EXPERIMENTS AND CORRELATIONS OF PHASE EQUILIBRIA OF ETHANOL-ETHYL ACETATE-WATER TERNARY MIXTURE

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The phase equilibrium behavior of the ternary mixture, containing two completely miscible pairs and one partially miscible binary pair, of ethanol, ethyl acetate, and water was reported in this study. The phase equilibria of this mixture include vapor-liquid equilibria of ethanol-ethyl acetate and ethanol-water binary mixtures; vapor-liquid-liquid equilibrium and vapor-liquid equilibrium (in the miscible region) of water-ethyl acetate binary mixture and ethanol-ethyl acetate-water ternary mixture. All the equilibrium measurements were conducted only with a simple condensed vapor recirculating apparatus. We observed that the equilibrium was difficult to be attained by this simple apparatus in the water-rich region, $x_1 > 0.988$, of the ethyl acetate-water binary constituent system, since the condensed vapor phase has smaller density and immiscible to the liquid phase. Thus a complete dew point curve can not be constructed. However, this difficulty was overcome by using an isobaric coexistence equation.

The binary interaction parameters of the models of UNIQUAC, NRTL, and modified Wilson of Huang and Lee [1994] were obtained based on the various correlations of VLE, LLE, and VLE of various mixtures of the constituent components. Then those interaction parameters were used to estimate the ternary VLE and LLE of the present mixtures. Comparisons were made between the estimated results and the experimental data. Selection of the best fitted model and interaction parameters can be determined through the various correlations and analysis of the estimated results.

Introduction

Most of the separation processes involving phase equilibrium, such as distillation and absorption in the chemical industry need more isobaric than isothermal data. Always, the required equilibrium data unavailable by experiment are estimated by correlation models with parameters determined from the available experimental data.

The very popular activity coefficient models, such as Wilson, NRTL, and UNIQUAC, were developed from the binary mixtures, and have the advantage of application to multicomponent mixtures merely with the constituent binary pair parameters. Unfortunately, this is not always successful if partially miscible binary pairs appear to a multicomponent mixture. Two alternatives, directly correlating with multicomponent experimental data or modifying the activity coefficient model, are considered having various degrees of success to solve this difficulty. However, the former approach is not very convenient, since a complete experimental data set of a multicomponent mixture is not so easy to attain as that of binary mixtures.

In general, there are three types of ternary

mixtures with at least one partially miscible binary pair. Type I mixtures contain only one partially miscible binary pair, Type II mixtures have two pairs, and Type III mixtures have three pairs. Among these three different types, Type III mixtures seldomly happen in industry. While Type II mixtures, without any plait point in the ternary composition phase diagram, are usually predicted without difficulty by local composition models if the binary solubility data of these two partially miscible pairs and the vapor-liquid equilibrium data of the miscible pair are available (Joy and Kyle, 1969; Simonetty *et al.*, 1982). Abrams and Prausnitz (1975) even mentioned that the interaction parameters of the correlation models of the totally miscible binary pair have little influence on the correlation results. Unfortunately, the same correlation for Type II mixtures can not be successfully applied to that for Type I mixtures. The estimated values are obviously deviated from the experimental values especially near the plait point (Joy and Kyle, 1969; Guffey and Wehe, 1972; Marina and Tassios, 1973; van Zandijcke and Verhoeve, 1974; Abrams and Prausnitz, 1975; Sugi *et al.*, 1976; Sugi and Katayama, 1978; Sorensen *et al.*, 1979; Sorensen *et al.*, 1980).

In 1982, Simonetty *et al.* divided Type I mixtures into three classes by the mutual solubilities of the partially miscible binary pair as the following.

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System	x_2^I	x_2^{II}
IA	>0.01	<0.86
IB	>0.01	>0.86
IC	<0.01	>0.99

They regressed with additional tie line data by the models of NRTL, LEMF, and UNIQUAC, and concluded that the correlations of Type IC were the worst. This result was identical to that of Renon and Prausnitz (1968). However, Joy and Kyle (1969) correlated the same type of mixtures with NRTL, and Anderson and Prausnitz (1978) with UNIQUAC, and gave the opposite results from Simonetty *et al.* that Type IC was the best. Unfortunately, this approach of determining model parameters with tie line will cause the loss of accuracy for predicting binary vapor-liquid equilibrium (Anderson and Prausnitz, 1978; Nagata and Usui, 1989).

In order to improve the capabilities of representing ternary LLE by the commonly used local composition models, Cha and Prausnitz (1985) suggested multiplication of an arbitrary parameter to the UNIQUAC model. This additional parameter reduces to unity when the model is applied to binary mixtures. This modification makes UNIQUAC model possibly represent ternary LLE and binary VLE simultaneously with high accuracy, but has the disadvantages of an additional parameter and of the application restricted only to binary and ternary mixtures. Some other researchers had also tried different modifications of the UNIQUAC, NRTL and Wilson models to solve this problem, those were Nagata (1989) with the UNIQUAC model, Connemann *et al.* (1990) with the NRTL model, Hiranuma (1974, 1983), Nagata *et al.* (1975), Tsuboka and Katayama (1975), Nishimura *et al.* (1985), Nagata and Watanabe (1992) with the Wilson model.

