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A COMPARISON OF SUPERCRITICAL PARTITION AND SUPERCRITICAL ADSORPTION CHROMATOGRAPHIES

Uğur AKMAN[*] *and Z. Sermin (GÖNENÇ) SUNOL*
Department of Chemical Engineering
Boğaziçi University, Bebek 80815, İstanbul - TURKEY

Aydın K. SUNOL
Department of Chemical Engineering
University of South Florida, Tampa, FL 33620 - USA

ABSTRACT

Implications of the partial molar volume of solute in the stationary-phase material in both supercritical partition chromatography and supercritical adsorption chromatography are discussed within the framework of a thermodynamic model of solute retention. Using experimental retention data and the thermodynamic model it is illustrated that, in supercritical partition chromatography, relationships among solubility, sorption and retention are confounded by the effects (pressure dependence) of the partial molar volume of solute in the stationary-phase material, and possible swelling of the stationary-phase material by the supercritical mobile-phase fluid. For the first time in literature, a supercritical sorption isotherm is imbedded in the thermodynamic model of solute retention in order to simulate temperature, pressure and density dependence of solute retention in supercritical adsorption chromatography. Unlike the behavior predicted by the model of solute retention in supercritical partition chromatography, simulation of pressure dependence of solute retention in supercritical adsorption chromatography with the aid of supercritical sorption isotherm does not show a retention minimum, and the retention coefficient exhibits an asymptotic decrease to zero with increasing pressure as expected. It is demonstrated that, in supercritical adsorption chromatography, the direct inverse relationship present between solute's solubility and sorption also exists between solubility (solvent power) and retention but as weighted by the molar volume of the mobile phase.

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[*] *author to whom correspondence should be addressed*

INTRODUCTION

Supercritical-fluid chromatography (SFC) has gained considerable interest in recent years as an attractive separation technique. The well known advantages of supercritical-fluid solvents (e.g., the ability to adjust solvent power and selectivity with small temperature and/or pressure perturbations, high solute-loading capacities even at low-temperature applications, ease of solvent regeneration, non-toxicity) make SFC a potential alternative to conventional chromatographic separation methods.

The retention mechanism of solutes in SFC is the key factor understanding of which would facilitate modeling and thus applications of supercritical-fluid-aided large-scale chromatographic separations. In conventional chromatographic separations, behavior of solute retention depends on the strength of sorption of the solute on the stationary-phase material. Separation effect in conventional chromatographic operations is enhanced by capitalizing on the solute-dependent temperature effects of the strength of sorption; i.e., through temperature programming. In SFC, however, mechanism of solute retention is quite complex since the above-mentioned properties of supercritical solvents give rise to high-level interactions among solute(s), stationary-phase material and supercritical mobile-phase fluid. Separation effect in SFC is enhanced by capitalizing on temperature and pressure (density) dependence of these complex interactions; e.g., through density programming.

The effects of temperature, pressure, mobile-phase (almost exclusively CO_2) density and stationary-phase material (in capillary or packed columns) on behavior of solute retention in SFC have been subject to extensive experimental and theoretical research**1-16**. At constant temperatures, experimental retention coefficients of solutes show an asymptotic decrease to zero with increasing pressure (5-40 MPa). Highest slope of the retention coefficient with respect to pressure is encountered around the critical temperature and pressure of the mobile-phase fluid. In retention-pressure plane, retention isotherms exhibit around the critical point a crossover region which is similar to that encountered in solubility of solutes in supercritical fluids. In retention-density plane, the crossover of the retention isotherms completely disappear as is the case of solubility isotherms when plotted against supercritical-phase density. Even though the pressure (density) and temperature dependence of solubility and retention show similarities, an exact relationship between solubility and retention cannot be derived since the mobile phase in SFC is at infinitely-dilute state; whereas bulk solubility of solutes in supercritical fluids, in general, represent conditions far from being infinitely dilute.

