988 J. Chem. Eng. Data 2006, 51, 988−991

Liquid−Liquid Equilibria for Ternary Mixtures (an Ionic Liquid + Benzene + Heptane or Hexadecane) at $T = 298.2$ K and Atmospheric Pressure

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The liquid−liquid equilibria data for the ionic liquids 1-ethyl-3-methylimidazolium octyl sulfate and 1-methyl-3-octylimidazolium diethylenglycol monomethyl ether sulfate was investigated at $T = 298.2$ K and atmospheric pressure to determine their potential as solvents for extracting an aromatic compound from alkanes. The cloud point method was used to determine the binodal curve data. The effects of the increase in chain length of the alkane for the ternary mixtures [an ionic liquid + an aromatic compound + an alkane] are discussed. The liquid−liquid equilibria data obtained were also used to calculate the selectivity values.

Introduction

Liquid−liquid equilibria (LLE) data can provide important technical information in developing processes for separation or extraction of desired products (extract) from mixtures of hydrocarbons (e.g., the separation of aromatic and aliphatic compounds).[1,2] Aromatic and aliphatic compounds are present in refinery products and are mainly derived from naphtha cuts or from the Fischer−Tropsch process.[3] The content of gasoline should have higher aromatic compound content than aliphatic compound content to achieve a higher octane number.[4] Traditionally, volatile organic compounds (VOCs) have been used for the separation of aromatic and aliphatic compounds, and they have a harmful effect on the environment.[5] Therefore, the importance of investigating effective and environmentally benign solvents for separation processes is crucial for sustainable development.[6]

In the last 10 years a new class of compounds (ionic liquids) has been investigated for its thermochemical properties. Ionic liquids (ILs) may be a key solvent to meet the challenges in separation processes, which are process efficiency improvement and minimization of emission of organic solvent.[6,7] ILs are organic salts; ILs have negligible vapor pressure; and some are liquids at room temperature.[6] Some ionic liquids are highly soluble in water, which makes them easily recoverable and reusable.[7] Recovery is an important economic factor in solvent extraction processes.[6]

In previous work by Letcher and Deenadayalu,[7] LLE data was presented for the IL 1-methyl-3-octylimidazolium chloride (MeOctImCl) as the solvent in the extraction of benzene from alkanes (heptane, dodecane, and hexadecane). Selvan et al.[8] have also determined the LLE data for two different ternary systems (ionic liquid + toluene + heptane), where the ILs were 1-ethyl-3-methylimidazolium triiodide (EtMeImI$_3$) at 308 K and 1-butyl-3-methylimidazolium triiodide (BuMeImI$_3$) at 318 K.

In this work, binodal curve data and tie-line data for the ternary mixture (ionic liquid + aromatic compound + alkane) were determined at $T = 298.2$ K. The ILs used in this work are 1-ethyl-3-methylimidazolium octyl sulfate [EMIM][OcSO$_4$] or 1-methyl-3-octylimidazolium diethylenegycol monomethyl ether sulfate [MOcIM][MDEGSO$_4$]. The structures of the ILs are given in Figure 1.[9] The aromatic compound is benzene, and the alkanes are heptane or hexadecane. From the experimental data, selectivity values were calculated to determine the feasibility of the ionic liquids for solvent extraction processes.

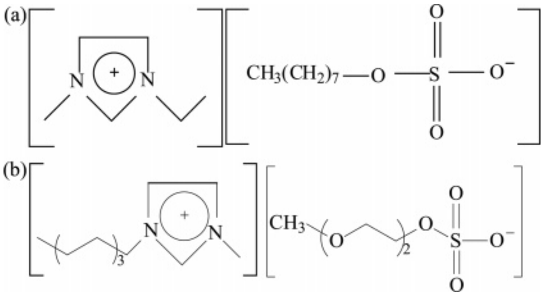

Figure 1. (a) 1-Ethyl-3-methylimidazolium octyl sulfate ($C_{14}H_{28}N_2O_4S$). (b) 1-Methyl-3-octylimidazoliumdiethylenegycolmonomethyl ether sulfate ($C_{17}H_{34}N_2O_6S$).

