Liquid−Liquid Equilibrium Studies on Toluene + Heptane + Solvent

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Liquid−liquid equilibria of the ternary systems toluene−heptane−tetraethylene glycol, toluene−heptane−*N*−formylmorpholine, toluene−heptane−(tetraethylene glycol + *N*-formylmorpholine), and toluene−heptane−(tetraethylene glycol + *N*-methylpyrrolidone) have been determined at 40 °C. The capacity and selectivity data of the solvent systems were obtained and compared. The data were correlated using Bachman, Othmer−Tobias, and Hand models.

Introduction

In the petroleum industry, many solvents such as *N*-methylpyrrolidone (NMP) (Muller, 1973), *N*-formylmorpholine (NFM) (Cinelli et al., 1972), glycols (Symoniak et al., 1981; Taher and Emina, 1996), and sulfolane (Deal et al., 1959; Voetter and Kosters, 1963; Broughton and Asselin, 1967) are used for the extraction of aromatics from multicomponent hydrocarbon mixtures, because of their high selectivity and solvency for low molar mass monocyclic aromatic hydrocarbons (C_6−C_9). Solvents for extraction should have high selectivity for aromatics, high capacity, capability to form two phases at reasonable temperatures, capability of rapid phase separation (high density and low viscosity), and good thermal stability, and they should be noncorrosive and nonreactive (Taher and Emina, 1996; Rawat et al., 1972; Rawat and Gulati, 1976a; Rawat and Naithani, 1993). Work is still in progress to find other solvents with these properties (Rawat et al., 1976; Rawat and Gulati, 1976b; Lo et al., 1983; Awwad et al., 1988; Salem, 1993). An alternate approach is to use a combination of solvents to balance the selectivity and solvency functions (Muller and Hochfeld, 1967; Rawat and Gulati, 1981; Nagpal and Rawat, 1981; Masurina et al., 1995; Rogozkin et al., 1981; Paulino, 1985; Klaus and Werner, 1983; Vasilev et al., 1984). Such a combination of solvents is reported to give the advantages of lower consumption of energy and lower solvent-to-feed ratio, with an effect on the dimensions of the column (Rawat and Gulati, 1981). Ternary-phase equilibrium data are essential for the proper understanding of solvent extraction processes, selection of solvents, and design of extractors. Studies of the liquid−liquid equilibrium of benzene−*n*-heptane−solvent systems are well-covered in the literature, while phase-equilibrium data published on toluene−*n*-heptane−solvent systems, which are also required for process design, are inadequate. Toluene is always associated with benzene in reformate. Data on toluene−*n*-heptane−sulfolane/NMP systems are available at 25−50 °C (Rawat and Gulati, 1981; Nagpal and Rawat, 1981; Tripathi et al., 1975; Hassan et al., 1988), while data on toluene−*n*-heptane−NFM systems are reported only at 25 °C (Cinelli et al., 1972). To our knowledge, phase-equilibrium data on toluene−*n*-heptane−tetraethylene glycol (tetra)/combination solvent systems have not been published so far in the literature.

In the present investigation, liquid−liquid equilibria of toluene−heptane hydrocarbon systems have been reported with tetra, NFM, tetra + NFM (mass ratio 70:30), and tetra + NMP (mass ratio 70:30) at 40 °C.

Experimental Section

The equilibrium data for the toluene−*n*-heptane−solvent/combination solvent systems were determined at 40 °C using a glass-jacketed mixer−settler (Krishna et al., 1987) The mixer−settler temperature was maintained within ±0.05 °C by circulation of thermostated water. Feed and solvent/combination solvent of known composition and mass were introduced into the mixer−settler and stirred for 10 min, which is a sufficient length of time, as determined in trial experiments, for establishment of equilibrium between phases. The equilibrium phases were then allowed to settle for 10 min and were separately withdrawn, weighed, and analyzed by standard methods (Rawat and Gulati, 1976b). All solvents used were soluble in water. The solvents were present only in small quantities in the raffinate phase, and so the raffinate phase was made solvent-free by washing with water. The quantitative removal of hydrocarbons from extract solutions was done using azeotropic distillation with water. The extract phase was placed in a distillation flask (250° mL) and diluted with an almost equal mass of water before the flask was connected to the column (32 in. long, 1 in. i.d.) filled with heli-packing. The ascending vapors were condensed in a vertical condenser with coolant water at 0−5 °C. Since water forms a heteroazeotrope with these hydrocarbons, the condensate was collected in a buret from which the hydrocarbon layer was drawn and weighed. The compositions of the extract and raffinate were determined by refractive index measurements and by using calibration charts of the toluene−*n*-heptane binary system. Mass fraction measurements of the extract phase were reproducible to within ±0.005, while the precision in the composition measurement of the raffinate phase was estimated to be

