Liquid-Liquid Equilibria in Ternary System Toluene-*n*-Heptane-Sulfolane

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Liquid-liquid equilibrium data for the system toluene-*n*-heptane-sulfolane are obtained at 25°, 40°, and 50°C. The distribution coefficients and selectivity data are included.

Ternary-phase equilibrium data are essential for proper understanding of solvent extraction processes and for the selection of solvents in the petroleum refining or petrochemical industry, particularly in the recovery of benzene, toluene, or xylenes from catalytic reformates. Although sulfolane (*2, 3, 9*) has been extensively used as a solvent for recovery of high-purity aromatics from reformed naphthas, to the authors' knowledge, phase equilibrium data on this system have not been published in the literature. In the present work, liquid-liquid equilibria of the toluene-*n*-heptane-sulfolane system have been studied at 25°, 40°, and 50°C. Included are the phase equilibrium diagrams, distribution coefficients, selectivity data, and tie line correlation curves for the system.

Experimental

Materials. Toluene obtained from BDH, Poole, England, and *n*-heptane from Prolabo, Rhone-Poulenc, France, were purified in an Oldershaw column using a high reflux ratio. A heart cut was collected by discarding the first 10% distillate and the last 10% residue. The purified materials were dried over molecular sieves before use. Sulfolane solvent obtained from Phillips Petroleum Co., USA, was also purified similarly but under a reduced pressure of 10 mm Hg. The physical properties of the three chemicals given in Table I compare well with those reported in the literature (*4, 7*).

Procedure. The liquid-liquid equilibrium data for the ternary system were determined both by analysis and by titration methods (*1*). The procedures used in the determination of the equilibrium data followed established techniques.

Binodal curve determination. Depending upon the region of binodal curve (i.e., whether *n*-heptane- or sulfolane-rich phase), homogeneous synthetic samples of known compositions were titrated in a thermostated glass-stoppered bottle to the appearance of turbidity. The temperature in the glass-stoppered bottle was maintained to within ±0.1°C of the desired temperature. The addition of appropriate amounts of sulfolane to a miscible mixture of *n*-heptane+toluene and that of *n*-heptane to a homogeneous mixture of toluene+sulfolane rendered the system immiscible. The titrant was added in small increments from a jacketed microburet maintained at constant temperature, and the contents of the glass-stoppered bottles were shaken vigorously for proper mixing and equilibrium. The amount of titrant thus added was calculated from its volume and density at that temperature. The composition of the ternary mixture at the first appearance of turbidity gave one point on the binodal curve.

Tie line data determination. Tie lines for the present system were obtained by mixing a known weight of the *n*-heptane-toluene mixture with an equal weight of sulfolane in a mixer settler. The mixer settler was maintained to within ±0.1°C of the desired temperature. The hydrocarbon feed mixture was varied from 10 to about 80% toluene, and each time the solvent-to-feed ratio was maintained at about 1:1 in order to get the tie lines equally distant from each other. Near the plait point and with feed containing 70-80 wt % toluene, the solvent-to-feed ratio was changed to 0.5:1 to provide more raffinate phase for analysis. The mixer settler was provided with a good mechanical mixing device, and equilibrium was attained in about 25 min. After proper attainment of equilibrium and phase separation, the equilibrated phases were removed and weighed to make a material balance and subsequent check of the tie line data.

Analysis of extract phase. Since the extract phase contained more solvent, the hydrocarbon portion was recovered from a known amount of the phase by dilution with water and subsequent heteroazeotropic distillation in a distillation assembly equipped with a small packed column (10 mm diam, 15 cm long) and a cold condenser. The hydrocarbons were carried over to the top of the distillation column along with the water, condensed, and finally collected in a jacketed receiver. The hydrocarbon portion was separated, weighed accurately, and its refractive index determined at 20°C. The composition of the hydrocarbon portion was established through a previously determined calibration curve of *n*-heptane-toluene mixture. The material balance of the total amount charged to the distillation assembly and the hydrocarbon part recovered in the receiver, coupled with the composition of the latter, determined the composition of the entire extract phase. The accuracy of the results was checked by carrying out similar distillation of a series of synthetic mixture of the ternary mixture and subsequent determination of refractive index of the hydrocarbon portion thus recovered. The precision in the composition measurement of the extract phase is estimated to be within ±0.005 wt fraction.

