Various Thermodynamic Properties for Binary Systems with Tertiary Ethers

A. Heine, K. Fischer, and J. Gmehling*

Universität Oldenburg, Technische Chemie, Fachbereich 9, Postfach 2503, 26111 Oldenburg, Germany

---

Isothermal *P*, *x* data and excess enthalpies (H^E) were measured for the binary systems 2-methyl-1-butene + methyl *tert*-butyl ether, 2-methyl-1-pentene + *tert*-amyl ethyl ether, *tert*-amyl ethyl ether + ethanol, and *tert*-amyl methyl ether + *tert*-amyl ethyl ether at approximately 363 K using a static apparatus and an isothermal flow calorimeter. Temperature dependent parameters were fitted simultaneously to the experimental data. Infinite dilution activity coefficients (γ_i^∞) were derived from the vapor−liquid equilibrium (VLE) data in the dilute region using a flexible Legendre polynomial.

Introduction

Since the first attempts for the reduction of lead additives to gasoline in the 1980s, tertiary ethers or so-called oxygenates have become of fundamental importance. Their presence in gasoline is even required by law (at least in the United States, 2 mass % oxygen). The oxygenates increase the octane number of the fuels and decrease the amount of carbon monoxide emitted by combustion. Furthermore they are preferred compared to light alcohols because of their similarity to hydrocarbons and their low volatility. The conversion to ethers also helps to reduce the amount of light olefins present in gasoline, which are responsible for smog and the ozone formation. But also the disadvantageous emission of formaldehyde and polycyclic aromatics (traces) is currently discussed (Fadopé, 1995).

In 1994 6.2 million tons of methyl *tert*-butyl ether (MTBE) was produced in the U.S. (*Chem. Eng. News*, 1995), and the production capacity is still increasing to meet the growing demand for oxygenates. Due to the insufficient supply of MTBE there is also a large interest in the heavier tertiary ethers (e.g., *tert*-amyl methyl ether (TAME) or *tert*-amyl ethyl ether (TAEE)).

The most commonly used production method for MTBE, TAME, or TAEE is based on an acid catalyzed (often acid ion exchange resins) chemical reaction of methanol or ethanol with isobutene from the C_4-fraction or the isoamylenes from the C_5-fraction (2-methyl-1-butene, 2-methyl-2-butene), respectively, from the steam cracking process. Currently, the intensive research activity (reaction equilibria, kinetics, and catalysts) for the isobutene and isoamylene conversion is indicated by several publications (Rihko et al., 1994; Jensen and Datta, 1995; Kitchaiya and Datta, 1995; Zhang and Datta, 1995a,b; Oost and Hoffmann, 1995).

Because of the various advantages of reactive distillation, such as enhanced conversion and selectivity, minimization of separation and recycle problems, and direct use of the reaction enthalpy, vapor−liquid equilibria (VLE) of systems with alcohols, isoalkenes, and tertiary ethers become important for the design of the distillation columns. In this study experimental vapor−liquid equilibria, excess molar enthalpies (H^E), and activity coefficients at infinite dilution (γ^∞) for four binary systems and, additionally, azeotropic

Table 1. Pure Components Specifications

compound	source	water content (mass %)
tert-amyl ethyl ether	Erdölchemie GmbH	0.015[a]
tert-amyl methyl ether	Erdölchemie GmbH	0.014[a]
ethanol	Scharlau	0.008[a]
2-methyl-1-butene	Erdölchemie GmbH	0.011[b]
2-methyl-1-pentene	Phillips Petroleum	0.004[b]
methyl *tert*-butyl ether	Riedel-de Haën	0.005[a]

[a] After drying with metallic sodium. [b] After drying with molecular sieve.

