532 *J. Chem. Eng. Data* **1999,** *44,* 532−538

Vapor−Liquid Equilibria and Vapor Pressure Data for the Systems Ethyl *tert*-Butyl Ether + Ethanol and Ethyl *tert*-Butyl Ether + Water

Jürgen Rarey, Sven Horstmann, and Jürgen Gmehling*

Technische Chemie, Carl von Ossietzky Universitaet Oldenburg, Postfach 2503, D-26111 Oldenburg, Germany

Accurate isothermal vapor−liquid equilibrium data for the systems ethyl *tert*-butyl ether + ethanol at 24.8, 50, 65, and 90 °C and ethyl *tert*-butyl ether + water at 25.1 and 40 °C as well as pure component vapor pressures for ethyl *tert*-butyl ether were measured using a computer-operated static apparatus. Activity coefficients at infinite dilution and azeotropic compositions for the different temperatures were derived from the experimental *P*−*x* data. The data were simultaneously correlated together with published data with the help of either the UNIQUAC, NRTL, or Wilson model. However, the new data for the system ethyl *tert*-butyl ether + ethanol are in disagreement with some of the older data by Peng and Chao (Peng, C.-L.; Chao, K.-C. *DIPPR Data Ser.* **1994**, *2*, 23−27) and the pure component vapor pressure data for ethyl *tert*-butyl ether by Daubert (Daubert, T. E. *AIChE Data Ser.* **1991**, *1*, 80−88).

Introduction

tert-Butyl and *tert*-amyl ethers have gained great importance during recent years as fuel additives to reduce the CO content in the exhaust gas of cars by increasing the amount of oxygen in gasoline and as substitutes for tetraethyl lead, which was formerly used to increase the octane number. A great part of the methanol available worldwide and large amounts of the different isobutenes from C_4-raffinate are used for the production of MTBE (methyl *tert*-butyl ether). To manufacture even larger amounts of ethers as fuel additives, ethanol and higher alcohols and 2-methylbutenes are also used to produce ethyl *tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), and *tert*-amyl ethyl ether (TAEE).

For the production of these compounds a precise knowledge of the pure component and mixture behavior (phase equilibria, excess properties) of the compounds included in the process is of great importance. Moreover gasoline oxygenates pose environmental problems as groundwater contaminants. In this work accurate vapor−liquid equilibrium data for the system ethyl *tert*-butyl ether (ETBE) + ethanol as well as the system ethyl *tert*-butyl ether + water were measured at different temperatures. In addition, vapor pressure data were measured for ethyl *tert*-butyl ether for comparison with earlier data.

Experimental Section

Purity of Materials. Ethanol (99.8 wt %) was purchased from Barker, ethyl *tert*-butyl ether (94 wt %) was supplied by Veba Oel AG, and bidistilled water was prepared at our laboratory. ETBE was further purified by extraction of the alcohol impurities with water. Ethanol and ETBE were dried over a molecular sieve. All components were further purified and degassed by distillation as described previously by Fischer and Gmehling (1994). The properties and purities (as determined by GLC and Karl Fischer titration) of the pure components are given in Table 1.

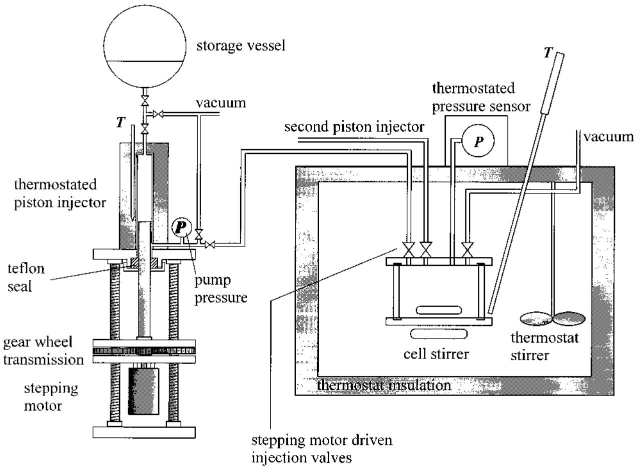

Figure 1. Schematic diagram of the computer-operated static apparatus.

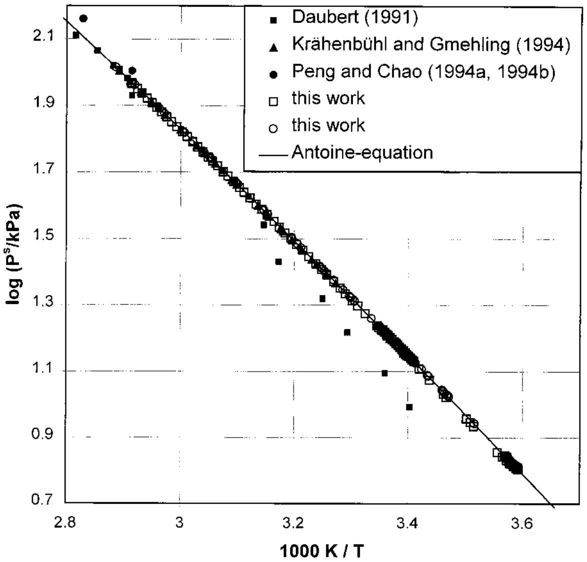

Figure 2. Pure component vapor pressure of ETBE as a logarithmic function of inverse temperature.

Apparatus and Procedure. A computer-operated static apparatus was used for the pure component vapor pressure and vapor−liquid equilibrium (VLE) measurements. Following the idea proposed by Gibbs and Van Ness (1972)

---

* Corresponding author. E-mail: Gmehling@tech.chem.uni-oldenburg.de.