The improvement of correlation had also been tried by considering the nonrandomness parameter of NRTL model as an adjustable parameter. However, van Zandijcke and Verhoeve (1974), De Fre and Verhoeve (1976), and Sugi and Katayama (1978) had pointed out that the results obtained by a flexible α_{ij} are not better than by a fixed value. Huang and Lee (1994) modified the three-parameters modified Wilson model proposed in Hiranuma's paper (1974) and obtained a better correlation than by other modifications for ternary LLE. de Pablo and Prausnitz (1988) improved the LLE correlation near the critical region by introducing an exponential function of a suitable distance from the critical point to the conventional models, such as NRTL and van Laar. This semi-theoretical correction was also applied to simultaneous correlations of isothermal VLE and LLE including the liquid-liquid critical region.

In this research we would not try to modify and model for better correlation but to study the phase behavior of Type I ternary mixture of ethanol, ethyl acetate, and water. The experimental VLE, LLE, and VLLE data sets of this ternary mixture and its three constituent binary pairs were individually correlated to determine the most suitable model parameters for estimating VLE and LLE of this ternary mixture as given in the later part of this study. The models applied in this study were UNIQUAC, NRTL, and Huang and Lee's modified Wilson.

Usually, the binary parameters of a binary mixture can be estimated from a set of experimental binary LLE data. Therefore, one parameter in the three-parameter NRTL model has to be kept constant. It is obvious that the non-randomness factor α_{ij} is the most suitable choice. For convenience, α_{ij} in the NRTL model was specified according to the rules proposed by Renon and Prausnitz (1968) through this work.

1. Experimental Work

Three chemicals, ethanol, ethyl acetate, and water were used in this study. The experiments included binary VLE (in totally miscible region) of mixtures of ethanol-water, ethanol-ethyl acetate, and water-ethyl acetate; binary VLLE (in partially miscible region) of water-ethyl acetate; and ternary VLE and VLLE of all three constituent components. All six experiments were conducted at atmospheric pressure.

1.1 Chemicals

The chemicals used were de-ionized distilled water, generated by a Minipore distilled water generator (Millipore Corporation, Bedford, MA), ethanol (Riedel-deHaen, 99.8% purity), and ethyl acetate (Merck, 99.7% purity). All chemicals were used without further purification.

1.2 Experimental procedure

The most important part of the experimental apparatus is the Othmer type recirculating still. This still was designed to avoid liquid entrainment by placing baffles on the chamber wall of the vapor path, and to avoid rectifying effect attributed to vapor heat loss by insulating vapor path with double jackets, in which the heating oil flowed through the inner jacket and the vacuum was kept to 10^{-6} kPa in the outer jacket. This still was used to carry out both experiments of vapor-liquid equilibrium and vapor-liquid-liquid equilibrium.

A cell with inner volume of 3 ml was used to conduct liquid-liquid equilibrium experiment. The desired temperature was maintained by the heating oil flowing through jacket between the inner and outer walls.

A. Vapor-liquid equilibrium The vapor and

liquid temperatures were measured with thermometers with scale calibrated to ± 0.1 K. The liquid sample, about 300 ml, was fed into the still and stirred to keep liquid phase uniform during experiment. An electrical heater supplied heat to evaporate liquid steadily. The time needed for each run to reach equilibrium was about an hour. The equilibrium temperature and pressure were recorded. The vapor and liquid samples of 1 ml in volume were collected from different ports of still for GC analysis.

The experiment of water-ethyl acetate mixture in the miscible region appeared an interesting phenomenon occurred in the range of water mole fraction larger than 0.988. Where the condensed vapor rich in more volatile ethyl acetate component, was coincidentally in the immiscible region accumulated on the returning path to still. Kato *et al.* (1970) used bubble-dew point apparatus to overcome this difficulty. But we merely used this simple apparatus to achieve the experimental work purposefully. The procedure of this part was described later in the section of experimental results and discussion.

B. Vapor-liquid-liquid equilibrium The same apparatus for vapor-liquid equilibrium was also used for vapor-liquid-liquid equilibrium. The experimental procedure was identical to that described in the previous section except that 3 ml of liquid sample was taken from still and fed to a liquid-liquid equilibrium cell that was kept at the same temperature of VLE equilibrium system. In order to ensure that the liquid phase was well mixed in the still, three samples were separately taken from different positions of still. Two liquid phases will obviously appear in the LLE cell, and then 1 μ l of each phase was taken separately for GC analysis. The GC analysis shows perfect agreement of all three samples.

Unfortunately, there exists difficulty to apply the same VLE apparatus to perform VLE experiment over the whole concentration range. This difficulty occurs at the very dilute concentration of ethyl acetate in the ethyl acetate-water binary mixture. The condensed vapor consisting of the more volatile component, ethyl acetate, accumulated on the top of liquid phase in the return channel, instead of recycling back to the still which was even vehemently stirred. However, this difficulty had been overcome as discussed in the later section.

1.3 Method of analysis

The compositions of vapor and liquid phase samples were analyzed by GC (China Chromatography Co., 8700T, Taipei). The followings are the accessories and operating conditions of GC for different systems.

A. Ethanol-ethyl acetate binary mixture
Detector: FID; column: 80/100 Porapak Q of 2 m length; carrier gas: nitrogen gas of flow rate of 55 ml/min; injection port temperature: 463.2 K; oven

temperature: 453.2 K; detector temperature: 453.2 K; injection sample volume 0.8 μ L.

B. Ethanol-water and water-ethyl acetate binary mixtures; ethanol-ethyl acetate-water ternary mixture
Detector: TCD; column: 80/100 Porapak Q of 2.5 m length; carrier gas: helium gas of flowrate of 32 ml/min; injection port temperature: 463.2 K; oven temperature: 463.2 K; detector temperature: 393.2 K; TCD current: 220 mA; injection sample volume 0.8 μ L.

