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Vapor−Liquid Equilibrium Data, Excess Enthalpy Data, and Azeotropic Data for the Binary System Dibutyl Ether + *o*-Xylene

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For the binary system dibutyl ether + *o*-xylene, isothermal and isobaric vapor−liquid equilibrium (VLE) data were measured with the static synthetic and the dynamic method. Additionally, excess enthalpy (H^E) data were determined by means of an isothermal flow calorimeter, and azeotropic data were investigated using a spinning band column. The experimental data from this work were correlated using linear temperature-dependent UNIQUAC interaction parameters.

Introduction

For the design and optimization of separation processes, a reliable knowledge of the phase equilibrium behavior is essential. For the binary system dibutyl ether and *o*-xylene, only azeotropic data are available in the literature.[1−4] In this study, isothermal vapor−liquid equilibrium (VLE) data for this system were measured with the static synthetic method in two different apparatuses at (323.15 and 413.15) K. Isobaric vapor−liquid equilibrium (VLE) data were measured with the dynamic method at 51 kPa with a Swietoslawsky ebulliometer. To describe the temperature dependence of the activity coefficients given by the Gibbs−Helmholtz equation

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

excess enthalpy (H^E) data were measured at 323.15 K with an isothermal flow calorimeter. Additionally, azeotropic data were measured at (323, 363, and 413) K by means of a spinning band column.

The experimental data were correlated with the UNIQUAC model using linear temperature-dependent interaction parameters. The experimental data from this work are compared to the azeotropic data of other authors.

Experimental Section

Chemicals. Dibutyl ether and *o*-xylene were purchased from a commercial source. Both components were dried over molecular sieves and then distilled and degassed as described by Fischer and Gmehling.[5] The final purity and water content were determined by gas chromatography and Karl Fischer titration and are given in Table 1.

Table 1. Properties of the Pure Components

component	supplier	purity/%	10^{-6} $w(H_2O)$
dibutyl ether	Acros	> 99.9	<15
o-xylene	Acros	> 99.8	<15

Apparatus and Procedures. The VLE measurements (isothermal *P*, *x* data) were carried out in two different computer-operated static devices[6,7] following the principle proposed by Gibbs and Van Ness.[8] The principle of the measurements was the same for both devices. The experimental setup is schematically shown in Figure 1. The thermostatted, purified, and degassed compounds were filled into the thermoregulated equilibrium cell of known volume by means of precise piston injectors, which were driven by stepping motors. The pressure inside the equilibrium cell was measured with a pressure sensor. In the case of the measurement at 323.15 K, a sensor model 245A, Paroscientific, was used, and in the case of the measurement at 413.15 K, a sensor model PAA 25 HTC, (0 to 2) bar, Keller, was utilized, respectively. The pressure sensors were calibrated against a primary standard using a pressure balance (Desgranges et Huot). For the temperature measurement, a Pt100 resistance thermometer (model 1560, Hart Scientific), which was calibrated against a certified reference temperature probe (Wika), was employed in both cases. The feed compositions were determined from the known quantities of liquids injected into the equilibrium cell by the piston injectors. The liquid-phase compositions were obtained by solving mass and volume balance equations which were also taking the vapor−liquid

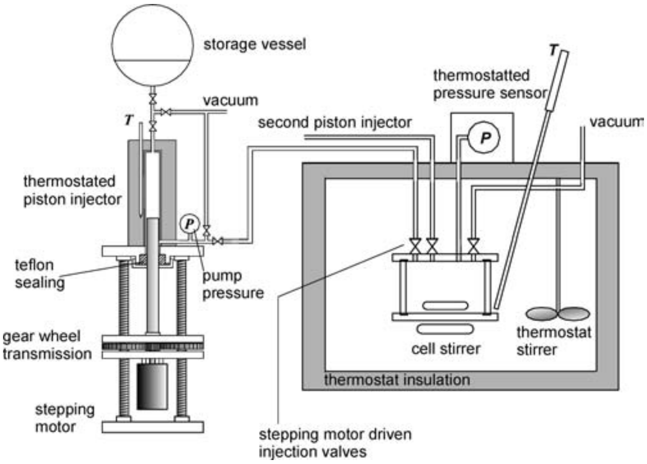

Figure 1. Schematic diagram of the computer-operated static apparatus.

