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Liquid−Liquid Equilibria for Mixtures of an Alkane + an Aromatic Hydrocarbon + 1,4-Dicyanobutane at 298.15 K

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Liquid−liquid equilibrium results for mixtures of an alkane + an aromatic hydrocarbon + 1,4-dicyanobutane at 298.15 K are reported, where the alkane is hexane or nonane or dodecane or hexadecane and the aromatic hydrocarbon is benzene or methylbenzene or 1,2-dimethylbenzene, or 1,3-dimethylbenzene, or 1,4-dimethylbenzene or 1,3,5-trimethylbenzene or ethylbenzene. The results show that there is a small increase in the two-phase region as the chain length of the alkane is increased. The type of aromatic hydrocarbon present in the mixture has a noticeable effect on the slopes of the tie lines. There is also an increase in the area of the two phase-region with increasing substitution of methyl groups on the benzene ring. NRTL and UNIQUAC models were correlated to the data. The results show that 1,4-dicyanobutane may be used as a solvent for the separation of aromatic and aliphatic hydrocarbons.

Introduction

The separation of pure aromatic and aliphatic compounds from their mixtures is an important goal in chemical operations (e.g. Fischer−Tropsch synthesis) that produce both types of compounds. In this work we have used 1,4-dicyanobutane (DCB) as a potential solvent for this separation. This compound has a very high boiling point (593 K), and this will allow for the easy isolation of both low-boiling aromatics and aliphatic compounds. It is a chainlike molecule with two polar terminal groups and has a similar structure to that of succinonitrile. The latter compound has been highlighted by Tiegs et al. (1986) as having a high capacity for separating aromatic and aliphatic hydrocarbons. Our interest in 1,4-dicyanobutane stems from the comments of Tiegs et al. (1986).

In this work the liquid−liquid equilibrium results for mixtures of an alkane + an aromatic hydrocarbon + 1,4-dicyanobutane at 298.15 K are reported, where the alkane is hexane or nonane or dodecane or hexadecane and the aromatic hydrocarbon is benzene or methylbenzene or 1,2-dimethylbenzene or 1,3-dimethylbenzene or 1,4-dimethylbenzene or 1,3,5-trimethyl benzene or ethylbenzene. An exhaustive literature search for liquid−liquid equilibrium data for the mixtures investigated here showed that this work has not been published before.

The binodal curve data have been summarized by the Hlavatý equation (Hlavatý, 1972), a β function, and a log γ function, following the work of Letcher et al. (1990). The NRTL model (Renon and Prausnitz, 1968) and the UNIQUAC model (Abrams and Prausnitz, 1975) were used to correlate the tie line data.

Table 1. Details of the Chemicals: Purities, UNIQUAC Structural Parameters, and Refractive Indicies

compound	purity (%)	UNIQUAC structural parameters		n_D^{25}	
		r	*q*	exp	lit[a]
n-hexane	99	4.50	3.86	1.3728	1.3723
n-nonane	99.8	6.52	5.48	1.4052	1.4031
n-dodecane	>99	8.55	7.10	1.4275	1.4269
n-hexadecane	99	11.24	9.26	1.4325	1.4325
1,4-dicyanobutane	>99	4.64	3.91	1.4365	
benzene	99	3.19	2.40	1.4990	1.4979
methylbenzene	99	3.92	2.98	1.4940	1.4940
1,2-dimethylbenzene	99	4.66	3.54	1.5018	1.5029
1,3-dimethylbenzene	99	4.66	3.54	1.4943	1.4946
1,4-dimethylbenzene	>99	4.66	3.54	1.4925	1.4932
1,3,5-trimethylbenzene	98	5.39	4.10	1.4965	1.4968
ethylbenzene	99	4.60	3.52	1.4928	1.4932

[a] Riddick et al. (1986). No literature value could be found for 1,4-dicyanobutane.

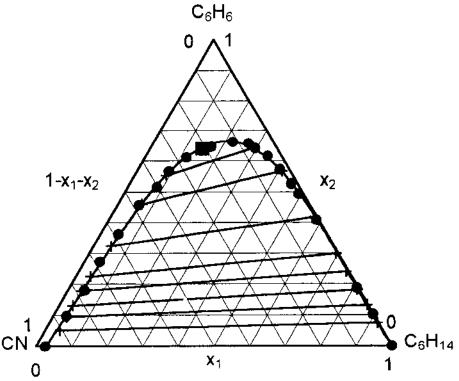

Figure 1. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_2C_6H_6 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

Experimental Section

The binodal curves were determined at 298.15 K using the cloud point method described in detail by Letcher and Siswana (1992). The tie lines were determined using the refractive index method described in detail by Briggs and Comings (1943). The accuracy of this technique was established in a previous paper (Letcher and Naicker, 1998) by comparing results obtained in our laboratory with literature values for a test system and was found to be within 0.005 mole fraction.