10.1021/je980229i CCC: $18.00

Table 1. Mass Percent GLC Purities and Water Content of Pure Components

component	supplier	purity/wt %	water content/wt ppm
ETBE	Veba Oel AG	99.8	135
ethanol	Barker	99.95	200
water		not analyzed	

the total pressure P is measured for different overall compositions at constant temperature. The apparatus was described previously by Rarey and Gmehling (1993) and has a range of applicability from 5 to 95 °C and from 0 to 3 bar. The pressure inside the equilibrium cell was monitored using a Digiquartz pressure sensor (Model 245A, Paroscientific), and the temperature was measured by means of a Pt100 resistance thermometer (Model 1506, Hart Scientific) in the oil bath close to the cell. The liquid-phase compositions were calculated from known total compositions by solving the mass and volume balance, taking into account the vapor−liquid equilibrium. At low to normal pressures and separation factors not too far from unity, the liquid compositions are very close to the total compositions. In the case of systems such as ETBE−water studied in this work, liquid and total compositions differ significantly due to the strong real liquid-phase behavior. The total compositions were obtained from exactly known

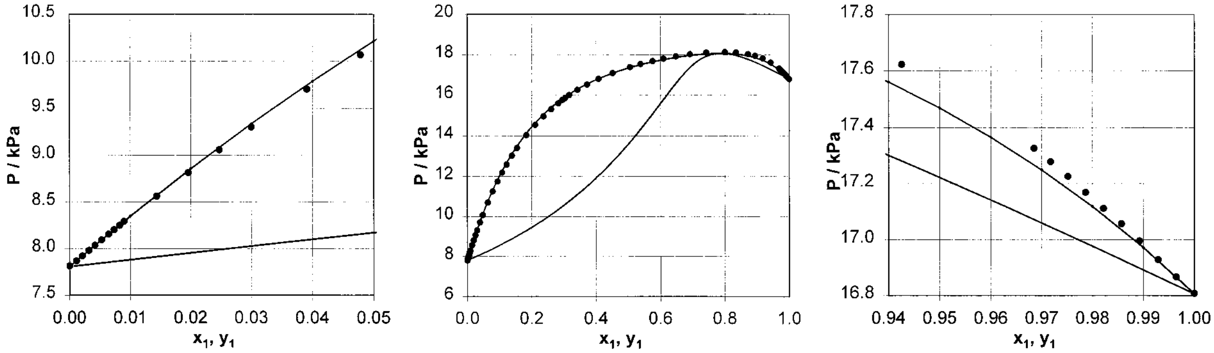

Figure 3. Different $P-x(y)$ diagrams for the system ETBE (1) + ethanol (2) at 24.8 °C: experimental (●); NRTL model (—).

Table 2. Experimental Vapor Pressure Data for Ethyl *tert*-Butyl Ether

T/K	P_i^s/kPa	T/K	P_i^s/kPa	T/K	P_i^s/kPa	T/K	P_i^s/kPa
(a) Between 278.28 and 343.33 K (Sample 1)							
278.283	6.370	285.476	9.061	298.122	16.824	327.300	54.109
278.300	6.384	288.368	10.526	298.191	16.831	328.028	55.511
278.321	6.370	288.795	10.752	298.612	17.099	329.046	57.533
278.335	6.405	290.871	11.854	298.885	17.318	330.069	59.631
278.345	6.430	292.410	12.805	300.751	18.848	331.070	61.733
278.408	6.387	293.211	13.516	301.917	19.850	332.091	63.955
278.449	6.466	293.440	13.654	302.809	20.622	333.089	66.193
278.579	6.428	293.693	13.819	303.927	21.649	334.111	68.527
278.581	6.495	293.964	13.991	304.829	22.500	335.123	70.922
278.731	6.526	294.236	14.051	305.838	23.519	336.135	73.374
278.858	6.559	294.251	14.178	306.970	24.649	337.121	75.843
278.974	6.514	294.438	14.141	307.863	25.586	338.108	78.364
279.006	6.594	294.530	14.360	308.819	26.650	339.047	80.842
279.155	6.625	294.750	14.307	310.001	27.955	340.024	83.487
279.304	6.657	294.795	14.542	311.050	29.189	341.110	86.500
279.420	6.696	295.069	14.724	312.070	30.417	342.048	89.169
279.422	6.638	295.346	14.911	313.120	31.734	343.111	92.288
279.542	6.769	295.619	15.097	314.080	32.969	343.171	92.466
279.770	6.897	295.916	15.301	315.068	34.285	343.219	92.615
279.858	6.957	296.195	15.494	316.071	35.662	343.255	92.724
279.880	6.785	296.509	15.718	317.257	37.352	343.283	92.804
279.971	6.988	296.797	15.923	318.221	38.741	343.296	92.849
280.052	7.007	296.840	15.807	319.161	40.149	343.305	92.875
280.103	7.017	297.111	16.146	320.307	41.921	343.313	92.898
280.135	7.019	297.280	16.119	321.368	43.620	343.317	92.916
280.146	7.020	297.386	16.334	322.231	45.025	343.320	92.932
280.396	6.963	297.669	16.531	323.351	46.932	343.325	92.941
281.111	7.186	297.932	16.714	324.369	48.696		
284.460	8.601	297.961	16.863	325.234	50.247		
284.958	8.834	297.961	16.861	326.332	52.272		
(b) Between 284.35 and 346.51 K (Sample 2)							
284.348	8.758	292.994	13.353	297.076	16.148	313.000	31.904
288.050	10.549	292.997	13.356	298.213	16.997	317.145	37.488
288.245	10.651	293.004	13.360	298.224	16.986	317.801	38.423
288.620	10.819	293.005	13.362	298.395	17.129	317.946	38.731
288.857	10.958	293.009	13.363	298.505	17.237	322.571	46.099
288.992	11.055	293.010	13.365	299.781	18.240	322.790	46.327
291.032	12.181	293.015	13.368	302.442	20.514	322.933	46.743
291.049	12.190	293.018	13.370	302.454	20.506	327.484	54.904
291.139	12.243	293.024	13.371	303.070	21.049	327.649	55.231
291.169	12.263	293.026	13.375	303.095	21.063	327.752	55.595
292.063	12.796	293.030	13.376	303.282	21.289	328.869	57.566
292.966	13.337	293.033	13.369	304.335	22.263	331.001	62.144
292.967	13.337	293.034	13.380	305.882	23.784	332.614	65.730
292.970	13.339	293.041	13.383	307.057	24.986	332.777	66.082
292.976	13.343	293.051	13.389	307.367	25.312	336.538	75.042
292.978	13.343	293.051	13.390	307.964	25.920	337.600	77.768
292.981	13.345	293.390	13.597	308.192	26.214	342.604	91.613
292.984	13.347	293.619	13.760	311.330	29.766	346.506	103.678
292.987	13.349	293.788	13.899	311.968	30.575		
292.989	13.352	294.032	14.029	312.894	31.718		
292.994	13.354	294.663	14.455	313.000	31.806		

