Glossary

K	equilibrium ratio y/x
K_{CO_2}	equilibrium ratio for carbon dioxide
$K_{neo\text{-}C_5}$	equilibrium ratio for neopentane
P	pressure
T	temperature
x	mole fraction of component in liquid phase
y	mole fraction of component in vapor phase

Registry No. CO_2, 124-38-9; neopentane, 463-82-1.

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Vapor-Liquid Equilibria for Binary Mixtures of Butyl Ether with 2-Furaldehyde and with 2-, 3-, and 4-Heptanone

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Isomeric effect on group-contribution liquid-activity models has been investigated by accurate measurement of vapor-liquid equilibria of butyl ether separately with 2-, 3-, and 4-heptanone, each on two isotherms. We also report data for butyl ether and 2-furaldehyde on two isotherms. The data reported satisfy thermodynamic consistency tests. The results of our measurements are correlated with five thermodynamic models by using the maximum likelihood parameter estimation method. A previously unavailable pair of UNIFAC interaction parameters for the furfural group with an ether group are also estimated from our data.

Introduction

Highly accurate vapor-liquid equilibria (VLE) are important to the design of separation processes and in the testing and further development of thermodynamic models. Recent group-contribution activity-coefficient models, e.g., UNIFAC (*1*, *2*) or TOM (*3*, *4*), are useful predictive models, but they do have some limitations. For example, the UNIFAC model cannot differentiate between some isomers, while isomeric mixtures do occur quite often in chemical processing. The TOM Project differentiates between isomers (*5*), but its further development will need additional accurate measurements, such as the data reported here. In this study the VLE of butyl ether separately with three isomers of heptanone were measured, and the experimental data compared with the predictions of the UNIFAC model. We have also measured the VLE of butyl ether with 2-furaldehyde (or furfural) and used these data to estimate the previously unavailable UNIFAC interaction parameters for the furfural group with an ether group.

In this study we report the results of our measurements of the pure component vapor pressures of butyl ether, and of 2-, 3-, and 4-heptanone, and the binary VLE of butyl ether separately with 2-heptanone at 363.15 and 393.22 K, with 3-heptanone and 4-heptanone at 363.15 and 393.15 K, and with furfural at 368.15 and 388.15 K. Our experimental data satisfy the thermodynamic consistency tests. Data reduction was carried out to determine the excess molar Gibbs free energies, G^E, for each isotherm, and to calculate molar heat of mixing using the Gibbs-Helmholtz relation.

Experiments

The experimental equipment and operating procedure have been described previously (*5*). Due to the rapid oxidation and autooxidation of furfural, the special methods of handling furfural previously reported (*6*) were used. The VLE measurements for both pure components and mixtures were made with a Stage-Muller dynamic still. The temperature was measured with a platinum resistance thermometer (Rosemount Model 162N) accurate to 0.02 K with a resolution of 0.001 K. Pressure was measured with an accuracy of 0.02 kPa by using a Wallace-Tiernan Model FA-187 precision mercury manometer. Vapor and liquid equilibrium 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 for accurate VLE measurements, we checked the purity of each chemical first by measuring its area fraction by gas chromatography, and then by comparing its pure component vapor pressure measured in the Stage-Muller still with data reported in the literature. In this study all chemicals used were from the Aldrich Chemical Co. Butyl ether was Gold Label quality of 99.9% purity by GC analysis as received. However, butyl ether is highly hygroscopic, and we found that it was rapidly contaminated by moisture. Therefore, when measuring the butyl ether vapor pressure, we constantly checked the water content of the solution in our still by gas chromatography. When the water content was above 0.1%, the still contents were replaced with fresh anhydrous butyl ether. Our measured butyl ether vapor pressure data are shown in Table I, and compared, in Table II, with predictions using Antoine constants reported in literature (*7*). We believe our vapor pressure data to be correct and that the higher vapor pressures reported previously in the literature are likely to result from contamination by water. The Antoine constants for furfural were found to be the same as in our previous report (*6*). The heptanones did not satisfy our purity tests as received and were purified to 99.9% by using a 13-stage Oldershaw distillation column at low pressure under a nitrogen blanket. The vapor pressures of three purified hep-

