Thermochimica Acta, 202 (1992) 51–63
Elsevier Science Publishers B.V., Amsterdam

Prediction of ternary excess enthalpies using the PRSV and PRSV2 equations of state

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(Received 24 September 1991)

Abstract

Binary excess enthalpies for a variety of mixtures at low pressures are well represented by use of the PRSV and PRSV2 equations of state. The Huron–Vidal mixing rules from excess Gibbs energy models are used for the calculation of the parameters in the equations of state. This method is easily extended to predict ternary excess enthalpies without introducing any ternary parameters. Calculated results agree with the published data for highly non-ideal mixtures containing non-polar, polar and associating substances.

INTRODUCTION

In previous studies [1–3], the good capabilities of the Stryjek–Vera modifications of the Peng–Robinson equation of state, called the PRSV and PRSV2 [4,5], in predicting multicomponent vapor–liquid and liquid–liquid equilibria (VLE and LLE) of strongly non-ideal systems at low and high pressures were reported by use of the Huron–Vidal mixing rule [6].

Excess enthalpy (H^E) data provide another test for thermodynamic models. Recently, several investigators have discussed the use of equations of state and mixing rules for the calculation of H^E data at ambient pressure [7–9]. However, the calculations of ternary H^E data have not been shown.

The purpose of the present work is to demonstrate the ability of the PRSV and PRSV2 equations of state coupled with the Huron–Vidal mixing rules in predicting ternary H^E data from binary data alone for strongly non-ideal mixtures. In this work the NRTL and residual part of UNIQUAC excess Gibbs energy (G^E) models are selected to evaluate G^E at infinite pressure in the Huron–Vidal mixing rule.

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0040-6031/92/$05.00

THE PRSV AND PRSV2 EQUATIONS OF STATE

The PRSV and PRSV2 equations of state retain the cubic term in the volume form of the Peng–Robinson equation [10], namely

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{1}$$

with

$$a = \left(0.457235 R^2 T_c^2 / P_c\right)\alpha \tag{2}$$

$$b = 0.077796 RT_c / P_c \tag{3}$$

where

$$\alpha = \left[1 + \kappa\left(1 - T_R^{0.5}\right)\right]^2 \tag{4}$$

Stryjek and Vera [4,5] have proposed the following expressions for the term κ:

$$\text{PRSV: } \kappa = \kappa_0 + \kappa_1\left(1 + T_R^{0.5}\right)\left(0.7 - T_R\right) \tag{5a}$$

$$\text{PRSV2: } \kappa = \kappa_0 + \left[\kappa_1 + \kappa_2\left(\kappa_3 - T_R\right)\left(1 - T_R^{0.5}\right)\right]\left(1 + T_R^{0.5}\right)\left(0.7 - T_R\right) \tag{5b}$$

where

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \tag{6}$$

and κ_1, κ_2 and κ_3 are pure component adjustable parameters, which are available in the literature [4,5,11] together with the critical constants and the acentric factor. When $\kappa_2 = 0$ in eqn. (5b), the PRSV form is recovered.

MIXING RULE

Huron and Vidal [6] presented a method for deriving mixing rules for cubic equations of state from G^E (or activity coefficient) models on the basis of the assumption that G^E from an equation of state at infinite pressure equals G^E from a liquid solution model. Their procedure yields the following mixing rule for mixtures:

$$a = b\left(\sum_i x_i \frac{a_{ii}}{b_i} - cG_\infty^E\right) \tag{7}$$

$$b = \sum_i x_i b_i \tag{8}$$

where c is the numerical constant equal to $2\sqrt{2}/\ln[(2+\sqrt{2})/(2-\sqrt{2})]$ for the present equations of state.

For the expression of G_∞^E, the previous study [3] has successfully combined the equations of state and the three local composition models in the prediction of multicomponent vapor–liquid equilibria at low pressures. Among the models, in this work, the NRTL [12] and residual part of UNIQUAC [13] models were employed to represent G_{∞}^{E}.

The NRTL model is

$$G_{\infty}^{E}/RT = \sum_{i} x_i \left(\sum_{j} \tau_{ji} G_{ji} x_j \Big/ \sum_{k} G_{ki} x_k \right) \tag{9}$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{10}$$

$$\tau_{ij} = a_{ij}/T \tag{11}$$

where α_{ij} $(=\alpha_{ji})$ is a non-randomness constant. The values of α_{ij} for binary systems were taken from a previous paper [1].

