

Literature Cited

- (1) Potter, R. W., II, Clyne, M. A., *J. Res. U.S. Geol. Surv.*, **6**, 701 (1978).
 (2) Potter, R. W., II, Babcock, R. S., Brown, D. L., *J. Res. U.S. Geol. Surv.*, **5**, 389 (1977).
 (3) Linke, W. F., "Solubilities of Inorganic and Metal Organic Compounds", 4th ed., Vol. 2, American Chemical Society, Washington, D.C., 1965.
 (4) Volz-Fladrich, H., *Freiberg. Forschungsh. C*, **134**, 1 (1962).

Received for review May 21, 1979. Accepted July 24, 1979.

Equilibrium Phase Properties of the Toluene-Hydrogen Sulfide and *n*-Heptane-Hydrogen Sulfide Binary Systems

Heng-Joo Ng, Harish Kalra, Donald B. Robinson,* and Hironobu Kubota

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

Vapor and liquid equilibrium phase compositions have been determined for the toluene-hydrogen sulfide and *n*-heptane-hydrogen sulfide binary systems at temperatures of 100.0, 175.0, 250.0, and 400.0 °F at several pressures between the vapor pressure of the hydrocarbon component and the vapor pressure of hydrogen sulfide or the critical pressure for the system, whichever was higher. Refractive index measurements were made on the equilibrium vapor and liquid phases for the hydrogen sulfide-*n*-heptane system at the three lower temperatures. These measurements were used with the phase composition data to calculate the equilibrium phase densities using the Lorentz-Lorenz molar refractivity relationship.

Introduction

Hydrogen sulfide is frequently found in naturally occurring hydrocarbon reservoirs and it is one of the more common nonhydrocarbon components found in substitute fuel mixtures derived from heavy oils, bitumen, or coal. Thus any method used for calculating the properties or phase behavior of these complex mixtures must be capable of coping with the presence of hydrogen sulfide. Normally, calculation methods require a knowledge of the properties of the pure components in the system, and in the case of hydrocarbon-nonhydrocarbon mixtures, they require at least one characteristic parameter for each possible hydrocarbon-nonhydrocarbon binary pair that could be formed from the mixture. In cases where the individual hydrocarbon components in the higher molecular weight fractions are not identified, it is common practice to at least attempt to characterize the fraction according to its paraffinic, aromatic, naphthenic, and sometimes olefinic content. Thus the binary interactions between the nonhydrocarbons and the fractions must be estimated. In order to make good estimates of these parameters, it is essential to have at least some values based on experimental data for selected representatives of each group.

The object of the work presented in this paper was to obtain experimental data which would make it possible to calculate binary interaction parameters for hydrogen sulfide with *n*-heptane, a C₇ paraffin, and toluene the C₇ aromatic. The work represents a continuation of the studies on related systems which have recently been reported by Ng and Robinson (10, 11) and Kalra et al. (9). No previous studies were found in the literature on the *n*-heptane-hydrogen sulfide system. The only previous work on the toluene-hydrogen sulfide system was that of Gerrard

(6) on the solubility of hydrogen sulfide in toluene at a total pressure of 754 mmHg over a temperature range from -8 to +20 °C.

Experimental Method

The experimental methods used in this work were the same in all respects as those described by Kalra et al. (9) and by Ng and Robinson (10, 11) for their work on carbon dioxide with toluene and *n*-heptane and carbon dioxide and hydrogen sulfide with methylcyclohexane. The variable volume equilibrium cell described in detail by Besserer and Robinson (2, 3) was used for the studies on hydrogen sulfide and *n*-heptane at 100, 175, and 250 °F. Refractive index measurements were made on the equilibrium vapor and liquid phases at each temperature. The fixed volume cell described in detail by Ng and Robinson (10) was used for this system at 400 °F and also for all of the work on hydrogen sulfide and toluene. No refractive index measurements were made on the hydrogen sulfide-toluene system.

Samples of the vapor phase were obtained from the variable volume cell using the technique explained by Besserer and Robinson (2, 3) and from the constant volume cell using a specially designed valve described by Kalra and Robinson (8). Samples of the liquid phase from the variable volume cell were obtained by trapping a sample of the equilibrium liquid in one chamber of a four-way ball valve and then vaporizing it into a stream of circulating hot helium. A similar sample of the liquid from the constant volume cell was obtained by using a device similar to that described by Frødenlund et al. (5). In all cases, the methods permitted the removal of microsamples so that the cell conditions were not materially altered during the sampling process.

