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EFFECT OF THE PARTIAL MOLAR VOLUME OF THE SOLUTE IN THE STATIONARY PHASE ON RETENTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

Retention in supercritical fluid chromatography is a dynamic mechanism, involving intermolecular interactions in the mobile and stationary phases. A simple thermodynamic model, describing solute retention, has been investigated on the basis of macroscopic thermodynamic variables of the solute partial molar volume in the stationary and mobile phases. Solute–solvent interactions in the mobile phase are dominant at lower pressures. Solute–stationary phase interactions have an important role in solute retention in capillary supercritical fluid chromatography. The interaction of the solute with the five different stationary phases reflects the polarizability differences between these phases, as shown by the partial molar volume of the solute in the stationary phase.

INTRODUCTION

Retention in supercritical fluid chromatography (SFC) is a complex function of temperature, density, eluent composition and the intermolecular interactions between the solute and the mobile and stationary phases. Solute–solvent interactions in the fluid mobile phase can be expressed on the basis of the macroscopic thermodynamic quantity of the partial molar volume of the solute in the mobile phase at infinite dilution, $\bar{v}_i^{\mathrm{mp},\infty}$. Pressure effects on solute retention in SFC are well established. This parameter incorporates changes in chemical potential of the solute with pressure $(\partial\mu_i/\partial P)_{T,n}$. In supercritical fluid solutions the chemical potential of the solute can be changed dramatically by small variations of pressure[1,2]. Interaction of the solute with the stationary phase can be described by the fundamental solution property of the partial molar volume of the solute in the stationary phase at infinite dilution, $\bar{v}_i^{\mathrm{sp},\infty}$.

A simple thermodynamic model for solute retention in SFC has been proposed by Van Wasen and co-workers[3,4] and Yonker and co-workers[5,6], based on the macroscopic thermodynamic parameters of $\bar{v}_i^{\mathrm{mp},\infty}$ and $\bar{v}_i^{\mathrm{sp},\infty}$. Martire and Boehm[7,8] have outlined a unified theory of adsorption chromatography, applied to gas, liquid and supercritical mobile phases, based on a more complex statistical thermodynamic model describing solute retention. The thermodynamic model of Yonker and

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co-workers[5,6] has been used to correlate solute retention as a function of pressure, based on the solution thermodynamic parameters of the partial molar volume ($\bar{v}_i^{\mathrm{mp},\infty}$, $\bar{v}_i^{\mathrm{sp},\infty}$). Both approaches provide similar insights into the SFC retention process.

In this paper, development of the retention model is extended by studies of various bonded stationary phases in capillary SFC over a wide range of pressures. The roles of both the mobile and stationary phases on retention were studied experimentally. The partial molar volume of the solute in the stationary phase has been used to determine whether the retention process is based on adsorption or partitioning into the bonded phase. Both fundamental solution parameters, $\bar{v}_i^{\mathrm{mp},\infty}$ and $\bar{v}_i^{\mathrm{sp},\infty}$, have been studied to gain a greater insight into the retention mechanism in SFC.

THEORY

Solute retention in SFC as a function of pressure at constant temperature for a pure fluid mobile phase is expressed by[3,5]

$$(\partial \ln k'/\partial P)_T = \frac{1}{RT}(\bar{v}_i^{\mathrm{mp},\infty} - \bar{v}_i^{\mathrm{sp},\infty}) - K \tag{1}$$

where k' is the solute capacity factor, P is the mobile-phase pressure, R is the gas constant, T is the absolute temperature and K is the isothermal compressibility of the fluid solution. The solute concentration is considered to be at infinite dilution and solute retention will therefore be independent of concentration. Thus, the partial molar volumes are determined at infinite dilution of the solute in the fluid mobile phase ($\bar{v}_i^{\mathrm{mp},\infty}$) and stationary phase ($\bar{v}_i^{\mathrm{sp},\infty}$). The assumptions made in eqn. 1 are that the molar volume of the stationary phase and the volumes of the stationary phase and mobile phase are independent of pressure. Under infinite dilution conditions, generally relevant to SFC, the isothermal compressibility of the fluid solution is equal to the isothermal compressibility of the pure mobile phase.

