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Liquid–Liquid Equilibria for the System Toluene–Isooctane–Diethylene Glycol Methyl Ether

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Liquid–liquid equilibrium data for the system toluene–isooctane–diethylene glycol methyl ether have been measured at 298 K. The data were correlated by the UNIFAC, UNIQUAC, and NRTL equations. The UNIQUAC and NRTL interaction parameters for the system are reported.

Introduction

The separation of aromatic and saturated hydrocarbons is often performed industrially by solvent extraction. A recent study (*1*) based on the UNIFAC (*2*) group contribution method found that a molecular structure corresponding to diethylene glycol methyl ether (DM) could be a potential solvent for aromatic–paraffinic separations. In the present work the liquid–liquid equilibrium for the system toluene–isooctane–diethylene glycol methyl ether (DM) was measured at 298 K. This paper reports the results of these measurements and their correlation by the UNIFAC (*2*), UNIQUAC (*3*), and NRTL (*4*) equations.

Experimental Section

Chemicals. Toluene (Merck, chromatography grade, density 0.87 g cm^{-3}), isooctane (Merck, analysis grade, density 0.69 g cm^{-3}), and diethylene glycol methyl ether (Dowanol DM, Dow Chemical, specific gravity at 25/25 °C 1.020) were used as supplied by the manufacturers. A chromatographic analysis on them showed major peak areas of more than 99.9%. The diethylene glycol methyl ether (DM) was dried with molecular sieves before being used and was kept under a dry atmosphere in a decanter with a molecular sieve column at the top.

Apparatus and Procedure. The experimental measurements were carried out in a thermostated glass cell of 155 cm^3 capacity, having two ports at the top for the titration and two side ports for sampling of the liquids. These last ports were made from Teflon tubing with threaded needle valves in order to reduce the dead volume to a minimum. Good mixing for volumes of up to 75 cm^3 was obtained by means of a magnetic stirrer in conjunction with two side baffles. A Plexiglas cap, placed over the mixing flask, allowed the experiments to be conducted in a dry nitrogen atmosphere, so as to prevent the highly hygroscopic DM from absorbing water.

The binodal curve was first determined by the titration method (*5*). The composition of the mixture at each saturation point was calculated from the measured weight of liquid (pure solvent or mixture of known composition) placed initially inside the flask and the measured volumes and densities of the solvents (or solutions) added from the burets. The densities of the liquids were measured in a PAAR DM 55 density meter.

In order to establish the binodal curve with more precision, some of the saturation points were redetermined. During the reevaluation, pure components or binary mixtures were used to titrate a binary or ternary mixture of known composition, chosen so as to reach the binodal curve by moving perpendicularly to it. Once turbidity became visible, a measured volume of the original mixture was added in order to break the saturation point moving toward the region of total miscibility, hence determining each saturation point twice.

Table I. Binodal-Curve Data for the System DM (1)–Toluene (2)–Isooctane (3) at 298 K

DM-rich phase			isooctane-rich phase		
$x(1)$	$x(2)$	$x(3)$	$x(1)$	$x(2)$	$x(3)$
0.900	0.000	0.100	0.049	0.000	0.951
0.891	0.008	0.101	0.058	0.075	0.867
0.816	0.063	0.121	0.074	0.133	0.793
0.751	0.107	0.142	0.099	0.172	0.729
0.695	0.139	0.165	0.121	0.201	0.678
0.645	0.166	0.189	0.152	0.225	0.623
0.594	0.189	0.217	0.198	0.243	0.559
0.547	0.207	0.246	0.250	0.250	0.500
0.502	0.220	0.278	0.313	0.248	0.439
0.462	0.228	0.310	0.371	0.243	0.386
0.425	0.234	0.341	0.422	0.237	0.341
			0.464	0.230	0.306

Table II. Tie-Line Data for the System DM (1)–Toluene (2)–Isooctane (3) at 298 K

DM-rich phase			isooctane-rich phase		
$x(1)$	$x(2)$	$x(3)$	$x(1)$	$x(2)$	$x(3)$
0.860	0.033	0.107	0.050	0.046	0.904
0.831	0.054	0.115	0.053	0.072	0.875
0.775	0.094	0.131	0.064	0.121	0.815
0.726	0.124	0.150	0.082	0.163	0.755
0.662	0.160	0.178	0.112	0.200	0.688

The tie lines were established by charging the mixing cell with a ternary mixture of known composition, corresponding to a point inside the two-phase region. This liquid was allowed to mix for several hours before the agitation was stopped to let the two phases separate. After some hours, samples of both phases were taken for analysis in a gas chromatograph.

