

A Modified Adsorption Model for Retention of Nonpolar Solutes in Reversed Phase Liquid Chromatography

Won Jo Cheong

Department of Chemistry, Inha University, Incheon 402-751

Received July 5, 1993

The adsorption model in reversed phase liquid chromatography has been critically examined. It has been found that use of the Everett type surface activity coefficient for the solute in the stationary phase is not useful to study the retention characteristics of a nonpolar solute. We suggest a modified model. In this model it is assumed that the displaced modifier molecules from the surface monolayer do not transfer into the bulk mobile phase but stick to the nonpolar solute which has displaced them. In addition, we prefer to use an apparent stationary phase activity coefficient of the solute instead of the Everett type activity coefficient. This modified adsorption model well explains the mobile and stationary phase effects on the solute retention upon variation of mobile phase composition.

Introduction

A quantitative theory of the adsorption mechanism of solute retention in reversed phase liquid chromatography has been theoretically established in a series of studies¹⁻⁴. A peculiar feature of this model is the use of the surface activity coefficient developed by Everett^{5,6} for the solute in the stationary phase. According to their work, the major factors on which the solute retention depends are the solute activity coefficient in the mobile phase and the interfacial surface tensions. The Everett type activity coefficient is often assumed to be an insignificant contribution to variation of solute retention. The stationary phase effect was considered by incorporation of the interfacial surface tension between the ligand and solute and that between the ligand and the mobile phase. The mobile phase effect was also considered *via* the solute activity coefficient in the mobile phase¹⁻⁴. Nevertheless the above studies focussed on stationary phase effects. The mobile and stationary phase effects have not been compared simultaneously. In order to consider the mobile phase effect, the solute activity coefficients in the mobile phase must be known. Recently, there appeared in the literature such data for a homologous series of alkylbenzenes in mixtures of methanol, acetonitrile, isopropanol, and tetrahydrofuran with water⁷. In this study we will examine a modification of the adsorption model to describe more reasonably the retention characteristics of nonpolar solutes. The purpose of this study is to examine the mobile and stationary phase effects on solute retention of alkylbenzenes in reversed phase liquid chromatography using the conventional and modified adsorption models comparatively.

Theory

In discussion below superscript *s* denotes the surface interface (stationary phase), and *m*, the mobile phase, and subscript 1, the solute, 2, the solvent matrix (phase), *w*, water and *o*, the organic modifier. The capacity factor can be expressed as follows:

$$k' = n^s_1/n^m_1 = (\gamma^m_1/\gamma^s_1) (n^s_2/n^m_2) \quad (1)$$

where n^s_1 , n^m_1 are the number of moles of the solute in

the stationary and mobile phase, γ^m_1 , γ^s_1 , the Raoult's law based activity coefficients of the solute in the mobile and stationary phase, and n^s_2 , n^m_2 are the number of moles of the stationary and mobile phase respectively.

The Adsorption Model. In the conventional adsorption model¹⁻⁴, it is assumed that the solute is distributed between the bulk mobile phase and the interfacial phase composed of a monolayer of adsorbed mobile phase on the hydrophobic ligand surface. The unique definition by Everett^{13,14} for the solute activity coefficient in the surface interface was used. The effective surface phase activity coefficient (γ^s_1) that is formally consistent with Eq. (1) is related to the Everett type activity coefficient (γ^{s*}_1) as follows^{13,14}:

$$\gamma^s_1 = \gamma^{s*}_1 - A_1 N(RT)^{-1} (\sigma_{sm} - \sigma_{s1}) \quad (2)$$

where A_1 is the surface contact area of the solute with the ligand, N , Avogadro number, σ_{sm} , the interfacial surface tension between the surface and the bulk mobile phase, and σ_{s1} , the interfacial surface tension between the surface and pure bulk solute.

