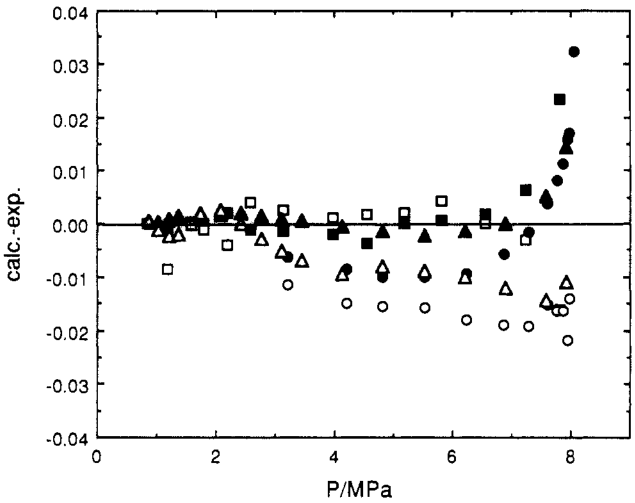

Figure 6. Deviation plot for isotherms at 344.3 K. Calculated compositions were determined from the Peng-Robinson equation using k_{ij} = 0.134. Liquid composition deviations, filled symbols; vapor composition deviations, open symbols. ■, this work; ●, ref *7*; ▲, ref *5*.

whereas the *n*-butane was subcritical. The best interaction parameters obtained for both equations, determined by minimizing the deviation of the calculated liquid composition curves from the experimental data, are displayed in Table V. At the lower temperature, the vapor-phase compositions from the PR equation were in good agreement with experiment, but the SRK compositions were too rich in CO_2. At the higher temperature, both equations of state predicted vapor compositions with too much butane.

The molar volume of the liquid mixture, as predicted by the SRK equation, was always larger than the values obtained with the PR equation. The molar volumes decreased with pressure up to a minimum, then increased until the critical point was reached. Molar volumes were not measured in this study.

Comparison with Previous Studies

The data values obtained at 71.10 °C were compared to those reported by Olds et al. (*5*) and Hsu et al. (*7*) and to calculated values at the corresponding pressures from the Peng-Robinson equation of state using the interaction parameter listed in Table V. Above 7 MPa systematic deviations (of opposite sign for liquid and vapor) show up for all the data because the calculated critical point from the PR equation at this temperature is at P = 8.06 MPa, lower than the 8.217 MPa that has been observed. Both the liquid and vapor compositions from this work are in good agreement with the PR equation below 7 MPa, but the vapor compositions of Olds et al. and both the liquid and vapor compositions of Hsu et al. are higher than the calculated values by 0.01 or more over much of the pressure range. A deviation plot showing both liquid and vapor composition deviations is given in Figure 6.

Acknowledgment

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Liquid–Liquid Equilibria for the Hexane–Benzene–Dimethyl Sulfoxide Ternary System

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Liquid–liquid equilibrium data for the hexane–benzene–dimethyl sulfoxide system were measured at 10, 25, and 50 °C. The experimental data were correlated by using the NRTL and the UNIQUAC models.

Introduction

Liquid–liquid equilibrium data are useful for the design of liquid extraction processes. Because dimethyl sulfoxide (DMSO) is a versatile solvent for a broad range of liquids, phase equilibrium studies of the ternary mixtures of dimethyl sulfoxide has received a great deal of attention (*1–3*). The purpose of the present study was to investigate the liquid–liquid equilibria for the hexane–benzene–dimethyl sulfoxide system at 10, 25, and

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Table I. Tie-Line Data for the Hexane (1)–Benzene (2)–Dimethyl Sulfoxide (3) System, wt %

