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Isobaric Vapor−Liquid Equilibria for Binary and Ternary Mixtures of Propanal, Propanol, and Propanoic Acid

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Vapor−liquid equilibrium (VLE) data for the associating ternary system propanal + propanol + propanoic acid and three constituent binary systems were determined at different liquid phase compositions using a novel pump ebulliometer at 101.325 kPa. The vapor-phase compositions of these binary systems were calculated from *Tpx* according to the function of molar excess Gibbs energy by the Barker's method. Moreover, the experimental *T*, *x* data are used to estimate Wilson, nonrandom two-liquid (NRTL), Margules, van Laar, and universal quasichemical activity coefficient (UNIQUAC) model parameters from regression, and these parameters in turn are used to calculate vapor-phase compositions. The activity coefficients of the solution were correlated with the Wilson, NRTL, Margules, van Laar, and UNIQUAC models through the fit of the least-squares method. The VLE data of the ternary system were well-predicted from these binary interaction parameters of Wilson, NRTL, Margules, van Laar, and UNIQUAC model parameters without any additional adjustment to build the thermodynamic model of VLE for the ternary system and obtain the vapor-phase compositions 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

Most systems of industrial interest show deviations from the ideal behavior; for example, carboxylic acid systems remain a challenging problem since the systems show extremely nonideal behaviors. The associating solution systems containing carboxylic acid disclosed the nonideal behavior through the formation of hydrogen bonding between oxygen and hydrogen in the carboxylic group; therefore, it is very significant that the vapor−liquid equilibrium (VLE) data containing carboxylic acid for the systems are correlated and predicted. Propanoic acid is an important organic acid with wide applications in the chemical industry. In the chemical industrial process, the oxidation reaction of propanol with a strong oxidant is the most common and important technology for the synthesis of propanoic acid. However, the resultant products contain byproduct propanal and other mixtures. The VLE data of propanal + propanol + propanoic acid ternary system and the constituent binary systems are indispensable in the distillation separation process to the product of the oxidation reaction of propanol with strong oxidants through correlation and prediction, while some of the isobaric VLE data on the associating systems containing carboxylic acid are correlated and predicted in previous literature. Wisniak and Tamir reported in detail that the strategies for vapor-phase and liquid-phase nonideal behaviors containing carboxylic acid associating systems were explored to build the theory and model of the correlation and prediction of multicomponent associating systems.[1−5] Chuang and co-workers have developed a new correlation for the prediction of the VLE of methyl acetate−water−ethanoic acid mixtures.[6] Although the VLE data of the associating mixture containing carboxylic acid were previously reported by the different research groups,[7−11] respectively, the associating systems have been extensively studied because of the extensive association effects occurring in them and the difficulty of properly calculating the activity coefficients. Nominally, the system is binary, but in practice it is multicomponent. Therefore, the challenge for the VLE data of the associating systems has evoked more and more researchers to focus on new strategies for exploring them. Moreover, the isobaric VLE data of propanal + propanol + propanoic acid ternary system and constituent binary systems have not been found in the previous literature. Therefore, to provide the correlation and prediction for VLE data on the separation process of the propanol oxidation reaction, it is indispensable for these systems studied on the VLE data of the constituent binary and ternary systems. Herein, this paper reports that a correlation for the prediction of the VLE of these systems has been developed. The VLE data for the propanal−propanol−propanoic acid ternary system and constituent binary systems were measured by the total pressure−temperature−liquid phase mole composition (*p*, *T*, *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.[12] Owing to the association of propanoic acid molecules, the Hayden−O'Connell (HOC) model was used to correct the nonideality of vapor phase. However, the nonideality of the liquid phase was corrected by the calculation of its activity coefficient obtained from *Tpx* based on the function of molar excess Gibbs energy by the indirect method, and Wilson, nonrandom two-liquid (NRTL), Margules, van Laar, and universal quasichemical activity coefficient (UNIQUAC) models as the function of *T*−*x* through the fit of the least-squares method, respectively. Wilson, NRTL, Margules, van Laar, and UNIQUAC models were applied to correlate the VLE data for the three constituent binary systems. The VLE data of the ternary

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Table 1. Physical Properties of the Pure Compounds: Densities ρ, Refractive Indexes n_D at 298.15 K, and Normal Boiling Temperatures T_b

	ρ/kg·m^{-3}		n_D		T_b/K	
compound	expt	lit.[a]	expt	lit.[a]	expt	lit.[a]
propanal	797.21	797.64	1.3634	1.3636	321.18	321.18
propanol	803.62	803.32	1.3856	1.3850	370.27	370.36
propionic acid	992.86	993.24	1.3858	1.3869	412.91	414.1

[a] Riddick et al.[13]

system were well-predicted from these binary interactive parameters of Wilson, NRTL, Margules, van Laar, and UNIQUAC models without any additional adjustment to build the thermodynamic model of VLE for the ternary system and obtain the vapor-phase compositions and the calculated bubble-point temperature. These VLE data can be used as the design and simulation of the distillation of these binary and ternary systems. The excess Gibbs 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.

