

Ternary Liquid–Liquid Equilibria for Mixtures of an Alkane + an Aromatic Compound + 1,3-Dimethyl-2-imidazolidinone at 298.2 K and 1 atm

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The binodal curves and liquid–liquid equilibrium data are presented for mixtures of (an alkane + an aromatic compound + 1,3-dimethyl-2-imidazolidinone) at 298.2 K. The aromatic compounds were benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, and ethylbenzene. The solubility of the aromatic compounds is higher in the alkane layer than in the 1,3-dimethyl-2-imidazolidinone (DMI) layer. The effectiveness of extracting an aromatic compound from mixtures containing an alkane using the solvent DMI is discussed in terms of the ratio of solubilities in the two phases. The results have been fitted to the Hlavatý equation, the β -density function, and the logarithmic γ function. The binodal curves obtained from these equations have been compared with the experimental binodal curves. The NRTL and UNIQUAC equations were used to correlate the experimental tie lines. There are no data in the literature for the mixtures discussed in this paper.

Introduction

This work is part of our investigation into finding suitable solvents for separating aromatic compounds from aliphatic compounds using solvent extraction. In the petroleum industry aromatic compounds are derived mainly from naphtha cuts. The nonaromatic portion of the reformed naphtha has the same boiling point as that of the aromatic compounds, and separation by distillation is difficult as most of these compounds form azeotropes. Liquid–liquid extraction has become commercially viable, as it permits the extraction of the light aromatics from a wide boiling range (Rawat et al., 1972) and does not involve an expensive heating process.

In a previous study by Letcher and Naicker (1998) liquid–liquid equilibrium measurements were made on the mixtures (an alkane + an aromatic compound + *N*-methyl-2-pyrrolidone), where the aromatic compound refers to toluene, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, and ethylbenzene. In this previous work it was shown that *N*-methyl-2-pyrrolidone (NMP) makes a suitable solvent for extracting aromatic compounds from aliphatic mixtures, and NMP is indeed the basis of a commercial process, namely the Arosolvan process (Muller and Hoehfeld, 1967) for this extraction. The results showed that the efficacy of the process decreases with decreasing alkane chain length.

We believe that it is the *N*'-alkylated amide group that is responsible for much of the solvent extraction property. In this work a solvent similar to NMP but containing an extra *N*-methyl group also adjacent to the carbonyl group is used (see structures a and b). The additional methyl group increases the basic character of the carbonyl functionality because the methyl group is electron donating.

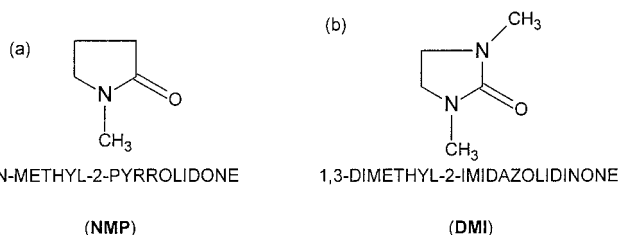
The purpose of this work was to compare the liquid–liquid equilibrium results of the 1,3-dimethyl-2-imidazolidinone

Table 1. Physical Properties of the Pure Components at 298.2 K: Refractive Indices n_D , Molar Volumes V_m , and Surface and Volume Parameters, Q and R

compound	n_D		V_m	Q	R
	lit. ^a	exp	cm ³ ·mol ⁻¹		
DMI	1.4707 ^b	1.4701	108.52	1.904	2.6908
hexadecane	1.4325	1.4322	294.07	9.256	11.2432
tetradecane	1.4269	1.4269	261.04	8.176	9.8945
octane	1.3950	1.3959	163.51	4.936	5.8484
benzene	1.4979	1.4985	89.41	2.400	3.1879
ethylbenzene	1.4932	1.4942	123.08	3.508	4.5972
toluene	1.4941	1.4939	106.86	3.816	3.9229
mesitylene	1.4964	1.4979	139.58	4.104	5.3929
<i>o</i> -xylene	1.5029	1.5030	121.20	3.536	3.3395
<i>m</i> -xylene	1.4946	1.4953	123.43	3.536	3.3395
<i>p</i> -xylene	1.4932	1.4930	123.93	3.536	3.3395

^a Riddick et al. (1986). ^b Rosenfarb et al. (1976).

with those of the published NMP mixtures in an attempt to further understand the extraction process involved.



In this study the liquid–liquid equilibrium data for the mixtures (an alkane + an aromatic compound + 1,3-dimethyl-2-imidazolidinone) were determined at 298.2 K. The results are discussed in terms of the selectivity parameter (S), which was defined in a previous paper (Letcher and Deenadayalu, 1999). The Hlavatý equation (Hlavatý, 1972), the β -density function, and the logarithmic

