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Phase Equilibria of Alkanes in Natural Gas Systems. 2. Alkanes in Ethane

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A previously reported novel chromatographic technique for measuring capacity factors to yield infinite dilution activity coefficients for liquid and solid *n*-alkanes in compressed gases can be used to estimate solubilities, virial coefficients, partial molar volumes, and partial molar enthalpies at infinite dilution. This paper reports experimental capacity factors and their corresponding solubilities for the *n*-alkanes from $C_{24}H_{50}$ to $C_{36}H_{74}$ in C_2H_6 from 308.2 to 348.2 K and from 80 to 240 bar. The results are interpreted according to the physical differences observed between even- and odd-numbered solid *n*-alkanes.

Introduction

In previous papers we have presented a sound method for measuring phase equilibria of the *n*-alkanes in natural gases (Suleiman *et al.*, 1993). New experimental capacity factors and the corresponding solubilities were presented for the *n*-alkanes from C_7H_{16} to $C_{36}H_{74}$ in CH_4 from 293.2 to 423.2 K and from 120 to 240 bar (Suleiman and Eckert, 1995). These phase equilibria data are important to overcome the deposition of solids in natural gas pipelines, as well as for understanding size differences and dispersion forces. The chromatographic technique presented can be used to estimate solubilities, virial coefficients, partial molar volumes, and partial molar enthalpies at infinite dilution from the experimentally determined capacity factors. This paper reports experimental capacitance factors and their corresponding solubilities for the heavy saturated hydrocarbons from $C_{24}H_{50}$ to $C_{36}H_{74}$ in C_2H_6 from 308.2 to 348.2 K and from 80 to 240 bar.

Because of the high solubility of the liquid paraffins (*e.g.*, C_7H_{16} to $C_{18}H_{38}$) in C_2H_6 at the conditions studied, they were not investigated. The chromatographic method used for this investigation works best for low solubilities (*i.e.*, $< 10^{-2}$) (high capacity factors). For more soluble systems, the capacity factors are very small, and there is excessive uncertainty in the degree of retention ($t_r \sim t_0$). The lower *n*-alkanes could be studied at lower pressures; however, as one approaches the critical pressure of ethane ($P_c = 48.8$ bar), other problems such as absorption of the solvent in the stationary phase become significant.

Experimental Method

The experimental apparatus has been described in detail elsewhere (Suleiman *et al.*, 1993; Suleiman and Eckert, 1995). The relation between the solubility of a solute *i*, y_i (mole fraction), in a supercritical fluid (SCF) or dense gas and the experimentally determined capacity factors, k_i, is

$$y_i = \left|\frac{P_{i,\mathrm{sat}}V^{\mathrm{s}}}{k^{\circ}_{\mathrm{H},i}V^{\mathrm{m}}V^{\mathrm{s}}_{\mathrm{m}}}\exp\left(\frac{V_i(P^{\circ} - P_{i,\mathrm{sat}})}{RT}\right)\right|\frac{V^{\mathrm{m}}_{\mathrm{m}}}{k_i} = |C_i(T)|\frac{V^{\mathrm{m}}_{\mathrm{m}}}{k_i} \qquad (1)$$

where $P_{i,\mathrm{sat}}$ is the saturation pressure and $k^{\circ}_{\mathrm{H},i}$ is the Henry constant of solute *i* in the stationary phase at the reference pressure P°. The quantities V^{s}, V^{m}, $V^{\mathrm{s}}_{\mathrm{m}}$, and $V^{\mathrm{m}}_{\mathrm{m}}$ are the physical volumes and the molar volumes of the stationary and mobile phases, respectively. $C_i(T)$ is a constant for a particular chromatographic column, temperature, and solute *i*. To determine $C_i(T)$ for a solute *i* at a particular temperature, it is necessary either to measure at least one solubility value at that temperature with an independent technique or to predict it. Once $C_i(T)$ is known, the entire solubility isotherm can be determined rapidly by utilizing the experimentally measured chromatographic capacity factors. For solids, $C_i(T)$ reduces to

$$C_i(T) = \left|\frac{V^{\mathrm{s}}}{V^{\mathrm{m}}V^{\mathrm{s}}_{\mathrm{m}}}\right|\frac{1}{\gamma_i^{\infty}}\frac{P_{i,\mathrm{sub}}}{P_{i,\mathrm{vap}}} \qquad (2)$$