The interfacial surface tension can be rewritten in terms of the bulk surface tension using Fowke's approximation⁸.

$$\sigma_{sm} = \sigma_s + \sigma_m - 2(\sigma_s \sigma^d_m)^{1/2} \quad (3)$$

$$\sigma_{s1} = \sigma_s + \sigma_1 - 2(\sigma_s \sigma_1)^{1/2} \quad (4)$$

σ_s is the bulk surface tension of the hydrophobic ligand, σ_m , the bulk surface tension of the mobile phase, σ^d_m , the dispersion portion of the bulk surface tension of the mobile phase, and σ_1 , the surface tension of the pure solute. The dispersion part of the surface tension of a polar solvent is close to the surface tension of hydrocarbons^{8,9}. Thus we make a further approximation that:

$$\sigma^d_m = \sigma_1 \quad (5)$$

Combining Eq. (3), (4), and (5) Eq. (6) results.

$$\sigma_{sm} - \sigma_{s1} = \sigma_m - \sigma_1 \quad (6)$$

From Eq. (2) and (6), we obtain:

$$\gamma^s_1 = \gamma^{s*}_1 - A_1 N(RT)^{-1} (\sigma_m - \sigma_1) \quad (7)$$

By application of the definition of the capacity factor and

use of the Everett type surface activity coefficient, an expression of $\ln k'$ is obtained as follows:

$$\ln k' = \ln \gamma_{m_1}^m - \ln \gamma_{s_1}^s + A_1 N (RT)^{-1} (\sigma_m - \sigma_1) + \ln (n_o^s) - \ln [V_m d_m \{w_o/M_o + (1-w_o)/M_w\}] \quad (8)$$

M_o is the molecular weight of the organic modifier, M_w , the molecular weight of water, w_o , the weight fraction of organic modifier in the mobile phase, d_m , the density of the mobile phase, and V_m , the void volume of the column. The number of moles of the monolayer (n_o^s) is regarded as the number of moles of the stationary phase (n_s^s in Eq. (1)). The last term of Eq. (8) is the number of moles of the mobile phase. The number of moles of the organic modifier in the monolayer is calculated as follows:

$$n_o^s = A_{sp} W_s / A_o N \quad (9)$$

where A_{sp} is the specific surface area of the stationary phase, W_s , the weight of stationary phase in the column, and A_o , the molecular contact area of the organic modifier with the ligand.

The physical meaning of an Everett type surface activity coefficient is not clear. The incorporation of an Everett type activity coefficient into the expression of capacity factor results in the separation of the surface interaction terms from the other terms. The Everett type surface activity coefficient of the solute is often regarded as an invariable term independent of mobile phase composition²⁻⁴.

It should be noted that in the conventional adsorption model it is not clear whether the displaced modifier molecules of the monolayer by a solute move into the bulk mobile phase or remain near the solute.

The Modified Adsorption Model. We modified the adsorption model by assuming that the displaced modifier molecules do not transfer into the bulk mobile phase but remain next to the solute which has replaced them. The observation by Scott and Kucera¹⁰ supports this assumption.

They equilibrated a column with an eluent and passed a large amount of solute through the column by eluting a solution of the solute in the eluent. While they observed a peak of the displaced modifier in normal phase liquid chromatography, they could not observe such a peak in reversed phase liquid chromatography. It implies that in reversed phase liquid chromatography the displaced modifier molecules remain near the surface.

In addition we abandoned the Everett type surface activity coefficient. An apparent stationary phase activity coefficient ($\gamma_{s_1}^s$) that is formally consistent with Eq. (1) can be as well defined for a solute which is adsorbed on a surface. In such a case, $RT \ln \gamma_{s_1}^s$ is equivalent to the partial molar excess free energy of transfer of the solute from its pure state onto a surface. The expression for $\ln k'$ is then obtained as follows:

$$\ln k' = \ln \gamma_{m_1}^m - \ln \gamma_{s_1}^s + \ln (n_o^s) - \ln [V_m d_m \{w_o/M_o + (1-w_o)/M_w\}] \quad (10)$$

A nonpolar solute adsorbed on the hydrophobic surface are favorably solvated with modifier molecules than water. It implies that the effective surface activity coefficient of a nonpolar solute is roughly invariable regardless of mobile phase composition. This will be further discussed later.

Table 1. Column Characteristics

Column characteristic	Lichrosorb RP-C ₁₈ ^f	Zorbax ODS ^g	Develosil ODS-5 ^h	Hypersil ODS ⁱ
V^a	3.77	2.492	2.492	1.661
d_s^b	0.5 ^f	0.783	0.8	0.8
V_m^c	2.26 ^k	1.414	1.495 ^h	1.150
W_s^d	1.885	1.95	1.99	1.329
A_{sp}^e	150 ^f	150 ^f	150 ^f	150 ^f

^a Column volume (mL); calculated using the column dimensions.

