Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures of Methanol, Ethanoic Acid, and Propanoic Acid

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Vapor−liquid equilibrium (VLE) data for the strongly associating ternary system methanol + ethanoic acid + propanoic acid and three constituent binary systems: methanol + ethanoic acid, methanol + propanoic acid, and ethanoic acid + propanoic acid have been determined by different liquid-phase compositions using a novel pump ebulliometer at 101.3 kPa. The vapor-phase compositions y of these binary systems had been calculated from $T-p-x$ according to the Q function of molar excess Gibbs energy by the indirect method. The experimental $T-x$ data are used to estimate Wilson, nonrandom two-liquid (NRTL), Margules, and van Laar model parameters, and these parameters in turn are used to calculate vapor-phase compositions y. The activity coefficients of the solution were correlated with its composition by the Wilson, NRTL, Margules, and van Laar models through the least-squares method. The VLE data of the ternary system were well-predicted from these binary interaction parameters of the Wilson, NRTL, Margules, and van Laar model parameters without any additional adjustment to build the thermodynamic model of VLE for the ternary system and obtain the vapor-phase compositions y and the calculated bubble points. The calculated bubble points with the model parameters of activity coefficients were in good agreement with the experimental data.

Introduction

Vapor−liquid equilibrium (VLE) data play a vital role in the design and operation of separation processes in the chemical industry. Such information can be obtained experimentally or estimated by using generalized methods for the calculation of the properties of mixtures. For an ideal system, it is relatively easy to estimate the VLE. However, most systems of industrial interest show deviations from the ideal behavior; for example, ethanoic acid systems remain a challenging problem since the systems show extremely nonideal behaviors. The strongly associating solution systems containing ethanoic acid disclosed the nonideal behavior through the formation of hydrogen bonding between oxygen and hydrogen in the carboxylic group. In the chemical industrial process, the reaction of methanol carboxylated with carbon monoxide is the most common and important technology for the synthesis of ethanoic acid.[1] Ethanoic acid is a kind of very important organic products, and its production shows the profiles of the organic chemical industry. At the present, the overwhelming majority of technology for the synthesis of ethanoic acid is through the reaction of methanol carboxylated with carbon monoxide. However, the resultant product contained the unreacted methanol, byproduct propanoic acid, and other mixtures. The VLE data of the methanol + ethanoic acid + propanoic acid ternary system and the constituent binary systems are indispensable in the distillation separation process to the product of methanol carboxylation, while the isobaric VLE data on these systems are almost not available in the literature. Arlt reported that the isothermal VLE data of a new apparatus for phase equilibria in reaction mixtures containing methanol with ethanoic acid and propanoic acid at (333 to 363) K.[2] Chuang and Xu have developed a new correlation for the prediction of the VLE of methyl acetate−methanol−water−ethanoic acid mixtures.[3,4] Although the VLE data of the mixture of methanol + ethanoic acid, methanol + propanoic acid, and ethanoic acid + propanoic acid were previously reported by the different research groups,[5−7] respectively, the isobaric VLE data of these systems have not been involved with the range of broad mole fraction, which have few VLE data about the systems. Moreover, to the best of our knowledge, the methanol + ethanoic acid + propanoic acid ternary system has been not investigated for thermodynamics properties. To provide some necessary basic thermodynamic data on the separation process of methanol carboxylation, therefore, it is very indispensable for these systems studied on the VLE data of the constituent binary and ternary systems. Herein, this paper reports the novel pump ebulliometer for the determination of experimental data for isobaric VLE at 101.325 kPa. That is to say, the VLE data for the methanol−ethanoic acid−propanoic acid system and constituent binary systems were determined by the total pressure−temperature−liquid mole composition ($T-p-x$) method using the novel pump-ebulliometer at 101.325 kPa, and the thermodynamic consistency of the experimental data for the binary systems was checked by the residual method. The Gibbs excessive free energy of binary systems in the overall range of liquid-mole composition was calculated by the liquid activity coefficient correlation to the Wilson model parameters using the experimental data. Moreover, the VLE data of the ternary system were well-predicted from these binary interaction parameters of Wilson, nonrandom two-

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liquid (NRTL), Margules, and van Laar model parameters without any additional adjustment to build the thermodynamic model of VLE for the ternary system and obtain the vapor-phase compositions y and the calculated bubble points.

Experimental Section

Materials. Methanol, ethanoic acid, and propanoic acid were obtained from Shanghai Chemistry Reagent Co., Ltd., purified by distillation in a laboratory column of 100 plates to a purity of more than 0.997 (mass fraction), as verified by gas chromatography analysis without any significant impurities. All of the chemicals were degassed using ultrasound and dried on a molecule sieve (pore diameter of 30 nm from Shanghai Chemistry Reagent Co., Ltd.). The purity of the materials was checked by comparing the measured densities, refractive indexes, and boiling points of the components with those reported by Riddick et al.[8] The densities were measured at 298.15 K using a bicapillary pycnometer previously described by Rao and Naidu,[9] with an accuracy of $\pm$ 0.01 $\text{kg}\cdot\text{m}^{-3}$, and the refractive indexes of the pure components were measured using an Abbe refractometer (Carl-Zeiss-Jena, precision $\pm$ 0.0001) at 298.15 K after calibration with standard liquids, supplied with the instrument. The temperature was controlled to $\pm$ 0.01 K with a thermostatted bath. The experimental values of these properties in comparison with the literature data are very similar (data not shown). Appropriate precautions were taken when handling the reagents to avoid volatilization.