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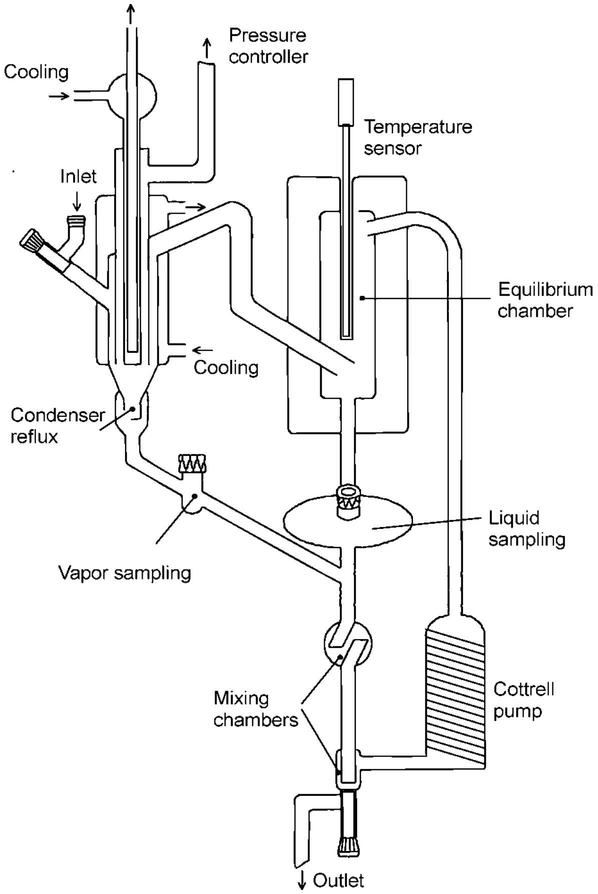

Figure 2. Schematic diagram of the Swietoslawsky ebouilliometer.

equilibrium into account. The experimental uncertainties for both setups are estimated to be $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa $+ 0.0005(P/\text{Pa})$, and $\sigma(x_i) = 0.0001$.

The isobaric VLE data were measured by means of a dynamic method using a Swietoslawski ebulliometer as described by Rogalski and Malanowski.[9] At a given pressure, which was regulated by an electronic pressure control, the boiling temperature of a mixture could be measured. When phase equilibrium was reached, i.e., a stable circulation was achieved and the boiling temperature was constant, the compositions of both phases could be determined by taking samples from the liquid and the condensed vapor phase, which were analyzed by gas chromatography (model 6890N, Agilent; column, FS-FFAP-CB-0.25, 50 m × 0.32 mm × 0.25 μm; detector TCD). Figure 2 shows a scheme of the device. The experimental errors for this setup depend on the investigated system and are estimated to be $\sigma(T) = 0.05$ K, $\sigma(P) = 20$ Pa $+ 0.0005(P/\text{Pa})$, and $\sigma(x_i) = 0.0002$.