Table 1. Suppliers, Purity, and Refractive Index n_D of the Pure Components at $T = 298.2$ K

			n_D	
components	suppliers	% purity	literature	experimental
[EMIM][OcSO$_4$]	Solvent Innovation	≥98		1.4710
[MOcIM][MDEGSO$_4$]	Solvent Innovation	≥98		1.4660
heptane	BDH Lab Supplies	≥99	1.3851[a]	1.3850
hexadecane	Sigma-Aldrich	≥99	1.4325[a]	1.4318
benzene	Merck	≥99.7	1.4980[b]	1.4972

[a] Ref 12. [b] Ref 13.

Experimental Section

Materials. The suppliers, purity, and refractive index of each substance used are given in Table 1. The IL was subjected to a low-pressure vacuum to remove traces of any volatile components including water. The ILs were stored in a desiccator to prevent any absorption of moisture.

Procedures. Two separate techniques were used to obtain the LLE data. First, the binodal curves were determined by titrating binary mixtures of known composition with the third component at $T = 298.2$ K. The end point was observed by the disappearance of turbidity in the sample.[7,8] This technique is

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10.1021/je050494l CCC: $33.50

Table 2. Composition of Points on the Binodal Curve at $T = 298.2$ K for Ternary Mixtures [Ionic Liquid (x_1) + Benzene (x_2) + Alkane ($1 - x_1 - x_2$)]

[EMIM][OcSO$_4$]				[MOIM][MDEGSO$_4$]			
heptane		hexadecane		heptane		hexadecane	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.0001	0.5103	0.0004	0.5288	0.0004	0.4618	0.0002	0.3119
0.0001	0.6187	0.0005	0.7860	0.0006	0.7707	0.0002	0.4867
0.0003	0.9997	0.0009	0.4971	0.0008	0.8011	0.0005	0.9447
0.0010	0.2310	0.0010	0.2851	0.0018	0.0000	0.0007	0.8316
0.0011	0.8127	0.0016	0.9984	0.0020	0.9980	0.0010	0.8372
0.0018	0.0000	0.0037	0.0000	0.0305	0.9695	0.0020	0.0000
0.0587	0.8852	0.1488	0.8511	0.1921	0.7902	0.0342	0.9658
0.1196	0.8804	0.1998	0.7831	0.3520	0.6120	0.0936	0.8511
0.1335	0.8106	0.3739	0.5586	0.5816	0.3590	0.1557	0.7831
0.2468	0.6757	0.5835	0.3097	0.7739	0.1212	0.3903	0.5586
0.8600	0.0000	0.7452	0.1500	0.8909	0.0000	0.6260	0.3097
		0.9944	0.0000			0.9526	0.0000

the "cloud point" method. The water bath temperature was maintained constant at $T = (298.2 \pm 0.2)$ K by means of a built-in temperature controller, and it was also monitored with a thermometer. In this work, a single sample was used to determine a single point on the binodal curve.[8,10]

Second, the liquid–liquid equilibrium tie-line data for the ternary system was determined. The calibration curves were obtained by relating the composition on the binodal curve to the refractive indices obtained at $T = 298.2$ K. Mixtures of the three components in the immiscible region were prepared with known overall composition, shaken well, left overnight, and allowed to separate into two-phase ternary mixtures.[7,11] The refractive index was obtained for each phase and was related to the calibration curve to obtain the composition of each phase. Each tie-line was checked to ensure that it passed through the composition of the overall mixture.[7,8] The precision of the technique for determination of the binodal curve points was better than 0.005 mole fraction and that for the composition of the tie-lines was better than 0.006 mole fraction.