Apparatus and Procedure. A new type of magnetic pump ebulliometer, described in detail by Qiu et al.,[10] was used for measuring the boiling points with different liquid-phase compositions. The apparatus was an all-glass dynamic recirculation still with a total volume of about $1.00 \cdot 10^{-4}$ m^3. During the run, the still was submerged in a constant temperature bath at about 3 °C below the equilibrium boiling point. The atmospheric pressure, p, was determined by a Fortin-type mercury barometer in experimental environments. Since the barometric pressure changed slightly, the experimental temperatures of the systems were automatically calibrated to that at 101.325 kPa with the self-adjusted pressure system. The equilibrium temperature, T, was measured to a precision of 0.1 K by means of a standard mercury thermometer. In each experiment, a known mass of the material was introduced from the injector into the still and heated at a fixed pressure of 101.325 kPa by an automatic pressure regulation system. The liquid mixtures of required composition were prepared gravimetrically, with the use of a Satorus electronic analytic balance (model ER-182A) with an accuracy of $\pm$ 0.0001 g. The values of mole fraction were reproducible to $\pm$ 0.0001 and have an uncertainty of 0.1 %. The ebulliometer was charged with the mixture of desired composition, and the boiler was then heated by Nichrome wire bound around the boiler. After the liquid mixture started boiling, the bubbles along with the drops of liquid spurted on the thermowell one by one. After adjusting the pressure to 101.325 kPa and when VLE was attained, the temperature was measured. The liquid-phase mole fraction of component i, x_i, could be calculated from the known mass of the material added to the still. The vapor-phase mole fraction of component i, y_i, was calculated from the experimental $T-p-x$ data by an indirect method based on the Q function (the function of molar excess Gibbs energy),[11] and the results were tested to meet rigorous thermodynamic consistency by the residual method.

Table 1. Antoine Coefficients of the Compounds

compound	A_i	B_i	C_i
methanol	7.19736	1574.99	238.86
ethanoic acid	6.42452	1479.02	216.82
propanoic acid	6.1742	1154.8	229.0

Results and Discussion

Correlation and Prediction of VLE Data of the Binary Systems. The activity coefficients γ_i of the components were calculated from

$$y_i \hat{\varphi}_i^{\text{V}} p = x_i \gamma_i \varphi_i^{\text{s}} p_i^{\text{s}} \exp\left[-\frac{V_i^{\text{L}}(p - p_i^{\text{s}})}{RT}\right] \tag{1}$$

where x_i and y_i are the liquid- and vapor-phase mole fractions of component i in equilibrium, $\hat{\varphi}_i^{\text{V}}$ is the fugacity coefficient of component i in the vapor mixture, φ_i^{s} is the fugacity coefficient of component i at saturation, V_i^{L} is the molar volume of component i in the liquid phase, R is the universal gas constant, and T is the experimental temperature. p is the total pressure, and p_i^{s} is the vapor pressure of pure component i. These vapor pressures were calculated from the Antoine equation

$$\log(p_i^{\text{s}}/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) + C_i} \tag{2}$$

where A_i, B_i, and C_i are Antoine constants and T is temperature in Kelvin. The constants A_i, B_i, and C_i are reported in Table 1, and their values were obtained from Shi et al.[12]

The fugacity coefficients for $\hat{\varphi}_1^{\text{V}}$ and $\hat{\varphi}_2^{\text{V}}$ were calculated by the expressions

$$\ln \hat{\varphi}_1^{\text{V}} = \frac{p}{RT}(B_{11} + {y_2}^2 \delta_{12}) \tag{3}$$

$$\ln \hat{\varphi}_2^{\text{V}} = \frac{p}{RT}(B_{22} + {y_1}^2 \delta_{12}) \tag{4}$$

where p is the total pressure and T is the experimental temperature, y_1 and y_2 are the vapor-phase mole fractions of compounds **1** and **2**, B_{11} and B_{22} are the virial coefficients of pure compounds **1** and **2**, and $\delta_{12} = 2B_{12} - B_{11} - B_{22}$, in which B_{12} is the second cross-virial coefficient.

Pitzer's correlation for the second virial coefficient was extended to mixtures by Reid et al.[13] To calculate B_{12} with the Tsonopoulos[14] modification for polar molecules by

$$B_{12} = \frac{RT_{\text{c12}}}{p_{\text{c12}}}(B^0 + \omega_{12}B^1 + a{T_{\text{r}}}^{-6} - b{T_{\text{r}}}^{-8}) \tag{5}$$

where a is the polarity parameter and b is the association parameter, T_{r} is the reduced temperature, and B^0 and B^1 are functions which depend exclusively on reduced temperature and can be represented satisfactorily by

$$B^0 = 0.083 - 0.422/{T_{\text{r}}}^{1.6} \tag{6}$$

$$B^1 = 0.139 - 0.172/{T_{\text{r}}}^{4.2} \tag{7}$$

The mixing rules proposed by Prausnitz[15] for the calculation of ω_{12}, T_{c12}, and p_{c12} are

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{8}$$

where ω_1 and ω_2 are the acentric factors of compounds **1** and **2**, and

$$T_{c12} = (1 - k_{ij})(T_{c1}T_{c2})^{0.5} \tag{9}$$

where T_{c1} and T_{c2} are the critical temperatures of compounds **1** and **2**, and k_{ij} is the binary interaction constant proposed by Lee and Chen,[16] $k_{ij} = 0.08$.

Also,

$$p_{c12} = \frac{Z_{c12}RT_{c12}}{V_{c12}} \tag{10}$$

where Z_{c12} is calculated by

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} \tag{11}$$

Z_{c1} and Z_{c2} are the critical compressibility factors of compounds **1** and **2**, respectively. V_{c12} is defined by the expression

$$V_{c12} = \left(\frac{{V_{c1}}^{1/3} + {V_{c2}}^{1/3}}{2}\right)^3 \tag{12}$$

where V_{c1} and V_{c2} are the critical volumes of compounds **1** and **2**. Values of T_c, p_c, V_c, Z_c, and ω have been obtained from the literature[12] and are presented in Table 2. The fugacity coefficients at saturation φ_1^s and φ_2^s were calculated by the expressions

$$\varphi_1^s = \exp \frac{B_{11}p_1^s}{RT} \tag{13}$$

$$\varphi_2^s = \exp \frac{B_{22}p_2^s}{RT} \tag{14}$$

According to the thermodynamic principles, the activity coefficients γ_i of the components were calculated by the expression

$$Q = \frac{G^E}{RT} = \sum x_i \ln \gamma_i \tag{15}$$

At constant pressure, for a binary system comprised of species 1 and 2, this eq 15 becomes

$$\gamma_i = \exp\left\{Q + (1 - x_i)\left[\left(\frac{dQ}{dx_i}\right) + \frac{H_m^E}{RT^2}\left(\frac{dT}{dx_i}\right) - \frac{V_m^E}{RT}\left(\frac{dp}{dx_i}\right)\right]\right\} \quad (i = 1{,}2) \tag{16}$$

where Q is the function of molar excess Gibbs energy, G^E is the molar excess Gibbs energy, H_m^E is the molar excess enthalpy, and V_m^E is the molar excess volume.