Experimental Section

Materials. Propanal, propanol, 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 $w = 0.998$, as verified by gas chromatography analysis without any significant impurities. All of the chemicals were degassed using ultrasound and dried on a molecular sieve (pore diameter of 30 nm from Shanghai Chemistry Reagent Co. Ltd.). The bidistilled water was from our lab through manufacturing it ourselves. 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.[13] The densities were measured at 298.15 K using a bicapillary pycnometer previously described by Rao and Naidu,[14] with an uncertainty of ± 0.12 kg·m^{-3}, and the refractive indexes of the pure components were measured using an Abbe refractometer (Carl-Zeiss-Jena, with an uncertainty of ± 0.0012) at 298.15 K after the calibration with standard liquids, supplied with the instrument. The temperature was controlled to ± 0.01 K with a thermostatted bath. The experimental values of these properties in comparison with the literature data are very similar in Table 1. 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.[15] 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, to avoid the over-equilibrium boiling point of the system, the still was submerged in a constant temperature bath at about 3 °C below the equilibrium boiling point, which was obtained by the Nichrome wire in the tube to partially heat the known mass of the material. 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 a self-adjusted pressure system. The equilibrium temperature, T, was measured to an uncertainty of 0.12 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 Sartorius electronic analytic balance (model ER-182A) with an accuracy of ± 0.0001 g. The values of mole fraction were reproducible to ± 0.0001 with the 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 Tpx data based on the function of molar excess Gibbs energy by an indirect method,[16] and the results were tested to meet rigorous thermodynamic consistency by the residual method.[12]

Results and Discussion

Correlation and Prediction of VLE Data of the Binary Systems. The new strategies for the correlation and accurate prediction of the VLE data play a vital role of distillation and separation of process in the chemical industry. The usual technique for obtaining VLE data is by direct measurement to the system, that is to say, when the VLE is established and phases are sampled and analyzed. Normally, the experimental technique must be rather delicate to ensure meaningful results in the operation of equilibrium stills. Actually, when the vapor-phase components are sampled and analyzed, the whole compositions of components in solution and vapor have been changed with the vapor-phase components sampled. Accordingly, the behaviors of the system have been changed with the amount of compositions. Moreover, it has been long realized that the analysis of vapor−liquid composition for the infinite dilute solution is very difficult. In addition, for VLE measurements of mixtures containing a highly volatile compound, the accurate measurement of the vapor-phase composition can be difficult. Meanwhile, there is an added complexity when working with carboxylic acids because they associate in the vapor phase. This association can be represented by assuming that the organic acid exists as monomers and dimer molecules in equilibrium. This fact, coupled with the necessity for much analytical work, tends to enhance interest in exploring new methods for the determination of equilibrium data that do not involve sampling and analysis of the vapor-phase component.

Herein, the method used to reduce the Tpx data has been described by the previous work[17−20] and is similar to the method proposed by Barker.[18] It involves an iterative procedure to solve the following basic equation of VLE:

Table 2. Antoine Coefficients of the Compounds

compound	A_i	B_i	C_i
propanal	6.17413	1154.80	−44.15
propanol	6.74410	1375.14	−80.15
propanoic acid	6.67244	1617.06	−67.48

Table 3. Published Parameters[21] 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

	T_c	p_c	V_c		
compound	K	MPa	cm^3·mol^{-1}	Z_c	ω
propanal	496.0 ± 4.16	4.762 ± 0.12	223.0 ± 0.42	0.260 ± 0.00146	0.313
propanol	536.7 ± 5.08	5.168 ± 0.18	218.5 ± 0.56	0.253 ± 0.00239	0.624
propanoic acid	612.0 ± 5.16	5.370 ± 0.24	230.0 ± 0.82	0.242 ± 0.00459	0.536

