

# Extrapolation of High Pressure VLE Data and Simultaneous Representation of Excess Enthalpies by Using NRTL Equation\*

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**Abstract** The non-random two liquids (NRTL) equation together with the Pitzer/Curl Virial equation of state are used to investigate the simultaneous representation of excess enthalpies ( $h^E$ ) and vapour-liquid equilibria (VLE) and the VLE prediction from  $h^E$  data. The calculation strategy for properly determining NRTL parameters and the effect of their temperature dependence on the simultaneous correlation of  $h^E$  and VLE data and the VLE extrapolation are analysed in detail.

**Keywords** non-random two liquids (NRTL) equation, excess enthalpy, vapour-liquid equilibrium, prediction

## 1 INTRODUCTION

The phase equilibrium data and the caloric properties such as excess enthalpies ( $h^E$  data) are of great importance in the process and equipment design for petroleum and other chemical industries. The activity coefficient models (also called  $g^E$ -models), such as Wilson, NRTL (non-random two liquids), UNIQUAC, UNIFAC *etc.*<sup>[1]</sup>, are very successful in the description of phase equilibria, particularly of vapour-liquid equilibria. They are very attractive in the engineering calculation and process simulation because of their flexibility, robustness and the need of less computation time. However, the disadvantage of these models is that it is difficult to use them to describe equilibrium and other thermodynamic properties in a unified way. The simultaneous representation of phase equilibria and excess enthalpies and their mutual predictions by using activity coefficient models have been investigated for decades. Detailed reviews can be seen in the literature<sup>[2,3]</sup>. Generally the VLE (vapour-liquid equilibrium) and  $h^E$  data in a certain temperature range can be correlated simultaneously by using  $g^E$ -models such as NRTL and UNIQUAC equation if a strong temperature-dependence is introduced in the energy parameters, but the prediction of  $h^E$  data from experimental VLE is usually not satisfactory and the calculation results in the reverse direction are even worse<sup>[4,5]</sup>. The combination of cubic equations of state with  $g^E$ -models (in the form of  $g^E$ -mixing rules<sup>[6-8]</sup>) improves the simultaneous description of the VLE and  $h^E$  data but their mutual prediction remains unsatisfactorily<sup>[9-11]</sup>. In addition, strongly temperature-dependent model parameters are still necessary<sup>[12,13]</sup>, which often leads

to problems by the extrapolation of VLE and/or  $h^E$  data. Ji *et al.*<sup>[14,15]</sup> recently used a cubic 3-parameter equation of state<sup>[16]</sup> together with  $g^E$ -mixing rules to correlate simultaneously a single VLE isotherm at normal temperature and  $h^E$  data in a wide temperature range and found that the parameters obtained in this way can be used to predict VLE data satisfactorily even in the critical region.

In this work the application of  $g^E$ -models in the VLE extrapolation at high pressures and simultaneous representation of  $h^E$  data is investigated by using the NRTL equation as an example and the influence of different temperature dependence variants of the model parameters is analysed in detail.

## 2 THERMODYNAMIC BASIS

The relationship between the VLE data which follow from the excess Gibbs free energy ( $g^E$ ) and the derived quantities  $h^E$  (temperature dependence) and  $v^E$  (pressure dependence) can be expressed by the following integration

$$\frac{g^E}{T} = \frac{g_{T_0, p_0}^E}{T_0} + \int_{T_0}^T \left( -\frac{h^E}{T^2} \right) dT + \frac{1}{T} \int_{p_0}^p v^E dp \quad (1)$$

Because the excess volumes of liquid mixtures are usually very small in the case that the system is not located in the critical region, the third term on the right side of Eq. (1) can be neglected. This means that the VLE data at any temperatures and pressures below the critical point can in principle be predicted when the excess Gibbs free energy at a reference state is given and the temperature dependence of the  $g^E$ -model is correct.

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In this work, the NRTL equation is used as an example to describe the excess Gibbs free energy for the liquid phase in a wide temperature range

$$\hat{g}^E = \frac{g^E}{RT} = \sum_k x_k \left( \frac{\sum_l x_l G_{lk} \tau_{lk}}{\sum_l x_l G_{lk}} \right) \quad (2)$$

$$\tau_{ij} = \frac{\Delta g_{ij}/R}{T} = \frac{A_{ij}}{T} \quad G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$(\alpha_{ij} = \alpha_{ji}) \quad (3)$$

where  $A_{ij}$  and  $\alpha_{ij}$  represent the energy and the non-randomness parameter. The corresponding activity coefficients follow from

$$\ln \gamma_i = \frac{\sum_l x_l G_{li} \tau_{li}}{\sum_l x_l G_{li}} + \sum_l \frac{x_l G_{il}}{\sum_k x_k G_{kl}} \left[ \tau_{il} - \frac{\sum_k x_k G_{ki} \tau_{ki}}{\sum_k x_k G_{ki}} \right] \quad (4)$$

and serve to the calculation of the VLE under the equilibrium condition

$$x_i^V \varphi_i^* V p = x_i^L \gamma_i^* L f_i^{0L} \quad (i = 1, \dots, K) \quad (5)$$

where  $f_i^{0L}$  represents the fugacity of the pure liquid  $i$  at system temperature and pressure and  $\varphi_i^*$  the fugacity coefficient of component  $i$  in the vapour phase which is calculated by the Virial equation of state with Pitzer/Curl correlation<sup>[1]</sup> (see Appendix). The interaction parameter used in Eq. (A6) is set to zero during the calculations.

