Equilibrium Phase Properties of the Ethylcyclohexane–Hydrogen Sulfide and *n*-Propylcyclohexane–Hydrogen Sulfide Binary Systems

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Vapor and liquid equilibrium phase compositions have been determined for the ethylcyclohexane–hydrogen sulfide and *n*-propylcyclohexane–hydrogen sulfide binary systems at temperatures of 310.9, 352.6, 394.3, and 477.6 K and at several pressures from the vapor pressure of the less volatile component to the vapor pressure of hydrogen sulfide or to the critical pressure for the system, whichever was higher. The data were used to calculate equilibrium ratios for each component in the binary system.

Introduction

Hydrogen sulfide is frequently found in naturally occurring petroleum reservoirs and is a common component in fuels or other products derived from heavy oils, bitumen, or coal. Normally, the methods used for calculating the properties and behavior of these complex mixtures 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 hydrocarbon–nonhydrocarbon binary pair that could be formed from the components in the mixture.

It is seldom practical to quantitatively identify the individual hydrocarbon components in the higher molecular weight fractions of the mixtures under consideration, but it is common to try to characterize these fractions according to their paraffinic, aromatic, or naphthenic content. In order to make reasonable estimates of the binary parameters between the nonhydrocarbons and these fractions it is essential to have at least some values based on experimental data for selected binary pairs for each group.

The object of the work presented in this paper was to obtain experimental data on the behavior of hydrogen sulfide with ethylcyclohexane and with *n*-propylcyclohexane to assist in establishing characteristic hydrogen sulfide–naphthenic binary pairs. The work represents an extension of the work reported earlier by Ng et al. (*1*) on hydrogen sulfide with *n*-heptane and with toluene, by Ng and Robinson (*2*) on carbon dioxide and hydrogen sulfide with methylcyclohexane, and by Ng et al. (*3*) on methane and carbon dioxide with *m*-xylene.

No previous work was found in the literature on either of the binary pairs investigated here.

Experimental Method

The experimental method used in this work has already been described in considerable detail by Ng and Robinson (*2*, *4*). The design operating conditions for the equipment were from about 35 to 325 °C at pressures up to 25 MPa. The fluid mixtures under investigation were brought to equilibrium at prearranged pressure and temperature conditions in a stainless steel windowed cell having a volume of about 150 cm^3. Microsamples were withdrawn through specially designed valves from each equilibrium phase into an evacuated space. Heated helium was circulated through this space into a heated manifold to prevent condensation of the heavier component prior to injection into the gas chromatograph.

Materials Used

The hydrogen sulfide used in these studies was obtained from Matheson with a specified minimum purity in the liquid phase of 99.9 mol %. This material was distilled once and the condensed phase from the distillation was used for the experiments. This reduced contamination with carbon dioxide or mercaptans.

The ethylcyclohexane was obtained from Aldrich Chemicals and it was specified to have a purity of 99 mol % or greater. The *n*-propylcyclohexane was obtained from the Koch-Light Lab Ltd., England. It was specified to be of "pure grade" with a purity of 99 mol % or greater. Chromatograms were run on both of these materials but no detectable impurities were found. Both were used without further purification.

Experimental Measurements

The temperatures were measured by using iron–constantan thermocouples which had been calibrated against a platinum resistance thermometer. They are believed known to within ±0.06 K. The pressure of the cell contents was measured by using 0–6.89- and 0–20.7-MPa Heise Bourdon tube gauges which had been calibrated with a Ruska dead-weight gauge. The measurements are believed known to within ±0.1% of full scale.

The analysis of the liquid and vapor samples was carried out on a Hewlett-Packard Model 5730A chromatograph. A thermal conductivity detector was used for both systems.