Details of the chemicals are given in Table 1. The aromatic hydrocarbons and *n*-hexane were used without

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Table 2. Composition of the Points on the Binodal Curve at 298.15 K for the Mixtures $\{x_1C_6H_{14} + x_2C_6H_{6-R}(CH_3)_R$ or $C_6H_5CH_2CH_3 + (1 - x_1 - x_2)1,4\text{-}C_4H_8(CN)_2\}$

C_6H_6		$CH_3C_6H_5$		1,2-$(CH_3)_2C_6H_4$		1,3-$(CH_3)_2C_6H_4$	
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.027	0.000	0.027	0.000	0.027	0.000	0.027	0.000
0.037	0.098	0.029	0.083	0.028	0.078	0.031	0.061
0.047	0.178	0.037	0.176	0.032	0.149	0.034	0.238
0.045	0.272	0.043	0.246	0.036	0.229	0.035	0.328
0.052	0.362	0.050	0.335	0.044	0.304	0.041	0.384
0.062	0.457	0.053	0.412	0.053	0.468	0.040	0.469
0.084	0.515	0.063	0.481	0.067	0.534	0.048	0.536
0.092	0.567	0.082	0.558	0.086	0.599	0.060	0.606
0.120	0.611	0.106	0.609	0.113	0.651	0.079	0.676
0.171	0.647	0.141	0.653	0.180	0.708	0.104	0.733
0.224	0.663	0.154	0.661	0.320	0.640	0.130	0.752
0.270	0.658	0.291	0.658	0.433	0.548	0.188	0.740
0.297	0.643	0.399	0.578	0.590	0.393	0.337	0.647
0.344	0.617	0.487	0.502	0.669	0.328	0.450	0.543
0.401	0.573	0.544	0.449	0.748	0.247	0.513	0.480
0.457	0.526	0.641	0.354	0.829	0.169	0.600	0.392
0.494	0.493	0.711	0.286	0.910	0.088	0.669	0.322
0.586	0.407	0.814	0.184	1.000	0.000	0.740	0.253
0.809	0.186	0.901	0.097			0.830	0.162
0.897	0.102	0.949	0.050			0.894	0.096
1.000	0.000	1.000	0.000			0.960	0.038
						1.000	0.000

1,4-$(CH_3)_2C_6H_4$		1,3,5-$(CH_3)_3C_6H_3$		$CH_3CH_2C_6H_5$	
x_1	x_2	x_1	x_2	x_1	x_2
0.027	0.000	0.027	0.000	0.027	0.000
0.029	0.076	0.032	0.041	0.031	0.065
0.033	0.154	0.033	0.075	0.035	0.117
0.035	0.224	0.035	0.115	0.036	0.228
0.038	0.300	0.036	0.162	0.041	0.292
0.039	0.394	0.038	0.233	0.043	0.383
0.040	0.457	0.008	0.364	0.046	0.453
0.046	0.541	0.000	0.416	0.055	0.532
0.057	0.609	0.000	0.813	0.071	0.602
0.074	0.680	0.083	0.842	0.093	0.663
0.099	0.740	0.207	0.749	0.127	0.720
0.158	0.759	0.363	0.614	0.190	0.727
0.193	0.744	0.541	0.444	0.327	0.638
0.435	0.544	0.619	0.372	0.440	0.544
0.510	0.479	0.697	0.296	0.472	0.513
0.587	0.404	0.774	0.221	0.597	0.392
0.672	0.320	0.852	0.144	0.678	0.315
0.750	0.245	1.000	0.000	0.755	0.239
0.834	0.163			0.823	0.173
0.904	0.092			0.900	0.096
1.000	0.000			1.000	0.000

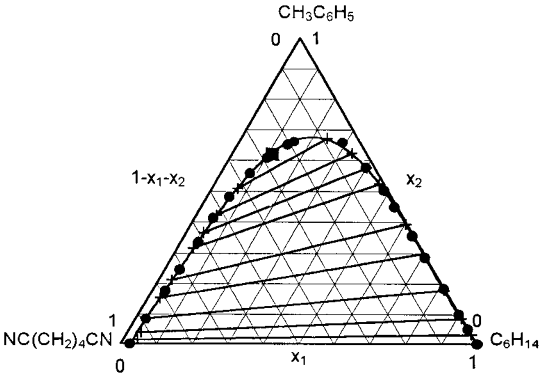

Figure 2. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_2C_6H_5CH_3 + (1- x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

