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Isothermal Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Methyl *tert*-Butyl Ether + Cyclohexane and Ethyl *tert*-Butyl Ether + Cyclohexane, *n*-Hexane, and *n*-Heptane in a Temperature Range from 298.15 to 393.15 K

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Isothermal vapor−liquid equilibrium (VLE) and excess enthalpy (H^E) data are reported for binary systems containing branched ethers and hydrocarbons. The vapor−liquid equilibrium data for methyl *tert*-butyl ether (MTBE) + cyclohexane at 308.15 K, for ethyl *tert*-butyl ether (ETBE) + cyclohexane, *n*-hexane + ethyl *tert*-butyl ether, and ethyl *tert*-butyl ether + *n*-heptane from 298.15 to 363.15 K were measured by means of a computer-controlled static apparatus. An isothermal flow calorimeter was used to obtain excess enthalpy data for the systems containing ethyl *tert*-butyl ether at 313.15 and 393.15 K. The experimental VLE and H^E data were compared with the data of other authors and have been used simultaneously for the correlation of temperature-dependent UNIQUAC parameters.

Introduction

In recent years, branched ethers have become important as fuel additives to reduce the CO content in the exhaust gas of automobiles by increasing the amount of oxygen in gasoline and substitution of tetraethyl lead, which was formerly used to increase the octane number. Methyl *tert*-butyl ether (MTBE) has not only been used since 1979 but also is the main oxygenated compound being used currently. This ether dissolves easily in water and the health risk caused by the contamination of drinking water from MTBE in some countries makes this compound a controversial gasoline additive. Ethyl *tert*-butyl ether (ETBE) has some important advantages over MTBE, such as being chemically more similar to hydrocarbons and having a lower solubility in water.[1−3] Finally, the higher boiling point of ETBE allows incorporation of more light feedstocks in gasoline, especially light cyclic alkanes that are also octane enhancers.[4]

Thus, reliable knowledge of thermodynamic properties of these substances and their mixture behavior is an important factor for process engineering design. The aim of this work is to measure vapor−liquid equilibrium and excess enthalpy data for the systems methyl *tert*-butyl ether + cyclohexane, ethyl *tert*-butyl ether + cyclohexane, *n*-hexane + ethyl *tert*-butyl ether, and ethyl *tert*-butyl ether + *n*-heptane for which experimental data are not available or only cover a limited temperature range. For the binary system methyl *tert*-butyl ether + cyclohexane experimental VLE[5,6] and H^E [7] data have been published. For the binary systems containing ethyl *tert*-butyl ether, VLE data have been measured by different authors,[4,8−10] and also the heats of mixing effects for the system ethyl *tert*-butyl ether + *n*-heptane have been investigated.[11] For the ternary system *n*-hexane + ethyl *tert*-butyl ether + *n*-heptane experimental VLE data have been measured by Reich et al.[12]

Table 1. Supplier, Purity, and Water Content of the Chemicals Used

component	supplier	purity mass %	water content mass ppm
methyl *tert*-butyl ether	Aldrich	>99.9	75
ethyl *tert*-butyl ether	Erdölchemie, Lyondell	>99.99	20
cyclohexane	Scharlau	>99.99	10
n-hexane	Fluka	>99.7	40
n-heptane	Scharlau	>99.99	15

Because of the importance of excess enthalpy data for the description of the temperature dependence of the activity coefficients from the Gibbs−Helmholtz equation,

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T}\right)_{P,x} = \frac{H_i^E}{R} \tag{1}$$

H^E data were measured in this project. The experimental VLE and H^E were compared to the data of the authors mentioned above and to values calculated with temperature-dependent UNIQUAC interaction parameters, which were fitted to the experimental data from this work and from the literature.

Experimental Section

Materials. Ethyl *tert*-butyl ether was supplied by Erdölchemie and Lyondell. The other chemicals were purchased from commercial sources. For the VLE measurements the chemicals were dried over molecular sieves, degassed, and distilled as described by Fischer and Gmehling.[13] For the H^E measurements, the chemicals were used

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Table 2. Experimental $P-x$ Data for the System Methyl *tert*-Butyl Ether (1) + Cyclohexane (2) at 308.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	20.03	0.1250	25.67	0.4735	36.88	0.9303	47.94
0.0023	20.14	0.1540	26.80	0.5182	38.07	0.9497	48.39
0.0048	20.27	0.1896	28.13	0.5653	39.28	0.9651	48.73
0.0078	20.43	0.2282	29.50	0.6136	40.49	0.9755	48.96
0.0105	20.56	0.2697	30.89	0.6623	41.69	0.9826	49.12
0.0160	20.83	0.3128	32.27	0.7106	42.86	0.9885	49.26
0.0263	21.35	0.3569	33.61	0.7578	43.97	0.9925	49.35
0.0393	21.99	0.4015	34.92	0.8021	45.01	0.9965	49.44
0.0561	22.74	0.4311	35.72	0.8433	45.96	0.9982	49.48
0.0755	23.60	0.4458	36.16	0.8768	46.73	1.0000	49.52
0.0990	24.60			0.9060	47.39		

