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Reviews

Excess Enthalpy Data in Binary Systems Containing a Supercritical Fluid and Their Correlation

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Excess enthalpy data measured in the critical regions were collected from the literature for the period of 1983−1995. The database contains 231 datasets of 23 binary systems (6434 data points) covering the temperature and pressure ranges of 263.15−573.15 K and 43.3−175 bar, respectively. The experimental data were correlated by Redlich−Kister equation. The following thermodynamic models were also tested: Peng−Robinson EOS, NRTL, and MHV1 models. A modified Peng−Robinson EOS with composition-dependent interaction parameters was proposed. The correlation of the excess enthalpy data in the database using this model provides good results.

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1. Introduction

Thermodynamic behavior of fluid mixtures in the vicinity of the critical point and in the supercritical region is currently a very active area of research [94-mch/kru]. About a decade ago, Christensen and co-workers reported that at conditions exceeding the critical point of one component the excess enthalpy of binary systems often shows large deviations from ideal behavior [85-mor/lev, 87-chr/iza]. Typically, the excess enthalpy goes through a deep minimum followed by a maximum of order 1000 J/mol at higher mole fractions. Some systems have only one maximum or minimum, but even these show very large values of excess enthalpies.

There is a high potential for utilizing these phenomena for development of heat pumps and other applications in heat exchange, heat transport, and heat storage [87-chr/iza]. Wormald [86-wor] has shown that the van der Waals equation of state can display all the features observed in the H^E in the critical region qualitatively with k_{ij} as the one adjustable parameter. Lewis et al. [77-lew/mos] used a modified Redlich−Kwong equation to calculate H^E for nitrogen + argon and argon + methane systems. Mosedale and Wormald [77-mos/wor] compared the van der Waals (VW), the Redlich−Kwong (RK), the Carnahan−Starling−van der Waals(CSVW), and Carnahan−Starling−Redlich−Kwong (CSRK) equations and found the CSRK equation yielded H^E values that agreed best with experimental H^E values. Christensen and co-workers [84-chr/chr, 84-chr/wal, 84-chr/zeb, 85-chr/zeb-1, 85-chr/zeb-2, 85-chr/zeb-3, 85-chr/cor] have calculated H^E values by using the RK, CSRK, Andrews−Redlich−Kwong (ARK), Peng−Robinson (PR), Soave (SRK), Carnahan−Strling−Soave (CSSRK), and Andrews−Soave (ASRK) equations for the ethane + Freon-22 system, the CSRK, ARK, ASRK, and CSSRK equations for the propane + Freon-12 system, the CSSRK, ASRK, and CSRK equations for the carbon dioxide + hexane and carbon dioxide + pyridine systems, and the RK and ASRK equations for carbon dioxide + toluene system. Gasielles et al. [89-gas/pan] predicted the excess enthalpies of the carbon dioxide + hexane + toluene ternary system at high temperatures and pressures using the Peng−Robinson equation of state. The main studies for correlation of excess enthalpy in high pressure and supercritical regions are listed in Table 1.

In the present work, we collected literature measurements of excess enthalpy in the critical region for the period of 1983−1995. Furthermore, we correlated all data sets in this database by the Redlich−Kister equation. We also tested three standard thermodynamic models (a cubic equation of state EOS, an equation for the excess Gibbs energy g^E, and a combined EOS−g^E model) to investigate which model gives the best correlation of the excess enthalpy data at the nearly critical and supercritical conditions.

Finally, for correlating S-shaped excess enthalpy curves we suggest the use of a modified Peng−Robinson with composition-dependent parameters.

2. Database of Excess Enthalpy

Tables 1−3 summarize the excess enthalpy data collected from the literature. The database covers the period of 1983−1995, and the reproducibility of all of the measurement is ±1 to ±2%. The database is divided into three parts according to the nature of the components:

I. Carbon Dioxide + Hydrocarbon Systems. This part of the database contains 166 datasets of 13 binary systems (4566 data points). The binary systems of part I are listed in Table 2.

II. Alkanol (or Hydrocarbon) + Hydrocarbon Systems. The second part of the database contains 25 data sets of 6 binary systems (703 data points). The binary systems of part II are listed in Table 3.

