J. Chem. Eng. Data **2003,** *48,* 23−28

Liquid−Liquid Equilibria for Mixtures of (Furfural + an Aromatic Hydrocarbon + an Alkane) at $T = 298.15$ K

Trevor M. Letcher,* Sandile Zondi, and Pavan K. Naicker†

School of Pure and Applied Chemistry, University of Natal, Durban 4041, South Africa

Liquid−liquid equilibrium results for mixtures of furfural + an aromatic hydrocarbon + an alkane at $T = 298.15$ K are reported, where an aromatic hydrocarbon is benzene or methylbenzene or 1,2-dimethylbenzene or 1,3-dimethylbenzene or 1,4-dimethylbenzene and an alkane refers to *n*-hexane or *n*-dodecane or *n*-hexadecane. The data were measured using the titration method and show a large solubility gap for all mixtures studied. The selectivity values are large, indicating that furfural is capable of separating aromatic hydrocarbons from aliphatic hydrocarbons by solvent extraction. The data were correlated with the UNIQUAC equation, the NRTL equation, and three analytical equations.

Introduction

The separation of aromatic and aliphatic hydrocarbons has been an area of active research,[1−4] and the search for new solvents that can be used in liquid−liquid extraction is ongoing.[3,4] To investigate the suitability of a new solvent for liquid−liquid extraction, it is usual to measure its phase equilibrium properties. In this work we report the liquid−liquid equilibrium results for the mixtures (furfural + an aromatic hydrocarbon + an alkane) at $T = 298.15$ K, where an aromatic hydrocarbon is benzene or methylbenzene or 1,2-dimethylbenzene or 1,3-dimethylbenzene or 1,4-dimethylbenzene and an alkane refers to *n*-hexane or *n*-dodecane or *n*-hexadecane. A search of the literature has indicated that data for mixtures presented here have not been reported previously. Furfural was chosen as it is a low-cost byproduct from the sugar industry, has a high boiling point (163 °C), and like other extractive solvents (e.g. *N*-methyl-2-pyrolidinone) is polar and has an aldehyde group.

The binodal curve data have been correlated with the Hlavatý equation,[5] a β function, and a log γ function.[6] The NRTL model[7] and the UNIQUAC model[8] were used to correlate the tie line data.

Experimental Section

Procedure. The binodal curves were determined at 298.15 K using the cloud point method, described in detail by Letcher and Siswana.[9] The tie lines were determined using the refractive index method, described in detail by Briggs and Comings.[10] The refractive index of each known composition on the binodal curve was related to a “composition” obtained by dropping a perpendicular onto the baseline of the two-phase region. This “composition” was then plotted against the refractive index, and this graph was used to determine unknown compositions from two-phase mixtures for which the overall composition was known. The line joining the compositions of each two-phase mixture (determined from the refractive index data) on the phase diagram should pass through the known overall composition point. This acted as a consistency check. The accuracy of this technique was established in a previous paper[4] by comparing results obtained in our laboratory with literature values for a test system and was found to be within 0.005 mole fraction. The temperature was controlled to within 0.01 K using a Tronac temperature controller used in conjunction with a calibrated Hewlett-Packard quartz thermometer.

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

	purity	UNIQUAC structural parameters[16]		n_D^{25}	
compound	% mole fraction	r	q^a	exp	lit.[15]
$C_5H_4O_2$	>99.0	3.17	2.481	1.4001	1.4001
C_6H_6	99.9	3.19	2.40	1.4990	1.4979
$C_6H_5CH_3$	99.8	3.92	2.98	1.4940	1.4940
1,2-$C_6H_4(CH_3)_2$	>99.0	4.66	3.54	1.5018	1.5029
1,3-$C_6H_4(CH_3)_2$	>99.0	4.66	3.54	1.4943	1.4946
1,4-$C_6H_4(CH_3)_2$	>99.0	4.66	3.54	1.4925	1.4932
$CH_3(CH_2)_4CH_3$	>99.0	4.50	3.86	1.3728	1.3723
$CH_3(CH_2)_{10}CH_3$	>99.0	8.55	7.10	1.4275	1.4269
$CH_3(CH_2)_{14}CH_3$	>99.0	11.24	8.26	1.4325	1.4325

[a] For non-hydrogen-bonding compounds $q' = q$.