Materials Used

The hydrogen sulfide used in these studies was obtained as a specially prepared sample from Thio-Pet Chemicals Limited, Fort Saskatchewan, Alberta, Canada. The liquid phase of this material was distilled once and the condensed phase from the distillation was used for the experiments. This minimized contamination with carbon dioxide and mercaptans. The purity of the material was at least 99.9 mol % as determined by chromatographic analysis. The toluene was research grade supplied by Phillips Petroleum Co. with a purity of 99.94 mol %. The *n*-heptane was supplied by Aldrich Chemicals at a stated purity of 99+ mol % but a chromatographic scan indicated it to be better than 99.9+ % pure. Both of these materials were used without further purification.

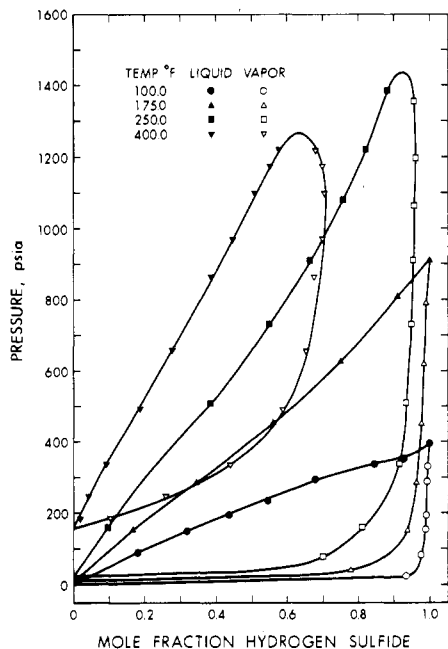


Figure 1. Equilibrium phase compositions for the *n*-heptane-hydrogen sulfide system.

Experimental Measurements

The iron-constantan thermocouples were calibrated against a platinum resistance thermometer certified by the National Research Council of Canada. Temperatures were measured to within ± 0.1 °F. The pressure of the cell contents was measured by using 0–2000 and 0–3000 psi Heise gauges which had been calibrated against a Ruska dead weight gauge. The accuracy of the gauges was known to within $\pm 0.1\%$ of full scale.

The samples of liquid and vapor from the variable volume equilibrium cell were analyzed by using a Hewlett-Packard Model 700 chromatograph and from the fixed volume cell by using a Hewlett-Packard Model 5830A chromatograph with thermal conductivity detectors. In both cases a 3 ft by $\frac{1}{8}$ in. diameter column packed with Porapak QS was used. Calibration was done by using the pure components in constant volume sample loops at pressures of about 200 mmHg or less. The response was linear with sample size at these conditions. The response factor of hydrogen sulfide relative to *n*-heptane was found to be 2.410 and relative to toluene was 2.652. At least two samples were taken from each phase and at least three analyses were made on each sample. Thus the compositions reported are the result of averaging at least six different analyses at the given conditions.

The repeatability of the analyses was normally within 0.2 mol %, and their accuracy is believed to be within ± 0.3 mol %.

The optical system used for the refractive index measurements made it possible to read the refractive indices within an accuracy of ± 0.0001 .

Results

The experimentally measured equilibrium phase compositions for the hydrogen sulfide-*n*-heptane system are presented in Table I and are shown graphically in Figure 1 for each of the four temperatures of 100, 175, 250, and 400 °F.

Whenever a slight change in pressure (usually in the order of 1–2%) occurred between liquid and vapor sampling, an interpolated value of the composition of the other phase was obtained so that the equilibrium ratios could be calculated at a constant pressure. Any error resulting from these interpolations is considered negligible. Table I also shows the experimentally

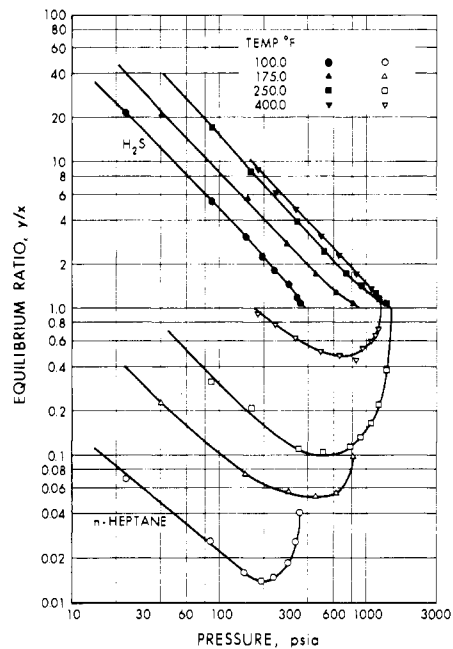


Figure 2. Equilibrium ratios for *n*-heptane and hydrogen sulfide in the *n*-heptane-hydrogen sulfide binary system.