Table 3. Experimental $P-x$ Data for the System Ethyl *tert*-Butyl Ether (1) + Cyclohexane (2)

298.15 K		328.15 K		363.15 K	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	12.99	0.0000	43.39	0.0000	132.45
0.0016	13.01	0.0014	43.42	0.0023	132.59
0.0032	13.02	0.0031	43.46	0.0045	132.73
0.0051	13.04	0.0050	43.51	0.0071	132.89
0.0088	13.07	0.0085	43.60	0.0096	133.03
0.0125	13.10	0.0123	43.69	0.0144	133.33
0.0180	13.15	0.0189	43.85	0.0236	133.89
0.0266	13.22	0.0277	44.05	0.0348	134.58
0.0389	13.31	0.0400	44.34	0.0496	135.44
0.0540	13.43	0.0553	44.68	0.0672	136.46
0.0725	13.57	0.0742	45.09	0.0881	137.64
0.0947	13.72	0.0968	45.55	0.1125	138.95
0.1205	13.89	0.1231	46.07	0.1396	140.37
0.1529	14.09	0.1558	46.68	0.1724	142.01
0.1887	14.30	0.1916	47.32	0.2077	143.70
0.2277	14.51	0.2306	47.97	0.2458	145.45
0.2690	14.71	0.2716	48.62	0.2857	147.17
0.3118	14.91	0.3142	49.25	0.3276	148.91
0.3557	15.10	0.3576	49.85	0.3699	150.59
0.3956	15.24	0.3929	50.31	0.3966	151.61
0.3999	15.28	0.4013	50.42	0.4125	152.19
0.4372	15.40	0.4339	50.81	0.4384	153.15
0.4431	15.44	0.4443	50.95	0.4543	153.70
0.4816	15.55	0.4777	51.31	0.4830	154.69
0.4854	15.59	0.4863	51.44	0.4952	155.12
0.5290	15.71	0.5243	51.82	0.5306	156.23
0.5782	15.86	0.5726	52.32	0.5801	157.78
0.6286	15.99	0.6220	52.79	0.6307	159.34
0.6793	16.12	0.6716	53.25	0.6816	160.75
0.7294	16.24	0.7206	53.67	0.7319	162.14
0.7773	16.34	0.7672	54.05	0.7798	163.36
0.8222	16.43	0.8112	54.38	0.8247	164.47
0.8592	16.49	0.8477	54.65	0.8616	165.33
0.8917	16.54	0.8801	54.86	0.8939	166.04
0.9192	16.58	0.9080	55.04	0.9211	166.67
0.9412	16.61	0.9307	55.18	0.9428	167.13
0.9588	16.64	0.9490	55.29	0.9601	167.48
0.9706	16.65	0.9628	55.37	0.9716	167.72
0.9789	16.66	0.9736	55.42	0.9796	167.86
0.9861	16.67	0.9814	55.47	0.9862	168.01
0.9909	16.68	0.9855	55.50	0.9907	168.14
0.9958	16.68	0.9890	55.54	0.9955	168.24
0.9979	16.68	0.9949	55.57	0.9975	168.30
1.0000	16.69	1.0000	55.60	1.0000	168.36

without degassing. In the case of ethyl *tert*-butyl ether, further purification was required before this procedure to remove small amounts of alcohol. Therefore, ethyl *tert*-butyl ether was washed several times with water. The final purities and water contents were checked by gas chromatography and Karl−Fischer titration, respectively. The properties of all components are listed in Table 1.

Table 4. Experimental H^E Data for the System Ethyl *tert*-Butyl Ether (1) + Cyclohexane (2)

313.15 K and 1.20 MPa		393.15 K and 1.69 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0625	80	0.0394	34
0.1249	148	0.0797	67
0.1874	201	0.1418	109
0.2499	241	0.2061	143
0.3124	269	0.2728	165
0.3748	287	0.3418	187
0.4373	294	0.4134	198
0.4998	292	0.4626	202
0.5623	282	0.5388	201
0.6248	263	0.6180	188
0.6874	235	0.7003	167
0.7499	202	0.7860	132
0.8124	161	0.8752	88
0.8749	113	0.9367	43
0.9375	59		

Table 5. Experimental $P-x$ Data for the System *n*-Hexane (1) + Ethyl *tert*-Butyl Ether (2)