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Table 1. Experimental Liquid–Liquid Equilibrium Compositions for Toluene–*n*-Heptane–Tetra Systems at 40 °C

mass fraction in raffinate phase			mass fraction in extract phase		
toluene	*n*-heptane	tetra	toluene	*n*-heptane	tetra
0.079	0.916	0.005	0.021	0.015	0.964
0.200	0.787	0.013	0.047	0.013	0.940
0.391	0.588	0.021	0.095	0.016	0.889
0.572	0.395	0.033	0.152	0.018	0.830
0.742	0.189	0.069	0.236	0.015	0.749
0.790	0.070	0.140	0.345	0.011	0.644

Table 2. Experimental Liquid–Liquid Equilibrium Compositions for Toluene–*n*-Heptane–NFM Systems at 40 °C

mass fraction in raffinate phase			mass fraction in extract phase		
toluene	*n*-heptane	NFM	toluene	*n*-heptane	NFM
0.064	0.906	0.030	0.039	0.030	0.931
0.171	0.784	0.045	0.089	0.034	0.877
0.271	0.661	0.068	0.155	0.047	0.798
0.410	0.398	0.192	0.308	0.110	0.582

Table 3. Experimental Liquid–Liquid Equilibrium Compositions for Toluene–*n*-Heptane–(tetra–NFM) Systems at 40 °C

mass fraction in raffinate phase			mass fraction in extract raffinate phase		
toluene	*n*-heptane	tetra–NFM	toluene	*n*-heptane	tetra–NFM
0.079	0.906	0.015	0.026	0.015	0.959
0.189	0.792	0.019	0.058	0.017	0.925
0.411	0.546	0.043	0.130	0.021	0.849
0.599	0.301	0.099	0.235	0.026	0.739
0.648	0.165	0.187	0.334	0.045	0.621
0.609	0.120	0.271	0.413	0.047	0.540

Table 4. Experimental Liquid–Liquid Equilibrium Compositions for Toluene–*n*-Heptane–(Tetra–NMP) Systems at 40 °C

mass traction in raffinate phase			mass traction in extract phase		
toluene	*n*-heptane	tetra–NMP	toluene	*n*-heptane	tetra–NMP
0.074	0.905	0.021	0.030	0.026	0.944
0.184	0.786	0.030	0.073	0.028	0.899
0.310	0.652	0.038	0.120	0.032	0.848
0.386	0.544	0.070	0.161	0.036	0.803
0.502	0.408	0.090	0.226	0.042	0.732
0.562	0.299	0.139	0.293	0.051	0.656
0.543	0.224	0.233	0.346	0.060	0.594

within ±0.003 mass fraction.The binodal curves were obtained on the basis of the equilibrium data (compositions of the extract and raffinate phases).

Results and Discussion

Liquid–liquid equilibrium data for different toluene–*n*-heptane-solvent systems at 40 °C are presented in Tables 1–4. The tie line data for the systems fit well on the binodal curves, indicating the accuracy of the experimental tie line data. The slopes of the tie lines are inclined toward the solvent, but the selectivity is greater than 1; thus, the extraction is possible. The error in the solute balance was found to be less than 2%.

For comparison purpose, binodal curves of all the systems are included in Figure 1. Binodal curve of the toluene–*n*-heptane–NMP system at 40 °C based on the reported data (Nagpal and Rawat, 1981) are also included in this diagram for comparison. Increase in the heterogeneous area in the ternary diagram results in an increase in selectivity and a decrease in capacity. As can be seen from the diagram, the selectivity and capacity vary in the following order:

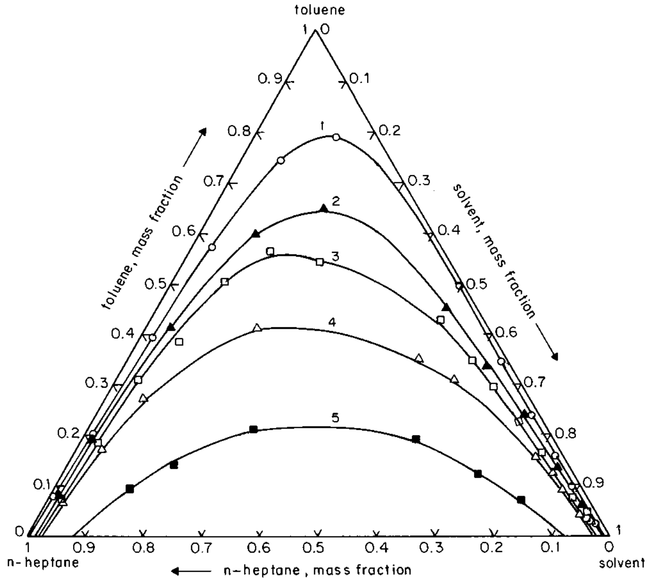

Figure 1. Comparison of the phase-equilibrium diagram for toluene–*n*-heptane–solvent systems at 40 °C. Solvents: 1, tetra; 2, tetra–NFM; 3, tetra–NMP; 4, NFM; 5, NMP.

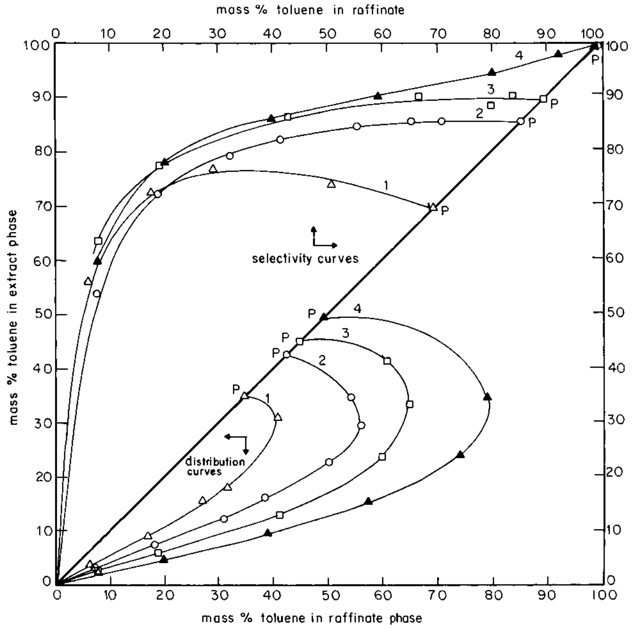

Figure 2. Selectivity and distribution curves for toluene–*n*-heptane–solvent systems at 40 °C. Solvents: 1, NFM; 2, tetra–NMP; 3, tetra–NFM; 4, tetra; P, plait point.

selectivity ←

tetra > tetra-NFM > tetra-NMP > NFM > NMP

capacity →

This indicates the solvent power (capacity) and its selectivity.

Similar conclusions can be drawn from the selectivity and distribution curves of the systems (Figure 2); the higher the distance of the curve from the diagonal, the higher the selectivity of the system.

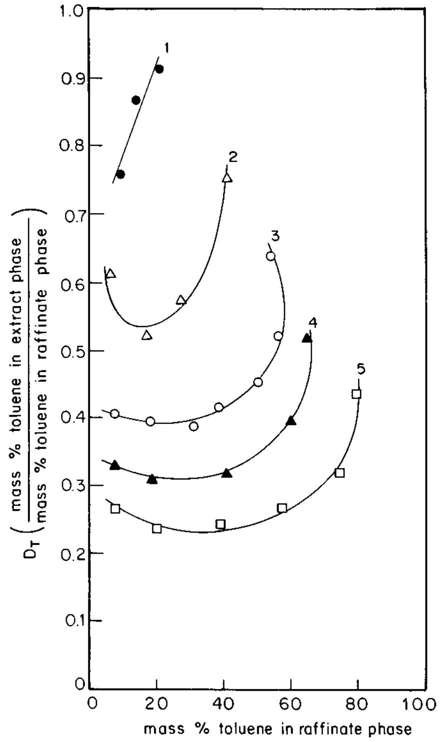

Figure 3. Comparison of capacity of solvents with toluene–heptane systems at 40 °C. Solvents: 1, NMP; 2, NFM; 3, tetra–NMP; 4, tetra–NFM; 5, tetra.