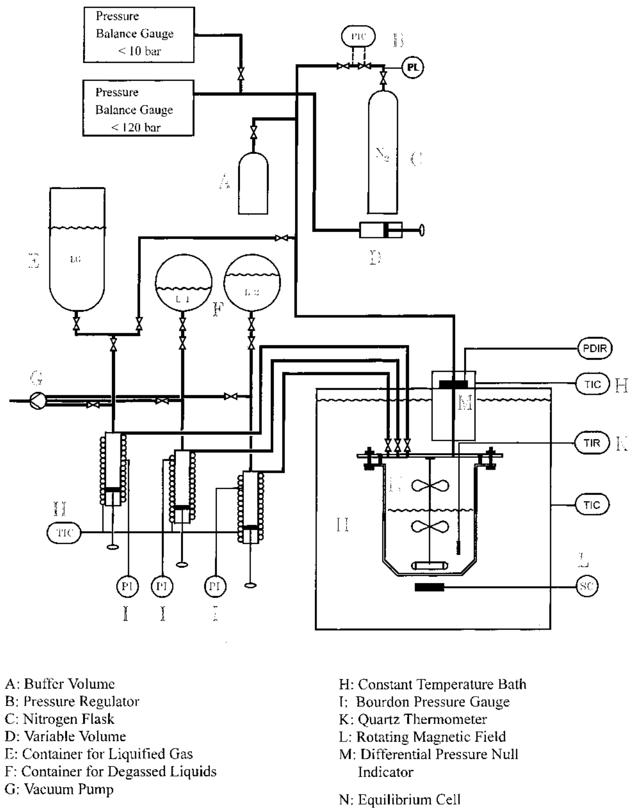

Figure 1. Scheme of the static apparatus.

---

* Corresponding author. Telephone: ++49 441 798 3831. Fax: ++49 441 798 3330. E-mail: gmehling@fb9tc.uni-oldenburg.de.

10.1021/je980203r CCC: $18.00

Table 2. Fitted NRTL Parameters[a]

component 1	component 2	T/K	α_{12}	g_{12}^0/(J mol^{-1})	g_{21}^0/(J mol^{-1})	g_{12}^1/(J mol^{-1} K^{-1})	g_{21}^1/(J mol^{-1} K^{-1})
2-methyl-1-butene	MTBE	362.86	0.3056	175.370	117.79	0.191 52	−0.824 09
2-methyl-1-pentene	TAME	362.82	0.3070	77.477	138.21	0.929 18	−1.274 20
TAME	TAEE	362.78	0.3040	−41.751	100.95	−0.399 03	0.221 19
TAEE	ethanol	362.82	0.4695	8745.800	−558.77	−17.8090	9.174 10[a]

[a] $\Delta g_{ij} = g_{ij}^0 + g_{ij}^1(T/\mathrm{K})$.

Table 3. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System 2-Methyl-1-butene (1) + Methyl *tert*-Butyl Ether (2) at 362.86 K

exptl data		NRTL		exptl data		NRTL		exptl data		NRTL	
x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa
0.000 00	277.80	0.0000	0.000	0.437 76	393.85	0.6021	0.144	0.868 10	504.98	0.9263	−0.129
0.016 95	282.35	0.0329	0.044	0.444 73	395.93	0.6088	−0.120	0.924 69	519.54	0.9590	−0.233
0.044 04	289.64	0.0833	0.072	0.496 53	409.09	0.6566	0.191	0.954 92	526.90	0.9758	0.123
0.068 19	296.08	0.1261	0.140	0.506 17	412.14	0.6652	−0.361	0.970 77	530.70	0.9844	0.368
0.094 67	303.19	0.1707	0.151	0.560 67	425.76	0.7117	0.129	0.979 62	533.21	0.9892	0.120
0.130 17	312.72	0.2274	0.128	0.564 18	427.14	0.7146	−0.336	0.986 99	535.10	0.9931	0.107
0.205 70	332.89	0.3368	0.083	0.624 91	442.76	0.7627	−0.285	0.991 38	535.98	0.9954	0.347
0.266 66	349.01	0.4157	0.105	0.692 03	459.91	0.8122	−0.159	0.994 65	537.05	0.9972	0.115
0.314 65	361.62	0.4727	0.141	0.745 31	473.51	0.8489	−0.080	0.997 32	537.68	0.9986	0.169
0.376 27	377.68	0.5403	0.256	0.807 10	489.29	0.8891	−0.037	1.000 00	538.53	1.0000	0.000

mean dev ΔP/kPa: 0.167
max dev ΔP/kPa: 0.368

Table 4. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System 2-Methyl-1-pentene (1) + *tert*-Amyl Methyl Ether (2) at 362.82 K

exptl data		NRTL		exptl data		NRTL		exptl data		NRTL	
x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa
0.000 00	111.05	0.0000	−0.000	0.289 36	144.61	0.4544	0.325	0.845 62	207.58	0.9159	0.029
0.008 56	112.21	0.0176	−0.139	0.357 56	152.49	0.5316	0.276	0.887 48	212.16	0.9399	0.099
0.017 33	113.27	0.0352	−0.152	0.411 81	158.68	0.5874	0.281	0.913 90	214.94	0.9546	0.239
0.025 50	114.34	0.0514	−0.254	0.466 22	165.39	0.6392	−0.244	0.939 40	218.08	0.9684	−0.069
0.038 99	115.55	0.0775	0.136	0.474 36	166.07	0.6466	−0.003	0.959 25	220.30	0.9789	−0.099
0.052 58	117.23	0.1030	0.065	0.524 38	171.85	0.6903	−0.135	0.976 51	222.10	0.9880	0.013
0.068 57	119.13	0.1321	0.057	0.526 87	172.48	0.6924	−0.480	0.986 98	223.15	0.9934	0.119
0.094 80	122.13	0.1778	0.157	0.584 52	178.95	0.7393	−0.457	0.992 70	223.75	0.9963	0.152
0.128 66	126.06	0.2333	0.200	0.648 17	185.73	0.7873	−0.108	0.996 28	224.45	0.9981	−0.145
0.180 75	132.19	0.3121	0.164	0.715 63	193.13	0.8344	0.027	1.000 00	224.71	1.0000	0.000
0.231 44	137.88	0.3818	0.364	0.786 66	200.90	0.8803	0.161				

