Isothermal Vapor−Liquid Equilibrium, Excess Enthalpy Data, and Activity Coefficients at Infinite Dilution for the Binary System Water + Methyl Lactate

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Isothermal vapor−liquid equilibrium at (283.15, 293.15, and 303.15) K and excess enthalpy data at (303.15 and 323.15) K have been measured for the binary reactive system water + methyl lactate. In addition, activity coefficients at infinite dilution have been determined in the temperature range of (303.15 to 333.15) K. Whereas a computer-operated static apparatus was used to obtain the isothermal $P-x$ data, the excess enthalpies were measured by means of a commercial isothermal flow calorimeter, and the infinite dilution activity coefficient measurements were carried out using the dilutor technique. The experimental VLE, H^E, and γ_i^∞ data were correlated simultaneously by using quadratic temperature-dependent UNIQUAC parameters.

Introduction

Lactic acid has attracted growing interest as a monomer in the production of biodegradable thermoplastics.[1] Highly purified lactic acid is needed to obtain these polymers. The esterification of lactic acid followed by distillation and hydrolysis has been proven[2,3] to be a suitable technique for purifying lactic acid through its methyl ester. These processes may be performed by reactive distillation. The conversion of lactic acid into methyl lactate is also of industrial interest because the lactic ester can be used as a solvent for varnishes.[4]

For the reliable design of a reactive distillation process, knowledge of the phase equilibrium behavior as well as of reaction kinetics is needed. The reaction rates of the lactic acid esterification with methanol and the hydrolysis reaction of the corresponding methyl ester have been already studied in detail.[5,6] In former studies, experimental VLE data for some of the nonreactive binary systems involved in this quaternary reactive system have already been measured.[7] Also, isobaric experimental VLE data for the reactive quaternary system methanol (1) + water (2) + methyl lactate (3) + lactic acid (4) have already been published.[8]

In this paper, the binary reactive system water (1) + methyl lactate (2) occurring in this quaternary system has been studied. A homogeneous maximum azeotrope has been reported for this system,[8] but experimental information is scarce. Therefore, isothermal VLE data at low temperatures (283.15 to 303.15) K are presented in this paper. To obtain recommended g^E-model parameters to describe the phase equilibrium behavior in a wider temperature range, additional excess enthalpy measurements were carried out at (303.15 and 323.15) K because excess enthalpy data are important for the reliable description of the temperature dependence of the activity coefficients following the Gibbs−Helmholtz equation[9]

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

Activity coefficients at infinite dilution provide the required information for the dilute range. Therefore, activity coefficients at infinite dilution are important for fitting binary g^E-model parameters[10] (e.g., for the UNIQUAC model). These data are also important for the selection of selective solvents (e.g., for extraction and extractive distillation) and for the design of thermal separation processes. In this paper, activity coefficients at infinite dilution were measured from (303.15 to 333.15) K.

All of the experimental data (VLE, H^E, and γ_i^∞) were correlated simultaneously to obtain reliable binary interaction parameters for the UNIQUAC model. The parameters obtained by the simultaneous fit lead to a reliable representation of the real behavior of this binary reactive system.[11]

Experimental Section

Chemicals. For the VLE measurements the chemicals were previously distilled and degassed following the procedure described by Fischer and Gmehling.[12] For the measurements of excess enthalpies H^E and activity coefficients at infinite dilution γ_i^∞, the chemicals were used without degassing.

Methyl (S)-(−)-lactate was purchased from Acros (Belgium) with a reported purity of 97%. After purification by vacuum distillation, the final purity was 99.9 wt % as determined by gas chromatography. The water content (75 ppm) of methyl lactate was determined by a Karl Fischer titration.

Apparatus and Procedure. A computer-driven static apparatus was used for the isothermal VLE measurements ($P-x$ data). This apparatus has been described previously[13] and has already been used to obtain reliable isothermal VLE data for binary reactive systems.[14] The evacuated VLE cell kept at constant temperature in a thermostatic oil bath was charged with the thermostated, purified, and degassed compounds. The pressure in the equilibrium cell was

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monitored using a Digiquartz pressure sensor (model 245A, Paroscientific). The temperature was measured with a Pt100 resistance thermometer (model 1506, Hart Scientific). The overall compositions were 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 were obtained by solving mass and volume balance equations taking into account the vapor−liquid equilibrium ($P-x$) behavior. All measurements were performed at low temperature (low system pressure). At this low pressure, the calculated liquid phase compositions are nearly identical to the feed compositions within ±0.0005. The experimental uncertainties of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 (P, Pa), and $\sigma(x_i) = 0.0001$.