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Table 2. Composition of Points on the Coexistence Curve at 298.2 K for Mixtures Hexadecane (1) + an Aromatic Compound (2) + DMI (3)

benzene		toluene		<i>o</i> -xylene		<i>p</i> -xylene		<i>m</i> -xylene		mesitylene		ethylbenzene	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.012	0.000	0.012	0.000	0.012	0.000	0.012	0.000	0.012	0.000	0.012	0.000	0.012	0.000
0.032	0.328	0.034	0.262	0.013	0.019	0.024	0.168	0.013	0.009	0.013	0.003	0.024	0.176
0.034	0.353	0.038	0.263	0.024	0.166	0.031	0.201	0.024	0.147	0.041	0.212	0.030	0.211
0.048	0.422	0.051	0.320	0.039	0.248	0.041	0.247	0.026	0.156	0.060	0.265	0.039	0.262
0.058	0.435	0.088	0.404	0.055	0.293	0.061	0.297	0.040	0.235	0.083	0.307	0.052	0.290
0.083	0.481	0.144	0.431	0.072	0.332	0.072	0.326	0.058	0.288	0.401	0.338	0.066	0.319
0.136	0.506	0.191	0.451	0.100	0.368	0.092	0.354	0.079	0.334	0.135	0.363	0.087	0.355
0.171	0.517	0.245	0.450	0.154	0.405	0.132	0.389	0.080	0.333	0.184	0.398	0.121	0.379
0.185	0.556	0.308	0.453	0.207	0.423	0.161	0.399	0.105	0.358	0.223	0.416	0.162	0.403
0.238	0.514	0.441	0.427	0.530	0.439	0.210	0.414	0.167	0.393	0.258	0.424	0.201	0.407
0.290	0.510	0.481	0.408	0.320	0.443	0.260	0.430	0.216	0.422	0.316	0.456	0.260	0.421
0.329	0.517	0.493	0.407	0.445	0.431	0.285	0.433	0.278	0.428	0.399	0.432	0.293	0.423
0.435	0.449	0.528	0.374	0.535	0.360	0.323	0.439	0.355	0.433	0.456	0.414	0.326	0.425
0.482	0.428	0.648	0.291	0.555	0.340	0.356	0.442	0.396	0.438	0.524	0.378	0.379	0.427
0.555	0.383	0.731	0.223	0.607	0.352	0.399	0.427	0.419	0.430	0.552	0.391	0.433	0.412
0.663	0.298	0.796	0.161	0.610	0.325	0.456	0.416	0.449	0.426	0.602	0.321	0.518	0.359
0.785	0.184	0.955	0.018	0.612	0.327	0.555	0.366	0.468	0.412	0.605	0.344	0.527	0.369
0.973	0.001	0.973	0.001	0.646	0.332	0.650	0.312	0.565	0.355	0.733	0.224	0.609	0.308
				0.702	0.256	0.829	0.139	0.575	0.320	0.751	0.214	0.742	0.208
				0.967	0.002	0.973	0.001	0.619	0.295	0.973	0.001	0.874	0.100
				0.973	0.001			0.662	0.292			0.973	0.001
								0.668	0.292				
								0.670	0.269				
								0.973	0.001				

Table 3. Composition of Points on the Coexistence Curve at 298.2 K for Mixtures Tetradecane (1) or Octane (1) + an Aromatic Compound (2) + DMI (3)

benzene		toluene		mesitylene		ethylbenzene	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
Tetradecane							
0.020	0.000	0.020	0.000	0.020	0.000	0.020	0.000
0.043	0.280	0.023	0.086	0.050	0.177	0.025	0.093
0.056	0.354	0.042	0.209	0.069	0.224	0.037	0.155
0.075	0.422	0.064	0.286	0.096	0.266	0.051	0.203
0.110	0.442	0.083	0.331	0.139	0.305	0.137	0.334
0.140	0.479	0.100	0.352	0.179	0.339	0.174	0.355
0.191	0.459	0.143	0.391	0.256	0.365	0.212	0.368
0.217	0.517	0.170	0.400	0.292	0.377	0.250	0.376
0.266	0.464	0.207	0.407	0.361	0.398	0.287	0.382
0.281	0.527	0.227	0.410	0.422	0.402	0.362	0.387
0.410	0.504	0.266	0.418	0.493	0.407	0.395	0.393
0.551	0.368	0.312	0.432	0.599	0.361	0.442	0.378
0.562	0.418	0.352	0.425	0.785	0.181	0.461	0.401
0.642	0.326	0.429	0.418	0.889	0.099	0.556	0.329
0.685	0.219	0.505	0.413	0.986	0.000	0.602	0.356
0.768	0.154	0.607	0.338			0.727	0.264
0.986	0.000	0.699	0.272			0.767	0.208
		0.828	0.141			0.986	0.000
		0.986	0.000				
Octane							
0.095	0.000	0.095	0.000	0.095	0.000	0.095	0.000
0.110	0.100	0.111	0.061	0.108	0.040	0.122	0.081
0.137	0.155	0.129	0.107	0.131	0.081	0.155	0.127
0.204	0.236	0.163	0.145	0.165	0.117	0.200	0.162
0.222	0.249	0.189	0.171	0.194	0.146	0.230	0.179
0.313	0.268	0.241	0.211	0.219	0.160	0.298	0.198
0.368	0.274	0.264	0.222	0.240	0.170	0.338	0.210
0.404	0.271	0.314	0.231	0.272	0.182	0.373	0.210
0.463	0.270	0.362	0.237	0.298	0.190	0.402	0.213
0.494	0.263	0.394	0.233	0.341	0.209	0.436	0.214
0.524	0.258	0.452	0.236	0.405	0.212	0.494	0.221
0.561	0.251	0.528	0.240	0.457	0.222	0.562	0.218
0.742	0.202	0.582	0.230	0.501	0.226	0.589	0.225
0.772	0.166	0.645	0.212	0.539	0.232	0.637	0.206
0.865	0.093	0.733	0.165	0.590	0.223	0.676	0.199
0.875	0.095	0.759	0.183	0.645	0.213	0.700	0.207
0.983	0.000	0.842	0.113	0.697	0.206	0.774	0.168
		0.871	0.099	0.740	0.194	0.919	0.054
		0.893	0.066	0.785	0.160	0.971	0.010
		0.983	0.000	0.854	0.112	0.983	0.000
				0.925	0.058		
				0.983	0.000		

γ function (Letcher et al., 1990) were used to correlate the binodal curves. The NRTL (Renon and Prausnitz, 1968)

and UNIQUAC (Abrams and Prausnitz, 1975) equations were used to correlate the experimental tie lines.