mean dev ΔP/kPa: 0.172
max dev ΔP/kPa: 0.480

data are presented. The experimental results were used to fit simultaneously temperature dependent NRTL parameters for the model.

These systems were studied as part of an ongoing investigation sponsored by Project 805c/94 of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

Experimental Section

The degassing and purification procedure of 2-methyl-1-butene, 2-methyl-1-pentene, MTBE, TAME, and TAEE was carried out in the same way as that described earlier (Fischer and Gmehling, 1994). 2-Methyl-1-butene was separated from a mixture of isoamylenes using a pilot plant distillation column of 4.50 m height with approximately 20 theoretical stages.

In Table 1 the supplier and the water content determined by Karl Fischer titration after purification are listed. The purities of the components used were also checked by gas chromatography and found to be greater than 99.98% in all cases.

The static apparatus and procedure of measurement have been described in detail elsewhere (Fischer and Gmehling, 1994). Using precise piston injectors, the desired amount of degassed liquids was introduced into the equilibrium cell. The steel equilibrium cell was located in a

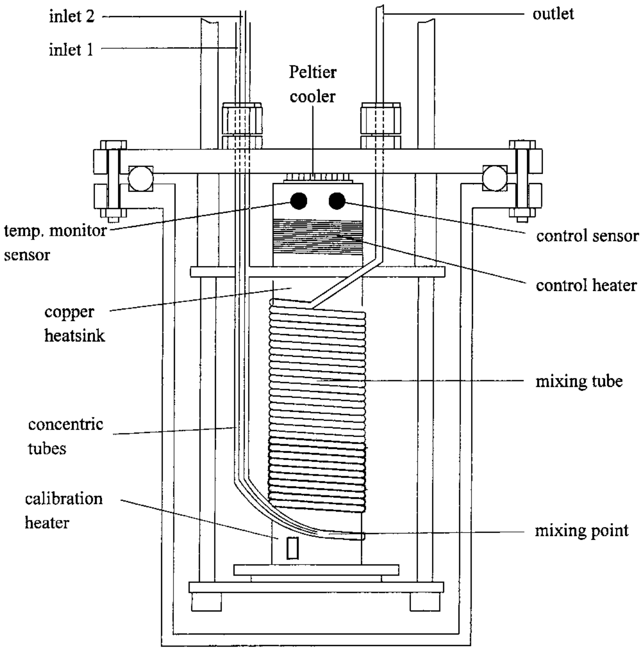

Figure 2. Scheme of the flow cell.

Table 5. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System *tert*-Amyl Ethyl Ether (1) + Ethanol (2) at 362.82 K

