

Research Article

Computation of Isobaric Vapor-Liquid Equilibrium Data for Binary and Ternary Mixtures of Methanol, Water, and Ethanoic Acid from T , p , x , and H_m^E Measurements

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Vapor-liquid equilibrium (VLE) data for the strongly associated ternary system methanol + water + ethanoic acid and the three constituent binary systems have been determined by the total pressure-temperature-liquid-phase composition-molar excess enthalpy of mixing of the liquid phase (p , T , x , H_m^E) for the binary systems using a novel pump ebulliometer at 101.325 kPa. The vapor-phase compositions of these binary systems had been calculated from Tpx and H_m^E based on the Q function of molar excess Gibbs energy through an indirect method. Moreover, the experimental T , x data are used to estimate nonrandom two-liquid (NRTL), Wilson, Margules, and van Laar model parameters, and these parameters in turn are used to calculate vapor-phase compositions. The activity coefficients of the solution were correlated with NRTL, Wilson, Margules, and van Laar models through fitting by least-squares method. The VLE data of the ternary system were well predicted from these binary interaction parameters of NRTL, Wilson, 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 and the calculated bubble points.

1. Introduction

New strategies for the correlation and accurate prediction of the vapor-liquid equilibrium (VLE) data play a vital role in the distillation and separation process in chemical industry. The common technique for obtaining VLE data is by direct measurement on the system. That is to say, when the VLE is established, and phases are sampled and analyzed. Consequently, the experimental technique must be rather highly accurate 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. Accordingly, the behavior of the systems has 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. 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 components.

Several methods have been explored for the calculation of component behavior from gross solution behavior. Van Ness and coworkers have suggested the classification of these methods into two categories, direct and indirect methods [1]. The direct methods involve calculation of vapor compositions by integration of the coexistence equation, a first-order differential equation derived from the Gibbs-Duhem equation relating phase compositions at equilibrium. Hala and coworkers have given a detailed discussion of the basic direct method [2], and Van Ness and coworkers have

discussed techniques for handling nonconstant temperature or pressure conditions as well as nonideal vapor phase behavior [1, 3]. Moreover, in the total pressure method one can calculate γ from T , p , x measurements using an indirect method discussed by Mixon et al. [4].

Of all the methods, the indirect methods involve first the measurement, by some appropriate means, the temperature and total pressure of the system, the liquid-phase compositions, and subsequent calculation of vapor-phase compositions there from. These methods usually involve ascertaining which of selected solution equations to the Gibbs-Duhem equation lead to the best fit to the experimental data, and of the determination of the parametric values producing the best fit. For example, Barker has developed a procedure based on the assumption that the excess free energy can be represented as a polynomial function of composition [5].

There is a basic difference in the degree of rigor associated with the direct method and the indirect method of Barker. In the former, one makes no assumptions about the solution behavior for the nature of molecular interactions. Solution behavior is determined directly from the experimental data. The Barker method necessitates the assumption of a particular model and the estimation of its parameters, this deficiency in the method of Barker has been recognized by Tao, who has presented another indirect method in which the necessity for the a priori assumption of a particular functional form for the excess free energy has been removed. Tao's procedure involves calculation of the activity coefficient essentially by integration of an equation resembling the coexistence equation. His procedure, though indirect, retains the rigor usually associated with the direct method [6]. The method of Tao appears specific to binary systems and does not seem to be easily generalized. However, an indirect method such as that of Barker is readily and easily generalized to ternary and higher-ordered systems, but this method retains the disadvantage of lacking rigor as compared with the direct method.

This paper presents the vapor-liquid compositions calculated based on the measurements of VLE data for temperature-total pressure-liquid-phase composition-molar excess enthalpy energy of mixing of the liquid phase (T , p , x , H_m^E) at 101.325 kPa according to the Q function of molar excess Gibbs energy through an indirect method. We know that the reaction of methanol carboxylated with carbon monoxide is the most common and important technology for synthesis of ethanoic acid in the chemical industrial process. Modeling the thermodynamic properties and correlating and predicting the phase equilibria of a mixture involving associating components forming hydrogen bonding such as carboxylic acid remain a challenging problem, since such systems show extremely nonideal behavior and the formation of monomer, dimer, and even trimer in vapor and liquid phase. In addition, for the VLE measurements of vapor-phase components containing a highly volatile compound such as carboxylic acid, the accurate measurement of the vapor-phase composition can be difficult. Many attempts have been made to describe the vapor-liquid equilibria of carboxylic acid containing mixtures using the concept of multiscale association [7]. Arlt reported the isothermal VLE

data of a new apparatus for phase equilibria in reaction mixtures containing water with ethanoic acid and propanoic acid at (333 to 363) K [8]. Xu and Chuang have developed a new correlation for the prediction of the vapor-liquid equilibrium of methyl acetate-methanol-water-ethanoic acid mixtures [9]. Sawistowski and Pilavakis explored the vapor-liquid equilibrium behavior of the quaternary system methyl acetate-methanol-water-ethanoic acid modeled by using the Margules equation in combination with Marek's method for the association of ethanoic acid [10]. Moreover, Guan et al. investigated that the isobaric vapor-liquid equilibria for water + ethanoic acid + *n*-pentyl acetate, isopropyl acetate, *N*-methyl pyrrolidone, or *N*-methyl acetamide were correlated and predicted by both the nonrandom two-liquid (NRTL) and universal quasichemical activity coefficient (UNIQUAC) models used in combination with the Hayden-O'Connell (HOC) method [11–14]. In our recent work, we have concluded that the VLE data for the associating systems containing the carboxylic acid system can be correlated and predicted [15, 16]. Although the VLE data of the mixture containing the associating systems were previously reported by the different research groups [17–21], respectively, the VLE data for the associating binary system containing the carboxylic acid have been still extensively studied because of the extensive association effects occurring in them and the difficulty of properly calculating the activity coefficients [22–25]. Nominally, the system is binary but in practice, it is multicomponent. Because the carboxylic acid monomer undergoes partial dimerization and even higher polymerization. This association is attributed to the formation of hydrogen bonds and occurs in both the vapor and liquid phase. 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. The VLE data for methanol + water + ethanoic acid ternary system and the constituent binary systems are indispensable in distillation separation process to the product of methanol carboxylation through the correlation and prediction by the new method, while some of the isobaric VLE data for these binary and ternary systems are correlated and predicted earlier [9–25]. To provide the new correlation and prediction for 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 using the new method. This paper reports a novel correlation and prediction for the VLE data for these systems containing the associating component that has been developed. The VLE data for methanol + water + ethanoic acid system and constituent binary systems were measured by the total pressure-temperature-liquid-phase composition-molar excess enthalpy of mixing of the liquid phase (p , T , x , H_m^E) for the binary systems using the novel pump-ebulliometer at 101.325 kPa. Owing to the association of ethanoic acid molecules, Marek's method in combination with Hayden-O'Connell (HOC) model was used to deal with the associating properties of the liquid and vapor phase and the nonideality of vapor phase, respectively [26–28]. However, the nonideality of liquid phase was corrected by the calculation of its activity coefficient, which was obtained

based on NRTL, Wilson, Margules, and van Laar models as the function of T , x through the nonlinear fit of the least-squares method. NRTL, Wilson, Margules, and van Laar models were applied to correlate the VLE data for the three constituent binary systems, and the model parameters together with the deviations of temperature and vapor-phase molar fractions calculated from T , p , x , H_m^E according to the Q function of molar excess Gibbs energy by the indirect method were obtained by the least-squares method. The VLE data of the ternary system were well predicted from these binary interaction parameters of NRTL, Wilson, Margules, and van Laar 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 points. The excess Gibbs free energies for these binary systems as the function of liquid-phase composition and activity coefficient were calculated through the activity coefficient correlation to NRTL model parameters with the experimental data.