The residual part of the UNIQUAC model is

$$G_{\infty}^{E}/RT = -\sum_{i} q_i x_i \ln\left(\sum_{j} \theta_j \tau_{ji} \right) \tag{12}$$

with

$$\theta_i = q_i x_i / \sum_{j} (q_j x_j) \tag{13}$$

$$\tau_{ij} = \exp(-a_{ij}/T) \tag{14}$$

where the pure component area parameter q is given in the monograph of Prausnitz et al. [14].

In both models, the binary energy parameters a_{ij} were assumed to be a linear function of temperature:

$$a_{ij} = C_{ij} + D_{ij}(T - 273.15) \tag{15}$$

The values of C_{ij} and D_{ij} were determined by the simplex method [15] which minimizes the sum of the squares of deviations in experimental and calculated H^{E} values.

EXCESS ENTHALPY

The excess enthalpy is calculated from the relation

$$H^{E} = \Delta H' - \sum_{i} x_i \, \Delta H_i' \tag{16}$$

where $\Delta H_i'$ and $\Delta H'$ are the enthalpy departure functions for pure components and mixtures. These functions can be obtained from eqn. (1) as follows [16]:

$$\Delta H' = (1/2\sqrt{2}b)[a - T(\partial a/\partial T)] \ln \frac{z + B(1-\sqrt{2})}{z + B(1+\sqrt{2})} + RT(z-1) \tag{17}$$

TABLE 1

Calculated results for binary systems at 298.15 K

System (1–2)	No. of data points	Model	Parameters									Absolute arithmetic mean deviations (J mol^{-1})		Ref.
			PRSV				PRSV2							
			C_{12} (K)	D_{12}	C_{21} (K)	D_{21}	C_{12} (K)	D_{12}	C_{21} (K)	D_{21}	α_{12}	PRSV	PRSV2	
Methanol–	18	I [a]	−557.35	−0.6115	190.08	−0.5326	−562.74	−0.5994	188.74	−0.5720	0.30	30.9	31.3	17
water		II [b]	−468.96	−1.3498	148.11	0.7182	−415.75	−0.9991	161.88	0.5387		18.3	18.8	
Water–	24	I	−214.60	10.6107	281.16	−6.8560	−223.31	10.2332	305.81	−6.9234	0.30	22.6	19.5	18
acetone [c]		II	49.39	2.4800	356.33	−0.9945	55.98	2.4900	354.35	−0.9597		14.6	13.1	
Ethanol–	10	I	−24.86	−0.3456	45.91	0.4266	−15.90	−0.1645	55.96	0.3193	0.30	1.0	0.7	19
1-propanol		II	23.59	0.1059	−15.92	−0.0871	26.30	0.0275	−20.28	−0.0231		0.8	0.9	
Ethanol–	20	I	670.66	1.4027	890.04	1.1981	628.31	1.2970	862.59	1.2658	0.35	16.6	15.1	20
cyclohexane		II	37.16	0.0275	1978.92	−0.7197	33.83	0.0080	1938.11	−0.2995		35.2	35.0	
1-Propanol–	18	I	496.53	1.1298	956.77	1.0707	503.86	1.1777	914.18	0.9370	0.35	22.1	22.0	20
cyclohexane		II	−0.50	−0.0369	1745.83	0.5021	19.22	0.0324	1818.93	−0.0399		14.3	15.6	
Ethanol–	12	I	270.84	−0.3583	1341.11	1.9842	115.47	−1.0085	1536.73	2.5730	0.35	15.6	14.8	19
n-heptane		II	−11.03	−0.0074	1790.63	−0.1201	−6.02	−0.0002	1881.13	−0.0531		37.0	37.0	
1-Propanol–	13	I	484.00	0.9462	1013.52	0.9475	492.04	0.8993	1018.14	0.8505	0.35	25.4	27.0	19
n-heptane		II	−86.86	−0.3297	2020.00	−3.7617	−155.34	−0.6552	1786.81	−0.2054		20.6	17.2	
Ethanol–	12	I	208.15	−0.7213	1386.95	1.9920	224.81	−0.6811	1385.79	1.9316	0.35	12.6	12.6	19
n-octane		II	−47.58	−0.1967	1832.93	−0.6510	−78.87	−0.3321	1914.05	−2.2666		31.8	30.8	
1-Propanol–	13	I	336.98	0.0916	1107.60	1.0157	313.14	0.0247	1093.94	0.9830	0.35	19.9	18.5	19
n-octane		II	−22.18	−0.0382	1750.42	0.1111	−85.96	−0.3351	1838.52	−1.8630		19.1	17.1	
2-Propanol–	17	I	145.89	−1.4438	945.88	−0.2123	161.17	−1.3693	925.22	−0.3339	0.35	24.5	24.8	21
benzene		II	−17.99	−0.6053	991.40	0.9950	4.91	−0.5148	947.88	0.9849		4.8	5.2	
2-Propanol–	18	I	202.70	−0.4007	956.28	1.3375	190.35	−0.4577	933.87	1.3909	0.35	17.2	15.9	22
cyclohexane		II	35.84	0.0061	1772.04	0.0186	46.54	0.0381	1741.81	0.4233		10.1	11.8	
Benzene–	24	I	262.07	0.0382	188.60	−0.0095	258.77	0.0234	187.00	−0.0066	0.30	0.9	0.9	20
cyclohexane		II	57.44	0.0080	91.79	−0.0089	56.09	0.0148	92.08	−0.0178		2.2	2.0	
Ethanol–	10	I	228.09	0.0115	958.18	−0.5117	222.26	−0.0349	962.68	−0.4516	0.35	21.6	21.8	23
benzene		II	12.43	0.0501	867.05	0.0077	10.14	0.0344	870.06	0.0372		6.3	6.2	
1-Propanol–	10	I	442.31	0.9227	806.97	−1.3136	447.58	0.8549	812.99	−1.3685	0.35	29.4	29.0	23
benzene		II	419.22	1.7562	920.45	0.4184	439.63	1.8030	912.25	0.4622		3.1	3.1	
Ethanol–	17	I	308.62	−0.1159	557.48	0.5242	274.63	−0.2576	543.31	0.5460	0.30	6.9	6.5	24