^b Packing density of stationary phase (g/mL). ^c Column void volume (mL). ^d Weight of stationary phase (g). ^e Specific surface area of silica substrate. ^f Used in Schoenmaker's work for the methanol/water system (13). ^g Used in Martire's work for the methanol/water system (14). ^h Used in Hanai's work for acetonitrile/water system (15). ⁱ Used in Cheong and Carr's work for the isopropanol/water and tetrahydrofuran/water system (7). ^j Based on reference (19). ^k Calculated assuming the total porosity is 0.6. ^l Based on references (18).

The Displacement Model. Another possible model is one where it is assumed that the displaced organic modifier molecules which were a part of the surface adsorbed monolayer transfer into the bulk mobile phase rather than stick to the solute. This concept is inherent in the model of normal phase chromatography¹¹. A similar idea was suggested by Regnier *et al.*¹² to explain the effect of varying the modifier concentration in the mobile phase on retention of proteins in reversed phase chromatography. The displacement model might be valid for the retention of polar solutes. For nonpolar solutes, however, this model is unlikely because a nonpolar solute on the nonpolar surface will be favorably solvated by less polar modifier molecules than water. The results of Scott and Kucera¹⁰ also argue against this model. For the above reasons, this model will not be considered in further discussion.

Results and Discussion

In order to compare these models capacity factor data¹³⁻¹⁶, surface tension data¹⁷, and activity coefficient data⁷ were collected from the literature along with the column specifications^{18,19}. The column characteristics are given in Table 1. Solute and solvent properties are assembled in Table 2. We assume that the effective surface area of the stationary phase is virtually independent of the mobile phase composition when wetting is good. We assume that complete wetting is achieved when the volume fraction (ϕ) of organic modifier in the mobile phase exceeds 0.3.

To facilitate the comparison of the various retention mechanisms it is essential to develop a standard of comparison. Examination of the relevant equations reveals that $\ln k'$ is composed of terms which are independent of ϕ and others which are not. All these equations can be written as follows:

$$\ln k'(\phi) = \text{Index} + F(\phi)$$

where the index is defined as the sum of all terms which are independent of ϕ . Such an equation can be re-written as follows:

Table 2. Solvent and Solute Properties

Solutes or solvents	Properties	
	A_1 or A_0^a (\AA^2)	σ_1 or σ_0^b (dyne/cm)
Solutes		
Benzene	51	28.17
Toluene	57.8	27.93
Ethylbenzene	65.5	28.49
Butylbenzene	80.8	28.73
Solvents		
Methanol	24.65	22.35
Acetonitrile	26.35	28.49
Isopropanol	39.95	20.82
Tetrahydrofuran	39.1	26.88

^aMolecular contact surface area (11). ^bSurface tension (17).

Table 3. Symbols, Definitions, and Description of the Variable Terms

Symbol	Definition	Description
A	$\ln k'$	Capacity factor term
B	$\ln \gamma^m_1$	Mobile phase activity coefficient term
C	$\ln [V_m d_m \{w_o/M_o + (1-w_o)/M_w\}]$	Mobile phase composition term
D	$A_1 N(RT)^{-1} \sigma_1$	Surface tension term

$$\text{Index} = \ln k'(\phi) - F(\phi) = \text{constant}$$

If a particular model is valid, its "index" must be independent of ϕ . If the "index" is not independent of ϕ the model is invalid. Thus we decided to use the model "index" for assessing the validity of any model.

Thus the expressions of indices for the conventional adsorption model (Index α) and the modified adsorption model (Index β) are obtained as follows:

$$\begin{aligned} \text{Index } \alpha &= [\ln k' - \ln \gamma^m_1 - A_1 N(RT)^{-1} \sigma_m \\ &\quad - \ln (V_m d_m \{w_o/M_o + (1-w_o)/M_w\})] \\ &= -\ln \gamma^s_1 - A_1 N(RT)^{-1} \sigma_1 + \ln (n^s_o) \end{aligned} \quad (11)$$

$$\begin{aligned} \text{Index } \beta &= [\ln k' - \ln \gamma^m_1 + \\ &\quad \ln (V_m d_m \{w_o/M_o + (1-w_o)/M_w\})] \\ &= -\ln \gamma^s_1 + \ln (n^s_o) \end{aligned} \quad (12)$$

