DETERMINATION AND PREDICTION OF THE ISOBARIC VAPOR-LIQUID-LIQUID EQUILIBRIUM DATA

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ABSTRACT

The prediction method of the isobaric vapor-liquid-liquid equilibria (VLLE) data for the system ethanol-water-1-butanol and ethanol-2-butanol-water was studied. The parameters for the activity coefficients models were determined from the constituent binary VLE data. With the parameters, the isobaric ternary VLLE data were predicted and compared with the experimental ones obtained in our previous study. Furthermore, a prediction method based on successive calculations of LLE at boiling point and VLE was studied. For this method, the two sets of the parameters were independently determined for LLE and VLE calculation. The VLLE data predicted by this method were in good agreement with the experimental ones.

INTRODUCTION

The phase equilibrium data is one of the basic and important physical properties for design and analysis of phase separation processes. For vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE), a number of measurements and predictions have been reported in literature and they seem to be successful. On the contrary, vapor-liquid-liquid equilibrium (VLLE) data, which are significantly important for the heterogeneous separation processes, have been reported scarcely due to the difficulty of their measurements. The static method and the dynamic method have been mainly used for the measurements. The static method, which is said to be the most accurate method for the measurement of phase equilibria and is widely used for the isothermal measurements, requires long time for settling the system. On the contrary, the dynamic method can achieve the equilibrium quickly and has been generally used for the isobaric measurements. However, when it comes to the measurements of VLLE, there is a problem of the recirculation of two liquid phases that appear in an apparatus for the VLLE measurements. So far, treatments of these two liquid phases in the VLE measurement apparatus have been studied by some researchers. For example, a dynamic VLE still equipped with an ultrasonic homogenizer in order to mix two liquid phases in the boiling flask was proposed by Gomis et al. [1]. In their apparatus, LLE measurements at boiling points are done independently in the water bath that is controlled at the boiling temperature. Also in

our previous study [2], a simple dynamic VLE still has been developed for both VLE and VLLE measurements. Although the still is very similar to the ordinary Gillespie type VLE still, VLE and VLLE measurements can be done in the same apparatus.

Another problem concerned with VLLE is its prediction. It is well known that the prediction of VLLE is not as precise as those of VLE and LLE. As studied by Lee et al. [3], the selection of the parameters for the VLLE prediction is very important since the parameters obtained from VLE data are very different from those obtained by LLE data. The predicted VLE or VLLE with the parameters determined by LLE data are sometimes poor. There seem to be no good indices to tell which parameters are better for prediction. In order to explore the cause, the accurate VLLE measurements are indispensable.

The purposes of this study are to predict the VLLE precisely. In our previous study, isobaric VLE and VLLE for binary and ternary systems have been measured at atmospheric pressure. In this paper, the parameters for the activity coefficients models are determined from the constituent binary VLE data. With the parameters, the isobaric ternary VLLE data are predicted and compared with the experimental ones Furthermore, a prediction method of ternary VLLE for these systems, and a parameter estimation method for LLE calculation are studied. The prediction method is based on successive calculations of LLE at boiling point and VLE. For each calculation, the different sets of parameters of activity coefficients models are independently determined and used. The predicted vapor phase compositions at VLLE are compared with the experimental ones.

PARAMETER ESTIMATION FOR ISOBARIC BINARY VLE AND VLLE DATA

Parameters of activity coefficient models, NRTL [4] and UNIQUAC [5], are determined by minimizing the following objective function.

$$OF = \sum_{k=1}^{m} \sum_{i=1}^{n} \left(\frac{\gamma_{i,k,\exp} - \gamma_{i,k,cal}}{\gamma_{i,k,\exp}} \right)^2 \tag{1}$$

where OF is the objective function, and $\gamma_{i,k,\exp}$ and $\gamma_{i,k,cal}$ are experimental and calculated activity coefficient of component i of the data number k, respectively, m is number of the data and n is number of components. The objective function was minimized by Marquardt method [6] and Simplex method proposed by Nelder and Mead [7]. If the two sets of parameters determined by both methods are different with each other, the one whose objective function is smaller than the other was taken. In this study, the non-randomness parameter, α, of the NRTL model was fixed at 0.2, and the values for van der Waals volume and surface parameter, r and q respectively, were taken from the literature [8].

The parameters determined from the binary VLE data for the system ethanol (1) – water (2) are shown in Table 1. Predicted VLE for the system with the parameters in Table 1 are compared with the experimental ones in Fig. 1. In the figure, the VLE data for the system in the literature [9-11] are also plotted. As can been seen in the figure, the experimental and the predicted VLE for the system are in good agreement with each other.

Table 1 Binary parameters of the NRTL and UNIQUAC models

System	Model	ΔA_{12}	ΔA_{21}	OF	$\Delta y_{1,avg}$	$\Delta y_{1,max}$	ΔT_{avg}	ΔT_{max}
Ethanol-Water	NRTL	-460.030	1791.37	0.0137	0.0044	0.0136	0.1507	0.4686
	UNIQUAC	-70.1587	398.992	0.0066	0.0029	0.0122	0.1123	0.3362
Water-1-Butanol	NRTL	3409.83	-426.999	0.3818	0.0129	0.0289	1.1576	2.8259
	UNIQUAC	498.762	183.167	0.2616	0.0100	0.0425	0.9634	2.3324
2-Butanol-Water	NRTL	-552.206	3344.64	0.6257	0.0202	0.0479	0.5278	0.9990
	UNIQUAC	79.2739	516.5409	0.4319	0.0165	0.0641	0.4177	2.6441

$\Delta A_{ij} = (g_{ij}-g_{jj}) / R$ for NRTL, $(u_{ij}-u_{jj}) / R$ for UNIQUAC
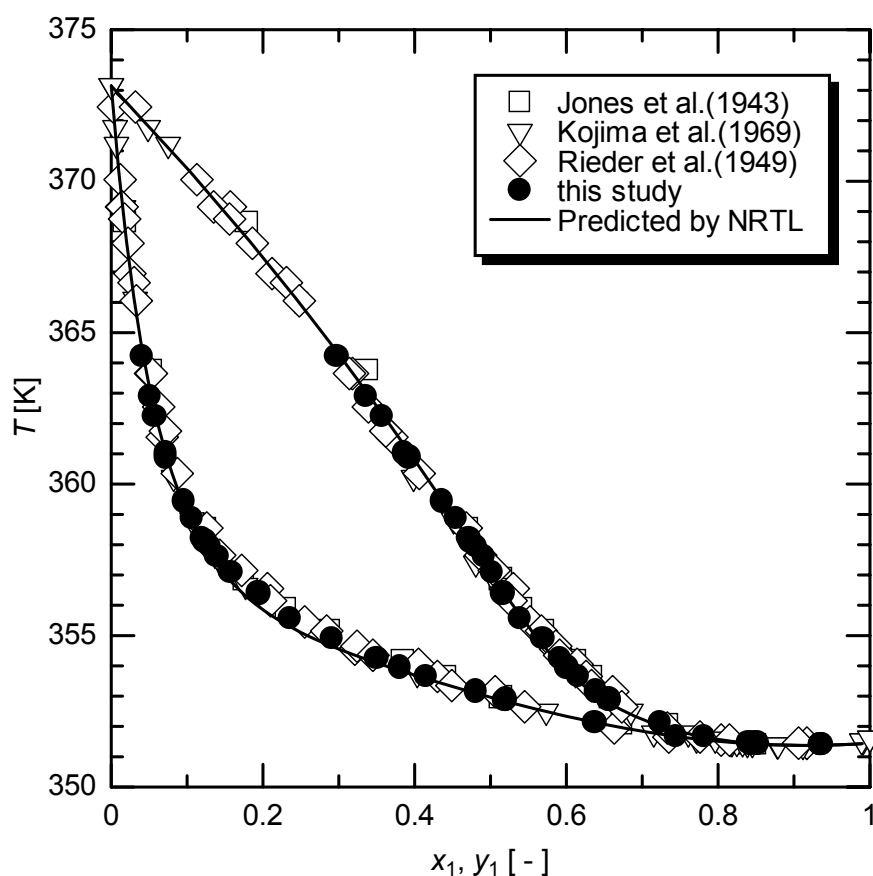

