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Solubilities of Hydrogen in Heavy Normal Paraffins at Temperatures from 323.2 to 423.2 K and Pressures to 17.4 MPa

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The solubilities of hydrogen in decane, eicosane, octacosane, and hexatriacontane were measured using a static equilibrium cell over the temperature range from 323.2 to 423.2 K and pressures to 17.4 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. In general, the two equations represent the experimental data well when a single interaction parameter is used for each binary system. The present data suggest that the interaction parameter, C_{ij}, is highly temperature dependent, and that the use of a second interaction parameter, D_{ij}, is not merited.

Introduction

Industrial processes such as petroleum refining, coal conversion, enhanced oil recovery, and supercritical separation have created great demand for phase equilibrium data for asymmetric mixtures. These mixtures, which involve small gas solute molecules (such as CO_2, hydrogen, methane, ethane, and CO) and heavy hydrocarbon solvents (effective carbon number of 10 or greater), pose a challenge to the current predictive models and the associated mixing theories.

As a part of our ongoing research dealing with the phase behavior of asymmetric mixtures, the solubilities of methane, ethane, CO_2, and CO in systematically-chosen solvents (heavy paraffinic, naphthenic, and aromatic hydrocarbons) have been measured and correlated *(1–7)*. In this study, we report new binary measurements for the solubility of hydrogen in the saturated heavy hydrocarbon solvents decane, eicosane, octacosane, and hexatriacontane. These data cover temperatures from 323.2 to 423.2 K and pressures to 17.4 MPa. The data have been correlated using the Soave–Redlich–Kwong (SRK) *(8)* and Peng–Robinson (PR) *(9)* equations of state. The binary interaction parameter, C_{ij}, has been regressed from the new experimental data.

A number of researchers have attempted to correlate the phase behavior of hydrogen + hydrocarbon binary systems. Prausnitz and co-workers modified the SRK equation of state (EOS) to improve the predictive capability for systems containing hydrogen *(10)*. The same kind of approach was pursued by Graboski and Daubert *(11)*. Lin compared the predictive abilities of the modified SRK equations of state with the original SRK equation and concluded that the original SRK EOS is better than the modified versions for systems containing a heavy hydrocarbon *(12)*. Preliminary analysis of the present data supports Lin's findings. We have therefore elected to use the original SRK and PR equations of states, along with the experimental values for the critical properties and acentric factor of hydrogen.

Experimental Section

Method. A variable-volume, static-type blind equilibrium cell was used in this study. For a given binary mixture of known composition, the bubble point pressure is identified graphically from the discontinuity in compressibility of the mixture as it passes from the two-phase state to the single-liquid-phase state. This method consists of introducing known amounts of well degassed pure components into a variable-volume, thermostated equilibrium cell. The effective volume of the equilibrium mixture is varied by the introduction or withdrawal of mercury. Two steel balls are placed in the equilibrium cell, and the cell is rocked 45° about the horizontal level to enhance the establishment of equilibrium. Details of the apparatus and experimental procedure are described by Darwish *(6, 7, 13)*. 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, which is dependent on the steepness of the pressure–composition relation, is on the order of 0.05 MPa for the systems studied here. A detailed error analysis is given by Darwish *(6, 13)*.

Materials. The hydrogen used in this study had a stated purity of 99.9995% and was supplied by Union Carbide Corp. Decane and eicosane were supplied by the Aldrich Chemical Co. and had stated purities of 99+% and 99%, respectively. Octacosane and hexatriacontane were supplied by Alfa Products, and both had reported purities of 99%. No further purification of these chemicals was attempted.

Results and Data Correlation

The hydrogen solubility measurements are presented in Table 1. In general, the lowest temperature at which each system was studied was dictated by the melting point of the solvent or the availability of literature data (for comparison purposes). The effect of temperature and pressure on the solubility of hydrogen in decane is shown in Figure 1. A similar trend of increasing solubility with increased temperature and pressure is observed for the other solvents studied.