The excess enthalpies are calculated by the temperature dependence of the activity coefficients given by

$$h_i^E = -RT^2 \left( \frac{\partial \ln \gamma_i}{\partial T} \right), \quad h^E = \sum_k x_k^L h_k^E \quad (6)$$

In order to describe thermodynamic properties in a wide temperature range, the introduction of an extra temperature dependence into the energy parameter of the NRTL equation is necessary<sup>[14,15]</sup>. In the following a linear function of temperature

$$A_{ij} = A_{ij}^c + A_{ij}^{TC}(T - 273.15) \quad (7)$$

or a quadratic one

$$A_{ij} = A_{ij}^c + A_{ij}^{TC}(T - 273.15) + A_{ij}^{T^2}(T - 273.15)^2 \quad (8)$$

is applied for the temperature dependence of the energy parameter  $A_{ij}$ . And the nonrandomness parameter  $\alpha_{ij}$  is taken either as a constant

$$\alpha_{ij} = \alpha_{ji} = \alpha_{ij}^c \quad (9)$$

or as a linear function of temperature

$$\alpha_{ij} = \alpha_{ji} = \alpha_{ij}^c + \alpha_{ij}^{TC}(T - 273.15) \quad (10)$$

Three variants of temperature dependence resulted from different combinations of  $\alpha_{ij}$  and  $A_{ij}$  are listed in Table 1 and investigated in detail. The excess Gibbs free energy at a reference state and its temperature dependence of the NRTL equation are determined by correlating simultaneously an experimental VLE isotherm at a low temperature and  $h^E$  data over a wide temperature range.

**Table 1** Temperature dependence of the model parameters

Temperature dependence	$\alpha_{ij}$	$A_{ij}$
Tfa	Eq. (10) (linear)	Eq. (7) (linear)
TFb	Eq. (9) (constant)	Eq. (8) (quadratic)
TFc	Eq. (10) (linear)	Eq. (8) (quadratic)

### 3 SIMULTANEOUS REPRESENTATION OF VLE AND $h^E$

Six non-ideal systems, the experimental VLE and  $h^E$  data of which are available in a wide temperature and pressure range, are investigated. In the calculation the VLE isotherm at 298.15 K is correlated simultaneously with several  $h^E$  isotherms by using following objective function

$$F_{\text{obj}} = 10^7 \times \frac{1}{N} \sum_1^N \left| \frac{p_{\text{exp}} - p_{\text{cal}}}{p_{\text{exp}}} \right|_n + \frac{1}{M \times N} \sum_1^M \left( \sum_1^N |h_{\text{exp}}^E - h_{\text{cal}}^E|_n \right)_m \quad (11)$$

in which a large weight is used for the VLE part in order to reproduce the VLE isotherm as accurate as possible.

The results of excess enthalpies calculated by using three different variants of temperature dependence for the NRTL parameters are presented in Fig. 1 in comparison with the experimental data<sup>[17-19]</sup>. The average deviations of the correlated  $h^E$  and VLE isotherm at 298.15K are listed in Tables 2 and 3, respectively. As shown in Fig. 1, if the temperature range of  $h^E$  isotherms is not wide the  $h^E$  data together with the VLE isotherm can be well correlated even by using linear temperature dependent model parameters (TFa). However, with the increase of the temperature range the use of TFa is not flexible enough for the simultaneous correlation, particularly of systems like ethanol+