$P_{i,\mathrm{vap}}$ is the vapor pressure of the hypothetical liquid solute at the temperature of interest. γ_i^{∞} is the activity coefficient at infinite dilution between solute *i* and the stationary phase in the chromatographic column. This was obtained using an application of regular solution theory (RST) (Hildebrand *et al.*, 1970). As explained in the previous paper, since the stationary phase is an octadecyl bonded phase to a silica support, and no solubility parameter for this material was available, a single solubility datum for $C_{10}H_{22}$ in CH_4 at 313.2 K (Rijkers *et al.*, 1992) was used to regress the constant $C_i(T)$, which provided γ_i^{∞} and therefore the solubility parameter of the stationary phase.

The solubility parameters for the *n*-alkanes from $C_{24}H_{50}$ to $C_{36}H_{74}$ were calculated using Fedors' group contribution method (Fedors, 1974). The temperature dependence of the solubility parameters was also suggested by Fedors. The expression in brackets, $|V^{\mathrm{s}}/V^{\mathrm{m}}V^{\mathrm{s}}_{\mathrm{m}}|$, was obtained from the physical information provided by the manufacturer of the chromatographic column. $P_{i,\mathrm{sub}}$ and $P_{i,\mathrm{vap}}$ were obtained from recent investigations in the measurement and prediction of $P_{i,\mathrm{sub}}$ (Drake, 1993) and $P_{i,\mathrm{vap}}$ (Morgan and Kobayashi, 1994). Since all solutions studied were highly diluted, the densities used in the calculations were pure fluid densities obtained from Younglove and Ely (1987).

The overall estimated experimental error in the measured capacity factors is approximately 5−10%, with the largest contributions (about 2−3% each) coming from the pressure drop across the column (2−4 bar), the flow variations from the constant pressure control (±0.2 mL/min), and the maxima of the retention times (±1−5 s). The error in the estimated solubilities is approximately 10−15%. The solvent density is known to 5% (Younglove and Ely, 1987), and the constant C_i is calculated with an estimated error of 10%. The large error in C_i is due to the inability to describe accurately the stationary phase.

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Table 1. Mole Fraction Solubility, *S*, and Capacity Factors, k_i, for $C_{24}H_{50}$ in C_2H_6

T/K		*P*/bar									
		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	17.0	15.0		13.0		9.1	7.1	5.0	2.9	
	k_i	0.10	0.12		0.14		0.22	0.30	0.47	0.97	
333.2	10^2S	14.0			10.0		9.5	7.9	6.7	5.1	3.3
	k_i	0.11			0.16		0.18	0.23	0.28	0.41	0.83
328.2	10^2S	5.0			3.9		2.7	2.2	1.8	1.4	0.86
	k_i	0.10			0.13		0.19	0.23	0.29	0.41	0.68
318.2	10^2S	7.5		5.8	5.6	5.0	3.9	3.1	2.3	1.5	0.8
	k_i	0.12		0.16	0.16	0.19	0.25	0.32	0.45	0.72	1.5
308.2	10^2S	5.1			4.0		2.7	2.3	1.8	1.4	0.87
	k_i	0.10			0.13		0.19	0.23	0.29	0.41	0.68

Table 2. Mole Fraction Solubility, *S*, and Capacity Factors, k_i, for $C_{25}H_{52}$ in C_2H_6

T/K		*P*/bar									
		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	14.0	13.0		11.0		7.8	6.1	4.3	2.5	
	k_i	0.12	0.14		0.16		0.25	0.34	0.53	1.1	
333.2	10^2S	13.0			8.5		8.0	7.9	6.6	5.4	3.7
	k_i	0.12			0.18		0.21	0.22	0.28	0.38	0.72
328.2	10^2S	14.0			11.0		7.8	6.7	5.6	5.0	3.3
	k_i	0.10			0.13		0.19	0.24	0.30	0.36	0.65
318.2	10^2S	5.7		4.5	4.2	3.8	2.9	2.2	1.7	1.1	0.57
	k_i	0.13		0.17	0.18	0.21	0.27	0.37	0.50	0.80	1.7
308.2	10^2S	5.5			3.0		2.0	1.7	1.3	1.3	0.69
	k_i	0.07			0.13		0.21	0.26	0.33	0.36	0.69