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Table I. Pure Component Vapor Pressures

temp, K	press., kPa	temp, K	press., kPa
2-Heptanone			
355.050	9.870	374.010	20.761
355.114	9.885	379.430	25.323
358.790	11.520	383.994	29.691
362.368	13.333	388.694	34.815
365.550	15.047	393.241	40.521
367.855	16.515	398.570	48.088
369.195	17.337	403.295	55.740
3-Heptanone			
354.743	11.050	383.422	32.582
358.551	12.928	388.829	39.133
363.150	15.510	393.150	45.117
368.075	18.750	398.825	54.015
373.905	23.273	404.277	64.025
378.195	27.114		
4-Heptanone			
358.408	14.540	388.555	43.171
363.405	17.721	393.628	50.950
369.989	22.690	398.496	59.150
377.660	29.934	403.769	69.393
383.650	36.628		
Butyl Ether			
355.716	14.436	383.822	39.909
359.845	16.962	388.213	45.980
363.280	19.328	393.125	53.685
368.264	23.232	398.295	63.110
373.215	27.750	403.540	73.745
378.390	33.218		

Table II. Comparison of Antoine Constants[a]

component	A	B	C	δP,[b] kPa	reference
butyl ether	6.36199	1578.979	220.947		this work
	5.92274	1298.256	191.144	1.726	*7*
furfural	5.58132	1138.837	155.741		*5*
2-heptanone	6.29277	1541.897	209.037		this work
	6.14611	1460.280	201.636	0.008	*8*
	6.08559	1420.790	197.370	0.167	*10*
3-heptanone	6.50078	1665.216	223.583		this work
	7.58830	2347.000	273.000	−2.984	*10*
4-heptanone	6.11097	1408.740	199.387		this work
	6.19102	1473.270	205.685	−2.776	*9*
	7.11820	2132.000	273.000	−0.425	*10*

[a] $\log P\ (\text{kPa}) = A - B/(T\ (°\text{C}) + C)$. [b] δP = mean deviation from data in Table I.

tanones, shown in Table I, are compared in Table II to predictions using Antoine constants reported in literature (*8–10*).

The packed column and conditions used in the gas chromatographic analysis were chosen for each mixture. The butyl ether/furfural mixture was analyzed by using a Porapak P column at an oven temperature of 180 °C. Mixtures of butyl ether with 2-heptanone and with 3-heptanone were analyzed with a Porapak P column at an oven temperature of 170 °C. A Porapak QS column at an oven temperature of 225 °C was used to analyze binary mixtures of butyl ether with 4-heptanone. In each case, the helium flow rate was 25 mL/min.

Calculations

An accurate determination of compositions relies on a good calibration of the gas chromatograph. The equation used for a binary mixture calibration was the Redlich–Kister expansion (*11*)

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

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 is the adjustable parameter in the correlation equation. Typically we used n = 3 or 4 in the calibrations and the parameters were determined from calibration data with gravimetrically prepared mixtures.

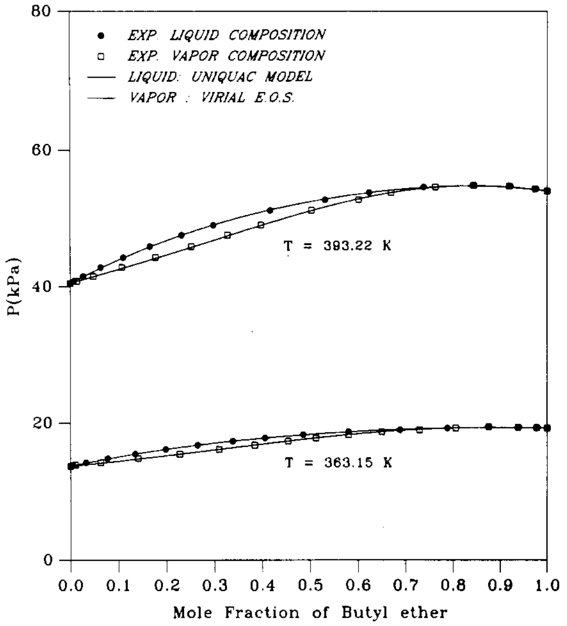

Figure 1. Butyl ether (1)/2-heptanone (2) VLE at 363.15 and 393.22 K.

Once the compositions had been determined, the activity coefficients were calculated from the equation

$$x_i\gamma_i\Phi_i^{s}P_i^{s}(\text{PF})_i = y_i\Phi_i^{v}P \qquad (2)$$

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 $(\text{PF})_i$ is the Poynting factor of species i. In this calculation, we considered both the use of an ideal vapor phase ($\Phi_i^v \doteq 1$) 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 (*12*). The Poynting factors were calculated by the method of Yen and Woods (*13*) and were only very slightly different from unity. The excess Gibbs free energies were then calculated from

$$G^{\text{EX}} = RT\sum_i x_i \ln \gamma_i \qquad (3)$$

The quality of these experimental data was examined by the thermodynamic point-to-point consistency test described by Fredenslund et al. (*2*). In this test the excess molar Gibbs free energies, G^{E}, were fitted to the Legendre polynomial expression

$$G^{\text{E}}/RT = x_1(1 - x_1)\sum_k^n a_k L_k(x_1) \qquad (4)$$

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

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

where n is the polynomial order used, typically three to five. Our data satisfied this point-to-point consistency test in that the deviations between calculated and experimental vapor-phase mole fractions were all less than 0.01 and the deviations in pressure were all less than 0.2 kPa.

