no ternary azeotrope exists, as there is no maximum, minimum, or saddle-point pressure in this figure. Thus, tetrahydrofuran can be useful for breaking the ethyl acetate and cyclohexane azeotrope. The situation of equal ethyl acetate/cyclohexane relative volatility, which is the formation of a pseudoazeotrope, disappears when the tetrahydrofuran liquid-phase mole fraction exceeds 70 mol % as is also shown in this figure.

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Correlation of Phase Equilibria of Naphtha Reformate with Sulfolane

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Liquid–liquid equilibria of the ternary systems *n*-hexane–benzene–sulfolane, *n*-heptane–toluene–sulfolane, and octane–xylene–sulfolane have been determined at temperatures of 30, 35, and 40 °C. The equilibria were measured with a thermostatically controlled Smith–Bonner cell. The work was then extended to a multicomponent system. A feed with a composition typical of a reformate containing 55% aromatics was extracted with sulfolane and the phase equilibria were determined. The data were correlated by using Hand's method and were found to be in good agreement with theoretical predictions using the UNIFAC method.

Introduction

The excellent performance of sulfolane as a solvent for the extraction of aromatics has been demonstrated by commercial operation of the sulfolane process over several years in a large number of units (*1*). Simultaneous extraction of BTX from both reformate and hydrotreated pyrolysis naphthas yields aromatic products of 99% purity (*2*). In the present investigation the liquid–liquid equilibria of four systems containing sulfolane have been determined and the data correlated by using Hand's equation. The UNIFAC method was subsequently applied to predict comparable data.

Experimental Investigation

Purity of Materials. The toluene and benzene used had a minimum purity of 99.5%. Sulfolane, obtained from Fluka AG, Chemical Fabrickin, Switzerland, was predistilled in a packed column of 2 m length and 10 cm diameter and had a maximum water content of 0.05%. Hexane, heptane, octane, and xylene were obtained from BDH Ltd, UK.

Table I. Experimental LLE Compositions for *n*-Hexane–Benzene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-hexane	benzene	sulfolane	*n*-hexane	benzene	sulfolane
0.990		0.009	0.006		0.993
0.851	0.131	0.018	0.015	0.083	0.891
0.705	0.26	0.034	0.047	0.181	0.771
0.512	0.392	0.995	0.088	0.281	0.62

Table II. Experimental LLE Compositions for *n*-Heptane–Toluene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-heptane	toluene	sulfolane	*n*-hexane	toluene	sulfolane
0.981		0.018	0.01		0.989
0.025	0.155	0.899	0.012	0.049	0.938
0.029	0.228	0.742	0.015	0.088	0.896
0.031	0.272	0.696	0.017	0.126	0.856

Table III. Experimental LLE Compositions for *n*-Octane–Xylene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-octane	xylene	sulfolane	*n*-octane	xylene	sulfolane
0.983		0.017	0.005		0.994
0.865	0.123	0.021	0.008	0.085	0.907
0.812	0.161	0.026	0.019	0.125	0.855
0.675	0.289	0.036	0.029	0.185	0.785

Table IV. Experimental LLE Compositions for Nonaromatics–Aromatics–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
non-aromatic	aromatic	sulfolane	non-aromatic	aromatic	sulfolane
0.845	0.144	0.012	0.007	0.048	0.944
0.783	0.204	0.013	0.012	0.072	0.916
0.731	0.255	0.014	0.016	0.142	0.842
0.550	0.422	0.029	0.02	0.231	0.749

Equilibrium Measurements. Measurements were made using a Smith–Bonner cell (*3*) controlled at a temperature of 30, 35, or 40 °C. Specific amounts of A (the nonaromatic) and the solute C (the aromatic) were introduced into the cell and agitated while maintained at a constant temperature by circulation

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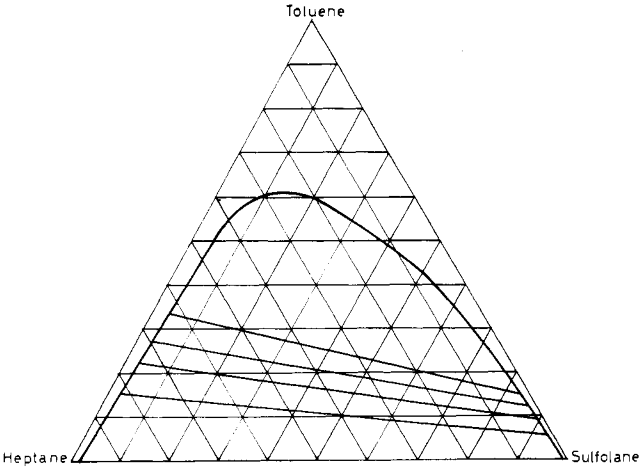

Figure 1. Ternary solubility diagram of the system toluene-heptane-sulfolane at 30 °C.