298.15 K		328.15 K		363.15 K	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	16.68	0.0000	55.57	0.0000	168.15
0.0024	16.69	0.0030	55.62	0.0032	168.27
0.0048	16.71	0.0063	55.67	0.0066	168.41
0.0077	16.73	0.0096	55.72	0.0105	168.56
0.0130	16.77	0.0133	55.78	0.0141	168.70
0.0185	16.80	0.0203	55.90	0.0211	168.98
0.0283	16.87	0.0296	56.06	0.0325	169.39
0.0388	16.93	0.0417	56.25	0.0463	169.92
0.0561	17.04	0.0572	56.49	0.0627	170.52
0.0751	17.16	0.0763	56.79	0.0827	171.21
0.0987	17.30	0.1001	57.15	0.1068	172.03
0.1269	17.46	0.1283	57.56	0.1352	172.99
0.1592	17.64	0.1607	58.01	0.1676	174.03
0.1989	17.85	0.2004	58.54	0.2063	175.22
0.2416	18.06	0.2431	59.09	0.2481	176.46
0.2873	18.28	0.2886	59.64	0.2928	177.68
0.3342	18.48	0.3355	60.16	0.3389	178.89
0.3817	18.68	0.3828	60.67	0.3856	180.04
0.4290	18.86	0.4300	61.13	0.4322	181.11
0.4687	19.00	0.4762	61.55	0.4697	181.85
0.4752	19.03	0.5121	61.84	0.4779	182.08
0.5114	19.14	0.5202	61.93	0.5126	182.71
0.5557	19.28	0.5565	62.20	0.5216	182.96
0.6017	19.41	0.6026	62.54	0.5571	183.54
0.6482	19.54	0.6492	62.86	0.5632	183.73
0.6944	19.65	0.6955	63.14	0.6034	184.35
0.7396	19.75	0.7408	63.38	0.6501	185.09
0.7832	19.83	0.7843	63.59	0.6966	185.72
0.8236	19.90	0.8240	63.77	0.7420	186.31
0.8608	19.95	0.8618	63.90	0.7857	186.79
0.8908	19.99	0.8917	63.99	0.8261	187.21
0.9167	20.02	0.9174	64.07	0.8632	187.51
0.9383	20.04	0.9389	64.11	0.8931	187.73
0.9555	20.05	0.9559	64.15	0.9188	187.88
0.9692	20.06	0.9694	64.17	0.9400	187.97
0.9785	20.07	0.9785	64.19	0.9569	188.04
0.9851	20.07	0.9849	64.20	0.9702	188.09
0.9895	20.08	0.9887	64.21	0.9791	188.11
0.9939	20.08	0.9926	64.22	0.9852	188.14
0.9962	20.08	1.0000	64.23	0.9903	188.18
0.9981	20.08			0.9937	188.19
1.0000	20.08			0.9971	188.20
				1.0000	188.22

Apparatus and Procedures. The vapor pressure and the isothermal $P-x$ data were measured with a computer-driven static apparatus. The experimental procedure for the determination of the VLE data is based on that proposed by Gibbs and Van Ness,[14] where the total pressure P for different overall compositions is measured at constant temperature. The apparatus was described previously[1,15] and can be used at temperatures between 278 and 368 K and pressures up to 0.3 MPa.

Table 6. Experimental H^E Data for the System *n*-Hexane (1) + Ethyl *tert*-Butyl Ether (2)

313.15 K and 1.20 MPa		393.15 K and 1.69 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0625	51	0.0529	32
0.1251	95	0.1054	61
0.1876	134	0.1837	100
0.2501	166	0.2613	127
0.3127	191	0.3381	144
0.3752	208	0.4143	155
0.4377	220	0.4898	159
0.5002	225	0.5397	159
0.5627	223	0.6141	153
0.6252	213	0.6878	141
0.6877	196	0.7609	118
0.7501	172	0.8334	92
0.8126	142	0.9052	54
0.8751	100	0.9527	29
0.9375	53		

Table 7. Experimental P−x Data for the System Ethyl *tert*-Butyl Ether (1) + *n*-Heptane (2)