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

$$x_1 = y_1 \qquad (5)$$

Substituting this equality into eq 2 indicates that the azeotropic composition can be determined from

$$\gamma_1\Phi_1^{s}P_1^{s}(\text{PF})_1\Phi_2^{v} - \gamma_2\Phi_2^{s}P_2^{s}(\text{PF})_2\Phi_1^{v} = 0 \qquad (6)$$

Table III. Experimental Vapor–Liquid Equilibria[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
Butyl Ether (1)/Furfural (2) at 368.15 K											
10.973	0.0000	0.0000	21.780	0.1786	0.5600	24.700	0.4591	0.6543	25.441	0.8014	0.7711
13.602	0.0219	0.2067	22.316	0.2021	0.5751	25.000	0.5271	0.6671	25.200	0.8601	0.8135
15.300	0.0381	0.3078	23.268	0.2751	0.6066	25.300	0.6002	0.6860	24.796	0.9045	0.8522
18.125	0.0806	0.4416	23.808	0.3317	0.6227	25.410	0.6749	0.7109	23.141	1.0000	1.0000
20.403	0.1284	0.5212	24.260	0.3794	0.6352	25.460	0.7277	0.7316			
Butyl Ether (1)/Furfural (2) at 388.15 K											
23.711	0.0000	0.0000	42.700	0.1750	0.5219	49.690	0.5313	0.6511	50.580	0.8099	0.7719
26.250	0.0112	0.1061	46.610	0.3065	0.5872	50.085	0.5869	0.6669	49.802	0.8798	0.8284
29.040	0.0256	0.1998	47.590	0.3559	0.6036	50.546	0.6529	0.6885	48.118	0.9505	0.9164
31.680	0.0421	0.2695	48.582	0.4163	0.6202	50.745	0.7461	0.7329	45.910	1.0000	1.0000
36.015	0.0784	0.3934									
Butyl Ether (1)/2-Heptanone (2) at 363.15 K											
13.723	0.0000	0.0000	16.161	0.1981	0.3090	18.303	0.4852	0.5801	19.447	0.8739	0.8752
13.909	0.0055	0.0105	16.775	0.2647	0.3838	18.748	0.5800	0.6499	19.371	0.9404	0.9379
14.256	0.0322	0.0633	17.345	0.3380	0.4535	18.995	0.6884	0.7295	19.304	0.9797	0.9776
14.833	0.0775	0.1409	17.813	0.4053	0.5125	19.247	0.7878	0.8055	19.271	1.0000	1.0000
15.501	0.1351	0.2277									
Butyl Ether (1)/2-Heptanone (2) at 393.22 K											
40.495	0.0000	0.0000	44.250	0.1107	0.1783	51.131	0.4177	0.5043	54.752	0.8414	0.8443
40.783	0.0073	0.0138	45.870	0.1663	0.2532	52.673	0.5327	0.6029	54.650	0.9222	0.9191
41.514	0.0273	0.0490	47.506	0.2323	0.3287	53.735	0.6245	0.6713	54.257	0.9770	0.9750
42.810	0.0639	0.1082	48.974	0.2986	0.3985	54.532	0.7389	0.7634	53.948	1.0000	1.0000
Butyl Ether (1)/3-Heptanone (2) at 363.15 K											
15.510	0.0000	0.0000	17.350	0.2006	0.2782	19.029	0.5134	0.5690	19.541	0.8861	0.8802
15.617	0.0108	0.0186	17.906	0.2799	0.3625	19.350	0.6088	0.6476	19.420	0.9509	0.9451
15.848	0.0323	0.0542	18.367	0.3537	0.4325	19.515	0.7062	0.7255	19.317	0.9860	0.9847
16.260	0.0722	0.1143	18.715	0.4339	0.5042	19.594	0.8036	0.8044	19.271	1.0000	1.0000
16.778	0.1278	0.1917									
Butyl Ether (1)/3-Heptanone (2) at 393.15 K											
45.117	0.0000	0.0000	49.118	0.1717	0.2328	53.905	0.5162	0.5640	55.110	0.8787	0.8735
45.893	0.0267	0.0426	50.498	0.2484	0.3181	54.603	0.6082	0.6406	54.704	0.9349	0.9291
46.800	0.0595	0.0892	51.627	0.3207	0.3883	55.045	0.7009	0.7133	54.350	0.9718	0.9686
47.844	0.1097	0.1557	52.598	0.4019	0.4629	55.308	0.7897	0.7904	53.764	1.0000	1.0000
Butyl Ether (1)/4-Heptanone (2) at 363.15 K											
17.534	0.0000	0.0000	18.818	0.1754	0.2233	19.973	0.4568	0.4935	19.585	0.9332	0.9188
17.670	0.0151	0.0212	19.238	0.2595	0.3112	20.185	0.5632	0.5830	19.350	0.9838	0.9793
17.919	0.0465	0.0654	19.566	0.3436	0.3902	20.202	0.6884	0.6858	19.271	1.0000	1.0000
18.323	0.1017	0.1374	19.813	0.4161	0.4568	19.982	0.8230	0.8046			
Butyl Ether (1)/4-Heptanone (2) at 393.15 K											
50.142	0.0000	0.0000	54.405	0.2449	0.2858	56.350	0.6050	0.6096	54.750	0.9399	0.9280
50.722	0.0297	0.0393	55.215	0.3382	0.3757	56.362	0.6632	0.6581	54.021	0.9838	0.9797
52.008	0.0897	0.1161	55.914	0.4316	0.4595	56.010	0.7877	0.7718	53.831	1.0000	1.0000
53.405	0.1667	0.2044	56.295	0.5227	0.5384	55.434	0.8670	0.8497			