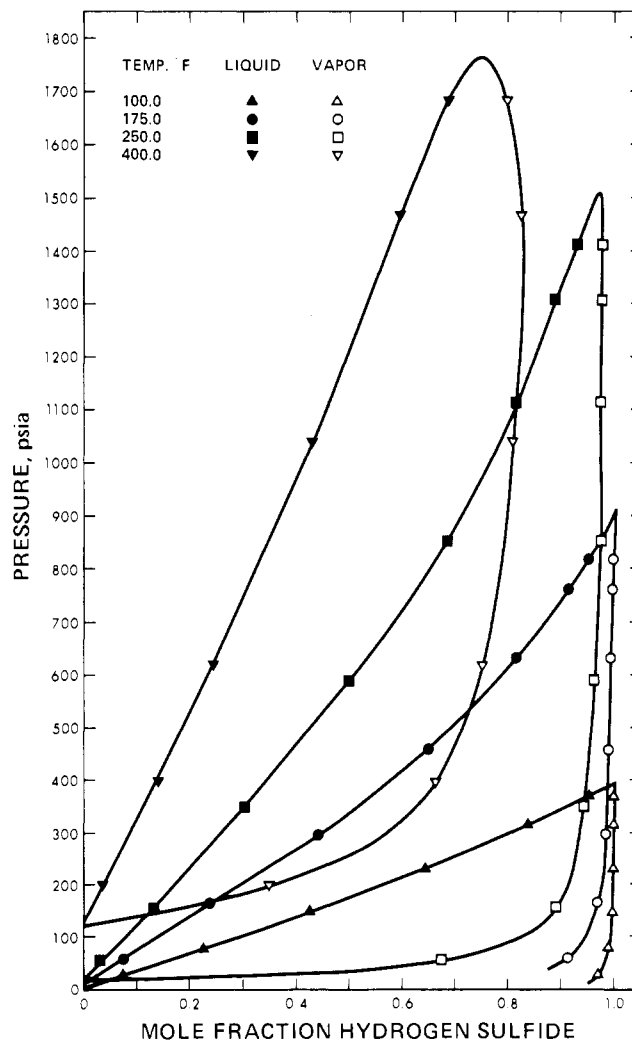


Figure 3. Equilibrium phase compositions for the toluene-hydrogen sulfide system.

measured equilibrium phase refractive indices and the calculated molar volumes at each of the three lower temperatures. The