Chemicals. All chemicals were supplied by ACROS. The purities of the chemicals were determined by gas chromatography, and the results are recorded in Table 1. Furfural was distilled twice, and the middle fraction from the second distillation was used in this work. *o*-Xylene, *m*-xylene, *p*-xylene, and *n*-hexane were distilled and the middle fraction used in this work. All other chemicals were not treated further.

Results

The compositions of points on the binodal curve for the mixtures ($C_5H_4O_2 + C_6H_{6-m}(CH_3)_m + CH_3(CH_2)_nCH_3$) at $T = 298.15$ K are reported in Table 2 where m is the number of methyl groups on the benzene ring and n is number of CH_2 units in the alkane. The compositions of conjugate phases for these mixtures (tie lines) are given in Table 3. The compositions of the plait points or critical points, which were determined following the method of Treybal,[11] are

---

* To whom correspondence should be addressed. E-mail: letcher@nu.ac.za. Fax: +27 31 260 2616.

† Presently on a Postdoctoral Grant to the Department of Chemical Engineering, The University of Tennessee, Knoxville, TN 37912.

10.1021/je010317u CCC: $25.00

Table 2. Composition of Points on the Binodal Curve for the Mixtures $\{(x_1)C_5H_4O_2 + (x_2)C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_nCH_3\}$ at $T = 298.15$ K

x_1	x_2	x_1	x_2	x_1	x_2
$C_5H_4O_2 + CH_3(CH_2)_4CH_3$					
$+ C_6H_6$		$+ C_6H_5CH_3$		$+ 1,2\text{-}C_6H_4(CH_3)_2$	
0.046	0.000	0.046	0.000	0.046	0.000
0.054	0.067	0.057	0.044	0.065	0.086
0.072	0.171	0.085	0.128	0.092	0.180
0.106	0.274	0.119	0.218	0.106	0.217
0.159	0.329	0.201	0.299	0.188	0.302
0.226	0.361	0.293	0.320	0.191	0.301
0.301	0.365	0.383	0.311	0.269	0.326
0.374	0.352	0.486	0.289	0.358	0.318
0.449	0.337	0.605	0.240	0.424	0.305
0.589	0.263	0.735	0.160	0.508	0.275
0.688	0.201	0.855	0.065	0.520	0.267
0.759	0.144	0.933	0.000	0.604	0.228
0.933	0.000			0.730	0.146
				0.907	0.023
				0.933	0.000
$C_5H_4O_2 + CH_3(CH_2)_4CH_3$					
$+ 1,3\text{-}C_6H_4(CH_3)_2$		$+ 1,4\text{-}C_6H_4(CH_3)_2$			
0.046	0.000	0.046	0.000		
0.056	0.054	0.056	0.039		
0.066	0.095	0.068	0.083		
0.108	0.230	0.116	0.226		
0.127	0.253	0.163	0.285		
0.178	0.303	0.193	0.303		
0.238	0.319	0.238	0.321		
0.250	0.321	0.276	0.329		
0.324	0.314	0.349	0.322		
0.351	0.314	0.426	0.299		
0.397	0.303	0.514	0.269		
0.486	0.281	0.610	0.224		
0.520	0.257	0.731	0.146		
0.605	0.230	0.883	0.036		
0.831	0.077	0.933	0.000		
0.859	0.051				
0.933	0.000				
$C_5H_4O_2 + CH_3(CH_2)_{10}CH_3$					
$+ C_6H_6$		$+ C_6H_5CH_3$		$+ 1,2\text{-}C_6H_4(CH_3)_2$	
0.055	0.000	0.055	0.000	0.055	0
0.061	0.086	0.063	0.107	0.074	0.145
0.097	0.350	0.079	0.199	0.11	0.316
0.142	0.449	0.108	0.327	0.147	0.414
0.213	0.507	0.129	0.395	0.232	0.472
0.291	0.500	0.157	0.443	0.311	0.465
0.352	0.486	0.197	0.473	0.359	0.452
0.421	0.463	0.267	0.483	0.451	0.417
0.500	0.423	0.384	0.451	0.512	0.388
0.661	0.305	0.409	0.446	0.658	0.292
0.844	0.137	0.589	0.348	0.773	0.195
0.986	0.000	0.737	0.227	0.986	0.000
		0.865	0.115		
		0.986	0.000		
$C_5H_4O_2 + CH_3(CH_2)_{10}CH_3$				$C_5H_4O_2 + CH_3(CH_2)_{14}CH_3$	
$+ 1,3\text{-}C_6H_4(CH_3)_2$		$+ 1,4\text{-}C_6H_4(CH_3)_2$		$+ C_6H_6$	
0.055	0.000	0.055	0.000	0.025	0.000
0.075	0.204	0.063	0.114	0.029	0.163
0.130	0.395	0.099	0.304	0.041	0.317
0.199	0.468	0.201	0.477	0.067	0.423
0.266	0.482	0.258	0.485	0.123	0.542
0.318	0.476	0.319	0.477	0.161	0.567
0.384	0.453	0.379	0.455	0.203	0.582
0.497	0.399	0.438	0.429	0.247	0.583
0.564	0.358	0.553	0.365	0.298	0.569
0.638	0.306	0.645	0.304	0.365	0.546
0.788	0.185	0.759	0.210	0.456	0.492
0.943	0.038	0.911	0.069	0.613	0.366
0.986	0.000	0.988	0.000	0.784	0.203
				0.992	0.000

