1324 *J. Chem. Eng. Data* **2002,** *47,* 1324−1329

Vapor−Liquid Equilibrium for Mixtures of Water, Alcohols, and Ethers

Bolun Yang* and Huajun Wang

Chemical Engineering Department, Xi'an Jiaotong University, Xi'an, 710049 China

Vapor−liquid equilibrium data for five binary systems and a quaternary system, which were ethanol−water, ethanol−*tert*-butyl alcohol, ethanol−ethyl *tert*-butyl ether, *tert*-butyl alcohol−ethyl *tert*-butyl ether, *tert*-butyl alcohol−water, and water−ethanol−*tert*-butyl alcohol−ethyl *tert*-butyl ether were measured respectively with a modified Rose equilibrium still under isopiestic pressure (0.1013 MPa). The data are correlated with the UNIFAC and Wilson models. The predicted vapor−liquid equilibrium for these systems agreed well with the experimental data.

Introduction

Recently, the demand for ethyl *tert*-butyl ether (ETBE) has increased rapidly with the increased utilization as a gasoline blender.[1] The process for the production of ETBE employs the method of liquid-phase synthesis from (EtOH) and isobutylene (IB). However, the IB source is limited only to catalytic-cracking or steam-cracking fractions; it is also used by other branches of the chemical industry as starting materials. On the other hand, *tert*-butyl alcohol (TBA) is a major byproduct in the ARCO process for the manufacture of propylene oxide.[2] It can provide an alternative route for the synthesis of ETBE by the etherification between EtOH and TBA. Since the reaction itself will produce water, the content of water in EtOH will become unimportant. Thus, it would reduce costs for the production of ETBE.

The kinetics were researched by using different catalysts. The process of reactive distillation combined with pervaporation has been investigated by the authors.[3−5] However, to our knowledge, there is relatively little vapor−liquid equilibrium data for this water−alcohol−ether system. Only the isothermal data of ETBE−H_2O and ETBE−EtOH, measured by a computer-driven static total pressure apparatus, has been reported by Rarey et al.[6]

For this reason, the purpose of this work is to measure the accurate isobaric vapor−liquid equilibrium data at different temperatures for the above system to supply basic data for the design and calculation of the combined process.

Thermodynamic Model

Basic Equations. For the highly nonideal system in which the polarities of each component is very different, the vapor−liquid equilibrium equation should be written as

$$y_i \hat{\phi}_i^V P = x_i \gamma_i f_i^0 \qquad (1)$$

P is system pressure, $\hat{\phi}_i^V$ is the fugacity coefficient of the gas phase calculated with the virial equation, and f_i^0 is the fugacity of the pure component at system temperature and pressure, which is given by the Poynting equation. The vapor pressure of the pure component can be calculated from the Antoine equation. The activity coefficient, γ_i, can be calculated by either the Wilson or the UNIFAC method.

The mole fraction for both the vapor and the liquid phase should be consistent with the normalizing condition expressed as the dew point and the bubbling point equations, respectively.

$$\sum_i^m y_i = 1 \qquad (2)$$

$$\sum_i^m x_i = 1 \qquad (3)$$

Equations 1−3 will be the basic model for this system.

Activity Coefficient. Wilson and UNIFAC methods have been used in this work to calculate the activity coefficient γ_i. In the Wilson method, the activity coefficient γ_i is expressed as

$$\ln \gamma_i = -\ln\left(\sum_{j=1}^N x_j \Lambda_{ij}\right) + 1 - \sum_{k=1}^N \frac{x_k \Lambda_{ki}}{\sum_{j=1}^N x_j \Lambda_{kj}} \qquad (4)$$

where

$$\Lambda_{ij} = \frac{V_j}{V_i} \exp\left[-\frac{\lambda_{ij}}{RT}\right]$$

are Wilson parameters. λ_{ij} is the binary interaction coefficient. It can be obtained by fitting the experimental data.

In the UNIFAC method, the activity coefficient γ_i is expressed as combinatorial and residual parts,

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \qquad (5)$$

where

$$\ln \gamma_i^c = \ln\left(\frac{\phi_i}{x_i}\right) + \frac{z}{2} q_i \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \frac{\phi_i}{x_i} \sum_j (x_j l_j) \qquad (6)$$

---

* To whom correspondence should be addressed. E-mail: blunyang@xjtu.edu.cn. Tel.: +8629-2668569.