Table I. Equilibrium Phase Properties of the *n*-Heptane-Hydrogen Sulfide System

pressure, psia	composition ^a		refractive index ^b		molar volume ^c		equilib ratios		
	x _{H₂S}	y _{H₂S}	n _L	n _V	V _L	V _V	K _{H₂S}	K _{n-C₇}	
									100 °F
23.2	0.043 ^d	0.933	1.3772	1.0003	142	57200	21.7	0.070	
81.9	0.166 ^d	0.977	1.3738	1.0030	130	5170	5.89	0.028	
88.0	0.180	0.978 ^d	1.3736	1.0033	129	4690	5.43	0.026	
148	0.311 ^d	0.988	1.3698	1.0059	116	2560	3.18	0.017	
149	0.318	0.989 ^d	1.3697	1.0060	115	2510	3.11	0.016	
194	0.435	0.992	1.3664	1.0081	104	1840	2.28	0.014	
234	0.538 ^d	0.992	1.3630	1.0101	93.4	1480	1.84	0.017	
236	0.545	0.991	1.3628	1.0102	92.7	1470	1.82	0.020	
293	0.675 ^d	0.993	1.3571	1.0134	79.8	1110	1.47	0.022	
294	0.680	0.994 ^d	1.3570	1.0135	79.3	1100	1.46	0.019	
332	0.819 ^d	0.996	1.3524	1.0154	64.9	958	1.22	0.022	
335	0.845	0.996 ^d	1.3519	1.0159	62.1	928	1.18	0.026	
351	0.927	0.997 ^d	1.3494	1.0169	53.3	871	1.08	0.041	
									175.0 °F
40.5	0.037 ^d	0.780	1.3554	1.0017	152	13370	21.1	0.229	
151	0.164 ^d	0.937	1.3503	1.0060	140	2830	5.71	0.075	
154	0.167	0.937 ^d	1.3502	1.0061	139	2780	5.61	0.076	
286	0.347	0.963 ^d	1.3438	1.0112	121	1430	2.78	0.057	
289	0.351 ^d	0.963	1.3436	1.0114	121	1400	2.74	0.057	
451	0.556 ^d	0.976	1.3335	1.0190	99.6	815	1.76	0.054	
455	0.561	0.977 ^d	1.3332	1.0192	99.1	805	1.74	0.052	
619	0.745 ^d	0.985	1.3191	1.0287	80.4	528	1.32	0.059	
625	0.750	0.986 ^d	1.3186	1.0290	79.9	521	1.31	0.056	
790	0.896 ^d	0.992	1.2986	1.0413	65.6	361	1.11	0.077	
807	0.908	0.991 ^d	1.2961	1.0428	64.5	349	1.09	0.098	
									250.0 °F
87.8	0.041 ^d	0.702	1.3287	1.0050	163	5120	17.1	0.311	
159	0.094 ^d	0.812	1.3270	1.0073	158	2960	8.64	0.208	
162	0.096	0.810 ^d	1.3270	1.0076	158	2850	8.44	0.210	
338	0.234 ^d	0.916	1.3217	1.0145	143	1220	3.91	0.110	
509	0.385 ^d	0.933	1.3149	1.0221	127	774	2.42	0.109	
509	0.384	0.935 ^d	1.3148	1.0221	127	770	2.43	0.106	
729	0.549	0.948	1.3029	1.0331	110	500	1.73	0.115	
909	0.665 ^d	0.953	1.2954	1.0442	97.2	371	1.43	0.140	
912	0.667	0.955 ^d	1.2901	1.0444	98.6	367	1.43	0.135	
1063	0.749 ^d	0.957	1.2771	1.0563	91.2	289	1.28	0.171	
1079	0.757	0.959 ^d	1.2756	1.0578	90.6	280	1.27	0.169	
1198	0.811 ^d	0.959	1.2630	1.0710	86.5	228	1.18	0.217	
1221	0.821	0.960 ^d	1.2603	1.0744	85.8	218	1.17	0.224	
1354	0.871 ^d	0.957	1.2424		83.7		1.10	0.333	
1385	0.880	0.954 ^d					1.08	0.383	
									400.0 °F
182	0.0177	0.104					8.89	0.912	
242	0.0414	0.260					6.29	0.772	
334	0.0929	0.443					4.77	0.614	
488	0.188	0.589					3.13	0.506	
652	0.279	0.652					2.34	0.483	
856	0.386	0.677					1.76	0.449	
964	0.447	0.760					1.57	0.542	
1093	0.514	0.707					1.38	0.603	
1168	0.552	0.704					1.28	0.661	
1213	0.578	0.676					1.17	0.732	

^a Mole fraction. ^b Relative to vacuum at 6328 Å. ^c Calculated from refractive index and composition data (cm³/g-mol). ^d Interpolated isobarically from the other equilibrium phase.

equilibrium ratios calculated from the measured phase compositions are given for all four temperatures and are shown graphically in Figure 2.

The experimental results of the phase compositions and the calculated equilibrium ratios for the hydrogen sulfide-toluene system are presented in Table II and in Figures 3 and 4 for all four temperatures.

Discussion

The molar volumes of the equilibrium phases reported at the three lower temperatures in Table I were calculated from the measured phase compositions and refractive indices using the Lorentz-Lorenz molar refractivity relationship as explained in

the earlier papers by Besserer and Robinson (2, 3). The molar refractivity is expressed in terms of the refractive index and molar density as follows:

$$R_{LL} = \frac{n^2 - 1}{n^2 + 1} \frac{1}{\rho_m}$$

The molar refractivity for a mixture is calculated as the molar average of the pure component values by

$$R_{LLM} = \sum_i z_i R_{LLi}$$

where z_i is the mole fraction of any component i in the phase for which the molar refractivity is required.

