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Solubilities of Hydrogen in Aromatic Hydrocarbons from 323 to 433 K and Pressures to 21.7 MPa

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The solubilities of hydrogen in benzene, naphthalene, phenanthrene, and pyrene were measured using a static equilibrium cell over the temperature range from 323.2 to 433.2 K and pressures to 21.7 MPa. The uncertainty in these new solubility measurements 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 (EOS). In general, the two equations represent the experimental data well when a single interaction parameter (C_{ij}) is used for each isotherm. The data suggest that the EOS C_{ij} interaction parameter is highly temperature dependent.

Introduction

Mixtures which contain small gas molecules (such as hydrogen, methane, ethane, carbon monoxide, and carbon dioxide) in heavy hydrocarbon solvents provide a severe test of the current predictive models and their associated mixing theories. In this work, measurements were made of the solubilities of hydrogen in selected aromatic solvents (benzene, naphthalene, phenanthrene, and pyrene) in the temperature range from 323.2 to 433.2 K and pressures to 21.7 MPa. The data have been correlated using the SRK (Soave, 1972) and PR (Peng and Robinson, 1976) equations of state. The present measurements complement our recent work on hydrogen in the *n*-paraffins decane, eicosane, octacosane, and hexatriacontane (Park et al., 1995).

Several experimental studies of the hydrogen solubility in benzene are available in the literature. Connolly reported smoothed data for vapor−liquid equilibrium ($T-P-x-y$) at elevated temperatures (433.2−533.2 K) (Connolly, 1962). Thompson and Edmister provided vapor−liquid equilibrium data for hydrogen binary mixtures with benzene and cyclohexane (Thompson, 1965). Brainard and Williams also measured data on the hydrogen binary systems of benzene and cyclohexane, along with quaternary vapor−liquid equilibrium data for the system containing hydrogen, benzene, cyclohexane, and hexane (Brainard and Williams, 1967). Similarly, measurements on hydrogen and phenanthrene binary systems were reported by Malone and Kobayashi (1990). These measurements are compared with the data of the present work. No literature data on hydrogen in naphthalene or pyrene are available for comparison.

Experimental Method

Details regarding the apparatus and experimental procedure have been described by Darwish (Darwish, 1991; Darwish et al., 1993) and are summarized briefly here.

A schematic diagram of the apparatus is shown in Figure 1. Phase equilibrium is established in a variable-volume, thermostated, static-type blind cell. This equilibrium cell (EC; refer to Figure 1) is a 25 cm^3, 316 stainless steel microreactor. It is housed in a constant-temperature bath (BATH 1). Two steel balls are placed in the equilibrium cell, and the cell is 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.

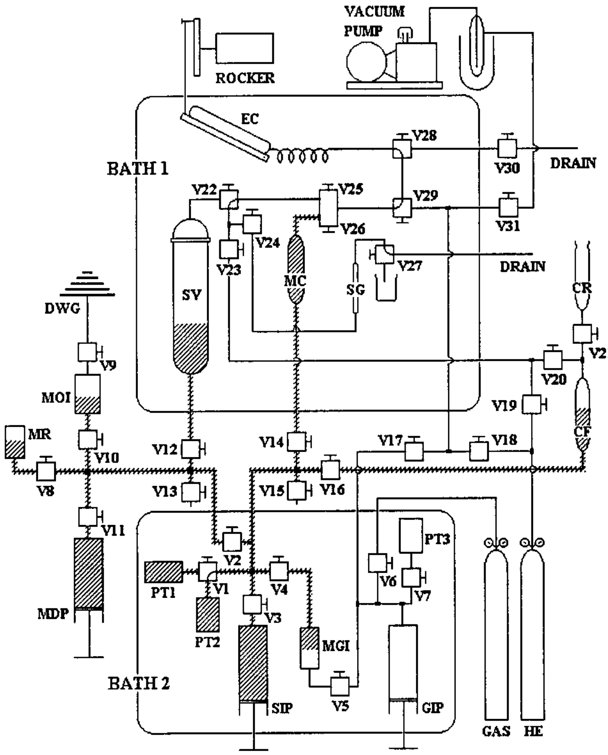

Figure 1. Schematic diagram of the experimental apparatus: (CF) cleaning fluid cylinder, (CR) cleaning fluid reservoir, (DWG) dead weight gauge, (EC) equilibrium cell, (GAS) solute gas, (GIP) solute gas injection pump, (HE) helium gas, (MDP) mercury displacement pump, (MGI) mercury−gas interface, (MC) mercury storage cell, (MOI) mercury−oil interface, (MR) mercury reservoir, (PT) pressure transducer, (SG) sight glass, (SIP) solvent injection pump, (SV) solvent storage cell, (V) valve.