Table 3. Compositions of the Points on the Binodal Curve at 298.15 K for the Mixtures $\{x_1C_nH_{2n+2} + x_2C_6H_6 + (1- x_1 - x_2)1,4\text{-}C_4H_8(CN)_2\}$

C_9H_{20}		$C_{12}H_{26}$		$C_{16}H_{34}$	
x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000	0.000	0.000	0.000	0.000
0.006	0.106	0.002	0.093	0.001	0.089
0.007	0.208	0.003	0.199	0.001	0.208
0.010	0.289	0.005	0.279	0.002	0.300
0.014	0.386	0.009	0.386	0.003	0.388
0.021	0.468	0.011	0.482	0.004	0.476
0.031	0.536	0.016	0.548	0.007	0.552
0.036	0.586	0.022	0.612	0.011	0.633
0.040	0.608	0.039	0.684	0.020	0.703
0.068	0.670	0.073	0.741	0.041	0.761
0.076	0.684	0.097	0.764	0.073	0.798
0.105	0.709	0.100	0.762	0.110	0.812
0.125	0.719	0.186	0.763	0.187	0.779
0.154	0.732	0.287	0.690	0.283	0.702
0.166	0.731	0.388	0.603	0.380	0.613
0.220	0.720	0.496	0.495	0.447	0.546
0.236	0.713	0.581	0.412	0.538	0.455
0.300	0.667	0.662	0.333	0.641	0.354
0.384	0.597	0.750	0.244	0.749	0.246
0.503	0.488	0.829	0.165	0.832	0.162
0.612	0.378	0.908	0.089	0.918	0.079
0.907	0.092	1.000	0.000	1.000	0.000
1.000	0.000				

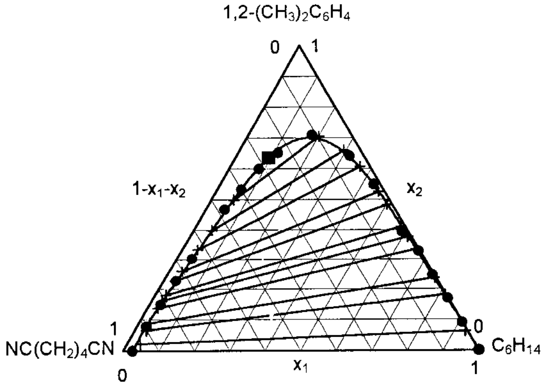

Figure 3. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_21,2\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

further treatment and 1,4-dicyanobutane was stored under 4 A molecular sieves. The purities of the chemicals were determined by gas chromatography, and the results are recorded in Table 1. The temperature was controlled to within 0.01 K using a Tronac temperature controller used in conjunction with a calibrated Hewlett-Packard quartz thermometer.

Results

The compositions of mixtures on the binodal curve are reported in Tables 2 and 3. The compositions of equilibrium mixtures (tie lines) are given in Tables 4 and 5. The compositions of the plait points or critical points, which were determined following the method of Treybal (1946), are given in Tables 6 and 7. The ternary phase diagrams showing the binodal curve together with tie lines and plait points are given in Figures 1−10. The ability of 1,4-dicyanobutane to separate aromatic hydrocarbons and aliphatic hydrocarbons is indicated by the selectivity S, defined as $S = (x_2'/x_3')(x_2''/x_3'')$ and is presented in Tables 4 and 5. The prime refers to the alkane-rich phase, and the double prime refers to the DCB-rich phase. The magnitude of S increases with a decrease in the overall concentration of the aromatic compound.

