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Isothermal Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Water + 1,2-Ethanediol and Propene + Acetophenone[†]

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Isothermal vapor−liquid equilibrium $P-x$ data for the two binary systems water + 1,2-ethanediol and propene + acetophenone were measured by means of a computer-operated static apparatus. Additionally, excess enthalpy (H^E) data for the binary system propene + acetophenone were measured with an isothermal flow calorimeter. The experimental data are presented using temperature-dependent interaction parameters for the UNIQUAC model which were fitted simultaneously to all measured data. The experimental results were compared with the data of other authors.

Introduction

A reliable knowledge of the phase equilibrium behavior is a prerequisite for the 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 ASOG, UNIFAC, Mod. UNIFAC (Dortmund), or Mod. UNIFAC (Lyngby) can be employed. For the revision and extension of these methods, the systematic extension of the existing database is desired.

In this paper, isothermal $P-x$ data measured with a computer-controlled static apparatus are presented for the systems water (1) + 1,2-ethanediol (2) at 333.15 K and 353.15 K and propene (1) + acetophenone (2) at 323.27 K. For the binary system propene (1) + acetophenone (2), also excess enthalpy data at 323.15 K were measured. For this purpose, an isothermal commercial flow calorimeter was used. Excess enthalpy data are important for a correct description of the temperature dependence of activity coefficients following the Gibbs−Helmholtz equation

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

The experimental vapor−liquid equilibrium (VLE) and H^E data of this work are presented together with the calculated results using temperature-dependent UNIQUAC interaction parameters.

The presented systems were studied as part of an ongoing investigation sponsored by Project 805(B)/98 of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

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

component	supplier	purity/% GC	water content/ mass ppm
water			
1,2-ethanediol	Riedel-de-Haën	>99.99	40
propene	Messer Griesheim	99.5	not analyzed
acetophenone	Riedel-de-Haën	>99.3	not analyzed

Experimental Section

Materials. 1,2-Ethanediol and acetophenone were purchased from Riedel-de-Haën and dried over moleculare sieves. Water was distilled twice in our laboratory. For the VLE measurements, these chemicals were degassed and distilled as described by Fischer and Gmehling (1994).[1] For the H^E measurements, the chemicals were used without degassing. Propene was purchased from Messer Griesheim and was used without 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.[2] For the measurement of the binary system water (1) + 1,2-ethanediol (2), a computer-operated static apparatus was used. The apparatus, the measurement procedure, and the accuracy of the data have been described previously.[3,4] For the measurement of the system propene + acetophenone, the static apparatus of Kolbe and Gmehling[5] was employed. A detailed description of this apparatus was given by Fischer and Gmehling.[1] 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 thermoregulated equilibrium cell by means of precise piston injectors. In the case of the computer-controlled equipment, the injectors are driven by stepping

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Table 2. Experimental $P-x$ Data for the System Water (1) + 1,2-Ethanediol (2) at 333.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	0.22	0.47769	9.27	0.93601	18.74
0.00327	0.28	0.53779	10.49	0.95154	19.04
0.00949	0.39	0.59256	11.61	0.96334	19.22
0.01634	0.51	0.64202	12.64	0.97303	19.43
0.02723	0.71	0.68626	13.55	0.98075	19.58
0.04142	0.96	0.72541	14.37	0.98667	19.70
0.06340	1.35	0.75942	15.09	0.99114	19.78
0.09276	1.87	0.78920	15.72	0.99405	19.83
0.13218	2.58	0.78979	15.81	0.99597	19.87
0.17827	3.43	0.82005	16.42	0.99740	19.92
0.23101	4.42	0.84816	16.99	0.99841	19.89
0.28891	5.52	0.87391	17.50	0.99915	19.88
0.34875	6.69	0.89719	17.94	0.99968	19.92
0.41455	7.99	0.91800	18.38	1.00000	19.93

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 of 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 water (1) + 1,2-ethanediol (2) system, the liquid composition is identical within $\Delta x = \pm 0.0002$ with the feed composition. For the system propene (1) + acetophenone (2), the corrections are within $\Delta x = \pm 0.025$.