Degassed liquid solvent is stored, at the operating temperature of the experiment, in a solvent storage cell (SV) contained inside the high-temperature air oven (BATH 1). The equilibrium cell and solvent storage cell are from High Pressure Equipment, Inc.

Injection of solvent into the initially-evacuated equilibrium cell is done volumetrically by injecting mercury at

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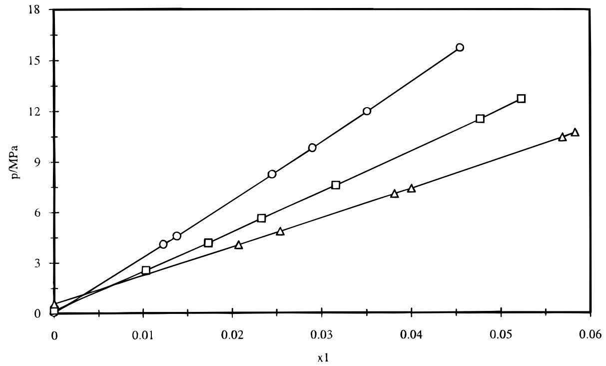

Figure 2. Solubility of hydrogen in benzene: (○) 323.2 K; (□) 373.2 K; (△) 423.5 K.

Table 1. Solubility of Hydrogen (1) in Aromatic Hydrocarbons (2)

x_1	p/MPa	x_1	p/MPa
	Benzene, 323.2 K		
0.0123	4.07	0.0290	9.80
0.0138	4.56	0.0351	11.97
0.0245	8.22	0.0455	15.73
	Benzene, 373.2 K		
0.0103	2.55	0.0316	7.57
0.0173	4.15	0.0477	11.51
0.0233	5.60	0.0523	12.71
	Benzene, 423.2 K		
0.0207	4.05	0.0400	7.40
0.0254	4.85	0.0569	10.44
0.0381	7.07	0.0585	10.73
	Naphthalene, 373.2 K		
0.0157	5.29	0.0362	12.35
0.0165	5.50	0.0530	18.53
0.0346	11.80	0.0553	19.39
	Naphthalene, 423.2 K		
0.0166	4.29	0.0385	9.95
0.0189	4.84	0.0470	12.46
0.0273	7.06	0.0534	14.08
0.0337	8.77	0.0567	15.21
	Phenanthrene, 383.2 K		
0.0165	6.33	0.0398	15.78
0.0228	8.85	0.0492	19.79
0.0328	12.83	0.0535	21.69
	Phenanthrene, 423.2 K		
0.0187	5.89	0.0391	12.53
0.0226	7.14	0.0514	16.74
0.0354	11.31	0.0557	18.35
	Pyrene, 433.2 K		
0.0158	5.17	0.0358	11.91
0.0185	6.05	0.0498	16.97
0.0325	10.80	0.0575	19.73

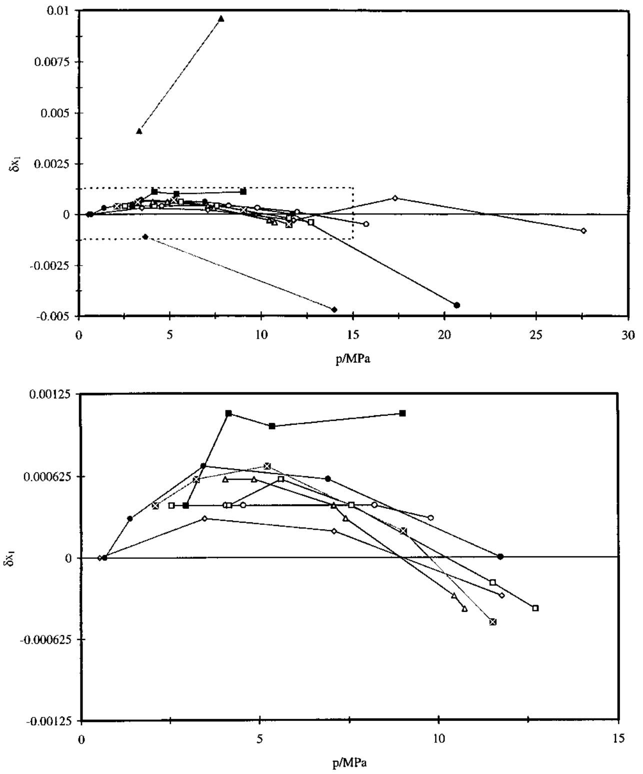

Figure 3. (a, top) Comparison of hydrogen solubilities in benzene. δx_1 is the deviation of the predicted solubility using the SRK EOS from that measured. This work: (○) 323.3 K; (□) 373.2 K; (△) 423.2 K. Brainard and Williams (1967): (▲) 366.5 K; (◆) 422.0 K. Connolly (1962): (white × in black box) 433.2 K. Thompson and Edmister (1965): (◇) 338.7 K; (●) 394 K; (■) 433.2 K. (- - -) See part b (bottom).