Table 3. Composition of Conjugate Phases for the Mixtures $\{(x_1)C_5H_4O_2 + (x_2)C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_nCH_3\}$ at $T = 298.15$ K and the Selectivity, S

x_{11}	x_{21}	x_{13}	x_{23}	S
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_4CH_3$				
0.695	0.194	0.085	0.216	5.7
0.597	0.257	0.119	0.289	3.6
0.523	0.299	0.159	0.328	2.6
0.396	0.353	0.262	0.368	1.4
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_4CH_3$				
0.804	0.111	0.090	0.142	7.1
0.720	0.172	0.140	0.240	4.1
0.642	0.219	0.192	0.292	2.8
0.562	0.257	0.266	0.315	1.9
$C_5H_4O_2 + 1,2\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$				
0.810	0.090	0.102	0.210	2.9
0.754	0.126	0.133	0.255	2.5
0.690	0.172	0.178	0.294	2.2
0.605	0.225	0.268	0.320	1.7
0.520	0.267	0.345	0.318	1.3
$C_5H_4O_2 + 1,3\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$				
0.754	0.134	0.115	0.240	3.2
0.716	0.160	0.143	0.277	2.7
0.652	0.199	0.187	0.307	2.2
0.580	0.235	0.301	0.324	1.5
$C_5H_4O_2 + 1,4\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$				
0.873	0.046	0.098	0.156	2.7
0.814	0.087	0.135	0.255	2.1
0.757	0.131	0.194	0.305	1.9
0.675	0.185	0.279	0.329	1.6
0.610	0.222	0.370	0.317	1.3
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{10}CH_3$				
0.763	0.220	0.090	0.311	25
0.690	0.281	0.105	0.382	13
0.602	0.348	0.141	0.447	6.4
0.535	0.399	0.189	0.492	3.9
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_{10}CH_3$				
0.858	0.123	0.078	0.198	24
0.760	0.208	0.107	0.329	11
0.653	0.296	0.150	0.435	5.5
0.583	0.345	0.196	0.473	3.4
0.492	0.400	0.260	0.480	2.0
$C_5H_4O_2 + 1,2\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$				
0.841	0.135	0.091	0.239	16
0.790	0.180	0.110	0.323	11
0.742	0.220	0.142	0.404	6.5
0.679	0.275	0.199	0.460	4.4
0.578	0.347	0.301	0.468	2.3
$C_5H_4O_2 + 1,3\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$				
0.851	0.128	0.081	0.246	17
0.800	0.171	0.106	0.338	9.7
0.748	0.218	0.141	0.410	7.0
0.683	0.275	0.180	0.456	5.2
0.587	0.343	0.253	0.483	2.7
$C_5H_4O_2 + 1,4\text{-}C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$				
0.859	0.121	0.095	0.290	13
0.811	0.168	0.117	0.373	11
0.742	0.226	0.149	0.438	6.7
0.670	0.287	0.202	0.472	4.6
0.625	0.321	0.230	0.481	3.6
0.550	0.368	0.302	0.478	2.1
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{14}CH_3$				
0.667	0.315	0.077	0.446	19
0.621	0.356	0.093	0.493	13
0.565	0.406	0.124	0.541	8.7
0.480	0.475	0.181	0.580	4.3
0.411	0.519	0.235	0.585	2.3