Table 4. VLE Data for the Propanal (1) + Propanol (2), Propanal (1) + Propanoic Acid (2), and Propanol (1) + Propanoic Acid (2) Three 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
Propanal (1) + Propanol (2)								
0.0000	370.27	370.36	0.0000	0.860279	0.944537	1.000000	0.969117	0.000000
0.0399	367.65	367.58	0.1191	0.869344	0.951445	0.999766	0.967533	−0.005812
0.0800	364.40	364.82	0.2650	0.878246	0.956859	0.999052	0.964828	−0.011259
0.1199	361.70	362.12	0.3673	0.886896	0.961010	0.997856	0.961303	−0.016281
0.1599	359.08	359.45	0.4566	0.895357	0.964171	0.996160	0.957155	−0.020906
0.1999	356.55	356.85	0.5337	0.903604	0.966529	0.993956	0.952571	−0.025113
0.2399	354.10	354.32	0.6005	0.911628	0.968245	0.991233	0.947692	−0.028889
0.2798	351.72	351.86	0.6585	0.919403	0.969450	0.987988	0.942641	−0.032215
0.3198	349.43	349.48	0.7085	0.926956	0.970258	0.984194	0.937478	−0.035093
0.3598	347.20	347.18	0.7520	0.934255	0.970753	0.979847	0.932284	−0.037502
0.3998	345.11	344.96	0.7887	0.941285	0.971004	0.974937	0.927106	−0.039426
0.4398	342.99	342.83	0.8220	0.948028	0.971067	0.969453	0.921982	−0.040852
0.4799	340.99	340.78	0.8502	0.954483	0.970987	0.963371	0.916928	−0.041765
0.5199	339.08	338.81	0.8743	0.960596	0.970797	0.956711	0.911985	−0.042147
0.5602	337.23	336.92	0.8953	0.966406	0.970523	0.949397	0.907121	−0.041981
0.6002	335.38	335.13	0.9141	0.971803	0.970192	0.941529	0.902415	−0.041255
0.6402	333.77	333.41	0.9288	0.976807	0.969818	0.933051	0.897838	−0.039956
0.6819	332.07	331.71	0.9428	0.981580	0.969397	0.923559	0.893207	−0.037973
0.7201	330.58	330.21	0.9539	0.985531	0.968992	0.914276	0.889092	−0.035580
0.7601	329.07	328.72	0.9640	0.989212	0.968558	0.903952	0.884916	−0.032469
0.8001	327.63	327.30	0.9726	0.992399	0.968118	0.893012	0.880874	−0.028725
0.8402	326.22	325.95	0.9802	0.995072	0.967677	0.881429	0.876958	−0.024319
0.8801	324.89	324.66	0.9865	0.997186	0.967242	0.869295	0.873196	−0.019275
0.9201	323.64	323.44	0.9919	0.998733	0.966812	0.856530	0.869559	−0.013540
0.9601	322.35	322.28	0.9966	0.999680	0.966391	0.843171	0.866057	−0.007114
1.0000	321.18	321.18	1.0000	1.000000	0.965983	0.829265	0.862698	0.000000
Propanal (1) + Propanoic Acid (2)								
0.0000	412.91	411.98	0.0000	1.054286	0.959977	1.000000	0.969007	0.000000
0.0400	400.83	400.69	0.3539	1.051850	0.970720	1.000092	0.962426	0.002110
0.0800	391.16	390.95	0.5533	1.048803	0.975368	1.000373	0.952799	0.004155
0.1200	382.83	382.63	0.6833	1.045545	0.977182	1.000849	0.942491	0.006091
0.1600	375.66	375.53	0.7696	1.042189	0.977656	1.001525	0.932380	0.007892
0.2000	369.50	369.43	0.8280	1.038812	0.977485	1.002405	0.922756	0.009537
0.2396	364.22	364.21	0.8684	1.035499	0.977009	1.003481	0.913767	0.011000
0.2800	359.51	359.55	0.8980	1.032187	0.976375	1.004794	0.905128	0.012314
0.3200	355.40	355.48	0.9195	1.029005	0.975685	1.006312	0.897056	0.013428
0.3601	351.35	351.86	0.9373	1.025930	0.974973	1.008058	0.889393	0.014354
0.4001	348.46	348.61	0.9482	1.022994	0.974267	1.010027	0.882127	0.015081
0.4400	345.53	345.69	0.9579	1.020208	0.973577	1.012222	0.875214	0.015606
0.4801	342.83	343.02	0.9656	1.017561	0.972904	1.014668	0.868566	0.015928
0.5200	340.39	340.58	0.9718	1.015089	0.972256	1.017345	0.862216	0.016042
0.5600	338.14	338.33	0.9769	1.012778	0.971631	1.020279	0.856088	0.015944
0.6000	336.06	336.24	0.9811	1.010642	0.971028	1.023470	0.850175	0.015631
0.6400	334.20	334.30	0.9845	1.008686	0.970446	1.026926	0.844454	0.015100
0.6800	332.36	332.49	0.9875	1.006915	0.969885	1.030654	0.838908	0.014348
0.7201	331.07	330.79	0.9894	1.005331	0.969342	1.034672	0.833506	0.013369
0.7601	329.09	329.19	0.9921	1.003946	0.968819	1.038970	0.828262	0.012165
0.8001	327.60	327.68	0.9939	1.002761	0.968311	1.043565	0.823148	0.010730
0.8400	326.20	326.26	0.9955	1.001782	0.967821	1.048454	0.818164	0.009066
0.8800	324.86	324.90	0.9969	1.001010	0.967343	1.053673	0.813276	0.007162
0.9201	323.58	323.60	0.9981	1.000451	0.966877	1.059233	0.808474	0.005013
0.9600	322.36	322.37	0.9991	1.000114	0.966425	1.065105	0.803785	0.002632
1.0000	321.18	321.18	1.0000	1.000000	0.965983	1.071343	0.799165	0.000000
Propanol (1) + Propanoic Acid (2)								
0.0000	412.91	411.98	0.0000	1.024590	0.933879	1.000000	0.969007	0.000000
0.0399	408.17	408.26	0.1693	1.022826	0.943349	1.000037	0.966917	0.000936
0.0801	404.83	404.94	0.2809	1.021107	0.950230	1.000148	0.963508	0.001809
0.1200	401.87	401.97	0.3734	1.019456	0.955265	1.000335	0.959404	0.002607
0.1600	399.20	399.28	0.4512	1.017859	0.959052	1.000600	0.954902	0.003336
0.2000	396.77	396.83	0.5173	1.016321	0.961930	1.000944	0.950205	0.003993
0.2399	394.54	394.59	0.5742	1.014846	0.964129	1.001368	0.945446	0.004574
0.2798	392.49	392.52	0.6235	1.013430	0.965823	1.001874	0.940685	0.005081
0.3199	390.58	390.60	0.6669	1.012069	0.967135	1.002469	0.935944	0.005515
0.3599	388.80	388.81	0.7051	1.010775	0.968141	1.003149	0.931287	0.005870
0.4000	387.13	387.14	0.7392	1.009542	0.968918	1.003921	0.926682	0.006147
0.4399	385.60	385.58	0.7690	1.008381	0.969492	1.004781	0.922218	0.006343
0.4800	384.10	384.11	0.7969	1.007282	0.969914	1.005739	0.917832	0.006458
0.5200	382.72	382.72	0.8214	1.006255	0.970211	1.006792	0.913560	0.006492
0.5600	381.35	381.40	0.8447	1.005299	0.970405	1.007944	0.909387	0.006441
0.6000	380.16	380.16	0.8641	1.004415	0.970515	1.009198	0.905313	0.006306
0.6400	378.98	378.98	0.8828	1.003606	0.970555	1.010558	0.901334	0.006085
0.6800	377.86	377.85	0.8998	1.002873	0.970534	1.012024	0.897460	0.005776
0.7201	376.77	376.77	0.9158	1.002217	0.970467	1.013605	0.893645	0.005377
0.7601	375.74	375.74	0.9305	1.001642	0.970359	1.015297	0.889922	0.004889
0.8001	374.76	374.75	0.9440	1.001150	0.970214	1.017105	0.886276	0.004310
0.8400	373.81	373.81	0.9567	1.000743	0.970041	1.019030	0.882714	0.003640
0.8800	372.90	372.90	0.9685	1.000422	0.969841	1.021082	0.879212	0.002875
0.9201	372.03	372.02	0.9796	1.000189	0.969617	1.023268	0.875767	0.002012
0.9600	371.18	371.18	0.9903	1.000048	0.969376	1.025575	0.872402	0.001056
1.0000	370.27	370.36	1.0000	1.000000	0.969117	1.028022	0.869086	0.000000

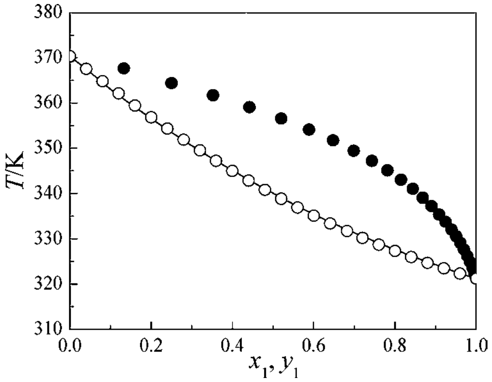

Figure 1. $T-x_1-y_1$ diagram for propanal (1) + propanol (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature.

