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Liquid–Liquid Equilibria for the Ternary Systems γ-Butyrolactone–*n*-Heptane–Benzene, γ-Butyrolactone–*n*-Heptane–Toluene, and γ-Butyrolactone–*n*-Heptane–*p*-Xylene

Akl M. Awwad,* Muna A. Salman, and Fatin A. Hassan

Scientific Research Council, Petroleum Research Center, Jadiriyah, P.O. Box 10039, Baghdad, Iraq

Liquid–liquid equilibrium data for the system γ-butyrolactone–*n*-heptane–benzene, γ-butyrolactone–*n*-heptane–toluene, and γ-butyrolactone–*n*-heptane–*p*-xylene are obtained at 298.15 K. Distribution coefficients and selectivity at 298.15 K were calculated. The selectivity for extraction of benzene from *n*-heptane by extraction with γ-butyrolactone is better than that for extraction of toluene or *p*-xylene from *n*-heptane.

Introduction

In recent years, the petroleum industry has given much attention to the highly polar, high density, and high boiling point solvents such as dimethyl sulfoxide (*1*), *N*-formylmorpholine (*2*), *N*-methylpyrrolidone (*3*), glycols (*4*), and sulfolane (*5*). This interest has resulted from their high selectivity and solvency for low molar mass monocyclic aromatic hydrocarbons (C_6–C_9). γ-Butyrolactone ($C_4H_6O_2$) is a new solvent for the recovery of aromatic hydrocarbons. Therefore, we have initiated a program to study its efficiency for extraction of benzene, toluene, and xylenes from reformates. Ternary phase equilibrium data are essential for the proper understanding of solvent extraction processes. To our knowledge phase equilibrium data on these systems have not been published in the literature. The present work reports the phase diagrams, distribution coefficients, tie line data, and selectivity for the systems γ-butyrolactone-*n*-heptane-benzene, γ-butyrolactone–*n*-heptane–toluene, and γ-butyrolactone–*n*-heptane–*p*-xylene at 298.15 K.

Experimental Section

Materials. The *n*-heptane (stated purity of 99.5 mol %), benzene (stated purity of 99.5 mol %), toluene (stated purity of 99.5 mol %), *p*-xylene (stated purity of 99.5 mol %), and γ-butyrolactone (stated purity of 99 mol %) were obtained from Fluka AG and used without further purification. All liquids were kept over freshly activated molecular sieve of Type 4A (Union Carbide) and filtered before use. The purity of all the liquids was confirmed by gas–liquid chromatographic analysis. Densities, ρ, and refractive indices, n_D, of the pure liquids at 298.15 K are compared with data from the literature in Table I.

Procedure. Liquid–liquid equilibria data for the ternary systems were determined by a standard turbidimetric method (*9*) using an apparatus similar to that described elsewhere (*10*).

Binodal Curves Determination. Homogeneous synthetic mixtures of known compositions of *n*-heptane–benzene, *n*-heptane–toluene, *n*-heptane–*p*-xylene, γ-butyrolactone–benzene, γ-butyrolactone–toluene, and γ-butyrolactone–*p*-xylene were titrated in a thermostated bottle to the appearance of turbidity. The thermostat temperature was controlled by a temperature controller and maintained a constant temperature within ±0.01 °C. The temperature was measured with a Hewlett-Packard quartz thermometer calibrated against a gallium temperature standard. The addition of γ-butyrolactone to a miscible mixture of *n*-heptane–benzene, *n*-heptane–toluene, *n*-heptane–*p*-xylene and the addition of *n*-heptane to a homogeneous mixture of γ-butyrolactone–benzene, γ-butyrolactone–toluene, and γ-butyrolactone–*p*-xylene rendered the systems immiscible. The titrant was added in small increments from the jacketed microburet and the contents of the bottle were mixed for proper mixing and equilibrium with a Teflon-coated magnetic rod. The amount of titrant thus added was calculated from its volume and density measured at 298.15 K with an Anton Paar digital dosimeter (Model DMA 60). Composition of the ternary mixture at the first appearance of turbidity gave one point on the binodal curve.