Fig. 1 Boiling and dew point for the system ethanol (1) - water (2) with those predicted by activity coefficient models

The parameters for the systems water (1) – 1-butanol (2) and 2-butanol (1) – water (2) are also shown in Table 1. The comparison of boiling and dew points between the experimental and the predicted ones for these systems are shown in Figs. 2 and 3, respectively. In these figures, the VLE data in the literature [12-20] and those predicted by ASPEN Plus are also plotted. For both systems, the predicted compositions of water in the organic liquid phase at VLLE are richer than the experimental ones. In order to investigate the cause of these deviations, various

types of the objective functions were tested. However, the results showed the same tendency. From these results of predictions, the sizes of two liquid phases regions at boiling points predicted by the parameters determined with VLE data for these two binary systems tend to become larger than the experimental ones.
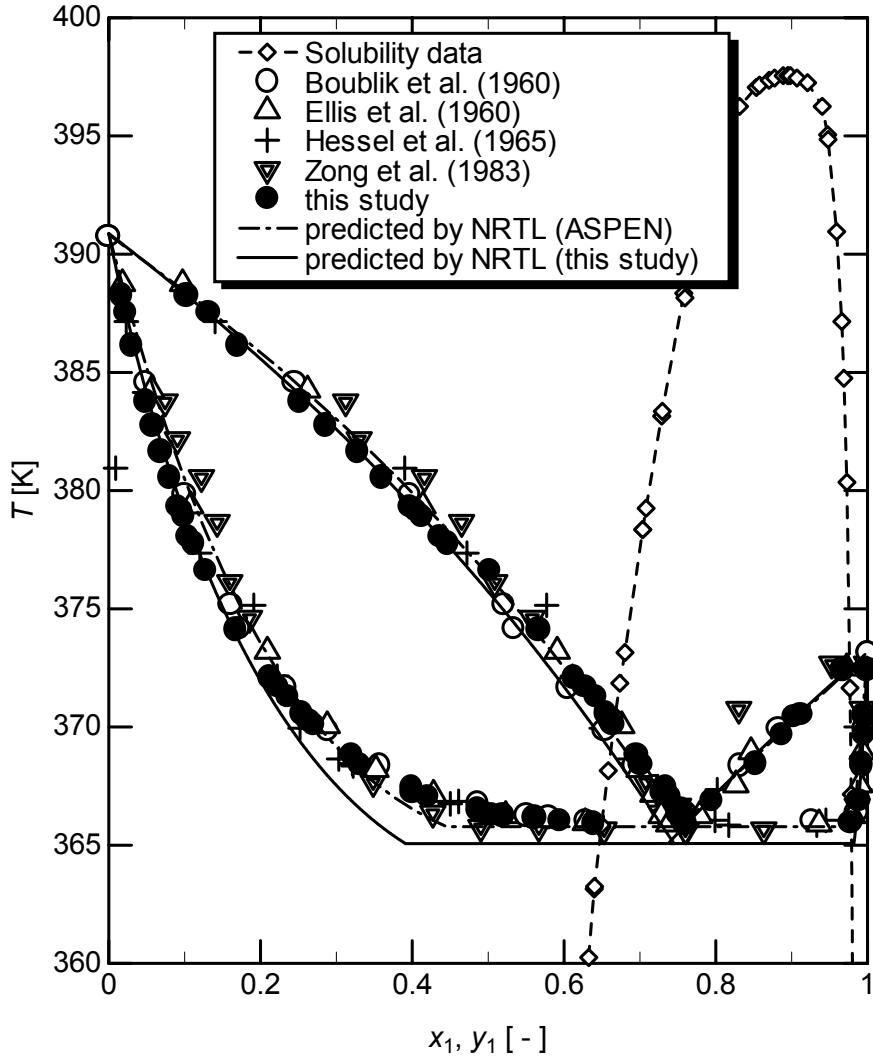

Fig. 2 Boiling and dew point for the system water (1) − 1-butanol (2) with those predicted by activity coefficient models
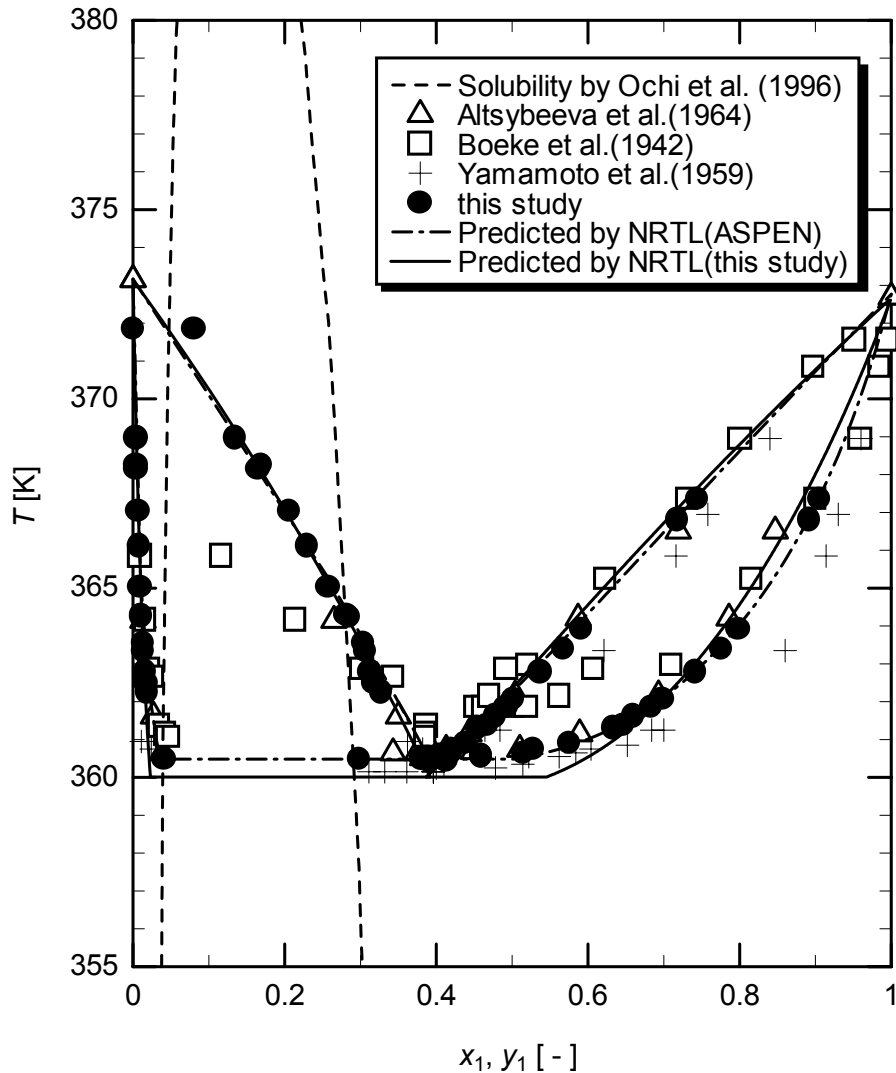
Fig. 3 Boiling and dew point for the system 2-butanol (1) – water (2) with those predicted by activity coefficient models