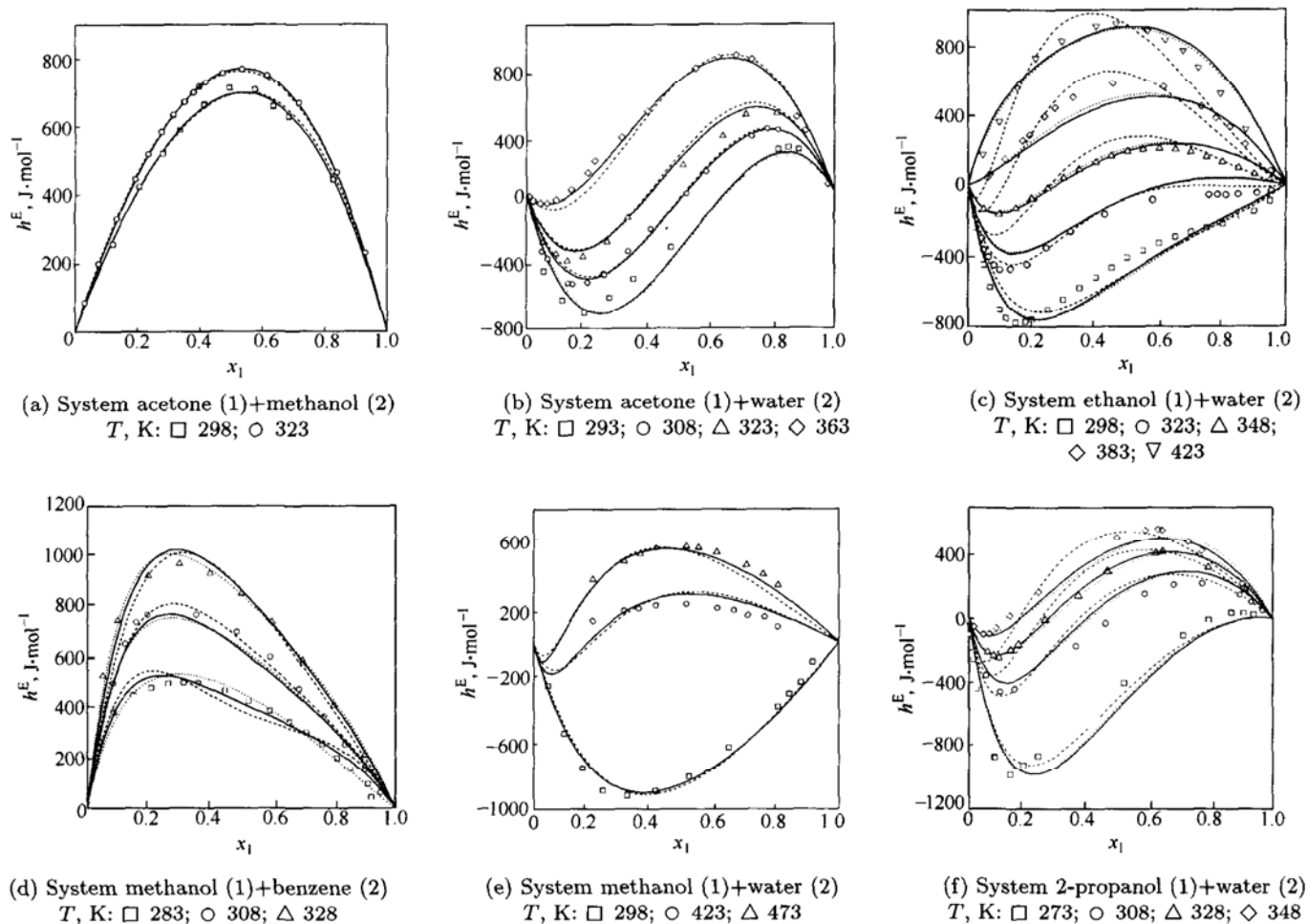


Figure 1 Correlation results of  $h^E$  data simultaneous with a VLE isotherm at 298 K by using NRTL equation with different variants of temperature dependence  
 - - - - TFa; — TFb; ····· TFc

Table 2 Simultaneous correlation results of  $h^E$  data and the VLE isotherm at 298.15 K by using the NRTL equation

System	Data points	$T, K$	$p, MPa$	NRTL, $\delta(h^E), J \cdot mol^{-1}$		
				TFa	TFb	TFc
acetone + water <sup>[17]</sup>	9	293	0.1	14.23	11.84	11.68
	14	308	0.1	10.28	8.37	8.74
	10	323	0.1	12.13	9.03	9.08
	18	363	0.3	13.64	8.38	8.35
methanol + benzene <sup>[18]</sup>	16	283	0.1	17.12	7.76	9.69
	13	308	0.1	6.46	10.19	10.27
	10	328	0.1	11.55	6.22	8.94
methanol + water <sup>[19]</sup>	12	298	0.1	16.25	15.38	15.37
	10	423	20	20.47	17.04	17.05
	10	473	20	15.22	9.60	9.60
ethanol + water <sup>[18]</sup>	23	298	0.1	17.17	14.60	16.41
	17	323	0.4	7.00	14.73	15.04
	19	348	0.4	10.68	5.19	5.90
	16	383	1.0	13.01	9.83	8.01
	16	423	4.0	14.74	9.41	8.09
	acetone + methanol <sup>[17]</sup>	10	298	0.1	4.03	2.94
2-propanol + water <sup>[17]</sup>	20	323	0.1	2.14	1.80	1.60
	15	273	0.1	19.07	21.03	19.16
	13	308	0.1	10.56	12.18	11.86
	17	328	0.1	14.93	3.85	5.67
	15	348	0.1	17.48	9.08	10.75
mean correlation deviation				12.77	9.93	10.19