At constant pressure, $dp/dx_i = 0$, substitution into eq 16 reduced it to

$$\gamma_i = \exp\left\{Q + (1 - x_i)\left[\left(\frac{dQ}{dx_i}\right) + \frac{H_m^E}{RT^2}\left(\frac{dT}{dx_i}\right)\right]\right\} \tag{17}$$

Compared with the term dQ/dx_i of $[(dQ/dx_i) + (H_m^E/RT^2)(dT/dx_i)]$, the term $(H_m^E/RT^2)(dT/dx_i)$ can be nearly negligible, so this equation yields

$$\gamma_i = \exp\left[Q + (1 - x_i)\left(\frac{dQ}{dx_i}\right)\right] \tag{18}$$

Table 2. Published Parameters[12] Used to Calculate Fugacity Coefficients: Critical Temperature T_c, Critical Pressure p_c, Critical Volume V_c, Critical Compression Z_c, and Acentric Factor ω of Pure Compounds

compound	T_c / K	p_c / MPa	V_c / $m^3 \cdot kmol^{-1}$	Z_c	ω
methanol	512.6	8.096	0.118	0.224	0.559
ethanoic acid	594.4	5.786	0.171	0.200	0.454
propanoic acid	612.0	5.370	0.230	0.242	0.536

For the binary system at the VLE state, the activity coefficients γ_i of the components as functions of the excess Gibbs energy are as follows:

$$\begin{aligned} \gamma_1 &= \exp\left[Q + (1 - x_1)\left(\frac{dQ}{dx_1}\right)\right] \\ \gamma_2 &= \exp\left[Q - x_1\left(\frac{dQ}{dx_1}\right)\right] \end{aligned} \tag{19}$$

From eq 1, this equation is rearranged to obtain

$$y_i = x_i\gamma_i\varphi_i^s p_i^s \exp[V_i^L(p - p_i^s)/RT]/\hat{\varphi}_i^V p$$

Because $\sum y_i = 1$, the binary system in the equation may be summed to give

$$\frac{x_1\gamma_1\varphi_1^s p_1^s \exp[V_1^L(p - p_1^s)/RT]}{\hat{\varphi}_1^V p} + \frac{x_2\gamma_2\varphi_2^s p_2^s \exp[V_2^L(p - p_2^s)/RT]}{\hat{\varphi}_2^V p} = 1 \tag{20}$$

In eq 20, solved for y_i by the difference method. Suppose that [0, 1] is subdivided into n subintervals $[x_k, x_{k+1}]$ of equal step size $h = 1/n$ by using $x_k = kh$ for $k = 0, 1, ..., n$. In k difference point, we obtain

$$F_k = 1 - \left(\frac{x_1\gamma_1\varphi_1^s p_1^s \exp[V_1^L(p - p_1^s)/RT]}{\hat{\varphi}_1^V p}\right)_k - \left(\frac{x_2\gamma_2\varphi_2^s p_2^s \exp[V_2^L(p - p_2^s)/RT]}{\hat{\varphi}_2^V p}\right)_k = 0 \tag{21}$$

Meanwhile, eq 17 may be shown as follows:

$$\gamma_i|_k = \exp\left[Q_k + (1 - x_i|_k)\frac{(Q|_{k+1} - Q|_{k-1})}{2/h} + \frac{H^E}{RT^2}\left(\frac{dT}{dx_i}\right)\Bigg|_k\right] \tag{22}$$

Also, eq 18 becomes

$$\gamma_i|_k = \exp\left[Q_k + (1 - x_i|_k)\frac{(Q|_{k+1} - Q|_{k-1})}{2/h}\right] \tag{23}$$

Equation 21 is linearized to obtain:

$$-F_k = \Delta Q|_{k-1}\left(\frac{\delta F_k}{\delta Q|_{k-1}}\right) + \Delta Q|_k\left(\frac{\delta F_k}{\delta Q|_k}\right) + \Delta Q|_{k+1}\left(\frac{\delta F_k}{\delta Q|_{k+1}}\right) \tag{24}$$

The number of n linear equation from eq 22 is solved for $\Delta Q|_k$ by the chasing method.

$$Q_k^{j+1} = Q_k^j + t\Delta Q_k^j \tag{25}$$

where t is the relaxation factor; finally, $y_{ik}(k = 1 \sim n)$ is obtained by the difference method.

There are many methods concerning the correlation and prediction of VLE data. The model-free approach data treatment of VLE is also one of the best strategies for the correlation and prediction of VLE data. The model-free computation technique of Mixon et al. is explored as a complementary tool for the assessment of VLE data and for further analysis of binary systems that satisfy standard consistency tests but are not satisfactorily modeled by classical G^E expressions.[17] However,

Table 3. VLE Data for the Methanol (1) + Ethanoic Acid (2), Methanol (1) + Propanoic Acid (2), and Ethanoic Acid (1) + Propanoic Acid (2) Binary Systems at 101.325 kPa: Liquid-Phase Mole Fraction x_1, Experimental Boiling-Point Temperature T_{exp}, Calculated Bubble-Point Temperature T_{cal}, Vapor-Phase Mole Fraction y_1, Activity Coefficients γ_1 and γ_2 using the Wilson Equation Correlation, Fugacity Coefficients $\hat{\varphi}_1^V$ and $\hat{\varphi}_2^V$, and Excess Gibbs Energy G^E/RT

