High-Pressure Vapor–Liquid Equilibrium Phase Properties of the Isopentane–Hydrogen Sulfide and Neopentane–Hydrogen Sulfide Binary Systems

Ah-Dong Leu and Donald B. Robinson*

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

Vapor- and liquid-phase compositions were determined at 50, 80, 110, and 140 °C for both the isopentane (2-methylbutane)–hydrogen sulfide and the neopentane (2,2-dimethylpropane)–hydrogen sulfide binary systems. Measurements were made at pressures from the vapor pressure of the pentanes to the critical pressure for the binary systems at each temperature. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The critical temperatures and corresponding critical pressures were measured and the critical loci were constructed for both binary systems.

Introduction

For predicting the phase behavior and other thermodynamic properties of multicomponent systems of industrial interest, reliable interaction parameters are required for each of the possible binary paris which can be formed from the components in the mixture. A literature survey pertaining to the phase behavior of C_5-alkane–hydrogen sulfide (H_2S) binaries has revealed that the work of Reamer et al. (1) on the n-pentane–hydrogen sulfide system represents the only data available. In view of this and as a continuation of a program to provide data on binary systems of interest to the petroleum and natural gas industry, it was decided that an experimental study of the isopentane– and neopentane–hydrogen sulfide binary systems at temperatures up to the critical region of hydrogen sulfide would be carried out. Data from the study will be useful for developing improved generalized equation of state parameters for C_5-alkane–H_2S mixtures.

The transparent variable-volume vapor–liquid equilibrium cell used for this work made it possible to observe and determine the behavior of each system in the neighborhood of the critical point. As a result of these observations, it was possible to construct the critical loci for both systems.

Experimental Section

The experiments were carried out in a variable-volume vapor–liquid equilibrium cell consisting of a transparent sapphire cylinder mounted between two steel headers. This has been described in detail by Robinson et al. (2). The body of the cell was 2.54-cm inside diameter with a length of 15.2 cm. The cell had a working capacity of about 45 cm³. The main cell and all the necessary auxiliary lead lines and valves were mounted inside a controlled temperature bath. The method of operation was basically the same as that described previously by Leu and Robinson (3).

Prior to commencement of an experimental run, the equipment was thoroughly cleaned and evacuated. It was then charged with the appropriate pentane isomer and hydrogen sulfide. The temperature of the cell was set to the desired value. The pressure was adjusted to the required values by varying the volume of the cell contents with the piston.

Equilibrium was attained by mechanically rocking the entire assembly about a horizontal axis. The gas phase was sampled first by continuously drawing off a vapor stream through the sampling valve under isobaric isothermal conditions. The withdrawn vapor was mixed with a stream of heated helium and circulated through the chromatographic switching valve. Samples were taken for analysis through the switching valve at periodic intervals. After the remainder of the vapor phase plus a small interface portion of the liquid was removed, the liquid phase was analyzed by using a similar procedure. At the completion of each pressure point, a new set of conditions was established by adjusting pressure and/or adding more material. The equilibration and sampling sequences were then repeated.

The critical point was obtained at isothermal conditions by adjusting pressure and/or adding more material. As equilibrium was approached in the vicinity of the critical region, minor isothermal adjustments in the pressure were made to observe changes along the phase boundary and to note the critical opalescence. When the critical pressure had been determined, the pressure was increased well into the single-phase region so that the system could be sampled and analyzed to obtain the composition at critical point.

Temperatures were measured with iron–constantan thermocouples which had been calibrated against a platinum resistance thermometer. Each temperature was read out on a digital voltmeter (HP-3455A). Temperatures are believed known to within ±0.1 °C.

