Thermochimica Acta, 235 (1994) 1-10
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01539-F

Prediction of ternary excess enthalpies at high pressures using an equation of state

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(Received 26 July 1993; accepted 3 August 1993)

Abstract

Predictions of the ternary excess enthalpies H^E for the carbon dioxide(1)–*n*-hexane(2)–toluene(3) system in the vicinity of the critical region and of the methane(1)–carbon dioxide(2)–hydrogen sulfide(3) system in the gaseous region were performed by use of the PRSV equation of state with the NRTL mixing rule. Good predictions are obtained without adding any ternary parameters.

LIST OF SYMBOLS

a	parameter of the equation of state
a_{ij}	binary interaction parameter
B	coefficient defined by eqn. (4)
b	parameter of the equation of state
C_{ij}, D_{ij}	coefficients of eqn. (11)
c	numerical constant
G^E_∞	excess Gibbs energy at infinite pressure
H^E	excess enthalpy
$\Delta H'$	enthalpy departure function
P	total pressure
R	gas constant
T	absolute temperature
v	molar volume
x	mole fraction
z	compressibility factor

Greek letters

α, β	amounts of liquid and vapor mixtures in equilibrium
α_{ij}	non-randomness parameter
τ	binary parameter defined by eqn. (10)
ω	acentric factor
κ_1	pure component parameter

Subscripts

c	critical property
i, j	components
m	actual composition of mixture
l, g	liquid and vapor phases
∞	at infinite pressure

Superscript

E	excess property

INTRODUCTION

The excess enthalpies H^E of mixtures at high pressures can be measured efficiently with a flow calorimeter. The H^E data provide a useful test for a variety of equation of state models. In a previous work [1], it was shown that the Stryjek–Vera modification of the Peng–Robinson (PRSV) equation of state [2, 3] coupled with the NRTL mixing rule [4] gives a good capability of representing various kinds of binary H^E data at high pressures, including supercritical conditions. For ternary systems at high pressures, Casielles et al. [5] and Barry et al. [6] have discussed the representation of ternary H^E data using equations of state.

The present work shows the abilities of the PRSV equation of state with the NRTL mixing rule in predicting ternary H^E data from constituent binary data alone. The ternary systems carbon dioxide(1)–*n*-hexane(2)–toluene(3) in the vicinity of the critical region and methane(1)–carbon dioxide(2)–hydrogen sulfide(3) in the gaseous region are studied in this work.

CALCULATION OF EXCESS ENTHALPY

The excess enthalpy H^E is given by the equation

$$H^E = \Delta H' - \sum_i x_i \, \Delta H'_i \tag{1}$$

The enthalpy departure functions for pure components and mixtures, $\Delta H'_i$ and $\Delta H'$, can be obtained from an equation of state using the thermodynamic relation [7]

$$\Delta H' = \int_\infty^v [T(\partial P/\partial T)_v - P] \, \mathrm{d}v + RT(z-1) \tag{2}$$

where for the PRSV equation of state chosen here

$$\Delta H' = (1/2\sqrt{2}b)[a - T(\partial a/\partial T)] \ln \frac{z + B(1-\sqrt{2})}{z + B(1+\sqrt{2})} + RT(z-1) \quad (3)$$

with

$$B = \frac{bP}{RT} \quad (4)$$

$$z = \frac{Pv}{RT} \quad (5)$$

The derivative of parameter a with respect to T, $\partial a/\partial T$, is obtained analytically from its temperature dependence form and the mixing rule.

For mixtures, the following NRTL mixing rule proposed by Huron and Vidal [4] was used for the calculation of the parameters in the PRSV equation of state

$$a = b\left(\sum_i x_i \frac{a_i}{b_i} - cG^{\mathrm{E}}_{\infty}\right) \quad (6)$$

$$b = \sum_i x_i b_i \quad (7)$$

where c is a numerical constant equal to $2\sqrt{2}/\ln[(2+\sqrt{2})/(2-\sqrt{2})]$ for the equation of state. The NRTL equation [8] was utilized to represent the excess Gibbs free energy at infinite pressure G^{E}_{∞}

$$G^{\mathrm{E}}_{\infty}/RT = \sum_i x_i \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} \quad (8)$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \quad (9)$$

$$\tau_{ij} = a_{ij}/T \quad (10)$$

where α_{ij} ($=\alpha_{ji}$) is a non-randomness constant. The binary energy parameters a_{ij} were assumed to be expressed by a linear function of temperature

$$a_{ij} = C_{ij} + D_{ij}(T - 273.15) \quad (11)$$

The simplex method of Nelder and Mead [9] was used to determine the adjustable parameters, C_{ij} and D_{ij}, by minimizing the sum of squares of deviations in experimental and calculated H^{E} values.