Note:  $\delta(h^E) = |h_{exp}^E - h_{cal}^E|$

water and 2-propanol + water, in which the excess enthalpies are relatively sensitive to the temperature change. In such cases a stronger temperature function is necessary. By introducing a quadratic temperature function in the energy parameters of the NRTL equation (*TFb* and *TFc*) the correlation of the  $h^E$  data can be improved obviously, especially at high temperatures. The overall average deviation of excess enthalpies for the six systems studied amounts to  $9.9 \text{ J}\cdot\text{mol}^{-1}$  for *TFb* (with temperature independent non-randomness parameter), about 20% less than that of *TFa* ( $12.8 \text{ J}\cdot\text{mol}^{-1}$ ). As will be shown later, this improvement is of importance for the VLE extrapolation at high temperatures and pressures. It is to note that the further introduction of a temperature dependence in the non-randomness parameter (*TFc*) leads to only slight decrease of the VLE calculation while the accuracy of the excess enthalpy description almost keeps unchanged.

#### 4 EXTRAPOLATION OF VLE DATA

As can be seen in Eq. (1), VLE data cannot be

reliably predicted from  $h^E$  information alone because there are other uncertainties except the temperature dependency. Figs. 2 and 3 illustrate an example in

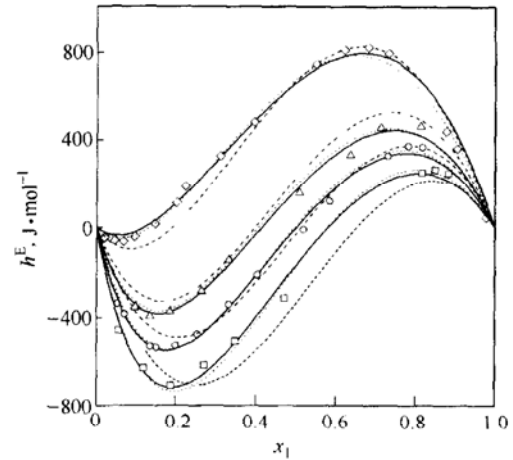


Figure 2  $h^E$  data of system acetone (1) + water (2) correlated by using NRTL equation with different variants of temperature dependence  
T, K: □ 293; ○ 308; △ 323; ◇ 363  
--- *TFa*; — *TFb*; - - - *TFc*

Table 3 VLE prediction results by using the NRTL equation

System	Data points	T K	NRTL						PSRK <sup>[20]</sup>	
			<i>TFa</i>		<i>TFb</i>		<i>TFc</i>		$\delta_{\text{rel}}(p)$	$\delta(y)$
			$\delta_{\text{rel}}(p)$	$\delta(y)$	$\delta_{\text{rel}}(p)$	$\delta(y)$	$\delta_{\text{rel}}(p)$	$\delta(y)$		
acetone + water <sup>[21,22]</sup>	13	298	1.56	1.14	1.78	1.25	1.71	1.25		
	9	333	1.99	1.25	1.60	1.26	1.60	1.26		
	22	373	1.97	0.74	2.05	0.68	2.05	0.69	2.4	0.7
	14	423	1.40	1.58	1.37	1.39	1.12	1.33	3.0	1.6
	25	473	6.92	2.96	5.20	2.18	4.74	2.04	3.6	1.2
methanol + benzene <sup>[23,24]</sup>	9	298	1.47	1.69	0.85	0.92	0.21	0.37		
	10	373	3.13	1.39	2.87	0.78	2.84	0.92	1.9	1.1
	10	413	8.06	2.47	4.25	0.92	4.27	0.92	2.3	1.4
	10	453	13.79	3.48	2.86	1.84	2.76	1.87	4.8	2.0
	10	473	16.73	3.72	2.69	2.27	11.86	5.14		
methanol + water <sup>[22,25]</sup>	9	298	2.13	0.81	2.30	0.89	2.30	0.90		
	12	373	1.34	1.22	1.45	1.44	1.44	1.43	2.2	0.9
	11	423	1.64	1.20	1.96	1.41	1.94	1.39	1.3	1.4
	11	473	1.87	1.70	2.14	1.90	2.12	1.88	1.2	1.0
	ethanol + water <sup>[26,27,28]</sup>	10	298	1.41	1.00	1.63	1.33	1.42	1.00	
19		363	1.07	0.91	1.22	1.19	1.08	1.10		
17		423	3.74	2.07	2.31	1.08	2.30	0.99	2.3	0.8
17		473	3.82	2.54	1.61	0.99	1.73	0.95	2.4	0.8
acetone + methanol <sup>[22,23]</sup>	12	298	0.22	1.96	0.22	1.96	0.22	1.96		
	12	372	0.38	0.63	0.26	0.58	0.27	0.58	2.7	1.3
	15	423	0.95	1.56	0.92	1.53	0.92	1.53	1.0	1.8
	10	473	2.15	2.52	2.03	2.74	2.10	2.79	3.6	3.2
2-propanol + water <sup>[21,28]</sup>	14	298	1.03	1.66	0.96	1.09	1.23	1.18		
	16	333	2.90	1.64	1.48	2.80	1.63	2.80		
	21	353	3.63	3.06	1.41	1.52	1.47	1.51		
	19	423	8.67	4.91	4.34	0.89	3.31	0.62		
	18	473	10.19	5.14	5.47	1.59	1.83	0.62		
mean correlation deviation of isotherms at 298.15K			1.30	1.38	1.29	1.24	1.18	1.11		
mean prediction deviation			4.68	2.16	2.18	1.46	2.83	1.63	2.7	1.5