A commercial isothermal flow calorimeter (model 7501, Hart Scientific) was used for the determination of the excess enthalpy data. This apparatus has already been described in detail.[15] The calorimeter consists of two solvent pumps (ISCO, LC 2600, 260 cm^3), a thermostated flow cell equipped with a pulsed heater and a Peltier cooler, and a back-pressure regulator to prevent evaporation. The Peltier cooler operates at constant power, producing constant heat loss from the calorimeter cell. The temperature of the cell is kept constant by adjusting the frequency of the pulsed heater to compensate for the cooling from the Peltier and the heat of mixing effect. The uncertainty of the experimental values was estimated to be less than ±1% of the H^E values measured.

The activity coefficients at infinite dilution were obtained by using the dilutor technique. The reliability of the dilutor that was used has already been proven.[10] The helium carrier gas is saturated with the solvent in the presaturation cell. After saturation, the carrier gas passes through the measurement cell, which is filled with the solvent and the highly diluted solute. The solute in equilibrium with the vapor phase is slowly removed from the cell by the carrier gas. The variation of the solute concentration in the vapor phase is recorded by gas chromatography using a TCD detector. Both the presaturation and measurement cells (~100 cm^3) are equipped with eight thin stainless steel capillaries through which the carrier gas is introduced. The activity coefficients at infinite dilution can be determined by the decrease in the solute concentration with time. In our measurements, about 24 h was needed to obtain one experimental data point. The accuracy of the γ_i^∞ determination is estimated to be within ±2.5%.

Results and Discussion

The VLE data of the binary system water (1) + methyl lactate (2) were measured at low temperatures (283.15, 293.15, and 303.15) K to avoid chemical reaction. No pressure increase inside the equilibrium cell was observed during the VLE determination, which leads us to conclude that no reaction takes place in the low-temperature range covered. The results of the VLE measurements are presented in Table 1 and Figure 1. The system shows a strong positive deviation from Raoult's law.

The excess enthalpies obtained from the heat of mixing measurements at (303.15 and 323.15) K are shown in Table 2 and Figure 2. During the H^E measurements at a temperature of 323.15 K, no reaction was observed because of the short residence time in the calorimeter cell caused by the flow principle.

The experimental activity coefficients at infinite dilution for this binary reactive system at different temperatures (303.15 to 333.15 K) shown in Table 3 were obtained by using the equation given by Krummen et al.[10]

$$\gamma_i^\infty = -\frac{n_{\text{solv}}RT}{\varphi_i^S P_i^S\left(\frac{F_{\text{He}}(1 + P_{\text{solv}}^S/P)}{a} + V_g\right)} \qquad (2)$$

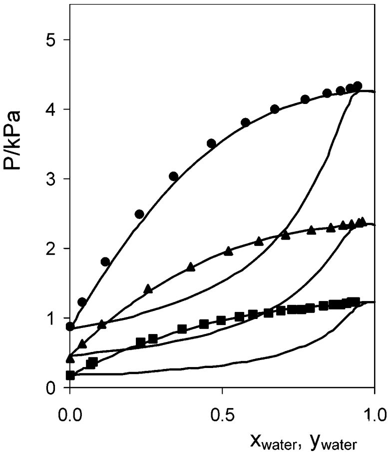

Figure 1. Experimental and calculated $P-x(y)$ data for the binary system water (1) + methyl lactate (2): ■, 283.15 K; ▲, 293.15 K; ●, 303.15 K; −, UNIQUAC.

