Glossary

P	total pressure, bar
P_c	critical pressure, bar
P_i^s	vapor pressure of pure component i, bar
R	gas constant, cal K^{-1} mol^{-1}
T	temperature, K
T_c	critical temperature, K
T_r	reduced temperature
v_i	liquid molar volume of pure component i
x_i	liquid-phase mole fraction of component i
y_i	vapor-phase mole fraction of component i
Z_{RA}	modified Rackett parameter

Greek Letters

γ_i	activity coefficient of component i
Λ	Wilson binary parameter
λ	Wilson energy parameter, cal mol^{-1}

Registry No. $C_2Cl_2F_4$, 76-14-2; $C_2Cl_4F_2$, 76-12-0; $C_2Cl_3F_3$, 76-13-1.

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Vapor–Liquid Equilibria of Tetrahydrofuran Systems

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Accurate vapor–liquid equilibrium data have been measured for tetrahydrofuran separately with hexane, with cyclohexane, and with ethyl acetate at both 313.15 and 333.15 K, for ethyl acetate with cyclohexane at 313.15 K, and for a ternary mixture of ethyl acetate, cyclohexane, and tetrahydrofuran at 313.15 K. The binary data reported satisfy thermodynamic consistency tests. The results of our measurements are correlated with five thermodynamic models using the maximum likelihood parameter estimation method. The ternary data are predicted accurately by both the multicomponent Wilson and NRTL models using parameters obtained from the binary vapor–liquid equilibrium data. Also, tetrahydrofuran is found to be an effective azeotropic distillation agent for changing the relative volatility of ethyl acetate to cyclohexane and breaking the azeotrope.

Introduction

Accurate vapor–liquid equilibrium (VLE) data are important to the design of separation processes and in the testing and further development of thermodynamic models. There are few VLE studies for cyclic ethers (e.g., furfural, tetrahydrofuran) with hydrocarbons or with oxyhydrocarbons, even though cyclic ethers have been found to be useful in breaking azeotropes (*1*). For example, furfural has been used as an extractive distillation agent in separating saturated and unsaturated hydrocarbons. Therefore, studies of these systems are both important to the chemical industry and helpful in improving the predictive ability of the UNIFAC (*2*, *3*) and TOM (*4*, *5*) group-contribution activity-coefficient models.

In this study we report the results of our measurements for binary mixtures of tetrahydrofuran separately with hexane, with cyclohexane, and with ethyl acetate at both 313.15 and 333.15 K, for ethyl acetate with cyclohexane at 313.15 K, and for a ternary mixture of ethyl acetate, cyclohexane, and tetrahydrofuran at 313.15 K. From the data we obtain the excess molar Gibbs free energy, G^E, for each isotherm. For mixtures for which G^E is available at two temperatures we also calculate molar heats of mixing which we compare with direct measurements of this quantity. Our experimental data are of high quality, as evidenced by this comparison and by using thermodynamic consistency tests.

Experiments

The experimental equipment and operating procedure have been described previously (*6*). The VLE measurements were done with a Stage-Muller dynamic still, temperature measurements were made with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K, and pressures were measured with an accuracy of 0.02 kPa with a Wallace-Tiernan Model FA-187 precision mercury manometer. The vapor and liquid samples were analyzed by a Hewlett-Packard Model 5730 gas chromatograph with a Model 3390 integrator, after calibration with gravimetrically prepared samples. The compositions determined are accurate to better than 0.005 in mole fraction.

Since the purity of chemicals is essential to obtaining accurate VLE measurements, a check of the purity is very important. We checked the purity of each component first by gas chromatography, and then by comparing its vapor pressure measured in the Stage-Muller still with data in the literature. If the area fraction was greater than 0.995, and the vapor pressures were within 0.1 kPa of the reported vapor pressure data, we used the chemical for VLE measurements without purification. In this study all chemicals used were gold label quality from Aldrich Chemical Co. Tetrahydrofuran, cyclohexane, and ethyl acetate, as received, satisfied these purity tests. Our measured vapor pressure data, shown in Table I, agree with those reported in literature (*7*), as seen in Table II. However, tetrahydrofuran is hygroscopic at room temperature; tetrahydrofuran contamination by moisture is evident as anomalous vapor pressures. When this occurred, molecular sieves were used to remove the water. Hexane, which did not satisfy the purity tests, was purified by using a 13-stage Oldershaw distillation column at low pressure under a nitrogen blanket. The vapor