Butanone–benzene	23	I	−116.92	0.3780	238.85	−0.0718	−114.27	0.3614	237.36	−0.0280	0.30	4.3	3.5	25
		II	−119.34	−0.0125	179.73	0.0109	−118.06	−0.0025	176.42	−0.0012		1.0	0.8	
Methanol–acetonitrile	14	I	354.34	0.2809	564.42	0.0982	347.25	0.2436	560.73	0.0904	0.30	0.8	1.2	26
		II	227.71	0.4730	361.34	−0.2745	236.02	0.5128	358.32	−0.2971		1.0	0.7	
Methanol–benzene	10	I	224.02	−0.0266	1078.58	0.2183	240.89	0.0235	1074.22	0.3249	0.35	17.7	16.0	23
		II	42.52	0.2274	1099.93	−0.8090	32.22	0.1746	1102.24	−0.8259		3.0	2.2	
Acetonitrile–benzene	16	I	318.73	−0.0017	−30.02	−0.0120	321.90	−0.0127	−30.23	0.0066	0.30	1.8	1.5	27
		II	120.13	−0.0198	−5.65	−0.0259	304.57	1.1057	−59.35	−0.4939		1.3	1.3	
Ethanol–ethyl acetate	13	I	299.01	−0.9673	848.47	1.4325					0.30	6.2		28
		II	373.69	1.1321	545.47	0.8507						5.8		
Ethyl acetate–cyclohexane	15	I	328.70	−0.2857	505.37	−0.3175					0.30	3.4		29
		II	169.27	0.2245	394.37	0.9825						5.3		
Acetonitrile–trichloromethane	15	I	321.72	−1.0489	−27.01	3.5457					0.30	2.9		30
		II	132.52	−0.2274	92.88	2.3422						3.9		
Trichloromethane–benzene	22	I	−90.83	1.2847	303.89	0.1044					0.30	1.2		31
		II	−50.02	0.6841	136.45	−0.1259						1.0		
Methanol–tetrachloromethane	19	I	287.93	1.3311	1180.12	2.0224					0.35	17.8		32
		II	−669.15	−1.6084	988.41	−9.8998						16.5		
Benzene–tetrachloromethane	16	I	70.44	−0.6355	−64.41	0.3372					0.30	0.8		27
		II	36.31	0.2218	−7.18	−0.1720						1.0		

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[a] I, NRTL model.

[b] II, residual part of UNIQUAC model.

[c] At 323.15 K.

where

$$B = \frac{bP}{RT} \tag{18}$$

$$z = \frac{Pv}{RT} \tag{19}$$

The derivative of parameter a with respect to T is analytically obtained from its temperature dependence form and mixing rule. For all the systems studied here, the pressure was assumed to be atmospheric.