The excess enthalpies of mixing in the two-phase region from an equation of state have been derived by Lewis et al. [10] and Casielles et al. [5]. A mixture is the sum of amounts α of liquid mixture and β of vapor mixture. The vapor and liquid equilibrium compositions are x_{g} and x_{l} respectively. When the actual composition of the mixture is given by x_{m}, the following equations must be satisfied

TABLE 1

Binary parameters and absolute arithmetic mean deviations for binary systems

Temperature in K	Pressure in MPa	No. of data points	Parameters					Abs. arith. mean dev. in J mol^{-1}	Ref.
			C_{12} in K	D_{12}	C_{21} in K	D_{21}	α_{12}		
Carbon dioxide(1)–*n*-hexane(2)									
308.15	7.50	29	468.43	−3.9192	4041.90	22.6331	0.40	76.8	12
	12.50	22	1191.36	0.4626	−275.74	−4.1402	0.40	10.0	12
358.15	7.50	29	1260.02	16.0620	3141.02	14.6799	0.40	76.7	12
	12.50	31	925.63	5.5348	−75.13	−2.5678	0.40	19.0	12
413.15	7.50	30	−328.21	22.6738	−420.85	−1.9436	0.40	48.6	12
	12.50	28	1244.89	4.5452	−107.95	−2.8971	0.40	22.5	12
470.15	7.50	31	433.85	16.2852	−140.96	1.1117	0.40	38.7	13
	12.50	31	1438.16	2.3811	−2.05	−1.8546	0.40	23.6	13
573.15	7.50	30	1502.38	−4.8174	−1442.33	7.2179	0.40	37.0	13
	12.50	39	2299.92	−1.7638	−942.23	5.5824	0.40	41.1	13
Carbon dioxide(1)–toulene(2)									
308.15	7.60	28	534.09	−2.0456	−19.95	−0.6597	0.40	76.4	14
	12.67	25	985.74	0.6314	−162.62	−2.7844	0.40	2.3	14
358.15	7.60	27	655.32	6.7235	−705.58	−4.6255	0.40	17.4	14
	12.67	25	432.55	0.8824	46.27	−1.2334	0.40	9.3	14
413.15	7.60	28	−726.33	26.2765	−574.94	−1.1498	0.40	25.0	14
	12.67	28	11.66	8.1646	−3.17	−0.8272	0.40	10.4	14
470.15	7.60	26	73.25	7.4236	−165.85	−0.4097	0.40	39.3	15
	12.67	24	472.85	3.7539	−114.69	−1.2095	0.40	18.8	15
573.15	7.60	34	1761.59	−5.6029	−325.39	0.9440	0.40	191.5	15
	12.67	38	302.88	8.6600	−242.76	−0.2399	0.40	55.3	15