Three equations have been fitted to this work following the work of Hlavatý (1972). The coefficients A_i relate to the modified Hlavatý equation,

$$x_2 = A_1x_A \ln x_A + A_2x_B \ln x_B + A_3x_Ax_B$$

Table 4. Composition of Conjugate Phases at 298.15 K for the Mixtures {$x_1C_6H_{14} + x_2C_6H_{6-R}(CH_3)_R$ or $C_6H_5CH_2CH_3 + (1 - x_1 - x_2)$1,4-$C_4H_8(CN)_2$}

C_6H_6					$CH_3C_6H_5$				
x_1'	x_2'	x_1''	x_2''	S	x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.027	0.000		1.000	0.000	0.027	0.000	
0.923	0.074	0.042	0.051	434.8	0.969	0.031	0.041	0.013	4447.8
0.864	0.132	0.040	0.094	305.2	0.913	0.085	0.039	0.037	1177.8
0.813	0.181	0.040	0.131	191.5	0.818	0.179	0.036	0.084	690.8
0.753	0.240	0.040	0.177	152.0	0.699	0.298	0.034	0.151	594.2
0.695	0.299	0.042	0.224	163.7	0.604	0.392	0.037	0.213	367.6
0.575	0.418	0.050	0.323	116.1	0.463	0.524	0.045	0.315	80.9
0.409	0.567	0.069	0.461	24.1	0.402	0.575	0.050	0.365	40.1
0.293	0.642	0.091	0.552	6.4	0.336	0.624	0.058	0.421	19.1
					0.242	0.672	0.073	0.508	6.4

1,2-$(CH_3)_2C_6H_4$					1,3-$(CH_3)_2C_6H_4$				
x_1'	x_2'	x_1''	x_2''	S	x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.027	0.000		1.000	0.000	0.027	0.000	
0.932	0.061	0.040	0.020	390.5	0.904	0.090	0.044	0.022	648.8
0.816	0.181	0.034	0.065	889.9	0.830	0.161	0.042	0.043	396.4
0.759	0.236	0.032	0.089	449.6	0.742	0.248	0.039	0.071	323.9
0.658	0.334	0.030	0.138	238.2	0.710	0.281	0.038	0.083	320.7
0.614	0.376	0.030	0.161	195.2	0.641	0.351	0.036	0.112	340.0
0.579	0.410	0.031	0.182	165.8	0.514	0.480	0.034	0.176	382.3
0.504	0.482	0.034	0.229	116.2	0.362	0.624	0.035	0.281	116.2
0.458	0.525	0.037	0.261	82.4	0.203	0.735	0.042	0.444	13.7
0.366	0.605	0.045	0.334	38.6					
0.295	0.658	0.052	0.398	19.3					
0.201	0.704	0.064	0.498	6.5					

1,4-$(CH_3)_2C_6H_4$					1,3,5-$(CH_3)_3C_6H_3$				
x_1'	x_2'	x_1''	x_2''	S	x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.027	0.000		1.000	0.000	0.027	0.000	
0.911	0.089	0.040	0.022	5926.3	0.860	0.139	0.041	0.013	8145.1
0.769	0.224	0.035	0.063	468.9	0.641	0.346	0.039	0.044	539.2
0.659	0.331	0.032	0.103	266.7	0.536	0.447	0.038	0.066	369.8
0.560	0.429	0.031	0.150	212.9	0.474	0.508	0.037	0.083	316.2
0.484	0.504	0.032	0.192	174.0	0.381	0.601	0.034	0.118	237.6
0.484	0.504	0.032	0.192	174.0	0.381	0.601	0.034	0.118	237.6
0.420	0.566	0.033	0.235	127.5	0.289	0.688	0.029	0.168	142.8
0.364	0.618	0.035	0.278	84.5	0.225	0.744	0.024	0.220	82.1
0.280	0.688	0.039	0.355	36.4	0.161	0.793	0.014	0.298	39.2
0.200	0.738	0.042	0.448	13.5					

$CH_3CH_2C_6H_5$				
x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.027	0.000	
0.786	0.208	0.037	0.060	6.2
0.655	0.336	0.033	0.110	6.4
0.487	0.500	0.033	0.197	5.8
0.424	0.559	0.035	0.239	5.2
0.370	0.606	0.037	0.279	4.6
0.330	0.639	0.039	0.312	4.1
0.290	0.669	0.042	0.350	3.6
0.220	0.708	0.047	0.424	2.8

Table 5. Composition of Conjugate Phases at 298.15 K for the Mixtures {$x_1C_nH_{2n+2} + x_2C_6H_6 + (1 - x_1 - x_2)$1,4-$C_4H_8(CN)_2$}

C_9H_{20}					$C_{12}H_{26}$				
x_1'	x_2'	x_1''	x_2''	S	x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.000	0.000		1.000	0.000	0.000	0.000	
0.796	0.195	0.003	0.127	151.2	0.788	0.205	0.000	0.113	229.0
0.633	0.360	0.009	0.250	160.4	0.597	0.398	0.005	0.246	218.8
0.509	0.484	0.015	0.356	121.1	0.498	0.497	0.008	0.326	202.8
0.423	0.564	0.020	0.434	58.0	0.382	0.608	0.011	0.434	78.4
0.357	0.622	0.025	0.496	28.0	0.289	0.688	0.015	0.531	24.7
0.319	0.650	0.029	0.532	17.3	0.222	0.734	0.022	0.606	10.3
0.250	0.698	0.040	0.599	8.1	0.167	0.769	0.033	0.670	5.4