Table II. Equilibrium Phase Properties of the Hydrogen Sulfide-Toluene System

pressure, psia	composition ^a		equilib const	
	$x_{\text{H}_2\text{S}}$	$y_{\text{H}_2\text{S}}$	$K_{\text{H}_2\text{S}}$	K_{toluene}
		100.0 °F		
29.5	0.077	0.971	12.8	0.031
79.3	0.226	0.990	4.39	0.013
150	0.427	0.996	2.33	0.0065
230	0.643	0.998	1.55	0.0070
317	0.836	0.998	1.19	0.014
370	0.954	0.999	1.05	0.015
		175.0 °F		
59.6	0.071	0.913	12.8	0.094
165	0.238	0.971	4.08	0.038
296	0.442	0.985	2.23	0.027
459	0.651	0.991	1.52	0.027
632	0.817	0.995	1.22	0.028
762	0.914	0.996	1.09	0.038
818	0.953	0.998	1.05	0.045
		250.0 °F		
54.5	0.031	0.677	21.5	0.334
154	0.135	0.891	6.60	0.126
350	0.305	0.944	3.09	0.081
589	0.502	0.963	1.92	0.074
853	0.686	0.975	1.42	0.081
1114	0.816	0.975	1.20	0.136
1309	0.891	0.975	1.09	0.228
1413	0.932	0.978	1.05	0.324
		400.0 °F		
200	0.037	0.352	9.53	0.673
399	0.142	0.666	4.70	0.389
619	0.247	0.752	3.04	0.330
1036	0.433	0.807	1.87	0.340
1468	0.598	0.826	1.38	0.434
1679	0.689	0.797	1.16	0.652

^a Mole fraction.

The refractivity of *n*-heptane was obtained directly from the results reported by Kalra et al. (9) in their work on the carbon dioxide-*n*-heptane system.

The refractivity of hydrogen sulfide was based on an empirical relationship used previously by Hadrich (7) for hydrocarbons. This relationship is

$$f(n) = \frac{n^2 - 1}{n^2 + 2} = A\rho_m^B e^{-CT}$$

where *A*, *B*, and *C* are characteristic constants of the material and depend on the wavelength of light.

In order to evaluate the constants in this equation, we made refractivity measurements on pure hydrogen sulfide at 100 °C up to its vapor pressure and at 250 °F at pressures from 290 to 1988 psia. Single measurements were also made for the vapor at 80, 50, and 40 °F, and for the liquid and vapor at -35 and -100 °F. The molar density of hydrogen sulfide at each condition was predicted with the Benedict-Webb-Rubin equation of state (7) using the improved constants reported by Bishnoi et al. (4). A plot of $-\ln f(n)$ against $-\ln \rho_m$ was prepared. A linear least-squares fit of these data gave a slope *B* of 0.995 and an intercept Ae^{-CT} of 9.42 cm³/g-mol. It was found that a single line represented the data for all temperatures and hence the relationship for determining the refractivity of hydrogen sulfide was obtained from

$$R_{LL} = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{1}{\rho_m} = 0.42(\rho_m^{-0.005})$$

where ρ_m is the molal density of hydrogen sulfide at the experimental temperature and pressure.

The reliability of the molal volumes of the saturated liquids is believed to be within $\pm 1.3\%$ and of the saturated vapors,

