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Isothermal Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Propylene Oxide + 2-Methylpentane and Difluoromethane (R32) + Pentafluoroethane (R125)[†]

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Isothermal *P*−*x* (vapor−liquid equilibria) and excess enthalpy (H^E) data for the two binary systems propylene oxide + 2-methylpentane and difluoromethane + pentafluoroethane were measured by means of the static technique and an isothermal flow calorimeter, respectively. The experimental data are presented using temperature-dependent interaction parameters for the nonrandom two-liquid model, which were fitted simultaneously to all measured data. From the experimental *P*−*x* data, the azeotropic conditions were determined for both systems. The experimental results from this work were compared with the data of other authors.

Introduction

Experimental phase equilibrium data are required for a proper synthesis, design, and optimization of separation processes. For the description of the required separation factors of the system to be separated, excess Gibbs energy (G^E) models or equations of state can be used, which allow the prediction of the phase equilibrium behavior of multicomponent systems from binary data alone. If there are no experimental data available, group contribution methods, such as UNIFAC, mod. UNIFAC (Dortmund), or PSRK, can be employed. For the extension of these methods, the systematic extension of the existing database is desired.

In this paper, isothermal *P*−*x* data were measured with the help of two static devices. For the system propylene oxide + 2-methylpentane at 323.15 K, a computer-controlled apparatus was employed. For the system difluoromethane + pentafluoroethane at 308.15 K, a manual apparatus was used which can be applied to higher temperatures and pressures. Additionally, excess enthalpy data was measured for both systems at the same temperature using a commercial isothermal flow calorimeter. Excess enthalpy data are important for the description of the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation

$$\left(\frac{\partial \ln \gamma_\mathrm{i}}{\partial\, 1/T}\right)_{P,x} = \frac{\bar{H}_i^{\mathrm{E}}}{R} \qquad (1)$$

While for the system propylene oxide + 2-methylpentane no experimental data are available in the literature, there are published vapor−liquid equilibria (VLE) data and azeotropic points for the system difluoromethane + pentafluoroethane.[1−18] Therefore, for this system, the experimental results of this work can be used to validate the consistency of all experimental data.

The presented systems were studied as part of an ongoing investigation sponsored by Project 805(B)/99 of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

Experimental Part

Materials. The liquids propylene oxide and 2-methylpentane were purchased from Aldrich and dried over molecular sieves. For the VLE measurements, they were degassed and distilled as described by Fischer and Gmehling (1994).[19] For the H^E measurements, they were used without degassing. The liquefied gases difluoromethane and pentafluoroethane were purchased from Lancaster (for the VLE measurements) and were supplied by Solvay (for the H^E measurements), respectively. They were used without any further purification. The suppliers and final purities as determined by gas chromatography and Karl Fischer titration are listed in Table 1.

Apparatus and Procedure. The VLE measurements (isothermal *P*−*x* data) were carried out in two different static devices following the principle proposed by Gibbs and Van Ness.[20] For the measurement of the binary system propylene oxide + 2-methylpentane, a computer-operated static apparatus was used. The apparatus, the measurement procedure, and the accuracy of the data has been described previously.[21,22] For the measurement of the system difluoromethane + pentafluoroethane, the static apparatus of Kolbe and Gmehling (1985)[23] was employed. A detailed description of this apparatus was given by Fischer and Gmehling (1994).[19] The experimental uncertainties for both setups are $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 (P/Pa), and $\sigma(x_i) = 0.0001$. The principle of measurement is the same for both devices. The thermostated, purified, and degassed compounds are filled into the thermostated equilibrium cell by means of precise piston injectors. In the case of the computer-controlled equipment,

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Table 1. Suppliers, Purities, and Water Contents of the Chemicals Used

component	supplier	purity/ % GC	water content/ mass ppm
propylene oxide	Aldrich	>99.99	180
2-methylpentane	Aldrich	99.98	<10
difluoromethane	Lancaster, Solvay	98	not analyzed
pentafluoroethane	Lancaster, Solvay	99	not analyzed