The descriptions of variable terms are given in Table 3. The relative contributions of the variable terms to the variation in $\ln k'$ with respect to mobile phase composition are compared in Figure 1 for a typical solute (ethylbenzene). When a single nonpolar solute is considered, the surface interaction effect reduces to the effect of the mobile phase surface tension. As shown in Figure 1 the surface interaction effect (term D) is not a major factor for variation of solute retention. The activity coefficient of the solute (term B) in the mobile phase is the dominant contribution to variation of solute retention (term A). The variation in the number of

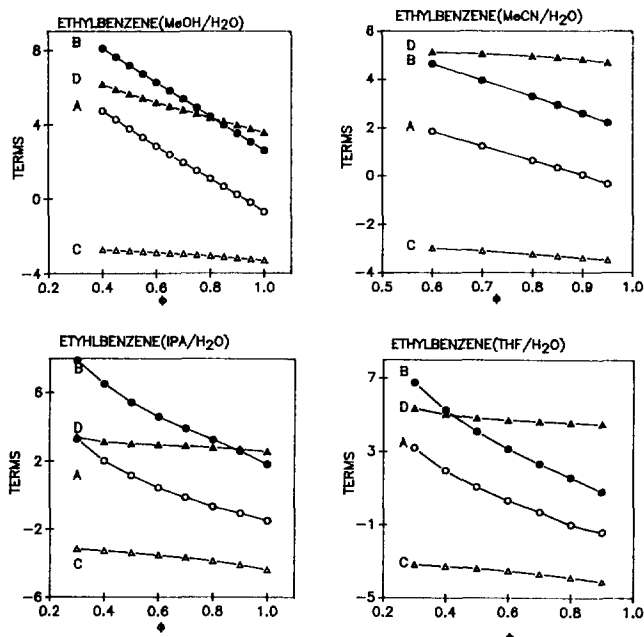


Figure 1. Comparison of the variable terms with respect to volume fraction of organic cosolvent for ethylbenzene. Symbols: (○); term A, (●); Term B, (△); Term C, (▲); Term D (See text).

a. methanol/water system, b. acetonitrile/water system, c. isopropanol/water system, d. tetrahydrofuran/water system.

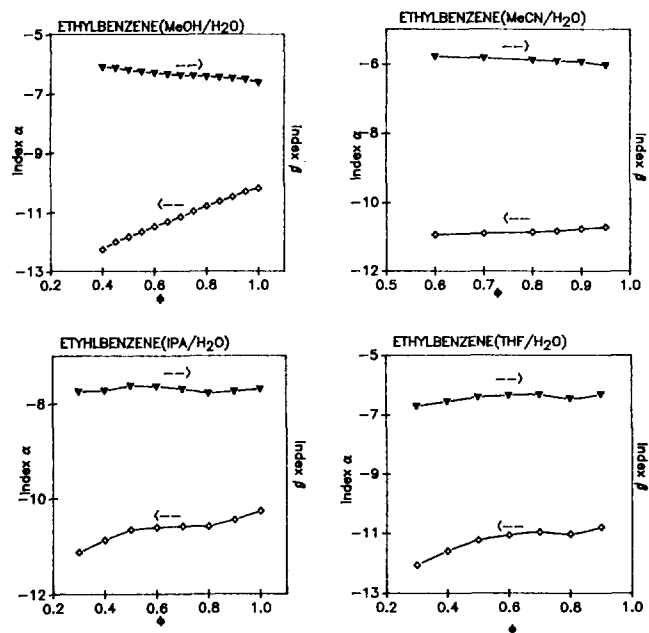


Figure 2. Indices vs. volume fraction of organic cosolvent for ethylbenzene. Symbols: (◇); Index α (the conventional adsorption model), (▼); Index β (the modified adsorption model).

a. methanol/water system, b. acetonitrile/water system, c. isopropanol/water system, d. tetrahydrofuran/water system.

moles of the mobile phase (term C) is minor compared to any of the other terms.

Now let us examine the variation in the indices with respect to mobile phase composition. Plots are shown in Figure

2. It is evident that the indices of the modified adsorption model are much less variable than those of the adsorption model for the methanol/water, isopropanol/water and tetrahydrofuran/water systems. On the other hand both indices are invariant for the acetonitrile/water system. It should be noted that the composition range for the acetonitrile/water system is limited ($0.6 < \phi_{org} < 0.95$) and the surface tension of the mobile phase (term D) is virtually constant over this range. The surface tension of the mobile phase for the isopropanol/water system and the tetrahydrofuran/water system does not vary as much as it does for the methanol/water system. Thus the discrepancies between the two models for the three solvent systems are not as large as that for the methanol/water system (Figure 2).