For the determination of the excess enthalpy data, a commercial isothermal flow calorimeter (model 7501, Hart Scientific) described by Gmehling[10] was used. In this apparatus, two syringe pumps (model LC-2600, ISCO) provided a flow of constant composition through a calorimeter cell (placed in a thermostat) equipped with a pulsed heater and a Peltier cooler. The Peltier cooler working at constant power caused a constant heat loss from the calorimeter cell. To keep the temperature constant, this heat flow was compensated by the pulsed heater. The enthalpy of mixing was obtained from the change of frequency of the pulsed heater between the baseline (pure components) and the investigated mixture. The endothermic heat effects caused an increase and exothermal heat effects caused a decrease in the frequency. A back-pressure regulator served to keep the pressure at a constant level at which evaporation and degassing effects could be prevented. The estimated experimental uncertainties of this device are $\sigma(T) = 0.03$ K, $\sigma(H^E) = 2\ \text{J}\cdot\text{mol}^{-1} + 0.01\ (H^E/(\text{J}\cdot\text{mol}^{-1}))$, and $\sigma(x_i) = 0.0001$.

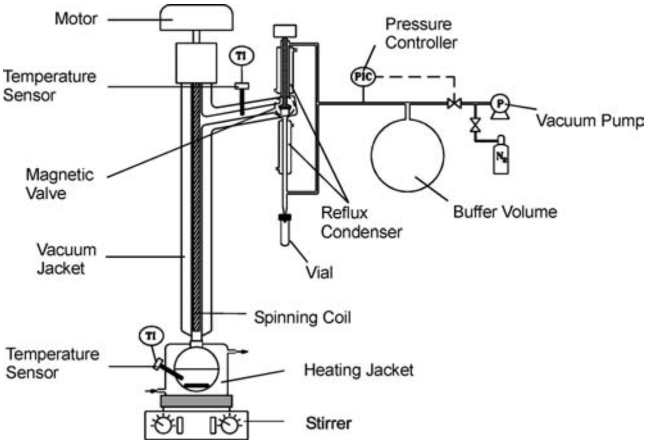

Figure 3. Schematic diagram of the spinning band column.

For the measurements of the azeotropic data, a commercially available microspinning band column with an electronically controlled reflux ratio from NORMAG GmbH (Hofheim, FRG) described by Gmehling and Bölts[11] was used. This equipment allows measurements up to a pressure of 3.5 bar. The experimental setup is schematically shown in Figure 3. Depending on the liquid load and the number of revolutions of the spinning band (optimum speed 2000 rpm), up to 50 theoretical stages at a low-pressure drop can be realized. Since the reflux is realized on the basis of a vapor dividing principle, not only homogeneous but also heterogeneous pressure maximum azeotropes can be determined. The determination of the composition of the homogenized distillate was performed, e.g., by gas chromatography (see above GC method). With the help of a vacuum pump for pressures below atmospheric and a reservoir of compressed nitrogen in the case of higher pressures in connection with the manostat (Kobold type DCMI (0.2 to 1.6) bar or type DGM6

Table 2. Experimental and Predicted (UNIQUAC) Vapor−Liquid Equilibrium Data (*P*, *x* Data) for the Binary System Dibutyl Ether (1) + *o*-Xylene (2) at 323.15 K

x_1	P_{exp} kPa	$y_{1,\text{pred}}$	P_{pred} kPa	$(P_{\text{exp}} - P_{\text{pred}})/P_{\text{exp}}$
0.0000	3.598	0.0000	3.529	0.0192
0.0096	3.602	0.0108	3.533	0.0191
0.0325	3.611	0.0364	3.544	0.0186
0.0607	3.622	0.0673	3.556	0.0183
0.0991	3.636	0.1082	3.569	0.0184
0.1475	3.651	0.1587	3.586	0.0177
0.2081	3.666	0.2202	3.602	0.0174
0.2749	3.680	0.2863	3.618	0.0167
0.3431	3.691	0.3525	3.629	0.0168
0.3649	3.693	0.3735	3.633	0.0162
0.4090	3.698	0.4157	3.637	0.0165
0.4246	3.696	0.4306	3.638	0.0156
0.4704	3.700	0.4742	3.642	0.0156
0.4945	3.699	0.4971	3.644	0.0149
0.5741	3.698	0.5730	3.644	0.0147
0.6607	3.693	0.6561	3.640	0.0144
0.7475	3.683	0.7407	3.632	0.0139
0.8235	3.669	0.8164	3.620	0.0134
0.8883	3.656	0.8823	3.608	0.0132
0.9388	3.644	0.9348	3.596	0.0133
0.9817	3.634	0.9803	3.585	0.0135
1.0000	3.630	1.0000	3.580	0.0139