1.4 Calibration curves

The calibration curves of all systems were constructed separately in this study.

A. Binary mixtures To construct this calibration curve, samples of known compositions were injected into GC for analysis, and the peak area ratios of the constituent components were then calculated by GC integrator. The calibration curve relating mixture composition and peak area ratio was then plotted for future use to determine the unknown composition of the same mixture. Two calibration curves for ethanol-water and ethanol-ethyl acetate mixtures were determined, respectively.

For a partially miscible mixture we have to know the overall composition. Thus, a solvent was added to dissolve this partially miscible mixture to a single phase, which was then injected into GC for analysis. The peak area ratios (the original solvent-free mixture) and compositions were used to plot the calibration curve. In this study, ethanol was used as solvent for water-ethyl acetate system.

B. Ternary mixtures The calibration curve of ethanol-water-ethyl acetate ternary mixture was determined from those of ethanol-water and ethanol-ethyl acetate and the peak area ratio percentage of each constituent component of the ternary mixture.

Components	Ethanol	Ethyl acetate	Water
Peak area %	A_1	A_2	A_3
Mole fraction	x_1	x_2	x_3

Where $A_1 + A_2 + A_3 = 100$, and $x_1 + x_2 + x_3 = 1$. Then the value of $A_1/(A_1 + A_2)$ and the calibration curve of ethanol-ethyl acetate will give x_1/x_2 , and the value of $A_1/(A_1 + A_3)$ and the calibration curve of ethanol-water will give x_1/x_3 . Let $x_1/x_2 = a$ and $x_1/x_3 = b$. Then, $x_1 + x_1/a + x_1/b = 1$. Finally, we have $x_1 = ab/(a + b + ab)$, $x_2 = b/(a + b + ab)$, and $x_3 = a/(a + b + ab)$ for each component of a ternary mixture.

2. Data Reduction

For the present ternary mixture, both vapor-liquid equilibrium and liquid-liquid equilibrium needed to be considered since this ternary mixture forms a partially miscible pair. The other conditions

for vapor-liquid and liquid-liquid equilibria in addition to the uniform temperature and pressure in the entire system are:

$$\hat{f}_i^l = \hat{f}_i^v, \quad i = 1, 2, 3 \quad (1)$$

and

$$\hat{f}_i^l = \hat{f}_i^{II}, \quad i = 1, 2, 3 \quad (2)$$

respectively.

If the vapor phase fugacity of component i is expressed by fugacity coefficient and partial pressure, and liquid phase fugacity is represented by activity coefficient and other relevant thermodynamic properties of that component, we will have the rigorous thermodynamic equation for vapor-liquid equilibrium and liquid-liquid equilibrium as

$$y_i P \hat{\phi}_i^v = x_i \gamma_i P_i^s \phi_i^s \exp \left[\frac{v_i^l (P - P_i^s)}{RT} \right], \quad i = 1, 2, 3 \quad (3)$$

and

$$(x_i \gamma_i)^I = (x_i \gamma_i)^{II}, \quad i = 1, 2, 3 \quad (4)$$

Where $\hat{\phi}_i^v$ and γ_i are the fugacity coefficient and activity coefficient of component i respectively, and superscripts I and II refer to the equilibrated liquid phases.

The liquid molar volume, v_i^l , and the saturated vapor pressures of each component were calculated by the modified Rackett equation (Spencer and Danner, 1972) and Antoine equation (Antoine, 1888) respectively.

The fugacity coefficient of component i in the vapor phase was calculated with the following equation

$$\ln \hat{\phi}_i^v = \frac{1}{RT} (2 \sum_{j=1}^3 y_j B_{ij} - B_{mix}), \quad i = 1, 2, 3 \quad (5)$$

Here, the pure component and the cross virial coefficients were estimated with the Hayden and O'Connell's correlation (1975). The activity coefficient models of UNIQUAC, NRTL, and modified Wilson of Huang and Lee were used to correlate the experimental data.

In this study, the model parameters of binary and ternary vapor-liquid equilibrium, and ternary liquid-liquid and vapor-liquid-liquid equilibrium were determined by the maximum likelihood principle, on which the assumption was imposed that errors were random and independent. The objective function for binary and ternary vapor-liquid equilibrium correlation was chosen as

$$Q_1 = \sum_{i=1}^N \left[\frac{(P_i^{\text{exp}} - P_i^{\text{cal}})^2}{\sigma_{P_i}^2} + \frac{(T_i^{\text{exp}} - T_i^{\text{cal}})^2}{\sigma_{T_i}^2} + \frac{(x_{ji}^{\text{exp}} - x_{ji}^{\text{cal}})^2}{\sigma_{x_{ji}}^2} + \frac{(y_{ji}^{\text{exp}} - y_{ji}^{\text{cal}})^2}{\sigma_{y_{ji}}^2} \right] \quad (6)$$