Results

The solubility curve and tie-line data for the ternary mixtures (ionic liquid + aromatic compound + alkane) are presented in Tables 2 and 3, respectively. The ternary phase diagrams are given in Figures 2 to 5. Figures 6 and 7 are plots of the distribution of benzene in the ionic liquid-rich and organic-rich phases for the ionic liquids [EMIM][OcSO$_4$] and [MOcIM]-[MDEGSO$_4$], respectively. The distribution ratio is defined as the ratio of the mole fraction of the aromatic compound in the ionic liquid-rich phase to the mole fraction of the aromatic compound in the alkane-rich phase.

The selectivity values calculated from the tie-line data for this work is given in Table 4. Selectivity values calculated from literature (refs 7 and 8) are also given in Table 4. The selectivity values (S) were calculated from eq 1:

$$S = (x_2''/x_3'')/(x_2'/x_3') \tag{1}$$

where x_i'' denotes the composition of component $i = 1$, 2, and 3 in the ionic liquid-rich phase; x_i' is the composition of

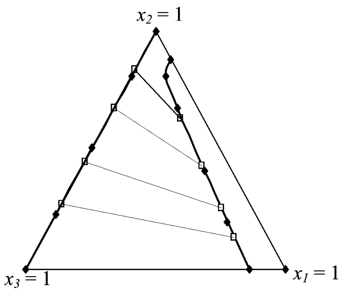

Figure 2. Binodal curve and tie-line data for the ternary mixtures {[EMIM]-[OcSO$_4$] (x_1) + benzene (x_2) + heptane (x_3)} at $T = 298.2$ K: ◆, binodal curve data; ◇, tie-line data.

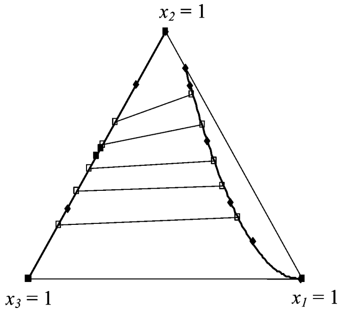

Figure 3. Binodal curve and tie-line data for the ternary mixtures {[EMIM]-[OcSO$_4$] (x_1) + benzene (x_2) + hexadecane (x_3)} at $T = 298.2$ K: ◆, binodal curve data; ◇, tie-line data.

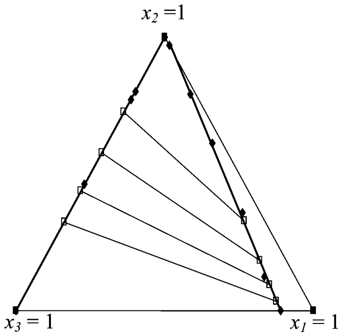

Figure 4. Binodal curve and tie-line data for the ternary mixtures {[MOcIM][MDEGSO$_4$] (x_1) + benzene (x_2) + heptane (x_3)} at $T = 298.2$ K: ◆, binodal curve data; ◇, tie-line data.

Table 3. Composition of the Conjugate Solutions, x_2', x_3' and x_2'', x_3'' at $T = 298.2$ K for Ternary Mixtures [An Ionic Liquid (x_1) + Benzene (x_2) + an Alkane (x_3)]

	[EMIM][OcSO$_4$]					[MOIM][MDEGSO$_4$]				
	alkane-rich phase		ionic liquid-rich phase			alkane-rich phase		ionic liquid-rich phase		
aromatic compound	x_2'	x_3'	x_2''	x_3''	selectivity (S)	x_2'	x_3'	x_2''	x_3''	selectivity (S)
					Heptane					
benzene	0.8410	0.1585	0.6321	0.0898	1.3	0.3250	0.6750	0.0330	0.1093	0.6
	0.6766	0.3227	0.4368	0.1026	2.0	0.4374	0.5626	0.0915	0.1012	1.2
	0.4531	0.5460	0.2577	0.1191	2.6	0.5785	0.4214	0.1854	0.0883	1.5
	0.2737	0.7252	0.1344	0.1316	2.7	0.7241	0.2758	0.3256	0.0690	1.8
					Hexadecane					
benzene	0.3525	0.6458	0.3886	0.0972	7.3	0.7029	0.2946	0.5798	0.0421	5.8
	0.4439	0.5545	0.4778	0.0811	7.4	0.5521	0.4460	0.4371	0.0505	7.0
	0.2160	0.7820	0.2458	0.1119	8.0	0.3929	0.6057	0.3194	0.0543	9.0
	0.5416	0.4571	0.6125	0.0565	9.1	0.2187	0.7807	0.1906	0.0547	12.4
	0.6326	0.3663	0.7588	0.0231	19.0					