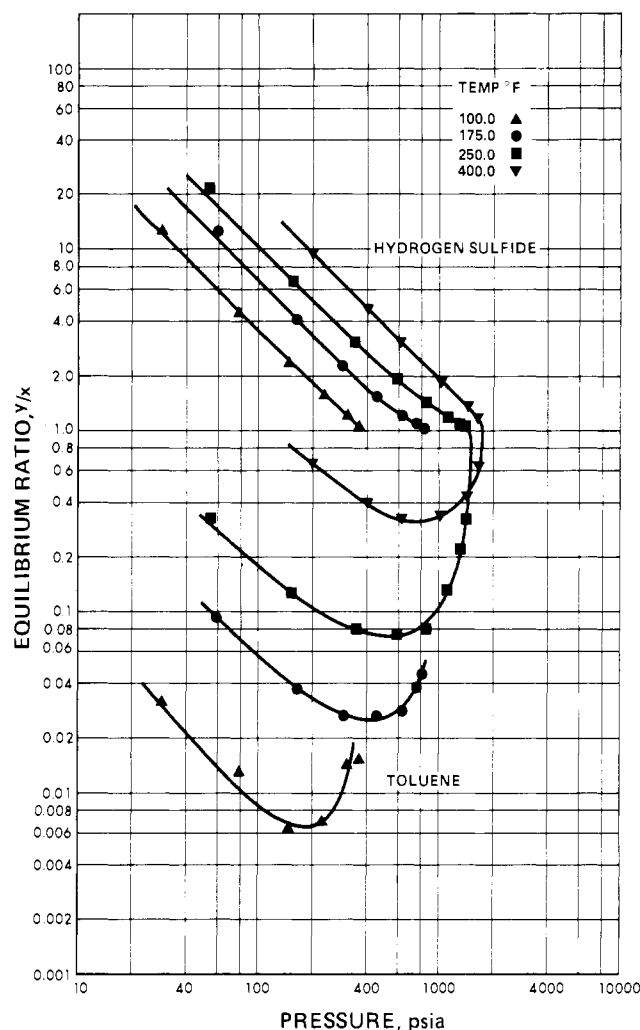


Figure 4. Equilibrium ratios for toluene and hydrogen sulfide in the toluene-hydrogen sulfide binary system.

within $\pm 1.1\%$. The errors in the vapor molal volumes may be somewhat higher in regions where the refractive index approaches unity.

The critical pressures at the two higher temperatures can be estimated for both systems from Figures 2 and 4 because in a binary system the isothermal equilibrium ratios converge to unity at the critical pressure. For the *n*-heptane-hydrogen sulfide system, the critical pressures at 250 and 400 °F are estimated to be 1450 and 1260 psia, respectively. For the toluene-hydrogen sulfide system, the corresponding pressures are 1510 and 1750 psia at the same temperatures.

Glossary

<i>A</i> , <i>B</i> , <i>C</i>	constants in equation describing effect of density and temperature on refractive index
<i>K</i>	equilibrium ratio
<i>n</i>	refractive index
R_{LL}	Lorentz-Lorenz molal refractivity, cm ³ /mol
ρ	density, mol/cm ³
<i>T</i>	absolute temperature, K
<i>V</i>	molal volume, cm ³ /mol
<i>x</i>	mole fraction in liquid phase
<i>y</i>	mole fraction in vapor phase
<i>z</i>	mole fraction in any mixture

Subscripts

<i>i</i>	any component in a mixture
<i>L</i>	liquid phase
<i>M</i>	mixture

m molal
V vapor phase

Literature Cited

- (1) Benedict, M., Webb, G. B., Rubin, L. C., *J. Chem. Phys.*, **6**, 334 (1940).
- (2) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49**, 651 (1971).
- (3) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 298 (1973).
- (4) Bishnoi, P. R., Miranda, R. D., Robinson, D. B., *Hydrocarbon Process.*, **53** (11), 197 (1974).
- (5) Fredenslund, A., Mollerup, J., Christiansen, L. J., *Cryogenics*, **13**, 414 (1973).
- (6) Gerrard, W., *J. Appl. Chem. Biotechnol.*, **22**, 623 (1972).
- (7) Hadrich, J., *J. Chem. Phys.*, **64**, 2265 (1976).
- (8) Kalra, H., Robinson, D. B., *Cryogenics*, **15**, 409 (1975).
- (9) Kalra, H., Kubota, H., Robinson, D. B., Ng, H.-J., *J. Chem. Eng. Data*, **23**, 317 (1978).
- (10) Ng, H.-J., Robinson, D. B., *J. Chem. Eng. Data*, **23**, 325 (1978).
- (11) Ng, H.-J., Robinson, D. B., *Fluid Phase Equilib.*, **2**, 283 (1979).

Received for review May 21, 1979. Accepted September 17, 1979. The financial assistance provided for this work by the Alberta Research Council and the Gas Processors Association is greatly appreciated.

Solubility of Sulfur Dioxide in Water-Acetonitrile Solutions

John J. Byerley,* Garry L. Rempel, and V. Thang Le

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

The solubilities of sulfur dioxide in water-acetonitrile solutions were determined at 25 and 50 °C and total pressure of 101.3 kPa. The solubilities are expressed in grams of sulfur dioxide dissolved/100 g of solute gas-free solution. At 25 °C two phases are observed when the overall composition lies between 20 and 80 wt % acetonitrile. The composition of each phase remains constant but the fraction of each phase is altered as the overall composition changes. Above 40 °C only one phase is observed for the entire composition range.