10.1021/je010223k CCC: $22.00

Table 1. Group Number and Category for Each Component

components	molecular formula	group number and category
ETBE	$C_6H_{14}O$	$4CH_3$ 1C $1CH_2O$
TBA	$C_4H_{10}O$	$3CH_3$ 1OH 1C
EtOH	C_2H_6O	$1CH_3$ $1CH_2$ 1OH
H_2O	H_2O	$1H_2O$

Table 2. Group Volume R_k and Surface Area Q_k Parameters

	CH_3	CH_2	C	OH	H_2O	CH_2O
R_k	0.9011	0.6744	0.2195	1.000	0.9200	0.9183
Q_k	0.8480	0.5400	0.0000	1.2000	1.4000	0.7800

Table 3. Group-Interaction Parameters (a_{mn}/K)

	n					
m	CH_3	CH_2	C	OH	H_2O	CH_2O
CH_3	0.0	0.0	0.0	986.5	1318.0	251.5
CH_2	0.0	0.0	0.0	986.5	1318.0	251.5
C	0.0	0.0	0.0	986.5	1318.0	251.5
OH	156.4	156.4	156.4	0.0	353.5	28.06
H_2O	300.0	300.0	300.0	−229.1	0.0	540.5
CH_2O	83.36	83.36	83.36	237.7	−314.7	0.0

Table 4. Antoine Parameters

	EtOH	TBA	H_2O	ETBE
ANT1	−75.7609	21.74757	−31.3974	6.67820
ANT2	−3100.647	−2658.29	−2046.366	−1066.84
ANT3	−40.50064	−95.5000	−75.40224	208.24
ANT4	−0.08814077	0	−0.012054280	0
ANT5	20.81208	0	9.165751	0
ANT6	0.00005045333	0	$0.4879195 \times 10^{-17}$	0
ANT7	2.00000	0	6.00000	0

and

$$\ln \gamma_i^{R} = \sum_k \nu_k^{(i)}(\ln \Gamma_k - \ln \Gamma_k^{(i)}) \qquad (7)$$

Some parameters[7] used in the UNIFAC method for the research system are shown in Tables 1−3.

The Antoine equation is used to calculate the vapor pressure of the pure components, P^s.

$$\ln(P^{s}) = \mathrm{ANT1} + \mathrm{ANT2}/(T + \mathrm{ANT3}) + (\mathrm{ANT4} \times T) + (\mathrm{ANT5} \times \ln(T)) + (\mathrm{ANT6} \times T^{\mathrm{ANT7}}) \qquad (8)$$

where T is the temperature and the Antoine parameters are shown in Table 4.

Prediction Procedures. The liquid-phase composition and initial temperature were designated at the isopiestic pressure. A series of calculations by iteration using eqs 1−3 were carried out to determine the gas-phase composition and the bubbling point temperature for each of the binary systems and the quaternary system.

Experimental Section

Materials. ETBE was synthesized in our laboratory and was purified by the following procedure. The crude ETBE was washed several times with bidistilled water to extract the impurities of alcohol. Then, it was distillated to remove IB and dried over a molecular sieve. EtOH and TBA were purchased as analytically pure reagents from Xi'an Chemical Reagent (Xi'an, China). The purity of the reagents was greater than 99.9 mass % as confirmed by gas chromatography. Bidistilled water was prepared in our laboratory.

Equipment and Procedure. A modified Rose equilibrium still was used to measure the vapor−liquid equilibrium data for the research systems. The total volume of the still was 100 cm^3. The energy was applied to the still with the help of electrical heating, controlled by a manostat.

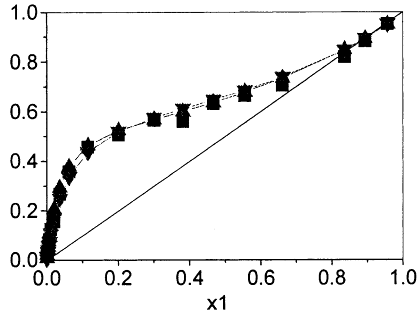

Figure 1. VLE for EtOH(1) + H_2O(2): ■, experimental; ▲, UNIFAC method; ▼, Wilson method.

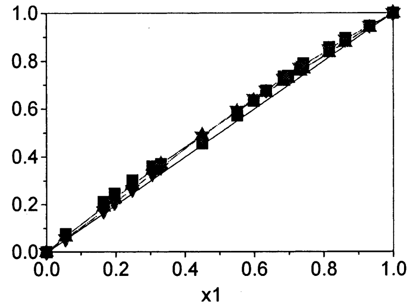

Figure 2. VLE for EtOH(1) + TBA(2): ■, experimental; ▲, UNIFAC method; ▼, Wilson method.

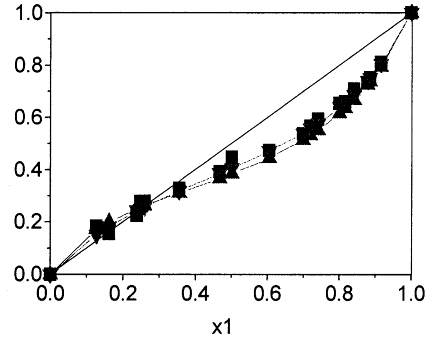

Figure 3. VLE for TBA(1) + ETBE(2): ■, experimental; ▲, UNIFAC method; ▼, Wilson method.