Table I. Physical Properties of the Pure Liquids at 298.15 K

	ρ/g cm^{-3}		n_D	
liquid	obsd	lit.	obsd	lit.
n-heptane	0.679 50	0.67951[a]	1.385 09	1.3851[a]
benzene	0.873 66	0.87363[c]	1.479 99	1.49792[b]
toluene	0.862 10	0.86222[c]	1.493 88	1.4939[b]
p-xylene	0.856 61	0.85669[b]	1.493 22	1.49325[b]
γ-butyrolactone	1.124 21	1.1254[d]	1.434 77	1.4348[d]

[a] Reference *7*. [b] Reference *6*. [c] Reference *8*. [d] Reference *12*.

Tie Line Data Determination. Tie lines for the present systems were obtained by mixing a known weight of the *n*-heptane–benzene, *n*-heptane–toluene, and *n*-heptane–*p*-xylene mixtures with an equal weight of γ-butyrolactone in a thermostated cell. The two-phase mixture was stirred for at least 2 h and allowed to settle for at least 6 h. Once equilibrium had been reached, samples of both phases were carefully withdrawn with glass syringes. The samples were analyzed by gas–liquid chromatography (Pye Unican, Model 204) equipped with a flame ionization detector and connected to an integration unit (Spectra Physics). A 6 ft × $^1/_8$ in. stainless steel column packed with Carbowax 20M on Chromsorb W and operating at 160 °C was used for analysis. The flow rate of nitrogen carrier gas was kept constant at 30 cm^3 min^{-1}. Samples of known concentration were injected for calibration purposes. Mass fraction measurements were reproducible to within ±0.004.

Results and Discussion

Experimental data for the binodal curves for the systems γ-butyrolactone–*n*-heptane–benzene, γ-butyrolactone–*n*-heptane–toluene, and γ-butyrolactone–*n*-heptane–*p*-xylene at 298.15 K are illustrated in Figures 1, 2, and 3. The tie line data indicating the composition of the two phases are reported in Tables II, III, and IV. Plait points were determined by a construction method (*11*) in the rectangular coordinate system. The projection points corresponding to the ends of the tie lines were found to tie on a smooth curve within the limits of ex-

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Table II. Tie Line Data, Distribution Coefficients, and Selectivities for the System γ-Butyrolactone–n-Heptane–Benzene at 298.15 K

γ-butyrolactone phase, wt %			n-heptane phase, wt %					
C_6H_6	n-C_7H_{16}	$C_4H_6O_2$	C_6H_6	n-C_7H_{16}	$C_4H_6O_2$	K_1	K_2	S
11.29	6.52	82.19	5.37	94.07	0.56	2.09	0.07	30.22
33.08	8.10	58.82	16.70	82.10	1.20	1.98	0.10	20.08
38.80	9.17	52.03	24.90	72.86	2.24	1.55	0.13	12.37
42.36	10.56	47.08	28.26	69.37	2.37	1.50	0.15	9.85
49.14	11.79	39.07	33.50	63.74	2.76	1.42	0.19	7.91
52.75	14.50	32.75	39.56	57.30	3.14	1.33	0.25	5.27
54.60	18.10	27.30	44.10	51.20	4.70	1.24	0.35	3.50

Table III. Tie Line Data, Distribution Coefficients, and Selectivities for the System γ-Butyrolactone–n-Heptane–Toluene at 298.15 K

γ-butyrolactone phase, wt %			n-heptane phase, wt %					
C_7H_8	n-C_7H_{16}	$C_4H_6O_2$	C_7H_8	n-C_7H_{16}	$C_4H_6O_2$	K_1	K_2	S
4.40	4.79	90.01	3.34	96.13	0.53	1.32	0.05	26.43
12.09	5.62	82.29	8.72	90.66	0.62	1.39	0.06	22.37
15.30	6.04	78.66	11.80	87.45	0.75	1.30	0.07	10.76
19.40	7.30	73.30	14.35	84.07	0.38	1.35	0.08	15.00
24.80	7.80	67.40	19.00	79.80	1.20	1.31	0.10	13.35
32.30	8.80	58.90	25.70	72.70	1.80	1.26	0.12	10.38
38.90	9.50	51.60	32.80	65.08	2.12	1.19	0.15	8.12
49.70	13.85	36.45	44.08	51.36	4.56	1.13	0.27	4.18
50.90	14.90	34.20	46.60	47.70	5.70	1.09	0.31	3.50
53.90	18.70	27.40	51.20	40.14	8.66	1.05	0.47	2.26

Table IV. Tie Line Data, Distribution Coefficients, and Selectivities for the System γ-Butyrolactone–n-Heptane–p-Xylene at 298.15 K