Note: ① The VLE isotherm at 298.15 K is correlated simultaneously with  $h^E$  data;

②  $\delta_{\text{rel}}(P) = |1 - p_{\text{cal}}/P_{\text{exp}}| \times 100\%$ ;  $\delta(y) = |y_{\text{exp}} - y_{\text{cal}}| \times 100\%$

which the VLE isotherms of system acetone + water at 373 K and 473 K calculated by using NRTL equation with parameters obtained directly from  $h^E$  cor-

relation. In spite of an accurate  $h^E$  representation by using quadratic temperature dependent energy parameters (Fig. 2) the results are very poor and even a wrong type of azeotropes is predicted.

Here the NRTL parameters obtained by simultaneous correlation of  $h^E$  information and the VLE isotherm at 298.15 K are used to predict VLE data at high temperatures and pressures. Six systems with different non-ideality, of which the experimental high pressure VLE data are available, are calculated. For each system the calculations are only up to a temperature near the critical point because of the inherent limitation of  $g^E$ -models in the critical region. The deviations of the calculated VLE data from the experimental ones by using three different temperature dependence variants are summarised in Table 3. The predicted VLE isotherms are also presented in  $p$ - $x$ -diagrams in Fig. 4. For weakly non-ideal systems like methanol + water and acetone + methanol all the three temperature dependence variants give similar results and the predictions are satisfactory even at a temperature relatively near the critical point. In the

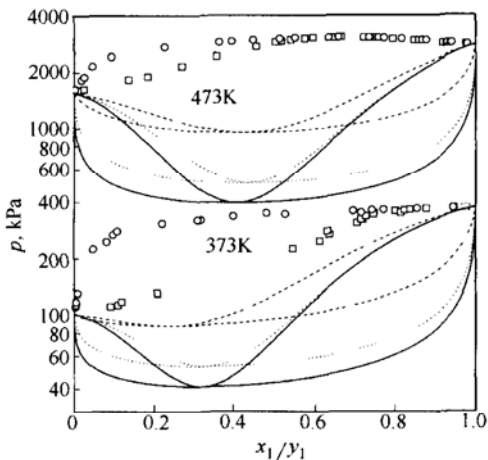
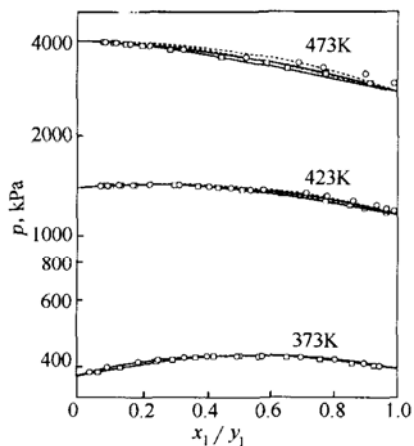
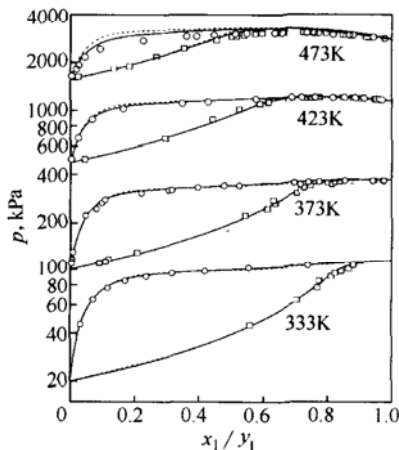


