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Solubilities of Nitrogen in Heavy Normal Paraffins from 323 to 423 K at Pressures to 18.0 MPa

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The solubilities of nitrogen in selected *n*-paraffin hydrocarbons (decane, eicosane, octacosane, hexatriacontane) were measured using a static equilibrium cell over the temperature range from 323.2 to 423.2 K at pressures to 18.0 MPa. The uncertainty in the measured solubilities is estimated to be less than 0.001 in mole fraction. The data were analyzed using the Soave−Redlich−Kwong (SRK) and Peng−Robinson (PR) equations of state. In general, the two equations represent the experimental data well when a single interaction parameter C_{ij} is used for each binary system. The data display a trend of increasing solubility of nitrogen with increased temperature, pressure, and *n*-paraffin chain length.

Introduction

Industrial processes such as petroleum refining, coal conversion, enhanced oil recovery, and supercritical separations have created a demand for phase equilibrium data for mixtures of light solute gases (e.g., methane, ethane, carbon dioxide, carbon monoxide, hydrogen, and nitrogen) with heavy hydrocarbon solvents. Such mixtures challenge current predictive models for describing vapor−liquid phase behavior. Prior to the work reported here, we have measured the solubilities of methane, ethane, hydrogen, carbon dioxide, and carbon monoxide in systematically chosen solvents, including heavy paraffinic, naphthenic, and aromatic hydrocarbons (Anderson et al., 1986; Darwish, 1991; Darwish et al., 1993; Gasem and Robinson, 1985; Gasem et al., 1989; Park et al., 1995; Srivatsan et al., 1995).

In this study, we report measurements of the solubility of nitrogen in decane, eicosane, octacosane, and hexatriacontane. These data cover the temperature range 323.2−423.2 K at pressures up to 18.0 MPa, and they complement our results for nitrogen in naphthenic and aromatic solvents (Gao et al., 1999a). The data have been correlated using the Soave−Redlich−Kwong (SRK) (Soave, 1972) and Peng−Robinson (PR) (Peng and Robinson, 1976) equations of state (EOSs), with the necessary binary interaction parameter C_{ij} regressed from the experimental data.

Experimental Method

A variable-volume, static-type blind equilibrium cell was used in this study. The apparatus and procedures have been described previously (Gao et al., 1999b). The measurement uncertainties are estimated to be 0.1 K in temperature and less than 0.001 in mole fraction. The estimated uncertainty in the bubble point pressure is on the order of 0.07 MPa for the systems studied here. A detailed error analysis is given by Darwish (1991).

Materials

Nitrogen having a stated purity of 99.99+ mol % was supplied by Liquid Air, Inc. The decane, eicosane, and octacosane were supplied by the Aldrich Chemical Co., with stated purities of 99+ mol %. The hexatriacontane was from Alfa Chemical Company with a purity of 99+ mol %. No further purification of these chemicals was attempted.

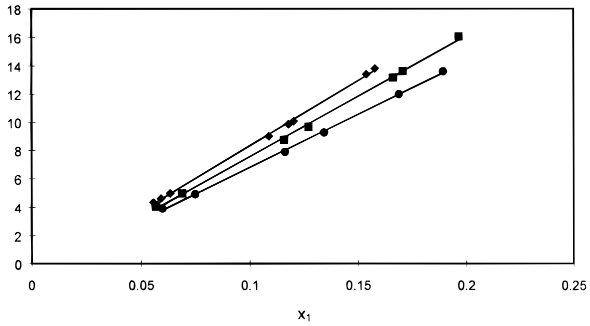

Figure 1. Solubility of nitrogen (1) in decane (2) at (◆) 344.3 K, (■) 377.6 K, and (●) 410.9 K.

Results and Data Correlation

The experimental data are presented in Table 1. The effects of temperature and pressure on the solubilities are illustrated in Figure 1 for nitrogen in decane. A trend of increasing solubility (liquid mole fraction of nitrogen) with increased temperature and pressure is observed; results for the other systems are similar. The solubility of nitrogen in the *n*-paraffins increases with the chain length of the solvent molecule.