The partial molar volume of the solute in the mobile phase at infinite dilution can be evaluated by

$$\bar{v}_i^{\mathrm{mp},\infty} = (\partial V/\partial n_1)_{T,P,n_2} = K_2 V_2\,(\partial P/\partial n_1)_{T,P,n_2} \tag{2}$$

where V is the volume of the binary solution, n_1 and n_2 are the number of moles of solute and solvent, respectively, K_2 is the isothermal compressibility of the pure fluid and V_2 is the molar volume of the pure fluid[6]. The partial molar volume of the solute in the mobile phase can be divided into two parts: K_2V_2, which is dependent on the pure fluid, and $(\partial P/\partial n_1)_{T,P,n_2}$, which is dependent on the attractive or repulsive intermolecular interactions in the binary solution.

There are three pressure regimes of interest to retention in eqn. 1. The first regime exists at low pressures, where $|\bar{v}_i^{\mathrm{mp},\infty}| \gg |\bar{v}_i^{\mathrm{sp},\infty}|$. As the isothermal compressibility of the fluid is greatest in the low-pressure region near the critical point of the fluid, a minimum in $\bar{v}_i^{\mathrm{mp},\infty}$ is observed where K_2 is a maximum[4,9–11]. Eqn. 1 for this pressure region is reduced to

$$(\partial \ln k'/\partial P)_T \approx \bar{v}_i^{\mathrm{mp},\infty}/RT - K \tag{3}$$

The derivative $(\partial P/\partial n_1)_{T,P,n_2}$ in eqn. 2 will be negative at low pressure because as a solute is added to the fluid at constant volume and temperature, the overall pressure of the system decreases with attractive solute–fluid intermolecular interactions. Negative partial molar volumes have been observed for supercritical fluids[1,2,4,11]. Therefore the slope of retention calculated from eqn. 3 would be negative.

The second pressure region of importance occurs when $\bar{v}_i^{\mathrm{mp},\infty} = \bar{v}_i^{\mathrm{sp},\infty}$; then eqn. 1 is reduced to

$$(\partial \ln k'/\partial P) \approx -K \tag{4}$$

In this case, the slope of solute retention is similar to the isothermal compressibility of the fluid. At these pressures the compressibility of the fluid is small; therefore the slope in eqn. 4 will be approximately zero.

The final pressure region of interest is at higher pressures, where $\bar{v}_i^{\mathrm{mp},\infty}$ is positive and greater than $\bar{v}_i^{\mathrm{sp},\infty}$. This pressure region is defined when the reduced density for the fluid is greater than 1.6. In this region, K_2 and K are very small, and $\bar{v}_i^{\mathrm{mp},\infty}$ has a small positive value[1]. Eqn. 1 cannot be simplified, as both $\bar{v}_i^{\mathrm{mp},\infty}$ and $\bar{v}_i^{\mathrm{sp},\infty}$ play a role in solute retention. With $\bar{v}_i^{\mathrm{mp},\infty}$ being positive at higher pressures, the derivative $(\partial P/\partial n_1)_{T,P,n_2}$ is positive. Under these conditions, $(\partial P/\partial n_1)_{T,P,n_2}$ represents possible repulsive interactions occurring in the fluid mobile phase at higher densities. If the value of $\bar{v}_i^{\mathrm{sp},\infty}$ reflects attractive interactions between the solute and the bonded stationary phase, then $\bar{v}_i^{\mathrm{sp},\infty} < V_i$ (where V_i is the molar volume of the solute). When repulsive interactions between the solute and stationary phase occur, it is possible for $\bar{v}_i^{\mathrm{sp},\infty} > V_i$. Finally, if the solute is adsorbed on the surface of the bonded stationary phase, then $\bar{v}_i^{\mathrm{sp},\infty} \approx V_i$, because the solute mainly interacts with itself.

Solute retention for naphthalene as a function of pressure with carbon dioxide as the mobile phase was studied with various column types at 35 and 45°C. The $\bar{v}_i^{\mathrm{sp},\infty}$ values are regressed from the least-squares fit of the experimental data to the calculated theoretical data to determine the apparent retention mechanism and the role of the stationary phase in solute retention in SFC.