PREDICTION OF ISOBARIC TERNARY VLLE WITH THE PARAMETERS DETERMINED BY BINARY VLE DATA

Predictions of isobaric ternary VLLE for the systems ethanol (1) – water (2) – 1-butanol (3) and ethanol (1) – 2-butanol (2) – water (3) were done with the parameters determined by the isobaric constituent binary VLE and VLLE data. Since isobaric VLE data for the system ethanol – 1-butanol and ethanol – 2-butanol were not measured in this study, the parameters for those systems were taken from literature [8]. The result for the system ethanol – water – 1-butanol is shown in Fig. 4. As can be seen in the figure, the predicted two liquid phase region at boiling point is larger than the experimental one. Experimental boiling points are compared with the predicted ones in Fig. 5. Although the predicted boiling points seems to be in good agreement in the figure, the liquid phase compositions are very different from the experimental ones. Thus, these parameters cannot predict the isobaric VLLE data for this system accurately.
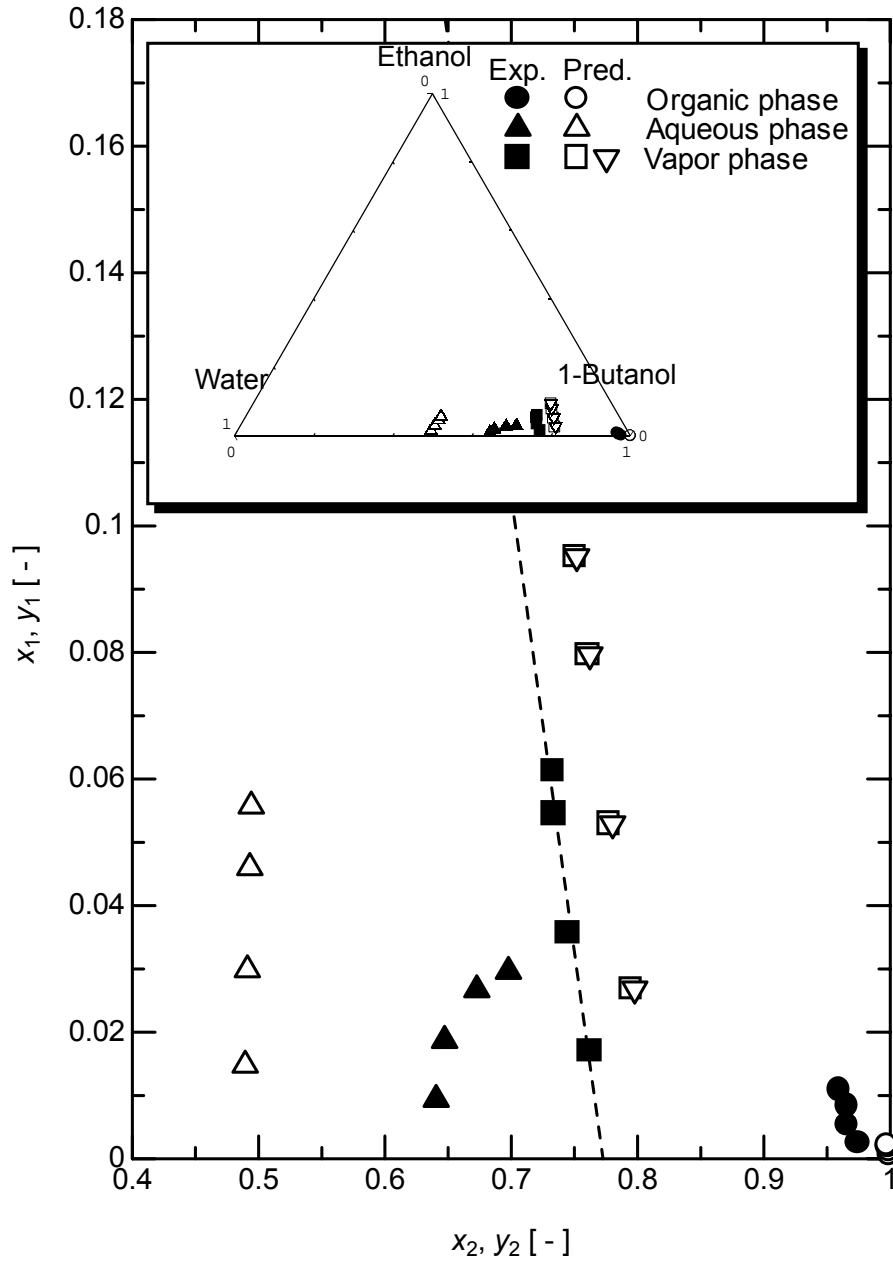
Fig. 4 Comparison between experimental and predicted compositions at VLLE for the system ethanol (1) – water (2) – 1-butanol (3)
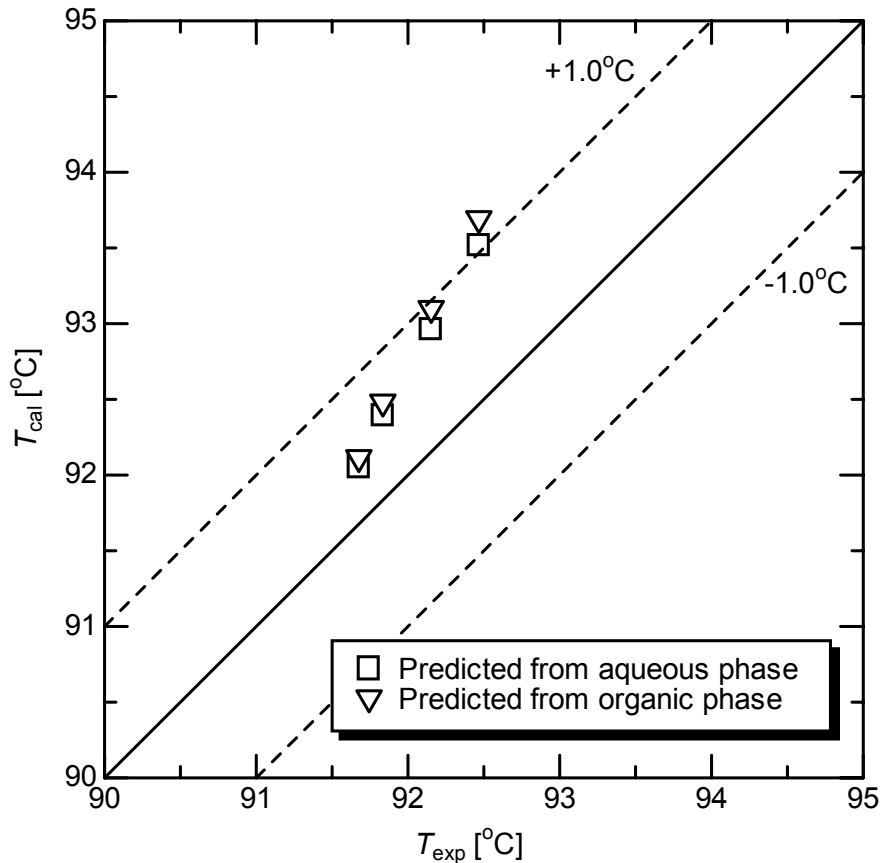
Fig. 5 Comparison between experimental and predicted boiling points at VLLE for the system ethanol (1) – water (2) – 1-butanol (3)

