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Isothermal *P*, *x* Data and Excess Enthalpies for Two Binary Systems

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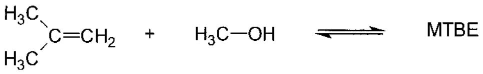
Isothermal *P*, *x* data and excess enthalpies were measured for the binary systems isobutane + diethyl ether and *tert*-amyl methyl ether (TAME) + 2-methyl-2-propanol (*tert*-butyl alcohol) at 323 K using a static apparatus and an isothermal flow calorimeter. Linear temperature dependent NRTL parameters were fitted simultaneously to the experimental *P*, *x*, and H^E data. Activity coefficients at infinite dilution (γ_i^∞) were derived from the *P*, *x* data in the dilute region using a flexible Legendre polynomial.

Introduction

A large number of organometallic compounds, especially tetramethyl lead (TML) or tetraethyl lead (TEL), are known to act as octane enhancers. These enhancers were generally used to improve the gasoline octane number, until their admixture began to be reduced stepwise worldwide. The resulting deficiency of high-octane fuels was compensated for by improvements in refinery processes, as well as by the use of alternative octane enhancers such as the so called fuel oxygenates. Considering the various oxygenates, only alcohols and ethers are used to any significant extent. They are preferred over other octane enhancers because of lower costs, availability, handling, and their physical and chemical properties, which are similar to gasoline components. Methyl *tert*-butyl ether (MTBE) is the most important ether used as an oxygenate. It is produced by the following reaction of isobutene with methanol:



This acid catalyzed reaction is often directly combined with the separation of the product in a distillation column (reactive rectification) since higher conversions than the equilibrium conversion can be achieved. Because of limited capacities for the production of both methanol and isobutene, also higher alcohols (ethanol, 2-propanol) and isoamylenes (2-methyl-1-butene, 2-methyl-2-butene) are of increasing interest to be converted to the different tertiary ethers: ethyl *tert*-butyl ether (ETBE), isopropyl *tert*-butyl ether (IPTBE), *tert*-amyl ethyl ether (TAME), and *tert*-amyl ethyl ether (TAEE).

For the design of the conversion columns, besides the kinetic information of the reaction, also the phase equilibrium behavior of the mixtures is important. Because of the high selectivity of isoalkenes to react with alcohols, there is no need to separate the C4 or C5 fractions, for example from the steam cracking process after the diene removal, before the conversion forming the tertiary ethers.

In a previous work, *P*, *x*, and H^E data of different binary systems with tertiary ethers were measured (Heine et al., 1999). In this work, *P*, *x*, and H^E data for the binary systems isobutane + diethyl ether and TAME + 2-methyl-2-propanol at ~323 K are presented.

Table 1. Pure Component Specifications

compd	supplier	water content/(mass %)
diethyl ether	Scharlau	0.0015[a]
isobutane	Messer-Griesheim	na[c]
tert-butyl alcohol	Riedel de Haen AG	0.0060[b]
TAME	Erdölchemie GmbH	0.0030[a]

[a] After drying with molecular sieve and distillation. [b] After drying with metallic sodium and distillation. [c] After drying with P_2O_5 and distillation.

These systems were studied as part of an ongoing investigation sponsored by Project 805c/95, Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

Experimental Section

VLE Measurements. The degassing and purification procedure of TAME, *tert*-butyl alcohol, and diethyl ether was carried out in the same way as that described earlier (Fischer and Gmehling, 1994). Liquid isobutane was transferred from the transport gas cylinder into a stainless steel container, filled with P_2O_5 to remove traces of water. After drying for 24 h, the liquid was distilled directly into the piston injectors. In Table 1 the supplier and the water content after purification, determined by Karl Fischer titration, are listed. The purities of the components were also checked by gas chromatography and obtained to be greater than 99.98% in all cases.