Table 1. Experimental $P-x$ Data for the System Water (1) + Methyl Lactate (2)

283.15 K		293.15 K		303.15 K	
x_1	P/kPa	x_1	P/kPa	x_1	P/kPa
0.0000	0.17	0.0000	0.43	0.0000	0.87
0.0673	0.34	0.0394	0.63	0.0399	1.22
0.0753	0.36	0.1051	0.91	0.1149	1.80
0.2320	0.66	0.2561	1.41	0.2264	2.49
0.2701	0.71	0.3944	1.74	0.3409	3.04
0.3687	0.84	0.5194	1.97	0.4659	3.50
0.4400	0.91	0.6218	2.11	0.5759	3.80
0.4941	0.96	0.7066	2.19	0.6707	3.99
0.5570	1.01	0.7935	2.25	0.7723	4.14
0.6007	1.06	0.8559	2.29	0.8438	4.22
0.6523	1.08	0.8969	2.33	0.8899	4.26
0.6912	1.10	0.9257	2.35	0.9216	4.29
0.7292	1.12	0.9461	2.37	0.9436	4.32
0.7607	1.13	0.9582	2.38		
0.7883	1.15				
0.8323	1.17				
0.8648	1.19				
0.8895	1.20				
0.9083	1.21				
0.9228	1.22				
0.9341	1.23				

Table 2. Experimental H^E Data for the System Water (1) + Methyl Lactate (2)

303.15 K and 14.10 MPa		323.15 K and 14.10 MPa	
x_1	H^E/J·mol^{-1}	x_1	H^E/J·mol^{-1}
0.0632	−16.50	0.0632	16.74
0.1202	−38.84	0.1202	14.92
0.2190	−88.40	0.2190	−1.83
0.3016	−120.4	0.3016	−19.31
0.3718	−144.2	0.3718	−36.22
0.4321	−166.6	0.4321	−55.96
0.5083	−200.6	0.5083	−92.63
0.5711	−230.8	0.5711	−123.5
0.6397	−269.1	0.6397	−160.7
0.7195	−316.4	0.7195	−206.1
0.7803	−351.2	0.7803	−239.5
0.8419	−377.0	0.8419	−268.6
0.8988	−372.8	0.8988	−270.9
0.9411	−321.0	0.9411	−230.9
0.9796	−164.7	0.9796	−120.5

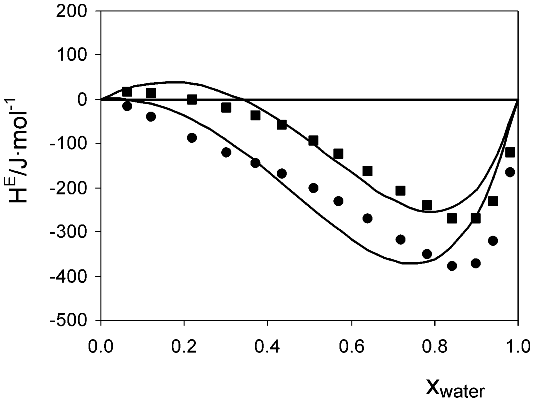

Figure 2. Experimental and calculated excess enthalpy data for the binary system water (1) + methyl lactate (2): ●, 303.15 K; ■, 323.15 K; —, UNIQUAC.

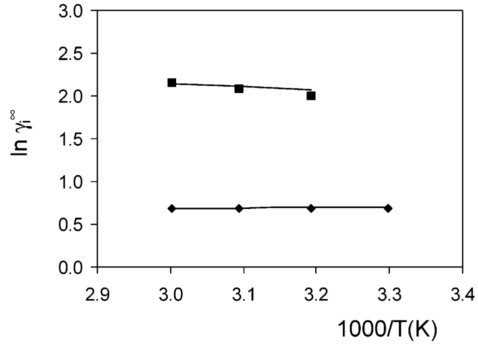

Figure 3. Activity coefficients at infinite dilution for the binary system water (1) + methyl lactate (2). Experimental values: ◆, γ_1^∞; ■, γ_2^∞; —, UNIQUAC.

Table 3. Experimental and Calculated (UNIQUAC) Activity Coefficients at Infinite Dilution for the System Water (1) + Methyl Lactate (2)

T/K	$\gamma_{1\text{exptl}}^\infty$	$\gamma_{1\text{calcd}}^\infty$	$\gamma_{2\text{exptl}}^\infty$	$\gamma_{2\text{calcd}}^\infty$
303.15	1.998	2.007		
313.15	1.998	2.002	7.396	7.924
323.15	1.982	1.993	8.023	8.238
333.15	1.982	1.981	8.636	8.515

where n_{solv} is the number of moles of the solvent in the measurement cell, R (J·mol^{-1}·K^{-1}) is the general gas constant, T(K) is the absolute temperature, φ_i^{S} is the saturation fugacity coefficient of solute i, which is determined by using second virial coefficients, P_i^{S}(Pa) is the saturation vapor pressure of solute i, $\dot{F}_{\text{He}}$ (m^3·s^{-1}) is the carrier gas flow, P(Pa) is the measured pressure, V_{g} (m^3) is the vapor-space volume of the measurement cell, and a is the measured slope of the logarithm of the peak area for solute i versus time.

