J. Chem. Eng. Data **1999,** *44,* 185−189

Solubilities of Nitrogen in Selected Naphthenic and Aromatic Hydrocarbons at Temperatures from 344 to 433 K and Pressures to 22.8 MPa

Wuzi Gao, Khaled A. M. Gasem, and Robert L. Robinson, Jr.*

School of Chemical Engineering, Oklahoma State University, Stillwater, Oklahoma 74078-0537

The solubilities of nitrogen in selected naphthenic (cyclohexane and *trans*-Decalin) and aromatic (benzene, naphthalene, 1-methylnaphthalene, phenanthrene, pyrene) solvents were measured using a static equilibrium cell over the temperature range from 344.3 to 433.2 K at pressures to 22.8 MPa. The uncertainty in these measurements is estimated to be less than 0.001 in mole fraction. The Peng−Robinson equation of state was shown to represent the experimental data with root-mean-square deviations of about 0.002 when a single interaction parameter (C_{ij}) is used for each binary system.

Introduction

In the recent past, we have obtained substantial amounts of data on equilibrium phase compositions for binary mixtures of heavy hydrocarbon solvents with a variety of supercritical solutes, including hydrogen, methane, ethane, carbon monoxide, and carbon dioxide (Anderson et al., 1986; Darwish, 1991; Darwish et al., 1993; Gasem et al., 1989; Gasem and Robinson, 1985; Park et al., 1995a,b; Srivatsan et al., 1995). The present data on nitrogen-containing systems complement our earlier studies.

The data we have acquired are designed to facilitate the development and testing of models for predicting the phase behavior of asymmetric mixtures, which contain small gas molecules in heavy hydrocarbon solvents. Such mixtures provide a severe test of current predictive models and their associated mixing theories (Park et al., 1995).

In the present work, measurements were made of the solubilities of nitrogen in several naphthenic (cyclohexane and *trans*-Decalin) and aromatic (benzene, naphthalene, 1-methylnaphthalene, phenanthrene, pyrene) hydrocarbons. The data have been correlated using the Peng−Robinson (Peng and Robinson, 1976) equation of state (PR EOS). Some literature information exists for nitrogen + cyclohexane, nitrogen + benzene, and nitrogen + naphthalene within our range of experimental conditions; however, no data have been reported previously for the other systems. Thus, the present measurements provide valuable new information.

Experimental Method

The experimental apparatus and procedures have been described by Darwish (Darwish, 1991; Darwish et al., 1993) and are summarized briefly here.

Phase equilibrium is established in a variable-volume, thermostated, static-type blind cell. Two steel balls are placed in the equilibrium cell, and the cell can be rocked 45° above and below the horizontal position to hasten the establishment of equilibrium. The effective volume of the cell can be varied by the introduction or withdrawal of mercury.

A known amount of degassed liquid solvent is injected volumetrically into the initially evacuated equilibrium cell. A known amount of solute gas is then injected into the rocking cell from a gas-injection pump. After each solute injection, the bubble point pressure of the mixture is determined by sequentially injecting known amounts of mercury into the equilibrium cell to alter the system volume. After each mercury injection, the equilibrium cell is rocked to bring the system to equilibrium, and the pressure is recorded. The bubble point pressure (for the mixture of known composition) is identified graphically from the discontinuity in a pressure vs total-volume-of-mercury-injected plot as the mixture passes from the more compressible two-phase state to the less compressible single-liquid-phase state. Additional solute is then added to the cell and the above procedure repeated at the new (higher) solute mole fraction.

Measurement uncertainties are estimated to be 0.1 K in temperature, 0.007 MPa in pressure, and less than 0.001 in composition (mole fraction). However, the estimated uncertainties (ϵ_{bp}) in the reported bubble point pressures (p_{bp}) at a specified mole fraction range from less than 0.1 MPa for the benzene system to about 0.5 MPa for the phenanthrene system, since $(\epsilon_{bp})^2 = (\epsilon_p)^2 + (d[p_{bp}]/dx)^2(\epsilon_x)^2$. Thus the total uncertainty in the reported bubble point pressure (at specified mole fraction) depends on both pressure and composition uncertainties and, in addition, the steepness of the bubble point pressure vs composition curve.