The static apparatus and procedure of measurement have been described in detail previously (Fischer and Gmehling, 1994). Using piston injectors, the desired amount of degassed liquids is introduced into the stainless steel equilibrium cell. A constant-temperature bath thermostats the equilibrium cell within ±0.03 K. Temperature is measured by a platinum resistance thermometer (Hart Scientific, Model 1506). The stirrer in the equilibrium chamber is driven by a rotating magnetic field. Using a differential pressure null indicator, the system equilibrium pressure is exactly compensated for by nitrogen. Absolute pressures up to 1000 kPa are precisely measured using a balance gauge (Desgranges & Huot, type 8000 S). For the determination of the feed composition, the liquid volume changes in the piston injectors are recorded at given conditions, 4000 kPa and 293.15 or 303.15 K in the case of

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Table 2. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System Isobutane (1) + Diethyl Ether (2) at 322.70 K[a]

exptl data		calcd (NRTL)		exptl data		calcd (NRTL)		exptl data		calcd (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	168.29	0.0000	0.00	0.115 43	237.28	0.3673	−1.63	0.895 08	623.96	0.9686	3.54
0.000 56	168.58	0.0026	0.05	0.146 12	254.35	0.4305	−1.41	0.917 36	634.94	0.9755	3.22
0.001 49	169.26	0.0068	−0.08	0.180 68	273.27	0.4914	−1.15	0.938 77	645.68	0.9820	2.70
0.003 56	170.63	0.0161	−0.19	0.225 51	297.21	0.5679	−0.61	0.954 56	653.98	0.9868	2.01
0.004 40	171.23	0.0198	−0.30	0.279 14	325.17	0.6236	0.13	0.964 92	659.29	0.9898	1.67
0.007 32	173.14	0.0326	−0.46	0.342 20	357.19	0.6866	1.09	0.974 25	664.02	0.9926	1.44
0.008 85	174.28	0.0392	−0.68	0.406 66	389.28	0.7395	1.96	0.981 18	667.74	0.9946	1.06
0.020 58	181.41	0.0872	−0.83	0.469 78	420.23	0.7831	2.72	0.986 10	670.23	0.9960	0.94
0.022 70	182.82	0.0955	−0.98	0.495 51	432.06	0.7990	3.60	0.989 21	671.69	0.9969	0.98
0.025 49	184.81	0.1062	−1.32	0.542 30	454.61	0.8257	4.05	0.991 37	673.00	0.9975	0.71
0.029 52	187.40	0.1213	−1.52	0.591 19	477.99	0.8509	4.44	0.996 07	675.46	0.9989	0.52
0.035 11	190.82	0.1415	−1.65	0.642 43	502.33	0.8748	4.97	0.997 93	676.51	0.9994	0.38
0.041 81	195.16	0.1648	−2.04	0.694 14	526.92	0.8969	4.96	0.998 86	677.15	0.9997	0.20
0.049 02	199.30	0.1888	−1.95	0.745 00	551.18	0.9169	4.94	0.999 63	677.57	0.9999	0.14
0.059 81	205.58	0.2228	−1.92	0.791 34	573.31	0.9339	4.83	1.000 00	677.90	1.0000	0.00
0.073 80	213.74	0.2636	−1.95	0.829 68	591.93	0.9472	4.42				
0.093 21	224.82	0.3149	−1.86	0.865 39	609.35	0.9591	4.00				

[a] Mean deviation ΔP/kPa = 0.88; maximum deviation ΔP/kPa = 4.96.

Table 3. Experimental and Calculated (NRTL) Vapor−Liquid Equilibrium Data for the System TAME (1) + *tert*-Butyl Alcohol (2) at 322.73 K[a]