The selection of a solvent for an extraction study depends on the solvent power measured by the solute distribution coefficient

$$K_i = \frac{x_i^{\mathrm{e}}}{x_i^{\mathrm{r}}} \tag{1}$$

and also on its selectivity

$$S_{ij} = \frac{K_i}{K_j} = \frac{x_i^{\mathrm{e}}}{x_j^{\mathrm{e}}}\frac{x_j^{\mathrm{r}}}{x_i^{\mathrm{r}}} \tag{2}$$

where K is the partition coefficient, S is the selectivity factor, x is the liquid-phase concentration (mass fraction), and superscripts e and r are the extract phase and the raffinate phase, respectively.

The capacity (K_i) and selectivity of the solvents toward toluene with respect to heptane estimated by eqs 1 and 2 are presented in Figures 3 and 4, respectively. Selectivity decreases as the percentage of aromatics in the feed increases, while solubility increases with the increase in the aromatic content of the feed as expected.

Tetra, although highly selective, has a small capacity for extraction of aromatics from paraffins, while NMP has very high capacity (0.76–0.91) (Nagpal and Rawat, 1981) for extracting toluene from heptane but its selectivity is very poor. In the case of recovery of aromatics from reformates, a solvent with the largest possible capacity and highest selectivity toward aromatics is preferred. Combination solvent systems (tetra–NFM and terta –NMP), although less selective, have higher capacity compared to that of pure tetra. These combinations have higher selectivity and lower capacity compared to those of pure NFM and NMP, but their capacity is reasonable relative to sulfolane (0.415–0.629) (Tripathi et al., 1975), which is considered to be one of the most powerful solvents for aromatics extraction. Moreover, viscosities of the combination solvent systems are very low relative to the viscosity of the pure tetra, which should improve the extraction efficiency. Thus, the new combination solvent systems (tetra–NFM and tetra–NMP) appear to be attractive for extraction of aromatics from naphtha reformate.

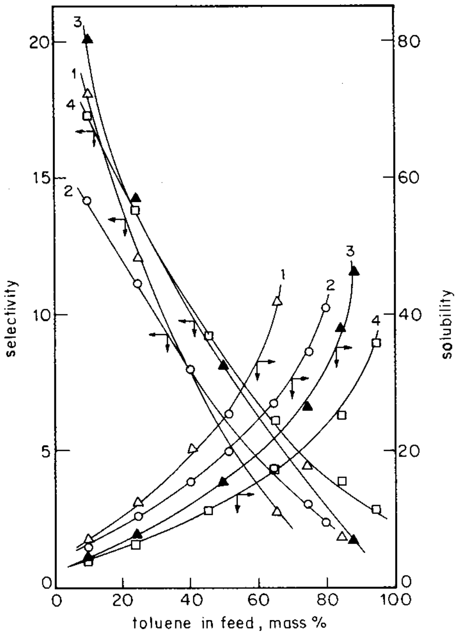

Figure 4. Selectivity and solubility curves with the change of composition of feed for toluene–n-heptane–solvent systems at 40 °C. Solvents: 1, NFM; 2, tetra–NMP; 3, tetra–NFM; 4, tetra.

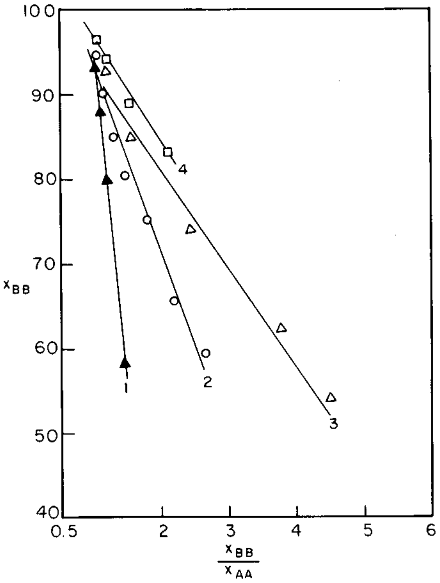

Figure 5. Bachman correlation for toluene–n-heptane–solvent systems at 40 °C. Solvents: 1, NFM; 2, tetra–NMP; 3, tetra–NFM; 4, tetra.