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Table I. The Vapor Pressures of Pure Substances

temp, K	press., kPa	temp, K	press., kPa	temp, K	press., kPa
		Tetrahydrofuran			
306.079	30.260	321.514	55.079	335.679	90.525
310.336	35.944	324.796	62.100	336.162	91.940
312.865	39.740	328.041	69.688	338.661	99.924
315.007	43.124	330.475	75.827	339.332	102.200
319.226	50.638	332.815	82.130		
		Hexane			
307.460	29.790	318.735	46.010	333.150	76.340
312.120	35.797	323.449	54.615	339.235	93.233
313.150	37.220	328.107	64.332		
		Cyclohexane			
307.520	19.540	320.935	33.348	340.050	65.760
313.150	24.614	328.196	43.616		
314.905	26.438	334.487	54.328		
		Ethyl Acetate			
308.241	20.218	325.892	42.280	333.457	56.381
311.930	23.762	330.072	49.680	338.238	67.100
316.174	28.460	330.808	51.100	343.987	82.130
321.069	34.905	330.821	51.130		

Table II. Comparison of Antoine Constants

$$\log P\ (\mathrm{kPa}) = A - \frac{B}{T\ (^\circ\mathrm{C}) + C}$$

component	A	B	C	δP,[a] kPa	reference
tetrahydrofuran	6.441 02	1384.21	246.153		this work
	6.593 72	1446.15	249.982	0.3782	Koizumi[b]
	6.120 23	1202.39	226.267	0.0236	Scott
hexane	6.137 06	1245.97	232.883		this work
	5.727 63	1031.94	208.304	0.0121	Letcher
	6.01098	1176.10	224.899	0.0816	Willingham
cyclohexane	6.15159	1301.67	233.445		this work
	6.005 69	1223.27	225.089	0.0392	Boublik
	5.975 61	1206.73	223.233	0.0352	Willingham
	5.982 26	1211.25	223.869	0.0317	Cruickshank
ethyl acetate	6.224 39	1243.97	217.792		this work
	6.202 29	1232.54	216.587	0.0125	Ambrose
	6.227 10	1245.17	217.904	0.0090	Mertl

[a] δP is the average absolute deviation from data in this work. [b] As reported in ref 7.

pressures of purified hexane, shown in Table I, agree with those reported in literature (*7*), as shown in Table II.

Because the normal boiling points of some of the substances studied are close, it is difficult to separate them by gas chromatography. Therefore, the packed column and conditions used needed to be chosen for each mixture. The tetrahydrofuran and hexane mixture was analyzed by using a Porapak P column at an oven temperature of 140 °C. The tetrahydrofuran and cyclohexane mixture was analyzed by using a Porapak QS column at an oven temperature of 180 °C. A Porapak T column at an oven temperature of 130 °C was used to analyze binary mixtures of ethyl acetate separately with tetrahydrofuran and with cyclohexane, and to analyze ethyl acetate/cyclohexane/tetrahydrofuran ternary mixtures. In each case the helium flow rate was 25 mL/min.

Calculations

An accurate determination of compositions relies on a careful calibration of the gas chromatograph. The equation used for the binary calibrations is the Redlich–Kister expansion (*8*)

$$x_1 = A_1 + A_1(1 - A_1)\sum_{j=0}^{n} p_j(2A_1 - 1)^j \tag{1}$$

where x_i is the mole fraction of component i, A_i is the area fraction of component i in GC analysis, and p_j are the adjustable parameters, typically with $n = 3$ or 4. The parameters in eq 1 were determined from calibration data with gravimetrically prepared mixtures. For a ternary mixture, an empirical equation based on the extension of eq 1 was used

$$x_1 = A_1 + G_{12} + G_{13} + G_{123}$$
$$x_2 = A_2 - G_{12} + G_{23} + G_{213}$$
$$x_3 = 1 - x_1 - x_2 \tag{2}$$

where

$$G_{ij} = A_iA_j\sum_{k=0}^{n} p_k(A_i - A_j)^k$$

$$G_{ijk} = A_iA_jA_k(q_0 + \sum_{l=1}^{m}(q_l(A_i - A_j)^l + r_l(A_i - A_k)^l))$$

p_k, q_l, r_l are adjustable parameters, with $m = 1$ or 2.

Once the compositions have been determined, the activity coefficients were calculated from the equations

$$x_i\gamma_i\Phi_i^{\mathrm{s}}P_i^{\mathrm{s}}(\mathrm{PF})_i = y_i\Phi_i^{\mathrm{v}}P \tag{3}$$

where Φ_i^{s} and Φ_i^{v} are fugacity coefficients of the pure saturated liquid and the species in the vapor, respectively, P_i^{s} is the saturated vapor pressure, and $(\mathrm{PF})_i$ is the Poynting factor of species i. In this calculation, we considered both the use of an ideal vapor phase ($\Phi_i^{\mathrm{v}} = 1$) and the use of a second virial coefficient correction for Φ_i^{v} and Φ_i^{s} using virial coefficients from the correlation of Hayden and O'Connell (*9*). The Poynting factors were calculated by the method of Yen and Woods (*10*), and the excess Gibbs free energies were calculated from