exptl data		calcd (NRTL)		exptl data		calcd (NRTL)		exptl data		calcd (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	23.16	0.0000	0.00	0.245 88	28.63	0.3721	−0.10	0.725 14	31.71	0.7111	0.12
0.000 87	23.28	0.0019	−0.11	0.286 20	29.17	0.4118	−0.03	0.762 64	31.67	0.7354	0.08
0.006 00	23.37	0.0132	−0.05	0.295 54	29.32	0.4205	−0.05	0.820 16	31.41	0.7770	0.08
0.011 00	23.48	0.0239	−0.03	0.320 86	29.61	0.4431	−0.01	0.880 85	30.81	0.8301	0.17
0.015 62	23.68	0.0337	−0.10	0.324 21	29.73	0.4460	−0.09	0.946 77	29.90	0.9080	0.09
0.023 78	23.84	0.0505	−0.03	0.358 55	30.14	0.4746	−0.08	0.970 38	29.43	0.9445	0.04
0.029 91	24.03	0.0628	−0.06	0.377 51	30.27	0.4895	−0.01	0.981 04	29.19	0.9630	0.01
0.039 77	24.30	0.0820	−0.08	0.386 88	30.45	0.4967	−0.09	0.987 23	29.03	0.9745	0.00
0.060 23	24.81	0.1199	−0.06	0.412 44	30.66	0.5157	−0.05	0.990 46	29.01	0.9807	−0.08
0.082 66	25.33	0.1585	−0.03	0.446 35	30.89	0.5396	0.01	0.992 98	28.85	0.9857	0.01
0.112 21	26.01	0.2052	−0.03	0.479 95	31.04	0.5621	0.11	0.994 72	28.83	0.9891	0.02
0.140 85	26.64	0.2465	−0.04	0.539 92	31.40	0.6000	0.09	1.000 00	28.65	1.0000	0.00
0.172 78	27.33	0.2886	−0.90	0.614 61	31.70	0.6447	0.06				
0.205 36	27.86	0.3278	−0.02	0.680 38	31.74	0.6836	0.17				

[a] Mean deviation ΔP/kPa = 0.03; maximum deviation ΔP/kPa = 0.90.

Table 4. Experimental and Calculated (NRTL) Excess Enthalpies for the System Isobutane (1) + Diethyl Ether (2) at 323.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0501	43.79	1.47
0.1002	85.89	0.45
0.2003	156.82	−1.27
0.3004	206.99	−0.04
0.4005	239.31	0.48
0.5005	252.07	1.17
0.6005	246.66	−0.16
0.7004	219.60	−0.86
0.8003	169.46	−0.43
0.9002	96.54	−0.12
0.9501	51.11	0.15

Table 5. Experimental and Calculated (NRTL) Excess Enthalpies for the System TAME (1) + *tert*-Butyl Alcohol (2) at 323.15 K

x_1	H^E/(J mol^{-1})	ΔH^E/(J mol^{-1})
0.0362	60.05	14.81
0.0735	135.37	16.33
0.1515	301.18	8.73
0.2343	472.28	−1.50
0.3225	635.24	−6.96
0.3688	709.13	−6.44
0.4166	778.60	−6.90
0.4660	831.08	1.93
0.5171	877.20	5.97
0.6249	921.83	11.39
0.7407	869.37	2.09
0.8653	602.34	9.27
0.9313	376.27	−12.84
0.9626	194.13	18.34

tert-butyl alcohol in order to exceed the melting point of *tert*-butyl alcohol.

After injection of the first compound, the vapor pressure of the pure component was determined, and finally the second component was added stepwise. Paying special attention to the dilute region, at the beginning only small amounts of the second component were injected. When equilibrium was reached (normally after 15−25 min), the pressure was measured for the given temperature and feed composition. The same procedure, restarted with the second component, provided P, x data across the entire concentration range. In both measurements the two resulting parts of the isothermal P, x data were overlapping within the range of accuracy of the measurements. To obtain isothermal P, x data, two different corrections on the raw data are required, as described in the literature (Fischer and Gmehling, 1994). All quasi-isothermal data were converted to the average temperature. To account for the small amounts of the components in the vapor phase, the feed composition was corrected by an iterative flash

Table 6. Fitted NRTL Parameters[a]

compd 1	compd 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})
isobutane	diethyl ether	322.70	0.2983	931.705	147.999	−0.753 624	−1.390 02
TAME	*tert*-butyl alcohol	322.73	0.3655	6856.30	−596.246	−11.827 7	−0.473 108

[a] $g_{ij}/(\text{J mol}^{-1}) = [g_{ij}^0/(\text{J mol}^{-1})] + [g_{ij}^1/(\text{J mol}^{-1}\ \text{K}^{-1})]\ (T/\text{K})$.