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

which must be solved by iteration since both γ_i and Φ_i^V are functions of composition.

Results and Discussion

All binary vapor–liquid equilibrium data we measured are listed in Table III. The experimental VLE data were correlated by five liquid activity coefficient models using the maximum likelihood parameter estimation method. The results of the correlation are compared and the model parameters given in Table IV. The experimental data together with the model results which led to the best correlation are plotted in Figures 1–4. All binary azeotropic compositions and pressures calculated in this work are listed in Table V.

Molar heats of mixing, H^E, were estimated from the fitted excess molar Gibbs free energies at two temperatures by the Gibbs–Helmholtz relation

$$H^E = \frac{\partial(G^E/T)}{\partial(1/T)} \qquad (7)$$

where the partial differentiation was calculated by the finite difference approximation. The molar heats of mixing calculated from isothermal VLE data by using five two-constant liquid activity coefficient models for butyl ether with the 2- and 4-heptanone agree with directly measured data for these systems (*14*) as shown in Figures 5 and 6. We also calculated the heats of mixing using the Legendre polynomial expressions for G^E with parameters obtained in the point-to-point consistency test. However, these results differ from the measured heats of mixing, as shown in Figure 7. In particular, the higher the order of Legendre polynomial used for the G^E model, the more oscillatory were the estimated heats of mixing. From this we see that, in the calculation of the molar heats of mixing from the temperature dependence of a G^E model, the use of a Legendre polynomial with the number of adjustable parameters ≥ 3, even though it is more flexible, may lead to misleading results. In contrast, the predictions from the two-constant liquid activity coefficient models, with parameters fit at each temperature, are in good agreement with data obtained from direct heats of mixing measurements. The possible problem arising from the use of too high an order Legendre polynomial when fitting G^E data is especially apparent for the systems studied

Table IV. Comparison of Five Two-Constant Activity-Coefficient Models[a]