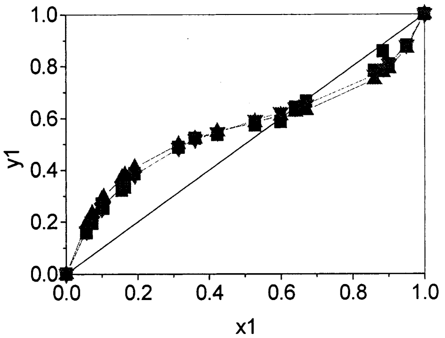

Figure 4. VLE for ETBE(1) + EtOH(2): ■, experimental; ▲, UNIFAC method; ▼, Wilson method.

A mercury thermometer was used and the accuracy of temperature measurements was estimated to be ±0.01 K. The temperature data obtained under atmospheres can be corrected as the one in the 0.1013 MPa by using the Tronton ruler and the Clausius−Clapeyron equation to compare with the literature results.

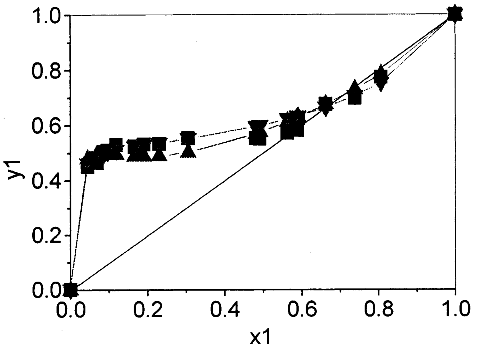

Figure 5. VLE for TBA(1) + H_2O(2): ■, experimental; ▲, UNIFAC method; ▼, Wilson method.

Table 5. Wilson Binary Interaction Coefficient

component *i*	component *j*	λ_{ij} (J/mol)	λ_{ji} (J/mol)
EtOH	TBA	2065.5	−1380.1
EtOH	ETBE	4887.8	−958.9
EtOH	H_2O	3178.4	3466.0
TBA	ETBE	1527.4	722.2
TBA	H_2O	5256.5	5916.8

During the operation, a given liquid solution was charged into the equilibrium still and heated. The vapor was condensed in the condenser by the circulation of cooling water and was delivered to the mixing chamber through the vapor-phase sampling port. In the mixing chamber they were mixed again and returned to the boiling still for recirculation. The vapor−liquid equilibrium was usually reached after about 60 min.

The samples of the equilibrium were taken out from a vapor and liquid sampling port, respectively. All the components were analyzed by the gas chromatograph with a 3-m column of Gaskuropack 54 as packing material at 463 K using a TCD detector. Hydrogen at 0.12 MPa was used as the carrier gas. Separation was achieved for all components.

To confirm the reliability of the experimental apparatus and the operation method, the data for the EtOH−H_2O system was first compared with literature results.[8] Graphs of gas-phase composition (y) versus liquid-phase composition (x) for this work and the literature were plotted to fit the function relation of (y) with (x). Then, based on the $T-x$ data from the literature, the gas-phase composition (y) for both this work and the literature were calculated by using the above two functions, respectively. In a comparison of these values of (y), it was found that the experimental results of this work agreed well with the literature results; the mean deviation for y was only 0.009. This fact indicates that the apparatus used in this work is reliable.

The Herington method[9] was used to check the thermodynamic consistency. All binary VLE data of this work were thermodynamically consistent.

Results and Discussion

Binary System. The VLE results of binary systems at 0.1013 MPa are shown in Figures 1−5. In these figures, the square marks show the results of experimental measurements, and the upward and downward pointing triangles show the prediction results. In the EtOH−TBA binary system, the results show a very good linear relation. This means that this system is close to an ideal system. The reasons could be that EtOH and TBA are two kinds of alcohols and that the interaction between EtOH and TBA is close to that of a pure substance. Therefore, the vapor pressure of the mixture obeys Raoult's law. However, a maximum positive deviation from the ideal is observed for the EtOH−H_2O, TBA−ETBE, EtOH−ETBE, and TBA−H_2O systems when an azeotrope is present.

With the help of least-squares nonlinear regression, Wilson binary interaction coefficients shown in Table 5 can be obtained.

With the use of the above parameters, calculated results for vapor−liquid equilibrium in the Wilson method can be obtained (marked by an upward pointing triangle). The results calculated by the UNIFAC method are also shown in Figures 1−5 (marked by downward pointing triangles).

Tables 6−9 show the deviation data of the vapor−liquid equilibrium between experimental and predicted results for each binary system in detail at P = 0.1013 MPa.