Thorough understanding of the behavior of solute retention in SFC requires characterization of complex intermolecular interactions present among the solute(s), mobile-phase fluid and the stationary-phase material. It is known that thermophysical properties of

the stationary-phase material (polymeric substances have been used almost exclusively in SFC columns) have profound effects in the mechanism of solute retention. Extraordinary properties of supercritical fluids, such as CO_2, cause significant degree of swelling of the polymeric stationary-phase materials at elevated pressures[8,12]. The degree of swelling decreases with increasing degree of cross-linking of the stationary-phase material. Change in volume of the stationary phase due to penetration of the supercritical fluid introduces difficulties in thermodynamic modeling of solute retention in SFC. On the other hand, the activity of the solute molecules within the polymeric stationary phase (whether swollen by the supercritical solvent or not), characterized by the solute's partial molar volume at infinite dilution in the stationary phase ($\overline{V}_{st}^{\infty}$), is the key issue, still to be resolved both experimentally and theoretically. Even though the conditions of partition chromatography prevail in almost all SFC experiments with polymeric stationary-phase materials, due to lack of extensive data, pressure and temperature dependence of $\overline{V}_{st}^{\infty}$ cannot be incorporated rigorously into thermodynamic modeling of solute retention. Furthermore, however the effects of stationary-phase swelling is small, in general, the stationary phase consists of the molecules of the polymeric substance, solute(s) and mobile phase fluid. Therefore, when the solute(s) is partitioned into the stationary phase, a rigorous thermodynamic model should include an accurate description (which has to be derived from independent set of experiments) of multi-component interactions as a function of temperature and pressure.

If the stationary-phase material is solid (e.g., activated carbon), then the solute is adsorbed on the surface of the adsorbent, and $\overline{V}_{st}^{\infty}$ simply becomes the solid-state molar volume of the solute[6,7]. Therefore, in supercritical adsorption chromatography, relationships among solubility, sorption and retention are not confounded by the effects (pressure dependence) of the partial molar volume of the solute in the stationary-phase material and possible swelling of the stationary-phase material by the supercritical mobile-phase fluid. However, the literature lacks works done on supercritical adsorption chromatography.

The object of this work is to comparatively investigate, within the framework of a thermodynamic model of solute retention, the relationships among solubility, sorption, and retention in supercritical partition chromatography and in supercritical adsorption chromatography. The main purpose is to identify the relationships among solubility, sorption and retention by incorporating an equation-of-state-based sorption isotherm into a general thermodynamic model of solute retention for supercritical adsorption chromatography in which there are no confounding effects of possible pressure dependence of the partial molar volume of the solute and/or stationary-phase swelling.

THERMODYNAMIC MODELING

In chromatography (as in adsorption columns), movement and distribution of the solute between the fluid (mobile) and adsorbent (stationary) phases can be described with the following partial differential equation:

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial z} - \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial n}{\partial t} \tag{1}$$

Since, in chromatography, the mobile and stationary phases are in local thermodynamic equilibrium, the stationary- and mobile-phase concentrations of the solute are related through the sorption isotherm as:

$$\frac{\partial n}{\partial t} = \frac{dn^*}{dc}\left(\frac{\partial c}{\partial t}\right) \tag{2}$$

Substitution of Eq.2 into Eq.1 leads to following hyperbolic partial differential equation:

$$\frac{\partial c}{\partial t} = -\omega\frac{\partial c}{\partial z} \tag{3}$$

In Eq.3, the propagation velocity of the solute depends on the sorption isotherm, interstitial mobile-phase velocity and volumetric phase holdups as follows:

$$\omega = \left\{ v \Big/ \left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{dn^*}{dc} \right] \right\} \tag{4}$$

In chromatography, the dimensionless retention coefficient (capacity factor) of the solute is defined based on the retention times of the solute and an inert substance (which is not adsorbed by the stationary phase) as:

$$k = \frac{\tau - \tau_o}{\tau_o} \tag{5}$$

The retention times of the inert substance and the solute are given as:

$$\tau_o = L/v \qquad\qquad \tau = L/\omega \tag{6}$$

When these definitions of the retention times are used in Eq.5, the capacity factor of the solute can also be expressed as (for the infinitely-dilute region where the sorption isotherm is linear):

$$k = \frac{dn^*}{dc}\left(\frac{1-\varepsilon}{\varepsilon}\right) = \frac{n^*}{c}\left(\frac{1-\varepsilon}{\varepsilon}\right) = \frac{x^*\rho_{st}}{y\rho_{mb}}\left(\frac{1-\varepsilon}{\varepsilon}\right) \tag{7}$$