Table 3. Mole Fraction Solubility, *S*, and Capacity Factors, k_i, for $C_{28}H_{58}$ in C_2H_6

T/K		*P*/bar									
		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	13.0	11.0		9.2		5.6	3.9	2.4	1.1	
	k_i	0.13	0.15		0.18		0.33	0.50	0.90	2.4	
333.2	10^2S	12.0			9.1		6.2	5.8	4.0	2.5	1.6
	k_i	0.12			0.16		0.25	0.28	0.43	0.75	1.5
328.2	10^2S	12.0			8.7		5.8	5.0	3.5	2.7	1.8
	k_i	0.11			0.15		0.24	0.29	0.43	0.61	1.1
318.2	10^2S	2.0		1.6	1.6	1.5	1.1	0.92	0.73	0.51	0.30
	k_i	0.21		0.28	0.28	0.30	0.40	0.51	0.67	1.0	1.9
308.2	10^3S	21.0			15.0		9.9	8.5	5.8	4.3	2.50
	k_i	0.11			0.15		0.24	0.29	0.43	0.61	1.1

Although the solubility parameter of the stationary phase is regressed from one known solubility datum, the number obtained for an octadecyl bonded phase to a silica support (19.8 $MPa^{1/2}$), does not support that of octadecane (16.6 $MPa^{1/2}$). However, the bonded octadecyl is not expected to behave as a free octadecane molecule.

Results and Discussion

Tables 1–7 present experimental capacity factors and their corresponding solubilities for the *n*-alkanes from $C_{24}H_{50}$ to $C_{36}H_{74}$ in C_2H_6 at temperatures from 308.2 to 348.2 K and at pressures from 80 to 240 bar. The only available published solubility data for these systems in C_2H_6 is that of Moradinia and Teja (1986, 1987, 1988). Figure 1 presents a comparison of the solubility of $C_{28}H_{58}$ in C_2H_6 at 308.2 K. All of the predicted solubilities from this investigation agree, within the experimental error (10–15%), with those of Moradinia and Teja. Like Moradinia and Teja's results, the solubilities of the solid even- and odd-numbered *n*-alkanes in ethane follow different trends. This behavior, which comes from the different trends in their solid phase properties (*e.g.*, sublimation pressure), is a result of the different packing arrangements in the solid structure (Moradinia and Teja, 1986). This behavior was also observed for the solid *n*-alkanes in methane (Suleiman and Eckert, 1995).

If one looks at how the solubility varies with temperature, one sees a rather complicated picture. Figure 2 presents the solubility of hexatriacontane ($C_{36}H_{74}$), in ethane at various temperatures (308.2 to 348.2 K). First, the normal melting temperature, T_m, of $C_{36}H_{74}$ is reached throughout the temperatures studied; therefore, we are dealing with both solid and liquid solubilities. Although T_m for $C_{36}H_{74}$ is ~348 K, the melting point depression of the heavy *n*-alkanes (*e.g.*, $C_{28}H_{58}$) has been found in CO_2 to be approximately 10 to 15 K (McHugh et al., 1984; Hess, 1987). A similar or perhaps larger melting point depression has been observed in ethane by V. S. Smith (Georgia Institute of Technology, personal communication, 1994). A possible explanation for the results presented is that there are two crossover regions, one for the solute in its liquid form (upper region) and one for when the solute is in its solid state (lower region). This behavior is very interesting, since the injection into the chromatographic system is

Table 4. Mole Fraction Solubility, *S*, and Capacity Factors, k$_i$, for $C_{29}H_{60}$ in C_2H_6

		P/bar									
T/K		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	12.0	10.0		8.6		4.9	3.2	1.8	0.71	
	k_i	0.13	0.15		0.19		0.36	0.58	1.2	3.5	
333.2	10^2S	9.7			6.5		6.0	4.3	3.6	2.6	1.5
	k_i	0.14			0.22		0.25	0.37	0.46	0.72	1.62
328.2	10^2S	9.6			7.1		5.4	4.0	3.3	2.3	1.4
	k_i	0.13			0.18		0.25	0.35	0.45	0.71	1.4
318.2	10^2S	1.5		1.1	1.2	1.1	0.85	0.70	0.54	0.37	0.22
	k_i	0.24		0.32	0.31	0.33	0.45	0.56	0.75	1.2	2.2
308.2	10^3S	18.0			13.0		7.9	5.9	4.7	3.1	1.7
	k_i	0.11			0.15		0.25	0.35	0.45	0.71	1.4