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Table 1. Main Studies for Correlation of Excess Enthalpy in High-Pressure and Supercritical Regions

authors	year	systems	data sets	status	models	journals
K. L. Lewis, S. E. Mosedale, C. J. Wormald	1977	6	34	low temperature, high pressure	modified RK, RK, van der Waals, SCRK, SCVW	*J. Chem. Thermodyn.*
J. J. Christensen, R., M. Izatt, et al.	1984	5	62	supercritical	RK, CSRK, ARK, PR, SRK, CSSRK, ASRK	*J. Chem. Thermodyn.*
	1985					
D. M. Zebolsky, J. A. R. Renuncio	1994	4		supercritical	MDS, FSC, PANV, PR, SRK, PYSRK	*J. Supercrit. Fluids*
H.-M. Lin, M.-J. Lee	1994	90		high temperature, high pressure	CCOR (cubic chain-of-rotators)	*Fluid Phase Equilib.*
R. Cesar Castells, et al.	1994	1	7	supercritical	PR	*J. Chem. Soc., Faraday Trans.*
K. Kurihara, K. Kojima	1995	11		high temperature, high pressure	EOS−g^E(VP), NRTL, EOS−g^E(MHV2), PSRK	*Fluid Phase Equilib.*
M. S. Gruszkiewicz, J. B. Ott	1996	4	52	high temperature, high pressure	van der Waals, RK, SRK, PR	*Fluid Phase Equilib.*

III. Fluorocarbon + Hydrocarbon Systems. The third part of the database contains 40 data sets of 4 binary systems (1165 data points). The binary systems of part III are listed in Table 4.

3. Analysis of the Database

At isothermal and isobaric conditions, the following cases are found when analyzing the excess enthalpy database:

I. The excess enthalpy shows very large negative or positive values (Figures 1-1, 1-2).

II. The excess enthalpy−composition plot changes sign and goes from large negative to large positive values (or vice versa).

III. Varying temperature at isobaric conditions, the excess enthalpy goes from a large minimum to a large maximum (or vice versa) (Figure 1-5, 1-6).

IV. Varying pressure at isothermal conditions, the excess enthalpy goes from a large minimum to a large maximum (or vice versa) (Figure 1-7, 1-8).

Figure 2 shows a three-dimensional diagram ($T-P-H^E$) based on experimental data for the equimolar mixture of carbon dioxide + pentane [83-pan/ren-3, 87-chr/iza]. When the two fluids are mixed at a temperature near the critical temperature of pentane (T_c = 469.7 K), large positive values of excess enthalpy are observed. This is in contrast to the large negative excess enthalpies that are measured at lower temperatures near the critical temperature of carbon dioxide (T_c = 304.1K). However, even at these temperatures, the excess enthalpy can also show both positive and negative values depending on pressure.

4. Data Reduction by Redlich−Kister Equation

The Redlich−Kister equation (R−K) [48-red/kis] is a flexible function commonly used for correlating binary excess enthalpy data. It is an empirical power expansion of the following form

$$H^E = x_1x_2\sum_{k=0}^{N-1}A_k(x_1 - x_2)^k \tag{1}$$

where A_k is an adjustable parameter, x_i (i = 1 or 2) is the mole fraction of component i, and N is the number of adjustable parameters.

All datasets of the excess enthalpy database were correlated by the Redlich−Kister equation. The results of the correlation are shown in Tables 5,6 and Figure 3. An algorithm suggested by Marquardt [63-mar], based on an earlier suggestion of Levenberg [44-lev], had been used in the data reduction. A suitable objective function to be minimized is

$$\mathrm{OF} = \sum_{i=1}^{n}\left[\frac{(H^E_{\mathrm{cal}} - H^E_{\mathrm{exp}})_i}{\sigma}\right]^2, \quad \sigma = \sqrt{\frac{\sum_{i=1}^{n}(H^E_{\mathrm{cal}} - H^E_{\mathrm{exp}})_i^2}{n}} \tag{2}$$

where n is the number of experimental data for a given system, σ is standard deviation.