model	temp, K	Λ_{12}	Λ_{21}	δP, kPa	δy_1
Butyl Ether (1)/Furfural (2)					
Margules	368.15	1.55756	−0.16012	0.148	0.0059
	388.15	1.44896	−0.10889	0.392	0.0077
Van Laar	368.15	1.73726	1.43330	0.143	0.0051
	388.15	1.55089	1.35421	0.392	0.0085
Wilson	368.15	0.24003	0.47987	0.059	0.0054
	388.15	0.30255	0.48952	0.140	0.0052
NRTL[b]	368.15	1647.770	4044.316	0.088	0.0041
	388.15	1865.113	3533.111	0.336	0.0076
UNIQUAC	368.15	1700.010	53.903	0.108	0.0045
	388.15	1705.583	17.813	0.300	0.0040
Butyl Ether (1)/2-Heptanone (2)					
Margules	363.15	0.43842	0.01657	0.044	0.0020
	393.22	0.41864	0.04931	0.076	0.0030
Van Laar	363.15	0.42252	0.45402	0.044	0.0020
	393.22	0.37261	0.47561	0.069	0.0029
Wilson	363.15	0.86219	0.73228	0.036	0.0019
	393.22	1.01634	0.61020	0.050	0.0026
NRTL	363.15	1074.082	287.309	0.036	0.0019
	393.22	2057.398	−488.244	0.055	0.0027
UNIQUAC	363.15	774.224	−430.734	0.043	0.0020
	393.22	1262.816	−804.929	0.055	0.0027
Butyl Ether (1)/3-Heptanone (2)					
Margules	363.15	0.35999	0.035701	0.012	0.0012
	393.15	0.34499	0.06332	0.121	0.0022
Van Laar	363.15	0.32733	0.39847	0.011	0.0012
	393.15	0.28744	0.42487	0.104	0.0021
Wilson	363.15	1.00601	0.66595	0.011	0.0012
	393.15	1.19740	0.53396	0.104	0.0022
NRTL	363.15	1587.551	−370.213	0.011	0.0012
	393.15	2585.218	−1102.378	0.109	0.0021
UNIQUAC	363.15	1041.332	−683.923	0.012	0.0012
	393.15	1518.542	−1027.368	0.109	0.0021
Butyl Ether (1)/4-Heptanone (2)					
Margules	363.15	0.34772	0.03640	0.021	0.0021
	393.15	0.32463	0.00233	0.071	0.0027
Van Laar	363.15	0.32264	0.39268	0.025	0.0018
	393.15	0.32236	0.32687	0.071	0.0027
Wilson	363.15	1.00476	0.67144	0.025	0.0018
	393.15	0.85251	0.83591	0.071	0.0027
NRTL	363.15	1553.198	−357.483	0.025	0.0018
	393.15	450.966	637.170	0.056	0.0022
UNIQUAC	363.15	967.613	−631.036	0.024	0.0019
	393.15	126.394	103.011	0.089	0.0029

[a] Λ_{ij} = binary model parameters. δP = absolute average deviation of pressure. δy_1 = absolute average deviation of vapor mole fraction. [b] NRTL: $\alpha_{12} = 0.3$.

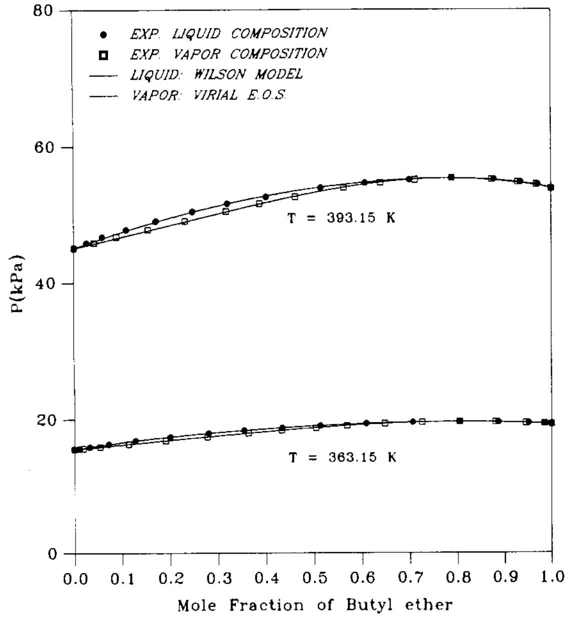

Figure 2. Butyl ether (1)/3-heptanone (2) VLE at 363.15 and 393.15 K.

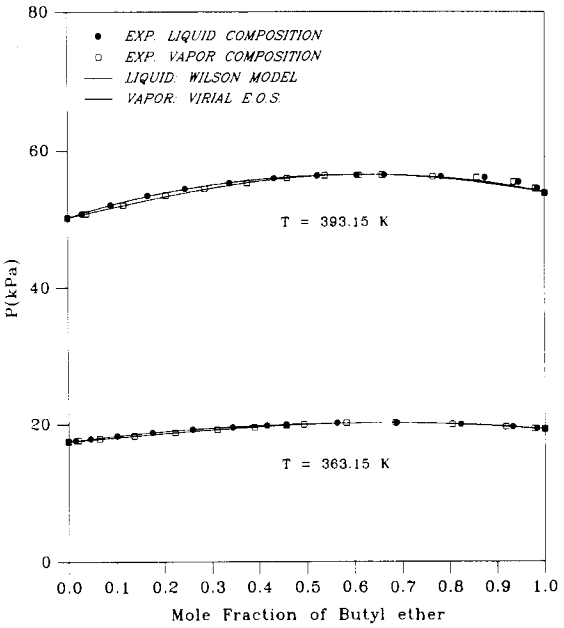

Figure 3. Butyl ether (1)/4-heptanone (2) VLE at 363.15 and 393.15 K.