Pressures were measured using a strain gauge pressure transducer of Statham UTC-UC3/UGP4-200 (0–200 psig; 0.15% full scale (FS)) and –500 (0–500 psig; 0.15% FS) for the vapor pressure of the pure pentane isomer and of Druck PTX-150/HP-4000 (0–4000 psig; 0.1% FS) for measuring the binary mixture and the hydrogen sulfide. They were calibrated with a precision dead-weight gauge. Each pressure was read out on a digital voltmeter (HP-3455A). The pressures are believed known to within ±0.2% of full scale for the Statham and ±0.1% of full scale for the Druck transducers, respectively.

The phase compositions were determined using a Hewlett-Packard Model 5750B gas chromatograph coupled with an HP-3353 data acquisition system. A thermal conductivity detector on isothermal mode was used. Calibration was made for each component using a gravimetric method. The column was made from 3.18-mm-diameter stainless steel tubing and was 2.44 m long. It was packed with Porapak-QS and maintained at 145 °C for the isopentane–hydrogen sulfide binary system and at 135 °C for the neopentane–hydrogen sulfide system.

Relative response factors were obtained from peak areas vs sample size. The response factors for converting area fraction to mole fraction for hydrogen sulfide were 1.9088 and 2.0960 for isopentane and neopentane, respectively. At least eight samples of each phase were taken for analysis. The reported compositions are the result of averaging at least six determi-

* To whom correspondence should be addressed.

Table I. Equilibrium Pressure P, Liquid-Phase Mole Fraction x_3, Vapor-Phase Mole Fraction y_3, and Equilibrium Ratios $K_i = y_i/x_i$ of the Isopentane (1) + Hydrogen Sulfide (3) System at Temperature t

P/MPa	x_3	y_3	K_3	K_1
		$t = 50.0\ °C$		
0.210	0.0	0.0		1.00
0.310	0.031	0.390	12.6	0.630
0.696	0.142	0.736	5.18	0.308
1.241	0.305	0.856	2.81	0.206
2.241	0.588	0.930	1.58	0.170
2.923	0.797	0.967	1.21	0.164
3.275	0.910	0.981	1.08	0.211
3.544	0.987	0.995	1.01	0.385
3.620	1.0	1.0	1.00	
		$t = 80.0\ °C$		
0.470	0.0	0.0		1.00
0.531	0.011	0.134	12.2	0.876
0.758	0.047	0.384	8.15	0.647
1.344	0.147	0.652	4.43	0.408
2.475	0.370	0.834	2.25	0.263
4.213	0.672	0.909	1.35	0.278
5.212	0.844	0.950	1.13	0.324
5.798	0.930	0.970	1.04	0.426
6.295	0.993	0.996	1.00	0.571
6.447	1.0	1.0	1.00	
		$t = 110.0\ °C$		
0.912	0.0	0.0		1.00
0.952	0.009	0.076	8.44	0.933
1.282	0.048	0.278	5.79	0.758
1.868	0.125	0.507	4.06	0.564
2.758	0.232	0.655	2.82	0.449
3.447	0.327	0.741	2.27	0.384
4.275	0.421	0.792	1.88	0.360
4.944	0.506	0.812	1.61	0.380
6.088	0.650	0.851	1.31	0.427
6.819	0.732	0.861	1.15	0.519
7.632	0.823	0.890	1.08	0.624
8.281	0.882	0.906	1.03	0.796
8.377	0.895^a	0.895	1.00	1.00
		$t = 140.0\ °C$		
1.608	0.0	0.0		1.00
1.758	0.014	0.071	5.07	0.942
2.351	0.071	0.277	3.95	0.778
3.489	0.174	0.460	2.64	0.654
5.061	0.327	0.612	1.87	0.576
6.143	0.441	0.650	1.47	0.626
6.681	0.520	0.661	1.27	0.707
7.157	0.583	0.660	1.13	0.816
7.315	0.630^a	0.630	1.00	1.00

^{a} Critical composition.

nations. The precision of the analysis was generally better than 0.001 mole fraction.

In determining the physical properties in the critical region, the experimental temperature was considered to be the critical temperature. The corresponding critical pressure was determined by averaging the two values obtained in the immediate vicinity of but on either side of the critical point from isothermal compression and expansion observations. The associated composition was determined as described above.