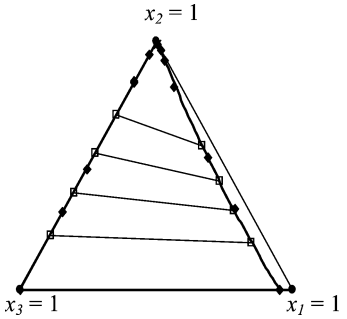

Figure 5. Binodal curve and tie-line data for the ternary mixtures {[MOcIM][MDEGSO$_4$] (x_1) + benzene (x_2) + hexadecane (x_3)} at T = 298.2 K: ◆, binodal curve data; ◇, tie-line data.

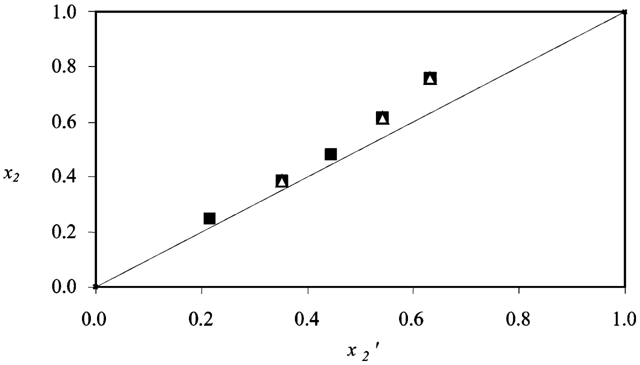

Figure 6. Distribution of the aromatic compound in the ionic liquid-rich and organic-rich phase, where the ionic liquid is [EMIM][OcSO$_4$]: ■, benzene distribution in {[EMIM][OcSO$_4$] + heptane}; △, benzene distribution in {[EMIM][OcSO$_4$] + hexadecane}.

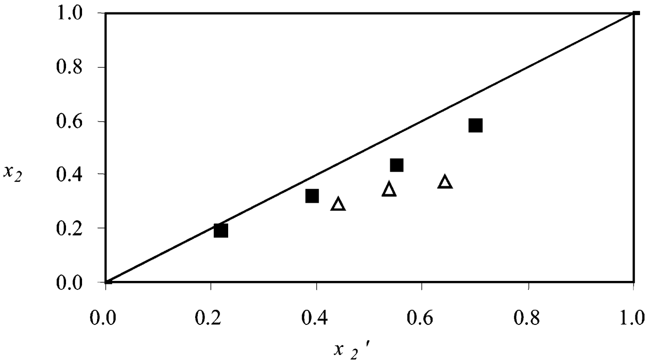

Figure 7. Distribution of the aromatic compound in the ionic liquid-rich and organic-rich phase, where the ionic liquid is [MOcIM][MDEGSO$_4$]: ■, benzene distribution in {[MOcIM][MDEGSO$_4$] + heptane}; △, benzene distribution in {[MOcIM][MDEGSO$_4$] + hexadecane}.

Table 4. Selectivity Values of Ionic Liquids from the Literature and This Work

	selectivity		
solute	[EMIM][OcSO$_4$]^a	[MOIM][MDEGSO$_4$^{a}	MeOctImCl^b
	Benzene		
heptane	1.3−2.7	0.6−1.8	0.9−6.0
dodecane			11.6−35.1
hexadecane	7.3−19.0	5.8−12.4	5.3−43.2

[a] This work. [b] Ref 7.

component i in the alkane-rich phase when $i = 2$, the solute is an aromatic compound and when $i = 3$, it is an alkane.