Table 2. Experimental *P*−*x* Data for the System Propylene Oxide (1) + 2-Methylpentane (2) at 323.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	72.19	0.42731	150.39	0.89325	175.54
0.00547	74.10	0.48023	155.10	0.91740	175.75
0.01095	75.88	0.53087	159.06	0.93628	175.73
0.01724	77.89	0.57750	162.31	0.95210	175.61
0.02336	79.82	0.60965	164.25	0.96497	175.40
0.03602	83.58	0.62105	165.03	0.97499	175.18
0.05277	88.36	0.64957	166.58	0.98280	174.95
0.07416	93.98	0.66073	167.27	0.98795	174.77
0.10258	100.99	0.68913	168.66	0.99155	174.65
0.13562	108.36	0.69700	169.12	0.99380	174.55
0.17404	116.12	0.72828	170.51	0.99606	174.45
0.21717	123.82	0.76597	172.08	0.99835	174.35
0.26393	131.10	0.80172	173.38	0.99917	174.30
0.31782	138.41	0.83510	174.40	1.00000	174.27
0.37253	144.80	0.86585	175.11		

the injectors are driven by stepping motors. In the other case, manual piston pumps (Model 2200-801, RUSKA) are used for injecting the compounds. When phase equilibrium is reached, the pressure in the equilibrium cell is measured with a pressure sensor (Model 245A, Paroscientific) and a dead weight pressure gage (Desgranges & Huot), respectively. For the temperature measurement, a Pt100 resistance thermometer (Model 1506, Hart Scientific) is used in both cases. The liquid-phase compositions can be obtained from exactly known volumes and densities of the liquids injected into the cell. The difference between feed and equilibrium composition is corrected by solving the mass and volume balance taking into account the measured $P-x$ data. At low pressures as in the case of the propylene oxide + 2-methylpentane system, the liquid composition is identical within $\Delta x = \pm 0.003$ with the feed composition. For the system difluoromethane + pentafluoroethane, the corrections are within $\Delta x = \pm 0.005$.

For the determination of excess enthalpy data, a commercial isothermal flow calorimeter (Model 7501, Hart Scientific) described by Gmehling (1993)[24] was used. In this apparatus, two syringe pumps (Model LC-2600, ISCO) provide a flow of constant compositions through a calorimeter cell (placed in a thermostat) equipped with a pulsed heater and a Peltier cooler. The Peltier cooler operates at constant power, resulting in a constant heat loss from the calorimeter cell. To keep the temperature constant, this heat flow is compensated by the pulsed heater. The heat of mixing effects are obtained from the change of the frequency of the pulsed heater. When starting with the mixing experiments, endothermal heat effects cause an increase and exothermal heat effects cause a decrease of the frequency. A back-pressure regulator maintains the pressure at a constant level at which evaporation and degassing effects can be prevented. The experimental uncertainties of this device are $\sigma(T) = 0.03$ K, $\sigma(H^E) = 2$ J mol^{-1} + 0.01 (H^E/J mol^{-1}), and $\sigma(x_i) = 0.0001$.

Table 3. Experimental H^E Data for the System Propylene oxide (1) + 2-Methylpentane (2) at 323.15 K and 1.14 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0895	404	0.5547	1232	0.8134	805
0.1719	702	0.6045	1202	0.8486	691
0.2479	920	0.6514	1156	0.8820	564
0.3184	1066	0.6954	1084	0.9137	431
0.3838	1164	0.7370	1003	0.9439	289
0.4447	1217	0.7763	911	0.9726	139
0.5015	1240				