2. Modeling Section

There is an added complexity when working with carboxylic acids because they associate in the vapor and liquid phases. This association can be represented by assuming that the organic acid exists as monomer and dimer according to the Marek's method [26, 27]. This fact, coupled with the necessity for much analytical work, tends to enhance interest in exploring the new strategies for correlation and prediction of the VLE data for the systems containing the associating carboxyl acid.

According to the Marek's chemical theory, there are monomer and dimer carboxylic acid molecules in both liquid and vapor phases. The equilibrium constant of vapor-phase dimerization, C_E^V , is calculated by the expression

$$C_E^V = \frac{y_D^*}{(y_M^*)^2 p} \quad (1)$$

and the equilibrium constant of liquid-phase dimerization, C_E^L , is calculated by the expression

$$C_E^L = \frac{x_D^*}{(x_M^*)^2}. \quad (2)$$

In equations mentioned above, y_D^* and x_D^* are the mole fractions of dimers of ethanoic acid molecules in both vapor and liquid phases, respectively, and C_E^V can be defined as the function of temperature by the expression obtained from the literature [27]

$$C_E^V = \exp\left(\frac{7290}{T} - 21.980\right), \quad (3)$$

where C_E^V was presented in kPa^{-1} and T in K.

When the dimers of ethanoic acid molecules mainly exist, the binary system for the methanol or water (1) + ethanoic acid (2) is nominally binary; however, it is actually ternary for the methanol or water (1) + monomer ethanoic acid (M) + dimer ethanoic acid (D) system. In this system, the

mole fractions of vapor-liquid equilibrium phases are y_1^* , y_M^* , y_D^* , x_1^* , x_M^* , and x_D^* , respectively. Therefore, the VLE relations of the nonassociating and associating components are individually calculated by the expressions

$$\begin{aligned} p y_1^* \Phi_1 &= p_1^s x_1^* \gamma_1, \\ p y_M^* \Phi_M &= p_M^s x_M^* \gamma_M, \\ p y_D^* \Phi_D &= p_D^s x_D^* \gamma_D. \end{aligned} \quad (4)$$

In (4), the actual mole fractions can be denoted by the apparent mole fractions of easily determined components (y_1 , y_2 , x_1 , and x_2 multiplied by a modified coefficient. Likewise, the measured apparent vapor pressure saturated of ethanoic acid (p_2^s) multiplied by a modified coefficient can also denote the actual vapor pressures saturated of monomer and dimer ethanoic acid (p_M^s , p_D^s). Consequently, the apparent compositions and vapor pressures saturated substitute for the actual ones, and the VLE relation of the nonassociating component, methanol or water (1), is expressed by

$$p y_1 \alpha_1 \Phi_1 = p_1^s x_1 \beta_1 \gamma_1, \quad (5)$$

where

$$\alpha_1 = \frac{2}{(2 - y_2)} \frac{1 - y_2 - \sqrt{1 + 4C_E^V p y_2 (2 - y_2)}}{1 + \sqrt{1 + 4C_E^V p y_2 (2 - y_2)}}, \quad (6)$$

$$\beta_1 = \frac{2}{(2 - x_2)} \frac{1 - x_2 - \sqrt{1 + 4C_E^L p x_2 (2 - x_2)}}{1 + \sqrt{1 + 4C_E^L p x_2 (2 - x_2)}}, \quad (7)$$

and for ethanoic acid (2), which is the associating component, its relation is expressed by

$$p y_2 \alpha_2 \Phi_2 = p_2^s \theta_2^s x_2 \beta_2 \gamma_2, \quad (8)$$

where

$$\alpha_2 = \frac{2}{1 + \sqrt{1 + 4C_E^V p y_2 (2 - y_2)}}, \quad (9)$$

$$\beta_2 = \frac{2}{1 + \sqrt{1 + 4C_E^L x_2 (2 - x_2)}}, \quad (10)$$

$$\theta_2^s = \frac{-1 + \sqrt{1 + 4C_E^V p_2^s}}{2C_E^V p_2^s}. \quad (11)$$

In (5) to (11), α_1 and α_2 can be regarded as modified coefficients for the deviation from ideality in vapor phase on account of association. The fugacity of coefficients Φ_1 and Φ_2 is not negligible, and their values were obtained through the HOC model [28]. From another point of view, θ_2^s can be viewed as a modified coefficient for the vapor pressure of the associating component. Moreover, β_1 and β_2 denote modified coefficients of the deviation from ideality in the liquid phase by reason of the existence of association, and γ_1 and γ_2 express the deviation from ideality in liquid

TABLE 1: Physical properties of the pure compounds: densities ρ , refractive indexes n_D at 298.15 K and normal boiling points T_b .

Compound	$\rho/\text{kg}\cdot\text{m}^{-3}$		n_D		T_b/K	
	expt	lit ^a	expt	lit ^a	expt	lit ^a
Methanol	786.44	786.37	1.3264	1.3265	337.71	337.69
Water	997.01	997.05	1.3324	1.3325	373.16	373.15
Ethanoic acid	1043.90	1043.92	1.3716	1.3718	391.53	391.15

^aRiddick et al. [29].

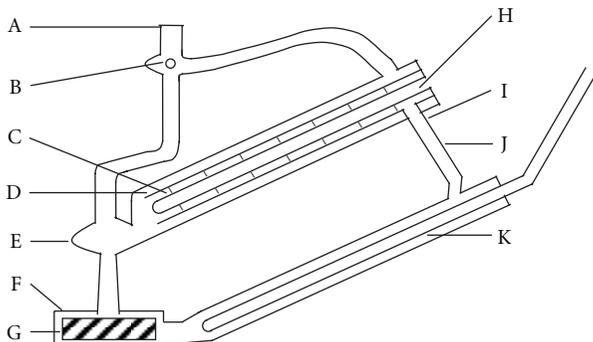


FIGURE 1: Schematic illustration for the structure of pump ebulliometer. (A) Normal distilling adaptor; (B) feed inlet; (C) coiled glass thread; (D) constant temperature introducing tube; (E) mixed vial section; (F) magnetic recirculating bump; (G) magnetic stirrer; (H) measured thermowell (filled with conducting oil); (I) tube window to observe in VLE status; (J) internal heating tube; (K) part-heating tube (resistance heating wire inserted).

phase because of other factors. Herein, in liquid phase, the modified coefficients of deviation from ideality, β_1 and β_2 , can be incorporated to the activity coefficients, γ_1 and γ_2 , respectively. So (5) and (8) are obtained by the expressions

$$p\gamma_1\alpha_1\Phi_1 = p_1^s x_1 \gamma_1, \quad (12)$$

$$p\gamma_2\alpha_2\Phi_2 = p_2^s \theta_2^s x_2 \gamma_2. \quad (13)$$

3. Experimental Section

3.1. Materials. Methanol (99.8 mass %) and ethanoic acid (99.8 mass %) were purchased from Sigma. The purities of the chemicals are provided by the manufacturer's specifications. Ultra sound was used to dispel the solvent air in the materials, which were dried on molecular sieve (pore diameter 30 nm from Fluka) to remove all possible traces of moisture before use, but no other treatments were applied. The densities and refractive indices at 298.15 K and normal boiling points at 101.325 kPa of the pure component were compared with the literature values of Riddick et al. [29]. The results show that the measured values are approximately in agreement with those of the literature, as presented in Table 1. The measurement method of the composition dependence of densities and refractive indices has been previously reported [30].