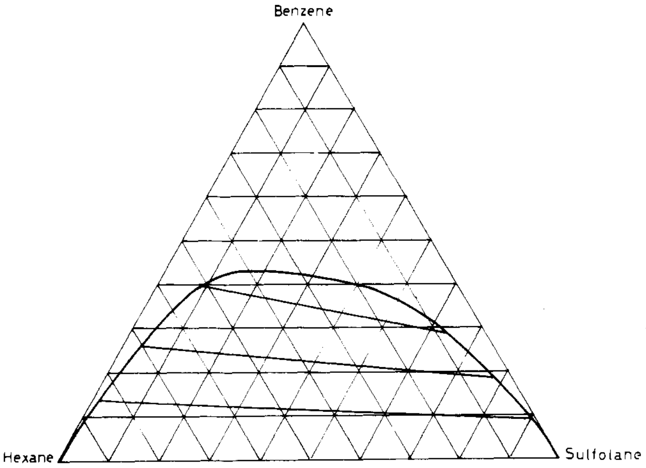

Figure 2. Ternary solubility diagram of the system benzene-hexane-sulfolane at 30 °C.

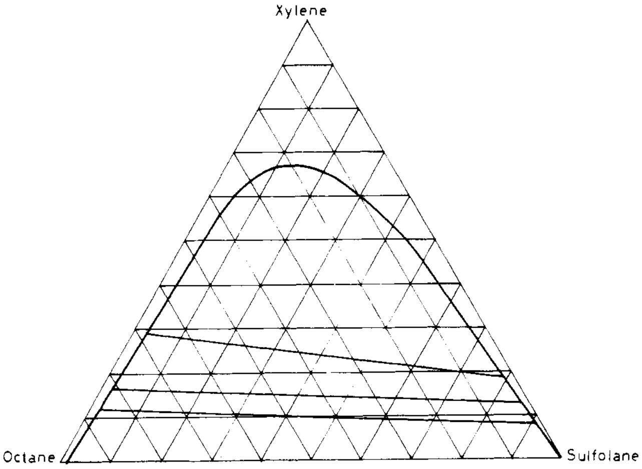

Figure 3. Ternary solubility diagram of the system xylene-octane-sulfolane at 30 °C.

of water through the external jacket from a thermostatic bath. The mixture was then titrated slowly against sulfolane until turbidity appeared, and continued until the turbidity disappeared. Repeating this procedure at various compositions enabled a complete set of curves to be obtained (*4*).

Method of Analysis. Analyses were performed using an Abbe refractometer supplied by American Optics. The solubility diagrams are shown in Figures 1-5, and the data are given in Tables I-VI.

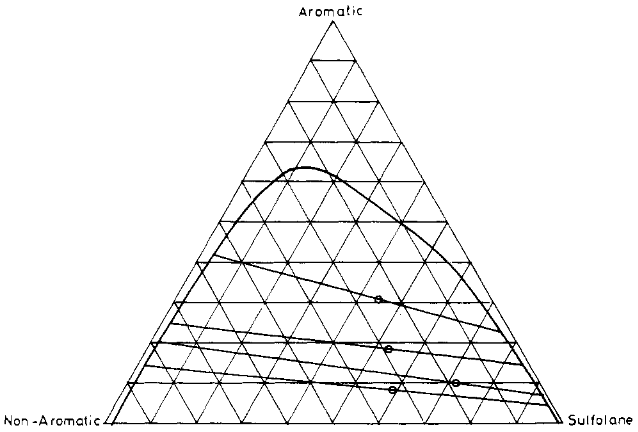

Figure 4. Solubility diagram of the system aromatics-nonaromatics-sulfolane at 30 °C.