Experimental Section

Chemicals. The aromatic compounds were found to have purities greater than 99 mol %, as determined by gas-liquid chromatography, and were stored under 4 Å molecular sieves. The chemical DMI was obtained from Acros and had a purity greater than 98 mol %. DMI was not purified further, since it is an expensive solvent and we found a substantial loss of solvent took place through distillation for a meager increase in purity. The alkanes were supplied by Acros and had a purity greater than 99 mol % and were also used without further treatment.

Procedure. The binodal curves were determined at 298.2 K and 1 atm pressure using the cloud point method described by Letcher and Siswana (1992). The precision of the technique was better than 0.004 mole fraction. Tie lines were determined using the refractive index method described by Briggs and Comings (1943). Plait points were determined following the method of Treybal (1946). The precision of the technique in determining the composition of the tie lines was better than 0.01 mole fraction.

Refractive indices, molar volumes, and volume and surface parameters of pure compounds at 298.2 K are given in Table 1.

Results

The compositions of the mixtures (mole fractions) on the binodal curve at 298.2 K are given in Tables 2 and 3. The compositions of the conjugate phases are given in Tables 4 and 5. The compositions of the plait points were determined following the method of Treybal et al. (1946) and are given in Table 6. The binodal curves and tie line results have been plotted in Figure 1. Three equations have been fitted to these data following the work of Hlavaty.

The coefficients A_i relate to a modified Hlavaty equation:

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B \quad (1)$$

The coefficients B_i relate to a β function equation:

$$x_2 = B_1 (1 - x_A)^{B_2} x_3^{B_3} \quad (2)$$

Table 4. Compositions of the Conjugate Solutions, x_1' , x_2' and x_1'' , x_2'' at 298.2 K for the System Hexadecane (1) + an Aromatic Compound (2) + DMI (3)

DMI-rich phase		hexadecane-rich phase	
x_1'	x_2'	x_1''	x_2''
Benzene			
0.053	0.411	0.236	0.527
0.035	0.353	0.314	0.508
0.023	0.288	0.405	0.470
0.018	0.238	0.491	0.420
0.014	0.173	0.603	0.343
0.013	0.124	0.702	0.264
0.013	0.046	0.875	0.104
Toluene			
0.018	0.156	0.118	0.417
0.014	0.079	0.247	0.468
0.014	0.072	0.423	0.429
0.014	0.062	0.549	0.361
0.014	0.048	0.611	0.320
0.014	0.036	0.756	0.205
0.015	0.000	0.882	0.089
<i>o</i> -Xylene			
0.032	0.226	0.422	0.430
0.021	0.181	0.501	0.394
0.015	0.121	0.640	0.302
0.014	0.108	0.675	0.274
0.013	0.086	0.728	0.230
0.013	0.066	0.774	0.189
0.013	0.026	0.864	0.105
<i>m</i> -Xylene			
0.036	0.226	0.401	0.429
0.026	0.183	0.504	0.390
0.021	0.156	0.537	0.373
0.071	0.110	0.625	0.317
0.014	0.091	0.667	0.286
0.037	0.049	0.824	0.151
0.013	0.019	0.918	0.058
<i>p</i> -Xylene			
0.013	0.046	0.177	0.408
0.014	0.030	0.333	0.440
0.014	0.023	0.459	0.412
0.014	0.015	0.514	0.388
0.015	0.011	0.796	0.181
0.015	0.009	0.918	0.058
Mesitylene			
0.051	0.245	0.345	0.442
0.039	0.213	0.414	0.428
0.034	0.197	0.446	0.416
0.018	0.125	0.632	0.306
0.014	0.087	0.745	0.215
0.012	0.051	0.870	0.101
Ethylbenzene			
0.017	0.158	0.260	0.429
0.014	0.125	0.376	0.419
0.012	0.100	0.432	0.402
0.012	0.089	0.522	0.361
0.012	0.059	0.673	0.265
0.013	0.027	0.814	0.150
0.014	0.013	0.890	0.082

and the coefficients C_i relate to a log γ equation:

$$x_2 = C_1(-\ln x_A)^{C_2} x_A^{C_3} \quad (3)$$

where

$$x_A = (x_1 + 0.5x_2 - x_1^0)/(x_{11}^0 - x_1^0) \quad (4)$$

$$x_B = (x_{11}^0 - x_1 - 0.5x_2)/(x_{11}^0 - x_1^0) \quad (5)$$

and x_1 refers to the mole fraction of an alkane, x_2 refers to the mole fraction of an aromatic compound, and x_{11}^0 and x_1^0 are the values of x_1 on the binodal curve which cuts the $x_2 = 0$ axis.