At the inception of this work, we performed measurements for two isotherms of nitrogen + decane at 344.3 K and 410.9 K to compare with the data of Tong (1994). These measurements were done to verify our experimental apparatus and techniques. The consistency of results from these two studies was evaluated by the comparisons shown in Figure 1. Results are shown in terms of deviations (δx) of the solubilities (liquid mole fraction nitrogen) from values predicted using the PR EOS, using temperature independent C_{ij} values determined from the combined data sets. The difference in the δx values between data sets (not the magnitude of the deviation of either set from the reference EOS model) is of interest in these comparisons, since the difference in δx between data sets is independent

---

* Corresponding author. E-mail: rrobins@okway.okstate.edu.

10.1021/je980187y CCC: $18.00

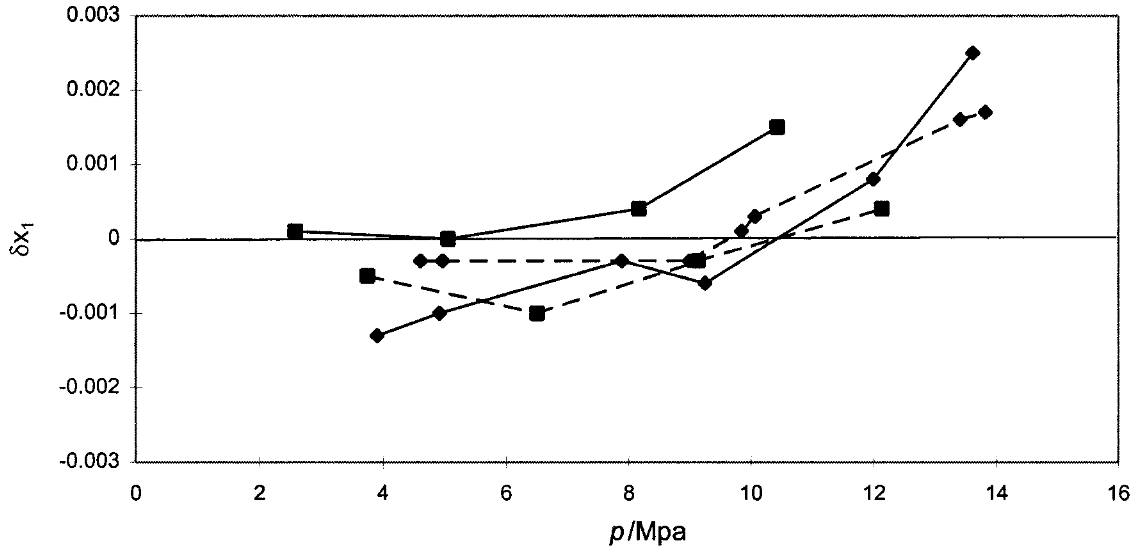

Figure 1. Comparison of solubility data for nitrogen (1) in decane (2): (◆) Tong (1994); (■) this work. Dashed lines for 344.3 K and solid lines for 410.9 K. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

of the reference model employed. That is, for two data sets A and B, at a fixed temperature and pressure, $\delta x_A - \delta x_B = [(x_{expt}) - (x_{EOS})]_A - [(x_{expt}) - (x_{EOS})]_B = (x_{expt})_A - (x_{expt})_B$. The results for nitrogen + decane are in good agreement; maximum differences in the two data sets are on the order of 0.001 in nitrogen mole fraction. Following this confirmation, we proceeded with measurements on the systems reported here.