Correlation of Data

The first empirical equation describing the distribution of components in the three-component two-phase liquid system was due to Bachman.

$$X_{\mathrm{BB}} = r + b(X_{\mathrm{BB}}/X_{\mathrm{AA}}) \tag{3}$$

where X_{AA} and X_{BB} are concentration (mass fraction) of

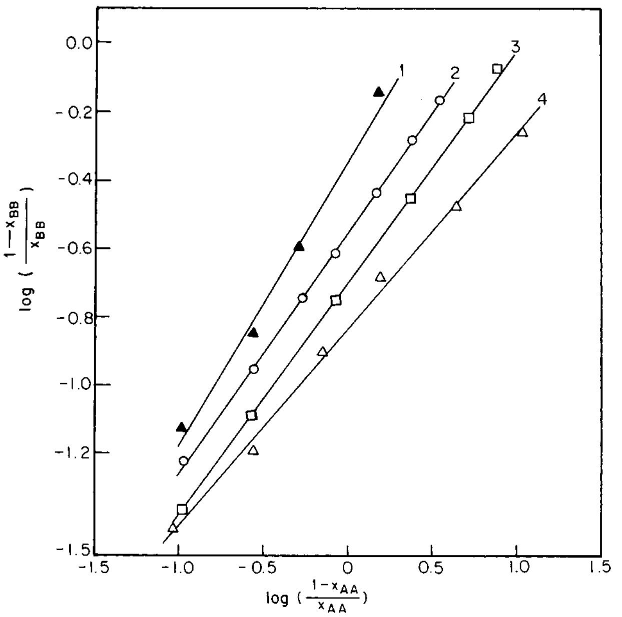

Figure 6. Othmer–Tobias correlation for toluene–*n*-heptane–solvent systems at 40 °C. Solvents: 1, NFM; 2, tetra–NMP; 3, tetra–NFM; 4, tetra.

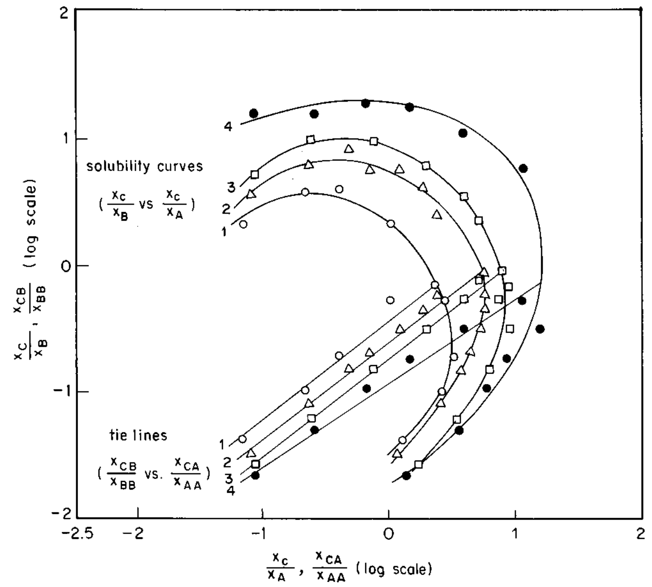

Figure 7. Hand correlation and plait point determination for toluene–*n*-heptane–solvent systems at 40 °C. Solvents: 1, NFM; 2, tetra–NMP; 3, tetra–NFM; 4, tetra.

components A (*n*-heptane) and B (solvent) in phase A (*n*-heptane-rich phase) and phase B (solvent-rich phase), respectively, and *r* and *b* are constants.

Othmer and Tobias proposed that

$$\frac{1 - x_{AA}}{x_{AA}} = K\left(\frac{1 - x_{BB}}{x_{BB}}\right)^n \tag{4}$$

where *K* and *n* are constants. On logarithmic coordinates this equation gives a straight line.

Hand correlated the concentration of the solute in the two conjugate solutions by the following equation

$$\frac{x_{CA}}{x_{AA}} = K\left(\frac{x_{CB}}{x_{BB}}\right)^r \tag{5}$$

where X_{CA} and X_{CB} are mass fractions of component C (toluene) in phases A and B, respectively, and *K* and *r* are constants. The logarithmic plot of X_{CA}/X_{AA} against X_{CB}/X_{BB} is rectilinear. Treybal illustrated the method of estimation of plait points on Hand's coordinates (Treybal, 1963).

Experimental data were plotted using these coordinates, and the plots are shown in Figures 5–7. Since the data show little scattering from a straight line, they are judged acceptable on an empirical basis, indicating internal consistency of the experimental data. The estimation at plait points for the system is also presented in Figure 7 by the use of Treybal's method.

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