RESULTS

Binary systems

Table 1 presents the calculated results for binary systems including various kinds of compounds. The PRSV and PRSV2 equations of state can reproduce binary data with equally good accuracy. Figures 1–3 show examples of typical sets of binary data. The residual part of the UNIQUAC model in the Huron–Vidal mixing rule gives slightly better results than the NRTL model for the present systems except for some alcohol–saturated hydrocarbon mixtures.

Ternary systems

The binary parameters listed in Table 1 were used to predict ternary H^E data for ten highly non-ideal systems at 298.15 K. Table 2 presents the absolute arithmetic mean deviations between the predicted and experimental values. The largest deviation is about 40 J mol^{-1}. The predictions from binary data alone are considered successful, and are comparable with those obtained from the usual methods which use liquid solution models to represent the non-ideality of liquid mixtures. A survey of the results indicates that the PRSV2 equation of state does not markedly improve the prediction accuracy of ternary H^E data compared with the PRSV equation. Two typical examples are graphically shown in Fig. 4. The NRTL model for expression of G_∞^E shows slightly better overall performance than the residual part of the UNIQUAC model for the systems studied here.

CONCLUSIONS

The PRSV and PRSV2 equations of state coupled with the Huron–Vidal mixing rules from the NRTL and residual UNIQUAC models were extended for the calculation of excess enthalpies of strongly non-ideal systems at low pressures. The present approach gives good prediction of

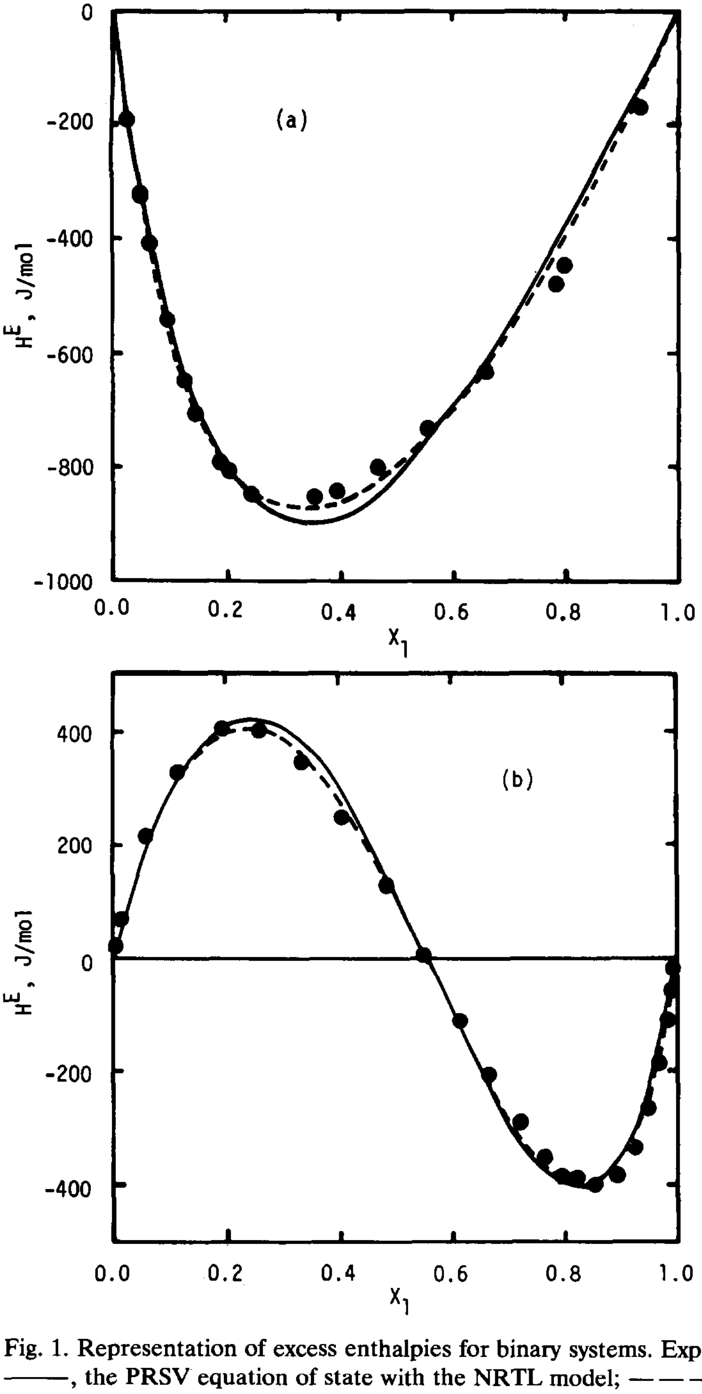

Fig. 1. Representation of excess enthalpies for binary systems. Experimental: ●. Calculated: ———, the PRSV equation of state with the NRTL model; — — —, the PRSV equation of state with the residual part of the UNIQUAC model. (a) Methanol(1)–water(2) at 298.15 K (data of Lama and Lu [17]); (b) water(1)–acetone(2) at 323.15 K (data of Villamanan and Van Ness [18]).