At equilibrium, the chemical potential of the solute in the stationary and mobile phases are equal. Therefore[5]:

$$\mu_{st} = \mu_{mb} = \mu_{st}^{\infty} + RT \ln x^{*} = \mu_{mb}^{\infty} + RT \ln y \tag{8}$$

The pressure dependence of the capacity factor can be obtained by combining Eq.7 and Eq.8 and differentiating the resulting equation with respect to pressure at constant temperature and mobile-phase mole fraction of the solute:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,y} = \frac{1}{RT}\left[\left(\frac{\partial \mu_{mb}^{\infty}}{\partial P}\right)_{T,y} - \left(\frac{\partial \mu_{mb}^{\infty}}{\partial P}\right)_{T,y}\right] + \frac{\partial}{\partial P}\left\{\ln\left[\frac{\rho_{st}}{\rho_{mb}}\left(\frac{1-\varepsilon}{\varepsilon}\right)\right]\right\}_{T,y} \tag{9}$$

The last term in Eq.9 is the pressure derivative of the ratio of stationary- and mobile-phase moles; $\rho_{st}(1-\varepsilon)$ and $\rho_{mb}\varepsilon$, respectively. In SFC, the stationary-phase materials used in capillary or packed columns are exclusively polymeric substances which are insoluble in the supercritical-fluid phase. However, molecules of supercritical fluids, such as CO_2, are small enough to diffuse easily into glassy as well as rubbery polymers to produce a significant degree of swelling[8]. The degree of swelling decreases with increasing degree of cross-linking in the stationary-phase material[8,9]. Experimental results[8] show that the degree of swelling (change in the volume of stationary phase) and sorption of supercritical-fluid molecules within swollen polymers increase with increasing solvent power (with increasing pressure/density) of the supercritical-fluid solvent[8]. Therefore, the degree of swelling may significantly affect the pressure dependence of the last term in Eq.9; i.e., both the molar density of the stationary phase and the volumetric holdups of the stationary and mobile phases may significantly change with pressure. Molar density of the swollen stationary phase and volumetric phase holdups can be evaluated -at least qualitatively- through polymer/supercritical-fluid phase-equilibrium calculations by using Flory equation for the stationary phase and a suitable equation of state (e.g., Peng-Robinson equation of state) for the mobile phase[8,9,11]. However, in SFC literature, possible effects of stationary-phase swelling has mostly been ignored in thermodynamic modeling of solute retention. This is because of two reasons: there is only limited experimental work since the research on polymers swollen by supercritical fluids is at its onset, and the stationary-phase materials used in SFC are mostly cross-linked polymers. On the other hand, the change in volume of the stationary phase due to penetration of solute molecules is negligible if the solute is at infinite dilution in the supercritical mobile phase.

Therefore, if the possible effects of stationary-phase swelling are ignored, the last term in Eq.9 is independent of pressure except for the molar density of the mobile phase. Since pressure derivative (at constant temperature and composition) of the chemical potential is defined as the partial molar volume of the solute, Eq.9 can be written as:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,y} = \frac{\overline{V}_{mb}^{\infty} - \overline{V}_{st}^{\infty}}{RT} - \kappa_{mb} \tag{10}$$

where, isothermal compressibility of the mobile phase is given by:

$$\kappa_{mb} = \left(\frac{\partial \ln \rho_{mb}}{\partial P}\right)_{T} \tag{11}$$

In Eq.10, the partial molar volume of solute at infinite dilution in the supercritical mobile phase ($\overline{V}_{mb}^{\infty}$) can be evaluated either from infinite-dilution supercritical-phase density data or from an equation of state adjustable parameter(s) of which has to be obtained from supercritical-solvent/solute solubility data. Although the former is the desired method, the lack of extensive infinite-dilution solubility data bars this option.