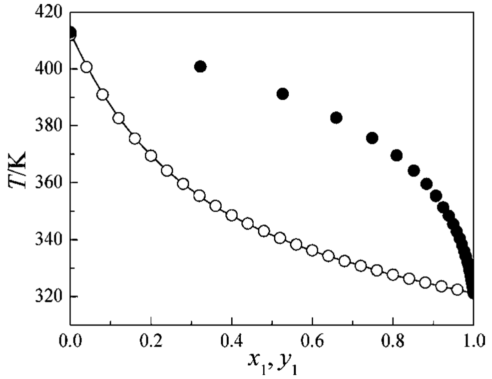

Figure 2. $T-x_1-y_1$ diagram for propanal (1) + propanoic acid (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature.

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

where x_i and y_i are the mole fractions of component i in the liquid and vapor phases, respectively. $\hat{\varphi}_i^{V}$ and φ_i^{s} are the fugacity coefficients of component i in the vapor mixture and the pure vapor at saturation, respectively. 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

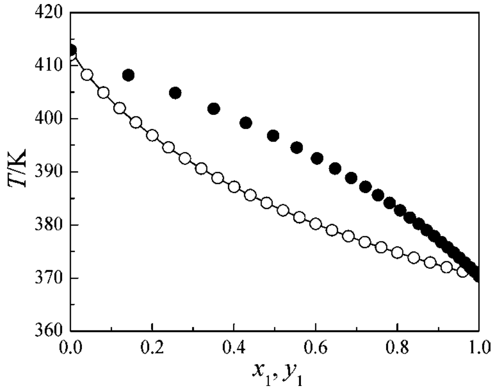

Figure 3. $T-x_1-y_1$ diagram for propanol (1) + propanoic acid (2) at 101.325 kPa: ●, vapor-phase mole fraction y_1; ○, liquid-phase experimental temperature; —, Wilson correlation temperature.

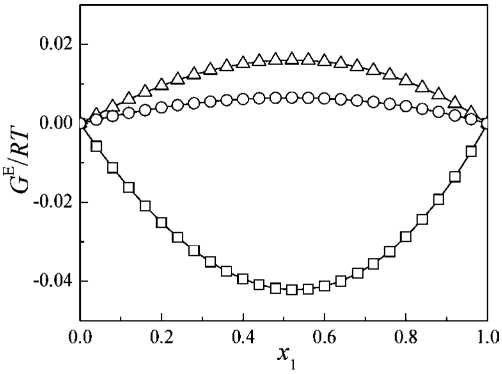

Figure 4. Excess Gibbs energy functions (G^E/RT) versus liquid-phase mole fraction of component 1 (x_1) diagram: △, propanal (1) + propanoic acid (2); ○, propanol (1) + propanoic acid (2); □, propanal (1) + propanol (2).

Table 5. Correlation Parameters for Activity Coefficients and Absolute Average Deviation for Studied Systems

equation	parameters or deviations	propanal (1) + propanol (2)	propanal (1) + propanoic acid (2)	propanol (1) + propanoic acid (2)
Wilson[a]	Λ_{12}/J·mol^{-1}	−260.46 ± 2.57	−95.32 ± 1.03	10.45 ± 0.14
	Λ_{21}/J·mol^{-1}	150.68 ± 1.68	139.58 ± 1.48	12.25 ± 0.21
	dT/K	0.23	0.16	0.17
	dy	0.0052	0.0044	0.0036
NRTL[a]	$(g_{12} - g_{11})$/J·mol^{-1}	−110.78 ± 0.87	15.45 ± 0.15	10.28 ± 0.18
	$(g_{21} - g_{22})$/J·mol^{-1}	12.93 ± 0.24	35.26 ± 0.20	20.36 ± 0.26
	α_{12}	0.6	0.4	0.7
	dT/K	0.27	0.17	0.09
	dy	0.0057	0.0088	0.0029
Margules[b]	A_{12}	−0.45 ± 0.02	−0.36 ± 0.01	0.64 ± 0.03
	A_{21}	−0.30 ± 0.01	0.16 ± 0.01	0.47 ± 0.02
	dT/K	0.22	0.33	0.12
	dy	0.0070	0.0091	0.0039
van Laar[b]	A_{12}	−0.10 ± 0.006	0.041 ± 0.001	0.01 ± 0.001
	A_{21}	−0.30 ± 0.008	0.11 ± 0.005	0.02 ± 0.002
	dT/K	0.26	0.12	0.13
	dy	0.0061	0.0094	0.0037
UNIQUAC[a]	$(u_{12} - u_{11})$/J·mol^{-1}	−1572.46 ± 5.68	867.36 ± 3.64	−2643.59 ± 4.78
	$(u_{21} - u_{22})$/J·mol^{-1}	2578.28 ± 6.75	786.68 ± 3.52	2865.47 ± 4.86
	dT/K	0.54	0.62	0.58
	dy	0.0072	0.0075	0.0033