5. Correlation by Thermodynamic Models

5.1. Cubic Equation of State. In this work, we chose the Peng−Robinson EOS as a representative of cubic

Table 2. Excess Enthalpy Data of Carbon Dioxide + Hydrocarbon Systems

name of system	literature	range of T (K)	range of P (bar)
carbon dioxide + methanol	86-cor/chr-1	308.15−573.15	75−125
carbon dioxide + ethane	83-pan/ren-2	293.15−323.15	75.8
carbon dioxide + ethanol	88-cor/rza-2	308.15−473.15	50−149.1
carbon dioxide + propan-1-ol	86-cor/chr-1	308.15−473.15	75−125
carbon dioxide + butan-1-ol	86-cor/chr-1	308.15−473.15	75−125
carbon dioxide + pyridine	84-chr/chr, 85-chr/zeb-3	308.15−573.15	75−125
carbon dioxide + pentane	83-pen/ren-3, 87-chr/rza	308.15−573.15	75.8−124.5
carbon dioxide + cyclohexane	83-chr/chr, 88-chr/cor, 88-cor/rza-1	308.15−573.15	75−143.9
carbon dioxide + hexane	84-chr/wal, 85-chr/zeb	308.15−573.15	75−125
carbon dioxide + toluene	83-pen/ren-4, 85-chr/zeb-1, 86-cor/chr-2, 88-cor/chr	308.15−573.15	69.8−175
carbon dioxide + octan-1-ol	86-cor/chr-1	308.15−473.15	75−125
carbon dioxide + nonane	91-cor/gun	308.15−413.15	75−125
carbon dioxide + deecane	83-pan/ren-1, 86-chr/cor	283.15−573.15	75.8−125

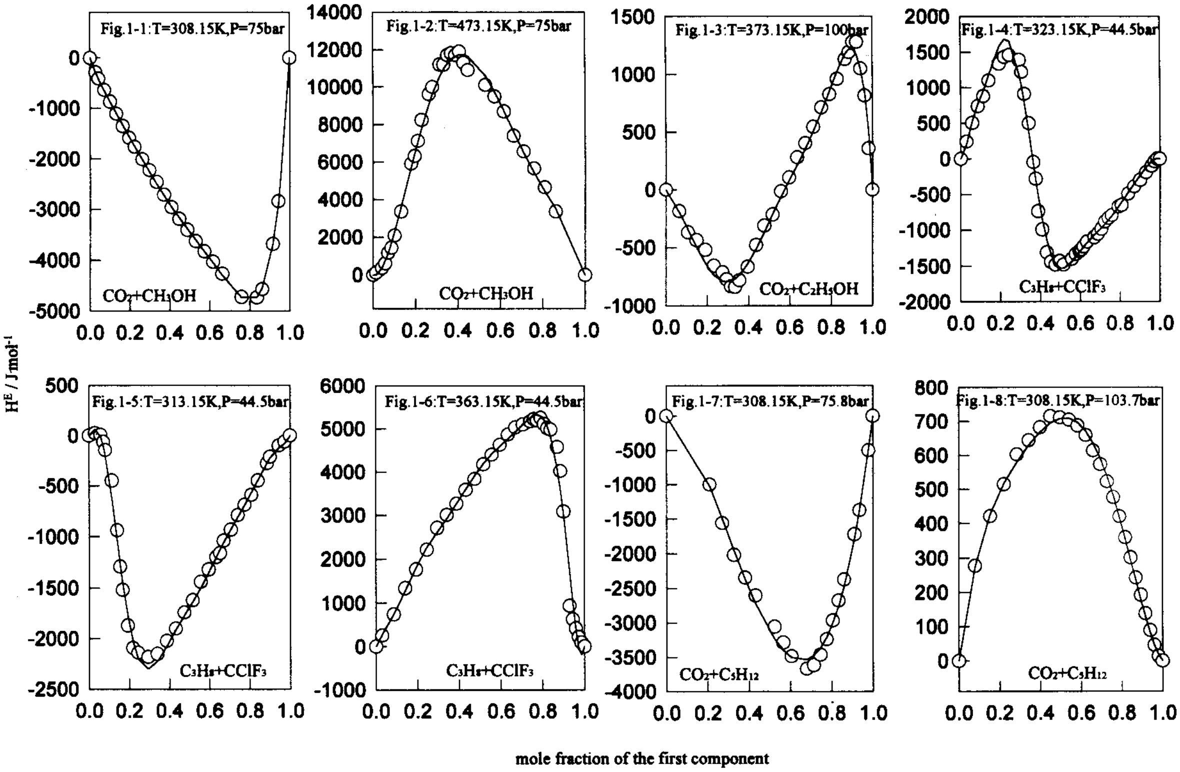

Figure 1. Some H^E curves in the database: ○, experimental data; —, correlated by the R−K equation.