Separation of hydrogen sulfide and ethylcyclohexane was achieved by using a 1.83 m long by 3.2 mm diameter column packed with 10% UC W98 on 80–100 mesh Porapak S together with a 1.37 m long by 3.2 mm diameter column packed with 50–80 mesh Porapak QS. The same columns were used for the hydrogen sulfide and *n*-propylcyclohexane system. In both cases the columns were operated by using a bypass technique whereby the two columns were connected with a four-port valve in such a way that the hydrogen sulfide was allowed to pass through both columns, but the heavier components were allowed to pass through only the first column.

The chromatograph was calibrated by using the pure components at pressures less than about 20 kPa where the response was linear. The response factor of hydrogen sulfide relative to ethylcyclohexane was 2.7322 and relative to *n*-propylcyclohexane was 3.0211.

At least two samples of each phase were taken for analysis and at least three chromatograms were run on each sample. The reported compositions therefore represent an average of at least six determinations. The repeatability of the analysis was generally within 0.2 mol %.

Results

The results of the direct experimental measurements of the equilibrium liquid and vapor phase compositions for the ethyl-

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Table I. Equilibrium Phase Properties of the Ethylcyclohexane-Hydrogen Sulfide System

press., MPa	x_{H_2S}	y_{H_2S}	K_{H_2S}	$K_{ethylcyclohexane}$
		T = 310.9 K		
0.170	0.0490	0.9811	20.0	0.0199
0.465	0.1495	0.9936	6.65	0.00753
0.972	0.3060	0.9964	3.26	0.00519
1.54	0.5362	0.9975	1.86	0.00539
2.21	0.8178	0.9988	1.22	0.00659
2.52	0.9447	0.9995	1.06	0.00904
2.66	0.9840	0.9998	1.02	0.0125
		T = 352.6 K		
0.273	0.0465	0.9324	20.1	0.0709
0.848	0.1518	0.9770	6.44	0.0271
1.72	0.3157	0.9876	3.13	0.0181
3.25	0.5822	0.9921	1.70	0.0189
4.59	0.8014	0.9947	1.24	0.0267
5.67	0.9443	0.9971	1.06	0.0521
6.10	0.9841	0.9988	1.01	0.0755
		T = 394.3 K		
0.383	0.0362	0.8067	22.3	0.201
1.14	0.1273	0.9332	7.33	0.0765
2.36	0.2767	0.9644	3.49	0.0492
4.42	0.5045	0.9769	1.94	0.0466
6.39	0.6820	0.9801	1.44	0.0626
8.68	0.8604	0.9801	1.14	0.143
9.65	0.9198	0.9787	1.06	0.266
		T = 477.6 K		
0.820	0.0163	0.3444	21.1	0.666
1.65	0.0735	0.6593	8.97	0.368
3.92	0.2368	0.8325	3.52	0.219
6.63	0.4109	0.8742	2.13	0.214
8.82	0.5437	0.8814	1.62	0.260
11.13	0.6702	0.8698	1.30	0.395
12.50	0.8313	0.8416	1.01	0.939

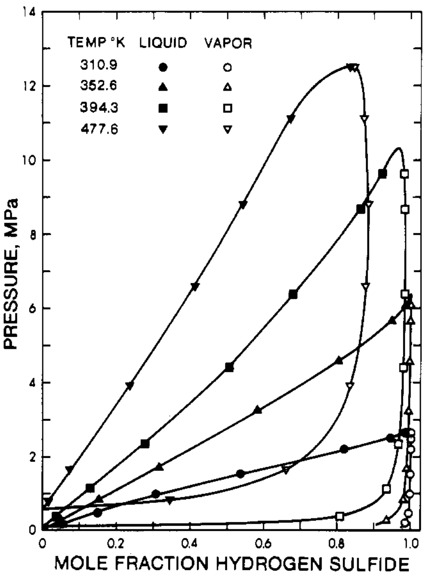

Figure 1. Pressure-equilibrium phase composition diagram for the ethylcyclohexane-hydrogen sulfide system.

cyclohexane-hydrogen sulfide system are presented in Table I and are shown graphically in Figure 1 for each of the four isotherms at 310.9, 352.6, 394.3, and 477.6 K. The calculated equilibrium ratios for each component in the binary system at each of the four temperatures are also presented in Table I and are shown graphically in Figure 2.