exptl data		NRTL		exptl data		NRTL		exptl data		NRTL	
x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa
0.000 00	154.35	0.0000	0.000	0.141 61	164.36	0.1668	−0.084	0.432 32	160.49	0.2887	0.120
0.000 97	154.44	0.0019	0.047	0.155 42	164.75	0.1762	−0.217	0.449 23	159.87	0.2937	0.167
0.001 97	154.73	0.0038	−0.103	0.165 74	164.85	0.1829	−0.183	0.461 33	159.40	0.2973	0.196
0.002 90	154.79	0.0056	−0.024	0.175 49	164.88	0.1888	−0.111	0.485 97	158.52	0.3046	0.123
0.004 50	155.05	0.0086	−0.068	0.182 86	164.91	0.1931	−0.083	0.492 71	157.96	0.3066	0.407
0.006 46	155.36	0.0122	−0.105	0.190 19	164.93	0.1973	−0.072	0.511 78	157.04	0.3124	0.507
0.008 95	155.68	0.0167	−0.092	0.197 67	165.04	0.2013	−0.156	0.531 63	156.04	0.3185	0.588
0.011 42	156.00	0.0211	−0.091	0.204 90	164.99	0.2051	−0.095	0.552 91	154.85	0.3253	0.709
0.014 35	156.41	0.0262	−0.135	0.212 52	165.00	0.2090	−0.115	0.575 95	153.43	0.3329	0.875
0.017 66	156.83	0.0318	−0.144	0.219 96	164.93	0.2127	−0.068	0.600 52	151.87	0.3415	0.952
0.021 33	157.36	0.0378	−0.247	0.227 63	164.92	0.2163	−0.088	0.627 54	149.99	0.3516	1.013
0.025 44	157.73	0.0443	−0.159	0.235 24	164.77	0.2199	0.013	0.651 15	148.16	0.3612	1.064
0.030 07	158.27	0.0514	−0.197	0.243 31	164.72	0.2235	0.007	0.675 51	146.03	0.3720	1.153
0.034 92	158.72	0.0586	−0.160	0.253 64	164.67	0.2280	−0.036	0.702 54	143.55	0.3852	1.076
0.041 23	159.41	0.0675	−0.255	0.265 26	164.53	0.2328	−0.033	0.732 80	140.27	0.4022	1.067
0.051 19	160.29	0.0807	−0.276	0.278 46	164.39	0.2381	−0.061	0.767 02	136.04	0.4248	0.921
0.062 36	161.12	0.0944	−0.255	0.291 59	164.19	0.2431	−0.063	0.805 67	130.25	0.4564	0.748
0.073 95	161.95	0.1074	−0.317	0.307 54	163.91	0.2490	−0.059	0.845 79	122.81	0.4994	0.545
0.085 70	162.49	0.1197	−0.199	0.322 43	163.64	0.2542	−0.081	0.890 62	112.18	0.5673	0.360
0.098 46	163.09	0.1319	−0.187	0.342 86	163.19	0.2611	−0.069	0.940 86	96.275	0.6900	0.311
0.112 60	163.65	0.1444	−0.187	0.376 16	162.37	0.2718	−0.080	1.000 00	70.482	1.0000	0.000
0.127 51	164.12	0.1564	−0.187	0.404 04	161.48	0.2803	0.025				

mean dev ΔP/kPa: 0.288
max dev ΔP/kPa: 1.153

Table 6. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System *tert*-Amyl Methyl Ether (1) + *tert*-Amyl Ethyl Ether (2) at 362.78 K

exptl data		NRTL		exptl data		NRTL		exptl data		NRTL	
x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa	x_1	P/kPa	y_1	ΔP/kPa
0.000 00	71.591	0.0000	0.000	0.341 87	85.097	0.4460	−0.077	0.835 42	104.57	0.8875	−0.043
0.010 46	72.029	0.0161	−0.028	0.395 69	87.221	0.5038	−0.080	0.888 92	106.73	0.9256	−0.076
0.017 97	72.339	0.0275	−0.044	0.437 99	88.885	0.5472	−0.075	0.938 81	108.74	0.9598	−0.105
0.023 43	72.589	0.0358	−0.080	0.461 53	89.739	0.5707	−0.000	0.965 78	109.74	0.9777	−0.039
0.028 64	72.749	0.0436	−0.036	0.484 20	90.678	0.5929	−0.044	0.980 12	110.38	0.9871	−0.115
0.037 10	73.101	0.0563	−0.056	0.497 60	91.166	0.6057	−0.003	0.987 45	110.63	0.9919	−0.071
0.050 68	73.619	0.0763	−0.043	0.546 51	93.130	0.6516	−0.035	0.992 25	110.79	0.9950	−0.040
0.068 84	74.331	0.1027	−0.043	0.597 66	95.132	0.6975	−0.015	0.995 91	110.94	0.9974	−0.049
0.102 93	75.676	0.1508	−0.052	0.661 52	97.677	0.7521	−0.033	0.998 42	111.03	0.9990	−0.036
0.172 12	78.379	0.2435	−0.039	0.698 23	99.168	0.7823	−0.071	1.000 00	111.06	1.0000	0.000
0.238 30	80.993	0.3264	−0.051	0.738 36	100.71	0.8143	−0.024				
0.295 22	83.229	0.3936	−0.047	0.783 50	102.50	0.8490	−0.024				

mean dev ΔP/kPa: 0.049
max dev ΔP/kPa: 0.115

Table 7. Activity Coefficients at Infinite Dilution

			quasi experimental using the Legendre polynomial		calculated using NRTL	
component 1	component 2	T/K	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
2-methyl-1-butene	MTBE	362.86	1.02	1.03	1.02	1.02
2-methyl-1-pentene	TAME	362.82	1.01	1.03	1.03	1.03
TAME	TAEE	362.78	1.01	1.01	1.00	1.00
TAEE	ethanol	362.82	4.37	3.89	4.41	3.92