$$G^{\mathrm{EX}} = RT\sum_i x_i \ln \gamma_i \tag{4}$$

All of the binary vapor–liquid equilibrium data we measured, which are listed in Table III, satisfy the thermodynamic point-to-point consistency test (*3*). In this test the excess molar Gibbs free energies, G^{E}, were correlated by using the Legendre polynomial expression

$$G^{\mathrm{E}}/RT = x_1(1 - x_1)\sum_k^n a_kL_k(x_1) \tag{5}$$

$$L_k(x_1) = [(2k - 1)(2x_1 - 1)L_{k-1}(x_1) - (k - 1)L_{k-2}(x_1)]/k$$

$$L_0(x_1) = 1; \quad L_1(x_1) = 2x_1 - 1$$

where n is the polynomial order used, typically three to five.

Molar heats of mixing, H^{E}, were obtained from excess molar Gibbs free energies fitted to our data at two temperatures by using

$$H^{\mathrm{E}} = \frac{\partial(G^{\mathrm{E}}/T)}{\partial(1/T)} \tag{6}$$

where the partial derivative was approximated by a finite difference since the isotherms in our measurements were separated by only 20 K.

If a binary mixture forms an azeotrope, at the azeotropic composition

$$x_1 = y_1 \tag{7}$$

Substituting this equality in eq 3 indicates that the azeotropic composition can be determined from

$$\gamma_1\Phi_1^{\mathrm{s}}P_1^{\mathrm{s}}(\mathrm{PF})_1\Phi_2^{\mathrm{v}} - \gamma_2\Phi_2^{\mathrm{s}}P_2^{\mathrm{s}}(\mathrm{PF})_2\Phi_1^{\mathrm{v}} = 0 \tag{8}$$

which must be solved by iteration since both γ_i and Φ_i^{v} are

Table III. Binary Experimental Vapor-Liquid Equilibrium Data[a]

P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1	P, kPa	x_1	y_1
Tetrahydrofuran (1)/Cyclohexane (2) at 333.15 K											
51.960	0.0000	0.0000	69.450	0.2880	0.4354	79.821	0.6483	0.7180	83.100	0.9300	0.9328
52.760	0.0085	0.0259	72.300	0.3566	0.5026	81.020	0.7214	0.7681	83.130	0.9644	0.9646
55.300	0.0373	0.0913	74.665	0.4288	0.5590	81.803	0.7809	0.8123	83.140	0.9851	0.9848
58.522	0.0786	0.1719	76.850	0.5139	0.6209	82.460	0.8342	0.8528	83.114	0.9982	0.9970
62.670	0.1554	0.2874	78.420	0.5780	0.6687	82.875	0.8871	0.8955	83.110	1.0000	1.0000
66.460	0.2162	0.3669									
Tetrahydrofuran(1)/Cyclohexane (2) at 313.15 K											
24.614	0.0000	0.0000	31.580	0.1922	0.3491	38.040	0.5629	0.6609	40.330	0.9361	0.9347
24.930	0.0058	0.0153	32.803	0.2434	0.4051	38.818	0.6359	0.7120	40.340	0.9585	0.9573
25.393	0.0158	0.0405	34.254	0.3091	0.4677	39.650	0.7498	0.7879	40.295	0.9831	0.9821
26.160	0.0334	0.0828	35.223	0.3575	0.5081	40.005	0.8088	0.8313	40.274	0.9884	0.9874
27.342	0.0599	0.1458	36.030	0.4038	0.5483	40.140	0.8553	0.8672	40.246	0.9925	0.9919
28.770	0.0959	0.2086	37.206	0.4696	0.6043	40.310	0.9003	0.9040	40.200	1.0000	1.0000
Tetrahydrofuran (1)/Hexane (2) at 313.15 K											
37.220	0.0000	0.0000	43.040	0.2470	0.3228	44.830	0.7113	0.6773	41.770	0.9484	0.9204
37.624	0.0108	0.0192	44.076	0.3462	0.4094	44.282	0.7923	0.7445	40.882	0.9793	0.9658
38.780	0.0459	0.0792	44.670	0.4253	0.4687	43.625	0.8469	0.7979	40.334	0.9959	0.9929
40.171	0.0967	0.1536	45.020	0.4975	0.5224	42.705	0.9078	0.8661	40.200	1.0000	1.0000
41.725	0.1661	0.2402	45.113	0.6195	0.6106						
Tetrahydrofuran (1)/Hexane (2) at 333.15 K											
76.340	0.0000	0.0000	88.440	0.3061	0.3695	91.230	0.7067	0.6823	85.690	0.9528	0.9305
77.092	0.0123	0.0205	90.115	0.3987	0.4470	90.365	0.7878	0.7523	84.250	0.9809	0.9699
79.193	0.0483	0.0752	91.125	0.4813	0.5109	88.980	0.8600	0.8185	83.275	0.9967	0.9947
82.670	0.1093	0.1696	91.647	0.5790	0.5854	87.375	0.9108	0.8768	83.100	1.0000	1.0000
85.900	0.2026	0.2707	91.600	0.6249	0.6191						
Tetrahydrofuran (1)/Ethyl Acetate (2) at 313.15 K											
25.050	0.0000	0.0000	28.850	0.1974	0.2881	34.556	0.5660	0.6722	39.050	0.9050	0.9339
25.250	0.0079	0.0143	30.650	0.3133	0.4299	35.708	0.6474	0.7400	39.840	0.9614	0.9729
26.043	0.0468	0.0832	32.229	0.4058	0.5217	36.959	0.7339	0.8077	40.159	0.9898	0.9923
27.238	0.1118	0.1769	33.905	0.5233	0.6362	38.040	0.8194	0.8726	40.200	1.0000	1.0000
Tetrahydrofuran (1)/Ethyl Acetate (2) at 333.15 K											
55.858	0.0000	0.0000	62.400	0.1940	0.2736	71.880	0.5234	0.6184	80.365	0.8736	0.9061
56.160	0.0074	0.0123	65.115	0.2800	0.3776	74.052	0.6095	0.6949	81.570	0.9262	0.9455
57.492	0.0465	0.0737	67.754	0.3879	0.4846	76.462	0.7067	0.7758	82.210	0.9554	0.9661
59.500	0.1068	0.1589	70.509	0.4727	0.5742	78.631	0.7966	0.8464	83.100	1.0000	1.0000
Ethyl Acetate (1)/Cyclohexane (2) at 313.15 K											
24.620	0.0000	0.0000	32.434	0.3414	0.4158	32.630	0.5896	0.5411	28.450	0.9142	0.8145
25.150	0.0043	0.0242	32.738	0.4375	0.4645	32.208	0.6837	0.5941	26.765	0.9641	0.9109
28.928	0.0858	0.2033	32.828	0.4875	0.4883	31.395	0.7715	0.6563	25.375	0.9958	0.9871
30.745	0.1642	0.2976	32.780	0.5177	0.5039	30.183	0.8526	0.7346	25.050	1.0000	1.0000
31.830	0.2572	0.3666									