Table 4. Experimental *P*−*x* Data for the System Difluoromethane (1) + Pentafluoroethane (2) at 308.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	1778.8	0.43139	2040.9	0.75306	2166.4
0.00439	1783.9	0.43530	2046.1	0.78323	2172.9
0.02167	1795.7	0.47359	2062.5	0.81890	2180.9
0.04553	1819.3	0.49698	2074.5	0.87254	2189.2
0.08106	1840.5	0.53291	2090.9	0.91899	2193.3
0.09187	1845.7	0.55997	2102.8	0.95262	2193.7
0.12935	1870.0	0.58930	2115.2	0.96984	2193.7
0.17193	1893.4	0.61610	2122.2	0.98226	2192.5
0.23104	1929.6	0.61778	2125.7	0.99023	2192.0
0.26228	1947.2	0.64551	2133.4	0.99619	2191.3
0.32483	1985.2	0.67741	2144.2	0.99940	2191.0
0.38260	2015.8	0.71226	2155.4	1.00000	2191.0

Table 5. Experimental H^E Data for the System Difluoromethane (1) + Pentafluoroethane (2) at 308.15 K and 5.13 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0880	25	0.5499	150	0.8105	130
0.1692	50	0.5999	155	0.8461	115
0.2444	73	0.6470	157	0.8800	97
0.3142	95	0.6913	155	0.9122	76
0.3792	114	0.7332	150	0.9428	52
0.4399	129	0.7729	142	0.9721	26
0.4967	141				

Table 6. NRTL Interaction Parameters Fitted Simultaneously to Isothermal *P*−*x* and H^E Data

component 1	component 2	i	j	a_{ij}/J·mol^{-1}	b_{ij}/J·mol^{-1}·K^{-1}
propylene oxide	2-methylpentane	1	2	2568.22	−0.9083
		2	1	3866.00	−9.8579
				$\alpha_{ij} = 0.4700$	
difluoromethane	pentafluoroethane	1	2	3098.73	−1.8390
		2	1	−1466.42	−0.4816
				$\alpha_{ij} = 0.2698$	

Table 7. Pure-Component Parameters: Antoine Coefficients A_i, B_i, and C_i for Equation 3

component	A_i	B_i/K	C_i/K
propylene oxide	6.14068	1086.37	−44.556
2-methylpentane	5.99313	1151.40	−44.673
difluoromethane	6.63072	989.04	−7.536
pentafluoroethane	6.35399	898.86	−18.558

Results

The experimental $P-x$ and H^E data for the investigated systems are listed in Tables 2−5. For both systems, temperature-dependent nonrandom two-liquid (NRTL)[25] parameters were fitted simultaneously to the experimental VLE and H^E data from this work. To describe the temperature dependence of the interaction parameters, the following expression was used

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

The obtained linear temperature-dependent parameters are presented in Table 6. The required constants of the Antoine equation

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

were taken from the Dortmund Data Bank (DDB 2003) and

Table 8. Experimental and Calculated (NRTL) Azeotropic Conditions for Both Systems

component 1	component 2	T/K	$y_{1,\mathrm{az}}$(exp)	P_{az}(exp)/kPa	$y_{1,\mathrm{az}}$(calc)	P_{az}(calc)/kPa
propylene oxide	2-methylpentane	323.15	0.925	175.77	0.9312	174.85
difluoromethane	pentafluoroethane	308.15	0.948	2193.8	0.9440	2192.0

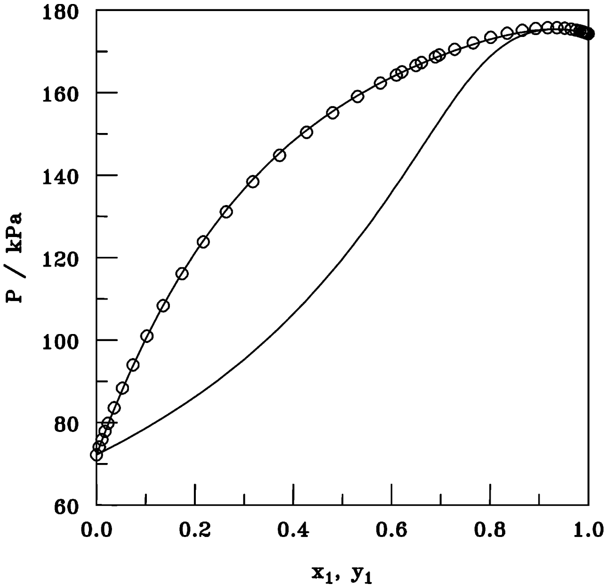

Figure 1. Experimental and predicted P−x(y) behavior of the system propylene oxide (1) + 2-methylpentane (2) at 323.15 K: ○, this work; solid line, NRTL.