Comparisons of our nitrogen + decane data with those of Azarnoosh and McKetta, 1963, and those of Llave and Chung, 1988, at 344.3 K, 377.6 K, and 410.9 K are shown in Figures 2−4. The comparisons are shown in terms of the deviation δx in the solubility (liquid mole fraction) predicted by the PR EOS from the measured value, that is, $\delta x = x_{\text{expt}} - x_{\text{EOS}}$. The solubility values for the EOSs were calculated using values of the interaction parameter C_{ij} regressed from our data at each temperature of interest. These figures facilitate a sensitive analysis of differences in data sets. The difference in the deviations between data sets (not the magnitude of the deviation of either set from the reference equation) is of interest in these data comparisons, since the difference in deviations (δx) between data sets is independent of the reference model employed.

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Table 1. Solubility of Nitrogen in *n*-Paraffin Hydrocarbons

x_1	p/MPa	x_1	p/MPa
Decane			
344.3 K			
0.0556	4.33	0.1178	9.84
0.0590	4.61	0.1202	10.06
0.0633	4.97	0.1539	13.40
0.1087	8.99	0.1578	13.81
377.6 K			
0.0568	4.05	0.1662	13.15
0.0689	4.97	0.1708	13.63
0.1158	8.73	0.1967	16.04
0.1271	9.66		
410.9 K			
0.0598	3.91	0.1343	9.25
0.0749	4.92	0.1690	11.99
0.1162	7.89	0.1894	13.61
Eicosane			
323.2 K			
0.0610	4.49	0.1292	10.61
0.0689	5.13	0.1413	11.90
0.0704	5.25	0.1789	16.22
0.0967	7.54	0.1866	17.23
373.2 K			
0.0629	4.03	0.1364	9.74
0.0715	4.61	0.1639	12.10
0.1199	8.33	0.1905	14.61
423.2 K			
0.0679	3.83	0.1445	8.89
0.0930	5.38	0.1728	11.09
0.1278	7.76	0.2121	14.24
Octacosane			
348.2 K			
0.0726	4.30	0.1900	13.70
0.1108	6.93	0.1909	13.70
0.1245	8.04	0.2181	16.47
0.1334	8.70		
373.2 K			
0.0862	4.87	0.1698	10.89
0.0988	5.63	0.2071	14.18
0.1466	9.08	0.2289	16.10
423.2 K			
0.0896	4.46	0.1951	11.07
0.1010	5.11	0.2320	13.94
0.1689	9.31	0.2578	16.01
Hexatriacontane			
373.2 K			
0.1054	5.30	0.2089	12.23
0.1197	6.10	0.2628	16.81
0.1934	11.10	0.2749	17.99
423.2 K			
0.1185	5.28	0.2263	11.71
0.1240	5.56	0.2747	15.21
0.2040	10.22	0.2970	17.11

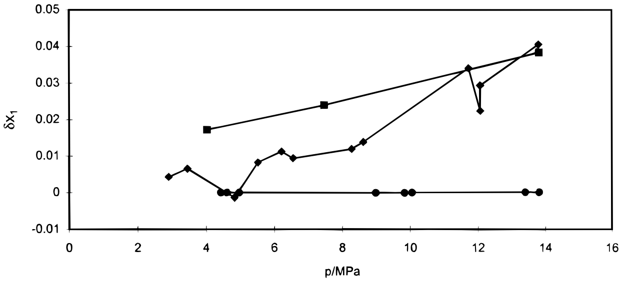

Figure 2. Comparison of solubility data for nitrogen (1) in decane (2) at 344.3 K: (●) this work; (◆) Azarnoosh and McKetta; (■) Llave and Chung. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

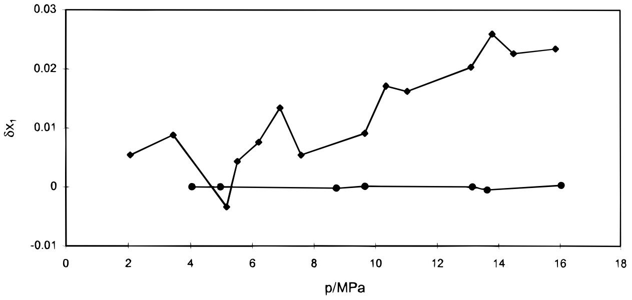

Figure 3. Comparison of solubility data for nitrogen (1) in decane (2) at 377.6 K: (●) this work; (◆) Azarnoosh and McKetta. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