298.15 K		328.15 K		363.15 K	
x_1	P kPa	x_1	P kPa	x_1	P kPa
0.0000	6.08	0.0000	23.04	0.0000	78.40
0.0022	6.11	0.0036	23.20	0.0069	79.14
0.0046	6.15	0.0071	23.34	0.0143	79.94
0.0071	6.18	0.0110	23.50	0.0221	80.76
0.0118	6.25	0.0147	23.65	0.0296	81.54
0.0167	6.32	0.0219	23.93	0.0372	82.33
0.0255	6.44	0.0342	24.43	0.0506	83.71
0.0372	6.59	0.0491	25.01	0.0656	85.28
0.0537	6.82	0.0684	25.76	0.1054	89.29
0.0726	7.07	0.0913	26.64	0.1267	91.42
0.0961	7.37	0.1180	27.65	0.1517	93.90
0.1254	7.74	0.1485	28.79	0.1977	98.39
0.1576	8.14	0.1825	30.03	0.2281	101.32
0.1972	8.62	0.2226	31.46	0.2644	104.77
0.2401	9.12	0.2644	32.92	0.3032	108.41
0.2857	9.64	0.3082	34.42	0.3441	112.20
0.3327	10.16	0.3531	35.92	0.3860	115.98
0.3803	10.67	0.3986	37.42	0.4283	119.78
0.4290	11.19	0.4438	38.88	0.4694	123.49
0.4679	11.58	0.4685	39.66	0.4704	123.53
0.4752	11.66	0.4882	40.29	0.5117	127.16
0.5104	12.01	0.5112	41.00	0.5121	127.15
0.5193	12.11	0.5306	41.62	0.5513	130.60
0.5546	12.45	0.5555	42.37	0.5565	130.99
0.6004	12.90	0.5711	42.87	0.5892	133.87
0.6468	13.35	0.6015	43.78	0.6027	134.95
0.6929	13.79	0.6480	45.19	0.6493	138.93
0.7381	14.22	0.6943	46.59	0.6958	142.83
0.7815	14.64	0.7395	47.93	0.7411	146.64
0.8219	15.02	0.7831	49.22	0.7848	150.31
0.8590	15.37	0.8236	50.42	0.8254	153.67
0.8890	15.65	0.8608	51.51	0.8626	156.76
0.9150	15.89	0.8908	52.39	0.8926	159.25
0.9367	16.09	0.9168	53.15	0.9184	161.39
0.9540	16.25	0.9385	53.78	0.9398	163.16
0.9678	16.38	0.9558	54.30	0.9568	164.57
0.9772	16.47	0.9695	54.70	0.9702	165.67
0.9839	16.53	0.9788	54.97	0.9791	166.39
0.9886	16.58	0.9854	55.16	0.9852	166.92
0.9934	16.62	0.9897	55.28	0.9902	167.32
0.9958	16.64	0.9941	55.41	0.9937	167.61
0.9979	16.66	0.9963	55.47	0.9971	167.91
1.0000	16.68	0.9981	55.53	0.9986	168.02
		1.0000	55.59	1.0000	168.15

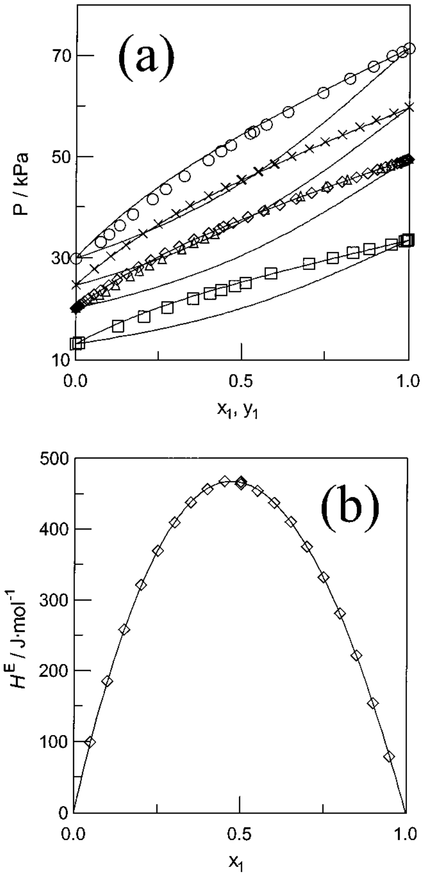

Figure 1. Experimental and calculated mixture behavior of the binary system methyl *tert*-butyl ether (1) + cyclohexane (2). (a) Vapor−liquid equilibrium: experimental data from this work at 308.15 K (◇), del Río et al.[5] at 298.15 (□), 308.15 (△), and 318.15 K (○), and Segovia et al.[6] at 313.15 K (×). (b) Excess enthalpies: experimental data from Zhu et al.[7] at 298.15 K (◇); (−) UNIQUAC.

Table 8. Experimental H^E Data for the System Ethyl *tert*-Butyl Ether (1) + *n*-Heptane (2)

313.15 K and 1.20 MPa		393.15 K and 1.69 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0625	51	0.0527	34
0.1250	101	0.1050	67
0.1875	147	0.1831	104
0.2500	186	0.2604	130
0.3124	216	0.3371	148
0.3749	236	0.4132	158
0.4374	249	0.4887	163
0.4999	252	0.5386	162
0.5624	248	0.6131	158
0.6249	237	0.6869	144
0.6874	218	0.7601	124
0.7500	190	0.8328	90
0.8125	152	0.9048	57
0.8750	109	0.9525	27
0.9375	57		

The thermostated, purified, and degassed compounds are charged into the VLE cell, which is evacuated and kept in a thermostatic oil bath. The pressure inside the cell is monitored with a Digiquartz pressure sensor (Model 245A, Paroscientific), and the temperature is measured with a Pt100 resistance thermometer (Model 1506, Hart Scientific). The overall compositions are determined from the known quantities of liquids injected into the equilibrium cell with stepping-motor-driven injection pumps and automatic valves. The liquid-phase composition is obtained by solving mass and volume balance equations which also account for the vapor−liquid equilibrium. At the low pressures of this investigation, the calculated liquid-phase compositions are identical to the feed compositions within ±0.001 mol fraction. The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K; $\sigma(P) = 20$ Pa + 0.0001 (P/Pa); and $\sigma(x_i) = 0.0001$.