Where $j=1$ for a binary, and $j=1, 2$ for a ternary system. The pressure and temperature standard deviations, σ_P and σ_T , were estimated by the accuracy of the measuring equipments mentioned earlier. The standard deviations of liquid and vapor compositions were determined by the inaccuracy of calibration curve. All the standard deviations used for our calculations were $\sigma_P=1$ kPa, $\sigma_T=0.1$ K, and $\sigma_x=\sigma_y=0.003$. The objective function for ternary liquid-liquid equilibrium correlation was chosen as

$$Q_2 = \sum_{i=1}^N \left[\frac{(x_{1i}^{\text{exp}'} - x_{1i}^{\text{cal}'})^2}{\sigma_{x_{1i}'}^2} + \frac{(x_{2i}^{\text{exp}'} - x_{2i}^{\text{cal}'})^2}{\sigma_{x_{2i}'}^2} + \frac{(x_{1i}^{\text{exp}''} - x_{1i}^{\text{cal}''})^2}{\sigma_{x_{1i}''}^2} + \frac{(x_{2i}^{\text{exp}''} - x_{2i}^{\text{cal}''})^2}{\sigma_{x_{2i}''}^2} \right] \quad (7)$$

The objective function for ternary vapor-liquid-liquid equilibrium correlation was chosen as

$$Q_3 = \sum_{i=1}^N \left[\frac{(P_i^{\text{exp}} - P_i^{\text{cal}})^2}{\sigma_{P_i}^2} + \frac{(T_i^{\text{exp}} - T_i^{\text{cal}})^2}{\sigma_{T_i}^2} + \frac{(y_{1i}^{\text{exp}} - y_{1i}^{\text{cal}})^2}{\sigma_{y_{1i}}^2} + \frac{(y_{2i}^{\text{exp}} - y_{2i}^{\text{cal}})^2}{\sigma_{y_{2i}}^2} + \left[\frac{(x_{1i}^{\text{exp}'} - x_{1i}^{\text{cal}'})^2}{\sigma_{x_{1i}'}^2} + \frac{(x_{2i}^{\text{exp}'} - x_{2i}^{\text{cal}'})^2}{\sigma_{x_{2i}'}^2} + \frac{(x_{1i}^{\text{exp}''} - x_{1i}^{\text{cal}''})^2}{\sigma_{x_{1i}''}^2} + \frac{(x_{2i}^{\text{exp}''} - x_{2i}^{\text{cal}''})^2}{\sigma_{x_{2i}''}^2} \right] \right] \quad (8)$$

The advantage of maximum likelihood principle is that all the measured variables of temperature, pressure, compositions of vapor and liquid, are taken into consideration.

The binary pair parameters of water-ethyl acetate obtained from mutual solubility data were determined by solving the isoactivity equation with the mathematical technique of Newton-Raphson method.

3. Experimental Results and Discussion

The experimental result of ethanol-water system was plotted in Fig. 1 along with those obtained from the literature (Gmehling *et al.*, 1981). Among those data there exist very slight discrepancies attributed to the different atmospheric pressure measurements at the different locations where those experiments were

Fig. 1 Comparisons of the present experimental results and those from literature for ethanol and water

Fig. 2 T - x - y diagram of ethanol and water at atmospheric pressure

conducted.

Here, the phase equilibrium experiments of different mixtures conducted in this study were given and discussed in the following three parts.

3.1 Vapor-liquid equilibria of ethanol-water and ethanol-ethyl acetate binary mixtures

These two binary mixtures are completely miscible. The experimental VLE data of these two mixtures were shown in **Fig. 2** and **Fig. 3** respectively. The experimental data had been checked and ensured satisfaction by Herington consistency test.

The activity coefficient models of UNIQUAC, NRTL, and modified Wilson by Huang and Lee had been tried to correlate the experimental data. The model parameters and the standard deviations of fit of three models were given in **Table 1**. The estimated equilibrium diagrams along with experimental data of two mixtures were given as **Fig. 2** and **Fig. 3** respectively. It is obvious that all three models are suitable to these two mixtures.

3.2 Vapor-liquid equilibrium and vapor-liquid-liquid equilibrium of water-ethyl acetate binary mixture

The vapor-liquid equilibrium of water-ethyl acetate mixture was carried out at the totally miscible region, and the vapor-liquid-liquid equilibrium experiment was in the partially miscible region and carried out with the identical equilibrium still for totally miscible mixture. All the experimental data were given in **Table 2**. Difficulty was experienced to obtain the equilibrium when water concentration in liquid phase is larger than 0.988. Since the condensed phase is a lighter ethyl acetate-rich mixture and is immiscible to the water-rich phase in the still,

Fig. 3 T - x - y diagram of ethanol and ethyl acetate at atmospheric pressure

such that it can not recycle back to the vehemently stirred still. Thus, the phase equilibrium data at the region of very dilute ethyl acetate concentration was missing. In order to obtain a complete phase diagram of this system, the coexistence equation (van Ness and Abbott, 1982; Raal and Brouckaert, 1992) was applied to estimate temperature and vapor composition (T - y) relation. The coexistence equation was briefly discussed in the following.