$C_{16}H_{34}$				
x_1'	x_2'	x_1''	x_2''	S
1.000	0.000	0.000	0.000	
0.925	0.072	0.000	0.036	643.3
0.755	0.237	0.000	0.132	206.2
0.521	0.474	0.003	0.305	194.0
0.426	0.570	0.004	0.392	219.3
0.355	0.639	0.004	0.464	127.4
0.302	0.688	0.005	0.522	60.8
0.273	0.710	0.006	0.555	33.1
0.224	0.750	0.008	0.614	17.8
0.153	0.793	0.018	0.703	5.8

Table 6. Compositions of Critical Points or Plait Points for the Mixtures {$x_1C_6H_{14} + x_2C_6H_{6-R}(CH_3)_R$ or $C_6H_5CH_2CH_3 + (1 - x_1 - x_2)$1,4-$C_4H_8(CN)_2$}

x_1	x_2	$1 - x_1 - x_2$
	C_6H_6	
0.150	0.639	0.211
	$CH_3C_6H_5$	
0.115	0.620	0.265
	1,2-$(CH_3)_2C_6H_4$	
0.095	0.634	0.271
	1,3-$(CH_3)_2C_6H_4$	
0.069	0.652	0.279
	1,4-$(CH_3)_2C_6H_4$	
0.067	0.653	0.280
	$CH_3CH_2C_6H_5$	
0.077	0.617	0.306

Table 7. Compositions of Critical Points or Plait Points for the Mixtures {$x_1C_nH_{2n+2} + x_2C_6H_6 + (1 - x_1 - x_2)$1,4-$C_4H_8(CN)_2$}

x_1	x_2	$1 - x_1 - x_2$
	C_9H_{20}	
0.105	0.717	0.178
	$C_{12}H_{26}$	
0.074	0.748	0.178
	$C_{16}H_{34}$	
0.065	0.801	0.134

The coefficients B_i relate to a β function,

$$x_2 = B_1(1 - x_A)^{B_2}x_A{}^{B_3}$$

The coefficients C_i relate to a log γ equation,

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

where

$$x_A = x_1 + \frac{1}{2}x_2 - x_1^0/(x_{11}^0 - x_1^0)$$

and

$$x_B = x_{11}^0 - x_1 - \frac{1}{2}x_2/(x_{11}^0 - x_1^0)$$

where x_1 refers to the mole fraction of the alkane, x_2 refers to the mole fraction of the aromatic hydrocarbon, and x_{11}^0 and x_1^0 refer to the mole fraction of the alkane when the value of $x_2 = 0$. The coefficients A_i, B_i, and C_i are given in Table 8 together with the standard deviations, σ, which are defined as:

$$\sigma = \{\sum(x_{2,\mathrm{calc}} - x_{2,\mathrm{exp}})^2/(n - 3)\}^{1/2}$$

where n is the number of data points.

Tie Line Correlation. The NRTL model of Renon and Prausnitz (1968) and the UNIQUAC model of Abrams and Prausnitz (1975) are used to correlate the tie line data. The data were correlated using a computer program that

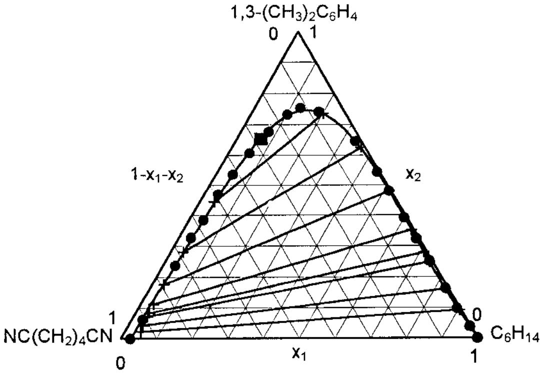

Figure 4. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_21,3\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