Materials. The nitrogen had a stated purity of 99.995+ mol % and was supplied by Sooner Airgas, Inc. The decane (99+%), cyclohexane (99.9+%), *trans*-Decalin (99%), benzene (99.9+%), naphthalene (99+%), 1-methylnaphthalene (95%), phenanthrene (98%), and pyrene (98%) were supplied by Aldrich Chemical Co. No further purification of these chemicals was attempted.

Results and Discussion

The experimental data are presented in Tables 1 and 2. As expected, a trend of increasing nitrogen solubility with increasing temperature and pressure is observed for each of the solvents studied.

The PR EOS (Peng and Robinson, 1976) was used to correlate the experimental data:

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

where

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

$$b = 0.08664RT_c/p_c \tag{3}$$

$$a_c = 0.42748R^2T_c^{\,2}/p_c \tag{4}$$

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

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

where p is the pressure, R is the gas constant, T is the temperature, a and b are EOS constants, v is the molar 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 PR EOS to mixtures, the values of a and b were determined using the mixing rules (Gasem et al., 1989):

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

$$b = 0.5\sum_i^N \sum_j^N z_i z_j (1 + D_{ij})(b_i + b_j) \tag{8}$$

where z_k represents the mole fraction of component "k" in a mixture and N is the number of components in the mixture.

Table 1. Solubility of Nitrogen in Naphthenic Hydrocarbons

x_1	P/MPa	x_1	P/MPa
	Cyclohexane		
	366.5 K		
0.0168	2.08	0.0655	7.59
0.0292	3.46	0.0749	8.72
0.0400	4.68	0.0898	10.49
0.0500	5.80	0.0999	11.71
	410.9 K		
0.0187	2.16	0.0768	7.66
0.0349	3.51	0.0950	9.17
0.0497	5.08	0.1174	11.62
0.0650	6.34	0.1240	12.13
	trans-Decalin		
	344.3 K		
0.0292	4.15	0.0704	10.44
0.0426	6.05	0.0758	11.48
0.0592	8.65	0.0942	14.57
	377.6 K		
0.0310	3.93	0.0746	10.10
0.0452	5.99	0.0897	12.21
0.0599	7.86	0.1016	14.15
	410.9 K		
0.0313	3.74	0.0748	9.07
0.0482	5.75	0.0901	11.12
0.0598	7.19	0.1105	13.85

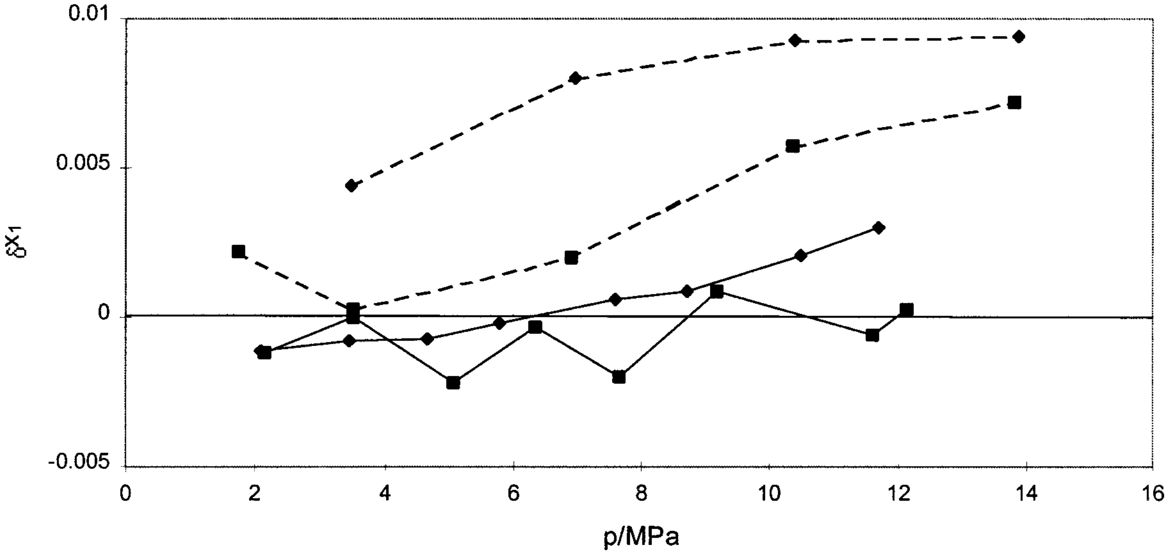

Figure 2. Comparison of solubility data for nitrogen (1) in cyclohexane (2): solid lines, this work; dashed lines, Shibate and Sandler (1989). (◆) 366.5 K; (■) 410.9 K. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