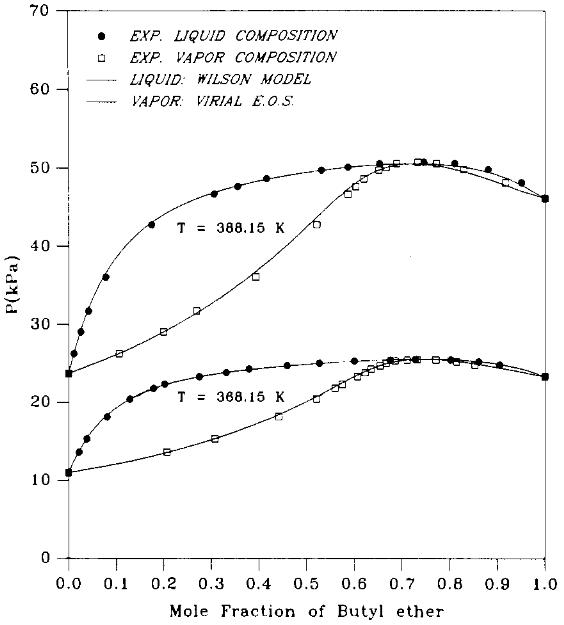

Figure 4. Butyl ether (1)/2-furaldehyde (2) VLE at 368.15 and 388.15 K.

Table V. Azeotropic Data for Butyl Ether (1) Systems

component 2	temp, K	x_1^{az}	P^{az}, kPa
2-heptanone	363.15	0.8930	19.385
2-heptanone	393.22	0.8467	54.814
3-heptanone	363.15	0.8080	19.589
3-heptanone	393.15	0.7925	55.308
4-heptanone	363.15	0.6540	20.190
4-heptanone	393.15	0.6205	56.373
furfural	368.15	0.7424	25.528
furfural	388.15	0.7361	50.769

here which have quite small excess Gibbs free energies and enthalpies of mixing.

From the data reduction of our experimental VLE data for butyl ether and furfural, we have estimated the values for the previously unavailable UNIFAC interaction parameters for the furfural with an ether group given in Table VI. The activity coefficients for butyl ether with the heptanones determined from

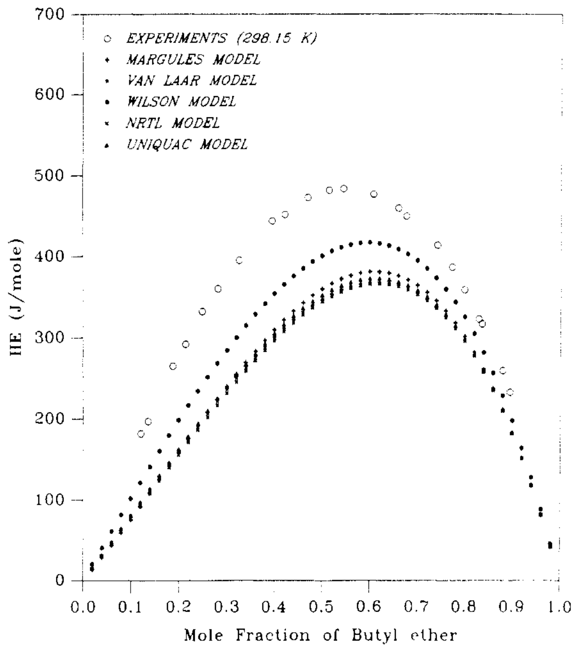

Figure 5. H^E for butyl ether with 2-heptanone, calculated from VLE data at 363.15 and 393.22 K.