At isobaric condition the coexistence equation (van Ness and Abbott, 1982) can be simplified to the

Table 1 The model parameters and the standard deviations of fit with the UNIQUAC, NRTL and modified Wilson models for ethanol-water and ethanol-ethyl acetate binary systems

No.	System	Model	$A_{12}^{b)}$	$A_{21}^{b)}$	α	$\sigma^a)$
1	ethanol (1) water (2)	UNIQUAC	86.27 ± 8.85	-419.31 ± 20.34	0.3	1.7503
		NRTL	-74.20 ± 6.27	694.07 ± 14.22		1.7501
		mod. Wilson	-451.51 ± 8.58	-64.71 ± 6.03		2.2944
2	ethanol (1) ethyl acetate (2)	UNIQUAC	183.33 ± 3.51	-570.62 ± 10.07	0.3	1.5289
		NRTL	128.18 ± 18.78	153.70 ± 19.12		1.6057
		mod. Wilson	101.97 ± 5.26	-209.87 ± 8.19		1.5684

a) $\sigma = [SUMSQ/(k-n)]^{1/2}$; ($SUMSQ$ =weighted sum of square $= \sum_{i,j}^k \left(\frac{\Delta z_{ij}}{\sigma_{ij}} \right)^2$, k =total number of data points, m = total number of measured variables per data point, n =total number of parameter, Δz =residual, σ =standard deviation)

b)

Model	A_{12}	A_{21}
UNIQUAC	$-(u_{12}-u_{22})/R$	$-(u_{21}-u_{11})/R$
Wilson	$\ln(\nu_2^f/\nu_1^f) \times [-(\lambda_{12}-\lambda_{11})]$	$\ln(\nu_1^f/\nu_2^f) \times [-(\lambda_{21}-\lambda_{22})]$
NRTL	$(g_{12}-g_{22})/R$	$(g_{21}-g_{11})/R$

Table 2 Vapor-liquid and liquid-liquid equilibrium data and activity coefficients of water and ethyl acetate at atmospheric pressure

P (kPa)	T (K)	x_1	y_1	γ_1	γ_2
101.5	350.3	0.000	0.000	—	1.0000
100.9	349.1	0.028	0.076	6.8901	0.9854
101.2	349.5	0.018	0.063	8.7136	0.9792
101.3	348.7	0.030	0.098	8.3734	0.9796
101.3	347.9	0.043	0.140	8.6962	0.9709
101.3	347.7	0.048	0.159	8.8068	0.9616
101.3	347.4	0.053	0.163	8.2594	0.9715
101.2	346.7	0.067	0.190	7.8487	0.9750
101.3	345.9	0.095	0.239	7.1955	0.9708
101.2	345.1	0.132	0.273	6.1075	0.9918
101.2	344.8	0.150	0.276	5.5267	1.0171
101.1	344.2	0.224	0.313	4.2891	1.0776
101.1	344.2	0.998	0.313	0.9715	69.0788
100.4	372.8	1.000	1.000	1.000	—

P (kPa)	T (K)	x_1'	x_1''
101.1	344.2	0.224	0.988

form of

$$\theta dT = (y_1 - x_1) d \ln \frac{\gamma_1^v}{\gamma_2^v} + \frac{y_1 - x_1}{y_1(1 - y_1)} dy_1 \quad (9)$$

where

$$\theta = \frac{x_1 \Delta H_1^v + x_2 \Delta H_2^v}{RT^2}$$

Where ΔH_1^v and ΔH_2^v are the heats of vaporization of components 1 and 2. If vapor phase was assumed

ideal, then Equation (9) became

$$\theta dT = \frac{y_1 - x_1}{y_1(1 - y_1)} dy_1 \quad (10)$$

The relation of heat of vaporization and temperature can be described by Watson relation (Reid *et al.*, 1988)

$$\Delta H_{i2}^v = \Delta H_{i1}^v \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^n \quad (11)$$

The power integer n was determined by Viswanath-Kuloor method (Reid *et al.*, 1988)

$$n = (0.00264 \frac{\Delta H_b^v}{RT_b} + 0.8794)^{10} \quad (12)$$

and the heat of vaporization at boiling point T was determined by Vetere method (Reid *et al.*, 1988)

$$\Delta H_b^v = RT_c T_{br} \cdot \frac{0.4343 \ln P_c - 0.69431 + 0.89584 T_{br}}{0.37691 - 0.37306 T_{br} + 0.15075 P_c^{-1} T_{br}^{-2}} \quad (13)$$

The estimated T - y relation by coexistence equation was compared to the result reported by Kato *et al.* (1970) by experiment of bubble point and dew point method. From Fig. 4 and 5, we can see that the estimated T - y curves by coexistence equation agree to the experimental values of Kato and his coworkers fairly well.

Two groups of correlations were made from different experimental data sets but with the same activity coefficient models of UNIQUAC, NRTL, and modified Wilson of Huang and Lee. In the first

Fig. 4 T - x - y diagram of water and ethyl acetate at atmospheric pressure: (Data for VLE were used to correlated the parameters of the UNIQAC, NRTL, and modified Wilson models)

Fig. 5 T - x - y diagram of water and ethyl acetate at atmospheric pressure: (Data for LLE were used to correlated the parameters of the UNIQAC, NRTL, and modified Wilson models)

correlation, all VLE data were used. The vapor-liquid equilibrium behaviors estimated by the above models were also shown in Fig. 4. The experimental and the estimated data agreed in each other very well as expected. For the second correlation, the LLE data were used and the estimated VLE behaviors were shown in Fig. 5. We also calculated RMSD (not

shown in the paper) of each model for two correlations. We obtained slight differences between the estimated data generated by UNIQAC and NRTL models for two correlations except the modified model of Huang and Lee. This was obviously observed in Fig. 5. This estimated result was identical to Raal and Brouchaert's (1992) that correlation from LLE data is not suitable to VLE prediction. Since it is well known that it is difficult to find a set of parameters which can simultaneously correlate both VLE and LLE accurately. We might explain that the agreement between the experimental and estimated data of two different correlations by UNIQAC and NRTL models was a special case for the present system.