3.2. Apparatus and Procedure. A new type of magnetic pump ebulliometer described in detail by Qiu et al. [31] was used

to measure the boiling points with different liquid phase compositions at the 101.325 kPa. The experimental main apparatus for pump-ebulliometer is schematically shown in Figure 1. The recirculation still is entirely constructed from borosilicate glass. The main parts are a magnetic recirculating bump (F), a magnetic stirrer (G), a thermo-well (filled with a conducting oil) provided to enable good measurement of equilibrium temperature (H), a part-heating tube (resistance heating wire inserted) (K), and a tube window to observe in VLE status (I). The apparatus is an all-glass dynamic recirculation still with total volume of about $1.00 \times 10^{-4} \text{ m}^3$. During the run, to avoid the over heating, 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 part-heating tube (K) to partially heat the known mass of the material. The equilibrium pressure was measured using a Fischer digital manometer with a precision of $\pm 0.01 \text{ kPa}$. The pressure measurement for the manometer had an uncertainty of $\pm 0.07 \text{ kPa}$, as provided by the manufacturer's specifications. The total uncertainty of calibration and pressure measurement is estimated to be $\pm 0.15 \text{ kPa}$ because of the uncertainty of the calibration and measurement errors. Since the barometric pressure changed slightly, the experimental temperatures of the systems were automatically calibrated to that at 101.325 kPa with self-adjusted pressure system. The temperature was measured using a Heraeus QuaT100 quartz thermometer with a thermosensor, with an accuracy of $\pm 0.01 \text{ K}$. The calibration of the thermometers was carried out at the accredited calibration laboratory (Quality and Technique Bureau, Anhui). The total uncertainty of calibration and temperature measurement is evaluated to be $\pm 0.085 \text{ K}$ because of the uncertainty of the calibration, the probe's position, and the pressure fluctuations. The equilibrium temperature, T , was measured by means of the thermosensor inserted into the thermowell (filled with conducting oil) (H). In each experiment, a known mass of the material was introduced from the injector into the still from feed inlet (B) and heated to equilibrium boiling point of the system 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 $\pm 0.0001 \text{ g}$. The values of mole fraction were reproducible to ± 0.0001 and have uncertainty of 0.01%. The ebulliometer was charged with the mixture of desired composition, and the boiler was then heated by nichrome wire wound around the boiler. After the liquid mixture started boiling, the bubbles along with the drops of liquid slowly spurted on the

thermowell one by one through the tube window observed in VLE status (I). When the VLE state was attained by adjusting the pressure to 101.325 kPa, it remained constant for 20 min to ensure the stationary state, and then the boiling temperature was measured.

A flow microcalorimeter (model 2107, LKB produkter, Bromma, Sweden) was applied to measure the molar excess enthalpies, H_m^E , of the mixtures. The electrical-calibration apparatus and its operating procedure have been described elsewhere by Francesconi and Comelli [34]. Two automatic burets (ABU, Radiometer, Copenhagen, Denmark) were used to pump liquids through the mixing cell of the calorimeter. The performance of the calorimeter was checked by measuring the H_m^E of the test mixture hexane + cyclohexane system reported by Gmehling [35]. Agreement with literature is better than 0.5% over the central range of mole fraction of hexane.

The uncertainties in mole fraction and H_m^E are estimated to be 0.0005 and 0.5%, respectively. 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 , and H_m^E data based on the Q function (the function of molar excess Gibbs energy) by the indirect method.

4. Results and Discussion

4.1. Calculation of Vapor-Phase Mole Fraction y for the Binary Systems from Tpx and H_m^E . The vapor-phase mole fraction y_i of the components was calculated from

$$y_i \Phi_i p = x_i \gamma_i p_i^s, \quad (14)$$

and the fugacity of coefficients Φ_i of the components was obtained by the expression

$$\Phi_i = \frac{\hat{\varphi}_i^V}{\varphi_i^s} \exp \left[-\frac{V_i^L (p - p_i^s)}{RT} \right], \quad (15)$$

where $\hat{\varphi}_i^V$ 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, T is the experimental temperature, p is the total pressure (101.325 kPa), and p_i^s is the vapor pressure of pure component i . The Antoine equations were applied to calculate the values of these vapor pressures. The Antoine constants A_i , B_i , C_i , and the values of T_c , p_c , V_c , Z_c and ω were obtained from Shi et al. [36], as shown in Table 2. 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 [37].

According to the Gibbs-Duhem equation, any extensive molar thermodynamic property of a given phase, such as the Gibbs and Helmholtz energies, the enthalpy, and molar volume, must satisfy the following differential relation:

$$\left(\frac{\partial M}{\partial T} \right)_{p, x_j \neq i} dT + \left(\frac{\partial M}{\partial p} \right)_{T, x_j \neq i} dp - \sum_{i=1}^C x_i d\bar{M}_i = 0. \quad (16)$$

In (16) M is a general molar property, x_i the molar fraction of component i in the phase under consideration, $x_{j \neq i}$ the pertinent set of compositions, C the number of components, and \bar{M}_i the partial contribution of component i to M .

When considering VLE, the molar excess Gibbs energy, G^E , can be evaluated from measurable (T , p , x) data using activity coefficient relations. Replacing M by G^E/RT in the following equation yields the well-known relation

$$-\frac{H_m^E}{RT^2} dT + \frac{V_m^E}{RT} dp - \sum_{i=1}^C x_i d \ln \gamma_i = 0, \quad (17)$$

where H_m^E and V_m^E are the molar excess enthalpy and volume of mixing of the liquid phase. According to the thermodynamic principles, the activity coefficients γ_i of the components were calculated from the expression as follows:

$$Q = \frac{G^E}{RT} = \sum_{i=1}^C x_i \ln \gamma_i, \quad (18)$$

where Q is the function of molar excess Gibbs energy and combining (17) and (18) yields

$$d \left(\frac{G^E}{RT} \right) - \sum_{i=1}^C \ln \gamma_i dx_i = \sum_{i=1}^C x_i d \ln \gamma_i = -\frac{H_m^E}{RT^2} dT + \frac{V_m^E}{RT} dp. \quad (19)$$

Application to a binary system gives

$$d \left(\frac{G^E}{RT} \right) - \ln \frac{\gamma_1}{\gamma_2} dx_1 = -\frac{H_m^E}{RT^2} dT + \frac{V_m^E}{RT} dp. \quad (20)$$

Simultaneous solution of (18) and (20) yields

$$\begin{aligned} \ln \gamma_1 &= \frac{G^E}{RT} + x_2 \left[\frac{d}{dx_1} \left(\frac{G^E}{RT} \right) + \frac{H_m^E}{RT^2} \frac{dT}{dx_1} - \frac{V_m^E}{RT} \frac{dp}{dx_1} \right], \\ \ln \gamma_2 &= \frac{G^E}{RT} - x_1 \left[\frac{d}{dx_1} \left(\frac{G^E}{RT} \right) + \frac{H_m^E}{RT^2} \frac{dT}{dx_1} - \frac{V_m^E}{RT} \frac{dp}{dx_1} \right]. \end{aligned} \quad (21)$$

