Infinite-Dilution Partial Molar Properties of Azulene and Acenaphthylene in Supercritical Carbon Dioxide

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The effects of temperature and pressure on retention of azulene and acenaphthylene in supercritical fluid chromatography are investigated within 33−58 °C and 74−150 bar. The retention factors are used to derive the infinite-dilution partial molar volumes of the two solutes in supercritical carbon dioxide and infinite-dilution molar enthalpies of the transfer of azulene from the stationary phase to supercritical CO_2. The partial molar volumes are converted to quantities characterizing short-range interactions between CO_2 and the aromatic hydrocarbon. The results obtained by analyzing the retention data in the usual way are compared with a more refined treatment that takes account of the pressure- and temperature-dependent dissolution of CO_2 in the stationary polymer (poly(dimethylsiloxane)) within the column. The corrections for composition changes in the stationary phase employ a combination of the Flory−Huggins theory, the regular solution theory, and the Panayiotou−Vera lattice-fluid model. Application of the composition correction makes the partial molar volumes and the transfer enthalpies more negative. It has recently been noted [Liu, H.; O'Connell, J. P. *Ind. Eng. Chem. Res.* **1998**, *37*, 3323] that the chromatographic values of partial molar volumes appear to be systematically less negative than those derived from solubility data. Therefore, the composition correction may help to reconcile the disparity between the chromatographic and the solubility values of partial molar volumes.

Introduction

In addition to its significance as an analytical and/or preparative separation method, supercritical fluid chromatography (SFC) has also become a recognized source of thermodynamic information related to the transfer of solute between the mobile and the stationary phases. If the exact mass of the stationary polymer in the column is known, SFC retention data may yield the partition coefficient of the solute between both phases[1,2] or the solute−polymer interaction parameter.[2] If the mass of stationary polymer is not known exactly but remains constant during the measurements, variations in the solute retention factor with pressure, temperature, or composition of the mobile-phase fluid may be used to measure partial molar volume,[3−11] partial molar enthalpy,[5−7] or composition derivative of the fugacity coefficient of the solute,[12] respectively. In principle, the partial molar properties mentioned can be obtained for either phase of the chromatographic system provided that the respective property in the other phase is known or may be reliably estimated. Because of the continued interest in the use of supercritical fluids as solvents and reaction media, these applications of SFC focus on the solute partial molar properties in the mobile (supercritical) phase. The modern instrumentation makes it possible to work with very small amounts of solutes so that the partial molar properties obtained approach those at infinite dilution of the solute.

With a few exceptions,[6,7] applications of SFC to determine the partial molar properties of solutes were based on a simplified thermodynamic description of the problem. Namely, the pressure and/or temperature variations in the equilibrium proportion of the mobile-phase fluid in the stationary phase were usually neglected so that the observed variations in the solute retention factor were attributed entirely to what happened in the mobile phase. However, the changes in phase ratio and in composition of the stationary phase are translated into the measured retention factors, and therefore, they affect the resultant partial molar properties. The present work makes use of an earlier theoretical treatment[13,14] to take the composition changes into account when reducing retention factor data to partial molar properties. The solutes are azulene and acenaphthylene; to the authors' knowledge, no information on the partial molar properties of these two aromatic hydrocarbons in supercritical CO_2 has yet been available.

Experimental Section

Measurements were performed using a Dionex Series D-600 supercritical fluid chromatograph equipped with a pneumatically operated injection valve, a flame ionization detector, and a 10 m long Dionex SB Methyl-100 capillary column with an internal diameter of 50 μm, containing a 0.25 μm film of cross-linked poly(dimethylsiloxane) (PDMS). The solutes were purchased from Aldrich (Seoul, Republic of Korea) and used as received. The injection solutions were prepared by dissolving 1.2 mg of either solute in 10 mL of methylene chloride. The injection valve was fitted with a 500 nL rotor, and the split ratio was 1:15 (column flow rate:split flow rate). The retention factor of acenaphthylene was measured along three isotherms within 48−58 °C, and the retention factor of azulene along five isotherms within 33−58 °C, separately for each solute. All measurements

