Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Propane + Dimethyl Ether and Propene + Dimethyl Ether at Temperatures from (298 to 323) K

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Isothermal vapor−liquid equilibrium (VLE) data for the binary systems propane + dimethyl ether and propene + dimethyl ether were determined experimentally with the static synthetic and the static analytic methods. Additionally, excess enthalpy (H^E) data were determined by means of an isothermal flow calorimeter. For the system propane + dimethyl ether, the azeotropic compositions were derived graphically from the VLE data. The experimental data from this work were correlated by using a linear temperature dependence for the UNIQUAC interaction parameters and by treating the real vapor phase behavior with the Soave−Redlich−Kwong equation of state. On the basis of this correlation, the new data were compared to values taken from the literature.

Introduction

For the synthesis and design of separation processes, a reliable knowledge of the phase equilibrium behavior is needed. For the binary systems propane + dimethyl ether and propene + dimethyl ether, only isothermal $P-x$ data[1,2] or ancient complete (isothermal $P-xy$ data) vapor−liquid equilibrium (VLE) data[3] are available in the literature. From these data, the partition coefficients (K factors) and relative volatilities (α_{ij}) cannot be evaluated beyond doubt. In this study, isothermal $P-x$ data at 298 and 313 K for the system propane + dimethyl ether and at 313 K for the system propene + dimethyl ether were measured using a computer controlled apparatus applying the synthetic static technique. Additionally, isothermal $P-xy$ data at 313 K were determined by analytic measurements for both systems. To describe the temperature dependence of the activity coefficients given by the Gibbs−Helmholtz equation,

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

the excess enthalpy (H^E) data for both systems were also measured at 323 K by means of an isothermal flow calorimeter. The experimental VLE and H^E data were correlated with the UNIQUAC model (linear temperature-dependent interaction parameters) considering the real vapor phase behavior with the SRK equation of state (EoS).[4] Thus, the experimental data from this work could be compared to the data of the other authors.

Experimental Section

Chemicals. All chemicals (liquefied gases) were purchased from commercial sources (purity checked by gas chromatography > 99.8 mol %). Since they were, as delivered, free from volatile components such as air, they were used without any further purification.

Apparatus and Procedures. The isothermal $P-x$ data were measured with a computer driven static apparatus. The synthetic experimental procedure is based on that proposed by Gibbs and Van Ness,[5] where the total pressure P is measured for different overall compositions at constant temperature. A similar apparatus has been described previously.[6,7] The apparatus used in this work can be operated at temperatures between 278 and 420 K and pressures up to 2 MPa. The thermostated 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 calibrated pressure sensor (model TJE-CP-lg, Sensotec), and the temperature is measured with a Pt100 resistance thermometer (model 1560, Hart Scientific). The overall compositions are determined from the known quantities of liquids injected into the equilibrium cell by stepping motor driven injection pumps and automatic valves. The liquid phase compositions are obtained by solving mass and volume balance equations also accounting for the vapor−liquid equilibrium. At the experimental conditions in this work, the estimated experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa $\pm$ 0.0001 (P/Pa), $\sigma(x_i) = 0.0005$.

For the measurements of the complete VLE data (isothermal $P-xy$ data) a magnetically stirred equilibrium cell made of Hastelloy C-276 was used. It is schematically shown in Figure 1. This setup can be applied for the experimental determination of phase equilibrium data such as V(L)LE or gas solubility data at temperatures of about 270 to 470 K and pressures up to 10 MPa. The thermoregulation of the cell is performed with a metal jacket heated electrically or with an external thermostat enabling the temperature to be constant within ±0.05 K. The pressure inside the cell is monitored with a calibrated pressure sensor (model PDCR 4010, Druck), and the temperature is measured with a Pt100 resistance ther-

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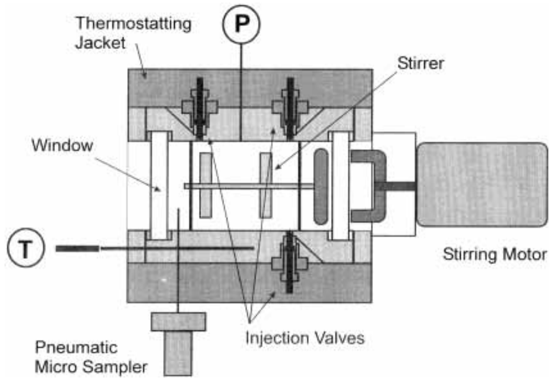

Figure 1. Schematic diagram of the equilibrium cell with sampling device.