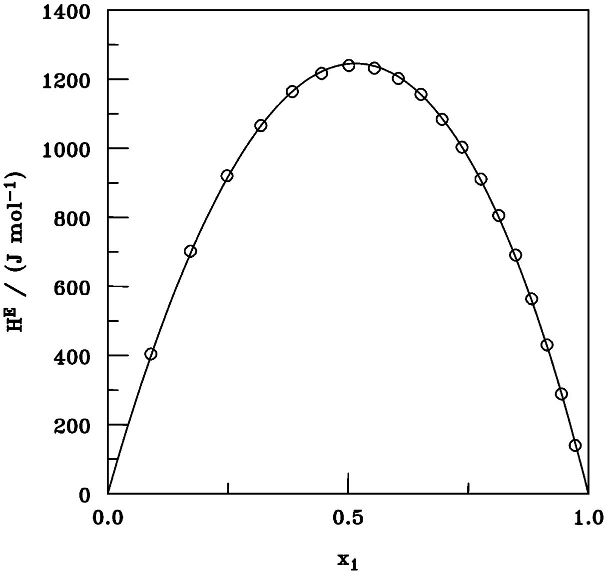

Figure 2. Experimental and predicted excess enthalpy data for the system propylene oxide (1) + 2-methylpentane (2) at 323.15 K: ○, this work; solid line, NRTL.

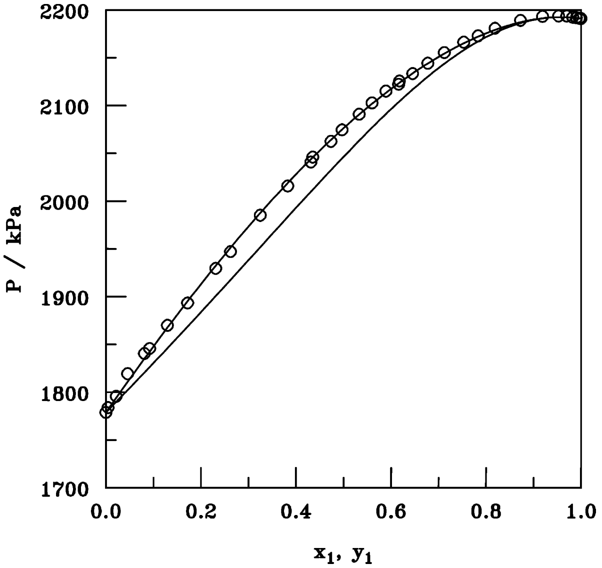

Figure 3. Experimental and predicted P−x(y) behavior of the system difluoromethane (1) + pentafluoroethane (2) at 308.15 K: ○, this work; solid line, NRTL.

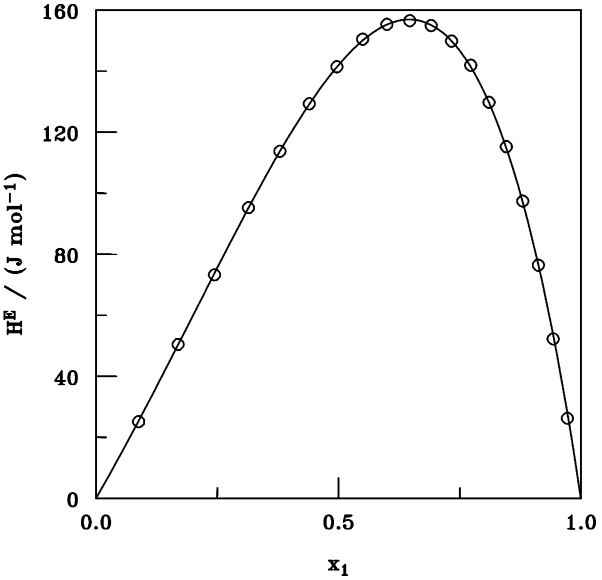

Figure 4. Experimental and predicted excess enthalpy data for the system difluoromethane (1) + pentafluoroethane (2) at 308.15 K: ○, this work; solid line, NRTL.