Table 7. Antoine Constants[a]

component	A	B	C
isobutane	6.64598	1324.67	24.543
diethyl ether	6.11080	1090.64	−41.950
TAME	5.97464	1208.39	−55.243
tert-butyl alcohol	6.35843	1107.06	−101.049

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

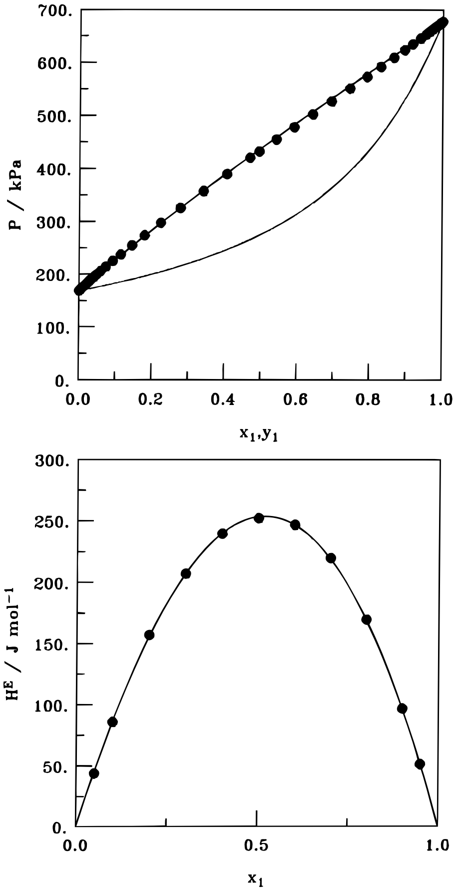

Figure 1. Experimental P, x, and H^E data (●) and calculated P, x, y, and H^E behavior (—, NRTL) for the system isobutane (1) + diethyl ether (2) at 323 K.

calculation to get the exact composition of the liquid phase. For the estimation of the required vapor composition the coefficients of a flexible Legendre polynomial were fitted to the P, x data to obtain the activity coefficients. Ideal vapor-phase behavior was assumed to determine the total amount of components in the vapor phase.

H^E Measurements. A commercial isothermal computer-driven flow calorimeter (Hart Scientific, Model 7501) and the procedure used in the present study are the same as those outlined by Gmehling (1993). In this type of calorimeter, the heat effects which occur during mixing are compensated for with the help of a pulsed electric heater. A Peltier cooler allows us to control the frequency of the pulsed heater and to set the baseline, so that exothermic heat of mixing effects can also be determined. A total flow rate of 40 cm^3 h^{-1} was chosen. Pure component densities and the molar masses provide the total mole flow. The accuracy of the experimental H^E data is estimated to be better than ±1%.

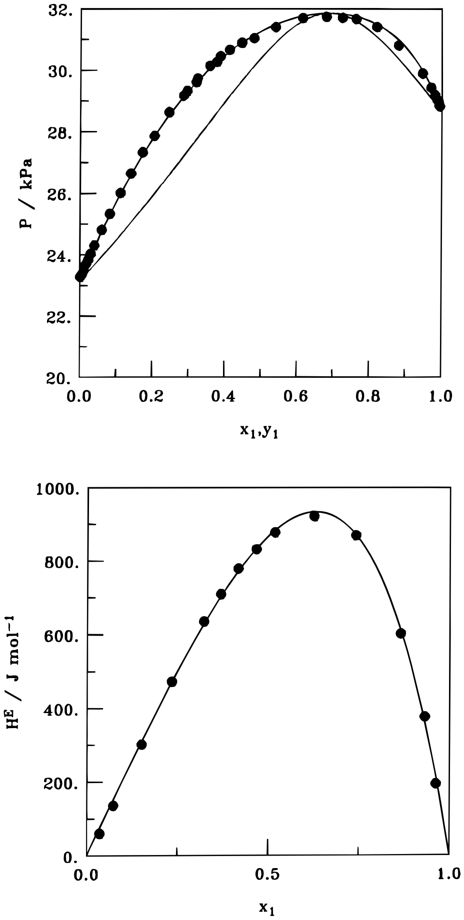

Figure 2. Experimental P, x, and H^E data (●) and calculated P, x, y, and H^E behavior (—, NRTL) for the system TAME (1) + *tert*-butyl alcohol (2) at 323 K.