given in Table 4. The ternary phase diagrams showing the binodal curve together with tie lines and plait points are given in Figure 1. The ability of furfural to separate aromatic and aliphatic hydrocarbon mixtures is indicated by the selectivity, S, defined as[12,13]

$$S = (x_2'/x_3')/(x_2''/x_3'')$$

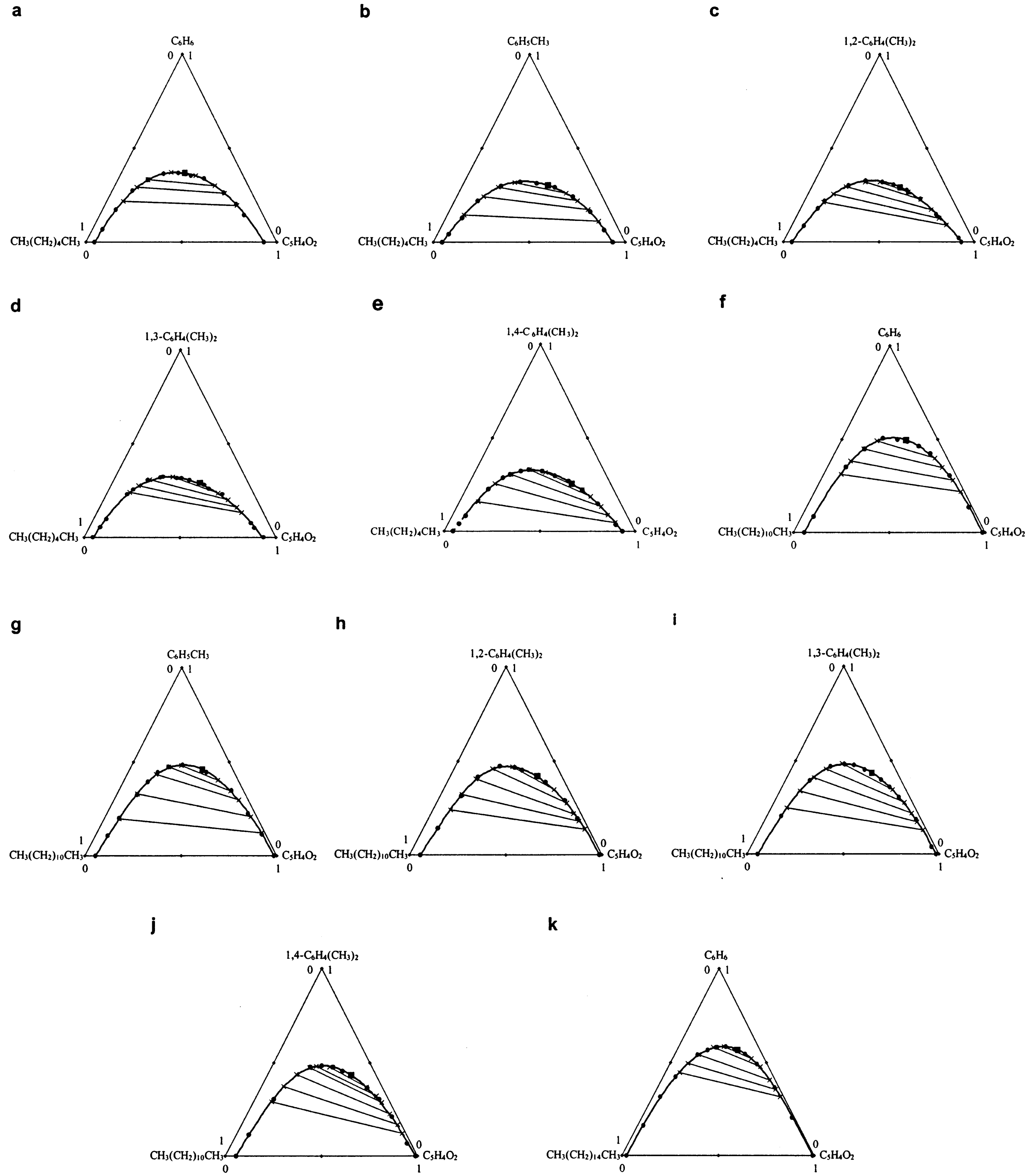

Figure 1. Liquid−liquid equilibrium results for the following mixtures: a, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; b, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; c, $\{(x_1)C_5H_4O_2 + (x_2)1,2\text{-}C_6H_4CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; d, $\{(x_1)C_5H_4O_2 + (x_2)1,3\text{-}C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; e, $\{(x_1)C_5H_4O_2 + (x_2)1,4\text{-}C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; f, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; g, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; h, $\{(x_1)C_5H_4O_2 + (x_2)1,2\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; i, $\{(x_1)C_5H_4O_2 + (x_2)1,3\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; j, $\{(x_1)C_5H_4O_2 + (x_2)1,4\text{-}C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; k, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_{14}CH_3\}$ at $T = 298.15$ K. ●, points on the binodal curve; ×, points connecting conjugate phases; ■, critical or plait point.

and presented in Table 3. The ′ refers to the furfural rich phase, and the ″ refers to the aliphatic rich phase.

Three equations have been fitted to the binodal curve data following the work of Hlavatý[5] and Letcher et al.[6] The coefficients A_i relate to the modified Hlavatý equation[5]

$$x_2 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_A x_B$$

Table 4. Compositions of Plait Points for the Mixtures $\{(x_1)C_5H_4O_2 + (x_2)C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_nCH_3\}$ at T = 298.15 K

	x_1	x_2
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_4CH_3$	0.334	0.365
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_4CH_3$	0.445	0.302
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	0.464	0.292
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	0.458	0.289
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	0.540	0.256
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{10}CH_3$	0.339	0.494