Table 5. Mole Fraction Solubility, *S*, and Capacity Factors, k$_i$, for $C_{32}H_{66}$ in C_2H_6

		P/bar									
T/K		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	10.0	8.5		6.2		3.2	2.1	1.1	3.8	
	k_i	0.14	0.17		0.23		0.46	0.76	1.6	5.3	
333.2	10^2S	7.9			5.3		4.5	3.5	2.7	1.8	1.3
	k_i	0.16			0.25		0.31	0.42	0.58	0.98	1.8
328.2	10^2S	6.1			4.4		3.3	2.4	2.0	1.4	0.86
	k_i	0.14			0.20		0.28	0.41	0.53	0.80	1.58
318.2	10^3S	8.3		6.3	6.4	5.7	4.7	4.3	2.9	1.9	1.2
	k_i	0.27		0.36	0.36	0.41	0.52	0.58	0.88	1.4	2.6
308.2	10^3S	9.4			6.8		4.5	3.2	2.5	1.4	0.91
	k_i	0.13			0.18		0.28	0.40	0.53	0.97	1.6

Table 6. Mole Fraction Solubility, *S*, and Capacity Factors, k$_i$, for $C_{33}H_{68}$ in C_2H_6

		P/bar									
T/K		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	9.8	7.9		6.2		3.2	2.1	1.1	0.38	
	k_i	0.14	0.18		0.24		0.49	0.83	1.8	6.0	
333.2	10^2S	4.1			3.4		3.4	3.4	2.5	1.9	1.5
	k_i	0.31			0.39		0.42	0.44	0.61	0.89	1.5
328.2	10^2S	5.0			3.6		2.8	1.8	1.6	1.1	0.64
	k_i	0.15			0.22		0.30	0.49	0.57	0.87	1.9
318.2	10^3S	7.5		5.9	5.7	4.7	4.0	3.6	2.4	1.5	0.87
	k_i	0.26		0.34	0.35	0.44	0.53	0.61	0.94	1.5	3.0
308.2	10^3S	7.7			5.3		3.4	2.4	1.9	1.3	0.70
	k_i	0.13			0.19		0.30	0.43	0.57	0.87	1.7

Table 7. Mole Fraction Solubility, *S*, and Capacity Factors, k$_i$, for $C_{36}H_{74}$ in C_2H_6

		P/bar									
T/K		240	220	210	200	180	160	140	120	100	80
348.2	10^2S	8.2	6.5		4.9		2.4	1.5	0.73	0.23	
	k_i	0.16	0.21		0.28		0.61	1.1	2.4	9.0	
333.2	10^2S	3.6			3.2		2.7	2.4	1.9	1.4	0.83
	k_i	0.35			0.41		0.52	0.61	0.81	1.2	2.7
328.2	10^3S	33.0			23.0		17.0	9.6	9.9	6.5	4.1
	k_i	0.17			0.24		0.34	0.64	0.65	1.1	2.1
318.2	10^3S	3.7		3.1	2.9	2.3	2.1	1.9	1.3	0.85	0.50
	k_i	0.35		0.43	0.47	0.60	0.68	0.76	1.2	1.9	3.5
308.2	10^4S	4.5			3.3		2.1	1.5	1.1	0.71	0.46
	k_i	0.14			0.20		0.32	0.45	0.63	1.1	1.7

independent of the physical state of the solute. Even at the conditions where the solute is in its solid form, since the injections are done with the solids dissolved in pentane, the actual molecules injected are difficult to visualize as solids.