	DMSO-rich phase			hexane-rich phase		
temp, °C	1	2	3	1	2	3
10	0.87	0	99.13	99.55	0	0.45
	1.45	5.32	93.23	91.75	7.78	0.46
	1.99	10.69	87.32	83.29	16.23	0.48
	2.47	17.53	80.00	75.73	25.99	0.48
	3.54	24.55	71.91	65.16	34.36	0.48
	3.41	28.07	68.51	57.05	41.94	1.01
	3.70	31.29	65.01	53.62	45.46	0.92
25	1.28	0	98.72	99.30	0	0.70
	1.98	5.44	92.58	93.11	6.46	0.43
	2.97	10.54	86.48	85.46	14.07	0.47
	3.46	16.93	79.61	77.52	21.85	0.63
	4.64	23.44	71.92	70.73	28.92	0.35
	5.31	28.13	66.55	63.34	35.04	1.62
	5.65	34.15	60.20	56.88	40.52	2.60
50	2.27	0	97.73	98.68	0	1.32
	3.13	5.78	91.09	90.31	8.22	1.47
	4.17	13.80	81.95	79.12	18.32	2.56
	5.06	17.29	77.65	75.06	21.62	3.31
	7.26	24.11	68.64	65.53	30.10	4.38
	6.87	28.78	64.36	59.11	35.51	5.39

50 °C. The experimental data were correlated by using the NRTL and the UNIQUAC models.

Experimental Section

Materials. Dimethyl sulfoxide was obtained from Alfa Products, and hexane was obtained from Mallinkrodt, Inc. Although both solvents had a stated minimum purity greater than 99 wt %, they were further purified by use of a Bughi-R rotary evaporator operated near atmospheric pressure. Benzene was obtained from the J. T. Baker Chemical Company with a stated minimum purity of 99.9 wt %. The purities of all the chemicals were checked by gas chromatography and were found to be greater than 99.9 wt % after purification.

Procedure. Experimental measurements were made in the two-phase region for the hexane–benzene–dimethyl sulfoxide ternary system. Sample mixtures of hexane–benzene–dimethyl sulfoxide were prepared and placed in Supelco sample bottles and sealed with Teflon lined septum caps. The samples were shaken vigorously in a Magin Whirl Blue M shaker bath controlled at a temperature of 10, 25, or 50 °C (±0.2 °C). After equilibrium was attained, the two phases were allowed to separate and small samples of approximately 25 μL were withdrawn from each phase. When collecting samples from the heavier phase, the syringe was inserted directly into the heavy phase and small sample quantities were repeatedly withdrawn and injected. This technique was used to prevent any contamination of the sample by the lighter phase. A sample was then withdrawn and diluted with 1.5 mL of carbon disulfide solvent to prepare for analysis. The sample analysis was performed with a gas chromatograph (Hewlett-Packard 5793) equipped with a single-channel flame ionization detector and an electronic integrator (Hewlett-Packard 3390). A stainless steel column of 1.5 m long × 3.2 mm diameter packed with 2% OV-101 methyl silicone fluid on a Chromasorb W-HP 100/120 Hewlett-Packard packing was used. A capillary column chromatograph (Hewlett-Packard 5792) employing a 12 m long × 6 mm diameter cross-linked methyl silicone column, constructed of fused silica, along with an integrator was used to analyze for extremely low concentrations. The flow rate of nitrogen carrier gas was kept constant at 30 mL/min. The column temperature was programmed for an initial temperature range of 45–80 °C and a final temperature range of 140–167 °C. The heating rate was 36 °C/min. The compositions of the liquid phases were determined by using an area analysis of the peak size of each component. The gas chromatograph was calibrated with two series of mixtures of known compositions. One series was rich in dimethyl sulfoxide and the other was rich in hexane. Calibration curves were obtained by using several chromatograms for each mixture. For each sample, three analyses were performed to obtain the mean value. The average absolute deviation from the mean value was estimated to be 0.05 wt %.