3.3 Vapor-liquid equilibrium and vapor-liquid-liquid equilibrium of ethanol-ethyl acetate-water ternary mixture

The experimental ternary VLE and VLLE data were listed in **Tables 3** and **4** respectively.

In the following section, all experimental ternary VLE and LLE data will be used to test the capability of the models of UNIQAC, NRTL, and modified Wilson by Huang and Lee for simultaneously estimating ternary VLE and LLE from binary parameters.

4. Estimation of Ternary VLE and LLE

It is known that an accurate estimation of phase equilibrium is highly dependent upon the model. However, if the estimation is with specified model, it will be dependent on the experimental data used. Here, we try to obtain the most appropriate interaction parameters from different experimental data sets for the future estimating ternary vapor-liquid and liquid-liquid equilibria. We generated eleven cases of correlations with different experimental data sets. The eleven cases were given in the followings.

1. All the binary parameters were correlated by VLE data of the constituent binary pairs, except water-ethyl acetate parameters were determined by VLE data in the totally miscible region.
2. All the binary parameters were correlated by VLE data of the constituent binary pairs, except water-ethyl acetate parameters were determined by LLE data in the partially miscible region.
3. All six binary parameters were correlated by ternary LLE data in the partially miscible region.
4. All six binary parameters were correlated by ternary VLLE data in the partially miscible region.
5. All six binary parameters were correlated by ternary VLE data in the totally miscible region.
6. The binary parameters of water-ethyl acetate binary mixture were correlated by ternary LLE data, and the others were correlated by VLE data

Table 3 Vapor-liquid equilibrium data of ethanol-ethyl acetate-water ternary mixtures at atmospheric pressure

$P(\text{kPa})$	$T(\text{K})$	x_1	x_2	y_1	y_2	$P(\text{kPa})$	$T(\text{K})$	x_1	x_2	y_1	y_2
100.4	351.3	0.949	0.011	0.929	0.024	101.3	347.4	0.693	0.174	0.596	0.288
100.4	351.1	0.935	0.015	0.913	0.033	101.3	347.1	0.626	0.180	0.523	0.297
100.5	350.8	0.910	0.022	0.881	0.049	101.3	346.8	0.546	0.188	0.472	0.328
100.5	350.4	0.861	0.035	0.821	0.077	101.3	346.2	0.524	0.219	0.448	0.357
100.5	350.0	0.806	0.048	0.761	0.105	101.3	345.8	0.502	0.254	0.425	0.385
100.7	349.4	0.740	0.064	0.694	0.140	101.2	345.4	0.459	0.318	0.387	0.429
100.9	349.1	0.679	0.079	0.634	0.173	101.2	345.4	0.416	0.296	0.354	0.428
100.8	348.7	0.623	0.093	0.580	0.204	101.2	345.5	0.383	0.280	0.330	0.431
100.8	348.3	0.574	0.105	0.538	0.232	101.2	345.5	0.364	0.270	0.316	0.431
100.5	346.7	0.022	0.917	0.035	0.805	101.5	344.3	0.215	0.498	0.194	0.554
100.7	345.6	0.042	0.870	0.058	0.758	101.5	344.2	0.192	0.554	0.178	0.575
100.5	345.4	0.069	0.847	0.091	0.741	101.5	344.2	0.219	0.508	0.197	0.558
100.4	344.5	0.086	0.793	0.102	0.694	101.5	344.4	0.258	0.460	0.226	0.534
100.5	344.0	0.116	0.717	0.124	0.650	101.5	344.6	0.318	0.435	0.275	0.508
100.5	343.8	0.140	0.640	0.137	0.615	101.6	344.9	0.372	0.401	0.320	0.483
100.7	344.0	0.206	0.587	0.193	0.584	101.6	345.2	0.424	0.369	0.361	0.459
100.8	344.1	0.255	0.549	0.235	0.559	101.6	345.6	0.489	0.327	0.413	0.428
101.2	344.5	0.319	0.501	0.287	0.530	101.6	346.1	0.574	0.272	0.480	0.384
101.2	344.6	0.370	0.463	0.327	0.508	101.6	346.2	0.509	0.240	0.432	0.376
101.3	344.9	0.428	0.421	0.372	0.481	101.5	348.4	0.016	0.954	0.030	0.876
101.3	345.3	0.492	0.374	0.422	0.451	101.5	347.3	0.026	0.925	0.041	0.835
101.3	345.7	0.558	0.326	0.471	0.418	101.5	346.6	0.038	0.901	0.056	0.797
101.3	346.2	0.624	0.276	0.527	0.378	101.3	344.9	0.064	0.859	0.086	0.755
101.3	346.7	0.681	0.233	0.575	0.343	101.3	345.6	0.104	0.823	0.133	0.725
101.3	347.1	0.728	0.197	0.621	0.307	101.3	344.9	0.150	0.748	0.173	0.663
101.3	347.6	0.768	0.168	0.663	0.276	101.3	344.7	0.210	0.684	0.223	0.622
101.3	347.6	0.758	0.168	0.655	0.275	101.2	344.8	0.283	0.620	0.286	0.587
101.2	347.5	0.740	0.169	0.637	0.277	101.3	344.9	0.382	0.535	0.361	0.539

Table 4 Vapor-liquid-liquid equilibrium data of ethanol-ethyl acetate-water ternary mixtures at atmospheric pressure

$P(\text{kPa})$	$T(\text{K})$	x'_1	x'_2	x'_1	x'_2	y_1	y_2
100.8	343.8	0.073	0.621	0.021	0.015	0.056	0.503
100.9	343.9	0.075	0.612	0.023	0.016	0.067	0.563
101.1	344.0	0.089	0.560	0.030	0.018	0.082	0.567
100.9	344.1	0.122	0.454	0.043	0.023	0.108	0.578
100.9	344.4	0.152	0.328	0.066	0.040	0.134	0.557
100.5	343.9	0.004	0.775	0.001	0.011	0.005	0.625
100.4	343.9	0.015	0.746	0.005	0.012	0.016	0.623
100.5	343.9	0.021	0.748	0.007	0.012	0.022	0.672
100.5	343.8	0.090	0.567	0.030	0.018	0.071	0.521
100.5	344.3	0.152	0.304	0.066	0.039	0.131	0.538

of the constituent binary pairs.