Table 5. Compositions of the Conjugate Solutions, x_1' , x_2' and x_1'' , x_2'' at 298.2 K for the System an Alkane (1) + an Aromatic Compound (2) + DMI (3)

DMI-rich phase		tetradecane-rich phase		DMI-rich phase		octane-rich phase	
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
Benzene							
0.093	0.427	0.334	0.522	0.124	0.149	0.367	0.274
0.071	0.381	0.397	0.500	0.112	0.115	0.501	0.266
0.037	0.257	0.189	0.391	0.106	0.091	0.596	0.246
0.027	0.182	0.689	0.303	0.103	0.072	0.660	0.224
0.024	0.148	0.741	0.256	0.100	0.047	0.763	0.173
0.021	0.042	0.916	0.082	0.098	0.023	0.886	0.086
0.021	0.013	0.973	0.021				
Toluene							
0.021	0.077	0.287	0.434	0.141	0.123	0.578	0.229
0.022	0.054	0.389	0.431	0.124	0.091	0.699	0.198
0.022	0.030	0.546	0.371	0.111	0.061	0.774	0.162
0.023	0.017	0.616	0.329	0.104	0.038	0.867	0.099
0.024	0.014	0.693	0.272	0.102	0.010	0.947	0.030
0.024	0.010	0.786	0.195				
0.024	0.008	0.862	0.125				
Mesitylene							
0.071	0.217	0.525	0.376	0.203	0.151	0.539	0.227
0.054	0.179	0.587	0.348	0.157	0.116	0.675	0.212
0.043	0.154	0.653	0.308	0.141	0.097	0.733	0.190
0.023	0.124	0.690	0.282	0.122	0.069	0.812	0.146
0.021	0.093	0.775	0.214	0.103	0.027	0.924	0.057
0.019	0.026	0.920	0.072				
Ethylbenzene							
0.066	0.254	0.435	0.387	0.178	0.151	0.656	0.210
0.053	0.226	0.689	0.373	0.141	0.115	0.725	0.187
0.035	0.170	0.650	0.307	0.124	0.090	0.802	0.147
0.029	0.138	0.728	0.254	0.115	0.069	0.844	0.118
0.025	0.108	0.778	0.208	0.106	0.044	0.903	0.072
0.022	0.076	0.864	0.135	0.100	0.021	0.961	0.020

Table 6. Compositions of Plait Points for the Mixtures (an Alkane + an Aromatic Compound + DMI) at 298.2 K and 1 atm Pressure Where x_1 and x_2 Are the Mole Fractions of an Alkane and an Aromatic Compound, Respectively

aromatic compound	x_1	x_2
Hexadecane		
benzene	0.171	0.514
toluene	0.051	0.316
<i>o</i> -xylene	0.167	0.405
<i>m</i> -xylene	0.165	0.395
<i>p</i> -xylene	0.028	0.188
mesitylene	0.113	0.339
ethylbenzene	0.097	0.352
Tetradecane		
benzene	0.130	0.459
toluene	0.100	0.354
mesitylene	0.239	0.361
ethylbenzene	0.166	0.351
Octane		
benzene	0.250	0.253
toluene	0.361	0.231
mesitylene	0.347	0.202
ethylbenzene	0.360	0.216

These equations have been used to correlate the binodal curve. The coefficients A_i , B_i , and C_i are given in Tables 7 and 8 together with the standard deviation, σ , which is defined as

$$\sigma = \left[\sum \{x_2(\text{calc}) - x_2(\text{exp})\}^2 / (n - 3) \right]^{1/2} \quad (6)$$

where n is the number of data points and 3 is the number of coefficients.