Equation (18) substituted into (21) reduced it to

$$\begin{aligned} \gamma_1 &= \exp \left[Q + (1 - x_1) \left(\frac{dQ}{dx_1} + \frac{H_m^E}{RT^2} \frac{dT}{dx_1} - \frac{V_m^E}{RT} \frac{dp}{dx_1} \right) \right], \\ \gamma_2 &= \exp \left[Q - x_1 \left(\frac{dQ}{dx_1} + \frac{H_m^E}{RT^2} \frac{dT}{dx_1} - \frac{V_m^E}{RT} \frac{dp}{dx_1} \right) \right]. \end{aligned} \quad (22)$$

For a binary system comprised of species 1 and 2 at VLE state, at constant pressure, $(dp/dx_1) = 0$, substitution into (22) reduced it to

$$\gamma_i = \exp \left[Q + (1 - x_i) \left[\left(\frac{dQ}{dx_i} \right) + \frac{H_m^E}{RT^2} \left(\frac{dT}{dx_i} \right) \right] \right], \quad (i = 1, 2). \quad (23)$$

The right-hand side, $(H_m^E/RT^2)(dT/dx_i)$, of (23) cannot be neglected. Proper use of (23) requires the availability

TABLE 2: Antoine coefficients of the compounds and published parameters [36] 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	A_i	B_i	C_i	T_c/K	p_c/MPa	$V_c/\text{m}^3 \cdot \text{kmol}^{-1}$	Z_c	ω
Methanol	7.19736	1574.99	-34.29	512.6	8.096	0.118	0.224	0.559
Water	7.07404	1657.46	-46.13	647.3	22.048	0.056	0.229	0.344
Ethanoic acid	6.42452	1479.02	-56.34	594.4	5.786	0.171	0.200	0.454

of heats of mixing as a function of composition and temperature. The activity coefficients γ_i of the components as functions of the excess Gibbs energy are as follows:

$$\gamma_1 = \exp \left\{ Q + (1 - x_1) \left[\left(\frac{dQ}{dx_1} \right) + \frac{H_m^E}{RT^2} \left(\frac{dT}{dx_1} \right) \right] \right\}, \quad (24)$$

$$\gamma_2 = \exp \left\{ Q - x_1 \left[\left(\frac{dQ}{dx_1} \right) + \frac{H_m^E}{RT^2} \left(\frac{dT}{dx_1} \right) \right] \right\}.$$

From (14), this equation is rearranged to obtain

$$y_i = \frac{x_i \gamma_i p_i^s}{\Phi_i p}. \quad (25)$$

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

$$\frac{x_1 \gamma_1 \phi_1^s p_1^s \exp \left[V_1^L (p - p_1^s) / RT \right]}{\hat{\phi}_1^V p} + \frac{x_2 \gamma_2 \phi_2^s p_2^s \exp \left[V_2^L (p - p_2^s) / RT \right]}{\hat{\phi}_2^V p} = 1. \quad (26)$$

In (26), solved for y_i by 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 $k = 0, 1, \dots, n$. In k difference point, we obtain

$$F_k = 1 - \left\{ \frac{x_1 \gamma_1 \phi_1^s p_1^s \exp \left[V_1^L (p - p_1^s) / RT \right]}{\hat{\phi}_1^V p} \right\}_k - \left\{ \frac{x_2 \gamma_2 \phi_2^s p_2^s \exp \left[V_2^L (p - p_2^s) / RT \right]}{\hat{\phi}_2^V p} \right\}_k = 0. \quad (27)$$

Meanwhile, (23) may be shown as follows:

$$\gamma_i|_k = \exp \left\{ Q_k + (1 - x_i|_k) \left[\frac{Q|_{k+1} - Q|_{k-1}}{2h} + \frac{H_m^E}{RT^2} \left(\frac{dT}{dx_1} \right) \Big|_k \right] \right\}. \quad (28)$$

And (27) is linearized to obtain:

$$-F_k = \Delta Q|_{k-1} \left(\frac{\delta F_k}{\delta Q|_{k-1}} \right) + \Delta Q|_k \left(\frac{\delta F_k}{\delta Q|_k} \right) + \Delta Q|_{k+1} \left(\frac{\delta F_k}{\delta Q|_{k+1}} \right). \quad (29)$$

The number of n linear equation from (28) is solved for $\Delta Q|_k$ by chasing method

$$Q_k^{j+1} = Q_k^j + t \Delta Q_k^j, \quad (30)$$

where t is relaxation factor, finally, y_{ik} ($k = 1 \sim n$) is obtained by difference method. The block diagram for calculation procedure was detailedly shown in Figure 2.

4.2. Calculation of Vapor-Phase Mole Fraction y for the Binary Systems from Model. There are many methods concerning the correlation and prediction of VLE data. The model-free approach data treatment of vapor-liquid equilibrium is also one of the best strategies for the correlation and prediction of VLE data. Wisniak's group has developed that the novel model-free computation techniques and limiting conditions have been applied to VLE data for azeotropic systems [42]. Moreover, Segura and coworkers reported that a model-free approach dealt with VLE data in application of ternary systems [38, 43]. For the three binary systems of this study, the activity coefficients were correlated with the NRTL [39], Wilson [40], Margules [41], and van Laar [44] equations, respectively. The interaction parameters optimized were achieved by the objective function (OF) minimized using the least-squares fitting as follows:

$$\text{OF} = \sum_{i=1}^N (x_{i,\text{cal}} - x_{i,\text{exp}})^2, \quad (31)$$

where N is the number of experimental points $x_{i,\text{cal}}$ and $x_{i,\text{exp}}$ are the liquid-phase mole fraction of component i calculated and experimental values from the (12) or (13) and from measured data, respectively.

Because carboxylic acids are always present in an associated form, like a dimer or trimer, in both the vapor and liquid phases even at low pressures, a significant deviation in fugacity coefficient may exist using the ideal gas assumption. To illustrate the deviation from ideal behavior, Marek's chemical theory and HOC model were applied to deal with the associating component and modify the deviation from idealities of vapor phase [26–28], respectively. 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 [37]. However, under isobaric conditions, the most volatile component cannot exist in the liquid state, only as superheated vapor. Hence, there is no way to calculate or measure this property for the molar volumes of the pure liquids. Therefore, the correct procedure for isobaric measurements is to calculate the overall values of A_{ij} and A_{ij} , as adjustable parameters,