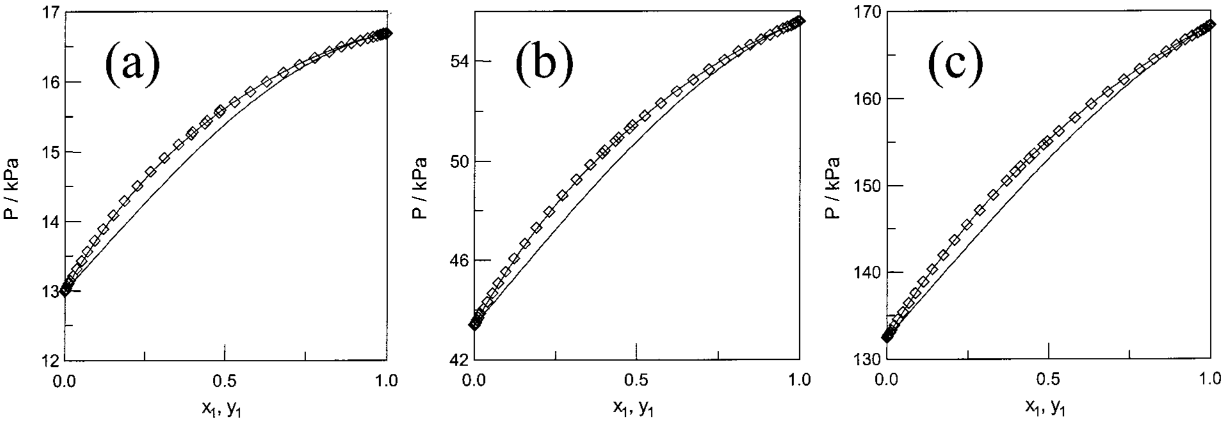

Figure 2. Experimental and calculated $P-x(y)$ data for the binary system ethyl *tert*-butyl ether (1) + cyclohexane (2): (◇) experimental data from this work at (a) 298.15, (b) 328.15, and (c) 363.15 K; (−) UNIQUAC.

Table 9. Temperature-Dependent UNIQUAC Interaction Parameters

component 1	component 2	i	j	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}
methyl *tert*-butyl ether	cyclohexane	1	2	19.628	−0.12441	
		2	1	48.756	−0.02894	
ethyl *tert*-butyl ether	cyclohexane	1	2	−11.047	−0.16454	6.534×10^{-4}
		2	1	86.930	−0.15888	2.904×10^{-4}
n-hexane	ethyl *tert*-butyl ether	1	2	46.802	−0.17568	-1.044×10^{-4}
		2	1	−4.8720	0.01995	2.898×10^{-4}
ethyl *tert*-butyl ether	*n*-heptane	1	2	36.108	−0.11921	-1.417×10^{-4}
		2	1	10.920	−0.06255	3.560×10^{-4}

Table 10. Pure Component Parameters: Antoine Coefficients A_i, B_i, and C_i, Relative van der Waals Volumes r_i and Surfaces q_i, and Liquid Densities

component	A_i	B_i/K	C_i/K	r_i	q_i	ρ_i (298.15 K) kg·dm^{-3}
methyl *tert*-butyl ether	6.25487	1265.40	−30.633	4.0678	3.632	0.7354
ethyl *tert*-butyl ether	6.21597	1279.69	−41.873	4.7422	4.172	0.7354
cyclohexane	5.97636	1206.47	−50.014	4.0464	3.240	0.7739
n-hexane	6.00266	1171.53	−48.784	4.4998	3.856	0.6550
n-heptane	6.01876	1264.37	−56.510	5.1742	4.396	0.6795

The commercial isothermal flow calorimeter (Model 7501, Hart Scientific) used for the determination of the excess enthalpy data was described previously.[16] In this apparatus, two syringe pumps (Model LC-2600, ISCO) provide a flow of constant composition through a thermostated calorimeter cell equipped with a pulsed heater and a Peltier cooler. The Peltier cooler operates at constant power producing a constant heat loss from the calorimeter cell, which is compensated by the pulsed heater. The required frequency is influenced by endothermal or exothermal heat effects, so that the heats of mixing can be determined from the observed frequency change between the baseline and the actual measurement. A back-pressure regulator serves to keep the pressure constant at a level for which evaporation and degassing effects can be prevented. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K; $\sigma(H^E) = 2$ J·mol^{-1} + 0.01 (H^E/J·mol^{-1}); and $\sigma(x_i) = 0.0001$.

