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Vapor−Liquid Equilibria and Excess Enthalpy Data for the Binary System Propionic Aldehyde + 2-Methyl-2-butanol at 333.15 K

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Isothermal vapor−liquid equilibrium (VLE) and excess enthalpy (H^E) data are reported for the system propionic aldehyde + 2-methyl-2-butanol at 333.15 K. The data were measured by means of a computer-operated static apparatus and isothermal flow calorimetry, respectively. The experimental data were correlated simultaneously by using linear temperature-dependent UNIQUAC parameters.

Introduction

For the synthesis and design of separation processes and for the extension of thermodynamic models (G^E models, equations of state, and group contribution methods), a reliable knowledge of the phase equilibrium behavior is needed. For the binary system propionic aldehyde + 2-methyl-2-butanol, no experimental information is available in the literature. In this study, isothermal $P-x$ data at 333.15 K were measured using a computer-controlled static apparatus. In addition, H^E data for this system were measured at the same temperature by means of an isothermal flow calorimeter.

Excess enthalpy data are important to describe the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation:

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

The VLE and H^E data are compared to values calculated by using temperature-dependent UNIQUAC interaction parameters, which were fitted simultaneously to the experimental data obtained in this work.

Experimental Section

Materials. The chemicals were purchased from commercial sources. For the VLE measurements, they were dried over molecular sieves, degassed, and distilled as described by Fischer and Gmehling.[1] For the H^E measurements the chemicals were used without degassing. The final purities and water contents were checked by gas chromatography (GC) and Karl Fischer titration, respectively. The purity was >99.99% (by GC) for both components, and the water content was 60 wt-ppm for propionic aldehyde and 15 wt-ppm for 2-methyl-2-butanol.

Apparatus and Procedures. The isothermal $P-x$ data were measured with a computer-driven static apparatus. The experimental procedure for the determination of the VLE data is based on that proposed by Gibbs and Van Ness,[2] in which the total pressure P is measured for different overall compositions at constant temperature. The apparatus has been described previously[3,4] and can be used at temperatures between 278 and 368 K and at pressures up to 0.3 MPa.

The thermostated, purified, and degassed 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 Digiquartz pressure sensor (model 245A, Paroscientific), and the temperature is measured with a Pt100 resistance thermometer (model 1506, 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 composition is obtained by solving mass and volume balance equations, taking into account the vapor−liquid equilibrium. At low system pressure as in this investigation, the calculated liquid phase compositions are identical to the feed compositions within ±0.002. The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 (P/Pa), $\sigma(x_i) = 0.0001$.

The commercial isothermal flow calorimeter (model 7501, Hart Scientific) used for the determination of the excess enthalpy data has been described previously.[5] 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 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, $\sigma(H^E) = 2\ \mathrm{J{\cdot}mol^{-1}} + 0.01\ (H^E/\mathrm{J{\cdot}mol^{-1}})$, $\sigma(x_i) = 0.0001$.

Results

The experimental VLE and H^E data are listed in Tables 1 and 2. The data are plotted in Figures 1 and 2 together

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Table 1. Vapor−Liquid Equilibrium Data for the System Propionic Aldehyde (1) + 2-Methyl-2-butanol (2) at 333.15 K

x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	16.87	0.3814	79.17	0.9014	138.73
0.0038	17.75	0.4315	85.29	0.9242	141.46
0.0078	18.62	0.4805	91.14	0.9434	143.81
0.0147	20.11	0.5276	96.62	0.9591	145.73
0.0211	21.49	0.5564	99.72	0.9714	147.27
0.0274	22.83	0.5722	101.71	0.9808	148.47
0.0429	26.11	0.5984	104.46	0.9870	149.24
0.0623	29.99	0.6134	106.38	0.9911	149.78
0.0873	34.72	0.6408	109.21	0.9939	150.14
0.1165	40.07	0.6835	113.96	0.9958	150.40
0.1506	45.91	0.7254	118.62	0.9977	150.65
0.1893	52.15	0.7658	123.14	0.9992	150.89
0.2315	58.60	0.8041	127.46	1.0000	150.93
0.2803	65.67	0.8400	131.56		
0.3308	72.56	0.8724	135.32		