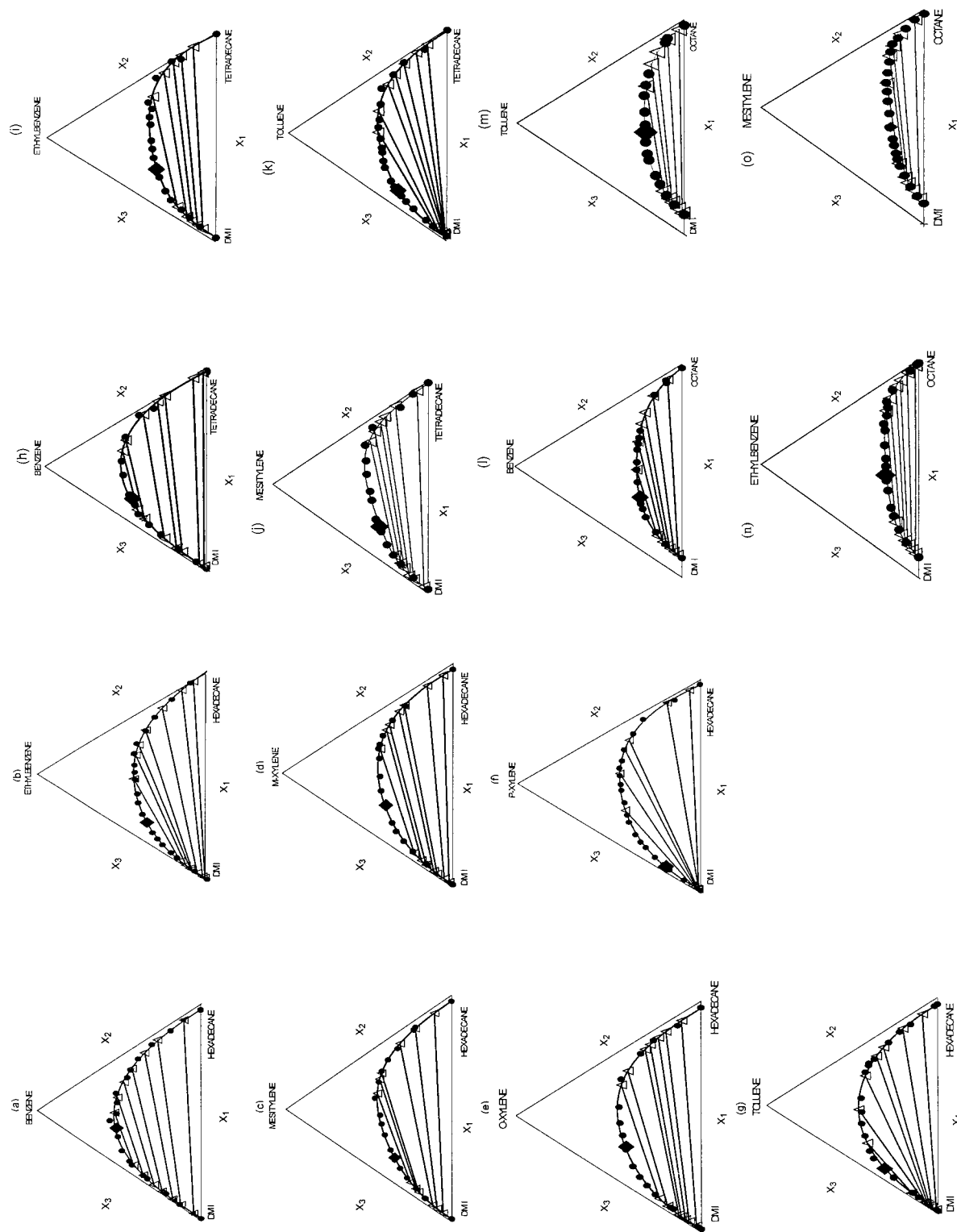


Figure 1. Binodal curves and tie lines for an alkane (1) + an aromatic compound (2) + DMI (3) at 298.2 K: (a–g) hexadecane; (h–k) tetradecane; (l–o) octane. (a) benzene; (b) ethylbenzene; (c) mesitylene; (d) m-xylene; (e) o-xylene; (f) p-xylene; (g) toluene; (h) benzene; (i) ethylbenzene; (j) mesitylene; (k) toluene; (l) benzene; (m) toluene; (n) ethylbenzene; (o) mesitylene. x_1 , x_2 , and x_3 are mole fractions.

Table 7. Coefficients $A_1, A_2, A_3, B_1, B_2, B_3$ and C_1, C_2, C_3 in Eqs 1, 2, and 3 Together with the Standard Errors and the Standard Deviation σ , Using the Experimental and Calculated x_2 Values at 298.2 K for Mixtures Hexadecane (1) + an Aromatic Compound (2) + DMI (3)

solute	A_1	A_2	A_3	σ	B_1	B_2	B_3	σ	C_1	C_2	C_3	σ
benzene	-0.165	-0.051	1.806	0.013	1.994	0.978	0.943	0.013	1.857	0.946	1.317	0.015
toluene	-0.132	-0.119	1.529	0.011	1.743	0.949	0.945	0.011	1.616	0.915	1.300	0.011
<i>o</i> -xylene	-0.338	-0.572	0.514	0.015	1.386	0.780	0.858	0.015	1.286	0.745	1.138	0.014
<i>m</i> -xylene	-0.159	-0.340	1.084	0.013	1.533	0.863	0.926	0.013	1.406	0.821	1.232	0.013
<i>p</i> -xylene	-0.273	-0.506	0.687	0.010	1.426	0.806	0.883	0.010	1.328	0.774	1.177	0.009
mesitylene	-0.075	-0.438	1.055	0.013	1.552	0.842	0.969	0.013	1.451	0.811	1.284	0.015
ethylbenzene	-0.287	-0.292	0.930	0.010	1.454	0.872	0.874	0.010	1.345	0.837	1.192	0.009

Table 8. Coefficients $A_1, A_2, A_3, B_1, B_2, B_3$ and C_1, C_2, C_3 in Eqs 1, 2, and 3 Together with the Standard Errors and the Standard Deviation σ , Using the Experimental and Calculated x_2 Values at 298.2 K for Mixtures an Alkane (1) + an Aromatic Compound (2) + DMI (3)

solute	A_1	A_2	A_3	σ	B_1	B_2	B_3	σ	C_1	C_2	C_3	σ
Tetradecane												
benzene	0.232	0.356	2.866	0.041	2.406	1.133	1.098	0.040	2.122	1.071	1.490	0.049
toluene	-0.250	-0.426	0.811	0.017	1.445	0.832	0.892	0.016	1.333	0.795	1.189	0.014
mesitylene	-0.145	-0.606	0.563	0.020	1.351	0.786	0.957	0.022	1.271	0.761	1.253	0.024
ethylbenzene	-0.410	-0.785	-0.083	0.014	1.097	0.671	0.806	0.014	1.026	0.641	1.042	0.013
Octane												
benzene	-0.429	-0.419	-0.070	0.009	0.769	0.738	0.733	0.009	0.721	0.712	1.003	0.008
toluene	-0.298	-0.397	0.016	0.008	0.703	0.730	0.785	0.009	0.657	0.702	1.049	0.008
mesitylene	-0.285	-0.644	-0.390	0.005	0.607	0.604	0.815	0.006	0.578	0.583	1.038	0.007
ethylbenzene	-0.400	-0.646	-0.563	0.007	0.583	0.614	0.752	0.009	0.555	0.595	0.982	0.009