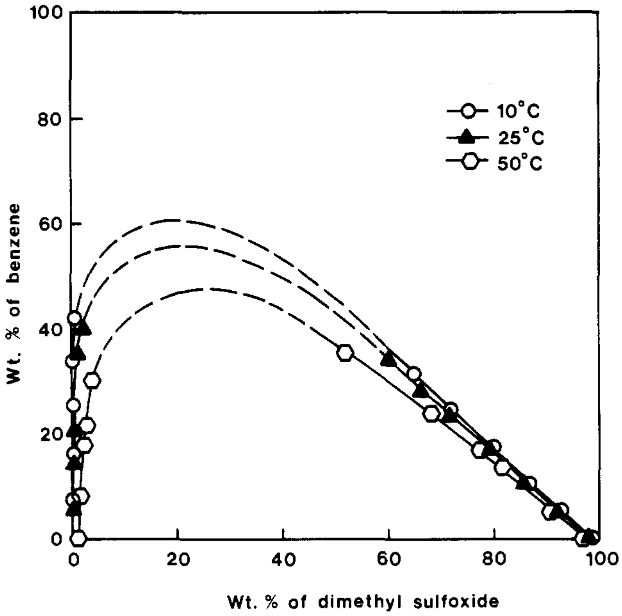

Figure 1. Effect of temperature on solubility for the hexane (1)–benzene (2)–dimethyl sulfoxide (3) system.

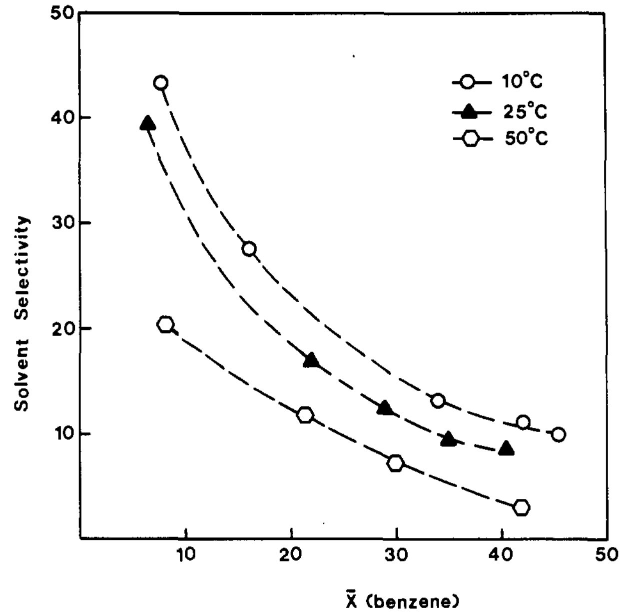

Figure 2. Solvent selectivity of dimethyl sulfoxide as a function of solvent-free benzene in the hexane-rich phase.

Results and Discussion

Experimental Results. The experimental tie-line data for the hexane–benzene–dimethyl sulfoxide system at 10, 25, and 50 °C are given in Table I. The temperature dependence of the solubility data is shown in Figure 1. The size of the two-phase region decreases with an increase in temperature near the plait point but was relatively unaffected at lower solute concentrations. The general trend of the solubility data for the hexane–benzene–dimethyl sulfoxide system studied herein is in good agreement with the data published by Nissema (*4*) for cyclohexane–benzene–dimethyl sulfoxide. The solvent selectivity for

Table II. UNIQUAC and NRTL Parameters for the Hexane (1)-Benzene (2)-Dimethyl Sulfoxide (3) System

		UNIQUAC parameters		NRTL parameters	
temp, °C	i-j	$(u_{ij}-u_{jj})/R$	$(u_{ji}-u_{ii})/R$	$(g_{ij}-g_{jj})/R$	$(g_{ji}-g_{ii})/R$
10	1-2	135.85	-28.50	370.07	-200.72
	1-3	739.73	49.44	1827.80	1030.10
	2-3	169.82	22.92	544.54	-118.61
25	1-2	93.11	-90.90	255.52	-221.34
	1-3	738.70	49.34	1900.20	817.34
	2-3	222.73	119.18	652.67	-277.14
50	1-2	119.14	-86.10	236.51	-212.12
	1-3	607.11	52.38	1212.0	754.43
	2-3	122.17	-25.53	390.68	-129.86

the hexane-benzene-dimethyl sulfoxide ternary system is given as a function of solvent-free weight composition in Figure 2. The solvent selectivity was defined as

$$S = \frac{(\text{wt \% benzene/wt \% hexane})_{\text{extract}}}{(\text{wt \% benzene/wt \% hexane})_{\text{raffinate}}} \qquad (1)$$

Because the values of the selectivities are greater than 1, the separation of benzene from hexane by extraction with dimethyl sulfoxide is feasible.