Table 3. Experimental and Predicted (UNIQUAC) Vapor−Liquid Equilibrium Data (P, x Data) for the Binary System Dibutyl Ether (1) + o-Xylene (2) at 413.15 K

x_1	P_{exp}/kPa	$y_{1,\text{pred}}$	P_{pred}/kPa	$(P_{\text{exp}} - P_{\text{pred}})/P_{\text{exp}}$
0.0000	90.39	0.0000	90.29	0.0011
0.0015	90.42	0.0018	90.32	0.0012
0.0048	90.49	0.0056	90.36	0.0013
0.0152	90.61	0.0175	90.51	0.0011
0.0319	90.83	0.0366	90.75	0.0009
0.0629	91.30	0.0714	91.16	0.0015
0.1112	91.90	0.1242	91.76	0.0015
0.1823	92.69	0.1996	92.56	0.0015
0.2736	93.56	0.2927	93.42	0.0015
0.3605	94.27	0.3789	94.12	0.0016
0.3749	94.40	0.3931	94.22	0.0019
0.4197	94.72	0.4367	94.52	0.0021
0.4596	94.98	0.4754	94.76	0.0023
0.4887	95.08	0.5034	94.92	0.0017
0.5665	95.42	0.5781	95.30	0.0013
0.6497	95.76	0.6577	95.62	0.0015
0.7337	96.03	0.7385	95.85	0.0018
0.8090	96.15	0.8114	95.99	0.0017
0.8714	96.22	0.8723	96.06	0.0017
0.9204	96.24	0.9205	96.08	0.0017
0.9609	96.25	0.9608	96.08	0.0018
0.9777	96.23	0.9776	96.07	0.0017
0.9913	96.22	0.9912	96.06	0.0016
1.0000	96.21	1.0000	96.06	0.0016

Table 4. Experimental and Predicted (UNIQUAC) Vapor−Liquid Equilibrium Data (T, x, y Data) for the Binary System Dibutyl Ether (1) + o-Xylene (2) at 50.60 kPa

x_1	y_1	T/K	$y_{1,\text{pred}}$	T_{pred}/K	$(y_{1,\text{exp}} - y_{1,\text{pred}})/y_{1,\text{exp}}$	$(T_{\text{exp}} - T_{\text{pred}})/T_{\text{exp}}$
0.0000	0.0000	393.04	0.0000	392.95	0.0000	0.0002
0.0299	0.0349	392.83	0.0341	392.80	0.0232	0.0001
0.0616	0.0694	392.75	0.0695	392.65	−0.0012	0.0003
0.1195	0.1319	392.42	0.1323	392.41	−0.0029	0.0000
0.2126	0.2289	392.10	0.2293	392.09	−0.0016	0.0000
0.2890	0.3059	391.89	0.3062	391.87	−0.0011	0.0001
0.3894	0.4056	391.52	0.4047	391.63	0.0022	−0.0003
0.4557	0.4687	391.44	0.4688	391.51	−0.0001	−0.0002
0.5619	0.5710	391.19	0.5707	391.37	0.0005	−0.0005
0.5776	0.5862	391.20	0.5857	391.35	0.0008	−0.0004
0.6476	0.6529	391.01	0.6528	391.29	0.0001	−0.0007
0.7384	0.7407	390.92	0.7403	391.24	0.0005	−0.0008
0.8227	0.8213	390.93	0.8225	391.23	−0.0015	−0.0008
0.8846	0.8840	390.89	0.8837	391.24	0.0004	−0.0009
0.9567	0.9564	390.85	0.9560	391.27	0.0004	−0.0011
1.0000	1.0000	390.80	1.0000	391.30	0.0000	−0.0013

(0.7 to 6) bar), the desired pressure can be kept constant. The temperature was determined with a resistance thermometer, and the pressure was monitored by means of a calibrated sensor (PDCR 4010, (0 to 3) bar, GE Sensing). The estimated accuracy is $\sigma(T) = 0.1$ K, $\sigma(p) = 0.20$ Pa $+ 0.0005(P/\text{Pa})$, and $\sigma(x_i) = 0.001$.