are listed in Table 7. To account only for the excess Gibbs energy (G^E), the coefficients A_i of the Antoine equation were adjusted to the experimental vapor pressures of the pure components during the fitting procedure. A comparison of the experimental pure-component vapor pressures with data from literature is a good test for the quality of degassing and purification of the chemicals used. The deviations between the pure-component vapor pressures from this work and values calculated with the Antoine equation are smaller than 1.0% for all substances.

A graphical representation of experimental VLE, H^E, and azeotropic data is shown in Figures 1−5 together with values calculated with the NRTL equation. As illustrated in the different diagrams, good agreement between experimental and calculated values was obtained. For both systems, the deviations for the bubble-point curves are less than 0.5% in pressure and the deviations between experimental and calculated excess enthalpies are less than 1% except the points at very small concentrations because of their small absolute values. For the system difluoromethane + pentafluoroethane, all isothermal VLE data from the literature in the temperature range from (263 to 323) K can also be described within $\Delta P = \pm 0.5\%$, although these data were not considered in the data regression. This fact validates the approach of this work. The simultaneous correlation of VLE and H^E facilitates a prediction of the phase

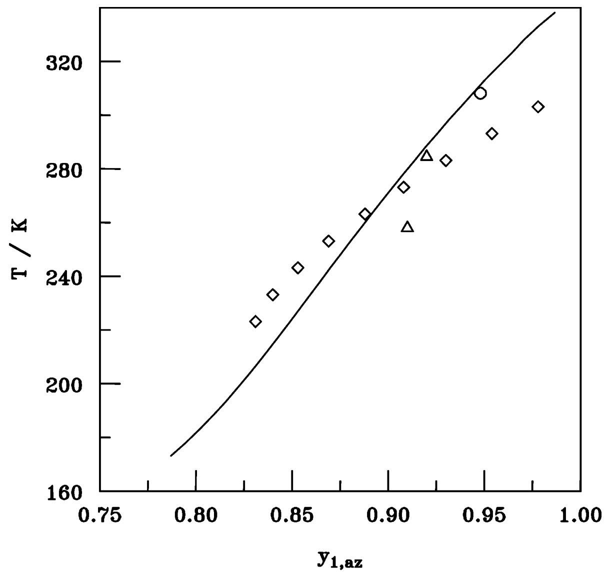

Figure 5. Experimental and predicted azeotropic data for the system difluoromethane (1) + pentafluoroethane (2): ○, this work; △, Barley et al.;[1] ◇, Shiflett and Sandler;[15] solid line, NRTL.

equilibrium behavior over large temperature and pressure ranges.

From the experimental $P-x$ data, the azeotropic conditions were derived graphically. The values can be described satisfactorily with the optimized NRTL parameters as shown in Table 8. Figure 5 contains a comparison between experimental azeotropic data for the system difluoromethane + pentafluoroethane from this work and other authors[26] and the calculated values with the NRTL parameters taken from Table 6.

Conclusions

Isothermal $P-x$ data were measured for the binary systems propylene oxide + 2-methylpentane and difluoromethane + pentafluoroethane using a static technique. Additionally, H^E data were measured with a commercial isothermal flow calorimeter. By use of these data, temperature-dependent NTRL parameters were fitted. VLE, H^E, and azeotropic data predicted with these parameters are in good agreement with experimental data. On the basis of these G^E model parameters, consistency of the data from this study and data from literature was verified.

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