[a] x_1, liquid mole fraction. y_1, vapor mole fraction.

functions of composition. The terms Φ_i^s and $(PF)_i$ were taken to be constants close to unity in this calculation.

Results and Discussion

We correlated our VLE data with five liquid activity coefficient models using the maximum likelihood parameter estimation method (11). The results are compared in Table IV. The experimental data together with the models which lead to the best correlation are plotted in Figures 1-4.

Our results show that, for the binary systems studied, the Wilson and NRTL local composition models lead to slightly better correlations of the data than the other models considered. Tetrahydrofuran forms an azeotrope with hexane and with cyclohexane, while it forms an almost ideal solution with ethyl acetate. Also ethyl acetate forms an azeotrope with cyclohexane. All binary azeotropic compositions and pressures determined in this work are listed in Table V. Also, the molar heats of mixing for tetrahydrofuran with hexane and with cyclohexane calculated from isothermal VLE data are in excellent agreement with the directly measured values (12) as shown in Figures 5 and 6.

Ternary VLE data measured for the ethyl acetate + cyclohexane + tetrahydrofuran mixture at 313.15 K are listed in Table VI. These ternary data were used to test the predictions

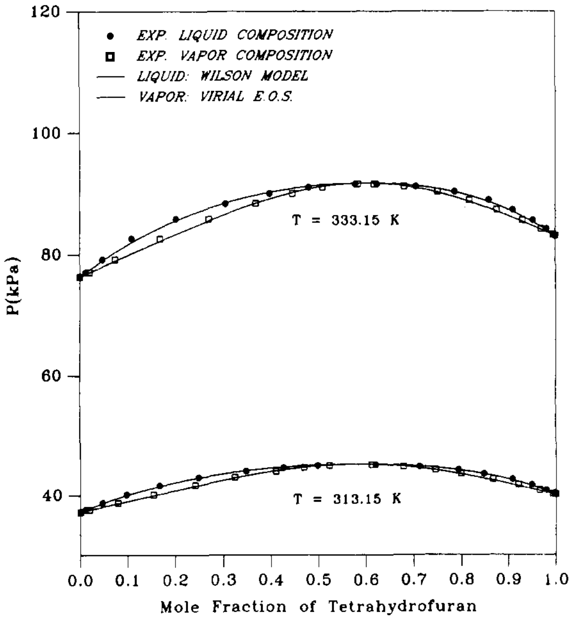

Figure 1. Binary VLE of tetrahydrofuran + hexane at 313.15 and 333.15 K.