Table 9. Representative Selectivity Values (S) and the Respective Tie Line Compositions at 298.2 K for the System an Alkane (1) + an Aromatic Compound (2) + DMI (3)

solute	tie line composition					
	selectivity (S)		DMI-rich phase		alkane-rich phase	
	DMI	NMP ^a	x_1'	x_2'	x_1''	x_2''
Hexadecane						
benzene	30		0.013	0.046	0.875	0.104
toluene	10	15	0.014	0.036	0.756	0.205
<i>o</i> -xylene	30	59	0.014	0.173	0.675	0.274
<i>m</i> -xylene	23	26	0.013	0.019	0.918	0.058
<i>p</i> -xylene	10	35	0.015	0.009	0.918	0.058
mesitylene	36	18	0.012	0.051	0.870	0.101
ethylbenzene	12	32	0.012	0.059	0.673	0.265
Tetradecane						
benzene	30		0.021	0.056	0.916	0.082
toluene	5		0.025	0.148	0.389	0.431
mesitylene	8		0.690	0.282	0.032	0.108
ethylbenzene	11		0.023	0.086	0.728	0.254
Octane						
benzene	3		0.102	0.067	0.763	0.173
toluene	9		0.102	0.031	0.947	0.030
mesitylene	4		0.103	0.027	0.924	0.057
ethylbenzene	10		0.100	0.021	0.961	0.020

^a Calculated from published tie line data.

Discussion

Hexadecane + an Aromatic + DMI. Previous work by Letcher and Naicker (1998) on mixtures of (an alkane + an aromatic compound + NMP) indicated that the shape of the binodal curve is not strongly dependent on the type of aromatic compound. This has also been found to be the case in this work. The minimum concentration (in mole fraction) for the solubility of the aromatic compound, over the whole composition range, in the mixture (hexadecane + an aromatic + DMI) was found to be 0.556, 0.456, 0.453, 0.427, 0.443, 0.442, and 0.438 for benzene, mesitylene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene, respectively. This reflects the magnitude of the area of the two-phase region. In the mixture (hexadecane + an aromatic + NMP) (Letcher and Naicker, 1998) the minimum concentration (in mole fraction) for the solubility of the

aromatic compound, over the whole composition range, was found to be 0.396, 0.383, 0.383, 0.370, 0.367, and 0.357 for toluene, *o*-xylene, *p*-xylene, ethylbenzene, *m*-xylene, and mesitylene, respectively. The two-phase region increases in the order toluene > *o*-xylene \approx *p*-xylene > *m*-xylene \approx ethylbenzene > mesitylene. In the two sets of data the order of immiscibility is similar except for mesitylene. It is assumed that the mesitylene molecule, which has three methyl groups, interacts less favorably with the DMI molecule than with the NMP molecule, resulting in a greater region of immiscibility for the DMI system than for the NMP system. The maximum solubility of DMI in hexadecane is 0.026 mole fraction, and the maximum solubility of hexadecane in DMI is 0.012 mole fraction at 293.2 K. For the (hexadecane + NMP) binary mixture, the solubility of hexadecane in NMP was 0.020 mole fraction and the solubility of NMP in hexadecane was 0.080 mole fraction at 298.2 K. There are no phase equilibrium data in the literature on the (hexadecane + benzene + NMP) mixture.

Tetradecane or Octane + an Aromatic + DMI. The minimum concentration (in mole fraction) for the solubility of the aromatic compound in the mixture (tetradecane + DMI) over the whole composition range was found to be 0.527, 0.401, 0.432, and 0.407 for benzene, ethylbenzene, toluene, and mesitylene, and for the mixture (octane + DMI) it was found to be 0.274, 0.225, 0.240, and 0.232, respectively. The solubility of DMI in tetradecane and octane is 0.014 and 0.017 mole fraction, respectively, and the solubility of tetradecane and octane in DMI is 0.020 and 0.095 mole fraction, respectively, at 298.2 K. The area of the two-phase region increases in the order benzene > toluene > ethylbenzene \approx mesitylene for both the tetradecane and octane mixtures.