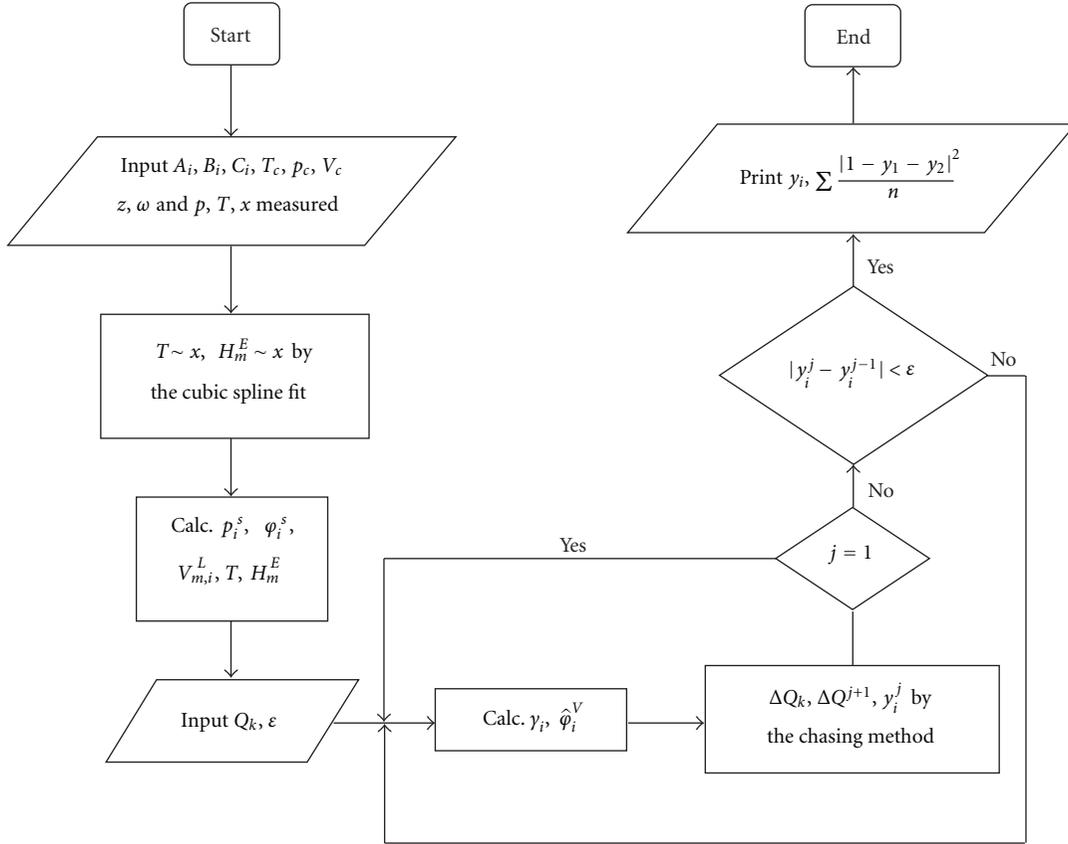


FIGURE 2: Block diagram for the calculation y by T, p, x , and H_m^E .

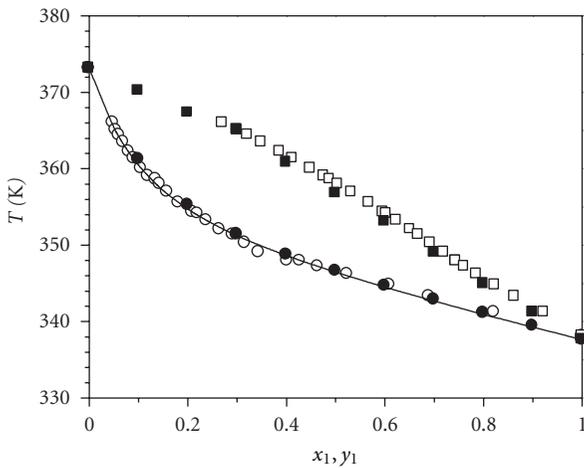


FIGURE 3: T - x_1 - y_1 diagram for methanol (1) + water (2) at 101.325 kPa: \square , vapor-phase mole fraction y_1 from Tpx and H_m^E ; \blacksquare , vapor-phase mole fraction y_1 from the literature [32, 33]; \circ , liquid-phase experimental temperature; \bullet , liquid-phase mole fraction x_1 from the literature [32, 33]; —, NRTL correlation temperature.

and not the values of the interaction excess energy. Hence, for Wilson model, A_{ij} and A_{ij} were reported as adjustable parameters.

The activity coefficients computed on the basis of NRTL model were used to evaluate 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 from the model, activity coefficients γ_1 and γ_2 using NRTL equation correlation, fugacity coefficients $\hat{\phi}_1^V$ and $\hat{\phi}_2^V$, and the molar excess enthalpies of mixing of the liquid phase H_m^E are included in Table 3. The T - x_1 - y_1 diagrams for the methanol (1) + water (2), methanol (1) + ethanoic acid (2), and water (1) + ethanoic acid (2) three binary systems at 101.325 kPa are shown in Figures 3, 4, and 5, respectively. The plot of excess Gibbs energy function G^E/RT versus liquid-phase mole fraction x_1 for the three binary systems is shown in Figure 6. All the mixtures exhibit deviations from ideality with a range that may be attributed to interactions leading to the formation of various associated aggregates. Observed nonideal behavior is indicative of the magnitude of experimental activity coefficients γ_i , as well as of the variation of excess Gibbs energy function, G^E/RT , with composition, as depicted in Figure 6. The obtained absolute maximum values of G^E/RT for the methanol (1) + water (2), methanol (1) + ethanoic acid (2), and water (1) + ethanoic acid (2) three binary systems are 0.1703, 0.0180, and 0.0892, respectively. The values of excess Gibbs energy

TABLE 3: VLE data for the methanol (1) + water (2), methanol (1) + ethanoic acid (2), and water (1) + ethanoic 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 NRTL equation correlation, fugacity coefficients $\hat{\phi}_1^V$ and $\hat{\phi}_2^V$, and molar excess enthalpies of mixing of the liquid phase H_m^E .

x_1	T_{exp}/K	T_{cal}/K	y_1	γ_1	$\hat{\phi}_1^V$	γ_2	$\hat{\phi}_2^V$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
Methanol (1) + water (2)								
0.0000	373.15	373.15	0.0000			1.0000	0.9882	0.00
0.0484	366.00	365.54	0.2704	2.1436	0.9852	1.0034	0.9875	225.74
0.0539	365.05	364.88	0.3009	2.1147	0.9849	1.0042	0.9875	248.74
0.0607	364.40	364.12	0.3213	2.0799	0.9846	1.0053	0.9874	276.88
0.0696	363.50	363.19	0.3492	2.0358	0.9843	1.0069	0.9874	312.53
0.0806	362.25	362.13	0.3866	1.9835	0.9839	1.0092	0.9873	354.36
0.0911	361.35	361.21	0.4126	1.9360	0.9836	1.0117	0.9872	392.94
0.1056	360.05	360.05	0.4492	1.8739	0.9832	1.0155	0.9871	443.59
0.1197	359.05	359.04	0.4762	1.8172	0.9829	1.0197	0.9870	489.29
0.1354	358.60	358.02	0.4885	1.7584	0.9826	1.0248	0.9869	538.32
0.1436	358.00	357.53	0.5047	1.7293	0.9824	1.0277	0.9869	562.20
0.1586	356.95	356.70	0.5323	1.6788	0.9822	1.0334	0.9868	602.83
0.1815	355.55	355.56	0.5677	1.6083	0.9819	1.0428	0.9867	659.52
0.2092	354.35	354.35	0.5969	1.5325	0.9815	1.0555	0.9865	719.43
0.2202	354.10	353.91	0.6031	1.5049	0.9814	1.0609	0.9865	741.25
0.2380	353.25	353.24	0.6237	1.4633	0.9812	1.0701	0.9864	772.62
0.2648	352.05	352.32	0.6519	1.4066	0.9809	1.0847	0.9862	812.77
0.2918	351.35	351.48	0.6681	1.3561	0.9807	1.1005	0.9861	846.82
0.3166	350.30	350.76	0.6923	1.3148	0.9805	1.1157	0.9860	870.15
0.3442	349.05	350.02	0.7197	1.2740	0.9803	1.1336	0.9859	889.06
0.4015	347.95	348.61	0.7431	1.2038	0.9800	1.1730	0.9856	909.80
0.4282	347.90	348.00	0.7443	1.1767	0.9798	1.1924	0.9854	911.28
0.4644	347.20	347.21	0.7613	1.1449	0.9796	1.2194	0.9853	903.04
0.5240	346.20	345.98	0.7860	1.1026	0.9793	1.2656	0.9850	869.55
0.6091	344.80	344.33	0.8231	1.0595	0.9789	1.3338	0.9845	783.83
0.6899	343.31	342.85	0.8633	1.0325	0.9785	1.3995	0.9840	666.92
0.8213	341.20	340.56	0.9221	1.0086	0.9779	1.5038	0.9832	419.31
1.0000	338.10	337.66	1.0000	1.0000	0.9771			0.00
Methanol (1) + ethanol acid (2)								
0.0000	390.15	391.04	0.0000			1.0000	0.9703	0.00
0.0359	387.32	386.23	0.1574	0.9388	0.9765	0.9999	0.9685	77.28
0.0410	386.21	385.56	0.1664	0.9393	0.9768	0.9999	0.9682	86.70
0.0648	383.89	382.68	0.2719	0.9419	0.9779	0.9997	0.9666	134.05
0.0741	382.73	381.90	0.3133	0.9428	0.9782	0.9996	0.9660	149.55
0.0859	381.20	380.60	0.3333	0.9441	0.9787	0.9995	0.9652	171.14
0.1040	380.03	379.06	0.3830	0.9460	0.9791	0.9992	0.9639	205.37
0.1280	378.46	377.35	0.4602	0.9485	0.9797	0.9988	0.9622	245.43
0.1629	375.62	374.70	0.5213	0.9521	0.9802	0.9981	0.9595	299.80
0.1919	373.21	372.43	0.5873	0.9551	0.9805	0.9973	0.9572	341.32
0.2510	369.31	368.44	0.6495	0.9609	0.9808	0.9954	0.9528	411.44
0.3391	364.35	363.56	0.7538	0.9692	0.9809	0.9916	0.9461	490.73
0.4401	358.54	357.71	0.8232	0.9776	0.9805	0.9857	0.9388	536.56
0.5829	351.77	350.75	0.8999	0.9874	0.9797	0.9748	0.9292	526.43
0.7050	346.47	346.39	0.9389	0.9936	0.9790	0.9633	0.9217	449.37
0.7509	344.90	344.06	0.9533	0.9955	0.9787	0.9583	0.9189	401.45
0.8109	342.81	342.35	0.9693	0.9974	0.9783	0.9515	0.9155	330.61
0.8711	341.60	340.75	0.9766	0.9988	0.9779	0.9442	0.9122	241.41
0.9161	339.65	340.00	0.9859	0.9995	0.9776	0.9384	0.9097	163.78
1.0000	338.15	337.66	1.0000	1.0000	0.9771			0.00