Table 8. Experimental and Calculated (NRTL) Excess Enthalpies for the System 2-Methyl-1-butene (1) + Methyl *tert*-Butyl Ether (2) at 363.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0276	7.64	0.00	0.3738	68.36	−0.68	0.7212	58.89	0.16
0.0551	14.91	−0.06	0.4250	71.52	−0.70	0.7688	52.15	0.16
0.1097	26.67	1.24	0.4756	72.53	−0.09	0.8160	44.56	−0.28
0.1636	39.69	−0.48	0.5258	72.58	0.00	0.8627	34.73	0.28
0.2170	48.83	−0.04	0.5754	70.82	0.46	0.9089	25.30	−0.78
0.2698	56.77	−0.06	0.6245	67.62	0.95	0.9547	14.29	−1.45
0.3221	63.36	−0.36	0.6731	64.48	0.00	0.9774	6.26	0.30

constant temperature bath, which was controlled within ±0.05 K. The temperature T was measured by means of Pt100 probes. The mixture in the cell was stirred using a magnetic stirrer driven by a rotating magnetic field. A differential pressure null indicator was used to adjust the nitrogen pressure in a reference system to the system pressure P. The nitrogen pressure was measured using a balance gauge. For the determination of the feed composi-

Table 9. Experimental and Calculated (NRTL) Excess Enthalpies for the System 2-Methyl-1-pentene (1) + *tert*-Amyl Methyl Ether (2) at 363.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0268	4.95	0.52	0.3667	50.28	−0.41	0.7150	45.13	−0.25
0.0536	10.09	0.57	0.4175	52.76	−0.34	0.7634	40.01	−0.09
0.1067	19.26	0.83	0.4680	54.42	−0.56	0.8114	33.49	0.45
0.1595	27.75	0.62	0.5181	54.30	−0.09	0.8590	25.91	1.05
0.2119	34.74	0.73	0.5679	53.95	−0.48	0.9063	17.94	1.02
0.2638	41.48	−0.08	0.6173	52.03	−0.37	0.9533	8.84	1.14
0.3154	46.40	−0.20	0.6663	49.24	−0.44	0.9767	4.47	0.64

Table 10. Experimental and Calculated (NRTL) Excess Enthalpies for the System *tert*-Amyl Ethyl Ether (1) + Ethanol (2) at 363.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0623	498.86	−29.40	0.5261	1280.96	30.52	0.9120	318.23	−20.73
0.1200	840.16	−36.75	0.6333	1099.82	10.60	0.9589	150.69	−11.03
0.2235	1216.32	−17.24	0.7215	899.14	−11.36	0.9589	152.04	−12.37
0.2235	1216.57	−17.48	0.7215	899.71	−11.92	0.9589	149.01	−9.35
0.3138	1345.82	24.18	0.7953	692.99	−20.30			
0.3931	1383.56	29.58	0.8581	498.59	−23.76			

Table 11. Experimental and Calculated (NRTL) Excess Enthalpies for the System *tert*-Amyl Methyl Ether (1) + *tert*-Amyl Ethyl Ether (2) at 363.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0566	2.96	0.10	0.4319	14.02	−0.12	0.7269	11.41	−0.28
0.1125	5.91	−0.18	0.4319	13.44	0.47	0.7269	11.25	−0.11
0.1125	6.23	−0.50	0.5328	13.75	0.31	0.8202	9.02	−0.78
0.2219	10.20	−0.34	0.5328	14.15	−0.09	0.8202	8.17	0.07
0.2219	10.25	−0.39	0.5328	13.73	0.32	0.9112	4.74	−0.23
0.3283	12.60	−0.06	0.6311	12.86	0.23	0.9112	4.48	0.03
0.3283	12.15	0.40	0.6311	13.07	0.03			

Table 12. Antoine Constants[a]

component	A	B	C
methyl *tert*-butyl ether	6.14854	1211.690	−35.719
tert-amyl methyl ether	5.97631	1208.391	−55.243
tert-amyl ethyl ether	5.92454	1216.990	−64.119
ethanol	7.23710	1592.864	−46.966
2-methyl-1-butene	5.98854	1048.876	−40.956
2-methyl-1-pentene	5.97520	1138.516	−48.446

[a] Constants for Antoine equation: log (P^s/kPa) = $A - B/(T/\mathrm{K} + C)$, taken from DDB.

tion, the liquid volume changes before and after injection in the piston injectors must be recorded at the given conditions (usually 5 MPa and 303 K).

The procedure was as follows: After the injection of the first solvent, the vapor pressure was determined and finally the second component was added stepwise. Paying special attention to the dilute region, at the beginning only small amounts were injected. When equilibrium was reached, the pressure was measured for the given temperature and feed composition. The same procedure, restarted with the second component, provides P, x data across the entire concentration range. In all measurements the two resulting parts of the isothermal P, x data were overlapping within the range of accuracy of the measurements. The precision of the determination of the mole fraction is estimated to be ±0.0001. A schematic representation of the static apparatus is shown in Figure 1.