7. The binary parameters of water-ethyl acetate binary mixture were correlated by ternary experimental data sets VLLE data, and the others were correlated by VLE data of the constituent binary pairs.
8. The binary parameters of water-ethyl acetate binary mixture were correlated by ternary VLE data, and the others were correlated by VLE data of the constituent binary pairs.
9. The binary parameters of water-ethyl acetate

mixture were correlated by its own LLE data, and the others were correlated by ternary LLE data.

10. The binary parameters of water-ethyl acetate mixture were correlated by its own LLE data, and the others were correlated by ternary VLLE data.
11. The binary parameters of water-ethyl acetate mixture were correlated by its own LLE data, and the others were correlated by ternary VLE data.

Only the parameters of the model which generated the best correlation were listed in **Table 5**. The root mean square deviations of the bubble point

Table 5 The optimum estimated parameter of the recommended model

Case	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	Model
1	101.97± 5.2	-209.87± 8.1	-451.51± 8.5	-64.71± 6.0	-905.98± 61.1	-209.41± 61.1	modified Wilson
2	101.97± 5.2	-209.87± 8.1	-451.51± 8.5	-64.71± 6.0	-1110.19± 35.3	-134.26± 11.7	modified Wilson
3	136.46±40.7	-288.77± 59.7	-377.87±65.9	-100.91±60.8	-1104.62± 31.4	-143.76± 8.9	modified Wilson
4	237.77±43.9	-407.53±145.8	-2709.08± 0.0	53.45±93.3	-929.07±201.9	-203.03±117.5	modified Wilson
5	185.25± 4.9	-574.47± 13.8	129.12±10.2	-512.85±26.6	-719.53± 15.7	35.03± 5.8	UNIQUAC
6	101.97± 5.2	-209.87± 8.1	-451.51± 8.5	-64.71± 6.0	-1126.25± 27.0	-129.11± 5.7	modified Wilson
7	101.97± 5.2	-209.87± 8.1	-451.51± 8.5	-64.71± 6.0	-1010.27± 95.5	-152.68± 28.9	modified Wilson
8	183.44± 3.5	-570.62± 10.0	86.27± 8.8	-419.31±20.3	-744.90± 15.5	50.13± 5.1	UNIQUAC
9	125.89±32.9	-296.83± 63.4	-435.00±66.2	-117.77±54.9	-1110.19± 35.3	-134.26± 11.7	modified Wilson
10	236.84±39.3	-342.30± 92.2	-2709.08± 0.0	5.48±56.3	-1110.19± 35.3	-134.26± 11.7	modified Wilson
11	41.71±13.9	-122.65± 17.2	-334.70±13.8	-134.74±11.3	-1110.19± 35.3	-134.26± 11.7	modified Wilson

Table 6 The root mean square deviations of bubble point temperatures and vapor composition of ternary VLE estimated by the parameters for each correlation

Case	RMSD								
	UNIQUAC			NRTL			mod. Wilson		
	ΔT	Δy_1	Δy_2	ΔT	Δy_1	Δy_2	ΔT	Δy_1	Δy_2
1	0.6	0.011	0.013	0.3	0.007	0.008	0.4	0.006	0.008
2	0.5	0.010	0.013	0.3	0.007	0.008	0.9	0.009	0.008
3	16.8	0.155	0.118	4.2	0.056	0.049	1.3	0.017	0.023
4	0.3	0.018	0.022	2.5	0.049	0.078	1.8	0.047	0.077
5	0.1	0.003	0.004	0.1	0.004	0.004	0.1	0.004	0.005
6	0.4	0.005	0.003	0.1	0.005	0.008	0.9	0.010	0.009
7	0.2	0.004	0.006	0.1	0.005	0.009	0.6	0.006	0.005
8	0.1	0.003	0.004	0.1	0.004	0.005	0.2	0.005	0.005
9	39.3	0.227	0.144	4.2	0.054	0.046	2.7	0.030	0.033
10	0.8	0.021	0.025	2.7	0.052	0.082	2.1	0.057	0.101
11	0.2	0.010	0.011	0.2	0.009	0.006	0.4	0.010	0.006

temperatures and the vapor compositions of ternary VLE estimated by the parameters for each correlation were listed in **Table 6**.

The followings were the detailed discussion of the correlation results by the cases given above. Our goal of studying the various correlations via different experimental data sets is to search the most appropriate parameters that would minimize the deviation between the estimated and experimental values for ternary VLE and LLE of the present mixture.