Table 3. Antoine Constants, van der Waals Surface and Volume Parameters, Liquid Density, Liquid Compressibility and Liquid Molar Volume (Used for Fitting Wilson Parameters) of ETBE, Ethanol, and Water

component	ETBE	ethanol	water
A_i	5.80300[a]	7.2371[b]	7.19621[b]
B_i/K	1066.84[a]	1592.86[b]	1730.63[b]
C_i/K	−64.910[a]	−46.966[b]	−39.724[b]
r_i	4.7422[b]	2.1055[b]	0.9200[b]
q_i	4.1720[b]	1.9720[b]	1.4000[b]
ρ_i/kg·dm^{-3} (25 °C)	0.7352[b]	0.7850[b]	0.9970[b]
χ_i/kPa^{-1}	1.4×10^{-6} [a]	1.0×10^{-6} [a]	4.5×10^{-7} [a]
v_i/dm^3·mol^{-1}	0.1359[b]	0.05869[b]	0.01807[b]

[a] Measured. [b] DDB (1998).

amounts of liquids injected into the measurement cell using stepping motor driven injection pumps and valves. Since the liquids were injected at pressures of about 1 MPa, the densities of the compounds at this pressure had to be calculated with the help of normal pressure densities and liquid compressibilities which were determined for every component during the measurements. The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K; $\sigma(P) = 20$ Pa $+ 0.0001(P/\text{Pa})$; $\sigma(x_i) = 0.0001$. A scheme of the apparatus is shown in Figure 1.

Results

Pure Component Vapor Pressures. The temperature T and pure component vapor pressure P_i^s for ETBE are reported in Table 2a,b (sorted by increasing temperature) and are shown in Figure 2 together with the data from different authors. Although the absolute temperature uncertainty is approximately 0.03 K, three digits are specified in the table. Differences between two temperatures show a reproducibility of approximately 0.001 K. The two measurements differ because different samples were used. Two charges of ETBE were prepared, and the two different sets of pure component vapor pressure data were determined to verify the quality of purification. Each measurement was performed by stepwise increasing the temperature of the equilibrium cell and measuring the

Table 4. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Ethanol (2) at 24.8 °C

x_1	P/kPa	$y_{1,\text{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\text{calc}}$	γ_1	γ_2
0.000 00	7.808	0.0000	3.7177	1.0000	0.304 25	15.857	0.6123	1.9021	1.1228
0.001 11	7.869	0.0087	3.7055	1.0000	0.317 16	16.017	0.6191	1.8611	1.1339
0.002 10	7.923	0.0163	3.6945	1.0000	0.342 64	16.270	0.6315	1.7850	1.1574
0.003 18	7.982	0.0245	3.6826	1.0000	0.372 57	16.534	0.6447	1.7028	1.1882
0.004 19	8.036	0.0319	3.6717	1.0000	0.408 33	16.811	0.6588	1.6139	1.2297
0.005 28	8.095	0.0399	3.6598	1.0000	0.451 74	17.098	0.6743	1.5182	1.2878
0.006 45	8.156	0.0481	3.6473	1.0001	0.505 54	17.392	0.6920	1.4155	1.3733
0.007 34	8.203	0.0544	3.6377	1.0001	0.538 31	17.542	0.7022	1.3606	1.4339
0.008 22	8.251	0.0603	3.6284	1.0001	0.575 71	17.688	0.7138	1.3041	1.5125
0.008 97	8.292	0.0654	3.6205	1.0001	0.609 83	17.805	0.7244	1.2578	1.5943
0.014 36	8.563	0.0998	3.5643	1.0003	0.648 46	17.921	0.7367	1.2107	1.7009
0.019 58	8.815	0.1302	3.5116	1.0006	0.692 22	18.025	0.7516	1.1637	1.8436
0.024 73	9.058	0.1577	3.4610	1.0009	0.742 38	18.102	0.7704	1.1173	2.0443
0.030 00	9.301	0.1837	3.4107	1.0013	0.800 46	18.132	0.7964	1.0729	2.3448
0.039 09	9.704	0.2239	3.3273	1.0022	0.834 82	18.116	0.8150	1.0512	2.5694
0.047 84	10.070	0.2579	3.2506	1.0033	0.872 48	18.033	0.8398	1.0315	2.8701
0.063 70	10.694	0.3106	3.1199	1.0057	0.894 51	17.951	0.8571	1.0220	3.0790
0.079 01	11.246	0.3528	3.0030	1.0086	0.917 93	17.822	0.8787	1.0136	3.3342
0.093 83	11.739	0.3875	2.8973	1.0121	0.942 59	17.624	0.9062	1.0068	3.6474
0.108 20	12.182	0.4166	2.8013	1.0159	0.968 47	17.326	0.9421	1.0021	4.0358
0.122 07	12.578	0.4412	2.7141	1.0201	0.971 77	17.278	0.9473	1.0017	4.0903
0.138 62	13.016	0.4669	2.6163	1.0257	0.975 16	17.227	0.9528	1.0013	4.1477
0.154 51	13.400	0.4886	2.5281	1.0318	0.978 65	17.169	0.9587	1.0010	4.2083
0.183 87	14.034	0.5225	2.3786	1.0447	0.982 15	17.112	0.9649	1.0007	4.2705
0.211 27	14.545	0.5487	2.2527	1.0587	0.985 69	17.057	0.9713	1.0004	4.3350
0.236 83	14.966	0.5694	2.1454	1.0738	0.989 25	16.995	0.9781	1.0003	4.4016
0.260 75	15.315	0.5863	2.0529	1.0895	0.992 90	16.929	0.9852	1.0001	4.4716
0.283 18	15.608	0.6004	1.9725	1.1059	0.996 44	16.867	0.9924	1.0000	4.5411
0.295 24	15.776	0.6074	1.9316	1.1154	1.000 00	16.807	1.0000	1.0000	4.6130

Table 5. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Ethanol (2) at 50 °C