x_1	T_{exp}/K	T_{cal}/K	y_1	γ_1	$\hat{\varphi}_1^V$	γ_2	$\hat{\varphi}_2^V$	G^E/RT
Methanol (1) + Ethanoic Acid (2)								
0.0000	390.15	391.04	0.0000	0.958025	0.974063	1.000000	0.970318	0.000000
0.0361	385.66	386.00	0.1710	0.959903	0.976582	0.999950	0.968405	–0.001530
0.0408	385.40	385.39	0.1900	0.960161	0.976836	0.999935	0.968116	–0.001720
0.0650	382.20	382.45	0.2785	0.961526	0.977942	0.999834	0.966529	–0.002710
0.0739	380.80	381.43	0.3076	0.962042	0.978276	0.999784	0.965912	–0.003060
0.0862	380.10	380.08	0.3451	0.962764	0.978684	0.999704	0.965037	–0.003540
0.1035	378.36	378.26	0.3932	0.963795	0.979167	0.999568	0.963774	–0.004200
0.1272	375.40	375.94	0.4515	0.965232	0.979688	0.999340	0.961998	–0.005080
0.1626	372.86	372.76	0.5252	0.967409	0.980233	0.998901	0.959290	–0.006310
0.1920	369.88	370.36	0.5769	0.969232	0.980527	0.998446	0.957022	–0.007260
0.2505	366.80	366.08	0.6602	0.972849	0.980822	0.997286	0.952526	–0.008930
0.3390	361.00	360.62	0.7523	0.978174	0.980818	0.994852	0.945891	–0.010890
0.4400	356.33	355.47	0.8259	0.983840	0.980467	0.991017	0.938667	–0.012220
0.5833	350.10	349.54	0.8967	0.990760	0.979697	0.983536	0.929096	–0.012330
0.7043	346.20	345.42	0.9378	0.995281	0.978954	0.975323	0.921610	–0.010720
0.7511	344.60	344.00	0.9506	0.996652	0.978661	0.971696	0.918853	–0.009670
0.8106	342.55	342.31	0.9650	0.998066	0.978288	0.966751	0.915454	–0.007970
0.8704	341.60	340.73	0.9776	0.999102	0.977917	0.961443	0.912154	–0.005880
0.9156	340.48	339.61	0.9861	0.999623	0.977641	0.957244	0.909735	–0.004030
1.0000	338.15	337.66	1.0000	1.000000	0.977135	0.949122	0.905384	0.000000
Methanol (1) + Propanoic Acid (2)								
0.0000	414.15	414.14	0.0000	1.001515	0.976205	1.000000	0.969630	0.000000
0.0763	395.38	395.52	0.4851	1.001757	0.982904	1.000008	0.959528	0.000141
0.0870	393.26	393.50	0.5242	1.001800	0.983210	1.000012	0.957933	0.000167
0.1462	384.54	384.05	0.6791	1.001991	0.983901	1.000044	0.949303	0.000328
0.1714	380.84	380.72	0.7237	1.002043	0.983904	1.000067	0.945805	0.000405
0.1860	378.82	378.93	0.7457	1.002064	0.983861	1.000083	0.943834	0.000451
0.1979	377.71	377.55	0.7619	1.002077	0.983809	1.000098	0.942258	0.000489
0.2237	375.50	374.76	0.7924	1.002092	0.983655	1.000136	0.938932	0.000573
0.3522	364.59	363.81	0.8872	1.001929	0.982512	1.000466	0.924027	0.000981
0.4068	360.88	360.21	0.9109	1.001772	0.981974	1.000688	0.918393	0.001128
0.4522	357.54	357.55	0.9264	1.001616	0.981531	1.000917	0.913965	0.001232
0.5095	355.31	354.53	0.9421	1.001397	0.980986	1.001266	0.908668	0.001332
0.5372	353.08	353.19	0.9484	1.001286	0.980730	1.001461	0.906212	0.001366
0.5729	352.43	351.57	0.9557	1.001141	0.980407	1.001737	0.903138	0.001395
0.6325	349.97	349.07	0.9658	1.000899	0.979885	1.002269	0.898216	0.001401
0.7321	345.08	345.40	0.9789	1.000524	0.979066	1.003363	0.890499	0.001283
0.7911	342.98	343.46	0.9849	1.000335	0.978608	1.004142	0.886188	0.001128
0.8586	340.98	341.42	0.9907	1.000161	0.978108	1.005161	0.881461	0.000866
0.9279	338.87	339.50	0.9957	1.000044	0.977620	1.006359	0.876812	0.000498
1.0000	337.07	337.66	1.0000	1.000000	0.977135	1.007777	0.872170	0.000000
Ethanoic Acid (1) + Propanoic Acid (2)								
0.0000	414.15	414.14	0.0000	1.026215	0.928110	1.000000	0.969630	0.000000
0.0990	410.46	410.88	0.1816	1.021545	0.941447	1.000248	0.966992	0.002334
0.1086	410.18	410.58	0.1974	1.021113	0.942510	1.000299	0.966589	0.002535
0.1192	409.95	410.25	0.2144	1.020640	0.943645	1.000361	0.966120	0.002753
0.1624	409.17	408.96	0.2805	1.018763	0.947864	1.000674	0.963966	0.003583
0.2125	407.64	407.52	0.3509	1.016685	0.952041	1.001163	0.961058	0.004432
0.2437	406.83	406.66	0.3918	1.015446	0.954305	1.001536	0.959063	0.004896
0.2548	406.71	406.36	0.4059	1.015016	0.955055	1.001682	0.958324	0.005050
0.2745	405.97	405.83	0.4302	1.014265	0.956318	1.001957	0.956978	0.005306
0.2943	405.32	405.31	0.4538	1.013529	0.957505	1.002256	0.955584	0.005545
0.3162	404.68	404.75	0.4792	1.012735	0.958728	1.002613	0.953998	0.005786
0.3433	404.08	404.06	0.5094	1.011782	0.960119	1.003091	0.951978	0.006048
0.3823	403.25	403.11	0.5508	1.010472	0.961905	1.003855	0.948973	0.006359
0.4362	401.90	401.83	0.6043	1.008778	0.963999	1.005057	0.944660	0.006656
0.4686	401.09	401.09	0.6346	1.007828	0.965072	1.005862	0.941994	0.006760
0.5057	400.29	400.27	0.6678	1.006802	0.966149	1.006863	0.938883	0.006809
0.5802	398.55	398.68	0.7298	1.004948	0.967879	1.009129	0.932487	0.006679
0.6722	396.75	396.83	0.7993	1.003049	0.969342	1.012414	0.924382	0.006091
0.7726	394.95	394.93	0.8676	1.001484	0.970250	1.016635	0.915359	0.004897
0.8725	392.75	393.16	0.9291	1.000472	0.970577	1.021522	0.906260	0.003127
1.0000	390.39	391.04	1.0000	1.000000	0.970318	1.028803	0.894531	0.000000

Wisniak's group have developed novel model-free computation techniques and limiting conditions which were applied to VLE data for azeotropy systems.[18] Moreover, Segura and co-workers reported that a model-free approach dealt with VLE data in application of the ternary systems.[19,20] Herein, the obtained activity coefficients were correlated with the Wilson,[21] NRTL (Renon and Prausnitz),[22] Margules,[23] and van Laar[24] equations. The optimum interaction parameters were obtained by minimization of the objective function (OF) by means of the least-squares fitting,

$$\mathrm{OF} = \sum [\ln \gamma_1 - f_1(\Lambda_{ij})]_k^2 + \sum [\ln \gamma_2 - f_2(\Lambda_{ij})]_k^2 \tag{26}$$

where γ_1 and γ_2 are the activity coefficients of component 1 and component 2 calculated by the Q function in the liquid