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

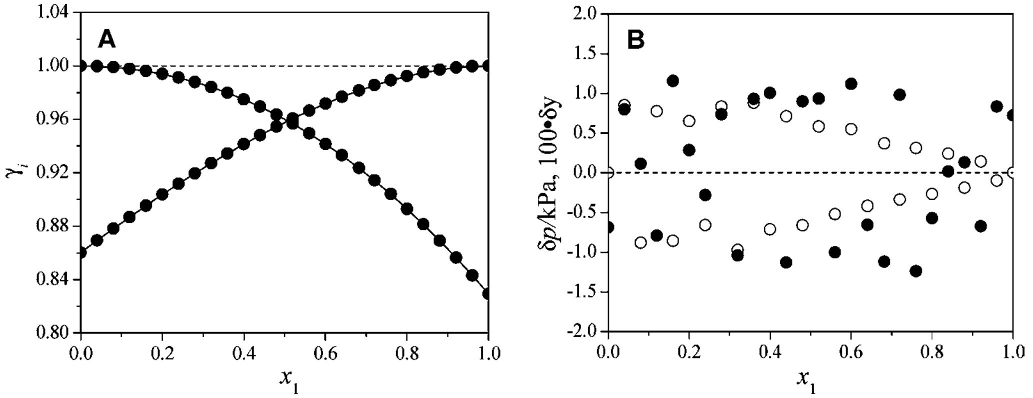

Figure 5. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for propanal (1) + propanol (2). ●, experimental data; —, calculated. (B) Residuals for the system propanal (1) + propanol (2). ●, pressure residuals; ○, vapor-phase mole fraction residuals ($100 \cdot \delta y$).

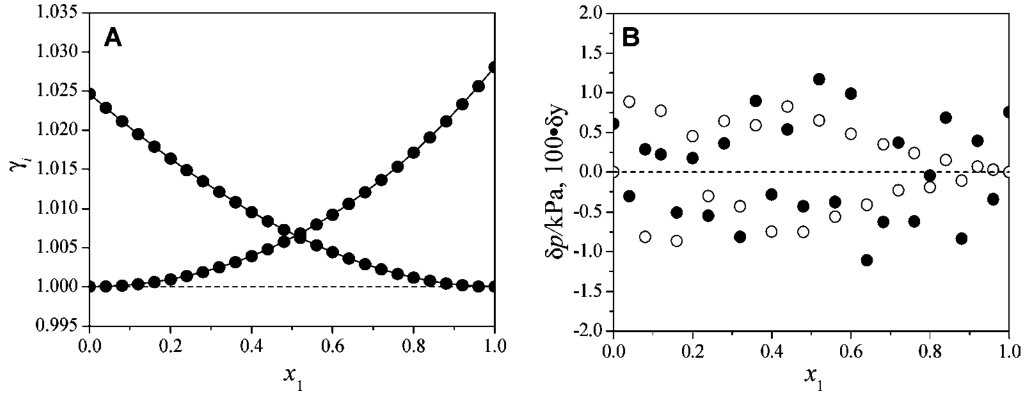

Figure 6. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for propanal (1) + propanoic acid (2). ●, experimental data; —, calculated. (B) Residuals for the system propanal (1) + propanoic acid (2). ●, pressure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

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

where A_i, B_i, and C_i are Antoine constants and T is the temperature in Kelvin. The constants A_i, B_i, and C_i are reported in Table 2, and their values were obtained from Shi et al.[21]

Because carboxylic acids are always present in an associated form, like a dimer or trimer, in both the vapor and the liquid phases even at low pressures,[1−5,7] a significant deviation in the fugacity coefficient may exist using the ideal gas assumption.[3] To account for nonideal behavior, a chemical theory is commonly used to calculate the fugacity coefficient in vapor. Herein, the HOC model was used for this purpose.[22,23] The Poynting correction factor was also included in the calculation of fugacity at the reference state. The liquid molar volumes were evaluated from the modified Rackett equation.[24] The fugacity coefficients for $\hat{\varphi}_i^{\mathrm{V}}$ and φ_i^{s} were calculated by the method of Hayden and O'Connell from the second virial coefficients. The association parameters, a and b, of the pure components in the polar contribution term of the Tsonopoulos method are obtained from the Tsonopoulos modification method.[24,25] The mixing rules were proposed by Prausnitz,[26] and k_{ij} is the binary interaction constant proposed by Lee and Chen,[27] $k_{ij} = 0.08$. The critical

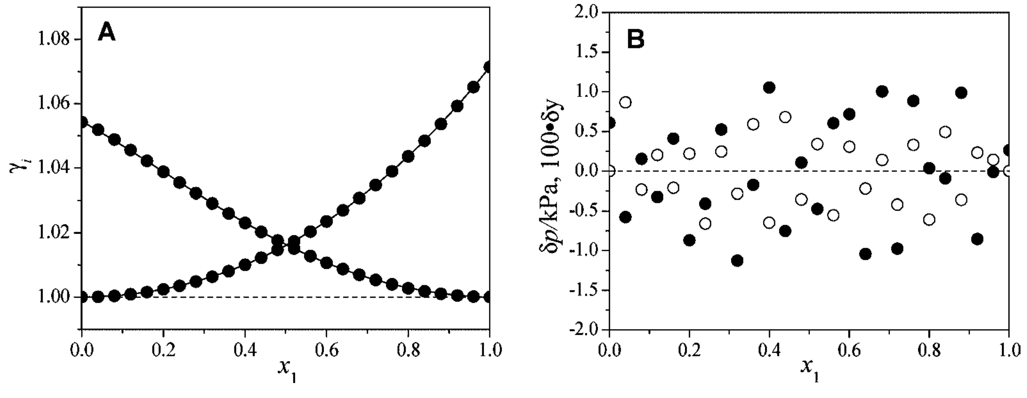

Figure 7. Consistency data treatment based on a statistically significant fit of the experimental bubble pressures at 101.325 kPa: (A) activity coefficients for propanol (1) + propanoic acid (2). ●, experimental data; —, calculated. (B) Residuals for the system propanol (1) + propanoic acid (2). ●, pressure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