x_1	P/kPa	$y_{1,\text{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\text{calc}}$	γ_1	γ_2
0.000 00	29.253	0.0000	3.7705	1.0000	0.306 96	49.578	0.5308	1.8200	1.1302
0.001 20	29.414	0.0071	3.7529	1.0000	0.318 50	49.700	0.5369	1.7838	1.1406
0.002 61	29.597	0.0153	3.7326	1.0000	0.344 17	50.279	0.5496	1.7081	1.1654
0.004 04	29.779	0.0233	3.7122	1.0000	0.374 36	50.872	0.5632	1.6270	1.1976
0.005 49	29.993	0.0313	3.6918	1.0001	0.410 41	51.482	0.5783	1.5408	1.2404
0.006 68	30.148	0.0377	3.6753	1.0001	0.454 23	52.098	0.5957	1.4499	1.2992
0.007 94	30.306	0.0444	3.6579	1.0001	0.508 59	52.719	0.6168	1.3557	1.3827
0.008 96	30.433	0.0497	3.6441	1.0002	0.541 60	53.005	0.6298	1.3071	1.4398
0.010 33	30.608	0.0567	3.6257	1.0002	0.579 26	53.268	0.6451	1.2580	1.5117
0.011 74	30.784	0.0637	3.6071	1.0003	0.613 69	53.448	0.6595	1.2184	1.5850
0.016 96	31.646	0.0883	3.5400	1.0005	0.652 52	53.582	0.6765	1.1786	1.6785
0.022 13	32.272	0.1109	3.4768	1.0009	0.696 58	53.646	0.6970	1.1387	1.8028
0.027 40	33.007	0.1323	3.4153	1.0013	0.747 12	53.576	0.7225	1.0988	1.9776
0.032 44	33.582	0.1514	3.3589	1.0019	0.805 54	53.210	0.7567	1.0601	2.2403
0.041 29	34.568	0.1820	3.2656	1.0029	0.839 94	52.818	0.7806	1.0413	2.4355
0.049 99	35.467	0.2091	3.1800	1.0042	0.877 49	52.158	0.8122	1.0243	2.6913
0.065 88	37.013	0.2523	3.0374	1.0070	0.899 40	51.595	0.8342	1.0163	2.8638
0.081 20	38.371	0.2879	2.9139	1.0104	0.922 48	50.917	0.8615	1.0096	3.0649
0.096 06	39.592	0.3180	2.8048	1.0141	0.946 55	49.943	0.8954	1.0045	3.2958
0.110 43	40.688	0.3437	2.7078	1.0182	0.971 93	48.702	0.9392	1.0012	3.5602
0.124 31	41.651	0.3659	2.6206	1.0227	0.975 00	48.549	0.9452	1.0010	3.5934
0.140 87	42.724	0.3896	2.5239	1.0286	0.978 03	48.328	0.9512	1.0007	3.6265
0.156 81	43.663	0.4100	2.4371	1.0349	0.981 10	48.191	0.9575	1.0005	3.6600
0.186 26	45.204	0.4424	2.2903	1.0483	0.984 09	48.011	0.9637	1.0004	3.6930
0.213 70	46.445	0.4678	2.1668	1.0629	0.987 18	47.817	0.9704	1.0002	3.7272
0.239 35	47.453	0.4882	2.0610	1.0786	0.990 36	47.571	0.9774	1.0001	3.7625
0.263 31	48.285	0.5049	1.9696	1.0952	0.993 54	47.336	0.9847	1.0001	3.7981
0.285 80	48.985	0.5189	1.8899	1.1124	0.996 76	47.203	0.9922	1.0000	3.8341
0.296 42	49.357	0.5250	1.8542	1.1211	1.000 00	46.957	1.0000	1.0000	3.8705

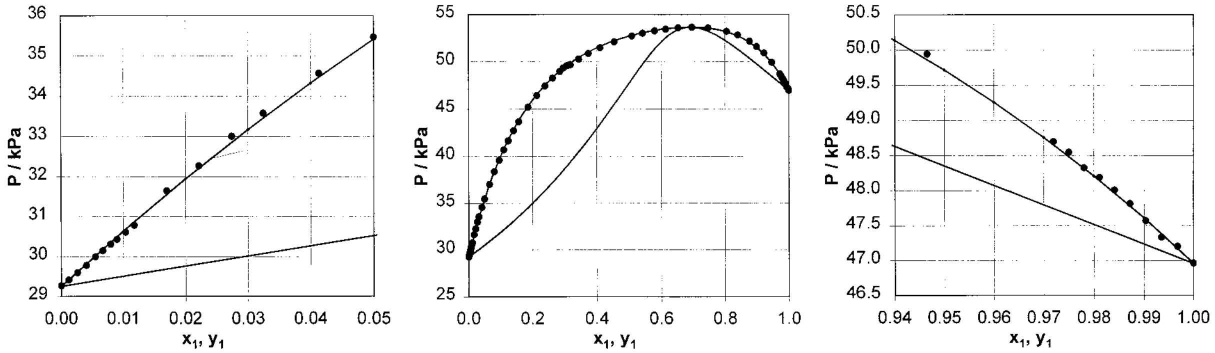

Figure 4. Different $P-x(y)$ diagrams for the system ETBE (1) + ethanol (2) at 50 °C: experimental (●); NRTL model (—).

Table 6. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Ethanol (2) at 65 °C

x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2
0.000 00	58.013	0.0000	3.5155	1.0000	0.306 24	88.944	0.4844	1.7626	1.1230
0.001 36	58.287	0.0064	3.4990	1.0000	0.315 03	89.387	0.4896	1.7378	1.1302
0.002 76	58.582	0.0129	3.4822	1.0000	0.340 59	90.266	0.5037	1.6696	1.1524
0.004 17	58.866	0.0192	3.4655	1.0000	0.370 70	91.150	0.5192	1.5964	1.1813
0.005 47	59.140	0.0251	3.4502	1.0001	0.406 69	92.067	0.5364	1.5179	1.2198
0.006 15	59.278	0.0280	3.4423	1.0001	0.450 53	92.976	0.5561	1.4339	1.2730
0.007 48	59.541	0.0338	3.4269	1.0001	0.505 02	93.796	0.5797	1.3448	1.3499
0.008 85	59.827	0.0396	3.4113	1.0001	0.538 10	94.156	0.5938	1.2978	1.4033
0.009 59	59.980	0.0427	3.4029	1.0002	0.575 92	94.445	0.6101	1.2497	1.4716
0.010 85	60.290	0.0479	3.3887	1.0002	0.610 56	94.595	0.6254	1.2103	1.5421
0.016 07	61.434	0.0686	3.3314	1.0004	0.649 66	94.620	0.6433	1.1704	1.6327
0.021 26	62.466	0.0878	3.2766	1.0007	0.694 14	94.436	0.6650	1.1304	1.7532
0.026 42	63.421	0.1058	3.2241	1.0011	0.745 28	93.913	0.6927	1.0909	1.9208
0.031 50	64.381	0.1225	3.1744	1.0016	0.804 43	92.762	0.7309	1.0537	2.1650
0.040 35	65.838	0.1493	3.0917	1.0026	0.839 35	91.717	0.7583	1.0361	2.3404
0.048 98	67.290	0.1732	3.0157	1.0038	0.877 26	90.127	0.7944	1.0208	2.5612
0.064 86	69.718	0.2122	2.8864	1.0064	0.899 45	88.869	0.8197	1.0138	2.7057
0.080 18	71.869	0.2449	2.7729	1.0096	0.922 57	87.312	0.8503	1.0080	2.8683
0.095 00	73.758	0.2727	2.6719	1.0132	0.946 97	85.283	0.8884	1.0037	3.0518
0.109 38	75.446	0.2969	2.5813	1.0172	0.972 77	82.652	0.9370	1.0009	3.2566
0.123 27	76.922	0.3180	2.4997	1.0215	0.975 75	82.309	0.9433	1.0007	3.2807
0.139 86	78.474	0.3407	2.4089	1.0272	0.978 74	81.964	0.9497	1.0006	3.3050
0.155 80	79.926	0.3604	2.3278	1.0333	0.981 77	81.630	0.9564	1.0004	3.3297
0.185 30	82.306	0.3924	2.1911	1.0463	0.984 80	81.297	0.9632	1.0003	3.3544
0.212 81	84.200	0.4179	2.0769	1.0603	0.987 85	80.959	0.9703	1.0002	3.3793
0.238 49	85.724	0.4389	1.9802	1.0751	0.990 84	80.564	0.9773	1.0001	3.4037
0.262 51	86.991	0.4564	1.8973	1.0906	0.993 84	80.193	0.9846	1.0000	3.4282
0.285 06	88.033	0.4714	1.8253	1.1066	0.996 88	79.820	0.9921	1.0000	3.4531
0.293 06	88.550	0.4765	1.8011	1.1126	1.000 00	79.431	1.0000	1.0000	3.4785