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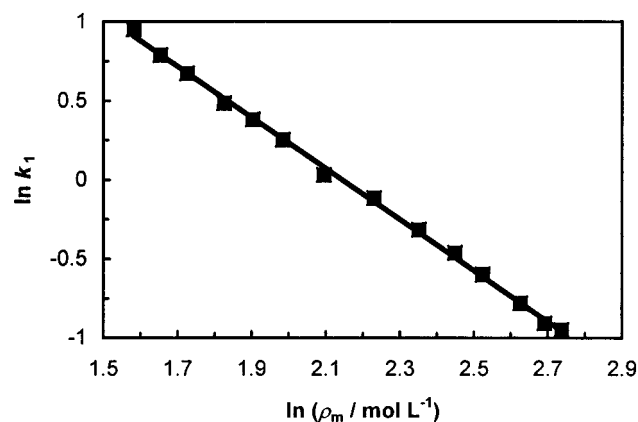‡ Academy of Sciences of the Czech Republic.

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Figure 1. Retention factor of azulene at 53 °C as a function of molar density of CO_2.
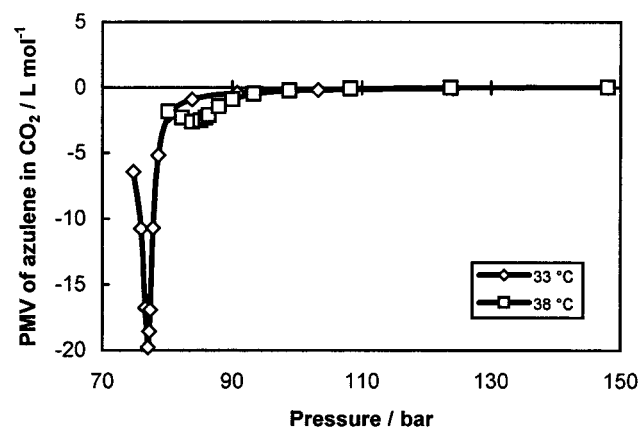

Figure 2. Pressure courses of the infinite-dilution partial molar volume of azulene in CO_2 at 33 and 38 °C.

were carried out in triplicate. The mobile phase holdup time, marked by injections of methane, did not drop below 9 min. Therefore, the difference between the column inlet pressure and the mean pressure in the column, calculated as described before[15] using the viscosity of CO_2 from the wide-range correlation by Vesovic et al.,[16] did not exceed 0.5 bar.

Data Analysis

The logarithmic plots of the solute retention factor, k_1, versus the molar density of CO_2, ρ_m, at the mean pressure in the column were smoothed with straight lines by least-squares linear regression. A sample plot is shown in Figure 1. The smoothed data were used to represent $\ln k_1$ as a function of temperature at a constant density of CO_2 so that a "grid" of $\ln k_1 = f(T, \rho_m)$ resulted for each solute. The isothermal pressure derivative of $\ln k_1$ and the isobaric temperature derivative of $\ln k_1$ were obtained from the density-involving derivatives using eqs 1 and 2,

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = \beta_{mT}\left(\frac{\partial \ln k_1}{\partial \ln \rho_m}\right)_T \tag{1}$$

$$\left(\frac{\partial \ln k_1}{\partial T}\right)_P = -\alpha_{mP}\left(\frac{\partial \ln k_1}{\partial \ln \rho_m}\right)_T - \frac{1}{T^2}\left(\frac{\partial \ln k_1}{\partial (1/T)}\right)_{\rho_m} \tag{2}$$