The tabulated results show that there is good agreement of the experimental data and the calculations by both of the Wilson and the UNIFAC methods, for all binary systems.

Table 6. VLE Deviation between Experimental and Predicted Results for the EtOH(1) + H_2O(2) System

	experimental results			calculation by UNIFAC method		deviation with UNIFAC method		calculation by Wilson method		deviation with Wilson method	
no.	T/K	x_1	y_1	γ_1	γ_2	ΔT (K)	Δy_1	γ_1	γ_2	ΔT (K)	Δy_1
1	372.97	0.0006	0.0233	6.7171	1.0000	0.04	0.0148	5.0000	1.0000	−0.03	0.0173
2	372.77	0.0015	0.0262	6.6663	1.0000	0.16	0.0054	4.9719	1.000	0.01	0.0107
3	372.33	0.0033	0.0442	6.5662	1.0000	0.34	0.0001	4.9173	1.0000	0.03	0.0089
4	371.87	0.0041	0.0553	6.5225	1.0001	0.15	0.0013	4.8933	1.0000	−0.22	0.0143
5	371.45	0.0058	0.0715	6.4307	1.0001	0.29	−0.0025	4.8428	1.0000	−0.23	0.0148
6	370.96	0.0077	0.0834	6.3303	1.0003	0.38	−0.0115	4.7873	1.0002	−0.27	0.0101
7	369.80	0.0121	0.1248	6.1062	1.0006	0.46	−0.0133	4.6623	1.0005	−0.47	0.0161
8	367.75	0.0210	0.1553	5.6872	1.0055	0.53	−0.0528	4.4244	1.0015	−0.79	−0.0139
9	364.68	0.0367	0.2677	5.0489	1.0019	0.22	−0.0264	4.0502	1.0044	−1.45	0.0180
10	362.16	0.0622	0.3585	4.2341	1.0149	0.60	−0.0197	3.5484	1.0119	−1.17	0.0214
11	358.79	0.1152	0.4571	3.1250	1.0453	0.33	−0.0066	2.8091	1.0361	−1.09	0.0188
12	356.56	0.2007	0.5061	2.1914	1.1163	0.26	−0.0183	2.1114	1.0942	−0.51	−0.0134
13	355.23	0.3005	0.5649	1.6654	1.2222	0.27	−0.0032	1.6663	1.1854	−0.06	−0.0105
14	354.28	0.3809	0.5589	1.4321	1.3208	0.16	−0.0416	1.4486	1.2757	−0.01	−0.0525
15	353.62	0.4664	0.6314	1.2767	1.4364	0.28	−0.0056	1.2928	1.3885	0.17	−0.0162
16	352.98	0.5549	0.6638	1.1731	1.5682	0.34	−0.0148	1.1829	1.5250	0.26	−0.0226
17	352.50	0.6615	0.7057	1.0937	1.7472	0.54	−0.0294	1.0954	1.7202	0.47	−0.0327
18	351.78	0.8365	0.8200	1.0229	2.1323	0.49	−0.0280	1.0197	2.1293	0.42	−0.0278
19	351.67	0.8939	0.8927	1.0103	2.3099	0.53	−0.0107	1.0080	2.2923	0.46	−0.0112
20	351.60	0.9569	0.9524	1.0019	2.5653	0.37	0.0006	1.0013	2.0490	0.32	−0.0007
			mean deviation			0.34	0.0153			0.42	0.0176

Table 7. VLE Deviation between Experimental and Predicted Results for the EtOH(1) + TBA(2) System