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_{10}CH_3$	0.382	0.457
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.452	0.419
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.433	0.433
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.435	0.435
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{14}CH_3$	0.318	0.565

The coefficients B_i relate to a β function[6]

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

The coefficients C_i relate to a log γ equation[6]

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

where

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

and

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

where x_1 refers to the mole fraction of furfural, x_2 refers to the mole fraction of the aromatic hydrocarbon, and x_{11}° and x_1° refer to the mole fraction of furfural when the value of $x_2 = 0$. The coefficients A_i, B_i, and C_i are given in Table 5 together with the standard deviation, σ, which is 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 nonrandom two-liquid (NRTL) model[7] and the universal quasichemical (UNIQUAC) model[8] are used to correlate the tie line data. The data were correlated using a computer program that minimized the following objective function using a simplex optimization routine.[14]

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

where x_{kli} is the experimental composition of component i in phase l for the kth tie line and $\bar{x}_{kli}$ is the calculated composition of component i in phase l for the kth tie line. For the UNIQUAC correlation the pure component structural parameters (r, q, and q') were calculated by the method outlined in the original paper[8] and are given in Table 1. The resulting binary interaction parameters and the root-mean-square (rms) deviations are reported in Tables 6 and 7. The symbols and notation used in these tables are consistent with the original work by Renon and Prausnitz[7] and Abrams and Prausnitz.[8]

Discussion

All the data reported here contribute new information to the literature. The mixtures (furfural + an aromatic hydrocarbon + an alkane) were studied in order to determine the suitability of furfural for separating aromatic–aliphatic hydrocarbon mixtures. The reason for choosing these aromatic hydrocarbons was to determine the effect that methyl substitution on the benzene ring had on the