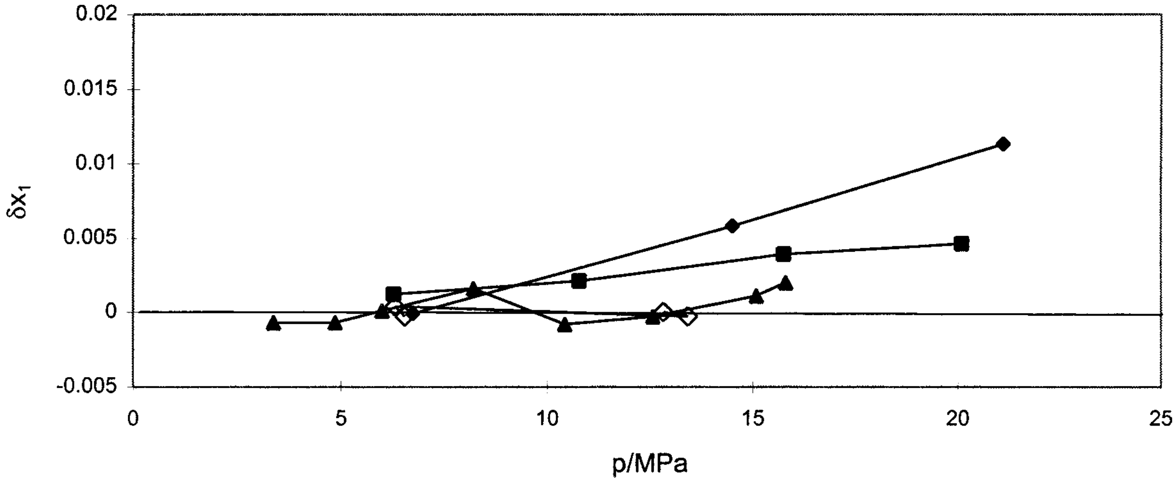

Figure 3. Comparison of solubility data for nitrogen (1) in benzene (2) at 373.2 K: (◆) Llave and Chung (1988); (■) Miller and Dodge (1940); (▲) this work; (◇) de Leeuw et al. (1989). (The data of de Leeuw et al. are at temperatures in the interval from 369.8 K to 378.8 K.) δx_1 is the difference between the measured solubility and that predicted by the PR equation.