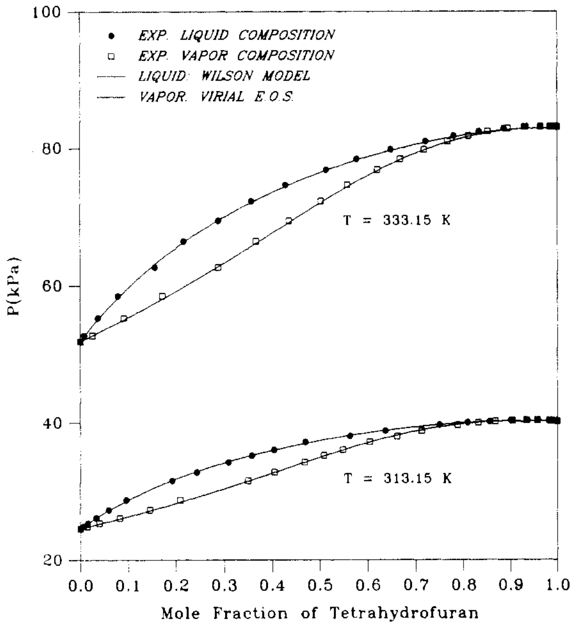

Figure 2. Binary VLE of tetrahydrofuran + cyclohexane at 313.15 and 333.15 K.

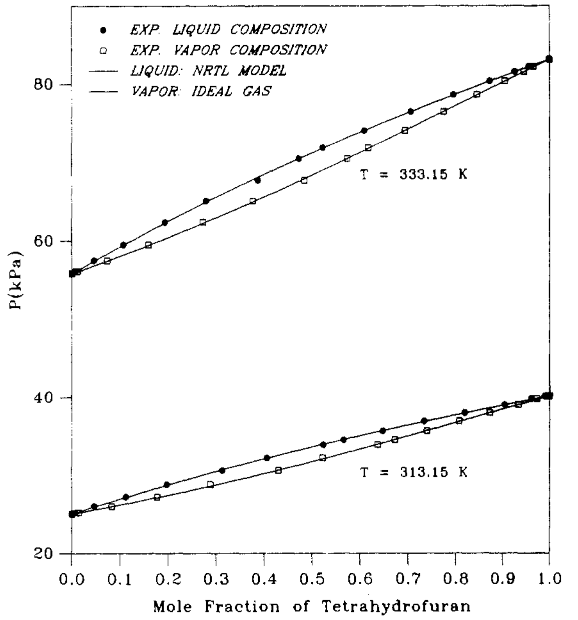

Figure 3. Binary VLE of tetrahydrofuran + ethyl acetate at 313.15 and 333.15 K.

of the five multicomponent liquid activity coefficient models considered earlier, using parameters obtained from only binary VLE data. The results, in Table VII, show that the multicomponent Wilson and NRTL models give excellent predictions. Indeed, the average absolute deviations in both vapor compositions and equilibrium pressures between the predictions and measurements are even smaller than was the case in the correlations of the binary data. However, the other models we considered gave poorer multicomponent predictions, even though they resulted in correlations of binary data of similar accuracy to the Wilson and NRTL models. The UNIFAC model with parameter values from the literature gave the poorest predictions.

The ternary data are also of interest in determining the effectiveness of tetrahydrofuran as an azeotropic distillation agent for the ethyl acetate + cyclohexane system. Figure 7 contains the vapor-liquid equilibrium envelope for this ternary system at 313.15 K calculated with multicomponent Wilson model. Clearly

Table IV. Comparison of VLE Data with Five Liquid Activity Models[a]