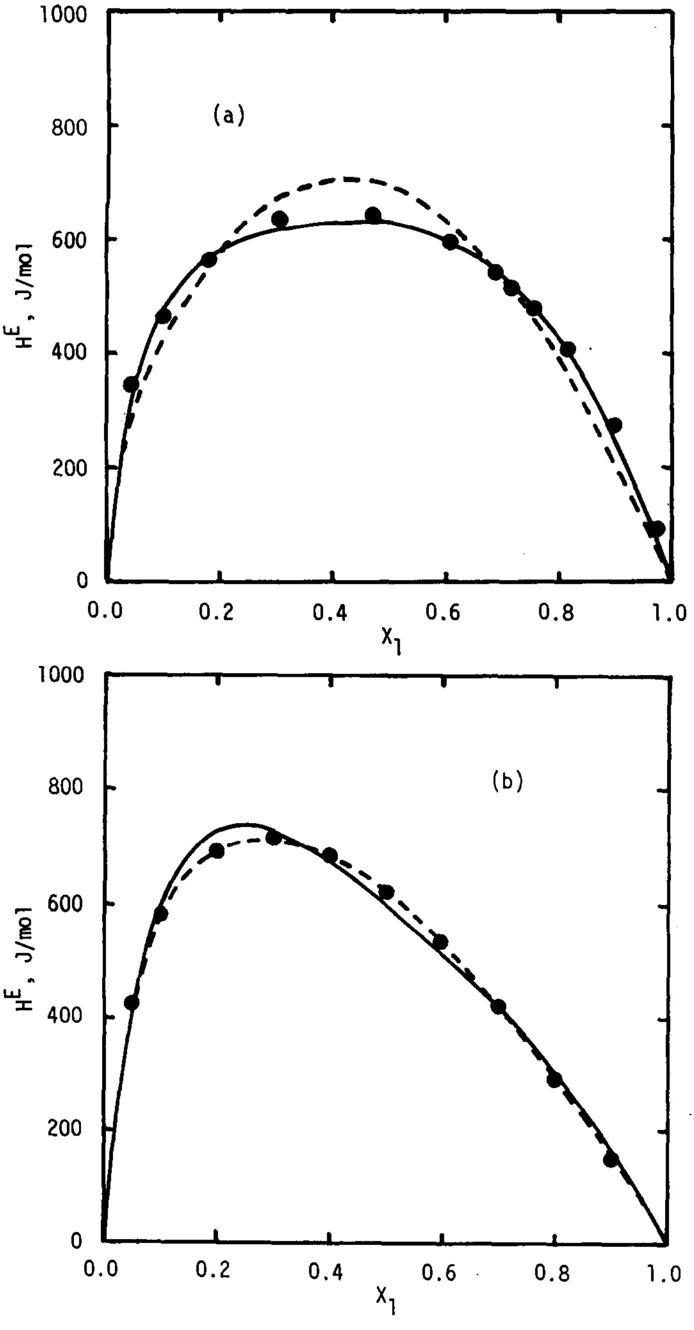

Fig. 2. Representation of excess enthalpies for binary systems. Experimental: ●. Calculated: ———, the PRSV equation of state with the NRTL model; — — —, the PRSV equation of state with the residual part of the UNIQUAC model. (a) Ethanol(1)–*n*-octane(2) at 298.15 K (data of Ramalho and Ruel [19]); (b) methanol(1)–benzene(2) at 298.15 K (data of Mrazek and Van Ness [23]).