	experimental results			calculation by UNIFAC method		deviation with UNIFAC method		calculation by Wilson method		deviation with Wilson method	
no.	T (K)	x_1	y_1	γ_1	γ_2	ΔT (K)	Δy_1	γ_1	γ_2	ΔT (K)	Δy_1
1	355.77	0.0000	0.0000			0.12	0.0000			0.13	0.0000
2	355.1	0.0548	0.0768	1.0275	1.0000	−0.26	0.0119	0.8786	0.9995	−0.52	0.0207
3	354.39	0.1650	0.2119	1.0229	1.0001	−0.41	0.0212	0.9068	0.9956	−1.1	0.0385
4	354.38	0.1963	0.2466	1.0217	1.0009	−0.26	0.0213	0.9143	0.9938	−1.05	0.0391
5	355.35	0.1969	0.2264	1.0216	1.0009	0.71	0.0004	0.9145	0.9937	−0.08	0.0182
6	354.04	0.2478	0.3012	1.0196	1.0015	−0.35	0.0199	0.9261	0.9901	−1.27	0.0370
7	353.74	0.3065	0.3601	1.0173	1.0023	−0.37	0.0164	0.9383	0.9850	−1.41	0.0309
8	355.02	0.3308	0.3704	1.0164	1.0028	1.01	0.0014	0.9431	0.9826	−0.05	0.0143
9	354.74	0.4492	0.4556	1.0120	1.0055	1.26	−0.0338	0.9632	0.9691	0.11	−0.0303
10	354.36	0.5506	0.5720	1.0086	1.0090	1.30	−0.0165	0.9765	0.9554	0.20	−0.0215
11	354.12	0.5982	0.6333	1.0071	1.0110	1.25	−0.0007	0.9816	0.9485	0.19	−0.0092
12	353.92	0.6341	0.6758	1.0061	1.0127	1.19	0.0079	0.9850	0.9430	0.18	−0.0028
13	353.69	0.6844	0.7350	1.0047	1.0154	1.15	0.0202	0.9891	0.9351	0.23	0.0071
14	353.64	0.6969	0.7368	1.0043	1.0162	1.14	0.0104	0.9900	0.9331	0.26	−0.0031
15	353.34	0.7414	0.7894	1.0033	1.0190	1.00	0.0221	0.9929	0.9259	0.21	0.0074
16	353.49	0.7313	0.7690	1.0035	1.0183	1.11	0.0109	0.9922	0.9276	0.30	−0.0035
17	352.98	0.8155	0.8573	1.0018	1.0244	0.90	0.0226	0.9965	0.9135	0.29	0.0082
18	352.70	0.8622	0.8962	1.0010	1.0284	0.76	0.0195	0.9981	0.9055	0.30	0.0067
19	352.29	0.9320	0.9462	1.0003	1.0354	0.57	0.0068	0.9995	0.8934	0.33	−0.0008
20	351.90	1.0000	1.0000			0.38	0.0000			0.38	0.0000
			mean deviation			0.77	0.0132			0.43	0.0150

Table 8. VLE Deviation between Experimental and Predicted Results for the TBA(1) + ETBE(2) System

	experimental results			calculation by UNIFAC method		deviation with UNIFAC method		calculation by Wilson method		deviation with Wilson method	
no.	T (K)	x_1	y_1	γ_1	γ_2	ΔT (K)	Δy_1	γ_1	γ_2	ΔT (K)	Δy_1
1	347.26	0.0000	0.0000			1.29	0.0000			1.25	0.0000
2	343.69	0.1268	0.1832	2.2009	1.0242	0.31	0.0113	1.8482	1.0136	−0.85	0.0317
3	345.16	0.1614	0.1559	2.0315	1.0382	2.04	−0.0439	1.7606	1.0920	0.79	−0.0265
4	344.00	0.2382	0.2245	1.7398	1.0792	1.12	−0.0254	1.5930	1.0479	−0.21	−0.0174
5	343.55	0.2480	0.2766	1.7092	1.0853	0.69	0.0211	1.5740	1.0519	−0.65	0.0278
6	343.12	0.2600	0.2778	1.6735	1.0932	0.26	0.0156	1.5514	1.0571	−1.09	0.0207
7	344.22	0.3552	0.3283	1.4450	1.1664	1.22	0.0173	1.3958	1.1078	−0.50	0.0102
8	344.82	0.4676	0.3923	1.2659	1.2782	1.30	0.0259	1.2565	1.1916	−0.06	0.0075
9	345.84	0.5014	0.4479	1.2251	1.3178	2.08	0.0639	1.2222	1.2223	0.74	0.0429
10	346.55	0.6051	0.4736	1.1288	1.4564	1.81	0.0289	1.1352	1.3385	0.58	0.0030
11	347.63	0.6986	0.5378	1.0701	1.6065	1.57	0.024	1.0775	1.4737	0.53	−0.0021
12	348.23	0.7189	0.5662	1.0601	1.6425	1.82	0.0348	1.0673	1.5078	1.82	0.0091
13	348.86	0.7407	0.5942	1.0505	1.6826	2.03	0.0424	1.0572	1.5464	1.10	0.0176
14	349.69	0.8004	0.6541	1.0289	1.8006	1.53	0.0380	1.0338	1.6643	0.80	0.0166
15	349.78	0.8161	0.6599	1.0243	1.8337	1.22	0.0244	1.0287	1.6985	0.55	0.0042
16	350.62	0.8403	0.7092	1.0181	1.8864	1.39	0.0412	1.0216	1.7542	0.81	0.0232
17	351.29	0.8785	0.7337	1.0103	1.9740	0.87	0.0073	1.0126	1.8497	0.44	0.0068
18	351.92	0.8852	0.7524	1.0092	1.9900	1.27	0.0147	1.0112	1.8675	0.86	0.0014
19	352.42	0.9160	0.8115	1.0048	2.0656	0.64	0.0172	1.0060	1.9536	0.36	0.0076
20	355.77	1.0000	1.0000			0.12	0.0000			0.13	0.0000
			mean deviation			1.23	0.0249			0.65	0.0138