Table 6. Thermodynamic Consistency for VLE of Propanal (1) + Propanol (2), Propanal (1) + Propanoic Acid (2), and Propanol (1) + Propanoic Acid (2) Three Binary Systems at 101.325 kPa[a]

equation	BIAS(p)/kPa	MAD(p)/kPa	BIAS(y)	MAD(y)
Propanal (1) + Propanol (2)				
Wilson	0.0565	0.7669	0.0001	0.0052
NRTL	−0.0746	0.7832	0.0002	0.0057
Margules	0.0314	0.4685	0.0010	0.0070
van Laar	0.0476	0.7635	0.0006	0.0061
UNIQUAC	0.0575	0.6357	0.0008	0.0072
Propanal (1) + Propanoic Acid (2)				
Wilson	0.0234	0.5492	0.0003	0.0044
NRTL	−0.0456	0.7621	0.0007	0.0088
Margules	−0.0645	0.4878	0.0009	0.0091
van Laar	0.0874	0.7608	0.0008	0.0094
UNIQUAC	0.0532	0.6765	0.0006	0.0075
Propanol (1) + Propanoic Acid (2)				
Wilson	−0.0104	0.5782	0.0001	0.0036
NRTL	−0.0246	0.4564	0.0005	0.0029
Margules	−0.0194	0.5854	0.0007	0.0039
van Laar	0.0286	0.5423	0.0006	0.0037
UNIQUAC	0.0342	0.5210	0.0008	0.0033

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

properties needed for data reduction by the previous method[28−30] are presented in Table 3.

The method of Barker data reduction assumes that there is an activity coefficient model based on molar excess Gibbs free energy that can predict the bubble-point pressure with higher accuracy than the experimental error of the measured total pressure. This method is an iterative method, which needs vapor-phase fugacities and liquid-phase activities to be calculated. The method for calculating fugacity coefficients was chosen to be the HOC model with the mixing rule. Liquid-phase activity coefficients were obtained from total vapor pressure based on the least-squares method, which due to its flexible nature is suitable for accurately predicting nonideal behavior of the liquid phase. The scheme for data reduction is reported in several previous publications.[11,17−20] The resultant vapor−liquid compositions were calculated through the Barker's method described based on the least-squares fit for calculating activity coefficients from results of total pressure−temperature−compositions.

In addition, 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. In contrast to previous approaches, model-free techniques are methods that do not require the assumption of a particular G^E model. In the model-free approach, the G^E function may be obtained numerically from experimental data by integrating the Gibbs−Duhem relation. The main feature of model-free techniques is their ability to overcome modeling pitfalls because, when performing data treatment, the right selection of an adequate G^E model is also a part of the problem.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.[31] However, Wisniak's group has reported that the novel model-free computation techniques and limiting conditions have been applied to VLE data for azeotropic systems.[32] Moreover, Segura and co-workers reported that a model-free approach dealt with VLE data in applications of ternary systems.[33,34] Herein, the obtained activity coefficients were correlated with the Wilson,[35] NRTL (Renon and Prausnitz),[36] Margules,[37] van Laar,[38] and UNIQUAC equations.

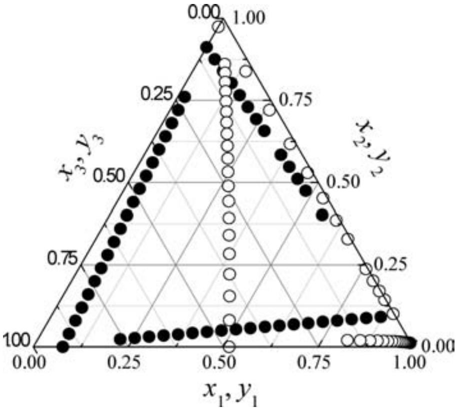

Figure 8. Diagram of VLE for the ternary system propanal (1) + propanol (2) + propanoic acid (3) at 101.325 kPa: ●, liquid-phase mole fraction; ○, vapor-phase mole fraction.

The optimum interaction parameters were obtained by minimization of the objective function (OF) by means of the least-squares fitting,

$$\mathrm{OF} = \sum[\ln\gamma_1 - f_1(\Lambda_{ij})]_k^2 + \sum[\ln\gamma_2 - f_2(\Lambda_{ij})]_k^2 \tag{3}$$

where γ_1 and γ_2 are the activity coefficients of component 1 and component 2 calculated by the function of excess Gibbs energy in the liquid phase, f_1 and f_2 the model equation calculated activity coefficients of component 1 and component 2, respectively, and Λ_{ij} the model interaction parameter; k ($k = 0, 1, ..., n$) is the different point for calculation.

The activity coefficients computed on the basis of the Wilson model were used to evaluate the dimensionless excess Gibbs function at 101.325 kPa for three binary systems over the overall range of composition. 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 4. The $T{-}x_1{-}y_1$ diagrams for the propanal (1) + propanol (2), propanal (1) + propanoic acid (2), and propanol (1) + propanoic acid (2) three binary systems at 101.325 kPa are shown in Figures 1 to 3. The plot of excess Gibbs energy function G^E/RT versus the liquid-phase mole fraction of x_1 is given in Figure 4. The values of excess Gibbs energy function G^E/RT are negative for propanal (1) + propanol (2) binary systems. However, for propanal (1) + propanoic acid (2) and propanol (1) + propanoic acid (2) two binary systems, the values of those are positive in the overall range of mole fraction. G^E/RT values follow the order propanal (1) + propanoic acid (2) > propanol (1) + propanoic acid (2) > propanal (1) + propanol (2). The absolute value of G^E/RT is maximized at an equimolar fraction in three binary systems. Comparing the values from the experimental temperature with the calculated temperature from the Wilson model, the values of those are very similar, as shown in Figures 1 to 3. The results have demonstrated that the present experimental method for the correlation and prediction of VLE data is reliable and accurate. Excess Gibbs energy functions (G^E/RT) versus the liquid-phase mole fraction (x_1) diagram for the three binary systems are shown in Figure 4. The optimum model interaction parameter of the liquid activity coefficient and the absolute average deviations are listed in Table 5. Herein, we obtained the results by the five different types of correlations for the prediction of activity coefficients