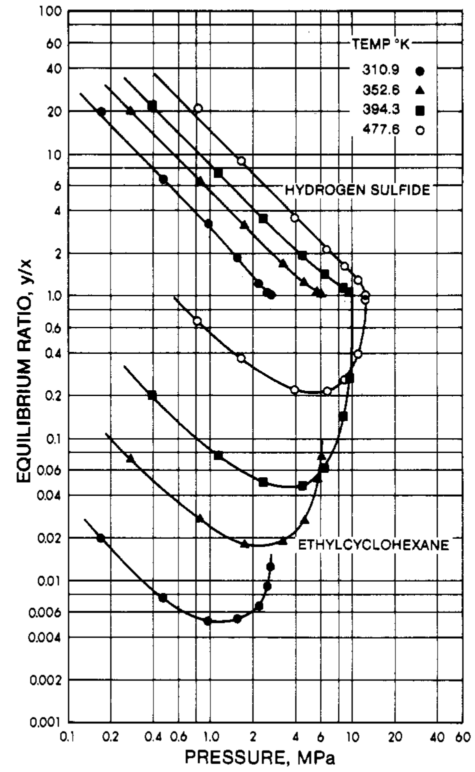

Figure 2. Equilibrium ratios for hydrogen sulfide and ethylcyclohexane in the ethylcyclohexane-hydrogen sulfide binary system.

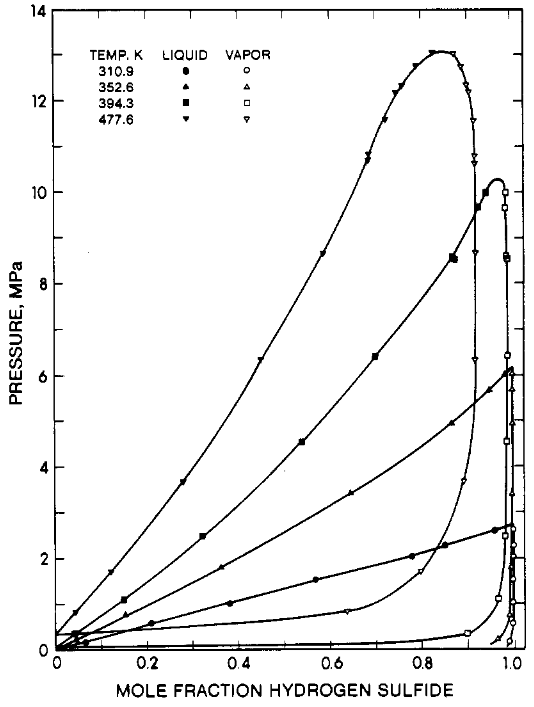

Figure 3. Pressure-equilibrium phase composition diagram for the *n*-propylcyclohexane-hydrogen sulfide system.

The results of the measurements for the *n*-propylcyclohexane-hydrogen sulfide system are presented in Table II and are shown graphically in Figure 3. The calculated equilibrium ratios for each component in the binary system at the four temperatures are also given in Table II and are shown graphically in Figure 4.

In this study, only two of the four temperatures studied for each system lay between the critical temperatures of the two pure components. Since the equilibrium ratios for each component converge to unity at the critical pressure corresponding to the given temperature, it is possible to determine two points on the critical locus for each of the binary pairs from the *K*-*P*