Correlation of the Experimental Data

Thermodynamic models, such as the NRTL and UNIQUAC, utilize the excess Gibbs energy and related activity coefficient to correlate liquid-liquid equilibrium data of ternary mixtures. A useful assumption of models for the excess Gibbs energy is that only experimental data of binary systems are needed to estimate multicomponent activity coefficients. The nonrandom two-liquid equation (NRTL) developed by Renon and Prausnitz (*5*) and the universal quasichemical equation (UNIQUAC) proposed by Abrams and Prausnitz (*6*) were derived by introducing the local composition concept into the quasichemical theory of Guggenheim (*7*). Although the NRTL and UNIQUAC equations have two adjustable parameters for each binary, the NRTL equation has a third parameter, α_{ij}, which represents the nonrandomness of the liquid mixture. A value for α_{ij} ranging from 0.2 to 0.5 was recommended by Renon and Prausnitz (*2*). Although NRTL and UNIQUAC models provide a method of correlating liquid-liquid equilibrium data, Sorensen et al. (*8*) concluded that these models were not fully successful for ternary systems. When an objective function that minimizes the activity differences or the differences between experimental and calculated compositions was used, the correlations improved (*9-11*). In the present study, the parameters τ_{ji} and τ_{ij} for the NRTL and UNIQUAC equations were obtained by using an iterative computer program developed to minimize the value of the objective function

$$F = \sum_{i}^{N}\sum_{l}^{2}\sum_{m}^{M}(x_{ilm} - \hat{x}_{ilm})^2 \qquad (2)$$

where i denotes the components, l denotes the phases, m denotes the tie lines, x represents the experimental composition, and $\hat{x}$ is the calculated composition. The parameter estimation was carried out by using an iterative computer program developed by Sorensen et al. (*8*) to minimize the value of the objective function. The estimated interaction parameters for the hexane-benzene-dimethyl sulfoxide system at 10, 25, and 50 °C are given in Table II. Although the nonrandomness parameter, α_{ij}, was set at a value of 0.2 in the present study, the effect of increasing the value of the nonrandomness parameter on the liquid-phase immiscibility was studied for the hexane-dibutyl ketone-dimethyl sulfoxide (*2*), and it was concluded that the domain of the liquid-phase immiscibility decreases with increase in the value of α_{ij}. The values predicted by using the NRTL and UNIQUAC models and the experimental tie lines at 10, 25, and 50 °C are plotted in Figures 3, 4, and 5, respectively. The mean deviations of the predicted values from the experimental data are larger near the plait point region, where there is more uncertainty in the predicted and experimental data. However, the deviation is of little consequence since practical extraction processes are usually not carried out in this region.

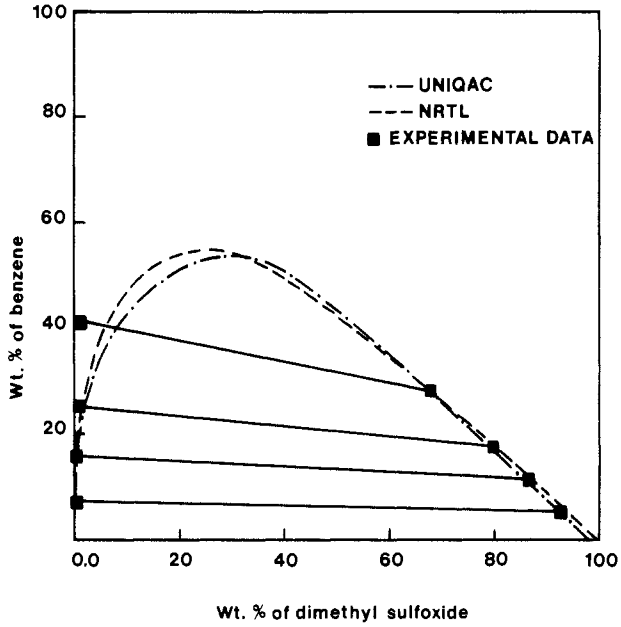

Figure 3. Liquid-liquid equilibria for the hexane (1)-benzene (2)-dimethyl sulfoxide (3) system at 10 °C.