where P is the pressure, T is the absolute temperature, α_{mP} is the isobaric expansivity of CO_2, and β_{mT} is the isothermal compressibility of CO_2. The properties of pure CO_2 were calculated from a Jacobsen−Stewart type modification of the BWR equation of state (EOS).[17]
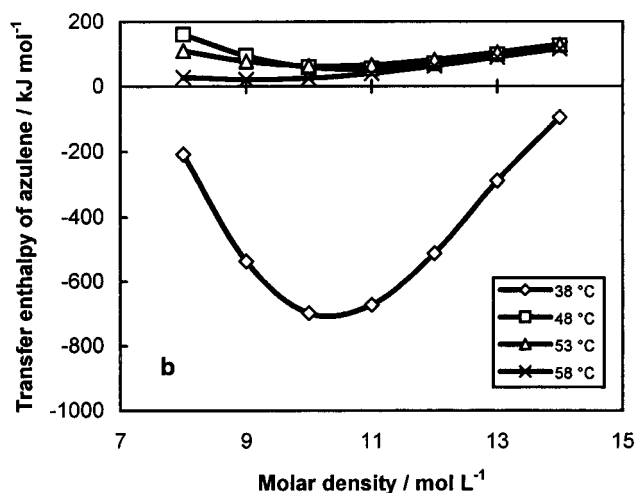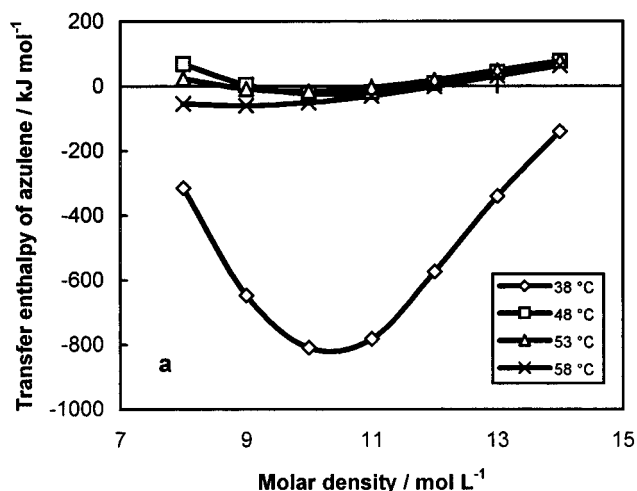

Figure 3. Infinite-dilution molar enthalpy of transfer of azulene from the stationary to the mobile phase, calculated with (a) and without (b) the correction for composition changes in the stationary phase.

The isothermal pressure derivative of $\ln k_1$ was converted to the infinite-dilution partial molar volume of the solute using eq 3,[13,14] where R is the molar gas constant,

$$\frac{\bar{v}_{1m}^{\infty}}{RT} = \left(\frac{\partial \ln k_1}{\partial P}\right)_T + \frac{\bar{v}_{1s}^{\infty}}{RT} + \beta_{mT} + \frac{V_s}{V_m}\beta_{sT\sigma} + \frac{1}{RT}\left(\frac{\partial \mu_{1s}^{\infty}}{\partial w_{3s}}\right)_{T,P,n_{2s}}\left(\frac{\partial w_{3s}}{\partial P}\right)_{T,\sigma} \tag{3}$$

$\bar{v}_{1m}^{\infty}$ and $\bar{v}_{1s}^{\infty}$ are the infinite-dilution partial molar volumes of the solute in CO_2 and in the stationary phase, respectively, $\beta_{sT\sigma}$ is the isothermal compressibility of the stationary phase at saturation with the dissolved CO_2, V_s and V_m are the geometric volumes of the stationary and the mobile phase in the column, respectively, μ_{1s}^{∞} is the infinite-dilution chemical potential of the solute in the stationary phase, and w_{3s} is the mass fraction of CO_2 in the stationary phase. Subscript n_{2s} refers to insolubility of the stationary polymer in CO_2, and subscript σ stresses saturation of the stationary phase with the dissolved CO_2. The infinite-dilution molar enthalpy of transfer of the solute from the stationary phase to the mobile phase, $\bar{h}_{1m}^{\infty} - \bar{h}_{1s}^{\infty}$, is related to the isobaric temperature derivative of k_1 by[13,14]