The behavior presented with $C_{36}H_{74}$ appears in all solutes studied ($C_{24}H_{50}$ to $C_{36}H_{74}$), because of their normal melting points between 323 and 348 K. For some of the other solutes the picture is more complicated since the so-called two crossover regions might be closer together. This behavior might also explain all of the inconsistencies observed by Smith (personal communication, 1994), when trying to measure the solubilities of the *n*-alkanes in ethane using a conventional flow method. Any misaccounted

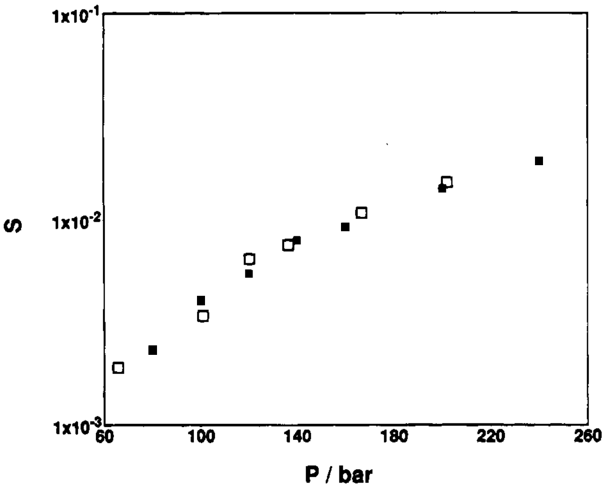

Figure 1. Mole fraction solubility, S, versus pressure, P, for $C_{28}H_{58}$ in C_2H_6 at 308.2 K: ■, this investigation; □, Moradinia and Teja (1986).

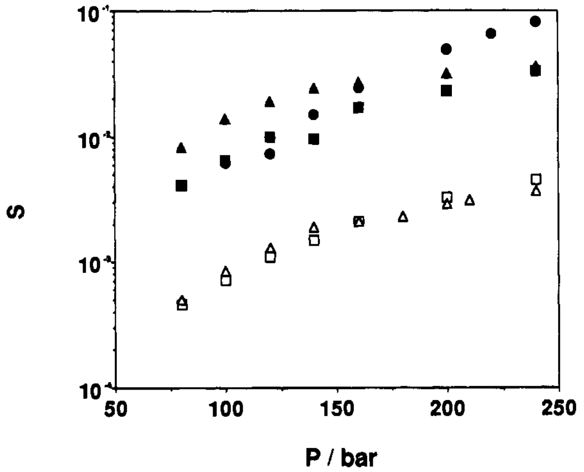

Figure 2. Mole fraction solubility, S, versus pressure, P, for $C_{36}H_{74}$ in C_2H_6 at various temperatures; □, 308.2 K; △, 318.2 K; ■, 328.2 K; ▲, 333.2 K; ●, 348.2 K.

thermal changes (*e.g.*, lines after high-pressure cell) would make the solubility change in unpredicted ways.

It is important to mention that another explanation of the effect of temperature in the solubility of the n-alkanes might be the inability to predict accurately the effect of temperature on $C_i(T)$. When one looks at eq 1, one notices that the shape of the solubility isotherm is given by the capacity factors and the density (nothing else depends on pressure). The constant $C_i(T)$ provides the location on the y-axis, and any errors in its prediction might be crucial to the picture presented in Figure 2. When looking at where the temperature effect comes in $C_i(T)$ (eq 2), one sees three temperature-dependent parameters: γ_i^∞, $P_{i,\mathrm{vap}}$, and $P_{i,\mathrm{sub}}$. The $\ln \gamma_i^\infty$ *vs* $1/T$ that provides RST seems to be reasonable temperature dependence for the temperature range studied (308.2 to 348.2 K). The $P_{i,vap}$ and $P_{i,sub}$ were determined according to the procedure described elsewhere (Suleiman, 1995), and they are supported not only with experimental data but also with reasonable consistency, since both correlations seem to agree within their limits at the triple point.