The increase in chain length of the alkane results in an increase in the two-phase area and reflects the reduction in the solubility of the nonpolar alkane in the polar DMI molecule. From the slope of the tie lines (see Figure 1), it can be seen that, in all cases, the aromatic compounds are more soluble in the alkane-rich phase than in the DMI-rich phase with a large skewing toward the DMI axis. This skewing increases with increasing carbon number of the

Table 10. Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid–Liquid Equilibria for the Mixtures [Hexadecane (1) + an Aromatic Compound (2) + DMI (3)] at 298.2 K, as Well as the rmsd Values

component		parameters (J·mol ⁻¹)			
		NRTL ^a		UNIQUAC	
<i>i</i> – <i>j</i>		<i>g</i> _{ij} – <i>g</i> _{ji}	<i>g</i> _{ji} – <i>g</i> _{ii}	Δu_{ij}	Δu_{ji}
Benzene					
(0.004) (0.012)					
1–2	2–1	–1233.97	–269.00	–73.28	6501.08
1–3	3–1	2917.42	11121.05	31.10	82.42
2–3	3–2	1710.48	1147.19	–47.04	4.98
Ethylbenzene					
(0.017) (0.007)					
1–2	2–1	–1395.00	–1601.66	–1077.93	829.82
1–3	3–1	6296.01	16309.34	1845.74	–56.00
2–3	3–2	16972.45	2732.77	–111.77	–1853.17
Toluene					
(0.009) (0.016)					
1–2	2–1	–2757.20	6802.29	5389.21	–2418.24
1–3	3–1	16892.67	12648.94	2791.77	–28.58
2–3	3–2	13858.01	5735.56	5367.14	–4353.73
Mesitylene					
(0.009) (0.014)					
1–2	2–1	–401.10	2809.60	–1026.20	407.52
1–3	3–1	7259.80	10187.06	990.72	426.40
2–3	3–2	4170.95	2036.59	–16.90	–2951.73
<i>o</i> -Xylene					
(0.006) (0.016)					
1–2	2–1	–1446.63	2587.23	5389.21	–2418.24
1–3	3–1	9407.37	14680.84	2791.77	–28.58
2–3	3–2	5903.54	825.30	5367.14	–4353.73
<i>m</i> -Xylene					
0.012) (0.0130)					
1–2	2–1	–1551.57	2373.20	–3045.99	283.77
1–3	3–1	22628.10	14787.92	–1640.08	3702.33
2–3	3–2	6238.18	344.03	381.32	–4979.29
<i>p</i> -Xylene					
0.013) (0.009)					
1–2	2–1	–2398.95	–1837.16	–5469.37	5597.21
1–3	3–1	14107.79	17254.34	1497.37	–95.40
2–3	3–2	11574.96	4362.54	–2176.04	–548.64

^a Calculated with $\alpha_{ij} = 0.35$ or 0.10 or 0.43 . The rms deviations are given in parentheses.

alkane molecule. As the alkane chain length increases, the plait point concentration changes from an alkane-rich composition to a DMI-rich composition (see Table 6). There are no binary data in the literature for (an alkane + DMI) mixtures.

The effectiveness of extracting the aromatic compound by DMI is given by its selectivity (*S*), which is the measure of the ability of DMI to separate an aromatic compound from an alkane:

$$S = (x_2/x_1)_{\text{DMI-rich phase}} / (x_2/x_1)_{\text{an alkane-rich phase}} \quad (7)$$

where the subscripts 2 and 1 represents an aromatic compound and an alkane, respectively (Letcher and Deenadayalu, 1999). This quantity is greater than unity for all the systems reported here, which means that extraction of the aromatic compound by DMI is possible. The selectivity is not constant over the whole two-phase region. Table 9 lists the maximum *S* values. The order of selectivity is mesitylene > benzene \approx *o*-xylene > *m*-xylene > ethylbenzene > toluene \approx *p*-xylene for the (hexadecane + an aromatic + DMI) mixtures. The *S* values for the mixtures (an alkane + an aromatic + NMP) were calculated from

Table 11. Values of the Parameters for the NRTL and UNIQUAC Equations, Determined from Ternary Liquid–Liquid Equilibria for the Mixtures [Tetradecane (1) + an Aromatic Compound (2) + DMI (3)] at 298.2 K, as Well as the rmsd Values

component		parameter (J·mol ⁻¹)			
		NRTL ^a		UNIQUAC	
<i>i</i> – <i>j</i>		<i>g</i> _{ij} – <i>g</i> _{ji}	<i>g</i> _{ji} – <i>g</i> _{ii}	Δu_{ij}	Δu_{ji}
Tetradecane					
Benzene					
(0.013) (0.019)					
1–2	2–1	3375.02	–4050.88	877.23	5704.44
1–3	3–1	14223.10	2482.08	1664.89	100.71
2–3	3–2	–5128.02	7889.77	248.55	507.07
Ethylbenzene					
(0.010) (0.016)					
1–2	2–1	–3009.33	6138.74	–2977.77	2510.09
1–3	3–1	6415.96	7247.63	–1640.35	3381.95
2–3	3–2	11751.51	–202.15	2334.60	–5228.48
Toluene					
(0.018) (0.016)					
1–2	2–1	–800.17	1875.12	–9207.83	673.12
1–3	3–1	2669.45	6913.89	–1676.34	6393.25
2–3	3–2	6317.01	2126.93	–306.16	8576.96
Mesitylene					
(0.005) (0.016)					
1–2	2–1	780.27	2500.82	–1162.25	427.78
1–3	3–1	10231.22	8559.54	–284.47	1714.95
2–3	3–2	4064.64	1088.12	2618.53	–4447.41
Octane					
Benzene					
(0.006) (0.040)					
1–2	2–1	–4654.68	–3156.59	–975.74	2949.55
1–3	3–1	14428.39	–1001.34	–2055.94	4948.83
2–3	3–2	–6664.75	8000.21	–564.75	–83.91
Etylbenzene					
(0.003) (0.048)					
1–2	2–1	1900.67	1584.83	436.32	4483.18
1–3	3–1	10396.03	–188.79	–2093.37	4472.62
2–3	3–2	–1378.73	6907.59	933.07	–606.40
Toluene					
(0.006) (0.043)					
1–2	2–1	–3612.91	3783.564	–3933.73	–1160.49
1–3	3–1	9044.65	426.75	–1208.05	3983.44
2–3	3–2	–548.17	3848.04	–94.68	–6962.99
Mesitylene					
(0.005) (0.058)					
1–2	2–1	3686.37	1890.77	399.56	–419.46
1–3	3–1	10296.73	–208.38	–172.00	1457.19
2–3	3–2	–1990.65	9735.31	–1654.55	–661.34

