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Vapor−Liquid Equilibria in the Propyl Acetate + Ethanoic Acid Binary System from (323.15 to 353.15) K: Measurement with a Static Method and Modeling with the NRTL, Wilson, UNIQUAC, and COSMO−SAC Approaches

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ABSTRACT: A static total pressure method was employed to determine the vapor pressures of pure propyl ethanoate (propyl acetate), pure ethanoic acid, and the corresponding propyl acetate + ethanoic acid binary system at different feeding compositions over the temperature range (323.15 to 353.15) K. The isothermal vapor−liquid equilibrium (VLE) data of the binary mixture at various temperatures were obtained from classical thermodynamic relations and mass-balance equations. The nonrandom two-liquid (NRTL), Wilson, and universal quasi-chemical (UNIQUAC) models were used to represent the nonideality of the liquid phase, and a modified Peng−Robinson equation of state was used to compute the properties of the vapor phase. The overall average relative deviations between the experimental equilibrium pressures and the NRTL, Wilson, and UNIQUAC models were (0.95, 0.96, and 0.94) %, respectively. The three models gave about the same equilibrium pressures and vapor compositions. A new version of the conductor-like screening model−segment activity coefficient (COSMO−SAC) model was applied to predict the VLE of propyl acetate + ethanoic acid mixtures, and good agreement with the experimental data was obtained.

INTRODUCTION

Ethanoic acid is often used as a raw material for the production of ethenyl acetate, acetic anhydride, acetate fiber, acetic ester, and so on.[1] Mixtures containing ethanoic acid in industrial processes are usually very complex and consist of many components and multiple phases, in which some components can form azeotropes with ethanoic acid. Azeotropic distillation with the help of an entrainer such as propyl ethanoate (propyl acetate) is always adopted in separations of such mixtures.[2] Some phase equilibrium data of propyl acetate + ethanoic acid binary mixtures have been reported in the literature. For instance, Othmer[3] provided the equilibrium compositions of the vapor and liquid phases of the propyl acetate + ethanoic acid mixture at atmospheric pressure but did not give the corresponding equilibrium temperature. Fu et al.[4] reported isobaric vapor−liquid equilibrium (VLE) data for the propyl acetate + ethanoic acid system at 760 mmHg. Recently, Xiao et al.[5] measured the liquid−liquid equilibrium (LLE) data of the ternary system water + ethanoic acid + propyl acetate at T = (298.15, 313.15, and 363.65) K under atmospheric pressure. Toikka and Toikka[6] briefly reviewed the VLE and LLE data in quaternary mixtures of ethanoic acid, propyl acetate, water, and *n*-propanol and discussed the azeotropic properties and the topological structure of the residue curve map at 313.15 K for this system. However, to our knowledge, very few binary VLE data for ethanoic acid and propyl acetate at low pressures have been reported in the literature. For that reason, new VLE measurements for binary mixtures of propyl acetate and ethanoic acid as well as for pure propyl acetate and pure ethanoic acid over the T range (323.15 to 353.15) K were performed in the current work using a static total pressure method. As is well-known, this method has the merit of avoiding the analysis of equilibrium compositions.

Besides the experimental measurement of phase equilibrium, the thermodynamic model is also an effective tool for understanding phase behavior, and it is often crucial for the simulation and optimization of industrial separation processes. Excess Gibbs models are always applied for the correlation of experimental data.[4,5] In the present work, the nonrandom two-liquid (NRTL),[7] Wilson,[8] and universal quasi-chemical (UNIQUAC)[9] models were applied to represent the nonideality of the liquid phase. The vapor phase at low pressure is often assumed to be an ideal mixture for the compounds without hydrogen bonding, dipole−dipole interactions, and so on. However, mixtures containing ethanoic acids cannot be simply considered as ideal mixtures because ethanoic acids are associating molecules with strong hydrogen-bonding interactions. Here, the modified Peng−Robinson equation of state (MPR EoS) presented by Liu et al.,[10,11] which is based on a large set of experimental data for associating fluids, was used to describe the nonideality of the vapor phase. In addition, the predictive conductor-like screening

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model−segment activity coefficient (COSMO−SAC) model was used to determine the VLE of propyl acetate + ethanoic acid, and the predictive capacity for this system was checked and confirmed.

■ EXPERIMENTAL SECTION

Chemicals. Propyl acetate (analysis purity grade, minimum mass fraction 0.99) was purchased from Shanghai Jingchun Reagent Company and ethanoic acid (analysis purity grade, minimum mass fraction 0.995) from Shanghai Chemical Regent Company. Before it was used in experiments, the ethanoic acid was distilled and recrystallized, and both the propyl acetate and ethanoic acid samples were dried using 0.4 nm molecular sieves. The exact purities of propyl acetate and ethanoic acid were determined by analysis using gas chromatography (Agilent 6890) with flame ionization detection, and they were found to be not less than 0.982 and 0.999 in mole fraction, respectively.

