Solubility of Hydrogen Sulfide in *n*-Eicosane at Elevated Pressure

Guo-xiang Feng and Alan E. Mather*

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

The solubility of H_2S in *n*-eicosane ($C_{20}H_{42}$) was measured at 50, 88, and 150 °C at pressures up to 7.6 MPa. Henry's constants were obtained from the data, and the interaction parameter in the Peng–Robinson equation of state was determined.

Introduction

Vapor–liquid equilibria for H_2S and alkane hydrocarbons are available for the lower members of the alkane series. However, few data exist for H_2S with alkanes of carbon number greater than 10. This work was undertaken to provide data to use in equations of state for the prediction of multicomponent vapor–liquid equilibria at elevated pressures.

Experimental Section

The experimental apparatus is similar to that used by Lee et al. (*1*). The equilibrium cell consisted of a Jerguson liquid level gauge (model 17-T-30) with a 250 cm³ tubular reservoir mounted at the top. The pressure in the cell was measured by a 0–10000-kPa digital Heise gauge, and the temperature of the fluid was measured using a calibrated iron–constantan thermocouple. The *n*-eicosane was supplied by the Aldrich Chemical Co. and had a purity of 99%. The H_2S and CO_2 were supplied by Matheson Canada Ltd., and each had a minimum purity of 99.5%. All substances were used as received. About 40 cm³ of *n*-eicosane was fed by gravity into the cell. The air bath was brought to the desired temperature, and the cell was evacuated to remove dissolved gases. Hydrogen sulfide was added in an amount monitored by the pressure. The vapor phase was recirculated by a magnetic pump and bubbled through the liquid for about 5 h until a steady value of the pressure indicated that the equilibrium had been reached. The pump was stopped, and a sample of the liquid phase, 0.4–4 cm³, was withdrawn into a tared sample bomb. The bomb was reweighed to obtain the mass of the sample and attached to a calibrated 100 cm³ buret. The valve was opened, and H_2S evolved and was collected in the buret. The amount of H_2S was calculated from the atmospheric pressure, room temperature, and volume collected. The residual H_2S in the *n*-eicosane was determined by injection of a sample of the liquid into a chromatograph and comparison with an injection of pure H_2S gas. A chromatograph with a 2.5-m-long column packed with Porapak Q was used. The total H_2S in the liquid phase was calculated from the sum of the gas and the residual content in the liquid. Duplicate analyses indicated that the precision of the results is ±0.002 mole fraction.

Results

To confirm the procedure and analytical technique, the solubility of CO_2 in *n*-eicosane was measured at 50 °C. The results are presented in Table I and plotted in Figure 1 for comparison with previous work. The data are seen to be in good agreement with those of Gasem and Robinson (*2*) and Schwarz and Prausnitz (*3*). The data of Huie et al. (*4*) were
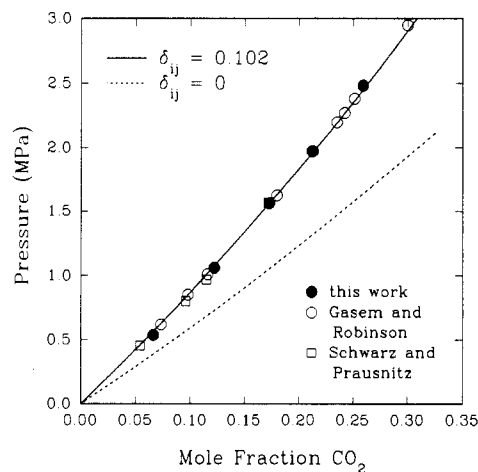
Figure 1. Comparison of data for the system CO_2 + *n*-eicosane at 50 °C.

Table I. Solubility of CO_2 in *n*-Eicosane

T, K	*P*, MPa	x_{CO_2}	*T*, K	*P*, MPa	x_{CO_2}
322.9	0.538	0.066	322.9	1.973	0.212
322.9	1.062	0.122	323.0	2.482	0.259
323.1	1.563	0.173			