Table 1. Experimental Vapor−Liquid Equilibrium Data ($P-x$ Data) for the Binary System Propane (1) + Dimethyl Ether (2) at 298.15 K and 313.10 K

$T = 298.15$ K		$T = 313.10$ K	
x_1	P/kPa	x_1	P/kPa
0.0000	589.60	0.0000	890.90
0.3848	836.79	0.0065	899.53
0.5118	880.24	0.0382	937.47
0.6436	915.17	0.0712	973.79
0.7737	939.37	0.1208	1023.5
0.8696	949.83	0.2037	1095.6
0.9268	952.64	0.2354	1119.9
0.9628	952.77	0.2775	1150.0
0.9810	952.37	0.3321	1185.4
0.9886	952.07	0.3887	1216.3
0.9924	951.81	0.3966	1222.6
0.9962	951.56	0.4729	1257.2
1.0000	951.25	0.5704	1297.0
		0.6700	1329.4
		0.7641	1352.3
		0.8422	1364.8
		0.9022	1369.9
		0.9470	1370.9
		0.9739	1370.1
		0.9853	1369.2
		0.9944	1368.5
		1.0000	1368.1

Table 2. Experimental Vapor−Liquid Equilibrium Data ($P-xy$ Data) for the Binary System Propane (1) + Dimethyl Ether (2) at 313.39 K

x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0000	0.0000	903.7	0.6670	0.7134	1344.0
0.0201	0.0415	926.1	0.7319	0.7639	1361.6
0.0384	0.0763	946.3	0.7762	0.7984	1370.9
0.0689	0.1289	977.7	0.8216	0.8363	1378.8
0.1303	0.2221	1037.0	0.8623	0.8699	1383.7
0.2013	0.3128	1098.6	0.9075	0.9107	1386.6
0.2909	0.4080	1164.8	0.9616	0.9615	1386.8
0.4324	0.5328	1252.4	0.9775	0.9774	1386.4
0.4945	0.5826	1280.8	0.9812	0.9812	1385.7
0.5509	0.6265	1304.6	0.9862	0.9861	1385.2
0.6061	0.6676	1324.4	1.0000	1.0000	1383.1

Table 3. Experimental Excess Enthalpy Data for the Binary System Propane (1) + Dimethyl Ether (2) at 323.15 K and 3.06 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0397	92	0.4900	626
0.0803	179	0.5411	625
0.1218	263	0.5935	608
0.1643	340	0.6472	575
0.2076	409	0.7023	529
0.2520	469	0.7587	458
0.2974	520	0.8167	368
0.3439	563	0.8762	25
0.3914	597	0.9373	125
0.4401	616		

Table 4. Experimental Vapor−Liquid Equilibrium Data ($P-x$ Data) for the Binary System Propene (1) + Dimethyl Ether (2) at 313.10 K

x_1	P/kPa	x_1	P/kPa
0.0000	891.60	0.5286	1339.6
0.0068	899.18	0.5793	1373.8
0.0542	945.55	0.6740	1439.1
0.1057	994.33	0.7633	1498.9
0.1680	1050.9	0.8379	1547.6
0.2325	1107.2	0.8967	1585.2
0.2940	1158.6	0.9419	1613.5
0.3546	1207.5	0.9704	1630.8
0.4032	1246.6	0.9833	1638.3
0.4169	1256.1	0.9952	1644.8
0.4696	1296.0	1.0000	1647.3
0.4856	1307.0		

Table 5. Experimental Vapor−Liquid Equilibrium Data ($P-xy$ Data) for the Binary System Propene (1) + Dimethyl Ether (2) at 313.32 K

x_1	y_1	P/kPa	x_1	y_1	P/kPa
0.0000	0.0000	896.2	0.8593	0.8967	1571.5
0.0307	0.0568	927.9	0.8925	0.9210	1591.6
0.0830	0.1432	977.1	0.9175	0.9395	1606.5
0.1125	0.1884	1004.6	0.9224	0.9432	1610.8
0.1353	0.2202	1024.5	0.9294	0.9482	1614.7
0.1845	0.2858	1065.6	0.9321	0.9502	1616.3
0.2687	0.3875	1139.1	0.9398	0.9558	1620.1
0.3753	0.4977	1227.5	0.9479	0.9618	1625.0
0.4971	0.6113	1324.0	0.9568	0.9683	1630.0
0.5986	0.6961	1399.1	0.9600	0.9708	1634.0
0.6823	0.7645	1458.4	0.9648	0.9743	1636.0
0.6890	0.7680	1463.0	0.9707	0.9786	1639.5
0.7365	0.8055	1493.8	0.9781	0.9840	1643.5
0.7618	0.8247	1510.2	0.9907	0.9932	1651.0
0.7769	0.8360	1520.0	0.9949	0.9963	1653.5
0.7987	0.8521	1534.0	1.0000	1.0000	1656.4
0.8213	0.8690	1548.2			