Apparatus and Operation Procedure. The experimental apparatus used in this work was composed mainly of a vacuum system, a thermostatic system, and a measurement system, and it has been described elsewhere.[12,13] First, a liquid sample with known total amount n_T and total mole fraction z_i of component i was injected into a glass equilibrium still with a volume of 45 cm^3. Next, to remove gas impurities from the liquid sample, the processes of freezing, degassing, and thawing were carried out and repeated (usually three times) until the vapor pressure above the frozen liquid sample was less than about 7 Pa. The equilibrium still was then placed in a water bath at a given temperature, which was controlled via a platinum resistance thermometer (± 0.05 K). The VLE was considered as reached when no temperature or pressure changes were observed after a given time (usually 1 h), and the equilibrium temperature T, pressure P^{exptl}, vapor-phase volume V^G, total amount n_T, and total mole fraction z_i were recorded as the original experimental data at equilibrium. The next experimental measurement was then carried by adjusting the temperature of the water bath to another value. It should be noted that the equilibrium temperature was measured using a mercury thermometer with an uncertainty of ± 0.02 K (which was calibrated by Shanghai Institute of Measurement and Testing Technology before use) rather than a platinum resistance thermometer, which was used only to control the temperature of the water bath. The equilibrium pressure was measured using a mercury pressure gauge and a cathetometer with an uncertainty of ± 0.04 mm. Five types of experimental data were determined experimentally: the total amount n_T, the total mole fraction z_i of component i, the equilibrium temperature T and pressure P^{exptl}, and the vapor-phase volume V^G. The other properties were determined using a thermodynamic model.

■ MODELS

The expressions for the NRTL, Wilson, and UNIQUAC activity coefficient models can be found elsewhere,[7−9] and are not repeated here. We provide only the main working equations for the MPR EoS[10,11] and the modified COSMO−SAC model.[14]

Modified PR Equation of State. The cubic Peng−Robinson (PR) equation of state[15] has a simple form and is often used for modeling of the phase equilibria of pure fluids or mixtures. To improve its precision and expand its application, Liu et al.[10,11] presented a modified PR EoS (MPR EoS) based on a new expression for the parameter $\alpha(T_r)$; the MPR EoS is given by the following equations:

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V \cdot (V + b) + b \cdot (V - b)} \tag{1}$$

$$a = \frac{0.45724 \cdot R^2 \cdot {T_c}^2}{P_c} \cdot \alpha(T_r) \tag{2a}$$

$$b = \frac{0.07780 \cdot R \cdot T_c}{P_c} \tag{2b}$$

$$\alpha(T_r) = 1 + (1 - T_r) \cdot \left(m + \frac{n}{{T_r}^2}\right) \tag{3}$$

where R is the gas constant, P_c and T_c are the critical pressure and temperature, respectively, and $T_r = T/T_c$ is the reduced temperature. The model parameters m and n are pure-component parameters that can be determined by fitting the vapor pressures or the saturated liquid densities of the pure compounds. The mixing rules are given by the following equations:

$$a = \sum_{i=1} \sum_{j=1} (x_i \cdot x_j \cdot a_{ij}) \tag{4a}$$

$$b = \sum_{i=1} (x_i \cdot b_i) \tag{4b}$$

$$a_{ij} = \sqrt{a_i \cdot a_j} \tag{5}$$

where x_i is the liquid phase mole fraction. Finally, φ_i, the fugacity coefficient of molecule i in the mixture, is calculated using the expression:

$$\ln \varphi_i = \frac{B_i}{B} \cdot (Z - 1) - \ln(Z - B) - \frac{A}{2\sqrt{2} \cdot B} \cdot \left(\frac{2 \cdot \sum_j (x_j \cdot A_{ij})}{A} - \frac{B_i}{B} \right) \cdot \ln\left[\frac{Z + (1 + \sqrt{2}) \cdot B}{Z + (1 - \sqrt{2}) \cdot B} \right] \tag{6}$$

where $A = (a \cdot P)/(R \cdot T)^2$, $B = (b \cdot P)/(R \cdot T)$, $A_{ij} = (a_{ij} \cdot P)/(R \cdot T)^2$, and $B_i = (b_i \cdot P)/(R \cdot T)$; $Z = (P \cdot V)/(R \cdot T)$ is the compressibility factor, which is calculated using:

$$Z^3 + (B - 1) \cdot Z^2 + (A - 2 \cdot B - 3 \cdot B^2) \cdot Z + B^2 + B^3 - A \cdot B = 0 \tag{7}$$

Equation 7 is solved to obtain Z, from which the vapor molar volume and the fugacity coefficient in the vapor phase can be computed at a given T and P.