The uniqueness of the conventional adsorption model lies in its emphasis on the surface interaction terms. When we examine the variation of solute retention upon change of mobile phase composition, this model is useful only if the Everett type activity coefficient is independent of mobile phase composition as previous studies²⁻⁴ assumed since this property is very difficult to measure. It is evident that the Everett type activity coefficient varies with respect to the mobile phase composition (see the variation of index α in Figure 2). If a limited range of mobile phase composition is considered so that the surface tension of the mobile phase is virtually invariant, the surface interaction terms are invariant as well and there is no reason why the surface interaction terms should be separated. We conclude that incorporation of the Everett type activity coefficient in the expression of $\ln k'$ does not help understand retention behaviors but makes the expression more complicated.

We will focus on the modified adsorption model in discussion below. We need to explore the thermodynamic meaning of the activity coefficient of a nonpolar solute in the mobile and stationary phases.

First the meaning of the activity coefficient of a nonpolar solute in a polar mobile phase is considered. $RT \ln \gamma_1^\infty$ is equivalent to the excess partial molar Gibbs free energy of transfer of the solute from its pure state to the solvent. It is composed of the vaporization energy of the solute (endoergic term, positive free energy change), the cavity formation energy of the solute in the solvent (endoergic term), and the interaction energy of the solute with the solvent (exoergic term, negative free energy change). An important factor is structural change of the solvent upon introduction of the solute. This effect is included in the cavity formation free energy.

When a nonpolar solute is introduced into a polar solvent, some of the solvent-solvent interactions such as hydrogen bonds are broken. This perturbation leads to the reinforcement of solvent molecules around the solute²⁰. This effect is so called *hydrophobic effect*²⁰. The enthalpic effects of perturbation and reinforcement are known to be roughly self-cancelling²⁰. The enthalpic effects of solute-solute interaction and solute-solvent interaction are also roughly self-cancelling²⁰. The overall enthalpic effect of the process is minor compared to entropic effect of reinforcement of surrounding solvent molecules. This entropy change is highly negative. This means highly positive Gibbs free energy of transfer. It results in a low solubility and a high activity coefficient of a nonpolar solute in a highly polar solvent. The driving

force for solution and mixing is, of course, the positive ideal entropy of mixing. When we consider a single solute in various solvents, a dominant factor for variation of solute activity coefficient is the cavity formation free energy which includes the perturbation effect of solvent structure.

Now let us consider a transfer free energy of a nonpolar solute from its pure state onto the hydrophobic ligand surface which is covered by an organic modifier monolayer. We can envision that the hydrophobic part of the organic modifier will orient towards the hydrophobic ligand and the polar part will interact with the polar bulk mobile phase. The polar groups of modifier molecules are already reinforced by polar groups of the bulk mobile phase. In this situation, cavity formation means cleavage of interaction between the hydrophobic part of the modifier and the hydrophobic ligand. The loss of this interaction is compensated by solute-ligand interaction. The interaction between the polar group of the modifier and the bulk mobile phase is not interrupted. In other words, a major contribution of the Gibbs free energy of transfer will be the solute vaporization energy (endoergic) and the interaction energy (exoergic) between the adsorbed solute and the hydrophobic part of the modifier around the solute. They are largely self-cancelling and the absolute magnitude of the solute vaporization energy is a little greater than that of the solute-modifier interaction. The difference is proportional to the contact area between the solute and the ligand. On the other hand, we can assume that the internal energy of the solute does not change by adsorption.