Using a suitable equation of state, and solubility-pressure equilibrium data in order to obtain interaction parameter(s), $\overline{V}_{mb}^{\infty}$ can be extracted from the following thermodynamic relationship**17**:

$$\lim_{y\to 0}\left(\frac{\partial \ln \hat{\phi}_{mb}}{\partial P}\right)_{T} = \left(\frac{\partial \ln \hat{\phi}_{mb}^{\infty}}{\partial P}\right)_{T} = \frac{\overline{V}_{mb}^{\infty}}{RT} - \frac{1}{P} \tag{12}$$

When Eq.10 is combined with Eq.12, the pressure derivative of solute retention can be expressed as:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,y} = \frac{1}{P} - \frac{\overline{V}_{st}^{\infty}}{RT} + \left(\frac{\partial \ln \hat{\phi}_{mb}^{\infty}}{\partial P}\right)_{T,y} - \kappa_{mb} \tag{13}$$

Substituting Eq.11 into Eq.13 and integrating from a reference pressure P_o one obtains:

$$\ln\left(\frac{k\rho_{mb}}{P\hat{\phi}_{mb}^{\infty}}\right)\Bigg|_{P} = \ln\left(\frac{k\rho_{mb}}{P\hat{\phi}_{mb}^{\infty}}\right)\Bigg|_{P_o} - \int_{P_o}^{P}\frac{\overline{V}_{st}^{\infty}}{RT}dP \qquad \text{(constant T, y}\to 0\text{)} \tag{14}$$

The partial molar volume of the solute at infinite dilution in the stationary phase ($\overline{V}_{st}^{\infty}$) characterizes the solute/stationary-phase interactions, and should be interpreted by considering the nature of the stationary-phase material. For a polymeric stationary phase, $\overline{V}_{st}^{\infty}$ represents the change in molar volume of the stationary phase (whether swollen or not) due to penetration of solute molecules only (i.e., if conditions of partition chromatography prevail). For a polymeric stationary phase, $\overline{V}_{st}^{\infty}$ is expected to be pressure dependent**7**. In literature, retention data have been correlated with limited success over usually limited experimental pressure range by assuming that $\overline{V}_{st}^{\infty}$ is insensitive to variations in pressure**7,14-16**. Assuming that $\overline{V}_{st}^{\infty}$ is constant, Eq.14 can be integrated to obtain a linear equation from the slope of which (i.e., the integrand of Eq.14) $\overline{V}_{st}^{\infty}$ can be extracted using retention-pressure data. For a

solid stationary phase (adsorption chromatography), $\overline{V}_{st}^{\infty}$ is constant and equal to molar volume of the solid solute (V_s) since the solute mainly interacts with itself.

When Eq.14 is used and $\overline{V}_{st}^{\infty}$ is regressed as a constant from retention-pressure data, the model generally predicts a temperature- and solute-dependent retention minimum as a function of pressure or density[7,14-16]. At a constant temperature, retention minimum, which is not observed experimentally[3,7], is predicted at pressures above the critical pressure of the solvent. This discrepancy may be due to the assumption of constant $\overline{V}_{st}^{\infty}$ and/or neglected effect of possible stationary-phase swelling.

In SFC literature, experimentally studied pressure range is in between 6-40 MPa and complete pressure dependence of solute retention (starting from atmospheric pressures) has not been studied. Within the studied pressure range, some investigators[9] pointed out the relationships between temperature and pressure dependence of solute retention and solubility of the solute in supercritical solvent. However, a direct relationship between retention and solubility should not be argued since, compared to a supercritical phase saturated with solute, in chromatography, the solute is at infinite dilution in the supercritical mobile phase. Even if the interactions between solvent/stationary-phase and solute/stationary-phase are neglected, local solvent structure about the solute in a saturated supercritical phase and in an infinitely-dilute mobile phase are quite different[7].

As can be understood from the above discussion, the uncertainty on the partial molar volume of solute in the stationary phase and possible effects of stationary-phase swelling make the understanding of solute retention in SFC difficult. Unfortunately, solute retention in SFC with solid stationary-phase material (e.g., activated carbon), for which $\overline{V}_{st}^{\infty}$ is constant equal to molar volume of the solute and there exists no swelling problem, has not been studied.