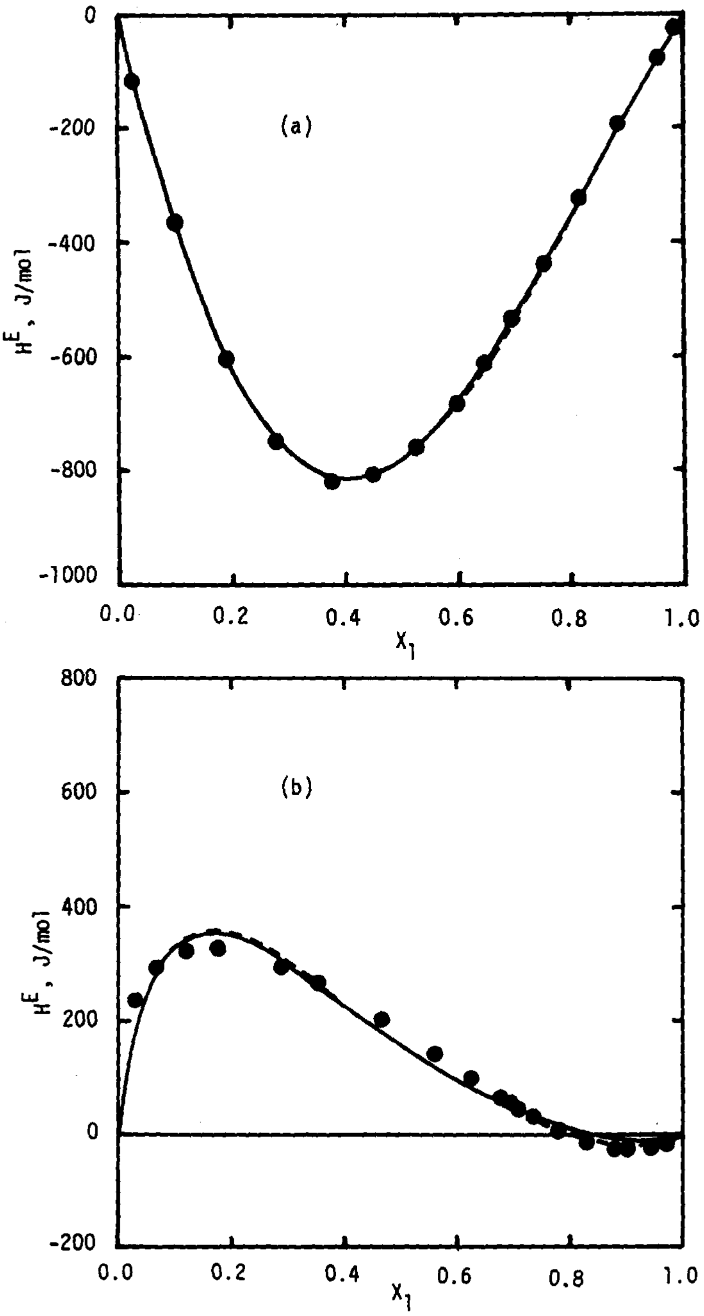

Fig. 3. Representation of excess enthalpies for binary systems. Experimental: ●. Calculated: ———, the PRSV equation of state with the NRTL model; — — —, the PRSV equation of state with the residual part of the UNIQUAC model. (a) Acetonitrile(1)–trichloromethane(2) at 298.15 K (data of Nagata and Kawamura [30]); (b) methanol(1)–tetrachloromethane(2) at 298.15 K (data of Nagata and Tamura [32]).

TABLE 2

Predicted results for ternary systems at 298.15 K

System	No. of data points	Absolute arithmetic mean deviation								Ref.
		δH^E (J mol^{-1})				$\delta H^E/H^E$ (%)				
		PRSV		PRSV2		PRSV		PRSV2		
		I [a]	II [b]	I	II	I	II	I	II	
Ethanol–1-propanol–cyclohexane	92	17.9	20.4	14.1	22.2	7.7	7.4	6.1	8.2	20
Ethanol–1-propanol–*n*-heptane	32	22.7	32.5	29.8	27.5	6.3	8.8	7.7	7.5	33
Ethanol–1-propanol–*n*-octane	30	13.5	33.8	11.8	35.1	3.6	10.4	3.2	11.2	33
2-Propanol–benzene–cyclohexane	67	27.1	32.3	27.3	29.2	3.3	3.6	3.2	3.4	22
Ethanol–1-propanol–benzene	59	27.5	10.8	31.3	8.0	6.0	2.6	6.4	2.1	34
Ethanol–2-butanone–benzene	42	11.4	5.6	9.4	6.2	1.9	0.9	1.6	1.0	35
Methanol–acetonitrile–benzene	55	20.5	40.3	19.5	32.8	2.5	4.9	2.4	4.1	26
Ethanol–ethyl acetate–cyclohexane	51	24.3	37.1			2.0	3.2			29
Acetonitrile–trichloromethane–benzene	64	15.9	40.8			5.9	19.3			31
Methanol–benzene–tetrachloromethane	45	23.4	30.1			8.1	8.4			32

[a] I, NRTL model.