Table 5. Hlavatý, β, and log γ Parameters and Their Standard Deviations for the Mixtures $\{(x_1)C_5H_4O_2 + (x_2)C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)\ CH_3(CH_2)_nCH_3\}$ at T = 298.15 K

	A_1	A_2	A_3	σ	B_1	B_2	B_3	σ	C_1	C_2	C_3	σ
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_4CH_3$	−0.108	0.001	1.341	0.013	1.426	1.001	0.949	0.014	1.285	0.953	1.300	0.005
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_4CH_3$	−0.040	−0.067	1.144	0.009	1.232	0.959	0.979	0.010	1.125	0.919	1.315	0.006
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	−0.067	0.129	1.389	0.008	1.359	1.080	0.979	0.008	1.213	1.023	1.357	0.003
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	−0.134	0.117	1.261	0.014	1.304	1.076	0.944	0.014	1.164	1.021	1.319	0.008
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	−0.0004	0.189	1.571	0.010	1.439	1.118	1.017	0.010	1.270	1.057	1.402	0.005
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{10}CH_3$	0.172	0.123	2.435	0.011	2.203	1.053	1.068	0.016	2.004	1.009	1.451	0.005
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_{10}CH_3$	0.197	0.182	2.453	0.015	2.171	1.083	1.087	0.015	1.963	1.037	1.479	0.012
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.196	0.174	2.388	0.013	2.101	1.079	1.085	0.015	1.909	1.034	1.479	0.007
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.146	0.183	2.371	0.007	2.122	1.081	1.066	0.008	1.944	1.041	1.469	0.002
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	0.167	0.208	2.439	0.008	2.161	1.093	1.077	0.009	1.962	1.049	1.474	0.009
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{14}CH_3$	0.395	0.286	3.277	0.046	2.783	1.110	1.144	0.044	2.517	1.062	1.548	0.009

Table 6. NRTL Binary Interaction Parameters and the Root-mean-square-deviations (rms) for the Mixtures[a] $\{x_1C_5H_4O_2 + x_2C_6H_{6-m}(CH_3)_m + (1\text{-}x_1\text{-}x_2)\ CH_3(CH_2)_nCH_3\}$

	$g_{12}g_{22}$ / J·mol^{-1}	$g_{21}g_{11}$ / J·mol^{-1}	$g_{13}g_{33}$ / J·mol^{-1}	$g_{31}g_{11}$ / J·mol^{-1}	$g_{23}g_{33}$ / J·mol^{-1}	$g_{32}g_{22}$ / J·mol^{-1}	rms
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_4CH_3$	817.2	−3106	−4252	−2422	−667.4	−1609	0.002
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_4CH_3$	−1160	−599.3	−3714	−2561	−806.0	−189.9	0.003
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	1522	−3090	−4289	−2030	−1770	3460	0.002
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	1700	−2865	−4299	−2133	−1712	3361	0.002
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	803.9	−3028	−4047	−2215	−1080	1542	0.003
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{10}CH_3$	514.7	−2992	−3241	−5057	−366.2	−1930	0.003
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_{10}CH_3$	−764.3	−1551	−3159	−4354	−250.7	−729.1	0.003
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	−966.7	−1551	−3215	−4212	−219.2	−679.7	0.004
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	−650.3	−1946	−3080	−4093	1750	−1833	0.003
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	62.02	−2467	−3026	−4186	2275	−1815	0.003
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{14}CH_3$	63.96	−1598	−2750	−5296	2665	−1743	0.003

[a] The α was optimized and a value of 0.3 yield the best results.