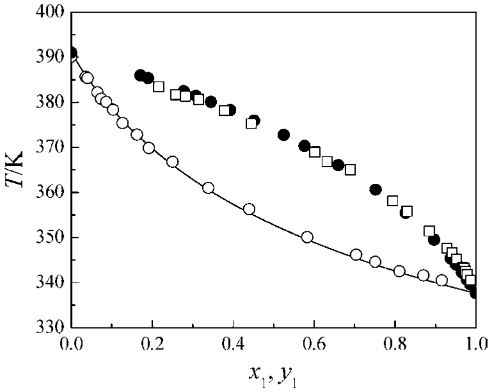

Figure 1. $T-x_1-y_1$ diagram for methanol (1) + ethanoic acid (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature; □, vapor-phase mole fraction y_1 from literature.[4]

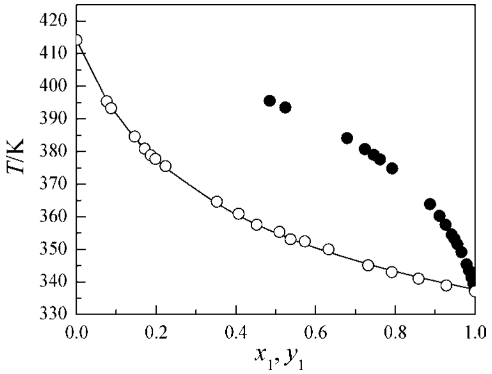

Figure 2. $T-x_1-y_1$ diagram for methanol (1) + propanoic acid (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature.

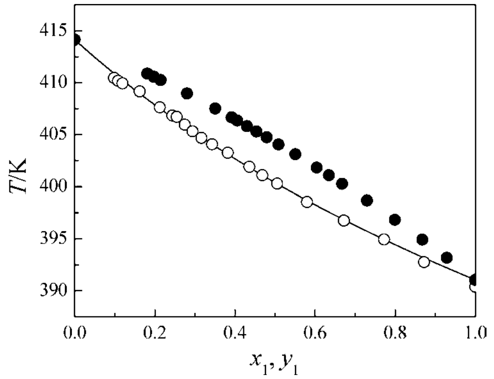

Figure 3. $T-x_1-y_1$ diagram for ethanoic acid (1) + propanoic acid (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature.

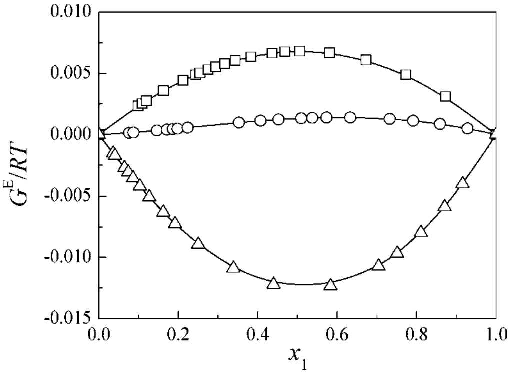

Figure 4. Excess Gibbs energy function (G^E/RT) versus liquid-phase mole fraction of component 1 (x_1) diagram for ethanoic acid (1) + propanoic acid (2), □; methanol (1) + propanoic acid (2), ○; and methanol (1) + ethanoic acid (2), △.

phase, f_1 and f_2 the model equation calculated activity coefficients of component 1 and component 2, respectively, Λ_{ij} the model interaction parameter, and $k(k = 0, 1, ..., n)$ the difference point to calculate.

Activity coefficients computed on the basis of the Wilson model were used to evaluate a dimensionless excess Gibbs function at 101.325 kPa for three binary systems over the overall range of composition. The liquid-phase mole fraction x_1, experimental boiling point temperature T_{exp}, calculated bubble-point temperature T_{cal}, vapor-phase mole fraction y_1, activity coefficients γ_1 and γ_2 using the Wilson equation correlation, fugacity coefficients $\hat{\varphi}_1^{\mathrm{V}}$ and $\hat{\varphi}_2^{\mathrm{V}}$, and dimensionless excess Gibbs energy G^E/RT are included in Table 3. $T-x_1-y_1$ diagrams for the methanol (1) + ethanoic acid (2), methanol (1) + propanoic acid (2), and ethanoic acid (1) + propanoic acid (2) binary systems at 101.325 kPa are shown in Figures 1 to 3. The plot of excess Gibbs energy function G^E/RT versus liquid-phase mole fraction of x_1 is given in Figure 4. The excess Gibbs energy function values are positive for ethanoic acid (1) + propanoic acid (2) and methanol (1) + propanoic acid (2) binary systems. However, for the methanol (1) + ethanoic acid (2) system, the values are negative. G^E/RT values follow the order ethanoic acid (1) + propanoic acid (2) > methanol (1) + propanoic acid (2) > methanol (1) + ethanoic acid (2). G^E/RT is maximized at an equimolar fraction in three binary systems. Compared with the values of the vapor-phase component from the literature,[4] the values of those from the paper are very similar, as shown in Figure 1. The results have demonstrated that the present experimental method for the correlation and prediction of VLE data is reliable and accurate. An excess Gibbs energy function (G^E/RT) versus liquid-phase mole fraction (x_1) diagram for the three binary systems is shown in Figure 4. The optimum model interaction parameters of the liquid activity coefficient and the absolute average deviations are listed in Table 4. Herein, we obtained the results by the four different types of correlations for the prediction of activity coefficients in these systems, which