$$\frac{\bar{h}_{1m}^{\infty}}{RT^2} - \frac{\bar{h}_{1s}^{\infty}}{RT^2} = \alpha_{mP} - \left(\frac{\partial \ln k_1}{\partial T}\right)_P + \frac{V_s}{V_m}\alpha_{sP\sigma} -$$
$$\frac{1}{RT}\left(\frac{\partial \mu_{1s}^{\infty}}{\partial w_{3s}}\right)_{T,P,n_{2s}}\left(\frac{\partial w_{3s}}{\partial T}\right)_{P,\sigma} \quad (4)$$

where $\bar{h}_{1m}^{\infty}$ and $\bar{h}_{1s}^{\infty}$ are the infinite-dilution partial molar enthalpies of the solute in CO_2 and in the stationary phase, respectively, and $\alpha_{sP\sigma}$ is the isobaric expansivity of the stationary phase at saturation with the dissolved CO_2.

In eqs 3 and 4, the quantities $\beta_{sT\sigma}$ and $\alpha_{sP\sigma}$, the phase ratio V_s/V_m, and the slopes $(\partial w_{3s}/\partial P)_{T,\sigma}$ and $(\partial w_{3s}/\partial T)_{P,\sigma}$ were calculated from the Panayiotou−Vera mean-field lattice model[18] as described before.[14,19] The elastic contribution to the derivative $(\partial \mu_{1s}^{\infty}/\partial w_{3s})_{T,P,n_{2s}}$ was neglected, and the mixing contribution was obtained from a combination of the Flory−Huggins and the regular solution theories,[20]

$$\left(\frac{\partial \mu_{1s}^{\infty}}{\partial w_{3s}}\right)_{T,P,n_{2s}} = \bar{v}_{1s}^{\infty}\frac{\phi_{2s}\phi_{3s}}{w_{2s}w_{3s}}\left[(\delta_1 - \delta_3)^2 - (\delta_1 - \delta_2)^2 - (\phi_{2s} - \right.$$
$$\left. \phi_{3s})(\delta_2 - \delta_3)^2 - RT\left(\frac{1}{\bar{v}_{1s}^{\infty}\phi_{2s}} - \frac{1}{\bar{v}_{2s}} + \frac{1}{\bar{v}_{3s}}\right)\right] \quad (5)$$

where $\bar{v}_{2s}$ and $\bar{v}_{3s}$ are the partial molar volumes of PDMS and dissolved CO_2 in the stationary phase, respectively, ϕ_{2s} and ϕ_{3s} are the volume fractions of the two components, and w_{2s} is the mass fraction of PDMS in the stationary phase. All these properties except $\bar{v}_{2s}$ were obtained from the Panayiotou−Vera mean-field lattice model as mentioned above; because of the very high molar mass of the PDMS in the column, the approximation $\bar{v}_{2s} \rightarrow \infty$ was adopted throughout the calculation. Symbols δ_1, δ_2, and δ_3 denote the solubility parameters of the subcooled liquid solute, PDMS, and the dissolved CO_2, respectively. The solubility parameter of PDMS was measured previously by gas chromatography,[21] and the value given by Prausnitz et al.[22] was used for the solubility parameter of the dissolved CO_2. The solubility parameter of subcooled liquid azulene was estimated as described by Prausnitz et al.,[22] using the cohesive energy calculated from the vapor pressures[23] of the solid and the liquid, and the molar volume of the subcooled liquid obtained from the modified Rackett equation[24] with the critical parameters for azulene estimated from the Joback correlation.[25] Within 303−363 K, the resultant solubility parameter of subcooled liquid azulene may be fitted by a quadratic polynomial in T as

$$\delta_1 = 30.186 - 2.452 \times 10^{-2}T - 8.6591 \times 10^{-6}T^2 \quad (6)$$

Because of the lack of necessary data, the solubility parameter of subcooled liquid acenaphthylene was approximated by that of structurally similar acenaphthene, calculated again from the vapor pressures[26] of the solid and the liquid, and from the molar volume of the subcooled liquid. Within 303−363 K, fitting of the results by a quadratic polynomial yields

$$\delta_1 = 33.116 - 5.482 \times 10^{-2}T + 4.5528 \times 10^{-5}T^2 \quad (7)$$