For the estimation results of ternary LLE, the prediction of the binodal curves with UNIQUAC, NRTL, and modified Wilson by Huang and Lee was compared to the experimental data. Several observations can be drawn from this study:

1. The results of the best correlations 1 and 2 are shown in **Fig. 6**. Actually, we obtained the estimated heterogeneous areas were larger than the experimental values of these cases except the model of modified Wilson by Huang and Lee in correlation 2. Figure 6 only showed the correlation

Fig. 6 Comparisons of the experimental liquid-liquid equilibria and the calculated results of correlations 1 and 2

Fig. 8 Comparisons of the experimental liquid-liquid equilibria and the calculated results of correlations 4, 7, and 10

Fig. 8 Comparisons of the experimental liquid-liquid equilibria and the calculated results of correlations 4, 7, and 10

of modified Wilson model by Huang and Lee which is superior to the UNIQUAC and NRTL models for these two cases.

2. The results of correlations 3, 6, and 9 are shown in Fig. 7. The model parameters of these cases are virtually suitable to estimate ternary LLE. Unfortunately the estimated LLE of water-ethyl acetate mixture by UNIQUAC and NRTL models in correlation 6 do not match experimental values very well. This figure only showed the best correlation models for these three cases.
3. The results of correlations 4, 7, and 10 are shown in Fig. 8. The estimated LLE of ternary mixture by these correlations is inferior to that by the correlations 3, 6, and 9. This figure only showed the best correlation models for these three cases.
4. The results of correlations 5, 8, and 11 are shown in Fig. 9. The estimated LLE of ternary mixture is worse than correlations 3, 6, 9, 4, 7, and 10. There exist large deviations between the estimated and experimental LLE of water-ethyl acetate mixture except those results in correlation 11. This figure only showed the best correlation models for these three cases.

The above observations can be summarized that if the binary pair parameters of water-ethyl acetate were obtained from mutual solubility data, the performances of all three models in representing ternary LLE can be improved successfully. Also, these results indicated that the modified Wilson of Huang and Lee is superior to the other two models in estimating ternary LLE. If we look into the estimation results for ternary VLE (shown in Table 6) similar to which given above for ternary LLE, we have

Fig. 9 Comparisons of the experimental liquid-liquid equilibria and the calculated results of correlations 5, 8, and 11

1. For correlations 1 and 2, the model parameters are suitable for ternary VLE estimations.
2. For correlations 3, 6, and 9, the root mean square deviations of different VLE estimations are large except for correlation 6.
3. For correlations 4, 7, and 10, correlation 7 provided the estimated VLE values match experimental values very well.
4. For correlations 5, 8, and 11, the estimated VLE values match experimental data quite well and are better than either correlations 3, 6, and 9 or

correlations 4, 7, and 10.

Through the discussions given above we may conclude that the reliable calculation of ternary VLE is obtainable if ternary VLE data were used for correlating model parameters. Unfortunately, the ternary equilibrium data were not always available. Thus, the phase behavior of ternary systems was always estimated by the parameters from the constituent binary mixtures. In this study, we observed that the ternary VLE estimated from the model parameters of the constituent binary pairs of the mixture with the NRTL model is better than that with the other two models.

Conclusion

The phase equilibrium of the ternary mixture, containing one partially miscible binary pair (ethyl acetate-water) of ethanol, ethyl acetate and water had been studied. Isobaric vapor-liquid equilibrium and vapor-liquid-liquid equilibrium data were measured for this ternary system and its three constituent binary systems at atmospheric pressure with a recirculating equilibrium apparatus. All experimental binary VLE data were thermodynamically consistent according to the Herington (1965) test and were well correlated by the models of UNIQUAC, NRTL, and modified Wilson by Huang and Lee.

The estimations of the ternary VLE and LLE by the models of UNIQUAC, NRTL, and modified Wilson by Huang and Lee have been tested. All the experimental data were used for 11 different correlations to estimate the parameters of these three models. This study concludes that 1) The ternary VLE estimated by the NRTL model with model parameters correlated by three binary pair experimental data is better than that by the other two models. 2) The performances of all three models in representing ternary LLE can be improved successfully if the binary pair parameters of water-ethyl acetate were obtained from mutual solubility data. 3) The modified Wilson of Huang and Lee's model is superior to UNIQUAC and NRTL models in estimating ternary LLE in this study.

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Nomenclature

A_1, A_2, A_3	= the peak area percentages of ethanol, ethyl acetate, and water for GC analysis
B_{ij}	= second virial coefficient for i - j pair
B_{mix}	= second virial coefficient of the mixture
D	= parameter defined in Eq. (1)
f	= fugacity
ΔH^v	= heat of vaporization
P	= total pressure
P_i^s	= vapor pressure of pure component i

Q_1	= objective function as defined by Eq. (6)
Q_2	= objective function as defined by Eq. (7)
Q_3	= objective function as defined by Eq. (8)
R	= gas constant
T	= absolute temperature
U	= upper area defined in consistency test figure
V	= lower area defined in consistency test figure
v_i^l	= molar liquid volume of pure component i
x_i	= liquid phase mole fraction of component i
y_i	= vapor phase mole fraction of component i
γ_i	= activity coefficient of component i
θ	= a function in the coexistence equation
σ^2	= variance of variable
$\hat{\phi}_i$	= fugacity coefficient of component i at P and T
ϕ_i^s	= fugacity coefficient of pure component i at P_i^s and T

<Superscripts>

cal	= calculated
exp	= experimental
I, II	= equilibrium liquid phase
l	= liquid phase
v	= vapor phase

<Subscripts>

c	= critical value
r	= reduced value
b	= boiling point

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