Table 4. Correlation Parameters for Activity Coefficients and Average Deviations for the Studied Systems

equation	parameters or deviations	methanol (1) + ethanoic acid (2)	methanol (1) + propanoic acid (2)	ethanoic acid (1) + propanoic acid (2)
Wilson[a]	Λ_{12}/J·mol^{-1}	10.00	280.00	10.12
	Λ_{21}/J·mol^{-1}	41.00	–271.13	12.15
	dT/K	0.49	0.43	0.18
	dy	0.0061	0.0079	0.0126
NRTL[a]	$(g_{12} - g_{11})$/J·mol^{-1}	–51.23	0.11	1.07
	$(g_{21} - g_{22})$/J·mol^{-1}	0.24	0.14	12.18
	α_{12}	0 0.36	0 0.001	10 0.15
	dT/K	0.51	0.42	0.19
	dy	0.0054	0.0080	0.0122
Margules[b]	A_{12}	0.01	0.01	0.01
	A_{21}	–0.23	0.02	0.02
	dT/K	0.34	0.47	0.18
	dy	0.0077	0.0072	0.0119
van Laar[b]	A_{12}	0.01	0.015	0.01
	A_{21}	0.001	0.012	0.02
	dT/K	0.61	0.46	0.19
	dy	0.0083	0.0072	0.0119

[a] Wilson interaction parameters (J·mol^{-1}); NRTL interaction parameters (J·mol^{-1}). [b] Margules and van Laar interaction parameters (dimensionless). $\mathrm{d}T = \sum|T_{\mathrm{exp}} - T_{\mathrm{cal}}|/N$; N: number of data points; T_{cal}: calculated bubble point from model, K; T_{exp}: experimental boiling-point temperature, K. $\mathrm{d}y = \sum|y_{\mathrm{cal}} - y_{\mathrm{mod}}|/N$; N: number of data points; y_{cal}: calculated vapor-phase mole fraction from $T-p-x$; y_{mol}: calculated vapor-phase mole fraction from model.

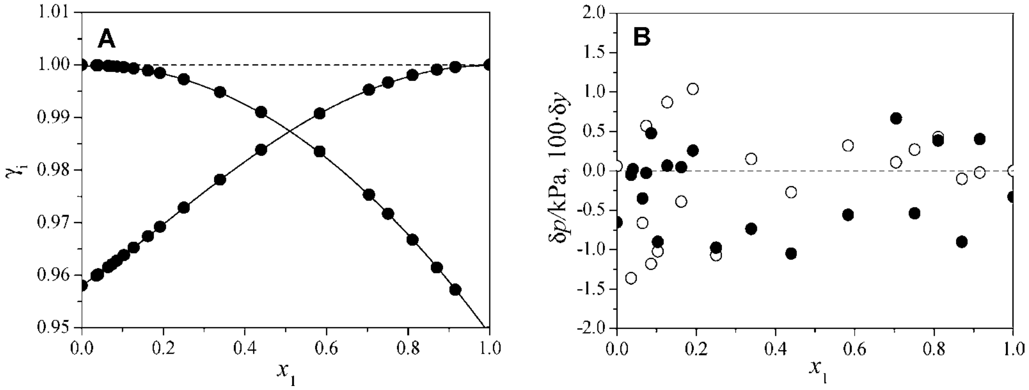

Figure 5. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for methanol (1) + ethanoic acid (2). ●, experimental data; —, calculated. (B) Residuals for the system methanol (1) + ethanoic acid (2). ●, pressure residuals; ○, vapor-phase mole fraction residuals (100·δy).

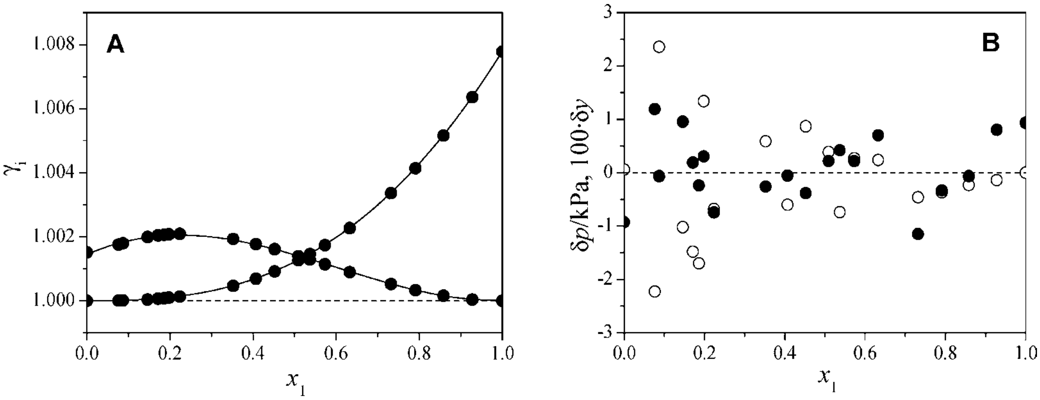

Figure 6. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for methanol (1) + propanoic acid (2). ●, experimental data; —, calculated. (B) Residuals for the system methanol (1) + propanoic acid (2). ●, pressure residuals; ○, vapor-phase mole fraction residuals (100·δy).

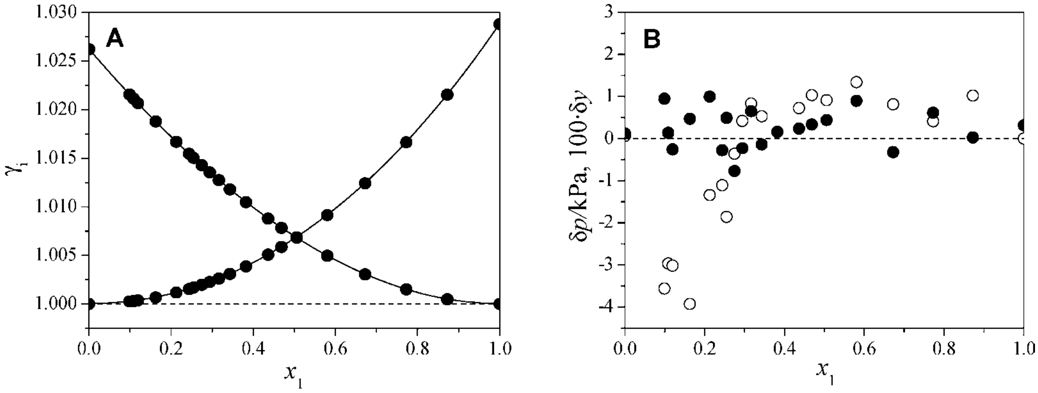

Figure 7. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for ethanoic acid (1) + propanoic acid (2). ●, experimental data; —, calculated. (B) Residuals for the system ethanoic acid (1) + propanoic acid (2). ●, pressure residuals; ○, vapor-phase mole fraction residuals (100·δy).