For the determination of the excess enthalpy data, a commercial isothermal flow calorimeter (Model 7501, Hart Scientific) described by Gmehling (1993)[6] 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 is working at constant power causing 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. Endothermal heat effects cause an increase, and exothermal heat effects cause a decrease of the frequency. A back-pressure regulator serves to keep 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 $\sigma(x_i) = 0.0001$.

Results

The experimental $P-x$ and H^{E} data for the investigated systems are listed in Table 2−5. For both systems, temperature-dependent UNIQUAC[7] parameters were fitted simultaneously to the experimental data. For the binary system water (1) + 1,2-ethanediol (2), additional H^{E} data from Matsumoto et al. (1977)[8] at 298.15 K and from Villamañan et al. (1984)[9] at 323.15 K were included in the data regression. For the system propene (1) + acetophenone (2), additional VLE data from Wilding et al. (1991)[10] were included. To describe the temperature dependence of the interaction parameters, the following expression was used

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

The fitted parameters are presented in Table 7.

Table 3. Experimental $P-x$ Data for the System Water (1) + 1,2-Ethanediol (2) at 353.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	0.77	0.47970	22.70	0.93584	44.50
0.00589	1.02	0.53926	25.58	0.95131	45.15
0.01148	1.28	0.59356	28.22	0.96310	45.72
0.02172	1.72	0.64277	30.61	0.97277	46.20
0.03311	2.22	0.68680	32.75	0.98043	46.56
0.04538	2.76	0.72475	34.59	0.98625	46.78
0.06678	3.70	0.72575	34.65	0.99085	47.02
0.09633	4.99	0.75803	36.16	0.99381	47.16
0.13585	6.71	0.78978	37.66	0.99579	47.26
0.18162	8.76	0.82003	39.10	0.99725	47.32
0.23460	11.15	0.84811	40.40	0.99816	47.36
0.29193	13.81	0.87384	41.61	0.99908	47.40
0.35156	16.60	0.89707	42.69	0.99965	47.41
0.41702	19.70	0.91785	43.67	1.00000	47.44

Table 4. Experimental $P-x$ Data for the System Propene (1) + Acetophenone (2) at 323.27 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.00000	0.34	0.39108	1314.8	0.79292	1802.8
0.00016	1.03	0.44197	1420.3	0.83818	1832.4
0.00108	4.95	0.49066	1507.9	0.88269	1866.5
0.00590	25.82	0.52670	1563.2	0.92200	1906.4
0.01323	57.58	0.56396	1613.2	0.95377	1951.4
0.02920	125.85	0.57348	1624.0	0.97487	1992.2
0.06196	261.43	0.59425	1648.1	0.99059	2030.9
0.09018	374.13	0.59453	1647.6	0.99767	2051.8
0.11367	465.38	0.61851	1672.5	0.99930	2056.2
0.14252	573.23	0.64818	1700.3	0.99987	2058.1
0.20909	806.01	0.68356	1728.9	1.00000	2058.9
0.26572	985.15	0.70576	1745.6		
0.32818	1160.8	0.74653	1773.2		

Table 5. Experimental H^{E} Data for the System Propene (1) + Acetophenone (2) at 323.15 K and 4.1 MPa

x_1	H^{E}/J·mol^{-1}	x_1	H^{E}/J·mol^{-1}	x_1	H^{E}/J·mol^{-1}
0.0702	54	0.4086	240	0.8115	142
0.1375	105	0.4889	250	0.8516	113
0.2020	148	0.5893	246	0.8905	82
0.2640	188	0.6828	218	0.9281	52
0.3235	213	0.7487	184	0.9646	25

Table 6. Pure-Component Parameters: Relative van der Waals Volumes r_i and Surfaces q_i and Antoine Coefficients A_i, B_i, and C_i

component	r_i	q_i	A_i	B_i/K	C_i/K
water	0.9200	1.400	7.19621	1730.63	−39.724
1,2-ethanediol	2.4088	2.248	6.88922	1851.88	−91.406
propene	2.2465	2.024	6.20726	905.70	−9.763
acetophenone	4.6941	3.608	6.35218	1774.63	−66.856

The required pure-component properties, such as the van der Waals properties r_i and q_i, and the constants of the Antoine equation

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

were taken from the Dortmund Data Bank (DDB 2003)) and are listed in Table 6. Also, the liquid densities at the experimental conditions required for the data treatment were taken from this source. To account only for the excess Gibbs energy, the coefficients A_i of the Antoine equation were adjusted to the experimental vapor pressures of the pure components during the fitting procedure. The deviations between experimental pure-component vapor pressures and values calculated with the Antoine equation are smaller than 1.1% for water and propene. Because of the very small absolute values for very small vapor pressures of 1,2-ethanediol and acetophenone, the deviations for these components are up to 20% but not above 0.12 kPa.