If a theoretical/experimental sorption isotherm capable of describing equilibrium sorption of a solute on a solid stationary phase from a supercritical phase is known, then complete pressure dependence of solute retention in SFC and its relationship with bulk solubility behavior can be investigated. For a solid stationary phase, all the assumptions leading to Eq.13 become valid. At constant temperature and constant mobile-phase mole fraction of the solute, the pressure derivatives of solute retention and solute loading of a solid stationary phase (adsorbent) are related through Eq.7 as:

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T,y} = \left[\frac{\partial \ln\left(n^*/\rho_{mb}\right)}{\partial P}\right]_{T,y} \tag{15}$$

For a solid stationary phase, Eq.14 can be integrated to obtain the following linear equation:

$$\ln\left(\frac{n^*}{P\hat{\phi}^{\infty}_{mb}}\right)\Bigg|_{P} = \ln\left(\frac{n^*}{P\hat{\phi}^{\infty}_{mb}}\right)\Bigg|_{P_o} - \frac{V_s}{RT}\left(P - P_o\right) \qquad \text{(constant T, y}\rightarrow 0\text{)} \qquad (16)$$

Eq.15 or Eq.16 can also be used to determine supercritical-phase sorption isotherm of a solute from retention-pressure data.

RESULTS AND DISCUSSION

In SFC literature, naphthalene-CO_2 is one of the commonly studied solute-solvent systems with various stationary-phase materials over wide range of pressures and temperatures. Figures 1.a and 1.b show the solubility of naphthalene in CO_2 as a function of pressure and fluid-phase density at different temperatures. Calculations were performed with the Peng-Robinson equation of state using the van der Waals one-fluid mixing rules and the non-quadratic combining rule of Panagiotopoulos and Reid[18]. Pure component parameters were obtained from the usual acentric-factor correlation. Binary interaction parameters for naphthalene-CO_2 were regressed as temperature dependent from a bulk solubility data[19]. In order to show both temperature and pressure effects, in this work, the retention data by Gönenç and Sunol[13-16] for naphthalene-CO_2-polydimethylsiloxane system (capillary column) were used. Figures 1.c and 1.d show the experimental and theoretical retention coefficient of naphthalene as a function of pressure and density of pure CO_2. The model (Eq.14) was fitted to retention data through linear regression by assuming constant $\overline{V}^{\infty}_{st}$ values. Molar density of pure CO_2 was obtained from an accurate correlation[20]. Infinite dilution fugacity coefficient of naphthalene in CO_2 was calculated from the Peng-Robinson equation of state as explained above. The values of $\overline{V}^{\infty}_{st}$ with which Eq.14 fits the data are –1166 cm^3/mole at 40 ^oC, –650 cm^3/mole at 45 ^oC and –422 cm^3/mole at 50 ^oC. Since the values of $\overline{V}^{\infty}_{st}$ are quite different than molar volume of solid naphthalene (110 cm^3/mole), even though effects of possible swelling of polydimethylsiloxane by supercritical CO_2 cannot be assessed, it can be concluded that naphthalene partitions into polydimethylsiloxane phase. With constant $\overline{V}^{\infty}_{st}$ assumption, the model cannot adequately describe the retention behavior at 40 ^oC (close to the critical temperature of CO_2) above approximately 9 MPa. The model also wrongly predicts temperature-dependent retention minima both in retention-pressure and retention-density planes. Retention minima cannot be explained physically since one expects the retention of the solute to decrease to a constant level (asymptotic approach to zero) as solvent power of the mobile phase increases with pressure/density. Even though the bulk solubility of naphthalene in CO_2 is as high as 10^{-2} (highly concentrated compared to infinite-dilution conditions in SFC), it is interesting to notice the strong relationship between solubility and retention coefficient. The crossover of both the solubility and retention

isotherms occur within approximately the same pressure range. Also, the retrograde temperature effects in the solubility-pressure and retention-pressure planes both disappear in the density plane. However, the theoretical retention isotherms do cross around 6 MPa; whereas, there is only one crossover region of the solubility isotherms.