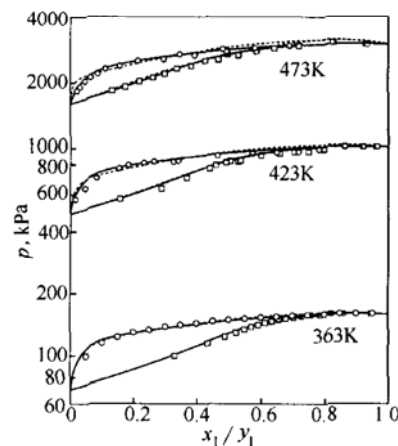
Figure 3 VLE predictions of system acetone (1) + water (2) by using NRTL equation with parameters obtained directly from  $h^E$  correlation  
 ○ exp.  $x_1$ ; □ exp.  $y_1$ ; ---  $TFa$ ;  
 —  $TFb$ ; - · - ·  $TFc$



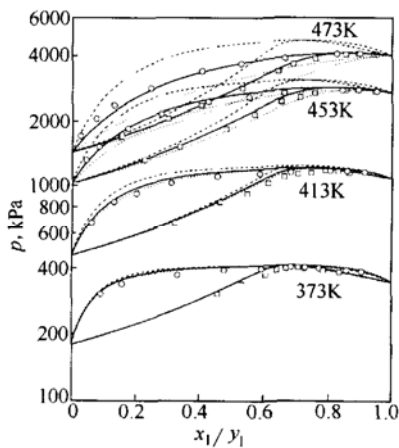
(a) acetone (1) + methanol (2)



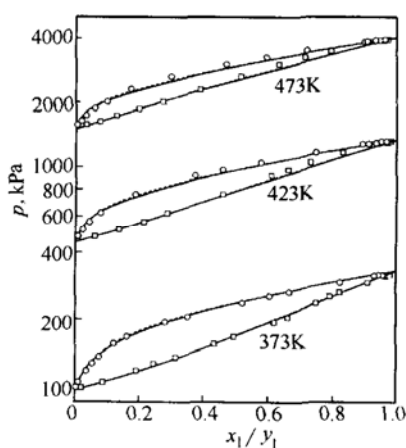
(b) acetone (1) + water (2)



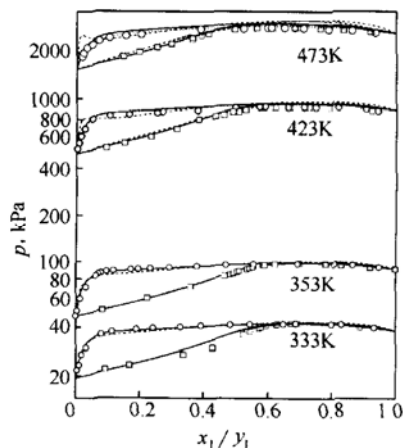
(c) ethanol (1) + water (2)



(d) methanol (1) + benzene (2)



(e) methanol (1) + water (2)



(f) 2-propanol (1) + water (2)

Figure 4 VLE predictions by using NRTL equation with different variants of temperature dependence  
 ○ exp.  $x_1$ ; □ exp.  $y_1$ ; ---  $TFa$ ; —  $TFb$ ; - · - ·  $TFc$

case of strongly non-ideal systems the linear temperature dependence variant (*TFa*) can give good results at temperatures not far away from the temperature range of the  $h^E$  data used, but with the increase of the system temperature the deviation of the calculated isotherms from experimental ones becomes large. In system 2-propanol + water even a miscibility gap which does not really exist is predicted at temperatures above 423 K. This is possibly due to the fact that the linear temperature function is still not flexible enough to describe the temperature dependence of the excess Gibbs free energy with a required accuracy. On the contrast, the *TFb* variant in which a quadratic temperature function is applied in the energy parameters of the NRTL equation can reproduce the VLE isotherms satisfactorily for all the six systems and at both low and high temperatures. However, just like the simultaneous correlation of  $h^E$  and VLE data carried out above, a further introduction of a temperature function in the nonrandomness parameter of the NRTL equation (*TFc*) does not lead to obvious improvement of VLE predictions in comparison with the results of *TFb*, and in the case of systems like methanol + benzene, the extrapolation at high temperatures even becomes worse. The possible reason is that the temperature dependence of the non-randomness parameter leads to a complicated temperature function in the NRTL equation so that the extrapolation is sometimes not reliable. For comparison Table 3 gives also the results calculated by Holderbaum and Gmehling<sup>[20]</sup> by using PSRK (predictive Soave-Redlich-Kwong) model. The overall average prediction deviation of the *TFb* variant is slightly smaller than that of PSRK.

## 5 CONCLUSIONS

The NRTL equation in combination with the Pitzer/Curl virial equation of state for the vapour phase is capable of representing simultaneously the VLE and  $h^E$  data in a relatively wide temperature and pressure range but an external temperature dependence is necessary to be introduced. The VLE data at high temperatures and pressures can be predicted reliably by using NRTL equation with parameters obtained from the simultaneous correlation of  $h^E$  data in a wide temperature range and a single VLE isotherm at low temperature. With quadratic temperature dependent energy parameters and a temperature independent non-randomness one the NRTL equation is not only flexible in simultaneous correlation of VLE and  $h^E$  data but also reliable in VLE extrapolation.