Results

The experimental VLE, excess enthalpy (H^{E}), and azeotropic data from this work are listed in Tables 2 to 6. Temperature-dependent interaction parameters for the UNIQUAC model were fitted to these data, and an ideal vapor-phase behavior was assumed. The temperature dependence of the parameters is given by the following equation

$$\Delta u_{ij}/\text{J}\cdot\text{mol}^{-1} = a_{ij} + b_{ij}\cdot T/\text{K} \tag{2}$$

The obtained parameters are given in Table 7. For the description of the pure component vapor pressures, Antoine coefficients given by the following equation

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

were fitted to experimental data from numerous authors taken from the Dortmund Data Bank.[12] The obtained parameters A_i, B_i, and C_i are given in Table 8 together with the van der Waals properties r_i and q_i for the UNIQUAC model. In the data tables, the modeling results and relative deviations between experimental data and calculated values are included.

The experimental and calculated data are graphically shown in Figures 4 to 7. For the fitting procedure and the calculations, the parameter A of the Antoine equation was adjusted to the experimental vapor pressures of the VLE to account only for the excess energy of the mixture. As can be seen in the different diagrams, the UNIQUAC model is able to reliably represent the phase equilibrium behavior of this binary system showing a homogeneous pressure maximum azeotrope. As indicated in the data tables, all obtained bubble point pressures and temperatures of the VLE data points are described within a relative error of 2 % even for the low pressure values. This is also valid for the excess enthalpy data except for the two data points in the diluted region. The experimental azeotropic pressures can be described with the UNIQUAC model within an uncertainty of 4 %, whereas the calculated azeotropic compositions show larger deviations (up to 12 %) from the experimental data points (cf. also Figure 7).

Table 5. Experimental and Predicted (UNIQUAC) Excess Enthalpy Data for the Binary System Dibutyl Ether (1) + o-Xylene (2) at 323.15 K and 1.100 MPa

x_1	$H^{\text{E}}_{\text{exp}}$/J·mol^{-1}	$H^{\text{E}}_{\text{pred}}$/J·mol^{-1}	$(H^{\text{E}}_{\text{exp}} - H^{\text{E}}_{\text{pred}})/H^{\text{E}}_{\text{exp}}$
0.0625	15.7	15.9	−0.0127
0.1249	29.5	29.6	−0.0034
0.1874	40.4	41.1	−0.0173
0.2499	50.1	50.5	−0.0080
0.3124	57.4	57.8	−0.0070
0.3749	63.2	63.2	0.0000
0.4374	66.5	66.0	0.0075
0.4999	67.5	67.0	0.0074
0.5624	66.5	66.8	−0.0045
0.6249	63.3	62.6	0.0111
0.6874	57.7	57.3	0.0069
0.7499	50.7	49.9	0.0158
0.8124	40.7	40.5	0.0049
0.8749	29.0	29.0	0.0000
0.9375	14.2	15.5	−0.0915

Table 6. Experimental and Predicted (UNIQUAC) Azeotropic Data for the Binary System Dibutyl Ether (1) + o-Xylene (2)