Table II. Equilibrium Phase Properties of the *n*-Propylcyclohexane–Hydrogen Sulfide System

press., MPa	x_{H_2S}	y_{H_2S}	K_{H_2S}	$K_{n\text{-propylcyclohexane}}$
		T = 310.9 K		
0.177	0.0642	0.9913	15.5	0.0093
0.585	0.2096	0.9981	4.76	0.0024
1.01	0.3810	0.9988	2.62	0.00194
1.54	0.5670	0.9992	1.76	0.00185
2.03	0.7804	0.9995	1.28	0.00228
2.28	0.8503	0.9996	1.18	0.00267
2.58	0.9598	0.9998	1.04	0.00498
		T = 352.6 K		
0.220	0.0455	0.9651	21.2	0.0366
0.752	0.1543	0.9892	6.41	0.0128
1.80	0.3623	0.9947	2.75	0.00831
3.40	0.6455	0.9966	1.54	0.00959
4.93	0.8676	0.9974	1.15	0.0196
5.65	0.9494	0.9983	1.05	0.0336
6.02	0.9832	0.9993	1.02	0.0417
		T = 394.3 K		
0.342	0.0418	0.8980	21.5	0.106
1.11	0.1505	0.9668	6.42	0.0391
2.47	0.3230	0.9823	3.04	0.0261
4.53	0.5400	0.9876	1.83	0.0270
6.40	0.7010	0.9886	1.41	0.0381
8.52	0.8748	0.9879	1.13	0.0966
8.56	0.8701	0.9864	1.13	0.105
9.65	0.9263	0.9857	1.06	0.194
9.99	0.9427	0.9839	1.04	0.281
		T = 477.6 K		
0.841	0.0448	0.6356	14.2	0.381
1.72	0.1215	0.7989	6.58	0.229
3.68	0.2805	0.8922	3.18	0.150
6.32	0.4515	0.9179	2.03	0.150
8.65	0.5909	0.9200	1.56	0.196
10.70	0.6850	0.9178	1.34	0.261
10.83	0.6888	0.9160	1.33	0.270
11.58	0.7249	0.9142	1.26	0.312
12.16	0.7463	0.9070	1.22	0.367
12.31	0.7620	0.8999	1.18	0.421
12.75	0.7912	0.8912	1.13	0.521
13.06	0.8270	0.8786	1.06	0.702

plot. The results of this treatment are shown in Figure 5, where the two critical points and the vapor pressure curves for each component in the binary pairs are shown. The position of the critical locus for the entire range has been estimated and is shown as a solid/dashed line.

As indicated earlier in this paper, the object of the work was to provide data from which characteristic binary interaction parameters could be established. As an example, the Peng–Robinson equation of state was used to determine the optimum binary interaction parameter to fit the data for both binary systems.

The binary interaction parameter δ_{ij} is defined by the relationship

$$a_m(1 - \delta_{ij})(a_i a_j)^{1/2}$$

The optimum values for δ_{ij} were obtained by comparing predicted and experimental values of bubble point pressure and dew point vapor compositions for each experimental liquid

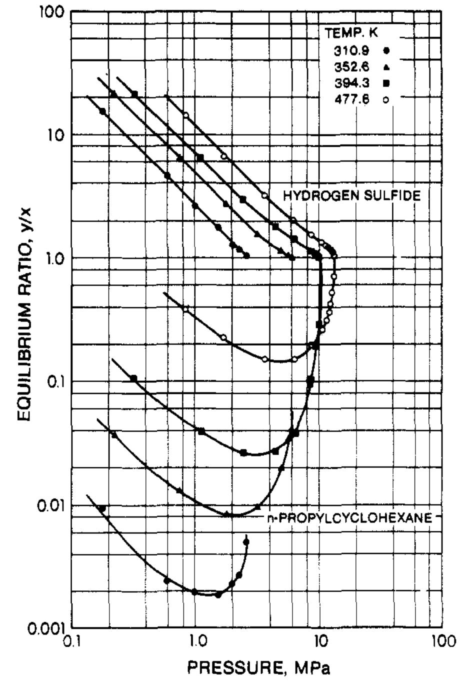

Figure 4. Equilibrium ratios for hydrogen sulfide and *n*-propylcyclohexane in the *n*-propylcyclohexane–hydrogen sulfide binary system.