The comparison for the system ethanol-2-butanol-water is shown in Fig. 6. Similar to ethanol-water-1-butanol system, the predicted two liquid phases region at boiling points is different from the experimental one, especially for the organic phase. Furthermore, the predicted boiling points for the region are about 15 K higher than the experimental ones, as shown in Fig. 7.

From the results of the predictions for these two ternary systems, the parameters determined with the constituent binary VLE data cannot be used for the prediction of the ternary VLLE data for these systems. In particular, the predictions of the compositions of the organic liquid phase are significantly poor. It seems that the parameters for LLE calculation is necessary for better prediction.
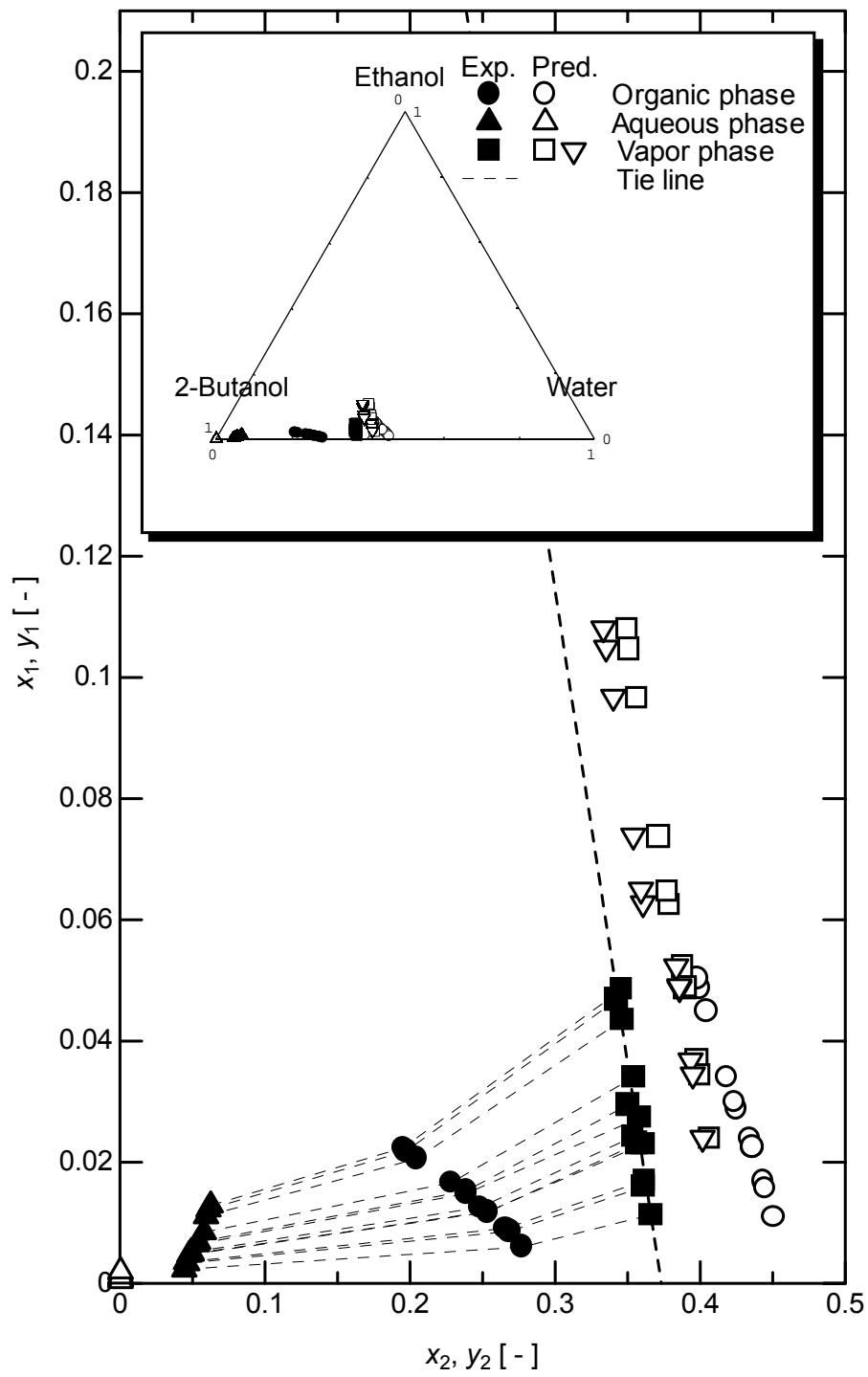
Fig. 6 Comparison between experimental and predicted compositions at VLLE for the system ethanol (1) – 2-butanol (2) – water (3)
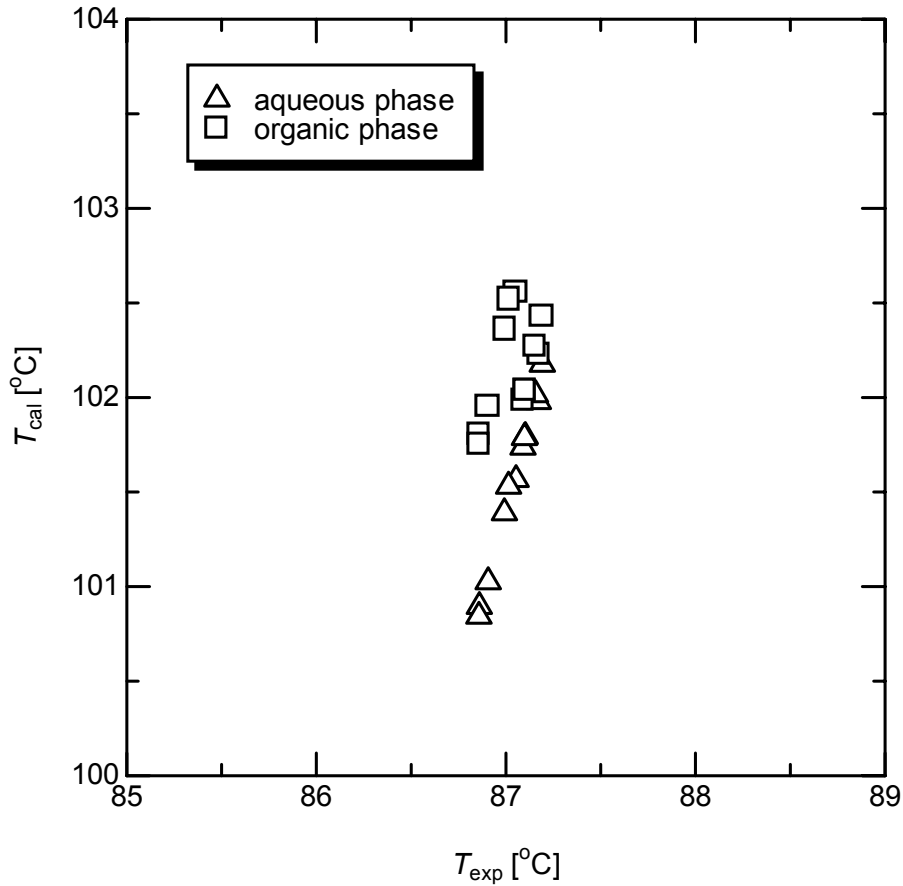
Fig. 7 Comparison between experimental and predicted boiling points at VLLE for the system ethanol (1) – 2-butanol (2) – water (3)