Table 7. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Ethanol (2) at 90 °C

x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2
0.000 00	159.051	0.0000	3.5515	1.0000	0.259 99	213.066	0.3824	1.8155	1.0995
0.000 18	159.132	0.0007	3.5493	1.0000	0.273 26	213.739	0.3904	1.7706	1.1096
0.000 40	159.234	0.0015	3.5466	1.0000	0.295 62	215.172	0.4032	1.7002	1.1276
0.001 40	159.722	0.0052	3.5344	1.0000	0.320 30	216.518	0.4165	1.6296	1.1491
0.002 23	160.116	0.0083	3.5242	1.0000	0.349 54	217.826	0.4313	1.5546	1.1767
0.003 44	160.640	0.0127	3.5095	1.0000	0.381 25	218.923	0.4467	1.4828	1.2091
0.004 54	161.158	0.0166	3.4963	1.0000	0.415 23	219.757	0.4627	1.4154	1.2469
0.006 31	161.941	0.0228	3.4752	1.0001	0.452 65	220.331	0.4803	1.3511	1.2921
0.008 20	162.713	0.0294	3.4528	1.0001	0.497 38	220.599	0.5015	1.2858	1.3513
0.010 53	163.748	0.0372	3.4256	1.0002	0.544 89	220.398	0.5251	1.2279	1.4209
0.014 82	165.548	0.0511	3.3767	1.0004	0.596 79	219.572	0.5525	1.1754	1.5058
0.020 81	167.961	0.0694	3.3105	1.0007	0.649 14	217.998	0.5825	1.1317	1.6032
0.030 15	171.457	0.0957	3.2119	1.0015	0.703 90	215.440	0.6173	1.0938	1.7214
0.041 56	175.457	0.1245	3.0985	1.0029	0.758 86	211.659	0.6571	1.0627	1.8624
0.052 66	179.052	0.1497	2.9951	1.0045	0.812 65	206.484	0.7030	1.0382	2.0289
0.065 70	182.921	0.1762	2.8814	1.0070	0.857 32	200.807	0.7489	1.0222	2.1941
0.081 43	187.112	0.2044	2.7543	1.0106	0.894 28	194.785	0.7949	1.0122	2.3523
0.101 55	191.835	0.2358	2.6060	1.0163	0.924 93	188.936	0.8407	1.0061	2.4994
0.120 85	195.786	0.2617	2.4770	1.0227	0.944 84	184.316	0.8753	1.0033	2.6028
0.139 33	199.084	0.2836	2.3640	1.0299	0.961 15	180.487	0.9072	1.0016	2.6919
0.161 39	202.543	0.3066	2.2411	1.0397	0.973 61	177.337	0.9342	1.0007	2.7624
0.182 35	205.380	0.3259	2.1350	1.0502	0.980 76	175.060	0.9508	1.0004	2.8037
0.202 32	207.749	0.3424	2.0425	1.0613	0.989 34	172.705	0.9719	1.0001	2.8541
0.221 27	209.735	0.3566	1.9618	1.0729	0.993 16	171.548	0.9817	1.0000	2.8767
0.237 45	211.011	0.3679	1.8978	1.0835	0.996 72	170.380	0.9911	1.0000	2.8980
0.239 36	211.399	0.3692	1.8905	1.0848	0.998 36	169.828	0.9955	1.0000	2.9078
0.254 08	212.327	0.3787	1.8363	1.0952	1.000 00	169.246	1.0000	1.0000	2.9176

Table 8. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Water (2) at 25.1 °C

x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2
0.901 17	19.801	0.8518	1.068	9.271	0.947 29	19.598	0.8685	1.026	15.245
0.906 67	19.781	0.8529	1.062	9.736	0.954 06	19.536	0.8734	1.021	16.770
0.912 01	19.771	0.8542	1.057	10.232	0.959 78	19.470	0.8785	1.017	18.298
0.917 45	19.764	0.8556	1.051	10.788	0.969 43	19.330	0.8901	1.011	21.548
0.922 91	19.739	0.8573	1.046	11.409	0.979 76	18.966	0.9092	1.005	26.395
0.928 69	19.712	0.8593	1.041	12.141	0.984 76	18.731	0.9226	1.003	29.515
0.934 49	19.689	0.8616	1.036	12.974	0.989 81	18.452	0.9404	1.002	33.397
0.940 20	19.653	0.8644	1.031	13.902	1.000 00	17.502	1.0000	1.000	