[b] II, residual part of UNIQUAC model.

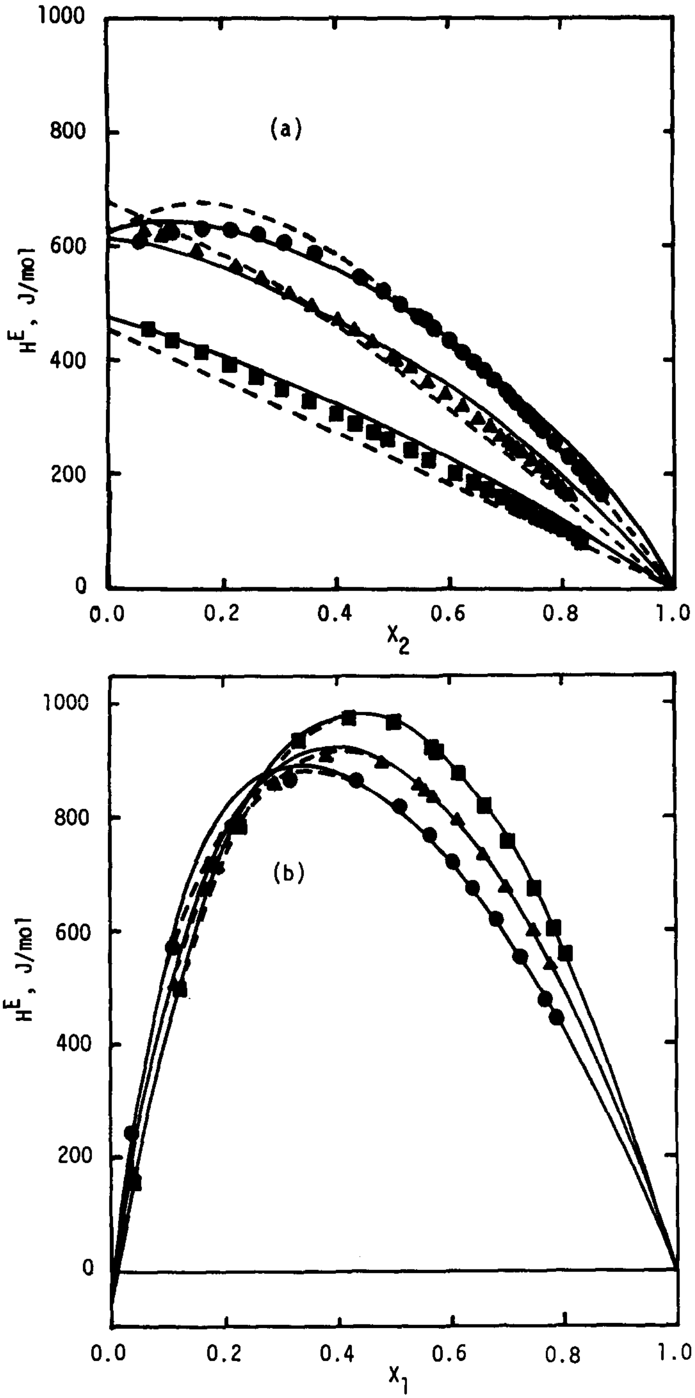

Fig. 4. Prediction of excess enthalpies for ternary systems at 298.15 K. (a) Ethanol(1)–1-propanol(2)–cyclohexane(3) (experimental: ●, $x_1' = 0.2493$; ▲, $x_1' = 0.4970$; ■, $x_1' = 0.7434$; data of Nagata and Kazuma [20]). (b) Ethanol(1)–2-butanone(2)–benzene(3) (experimental: ●, $x_2' = 0.2494$; ▲, $x_2' = 0.5000$; ■, $x_2' = 0.7521$; data of Nagata and Tamura [35]). Predicted: ——, the PRSV equation of state with the NRTL model; — — —, the PRSV equation of state with the residual part of the UNIQUAC model.

ternary H^E data from binary parameters alone. It is expected that this approach will be able to reproduce the H^E data at higher pressures.