Table 8. Activity Coefficients at Infinite Dilution

			quasi-exptl using the Legendre polynomial		calcd using NRTL	
component 1	component 2	T/K	γ_1^∞	γ_2^∞	γ_1^∞	γ_2^∞
isobutane	diethyl ether	322.70	1.29	1.11	1.13	1.15
TAME	*tert*-butyl alcohol	322.73	2.00	2.78	1.79	2.60

Results and Discussion

The experimental P, x data are listed in Tables 2 and 3, and the measured heat of mixing data are given in Tables 4 and 5. Linear temperature dependent interaction parameters were fitted for the NRTL model simultaneously to the P, x, and H^E data, using the Simplex−Nelder−Mead algorithm and assuming ideal behavior in the vapor phase. Figures 1 and 2 show the experimental values together with the curves calculated using the NRTL model. The parameters are listed in Table 6. The vapor pressures of the pure components were calculated using the Antoine

Table 9. Azeotropic Data for the System TAME (1) + *tert*-Butyl Alcohol (2)

T/K	P/kPa	y_1[a]
322.73	31.72	0.6836[b]
303.55	13.41	0.7932[c]
328.75	40.44	0.6401[c]
353.20	101.80	0.4383[c]

[a] Homogeneous pressure maximum azeotrope. [b] Obtained by static vapor−liquid equilibrium measurements. [c] Obtained by a rotating band distillation column.

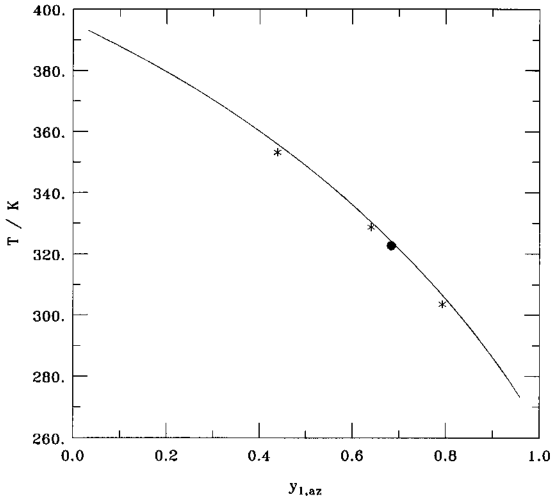

Figure 3. Experimental (●, static vapor−liquid equilibrium measurement; ∗, rotating band column) and calculated (−, NRTL) temperature dependence of the azeotropic composition for the system TAME (1) + *tert*-butyl alcohol (2).

constants taken from the Dortmund Data Bank (DDB). The parameters are given in Table 7. The pressure deviations $\Delta P = P_{\text{calc}} - P_{\text{expt}}$ and the calculated vapor compositions y_i for the different systems are listed in Tables 2 and 3. The enthalpy deviations $\Delta H^{\text{E}} = H^{\text{E}}_{\text{calc}} - H^{\text{E}}_{\text{expt}}$ are given in Tables 4 and 5. The experimental P, x data were used to derive γ^{∞} values with the help of a flexible Legendre polynomial as described earlier by Fischer and Gmehling (1994). They are compared with those calculated with the help of NRTL in Table 8.

The system isobutane + diethyl ether shows only a small positive deviation from Raoult's law. The nearly ideal behavior of this system is also expressed by small H^{E} values.

At 323 K the system TAME + *tert*-butyl alcohol shows a homogeneous pressure maximum azeotrope. In Table 9, experimental azeotropic data for this system, determined using a spinning band distillation column as described by Gmehling et al. (1995), are listed together with the azeotropic point derived from the maximum of the P, x data with the help of the Legendre polynomial. Figure 3 shows the temperature dependence of the experimental azeotropic composition for the system TAME + *tert*-butyl alcohol together with the calculated curve using the NRTL model. Obviously, the concentration of TAME in the azeotrope decreases with increasing temperature.

Conclusions

In this work, VLE and H$^{\text{E}}$ data were measured for two binary systems, using a static apparatus and an isothermal flow calorimeter. For each system the experimental results have been used to fit simultaneously NRTL parameters using a linear temperature dependence of the parameters. These parameters allow an accurate description of the real behavior (vapor−liquid equilibrium, H^{E}, γ^{∞}) of the systems investigated.

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