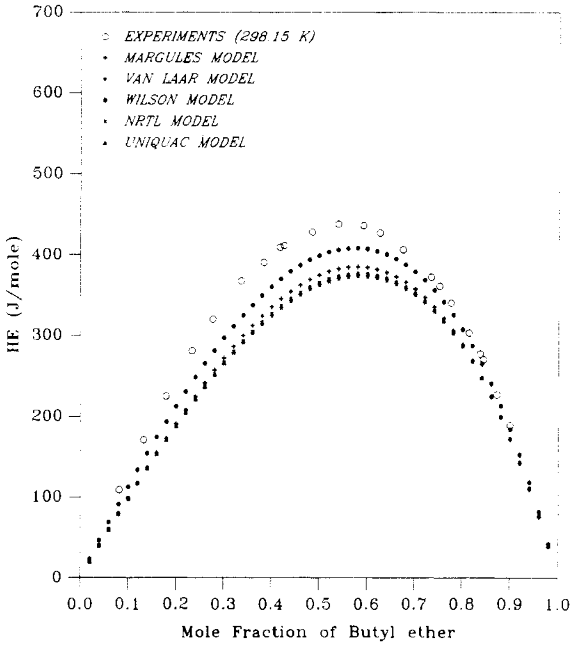

Figure 6. H^E for butyl ether with 4-heptanone, calculated from VLE data at 363.15 and 393.15 K.

Table VI. New UNIFAC Interaction Parameters Ether Group (1) with Furfural Group (2)

Data Reduction from VLE of Butyl Ether (1)/Furfural (2)

temp, K	a_{12}	a_{21}	δP, kPa	δy_1
368.15	380.6	-153.9	0.19	0.0032
388.15	276.4	-139.9	0.24	0.0070
two temp together	176.6	-69.26	0.12[b]	0.0042
			0.51[c]	0.0046

[a] a_{12}, a_{21} are UNIFAC interaction parameters. δP = standard deviation of pressure. δy_1 = standard deviation of vapor composition. [b] Standard deviation from data at 368.15 K. [c] Standard deviation from data at 388.15 K.

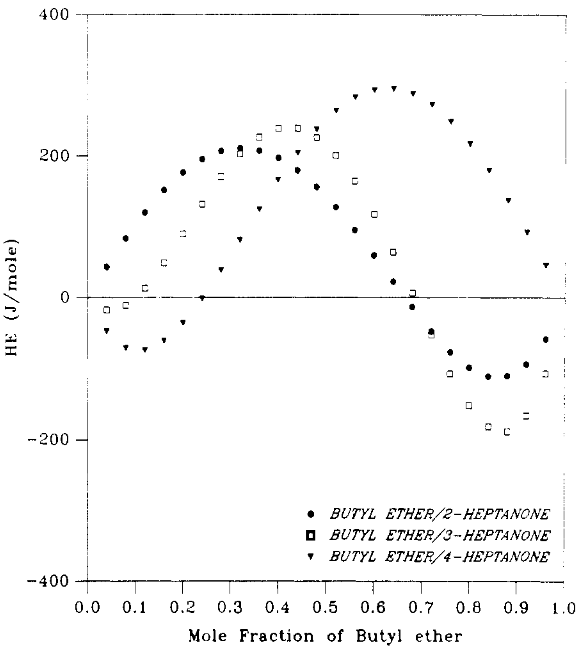

Figure 7. Improper estimation of H^E from VLE data from three-constant Legendre polynomial G model.

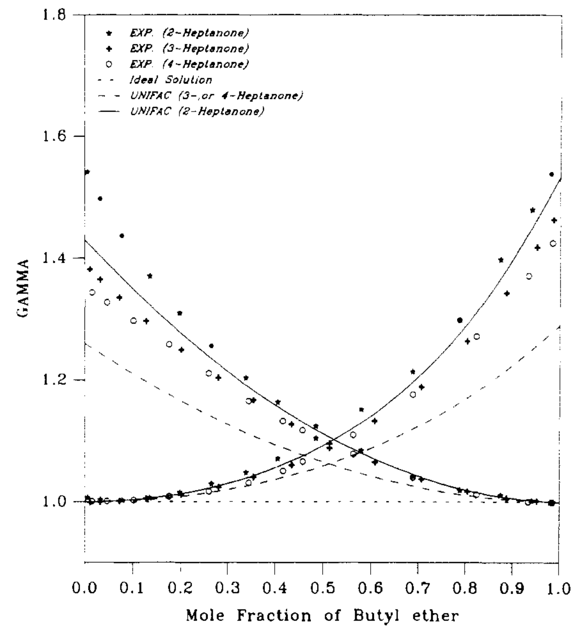

Figure 8. Activity coefficients of butyl ether system at 363.15 K.

our experiments are compared with those predicted by the UNIFAC model with the most recent parameters (*15*) in Figure 8. In the UNIFAC model, 2-heptanone is considered as having one CH_3CO, four CH_2, and one CH_3 groups; both 3-heptanone and 4-heptanone have two CH_3, three CH_2, and one CH_2CO groups. Thus the UNIFAC model can differentiate between the butyl ether/2-heptanone and the butyl ether/3- or 4-heptanone systems, but not between butyl ether with 3-heptanone or with 4-heptanone, so that the UNIFAC activity coefficient predictions for these two mixtures are the same. In fact, our results show that the activity coefficients for these mixtures are not much different from each other and that the activity coefficients predicted by UNIFAC model, even though slightly low, are acceptable. The UNIFAC model also gives reasonable predictions for the mixture of butyl ether with 2-heptanone.