^a Calculated with $\alpha_{ij} = 0.10$ or 0.35 . The rms deviations are given in parentheses.

the published tie line data (Letcher and Naicker, 1998). For the (hexadecane + an aromatic + NMP) mixtures, higher *S* values were obtained (see Table 9) for all the other aromatics except mesitylene and *m*-xylene. Although DMI is a more polar molecule, it is less selective than NMP. This could be due in part to the greater dipole–dipole interactions between the DMI molecules. The polarity difference between the DMI molecules and the aromatic compound must be greater than the polarity difference between the NMP and the aromatic compound, making DMI less favorable for the extraction of the aromatic compound. Overall, the order of selectivity of DMI for an aromatic compound in an alkane mixture is hexadecane > tetradecane > octane; that is, the selectivity decreases as the alkane carbon number decreases.

In the aromatic series, benzene, toluene, and xylene (ortho and meta), polarity increases as the molecular weight of the aromatic member increases (Fevre, 1964) due to the greater amount of π electrons which are subject to electromeric shifts within the ring (inductive effect of the methyl groups). Rawat et al. (1972) found that the solvent power for many extractive solvents was always greater for benzene than for toluene or xylenes. This is supported here for the DMI mixtures. Other factors such as smaller molecular size and lower molecular weight also help in the association of the benzene with the solvent molecule, making benzene more effectively extracted. The polarity difference between the solvent and an aromatic compound should not be too high for effective extraction. A low polarity difference between the solvent and the aromatic compound results in attractive forces between the different molecules, and as a result the aromatic molecules are preferentially pulled toward the solvent (Rawat et al., 1972). In extreme cases two polar groups attached symmetrically to the molecule can make the molecule nonpolar and we can expect the selectivity for *p*-xylene will be low. This is indeed the case as found in this work.

The electronegativity of NMP is less than the electronegativity for DMI. This is reflected in the greater dipole-dipole interactions between the DMI molecules (Langan and Salmon, 1987; Rosenfarb et al., 1976). The methyl groups increase the electronegativity of the oxygen atom (Pauling, 1948; Uosaki et al., 1990), since the methyl groups are electron donating. This property is important in understanding the selectivity.

The fitting of the Hlavatý equation (Hlavatý, 1972), the β -density function (Letcher et al., 1990), and the logarithmic γ function (Letcher et al., 1990) to our binodal curve data showed good correlation. The nonrandom two-liquid equation (NRTL) (Renon and Prausnitz, 1968) and the universal quasichemical equation (UNIQUAC) (Abrams and Prausnitz, 1975) were used to correlate the experimental data for the 15 ternary mixtures reported here. The equations and algorithms used in the calculation of the compositions of the liquid phases follow the method used by Walas (1985). The objective function, $F(P)$, used to minimize the difference between the experimental and calculated concentrations is defined as

$$F(P) = \sum_{i=1}^n [x'_{1i} - x'_{1i}(\text{calc})(PT)]^2 + [x'_{2i} - x'_{2i}(\text{calc})(PT)]^2 + [x''_{1i} - x''_{1i}(\text{calc})]^2 + [x''_{2i} - x''_{2i}(\text{calc})(PT)]^2 \quad (8)$$

where P is the set of parameters vector, n is the number of experimental points, $x'_{1i}(\text{exp})$, $x'_{2i}(\text{exp})$ and $x'_{1i}(\text{calc})$, $x'_{2i}(\text{calc})$ are the experimental and calculated mole fractions of one phase and $x''_{1i}(\text{exp})$, $x''_{2i}(\text{exp})$ and $x''_{1i}(\text{calc})$, $x''_{2i}(\text{calc})$ are the experimental and calculated mole fractions of the other phase. For the NRTL model, the nonrandomness parameter, α_{ij} , was set at a value of 0.10, 0.35, or 0.43 (see Tables 10 and 11). The NRTL equation was optimized for all parameters. The parameters calculated in this way, $g_{ij} - g_{ji}$, $g_{ji} - g_{ii}$, and Δu_{ij} , Δu_{ji} for the NRTL and UNIQUAC

equations, respectively, are shown in Tables 10 and 11. The model correlation parameters are included in Tables 10 and 11 together with the root-mean-square deviation (rmsd) values, defined below, which can be taken as a measure of the precision of the correlation:

$$\text{rmsd} = \left(\sum_i \sum_l \sum_m [x_{ilm}^{\text{exp}} - x_{ilm}^{\text{calc}}]^2 / 6k \right)^{1/2} \quad (9)$$

where x is the mole fraction and the subscripts i , l , and m designate the component, phase, and tie line, respectively, and k represents the number of interaction components. The correlation obtained with the NRTL model is significantly better than the UNIQUAC model.

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