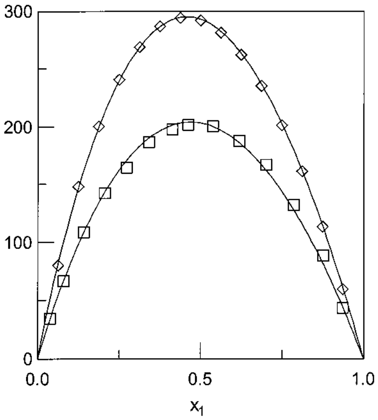

Figure 3. Experimental and calculated excess enthalpy data for the binary system ethyl *tert*-butyl ether (1) + cyclohexane (2): experimental data from this work at 313.15 (◇) and 393.15 K (□); (−) UNIQUAC.

Results

The experimental VLE and H^E data are listed in Tables 2−8. For all binary systems, linear or even quadratic temperature-dependent UNIQUAC[17] parameters were fitted to the experimental data from this work and from the literature. The temperature dependence of the interaction parameters is described by the expression,

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

The parameters are given in Table 9. The required van der Waals properties r_i and q_i and the coefficients A_i, B_i, and C_i for the Antoine vapor pressure equation

$$\log(P_i^s/\mathrm{kPa}) = A_i - \frac{B_i}{C_i + T/\mathrm{K}} \tag{3}$$

and the liquid densities at 298.15 K which were used in the calculations are presented in Table 10. To account for only the excess Gibbs energy, the parameters A_i were adjusted to the experimental pure component vapor pressures during the G^E model parameter fitting procedure.

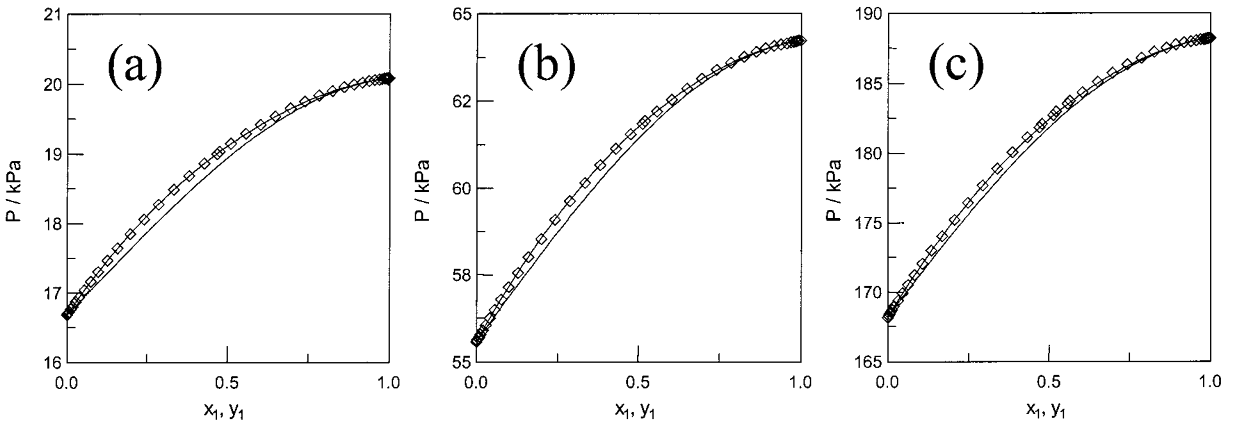

Figure 4. Experimental and calculated $P-x(y)$ data for the binary system *n*-hexane (1) + ethyl *tert*-butyl ether (2): (◇) experimental data from this work at (a) 298.15, (b) 328.15, and (c) 363.15 K; (−) UNIQUAC.

Table 11. Experimental and Predicted (UNIQUAC) Activity Coefficients at Infinite Dilution

component 1	component 2	T/K	γ_1^∞	γ_2^∞	source	γ_1^∞ calc	γ_2^∞ calc
methyl *tert*-butyl ether	cyclohexane	308.15	1.449	1.353	this work	1.413	1.344
		313.15	1.434	1.316	Segovia et al.[6]	1.395	1.330
		313.15	1.41	1.21	Pividal et al.[19]	1.395	1.330
		333.15	1.32	1.07	Pividal et al.[19]	1.377	1.279
ethyl *tert*-butyl ether	cyclohexane	298.15	1.295	1.195	this work	1.271	1.204
		328.15	1.223	1.146	this work	1.206	1.160
		363.15	1.160	1.109	this work	1.155	1.124
n-hexane	ethyl *tert*-butyl ether	298.15	1.167	1.173	this work	1.168	1.170
		328.15	1.122	1.127	this work	1.131	1.130
		363.15	1.096	1.094	this work	1.100	1.098
		333.15		1.11	Decros et al.[20]		1.125
ethyl *tert*-butyl ether	*n*-heptane	298.15	1.205	1.210	this work	1.188	1.187
		328.15	1.158	1.150	this work	1.145	1.143
		363.15	1.113	1.103	this work	1.111	1.108
		348.15	1.10		Decros et al.[20]	1.124	