mometer (model 1502, Hart Scientific) inside the metal body of the cell. Also in this device, known quantities of substances (liquids, liquefied gases, or gases) can be injected into the cell using piston injector pumps (model 2200-801, Ruska) or gas storage containers, respectively. Moreover, after equilibration and phase settling, samples can be taken from both phases and analyzed by gas chromatography. Therefore, small amounts of the substances are directly injected into the carrier gas stream using a pneumatically driven microsampler (ROLSI: rapid on-line sampler injector, Guilbot et al.[8]). The complete compact cell can be turned so that the cusp of the sampling capillary is immersed in the desired phase. For this purpose, the cell is equipped with sapphire windows which are sealed with PTFE. Because of the very small sample size, the equilibrium inside the cell is not disturbed. To avoid condensation and adsorption of high boiling components, the microsampler and the lines for the gas stream of the gas chromatograph are superheated.

The commercial isothermal flow calorimeter (model 7501, Hart Scientific) used for the determination of the excess enthalpy data has been described previously.[9] 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 is working 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

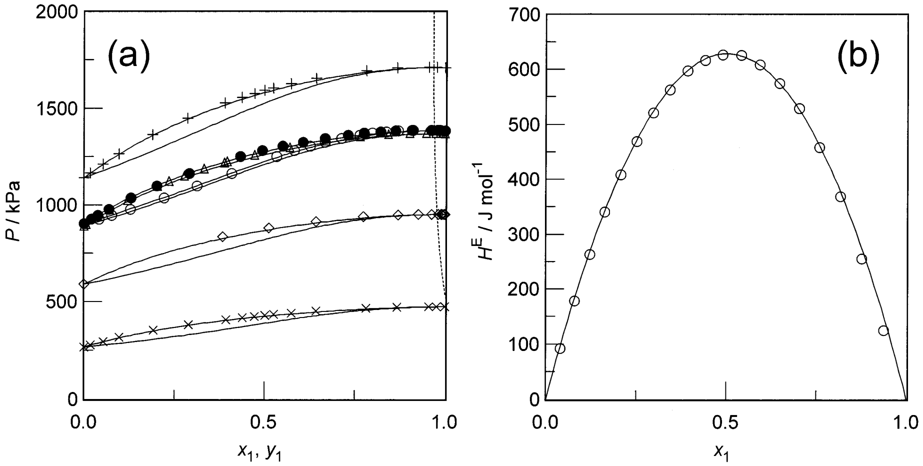

Figure 2. Experimental and predicted vapor−liquid equilibrium and excess properties for the binary system propane (1) + dimethyl ether (2). (a) Vapor−liquid equilibrium data: this work, synthetic $P-x$ data at 298.15 K (◇) and 313.10 K (△); this work, analytic $P-xy$ data at 313.39 K (●, ○); work of Giles and Wilson[1] at 273.15 K (×) and 323.15 K (+). (b) Excess enthalpy data at 323.15 K and 3.06 MPa: (○) this work; (—) UNIQUAC, real vapor phase; (- - -) azeotropic line, UNIQUAC, real vapor phase.

Table 6. Experimental Excess Enthalpy Data for the Binary System Propene (1) + Dimethyl Ether (2) at 323.15 K and 3.00 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0427	24	0.5088	156
0.0861	47	0.5597	155
0.1301	65	0.6115	152
0.1748	84	0.6641	145
0.2203	101	0.7177	133
0.2664	117	0.7722	116
0.3133	128	0.8277	93
0.3610	139	0.8841	67
0.4095	148	0.9415	33
0.4587	154		

Table 7. Experimental Azeotropic Conditions for the System Propane (1) + Dimethyl Ether (2)

T/K	$y_{az,1}$	P_{az}/kPa	source
298.15	0.945	952.9	synthetic VLE measurements
313.10	0.935	1371	synthetic VLE measurements
313.39	0.94	1388	analytic VLE measurements

Table 8. UNIQUAC Interaction Parameters (Eq 2) for the Binary Systems Treating the Real Vapor Phase with the SRK EoS (k_{ij} = 0, in the Classical Combining Rules)

component 1	component 2	i	j	a_{ij}/J·mol^{-1}	b_{ij}/J·mol^{-1}·K^{-1}
propane	dimethyl ether	1	2	1329.21	−2.8676
		2	1	−25.50	0.3873
propene	dimethyl ether	1	2	185.85	−0.1825
		2	1	134.81	−0.1155

determined from the observed frequency change between the baseline and the actual measurement. A back-pressure regulator serves to keep the pressure at a level at 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}), $\sigma(x_i)$ = 0.0001.