Comparisons of our data for the solubility of hydrogen in eicosane, octacosane, and hexatriacontane with those of Huang and co-workers *(14)* at 373.2 K are shown in Figures 2–4, respectively. Minor temperature variations of up to 0.2 K in Huang's data were neglected for the purposes of comparison. The comparisons are shown in terms of deviations of the experimental measurements from the solubility predicted using the SRK EOS (discussed below). The binary interaction parameter, C_{ij}, employed in the EOS predictions was obtained by fitting our data for the isotherm under study. Figures 2–4 indicate reasonable agreement between our data and those of Huang. While Sebastian et al. *(15)* have reported experimental measure-

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

x_1	p/MPa	x_1	p/MPa
Decane			
344.3 K			
0.0369	4.46	0.0958	12.46
0.0576	7.13	0.1094	14.46
0.0682	8.60	0.1288	17.39
373.2 K			
0.0418	4.41	0.0963	10.85
0.0557	5.96	0.1124	12.93
0.0760	8.36	0.1286	15.04
423.2 K			
0.0435	3.71	0.0914	8.13
0.0561	4.82	0.1232	11.32
0.0851	7.48	0.1264	11.66
Eicosane			
323.2 K			
0.0320	3.26	0.0964	10.51
0.0333	3.40	0.0978	10.71
0.0644	6.77	0.1152	12.91
0.0663	7.02		
373.2 K			
0.0273	2.23	0.0811	7.01
0.0296	2.41	0.0989	8.69
0.0371	3.09	0.1147	10.40
0.0686	5.81	0.1289	11.82
0.0776	6.73		
423.2 K			
0.0410	2.81	0.0874	6.24
0.0573	3.97	0.1064	7.75
0.0756	5.33	0.1246	9.30
Octacosane			
348.2 K			
0.0452	3.53	0.1139	9.59
0.0764	6.14	0.1296	11.11
0.0895	7.31	0.1487	13.10
373.2 K			
0.0572	4.02	0.1123	8.41
0.0614	4.34	0.1572	12.43
0.1076	8.00		
423.2 K			
0.0503	2.86	0.1235	7.47
0.0524	2.95	0.1407	8.74
0.0747	4.34	0.1511	9.53
0.0921	5.43	0.1728	11.24
0.1047	6.23		
Hexatriacontane			
373.2 K			
0.0677	4.11	0.1453	9.62
0.0813	4.99	0.2001	14.32
0.1287	8.32	0.2271	16.75
423.2 K			
0.0720	3.56	0.1545	8.39
0.0881	4.42	0.1941	11.08
0.1355	7.24	0.2080	12.00

ments for the solubility of hydrogen in decane at temperatures extending from 462.5 to 583.5 K, no literature data are available for direct comparison.

The SRK *(8)* and PR *(9)* cubic equations of state were used to correlate the experimental data. The Soave equation is given below; similar relations are given elsewhere for the Peng–Robinson equation *(9)*.

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

where

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

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

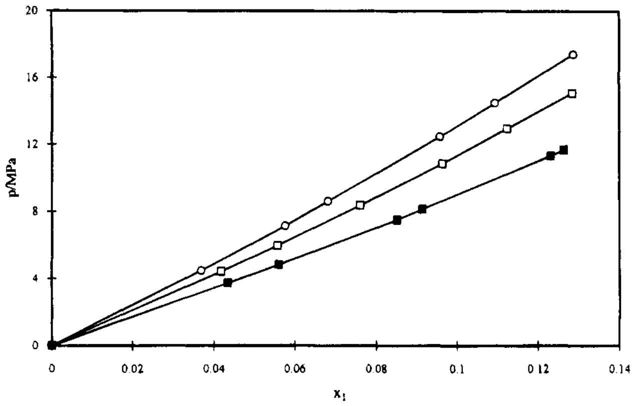

Figure 1. Solubility of hydrogen in decane: ○, 344.2 K; □, 373.2 K; ■, 423.2 K.