This method can also be used to determine partial molar volumes at infinite dilution, $\bar{V}_i^\infty$, from the density derivative of the capacity factors (van Wasen *et al.*, 1980; Shim and Johnston, 1991). Figure 3 presents the $\bar{V}_i^\infty$ for the solid paraffins studied in this investigation ($C_{24}H_{50}$ to $C_{36}H_{74}$) in C_2H_6 at 308.2 K. $\bar{V}_i^\infty$ values smaller than V_i (421−614 cm^3/mol) indicate the still strong solvent−solute interactions; however, there does not seem to be any trend as the carbon number of the solutes increases, not even between even- and odd-numbered n-alkanes. The lack of trends in the $\bar{V}_i^\infty$ results can also be observed from the solubilities of Moradinia and Teja (1986, 1987, 1988), converted to $\bar{V}_i^\infty$ using the argument of Kumar and Johnston (1988). This suggests that the solvation process for the n-alkanes in ethane is very complex, perhaps because of the different packing structures in the solid n-alkanes. Another explanation for these results may be that the inaccuracy of differentiating integral data does not support the precision required to understand the solvation process of the heavy paraffins in ethane. At least, the qualitative solvating picture seems to agree with the expected results, as well as with those observed in methane. Also, the decreasing $\bar{V}_i^\infty$ data with decreasing pressure agree with the behavior expected as one approaches the critical point of the solvent (Foster et al., 1989; Eckert et al., 1986; Abraham and Ehrlich, 1975; Khazanova and Saminskaya, 1968).

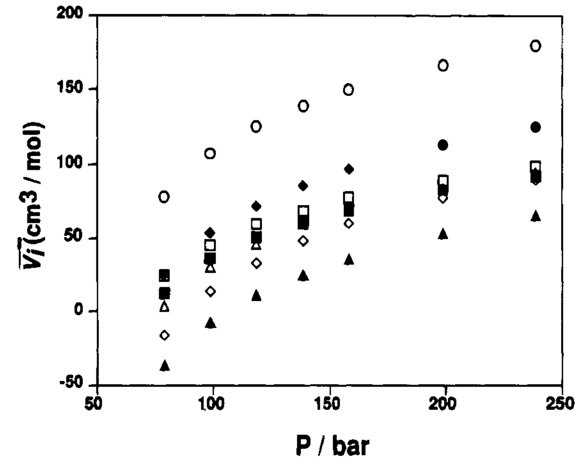

Figure 3. Partial molar volume at infinite dilution, $\bar{V}_i^\infty$, of various n-alkanes in ethane at 308.2 K: □, $C_{24}H_{50}$; ■, $C_{25}H_{52}$; △, $C_{28}H_{58}$; ▲, $C_{29}H_{60}$; ◇, $C_{32}H_{66}$; ◆. $C_{33}H_{68}$; ○, $C_{36}H_{74}$.

Although partial molar enthalpies at infinite dilution, $\bar{H}_i^\infty$, can be obtained from the temperature derivative of the capacity factors (van Wasen *et al.*, 1980; Shim and Johnston, 1991), we found that for the solids studied the relationship between the capacity factors and temperature was not linear over the range of temperatures studied. The nonlinearity of the log of the chromatographic capacity factors versus temperature has also been observed by Bartle *et al.* (1988) for various nonpolar solids in carbon dioxide. Bartle and co-workers found that the capacity factors first increased with increasing temperature, approached a maxima, and then decreased. Their explanation agrees with that offered in the interpretation of the effect of temperature in the solubility of solids in supercritical fluids, *retrograde vaporization* (Hoyer, 1985; Johnston and Eckert, 1981; McHugh, 1986; Wong and Johnston, 1986). This phenomenon consists of two competing effects: the density of the supercritical fluid (which decreases with increasing temperature) and the sublimation pressure of the solid (which increases with increasing temperature). Since the chromatographic capacitance factors are inversely proportional to the solubility, these effects are opposite to those observed in the study of the solubility of solids in SCFs. Our results follow this behavior; however, the melting point is within the temperature range studied, complicating our picture. At the highest temperature studied (348 K), the capacity factors are highest, but at this temperature all of the solutes studied were in their liquid state. The *retrograde vaporization* phenomenon was not observed for the liquid *n*-alkanes in methane, perhaps because of their higher saturation (vapor) pressure and/or the fact that our investigation was performed removed from the critical temperature of methane (190.7 K).