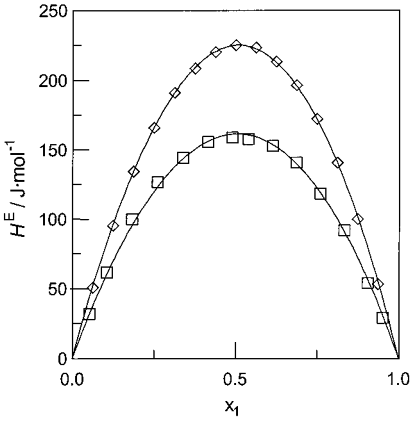

Figure 5. Experimental and calculated excess enthalpy data for the binary system *n*-hexane (1) + ethyl *tert*-butyl ether (2): experimental data from this work at 313.15 (◇) and 393.15 K (□); (−) UNIQUAC.

For all systems, small positive deviations from Raoult's law are observed. But no homogeneous pressure maximum azeotropes or miscibility gaps are formed. In Figures 1−7 the experimental data from this work are compared with the calculated values using the UNIQUAC parameters from Table 9. The first system methyl *tert*-butyl ether + cyclohexane was chosen to verify the reliability of the static apparatus used here. As can be seen in Figure 1, the data from this work are well described with the obtained UNIQUAC parameters. The data are also in agreement with the VLE data of Segovia et al.[6] The former measurements of del Rio et al.[5] show small deviations, especially in the diluted region of methyl *tert*-butyl ether at 308.15 and 318.15 K, resulting in small differences in the calculated activity coefficients. The new parameters fitted simultaneously to all experimental VLE and the H^E from Zhu et al.[7] data are recommended to describe this system in a temperature range from about 300 to 370 K.

For the three binary systems containing ethyl *tert*-butyl ether, only scarce experimental information is available in the literature and thus a large temperature range was covered in this investigation. So VLE data were measured at 298.15, 328.15, and 363.15 K and, additionally, H^E measurements were performed at 313.15 and 393.15 K. It can be seen in Figures 2, 4, and 6 that the experimental VLE data for all three systems (ethyl *tert*-butyl ether + cyclohexane, *n*-hexane + ethyl *tert*-butyl ether, and ethyl *tert*-butyl ether + *n*-heptane) are reliably described with the UNIQUAC parameters from Table 9. Also, the excess enthalpy data can be calculated with these parameters (see Figures 3, 5, and 7). The VLE data measured here are in agreement with most of the data in the literature[4,8] which are not included in the diagrams. However, the data of other authors[9,10] deviate from this work. For the system ethyl *tert*-butyl ether + *n*-heptane, experimental H^E data were measured by Mier et al.,[11] but there are discrepancies with our data (Figure 7). It is possible that this effect was caused by ethanol impurities in the ethyl *tert*-butyl ether used by those authors.

From the experimental VLE data of this work, activity coefficients at infinite dilution (γ_i^∞) were derived using a flexible Legendre polynomial.[18] They are listed in Table 11 together with experimental values of other authors[19,20] and the values calculated with the UNIQUAC parameters. For this comparison, the VLE data of Segovia et al.[6] for the system methyl *tert*-butyl ether + cyclohexane were treated