Analysis of raffinate phase. The composition of the raffinate phase was determined by washing a known amount of the phase with water in a separating funnel and subsequently shaking and allowing the phases to set-

Table I. Physical Properties of Chemicals Used

	Density, 20°C		Refractive index, 20°C		Boiling
Chemical	Exptl	Lit	Exptl	Lit	bp, °C
Toluene (*4*)	0.8668	0.8669	1.4968	1.4969	110.6
n-Heptane (*4*)	0.6836	0.6837	1.3875	1.3876	98.4
Sulfolane (*7*)	1.2628[a]	1.2631[a]	1.4829	1.4832	288.0

[a] At 30°C.

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tle. The lower layer containing the hydrocarbon portion was separated, weighed accurately, and its refractive index determined at 20°C. The composition of the hydrocarbon part was also determined through a previously obtained calibration curve of *n*-heptane–toluene mixture, and this coupled with the material balance of the total raffinate phase charged in the separating funnel and the amount of hydrocarbon portion separated gave the composition of the entire raffinate phase. Also, in the case of the raffinate phase, the accuracy of the composition measurements was checked by carrying out water washing of a series of synthetic ternary mixtures corresponding to raffinate-phase compositions and subsequent measurements of refractive index of the hydrocarbon part thus separated. The precision in the measurement of the composition of the raffinate phase is estimated to be within ±0.004 wt fraction.

Results and Discussion

The experimental data for the binodal curve at 25°, 40°, and 50°C are given in Table II, and the tie line data indicating the composition of the two phases at equilibri-

Table II. Solubility Data for Ternary System Toluene–*n*-Heptane–Sulfolane
Expressed in wt %

25°C			40°C			50°C		
Toluene	*n*-Heptane	Sulfolane	Toluene	*n*-Heptane	Sulfolane	Toluene	*n*-Heptane	Sulfolane
3.7	1.2	95.1	9.1	1.9	89.0	6.2	2.0	91.8
15.2	2.0	82.8	18.2	2.8	79.0	10.3	2.4	87.3
34.2	4.5	61.3	29.9	5.2	64.9	23.8	4.0	72.2
43.7	7.3	49.0	36.1	7.5	56.4	37.5	7.2	55.3
47.0	8.2	44.8	43.6	8.6	47.8	45.1	10.5	44.4
49.8	9.0	41.2	46.0	9.9	44.1	49.6	12.8	37.6
52.9	12.0	32.8	47.9	11.1	41.0	54.7	18.3	27.0
58.4	14.7	26.8	49.6	12.1	38.3	57.4	21.4	21.2
60.8	16.6	22.6	53.9	14.3	31.8	58.0	26.4	15.6
62.4	19.7	17.9	59.6	23.1	17.3	57.5	30.4	12.1
62.3	27.2	10.5	59.7	27.9	12.4	56.5	34.0	9.5
52.5	44.0	3.5	58.4	31.6	10.0	51.9	41.1	7.0
44.4	52.8	2.8	51.5	43.7	4.8	40.5	55.5	4.0
29.5	68.5	2.0	34.3	63.4	2.3	24.2	73.0	2.8
15.4	83.0	1.6	26.0	72.2	1.8	12.2	85.8	2.0
9.1	89.4	1.5	17.1	81.5	1.4			
				Established plait point				
50.8	8.9	40.3	47.1	10.1	42.8	46.3	11.2	42.5

Table III. Tie Line, Distribution Coefficient, and Selectivity Data for System Toluene–*n*-Heptane–Sulfolane