		313.15 K		333.15 K	
		AADY	AADP, kPa	AADY	AADP, kPa
		Tetarahydrofuran/Hexane			
Margules	(A)	0.0023	0.096	0.0029	0.180
	(B)	0.0014	0.100	0.0018	0.187
Van Laar	(A)	0.0023	0.091	0.0028	0.169
	(B)	0.0011	0.096	0.0017	0.177
Wilson	(A)	0.0022	0.084	0.0027	0.164
	(B)	0.0011	0.089	0.0016	0.169
NRTL	(A)	0.0022	0.091	0.0028	0.169
	(B)	0.0011	0.095	0.0017	0.179
UNIQUAC	(A)	0.0017	0.095	0.0028	0.165
	(B)	0.0011	0.095	0.0016	0.169
		Tetrahydrofuran/Cyclohexane			
Margules	(A)	0.0035	0.069	0.0020	0.095
	(B)	0.0032	0.068	0.0020	0.091
Van Laar	(A)	0.0035	0.069	0.0021	0.099
	(B)	0.0032	0.068	0.0020	0.092
Wilson	(A)	0.0035	0.068	0.0020	0.092
	(B)	0.0032	0.067	0.0019	0.089
NRTL	(A)	0.0036	0.069	0.0020	0.097
	(B)	0.0032	0.068	0.0020	0.089
UNIQUAC	(A)	0.0035	0.069	0.0020	0.107
	(B)	0.0032	0.067	0.0017	0.120
		Tetrahydrofuran/Ethyl Acetate			
Margules	(A)	0.0027	0.063	0.0013	0.079
	(B)	0.0036	0.077	0.0024	0.128
Van Laar	(A)	0.0028	0.064	0.0013	0.077
	(B)	0.0036	0.077	0.0017	0.088
Wilson	(A)	0.0027	0.063	0.0013	0.080
	(B)	0.0036	0.077	0.0024	0.127
NRTL	(A)	0.0027	0.063	0.0013	0.081
	(B)	0.0036	0.077	0.0024	0.128
UNIQUAC	(A)	0.0030	0.066	0.0014	0.100
	(B)	0.0037	0.081	0.0015	0.105
		Ethyl Acetate/Cyclohexane			
Margules	(A)	0.0043	0.174		
	(B)	0.0039	0.181		
Van Laar	(A)	0.0042	0.171		
	(B)	0.0038	0.179		
Wilson	(A)	0.0043	0.137		
	(B)	0.0026	0.147		
NRTL	(A)	0.0039	0.164		
	(B)	0.0034	0.172		
UNIQUAC	(A)	0.0040	0.168		
	(B)	0.0036	0.172		

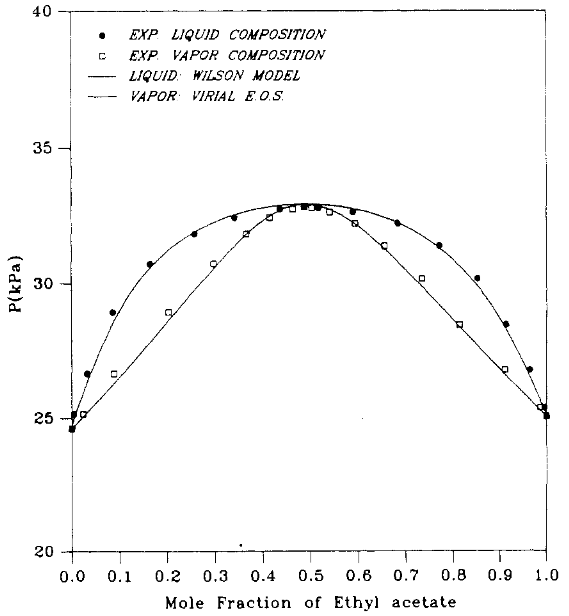

Figure 4. Binary VLE of ethyl acetate + cyclohexane at 313.15 K.

Table V. Azeotropic Data

mixture	temp, K	press., kPa	composn (1)
tetrahydrofuran (1)/hexane (2)	313.15	45.153	0.5881
tetrahydrofuran (1)/hexane (2)	333.15	91.639	0.6102
tetrahydrofuran (1)/cyclohexane (2)	313.15	40.313	0.9313
tetrahydrofuran (1)/cyclohexane (2)	333.15	83.137	0.9737
ethyl acetate (1)/cyclohexane (2)	313.15	32.822	0.4876

Table VI. Ternary Experimental Vapor-Liquid Equilibrium Data for Ethyl Acetate (1)/Cyclohexane (2)/Tetrahydrofuran (3) at 313.15 K[a]

P, kPa	x_1	x_2	y_1	y_2
32.479	0.1475	0.7543	0.2309	0.6160
33.924	0.2855	0.5900	0.3246	0.5086
33.982	0.4499	0.4317	0.4204	0.4359
33.217	0.6110	0.2755	0.5144	0.3476
32.224	0.7050	0.1877	0.5790	0.2821
34.115	0.1282	0.6684	0.1710	0.5288
35.038	0.2551	0.5150	0.2640	0.4456
34.921	0.3993	0.3765	0.3559	0.3789
34.187	0.5391	0.2388	0.3645	0.2485
33.044	0.6461	0.1644	0.5207	0.2418
35.540	0.1126	0.5729	0.1303	0.4518
36.156	0.2187	0.4381	0.2088	0.3816
35.883	0.3415	0.3235	0.2906	0.3231
34.024	0.5594	0.1436	0.4376	0.2033
36.748	0.0961	0.4851	0.1021	0.3868
37.140	0.1835	0.3615	0.1655	0.3189
36.808	0.2860	0.2664	0.2320	0.2671
36.022	0.3926	0.1668	0.3004	0.1992
35.060	0.4666	0.1201	0.3571	0.1617
37.850	0.0791	0.3944	0.0751	0.3248
37.993	0.1523	0.2896	0.1275	0.2631
37.609	0.2313	0.2134	0.1826	0.2146
36.830	0.3124	0.1369	0.2394	0.1570
36.061	0.3791	0.0956	0.2812	0.1234
38.652	0.0644	0.3121	0.0560	0.2673
38.573	0.1207	0.2319	0.0969	0.2146
38.213	0.1881	0.1669	0.1404	0.1710
37.528	0.2531	0.1068	0.1852	0.1230
36.905	0.3014	0.0737	0.2202	0.0922
39.257	0.0513	0.2448	0.0420	0.2175
39.050	0.0979	0.1840	0.0761	0.1765
39.350	0.0920	0.0784	0.0670	0.0849
38.122	0.1998	0.0814	0.1465	0.0929
37.620	0.2434	0.0545	0.1778	0.0674