DETERMINATION OF THE PARAMETERS WITH THE ISOBARIC TERNARY VLLE DATA

Determination of the Parameters for LLE Calculation

Based on the discussion above, the parameters for LLE calculation are independently determined from the LLE data of the isobaric ternary VLLE data, namely the liquid compositions. Though there are six parameters to be determined for a ternary system, it was hard to determine all of them at the same time. Recently, a regression method of the parameters with ternary LLE data was proposed by Katayama [21]. In the method, the parameters for the immiscible binary pair are preliminary determined from the binary LLE or solubility data. By fixing these parameters, the rest of the parameters are determined from the ternary LLE data by using the modified Marquardt method proposed by Katayama [21]. In this study, this Katayama method was used to determine the parameters for LLE calculation.

To determine the parameters from binary LLE data, the following objective function was employed.

$$OF = \sum_{k=1}^{m}\sum_{i=1}^{n}\left(a_{i,1,k} - a_{i,2,k}\right)^2 \tag{2}$$

where $a_{i,1,k}$ and $a_{i,2,k}$ are the activities of the component i of the data number k in the phase 1 and 2, respectively, and calculated as follows.

$$a_i = x_i \gamma_{i,cal} \tag{3}$$

To determine the parameters from ternary LLE data part of ternary VLLE data, equation (2) can be also used as the objective function. However, the LLE data predicted with the parameters determined from the equation (2) were not accurate. So the following objective function for the prediction of the ternary LLE data was employed, which is the difference of the experimental and predicted liquid composition in each phase.

$$OF = \sum_{k=1}^{m} \sum_{j=1}^{2} \sum_{i=1}^{n} \left(x_{i,j,k,\exp} - x_{i,j,k,cal} \right)^2 \tag{4}$$

where j is the phase 1 and 2, and m is the number of the data.

First of all, the parameters for the immiscible binary pairs are determined from the solubility data. Since the solubility data are not measured in this study, the data in the literature [16, 20] are used. The solubility data are smoothed by the polynomial function of the temperature for each system and the LLE data for a temperature can be read from this smoothed curve. Then the rest of the parameters were determined by the modified Marquardt method proposed by Katayama [21].

Parameter estimation and Prediction for the system Ethanol-2-Butanol-Water
The resultant parameters versus the temperature for the system 2-butanol-water are shown in Fig. 8. The parameters were correlated to the temperatures as a second order polynomial. The coefficients for the polynomial function are shown in Table 2. The rest of the parameters necessary for the ternary LLE prediction were determined by Katayama's method successfully. They are shown in Table 3. The parameters for the VLE calculations are directly determined from the activity coefficients data for both systems. The parameters are shown in Table 4.

Table 2 Temperature dependent parameters for LLE calculation

System	Pseudo Water(1)-1-Butanol(2)			2-Butanol(1)-Water(2)		
	a_{ij}	b_{ij}	c_{ij}	a_{ij}	b_{ij}	c_{ij}
NRTL						
ΔA_{12}	1.978×10^7	-1.084×10^5	148.5	-1981	11.81	-2.224×10^{-2}
ΔA_{21}	-1.713×10^7	9.378×10^4	-128.3	-2367	17.64	-1.587×10^{-2}
UNIQUAC						
ΔA_{12}	1.212×10^7	-6.631×10^4	90.73	-174.7	1.655	-4.166×10^{-3}
ΔA_{21}	-9.343×10^7	5.111×10^4	-69.91	-1261	7.486	-8.115×10^{-3}

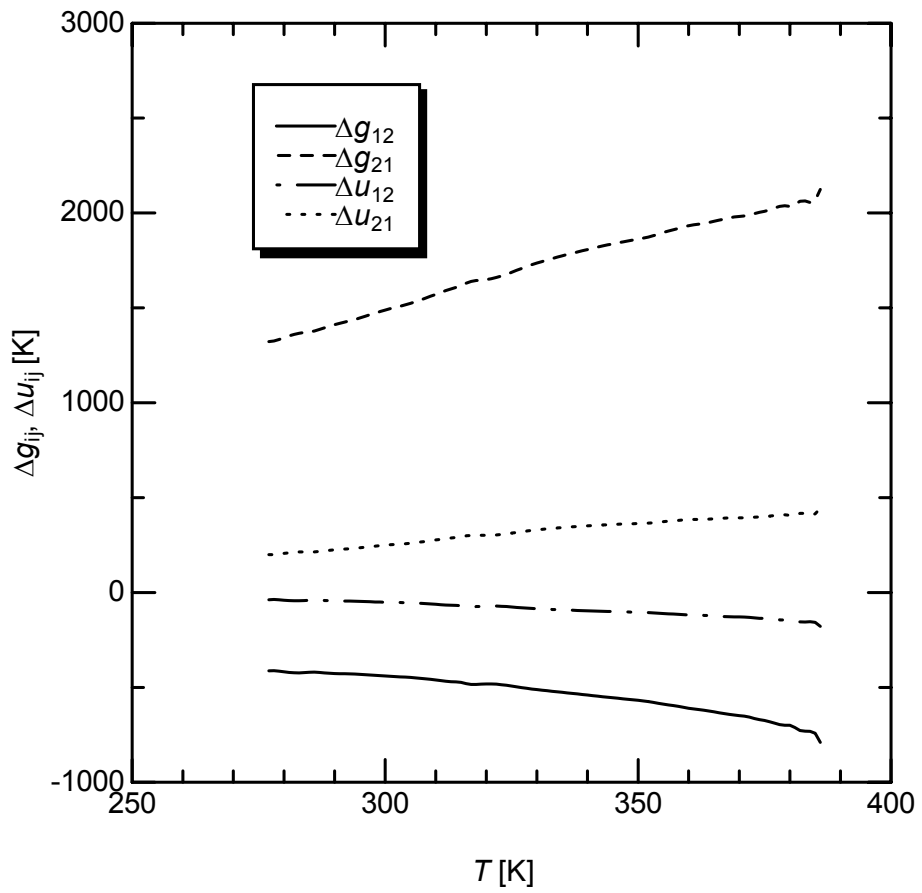$\Delta A_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2$