n-Hexane(1)–toulene(2)									
308.15	7.50	29	−304.68	−1.3312	27.44	−0.9656	0.30	7.1	16
	12.50	25	115.93	2.5188	11.64	−2.4660	0.30	3.5	16
358.15	7.50	24	2.50	−0.5171	120.58	−0.0561	0.30	6.0	16
	12.50	38	158.96	0.3835	266.15	0.4875	0.30	6.4	16
413.15	7.50	24	228.92	2.4691	38.62	−1.0749	0.30	3.1	16
	12.50	35	224.03	2.3154	70.82	−1.0078	0.30	6.5	16
470.15	7.50	30	−71.54	1.3138	264.02	−0.6811	0.30	2.4	16
	12.50	30	−118.36	−0.0363	223.88	−0.9618	0.30	4.9	16
573.15	7.50	27	−96.75	0.8702	231.09	−1.3101	0.30	8.6	16
	12.50	32	−137.70	0.7073	274.35	−0.9339	0.30	5.3	16
Methane(1)–carbon dioxide(2)									
293.15	0.507	4	318.74	−3.8720	312.76	1.4800	0.40	0.1	17
	1.520	5	438.66	1.6604	988.35	8.5942	0.40	0.4	17
305.15	0.507	4	320.46	−0.3309	1260.24	3.5505	0.40	0.8	17
	1.520	4	392.44	0.2565	468.74	1.0029	0.40	0.4	17
313.15	0.507	4	270.20	4.8846	420.64	22.1505	0.40	0.1	17
	1.520	4	545.14	1.8104	639.09	2.2021	0.40	0.4	17
Methane(1)–hydrogen sulfide(2)									
293.15	0.507	6	3301.83	−78.5112	117.55	−19.1459	0.40	0.2	18
	1.520	5	897.54	−4.6170	340.23	−8.3753	0.40	0.3	18
305.15	0.507	4	675.17	−5.1730	227.00	−2.9712	0.40	0.2	18
	1.520	4	423.97	−4.8512	553.92	−4.8003	0.40	3.3	18
313.15	0.507	4	125.47	−4.6880	155.63	−2.4777	0.40	2.1	18
	1.520	4	286.43	−2.3245	366.79	−4.8754	0.40	2.9	18
Carbon dioxide(1)–hydrogen sulfide(2)									
293.15	0.507	4	504.26	9.5846	−140.25	−5.7675	0.30	0.2	19
	1.419	4	695.71	1.7630	470.80	1.8936	0.30	0.4	19
305.15	0.507	4	525.77	−0.2547	55.39	0.2115	0.30	0.8	19
	1.520	5	661.93	−0.6269	295.04	1.0760	0.30	2.2	19
313.15	0.507	4	902.89	11.7091	−191.87	−1.6408	0.30	0.6	19
	1.520	4	579.31	2.3300	376.25	1.8359	0.30	2.0	19

$$x_l\alpha + x_g\beta = x_m \tag{12}$$

$$(1-x_l)\alpha + (1-x_g)\beta = 1 - x_m \tag{13}$$

where x_m, x_l and x_g are mole fractions of the same component. When we solve for α and β, the enthalpy departure of the mixture is given by

$$\Delta H' = \alpha(\Delta H'_m)_l + \beta(\Delta H'_m)_g \tag{14}$$

where $(\Delta H'_m)_l$ and $(\Delta H'_m)_g$ are the enthalpy departure functions of a liquid mixture of compositions x_l and a vapor mixture of composition x_g.

RESULTS

The two ternary systems carbon dioxide(1)–*n*-hexane(2)–toluene(3) and methane(1)–carbon dioxide(2)–hydrogen sulfide(3) were investigated at high pressures.

To use the PRSV equation of state, it is necessary to obtain pure component parameters for each component, T_c, P_c, ω, and κ_1, which are available in the literature [3, 11]. The values of α_{ij} for the related binary systems were taken from a previous paper [1], except for the two systems containing hydrogen sulfide. In this work, the values of α_{ij} for these systems were empirically assigned as follows: methane–hydrogen sulfide, 0.40; carbon dioxide–hydrogen sulfide, 0.30.

Table 1 presents the binary parameters for the related binary systems and absolute arithmetic mean deviations. Agreement with the experimental data seems to be acceptable.

*The carbon dioxide(1)–*n*-hexane(2)–toluene(3) system in the vicinity of the critical region*

The excess enthalpy data for this ternary system were studied at five temperatures between 308.15 and 573.15 K and at pressures of 7.50 and 12.50 MPa. The ternary H^E data were determined by adding carbon dioxide to an *n*-hexane–toluene mixture of known composition. Three mixtures with *n*-hexane mole fractions of 0.25, 0.50 and 0.75 were measured [20–24]. Two-phase regions appear at 308.15, 358.15, 413.15, 470.15 and 573.15 K and 7.50 MPa, and at 358.15, 413.15 and 470.15 K and 12.50 MPa. Large changes in sign and magnitude of the ternary H^E values with the variations in temperature, pressure and composition are observed.