COSMO−SAC Model. COSMO (conductor-like screening model)-based thermodynamic models were first proposed by Klamt et al.[16−20] The COSMO for real solvents (COSMO−RS) model developed by Klamt and co-workers[16−20] is a predictive activity coefficient model in which the only needed inputs that characterize a given compound are ab initio data. The model depends on universal parameters that were determined over a large set of experimental phase equilibrium data. Following the works of Klamt et al.,[16−20] Lin and Sandler[21] proposed the COSMO−SAC model based on the COSMO−RS model.[16−20] The original COSMO−SAC model has been used extensively to predict VLE and LLE data.[21] Recently, Hsieh et al.[14] proposed a modified version of the COSMO−SAC model in which they introduced a temperature-dependent parameter for the electrostatic interaction and considered the σ profiles of different functional groups that are involved in hydrogen bonding. This new version of the COSMO−SAC model has more universal parameters that were fitted to LLE data.[14] In this model, the activity coefficient $\gamma_{i/\mathrm{S}}$ of a solute i in the solution S is expressed as

$$\ln(\gamma_{i/\mathrm{S}}) = \ln(\gamma_{i/\mathrm{S}}^{\mathrm{SG}}) + n_i \cdot \sum_{\mathrm{s}}^{\mathrm{nHB\,,\,HB}} \sum_{m} p_i(\sigma_m^{\mathrm{s}}) \cdot \{\ln[\Gamma_{\mathrm{S}}^{\mathrm{s}}(\sigma_m^{\mathrm{s}})] - \ln[\Gamma_i^{\mathrm{s}}(\sigma_m^{\mathrm{s}})]\} \qquad (8)$$

where the $\ln(\gamma_{i/\mathrm{S}}^{\mathrm{SG}})$ term is the Guggenheim−Staverman combinational term,[22] given by

$$\ln(\gamma_{i/\mathrm{S}}^{\mathrm{SG}}) = \ln\left(\frac{\zeta_i}{x_i}\right) + \frac{z}{2} \cdot q_i \cdot \ln\left(\frac{\theta_i}{\zeta_i}\right) + l_i - \frac{\zeta_i}{x_i} \cdot \sum_j (x_j \cdot l_j) \qquad (9)$$

in which $\zeta_i = (x_i \cdot r_i)/\sum_j (x_j \cdot r_j)$ is the volume fraction of solute i, $z = 10$ is the coordination number, $\theta_i = (x_i \cdot q_i)/\sum_j (x_j \cdot q_j)$ is the area fraction, $l_i = z \cdot [(r_i - q_i)/2] - (r_i - 1)$, and $r_i = v_i^{\mathrm{molec}}/v_{\mathrm{ref}}$ and $q_i = A_i^{\mathrm{molec}}/A_{\mathrm{ref}}$ are the normalized volume and surface area, respectively, where v_i^{molec} and A_i^{molec} are the volume and surface area of solute i, respectively, as determined from ab initio calculations, $v_{\mathrm{ref}} = 6.669 \cdot 10^{-2}\ \mathrm{nm}^3$, and $A_{\mathrm{ref}} = 0.7953\ \mathrm{nm}^2$.

In eq 8, $n_i = A_i^{\mathrm{molec}}/a_{\mathrm{eff}}$ is the number of surface segments and $a_{\mathrm{eff}} = 0.0725\ \mathrm{nm}^2$ is an effective surface area.[23] The activity coefficient Γ of segment m having charge density σ_m is determined from the σ profile of the fluid as

$$\ln[\Gamma_j^{\mathrm{t}}(\sigma_m^{\mathrm{t}})] = -\ln\left[\sum_{\mathrm{s}}^{\mathrm{nHB\,,\,HB}} \sum_{n} p_j^{\mathrm{s}}(\sigma_n^{\mathrm{s}}) \cdot \Gamma_j^{\mathrm{s}}(\sigma_n^{\mathrm{s}}) \cdot \exp\left(\frac{-\Delta W(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}})}{RT}\right)\right] \qquad (10)$$

where the subscript j can refer to either a pure liquid i or the mixture S, the superscripts t and s represent either a hydrogen-bonded (HB) or non-hydrogen-bonded (nHB) segment,[23] and $p_{\mathrm{S}}(\sigma) = \sum_i [x_i \cdot A_i(\sigma)]/\sum_i (x_i \cdot A_i^{\mathrm{molec}})$ and $p_i(\sigma) = A_i(\sigma)/A_i^{\mathrm{molec}}$ are the normalized distributions of surface charge densities for the mixture S and molecule i, respectively, in which $A_i(\sigma) = A_i^{\mathrm{HB}}(\sigma) + A_i^{\mathrm{nHB}}(\sigma)$ is the sum of the surface areas of segments having a charge density σ, $A_i^{\mathrm{HB}}(\sigma)$ is the total surface area of the segments of charge σ that are around oxygen, nitrogen and fluorine atoms and hydrogen atoms connected to a N, O or F atom, and $A_i^{\mathrm{nHB}}(\sigma)$ is the sum of the areas of all of the other segments of charge σ. The σ profile $p_i(\sigma)$ of component i is given by

