High-Pressure Solubilities of Hydrogen and Methane in Toluene in the Presence of Ethane and Eicosane

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The effect of ethane on solubilities of hydrogen and methane in toluene was identified by measuring the solubility of a ternary gas containing hydrogen, methane, and ethane and comparing with the solubility of a binary gas containing hydrogen and methane only. The ternary gas solubilities were measured at pressures up to 13.88 MPa and at a temperature of 295 K. A significant increase in the methane solubility was observed in the presence of ethane, whereas the hydrogen solubilities were little affected. The solubilities of the binary gas at pressures up to 17.33 MPa and the ternary gas at pressures up to 12.16 MPa were measured in a toluene solution containing 20 mass % eicosane. The addition of eicosane to toluene increased the gas solubilities over those of toluene alone.

Introduction

In a multicomponent system, the solubility of one gas in a liquid is often affected by the presence of the others. Many studies have been carried out on binary gas mixtures, whereas solubility data on ternary gas mixtures are fairly limited. Simnick et al. (1980) measured vapor−liquid equilibria in a system containing hydrogen, methane, and tetralin (1,2,3,4-tetrahydronaphthalene: $C_{10}H_{12}$). The measurements were performed at 462 K and 663 K and pressures from 5.07 MPa to 25.33 MPa for several gas compositions. They reported substantial variations in the equilibrium ratio (K) values at high pressures. A decrease in hydrogen solubility with increased methane concentration in a system containing hydrogen, methane, and coal liquid was reported by Ding et al. (1985), who performed experiments in the temperature range 420 K to 680 K and the pressure range 4 MPa to 11 MPa. Liaw et al. (1991) measured the solubilities for hydrogen + methane + tetralin and hydrogen + ethane + tetralin systems at temperatures of 633 K and 653 K and pressures up to 12 MPa. The presence of methane or ethane in the systems affected the solubility of hydrogen in tetralin. At constant temperature and hydrogen partial pressure, the solubility of hydrogen in tetralin first increased as the methane and ethane partial pressures increased and then decreased.

The presence of heavier hydrocarbon gases in a hydrogen gas stream and the addition of heavy paraffinic compounds to an aromatic solvent are normally encountered in the absorption-stripping process used for the purification of high-pressure hydrogen from a hydrocracker off-gas. Hydrocracker off-gas is normally at pressures 13.88 MPa to 20.78 MPa and temperature 310 K and typically contains 70 mol % H_2, 25 mol % CH_4, and 5 mol % C_2^+. Absorption-stripping processes are normally preferred for hydrogen purification since hydrogen-rich gas is available at high pressure, reducing compression costs. In a previous study (Peramanu and Pruden, 1997), solubilities of pure hydrogen, pure methane, and a binary gas containing 73 mol % hydrogen and 27 mol % methane were measured to identify solvents that selectively absorb methane over hydrogen.

The pure solvents tested were *n*-heptane, *n*-octane, 2,2,4-trimethylpentane, 1-octene, cyclohexane, methylcyclohexane, benzene, toluene, ethylbenzene, *m*-xylene, 1,2,4-trimethylbenzene, pyridine, and quinoline. The mixed solvents tested were Petro-Canada supreme gasoline, Shell regular gasoline, and light cycle oil. Solubility parameter correlations and equation-of-state predictions were also delineated. For the mixed solvents the solubility parameter correlations and the equation-of-state predictions for hydrogen and methane solubilities were reported by Peramanu (1998).

It is important to test the effect of the presence of heavier hydrocarbon gases on the solubilities of hydrogen and methane since hydrocracker off-gases normally contain some C_2^+ components. If the methane solubility is increased significantly and the hydrogen solubility is not affected, there will be an improved separation using an absorption-stripping process. Since there are insufficient data available to substantiate this, solubility measurements were performed for a ternary gas containing hydrogen, methane, and ethane in toluene and were compared with binary gas solubility results measured in the same apparatus.

Often refineries utilize aromatic oils as absorbing oils, yet they have low gas solubilities compared to those of paraffinic oils. It was previously observed that adding a paraffinic solvent (C6−C8) to aromatic solvents increased the gas solubilities (Brainard and Williams, 1967). However, data related to the addition of heavier paraffins (wax) to aromatic solvents are not available. Therefore, a normal-paraffin, eicosane ($C_{20}H_{42}$), was added to toluene, and the solubilities of binary and ternary gas mixtures were measured in the solution.