As can be understood from the above discussion, interactions among solute, solvent and stationary-phase material, characterized by $\overline{V}_{st}^{\infty}$, play a key role in mechanism of retention. These interactions are temperature and pressure dependent. Even if effects of swelling of stationary-phase material by supercritical solvent is indeed negligible, when the solute dissolves in the stationary phase (i.e., if the conditions of partition chromatography prevail), the model with the assumption of constant $\overline{V}_{st}^{\infty}$ should only be used within the range of retention data from which $\overline{V}_{st}^{\infty}$ is obtained. Pressure and temperature dependent solvent selectivity and solute/stationary-phase interactions are the points of interest for commercial applications of SFC. Therefore, stationary-phase materials reported in the literature are exclusively polymeric substances which enables partitioning of solute(s) between supercritical mobile phase and stationary phase. Unfortunately, in the literature there is no work on supercritical adsorption chromatography. If solid adsorbents such as activated carbon are used as stationary-phase materials, it is possible to understand the retention mechanism under supercritical conditions and elucidate relationships between solubility and retention.

In SFC with a solid stationary-phase material there is no problem of swelling and $\overline{V}_{st}^{\infty}$ simply becomes the solid-state molar volume of the solute. Under such circumstances the sorption of the solute (adsorbate) onto adsorbent from supercritical mobile phase becomes the only key issue. Relationships between sorption and retention coefficient are summarized by Eq.7, Eq.15 and Eq.16. Akman and Sunol**[20,23]**, have modeled the supercritical sorption equilibrium for phenol/activated carbon/CO_2 system with the following equation-of-state-based isotherm:

$$q_y(y,T,P)=\frac{\left[\dfrac{\theta_1(T)f_y(y,T,P)}{\gamma^{\infty}(T)P^{sat}(T)}\right]}{\left\{\theta_2(T)+\left[\dfrac{f_y(y,T,P)}{\gamma^{\infty}(T)P^{sat}(T)}\right]^{\theta_3(T)}\right\}^{1/\theta_3(T)}} \tag{17}$$

This fugacity-dependent sorption isotherm can be used reliably (it has been shown that the particular isotherm can fully explain and qualitatively predict the behavior encountered in supercritical desorbers**[20,23]**) to predict retention behavior and relationships between solubility and retention in supercritical adsorption chromatography.

The fugacity-dependent sorption isotherm which gives carbon loadings of phenol when adsorbed from CO_2 phase is a highly nonlinear isotherm (very favorable type isotherm). Therefore, the isotherm should be evaluated in the limit as fluid-phase mole fraction of phenol goes to zero to ensure that the calculations are done in the linear region of the isotherm and at infinite-dilution conditions:

$$\frac{n^*}{\rho_{st} M_{st}} = \lim_{y \to 0} \{ q_y (y, T, P) \} = q^\infty \tag{18}$$

The use of Eq.18 in Eq.7 results in the following equation which can be used in simulation of solute retention in adsorption chromatography:

$$\ln k = \ln \left[\left(\frac{q^\infty}{\rho_{mb}} \right) \frac{\rho_{st} M_{st}}{y} \frac{1-\varepsilon}{\varepsilon} \right] \qquad \text{(constant y)} \tag{19}$$

Figures 2.a and 2.b show the solubility of phenol in CO_2 as a function of pressure and fluid-phase density at different temperatures**[20,23]**. Calculations were performed with the Peng-Robinson equation of state as explained before. Figures 2.c and 2.d show pressure and density dependence of the quantity $\ln(q^\infty / \rho_{mb})$ which is proportional to theoretical (simulated) retention coefficient of phenol as calculated from Eq.19 with $y=10^{-8}$ to ensure linearity of the isotherm at infinite-dilution conditions. Both pressure and density dependence of the simulated retention isotherms are similar to those of the experimental retention isotherms shown in Figure 1. It is interesting to note that neither pressure nor density dependence of the simulated retention isotherms show retention minima. Within complete pressure range there is only one crossover region in pressure dependence and none in density dependence of the simulated retention isotherms. In the limit, as pressure increases (as the solvent power of CO_2 increases), the simulated retention isotherms show asymptotic approach to zero as expected**[3,6,7]**. Therefore, in supercritical adsorption chromatography, temperature, pressure and density effects on retention coefficient are those effects on supercritical sorption equilibrium weighted by the molar volume of the mobile phase. It is known**[20,23]** that there is a one-to-one inverse relationship between solubility and sorption (as solubility of the solute -solvent power- increases amount of the solute adsorbed decreases). Therefore, the same inverse relationship, weighted by the molar volume of the mobile phase, exists between solubility (solvent power) and retention as Eq,15 and Eq.19 show.