Results and Discussion

Table 1 shows the resultant infinite-dilution partial molar volumes of azulene as functions of temperature and density of CO_2, and the results for acenaphthylene are listed in Table 2. The pressure dependence of partial molar volumes conforms
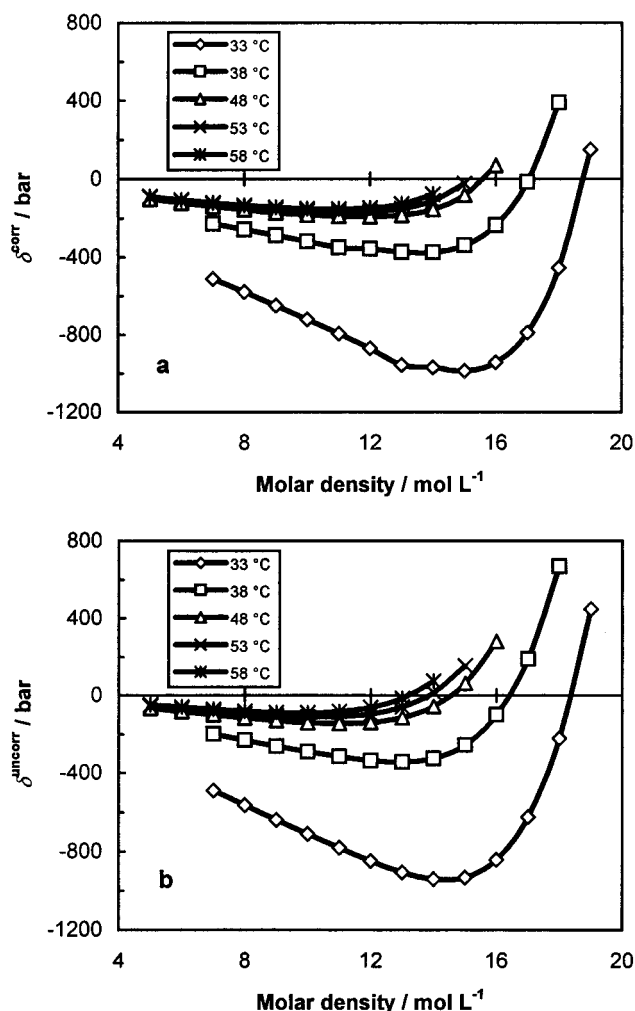

Figure 4. Quantity δ in the azulene−CO_2 system, calculated with (a) and without (b) the correction for composition changes in the stationary phase.

to the expected, typical pattern, as illustrated by Figure 2. In Tables 1 and 2, the partial molar volumes calculated from eqs 3 and 5 are compared with the values that result from the usual simplified treatment involving just the first three terms on the right-hand side (rhs) of eq 3. In both solutes, it turns out that the correction for composition changes in the stationary phase makes the solute partial molar volumes algebraically lower (more negative). Therefore, it appears that the composition correction helps us to reconcile the recently noted disparity[27] between the chromatographic values of $\bar{v}_{1m}^{\infty}$ and the values predicted from solubility data. The relative importance of the composition correction generally increases with decreasing magnitude of $\bar{v}_{1m}^{\infty}$ as the temperature moves farther away from the critical temperature of CO_2. However, the relatively small effect of the composition correction on the values of $\bar{v}_{1m}^{\infty}$ for azulene at 33 °C may partly be due to inadequacy of the mean-field theories near the critical point of CO_2, in particular, to underestimation of the derivative $(\partial w_{3s}/\partial P)_{T,\sigma}$, rather than to actual dominance of the mobile-phase effects in determining the slope $(\partial \ln k_1/\partial P)_T$. The partial molar volumes of azulene at 33 °C are gross approximations because of uncertainties in the CO_2 density that result from the near-critical enhancement in compressibility.