Table 9. Experimental Vapor−Liquid Equilibrium Data for ETBE (1) + Water (2) at 40 °C

x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2	x_1	P/kPa	$y_{1,\mathrm{calc}}$	γ_1	γ_2
0.000 00	7.399	0.0000		1.000	0.017 73	37.212	0.8024	52.072	1.014
0.000 13	9.118	0.1882	496.245	1.000	0.021 41	37.443	0.8037	43.329	1.018
0.000 26	10.847	0.3172	473.521	1.000	0.025 77	37.618	0.8046	36.111	1.022
0.000 39	12.368	0.4013	453.752	1.000	0.031 15	37.754	0.8053	29.935	1.028
0.000 51	13.698	0.4591	437.132	1.000	0.036 47	37.828	0.8057	25.593	1.033
0.000 66	15.221	0.5132	417.059	1.000	0.042 41	37.888	0.8060	22.022	1.040
0.000 81	16.639	0.5547	398.526	1.000	0.048 63	37.929	0.8062	19.213	1.046
0.000 95	17.846	0.5849	382.253	1.000	0.055 42	37.953	0.8064	16.858	1.054
0.001 09	18.988	0.6099	366.973	1.000	0.062 12	37.983	0.8065	15.042	1.061
0.001 23	20.021	0.6300	353.015	1.000	0.068 71	37.985	0.8066	13.598	1.069
0.001 50	21.864	0.6614	327.265	1.001	0.076 82	38.006	0.8067	12.163	1.078
0.001 87	23.907	0.6905	298.013	1.001	0.907 79	38.105	0.82785	1.057	9.653
0.002 43	26.441	0.7203	260.557	1.001	0.920 16	38.004	0.83221	1.046	10.842
0.003 18	28.910	0.7443	222.215	1.001	0.932 87	37.845	0.83825	1.035	12.388
0.004 11	31.045	0.7622	186.580	1.002	0.945 51	37.601	0.84666	1.025	14.388
0.005 22	32.760	0.7748	155.919	1.003	0.958 94	37.199	0.85992	1.016	17.277
0.006 80	34.295	0.7851	125.733	1.004	0.972 20	36.538	0.88080	1.008	21.365
0.008 72	35.418	0.7920	101.243	1.006	0.985 97	35.328	0.91900	1.002	27.872
0.011 38	36.305	0.7972	79.405	1.008	1.000 00	32.925	1.00000	1.000	1.000
0.014 38	36.858	0.8004	63.686	1.011					

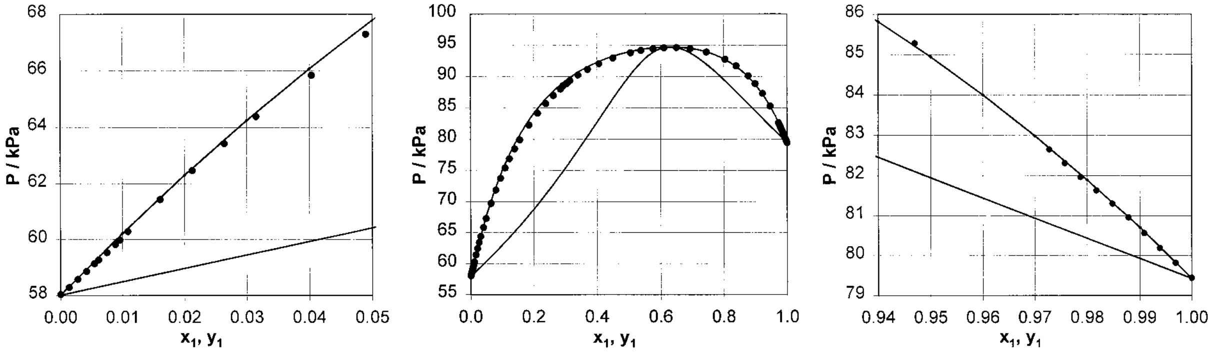

Figure 5. Different $P-x(y)$ diagrams for the system ETBE (1) + ethanol (2) at 65 °C: experimental (●); NRTL model (—).

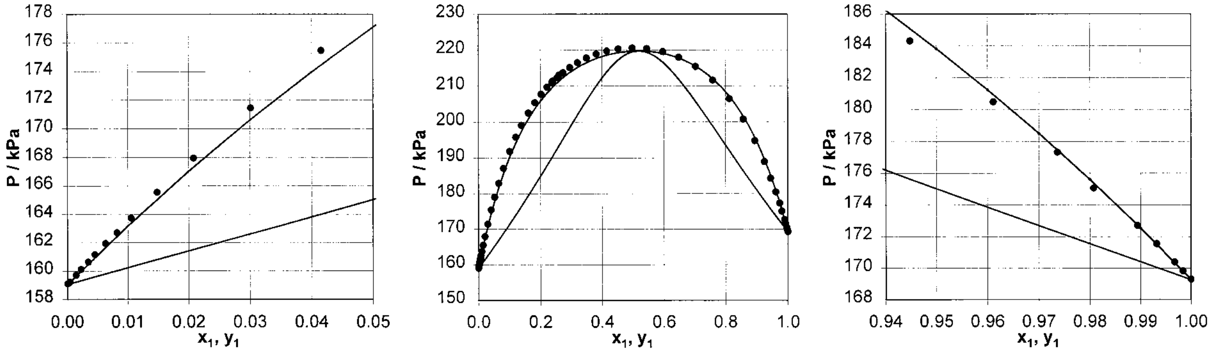

Figure 6. Different $P-x(y)$ diagrams for the system ETBE (1) + ethanol (2) at 90 °C: experimental (●); NRTL model (—).

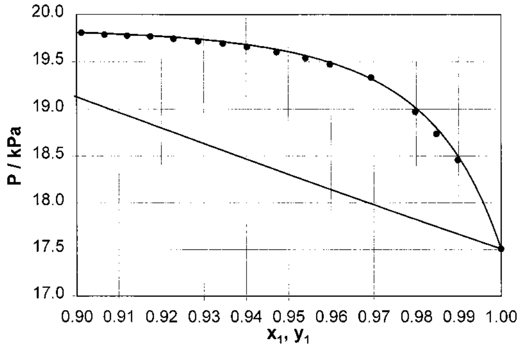

Figure 7. $P-x(y)$ diagram for the system ETBE (1) + water (2) at 25.1 °C: experimental (●); Wilson model (—).

vapor pressure over the whole temperature range and then repeating the measurement with stepwise cooling. At temperatures below 300 K heating and cooling measurements differ by about 1% in pressure, which leads to reversed temperature/pressure increases in the tables.

The data from this work were correlated with the help of the Antoine equation:

$$\log(P_i^{\mathrm{s}}/\mathrm{kPa}) = A_i - \frac{B_i}{C_i + (T/\mathrm{K})} \qquad (1)$$

The Antoine constants, derived with the help of a least squares linear regression of the logarithms of the vapor pressures as a function of inverse temperature, are given in Table 3 together with other required pure component data for all three components.

Vapor−Liquid Equilibrium Data. The liquid-phase composition x_1 for the first component and the system pressure P for the different VLE isotherms are given in Tables 4−9 together with the calculated vapor phase composition y_1 and activity coefficients γ_1 and γ_2 as determined from a correlation of the experimental $P-x$ data with the help of a Legendre polynomial (Kolbe and Gmehling, 1985) with up to six parameters. At 25 °C for the system ETBE + water, only the behavior on the ETBE rich side was determined. Graphical representations of the data are shown in Figures 3−8.