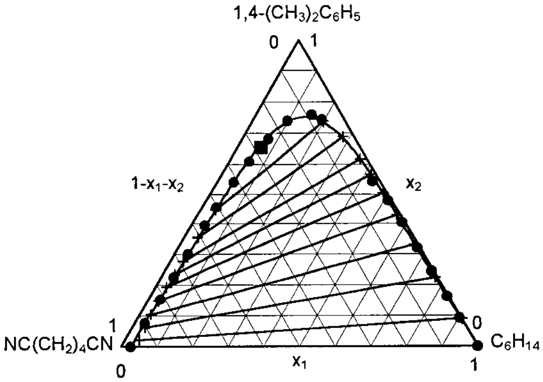

Figure 5. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_21,4\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

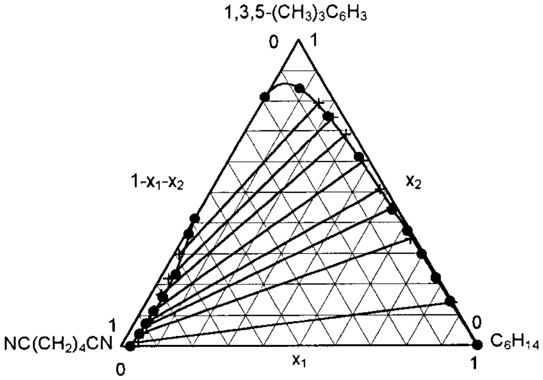

Figure 6. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_21,3,5\text{-}C_6H_3(CH_3)_3 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

minimized the objective function

$$OF = \sum_{k=1}^{n}\sum_{l=1}^{2}\sum_{i=1}^{3}(x_{kli} - \bar{x}_{kli})^2$$

where x_{nli} is the experimental composition of component i in phase l for the kth tie line and $\bar{x}_{nli}$ is the calculated composition of component i in phase l for kth tie line. n is the number of tie lines. In fitting the NRTL equation, the nonrandomness parameter α was set to 0.3. For the UNIQUAC correlation the pure component structural parameters (r and q) were calculated by the method outlined in the original paper by Abrams and Prausnitz (1975) and are given in Table 1. The resulting binary interaction parameters and the root-mean-square (rms) deviations are reported in Tables 9 and 10.

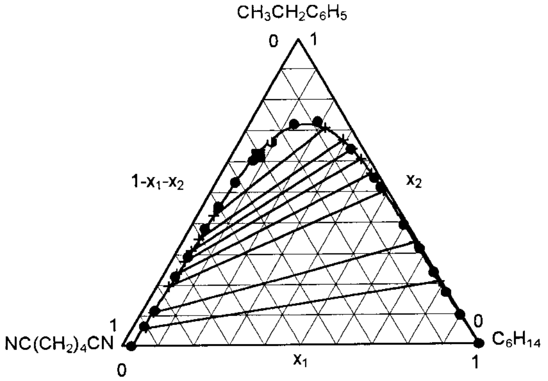

Figure 7. Liquid−liquid equilibrium results for the mixture $\{x_1C_6H_{14} + x_2C_6H_5CH_2CH_3 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

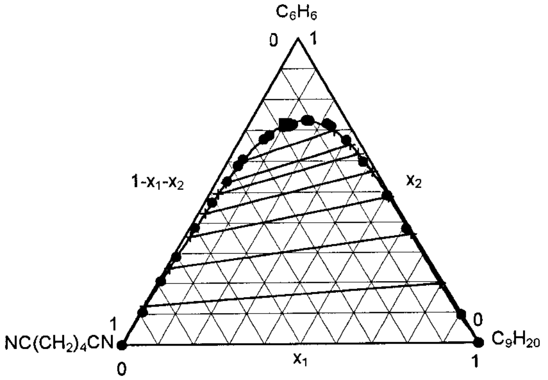

Figure 8. Liquid−liquid equilibrium results for the mixture $\{x_1C_9H_{20} + x_2C_6H_6 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

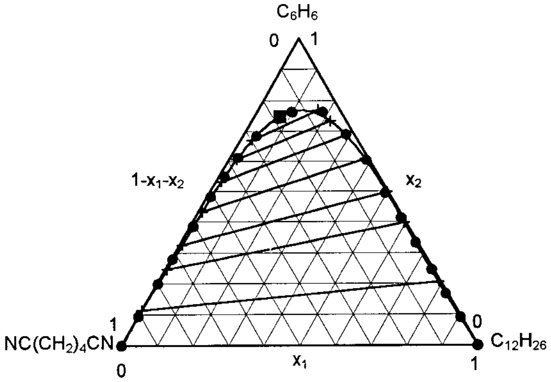

Figure 9. Liquid−liquid equilibrium results for the mixture $\{x_1C_{12}H_{26} + x_2C_6H_6 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