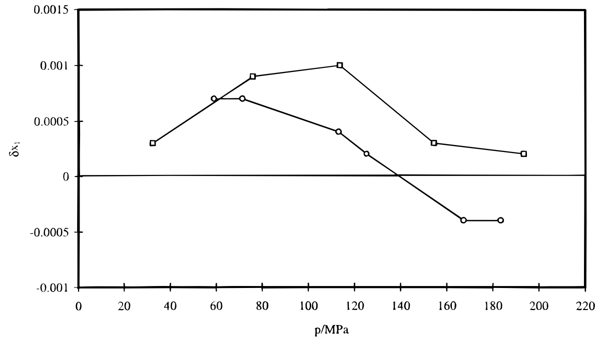

Figure 4. Comparison of hydrogen solubilities in phenanthrene at 423.2 K: (○) this work; (□) Malone and Kobayashi (1990). δx_1 is the deviation of the predicted solubility using the SRK EOS from that measured.

the bottom of the solvent cylinder, thus displacing an equal quantity of solvent into the rocking cell. The solvent injection pump (SIP) is from Temco, Inc. Solute gas is then injected into the rocking cell from a second Temco pump (GIP). After each solute injection, the bubble point pressure of the mixture is determined. This is done by sequentially injecting known amounts of mercury into the 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 the pressure vs total volume of mercury injected relation as the mixture passes from the more compressible two-phase state to the less compressible single-liquid-phase state.

The air bath housing the equilibrium cell (BATH 1) is thermostated by a proportional-integral (PI) controller supplied by Omega Engineering, Inc. The temperature of the air bath housing the injection pump (BATH 2) is controlled by a PI controller from Halikainen Instruments. The temperatures in the air baths are measured using platinum resistance thermometers equipped with digital displays from Fluke, Inc. Pressures are measured with transducers from Sensotec, Inc. The transducers are calibrated periodically against a Ruska Instrument Corp. dead weight tester (DWG) with a certification traceable to the National Bureau of Standards.

Measurement uncertainties are estimated to be 0.1 K in temperature and less than 0.001 in composition (mole fraction). The uncertainty in the bubble point pressure is dependent on the steepness of the pressure vs composition relation; it is estimated to be approximately 0.06 MPa for the systems studied here.

Table 2. SRK and PR Equation of State Representations of the Solubility of Hydrogen (1) in Aromatic Hydrocarbons (2)

		error in mole fraction		
T/K	C_{12} SRK parameter (PR parameter)	RMS	$\lvert\max\rvert$	SRK Henry's constant/MPa (PR Henry's constant/MPa)
		Benzene		
323.2	0.3479	0.0004	0.0005	306
	(0.3681)	(0.0003)	(0.0005)	(306)
373.2	0.4168	0.0004	0.0006	215
	(0.3991)	(0.0004)	(0.0005)	(216)
423.2	0.5450	0.0005	0.0006	1561
	(0.4627)	(0.0003)	(0.0004)	(1576)
323.2, 373.2, 423.2	0.3818	0.0028	0.0058	
	(0.3861)	(0.0019)	(0.0039)	
		Naphthalene		
373.2	0.3685	0.0006	0.0009	307
	(0.3895)	(0.0006)	(0.0008)	(308)
423.2	0.4278	0.0005	0.0007	238
	(0.4127)	(0.0004)	(0.0006)	(240)
373.2, 423.2	0.3865	0.0011	0.0016	
	(0.3971)	(0.0007)	(0.0010)	
		Phenanthrene		
383.2	0.3245	0.0005	0.0007	354
	(0.3766)	(0.0005)	(0.0007)	(354)
423.2	0.3665	0.0005	0.0007	291
	(0.3940)	(0.0004)	(0.0006)	(293)
383.2, 423.2	0.3376	0.0008	0.0012	
	(0.3824)	(0.0006)	(0.0009)	
		Pyrene		
433.2	0.4309	0.0005	0.0007	305
	(0.4620)	(0.0005)	(0.0006)	(306)

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

component	p_c/MPa	T_c/K	ω	ref
hydrogen	1.30	33.2	−0.218	Reid et al. (1977)
benzene	4.89	562.1	0.212	ESDU Engineering Series Data (1990)
naphthalene	4.05	748.4	0.302	API Monograph Series (1978)
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, E. A., Amoco Production Co., Tulsa, OK, personal communication, 1988.