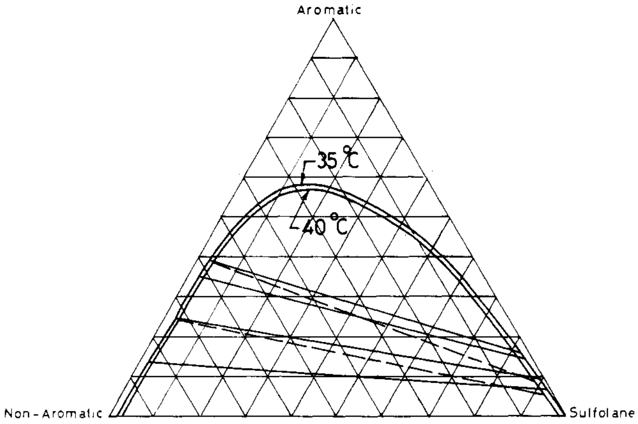

Figure 5. Solubility diagram of the system aromatics-nonaromatics-sulfolane at 35 and 40 °C.

Table V. Experimental LLE Compositions for Nonaromatics-Aromatics-Sulfolane at 35 °C

wt fraction in raffinate			wt fraction in extract		
nonaromatic	aromatic	sulfolane	nonaromatic	aromatic	sulfolane
0.842	0.135	0.023	0.017	0.06	0.923
0.73	0.245	0.025	0.02	0.09	0.88
0.66	0.313	0.027	0.025	0.115	0.86
0.58	0.39	0.03	0.035	0.145	0.82

Table VI. Experimental LLE Compositions for Nonaromatics-Aromatics-Sulfolane at 40 °C

wt fraction in raffinate			wt fraction in extract		
nonaromatic	aromatic	sulfolane	nonaromatic	aromatic	sulfolane
0.912	0.06	0.028	0.015	0.025	0.95
0.822	0.149	0.029	0.022	0.052	0.92
0.675	0.282	0.037	0.027	0.088	0.88
0.6	0.36	0.04	0.03	0.11	0.86

Correlation of Data

Geometrical methods for interpolation and extrapolation of tie line data have been devised by Brancker et al. (*5*), Sherwood (*6*), and Hand (*7*). While they are entirely graphical, these methods are useful for extrapolation. The first empirical equation describing the distribution of components in a three-component, two-phase liquid system was due to Bachman (*8*)

$$X_{BB} = r + b(X_{BB}/X_{AA}) \quad (1)$$

where r and b are constants.

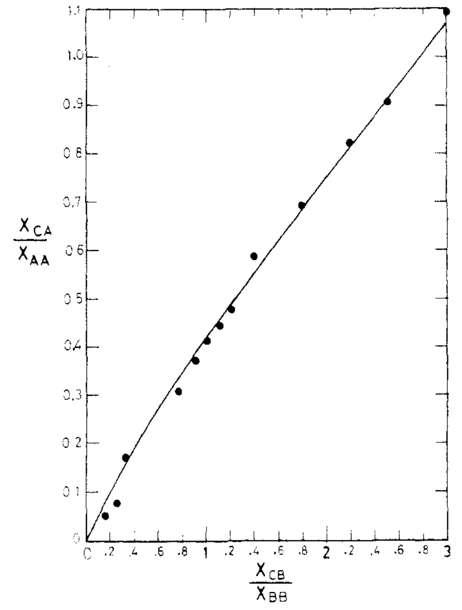

Figure 6. Equilibrium curve for the system aromatic–nonaromatic–sulfolane at 30 °C.

Othmer and Tobias (*9*) showed that this correlation is of limited use, because it is based on ternary systems composed of practically immiscible, nonconsolute components in the absence of the consolute component. They therefore proposed that

$$\frac{1 - X_{AA}}{X_{AA}} = K\left[\frac{1 - X_{BB}}{X_{BB}}\right]^{n} \tag{2}$$

On logarithmic coordinates this equation gives a straight line.

However, the method of Othmer and Tobias is also limited by the fact it does not include the concentration of the distributed component. Therefore, the most useful formula appears to be that of Hand which correlates the concentration of the solute in the two conjugate solutions. Hand's equation is represented by

$$\frac{X_{CA}}{X_{AA}} = K\left[\frac{X_{CB}}{X_{BB}}\right]^{r} \tag{3}$$

i.e., the logarithmic plot of X_{CA}/X_{AA} against (X_{CB}/X_{BB}) is rectilinear.