EXPERIMENTAL

The experimental system and approach has been described in detail elsewhere[12]. The capacity factors for naphthalene at 35 and 45°C in carbon dioxide from 80 to 350 atm with SE-33, OV-17, DB-5, OV-1 and SE-54 were measured. The chemical composition of the stationary phases in the capillaries is given in Table I. The dimensions of the capillary columns were 10 m × 100 μm I.D. A Varian (Walnut Creek, CA, U.S.A.) 8500 microprocessor-controlled high-pressure syringe pump provided a pulse-free mobile-phase flow and accurate fluid pressure. The column temperature was controlled with a constant-temperature air-bath to an accuracy of ±0.1°C. The system pressure was measured with a Bourdon tube-type pressure gauge in line between the pump and the capillary column in the oven. The retention time of naphthalene as a function of pressure was measured with a reporting integrator, having an accuracy of 0.1 s. The elution time of dichloromethane, which was the solvent used for naphthalene, was used for the t_0 measurement in the determination of k' for naphthalene at all pressures studied. The solute sample was injected with a Valco

TABLE I

PARTIAL MOLAR VOLUME OF NAPHTHALENE IN DIFFERENT STATIONARY PHASES ($\bar{v}_i^{\mathrm{sp},\infty}$ ± PROBABLE ERROR) FROM THE LEAST-SQUARES FIT OF EXPERIMENTAL RETENTION DATA

Column type	*Phenyl-to-methyl ratio of the polysiloxane stationary phase*	*Partial molar volume (cm³/mole)*		*Film thickness (µm)*
		35°C	*45°C*	
OV-1	0:100	197 ± 22	377 ± 3	0.20
DB-5	5:95	124 ± 9	284 ± 32	0.20
SE-54	5:95	84 ± 16	149 ± 11	0.20
OV-17	50:50	22 ± 20	244 ± 20	0.10
SE-33	0:100	347 ± 26	300 ± 23	0.20
		149 ± 30	299 ± 16	0.30
		68 ± 16	144 ± 10	0.40
V_i (naphthalene)		126.4	127.4	

(Houston, TX, U.S.A.) C14W HPLC injection value (0.2 µl rotor volume), which was mounted outside the oven. A flow restrictor was connected to the end of the capillary and controlled the flow of the mobile phase through the column. After expansion through the restrictor, the solute was detected with a flame ionization detector.

RESULTS AND DISCUSSION

Experimental partial molar volume data for naphthalene in carbon dioxide are available[2]. They permit the calculation of $\bar{v}_i^{\mathrm{mp},\infty}$ by means of a two-parameter cubic equation of state (EOS), such as the Peng–Robinson EOS[1,2,6]. The accuracy of the fit of the experimental data as one nears the critical point of the fluid becomes suspect, but further from the critical point the fit is improved. The binary interaction parameters for the calculation of $\bar{v}_i^{\mathrm{mp},\infty}$ of naphthalene calculated with the Peng–Robinson EOS were regressed from solubility data of naphthalene in carbon dioxide at 35 and 45°C[2]. The experimental data[1] and $\bar{v}_i^{\mathrm{mp},\infty}$ calculated from the Peng–Robinson EOS for naphthalene at 35 and 45°C are shown in Fig. 1. The trends in $\bar{v}_i^{\mathrm{mp},\infty}$ are similar to that reported by Van Wasen and Schneider[11] as a function of pressure and temperature determined from experimental retention studies in packed-column SFC. The calculation of solute retention in SFC is similar to that described by the authors previously[6]. In this work the partial molar volume of the solute in the stationary phase was obtained by a least-squares fit of the experimental data to eqn. 1. The data in Fig. 1 show a large negative $\bar{v}_i^{\mathrm{mp},\infty}$ value at 35°C for naphthalene. This is because the derivative $(\partial P/\partial n_1)_{T,P,n_2}$ in eqn. 2 is negative. As discussed in the Theory section, attractive intermolecular interactions between the solute and the solvent would cause $(\partial P/\partial n_1)_{T,P,n_2}$ to be negative. Therefore, carbon dioxide can be considered to cluster about naphthalene at these low pressures near the critical point. This affects the solubility of naphthalene in carbon dioxide[1,10]. At 45°C, $\bar{v}_i^{\mathrm{mp},\infty}$ is not as negative as at 35°C; therefore one might expect the slope of solute retention to be not as steep at 45°C as for naphthalene at 35°C. This is indeed seen for the cases studied in this work and was also reported by Van Wasen and Schneider[11] for packed-column SFC. The