T/K	P_{exp}/kPa	$y_{\text{az},1,\text{exp}}$	P_{pred}/kPa	$y_{\text{az},1,\text{pred}}$	$(P_{\text{exp}} - P_{\text{pred}})/P_{\text{exp}}$	$(y_{\text{az},1,\text{exp}} - y_{\text{az},1,\text{pred}})/y_{\text{az},1,\text{exp}}$
412.74	96.28	0.928	95.00	0.935	0.0133	−0.0074
363.47	19.91	0.698	19.82	0.685	0.0045	0.0185
322.91	3.46	0.488	3.60	0.548	−0.0405	−0.1225

Table 7. UNIQUAC Interaction Parameters for the Binary System

component 1	component 2	i	j	a_{ij}/J·mol^{-1}	b_{ij}/J·mol^{-1}·K^{-1}
dibutyl ether	o-xylene	1	2	188.85	1.8546
		2	1	−88.45	−1.8519

Table 8. Pure Component Properties (Antoine Parameters A_i, B_i, and C_i and van der Waals Properties r_i and q_i)

	dibutyl ether	o-xylene
A_i	6.38385	6.20976
B_i	1616.42	1539.63
C_i	−45.892	−51.234
r_i	6.0925	4.6578
q_i	5.176	3.536

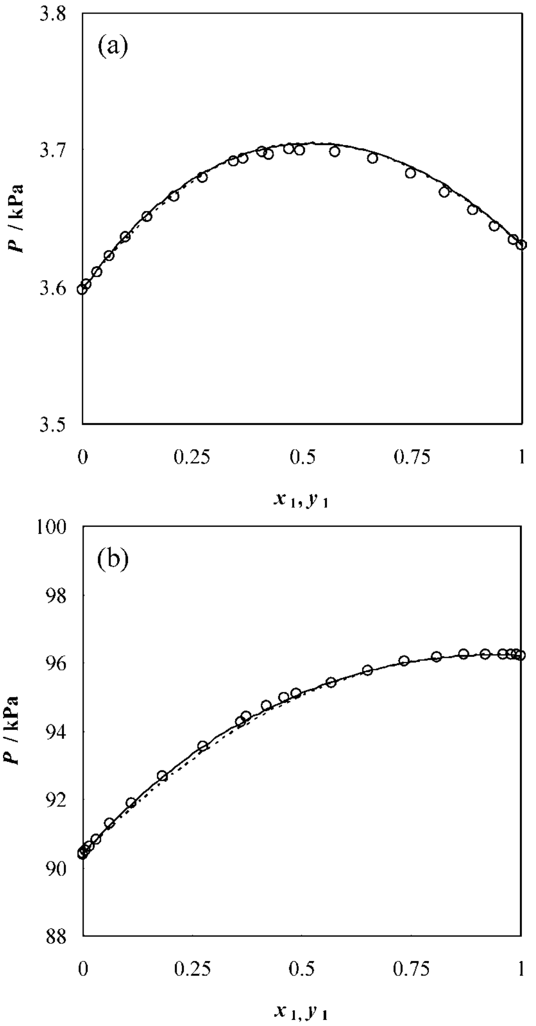

Figure 4. Experimental and predicted $P-x$ data for the system dibutyl ether (1) + *o*-xylene (2) at (a) 323.15 K and (b) 413.15 K: ○, experimental data; −, UNIQUAC (liquid phase); ····, UNIQUAC (vapor phase).

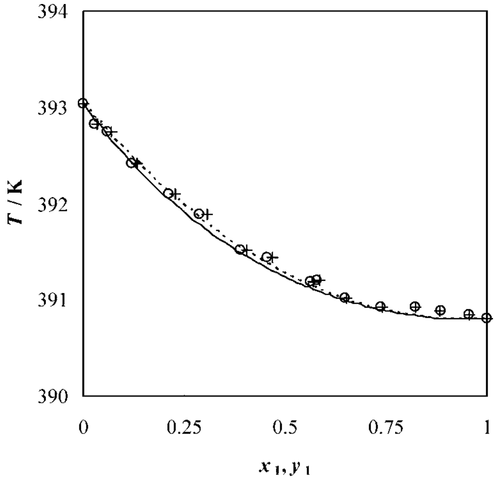

Figure 5. Experimental and predicted $T-x$ data for the system dibutyl ether (1) + *o*-xylene (2) at 50.60 kPa: ○, experimental data of the liquid phase; +, experimental data of the vapor phase; −, UNIQUAC (liquid phase); ····, UNIQUAC (vapor phase).