reveal that the deviations of Wilson, NRTL, Margules, and van Laar equations are reasonably small in Table 4. Since the superiority of one method over the others is not always obvious, practice must rely on experience and analogy. The comprehensive comparisons of four of the methods (Wilson, NRTL, van Laar, and Margules) were made in Table 4. From the data analysis, the temperature deviations between the experimental and the calculated values of four different types of model are very similar in the three binary systems, and the vapor mole fraction deviations between calculated values from $T-p-x$ and from the model are very similar. Therefore, the activity coefficient models are appropriate for representing the experimental data of the three binary systems. In Table 4, the absolute average deviations dT of the difference between the boiling-point temperature from the experiment and the bubbling-point temperature from calculation by Wilson model parameters for the three binary systems are (0.49, 0.43, and 0.18) °C, respectively. The absolute average deviations dy of the difference between vapor-phase mole fraction from $T-p-x$ calculation and from the Wilson model calculation are 0.0061, 0.0079, and 0.0126, respectively.

Thermodynamic Consistency Tests Based on VLE Calculations. Consistency tests are techniques that allow, in principle, the assessment of experimental VLE data on the basis of the Gibbs−Duhem equation. Much empiricism and arbitrariness is frequently observed in the analysis and application of consis-

Table 5. Thermodynamic Consistency for VLE of Methanol (1) + Ethanoic Acid (2), Methanol (1) + Propanoic Acid (2), and Ethanoic Acid (1) + Propanoic Acid (2) Binary Systems at 101.325 kPa[a]

equation	BIAS (p)/kPa	MAD (p)/kPa	BIAS (y)	MAD (y)
Methanol (1) + Ethanoic Acid (2)				
Wilson	–0.2368	0.4692	–0.0023	0.0061
NRTL	–0.0746	0.4621	–0.0005	0.0054
Margules	0.0215	0.4586	–0.0010	0.0077
van Laar	0.0385	0.2665	–0.0063	0.0083
Methanol (1) + Propanoic Acid (2)				
Wilson	0.0183	0.5493	0.0079	0.0079
NRTL	–0.0155	0.3655	0.0080	0.0080
Margules	–0.0435	0.4829	0.0072	0.0072
van Laar	0.0874	0.5083	0.0072	0.0072
Ethanoic Acid (1) + Propanoic Acid (2)				
Wilson	0.1011	0.6330	–0.0047	0.0126
NRTL	–0.0222	0.4756	–0.0040	0.0122
Margules	–0.0169	0.5841	–0.0041	0.0119
van Laar	0.2295	0.4200	–0.0040	0.0119

[a] BIAS: average of residuals. BIAS (θ) = $(1/N_d)\sum_{i=1}^{N_d}(\theta_{\mathrm{cal},i} - \theta_{\mathrm{exp},i})$. MAD: mean absolute deviation. MAD (θ) = $(1/N_d)\sum_{i=1}^{N_d}|\theta_{\mathrm{cal},i} - \theta_{\mathrm{exp},i}|$.

tency tests, a situation that may question their usefulness.[25−27] Perfect data satisfy exactly the Gibbs−Duhem relation, but acceptable data obey it within a tolerable limit (consistency criteria) which does not give a unique answer, regarding the quality of the data, when different consistency procedures are used. As with any approximation, application of consistency tests requires rigor, reasonable assumptions and models, and an examination of the data and results of the test. Herein, we use the assessment of the thermodynamic consistency test for VLE data, which is reported by the Wisniak group.[28] The results based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa were shown in Figures 5 to 7. The average of residuals and average absolute deviation for pressure and vapor-phase mole fraction for the four different models (Wilson, NRTL, Margules, and van Laar) of the three binary systems were illustrated in Table 5. We can conclude that the residuals show a random scatter distribution about the zero line, as confined also by the small numerical value of the bias of the vapor-phase composition, as shown in Table 5. Hence, the systems will be declared consistent although the systematic error was completely absorbed by the procedure used to fit the experimental bubble-point pressures, as can be deduced from the magnitude of δp residuals in Figures 5 to 7B. A plot of the activity coefficients reported in the paper, as shown in Figures 5 to 7A, indicates that the activity coefficients do approach x_i = 1.0 with a constant slope. It is confirmed that either the parameters of the Antoine equations used are accurate for treating the data or experimental accuracy may be present due to the small difference in boiling points of the components.

Prediction of VLE of the Ternary System. The binary interaction parameters of the Wilson, NRTL, Margules, and van Laar models given in Table 4 were used to predict the VLE data of the ternary system. VLE data for methanol (1) + ethanoic acid (2) + propanoic acid (3) at 101.325 kPa included liquid-phase mole fractions x_1, x_2, and x_3, experimental boiling-point temperature T_{exp}, calculated bubble-point temperature T_{cal}, vapor-phase mole fraction $y_{1,\mathrm{cal}}$, $y_{2,\mathrm{cal}}$, and $y_{3,\mathrm{cal}}$, activity coefficients γ_1, γ_2, and γ_3, and the average deviation in the bubble temperatures using the Wilson equation. Correlations are listed in Table 6. The absolute average and maximum deviation

Table 6. VLE Data for the Methanol (1) + Ethanoic Acid (2) + Propanoic Acid (3) Ternary System at 101.325 kPa: Liquid-Phase Mole Fraction x_1, x_2, and x_3, Experimental Boiling-Point Temperature T_{exp}, Calculated Bubble-Point Temperature T_{cal}, Vapor-Phase Mole Fraction $y_{1,\mathrm{cal}}$, $y_{2,\mathrm{cal}}$, and $y_{3,\mathrm{cal}}$, and Activity Coefficients γ_1, γ_2, and γ_3 Using Wilson Equation Correlation