Experimental Method

The apparatus used for solubility measurements was a flow system with countercurrent flow of gas and liquid under steady-state conditions. Peramanu and Pruden (1997) give a detailed description of the experimental apparatus and a schematic diagram. The apparatus consisted of two major units, an absorber and a stripper. The absorber had a 1.6 cm inside diameter and was packed

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Table 1. Solubilities of Binary (73 mol % H_2 and 27 mol % CH_4) and Ternary (73 mol % H_2, 21 mol % CH_4, and 6 mol % C_2H_6) Gases in Toluene at 295 K

	binary gas		ternary gas		
P/MPa	x_{H_2}	x_{CH_4}	x_{H_2}	x_{CH_4}	$x_{C_2H_6}$
6.99	0.0173[a]	0.0403[a]	0.0173	0.0348	0.0544
8.71	0.0217	0.0489	0.0217	0.0422	0.0657
10.44	0.0260[a]	0.0575[a]	0.0261	0.0492	0.0760
12.16	0.0304	0.0649	0.0307	0.0559	0.0836
13.88	0.0348[a]	0.0724[a]	0.0346	0.0617	0.0894
17.33	0.0440[a]	0.0867[a]			
20.78	0.0536[a]	0.0996[a]			

[a] Data from Peramanu and Pruden (1997).

with 4 mm glass spheres up to a height of 38 cm, and the stripper was 47 cm high with an inside diameter of 1.6 cm. The absorber was maintained at high pressure where the gas was absorbed in the liquid. The liquid was regenerated in the stripper, which was maintained at near atmospheric pressures. Pressures and liquid levels were measured and controlled with PID controllers with deviation from the set points less than 0.5% and 0.25%, respectively. The liquid flow rates were measured using a microflow meter with an accuracy of ±0.5%, the gas flow rates were measured using wet-test meters with an accuracy of ±0.25%, and the gas compositions were measured with a gas chromatograph.

A detailed experimental procedure has been described previously (Peramanu and Pruden, 1997). On start-up the gas and liquid flow rates were simultaneously increased to their desired values. The liquid flow rates were kept less than 0.4 L/h so as to ensure a complete saturation of the liquid. Once start-up was initiated, steady-state operation was normally reached within approximately 0.5 h.

Materials

The binary and ternary gas mixtures were obtained from Praxair. The binary gas mixture had 73 mol % H_2 and 27 mol % CH_4, and the ternary gas mixture had 73 mol % H_2, 21% CH_4, and 6% C_2H_6. Toluene was obtained from BDH with a minimum purity of 99.5%, and eicosane was obtained from Aldrich Chemicals and was 99% pure.

Solubility Calculation Method and the Errors Involved

The solubilities of gases in toluene at separator conditions were neglected because the solubilities of the experimental gases at atmospheric conditions were negligible compared to those at high pressure. To calculate the solubilities of mixed gases, the separator gas composition was analyzed, and the molar flow rates of the individual gas (G_i) were calculated from the total molar flow rate that was measured using a wet-test meter. The mole fraction of an individual gas (x_i) in the solvent was calculated using

$$x_i = \frac{G_i}{\sum_{j=1}^{C} G_j + L} \qquad (1)$$

where L is the molar liquid flow rate and C is the number of components in the gas mixture. The molar flow rates of the individual gases (G_i) were calculated from the volumetric flow rates of the separator gas assuming ideal gas conditions. The molar liquid flow rates (L) were calculated using molecular weight and density data (Reid et al., 1987). For the mixture containing toluene and

Table 2. Solubilities of Binary (73 mol % H_2 and 27 mol % CH_4) and Ternary (73 mol % H_2, 21 mol % CH_4, and 6 mol % C_2H_6) Gases in a Solution of Toluene + Eicosane (7.54 mol % Eicosane) at 295 K