Table 9. VLE Deviation between Experimental and Predicted Results for the ETBE(1) + EtOH(2) System

	experimental results			calculation by UNIFAC method		deviation with UNIFAC method		calculation by Wilson method		deviation with Wilson method	
no.	T (K)	x_1	y_1	γ_1	γ_2	ΔT (K)	Δy_1	γ_1	γ_2	ΔT (K)	Δy_1
1	351.90	0.0000	0.0000			0.38	0.0000			0.38	0.0000
2	348.65	0.0563	0.1583	3.3033	1.0045	1.39	−0.0353	2.7291	1.0034	0.44	−0.0062
3	347.60	0.0726	0.1946	3.1697	1.0075	1.26	−0.0385	2.6442	1.0056	0.16	−0.0063
4	346.31	0.0989	0.2686	2.9710	1.0139	1.25	−0.0180	2.5160	1.0104	−0.04	0.0164
5	346.76	0.1038	0.2534	2.9361	1.0153	1.91	−0.0420	2.4932	1.0115	0.59	−0.0074
6	345.06	0.1553	0.3220	2.6059	1.0339	2.04	−0.0491	2.2730	1.0258	0.57	−0.0164
7	344.32	0.1637	0.3348	2.2277	1.0377	1.55	−0.0463	2.2401	1.0287	0.06	−0.0143
8	343.54	0.1906	0.3858	2.4130	1.0510	1.46	−0.0241	2.1401	1.0390	−0.04	0.0053
9	341.62	0.3137	0.4882	1.8996	1.1405	1.54	−0.0112	1.7667	1.1093	0.15	0.0035
10	341.11	0.3595	0.5230	1.7563	1.1871	1.46	0.0009	1.6564	1.1465	0.14	0.0101
11	340.80	0.4225	0.5377	1.5906	1.2656	1.56	−0.0108	1.5246	1.2096	0.33	−0.0084
12	340.37	0.5273	0.5732	1.3775	1.4422	1.53	−0.0124	1.3477	1.3534	0.42	−0.0197
13	340.15	0.5992	0.5877	1.2665	1.6076	1.40	−0.0222	1.2512	1.4898	0.36	−0.0348
14	339.91	0.6401	0.6414	1.2138	1.7230	1.16	0.0169	1.2042	1.5860	0.14	0.0019
15	339.88	0.6706	0.6650	1.1788	1.8215	1.09	0.0345	1.1725	1.6685	0.09	0.0124
16	341.12	0.8600	0.7828	1.0334	2.8014	0.89	0.0352	1.0344	2.5288	0.14	0.0171
17	341.43	0.8845	0.8580	1.0230	2.9981	0.71	0.0818	1.0239	2.7019	0.04	0.0686
18	341.72	0.9000	0.8067	1.0173	3.1344	0.62	0.0157	1.0181	2.8276	0.00	0.0001
19	343.23	0.9500	0.8797	1.0044	3.6468	0.37	0.0102	1.0047	3.3123	0.01	0.0002
20	344.98	1.0000	1.0000			−0.99	0.0000			−0.99	0.0002
			mean deviation			1.23	0.0252			0.27	0.0281

Table 10. VLE Deviation between Experimental and Predicted Results for the TBA(1) + H_2O(2) System