$$p_i(\sigma) = p_i^{\mathrm{nHB}}(\sigma) + p_i^{\mathrm{HB}}(\sigma) = p_i^{\mathrm{nHB}}(\sigma) + {}_{p}^{i\mathrm{OH}}(\sigma) + {}_{p}^{i\mathrm{OT}}(\sigma) \qquad (11)$$

where $p_i^{\mathrm{nHB}}(\sigma)$ is the σ profile for surface segments that do not contribute to hydrogen bonding and $p_i^{\mathrm{OH}}(\sigma)$ (for OH in water and alcohol) and $p_i^{\mathrm{OT}}(\sigma)$ (for O in ketones, NO_2 in nitro compounds, and NH_2 in amines) are the σ profiles of segments that contribute to hydrogen bonding. The exchange energy between surface segments m and n with charge densities σ_m and σ_n, $\Delta W(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}})$, is given by

$$\Delta W(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}}) = c_{\mathrm{ES}} \cdot (\sigma_m^{\mathrm{t}} + \sigma_n^{\mathrm{s}})^2 - c_{\mathrm{hb}}(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}}) \cdot (\sigma_m^{\mathrm{t}} - \sigma_n^{\mathrm{s}})^2 \qquad (12)$$

where $c_{\mathrm{ES}} = A_{\mathrm{ES}} + B_{\mathrm{ES}}/T^2$ is a temperature-dependent parameter and $c_{\mathrm{hb}}(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}})$ is the hydrogen-bonding interaction energy, which is defined as

$$c_{\mathrm{hb}}(\sigma_m^{\mathrm{t}}, \sigma_n^{\mathrm{s}}) = \begin{cases} c_{\mathrm{OH\text{-}OH}}, & \mathrm{s} = \mathrm{t} = \mathrm{OH},\ \sigma_m^{\mathrm{t}} \cdot \sigma_n^{\mathrm{s}} < 0 \\ c_{\mathrm{OT\text{-}OT}}, & \mathrm{s} = \mathrm{t} = \mathrm{OT},\ \sigma_m^{\mathrm{t}} \cdot \sigma_n^{\mathrm{s}} < 0 \\ c_{\mathrm{OH\text{-}OT}}, & \mathrm{s} = \mathrm{OH},\ \mathrm{t} = \mathrm{OT},\ \sigma_m^{\mathrm{t}} \cdot \sigma_n^{\mathrm{s}} < 0 \\ 0 & \text{otherwise} \end{cases} \qquad (13)$$

The quantities A_{ES}, B_{ES}, $c_{\mathrm{OH-OH}}$, $c_{\mathrm{OT-OT}}$, and $c_{\mathrm{OH-OT}}$ are adjustable parameters, and their values can be found in the literature.[14] Here only the main working equations have been given; for further detailed information, see the papers by Lin and co-workers.[14,21−25]

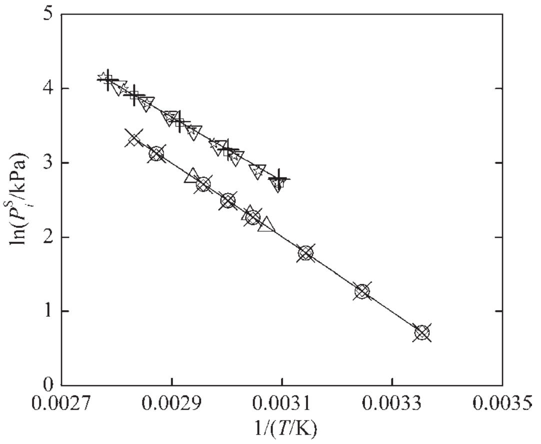

Figure 1. Comparison of the saturated vapor pressures P_i^{S} of pure propyl acetate and pure ethanoic acid obtained from various experiments (symbols) and calculations (lines) at different temperatures T. Solid lines, data calculated using the Antoine equation (Table 1); dotted lines, data calculated using the MPR EoS. For propyl acetate: +, this work; ☆, ref 27; ▽, ref 28; □, ref 26. For ethanoic acid: ×, this work; △, ref 29; ○, ref 12; ◇, ref 26.

■ RESULTS AND DISCUSSION

Vapor Pressures of Pure Compounds. To confirm the reliability of the experimental apparatus and operation and the purities of the liquid samples, the vapor pressures of pure propyl

Table 1. Critical Pressures (P_c) and Critical Temperatures (T_c),[26] Antoine Constants (A_i, B_i, C_i)[a,b], Parameters for the MPR EoS (m_i, n_i),[b] and Temperature (T) Range of Application

compound	P_c/MPa	T_c/K	A_i	B_i	C_i	m_i	n_i	range of T/K
propyl acetate	3.360	549.73	16.6567	4690.84	14.864	1.00610	0.054972	323.15 to 359.15
ethanoic acid	5.786	591.95	15.3519	3700.35	−45.353	1.11336	0.047769	298.15 to 353.15

[a] Antoine equation: $\ln(P_i^{\mathrm{S}}/\mathrm{kPa}) = A_i - B_i/[(T/\mathrm{K}) + C_i]$. [b] Obtained from fits to the experimental saturated vapor pressures P_i^{S}.