The predicted results for the system are listed in Table 2, together with the maximum and minimum values of each set of ternary H^E data. Figures 1 and 2, respectively, indicate the isotherms with $x_2/x_3 = 3$ at 7.50 and 12.50 MPa. Similar results are obtained for the other two series of ternary H^E determinations with $x_2/x_3 = 1/3$ and 1. Isotherms at some temperatures show a minimum and a maximum connected by a linear section which

TABLE 2

Predicted results for the carbon dioxide(1)-*n*-hexane(2)-toluene(3) system

Temperature in K	Pressure in MPa	No. of data points	H^E_{min} in J mol^{-1}	H^E_{max} in J mol^{-1}	Abs. arith. mean dev. in J mol^{-1}	Ref.
308.15	7.50	83	−4650.0	137.0	173.3	20
	12.50	76	−45.0	831.0	76.5	20
358.15	7.50	92	−2130.0	576.0	69.6	21
	12.50	84	−2100.0	242.0	139.3	21
413.15	7.50	84	−860.0	2200.0	123.9	22
	12.50	75	−966.0	984.0	91.2	22
470.15	7.50	82	146.0	4660.0	139.8	23
	12.50	74	91.0	2400.0	34.3	23
573.15	7.50	82	297.0	7120.0	258.8	24
	12.50	80	244.0	4300.0	83.2	24

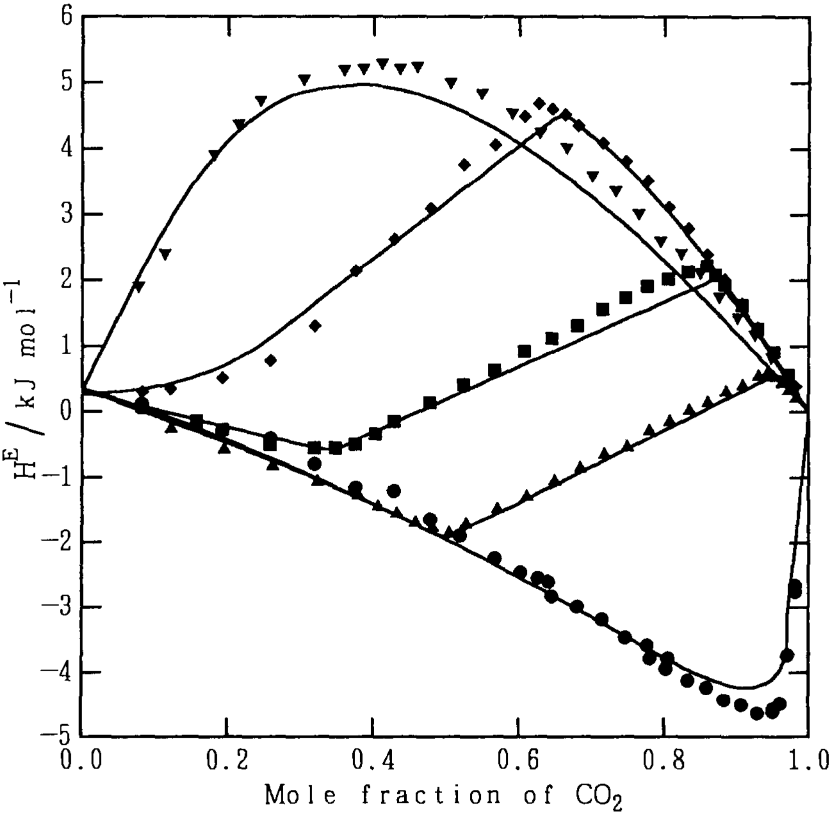

Fig. 1. Comparison of experimental and predicted excess enthalpies for the carbon dioxide(1)-*n*-hexane(2)-toluene(3) system at 7.50 MPa and $x_2/x_3 = 3$. Experimental: ●, at 308.15 K; ▲, at 358.15 K; ■, at 413.15 K; ◆, at 470.15 K; ▼, at 573.15 K. Predicted: ——.