Table 7. VLE Data for the Propanal (1) + Propanol (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 $y_{1,cal}$, $y_{2,cal}$, and $y_{3,cal}$, and Activity Coefficients γ_1, γ_2, and γ_3 Using the Wilson Equation Correlation[a]

x_1	x_2	x_3	T_{exp}/K	T_{cal}/K	y_1	y_2	y_3	γ_1	γ_2	γ_3
0.8686	0.0914	0.0400	325.11	325.67	0.9866	0.0120	0.0015	0.997946	0.865539	1.076494
0.8324	0.0876	0.0800	326.37	326.46	0.9846	0.0123	0.0031	0.997946	0.869839	1.069565
0.7962	0.0838	0.1200	327.68	327.99	0.9825	0.0126	0.0049	0.998204	0.874367	1.063038
0.7600	0.0800	0.1600	329.06	328.90	0.9801	0.0129	0.0069	0.998715	0.879121	1.056897
0.7238	0.0762	0.2000	330.50	330.84	0.9775	0.0133	0.0093	0.999473	0.884097	1.051131
0.6876	0.0724	0.2400	332.02	331.23	0.9744	0.0137	0.0119	1.000474	0.889294	1.045727
0.6515	0.0685	0.2800	333.63	333.93	0.9710	0.0140	0.0149	1.001719	0.894683	1.040668
0.6153	0.0647	0.3200	335.34	336.07	0.9671	0.0144	0.0184	1.003190	0.900318	1.035956
0.5601	0.4012	0.0387	337.06	336.97	0.8968	0.1006	0.0026	0.969970	0.945072	1.087394
0.5791	0.0609	0.3600	337.15	337.77	0.9626	0.0149	0.0225	1.004887	0.906169	1.031574
0.5429	0.0571	0.4000	339.10	338.59	0.9574	0.0153	0.0273	1.006807	0.912232	1.027513
0.4801	0.4741	0.0458	340.98	340.97	0.8530	0.1434	0.0036	0.959318	0.959029	1.082857
0.5067	0.0533	0.4400	341.18	341.54	0.9513	0.0158	0.0329	1.008943	0.918506	1.023763
0.4399	0.5106	0.0495	343.08	342.27	0.8255	0.1702	0.0043	0.953524	0.965224	1.079848
0.4400	0.5106	0.0494	343.08	343.69	0.8256	0.1701	0.0043	0.953528	0.965217	1.079870
0.4705	0.0495	0.4800	343.42	344.52	0.9441	0.0163	0.0396	1.011290	0.924986	1.020317
0.4001	0.5471	0.0528	345.26	346.01	0.7938	0.2012	0.0051	0.947469	0.970863	1.076486
0.4343	0.0457	0.5200	345.86	346.63	0.9354	0.0169	0.0477	1.013841	0.931670	1.017167
0.3601	0.5836	0.0563	347.55	347.30	0.7567	0.2374	0.0060	0.941143	0.975996	1.072662
0.3981	0.0419	0.5600	348.51	348.84	0.9250	0.0174	0.0576	1.016588	0.938553	1.014304
0.3619	0.0381	0.6000	351.41	351.23	0.9122	0.0180	0.0698	1.019524	0.945630	1.011722
0.2800	0.6565	0.0635	352.43	352.53	0.6632	0.3285	0.0083	0.927771	0.984736	1.063815
0.3257	0.0343	0.6400	354.61	353.74	0.8963	0.0186	0.0850	1.022638	0.952894	1.009415
0.2400	0.6930	0.0670	355.01	354.94	0.6048	0.3855	0.0097	0.920741	0.988360	1.058869
0.2895	0.0305	0.6800	358.16	356.44	0.8763	0.0192	0.1045	1.025918	0.960337	1.007375
0.1998	0.7294	0.0708	357.70	358.04	0.5366	0.4519	0.0114	0.913501	0.991503	1.053537
0.1599	0.7659	0.0742	360.45	360.57	0.4580	0.5286	0.0134	0.906056	0.994161	1.047967
0.2533	0.0267	0.7200	362.14	361.89	0.8504	0.0198	0.1298	1.029349	0.967949	1.005598
0.1201	0.8024	0.0775	363.28	362.65	0.3672	0.6172	0.0157	0.898417	0.996350	1.042124
0.0801	0.8389	0.0810	366.19	365.18	0.2618	0.7199	0.0184	0.890567	0.998089	1.035957
0.2172	0.0228	0.7600	366.62	366.14	0.8167	0.0202	0.1632	1.032921	0.975695	1.004074
0.0400	0.8753	0.0847	369.17	369.30	0.1399	0.8385	0.0216	0.882529	0.999381	1.029494
0.0000	0.9118	0.0882	372.20	372.40	0.0000	0.9748	0.0252	0.874282	1.000229	1.022808
0.0185	0.7601	0.2214	373.77	374.44	0.0735	0.8605	0.0661	0.900621	1.000634	1.018697
0.0216	0.7200	0.2584	374.39	375.12	0.0875	0.8339	0.0786	0.907703	1.000845	1.017357
0.0247	0.6801	0.2952	375.03	375.83	0.1022	0.8062	0.0916	0.914845	1.001079	1.016081
0.0278	0.6399	0.3323	375.70	376.30	0.1175	0.7772	0.1052	0.922132	1.001338	1.014844
0.0309	0.5998	0.3693	376.39	376.81	0.1335	0.7470	0.1195	0.929492	1.001617	1.013660
0.0340	0.5599	0.4061	377.11	377.45	0.1502	0.7155	0.1343	0.936905	1.001912	1.012532
0.0370	0.5198	0.4432	377.86	378.03	0.1673	0.6826	0.1501	0.944443	1.002237	1.011427
0.0401	0.4801	0.4798	378.62	378.74	0.1856	0.6480	0.1664	0.951991	1.002560	1.010392
0.0432	0.4401	0.5167	379.42	379.42	0.2049	0.6113	0.1837	0.959681	1.002902	1.009386
0.0463	0.4001	0.5536	380.26	380.54	0.2252	0.5727	0.2021	0.967452	1.003255	1.008417
0.0494	0.3598	0.5908	381.14	382.09	0.2467	0.5316	0.2218	0.975363	1.003624	1.007475
0.0525	0.3199	0.6276	382.05	382.14	0.2692	0.4882	0.2425	0.983272	1.003994	1.006578
0.0556	0.2799	0.6645	383.01	382.61	0.2932	0.4421	0.2647	0.991276	1.004372	1.005709
0.0587	0.2398	0.7015	384.02	384.42	0.3187	0.3927	0.2887	0.999372	1.004758	1.004867
0.0617	0.2000	0.7383	385.10	384.96	0.3453	0.3402	0.3145	1.007478	1.005160	1.004054
0.0648	0.1601	0.7751	386.23	385.93	0.3742	0.2834	0.3423	1.015663	1.005549	1.003270
0.0679	0.1199	0.8122	387.44	387.44	0.4054	0.2216	0.3730	1.023970	1.005948	1.002504
0.0710	0.0800	0.8490	388.72	389.52	0.4390	0.1546	0.4064	1.032266	1.006340	1.001766
0.0741	0.0399	0.8860	390.10	390.40	0.4755	0.0810	0.4435	1.040651	1.006738	1.001045
0.0772	0.0000	0.9228	391.59	391.67	0.5153	0.0000	0.4847	1.049031	1.007130	1.000347