Based on the above arguments, the Gibbs free energy of transfer from the pure solute state onto the hydrophobic surface will be a small positive value and the logarithm of the surface activity coefficient will be slightly higher than zero. We computed the logarithm of solute activity coefficient in the stationary phase using the literature column characteristics. The calculated $\ln \gamma_1^\infty$ based on the Schoenmakers' data¹³ ranges from -0.9 to -0.3 for benzene, toluene and ethylbenzene. We used the specific surface area reported by Slaats¹⁸. That was the only available data for the reversed stationary phase. We also employed the packing density reported by Engelhardt and Ahr¹⁹. The value of 0.5 for a home-packed column was employed because a home-packed LiChrosorb column was used by Schoenmakers *et al.*¹³. We also used solute molecular contact areas reported by Snyder¹¹. Snyder's data were collected for the stationary phases used in normal phase liquid chromatography. If we consider the complicated structure of the ligands in reversed phase liquid chromatography, the effective surface contact areas might be different. If we assume that the packing density of the column is 1.0 (g/ml) instead of 0.5, then the calculated $\ln \gamma_1^\infty$ will vary from -0.1 to 0.4 for the three benzene homologues, which is in agreement with the calculated data by Petrovic and coworkers²¹ who applied the UNIFAC approach in estimating activity coefficients of solutes in the mobile phase and also calculated the apparent activity coefficients of the solutes in the stationary phase. Based on Barman and Martire's data¹⁴ $\ln \gamma_1^\infty$ ranges from -0.5 to 0.6 for the five benzene homologues (benzene to *n*-butylbenzene). On the other hand $\ln \gamma_1^\infty$ ranges from -0.9 to -0.1 for the acetonitrile/water system, from 0.2 to 0.9 for the isopropanol/water system, and -1.0 to -0.3 for the tetrahydrofuran/water system (Figure 3). The systematic increase of \ln

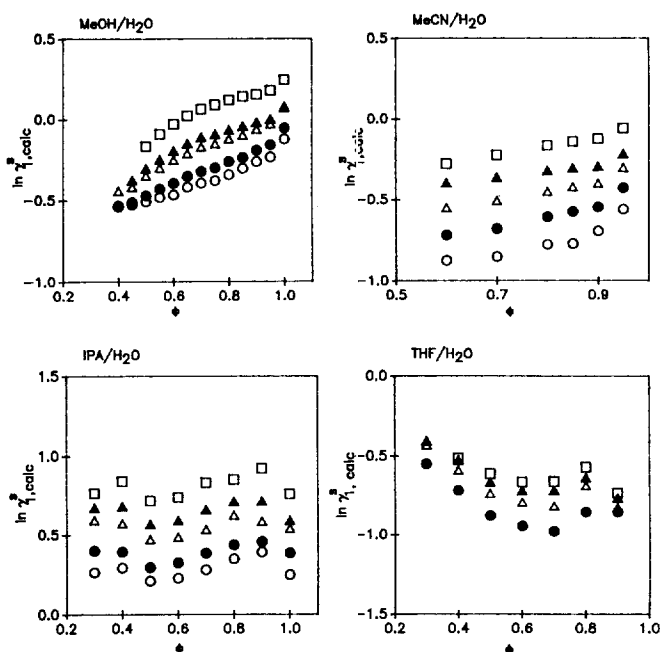


Figure 3. The computed $\ln \gamma_1$ vs. volume fraction of organic cosolvent. Symbols: (○); benzene, (●); toluene, (△); ethylbenzene, (▲); propylbenzene, (□); butylbenzene. a. methanol/water system, b. acetonitrile/water system, c. isopropanol/water system, d. tetrahydrofuran/water system.

γ_1 from benzene to butylbenzene is in agreement with the argument that the positive Gibbs free energy of solute transfer from the pure solute state onto the hydrophobic ligand surface will increase with solute-ligand contact area.

Let us examine how the modified adsorption model can be related to other theories. As far as we know, the only rigorous theory of retention in RPLC where factors related to measurable properties were employed was reported by Horvath and coworkers^{22,23}. This theory seems to be accepted in the general sense that the cavity formation energy of the solute in the mobile phase governs solute retention, especially for nonpolar solutes. On the other hand, a very fundamental and rigorous treatment of the retention mechanism has been reported by Martire and Boehm²⁴. This exhaustive theoretical study was based on the statistical thermodynamics.