Fig. 8 Temperature dependences of the model parameters for the system 2-butanol (1) – water (2)

Table 3 Binary interaction parameters for LLE calculation

System	Ethanol (1)-Water (2)-1-Butanol (3)		Ethanol (1)-2-Butanol (2)-Water (3)	
	NRTL	UNIQUAC	NRTL	UNIQUAC
ΔA_{12}	1193	485.1	-546.5	-186.3
ΔA_{13}	74.99	1447	-42.96	-385.3
ΔA_{21}	-1292	651.3	-1386	-1691
ΔA_{31}	-1741	387.9	-3073	-1095

$\Delta A_{ij}=(g_{ij}-g_{jj})/R$ for NRTL, $(u_{ij}-u_{jj})/R$ for UNIQUAC

Table 4 Binary interaction parameters for VLE calculation

System	Ethanol(1)-Water(2)-1-Butanol(3)		Ethanol(1)-2-Butanol(2)-Water(3)	
	NRTL	UNIQUAC	NRTL	UNIQUAC
ΔA_{12}	2433	-303.6	-469.4	-282.3
ΔA_{13}	-178.8	6.880	-175.5	84.00
ΔA_{21}	-19.77	631.1	1315	1001
ΔA_{22}	1657	626.1	-295.4	75.78
ΔA_{31}	749.3	378.0	851.6	94.44
ΔA_{32}	-285.3	-200.0	1541	181.6

$\Delta A_{ij}=(g_{ij}-g_{jj})/R$ for NRTL, $(u_{ij}-u_{jj})/R$ for UNIQUAC

The prediction method for the isobaric VLLE data is similar to the one proposed by Liu *et al.* [22], that is, VLE and LLE data are separately calculated with the correspondent parameters in Tables 2, 3 and 4. The procedure is as follows. Firstly, an overall liquid composition is given and the bubble point is set as the initial temperature. With this condition, isothermal LLE calculation is done and the compositions of the two liquid phases are calculated. For these compositions, the boiling points and the vapor phase compositions are independently determined by the bubble point calculation. If these boiling points are different with each other, the average value is used for the next LLE calculation. The procedure is repeated until the difference of the boiling points between the former and the present iteration becomes small enough for both liquid phases. So the predicted vapor phase compositions and boiling points are presented for both organic and aqueous liquid phases in this study. Since only the two liquid phases regions are studied in this paper, the phase stability analysis was omitted.