Sulfolane-rich phase, wt %			*n*-Heptane-rich phase, wt %			Distribution coefficient of toluene	Distribution coefficient of *n*-heptane	Selectivity
Toluene	*n*-Heptane	Sulfolane	Toluene	*n*-Heptane	Sulfolane			
				25°C				
3.3	0.8	95.9	8.3	90.4	1.3	0.398	0.009	44.2
8.3	1.0	90.7	23.0	75.6	1.4	0.358	0.013	28.0
12.7	1.2	86.1	30.9	67.5	1.6	0.411	0.018	22.8
15.4	1.4	83.2	37.5	59.7	2.8	0.411	0.023	17.9
20.3	2.0	77.7	45.5	51.3	3.2	0.446	0.039	11.4
27.3	2.6	70.1	54.8	39.9	5.3	0.498	0.065	7.7
32.3	3.9	63.8	60.3	29.8	9.9	0.536	0.131	4.1
				40°C				
3.9	1.0	95.1	9.4	89.1	1.5	0.415	0.011	37.7
5.0	1.1	93.9	12.8	85.4	1.8	0.391	0.013	30.1
9.5	1.4	89.1	23.6	74.4	2.0	0.402	0.019	21.2
11.8	1.7	86.5	29.0	68.8	2.2	0.407	0.024	16.9
16.9	2.1	81.0	38.2	59.3	2.5	0.442	0.035	12.6
20.2	2.6	77.2	46.5	49.4	4.1	0.434	0.053	8.2
27.1	3.4	69.5	53.2	39.8	7.0	0.509	0.085	6.0
26.9	4.4	58.7	58.6	28.0	13.4	0.629	0.157	4.0
				50°C				
3.8	1.2	95.0	9.6	88.5	1.9	0.395	0.014	28.2
8.9	1.5	89.6	22.8	74.7	2.5	0.390	0.020	19.5
12.6	1.9	85.5	30.2	66.9	2.9	0.417	0.028	14.9
16.4	2.3	81.3	38.3	58.6	3.1	0.429	0.039	10.9
21.2	2.7	76.1	45.5	48.8	5.7	0.466	0.055	8.5
26.6	3.9	69.5	52.2	39.1	8.7	0.509	0.099	5.1
34.6	4.6	60.8	56.0	30.5	13.5	0.618	0.152	4.1

um are reported in Table III. Included in Table III are the distribution coefficients for toluene and *n*-heptane and the selectivity data of the solvent at the three temperatures. Figure 1 illustrates the effect of temperature (25° and 50°C) on the phase equilibrium relationship of the ternary system; the tie line data at the two temperatures are also included in this figure.

The tie line data for the present system are observed to fit well in the smoothed binodal curve in Figure 1, indicating the accuracy of the experimental tie line data. The maximum difference between points on the binodal curve and the tie line data was of the order of ±0.005 wt fraction. The effect of the increase of temperature from 25° to 50°C on the slope of the tie lines is very small. The calculations of plait points for the present system are illustrated in Figure 2 by use of Treybal's (*8*) method on Hand's (*5*) coordinates.

The effectiveness of extraction of a solute (toluene) by the solvent (sulfolane) is given by its selectivity (β) which is a measure of the ability of sulfolane to separate toluene from *n*-heptane:

$$\beta = \frac{\text{Distribution coefficient of aromatics}}{\text{Distribution coefficient of nonaromatics}} = \frac{\%\ \text{Toluene in extract phase}/\%\ \text{toluene in raffinate phase}}{\%\ n\text{-Heptane in extract phase}/\%\ n\text{-heptane in raffinate phase}}$$

Figure 3 illustrates the effect of temperature on the distribution curve and the selectivity curve for the present system. The selectivity curve indicates that with the increase of temperature from 25° to 50°C, the selectivity of sulfolane for toluene decreases and eventually the ca-