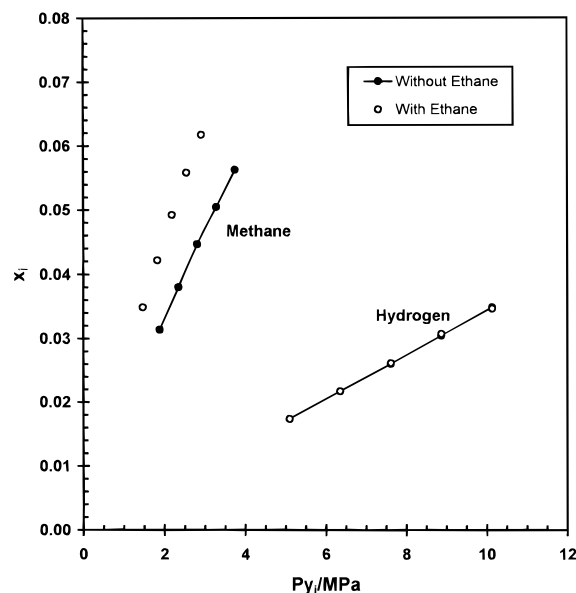|	binary gas			ternary gas			
P/MPa	x_{H_2}	x_{CH_4}	$x_{C_{20}H_{42}}$	x_{H_2}	x_{CH_4}	$x_{C_2H_6}$	$x_{C_{20}H_{42}}$
6.99	0.0196	0.0460	0.0704	0.0188	0.0385	0.0596	0.0666
8.71				0.0240	0.0471	0.0719	0.0650
10.44	0.0290	0.0645	0.0683	0.0290	0.0549	0.0834	0.0631
12.16				0.0335	0.0620	0.0895	0.0618
13.88	0.0393	0.0824	0.0662				
17.33	0.0479	0.0950	0.0646				

Figure 1. Solubilities (x_i) of hydrogen and methane in toluene versus their partial pressures (P_{y_i}) in the presence and absence of ethane at 295 K.

eicosane, the average molecular weight and average density were used to compute the molar liquid flow rates.

The experimental uncertainties involve the neglect of gas solubilities at separator conditions, the propagation of instrument errors on the calculated values of solubilities, and the reproducibility errors of the experiments. It was observed that at 10.44 MPa and 295 K the calculated values of the dissolved gas mole fractions were smaller by only 0.8% when the solubilities at separator conditions were neglected. The effects of instrument errors and random errors were calculated by performing the solubility experiments for pressures in the range of 6.99 MPa to 17.33 MPa. The maximum percentage difference ($100 \times |\Delta x_i|/x_i$) in the measured dissolved gas mole fractions due to propagation of instrument errors was less than 0.7% and that due to reproducibility of experiments was less than 1.1%. These indicate that the maximum uncertainty in the mole fraction values did not exceed 1.8%.

The solvent, toluene, was assumed to be nonvolatile since it did not appear in the gas phase at the high-pressure conditions involved in the experiments. This was also justified since there was no trace of toluene observed when the absorber exit gas was condensed.

It was assumed that liquid leaving the absorber was in equilibrium with the feed gas, and therefore the equilibrium gas compositions were taken as feed gas compositions. This is a fair assumption under the conditions of negligible dispersion and when the concentration variation in the gas phase is not significantly high. Owing to high gas flow rate and low liquid flow rates used in the experiments, the
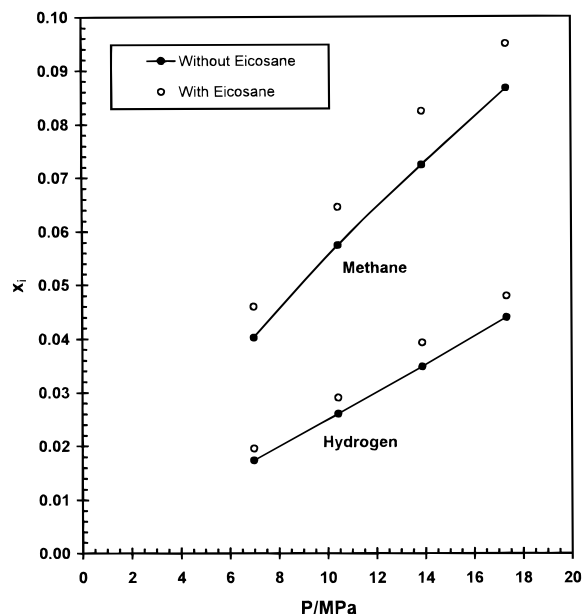
Figure 2. Effect of 7.54 mol % eicosane in toluene solution on the solubilities (x_i) of hydrogen and methane for a binary gas containing 73 mol % H_2 and 27 mol % CH_4 at 295 K.

maximum percentage variation in the hydrogen mole fraction was less than 3%, for methane it was less than 5%, and for ethane it was less than 7%.