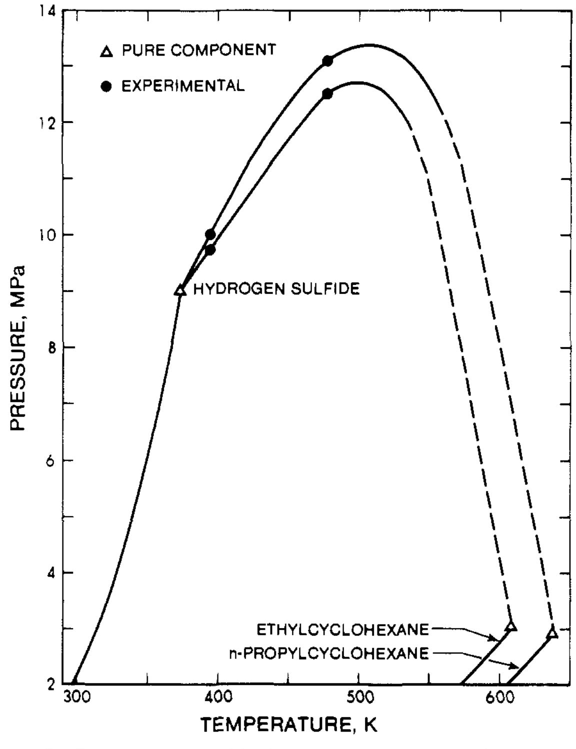

Figure 5. Estimated critical loci for the hydrogen sulfide–ethylcyclohexane and hydrogen sulfide–*n*-propylcyclohexane binary systems.

Table III. Goodness of Fit of the Experimental Data Using the Peng–Robinson Equation with Optimum Interaction Parameters

δ_{ij}	$\sum_{i=1}^{n}(\Delta P_i)^2$ [a]	$\sum_{i=1}^{n}(\Delta y_i)^2$ [b]	$\overline{\Delta P_i}^{+ve}$,[c] kPa	$\overline{\Delta P_i}^{-ve}$,[d] kPa	$\overline{\Delta y_i}^{+ve}$ [c]	$\overline{\Delta y_i}^{-ve}$ [d]	no. of points
			Ethylcyclohexane–Hydrogen Sulfide				
0.06	0.089	0.061	+0.0362 (n = 15)	−0.0507 (n = 13)	n = 0	−0.0222 (n = 28)	28
			n-Propylcyclohexane–Hydrogen Sulfide				
0.02	0.037	0.010	+0.0178 (n = 18)	−0.0352 (n = 16)	+0.00038 (n = 1)	−0.0118 (n = 33)	35

[a] $\Delta P_i = (P_i^{exptl} - P_i^{calcd})/P_i^{exptl}$. [b] $\Delta y_i = (y_i^{exptl} - y_i^{calcd})/y_i^{exptl}$. [c] $\overline{\Delta P_i}^{+ve}$ and $\overline{\Delta y_i}^{+ve}$ are arithmetic means of positive residuals. [d] $\overline{\Delta P_i}^{-ve}$ and $\overline{\Delta y_i}^{-ve}$ are arithmetic means of negative residuals.

composition. The values were obtained by varying the value of the interaction until a minimum in the pressure and composition predictions was achieved. The values were 0.06 ± 0.01 for the ethylcyclohexane–hydrogen sulfide pair and 0.02 ± 0.01 for the *n*-propylcyclohexane–hydrogen sulfide pair.

The sums of differences in bubble point pressures and vapor phase compositions at the optimum δ_{ij} value are presented in Table III. The arithmetic mean of the positive and negative pressure and vapor composition differences are also given in the table. The number of positive and negative points are indicated. Zero differences were considered positive for the averaging process.

Acknowledgment

Mr. S. S. Chung assisted in fitting the data to the Peng–Robinson equation of state.

Glossary

a	constant in equation of state
i, j	molecular species
K	equilibrium ratio, y/x
m	pertaining to a mixture
P	pressure
T	temperature
x	mole fraction in liquid phase
y	mole fraction in vapor phase
δ	binary interaction parameter

Registry No. Hydrogen sulfide, 7783-06-4; ethylcyclohexane, 1678-91-7; *n*-propylcyclohexane, 1678-92-8.