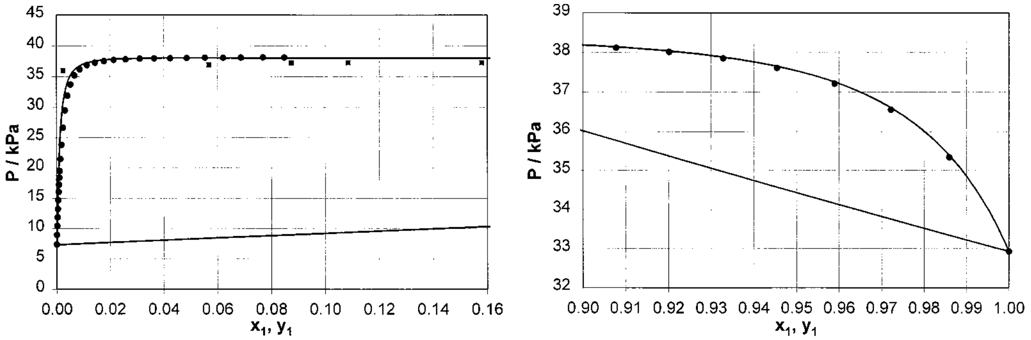

Figure 8. Different $P-x(y)$ diagrams for the system ETBE (1) + water (2) at 39.09 and 40 °C: experimental (this work, 40 °C, ●; Clark et al. (1997), 39.09 °C, ■; Wilson model, 40 °C, —).

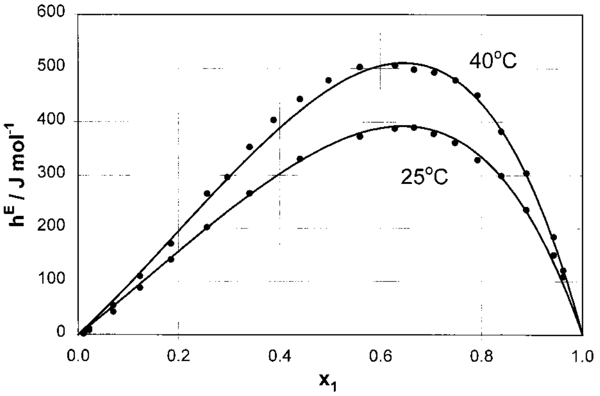

Figure 9. Experimental excess enthalpy data from literature for the system ETBE (1) + ethanol (2) (Mier et al. (1995) (●); NRTL model (—).

Data Treatment and Discussion

ETBE + Ethanol System. The measured VLE data for the system ETBE + ethanol were simultaneously correlated together with H^E data from literature with the help of the NRTL and UNIQUAC model. The experimental data are shown in Figures 3−6 together with the curves calculated with the same set of temperature-dependent NRTL interaction parameters. Figure 9 shows the consistency of the VLE data at different temperatures with the excess enthalpy data from Mier et al. (1995). For the calculated curve in Figure 9 again the same parameters were used. A similar good agreement of the data is achieved by the UNIQUAC model. The regressed interaction parameters for both models are given in Table 10. The following expression was used to describe the temperature dependence of the interaction parameters:

$$\Delta u_{ij}/\mathrm{K} = a_{ij} + b_{ij}(T/\mathrm{K}) + c_{ij}(T/\mathrm{K})^2 \qquad (2)$$

Figure 10 shows the data published by Peng and Chao (1994b) together with the curves calculated with the help of the temperature-dependent NRTL parameters from Table 10. It can be seen that in particular the data at higher temperature are in strong disagreement with the results from this work.

From the experimental data of this work, the activity coefficients at infinite dilution as well as the azeotropic composition were derived at different temperatures. In the case of activity coefficients at infinite dilution the values were obtained by regressing approximately 10 data points in the very dilute region with the help of a one parameter Legendre polynomial. The results are given in Table 11 and are shown in graphical form in Figures 11 and 12 in comparison with the results obtained by the UNIQUAC and NRTL models.

ETBE + Water System. The experimental VLE data for the system ETBE + water from this work were simultaneously correlated with the help of the Wilson model as the NRTL and UNIQUAC models were not able to describe the strong real VLE behavior of this partially immiscible system. Figures 7 and 8 show the experimental data together with the calculated curves. Due to their large scatter the data of Clark et al. (1997) were not used for the regression but are included in Figure 8. The interaction parameters and activity coefficients at infinite dilution calculated from these parameters are given in Tables 12 and 13.

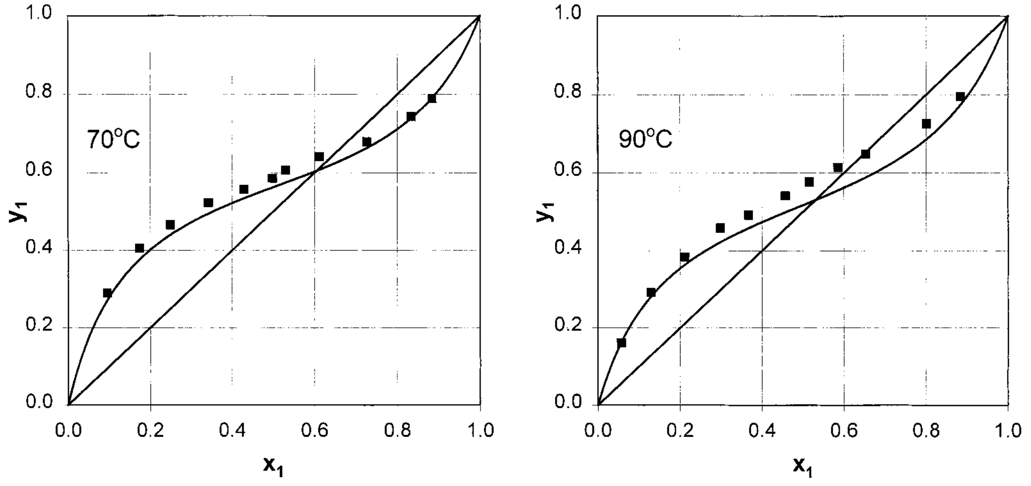

Figure 10. Experimental vapor−liquid equilibrium data by Peng and Chao for the system ETBE (1) + ethanol (2): experimental data (■), NRTL model (—).