A regression analysis of the solubility data for the system aromatics–nonaromatics–sulfolane, based on Hand's correlation, resulted in the equation

$$\frac{X_{CA}}{X_{AA}} = 0.414\left[\frac{X_{CB}}{X_{BB}}\right]^{0.885} \tag{4}$$

where *A*, *B*, and *C* refer to sulfolane, nonaromatics, and aromatics, respectively.

Figure 6 shows that the results predicted by Hand's correlation, when plotted against the experimental values, gave good agreement. The results of regression analysis of the data for this system at 35 °C resulted in the equation

$$\frac{X_{CA}}{X_{AA}} = 0.23\left[\frac{X_{CB}}{X_{BB}}\right]^{0.64} \tag{5}$$

and at 40 °C

$$\frac{X_{CA}}{X_{AA}} = 0.188\left[\frac{X_{CB}}{X_{BB}}\right]^{0.73} \tag{6}$$

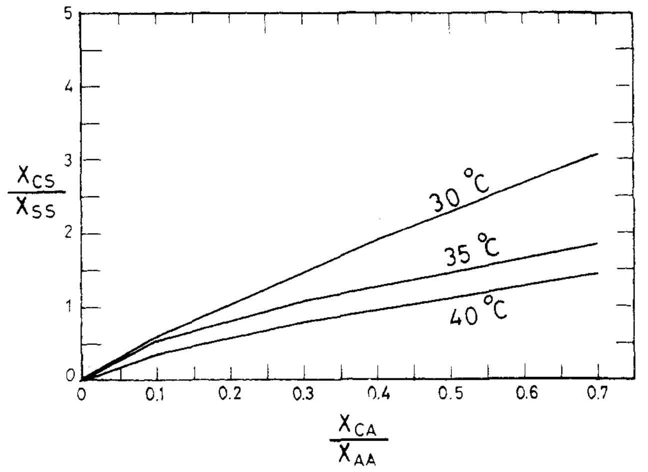

Figure 7. Hand's correlation for the system aromatic–nonaromatic–sulfolane at 30, 35, and 40 °C.

Table VII. Predicted LLE Compositions at 30 °C for the Aromatics–Nonaromatics–Sulfolane System[a]

wt fraction in raffinate			wt fraction in extract		
nonaromatic	aromatic	sulfolane	nonaromatic	aromatic	sulfolane
0.843	0.142	0.015	0.009	0.052	0.938
0.781	0.199	0.019	0.014	0.075	0.910
0.725	0.254	0.020	0.020	0.149	0.840
0.549	0.420	0.035	0.025	0.239	0.735

[a] Compositions of aromatics: benzene 46.80, toluene 32.29, xylene, 20.91 vol. %; nonaromatics: *n*-hexane 21.47, *n*-heptane 40.6, *n*-octane 37.91 vol. %.

Figure 7 represents Hand's correlation for the multicomponent system nonaromatics–aromatics–sulfolane at 30, 35, and 40 °C.

Computation of LLE Data by UNIFAC. Computation of the liquid–liquid equilibrium phase compositions involves solving eq 7 with material balance eq 8, 9, and 10, using an iterative procedure based on the Newton–Raphson method (*10*)

$$(\gamma X_i)^{\mathrm{I}} = (\gamma X_i)^{\mathrm{II}} \tag{7}$$

$$X_i^{\mathrm{F}} = \theta X_i^{\mathrm{I}} + (1 - \theta)X_i^{\mathrm{II}} \qquad (i = 1, 2, ..., N) \tag{8}$$

$$\sum_{i=1}^{N} X_i^{\mathrm{I}} = 1 \tag{9}$$

$$\sum_{i=1}^{N} X_i^{\mathrm{II}} = 1 \tag{10}$$

θ is the fraction extracted. The procedure involves estimation for θ and X_i^{I} and successive iteration until eq 7 is satisfied; the γ_i^{I} and γ_i^{II} are next calculated, using the compositions just obtained from the UNIFAC(*11*). New values of X_i^{II} and X_i^{I} are then calculated from the eq

$$X_i^{\mathrm{II}} = \frac{X_i^{\mathrm{F}}}{1 + (K_i - 1)\theta} \tag{11}$$

$$X_i^{\mathrm{I}} = K_i X_i^{\mathrm{II}} \tag{12}$$

where $K_i = X_i^{\mathrm{I}}/X_i^{\mathrm{II}}$ and θ are improved upon successive iter-