The experimental VLE, H^{E}, and the activity coefficients at infinite dilution (γ_i^∞) were correlated simultaneously by the UNIQUAC equation. Quadratic temperature-dependent interaction parameters were needed to fit the experimental data

$$\Delta u_{ij} = a_{ij} + b_{ij}T + c_{ij}T^2 \tag{3}$$

where Δu_{ij} and T are in K. The fitted parameters are listed in Table 4. The liquid densities at 298.15 K, van der Waals properties r_i and q_i, and coefficients A_i, B_i, and C_i of the Antoine equation

$$\log(P_i^{\text{S}}/\text{kPa}) = A_i - \frac{B_i}{C_i + T/\text{K}} \tag{4}$$

which were used for fitting the parameters were taken from the Dortmund Databank and are presented in Table 5. To account only for the excess Gibbs energy, parameters A_i were adjusted to the experimental pure-component vapor pressure during the parameter-fitting procedure.

Table 4. Temperature-Dependent UNIQUAC Interaction Parameters

component 1	component 2	i	j	a_{ij}/K	b_{ij}	c_{ij}/K^{-1}
water	methyl lactate	1	2	−287.830	0.33676	1.4237×10^{-3}
		2	1	429.347	−0.57968	-8.6995×10^{-4}

Table 5. Pure-Component Parameters Including Antoine Coefficients A_i, B_i, and C_i, Relative van der Waals Volumes r_i and Surfaces q_i, and Liquid Densities

compound	A_i	B_i	C_i	r_i	q_i	ρ(298.15 K)
water	7.19621	1730.63	−39.724	0.9200	1.4000	0.997000
methyl lactate	7.61880	2333.20		3.7811	3.3880	1.087131

In Figures 1 and 2, the experimental VLE and H^{E} data from this study are compared to the calculated data using the UNIQUAC equation. As can be seen, the VLE as well as the H^{E} behavior is fairly well described with the UNIQUAC parameters from Table 4. It seems that a homogeneous pressure maximum azeotrope is formed at high water concentrations. This maximum azeotrope has already been reported.[8] The activity coefficients at infinite dilution calculated with the UNIQUAC parameters are presented in Table 3. In Figure 3, the experimental activity coefficients at infinite dilution are compared to the calculated activity coefficients obtained with the UNIQUAC equation.

The values of the partial molar excess enthalpy at infinite dilution, $h_i^{\text{E},\infty}$, obtained by fitting a Redlich−Kister polynomial to the experimental calorimetric data are reported in Table 6. For associated solutions, differing $h_i^{\text{E},\infty}$ values can be expected as is also observed in the temperature range covered.[16] In Table 6, these values are compared with the values derived from the slopes of the linear plot of the measured ln(γ_i^∞) versus 1/T (Figure 3) according to the Gibbs−Helmholtz equation (eq 1). It can be seen that the $h_i^{\text{E},\infty}$ values obtained from the linear plot are in the range of the $h_i^{\text{E},\infty}$ values obtained from the calorimetric data.

Table 6. Partial Molar Excess Enthalpies at Infinite Dilution ($h_i^{\text{E},\infty}$) for the Binary System Water (1) + Methyl Lactate (2)

T/K	$h_1^{\text{E},\infty}$	$h_2^{\text{E},\infty}$	source
303.15	−327.8	−9543	calorimetric data
323.15	434.8	−5560	calorimetric data
303.15−333.15	265.8	−6726	activity coefficients at infinite dilution

Conclusions

Experimental VLE data at (283.15, 293.15, and 303.15) K, H^{E} data at (303.15 and 323.15) K, and activity coefficients at infinite dilution (303.15 to 333.15 K) are presented for the binary reactive system water (1) + methyl lactate (2). All of the experimental data were used to fit temperature-dependent UNIQUAC parameters simultaneously. Because very good agreement is obtained for all types of data, the new UNIQUAC parameters can be used reliably to describe this binary reactive system.

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