Table II. Solubility of H_2S in *n*-Eicosane

T, K	*P*, MPa	x_{H_2S}	*T*, K	*P*, MPa	x_{H_2S}
322.9	0.404	0.161	323.1	2.008	0.635
323.1	0.654	0.256	322.9	2.403	0.729
323.0	0.933	0.332	322.9	2.958	0.855
322.9	1.312	0.438	323.1	3.143	0.895
322.9	1.602	0.516			
361.3	0.544	0.128	361.3	3.693	0.715
361.2	1.144	0.259	361.3	4.403	0.749
361.3	1.584	0.355	361.3	5.228	0.824
361.3	2.349	0.505	361.2	6.065	0.875
361.2	3.044	0.609	361.2	6.338	0.908
423.2	0.458	0.0669	423.2	4.093	0.517
423.2	1.023	0.152	423.2	5.003	0.576
423.3	1.663	0.241	423.3	6.454	0.660
423.3	2.434	0.343	423.3	7.674	0.720
423.4	3.064	0.413			

shown to be in substantial disagreement with those of Gasem and Robinson, which were concluded to be accurate.

Data for the solubility of H_2S in *n*-eicosane were obtained at 50, 88, and 150 °C at pressures up to 7.6 MPa. The results are presented in Table II. The data were represented by the Krichevsky–Kasarnovsky equation:

$$\ln (f_2/x_2) = \ln H_{2,1} + (\bar{v}^\infty/RT)(P - P_1^\circ) \qquad (1)$$

A plot of $\ln (f_2/x_2)$ versus P was constructed (the vapor
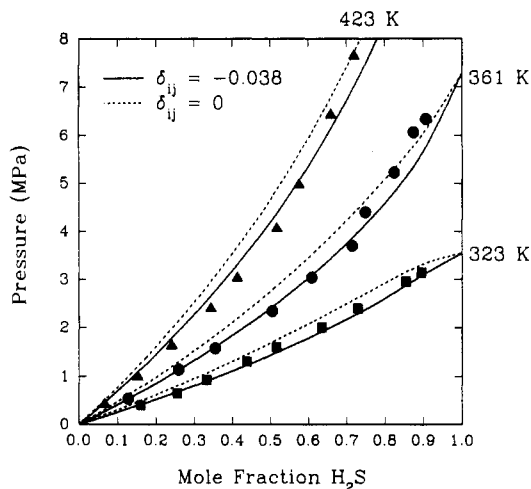
Figure 2. Solubility of H_2S in *n*-eicosane.

Table III. Henry's Constants of H_2S in *n*-Eicosane

T, K	$H_{2,1}$, MPa
323.1	2.42
361.2	4.07
423.3	6.42

pressure of *n*-eicosane is negligible even at the highest temperature), and values of $H_{2,1}$ were obtained from the intercept of the curve at $P = 0$. The fugacities of H_2S were obtained from Goodwin (5). Henry's constants are given in Table III.

The solubility data were correlated with the Peng–Robinson (6) equation of state. The pure component parameters required for the equation were obtained from Daubert and Danner (7). The optimum interaction parameter, δ_{ij}, in the

mixing rule of the equation of state was obtained by minimizing the error in the predicted bubble point pressure. The following objective function was used:

$$f(\delta_{ij}) = \left(\sum \frac{P_{exp} - P_{calc}}{P_{exp}}\right)\Big/NP \qquad (2)$$

where P_{exp} is the experimental bubble point pressure, P_{calc} is the calculated bubble point pressure, and NP is the number of data points. The use of a δ_{ij} of –0.038 for the *n*-eicosane–H_2S system results in a value of the objective function of 5.0%. This value of δ_{ij} allows the correlation of the solubility data over the complete range of composition at the three temperatures. These results of the correlation are compared with the experimental data in Figure 2. Reasonable agreement is found although the data at the highest temperature exhibit a skewed behavior.

Literature Cited

(1) Lee, J. I.; Mather, A. E.; Otto, F. D. *J. Chem. Eng. Data* **1978**, *23*, 78.
(2) Gasem, K. A. M.; Robinson, R. L., Jr. *J. Chem. Eng. Data* **1985**, *30*, 53.
(3) Schwarz, B. J.; Prausnitz, J. M. *Ind. Eng. Chem. Res.* **1987**, *26*, 2360.
(4) Huie, N. C.; Luks, K. D.; Kohn, J. P. *J. Chem. Eng. Data* **1973**, *18*, 311.
(5) Goodwin, R. D. Hydrogen Sulfide Provisional Thermophysical Properties from 188 to 700 K at Pressures to 75 MPa. Report No. NBSIR 83-1694; U.S. National Bureau of Standards: Boulder, CO, 1983.
(6) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59.
(7) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere Publishing Co.: Washington, DC, 1991.