Literature Cited

(1) Ng, H.-J.; Kalra, H.; Robinson, D. B.; Kubota, H. *J. Chem. Eng. Data* **1980**, *25*, 51.
(2) Ng, H.-J.; Robinson, D. B. *Fluid Phase Equilib.* **1979**, *2*, 283.
(3) Ng, H.-J.; Huang, S.-S.; Robinson, D. B. *J. Chem. Eng. Data* **1982**, *27*, 119.
(4) Ng, H.-J.; Robinson, D. B. *J. Chem. Eng. Data* **1978**, *23*, 325.
(5) Peng, D.-Y.; Robinson, D. B. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.

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Phenol Recovery from Water Effluents with Mixed Solvents

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The infinite-dilution distribution coefficients of phenol between water and six solvent mixtures—*n*-butyl acetate–*n*-octane, and isopropyl ether with *n*-butyl acetate, 1-octanol, benzene, carbon tetrachloride, and *n*-octane—have been determined at 25 °C. Such mixed solvent systems may be useful for phenol extraction from water in industrial processes. The mixtures exhibit negative and positive nonlinear distribution coefficient–volume fraction relationships. Maximum mixture distribution coefficients are obtained with approximately equivolume mixtures of isopropyl ether with 1-octanol.

Introduction

The aqueous effluents of petroleum refineries and plants processing petrochemicals, phenolic resins, and fossil fuels frequently contain phenol or phenolic compounds with concentrations reaching several percent (*1*). Phenol concentrations of about 2 mg/L affect organoleptic properties and are toxic to marine fauna (*2*). Such effluents may be treated by destructive oxidation processes or the phenols may be recovered by a suitable separation process such as solvent extraction. Recovery may be economically attractive because the quantity of phenols in effluents of a catalytic cracking plant can reach 100–200 kg/day (*3*). The comparative study carried out by Earhart et al. (*4*) concerning the recovery of phenol in aqueous effluents with concentrations over 50 ppm shows that liquid–liquid extraction is the most economic nondestructive process. The application of liquid–liquid extraction to waste water treatment has been reviewed by Kiezyk and Mackay (*5*), Earhart et al. (*4*), Bailey et al. (*6*), Little (*7*), and Mackay and Medir (*8*, *9*). Earhart et al. (*10*) have suggested an extraction process with two solvents. In a first stage a nonvolatile polar solvent such as butyl acetate is used to extract most of the phenol and in a second a nonpolar volatile solvent (isobutylene) recovers the remaining phenol and the dissolved polar solvent which has entered the aqueous phase.

The factors which influence the selection of solvents for phenol extraction have been discussed by Kiezyk and Mackay (*11*). The most important single factor is a favorable solvent–water distribution coefficient, which is a fundamental property of the solvent–solute–water system. It has been shown that mixed solvents can be more effective in phenol extraction than pure solvents, as has been subsequently discussed by Nakagawa et al. (*12*), Korenman (*13*, *14*), Medir and Mackay (*15*), and Gravelle and Panayiotou (*16*).

In this work data are presented for pure and mixed systems involving two solvents frequently used in phenol extraction processes, butyl acetate and isopropyl ether. Distribution coefficients at infinite dilution of phenol between water and mixtures of butyl acetate and isopropyl ether, butyl acetate and octane, isopropyl ether and octanol, isopropyl ether and benzene, isopropyl ether and carbon tetrachloride, and isopropyl ether and octane have been experimentally determined.

Experimental Part

To determine phenol distribution coefficients a two-liquid phase system was equilibrated by gently shaking the mixture of 50 mL of aqueous phenol solution of known concentration with 10 or 25 mL of pure or mixed solvent in a 250-mL Erlenmeyer flask in a water bath at 25 ± 0.1 °C. It was found by concentration–time measurements that an equilibration time of 24 h was sufficient to establish equilibrium. After shaking, the samples were allowed to stand for 2 h to allow phase separa-

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