The predicted VLLE for the system ethanol-2-butanol-water by this method are shown in Fig. 9. As can be seen in the figure, the predicted LLE favorably coincides with the experimental ones. The predicted vapor compositions are also in good agreement with the experimental ones. Fig. 10 shows the comparison between the predicted and experimental boiling points. Almost all of the predicted boiling points are within ±1.0 K of the experimental ones.
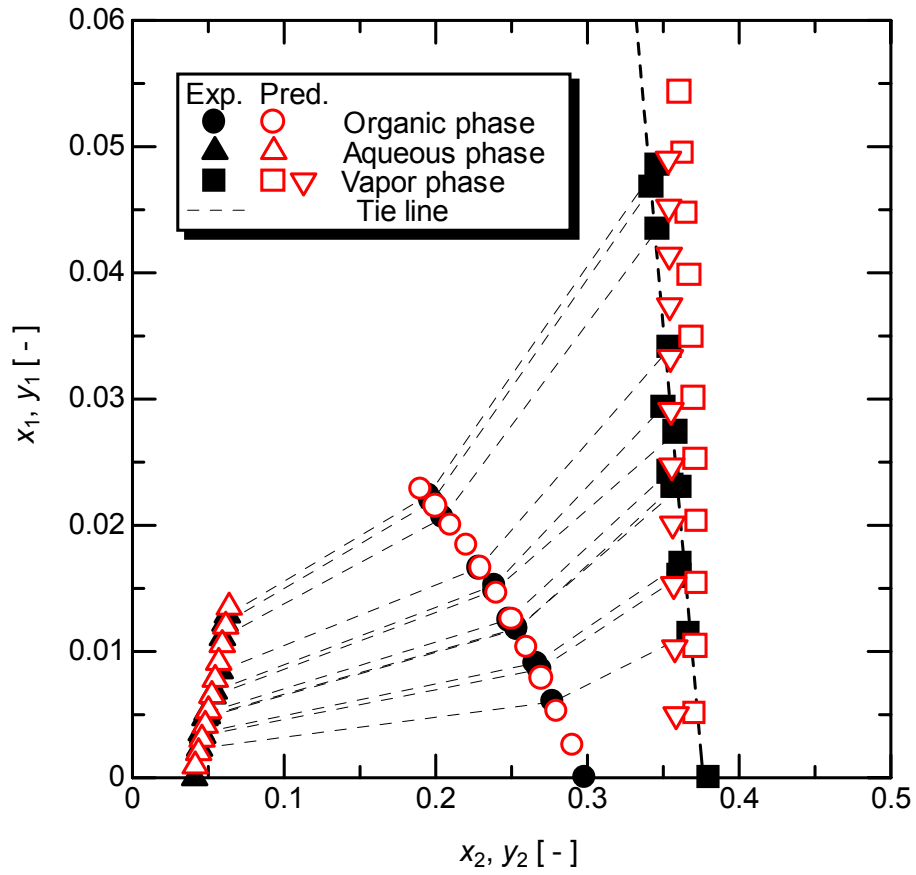
Fig. 9 Comparison between experimental and predicted isobaric ternary VLLE for the system ethanol (1) –2-butanol (2) – water (3) at 101.3 kPa
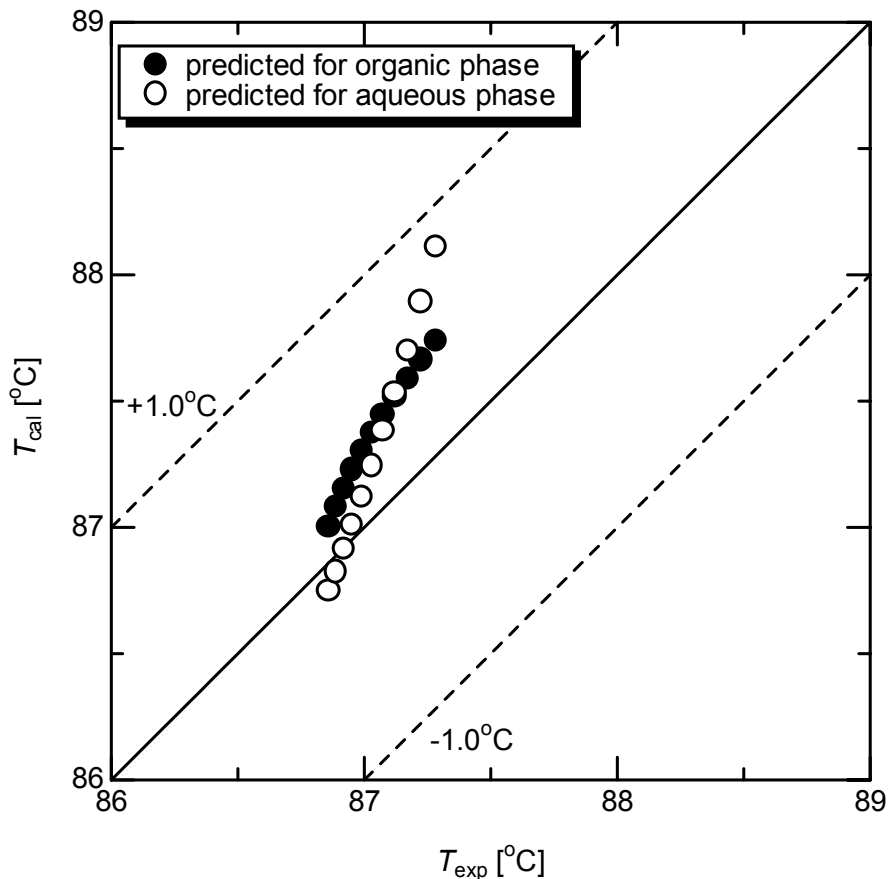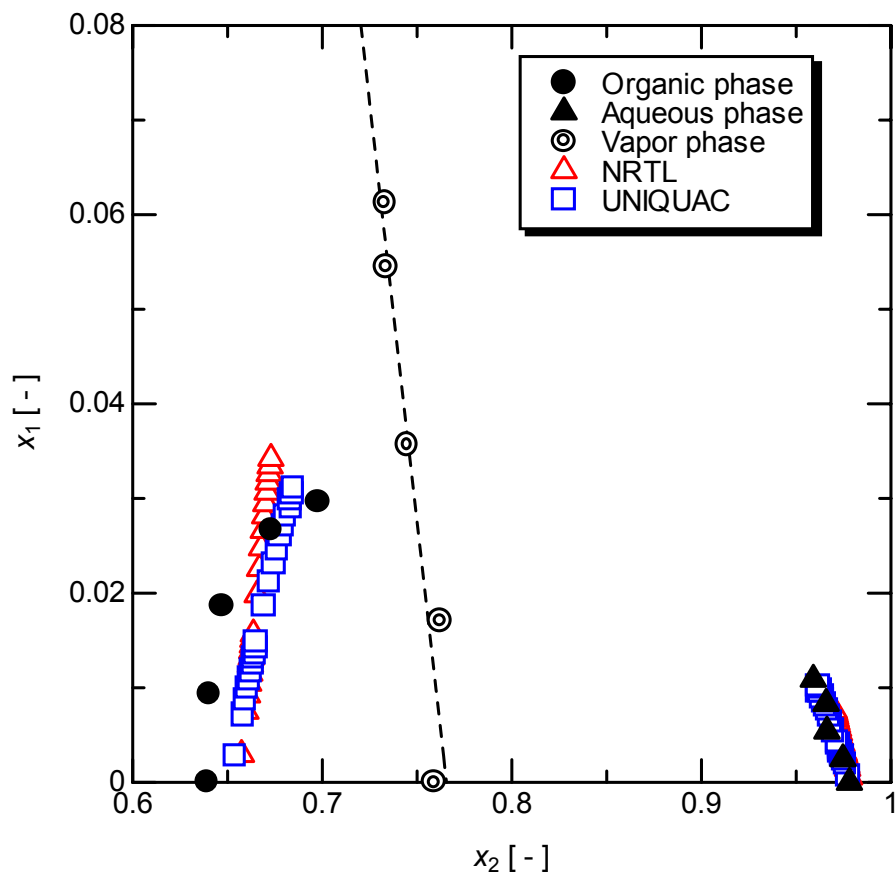
Fig. 10 Comparison between experimental and predicted compositions at VLLE for the system ethanol (1) – 2-butanol (2) – water (3)

Parameter Estimation and Prediction for the system Ethanol-Water-1-Butanol
For the system water-1-butanol, if the parameters determined by Katayama's method are used for prediction of ternary LLE at boiling points, the predicted LLE data deviate from the experimental ones as shown in Fig. 11. In the region where the composition of ethanol in the liquid phase is more than 0.02 mole fraction, the solubility of the organic liquid phase for this ternary system changes a lot, while the boiling points for this region doesn't change so much. The binary solubility data for this narrow temperature range changes slightly. Thus, the parameters from binary LLE data cannot predict this big solubility change.

In this study, the pseudo-binary LLE data are assumed by normalizing the compositions of water and 1-butanol in ternary LLE data of VLLE data, and the parameters for this binary immiscible pair are determined from the pseudo-binary LLE data. The parameters determined by this method are also shown in Table 2. The rest of the parameters necessary for the ternary LLE prediction are estimated by Katayama's method and shown in Table 3. The parameters for VLE calculation are determined from the isobaric ternary VLLE data for this system. They are shown in Table 4.

Fig. 11 Comparison between experimental and predicted isobaric ternary LLE with the parameters determined by Katayama's method for the system ethanol (1) – water (2) – 1-butanol (3)

The predicted VLLE for the system ethanol-water-1-butanol are shown in Fig. 12. The VLLE was calculated by the same way as for the system ethanol-2-butanol-water. The predicted compositions are in good agreement with the experimental ones. Fig. 13 shows the comparison between the predicted and experimental boiling points. Almost all of the predicted boiling points are within ±1.0 K of the experimental ones.