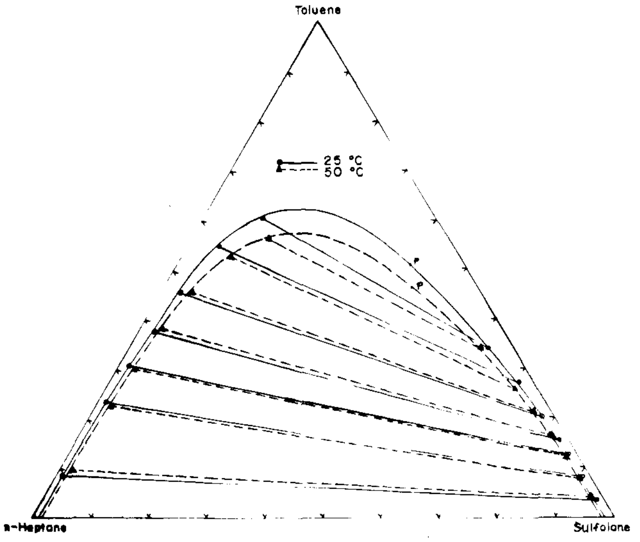

Figure 1. Phase equilibrium diagrams for toluene-*n*-heptane-sulfolane system

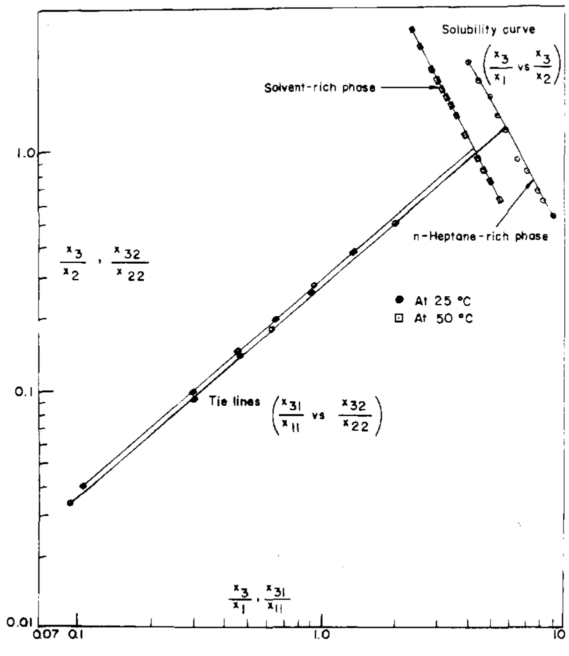

Figure 2. Plait point determination for toluene-*n*-heptane-sulfolane system

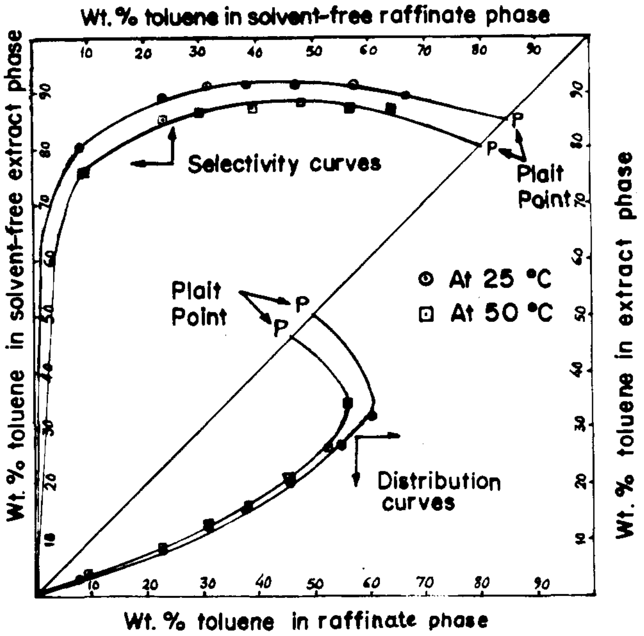

Figure 3. Selectivity and distribution curves for toluene-*n*-heptane-sulfolane system

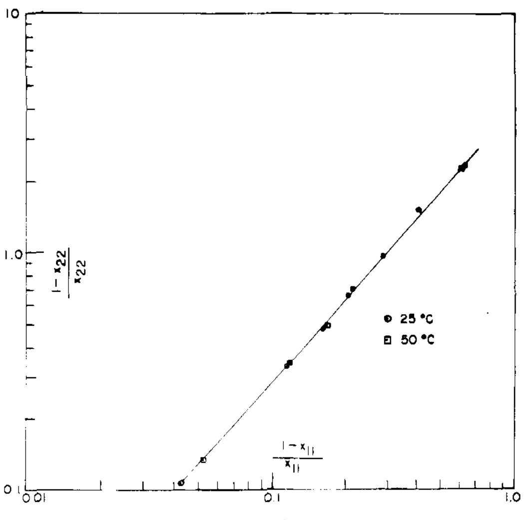

Figure 4. Othmer-Tobias correlation for toluene-*n*-heptane-sulfolane system

pacity of the solvent increases. This is also evident from the data reported in Table III.

Figure 4 shows the tie line correlation curve on the Othmer-Tobias (*6*) coordinates for the system at 25° and 50°C. Since the data do not exhibit much scatter from straight line, they are judged acceptable on the empirical basis, indicating internal consistency of the experimental data.