	experimental results			calculation by UNIFAC method		deviation with UNIFAC method		calculation by Wilson method		deviation with Wilson method	
no.	T (K)	x_1	y_1	γ_1	γ_2	ΔT (K)	Δy_1	γ_1	γ_2	ΔT (K)	Δy_1
1	373.05	0.0000	0.0000			−0.1	0.0000			−0.1	0.0000
2	357.27	0.0450	0.4505	15.0853	1.0211	0.88	−0.0279	9.6971	1.0235	0.44	−0.0111
3	355.49	0.0700	0.4647	10.1511	1.0461	−0.11	−0.0315	6.8747	1.0450	−0.50	−0.0231
4	354.93	0.0875	0.5029	8.0255	1.0673	−0.61	0.0053	5.7036	1.0623	−0.64	0.0113
5	354.80	0.0967	0.5095	7.1784	1.0794	−0.78	0.0129	5.2382	1.0717	−0.60	0.0074
6	354.76	0.1188	0.5284	5.6526	1.1108	−0.92	0.0343	4.3824	1.0951	−0.32	0.0186
7	354.60	0.1663	0.5226	3.7742	1.1870	−1.29	0.0343	3.2640	1.1500	0.00	0.0006
8	354.53	0.1910	0.5307	3.1999	1.2302	−1.39	0.0434	2.8924	1.1808	0.12	0.0033
9	354.45	0.2301	0.5332	2.5811	1.3024	−1.43	0.0443	2.4631	1.2327	0.31	−0.0023
10	354.25	0.3054	0.5523	1.9132	1.4514	−1.33	0.0503	1.9433	1.3442	0.56	0.0011
11	353.85	0.4804	0.5522	1.3151	1.8349	−0.81	−0.0166	1.3765	1.6755	0.97	−0.0429
12	353.86	0.4917	0.5507	1.2954	1.8613	−0.75	−0.0237	1.3547	1.7011	1.03	−0.0478
13	353.88	0.5626	0.5717	1.1964	2.0330	−0.47	−0.0411	1.2410	1.8765	1.26	−0.0505
14	353.60	0.5885	0.5814	1.1687	2.0987	−0.67	−0.0466	1.2076	1.9474	1.03	−0.0505
15	353.44	0.5911	0.6240	1.1661	2.1053	−0.82	−0.0056	1.2045	1.9547	0.88	−0.0089
16	353.36	0.6629	0.6752	1.1066	2.2987	−0.78	−0.0004	1.1304	2.1749	0.87	0.0105
17	353.50	0.7389	0.6982	1.0625	2.5283	−0.64	−0.0321	1.0742	2.4497	0.92	−0.0075
18	353.38	0.8065	0.7741	1.0347	2.7666	−0.88	0.0110	1.0393	2.7376	0.51	0.0203
19	354.15	0.9065	0.8655	1.0220	2.9361	−0.58	−0.0158	1.0088	3.2533	0.28	0.0000
20	355.92	1.0000	1.0000			0.28	0.0000			0.33	0.0124
			mean deviation			0.78	0.0238			0.61	0.0167

Table 11. Experimental VLE Data for the H_2O(1) + EtOH(2) + TBA(3) + ETBE(4) System

no.	T (K)	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
1	346.33	0.4111	0.3305	0.1569	0.1015	0.2352	0.3052	0.1329	0.3267
2	347.18	0.3177	0.2018	0.4069	0.0736	0.2456	0.1537	0.3607	0.2400
3	347.35	0.3638	0.2478	0.3109	0.0775	0.2712	0.2048	0.2907	0.2333
4	348.83	0.2807	0.4034	0.2547	0.0612	0.2346	0.3654	0.2203	0.1792
5	350.33	0.2312	0.3782	0.3501	0.0405	0.2320	0.3450	0.3092	0.1138
6	350.71	0.3019	0.2960	0.3719	0.0302	0.2743	0.2796	0.3471	0.0990
7	351.19	0.5243	0.2065	0.2465	0.0227	0.3526	0.2270	0.3006	0.1198
8	351.70	0.6726	0.1540	0.1608	0.0126	0.3767	0.2057	0.2994	0.1182
9	352.20	0.7733	0.1080	0.1169	0.0018	0.4006	0.1832	0.3060	0.1102
10	352.78	0.5124	0.2380	0.2496	0.0000	0.4157	0.1770	0.3087	0.0886

Table 12. Deviation between Experimental and Predicted Results for the H_2O(1) + EtOH(2) + TBA(3) + ETBE(4) System

	activity coefficients predicted by UNIFAC method				deviation with UNIFAC method				
no.	γ_1	γ_2	γ_3	γ_4	ΔT (K)	Δy_1	Δy_2	Δy_3	Δy_4
1	1.9587	1.0583	1.1993	2.5928	−0.81	−0.0605	0.0091	−0.0024	0.0538
2	2.2385	1.0387	1.1101	2.0224	−3.42	−0.0731	−0.0478	−0.0256	0.1465
3	2.1023	1.0445	1.1498	2.2326	−1.51	−0.0307	−0.0294	0.0155	0.0446
4	2.1488	1.0374	1.1257	2.2768	−0.31	−0.0062	−0.0173	−0.0030	0.0260
5	2.2946	1.0249	1.0924	2.1574	0.12	0.0108	−0.0241	−0.0014	0.0147
6	2.1747	1.0277	1.1327	2.1849	−0.01	−0.0054	−0.0158	−0.0019	0.0230
7	1.6984	1.1098	1.4395	3.5217	0.15	−0.0317	0.0018	0.0029	0.0270
8	1.4013	1.3113	2.0800	7.4124	0.52	−0.0326	0.0062	0.0172	0.0093
9	1.2234	1.6584	3.2723	12.113	−0.40	−0.0345	−0.0034	−0.0349	0.0728
10	1.6673	1.1202	1.4815		0.18	0.0229	−0.1007	−0.0208	0.0512
		mean deviation			0.74	0.0308	0.0255	0.0125	0.0469