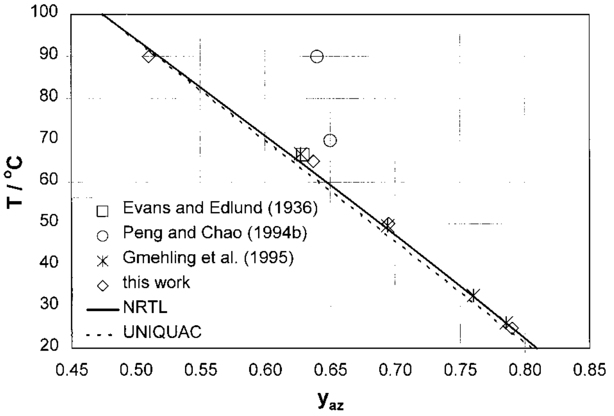

Figure 11. Experimental and calculated azeotropic compositions for the system ETBE (1) + ethanol (2).

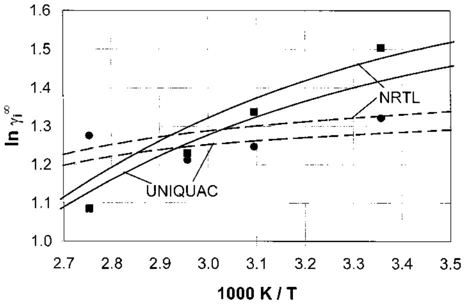

Figure 12. Experimental and calculated activity coefficients at infinite dilution for the system ETBE (1) + ethanol (2) (●, – -, (1) in (2); ■, —, (2) in (1)).

Table 10. Temperature-Dependent Interaction Parameters for the NRTL and UNIQUAC Model for the System ETBE (1) + Ethanol (2)

model	i	j	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}	
NRTL	1	2	−753.694	7.167 82	−0.012 321 6	$\alpha_{12} = 0.4691$
	2	1	339.475	−1.663 86	0.004 152 0	
UNIQUAC	1	2	−486.511	5.183 22	−0.007 979 2	
	2	1	176.611	−1.650 10	0.002 583 3	

Table 11. Azeotropic Composition, Pressure, and Activity Coefficients at Infinite Dilution for the System ETBE (1) + Ethanol (2) Derived from the Experimental VLE Data of This Work

T/K	$y_{az,1}$	P_{az}/kPa	γ_1^∞	γ_2^∞
297.95	0.790	18.14	3.75	4.50
323.15	0.695	53.66	3.48	3.81
338.15	0.637	94.69	3.36	3.42
363.15	0.510	220.61	3.58	2.96

Conclusions

Pure component vapor pressures for ETBE and isothermal VLE data for the systems ETBE−ethanol and ETBE−water were measured at different temperatures using a computer-driven static total pressure apparatus. Good agreement between all experimental $P-x$ data from this work as well as H^E data and azeotropic information from literature with the calculated values using the different G^E models can be achieved. For the ETBE−ethanol system, both the NRTL and UNIQUAC models give similar good representation of the data. The results for the system ETBE−water could only be correlated with the help of the Wilson equation due to the large positive deviation from Raoult's law.

Table 12. Wilson Interaction Parameters for the System ETBE (1) + Water (2)

i	j	a_{ij}/K
1	2	1015.45
2	1	1462.70

Table 13. Activity Coefficients at Infinite Dilution for the System ETBE (1) + Water (2) Derived from the Experimental VLE Data of This Work

T/K	γ_1^∞	γ_2^∞
298.25		17.5
313.15	520	33

Literature Cited

Clark, A. Q.; McBain, S. E.; Killner, J. (Vapour + Liquid) Equilibria of (Alkoxyalkanes + Alkanes, or *o*-Xylene, or Water, or Methanol) for Ether Mole Fractions 0 to 0.5, Between Temperatures 293 K and 323 K. *J. Chem. Thermodyn.* **1997**, *29*, 441−446.

Daubert, T. E. Vapor Pressure of 13 Pure Industrial Chemicals. *AIChE Data Ser.* **1991,** *1*, 80−88.

Evans, T. W.; Edlund, K. R. Tertiary Alkyl Ethers. Preparation and Properties. *Ind. Eng. Chem.* **1936**, *28*, 1186−1188.

Fischer, K.; Gmehling, J. $P-x$ and γ^∞ Data for the Different Binary Butanol−Water Systems at 50 °C. *J. Chem. Eng. Data* **1994**, *39*, 309−315.

Gibbs, R. E.; Van Ness, H. C. Vapor−Liquid Equilibria from Total-Pressure Measurements. A New Apparatus. *Ind. Eng. Chem. Fundam.* **1972**, *11*, 410−413.

Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. A Data Bank for Azeotropic Data−Status and Applications. *Fluid Phase Equilib.* **1995**, *103*, 51−76.

Kolbe, B.; Gmehling, J. Thermodynamic Properties of Ethanol + Water. I. Vapour-Liquid Equilibria, Measurements from 90 to 150 °C by the Static Methodol. *Fluid Phase Equilib.* **1985**, *23*, 213−226.

Krähenbühl, M.; Gmehling, J. Vapor Pressures of Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, Isopropyl *tert*-Butyl Ether, *tert*-Amyl Methyl Ether, and *tert*-Amyl Ethyl Ether. *J. Chem. Eng. Data* **1994**, *39*, 759−762.

Mier, W.; Oswald, G.; Tusel-Langer, E.; Lichtenthaler, R. N. Excess Enthalpy h^E of Binary Mixtures Containing Alkanes, Ethanol and Ethyl *tert*-Butyl Ether (ETBE). *Ber. Bunsen-Ges. Phys. Chem.* **1995**, *99*, 1123−1130.

Peng, C.-L.; Chao, K.-C. Vapor-Liquid Equilibrium in Binary Mixtures of *n*-Heptane + Ethyl *tert*-Butyl Ether. *DIPPR Data Ser.* **1994a**, *2*, 18−22.

Peng, C.-L.; Chao, K.-C. Vapor-Liquid Equilibrium in Binary Mixtures of Ethyl *tert*-Butyl Ether + Ethanol and *n*-Butyraldehyde + *n*-Propanol. *DIPPR Data Ser.* **1994b**, *2*, 23−27.

Rarey, J. R.; Gmehling, J. Computer-Operated Differential Static Apparatus for the Measurement of Vapor-Liquid Equilibrium Data. *Fluid Phase Equilib.* **1993**, *83*, 279−287.

Received for review September 16, 1998. Accepted January 21, 1999. The authors thank the "Fonds Der Chemischen Industrie" for financial support.

JE980229I