydrophobic interior and at the exterior surface of the cyclodextrin cavity; however, only the cavity exterior surface is active and usable for the solvent molecules, as the molecular sizes of solvent molecules (water and methanol) are too small compared to the dimensions of β-cyclodextrin cavity to bind to the cavity interior (Rohrbach, 1977). This is why we assume in the above theory section that the saturation capacities for solute molecules are larger than that for solvent molecules. We note from Figures 4-6 that the ideal model shows a larger deviation for *p*-cresol than for *m*- or *o*-cresol, showing *p*-cresol is of the larger saturation capacity than *m*- or *o*-cresol. For this case the larger saturation capacity for *p*-cresol may be caused by the smaller surface area required by an adsorbed molecule in the adsorbed phase for *p*-cresol than for *m*- or *o*-cresol.

Conclusion

A simple approach to modeling the solvent concentration dependence of solute distribution coefficient is presented. The ideal model, based on the classical multicomponent Langmuir isotherm, is modified according to the adsorption kinetics and the solvent association theory. Comparison of the ideal and modified models with the experimental results shows that the modified model obtains a significant improvement on the ideal model for the description of the distribution dependence. The results show that the deviation of the distribution dependence from ideal model is mainly from the uneven saturation capacities of components rather than from the solvent association in the mixed mobile phase.

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Notation

a_i, a'_i, a''_i = constants in multicomponent isotherm and distribution model
b_i, b'_i, b''_i, b_{ij} = constants in multicomponent isotherm and distribution model
c_i, c_j = concentration of component i or j in the mobile phase, mol^{-1}
$[c_j]$ = association equilibrium concentration of solvent j, mol^{-1}
k_{ai} = constants of adsorption rate for component i, $\mathrm{mol}^{-1}\cdot\mathrm{s}^{-1}$
k_{di} = constants of desorption rate for component i, s^{-1}
K = solute distribution coefficient or pseudo Henry constant
L = packed length of column, cm
q_i, q_j = concentration of component i or j in the adsorbed phase, mol^{-1}
q_i^{∞} = adsorption saturation concentration of component i in the adsorbed phase, mol^{-1}
t = time, s
u = superficial fluid velocity, $\mathrm{cm}\cdot\mathrm{s}^{-1}$
v = interstitial fluid velocity, $\mathrm{cm}\cdot\mathrm{s}^{-1}$

Greek letters

α_{ij} = coefficients for modified distribution model
ϵ = voidage of the packed column
μ = first moment of response peak, s

Subscripts

0 = cresol
1 = water
2 = methanol

Superscript

∞ = adsorption saturation

Literature Cited

Arve, B. H., and A. I. Liapis, "Modelling and Analysis of Elution Stage of Biospecific Adsorption in Fixed Beds," *Biotech. Bioeng.*, **30**, 638 (1987).

Boehm, R. E., and D. E. Martire, "A Unified Theory of Retention and Selectivity in Liquid Chromatography: 1. Liquid-Solid (Adsorption) Chromatography," *J. Phys. Chem.*, **84**, 3620 (1980).

Borówko, M., "Liquid Adsorption Chromatography with Multicomponent Mobile Phase," *J. Colloid Interf. Sci.*, **102**, 519 (1984).

Chase, H. A., "Prediction of the Performance of Preparative Affinity Chromatography," *J. Chromatog.*, **297**, 179 (1984).

Cox, G. B., and L. R. Snyder, "Preparative High Performance Liquid Chromatography Under Isocratic Conditions: III. The Consequences of Two Adjacent Bands Having Unequal Column Capacities," *J. Chromatog.*, **483**, 95 (1989).

Fallah, M. Z. E., S. Golshan-Shirazi, and G. Guichon, "Theoretical Study of the Effect of a Difference in Column Saturation Capacities for the Two-Components of a Binary Mixture on Their Elution Band Profiles and Separation in Nonlinear Chromatography," *J. Chromatog.*, **511**, 1 (1990).

Gu, T., G. J. Tsai, and G. T. Tsao, "Multicomponent Adsorption and Chromatographic with Uneven Saturation Capacities," *AIChE J.*, 1333 (1991).

Hiester, N., and T. Vermeulen, "Saturation Performance of Ion-exchange and Adsorption Columns," *Chem. Eng. Prog.*, **48**, 505 (1952).

Huang, J. X., and G. Guichon, "Competitive Adsorption Behaviour in HPLC: cis- and trans-Androsterone on Silica," *J. Colloid Interf. Sci.*, **128**, 577 (1989).

Jaroninec, M., B. Klepacka, and J. Narkiewicz, "Liquid Adsorption Chromatography with a Two-component Mobile Phase: I. Effects of Non-ideality of the Mobile Phase," *J. Chromatog.*, **170**, 299 (1979).

Jaroninec, M., J. K. Różylo, and W. Golkiewicz, "Liquid Adsorption Chromatography with a Two-component Mobile Phase II. Effects of Adsorbent Heterogeneity," *J. Chromatog.*, **178**, 27 (1979).

Katz, E. D., K. Ogan, and R. P. W. Scott, "Distribution of a Solute Between Two Phases: The Basic Theory and its Application to the Prediction of Chromatographic Retention," *J. Chromatog.*, **352**, 67 (1986).

Lin, B., Z. Ma, S. G. Shirazi, and G. Guiochon, "Study of the Representation of Competitive Isotherms and of the Intersection between Adsorption Isotherms," *J. Chromatog.*, **475**, 1 (1989).

Rohrbach, R. P., L. J. Rodriguez, and E. M. Eyring, "An Equilibrium and Kinetic Investigation of Salt-Cycloamylose Complexes," *J. Phys. Chem.*, **81**, 944 (1977).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Snyder, L. R., *Principles of Adsorption Chromatography*, Marcel Dekker, New York (1968).

Snyder, L. R., *High Performance Liquid Chromatography*, Vol. 3, Academic Press, New York (1983).

Soczewiński, E., "Solvent Composition Effects in Thin-Layer Chromatography Systems of Type Silica Gel-Electron Donor Solvent," *Anal. Chem.*, **41**, 179 (1969).

Whitham, G. B., *Linear and Non-linear Waves*, Wiley, New York (1974).

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