[a] x_i, liquid mole fraction of component i. y_i, vapor mole fraction of component i.

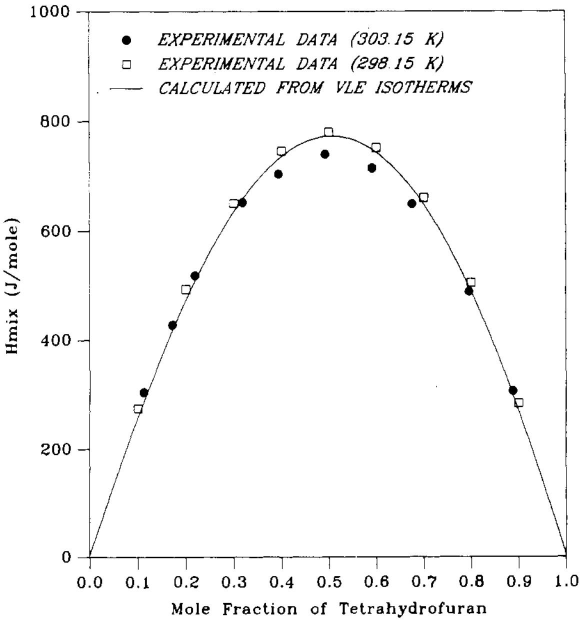

Figure 5. Heats of mixing of tetrahydrofuran + hexane.

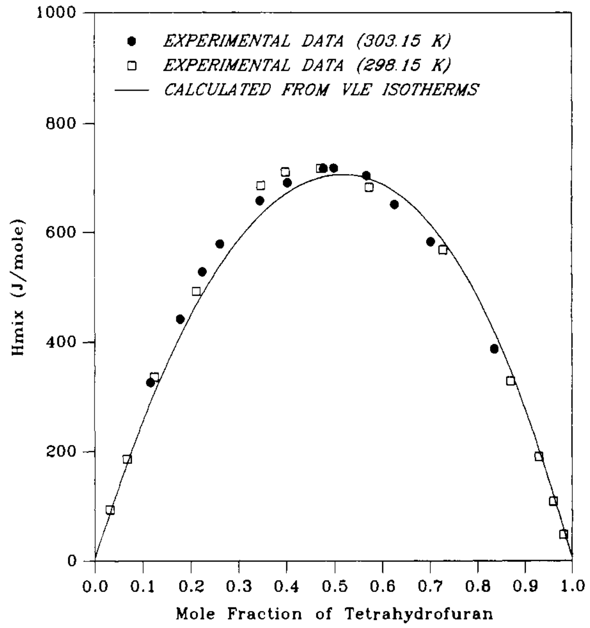

Figure 6. Heats of mixing of tetrahydrofuran + cyclohexane.

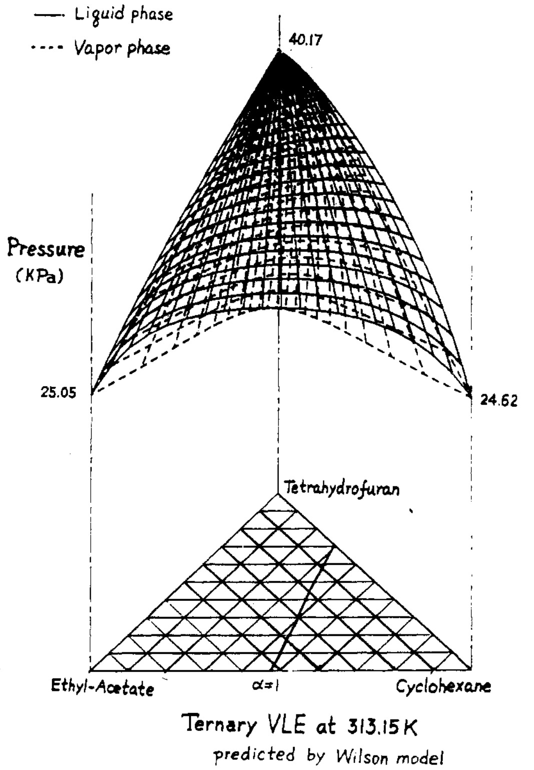

Figure 7. Ternary VLE of ethyl acetate + cyclohexane + tetrahydrofuran at 313.15 K.