TABLE 3: Continued.

x_1	T_{exp}/K	T_{cal}/K	y_1	γ_1	$\hat{\phi}_1^V$	γ_2	$\hat{\phi}_2^V$	$H_m^E/\text{J}\cdot\text{mol}^{-1}$
Water (1) + ethanoic acid (2)								
0.0000	390.15	391.04	0.0000			1.0000	0.9703	0.00
0.0665	387.22	387.67	0.1140	1.4161	0.9899	1.0025	0.9693	245.31
0.0749	387.00	387.31	0.1288	1.4046	0.9898	1.0031	0.9692	273.17
0.0855	386.48	386.88	0.1603	1.3903	0.9897	1.0040	0.9691	307.50
0.0995	385.86	386.34	0.1938	1.3722	0.9896	1.0054	0.9689	350.32
0.1507	384.16	384.60	0.2802	1.3117	0.9892	1.0121	0.9683	489.63
0.1722	383.44	383.96	0.3155	1.2888	0.9891	1.0156	0.9681	540.35
0.1926	382.99	383.39	0.3375	1.2684	0.9890	1.0193	0.9679	585.57
0.2168	382.39	382.77	0.3676	1.2458	0.9890	1.0242	0.9677	632.34
0.2502	381.53	381.98	0.4101	1.2171	0.9889	1.0316	0.9674	689.92
0.2936	380.94	381.06	0.4407	1.1838	0.9887	1.0425	0.9670	750.61
0.3303	380.20	380.36	0.4815	1.1589	0.9887	1.0528	0.9667	788.98
0.3756	379.40	379.57	0.5253	1.1318	0.9886	1.0666	0.9663	821.39
0.4465	378.27	378.48	0.5890	1.0965	0.9885	1.0908	0.9658	841.59
0.4946	377.61	377.82	0.6274	1.0768	0.9885	1.1087	0.9654	836.35
0.5615	376.80	376.99	0.6777	1.0543	0.9884	1.1355	0.9649	802.60
0.6036	376.24	376.51	0.7137	1.0427	0.9884	1.1533	0.9645	767.63
0.6517	375.59	376.00	0.7546	1.0315	0.9884	1.1746	0.9642	714.78
0.7067	375.11	375.46	0.7849	1.0213	0.9884	1.1998	0.9637	639.01
0.7045	375.11	375.48	0.7848	1.0217	0.9884	1.1988	0.9638	642.76
0.7507	374.71	375.05	0.8173	1.0148	0.9883	1.2207	0.9634	568.24
0.8008	374.31	374.62	0.8501	1.0091	0.9883	1.2451	0.9630	475.20
0.8723	373.80	374.05	0.9011	1.0035	0.9883	1.2809	0.9624	323.52
0.9116	373.54	373.76	0.9315	1.0016	0.9883	1.3009	0.9620	230.13
0.9546	373.24	373.45	0.9630	1.0004	0.9883	1.3231	0.9616	121.95
1.0000	373.15	373.15	1.0000	1.0000	0.9882			0.00

TABLE 4: Correlation parameters for activity coefficients, average deviation for studied systems and vapor-phase composition mean absolute deviation from the literatures.

Equation	Parameters or deviations	Methanol (1) + water (2)	Methanol (1) + ethanoic acid (2)	Water (1) + ethanoic acid (2)
NRTL ^a	$(g_{12} - g_{11})/\text{J}\cdot\text{mol}^{-1}$	-436.50	-85.50	-352.42
	$(g_{21} - g_{22})/\text{J}\cdot\text{mol}^{-1}$	1159.55	0.98	715.43
	α_{12}	0.241	0.30	0.23
	dT/K	0.28	0.51	0.33
	dy	0.0072	0.0054	0.0096
Wilson ^a	$\Lambda_{12}/\text{J}\cdot\text{mol}^{-1}$	389.37	50.46	644.71
	$\Lambda_{21}/\text{J}\cdot\text{mol}^{-1}$	368.45	95.58	-87.59
	dT/K	0.43	0.47	0.64
	dy	0.0036	0.0059	0.0053
Margules ^b	A_{12}	0.95	0.12	0.29
	A_{21}	0.65	-0.46	0.57
	dT/K	0.37	0.32	0.56
	dy	0.0049 (0.0057) ^c	0.0075 (0.0234) ^c	0.0086 (0.0123) ^c
van Laar ^b	A_{12}	0.86	0.24	0.32
	A_{21}	0.56	0.03	0.55
	dT/K	0.27	0.58	0.47
	dy	0.0069	0.0078	0.0098

^aWilson's interaction parameters ($\text{J}\cdot\text{mol}^{-1}$), NRTL's interaction parameters ($\text{J}\cdot\text{mol}^{-1}$). ^bMargules and van Laar interaction parameters (dimensionless). $dT = \sum |T_{\text{exp}} - T_{\text{cal}}|/N$; N : number of data points; T_{cal} : calculated bubble point from model, K; T_{exp} : experimental boiling point temperature, K. $dy = \sum |y_{\text{cal}} - y_{\text{mod}}|/N$; N : number of data points; y_{cal} : calculated vapor-phase mole fraction from T_{px} ; y_{mol} : calculated vapor-phase mole fraction from model. ^cThe values in parentheses from the literatures [38–41].