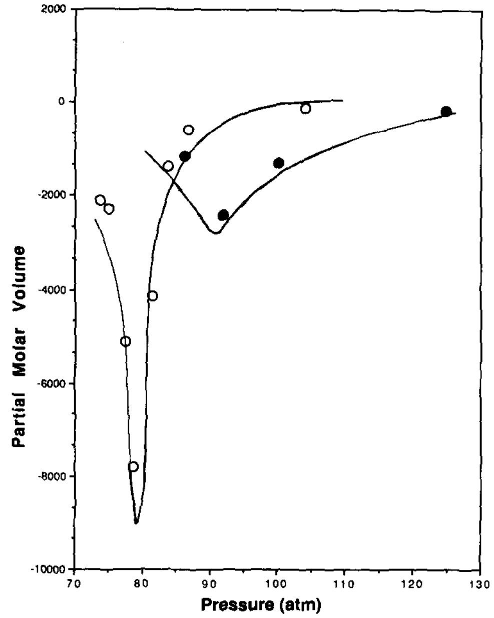

Fig. 1. Plot of the partial molar volume (in cm^3/mole) of naphthalene in carbon dioxide as a function of pressure at (○) 35 and (●) 45°C. Symbols, experimental data; lines, calculated data.

$\bar{v}_i^{\mathrm{mp},\infty}$ values in Fig. 1 become less negative and finally positive as pressure increases, thus reflecting the onset of possible repulsive interactions between the solute and solvent as pressure increases $[(\partial P/\partial n_1)_{T,P,n_2}>0]$.

In Fig 2, with DB-5 (phenylmethylpolysiloxane with a phenyl/methyl ratio of 95:5) at 35°C, naphthalene retention is plotted as a function of pressure. The solid line is calculated from eqn. 3, assuming $\bar{v}_i^{\mathrm{mp},\infty}$ is dominant, and is fixed to the first experimental data point. The Peng–Robinson EOS was used to calculate $\bar{v}_i^{\mathrm{mp},\infty}$ at 35°C. The experimental data and the solid line correlate fairly well at low pressures, but as the pressure increases the predicted slope becomes zero, and with still further increases in pressure the theoretical slope becomes positive. A positive slope indicates a net increase in solute retention (increased *k'*) with pressure.

The experimental results do not bear out this postulated retention mechanism at higher pressures. As pressure increased, the naphthalene retention asymptotically decreased, approaching a *k'* value of zero in all cases studied. Further increases in pressure up to 350 atm did not show the retention reversal theoretically calculated for Fig. 2. The theoretical retention reversal is caused by the overemphasis of the repulsive interactions between the solute and the fluid mobile phase in $\bar{v}_i^{\mathrm{mp},\infty}$ $[(\partial P/\partial n_1)_{T,P,n_2}>0]$ as pressure increases.

The experimental results for the DB-5 capillary column were used again with the theoretical retention slope calculated from eqn. 1, allowing $\bar{v}_i^{\mathrm{sp},\infty}$ to assume a value giving the best least-squares fit to the experimental data. These results are shown in Fig. 3. The least-squares value for $\bar{v}_i^{\mathrm{sp},\infty}$ was 124 cm^3/mole for naphthalene in this polyphenylmethylsiloxane stationary phase. The theoretical slope of retention fits the

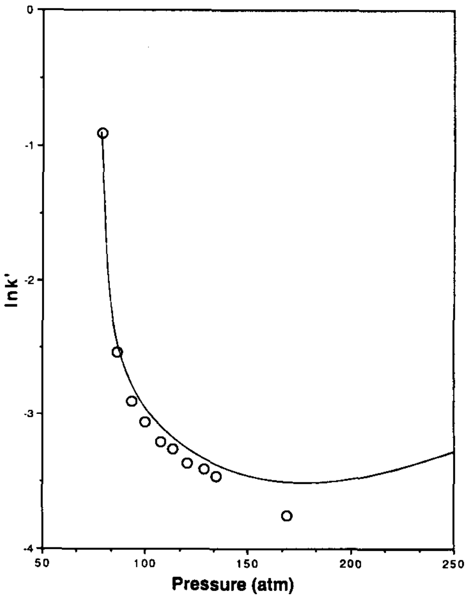

Fig. 2. Plot of experimental ln k' *versus* pressure for DB-5 at 35°C. The solid line was calculated from eqn. 3.