Table 7. UNIQUAC 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}	c_{ij}/J·mol^{-1}·K^{-2}
water	1,2-ethanediol	1	2	1248.07	−2.1720	
		2	1	−2116.50	2.0751	
propene	acetophenone	1	2	8445.28	−49.7174	0.08706576
		2	1	8100.75	−47.6228	0.06963779

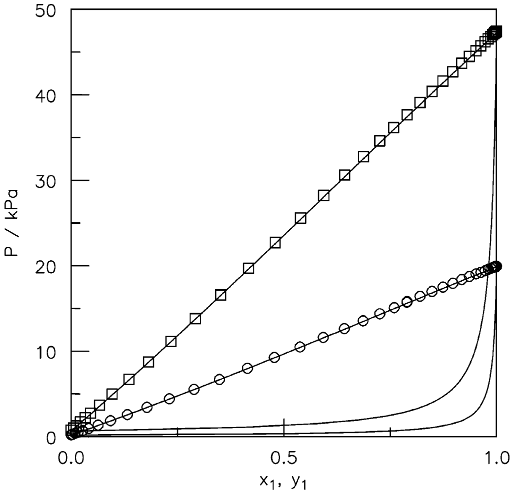

Figure 1. Experimental and predicted $P-x(y)$ behavior of the system water (1) + 1,2-ethanediol (2): ○, 333.15 K; □, 353.15 K; solid line, UNIQUAC.

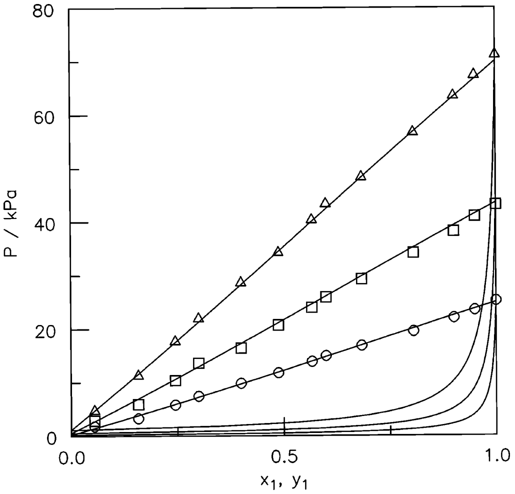

Figure 2. Experimental and predicted $P-x(y)$ behavior of the system water (1) + 1,2-ethanediol (2) by Nath and Bender (1983):[11] ○, 338.25 K; □, 350.85 K; △, 363.45 K; solid line, UNIQUAC.

A graphical representation of experimental VLE and H^E data from this work and other authors is given in Figures 1−5 together with values calculated with the UNIQUAC equation. As illustrated in different diagrams, good agreement between experimental and calculated values is obtained.

In Figure 1, the experimental $P-x$ data for the nearly ideal system water (1) + 1,2-ethanediol (2) from this study are presented. Figure 2 shows a comparison with three isothermal $P-x$ data sets for this system from Nath and Bender (1983)[11] which were not included in the data regression together with the UNIQUAC prediction. The correct description of the temperature dependence of the excess Gibbs energy is proved in Figure 3 where two isothermal H^E data sets from Matsumoto et al. (1977)[8] and from Villamañan et al. (1984)[9] are compared with the UNIQUAC predictions.