function G^E/RT are positive for methanol (1) + water (2) and water (1) + ethanoic acid (2) binary systems. However, for methanol (1) + ethanoic acid (2) system, the values of those are negative in the overall range of mole fraction. G^E/RT values follow the order methanol (1) + water (2) > water (1) + ethanoic acid (2) > methanol (1) + ethanoic acid (2). The absolute maximum value of G^E/RT is approximate at an equimolar fraction in three binary systems. Figures 3–5 show that the comparison of the predicted vapor-phase and experimental liquid-phase compositions with those of the literature [10, 11, 32, 33]. Comparing with the values of vapor-phase and liquid-phase component from the literatures, the values of those from the paper are in good agreement with the literature, as shown in Figures 3–5. The results have demonstrated that the methods for Tpx and H_m^E are appropriate for representing the experimental data of the three binary systems. The optimum model interaction parameter of liquid activity coefficient and the absolute average deviations for the different models, and from Tpx and H_m^E 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 reveal that the deviations of NRTL, Wilson, Margules, and van Laar equations are reasonably small in Table 4. For comparison, the mean deviations obtained by Gmehling and Onken [32, 33, 45, 46] are also shown in the Table 4. It can seem that two sets of deviation values are comparable. 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 (NRTL, Wilson, van Laar, and Margules) were made in Table 4. From the data analysis, the temperature deviations between the experimental and calculated values of four 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 H_m^E , 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 boiling point temperature from experiment and bubbling point temperature from calculation by NRTL model parameters for the three binary systems are 0.28°C, 0.51°C, and 0.33°C, respectively. And the absolute average deviations dy of the difference between vapor-phase mole fraction from Tpx and H_m^E calculation and from NRTL model calculation are 0.0072, 0.0054, and 0.0096, respectively.

4.3. Correlation and Prediction of VLE of Ternary System. The binary interaction parameters of the NRTL, Wilson, Margules, and van Laar model given in Table 4 were used to correlate and predict the VLE data of the ternary system. VLE data for methanol (1) + water (2) + ethanoic acid (3) at 101.325 kPa included liquid-phase mole fraction x_1 , x_2 , and x_3 , experimental boiling point temperature T_{exp} , calculated bubble point temperature T_{cal} , calculated vapor-phase mole fraction y_1 , y_2 , and y_3 , activity coefficients γ_1 , γ_2 , and γ_3 , the average deviation in the bubble temperatures of the ternary system using NRTL equation correlation listed in Table 5. The absolute average and maximum deviation

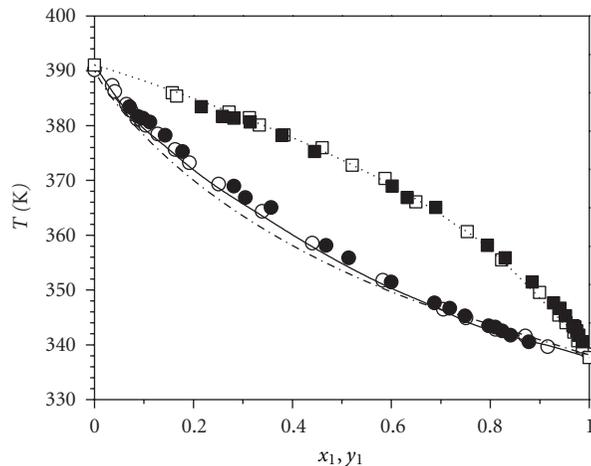


FIGURE 4: T - x_1 - y_1 diagram for methanol (1) + ethanoic acid (2) at 101.325 kPa: \square , vapor-phase mole fraction y_1 from Tpx and H_m^E ; \blacksquare , vapor-phase mole fraction y_1 from literature [10]; —, dot line, vapor-phase mole fraction y_1 with Block diagram for the calculation y by T , p , x , and H_m^E neglected from our previous work [15]; \circ , liquid-phase experimental temperature; \bullet , liquid-phase experimental temperature from literature [10]; - · - ·, dash dot, liquid-phase experimental temperature from our previous work [15]; —, NRTL correlation temperature.

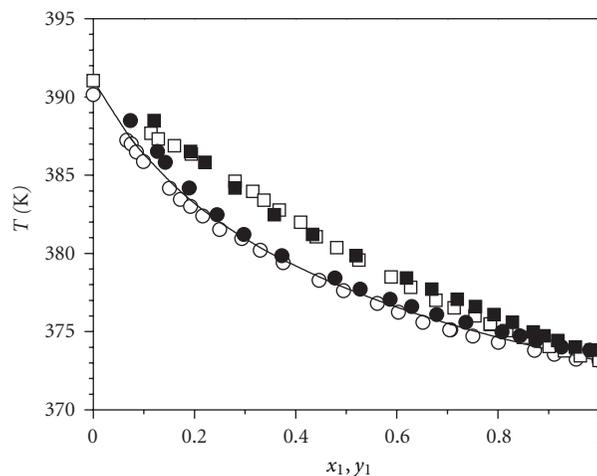


FIGURE 5: T - x_1 - y_1 diagram for water (1) + ethanoic acid (2) at 101.325 kPa: \square , vapor-phase mole fraction y_1 from Tpx and H_m^E ; \blacksquare , vapor-phase mole fraction y_1 from literature [11]; \bullet , liquid-phase experimental temperature from the literature; \circ , liquid-phase experimental temperature [11]; —, NRTL correlation temperature.

between the boiling point from experimental data and the bubble point from NRTL model calculation are 0.77°C and 1.94°C, respectively. The average and maximum deviations using Wilson, Margules, and van Laar equation individually are 0.79°C, 1.90°C, 0.85°C, 1.89°C, and 0.96°C, 1.91°C. Diagram of VLE for the ternary system methanol (1) + water (2) + ethanoic acid (3) at 101.325 kPa is shown in Figure 7.