Table 13. Deviation between Experimental and Predicted Results for the H_2O(1) + EtOH(2) + TBA(3) + ETBE(4) System

	activity coefficients predicted by Wilson method				deviation with Wilson method				
no.	γ_1	γ_2	γ_3	γ_4	ΔT (K)	Δy_1	Δy_2	Δy_3	Δy_4
1	1.8107	1.1299	1.3891	2.8226	0.36	−0.0160	0.0086	−0.0055	0.0125
2	2.1376	1.1106	1.1707	2.4910	−0.78	−0.0120	−0.0121	−0.0025	0.0266
3	1.9715	1.0020	1.2478	2.6630	−0.21	0.0090	−0.0094	0.0064	−0.0060
4	2.1034	1.0530	1.2225	2.7333	0.46	0.0060	0.0067	0.0031	−0.0158
5	2.2620	1.0472	1.1575	2.6728	0.53	0.0110	0.0045	0.0026	−0.0181
6	2.0894	1.0724	1.1910	2.8493	1.08	0.0174	0.0161	0.0043	0.0030
7	1.5817	1.2189	1.5228	3.8997	0.74	0.0032	0.0149	0.0071	0.0188
8	1.3316	1.4761	2.0650	5.6728	−0.09	−0.0219	−0.0240	0.0125	0.0334
9	1.1967	1.8384	2.8433	8.6251	−1.79	−0.0495	0.0345	0.0066	0.0906
10	1.5831	1.2001	1.5216	−	0.43	0.0464	0.1176	0.0164	0.0876
		mean deviation			0.65	0.0192	0.0248	0.0067	0.0312

Quaternary System. The measurements of the liquid phase and vapor phase for H_2O−EtOH−TBA−ETBE at 0.1013 MPa at different temperatures is shown in Table 10. The deviation between the experimental measurements and the predicted results are shown in Tables 11 and 12.

When these results are compared, it can be seen that both the Wilson and the UNIFAC methods give a good representation of the experimental data. The Wilson method is a little better than the UNIFAC method based on the mean deviations of ΔT and Δy.

Conclusions

Vapor−liquid equilibrium data have been reported for the H_2O−EtOH−TBA−ETBE system at different temperatures. A maximum positive deviation from Raoult's law for the TBA−ETBE, EtOH−ETBE, and TBA−H_2O systems was observed; an azeotrope will be formed in these binary systems. The binary interaction coefficient in the Wilson model can be obtained by fitting the VLE experimental data. With use of these parameters, the VLE for the multicomponent system can be predicted. The calculated results agreed with the experimental data. The UNIFAC method also can be considered when the VLE prediction in the multicomponent system contains water, alcohol, and a branched ether.

Literature Cited

(1) Sneesby, M. G.; Tade, M. O.; Datta, R.; Smith, T. N. Synthesis via Reactive Distillation. 1. Steady-State Simulation and Design Aspects. *Ind. Eng. Chem. Res.* **1997**, *36*, 1855−1869.

(2) Quitain, A.; Itoh, H.; Goto, S. Reactive Distillation for Synthesizing Ethyl *tert*-Butyl Ether from Bioethanol. *J. Chem. Eng. Jpn.* **1999**, *32*, 280−287.

(3) Yang, B. L.; Goto, S. Pervaporation with Distillation for the Production of Ethyl *tert*-Butyl Ether. *Sep. Sci. Technol.* **1997**, *32*, 971−981.

(4) Yang, B. L.; Yao, R. Q.; Yang, S. B. Catalytic Reaction Coupling with Pervaporation for the Production of Ethyl *tert*-Butyl Ether. *Petrochem. Technol.* **1999**, *28*, 77−81.

(5) Yang, B. L.; Yang, S. B.; Yao, R. Q. Synthesis of Ethyl *tert-B*utyl Ether from *tert*-Butyl Alcohol and Ethanol on Strong Acid Cation Exchange Resins. *React. Funct. Polym.* **2000**, *44*, 165−175.

(6) Rarey, J.; Horstmann, S.; Gmehling, J. Vapor Liquid Equilibria and Vapor Pressure Data for the Systems Ethyl *tert*-Butyl Ether + Ethanol and Ethyl *tert*-Butyl Ether + Water. *J. Chem. Eng. Data* **1999**, *44*, 532−538.

(7) Walas, S. M. *Phase Equilibria in Chemical Engineering;* Petrochemical Technology Press of China: Peking, 1991.

(8) Zheng, C. *Handbook of Chemical Technology Design*; Chemical Engineering Press of China: Peking, 1986.

(9) Herington, E. F. G. *J. Inst. Petrol.* **1951**, *37*,457−459.

Received for review August 6, 2001. Accepted February 1, 2002. This research was supported by the National Natural Science Foundation of China (Grant 200176044).

JE010223K