Table 2. Total Feeding Amount (n_T), Total Feeding Mole Fraction of Propyl Acetate (z_1), Vapor-Phase Volume (V^G), Equilibrium Temperature (T) and Pressure (P^{exptl}), and VLE Data Calculated Using Activity Coefficient Models for Propyl Acetate (1) + Ethanoic Acid (2) Binary Mixtures over the T Range (323.15 to 353.15) K

original experimental data				NRTL			Wilson			UNIQUAC		
n_T mol	z_1	V^G cm^3	P^{exptl} kPa	x_1	y_1	P^{calcd} kPa	x_1	y_1	P^{calcd} kPa	x_1	y_1	P^{calcd} kPa
						$T/K = 323.15$						
0.2782	0.0000	27.37	7.567	0.0000	0.0000	7.626	0.0000	0.0000	7.626	0.0000	0.0000	7.626
0.3132	0.0549	23.73	8.750	0.0549	0.1560	8.566	0.0549	0.1570	8.582	0.0549	0.1565	8.575
0.2525	0.1023	28.07	9.013	0.1022	0.2505	9.224	0.1022	0.2499	9.230	0.1022	0.2499	9.225
0.2389	0.1914	27.79	10.255	0.1913	0.3789	10.220	0.1913	0.3767	10.207	0.1913	0.3772	10.208
0.1948	0.3050	29.56	11.316	0.3049	0.4988	11.238	0.3049	0.4974	11.220	0.3049	0.4978	11.223
0.1892	0.4091	28.19	12.025	0.4090	0.5897	12.047	0.4090	0.5897	12.038	0.4090	0.5899	12.040
0.1697	0.4952	28.99	12.730	0.4951	0.6580	12.671	0.4951	0.6590	12.673	0.4951	0.6590	12.674
0.1586	0.6095	29.17	13.288	0.6094	0.7431	13.467	0.6094	0.7445	13.481	0.6094	0.7443	13.480
0.1577	0.6967	28.05	14.245	0.6966	0.8049	14.061	0.6966	0.8059	14.080	0.6966	0.8058	14.079
0.1476	0.8077	28.24	14.669	0.8076	0.8800	14.811	0.8076	0.8802	14.829	0.8076	0.8802	14.828
0.1796	0.8463	23.59	15.270	0.8463	0.9052	15.070	0.8463	0.9051	15.087	0.8463	0.9051	15.086
0.1622	0.9337	25.17	15.322	0.9337	0.9602	15.658	0.9337	0.9599	15.666	0.9337	0.9599	15.666
0.1527	1.0000	25.73	16.092	1.0000	1.0000	16.103	1.0000	1.0000	16.103	1.0000	1.0000	16.103
						$T/K = 333.15$						
0.2782	0.0000	27.40	12.045	0.0000	0.0000	12.114	0.0000	0.0000	12.114	0.0000	0.0000	12.114
0.3132	0.0549	23.92	13.515	0.0549	0.1337	13.239	0.0549	0.1339	13.243	0.0549	0.1338	13.242
0.2525	0.1023	26.72	13.891	0.1022	0.2253	14.112	0.1022	0.2254	14.115	0.1022	0.2254	14.115
0.2389	0.1914	26.23	15.502	0.1913	0.3600	15.557	0.1913	0.3599	15.558	0.1913	0.3600	15.560
0.1948	0.3050	29.63	17.196	0.3048	0.4896	17.129	0.3048	0.4894	17.127	0.3048	0.4895	17.130
0.1892	0.4091	28.10	18.485	0.4089	0.5853	18.386	0.4089	0.5852	18.385	0.4089	0.5853	18.387
0.1697	0.4952	29.09	19.347	0.4950	0.6548	19.333	0.4950	0.6548	19.333	0.4950	0.6547	19.334
0.1586	0.6095	29.17	20.281	0.6093	0.7388	20.498	0.6093	0.7389	20.498	0.6093	0.7388	20.498
0.1577	0.6967	28.04	21.564	0.6966	0.7991	21.333	0.6966	0.7992	21.334	0.6966	0.7991	21.334
0.1476	0.8077	28.26	22.207	0.8076	0.8734	22.345	0.8076	0.8735	22.347	0.8076	0.8734	22.345
0.1796	0.8463	23.67	22.803	0.8462	0.8989	22.685	0.8462	0.8989	22.687	0.8462	0.8989	22.686
0.1622	0.9337	25.14	23.155	0.9337	0.9564	23.438	0.9337	0.9563	23.439	0.9337	0.9564	23.438
0.1527	1.0000	25.66	24.006	1.0000	1.0000	23.993	1.0000	1.0000	23.993	1.0000	1.0000	23.993
						$T/K = 343.15$						
0.2782	0.0000	27.39	18.662	0.0000	0.0000	18.655	0.0000	0.0000	18.655	0.0000	0.0000	18.655
0.3132	0.0549	23.97	20.354	0.0549	0.1181	20.011	0.0549	0.1183	20.016	0.0549	0.1170	19.980
0.2525	0.1023	26.68	20.874	0.1022	0.2054	21.131	0.1022	0.2055	21.138	0.1022	0.2047	21.097
0.2389	0.1914	26.29	22.875	0.1913	0.3420	23.113	0.1913	0.3419	23.117	0.1913	0.3428	23.100
0.1948	0.3050	29.52	25.502	0.3048	0.4790	25.411	0.3048	0.4787	25.408	0.3048	0.4807	25.430
0.1892	0.4091	28.15	27.712	0.4089	0.5804	27.306	0.4089	0.5800	27.299	0.4089	0.5816	27.336
0.1697	0.4952	29.12	28.694	0.4949	0.6522	28.731	0.4949	0.6519	28.721	0.4949	0.6527	28.755
0.1586	0.6095	29.15	30.202	0.6092	0.7366	30.441	0.6092	0.7365	30.432	0.6092	0.7362	30.449
0.1577	0.6967	28.00	31.864	0.6965	0.7957	31.620	0.6965	0.7957	31.614	0.6965	0.7950	31.615
0.1476	0.8077	28.22	32.815	0.8076	0.8682	32.978	0.8076	0.8683	32.975	0.8076	0.8677	32.962
0.1796	0.8463	23.69	33.265	0.8462	0.8934	33.415	0.8462	0.8935	33.413	0.8462	0.8932	33.398
0.1622	0.9337	25.06	34.160	0.9337	0.9523	34.334	0.9337	0.9523	34.333	0.9337	0.9524	34.322
0.1527	1.0000	25.73	34.988	1.0000	1.0000	34.962	1.0000	1.0000	34.962	1.0000	1.0000	34.962
						$T/K = 353.15$						
0.2782	0.0000	27.41	28.205	0.0000	0.0000	27.933	0.0000	0.0000	27.933	0.0000	0.0000	27.933
0.3132	0.0549	24.02	29.951	0.0549	0.1073	29.590	0.0549	0.1084	29.634	0.0549	0.1050	29.497
0.2525	0.1023	26.75	30.653	0.1022	0.1903	31.010	0.1022	0.1915	31.073	0.1022	0.1886	30.898
0.2389	0.1914	26.77	33.020	0.1912	0.3260	33.635	0.1912	0.3261	33.695	0.1912	0.3274	33.569