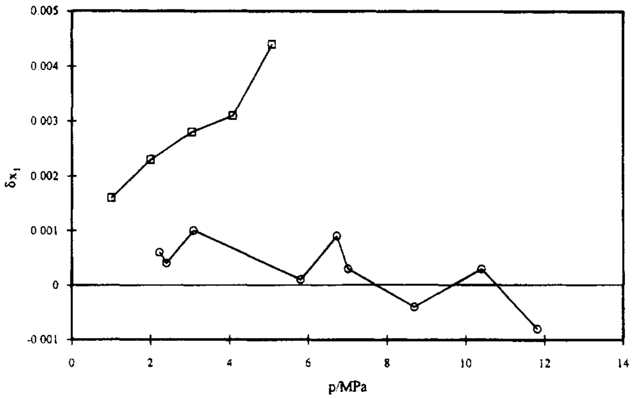

Figure 2. Comparison of solubilities for hydrogen in eicosane at 373.2 K: ○, this work; □, Huang *(14)*. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

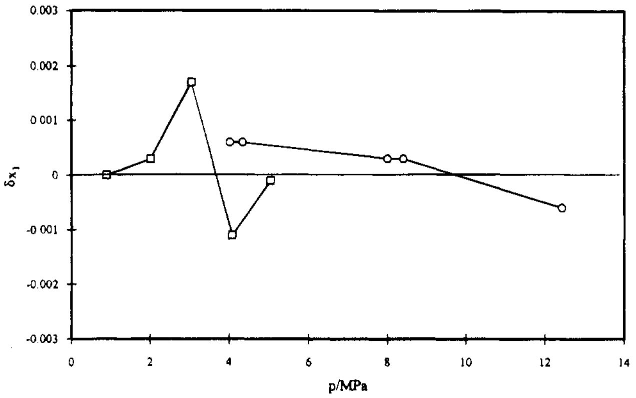

Figure 3. Comparison of solubilities for hydrogen in octacosane at 373.2 K: ○, this work; □, Huang *(14)*. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

and

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

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

$$k = 0.480 + 1.574\omega - 0.176\omega^2 \tag{6}$$

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 SRK or PR equations of state to mixtures, the values of a and b can be determined using the mixing

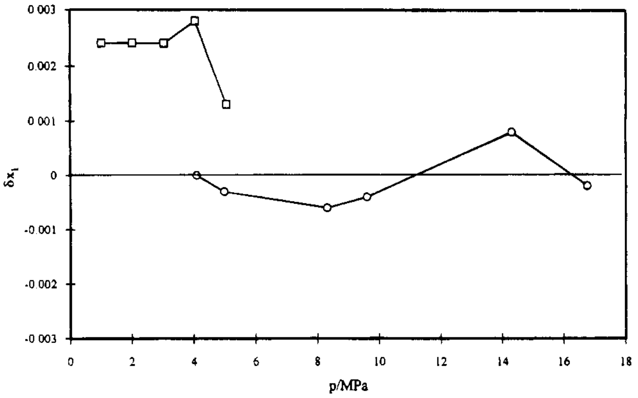

Figure 4. Comparison of solubilities for hydrogen in hexatriacontane at 373.2 K: ○, this work; □, Huang *(14)*. δx_1 is the deviation of the measured solubility from that predicted by the SRK equation.

Table 2. Critical Pressure, p_c, Critical Temperature, T_c, and Acentric Factor, ω, Used in the SRK and PR Equations of State

component	p_c/MPa	T_c/K	ω	ref
hydrogen	1.300	33.2	−0.218	19
decane	2.097	617.5	0.4885	16
eicosane	1.117	770.5	0.8738	16
octacosane	0.826	845.4	1.1073	16
hexatriacontane	0.682	901.1	1.2847	16

rules *(4)*

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

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

where z_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 a mixture.

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. Values of these parameters were determined by fitting the experimental data to minimize the objective function, SS, which represents the sum of squared errors in predicted bubble point pressures.

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

where n is the number of data points, p_{exp} is the experimental pressure, and p_{cal} is the calculated pressure. Further details of the data reduction technique used in this study are given by Gasem *(16)*. The input parameters for the pure components (acentric factors, critical temperatures, and critical pressures) required by the SRK and PR equations of state, together with their literature sources, are presented in Table 2. A detailed description for the asymptotic behavior correlation used to estimate the critical properties of the heavy normal paraffins is given elsewhere *(14, 17)*.