Analysis. The liquid samples from the tie-line experiments were analyzed in a gas chromatograph Hewlett Packard 5840 A with a thermal conductivity detector. The separation column consisted of a 2 m × $^1/_8$ in. stainless steel tube packed with OV 17 silicone on Chromosorb G1 AW DMCS 80-100 mesh from Perkin-Palmer. The separation of the three components started at 110 °C for the isooctane peak and finished at 250 °C for the DM peak, with a temperature rate of increase of 30 °C/min. The injector and detector temperatures were 250 °C. The carrier gas was helium, flowing at 15.5 cm^3/min. Sample volumes for analysis were 0.3 μL.

The compositions of the liquid phases were calculated from

$$x_i = \frac{K_i A_i}{\sum K_i A_i} 100 \qquad i = 1, 2, 3 \tag{1}$$

where K_i is a calibration factor and A_i the area of the peak of component i. A series of K_i values, applicable to zones of different compositions within the one-phase region close to the binodal curve, were determined by calibrating the chromatograph with two series of mixtures of known composition (one series rich in DM and the other rich in isooctane).

Results, Correlations, and Discussion

Table I shows the compositions, in molar fractions, of the binodal curve for both the DM-rich phase and the isooctane-rich phase.

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Table III. UNIQUAC and NRTL Parameters for the System DM (1)-Toluene (2)-Isooctane (3) at 298 K

	UNIQUAC parameters		NRTL parameters		
$i-j$	$(u_{ij}-u_{jj})/R$, K	$(u_{ji}-u_{ii})/R$, K	$(g_{ij}-g_{jj})/R$, K	$(g_{ji}-g_{ii})/R$, K	α
1 - 2	-27.768	-95.354	-23.558	201.52	0.200
1 - 3	3.604	220.99	356.95	804.86	0.200
2 - 3	113.58	-265.70	-303.60	354.54	0.200
av |calcd - exptl|	0.0014		0.0016		

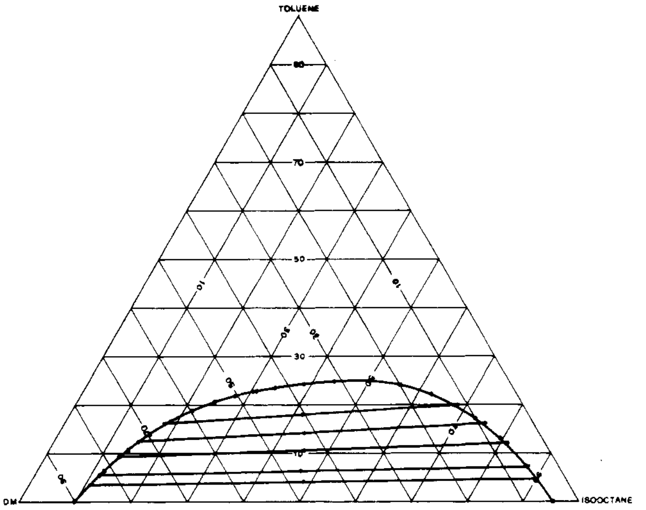

Figure 1. Liquid–liquid equilibria for the system diethylene glycol methyl ether (DM) (1)–toluene (2)–isooctane (3) at 298 K.

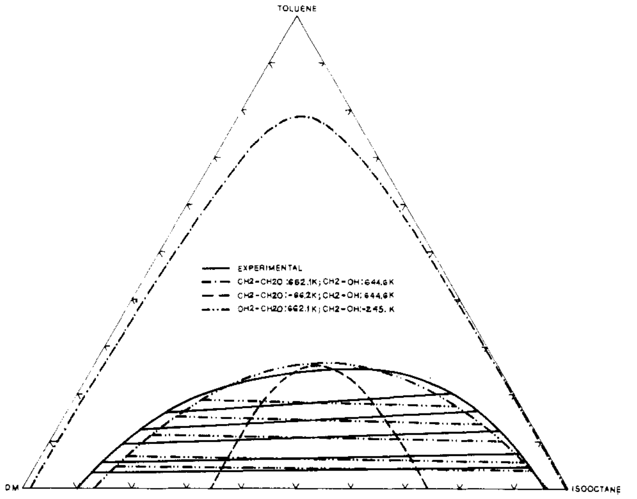

Figure 2. UNIFAC calculated liquid–liquid equilibria for the system diethylene glycol methyl ether (DM) (1)–toluene (2)–isooctane (3) at 298 K.