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Phase Equilibria in Ternary Systems with Carbon Dioxide, Water, and Carboxylic Acids at Elevated Pressures

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Vapor–liquid and vapor–liquid–liquid equilibrium compositions have been measured for the ternary systems CO_2 + H_2O + acetic acid at 313 and 333 K, CO_2 + H_2O + propionic acid at 313 K, and CO_2 + H_2O + *n*-butyric acid at 313 K, at pressures between 2.0 and 20.0 MPa. For all systems, a three-phase equilibrium region was observed at pressures comparable to the critical pressure of pure carbon dioxide. The extent of the three-phase equilibrium region increases with the hydrocarbon chain length of the acid, while the pressure for the appearance of three phases also increases with temperature. The distribution coefficient of the acids between the supercritical fluid phase and the aqueous phase at pressures above the critical pressure of pure carbon dioxide increases with the hydrocarbon chain length of the acid: higher molecular weight acids were found to be preferentially partitioned into the supercritical fluid phase. The experimental data for the ternary systems were correlated by using a cubic equation of state and a recently proposed density-dependent mixing rule with model parameters derived from binary data only.

Introduction

Methods of using a fluid above its critical temperature and pressure as a solvent for the separation of mixtures of components have received considerable attention recently (*1*, *2*). The use of supercritical solvents for the energy-efficient recovery of low molecular weight organic compounds from aqueous solutions has been recently proposed by several investigators. Paulaitis et al. (*3*), McHugh et al. (*4*), and Gilbert and Paulaitis (*5*) investigated the recovery of ethanol with carbon dioxide, ethylene, and ethane as solvents. Kuk and Montagna (*6*) presented results for the separation of ethanol and 2-propanol from aqueous solutions using supercritical carbon dioxide. Radosz (*7*) and Paulaitis et al. (*8*, *9*) have determined phase equilibria for the system 2-propanol + water + carbon dioxide. Fleck (*10*) presented results for the extraction of *n*-propyl alcohol using a variety of supercritical fluids. Panagiotopoulos and Reid (*11*, *12*) have determined phase equilibria for ternary systems with supercritical carbon dioxide, water, and acetone or 1-butanol.

There have been relatively few experimental investigations of equilibria between aqueous solutions of low molecular weight organic acids and supercritical fluids. Previous measurements include those of Snedeker (*13*) for the system carbon dioxide + water + acetic acid and Elgin and Weinstock (*14*) for the system C_2H_4 + water + acetic acid and the corresponding system with propionic acid. Francis (*15*) measured phase equilibria for the system subcritical carbon dioxide + water + acetic acid. Shimshick (*16*) has presented data for the extraction of acetic and *n*-butyric acid from aqueous solutions using supercritical carbon dioxide. The objective of the present work was the determination of the phase equilibrium behavior for the ternary systems supercritical carbon dioxide + water + one of the first three straight-chain aliphatic acids.

Experimental Section

Equipment and Procedures. The experimental apparatus used was a high-pressure visual cell with external recirculation of all phases present. A detailed description of the equipment and operating procedures is given elsewhere (*17*). Compositions were measured by gas chromatography with on-line sampling. The chromatographic response factors for the nonvolatile components were determined by analyzing standard mixtures prepared gravimetrically. The relative response factor for carbon dioxide was determined by measuring equilibrium data for mixtures for which data are available in the literature (*18*–*20*). The stability of the relative response factors was monitored by periodic injection of reference mixtures of the liquid components. An additional check for the validity of the chromatographic analysis was provided by the agreement of the results at high pressures with the known behavior of the binary CO_2 + H_2O system at low concentrations of organic acid. The validation of the experimental procedures and comparisons with literature data is given in ref *17*.

It was determined that the composition of the less-dense supercritical fluid phase could not be reproducibly determined at lower pressures ($\leq$6.0 MPa), primarily because of the small mass of sample injected. These data were not considered reliable and were not included in the data tables.

Materials. Analytical grade acetic acid (supplied by Mallinckrodt), propionic acid (Sigma Chemical Co.), and *n*-butyric

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