Results

The experimental VLE and excess enthalpy (H^E) data from this work are listed in Tables 1−6. From the system propane + dimethyl ether, the azeotropic conditions were derived graphically from the VLE data (the pressure maximum in the case of the $P-x$ data and K-factors and the pressure maximum in the case of the $P-xy$ data). The obtained values are given in Table 7. To the experimental data from this work, linear temperature-dependent interaction parameters for the UNIQUAC model were fitted simultaneously. The temperature dependence of the parameters is described by the following equation:

$$\Delta u_{ij}/\text{J·mol}^{-1} = a_{ij} + b_{ij}(T/\text{K}) \qquad (2)$$

The obtained parameters are given in Table 8. Since it was not possible to achieve a proper calculation of the vapor phase compositions, the real vapor phase behavior was considered using an EoS approach. The SRK EoS was used with the classical van der Waals mixing rules where the adjustable binary parameter k_{ij} was set to zero. The pure component critical data $T_{c,i}$ and $P_{c,i}$ and the acentric factors ω_i required for the EoS and the van der Waals properties r_i and q_i for the UNIQUAC model were taken from the Dortmund Data Bank (DDB 2003) and are given in Table 9. For the description of the pure component vapor pressures, coefficients for the Antoine equation for vapor pressures

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

were fitted to experimental data from numerous authors from this data compilation. The obtained parameters A_i, B_i, and C_i are also included in the table.

Table 9. Pure Component Properties (Antoine Parameters A_i, B_i, and C_i, van der Waals Properties r_i and q_i, Critical Data $T_{c,i}$ and $P_{c,i}$, and Acentric Factor ω_i)

	propane	propene	dimethyl ether
A_i	6.22361	6.20726	6.01540
B_i/K	942.43	905.70	814.24
C_i/K	−7.450	−9.763	−47.150
r_i	2.4766	2.2465	2.0461
q_i	2.2360	2.0240	1.9360
$T_{c,i}$/K	369.95	365.00	400.00
$P_{c,i}$/MPa	4.246	4.620	5.370
ω_i	0.1520	0.1480	0.1920

In Figures 2−5, the experimental data from this work and from other authors are compared to the calculated results of the modeling. For the system propene + dimethyl ether, an almost ideal behavior was observed showing only small positive deviations from Raoult's law. However, for the system propane + dimethyl ether even a homogeneous

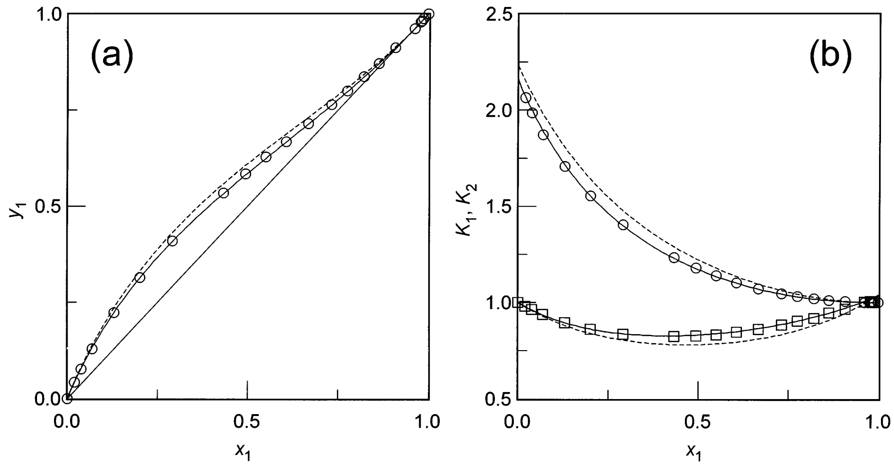

Figure 3. Experimental and predicted vapor−liquid equilibrium data for the binary system propane (1) + dimethyl ether (2) at 313.39 K. (a) *xy* diagram: (○) this work. (b) *K* factors: (○) this work; (—) UNIQUAC, real vapor phase; (- - -) UNIQUAC, ideal vapor phase.