To evaluate the accuracy of the experimental values, the solubilities of pure hydrogen and pure methane in toluene were compared (Peramanu and Pruden, 1997) with the literature data (Ipatiev and Levin, 1935; Brunner, 1985; Savvina, 1962; Lin et al., 1978). It was observed that for pure hydrogen solubility in toluene the percentage difference in the mole fraction was 1.2%, and for pure methane solubility in toluene the difference was 0.75%.

Results and Discussion

The experimental solubility results for the binary gas mixture and for the ternary gas mixture in toluene at 295 K are given in Table 1. Some of the data for binary gas solubilities in toluene were taken from the previous work (Peramanu and Pruden, 1997). Table 2 gives the solubilities of binary and ternary gases in a solution of toluene and eicosane containing 20 mass % (7.54 mol %) eicosane.

A direct comparison of binary gas and ternary gas solubilities cannot be made using Table 1 at system pressure (P) because the partial pressures of the individual gases are not equal. Therefore, the solubilities were compared using partial pressures of the gases as shown in Figure 1. The partial pressures (P_{y_i}) were calculated using the system pressure (P) and the component mole fraction (y_i) in the feed gas. The addition of ethane to hydrogen and methane gas mixture did not affect the hydrogen solubility, whereas the methane solubility increased by about 37%.

The solubilities of a binary gas mixture in toluene with and without eicosane are compared in Figures 2 and those of a ternary gas mixture are compared in Figure 3. Eicosane increased the solubilities of hydrogen, methane, and ethane. For the binary gas mixture, the increase in hydrogen solubility was 11.5% and for methane it was 12.5%. For the ternary gas mixture, the increase was 9.8% for hydrogen, 11.2% for methane, and 9.0% for ethane.

Conclusions

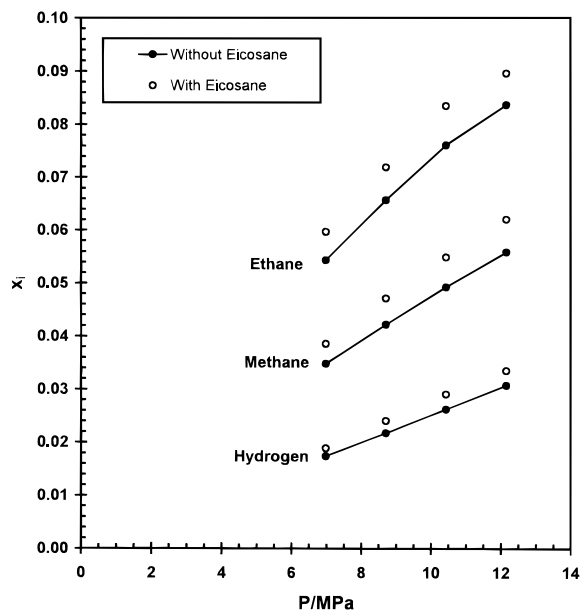The presence of 6 mol % ethane did not affect the hydrogen solubility in toluene, whereas methane solubility

Figure 3. Effect of 7.54 mol % eicosane in toluene solution on the solubilities (x_i) of hydrogen, methane, and ethane for a ternary gas containing 73 mol % H_2, 21 mol % CH_4, and 6 mol % C_2H_6 at 295 K.

increased significantly. This results in a higher selectivity for methane and a better separation from hydrogen in the presence of ethane.

The addition of a heavier paraffin, eicosane ($C_{20}H_{42}$), to toluene with a concentration of 7.54 mol % eicosane in the solution increased the gas solubilities by about 10%. This indicates that in the hydrogen purification process using an absorption-stripping process the absorption capacity of an aromatic solvent can be improved by adding a paraffin wax.

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