experimental data fairly accurately over the entire pressure range studied. In this instance at 35°C, no retention minimum is predicted for the retention of naphthalene with carbon dioxide. Therefore, the mobile phase alone does not control solute retention. The stationary phase has a role in the retention mechanism in SFC but the

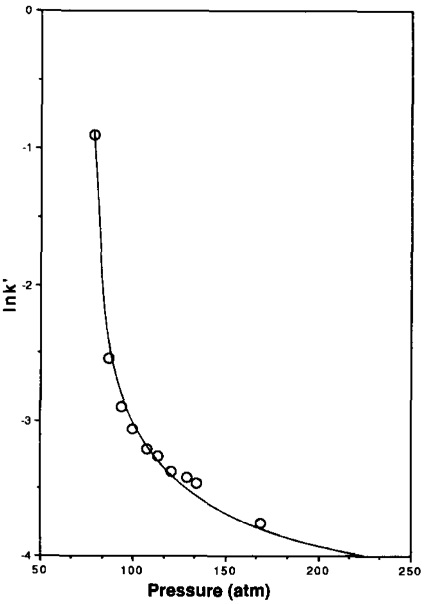

Fig. 3. Plot of experimental ln k' *versus* pressure for DB-5 at 35°C. The solid line was calculated from eqn. 1 with the least-squares value for $\bar{v}_i^{\text{sp},\infty}$ = 124 cm^3/mole.

exact role, be it an adsorption or partitioning process, remains to be defined.

Similar results at 45°C for naphthalene eluted from a capillary bonded with OV-17 by carbon dioxide are shown in Fig. 4. The calculated slope is based on a $\bar{v}_i^{\mathrm{sp},\infty}$ of 244 cm^3/mole, which was obtained from the least-squares fit to the experimental data. Once again, the data are fitted fairly accurately by the calculated slope over the entire pressure range studied. Similar results were obtained with all columns studied at both 35 and 45°C, as shown in Figs. 3 and 4 for naphthalene and carbon dioxide. No retention minimum was seen in the experimental solute retention values with increasing pressure up to and including 350 atm.

The partial molar volume of the solute in the stationary phase is an important thermodynamic parameter, related to the solute environment in the bonded polymeric phase. If there are no intermolecular interactions between the bonded polymeric stationary phase and the solute, then the solute is adsorbed on the interface region between the stationary phase and the fluid mobile phase. Solute adsorption on the surface of the polymer should give a $\bar{v}_i^{\mathrm{sp},\infty}$ value equal to the molar volume of the pure solute (V_i). This is because the solute is only capable of interacting with itself when it is adsorbed on the stationary phase. If the solute can partition into the bonded polymeric phase, then the possibility exists for attractive or repulsive intermolecular interactions between the solute and the stationary phase. If the intermolecular interactions are more attractive than in the pure solute, then $\bar{v}_i^{\mathrm{sp},\infty} < V_i$ would be expected to occur. On the other hand, if the intermolecular interactions are slightly repulsive (less attractive) between the solute and the stationary phase, then the total volume for the stationary phase–solute solution will increase with $\bar{v}_i^{\mathrm{sp},\infty} > V_i$. Through the study of $\bar{v}_i^{\mathrm{sp},\infty}$ under

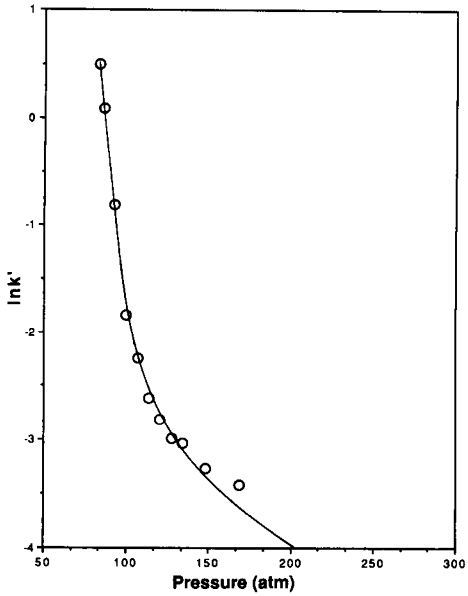

Fig. 4. Plot of experimental ln *k'* *versus* pressure for OV-17 at 45°C. The solid line was calculated from eqn. 1 with the least-squares value for $\bar{v}_i^{\mathrm{sp},\infty}$ = 244 cm^3/mole.