Table 7. UNIQUAC Binary Interaction Parameters and the Root-Mean-Square Deviations (rms) for the Mixtures $\{(x_1)C_5H_4O_2 + (x_2)C_6H_{6-m}(CH_3)_m + (1 - x_1 - x_2)CH_3(CH_2)_nCH_3\}$

	$\frac{u_{12} - u_{22}}{J \cdot mol^{-1}}$	$\frac{u_{21} - u_{11}}{J \cdot mol^{-1}}$	$\frac{u_{13} - u_{33}}{J \cdot mol^{-1}}$	$\frac{u_{31} - u_{11}}{J \cdot mol^{-1}}$	$\frac{u_{23} - u_{33}}{J \cdot mol^{-1}}$	$\frac{u_{32} - u_{22}}{J \cdot mol^{-1}}$	rms
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_4CH_3$	90.53	−173.1	−229.8	−52.3	−303.2	500.6	0.008
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_4CH_3$	69.61	−186.8	−219.9	−58.6	−335.2	548.4	0.008
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	118.6	−168.4	−288.6	85.4	−210.2	545.8	0.007
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	167.7	−209.1	−306.6	103.6	−265.2	811.0	0.006
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_4CH_3$	129.6	−178.1	−332.4	162.0	−225.1	513.1	0.005
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{10}CH_3$	230.4	−256.5	−292.6	208.5	−296.8	1073	0.014
$C_5H_4O_2 + C_6H_5CH_3 + CH_3(CH_2)_{10}CH_3$	171.5	−136.8	−235.2	68.7	−187.1	515.7	0.016
$C_5H_4O_2$ + 1,2-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	231.4	−142.0	−259.4	102.0	−160.2	493.3	0.015
$C_5H_4O_2$ + 1,3-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	232.4	−148.5	−266.5	104.0	−173.4	495.2	0.014
$C_5H_4O_2$ + 1,4-$C_6H_4(CH_3)_2 + CH_3(CH_2)_{10}CH_3$	69.18	−175.5	−315.4	234.8	−311.6	910.7	0.007
$C_5H_4O_2 + C_6H_6 + CH_3(CH_2)_{14}CH_3$	270.8	−253.9	−270.5	191.0	−233.0	1188	0.018

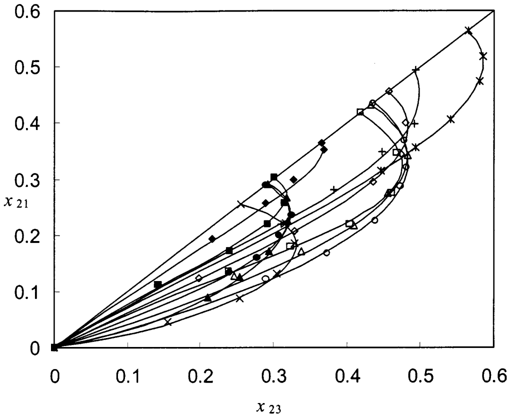

Figure 2. Distribution of the aromatic hydrocarbon between the furfural rich phase and the alkane compound rich phase at T = 298.15 K. x_{21} and x_{23} are the concentration of the aromatic hydrocarbon in the furfural rich phase and the concentration of the alkanol in the alkane rich phase, respectively. ◆, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; ■, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; ▲, $\{(x_1)C_5H_4O_2 + (x_2)$1,2-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; ●, $\{(x_1)C_5H_4O_2 + (x_2)$1,3-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; ○, $\{(x_1)C_5H_4O_2 + (x_2)$1,4-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_4CH_3\}$; +, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; ◇, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_5CH_3 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; □, $\{(x_1)C_5H_4O_2 + (x_2)$1,2-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; △, $\{(x_1)C_5H_4O_2 + (x_2)$1,3-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; ×, $\{(x_1)C_5H_4O_2 + (x_2)$1,4-$C_6H_4(CH_3)_2 + (1 - x_1 - x_2)CH_3(CH_2)_{10}CH_3\}$; ∗, $\{(x_1)C_5H_4O_2 + (x_2)C_6H_6 + (1 - x_1 - x_2)CH_3(CH_2)_{14}CH_3\}$.

phase equilibrium. Alkanes of three different chain lengths (6 and 12 and 16) were looked at to establish the effect of chain length on the phase equilibrium.

The area of the two-phase region for the mixtures (furfural + an aromatic hydrocarbon + an alkane) is significantly large, indicating the mutual immiscibility of the components of the mixture. As the number of carbon atoms in the alkane increases from 6 to 16, there is a small but significant increase in the area of the two-phase region, reflecting a decrease in the mutual solubility of the components as the alkane chain length increases. The number of methyl groups and their positions on the benzene ring do not have a dramatic effect on the ternary liquid−liquid equilibria for the mixtures looked at in this work.