## NOMENCLATURE

$A_{ij}$  energy parameters of the NRTL model in the  $g^E$ -mixing rule

$A_{ij}^C, A_{ij}^{TC}, A_{ij}^{T2}$	constant in the temperature dependent $A_{ij}$
$B$	second virial coefficient
$F_{objj}$	objective function used in the simultaneous correlation
$f^{(0)}, f^{(1)}$	Pitzer/Curl correlations
$f_i^{0L}$	standard fugacity of component $i$
$g^E$	molar excess Gibbs energy, J·mol <sup>-1</sup>
$\hat{g}^E$	dimensionless excess Gibbs energy ( $\hat{g}^E = g^E/RT$ )
$h$	molar enthalpy, J·mol <sup>-1</sup>
$k_{ij}$	interaction parameter
$P$	pressure, kPa
$R$	gas constant, J·mol <sup>-1</sup> ·K <sup>-1</sup>
$T$	thermodynamic temperature, K
<i>TFa, TFb, TFc</i>	temperature dependence variants
$v$	molar volume, dm <sup>3</sup> ·mol <sup>-1</sup>
$x_i$	mole fraction of component $i$ in liquid phase
$y_i$	mole fraction of component $i$ in vapor phase
$\alpha_{ij}$	non-randomness parameter of the NRTL-equation
$\alpha_{ij}^C, \alpha_{ij}^{TC}$	constant in $\alpha_{ij}$
$\omega$	acentric factor

## Superscripts

E	excess
L	liquid
V	vapour

## Subscripts

c	critical
$i, j, k, l$	component
r	reduced value
0	reference state

## REFERENCES

- 1 Walas, S.M., Phase Equilibria in Chemical Engineering, Butterworth-Heinemann, Newton (1985).
- 2 Nicolaides, G.L., Eckert, C.A., "Optimal representation of binary liquid mixture nonidealities", *Ind. Eng. Chem. Fundam.*, 17, 331–340 (1978).
- 3 Skold-Jorgensen, S., Rasmussen, P., Fredenslund, A., "On the temperature dependence of the UNIQUAC/UNIFAC models", *Chem. Eng. Sci.*, 35, 2389–2403 (1980).
- 4 Demirel, Y., Gecegormez, H., "Simultaneous correlation of excess Gibbs free energy and enthalpy of mixing by the UNIQUAC equation", *Can. J. Chem. Eng.*, 67, 455–461 (1989).
- 5 Demirel, Y., Gecegormez, H., "Simultaneous representation of excess enthalpy and vapour-liquid equilibrium data by the NRTL and UNIQUAC models", *Fluid Phase Equilibria*, 65, 111–133 (1991).
- 6 Huron, M.-J., Vidal, J., "New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures", *Fluid Phase Equilibria*, 3, 255–271 (1979).
- 7 Michelsen, M.L., "A modified Huron-Vidal mixing rule for cubic equations of state", *Fluid Phase Equilibria*, 60, 213–219 (1990).
- 8 Wong, D.S.H., Sandier, S.I., "A theoretically correct mixing rule for cubic equation of state", *AIChE J.*, 38, 671–680 (1992).
- 9 Adachi, Y., Sugie, H., "A new method to predict thermodynamic properties of mixtures by means of a cubic equation of state", *J. Chem. Eng. Japan*, 21, 57–63 (1988).
- 10 Lichtenstein, C., Rauzy, E., Berro, C., "Simultaneous representation of vapour-liquid equilibria and excess enthalpies of methanol-hydrocarbons systems using an equation of state", *Fluid Phase Equilibria*, 87, 37–51 (1993).