Materials

Gold Label, spectrophotometric grade isopentane (2-methylbutane) of 99+ mol % was obtained from Aldrich Chemicals Co. Research grade neopentane (2,2-dimethylpropane) of 99.86 mol % and chemically pure grade hydrogen sulfide of 99.5+ mol % were obtained from Matheson Gas Products Canada, Inc. The pentanes were used without further purification, but the hydrogen sulfide was distilled twice to minimize the contamination from carbon dioxide and mercaptans. Gas chromatograms were run on these compounds, but
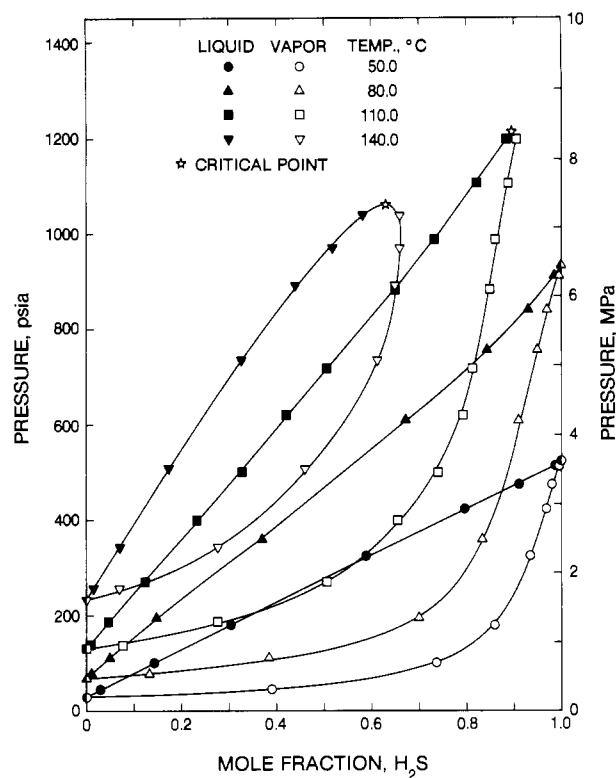

Figure 1. Equilibrium phase compositions for the isopentane–hydrogen sulfide binary system at four temperatures.
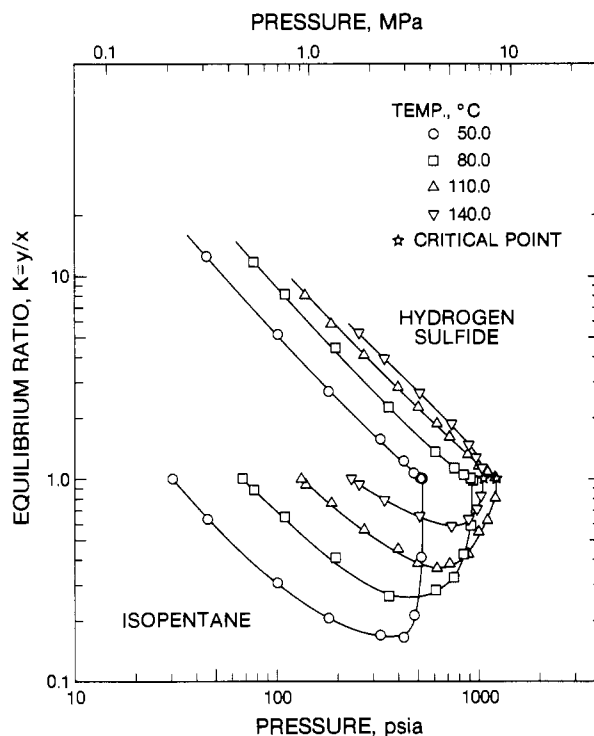

Figure 2. Equilibrium ratios for isopentane and hydrogen sulfide in the binary system.

no detectable impurities were found. The pentanes were degassed in the equilibrium cell before the addition of hydrogen sulfide.