Table II gives the molar fractions corresponding to the tie-line data.

Figure 1 shows the triangular diagram for the system at 298 K.

There is a good agreement between the experimental points corresponding to the tie-line data and those obtained from the binodal curve measurements. There are no experimental data available in the literature on this system for comparison.

Prediction of the liquid–liquid equilibrium on this system by the UNIFAC (*2*) group contribution method showed a correct qualitative behavior regarding mutual solubilities, but gave a poor quantitative agreement with the experimental data. The predicted two-phase region covered a larger area than the experimental one, with a calculated plait point at 78.4 mol % of toluene instead of the 23.4% measured experimentally.

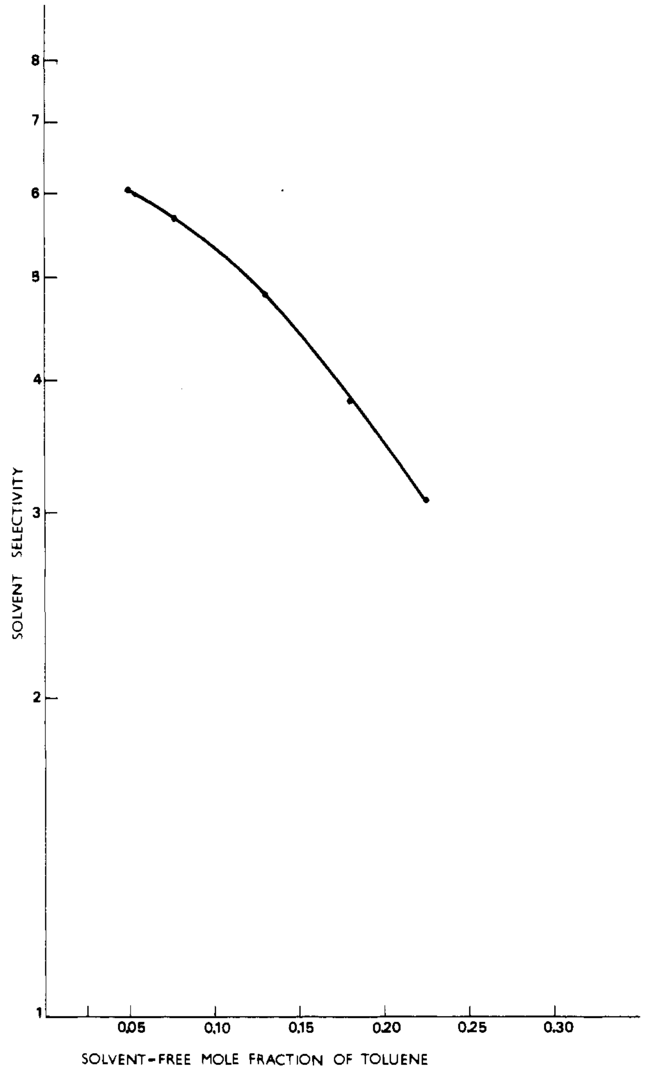

Figure 3. Solvent selectivity of the DM at 298 K as a function of solvent-free mole fraction of toluene in the isooctane-rich phase.

A study on the effect of the UNIFAC group interaction parameter values on the liquid–liquid equilibrium predictions for this system showed that only changes in the interaction parameters between the CH_2 and OH ($a_{CH_2,OH}$) and between CH_2 and CH_2O (a_{CH_2,CH_2O}) groups have a noticeable effect on the predicted mutual solubilities. A value of -66.2 K for the $a_{CH_2,OH}$ interaction parameter predicted a correct plait point but overcorrected the values of the mutual solubilities in the binary DM–isooctane. The best possible agreement between the calculated and the experimental binodal curve was obtained with a value of -245 K for the $a_{CH_2,OH}$ interaction parameter and the original parameters (*6*) for the remaining group interactions. The tie lines calculated with both the original value of 644.6 K (*6*) and with a value of -245 K for the $a_{CH_2,OH}$ interaction parameter predicted a preferential solubility of the solvent with respect to the toluene–isooctane pair opposite to that shown by the experiments. Figure 2 shows the liquid–liquid equilibria predicted by

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UNIFAC with the above interaction parameters.