The slope of the tie lines (Figure 1) indicates that the solubility of the aromatic hydrocarbon in the aliphatic rich phase increases as the carbon chain length of the alkane increases from 6 to 16. This is also reflected in Figure 2, which shows the distribution of the aromatic hydrocarbon in the aliphatic rich phase and in the furfural rich phase.

The significantly large two-phase region and the S values (ranging from 1.3 to 25) indicate that it is possible to use furfural as a solvent in liquid−liquid extraction processes for separating aromatic hydrocarbons from alkanes and related compounds.

Both the NRTL and UNIQUAC models are able to model the tie line data, but the NRTL model is the better of the two. This is most likely due to the fact that the NRTL model is a three-parameter model while the UNIQUAC model is a two-parameter model. The log γ is able to correlate the binodal curve better than the Hlavatý and the β functions.

Literature Cited

(1) Bennett, B.; Larter, S. R. Quantitative separation of aliphatic and aromatic hydrocarbons using silver ion-silica solid-phase extraction. *Anal. Chem.* **2000**, *72* (5), 1039−1044.

(2) Kabatek, R.; Browarzik, D. Role of azeotropy in true-boiling-point distillation of complex mixtures of aliphatics, aromatics and 1-butanol. *Fluid Phase Equilib.* **2001**, *178* (1−2), 131−147.

(3) Letcher, T. M.; Naicker, P. K. Liquid−Liquid Equilibria for Mixtures of an alkane + an aromatic hydrocarbon + 1,4-dicyanobutane at 298.15 K. *J. Chem. Eng. Data* **2000**, *45* (1), 104−109.

(4) Letcher, T. M.; Naicker, P. K. Ternary liquid−liquid equilibria for mixtures of an *n*-alkane + an aromatic hydrocarbon + *N*-methyl-2-pyrrolidone at 298.2 K and 1 atm. *J. Chem. Eng. Data* **1998**, *43*, 1034−1038.

(5) Hlavatý, K. Correlation of the binodal curve in a ternary mixture with one pair of immiscible liquids. *Collect. Czech. Chem. Commun.* **1972**, *37*, 4005−4007.

(6) Letcher, T. M.; Sewry, J. D.; Radloff, S. E. Liquid−liquid equilibria of benzene − water − n-alcohol at 298.15 K. *S. Afr. J. Chem.* **1990**, *43*, 56−58.

(7) Renon, H.; Prausnitz, J. M. Local composition in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135−144.

(8) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116−128.

(9) Letcher, T. M.; Sizwana, P. M. Liquid−liquid equilibria for mixtures of alkanol + water + a methyl substituted benzene at 25 °C. *Fluid Phase Equilib.* **1992**, *74*, 203-217.

(10) Briggs, S. W.; Comings, E. W. Effect of temperature on liquid−liquid equilibrium. Benzene-acetone−water and docasane-1,6-diphenylhexane-furfural systems. *Ind. Eng. Chem.* **1943**, *35*, 411−415.

(11) Treybal, R. E.; Weber, L. D.; Daley, J. F. The system acetone−water−1,1,2-trichloroethane. *Ind. Eng. Chem.* **1946**, *38*, 817−821.

(12) Perry, R. H.; Green, D. W. *Perry's Chemical Engineers Handbook*, 7th ed.; McGraw-Hill: New York, 1997.

(13) Letcher, T. M.; Redhi, G. G.; Radloff, S. E.; Domanksa, U. Liquid−liquid equilibria of the ternary mixtures with sulfolane at 303.15 K. *J. Chem. Eng. Data* **1996**, *41* (3), 634−638.

(14) Press: W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in C: The Art of Scientific Computing*; Cambridge University Press: New York, 1989.

(15) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(16) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2000.

Received for review December 4, 2001. Accepted September 25, 2002. This work was done under the auspices of a National Research Foundation (South Africa)−Forschungszentrum Juelich (Bundesrepublic Deutschland) collaboration program with additional support from the Natal University Research Grant.

JE010317U