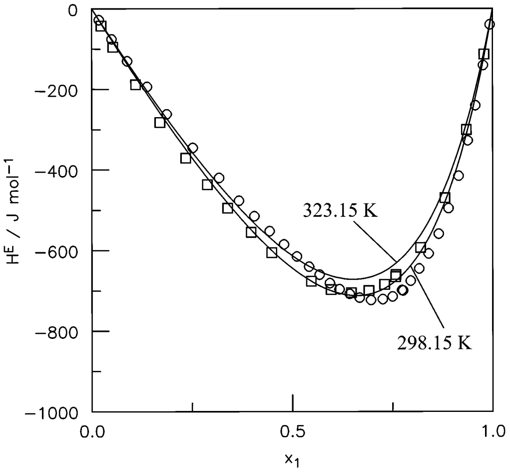

Figure 3. Experimental and predicted excess enthalpy data for the system water (1) + 1,2-ethanediol (2) by: ○, Matsumoto et al. (1977)[8] at 298.15 K; □, Villamañan et al. (1984)[9] at 323.15 K; solid line, UNIQUAC.

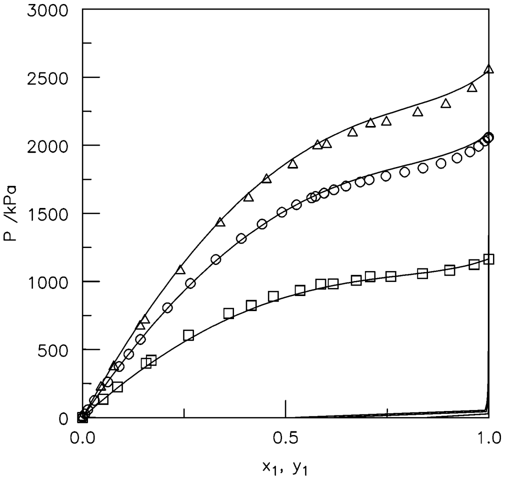

Figure 4. Experimental and predicted $P-x(y)$ behavior of the system propene (1) + acetophenone (2) (○) 323.27; by Wilding et al. (1991):[10] □, 298.15 K, △, 333.15 K; solid line, UNIQUAC.

The VLE results for the system propene (1) + acetophenone (2) from this work and from Wilding et al. (1991),[10] which show a positive deviation from Raoult's law, are presented in Figure 4 together with the calculated data (UNIQUAC). It can be seen from Figure 5 that the experimental H^E data are described reliably with the fitted UNIQUAC parameters.

Conclusions

Isothermal $P-x$ data were measured for the binary systems water (1) + 1,2-ethanediol (2) and propene (1) + acetophenone (2) using the static technique. Additionally, for the system propene (1) + acetophenone (2), H^E data were measured with a commercial isothermal flow calorimeter. From these data and the data of other authors, temperature-dependent interaction parameters for the UNIQUAC model were fitted. VLE and H^E data predicted with these parameters are in good agreement with experi-

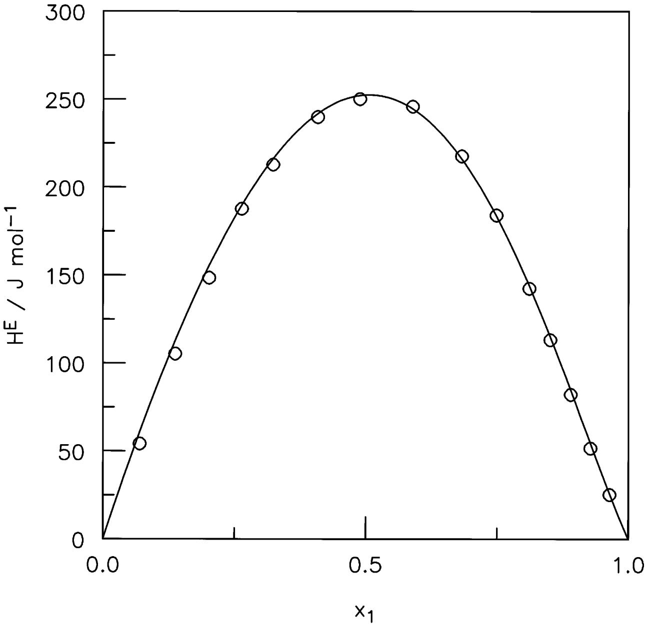

Figure 5. Experimental and predicted excess enthalpy data for the system propene (1) + acetophenone (2): ○, 323.15 K; solid line, UNIQUAC.

mental data. On the basis of the fitted G^E model parameters, a consistency of the data from this study and the data from the literature was indicated.

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