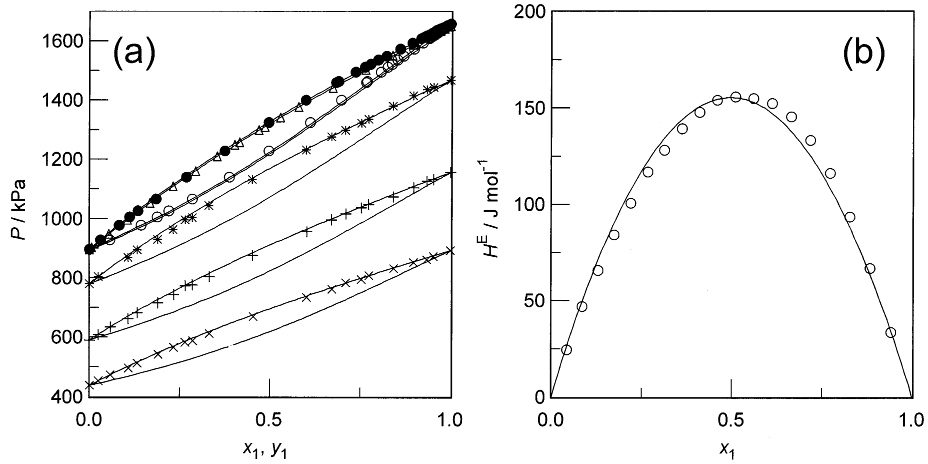

Figure 4. Experimental and predicted vapor−liquid equilibrium and excess properties for the binary system propene (1) + dimethyl ether (2). (a) Vapor−liquid equilibrium data: this work, synthetic *P*−*x* data at 313.10 K (△); this work, analytic *P*−*xy* data at 313.32 K (●, ○); work of Preuss and Moerke[2] at 288.2 K (×), 298.2 K (+), and 308.2 K (∗). (b) Excess enthalpy data at 323.15 K and 3.00 MPa: (○) this work; (—) UNIQUAC, real vapor phase.

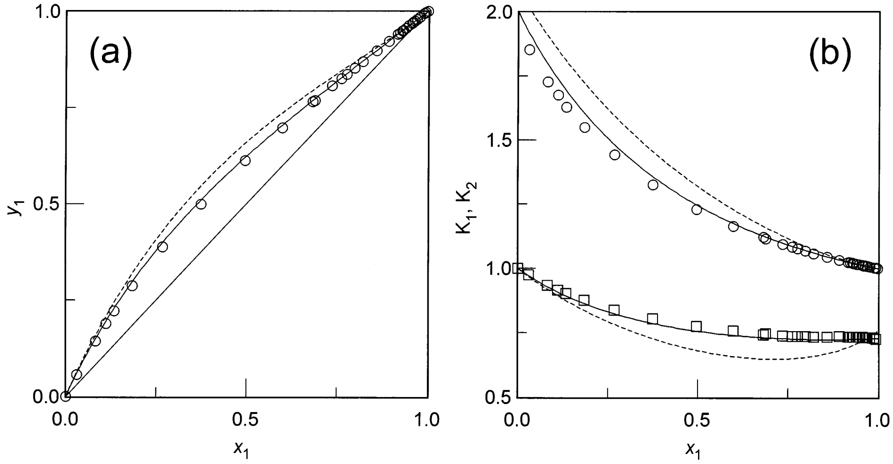

Figure 5. Experimental and predicted vapor−liquid equilibrium data for the binary system propene (1) + dimethyl ether (2) at 313.32 K. (a) *xy* diagram: (○) this work. (b) *K* factors: (○) this work; (—) UNIQUAC, real vapor phase; (- - -) UNIQUAC, ideal vapor phase.

pressure maximum azeotrope appears at temperatures above 278 K. The phase equilibrium behavior as well as the temperature dependence (heats of mixing data) for both systems can be correctly described with the regressed parameters, as can be seen in Figures 2 and 4. Also the experimental *P*−*x* data of Giles and Wilson[1] and of Preuss and Moerke[2] agree well with the calculations. For the propane + dimethyl ether binary system, the azeotropic line is included in the *P*−*x* diagram (Figure 2). As can be seen in Figures 3 and 5 (*x*−*y* diagram and *K* factors), the description of the vapor phase compositions (and of the relative volatilities) assuming ideal vapor phase behavior fails but considering the real vapor phase behavior, these systems can be reliably described.

Conclusions

Accurate isothermal $P-x$, $P-xy$, and H^E measurements were performed using different experimental techniques such as the static synthetic method, the static analytic method, and flow calorimetry. From these data, interaction parameters for the UNIQUAC g^E model using the SRK EoS and the classical van der Waals mixing rules for the description of the real vapor phase were obtained. With these parameters, the experimental data of this work were compared to the data of other authors. Due to the good agreement between experiments and calculations, the parameters given in Tables 8 and 9 can be recommended to describe the investigated systems in the temperature range from about 260 to 340 K.

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