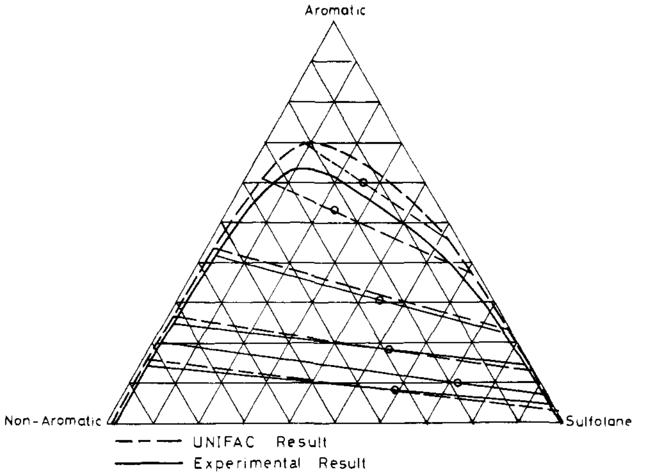

Figure 8. Comparison of predicted and experimental phase compositions of the system aromatics-nonaromatics-sulfolane at 30 °C.

ation until $\sum (X_i^{II}{}_{old} - X_i^{II}{}_{new}) < 10^{-8}$.

Results and Discussion

Figure 8 and Table VII demonstrate that the predicted phase compositions are in good agreement with the corresponding experimental values for the system aromatic-nonaromatic-sulfolane. The deviation of the predicted compositions near the plait point is characteristic of any prediction method but is of little consequence since practical extractions are never carried out near the plait point.

With regard to the effect of temperature on the selectivity and distribution coefficient, the selectivity of sulfolane will decrease with temperature since the heterogeneous area decreases with temperature. The slope of the tie lines is inclined toward the solvent, but the selectivity is greater than one; thus the extraction is possible.

Conclusions

It is concluded from the above results that the temperature had a modest effect on the miscibility range of the systems studied. On balance, considering both capacity and selectivity of sulfolane, with the systems studied better results were achieved at the lowest temperature of 30 °C.

Good agreement was obtained between data predicted by the UNIFAC method and experimental results as shown in Figure 8. The UNIFAC method is presently being applied to predict phase equilibria for actual naphtha cuts. The predicted values will be used to correlate data obtained on the extraction of naphtha by sulfolane, using a mixer-settler cascade. Work is also in progress to improve prediction near the plait point by improving the interaction parameters of UNIFAC.

Glossary

X_{BB}	concentration of solvent B in B phase in eq 1, 2, and 3
X_{AA}	concentration of solvent A in A phase in eq 1, 2, and 3
X_{CA}/X_{AA}	concentration of aromatics in nonaromatics phase per concentration of nonaromatics in nonaromatics phase in eq 4
X_{CB}/X_{BB}	concentration of aromatics in sulfolane phase per concentration of sulfolane in sulfolane phase in eq 4
r, b, n	constants
X_i^F	concentration of component i in feed
I	extract phase
II	raffinate phase
γ	activity coefficient

Registry No. Hexane, 110-54-3; benzene, 71-43-2; heptane, 142-82-5; toluene, 108-88-3; octane, 111-65-9; xylene, 1330-20-7; sulfolane, 126-33-0.

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Ultrasonic Velocity and Adiabatic Compressibility of Monochloroacetic Acid in Aqueous Ethanol at Various Temperatures

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Ultrasonic velocities of solutions of monochloroacetic acid in aqueous ethanol were measured at 25, 30, 35, and 40 °C by using a single-crystal interferometer at a frequency of 1.5 MHz. The ultrasonic velocity, density, and concentration were used to calculate adiabatic compressibility, intermolecular free length, and apparent molal compressibility. Bachem's relation has been found to be obeyed and the constants *A* and *B* of this relation of various solvents have also been reported.

Introduction

Accurate thermodynamic data on dilute electrolyte solutions are frequently needed. The sound velocity is a purely thermodynamic function. Many other thermodynamic properties of electrolyte solutions are determined from sound velocity (*1*, *2*). In recent years ultrasonic velocity studies in many of the aqueous and nonaqueous electrolytic solutions have led to new insights into the process of ion-ion and ion-solvent interactions (*3*-*11*). Ultrasonic velocity and adiabatic compressibility are quite sensitive to changes in ionic concentrations. Either or