CONCLUSIONS

If stationary-phase material is a polymeric substance, generally the solute is partitioned between supercritical mobile phase and stationary phase. Therefore, in supercritical partition chromatography, the retention coefficient is a measure of the partition

coefficient of the solute between the stationary phase (which is composed of the stationary-phase material, solute and solvent molecules) and supercritical mobile phase. In such a case, success of the thermodynamic model of isothermal solute retention, which neglects effects of possible swelling of the stationary phase by the supercritical mobile phase, depends on validity of the assumption of constant (pressure independent) $\overline{V}_{st}^{\infty}$. The use of constant $\overline{V}_{st}^{\infty}$ in fitting the model to retention data furnishes the thermodynamic model only with power of interpolation; when extrapolated to higher pressures outside the range of data, the model may predict temperature-dependent retention minimum which is not observed experimentally. For rigorous modeling of supercritical partition chromatography with a single-solute system, data on both ternary (polymer, solute, solvent) phase-equilibrium and stationary-phase swelling under supercritical conditions should be incorporated into the theoretical treatment.

In supercritical adsorption chromatography, the theoretical treatment is simplified as the problem of swelling disappears and $\overline{V}_{st}^{\infty}$ simply becomes the solid-state molar volume of the solute. In such a case, the retention coefficient is proportional to the ratio of supercritical sorption-equilibrium to mobile-phase molar density. When a theoretical supercritical sorption isotherm is included in the analysis, the theoretical model of solute retention does not predict retention minimum, and the retention coefficient shows an asymptotic decrease to zero with increasing pressure as expected. In supercritical adsorption chromatography, the relationships among solubility, sorption and retention are not confounded by the effects (pressure dependence) of $\overline{V}_{st}^{\infty}$ and stationary-phase swelling. Therefore, the direct inverse relationship present between solubility and sorption under supercritical conditions also exists between solubility (solvent power) and retention but as weighted by the molar volume of the mobile phase.

SYMBOLS

c	mobile-phase concentration of solute
f_y	fugacity of phenol in supercritical-fluid phase
k	dimensionless retention coefficient of solute
L	length of column
M_{st}	molecular weight of stationary phase material
n	stationary-phase (adsorbent) concentration (loading) of solute
n^*	stationary-phase (adsorbent) concentration (loading) at equilibrium with c
P	pressure
P^{sat}	vapor pressure of pure phenol

q_y	equilibrium adsorbent loading from supercritical-fluid phase
q^∞	equilibrium adsorbent loading from infinitely-dilute supercritical-fluid phase
R	universal gas constant
t	time
T	temperature
v	interstitial velocity of mobile phase
V_s	solid-state molar volume of solute
$\overline{V}^\infty_{mb}$	partial molar volume of solute at infinite dilution in mobile phase
$\overline{V}^\infty_{st}$	partial molar volume of solute at infinite dilution in stationary phase
x^*	stationary-phase mole fraction of solute at equilibrium with y
y	mobile-phase mole fraction of solute
z	axial direction
ε	volumetric mobile-phase holdup (column voidage)
$\hat{\phi}^\infty_{mb}$	infinite-dilution fugacity coefficient of solute in mobile phase
κ_{mb}	isothermal compressibility of mobile phase
γ^∞	infinite dilution activity coefficient of phenol
μ_{st}	chemical potential of solute in stationary phase
μ^∞_{st}	chemical potential of solute at infinite dilution in stationary phase
μ_{mb}	chemical potential of solute in mobile phase
μ^∞_{mb}	chemical potential of solute at infinite dilution in mobile phase
θ_i	temperature dependent parameters of isotherm
ρ_{st}	molar density of stationary phase
ρ_{mb}	molar density of mobile phase
τ	retention time of solute
τ_o	retention time of inert substance
ω	propagation velocity of solute

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Figure Captions

Fig.1. Solubility and Retention Coefficient of Naphthalene

Fig.2. Solubility and Simulated Retention Coefficient of Phenol