Figure 3 shows the infinite-dilution molar enthalpy of transfer of azulene from the stationary phase to the mobile phase, $\bar{h}_{1m}^{\infty} - h_{1s}^{\infty}$. Part a shows the values corrected for the composition

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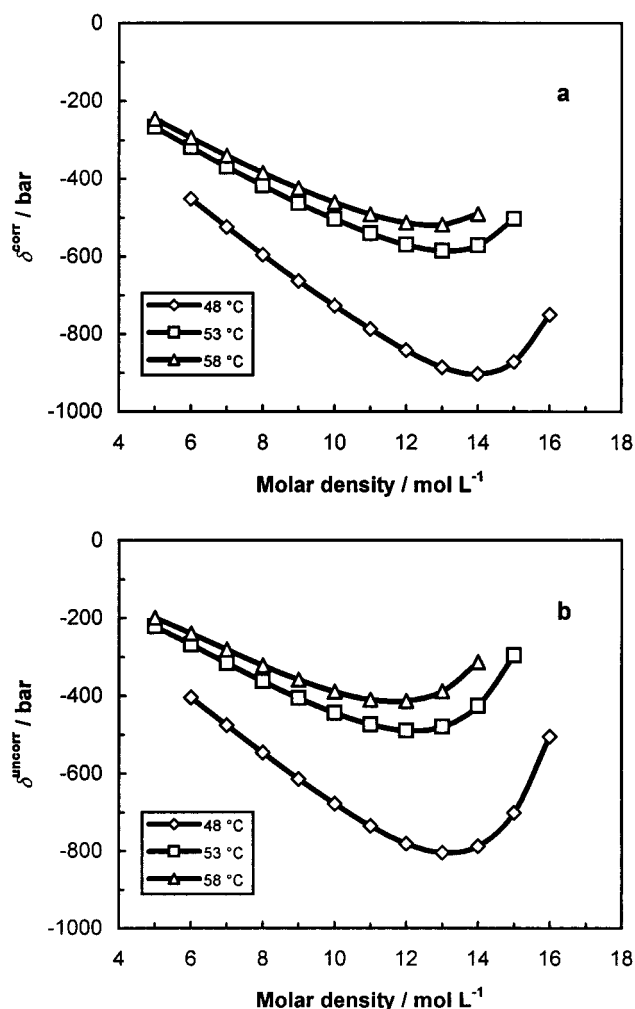
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TABLE 1: Infinite-Dilution Partial Molar Volumes of Azulene in CO_2, Calculated with and without the Composition Correction in the Stationary Phase

t/°C	ρ_m/mol L⁻¹	$\bar{v}_{1m}^{\infty}$/L mol⁻¹ composition correction		t/°C	ρ_m/mol L⁻¹	$\bar{v}_{1m}^{\infty}$/L mol⁻¹ composition correction	
		yes	no			yes	no
33	7	−6410	−6150	48	9	−656	−498
	8	−10700	−10500		10	−568	−438
	9	−16800	−16500		11	−442	−341
	10	−19800	−19500		12	−313	−229
	11	−16900	−16600		13	−195	−122
	12	−10700	−10400		14	−100	−36
	13	−5160	−4890		15	−31	24
	14	−2080	−2020		16	16	63
	15	−891	−841				
	16	−395	−352	53	5	−434	−258
	17	−169	−134		6	−461	−284
	18	−54	−26		7	−485	−312
	19	11	31		8	−488	−326
					9	−454	−310
38	7	−1810	−1580		10	−383	−263
	8	−2290	−2060		11	−295	−195
	9	−2600	−2380		12	−205	−120
	10	−2510	−2300		13	−124	−50
	11	−2100	−1900		14	−57	8
	12	−1430	−1350		15	−8	49
	13	−870	−801				
	14	−456	−396	58	5	−375	−207
	15	−210	−158		6	−386	−217
	16	−76	−32		7	−392	−229
	17	−3	33		8	−381	−229
	18	40	69		9	−344	−210
					10	−286	−170
48	5	−527	−344		11	−217	−117
	6	−584	−395		12	−148	−61
	7	−643	−456		13	−86	−10
	8	−678	−501		14	−34	33