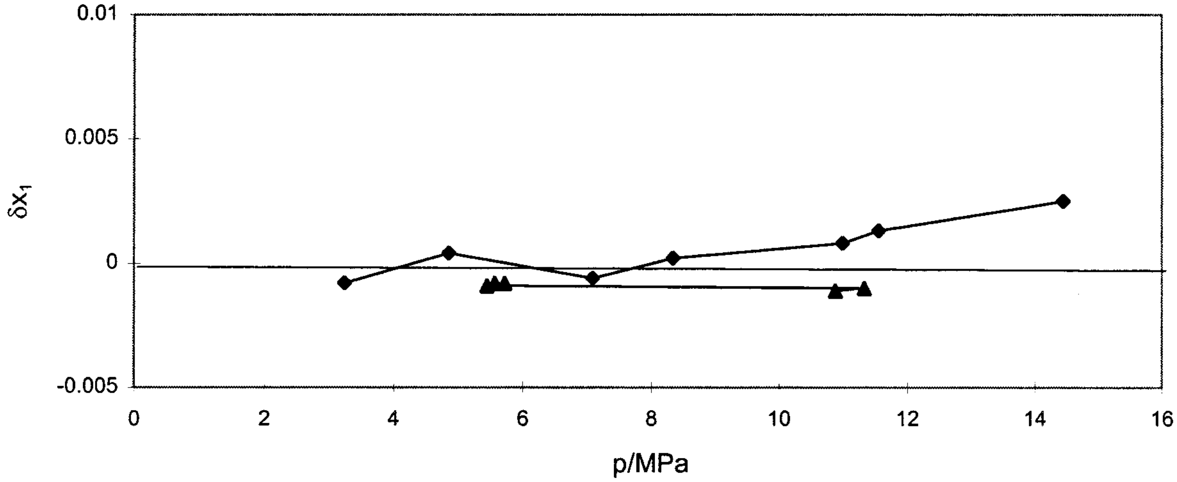

Figure 4. Comparison of solubility data for nitrogen (1) in benzene (2): (◆) this work at 410.9 K; (▲) de Leeuw et al. (1989). (The data of de Leeuw et al. are at temperatures in the interval from 404.6 K to 423.0 K.) δx_1 is the difference between the measured solubility and that predicted by the PR equation.

In eqs 7 and 8, the summations are over all chemical species, and C_{ij} and D_{ij} are empirical interaction parameters characterizing the binary interactions between components "*i*" and "*j*". Interaction parameter values were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of

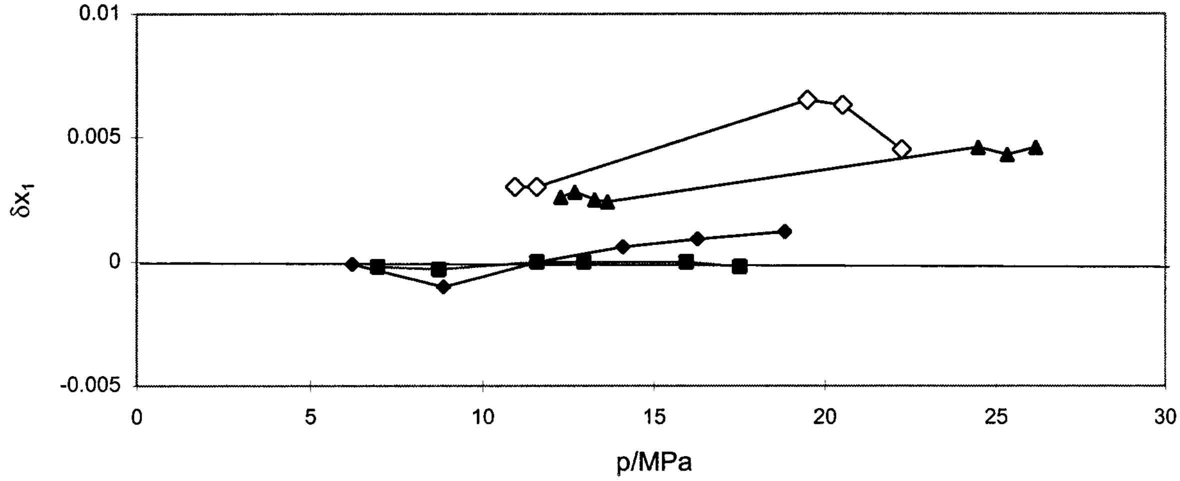

Figure 5. Comparison of solubility data for nitrogen (1) in naphthalene (2): (■) this work at 377.6 K; (◆) this work at 410.9 K; (▲) de Leeuw et al. (1989) at temperatures in the range from of 372.0 K to 387.2 K; (◇) de Leeuw et al. (1989) at temperatures in the range from 406.1 K to 422.1 K. δx_1 is the difference between the measured solubility and that predicted by the PR equation.

squared relative deviations in predicted bubble point pressures, i.e.:

$$SS = \sum_i^n \left(\frac{p_{calc} - p_{expt}}{p_{expt}} \right)_i^2 \qquad (9)$$

where n is the number of data points, p_{calc} is the calculated pressure, and p_{expt} is the experimental pressure. Further details of the data reduction technique are given by Gasem (Gasem and Robinson, 1985; Gasem, 1986). The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the PR EOS are presented in Table 3. In general, the root-mean-square deviations in the calculated bubble point pressures range from about 0.5% for the naphthalene system to 3.0% for the pyrene system.