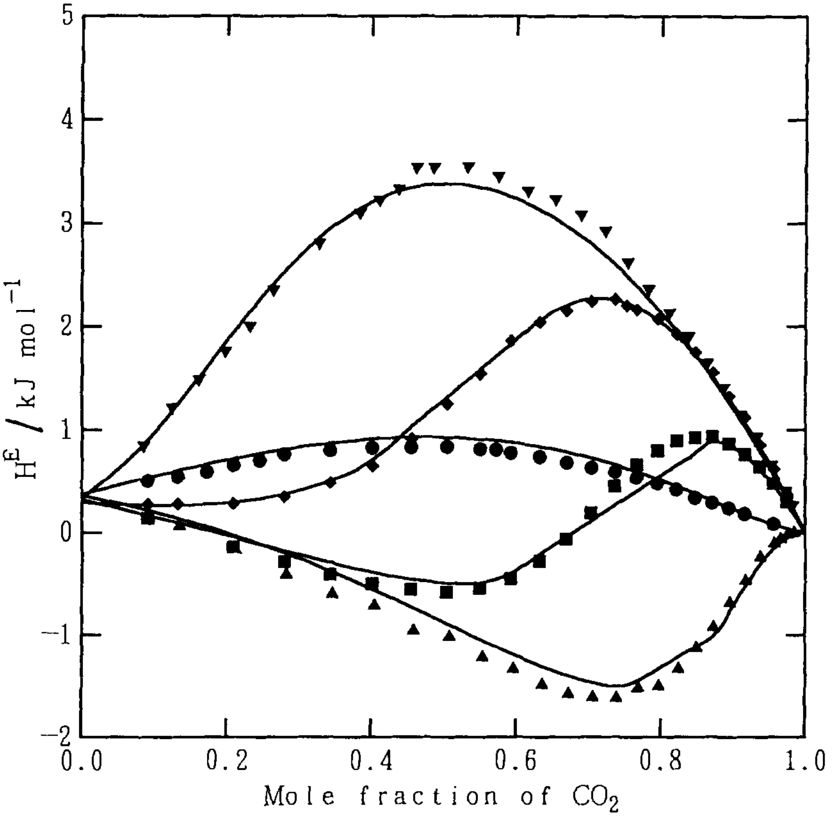

Fig. 2. Comparison of experimental and predicted excess enthalpies for the carbon dioxide(1)-*n*-hexane(2)-toluene(3) system at 12.50 MPa and $x_2/x_3 = 3$. Experimental: ●, at 308.15 K; ▲, at 358.15 K; ■, at 413.15 K; ◆, at 470.15 K; ▼, at 573.15 K. Predicted: ——.

corresponds to a two-phase region for the ternary mixture. The accuracy of the predictions by the present equation of state can be considered satisfactory.

In this work, the predictions of the H^E data in the two-phase region were made on the assumption that the boundaries of the two-phase region in the ternary mixture can be approximately expressed by the straight lines connecting the limits of those in the binary systems carbon dioxide-*n*-hexane and carbon dioxide-toluene, because the vapor-liquid equilibrium data for the ternary system are not reported and the shape of the two-phase region is unknown. Details of the calculational procedure for this estimation have been described by Casielles et al. [5]. In their work, the Peng-Robinson equation of state was employed to predict ternary H^E data for the same system from binary data alone. On the whole, the predictive ability of the present approach seems to be slightly better than that of Casielles et al. Further improvements of the ternary H^E predictions in the two-phase

TABLE 3

Predicted results for the methane(1)–carbon dioxide(2)–hydrogen sulfide(3) system

Temperature in K	Pressure in MPa	No. of data points	H^E_{min} in J mol^{-1}	H^E_{max} in J mol^{-1}	Abs. arith. mean dev. in J mol^{-1}	Ref.
293.15	0.507	5	29.9	50.6	3.6	6
	1.520	4	73.7	129.9	7.9	6
305.15	0.507	5	27.3	41.2	11.3	6
	1.520	3	57.2	99.1	4.7	6
313.15	0.507	4	25.9	32.3	2.9	6
	1.520	4	38.1	90.8	4.7	6

region might be obtained by using more accurate ternary vapor–liquid equilibrium data.

The methane(1)–carbon dioxide(2)–hydrogen sulfide(3) system in the gaseous region

Predictions of ternary H^E data for the gaseous mixtures were carried out at 293.15, 305.15 and 313.15 K and at 0.507 and 1.520 MPa. The experimental values of H^E under these conditions are small and endothermic [6]. The predicted results for the system are shown in Table 3.

The present equation of state provides good results for the ternary system. The mean percentage deviation between the experimental and predicted values of the ternary excess enthalpies is, in most cases, below 10%, and it is comparable with that of Barry et al. [6] who utilized the Redlich–Kwong and the Benedict–Webb–Rubin equations of state to represent the ternary H^E data using the binary interaction parameters obtained from the ternary data.

CONCLUSIONS

The PRSV equation of state coupled with the NRTL mixing rule was utilized for the prediction of ternary excess enthalpy data at high pressures. For the carbon dioxide(1)–*n*-hexane(2)–toluene(3) system in the vicinity of the critical region and for the methane(1)–carbon dioxide(2)–hydrogen sulfide(3) system in the gaseous region, the equation of state provides good predictions of ternary H^E data using only binary data.

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