Results and Discussion

The experimentally measured equilibrium liquid x_i and vapor y_i mole fractions for the isopentane (1)–hydrogen sulfide (3) system are given in Table I. The vapor- and liquid-phase
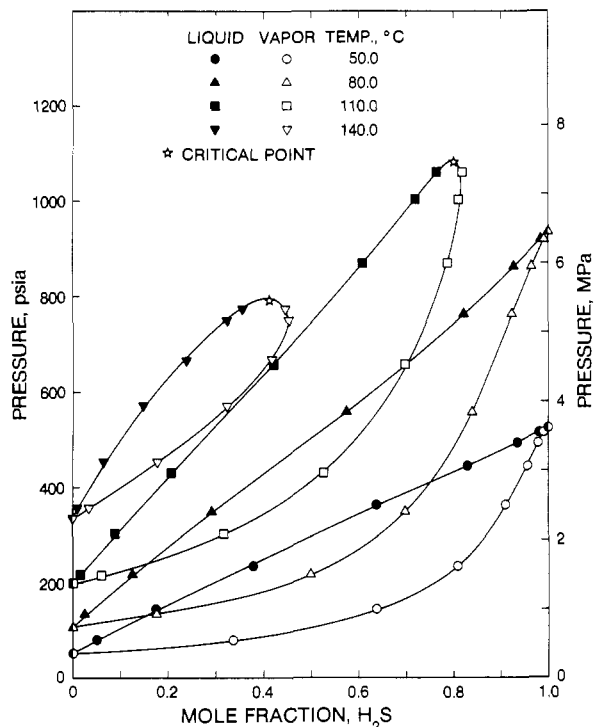
Figure 3. Equilibrium phase compositions for the neopentane–hydrogen sulfide binary system at four temperatures.
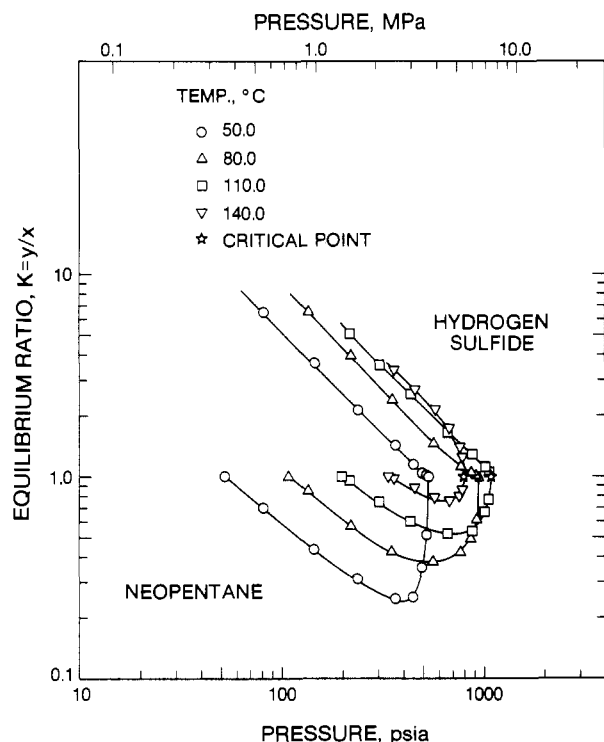

Figure 4. Equilibrium ratios for neopentane and hydrogen sulfide in the binary system.