The isothermal computer driven flow calorimeter from Hart Scientific and the procedure used in the present study is the same as that outlined by Gmehling (1993). The thermostated flow cell contains a mixing tube (length, approximately 150 cm) wound around a copper cylinder. The excess molar enthalpies are measured by compensation of the temperature effects by cooling and heating. Therefore a pulsed heater, a calibration heater, and a Peltier cooler are installed. A constant temperature of the flow cell is realized by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler and the heat of mixing. The H^E values can be obtained from differences between the measured frequency for the mixture and the frequency for the pure liquids. For the evaluation of the

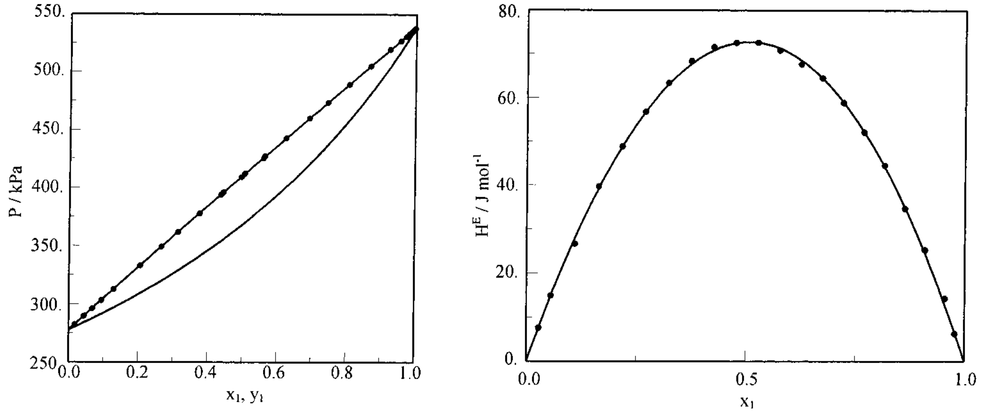

Figure 3. Experimental (●) and calculated (—, NRTL) behavior of 2-methyl-1-butene (1) + MTBE (2) at 90 °C.

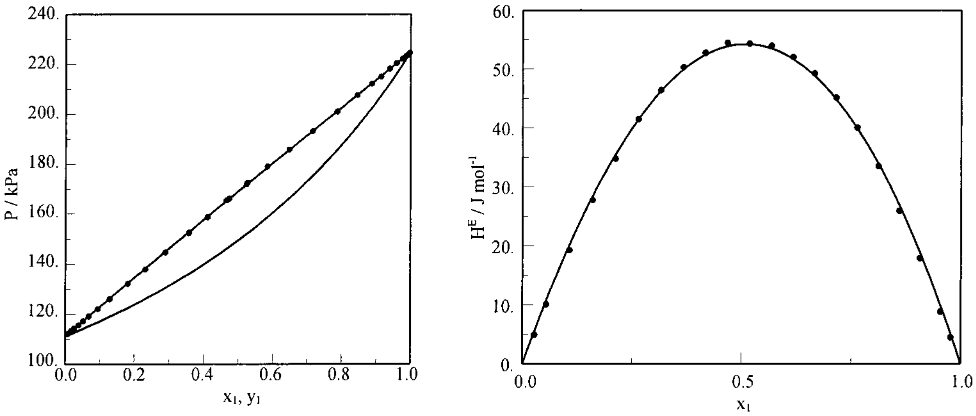

Figure 4. Experimental (●) and calculated (—, NRTL) behavior of 2-methyl-1-pentene (1) + TAME (2) at 90 °C.

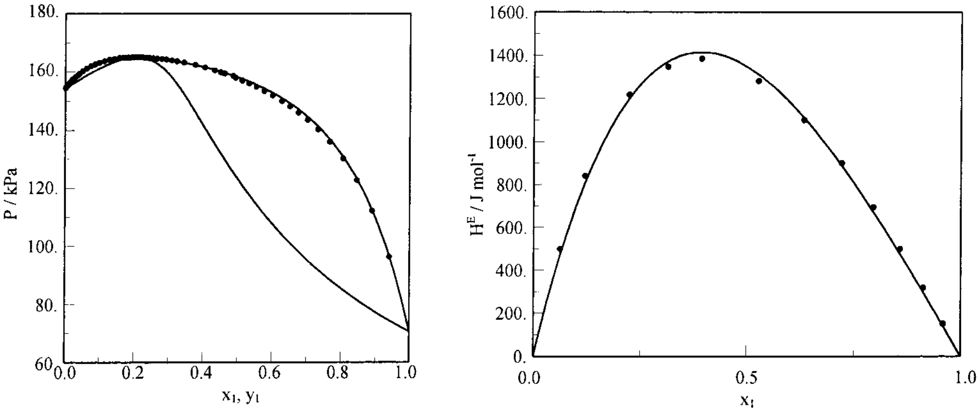

Figure 5. Experimental (●) and calculated (—, NRTL) behavior of TAEE (1) + ethanol (2) at 90 °C.