LIST OF SYMBOLS

a	parameter of the equations of state
a_{ij}	binary interaction parameter
B	coefficient defined by eqn. (18)
b	parameter of the equations of state
C_{ij}, D_{ij}	coefficients of eqn. (15)
c	numerical constant
G^E	excess Gibbs energy
G_∞^E	excess Gibbs energy at infinite pressure
H^E	excess enthalpy
$\Delta H'$	enthalpy departure function
P	total pressure
q	molecular geometric area parameter
R	gas constant
T	absolute temperature
v	molar volume
x	liquid mole fraction
z	compressibility factor

Greek letters

α	function of reduced temperature and acentric factor
α_{ij}	non-randomness parameter
θ	area fraction
τ	binary parameter
ω	acentric factor
κ	function of reduced temperature and acentric factor
κ_0	function of acentric factor
κ_1, κ_2, κ_3	pure component parameters

Subscripts

c	critical property
i, j	components
R	reduced temperature
∞	at infinite pressure

Superscript

E	excess property

REFERENCES

1 T. Ohta, Fluid Phase Equilib., 47 (1989) 1.
2 T. Ohta, Fluid Phase Equilib., 59 (1990) 329.
3 T. Ohta, Thermochim. Acta, 185 (1991) 283.
4 R. Stryjek and J.H. Vera, Can. J. Chem. Eng., 64 (1986) 323.
5 R. Stryjek and J.H. Vera, Can. J. Chem. Eng., 64 (1986) 820.
6 M.J. Huron and J. Vidal, Fluid Phase Equilib., 3 (1979) 255.
7 J.J. Christensen, R.L. Rowley and R.M. Izatt, Handbook of Heats of Mixing: Supplementary Volume, Wiley–Interscience, New York, 1988.
8 Y. Adachi and H. Sugie, J. Chem. Eng. Jpn., 21 (1988) 57.
9 P.A. Gupte and T.E. Daubert, Fluid Phase Equilib., 59 (1990) 171.
10 D.Y. Peng and D.B. Robinson, Ind. Eng. Chem. Fundam., 15 (1976) 59.
11 P. Proust and J.H. Vera, Can. J. Chem. Eng., 67 (1989) 170.
12 H. Renon and J.M. Prausnitz, AIChE J., 14 (1968) 135.
13 D.S. Abrams and J.M. Prausnitz, AIChE J., 21 (1975) 116.
14 J.M. Prausnitz, T.F. Anderson, E.A. Grens, C.A. Eckert, R. Hsieh and J.P. O'Connell, Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria, Prentice–Hall, Englewood Cliffs, NJ, 1980.
15 J.A. Nelder and R. Mead, Comput. J., 7 (1965) 308.
16 R.C. Reid, J.M. Prausnitz and B.E. Poling, The Properties of Gases and Liquids, 4th edn., McGraw-Hill, New York, 1987.
17 R.F. Lama and B.C.-Y. Lu, J. Chem. Eng. Data, 10 (1965) 216.
18 M.A. Villamanan and H.C. Van Ness, J. Chem. Eng. Data, 29 (1984) 429.
19 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 456.
20 I. Nagata and K. Kazuma, J. Chem. Eng. Data, 22 (1977) 79.
21 I. Nagata, H. Asano and K. Fujiwara, Fluid Phase Equilib., 1 (1978) 211.
22 I. Nagata, K. Fujiwara and Y. Ogasawara, J. Chem. Thermodyn., 10 (1978) 1201.
23 R.V. Mrazek and H.C. Van Ness, AIChE J., 7 (1961) 190.
24 I. Nagata, T. Ohta and S. Nakagawa, J. Chem. Eng. Jpn., 9 (1976) 276.
25 O. Kiyohara, G.C. Benson and J.-P.E. Grolier, J. Chem. Thermodyn., 9 (1977) 315.
26 I. Nagata and K. Tamura, Fluid Phase Equilib., 24 (1985) 289.
27 I. Nagata, K. Tamura and S. Tokuriki, Fluid Phase Equilib., 8 (1982) 75.
28 I. Nagata, T. Yamada and S. Nakagawa, J. Chem. Eng. Data, 20 (1975) 271.
29 I. Nagata and K. Tamura, J. Chem. Thermodyn., 16 (1984) 975.
30 I. Nagata and Y. Kawamura, Fluid Phase Equilib., 3 (1979) 1.
31 I. Nagata, K. Tamura and S. Tokuriki, Thermochim. Acta, 47 (1981) 315.
32 I. Nagata and K. Tamura, Fluid Phase Equilib., 15 (1983) 67.
33 R.S. Ramalho and M. Ruel, Can. J. Chem. Eng., 46 (1968) 467.
34 I. Nagata, K. Tamura and K. Gotoh, Thermochim. Acta, 104 (1986) 179.
35 I. Nagata and K. Tamura, J. Chem. Thermodyn., 22 (1990) 279.