Table II. Equilibrium Pressure P, Liquid-Phase Mole Fraction x_3, Vapor-Phase Mole Fraction y_3, and Equilibrium Ratios $K_i = y_i/x_i$ of the Neopentane (2) + Hydrogen Sulfide (3) System at Temperature t

P/MPa	x_3	y_3	K_3	K_2
	t = 50.0 °C			
0.359	0.0	0.0		1.00
0.558	0.052	0.336	6.47	0.700
0.993	0.175	0.638	3.66	0.438
1.627	0.378	0.807	2.13	0.310
2.496	0.639	0.910	1.43	0.249
3.061	0.830	0.957	1.15	0.254
3.392	0.935	0.977	1.05	0.354
3.551	0.983	0.991	1.01	0.529
3.620	1.0	1.0	1.00	
	t = 80.0 °C			
0.734	0.0	0.0		1.00
0.924	0.025	0.166	6.64	0.856
1.503	0.125	0.498	3.98	0.574
2.406	0.293	0.699	2.39	0.426
3.847	0.575	0.839	1.46	0.379
5.268	0.823	0.925	1.12	0.424
5.943	0.929	0.965	1.04	0.495
6.336	0.986	0.991	1.01	0.643
6.426	0.998	0.999	1.00	0.810
6.447	1.0	1.0	1.00	
	t = 110.0 °C			
1.358	0.0	0.0		1.00
1.482	0.012	0.061	5.08	0.950
2.082	0.089	0.317	3.55	0.750
2.965	0.207	0.527	2.55	0.597
4.530	0.422	0.698	1.65	0.523
5.992	0.609	0.788	1.29	0.543
6.915	0.719	0.812	1.13	0.670
7.315	0.765	0.819	1.07	0.770
7.453	0.802[a]	0.802	1.00	1.00
	t = 140.0 °C			
2.308	0.0	0.0		1.00
2.448	0.010	0.034	3.40	0.976
3.123	0.066	0.179	2.71	0.879
3.923	0.150	0.324	2.17	0.795
4.592	0.239	0.418	1.75	0.765
5.164	0.325	0.454	1.40	0.808
5.336	0.357	0.447	1.25	0.860
5.454	0.413[a]	0.413	1.00	1.00

[a] Critical composition.

Table III. Critical Temperature t_c and Corresponding Critical Pressure P_c on the Critical Locus of the Binary Systems

t_c/°C	P_c/MPa	t_c/°C	P_c/MPa
Isopentane–H_2S		Neopentane–H_2S	
110.0	8.377	110.0	7.453
140.0	7.315	140.0	5.454
	n-Pentane–H_2S[a]		
112.7	8.915	187.3	6.750
125.6	8.770	193.3	5.936
142.7	8.501	195.7	5.081
160.9	8.081	196.4	4.226
176.2	7.495		

[a] Reference 1.

envelopes for this system are shown in Figure 1 for four isotherms at 50.0, 80.0, 110.0, and 140.0 °C. 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.

The equilibrium phase composition for the neopentane (2)–H_2S (3) system are given in Table II and are shown in Figure 3 for each of the four isotherms at 50.0, 80.0, 110.0, and 140.0 °C. The calculated equilibrium ratios $K_i = y_i/x_i$ for each component in this binary system at each of the four isotherms are

also given in Table II and are shown in Figure 4.

The measured critical temperatures and corresponding pressures for these two binary systems are presented in Table III. The vapor pressure curves for the pure components and the critical properties at the conditions investigated in this work and the critical properties determined in earlier studies for n-pentane–hydrogen sulfide (1) are shown graphically in Figure 5. From this figure, it can be seen that the cricondenbar for the pentane isomer–hydrogen sulfide binary systems is in the following decreasing order: n-pentane– > isopentane– >
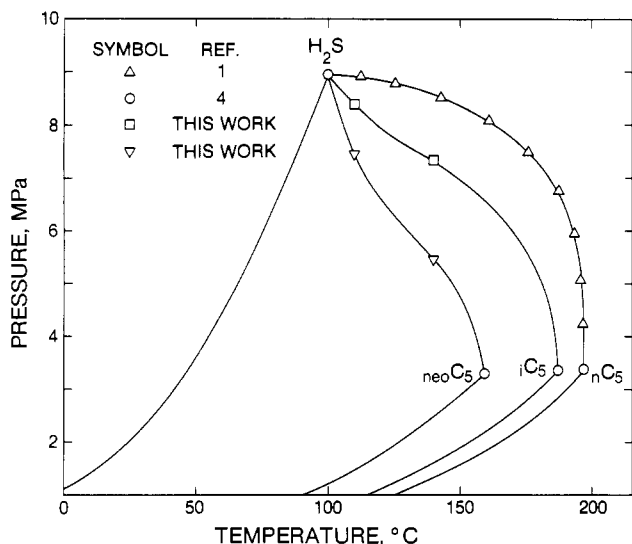
Figure 5. Critical loci in the isopentane (iC₅)–, neopentane (neoC₅)–, and *n*-pentane (*n*C₅)–hydrogen sulfide binary systems.