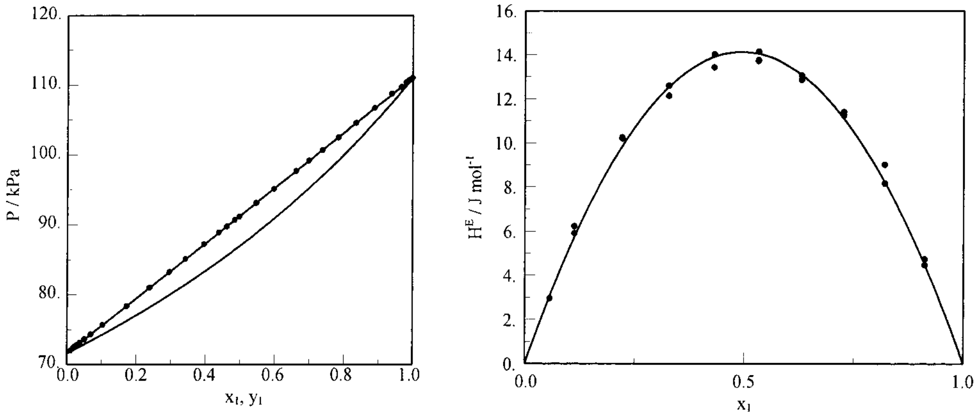

Figure 6. Experimental (●) and calculated (—, NRTL) behavior of TAME (1) + TAEE (2) at 90 °C.

data the energy per pulse is determined by calibration using a precise resistor. The flow cell is shown in Figure 2. For all experiments a total flow rate of 40 cm^3 h^{-1} was chosen. Pure component densities and the molar mass provide the total mole flow. The accuracy of the experimental H^E data is estimated to be better than ±1%.

Results and Discussion

To obtain isothermal P, x data from the raw data, two different corrections are required:

All quasi-isothermal data were converted to the average temperature using the slopes of the pure component vapor pressure curves as described previously (Fischer and Gmehling, 1994). Furthermore the feed composition was corrected to achieve the liquid-phase mole fractions x_i by an iterative flash calculation, to account for the small amounts of the components in the vapor phase. To estimate the required vapor composition y_i, the coefficients of a flexible Legendre polynomial are fitted to the P, x data to obtain activity coefficients. Ideal vapor-phase behavior has been assumed to determine the total amount of the components in the vapor phase. Since pressure and volume of the vapor phase were small, the difference between feed mole fraction and liquid mole fraction was less than 0.001.

For the calculation of the vapor composition at given liquid composition with the NRTL equation, temperature dependent interaction parameters were fitted simultaneously to the P, x and H^E data by using the Simplex–Nelder–Mead method. The resulting parameters are given in Table 2. The deviations $\Delta P = P_{calc} - P_{expt}$ and the calculated vapor phase mole fractions y_i for the different systems are listed together with the experimental P, x data in Tables 3–6. A homogeneous pressure maximum azeotrope for the system TAEE + ethanol was observed: $T =$

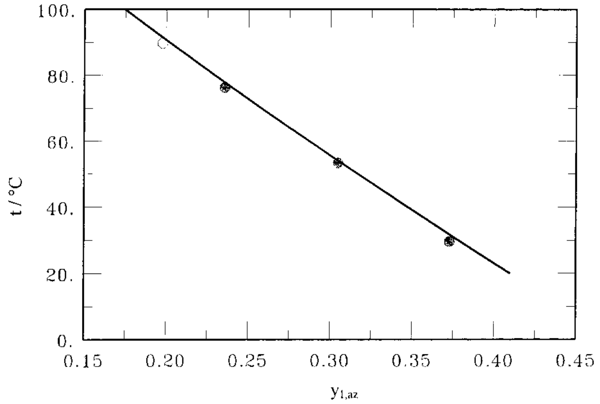

Figure 7. Experimental (○, this work; ●, results from Gmehling et al. (1994 and 1995)) and calculated (—, NRTL) temperature dependence of the azeotropic composition of TAEE (1) + ethanol (2).