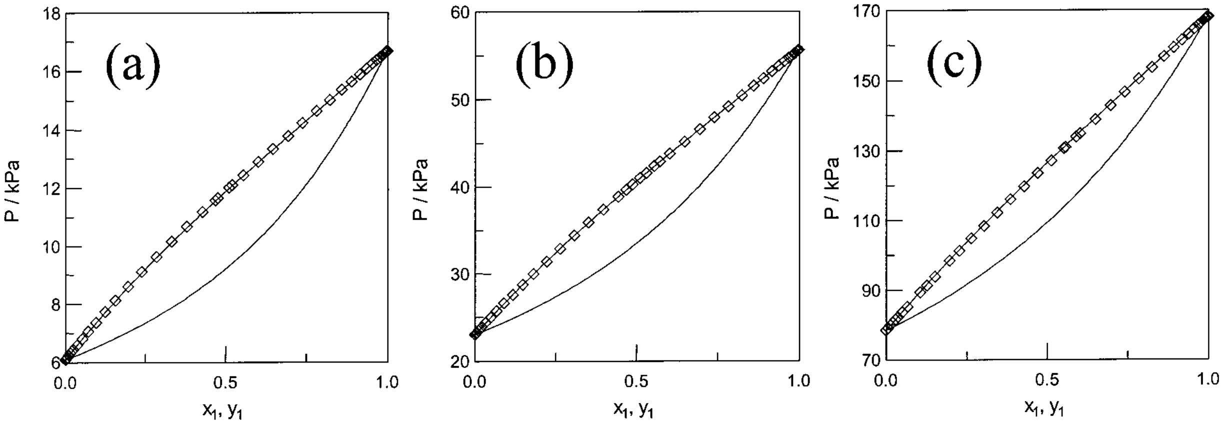

Figure 6. Experimental and calculated $P-x(y)$ data for the binary system ethyl *tert*-butyl ether (1) + *n*-heptane (2): (◇) experimental data from this work at (a) 298.15, (b) 328.15, and (c) 363.15 K; (−) UNIQUAC.

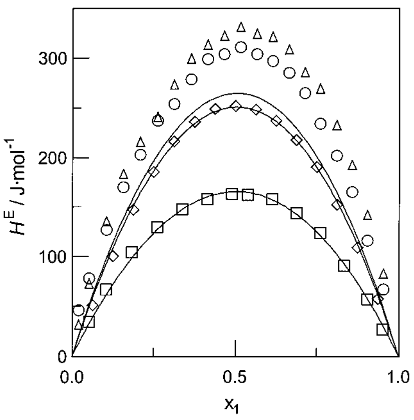

Figure 7. Experimental and calculated excess enthalpy data for the binary system ethyl *tert*-butyl ether (1) + *n*-heptane (2): experimental data from this work at 313.15 (◇) and 393.15 K (□); experimental data of Mier et al.[11] at 298.15 (△) and 313.15 K (○); (−) UNIQUAC.

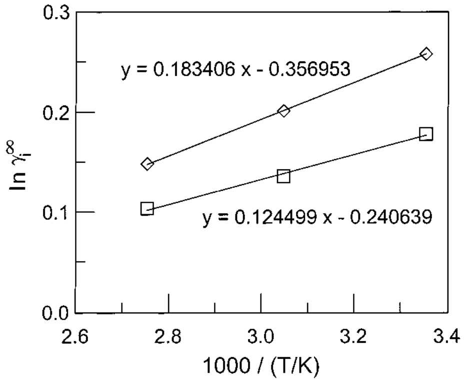

Figure 8. Activity coefficients at infinite dilution for the binary system ethyl *tert*-butyl ether (1) + cyclohexane (2): experimental values derived from the VLE data: γ_1^∞ (◇), γ_2^∞ (□); (−) linear regression.

in the same way to obtain the activity coefficients at infinite dilution. As can be seen, the temperature dependence of the mixture behavior can be described correctly with the UNIQUAC model.

Another proof of the consistency of our VLE and H^E data is shown for the system ethyl *tert*-butyl ether + cyclohexane. The partial molar excess enthalpies at infinite dilution ($H_i^{E,\infty}$) determined from the VLE data using the Gibbs−Helmholtz equation (eq 1) (compare Figure 8) are presented in Table 12 together with the values obtained by fitting a Redlich−Kister polynomial to the experimental calorimetric data.

Table 12. Partial Molar Excess Enthalpies at Infinite Dilution ($H_i^{E,\infty}$) for the Binary System Ethyl *tert*-Butyl Ether (1) + Cyclohexane (2)

T/K	$H_1^{E,\infty}$/J·mol^{-1}	$H_2^{E,\infty}$/J·mol^{-1}	source
330	1525	1035	VLE data
313.15	1440	995	calorimetric data
393.15	920	720	calorimetric data

An examination of the applicability of the binary UNIQUAC parameters to higher systems was performed with the help of the ternary VLE data of Reich et al.[12] for *n*-hexane + ethyl *tert*-butyl ether + *n*-heptane. These experimental data can be predicted within an average absolute error of 0.2 K in temperature and 0.007 in the vapor phase compositions y using the binary interaction parameters obtained in this work and those fitted to literature data for the system *n*-hexane + *n*-heptane.

Conclusions

In this project, experimental VLE and H^E data are presented. The data were used for a simultaneous correlation of temperature-dependent UNIQUAC interaction parameters which are able to represent all experimental data. From the experimental VLE data, activity coefficients at infinite dilution were derived. As can be seen from the different diagrams and tables, the experimental data can be predicted using the obtained temperature-dependent G^E model parameters. The data measured were compared with the data of other authors. Because of the good agreement with the literature data and the calculated values, the interaction parameters from this work can be recommended for the investigated ethyl *tert*-butyl ether systems in a temperature range from about 270 to 420 K. For the system methyl *tert*-butyl ether + cyclohexane the parameters can be recommended for temperatures from about 300 to 370 K because of the smaller temperature range covered by the experimental data.

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