γ-butyrolactone phase, wt %			n-heptane phase, wt %					
C_8H_{10}	n-C_7H_{16}	$C_4H_6O_2$	C_8H_{10}	n-C_7H_{16}	$C_4H_6O_2$	K_1	K_2	S
4.20	4.86	90.84	5.67	93.20	1.13	1.13	0.05	14.21
11.04	6.19	82.77	16.40	82.12	1.48	0.67	0.07	9.08
17.80	6.50	75.70	28.70	69.47	1.83	0.18	0.09	6.08
26.30	6.40	67.30	37.67	60.17	2.16	0.70	0.11	6.56
28.72	6.98	64.30	38.82	58.78	2.40	0.74	0.12	6.25
30.72	7.21	62.07	44.32	52.60	3.08	0.69	0.14	5.05
33.98	7.34	58.68	48.66	47.45	3.89	0.70	0.15	4.52
49.48	11.40	39.12	59.30	34.20	6.50	0.83	0.33	2.50
51.38	11.93	36.69	59.85	32.16	7.99	0.86	0.37	2.32

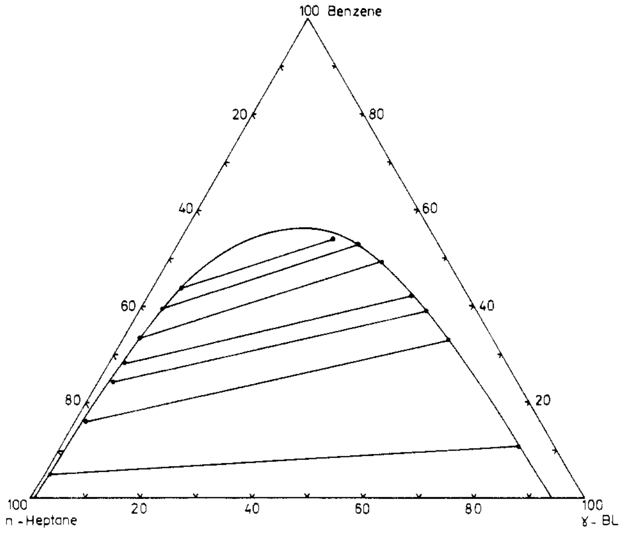

Figure 1. Phase equilibrium diagram for the γ-butyrolactone–n-heptane–benzene system at 298.15 K.

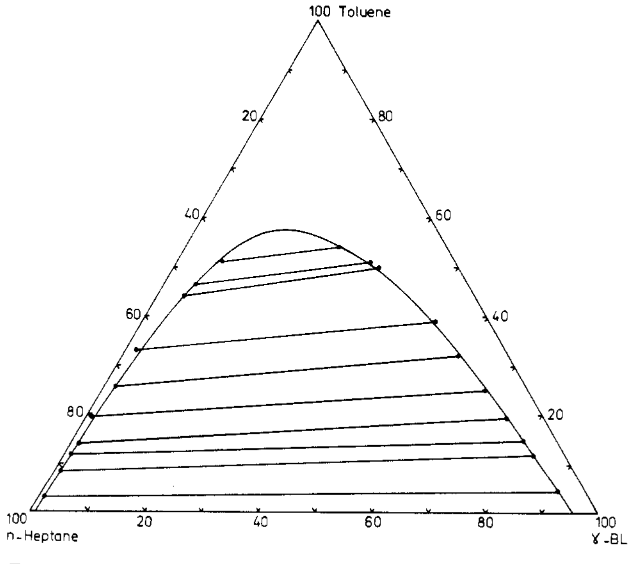

Figure 2. Phase equilibrium diagram for the γ-butyrolactone–n-heptane–toluene system at 298.15 K.

perimental errors. The distribution coefficients for benzene, toluene, and p-xylene in the n-heptane and γ-butyrolactone phases were calculated from the following formula:

$$K_1 = \frac{\text{wt \% of component } i \text{ in } \gamma\text{-butyrolactone phase}}{\text{wt \% of component } i \text{ in } n\text{-heptane phase}} \quad (1)$$

The obtained results are listed in Tables II, III, and IV. The selectivity (S) of γ-butyrolactone solvent for aromatic hydrocarbons was calculated from the relation

$$S = K_1/K_2 \quad (2)$$

where K_1 is the distribution coefficient of benzene or toluene or p-xylene and K_2 is the distribution coefficient of n-heptane in the two phases.