Table 2. Continued

original experimental data				NRTL			Wilson			UNIQUAC		
n_T		V^G	P^{exptl}			P^{calcd}			P^{calcd}			P^{calcd}
mol	z_1	cm^3	kPa	x_1	y_1	kPa	x_1	y_1	kPa	x_1	y_1	kPa
0.1948	0.3050	29.59	36.985	0.3047	0.4677	36.841	0.3047	0.4663	36.858	0.3047	0.4713	36.875
0.1892	0.4091	28.02	40.602	0.4088	0.5740	39.584	0.4088	0.5720	39.556	0.4088	0.5771	39.670
0.1697	0.4952	29.23	41.618	0.4948	0.6488	41.674	0.4948	0.6471	41.622	0.4948	0.6505	41.759
0.1586	0.6095	29.13	43.973	0.6091	0.7349	44.166	0.6091	0.7340	44.108	0.6091	0.7344	44.205
0.1577	0.6967	27.89	46.054	0.6964	0.7935	45.835	0.6964	0.7935	45.791	0.6964	0.7921	45.829
0.1476	0.8077	28.34	47.430	0.8075	0.8642	47.660	0.8075	0.8648	47.645	0.8075	0.8630	47.612
0.1796	0.8463	23.59	47.501	0.8462	0.8889	48.214	0.8462	0.8896	48.209	0.8462	0.8882	48.161
0.1622	0.9337	25.08	49.298	0.9337	0.9482	49.294	0.9337	0.9484	49.302	0.9337	0.9485	49.251
0.1527	1.0000	25.57	49.918	1.0000	1.0000	49.913	1.0000	1.0000	49.913	1.0000	1.0000	49.913

Table 3. Binary Interaction Parameters for Activity Coefficient Models and Relative Deviation Percent for Pressure (σ)[a]