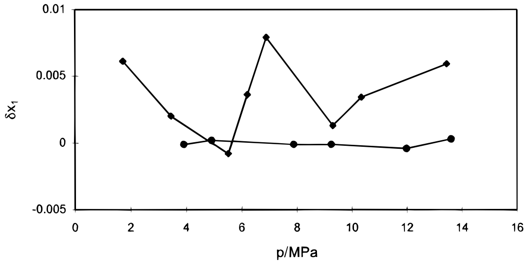

Figure 4. Comparison of solubility data for nitrogen (1) in decane (2) at 410.9 K: (●) this work; (◆) Azarnoosh and McKetta. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

Table 2. Critical Pressures p_c Critical Temperatures T_c and Acentric Factors ω Used in the Equations of State

component	p_c/MPa	T_c/K	ω	ref
nitrogen	3.390	126.2	0.039	Reid et al., 1987
decane	2.12	617.7	0.489	Reid et al., 1987
eicosane	1.11	767.0	0.907	Reid et al., 1987
octacosane	0.661	827.4	1.162	Gasem et al., 1993
hexatriacontane	0.428	864.0	1.423	Gasem et al., 1993

That is, for two data sets A and B, at a fixed temperature and pressure: $\delta x_A - \delta x_B = [(x_{expt})_A - (x_{EOS})] - [(x_{expt})_B - (x_{EOS})] = (x_{expt})_A - (x_{expt})_B$. Figures 2 and 3 show obvious disagreement between our data and those of Llave and Chung and of Azarnoosh and McKetta. Figure 4 (note the more sensitive scale on the y-axis relative to Figures 2 and 3) shows better agreement of our data at 410.9 K with those of Azarnoosh and McKetta, with deviations within 0.005 in mole fraction for most of the data points. No literature data for the other systems are available for comparison.

The RKS and PR EOSs were used to correlate the experimental data. The PR EOS is given below.

$$p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \tag{1}$$

where

$$a = a_c \alpha(T) \tag{2}$$

$$b = 0.07780 RT_c/p_c \tag{3}$$

and

$$a_c = 0.45724 R^2 T_c^{\ 2}/p_c \tag{4}$$

$$\alpha(T)^{1/2} = 1 + k(1 - T_r^{\ 1/2}) \tag{5}$$

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{6}$$

where p is the pressure, R is the gas constant, T is the temperature, a and b are EOS constants, v is the molar

Table 3. SRK and PR EOS Representations of the Nitrogen Solubility

T/K	SRK parameter (PR Parameter) C_{12}	deviation in predicted nitrogen mole fraction		SRK Henry's constant (PR Henry's constant) MPa
		rms	|max|	
		Decane		
344.3	0.2123	0.0006	0.0008	71.8
	(0.2050)	(0.0005)	(0.0010)	(72.1)
377.6	0.2089	0.0010	0.0015	65.9
	(0.1953)	(0.0007)	(0.0016)	(66.3)
410.9	0.2148	0.0013	0.0016	59.8
	(0.1901)	(0.0008)	(0.0018)	(60.2)
344.3, 377.6, and 410.9	0.2116	0.0011	0.0022	
	(0.1993)	(0.0015)	(0.0041)	
		Eicosane		
323.2	0.2847	0.0003	0.0006	66.8
	(0.2833)	(0.0002)	(0.0003)	(66.9)
373.2	0.2587	0.0004	0.0009	59.1
	(0.2492)	(0.0004)	(0.0007)	(59.7)
423.2	0.2361	0.0004	0.0006	51.8
	(0.2153)	(0.0006)	(0.0010)	(52.8)
323.2, 373.2, and 423.2	0.2714	0.0032	0.0071	
	(0.2635)	(0.0050)	(0.0098)	
		Octacosane		
348.2	0.4609	0.0009	0.0014	52.9
	(0.4356)	(0.0006)	(0.0011)	(53.3)
373.2	0.4647	0.0010	0.0019	49.8
	(0.4309)	(0.0007)	(0.0011)	(50.4)
423.2	0.4753	0.0018	0.0034	43.6
	(0.4209)	(0.0009)	(0.0011)	(44.5)
348.2, 373.2, and 423.2	0.4646	0.0014	0.0027	
	(0.4312)	(0.0015)	(0.0043)	
		Hexatriacontane		
373.2	0.6377	0.0033	0.0045	41.1
	(0.5939)	(0.0029)	(0.0037)	(41.7)
423.2	0.6895	0.0037	0.0048	36.2
	(0.6162)	(0.0027)	(0.0034)	(37.1)
373.2 and 423.2	0.6546	0.0052	0.0092	
	(0.6018)	(0.0035)	(0.0054)	