TABLE 5: VLE data for the methanol (1) + water (2) + ethanoic 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 , y_2 , and y_3 , activity coefficients γ_1 , γ_2 , and γ_3 using NRTL 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
0.7919	0.2080	0.0001	341.08	340.94	0.9108	0.0870	0.0022	1.0152	1.5155	0.9163
0.7502	0.1967	0.0531	342.79	342.12	0.9024	0.0882	0.0094	1.0156	1.5068	0.9294
0.6923	0.1816	0.1261	344.60	343.90	0.8886	0.0872	0.0242	1.0147	1.4953	0.9444
0.6623	0.1841	0.1536	345.45	344.77	0.8783	0.0910	0.0307	1.0152	1.4838	0.9493
0.5917	0.1645	0.2438	348.36	347.27	0.8561	0.0895	0.0544	1.0114	1.4719	0.9632
0.4619	0.4554	0.0827	349.12	348.30	0.7566	0.2242	0.0191	1.1037	1.2749	0.9612
0.4122	0.3196	0.2682	350.38	352.17	0.7339	0.1929	0.0732	1.0461	1.3352	0.9808
0.5333	0.1483	0.3184	350.67	349.55	0.8338	0.0881	0.0781	1.0072	1.4623	0.9722
0.4263	0.4203	0.1534	351.53	350.19	0.7359	0.2254	0.0387	1.0874	1.2853	0.9763
0.4946	0.1375	0.3679	351.93	351.19	0.8167	0.0869	0.0964	1.0040	1.4558	0.9772
0.3166	0.4774	0.2060	352.84	354.29	0.6481	0.2893	0.0627	1.1178	1.2310	1.0116
0.3959	0.3903	0.2138	353.19	351.89	0.7162	0.2258	0.0580	1.0733	1.2939	0.9847
0.2537	0.5812	0.1651	354.90	355.93	0.5880	0.3565	0.0555	1.1972	1.1675	1.0536
0.2148	0.6454	0.1398	356.16	357.08	0.5479	0.4013	0.0508	1.2669	1.1308	1.0932
0.1750	0.4020	0.4230	363.36	363.66	0.4673	0.3513	0.1814	1.0664	1.2364	1.0246
0.0585	0.9055	0.0360	364.18	364.83	0.2965	0.6797	0.0238	1.9547	1.0150	1.5148
0.1563	0.3589	0.4848	365.42	365.67	0.4367	0.3420	0.2213	1.0459	1.2516	1.0186
0.0478	0.9228	0.0294	366.09	365.86	0.2627	0.7164	0.0209	2.0514	1.0104	1.5759
0.1413	0.3246	0.5341	366.99	367.35	0.4109	0.3321	0.2570	1.0318	1.2630	1.0145
0.0404	0.9348	0.0248	367.10	366.66	0.2359	0.7454	0.0187	2.1259	1.0077	1.6231
0.0350	0.9435	0.0215	367.41	367.30	0.2142	0.7689	0.0169	2.1843	1.0059	1.6602
0.1290	0.2963	0.5747	368.56	368.80	0.3888	0.3218	0.2895	1.0214	1.2720	1.0116
0.0241	0.9592	0.0167	368.82	368.78	0.1626	0.8230	0.0144	2.2986	1.0032	1.7357
0.0203	0.9657	0.0140	369.63	369.35	0.1425	0.8449	0.0126	2.3510	1.0023	1.7687
0.0175	0.9704	0.0121	370.14	369.79	0.1266	0.8622	0.0112	2.3906	1.0017	1.7938
0.0154	0.9740	0.0106	370.54	370.13	0.1141	0.8759	0.0100	2.4220	1.0013	1.8136
0.0884	0.2313	0.6803	371.87	373.49	0.3017	0.3004	0.3979	1.0004	1.2864	1.0068
0.0779	0.2038	0.7183	373.44	375.08	0.2771	0.2814	0.4415	0.9933	1.2933	1.0050
0.0690	0.1805	0.7505	375.20	376.50	0.2548	0.2629	0.4822	0.9878	1.2987	1.0037
0.0625	0.1635	0.7740	375.65	377.59	0.2376	0.2480	0.5144	0.9841	1.3022	1.0030
0.0413	0.1802	0.7785	379.37	379.33	0.1656	0.2871	0.5473	0.9859	1.2885	1.0044
0.0359	0.1567	0.8074	379.87	380.59	0.1486	0.2617	0.5897	0.9812	1.2942	1.0032
0.0314	0.1369	0.8317	381.03	381.69	0.1338	0.2380	0.6282	0.9775	1.2986	1.0023
0.0280	0.1222	0.8498	381.64	382.55	0.1220	0.2192	0.6588	0.9749	1.3016	1.0018
Deviations			$dT = 0.77$							

5. Conclusions

VLE data for the ternary system methanol + water + ethanoic acid and three constituent binary systems at 101.325 kPa: methanol + water, methanol + ethanoic acid, and water + ethanoic acid were determined at different liquid-phase compositions using a novel pump ebulliometer. The equilibrium composition of the vapor phase was calculated from T , p , x , and H_m^E based on the Q function of excess Gibbs free energy by the indirect method. The experimental data were correlated using the NRTL, Wilson, Margules, and van Laar

equations. It was shown that the deviations of NRTL, Wilson, Margules, and van Laar equations are reasonably small. The VLE data of ternary system were predicted by NRTL, Wilson, Margules, and van Laar equation. The calculated bubble points accorded well with the 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 separation process in chemical industry. Moreover, the method will provide theoretical guidance for the research of VLE data of strongly associating system of vapor and liquid phase in nonideal behavior.

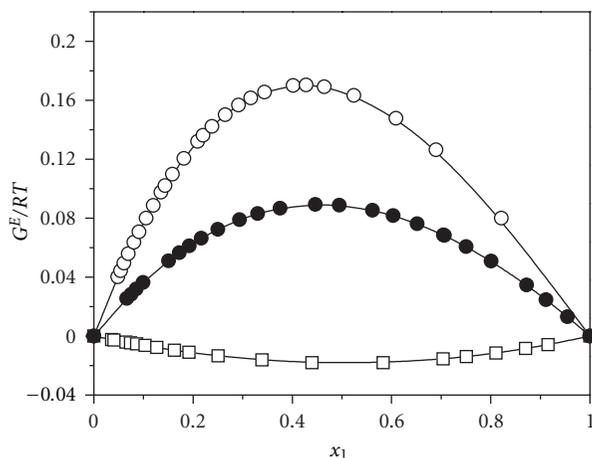


FIGURE 6: Excess Gibbs energy functions (G^E/RT) versus liquid-phase mole fraction of component 1 (x_1) diagram: \circ , methanol (1) + water (2); \bullet , water (1) + ethanoic acid (2); \square , methanol (1) + ethanoic acid (2).

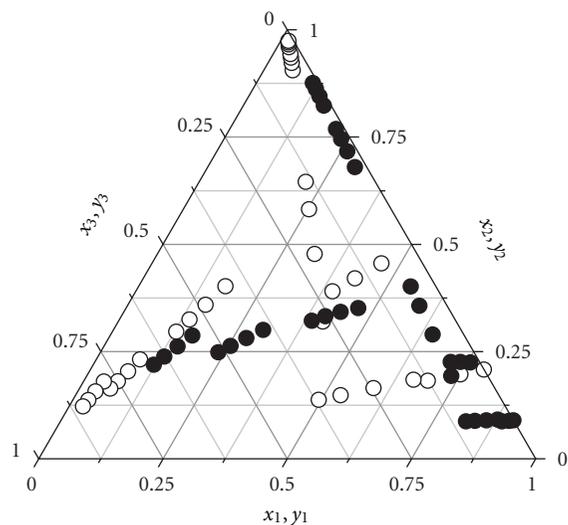


FIGURE 7: Diagram of VLE for the ternary system methanol (1) + water (2) + ethanoic acid (3) at 101.325 kPa: \circ , liquid-phase mole fraction; \bullet , vapor-phase mole fraction.

Acknowledgments

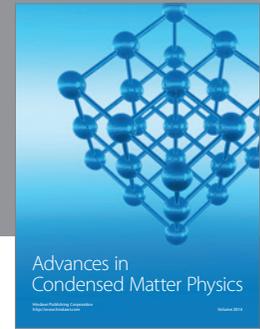
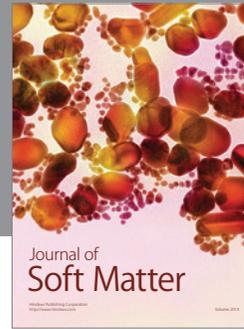
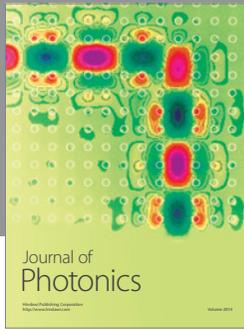
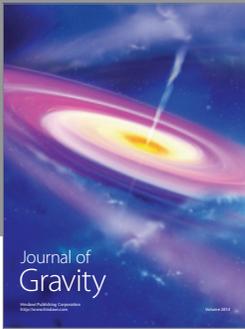
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