From the results above, the isobaric ternary VLLE data for these two systems are successfully predicted with the parameters obtained in this study.
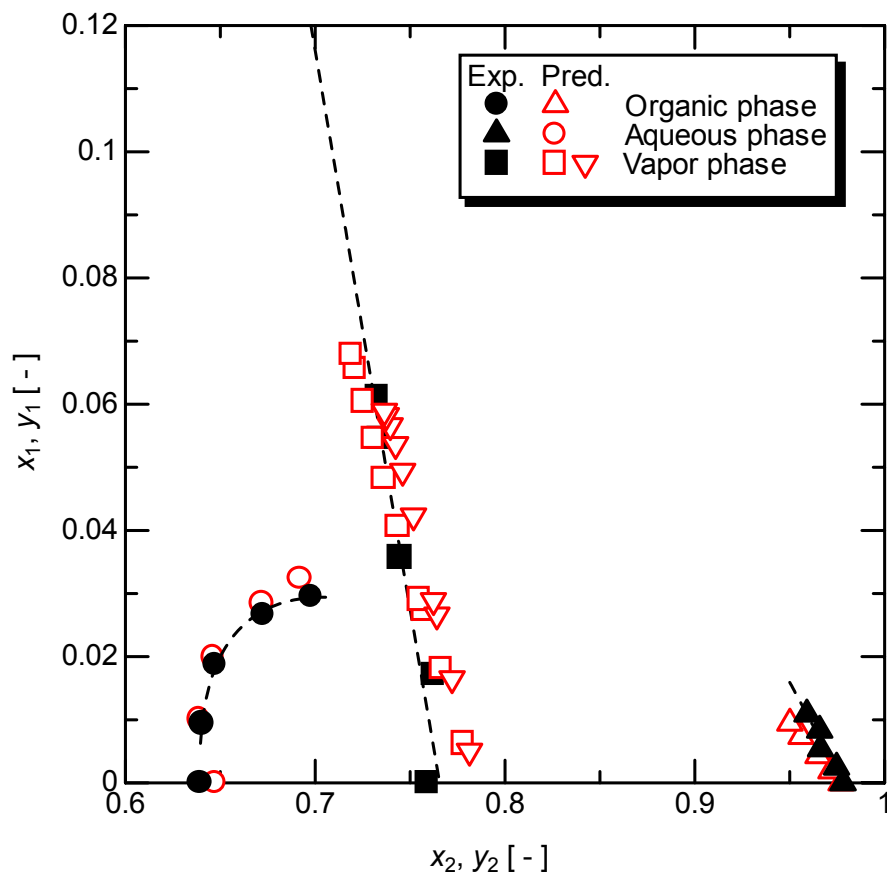
Fig. 12 Comparison between experimental and predicted isobaric ternary VLLE for the system ethanol (1) – water (2) – 1-butanol (3) at 101.3 kPa
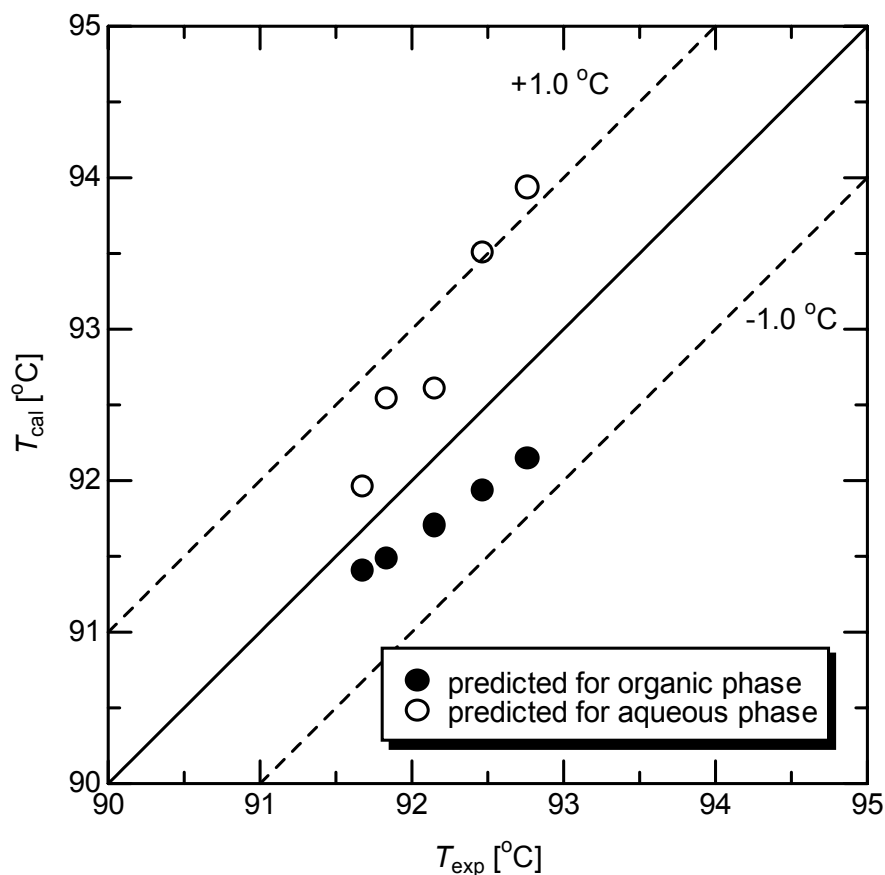
Fig. 13 Comparison between experimental and predicted vapor phase composition of 1-butanol at VLLE for the system ethanol (1) – water (2) – 1-butanol (3)

CONCLUSION

The predictions of the isobaric ternary VLLE data for the systems ethanol-water-1-butanol and ethanol-2-butanol-water with activity coefficient models are studied. The parameters determined from binary VLE data for the constituent binaries cannot be used for the prediction since the predicted LLE data at boiling points are very different from the experimental ones. Then the parameters for VLE and LLE calculation were independently determined from those data. Katayama's method was employed to determine the parameters for LLE calculation. For the system ethanol-2-butanol-water, the parameters were obtained by the method. For the system ethanol-water-1-butanol, however, the parameters for the binary immiscible pair determined from the binary LLE data were not suited for the prediction of ternary LLE at boiling points. So the pseudo-binary system was assumed by normalizing the compositions of binary immiscible pairs in the ternary LLE data. Using the parameters, better predictions for the ternary LLE data at boiling points were obtained. Finally, the isobaric ternary VLLE data are predicted by the successive calculation of the LLE and VLE. The predicted VLLE data were in good agreement with the experimental ones.

NOMENCLATURE

ΔA_{ij} = binary interaction parameter for component i and j [K]

a = activity   [-]

a_{ij} = coefficients for temperature dependent parameter   [K]

b_{ij} = coefficients for temperature dependent parameter   [-]

c_{ij} = coefficients for temperature dependent parameter   [K^{-1}]

g = binary interaction parameter of NRTL model   [J mol^{-1}]

m = number of the data   [-]

OF = objective function   [-]

q = van der Waals surface area parameter   [-]

R = gas constant (=8.314 J mol^{-1} K^{-1})   [J mol^{-1} K^{-1}]

r = van der Waals volume parameter   [-]

T = temperature   [K]

u = binary interaction parameter of UNIQUAC model   [J mol^{-1}]

x = mole fraction in the liquid phase   [-]

y = mole fraction in the vapor phase   [-]

Greeks

α = nonrandomness parameter of NRTL model   [-]

γ = activity coefficient   [-]

Subscript

cal = calculated value

exp = experimental value

i = component i

j = component j

j = phase number, in eq. 4

k = data number

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KEYWORD

Phase equilibrium, Vapor-liquid-liquid equilibrium, Prediction, Parameter estimation, Activity coefficient models