Discussion

[EMIM][OcSO$_4$]. The binodal curves (Figures 2 and 3) indicate that benzene is partially soluble in [EMIM][OcSO$_4$]. The solubility limit of benzene in [EMIM][OcSO$_4$] is 0.8804, and the solubility of [EMIM][OcSO$_4$] in benzene is 0.0003 mole fraction (Table 2). The amount of alkane that is soluble in [EMIM][OcSO$_4$] is 0.1400 and 0.0056, and the amount of [EMIM][OcSO$_4$] soluble in the alkane is 0.0018 and 0.0037 for heptane and hexadecane, respectively (Table 2). The alkane and aromatic compounds are completely soluble in all proportions.[7] The solubility of alkanes in [EMIM][OcSO$_4$] decreases in the order of heptane > hexadecane. The selectivity values range from 1 to 19 for the ternary system {[EMIM][OcSO$_4$] + benzene + an alkane} (Table 4). It can be seen in Figure 6 that a better separation can be obtained for benzene from hydrocarbons (alkanes) for the IL [EMIM][OcSO$_4$] since the benzene distribution ratio for the ternary system {[EMIM][OcSO$_4$] + benzene + heptane} lies mostly in the ionic liquid-rich phase.

[MOcIM][MDEGSO$_4$]. The binodal curves (Figures 4 and 5) show that benzene is partially soluble in the [MOcIM][MDEGSO$_4$]. The solubility limit for benzene in [MOcIM][MDEGSO$_4$] is 0.9695, and for [MOcIM][MDEGSO$_4$] in benzene it is 0.0305 mole fraction (Table 2). The amount of alkane that is soluble in [MOcIM][MDEGSO$_4$] is 0.1091 and 0.0474, and the amount of [MOcIM][MDEGSO$_4$] soluble in alkane is 0.0018 and 0.0020 for heptane and hexadecane, respectively (Table 2).

The selectivity values ranges from 0.6 to12.4 (Table 4), which implies that the separation of aromatic compounds from aliphatic compounds is possible. It is also observed in Figure 7 that benzene is distributed mainly in the alkane-rich phase. Increasing the number of stages and recycling the raffinate back to the extraction unit can enhance the separation of aromatic compounds from aliphatic compounds.[4]

These results are similar to the findings of Letcher and Deenadayalu[7] in that the selectivity increases in the order of heptane < hexadecane (Table 4). Heptane has the lowest selectivity value. This could be because heptane is more soluble in the ionic liquid than hexadecane. Work by Selvan et al.[8] had higher selectivity values (Table 4), this is possibly due to the iodide anion. The selectivity values in this work are greater than 1, which implies that the separation of an aromatic compound from an alkane is possible at $T = 298.2$ K.

Conclusion

The focus of this work was to obtain LLE data and to determine the selectivity values for the ILs 1-ethyl-3-methylimidazolium octyl sulfate or 1-methyl-3-octylimidazolium diethylenglycol monomethyl ether sulfate for the ternary system (ionic liquid + aromatic compound + alkane). The selectivity values obtained range from 1 to 19 and from 0.6 to 24 for [EMIM][OcSO$_4$] and[MOcIM][MDEGSO$_4$], respectively. This implies that the ILs [EMIM][OcSO$_4$] and [MOcIM][MDEGSO$_4$] are potential solvents for the separation of aromatic compounds from alkanes. Since these ILs [EMIM][OcSO$_4$] and [MOcIM][MDEGSO$_4$] are highly soluble in water, this will enhance their recoverability from the extract for re-use.

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Received for review November 24, 2005. Accepted February 20, 2006. K.C.N. thanks the National Research Foundation for their financial assistance.

JE050494L