Table VII. Prediction of Ternary VLE by Six Liquid Activity Models Using Binary Parameters Only and Incorporated with Virial Equation of State for Ethyl Acetate/Cyclohexane/Tetrahydrofuran

	313.15 K	
	AAD(Y_1) + (Y_2) + (Y_3)	AADP, kPa
Margules	0.0274	3.094
Van Laar	0.0093	1.542
Wilson	0.0019	0.073
NRTL	0.0020	0.076
UNIQUAC	0.0049	0.309
UNIFAC	0.0627	9.793

no ternary azeotrope exists, as there is no maximum, minimum, or saddle-point pressure in this figure. Thus, tetrahydrofuran can be useful for breaking the ethyl acetate and cyclohexane azeotrope. The situation of equal ethyl acetate/cyclohexane relative volatility, which is the formation of a pseudoazeotrope, disappears when the tetrahydrofuran liquid-phase mole fraction exceeds 70 mol % as is also shown in this figure.

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Correlation of Phase Equilibria of Naphtha Reformate with Sulfolane

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Liquid–liquid equilibria of the ternary systems *n*-hexane–benzene–sulfolane, *n*-heptane–toluene–sulfolane, and octane–xylene–sulfolane have been determined at temperatures of 30, 35, and 40 °C. The equilibria were measured with a thermostatically controlled Smith–Bonner cell. The work was then extended to a multicomponent system. A feed with a composition typical of a reformate containing 55% aromatics was extracted with sulfolane and the phase equilibria were determined. The data were correlated by using Hand's method and were found to be in good agreement with theoretical predictions using the UNIFAC method.

Introduction

The excellent performance of sulfolane as a solvent for the extraction of aromatics has been demonstrated by commercial operation of the sulfolane process over several years in a large number of units (*1*). Simultaneous extraction of BTX from both reformate and hydrotreated pyrolysis naphthas yields aromatic products of 99% purity (*2*). In the present investigation the liquid–liquid equilibria of four systems containing sulfolane have been determined and the data correlated by using Hand's equation. The UNIFAC method was subsequently applied to predict comparable data.

Table I. Experimental LLE Compositions for *n*-Hexane–Benzene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-hexane	benzene	sulfolane	*n*-hexane	benzene	sulfolane
0.990		0.009	0.006		0.993
0.851	0.131	0.018	0.015	0.083	0.891
0.705	0.26	0.034	0.047	0.181	0.771
0.512	0.392	0.995	0.088	0.281	0.62

Table II. Experimental LLE Compositions for *n*-Heptane–Toluene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-heptane	toluene	sulfolane	*n*-hexane	toluene	sulfolane
0.981		0.018	0.01		0.989
0.025	0.155	0.899	0.012	0.049	0.938
0.029	0.228	0.742	0.015	0.088	0.896
0.031	0.272	0.696	0.017	0.126	0.856

Table III. Experimental LLE Compositions for *n*-Octane–Xylene–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
n-octane	xylene	sulfolane	*n*-octane	xylene	sulfolane
0.983		0.017	0.005		0.994
0.865	0.123	0.021	0.008	0.085	0.907
0.812	0.161	0.026	0.019	0.125	0.855
0.675	0.289	0.036	0.029	0.185	0.785

Table IV. Experimental LLE Compositions for Nonaromatics–Aromatics–Sulfolane at 30 °C

wt fraction in raffinate			wt fraction in extract		
non-aromatic	aromatic	sulfolane	non-aromatic	aromatic	sulfolane
0.845	0.144	0.012	0.007	0.048	0.944
0.783	0.204	0.013	0.012	0.072	0.916
0.731	0.255	0.014	0.016	0.142	0.842
0.550	0.422	0.029	0.02	0.231	0.749

Experimental Investigation

Purity of Materials. The toluene and benzene used had a minimum purity of 99.5%. Sulfolane, obtained from Fluka AG, Chemical Fabrickin, Switzerland, was predistilled in a packed column of 2 m length and 10 cm diameter and had a maximum water content of 0.05%. Hexane, heptane, octane, and xylene were obtained from BDH Ltd, UK.

Equilibrium Measurements. Measurements were made using a Smith–Bonner cell (*3*) controlled at a temperature of 30, 35, or 40 °C. Specific amounts of A (the nonaromatic) and the solute C (the aromatic) were introduced into the cell and agitated while maintained at a constant temperature by circulation

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