Since a single interaction parameter (C_{ij}) represents the data for the present systems adequately, addition of a second parameter (D_{ij}) was not necessary (i.e., $D_{ij} = 0$ was employed). Using the optimized value of the interaction parameter, C_{ij}, the solubilities at fixed pressures were calculated. Results of the EOS representations of the solubilities are shown in Table 4. In general, the PR EOS is capable of describing the data with root-mean-square deviations less than 0.002 in mole fraction when one interaction parameter, C_{ij}, is regressed for each binary system. When a separate value of C_{ij} is used for each isotherm of a given system, representation of the data improves to about 0.001 in mole fraction.

The nitrogen systems show a relatively weak temperature dependence of C_{ij}, which is consistent with our previous studies of mixtures involving the solutes methane, ethane, and CO_2 (Anderson et al., 1986; Darwish, 1991; Darwish et al., 1993; Gasem et al., 1989; Gasem and Robinson, 1985; Park et al., 1995a,b; Srivatsan et al., 1995).

Our data for nitrogen + cyclohexane are compared with the previous measurements of Shibate and Sandler (1989) at 366.5 K and 410.9 K in Figure 2. Considerable disagreement exists between our data and those of Shibate and Sandler at both temperatures, with differences approaching 0.01 in mole fraction.

Comparisons of the present data for nitrogen + benzene at 373 K with those of Llave and Chung (1988), Miller and Dodge (1940), and de Leeuw et al. (1989) are shown in Figure 3. The solubility values for the PR EOS were calculated using values of the interaction parameter C_{ij}

Table 2. Solubility of Nitrogen in Aromatic Hydrocarbons

x_1	P/MPa	x_1	P/MPa
	Benzene		
	373.2 K		
0.0200	3.38	0.0624	10.43
0.0290	4.86	0.0750	12.57
0.0360	5.99	0.0888	15.09
0.0494	8.21	0.0929	15.81
	410.9 K		
0.0211	3.24	0.0788	11.00
0.0346	4.86	0.0832	11.56
0.0500	7.09	0.1035	14.44
0.0598	8.34		
	Naphthalene		
	377.6 K		
0.0250	6.96	0.0442	12.95
0.0307	8.73	0.0529	15.95
0.0401	11.59	0.0571	17.51
	410.9 K		
0.0257	6.22	0.0552	14.09
0.0350	8.87	0.0628	16.27
0.0460	11.62	0.0713	18.82
	1-Methylnaphthalene		
	344.3 K		
0.0206	7.22	0.0431	16.00
0.0255	9.25	0.0527	20.91
0.0387	14.63	0.0547	21.45
	377.6 K		
0.0189	5.16	0.0535	15.49
0.0335	9.44	0.0552	16.25
0.0399	11.33	0.0706	21.13
	410.9 K		
0.0203	4.96	0.0502	12.61
0.0296	7.18	0.0620	15.80
0.0449	11.08	0.0762	20.06
	Phenanthrene		
	383.2 K		
0.0222	10.47	0.0337	16.12
0.0241	11.45	0.0411	19.85
0.0300	14.33	0.0431	20.82
	410.9 K		
0.0254	10.44	0.0452	18.60
0.0298	12.47	0.0491	20.35
0.0404	16.74	0.0517	21.40
	Pyrene		
	433.2 K		
0.0178	7.59	0.0354	15.48
0.0256	11.09	0.0492	21.90
0.0310	13.50	0.0512	22.88