Discussion

Figures 1−10 show large two-phase regions which favor the use of DCB as an agent for the separation of alkane and aromatic compounds. The slopes of the tie lines indicate that 1,4-dicyanobutane is most effective as a separating agent at low aromatic and high DCB concentrations. This is also evident when looking at the values of

Table 8. Hlavatý, β, and log γ Parameters and Their Standard Deviations for the Mixtures $\{x_1C_nH_{2n+2} + x_2C_6H_{6-R}(CH_3)_R$ or $C_6H_5CH_2CH_3 + (1\text{-}x_1\text{-}x_2)1,4\text{-}C_4H_8(CN)_2\}$

	A_1	A_2	A_3	σ	B_1	B_2	B_3	σ	C_1	C_2	C_3	σ
$C_6H_{14} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	1.259	0.814	5.503	0.018	4.356	1.304	1.419	0.014	4.011	1.267	1.932	0.012
$C_6H_{14} + C_6H_5CH_3 + 1,4\text{-}C_4H_8(CN)_2$	1.184	0.815	5.425	0.010	4.386	1.309	1.406	0.023	4.178	1.294	1.942	0.015
$C_6H_{14} + 1,2\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	1.295	0.990	5.881	0.014	4.858	1.374	1.453	0.014	4.510	1.344	2.007	0.012
$C_6H_{14} + 1,3\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	1.671	1.441	7.223	0.024	6.461	1.533	1.600	0.016	5.960	1.500	2.221	0.012
$C_6H_{14} + 1,4\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	1.404	1.305	6.655	0.030	6.104	1.507	1.545	0.026	5.639	1.474	2.156	0.016
$C_6H_{14} + 1,3,5\text{-}C_6H_3(CH_3)_3 + 1,4\text{-}C_4H_8(CN)_2$	−0.256	1.078	4.296	0.030	4.818	1.420	1.171	0.030	4.499	1.392	1.753	0.016
$C_6H_{14} + C_6H_5CH_2CH_3 + 1,4\text{-}C_4H_8(CN)_2$	1.324	1.143	6.217	0.020	5.245	1.423	1.468	0.026	4.2101	1.317	1.916	0.018
$C_9H_{20} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	1.413	1.139	6.415	0.040	5.393	1.416	1.480	0.035	4.805	1.359	2.011	0.020
$C_{12}H_{26} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	1.602	1.389	7.150	0.030	6.176	1.489	1.536	0.018	5.645	1.450	2.216	0.014
$C_{16}H_{34} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	1.271	1.391	6.802	0.027	6.600	1.531	1.533	0.022	6.134	1.501	2.162	0.011

Table 9. NRTL Binary Interaction Parameters ($J\cdot mol^{-1}$) and the Root-Mean-Square (rms) Deviations for the Mixtures[a] $\{x_1C_nH_{2n+2} + x_2C_6H_{6-R}(CH_3)_R$ or $C_6H_5CH_2CH_3 + (1 - x_1 - x_2)1,4\text{-}C_4H_8(CN)_2\}$

	Δg_{12}	Δg_{21}	Δg_{13}	Δg_{23}	Δg_{23}	Δg_{32}	rms
$C_6H_{14} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−2750.81	3729.47	16 037.14	7350.82	5654.68	−2122.58	0.004
$C_6H_{14} + C_6H_5CH_3 + 1,4\text{-}C_4H_8(CN)_2$	−3297.45	3204.92	16 136.23	7600.61	5561.46	−1503.56	0.006
$C_6H_{14} + 1,2\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−3816.19	3066.60	16 116.56	7589.09	5452.32	−1198.74	0.005
$C_6H_{14} + 1,3\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−4632.19	2749.57	15 695.91	6748.09	6106.88	−1235.24	0.005
$C_6H_{14} + 1,4\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−4671.48	2690.33	16 712.58	7255.89	6167.25	−1287.06	0.004
$C_6H_{14} + 1,3,5\text{-}C_6H_3(CH_3)_3 + 1,4\text{-}C_4H_8(CN)_2$	−5393.56	1537.94	14 663.30	5772.99	6127.62	329.58	0.006
$C_6H_{14} + C_6H_5CH_2CH_3 + 1,4\text{-}C_4H_8(CN)_2$	−2972.06	1168.25	15 112.66	7702.93	5989.25	−639.38	0.005
$C_9H_{20} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−2941.26	6490.93	17 295.66	10739.65	5885.43	−1416.79	0.005
$C_{12}H_{26} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−3528.06	7568.73	16 361.32	11555.18	5967.28	−1277.52	0.005
$C_{16}H_{34} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−3562.89	9062.12	15 659.51	12663.06	6696.77	−1156.24	0.005

[a] $\alpha = 0.3$.