Introduction

The solubility of sulfur dioxide in water and other pure solvents has been investigated by many researchers; however, data on sulfur dioxide solubility in aqueous-nonaqueous solvent mixtures are very limited. Of particular interest is the system water-acetonitrile which has been proposed as a leaching and stabilizing medium in the hydrometallurgical processing of metallic minerals using sulfur dioxide (1-3).

In this paper, the solubility of sulfur dioxide in water-acetonitrile mixtures is examined at 25 and 50 °C over the complete composition range using both iodometric titration and chromatographic analytical techniques. A rather unexpected result was observed for the system which is the separation of two phases, a phenomenon which persisted in the range 20-80 wt % acetonitrile. An examination of the interaction of H₂O and SO₂ and CH₃CN and SO₂ using UV spectra was undertaken in an attempt to explain this phase separation.

Experimental Section

Materials. All chemicals were of reagent grade and were used directly without further purification. Acetonitrile was supplied by J. T. Baker. Sulfur dioxide (anhydrous) was obtained from Union Carbide Canada, Ltd. Aqueous solutions were made from distilled water free of carbon dioxide.

Sulfur Dioxide Solubility Experiments. The solubility of sulfur dioxide in water-acetonitrile solutions and the phase equilibria phenomena were studied in a 50-mL buret equipped with a water jacket. The circulating water was controlled to ± 0.1 °C. Sulfur dioxide was bubbled at a slow flow rate approximately 60 mL/min with the gas flow being from bottom to top of the buret. The gas exited through a spiral condenser in order to avoid excessive loss of acetonitrile. The sulfur dioxide concentration after saturation was measured by titrating excess iodine with standard thiosulfate solution using starch as the indicator. The

presence of acetonitrile in the analytical solution was determined not to interfere with the titration.

Phase Separation Experiments. In cases where there was a separation of two liquid phases upon sulfur dioxide saturation, the composition of each phase was determined by a gas chromatography technique using the internal normalization method. The GC measurements were made with a Hewlett-Packard F&M Scientific 700 laboratory chromatograph. The columns were stainless tubes 0.91 m long and 0.04 cm i.d. packed with 50-80 mesh Porapak Q. The carrier gas was helium (91.5% He-8.5% H₂) flowing at the rate of 30 mL/min. The temperatures of the injection port, the column oven, and the thermal conductivity detector were maintained at 165, 135, and 175 °C, respectively. Samples were injected by using either 10- or 25- μ L Hamilton microsyringes through a silicone rubber septum contained in the injection block. The sample sizes were 2 μ L for the water-rich phase and 5 μ L for the acetonitrile-rich phase. The identity of each component was checked by injecting pure samples and comparing the retention times. The chromatograms were recorded by using a standard millivolt recorder equipped with a disk integrator.

Spectrophotometric Experiments. In order to investigate the SO₂-CH₃CN and SO₂-H₂O interactions, we examined ultraviolet spectra of solutions of SO₂ in acetonitrile and SO₂ in water by using a Beckman DK spectrophotometer with two matched 1.0-cm cells. The wavelength region investigated was 250-300 nm. The temperature of the cells was controlled by using a thermostated cell holder. Stock solutions of SO₂ in distilled water and in pure acetonitrile (0.02-0.03 mol of SO₂/L) were prepared. The SO₂ content was verified by iodometry. From these stock solutions known solutions of SO₂-H₂O and SO₂-CH₃CN were prepared and their UV spectra measured. The range of solutions examined were as follows: SO₂-H₂O, 5×10^{-4} - 1×10^{-3} mol of SO₂/L; SO₂-CH₃CN, 3×10^{-3} - 5×10^{-3} mol of SO₂/L.

Results and Discussion

Sulfur Dioxide Solubility and Phase Separation at 25 °C. The solubility of sulfur dioxide in a number of water-acetonitrile mixtures at 25 °C and the total pressure of 101.3 kPa is summarized in Table I. Investigating this system over the range of pure water to pure acetonitrile produced a somewhat unusual result. As indicated in the table when the acetonitrile content was between 20 and 80 wt %, the sulfur dioxide saturated mixture was composed of two liquid phases. The upper layer (measured density of 0.975 g/mL) was the acetonitrile-rich phase and the lower layer (measured density 1.005 g/mL) was the water-rich phase. The notable feature of these data is the fact