[a] Deviations $dT = 0.44$; $\Delta T = 1.72$.

in these systems, which reveal that the deviations of Wilson, NRTL, Margules, van Laar, and UNIQUAC equations are reasonably small in Table 5. Since the superiority of one method over the others is not always obvious, practice must rely on experience and analogy. The comprehensive comparisons of five of the methods (Wilson, NRTL, Margules, van Laar, and UNIQUAC) were made in Table 5. From the data analysis, the temperature deviations between the experimental and the calculated values of five different types of model are very similar in the three binary systems, and the vapor-phase mole fraction deviations between calculated values from *Tpx* 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 5, the absolute average deviations *dT* of the difference between the boiling point temperature from experiment and the bubbling point temperature from calculation by Wilson model parameters for the three binary systems are (0.23, 0.16, and 0.17) °C, respectively. The absolute average deviations *dy* of the difference between vapor-phase mole fraction from *Tpx* calculations and from Wilson model calculations are 0.0052, 0.0044, and 0.0036, respectively.

Thermodynamic Consistency Tests Based on VLE Calculations. To analyze the punctual consistency for VLE data, we have followed the protocol suggested by Fredenslund et al.[12] 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 five different models (Wilson, NRTL, Margules, van Laar, and UNIQUAC) of the three binary systems are illustrated in Table

6. In the residual method,[12] a set of data is considered consistent if the averages of the absolute values of the residuals for vapor phase in mole fraction are smaller than 0.01. Moreover, if the pressure residuals are smaller than 1.33 kPa, the data are also considered consistent. We can conclude the residuals show a random scatter distribution about the zero line, as confirmed also by the small numerical value of the mean absolute deviation of the vapor-phase composition, as shown in Table 6. 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 zero 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, van Laar and UNIQUAC model given in Table 5 were used to predict the VLE data of the ternary system. VLE data for propanal (1) + propanol (2) + propanoic acid (3) at 101.325 kPa including the 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 $y_{1,\text{cal}}$, $y_{2,\text{cal}}$, and $y_{3,\text{cal}}$, activity coefficients γ_1, γ_2, and γ_3, and the average deviation in the bubble temperatures using the Wilson equation correlation are listed in Table 7. The absolute average and maximum deviation between the boiling point from experimental data and the bubble point from Wilson model calculation are (0.44 and 1.72) °C, respectively. Meanwhile, the average and maximum deviations using NRTL, Margules, van Laar, and UNIQUAC models individually are 0.48 °C, 1.65 °C; 0.53 °C, 1.76 °C; 0.60 °C, 1.82 °C; and 0.54 °C, 1.76 °C. The diagram of VLE for the ternary system propanal (1) + propanol (2) + propanoic acid (3) at 101.325 kPa is shown in Figure 8.

Conclusions

VLE data for the ternary system propanal + propanol + propanoic acid and three constituent binary systems, propanal + propanol, propanal + propanoic acid, and propanol + propanoic acid, were determined by different liquid-phase compositions using a novel pump ebulliometer at 101.325 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, van Laar, and UNIQFAC equations, respectively. It was shown that the deviations of Wilson, NRTL, Margules, van Laar, and UNIQFAC equations are reasonably small. The VLE data of ternary system were predicted by Wilson, NRTL, Margules, van Laar, and UNIQFAC equations. The calculated bubble points accorded well with the experimental data. The results show that the calculated bubble point is fitted by the models that satisfy the need for the design and operation of separation process in the chemistry industry. Moreover, the method will provide theoretical guidance for the research of VLE data of strongly associating systems of vapor and liquid phases in nonideal behavior.

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