Materials

The hydrogen used in this study had a stated purity of 99.995% and was supplied by Union Carbide Corp. The benzene, naphthalene, phenanthrene, and pyrene were supplied by the Aldrich Chemical Co. and had stated purities of 99.9+% 99+%, 98+%, and 99+%, respectively. No further purification of these chemicals was attempted.

Results and Data Correlations

The measurements of hydrogen solubilities in benzene, naphthalene, phenanthrene, and pyrene are presented in Table 1. The effect of temperature and pressure on the solubility of hydrogen in benzene is shown in Figure 2. A trend of increasing solubility with increased temperature and pressure is observed. The same trend is shown for hydrogen in naphthalene and phenanthrene, as well as in heavy normal paraffins (Park et al., 1995). Similar data for methane, ethane, and carbon dioxide binaries in the above solvents reveal a trend of decreasing solubilities with increased temperature (Anderson et al., 1986; Darwish et al., 1993; Gasem and Robinson, 1985; Gasem et al., 1989; Raff, 1989; Robinson, et al., 1994).

Comparisons of the present data with those of earlier researchers appear in Figures 3 and 4. The comparisons are limited to the data range of the current measurements. In these figures, the data are shown in terms of the deviation, δx_1, in the solubility (liquid mole fraction) predicted by the SRK EOS from the measured value, i.e., $\delta x_1 = x_1(\text{SRK}) - x_1(\text{exptl})$. The solubility values for the SRK EOS were calculated using values of the interaction parameter, C_{ij}, regressed from our data at the temperature of interest. In the comparisons with the data reported by Connolly (1962) and Thompson and Edmister (1965), the interaction parameter C_{ij} was extrapolated to the temperature of 433.2 K where their data exist. In the other comparisons, the C_{ij} values were linearly interpolated.

The solubility comparisons for hydrogen in benzene are shown in Figure 3. The data of Brainard are not shown since deviations of that work from the others were as large as 0.008 in mole fraction. The data in Figure 3 exhibit good agreement, with the scatter being generally less than 0.0005 mole fraction. A comparison of data for hydrogen in phenanthrene is shown in Figure 4; the scatter is again less than 0.0005 mole fraction.

The abilities of the SRK and PR equations of state to represent the solubility data from the present study are shown in Table 2. The details of the equations and the mixing rules employed are described in detail elsewhere (Park et al., 1995). The input parameters for pure components (critical temperature, T_c, critical pressure, p_c, and the acentric factor, ω) are given in Table 3. The table reveals that the EOSs are capable of describing the data with RMS errors less than 0.001 mole fraction when a single interaction parameter, C_{ij}, is used for each isotherm. Data reduction indicates that the interaction parameter C_{ij} is highly dependent on temperature. Moreover, the SRK and PR EOSs, in general, exhibit comparable abilities in representing the data using a single interaction parameter.

Henry's Constants

By definition, Henry's constant, $H_{1,2}$, of hydrogen (1) in a hydrocarbon solvent (2) is given as

$$H_{1,2} = \lim_{x_1 \to 0}(f_1/x_1) = \lim_{x_1 \to 0}(\varphi_1 p) \tag{1}$$

where f_1, x_1, and φ_1 are the fugacity, liquid mole fraction, and fugacity coefficient, respectively, of hydrogen. Estimates for Henry's constants were obtained for the present data using SRK and PR equations of state in accordance with the above definition. Values for Henry's constants, along with the interaction parameters associated with them, are given in Table 2. In general, the SRK EOS produces slightly lower $H_{1,2}$ values (~1% lower) than those obtained from the PR EOS.

Conclusions

Measurements have been obtained for the solubilities of hydrogen in benzene, naphthalene, phenanthrene, and pyrene at temperatures from 323.2 to 433.2 K and pressures up to 21.7 MPa. The present data exhibit good agreement with data available in the literature for benzene and phenanthrene. The data are well described by the SRK and PR equations of state. Interaction parameters for these equations, along with Henry's constants, have been obtained for the binary systems studied.

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