	NRTL			Wilson			UNIQUAC		
T	$(g_{12}-g_{22})/R$	$(g_{21}-g_{11})/R$	σ	$(\lambda_{12}-\lambda_{11})/R$	$(\lambda_{21}-\lambda_{22})/R$	σ	$(u_{12}-u_{22})/R$	$(u_{21}-u_{11})/R$	σ
K	K	K	%	K	K	%	K	K	%
323.15	−228.181	450.343	1.20	132.233	83.552	1.21	−14.515	81.194	1.21
333.15	−84.770	207.802	0.86	−79.293	198.777	0.87	113.368	−44.972	0.86
343.15	243.228	−116.766	0.81	−299.481	418.389	0.81	238.204	−132.182	0.79
353.15	466.643	−257.926	0.92	−411.401	602.184	0.93	330.924	−183.490	0.89

[a] $\sigma/\% = (100/N_p)\sum_{i=1}^{N_p}|P_i^{\text{calcd}} - P_i^{\text{exptl}}|/P_i^{\text{exptl}}$, where N_p is the number of data points.

acetate and ethanoic acid were first determined. Figure 1 shows our results for the experimental vapor pressures of pure propyl acetate and ethanoic acid over the $T = (323.15$ to $359.15)$ K and (298.15 to 353.15) K ranges, respectively. Experimental vapor pressures from the literature[12,26−29] and ones calculated using the Antoine equation and the MPR EoS are also provided in the figure. It can be seen that our measurements are in excellent agreement with the literature data, suggesting that the apparatus was working well and that the pure liquid samples were sufficiently pure to be further used for the measurements on mixtures.

VLE Data for Binary Mixtures. As mentioned above, the original experimental values are n_T, z_i, T, P^{exptl}, and V^G. From these original data, one can obtain the complete phase diagram with the help of simple thermodynamic models and mass-balance equations.

The mass-balance equations lead to

$$x_i = \frac{z_i - f\cdot y_i}{1-f} \qquad (14)$$

where y_i is the vapor-phase mole fraction and f is the vapor fraction, which is given by

$$f = \frac{V^G}{V_m^G\cdot n_T} \qquad (15)$$

in which $V_m{}^G$ is the molar volume of the vapor phase estimated using the MPR EoS.[10,11] The required values of the critical pressure P_c and temperature T_c for the MPR EoS were taken from the literature[26] and are listed in Table 1. Moreover, the values of the parameters m and n in the MPR EoS and the constants A_i, B_i, and C_i in the Antoine equation obtained by fitting the experimental vapor pressures of pure substances are also reported in Table 1.

The VLE condition is given by

$$y_i\cdot P\cdot \varphi_i^V = x_i\cdot\gamma_i\cdot P_i^S\cdot\varphi_i^S\cdot\exp[V_i^L\cdot(P-P_i^S)/(R\cdot T)] \qquad (16)$$

where P_i^S is the vapor pressure of component i, φ_i^V and φ_i^S are the fugacity coefficients of component i in the vapor mixture and the pure state, respectively (calculated using the MPR EoS),[10,11] and γ_i is the activity coefficient of component i in the liquid phase (calculated using the activity coefficient models). It should be noted that the parameter α_{ij} in the NRTL model was set to 0.3 here. The term $\exp[V_i^L\cdot(P - P_i^S)/(R\cdot T)]$ is the Poynting correction factor, which was set to 1 in the current work because the experimental pressure was low. Equations 14 to 16 were solved iteratively by self-substitution. The binary parameters of the activity coefficient models were optimized by using the Nelder−Mead simplex method[30] and the following objective function F:

$$F = \sum_{i=1}^{N_p}\left|\frac{P_i^{\text{calcd}} - P_i^{\text{exptl}}}{P_i^{\text{exptl}}}\right| \qquad (17)$$

where P^{calcd} and P^{exptl} denote the calculated and experimental equilibrium pressures and N_p is the number of data points.