Horvath's theory suggests a linear relationship between $\ln k'$ and the surface tension of the mobile phase if the correction factor for the microscopic surface tension is virtually constant or collinear with $\ln k'$. The adsorption theory¹⁻⁴ also leads to the same conclusion when a single solute is considered in various eluents if Fowke's approximation is used to convert the interfacial surface tension to the bulk surface tension terms. The theoretical concepts of these two approaches are totally different. In our modified adsorption model, the surface tension term is not used at all, but it shows good agreement between the theory and the measured data for a nonpolar solute as shown in this study. This can be explained by Table 4. The logarithm of the capacity factor is linearly correlated with the surface tension and also with $\ln \gamma_1^m$ over a wide range of mobile phase composition ($0.3 \leq \phi \leq 1.0$). Thus surface tension is also linearly correlated

Table 4. Results of Correlations of the Logarithmic Capacity Factor ($\ln k'$) with the Logarithmic Activity Coefficient ($\ln \gamma$) and Surface Tension (σ)^a

Solute	Correlation	Number of data point	Correlation coefficient
Benzene	$\ln k'$ vs. σ	8	0.9983
	$\ln k'$ vs. $\ln \gamma$	8	0.9983
Toluene	$\ln k'$ vs. σ	8	0.9984
	$\ln k'$ vs. $\ln \gamma$	8	0.9979
Ethylbenzene	$\ln k'$ vs. σ	8	0.9974
	$\ln k'$ vs. $\ln \gamma$	8	0.9993

^aBased on Schoenmakers' retention data (references 13) for the methanol/water system.

with the logarithm of activity coefficient. It should be noted that in the Horvath's solvophobic theory the surface tension term is related to the mobile phase effect and that in the conventional adsorption model the surface tension effect is relevant to the stationary phase. We showed that the major contribution to the solute retention is the mobile phase effect (solute activity coefficient in the mobile phase). Thus our model agrees with Horvath's theory in that view.

Snyder's linear correlation²⁵ of $\ln k'$ vs. ϕ also seems to be related to the observed linear correlation between $\ln \gamma_1^m$ vs. ϕ over a wide range of mobile phase composition⁷ assuming that the surface activity coefficient term plays only a minor role or that this term is also linear with respect to ϕ .

Acknowledgement. This work was supported by Inha University (1992 University Fund.)

References

- Locke, D. C. *J. Chromatogr. Sci.* **1977**, *15*, 393.
- Eon, C. H. *Anal. Chem.* **1975**, *47*, 1871.
- Colin, H.; Guiochon, G. *J. Chromatogr.* **1978**, *158*, 183.
- Hammers, W. E.; Meurs, G. J.; De Lingny, C. L. *J. Chromatogr.* **1982**, *24*, 169.
- Everett, D. H. *Trans. Faraday Soc.* **1964**, *60*, 1803.
- Everett, D. H. *Trans. Faraday Soc.* **1965**, *61*, 2478.
- Cheong, W. J.; Carr, P. W. *J. Chromatogr.* **1990**, *500*, 215.
- Fowkes, F. M. *J. Phys. Chem.* **1963**, *67*, 2538.
- Fowkes, F. M. *Predicting Attractive Forces at Interface, Symposium on Interfaces*; Washington, D. C., 1964.
- W. Scott, R. P.; Kucera, P. *J. Chromatogr.* **1977**, *142*, 213.
- Snyder, L. R. *Principles of Adsorption Chromatography*; Marcel Dekker: New York, 1968.
- Geng, X.; Regnier, F. E. *J. Chromatogr.* **1984**, *296*, 15.
- Schoenmakers, P. J.; Billiet, H. A. H.; de Galan, L. *J. Chromatogr.* **1983**, *282*, 107.
- Barman, B. N. *A Thermodynamic Investigation of Retention and Selectivity in Reversed Phase Liquid Chromatography, PhD. Thesis*; Dept. Chem., Georgetown University, Washington, D. C., 1985.
- Hanai, T.; Hubert, J. *J. Chromatogr.* **1984**, *299*, 197.
- Cheong, W. J.; Carr, P. W. *J. Chromatogr.* **1990**, *499*, 373.
- Cheong, W. J.; Carr, P. W. *J. Liq. Chromatogr.* **1987**, *10*,

- 561.
18. Slaats, E. H.; Markovski, W.; Fekete, J.; Poppe, H. *J. Chromatogr.* **1981**, 207, 299.
19. Engelhardt, E.; Ahr, G. *Chromatographia* **1981**, 14, 227.
20. Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley and Sons: New York, 1973.
21. Petrovic, S. M.; Lomic, S. L.; Sefer, I. *J. Chromatogr.* **1985**, 348, 49.
22. Horvath, C.; Melander, W.; Molar, I. *J. Chromatogr.* **1976**, 125, 129.
23. Horvath, C.; Melander, W. *J. Chromatogr. Sci.* **1977**, 15, 393.
24. Martire, D. E.; Bohem, R. E. *J. Phys. Chem.* **1983**, 87, 1045.
25. Snyder, L. R.; Dolan, J. W.; Gant, J. R. *J. Chromatogr.* **1979**, 165, 3.