Table 3. Critical Pressures, p_c, Critical Temperatures, T_c, and Acentric Factors, ω, Used in the PR Equation of State

component	p_c/MPa	T_c/K	ω	ref
nitrogen	3.39	126.2	0.039	Reid et al. (1987)
decane	2.12	617.7	0.489	Reid et al. (1987)
cyclohexane	4.07	553.5	0.212	Reid et al. (1987)
trans-Decalin	3.14	687.1	0.270	Reid et al. (1987)
benzene	4.89	562.2	0.212	Reid et al. (1987)
naphthalene	4.05	748.4	0.302	API Monograph Series (1978)
1-methylnaphthalene	3.60	772.0	0.310	Reid et al. (1987)
phenanthrene	3.30	873.2	0.540	API Monograph Series (1979a)
pyrene	2.60	938.2	0.830[a]	API Monograph Series (1979b)

[a] Turek, 1988.

Table 4. PR EOS Representations of the Solubility of Nitrogen in Naphthenic and Aromatic Hydrocarbons

		error in predicted solute mole fraction	
T/K	C_{12}	RMS[a]	$\lvert\mathrm{MAX}\rvert$
Cyclohexane			
366.5	0.184	0.0014	0.0029
410.9	0.161	0.0013	0.0021
366.5 and 410.9	0.176	0.0019	0.0047
trans-Decalin			
344.3	0.242	0.0006	0.0012
377.6	0.235	0.0008	0.0012
410.9	0.234	0.0010	0.0021
344.3, 377.6 and 410.9	0.238	0.0010	0.0027
Benzene			
373.2	0.196	0.0011	0.0021
410.9	0.184	0.0010	0.0020
373.2 and 410.9	0.192	0.0013	0.0033
Naphthalene			
377.6	0.288	0.0002	0.0002
410.9	0.285	0.0007	0.0011
377.6 and 410.9	0.287	0.0006	0.0012
1-Methylnaphthalene			
344.3	0.398	0.0008	0.0013
377.6	0.357	0.0011	0.0023
410.9	0.365	0.0009	0.0016
344.3, 377.6 and 410.9	0.376	0.0021	0.0031
Phenanthrene			
383.2	0.405	0.0009	0.0015
410.9	0.401	0.0013	0.0018
383.2 and 410.9	0.403	0.0011	0.0020
Pyrene			
433.2	0.496	0.0011	0.0018

[a] RMS = root mean square.

regressed from our data at each temperature of interest. The figure shows good agreement between our data and those of Miller and Dodge, with differences on the order of 0.002 mole fraction, while agreement with the data of Llave and Chung is less satisfactory. The data of de Leeuw et al. are in excellent agreement with ours. Comparison of our data at 411 K with those of de Leeuw et al. appears in Figure 4; agreement is within about 0.001 mole fraction.

Figure 5 contains a comparison of our data for nitrogen + naphthalene at 377 K and 411 K with those of de Leeuw et al. Differences in the data sets are on the order of 0.004 in their common range of pressures.

No literature data on the solubilities for the other systems are available for comparison.

Conclusions

Measurements have been obtained for the solubilities of nitrogen in cyclohexane, *trans*-Decalin, benzene, naphthalene, 1-methylnaphthalene, phenanthrene, and pyrene at temperatures from 344.3 K to 433.2 K at pressures up to 22.8 MPa. The data are described well by the PR EOS, using interaction parameters obtained from the data.

Literature Cited

Anderson, J. M.; Barrick, M. W.; Robinson, R. L., Jr. Solubilities of Carbon Dioxide in Cyclohexane and *trans*-Decalin at Pressures to 10.7 MPa and Temperatures from 323 to 423 K. *J. Chem. Eng. Data* **1986**, *31*, 172−175.

API Monograph Series: *Naphthalene*; Monograph No. 707; American Petroleum Institute: Washington, DC, 1978.

API Monograph Series: *Anthracene and Phenanthrene*; Monograph No. 708; American Petroleum Institute: Washington, DC, 1979a.