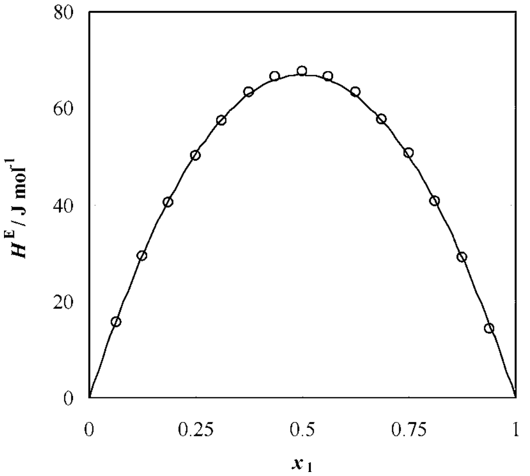

Figure 6. Experimental and predicted H^E data for the system dibutyl ether (1) + *o*-xylene (2) at 323.15 K and 1.100 MPa: ○, experimental data; and −, UNIQUAC.

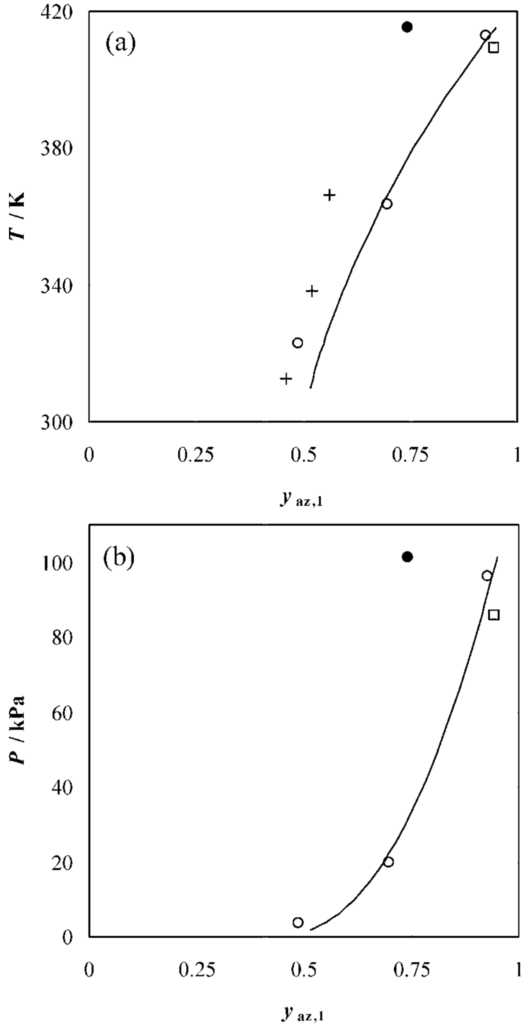

Figure 7. Experimental and predicted azeotropic data compared with data from the literature for the system dibutyl ether (1) + *o*-xylene (2): ○, experimental data from this work; ●, ref 1; +, ref 2; □, ref 3; −, UNIQUAC.

Conclusions

Isothermal VLE, excess enthalpy (H^E), and azeotropic data were measured using different techniques such as the static synthetic method, the dynamic method, flow calorimetry, and the spinning band column. From these data, linear temperature-dependent UNIQUAC parameters were fitted. Using these parameters, the azeotropic data from this work were compared to data of other authors. It was found that the calculated values are in good agreement with the new experimental data and data taken from the literature as discussed above.

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