volume, T_c is the critical temperature, p_c is the critical pressure, T_r is the reduced temperature, $\alpha(T)$ expresses the temperature dependence in the parameter a, and ω is the acentric factor.

To apply the equations of state to mixtures, the values of a and b were determined using the mixing rules (Gasem et al., 1989):

$$a = \sum_i^N \sum_j^N z_i z_j (1 - C_{ij})(a_i a_j)^{1/2} \tag{7}$$

$$b = \sum_i^N z_i b_i \tag{8}$$

where z_i is the mole fraction of component i in a mixture, z_j is the mole fraction of component j in a mixture, and N is the number of components in the mixture.

In eqs 7 and 8, the summations are over all chemical species, and C_{ij} is an empirical interaction parameter characterizing the binary interactions between components i and j. Values of this parameter were determined by fitting the experimental data to minimize the objective function SS, which represents the sum of relative differences in the calculated and experimental bubble point pressures at fixed temperatures and compositions:

$$\mathrm{SS} = \sum_i^n \left(\frac{p_{\text{calc}} - p_{\text{exp}}}{p_{\text{exp}}} \right)_i^2 \tag{9}$$

where n is the number of data points, p_{calc} is the calculated pressure, and p_{exp} is the experimental pressure. Further details of the data reduction technique used in this study were given by Gasem (Gasem et al., 1985; Gasem, 1986). The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) required by the EOSs, together with their literature sources, are presented in Table 2. The parameters for decane and eicosane are from Reid, 1987. Those for octacosane and hexatriacontane are from Gasem et al. (1993).

Details of the EOS representations of the solubilities are shown in Table 3. Both SRK and PR EOSs are capable of describing the data with rms errors of about 0.002 (0.003 for hexatriacontane) in mole fraction when one interaction parameter C_{ij} is used for each isotherm. When a single value of the interaction parameter is regressed for a given hydrocarbon solvent over the complete temperature range, the rms errors using SRK are 0.0011, 0.0032, 0.0014, and 0.0052 for nitrogen in decane, eicosane, octacosane, and hexatriacontane, respectively.

Henry's Constants

By definition, Henry's constant of a solute (1) in a solvent (2) is given as

$$H_{1,2} = \lim_{x_1 \to 0} (\hat{f}_1^{\,\mathrm{L}}/x_1) = \lim_{x_1 \to 0} (\hat{\varphi}_1^{\,\mathrm{L}} p) \tag{10}$$

where $\hat{f}_1^{\mathrm{L}}$, x_1, and $\hat{\varphi}_1^{\mathrm{L}}$ are the liquid-phase fugacity, the liquid mole fraction, and the liquid-phase fugacity coefficient, respectively, of the solute (component 1).. Estimates for Henry's constant were obtained for the present data using both the SRK and PR equations of state in accordance with the above definition. Values for the Henry's constants, along with the interaction parameters associated with them, are given in Table 3. In general, the SRK EOS produces lower $H_{1,2}$ values (~1%) than those obtained from the PR EOS.

Conclusions

Measurements have been obtained for the solubilities of nitrogen in selected *n*-paraffin hydrocarbons (decane, eicosane, octacosane, hexatriacontane) at temperatures from 323.2 K to 423.2 K at pressures up to 18.0 MPa. The data are described well by the SRK and PR EOSs. Interaction parameters and Henry's constants for the SRK and PR EOSs have been obtained for the binary systems studied.

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