Second virial coefficients, B_{12}, for the *n*-alkanes in ethane were obtained from the chromatographic capacity factors. The results compared well with those obtained from Moradinia and Teja (1986, 1987, 1988). Although no data were found for the solutes we studied in ethane, data exist for other *n*-alkanes in ethane, which show a decrease in B_{12} with increase in solute carbon number. Our results are in agreement with that trend. For example, B_{12} for $C_{28}H_{58}$ in C_2H_6 from our investigation is (-2073 ± 105) cm^3/mol at 308.2 K. Dymond and Smith (1980), tabulated -928 cm^3/mol for $C_{16}H_{34}$ in C_2H_6 at 348.2 K and -242 cm^3/mol for C_5H_{12} in C_2H_6 at 298.2 K. The comparison was done at different temperatures due to the lack of data at one temperature; however, the decreasing trend with increasing solute carbon number seems clear. The decrease in B_{12} agrees with the solvation picture presented by the $\bar{V}_i^\infty$ results. It is clear that the virial equation truncated after the second coefficient is inadequate to characterize Φ_i^∞ in systems at these densities; however, in this work, as in the work of Moradinia and Teja (1986, 1987, 1988), uncertainties in higher coefficients preclude their use.

In conclusion, chromatographic capacity factors and their corresponding solubilities for various *n*-alkanes in C_2H_6 have been presented. Partial molar volumes at infinite dilution have been obtained from the density derivative of the capacity factor data. Virial coefficients have also been obtained from the fugacity coefficients at infinite dilution.

Acknowledgment

The discussions with Frederic Pouillot, Martin S. Schiller, Professor Amyn S. Teja, and Vicky Smith are very much appreciated.

Nomenclature

B_{12}	second virial coefficient
$C_i\,(T)$	constant for a particular solute, chromatographic column, and temperature, T
$\bar{H}_i^\infty$	partial molar enthalpy at infinite dilution
k_i	chromatographic capacity factor
$k^\circ_{H,i}$	Henry constant for solute i in the stationary phase at the reference pressure, P° ($k^\circ_{H,i} = P_{i,\mathrm{vap}}\gamma_i^\infty$)
P	pressure
P°	reference pressure
$P_{i,\mathrm{sat}}$	saturation (vapor/sublimation) pressure of solute i
$P_{i,\mathrm{sub}}$	sublimation pressure of solute i
$P_{i,\mathrm{vap}}$	vapor pressure of solute i
R	universal gas constant
T	temperature
t_r	retention time of solute i
t_0	retention time of an unretained solvent
V^m	physical volume of the mobile phase inside the chromatographic column
V^s	physical volume of the stationary phase
V_m^m	molar volume of the mobile phase
V_m^s	molar volume of the stationary phase
V_i	molar volume of solute i
$\bar{V}_i^\infty$	partial molar volume of solute i at infinite dilution
y_i	mole fraction of solute i in the mobile phase (solubility)

Greek Letters

γ_i^∞	infinite dilution activity coefficient of solute i in the stationary phase
Φ_i^∞	fugacity coefficient of solute i in the mobile phase at infinite dilution

Superscripts

∞	infinitely diluted
m	mobile phase
o	reference state
s	stationary phase

Literature Cited

Abraham, K. P.; Ehrlich, P. Partial Molar Volume of a Polymer in Supercritical Solution. *Macromolecules* **1975**, *8*, 944–946.

Bartle, K. D.; Clifford, A. A.; Jacob, P. K.; Shilstone, G. F. Studies of the Temperature Dependence of Retention in Supercritical Fluid Chromatography. *J. Chem. Soc., Faraday Trans.* **1988**, *12*, 4487–4493.

Drake, B. D. Prediction of Sublimation Pressures of Low Volatility Solids. Ph.D. Thesis, Universtiy of South Carolina, 1993.

Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures. A Critical Compilation*; Offord University Press: New York, 1980.

Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Kim, S. Solute Partial Molal Volumes in Supercritical Fluids. *J. Phys. Chem.* **1986**, *90*, 2738–2746.

Fedors, R. F. A Method for Estimating Both the Solubility Parameters and Molar Volumes of Liquids. *Polym. Eng. Sci.* **1974**, *14*, 147.

Foster, N. R.; Macnaughton, S. J.; Chaplin, R. P.; Wells, T. Critical Locus and Partial Molar Volume Studies of the Benzaldehyde-Carbon Dioxide Binary System. *Ind. Eng. Chem. Res.* **1989**, *28*, 1903–1907.

Hess, B. S. Supercritical Fluids: Measurement and Correlation Studies of Model Coal Compound Solubility and the Modeling of Solid-Liquid-Fluid Equilibria. Ph.D. Thesis, University of Illinois, IL, 1987.