The experimental tie-line data were also correlated by using the UNIQUAC (*3*) and NRTL (*4*) models. The parameters ($u_{ij} - u_{jj}$) and ($u_{ji} - u_{ii}$) corresponding to the residual excess Gibbs energy contribution of the UNIQUAC equations and the interaction parameters ($g_{ij} - g_{jj}$) and ($g_{ji} - g_{ii}$) for the NRTL equations were estimated by using the method described by Sørensen et al. (*7*). The objective function used to estimate the model parameters was

$$F = \sum_k (\min) \sum_j \sum_i (x_{ijk} - \hat{x}_{ijk})^2 \qquad (2)$$

where the summation indices are $i = 1, 2$ phases, $j = 1, 2, ..., N$ components, and $k = 1, 2, ..., M$ tie lines. Here the x_{ijk} represent the experimental mole fractions and $\hat{x}_{ijk}$ the calculated ones, and min denotes the minimum value of the summation. For the NRTL model, the nonrandomness parameter α_{ij} was set at a value of 0.2.

The UNIQUAC and NRTL parameters, obtained by this procedure, are reported in Table III, together with the average absolute deviations between the experimental and calculated mole fractions.

The experimental measurements on this system showed a small two-phase region at 298 K. According to these results only toluene–isooctane mixtures with less than about 47 mol % of toluene could be separated by the use of diethylene glycol methyl ether. Figure 3 shows the selectivity of this solvent as a function of the solvent-free mole fraction of toluene in the isooctane-rich phase. The solvent selectivity was defined in term of mole fractions as

$$S = \frac{[x(2)^*/x(3)^*]_{\text{DM-rich phase}}}{[x(2)^*/x(3)^*]_{\text{isooctane-rich phase}}} \qquad (3)$$

where the indices 2 and 3 represent toluene and isooctane, respectively, and * indicates equilibrium values. The *S* values drop quite rapidly toward a value of 1 at low toluene concentrations. The above results and discussion indicate a low solvent capability of the diethylene glycol methyl ether for the separation of toluene–isooctane mixtures.

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Registry No. DM, 111-77-3; toluene, 108-88-3; isooctane, 540-84-1.

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Density Study of $Mg(NO_3)_2$–H_2O–HNO_3 Solutions at Different Temperatures

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Densities for the $Mg(NO_3)_2$–HNO_3–H_2O system have been measured experimentally; more than 140 measurements were made covering the ranges 30–70 wt % $Mg(NO_3)_2$ and 0–40 wt % HNO_3 at temperatures of 50–145 °C. A mathematical model for the observed density relationships has been developed.

Introduction

This study was undertaken to provide density data for $Mg(NO_3)_2$–HNO_3–H_2O solutions for the conversion of mass to volumetric flow rates for process simulation and design purposes. This activity is part of an effort to develope and demonstrate a simple process for the extractive distillation of nitric acid (*1*, *2*). The specific objectives of the study were to obtain density data for solutions containing 30–70 wt % $Mg(NO_3)_2$ and 0–15 wt % HNO_3 over the temperature range 50–145 °C. A mathematical model of the density data as a function of the weight percent of $Mg(NO_3)_2$ and HNO_3 and temperature was developed and is presented in this publication.

Experimental Section

The experimental procedure is described more completely elsewhere (*3*).

Reagents. Reagent-grade chemicals and demineralized water were used in the preparation of samples and in subsequent analyses. The magnesium nitrate used in these studies was Mallinckrodt $Mg(NO_3)_2 \cdot 6H_2O$ flake. For some tests with high $Mg(NO_3)_2$ concentrations, the original hexahydrate was dehydrated to $Mg(NO_3)_2 \cdot (2.1{-}2.2)H_2O$.

Density Measurements. The dilatometers used in this study were designed to contain ~35 mL and were fabricated of Pyrex glass for the study. Calibration was performed by observing and recording the level of the meniscus of water in the graduated regions when equilibrated at 30, 50, 70, and 90 °C.

Density Measurements. Reagents were weighed directly into 500-mL beakers for the preparation of solutions with magnesium nitrate concentrations of ≤55 wt %. Accurate

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