362.82 K, $P = 165.04$ kPa, and $x_{\text{TAEE}} = 0.1977$. The calculated γ^∞ values are listed in Table 7. They are compared with those derived from the Legendre polynomial using only data from the dilute region (quasi-experimental values). The results of the H^E measurements are given in Tables 8−11 together with the deviations $\Delta H^E = H^E_{\text{calc}} - H^E_{\text{expt}}$ between the experimental data and the calculated results using the NRTL model. In Table 12, the Antoine constants (A−C) used are given. The values were taken from the Dortmund Data Bank (DDB).

The experimental P, x data together with the calculated P, x, y curves using the fitted NRTL parameters (Δg_{ij}, α_{ij}) are shown in Figures 3−6. Small positive deviations from Raoult's law are observed for the systems 2-methyl-1-butene + MTBE, 2-methyl-1-pentene + TAME, and TAME + TAEE. The system TAEE + ethanol shows strong positive deviation from Raoult's law, which leads to the formation of a pressure maximum azeotrope. The quasi-experimental activity coefficients at infinite dilution are in good agreement with the calculated values using the NRTL model.

Figure 7 shows the temperature dependence of the azeotropic composition of the system TAEE + ethanol. In the considered temperature range, the measured point is in good agreement with the experimental data obtained using a rotating band column (Gmehling et al., 1994, 1995) and the calculated results. It can be seen that the concentration of ethanol in the azeotrope increases with increasing temperature.

The nearly ideal behavior of the systems 2-methyl-1-butene + MTBE, 2-methyl-1-pentene + TAME, and TAME + TAEE is also expressed by small H^E values. For all systems, good agreement between the experimental data and the calculated excess molar enthalpy curves using the fitted linear temperature dependent NRTL parameters (Figures 3−6) is obtained. In all cases endothermic behavior is observed.

Conclusions

In this work VLE, H^E, γ^∞, and azeotropic points were measured for mixtures containing tertiary ethers. For each system the experimental VLE and H^E data have been fitted simultaneously for the NRTL model using linear temperature dependent interaction parameters. These parameters allow an accurate description of the real behavior (VLE, H^E, γ^∞, y_{az}) of the systems investigated.

Acknowledgment

The authors thank B. Krentscher for carrying out all of the excess molar enthalpy measurements. Furthermore the authors are grateful to Erdölchemie, who provided the different *tert*-amyl ethers.

Literature Cited

Chem. Eng. News. Facts & Figures for the Chemical Industry. *Chem. Eng. News* **1995** *(June 26)*, 36.

Fadopé, C. M. Washington Meeting Examines the Safety of MTBE. *Chem. Eng.* **1995**, *4*, 40.

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.

Gmehling, J. Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters. *J. Chem. Eng. Data* **1993**, *38*, 143−146.

Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. *Azeotropic Data*; VCH: Weinheim, Germany, 1994.

Gmehling, J.; Menke, J.; Krafczyk, J.; Fischer, K. A Data Bank for Azeotropic Data-Status and Applications. *Fluid Phase Equilib.* **1995**, *103*, 51−75.

Jensen, K. L.; Datta, R. Ethers from Ethanol. 1. Equilibrium Thermodynamic Analysis of the Liquid-Phase Ethyl *tert*-Butyl Ether Reaction. *Ind. Eng. Chem. Res.* **1995**, *34*, 392−399.

Kitchaiya, P.; Datta, R. Ethers from Ethanol. 2. Reaction Equilibria of Simultaneous *tert*-Amyl Ethyl Ether Synthesis and Isoamylene Isomerization. *Ind. Eng. Chem. Res.* **1995**, *34*, 1092−1101.

Oost, C.; Hoffmann, U. Synthesis of Tertiary Amyl Methyl Ether (TAME): Influence of Internal and External Mass Tranfer Resistance. *Chem. Eng. Technol.* **1995**, *18*, 203−209.

Rihko, L. K.; Linnekoski, J. A.; Krause, A. O. I. Reaction Equilibria in the Synthesis of 2-Methoxy-2-methylbutane and 2-Ethoxy-2-methylbutane in the Liquid Phase. *J. Chem. Eng. Data* **1994**, *39*, 700−704.

Zhang, T.; Datta, R. Ethers from Ethanol. 3. Equilibrium Conversion and Selectivity Limitations in the Liquid-Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers. *Ind. Eng. Chem. Res.* **1995a**, *34*, 2237−2246.

Zhang, T.; Datta, R. Ethers from Ethanol. 4. Kinetics of the Liquid-Phase Synthesis of Two *tert*-Hexyl Ethyl Ethers. *Ind. Eng. Chem. Res.* **1995b**, *34*, 2247−2257.

Received for review August 20, 1998. Accepted December 1, 1998. The authors are grateful to Project 805 of the Design Institute for Physical Property Data (DIPPR) for financial support.

JE980203R