SFC conditions, a greater in-depth understanding of the intermolecular interactions between the solute and stationary phase can be obtained.

Table I contains the least-squares regressed $\bar{v}_i^{\mathrm{sp},\infty}$ values, obtained from fitting eqn. 1 to the experimental data for the five stationary phases studied by capillary SFC. Naphthalene should be able to interact more effectively with a polarizable stationary phase, such as OV-17, owing to the larger phenyl content of the bonded polymer. The ranking of naphthalene interactions with these five stationary phases is qualitatively OV-17 > SE-54 $\approx$ DB-5 > OV-1 $\approx$ SE-33. This is based on the decreasing percentage of phenyl groups in the bonded polymer (*cf.*, Table I). Intermolecular interactions between the solute and stationary phase are reflected in the $\bar{v}_i^{\mathrm{sp},\infty}$, regressed from the experimental data by means of eqn. 1. Naphthalene can interact very effectively with OV-17, and one obtains $\bar{v}_i^{\mathrm{mp},\infty} < V_i$. The least effective interaction should be with OV-1 and SE-33, as evidenced by $\bar{v}_i^{\mathrm{sp},\infty} > V_i$. A similar trend in $\bar{v}_i^{\mathrm{sp},\infty}$ is seen at 45°C, where $\bar{v}_i^{\mathrm{sp},\infty}$ decreases as the solute–stationary phase interaction increases. The qualitative agreement between $\bar{v}_i^{\mathrm{sp},\infty}$ from the proposed thermodynamic retention model and the postulated extent of intermolecular interaction between the solute and stationary phase is remarkable. The difference in $\bar{v}_i^{\mathrm{sp},\infty}$ as a function of temperature is probably due to the increased thermal energy in the system which contributes to higher thermal random motion in the polymer phase. This thermal motion precludes as effective of an intermolecular interaction between the solute and stationary phase at the higher temperature. This is reflected in the larger $\bar{v}_i^{\mathrm{sp},\infty}$ values at 45°C compared with 35°C. These results seem to establish the partitioning of the naphthalene solute into the bonded polymeric phase. This fact is also borne out when comparing the $\bar{v}_i^{\mathrm{sp},\infty}$ results for SE-33 as a function of stationary-phase film thickness. As the film thickness increases the bonded polymer would be a better solvent for the solute. This is reflected in the decrease in $\bar{v}_i^{\mathrm{sp},\infty}$ and an increase in solute retention with increasing film thickness for the SE-33 stationary phase.

Experimental data and $\bar{v}_i^{\mathrm{sp},\infty}$ values have been reported with a packed column (10-μm Whatman Partisil ODS-2) and carbon dioxide at 40°C by Brown *et al.*[13]. They reported an adsorption retention mechanism for naphthalene on the octadecyl-bonded stationary phase because they found that $\bar{v}_i^{\mathrm{sp},\infty} \approx V_i$ in this system. Studies performed by these workers on other solutes proved in conclusive owing to relatively large experimental uncertainties. The lack of accurate experimental $\bar{v}_i^{\mathrm{mp},\infty}$ values for different solutes as a function of pressure precludes the accurate extension of this technique to different solute–solvent–stationary phase systems[13]. The experimental methodology and theoretical retention calculation based on eqn. 1 do suggest the important potential for studying the intermolecular interactions of dilute solute-bonded polymeric phases.

CONCLUSIONS

Determination of $\bar{v}_i^{\mathrm{sp},\infty}$ on the basis of theory and the methodology discussed in this paper provides insights concerning the role of adsorption or partitioning processes in retention during SFC. If $\bar{v}_i^{\mathrm{sp},\infty} = V_i$, then solute adsorption at the stationary phase interface probably occurs. If $\bar{v}_i^{\mathrm{sp},\infty} > V_i$ or $\bar{v}_i^{\mathrm{sp},\infty} < V_i$ then a partition-like retention process must occur with slightly repulsive or attractive intermolecular interactions between the solute and stationary phase. The results presented in this paper are consistent with the extent of intermolecular interaction between naphthalene and the polarizable stationary phases studied. The extension of this work to different solutes awaits more accurate $\bar{v}_i^{\mathrm{mp},\infty}$ determinations.

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