Table 10. UNIQUAC Binary Interaction Parameters ($J\cdot mol^{-1}$) and the Root-Mean-Square (rms) Deviations for the Mixtures $\{x_1C_nH_{2n+2} + x_2C_6H_6 + (1 - x_1 - x_2)1,4\text{-}C_4H_8(CN)_2\}$

	Δu_{12}	Δu_{21}	Δu_{13}	Δu_{23}	Δu_{23}	Δu_{32}	rms
$C_6H_{14} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	207.35	−134.04	641.16	18.76	69.32	24.32	0.004
$C_6H_{14} + C_6H_5CH_3 + 1,4\text{-}C_4H_8(CN)_2$	94.91	−85.76	828.00	−7.29	102.84	6.02	0.003
$C_6H_{14} + 1,2\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−205.01	251.10	1405.91	−23.09	180.49	−56.65	0.004
$C_6H_{14} + 1,3\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−188.63	157.34	1219.86	−40.51	205.71	−70.42	0.004
$C_6H_{14} + 1,4\text{-}C_6H_4(CH_3)_2 + 1,4\text{-}C_4H_8(CN)_2$	−189.24	156.69	1509.95	−39.53	204.66	−70.91	0.003
$C_6H_{14} + 1,3,5\text{-}C_6H_3(CH_3)_3 + 1,4\text{-}C_4H_8(CN)_2$	−243.64	149.61	622.85	−35.55	261.79	−78.16	0.006
$C_6H_{14} + C_6H_5CH_2CH_3 + 1,4\text{-}C_4H_8(CN)_2$	−232.91	260.14	1125.55	−26.32	193.14	−61.34	0.003
$C_9H_{20} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−230.54	188.16	764.36	−15.03	97.59	−114.81	0.005
$C_{12}H_{26} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−224.98	219.58	586.66	−17.22	124.22	−115.28	0.004
$C_{16}H_{34} + C_6H_6 + 1,4\text{-}C_4H_8(CN)_2$	−221.07	253.14	603.05	−18.71	117.50	−118.17	0.003

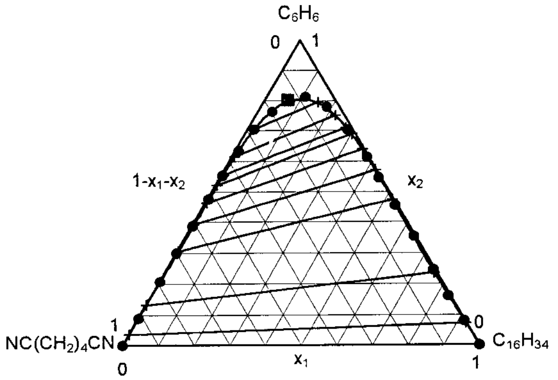

Figure 10. Liquid–liquid equilibrium results for the mixture $\{x_1C_{16}H_{34} + x_2C_6H_6 + (1 - x_1 - x_2)NC(CH_2)_4CN\}$ at 298.15 K: (●) points on the binodal curve; (×) points connecting conjugate phases; (■) critical or plait point.

the selectivity S presented in Tables 4 and 5.

An increase in the number of methyl groups on the benzene moiety results in an increase in the slope of the tie lines. The plait point "slides" down the binodal curve toward the region of high DCB concentration. In the extreme case of the trimethyl-substituted benzene, a mixture in which two of the binary pairs are immiscible is formed. An increase in the chain length of the alkane results in a slight increase in the size of the two-phase region.

The NRTL and UNIQUAC models correlate the data very well. The rms values from Tables 9 and 10 indicate that the UNIQUAC model fits the data marginally better than the NRTL model. The parameters obtained in this work will be used by us in predicting the infinite dilution activity coefficients for various hydrocarbons in DCB.

The Hlavatý, β, and log γ equations also correlate the data satisfactorily. A comparison of the standard deviations, σ, of the Hlavatý, β, and log γ equations with the root-mean-square deviations of the NRTL and UNIQUAC models shows that the NRTL and UNIQUAC models provide a better correlation of the experimental data. The NRTL and UNIQUAC models also allow for the determination of compositions of conjugate phases, which is not possible with the Hlavatý, β, and log γ equations.

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