Table 3. SRK and PR Equation of State Representations of the Solubility of Hydrogen (1) in Hydrocarbons (2)

T/K	SRK parameter (PR parameter) C_{12}	error in mole fraction RMS	error in mole fraction |MAX|	SRK Henry constant/MPa (PR Henry constant/MPa)
		Decane		
344.3	0.4200 (0.3935)	0.0011 (0.0008)	0.0015 (0.0011)	110.54 (112.14)
373.2	0.4685 (0.4135)	0.0008 (0.0005)	0.0011 (0.0010)	96.76 (98.43)
423.2	0.5835 (0.4620)	0.0008 (0.0004)	0.0012 (0.0006)	76.97 (78.59)
344.3, 373.2 and 423.2	0.4523 (0.4082)	0.0039 (0.0023)	0.0077 (0.0046)	
		Eicosane		
323.2	0.3682 (0.3781)	0.0007 (0.0006)	0.0010 (0.0008)	94.35 (95.04)
373.2	0.3849 (0.3656)	0.0006 (0.0004)	0.0010 (0.0007)	77.18 (78.12)
423.2	0.4070 (0.3490)	0.0005 (0.0002)	0.0008 (0.0004)	63.88 (72.25)
323.2, 373.2 and 423.2	0.3772 (0.3706)	0.0010 (0.0009)	0.0015 (0.0018)	
		Octacosane		
348.2	0.2911 (0.3283)	0.0005 (0.0003)	0.0009 (0.0007)	72.25 (72.91)
373.2	0.2560 (0.2915)	0.0005 (0.0002)	0.0006 (0.0003)	64.98 (65.74)
423.2	0.1697 (0.2056)	0.0005 (0.0006)	0.0009 (0.0011)	53.21 (53.99)
348.2, 373.2 and 423.2	0.2518 (0.2850)	0.0031 (0.0043)	0.0056 (0.0072)	
		Hexatriacontane		
373.2	0.0828 (0.1876)	0.0005 (0.0008)	0.0008 (0.0011)	56.38 (57.08)
423.2	−0.0560 (0.0695)	0.0005 (0.0008)	0.0007 (0.0013)	46.50 (47.19)
373.2 and 423.2	0.0425 (0.1509)	0.0050 (0.0059)	0.0052 (0.0097)	

The equation of state representations of the solubilities for the systems considered are shown in Table 3. In general, the SRK and PR equations are capable of describing the data with RMS errors within 0.001 in mole fraction when a single interaction parameter, C_{ij}, is used per isotherm. Using the physical properties given in Table 2, relatively large C_{ij} values are obtained for hydrogen + decane, with a decreasing trend for C_{ij} in the higher-carbon-number solvents. These atypical values for C_{ij} are attributed to the low value of the critical temperature of hydrogen and the resulting acentric factor ($\omega = -0.218$).

When a single interaction parameter is used for a given hydrocarbon solvent, the RMS errors are within 0.005. This level of variation is significantly beyond the precision of the experimental data and is an indication of a strong temperature dependence of the interaction parameter. Data regressions involving a second interaction parameter, D_{ij}, resulted in near-zero values for this parameter (not given here) and no significant improvement in the quality of the fit. This is in clear contrast to our previous studies of hydrocarbon mixtures involving methane, ethane, and CO_2 *(1−7)*.

The SRK and PR equations of state, in general, exhibit comparable abilities, with both representing the reported data within their experimental precision. However, some differences in the quality of fit are observed for the various hydrocarbons; specifically, the PR EOS produced better fits for decane, while the SRK EOS gave better results for hexatriacontane.

Henry Constants

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

$$H_{1,2} = \underset{\lim x_1 \to 0}{(f_1/x_1)} = \underset{\lim x_1 \to 0}{(\varphi_1 p)} \tag{10}$$

where f_1, x_1, and φ_1 are the fugacity, liquid mole fraction, and fugacity coefficient of hydrogen, respectively. Estimates for the Henry constant were obtained for the present data using SRK and PR equations of state in accordance with the above definition. Values for the Henry constant, along with the interaction parameters associated with them, are given in Table 3. These values are slightly (0.5–5%) lower than those obtained from the Krichevsky–Kasarnovsky equation *(18)*.

Conclusions

Data have been obtained for the solubility of hydrogen in decane, eicosane, octacosane, and hexatriacontane at temperatures from 323.2 to 423.2 K and pressures up to 17.4 MPa. These data are well described by the SRK and PR equations of state with a single interaction parameter for each isotherm. Interaction parameters for these equations, along with estimates for Henry constants, have been obtained for the binary systems considered.

The newly acquired data provide valuable information for the development of improved equation of state models and better understanding of the phase behavior of hydrogen + hydrocarbon mixtures.

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