API Monograph Series: *Four-Ring Condensed Aromatic Compounds*; Monograph No. 709; American Petroleum Institute: Washington, DC, 1979b.

Darwish, N. A. Binary Vapor-Liquid-Phase Equilibrium for Methane in Selected Heavy Normal Paraffins, Naphthenes, and Aromatics. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK, 1991.

Darwish, N. A.; Fathikalajahi, J.; Gasem, K. A. M.; Robinson, R. L., Jr. Solubility of Methane in Heavy Normal Paraffins at Temperatures from 323 to 423 K and Pressures to 10.7 MPa. *J. Chem. Eng. Data* **1993**, *38*, 44−48.

de Leeuw, V. V.; Poot, W.; de Loos, T. W.; de Swaan Arons, J. High-Pressure Phase Equilibria of the Binary Systems N_2 + Benzene, N_2 + *p*-Xylene, and N_2 + Naphthalene. *Fluid Phase Equilib.* **1989**, *49*, 75−101.

Gasem, K. A. M. Binary Vapor-Liquid Phase Equilibrium for Carbon Dioxide + Heavy Normal Paraffins. Ph.D. Dissertation, Oklahoma State University, Stillwater, OK, 1986.

Gasem, K. A. M.; Robinson, R. L., Jr. Solubilities of Carbon Dioxide in Heavy Normal Paraffins (C_{20}−C_{44}) at Pressures to 9.6 MPa and Temperatures from 323 to 423 K. *J. Chem. Eng. Data* **1985**, *30*, 53−56.

Gasem, K. A. M.; Bufkin, B. A.; Raff, A. M.; Robinson, R. L., Jr. Solubilities of Ethane in Heavy Normal Paraffins at Pressures to 7.8 MPa and Temperatures from 348 to 423 K. *J. Chem. Eng. Data* **1989**, *34*, 187−191.

Llave, F. M.; Chung, T. H. Vapor−Liquid Equilibria of Nitrogen−Hydrogen Systems at Elevated Pressures. *J. Chem. Eng. Data* **1988**, *33*, 123−128.

Miller, P.; Dodge, B. F. The System Benzene−Nitrogen Liquid−Vapor Phase Equilibria at Elevated Pressures. *Ind. Eng. Chem.* **1940**, *32*, 434−438.

Park, J.; Robinson, R. L., Jr.; Gasem, K. A. M. Solubilities of Hydrogen in Heavy Normal Paraffins at Temperatures from 323.2 to 423.2 K and Pressures to 17.4 MPa. *J. Chem. Eng. Data* **1995a**, *40*, 241−244.

Park, J.; Robinson, R. L., Jr.; Gasem, K. A. M. Solubilities of Hydrogen in Aromatic Hydrocarbons from 323 to 433 K and Pressures to 21.7 MPa. *J. Chem. Eng. Data* **1995b**, *40*, 70−73.

Peng, Y. D.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases & Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

Shibate, S. K.; Sandler, S. L. High-Pressure Vapor−Liquid Equilibria of Mixtures of Nitrogen, Carbon Dioxide, and Cyclohexane. *J. Chem. Eng. Data* **1989**, *34*, 419−424.

Srivatsan, S.; Yi, X.; Robinson, R. L., Jr.; Gasem, K. A. M. Solubilities of Carbon Monoxide in Heavy Normal Paraffins at Temperatures from 311 to 423 K and Pressures to 10.2 MPa. *J. Chem. Eng. Data* **1995**, *40*, 237−240.

Tong, J. Solubility Data for Nitrogen in n-Paraffins and Equation-of-State Methods To Describe Light Gas Solubilities in Hydrocarbons. M.S. Thesis, Oklahoma State University, Stillwater, OK, 1994.

Turek, E. A., Amoco Production Co., Tulsa, OK, personal communication, 1988.

Received for review August 10, 1998. Accepted November 9, 1998. This work was supported by the U. S. Department of Energy under Contract No. DE-FG-22-90PC90302.

JE980187Y