TABLE 2: Infinite-Dilution Partial Molar Volumes of Acenaphthylene in CO_2, Calculated with and without the Composition Correction in the Stationary Phase

t/°C	ρ_m/mol L⁻¹	$\bar{v}_{1m}^{\infty}$/L mol⁻¹ composition correction		t/°C	ρ_m/mol L⁻¹	$\bar{v}_{1m}^{\infty}$/L mol⁻¹ composition correction	
		yes	no			yes	no
48	6	−2170	−1940	53	10	−1190	−1050
	7	−2410	−2190		11	−956	−839
	8	−2570	−2360		12	−710	−610
	9	−2540	−2350		13	−482	−396
	10	−2270	−2110		14	−296	−221
	11	−1840	−1720		15	−160	−94
	12	−1380	−1280				
	13	−937	−851	58	5	−1040	−843
	14	−582	−508		6	−1070	−875
	15	−331	−267		7	−1100	−910
	16	−168	−113		8	−1090	−910
					9	−1010	−852
53	5	−1240	−1035		10	−868	−734
	6	−1320	−1110		11	−693	−579
	7	−1400	−1200		12	−513	−414
	8	−1430	−1240		13	−348	−261
	9	−1360	−1190		14	−213	−136

Figure 5. Quantity δ in the acenaphthylene−CO_2 system, calculated with (a) and without (b) the correction for composition changes in the stationary phase.

changes in the stationary phase (eqs 4 and 5), while part b displays the results of the usual simplified treatment retaining only the first two terms on the rhs of eq 4. Application of the composition correction shifts the transfer enthalpies toward more negative values. Because of the method of calculation, the uncertainty in the resultant enthalpies of transfer exceeds that in the partial molar volumes. At the temperatures and densities near the critical values of CO_2, the transfer enthalpies are dominated by large negative values of $\bar{h}_{1m}^{\infty}$. Farther away from the critical point, the interplay between $\bar{h}_{1m}^{\infty}$ and $\bar{h}_{1s}^{\infty}$ becomes

more subtle, as seen in the irregular behavior of the transfer enthalpy with temperature and density.

The infinite-dilution partial molar volumes of the solutes may be reduced to several well-behaved quantities characterizing short-range interactions between the solute and the near-critical solvent, such as the quantity δ,[28] the Krichevskii parameter,[29] or the generalized Krichevskii parameter.[30] The quantity δ may be written as

$$\delta = \bar{v}_{1m}^{\infty}\rho_m/\beta_{mT} \qquad (8)$$

Figure 4 shows the values of δ for azulene in CO_2, calculated with (a) and without (b) the correction for composition changes in the stationary phase, respectively. Figure 5 presents the δ values for acenaphthylene in CO_2. Application of the composition correction makes the δ values more negative. Overall shapes of the curves in Figures 4 and 5 are qualitatively consistent with the density course of δ in the naphthalene−CO_2 system as derived from high-accuracy density measurements.[31] The perturbations appearing in the 33 and 38 °C isotherms in Figure 4a are artifacts that result from problems in describing the two isotherms for pure CO_2 with the mean-field model.

The simplicity of the models used to handle the difficult correction for composition changes in the stationary phase may certainly be criticized. In the derivatives $(\partial w_{3s}/\partial P)_{T,\sigma}$ and $(\partial w_{3s}/\partial T)_{P,\sigma}$, experimental values, if available, would be preferred to the model estimates. Nevertheless, as regards the disparity[27]

between the chromatographic and solubility data on partial molar volumes, the correction seems to work in the right direction. An important problem of this study is the degree of mutual consistency of the various thermodynamic models involved in the data analysis and in the composition correction. The quantitative performance of the approximate models for the individual derivatives involved in the composition correction has yet to be tested with solutes for which independent data on partial molar volumes in CO_2 are available. The work in this direction is in progress.

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