x_1	x_2	x_3	T_{exp}/K	T_{cal}/K	y_1	y_2	y_3	γ_1	γ_2	γ_3
0.9048	0.0952	0.0000	340.18	340.13	0.9839	0.0161	0.0000	0.9995	0.9583	1.0042
0.8513	0.0000	0.1487	341.78	341.91	0.9900	0.0000	0.0100	1.0002	0.9462	1.0050
0.8323	0.0875	0.0802	342.88	342.22	0.9784	0.0161	0.0055	0.9995	0.9577	1.0052
0.7707	0.0811	0.1482	344.80	344.16	0.9728	0.0162	0.0111	0.9994	0.9583	1.0056
0.7592	0.1082	0.1326	344.99	344.45	0.9681	0.0219	0.0101	0.9990	0.9614	1.0058
0.7285	0.0766	0.1949	346.20	345.59	0.9683	0.0161	0.0156	0.9993	0.9592	1.0056
0.7029	0.1743	0.1228	347.04	346.16	0.9520	0.0379	0.0101	0.9974	0.9688	1.0066
0.6920	0.2165	0.0915	347.39	346.41	0.9448	0.0476	0.0076	0.9964	0.9720	1.0067
0.6606	0.0908	0.2486	348.81	348.00	0.9567	0.0211	0.0222	0.9986	0.9637	1.0058
0.6176	0.3008	0.0816	350.40	348.91	0.9191	0.0732	0.0076	0.9934	0.9790	1.0082
0.5862	0.0806	0.3332	351.97	351.05	0.9448	0.0211	0.0340	0.9984	0.9671	1.0053
0.5580	0.3682	0.0738	352.61	351.12	0.8946	0.0977	0.0077	0.9906	0.9837	1.0098
0.4884	0.4379	0.0737	354.32	354.00	0.8616	0.1297	0.0087	0.9870	0.9881	1.0118
0.5268	0.0724	0.4008	354.98	353.79	0.9328	0.0211	0.0461	0.9982	0.9707	1.0046
0.4787	0.0658	0.4555	357.19	356.23	0.9208	0.0211	0.0582	0.9982	0.9742	1.0040
0.4178	0.5192	0.0630	358.73	357.21	0.8181	0.1733	0.0086	0.9829	0.9918	1.0141
0.3648	0.5802	0.0550	361.55	359.90	0.7783	0.2133	0.0085	0.9797	0.9940	1.0159
0.3234	0.6278	0.0488	362.66	362.19	0.7415	0.2502	0.0083	0.9771	0.9955	1.0174
0.3931	0.0637	0.5432	363.02	361.19	0.8900	0.0246	0.0854	0.9977	0.9819	1.0033
0.3551	0.0575	0.5874	363.93	363.75	0.8732	0.0243	0.1025	0.9978	0.9855	1.0027
0.2671	0.6725	0.0604	366.17	365.79	0.6844	0.3037	0.0119	0.9735	0.9971	1.0189
0.2264	0.7224	0.0512	366.88	368.54	0.6307	0.3579	0.0113	0.9709	0.9980	1.0204
0.3037	0.0520	0.6443	368.56	367.62	0.8435	0.0253	0.1312	0.9979	0.9907	1.0021
0.1968	0.7587	0.0445	369.30	370.71	0.5852	0.4040	0.0108	0.9690	0.9986	1.0215
0.2609	0.0446	0.6945	371.42	371.32	0.8120	0.0247	0.1633	0.9982	0.9953	1.0016
0.1649	0.7999	0.0352	371.90	373.23	0.5282	0.4624	0.0094	0.9671	0.9990	1.0228
0.2291	0.0392	0.7317	373.09	374.40	0.7824	0.0241	0.1935	0.9985	0.9989	1.0012
0.1564	0.0222	0.8214	381.40	382.95	0.6847	0.0181	0.2972	0.9997	1.0075	1.0005
0.1333	0.0189	0.8478	386.33	386.19	0.6388	0.0170	0.3441	0.9999	1.0104	1.0003
0.1161	0.0165	0.8674	387.65	388.82	0.5981	0.0162	0.3858	1.0001	1.0125	1.0003
0.1065	0.0150	0.8785	388.95	390.39	0.5723	0.0154	0.4123	1.0002	1.0137	1.0002
0.0703	0.0302	0.8995	395.79	396.55	0.4434	0.0372	0.5193	0.9984	1.0174	1.0003
0.0521	0.0224	0.9255	398.72	400.42	0.3632	0.0309	0.6059	0.9991	1.0197	1.0002
Deviations			$dT = 0.95$					$\Delta T = 1.83$		

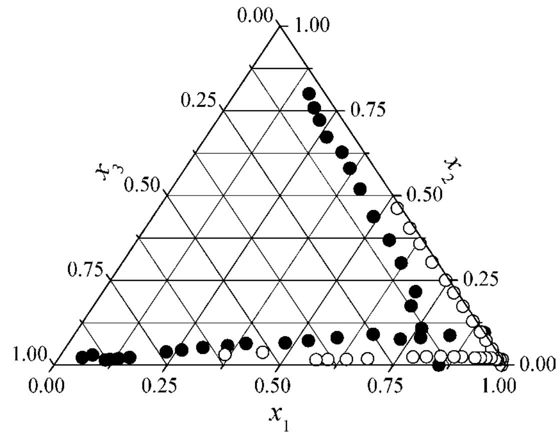

Figure 8. Diagram of the VLE for the ternary system methanol (1) + ethanoic acid (2) + propanoic acid (3) at 101.325 kPa: ●, liquid-phase mole fraction; ○, vapor-phase mole fraction.

between the boiling point from experimental data and the bubble point from Wilson model calculation are (0.95 and 1.83) °C, respectively. Meanwhile, the average and maximum deviations using the NRTL, Margules, and van Laar equation individually are (0.90 and 1.78) °C, (0.98 and 1.85) °C, and (1.01 and 1.89) °C. The diagram of VLE for the ternary system methanol (1) + ethanoic acid (2) + propanoic acid (3) at 101.325 kPa is shown in Figure 8.

Conclusions

VLE data for the ternary system methanol + ethanoic acid + propanoic acid and three constituent binary systems, methanol + ethanoic acid, methanol + propanoic acid, and ethanoic acid + propanoic acid, were determined by different liquid-phase compositions using a novel pump ebulliometer at 101.3 kPa. The equilibrium composition of the vapor phase was calculated from $T-p-x$ by the indirect method. The experimental data were correlated using the Wilson, NRTL, Margules, and van Laar equations. It was shown that the deviations of the Wilson, NRTL, Margules, and van Laar equations are reasonably small. The VLE data of ternary system were predicted by the Wilson, NRTL, Margules, and van Laar equations; the calculated bubble points accorded well with experimental data. The results show that the calculated bubble point is fitted by the models which satisfy the need for the design and operation of the separation process in the chemistry industry. Moreover, the method will provide theoretical guidance for the research of VLE data of a strongly associating system of the vapor and liquid phases in nonideal behavior.

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