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Nomenclature

x = liquid-phase composition (wt fraction)

Subscripts

1 = *n*-heptane
2 = sulfolane
3 = toluene
11, 31 = composition (wt fraction) of components 1 and 3, respectively, in phase 1 (*n*-heptane-rich phase)
22, 32 = composition (wt fraction) of components 2 and 3, respectively, in phase 2 (sulfolane-rich phase)

Literature Cited

(1) Alders, L., "Liquid-Liquid Extraction," 2nd ed., Chap. II, pp 34–45, Elsevier, Amsterdam, The Netherlands, 1959.
(2) Broughton, D. B., Asselin, G. F., Seventh World Petrol. Congr., Proc., Vol 4, 65 (1967).
(3) Deal, C. H., Evans, H. D., Oliver, E. D., Papadopoulus, M. N., Fifth World Petrol. Congr., Proc., Section III, 283 (1959).
(4) Dreishbach, R. R., "Physical Properties of Chemical Compounds," *Advan. Chem. Ser.*, Vol 15, American Chemical Society, Washington, D.C., 1955.
(5) Hand, D. B., *J. Phys. Chem.*, **34,** 1961 (1930).
(6) Othmer, D. F., Tobias, P. E., *Ind. Eng. Chem.*, **34,** 690 (1942).
(7) Rawat, B. S., Mallik, K. L., Gulati, I. B., *J. Appl. Chem. Biotechnol.*, **22,** 1001 (1972).
(8) Treybal, R. E., Weber, L. D., Daley, J. F., *Ind. Eng. Chem.*, **38,** 817 (1946).
(9) Voetter, H., Kosters, W. C. G., Sixth World Petrol. Congr., Proc., Vol III, 131 (1963).

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Isothermal Vapor-Liquid Equilibria for Systems Ethyl Ether–Carbon Dioxide and Methyl Acetate–Carbon Dioxide at High Pressures

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The isothermal vapor-liquid equilibrium data for the systems ethyl ether–carbon dioxide and methyl acetate–carbon dioxide were measured by a static method over a pressure range from 5 to 80 atm at 25° and 40°C. By use of the Lewis rule and the Redlich-Kwong equation of state for only carbon dioxide in the vapor phase, the activity coefficients of both components in the liquid phase and the fugacity coefficient of the solvent component in the vapor phase were evaluated with the thermodynamic relationships.

Carbon dioxide is one of the most important industrial gases, and the data on phase equilibria of systems containing carbon dioxide have been reported abundantly. However, vapor-liquid equilibrium data of carbon dioxide with one of the heavy components having normal boiling points at about 50°C are scarce.

In this study, the vapor-liquid equilibria for the systems ethyl ether–carbon dioxide and methyl acetate–carbon dioxide were measured at 25° and 40°C by a static method with a new apparatus.

The thermodynamic procedures were applied for determining the nonidealities of vapor and liquid phases of these systems. Thereafter, the nonidealities were compared and discussed between these two systems.

Apparatus and Operations

The schematic diagram of the experimental apparatus is shown in Figure 1. The solvent was fed from a solvent vessel H, and carbon dioxide from a gas cylinder I flowed through valves 1, 2, and 3 into an equilibrium cell A. The contents of the equilibrium cell were agitated by a magnetic stirrer operated by a separated solenoid M. At the center of the equilibrium cell, two windows, pyrex glass disk 3.5 cm in diameter and 2.5 cm thick each, were set, and the vapor-liquid interface was controlled to be at the center of the windows with a needle valve 8. The equilibrium cell was a stainless-steel cylinder, approximately 300 cm^3 in volume, and the operating maximum pressure was about 150 atm.

The liquid-phase sampler K was a small steel tube approximately 0.15 cm^3 in volume with a ball valve 4, and a needle valve 5 was approximately 2 cm^3. The ball valves 4, 6, and 7 were used with the sampling valves for avoiding the flushing phenomenon. The sample of gas phase was introduced to a container B of variable volume and expanded to about 0.1 atm. The sample of liquid phase was vaporized in an evaporator C and introduced to a liquid-phase container D, constantly maintained at about 0.1 atm. The variable volume container B was the same as the evaporator C, and the possible working volume ranged from 10 to 1000 cm^3.

The compositions of each phase sample were determined by direct comparison of the peak area ratio of the

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