Preparation of Y-Ba-Cu-O Superconducting Film on Ag Substrate by an Electrophoretic Deposition Method

Cheol-Hwa Kang, Cheol-Mo Jeong, Cheol-Woo Yi, and Keon Kim

Department of Chemistry, Korea University, Seoul 137-701

Received July 7, 1993

The preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ thick film on Ag substrate by electrophoretic deposition was directly studied. Electrophoretic deposition was carried out in solution, which was composed of presintered $\text{YBa}_2\text{Cu}_4\text{O}_8$ powder, sodium, and 2-propanol as a solvent. The deposited thick films were heat-treated in O_2 at 815°C for 12 hours and at 450°C for 12 hours. We succeeded in obtaining superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$ films on Ag substrate. Even though the chemical reactions at the $\text{YBa}_2\text{Cu}_4\text{O}_8/\text{Ag}$ interface occurred in the range of $10\ \mu\text{m}$, superconductivity was not depressed. The thickness of the films was in the range of $60\text{--}80\ \mu\text{m}$. The characteristics of the films were examined by electric resistance measurements, X-ray diffraction, and SEM observations.

Introduction

The discovery of the superconductor, Y-Ba-Cu-O¹ system, has led to intensive efforts at developing these ceramics into useful materials. Although a number of fabrication approaches have been studied, its applications were not easy due to the inherent brittleness of ceramic materials and the difficulties in forming the high T_c superconductor into desired shapes.

Thick-film fabrication techniques have been widely investigated because the prospect of coated superconducting materials offers a lot of promising advantages. Techniques such as plasma spraying², screen printing³, and sol-gel method⁴ have been utilized to make Y-Ba-Cu-O coatings.

We prepared good superconducting films deposited on Ag substrate using the electrophoretic method⁵. Electrophoretic deposition is an electrokinetic phenomenon in which charged particles suspended in a liquid vehicle are moved and deposited under the influence of an electric field.

This method has several advantages high throwing power, short deposition time and its versatility, etc.

Electrophoretic deposition method was used for beta-alumina ceramics⁶ and CdSe⁵ coating films. Recently, some groups prepared the thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ by this method^{7,8}. They used buffer layer or $\text{I}_2/\text{acetone}$ as electrolyte/solvent. Since the acetone has low boiling point (56°C), it easily boiled during this experiment. In our work, 2-propanol (its boiling point is 82°C) was used as solvent and Na was

utilized as electrolyte because I_2 was not dissolved in 2-propanol. Until now, $\text{YBa}_2\text{Cu}_3\text{O}_7$ compounds were only used as the ceramic powders of electrophoretic method because it was difficult to prepare $\text{YBa}_2\text{Cu}_4\text{O}_8$ samples. Lately we had prepared $\text{YBa}_2\text{Cu}_4\text{O}_8$ bulk samples⁹ at 1 atm in O_2 condition, therefore, we utilized $\text{YBa}_2\text{Cu}_4\text{O}_8$ samples as starting powders. When buffer layer is not used, interface chemical reaction is crucial. But the heat-treatment temperature of $\text{YBa}_2\text{Cu}_4\text{O}_8$ samples (815°C) is lower than that of $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples (about 915°C). The chemical reaction at the $\text{YBa}_2\text{Cu}_4\text{O}_8/\text{Ag}$ interface is less effective on their properties.

Experiment

Electrophoretic deposition was carried out in solution, which was composed of presintered $\text{YBa}_2\text{Cu}_4\text{O}_8$ ceramic powders (1.5 g), sodium, and 2-propanol (150 ml). The sodium was used in order to play electrolyte and to prevent the particle from settling during the deposition time.

Using the pyrolysis method of EDTA complex⁹, the stoichiometric amounts of high purity powders $\text{Y}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2$ were dissolved in purified de-ionized water together with EDTA and converted to metal-oxide powders by pyrolysis, and then $\text{YBa}_2\text{Cu}_4\text{O}_8$ powders were sintered at 815°C for 48 hours. This process offers the advantage of forming the fine particles to develop a suitable charge on the surface and to produce high densification in sintering process. The powders were ball-milled for 12 hours with