- 11 Orbey, H., Sandier, S.I., "A comparison of various cubic equation of state mixing rules for the simultaneous description of excess enthalpies and vapour-liquid equilibria", *Fluid Phase Equilibria*, **121**, 67—83 (1996).
- 12 Ohta, T., "Representation of excess enthalpies by the PRSV equation of state with the modified Huron-Vidal first order and Wong-Sandier mixing rules", *Fluid Phase Equilibria*, **129**, 89—103 (1997).
- 13 Djordjevic, B.D., Kjievcenin, M.L., Sarbanovic, S.P., "Simultaneous presentation of VLE,  $h^E$  and  $c_p^E$  by the PRSV equation of state with the modified van der Waals one-fluid and Huron-Vidal-Orbey-Sandler mixing rules", *Fluid Phase Equilibria*, **155**, 205—218 (1999).
- 14 Ji, W.-R., Stiebing, E., Lempe, D. A., "VLE extrapolation and simultaneous representation of caloric and volumetric properties by means of a cubic 3-parameter equation of state", *Fluid Phase Equilibria*, (2005). submitted
- 15 Ji, W.-R., Stiebing, E., Lempe, D.A., "Strukturoptimierte Dreiparameter-Zustandsgleichung (C3EOS) zur Beschreibung von Phasengleichgewichts und anderen thermophysikalischen Eigenschaften, Bericht zum DFG-Vorhaben LE 886/4-1, Merseburg (2004).
- 16 Ji, W.-R., Lempe, D. A., "A systematic study of cubic three-parameter equations for deriving a structurally optimized PVT relation", *Fluid Phase Equilibria*, **147**, 85—103 (1998).
- 17 Christensen, C, Gmehling, J., Rasmussen, P., Weidlich, U., Heat of Mixing Data Collection. Binary Systems, DECHEMA Chemistry Data Series, Vol. III, Part 1, Frankfurt/Main (1984).
- 18 Gmehling, J., Holderbaum, T., Heat of Mixing Data Collection. Binary and Multicomponent Systems (Supplements), DECHEMA Chemistry Data Series, Vol. III, Part 3, Frankfurt/Main (1989).
- 19 Wormald, C.J., Badock, C.J., Lloyd, M.J., "Excess enthalpies for (water + methanol) at  $T = 423$  K to  $T = 523$  K and pressures up to 20 MPa. A new flow mixing calorimeter", *J. Chem. Thermodyn.*, **28**, 603—613 (1996).
- 20 Holderbaum, T., Gmehling, J., "PSRK: A group contribution equation of state based on UNIFAC", *Fluid Phase Equilibria*, **70**, 251—265 (1991).
- 21 Gmehling, J., Onken, U., VLE Data Collection., Aqueous-Organic Systems. DECHEMA Chemistry Data Series, Vol. I, Part 1, Frankfurt/Main (1977).
- 22 Griswold, J., Wong, S.Y., "Phase equilibria of acetone-methanol-water system from 100°C into the critical region", *Chem. Eng. Progr. Symp. Ser.*, **48**, 18—34 (1952).
- 23 Gmehling, J., Onken, U., Arlt, W., VLE Data Collection. Organic Hydroxy Compounds: Alcohols (Supplement 1), DECHEMA Chemistry Data Series, Vol. I, Part 2c, Frankfurt/Main (1981).
- 24 Butcher, K.L., Medani, M.S., "Thermodynamic properties of methanol-benzene mixtures at elevated temperatures", *J. Appl. Chem.*, **18**, 100—107 (1968).
- 25 Gmehling, J., Onken, U., Rarey-Nies, J.R., VLE Data Collection. Aqueous Systems (Supplement 2), DECHEMA Chemistry Data Series, Vol.I, Part 1b, Frankfurt/Main (1988).
- 26 Gmehling, J., Onken, U., Arlt, W., VLE Data Collection. Aqueous-Organic Systems (Supplement 1), DECHEMA Chemistry Data Series, Vol. I, Part 1a, Frankfurt/Main (1981).
- 27 Pemberton, R.C., Mash, C.J., "Thermodynamic properties of aqueous non-electrolyte mixtures II. Vapour pressures and excess Gibbs energies for water + ethanol at 303.15 to 363.15 K determined by an accurate static method", *J. Chem. Thermodyn.*, **10**, 867—888 (1978).
- 28 Barr-David, F., Dodge, B.F., "Vapour-liquid equilibrium at high pressures. The systems ethanol-water and 2-propanol-water", *J. Chem. Eng. Data*, **4**, 107—120 (1959).

## APPENDIX

The Virial equation of state with Pitzer/Curl correlation is

$$pv = RT + Bp \quad (\text{A1})$$

where

$$B = \frac{RT_c}{p_c} [f^{(0)} + \omega f^{(1)}] \quad (\text{A2})$$

with

$$f^{(0)} = 0.1445 - \frac{0.33}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} \quad (\text{A3})$$

$$f^{(1)} = 0.073 - \frac{0.46}{T_r} - \frac{0.50}{T_r^2} - \frac{0.097}{T_r^3} - \frac{0.0073}{T_r^8} \quad (\text{A4})$$

For vapour mixtures the following mixing rule is used

$$B = \sum_l \sum_k x_l x_k B_{lk} \quad (\text{A5})$$

where  $B_{ij}$  is calculated by using pseudo-critical data, and

$$T_{cij} = (T_{ci} T_{cj})^{\frac{1}{2}} (1 - k_{ij}) \quad (\text{A6})$$

$$p_{cij} = 4T_{cij} \frac{p_{ci} v_{ci} / T_{ci} + p_{cj} v_{cj} / T_{cj}}{v_{ci}^{1/3} + v_{cj}^{1/3}} \quad (\text{A7})$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \quad (\text{A8})$$

The fugacity coefficient is given by

$$\varphi_i^{*V} = \exp \left[ \left( 2 \sum_k x_k B_k - B \right) p / RT \right] \quad (\text{A9})$$