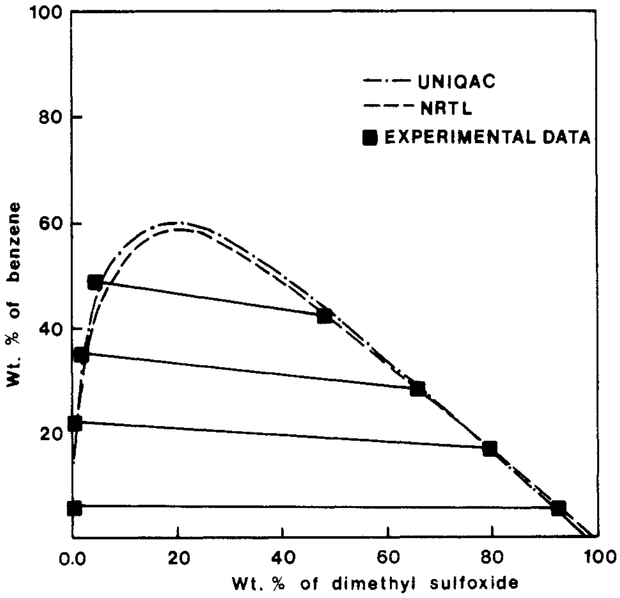

Figure 4. Liquid-liquid equilibria for the hexane (1)-benzene (2)-dimethyl sulfoxide (3) system at 25 °C.

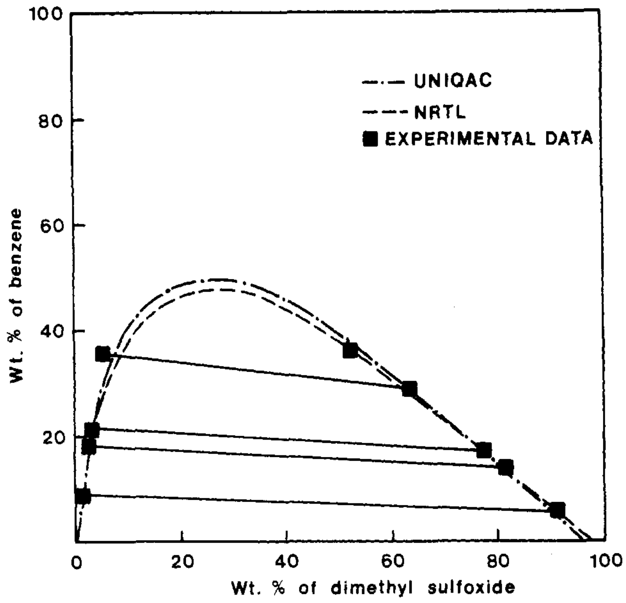

Figure 5. Liquid–liquid equilibria for the hexane (1)–benzene (2)–dimethyl sulfoxide (3) system at 50 °C.

Glossary

g_{ij}	energy parameter in the NRTL equation, K
α_{ij}	nonrandomness parameter in the NRTL equation
u_{ij}	energy parameter in the UNIQUAC equation, K
x_{ilm}	experimental mole fraction of component *i*, in phase *l* on tie line *m*
$\hat{x}_{ilm}$	calculated mole fraction of component *i*, in phase *l* on tie line *m*
$\bar{X}$	solvent-free composition, wt %
R	gas constant, cal/(mol K)

Subscripts

i, *j*	components
l	phases
m	tie lines

Registry No. DMSO, 67-68-5; hexane, 110-54-3; benzene, 71-43-2.

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