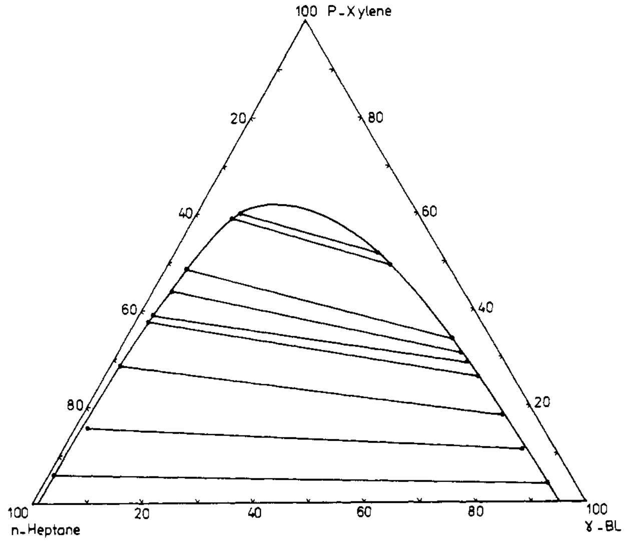

Figure 3. Phase equilibrium for the γ-butyrolactone–*n*-heptane–*p*-xylene system at 298.15 K.

Figures 1, 2, and 3 show that the slopes of the tie lines are steeper in the benzene system than that in the corresponding toluene and *p*-xylene systems; i.e., the plait point is located in the region of mixtures containing more γ-butyrolactone in the case of benzene. So the separation of benzene from *n*-heptane by extraction with γ-butyrolactone can be achieved in fewer stages than the separation of toluene and *p*-xylene from *n*-heptane. On the other hand, comparison of the solubility gaps in Figures 1, 2, and 3 shows that the capacity of γ-butyrolactone is a little greater for *p*-xylene than for benzene and toluene.

A comparison of the selectivities of γ-butyrolactone, *N*-formylmorpholine, dimethyl sulfoxide, glycols, sulfolane, and *N*-methylpyrrolidone was based on the liquid–liquid equilibria data available in the literature for the system solvent–benzene–*n*-heptane. The selectivity of γ-butyrolactone is higher than that of glycols, dimethyl sulfoxide, and *N*-methylpyrrolidone (*4*). γ-Butyrolactone has low selectivity for aromatic hydrocarbons compared to that of sulfolane (*13*). The selectivities of γ-butyrolactone and *N*-formylmorpholine are not comparable because the hydrocarbon models in the two cases are different.

Glossary

K_i	distribution coefficient of component *i*
n_D	refractive index
ρ	density, g cm^{-3}
S	selectivity (K_1/K_2)
γ-BL	γ-butyrolactone

Registry No. γ-Butyrolactone, 96-48-0; *n*-heptane, 142-82-5; benzene, 71-43-2; toluene, 108-88-3; *p*-xylene, 106-42-3.

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Excess Molar Volumes of Mixtures Containing Morpholine at 298.15 K

Aki M. Awwad,* Etamid I. Allos, and Salman R. Salman

Scientific Research Council, Petroleum Research Center, Jadiriyah, P.O. Box 10039, Baghdad, Iraq

Excess molar volumes were determined from precise density measurements at 298.15 K for morpholine + methanol, + acetone, + benzene, + chloroform, + dimethyl sulfoxide, and + dimethylformamide. The results are interpreted qualitatively in terms of various specific interactions.

Introduction

In a previous paper (*1*) the excess molar volumes morpholine + 2-ethoxyethanol were reported. Our interest in the morpholine derivatives arose from their high efficiency for the extraction of monocyclic aromatic hydrocarbons from petroleum products. We have initiated a program on studying the thermodynamic properties of these solvents. This paper reports the excess molar volumes of binary mixtures of morpholine + methanol, + benzene, + chloroform, + acetone, + dimethyl sulfoxide, and + dimethylformamide at 298.15 K.

Table I. Densities of the Pure Component Liquids at 298.15 K

liquid	ρ/g cm^{-3} obsd	ρ/g cm^{-3} lit.
methanol	0.786 65	0.786 64[b]
acetone	0.785 16	0.784 40[b]
chloroform	1.478 99	1.479 88[b]
benzene	0.873 61	0.873 72[a]
M	0.905 71	0.995 47[b]
DMSO	1.095 68	1.095 80[b]
DMF	0.943 93	0.943 97[b]

[a] Reference *3*. [b] Reference *4*.

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