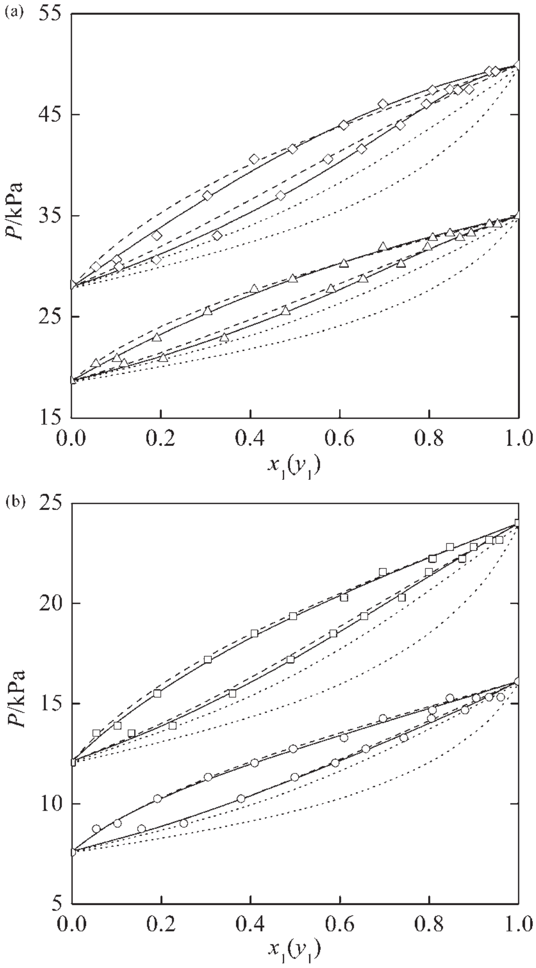

Figure 2. Comparison of binary VLE data for the propyl acetate (1) + ethanoic acid (2) system at various temperatures obtained from experiment (symbols) and theoretical calculations and predictions (lines). (a) 353.15 and 343.15 K; (b) 333.15 and 323.15 K. The generated coexistence compositions were determined using MPR + NRTL model. ◇, 353.15 K; △, 343.15 K; □, 333.15 K; ○, 323.15 K; solid lines, data calculated using NRTL; dashed lines, data predicted by the new version of COSMO−SAC;[14] dotted lines, data predicted by the original COSMO−SAC.[21]

The experimental temperature T, the total feeding amount n_T, the total mole fraction of liquid feeding z_1 for propyl acetate, the vapor-phase volume V^G, the experimental pressure P^{exptl}, and the calculated liquid- and vapor-phase mole fractions x_1 and y_1 for propyl acetate, and the pressure P^{calcd} are reported in Table 2. The binary parameters of the NRTL, Wilson, and UNIQUAC models and the corresponding average deviations can be found in Table 3. It can be seen from Table 2 that the composition of the liquid phase at equilibrium, x_1, was very similar to the total composition of the liquid feeding, z_1, which indicates that only a small amount of the feeding liquid sample was vaporized (i.e., the vapor fraction was small). This is due to the fact that the vapor-phase volume was very small (about 27 cm^3) after injection of the liquid sample (about 18 cm^3) into the equilibrium still (45 cm^3). Furthermore, the three different activity coefficient models gave about the same coexistence compositions and equilibrium pressures, and the average deviations were almost same for the three models. The pressure−composition diagrams of the propyl acetate + ethanoic acid mixture at four different temperatures are depicted in Figure 2. It should be noted that only the results calculated using the NRTL model are given in this figure, since the Wilson and UNIQUAC models produced the same results as NRTL and the calculated pressures obtained from NRTL are in good agreement with the experimental equilibrium pressures. Furthermore, the binary parameters for all of the models can be linearly correlated as functions of temperature. The linear expressions for each model are given below:

For the NRTL model:

$$(g_{12}-g_{22})/R = 24.1247 \cdot T - 8058.54 \qquad (18a)$$

$$(g_{21}-g_{11})/R = -24.4937 \cdot T + 8353.42 \qquad (18b)$$

For the Wilson model:

$$(\lambda_{12}-\lambda_{11})/R = -18.5109 \cdot T + 6094.98 \qquad (19a)$$

$$(\lambda_{21}-\lambda_{22})/R = 17.7551 \cdot T - 5678.15 \qquad (19b)$$

For the UNIQUAC model:

$$(u_{12}-u_{22})/R = 11.6115 \cdot T - 3759.44 \qquad (20a)$$

$$(u_{21}-u_{11})/R = -8.81260 \cdot T + 2910.13 \qquad (20b)$$

As a result, the isobaric or isothermal VLE data of propyl acetate + ethanoic acid mixtures over the T range (323.15 to 353.15) K can be smoothly predicted using these equations.

Predictions Using COSMO−SAC Models. In COSMO-like activity coefficient models, the only required input that characterizes a given compound is the so-called COSMO file, which is the output file from a COSMO ab initio quantum calculation. In this work, the COSMO files for propyl acetate and ethanoic acid were those from the VT 2005 database developed by Mullins et al.[22] The predicted pressure−composition diagrams are shown in Figure 2. It can be clearly seen that the predictions of the new version of COSMO−SAC[14] are more accurate than those of the original COSMO−SAC model[21] for the investigated mixture. This seems to indicate that the use of separate different σ profiles to distinguish hydrogen-bonding and non-hydrogen-bonding surface segments leads to a better representation of the propyl acetate and ethanoic acid associating system.

■ CONCLUSIONS

VLE data for propyl acetate + ethanoic acid binary mixtures over the T range (323.15 to 353.15) K have been determined using the static total pressure method and thermodynamic correlations. The NRTL, Wilson, and UNIQUAC activity coefficient models have been used to represent the nonideality of the liquid phase, and the MPR EoS has been used to describe the properties of the vapor phase. The VLE data are well-correlated by the three activity coefficient models, and the overall average relative deviations from the equilibrium pressures are (0.95, 0.96, and 0.94) % for the NRTL, Wilson, and UNIQUAC models, respectively. The predictive COSMO−SAC approach has been used to represent the binary VLE data of the propyl acetate + ethanoic acid system, and good agreement with the experimental data was obtained using the new version of COSMO−SAC.

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