neopentane–hydrogen sulfide. It also indicates that the shape of the critical locus is different for straight-chain and branched-chain C_5-alkanes.

The experimental data on the behavior of the pentane isomer–hydrogen sulfide binary systems will be useful for evaluating the optimum binary interaction parameters in equation of state modeling of systems containing these components.

Glossary

K	equilibrium ration, y/x
P	pressure, MPa, psia
t	temperature, °C
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Subscripts

i component ($i = 1$, isopentane; $i = 2$, neopentane; $i = 3$, hydrogen sulfide)

Registry No. H_2S, 7783-06-4; isopentane, 78-78-4; neopentane, 463-82-1.

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Isothermal Vapor–Liquid Equilibria for the 1,2-Dichloroethane–Anisole and Trichloroethylene–Anisole Systems

Gloria M. Foco, Susana B. Bottini, and Esteban A. Brignole*

Planta Piloto de Ingenieria Quimica, UNS-CONICET, C. C. 717-8000 Bahia Blanca, Argentina

Vapor–liquid equilibrium (VLE) data have been measured for the binaries 1,2-dichloroethane–anisole and trichloroethylene–anisole at 353 and 373 K and pressures below atmospheric. The data were reduced using Barker's method, and they were found to be thermodynamically consistent. In addition, VLE predictions by the UNIFAC activity coefficient model were compared to experimental data.

Introduction

The system 1,2-dichloroethane–trichloroethylene forms a homogeneous azeotrope, with a boiling temperature of 355 K at atmospheric pressure (*1*). The separation of these substances can be performed by extractive distillation. Among the potential solvents, aromatic ethers show some attractive properties, like low volatility, high thermal stability, and relatively high polarity. The evaluation of their solvent properties for this specific separation is hindered by the lack of VLE data of the aromatic ethers with 1,2-dichloroethane and trichloroethylene.

In the present work, vapor–liquid equilibrium data for the binary mixture of 1,2-dichloroethane and trichloroethylene with anisole (methyl phenyl ether) were measured at 353 and 373 K, and interaction coefficients for the UNIQUAC equation (*2*) were computed. Comparison of the experimental data with

vapor–liquid equilibrium predictions by the UNIFAC group contribution method (*3*) indicates the need for using two different ether groups: paraffinic and aromatic.

Experimental Section

The experimental measurements were carried out in a glass, 230-cm³ capacity, recirculating still (Rock and Siege type, Normag). The equilibrium temperature was measured with a 100-Ω Pt resistance thermometer, via a digital meter (Systemteknik AB, S1220), with an accuracy of 0.01 K. The pressure was measured to within 1 mbar with a pressure controller (Normag) using a piezoresistive sensor.

The equilibrium vapor and liquid compositions were obtained by gas chromatography (Varian 3700 with a Hewlett Packard 3392 integrator), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used, together with a 2-m, ¹/₈-in.-o.d. stainless steel separation column, packed with Porapak Q 50/80. The injector, oven, and detector temperatures were set at 493, 483, and 493 K, respectively. The carrier gas was nitrogen, with a flow of 25 cm³/min. The chemicals used were chromatographic grade commercial reagents: anisole from Baker Chemical Co., trichloroethylene from Carlo Erba, and 1,2-dichloroethane from Mallinkrodt. Their purities, as measured by gas chromatography, were better than 99.9%.