Table 2. Excess Enthalpy Data for the System Propionic Aldehyde (1) + 2-Methyl-2-butanol (2) at 333.15 K and 1.58 MPa

x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0730	373	0.4992	1454	0.8177	907
0.1425	693	0.5503	1450	0.8568	753
0.2088	952	0.5993	1420	0.8945	581
0.2721	1148	0.6464	1353	0.9308	398
0.3327	1280	0.6917	1271	0.9660	198
0.3906	1375	0.7353	1167		
0.4461	1432	0.7773	1043		

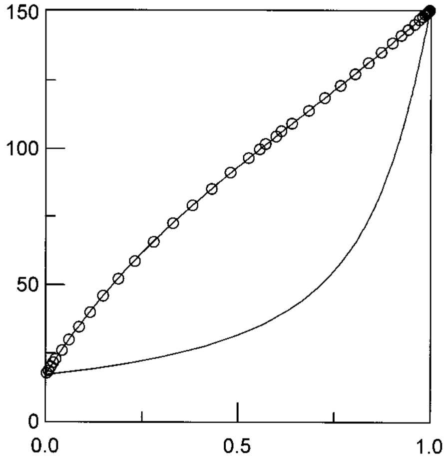

Figure 1. Experimental and calculated *P*-*x*(*y*) behavior of the system propionic aldehyde (1) + 2-methyl-2-butanol (2) at 333.15 K: ○, experimental data; —, UNIQUAC.

with calculated values using the UNIQUAC model.[6] This system shows small positive deviations from Raoult's law and is miscible over the entire concentration range. The UNIQUAC interaction parameters were obtained by a simultaneous correlation of the experimental data. The linear temperature dependence of the parameters is described by the expression

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

The parameters for eq 2 are given in Table 3. The van der Waals properties r_i and q_i and the parameters A_i, B_i, and C_i of the Antoine equation for vapor pressures

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

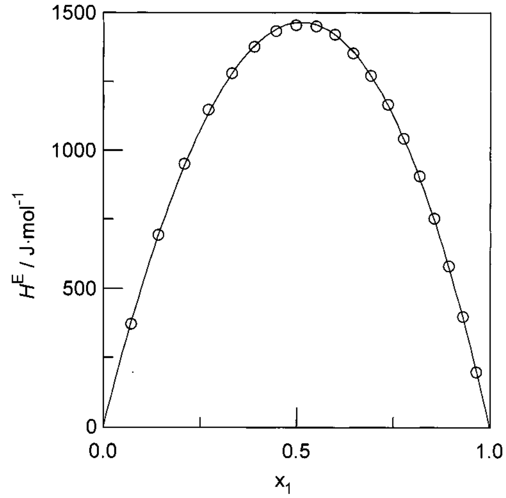

Figure 2. Experimental and calculated excess enthalpy data for the system propionic aldehyde (1) + 2-methyl-2-butanol (2) at 333.15 K: ○, experimental data; —, UNIQUAC.

Table 3. Linear Temperature-Dependent UNIQUAC Interaction Parameters for the System Propionic Aldehyde (1) + 2-Methyl-2-butanol (2)

component 1	component 2	i	j	a_{ij}/J·mol^{-1}	b_{ij}/J·mol^{-1}·K^{-1}
propionic acid	2-methyl-2-butanol	1	2	1432.93	−6.6313
		2	1	501.89	3.1399

Table 4. Pure Component Parameters Used for the Calculations: Relative van der Waals Volumes r_i, van der Waals 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
propionic aldehyde	2.5735	2.336	5.51662	830.80	−84.480
2-methyl-2-butanol	4.1279	3.588	6.50862	1284.76	−89.753

used for the calculations are listed in Table 4. To consider only the excess Gibbs energy, the parameters A_i were adjusted to the experimental pure component vapor pressures during the G^E model parameter fitting procedure.

Conclusions

In this work experimental VLE and H^E data are presented for the system propionic aldehyde + 2-methyl-2-butanol. As can be seen from the diagrams, the linear temperature-dependent UNIQUAC parameters given in Table 3 are able to describe the phase equilibrium behavior and the excess enthalpy data, which represent the temperature dependence of the activity coefficients. The maximum deviation between the calculated and experimental data is below 0.3% in pressure and below 2.5% in excess enthalpy. Thus, the obtained parameters can be recommended for this system in a temperature range from about 300 to 370 K.

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