Hildebrand, J. H.; Prausnitz J. M.; Scott, R. L. *Regular and Related Solutions; The Solubility of Gases, Liquids, and Solids;* van Nostrand Reinhold New York, 1970.

Hoyer, G. G. Extraction with Supercritical Fluids: Why, How, and So What. *CHEMTECH* **1985**, *15*, 440–448.

Johnston, K. P.; Eckert, C. A. An Analytical Carnahan-Starling-van der Waals Model for the Solubility of Hydrocarbon Solids in Supercritical Fluids. *AIChE J.* **1981**, *27*, 773–779.

Khazanova, N. E.; Saminskaya, E. E.; Volume Properties of Binary Gaseous Solutions Close to the Critical Pressures and Temperatures of the Pure Components. *Russ. J. Phys. Chem.* **1968**, *42*, 676–682.

Kumar, S. K.; Johnston, K. P. Modeling the Solubility of Solids in Supercritical Fluids with Density as the Independent Variable. *J. Supercrit. Fluids* **1988**, *1*, 15–22.

McHugh, M. *Extraction with Supercritical Fluids. and Recent Developments in Separation Science*; CRC Press: Boca Raton, FL, 1986.

McHugh, M. A.; Seckner, A. J.; Yogan, T. J. High Pressure Phase Behavior of Binary Mixtures of Octacosane and Carbon Dioxide. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 493.

Moradinia, I.; Teja, A. S. Solubilities of Solid n-Octacosane, n-Triacontane and n-Dotriacontane in Supercritical Ethane. *Fluid Phase Equilib.* **1986**, *28*, 199–209.

Moradinia, I.; Teja, A. S. Solubilities of Five Solid n-alkanes in Supercritical Ethane. *Supercrit. Fluids; ACS Symp. Ser.* **1987**, *329*, 130–137.

Moradinia, I.; Teja, A. S. Solubilities of Solid n-Nonacosane and n-Tritriacontane in Supercritical Ethane. *J. Chem. Eng. Data* **1988**, *33*, 240–242.

Morgan, D. L.; Kobayashi, R. Direct Vapor Pressure Measurements of Ten n-Alkanes in the C10 to C28 Range. *Fluid Phase Equilibr.* **1994**, *97*, 211–242.

Rijkers, M. P. W. M.; Malais, M.; Peters, C. J.; de Swann Arons, J. Measurement on the Phase Behavior of Binary Hydrocarbon Mixtures for Modeling the Condensation Behavior of Natural Gas. Part I. The System Methane + Decane. *Fluid Phase Equilib.* **1992**, *71*, 143–168.

Shim, J. J.; Johnston, K. P. Phase Equilibria, Partial Molar Enthalpies, and Partial Molar Volumes Determined by Supercritical Fluid Chromatography. *J. Phys. Chem.* **1991**, *95*, 353–360.

Suleiman, D. Measurement and Prediction of Phase Equilibrium Properties at Infinite Dilution: Alkanes in Natural Gases and Organic Solvents in Aqueous Solutions. Ph.D. Thesis, Georgia Institute of Technology, Atlanta, GA, 1995.

Suleiman, D.; Eckert, C. A. Phase Equilibria of Alkanes in Natural Gas Systems. 1. Alkanes in Methane. *J. Chem. Eng. Data* **1995**, *40*, 2–11.

Suleiman, D.; Gurdial, G. S.; Eckert, C. A. An Appparatus for Phase Equilibria of Heavy Paraffins in Supercritical Fluids. *AIChE J.* **1993**, *39*, 1257–1260.

van Wasen, U.; Swaid, I.; Schneider, G. M. Physicochemical Principles and Applications of Supercritical Fluid Chromatography. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 575–587.

Wong, J. M.; Johnston, K. P. Solubilization of Biomolecules in Carbon Dioxide Based Supercritical Fluids. *Biotechnol. Prog.* **1986**, *2*, 29.

Younglove, B. A.; Ely, J. F. Thermophysical Properties of Fluids. II. Methane, Ethane, Propane, Isobutane, and Normal Butane. *J. Phys. Chem. Ref. Data* **1987**, *16*, 577–798.

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