Table 3. Excess Enthalpy Data of Alkanol (or Hydrocarbon) + Hydrocarbon Systems

name of system	literature	range of T (K)	range of P (bar)
ethane + methanol	89-sip/gra	298.15−348.15	75−150
ethane + ethanol	90-ott/sip	323.15−348.15	50−150
ethane + butan-1-ol	91-sip/ott-2	323.15−348.15	50−150
propane + methanol	91-sip/ott-1	373.15	50−150
propane + propan-1-ol	90-sip/ott	368.15	50−150
hexane + toluene	87-fau/chr	573.15	75−125

equation of state. The Peng−Robinson EOS shows an improved performance about heat capacity in the critical region, and it has the following form [76-pen/rob] The

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V^2 + 2bV - b^2)} \tag{3}$$

mixing rules are given by

$$a = \sum_{i=1}^{c}\sum_{j=1}^{c} x_i x_j a_{ij} \tag{4}$$

$$b = \sum_{i=1}^{c} x_i b_i \tag{5}$$

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \tag{6}$$

where a is the energy parameter, b is the size parameter of the Peng−Robinson EOS and c is the number of components. Excess enthalpy H^E can be calculated by the

Table 4. Excess Enthalpy Data of Fluorocarbon + Hydrocarbon Systems

name of system	literature	range of T (K)	range of P (bar)
chlorodifluoromethane + ethane	84-chr-zeb	293.15−383.15	51.5
chlorotrifluoromethane + propane	86-chr/fau	293.15−383.15	44.5
dichlorodifluoromethane + propane	85-chr/cor	353.15−398.15	44.5
dichlorodifluoromethane + N,N-dimethylacetamide	83-sch/pos	263.15−413.15	43.3−45.3

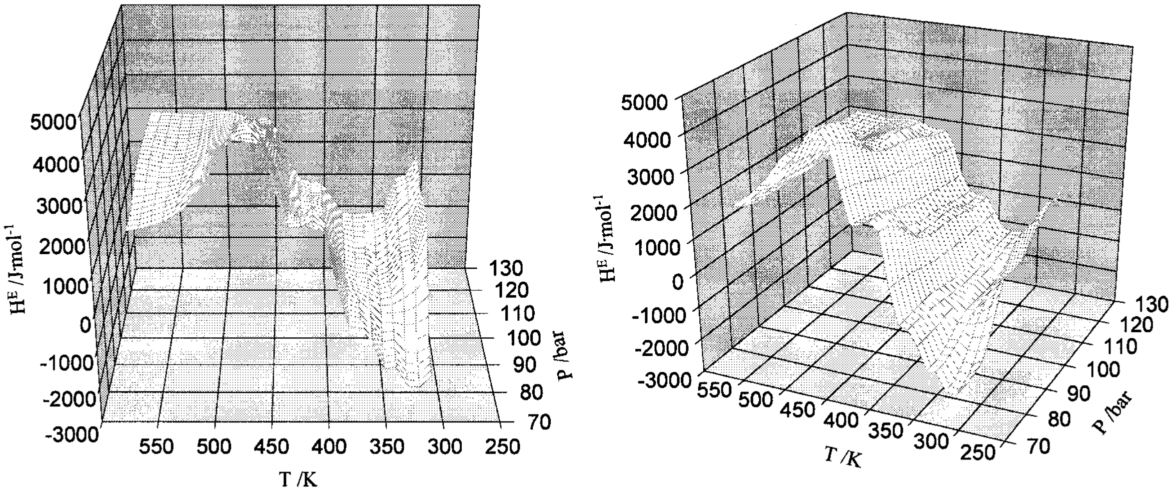

Figure 2. $T-P-H^E$ plot for carbon dioxide + pentane system (from different view angle, $x = 0.5$). CO_2: $T_c = 304.1$ K, $P_c = 74.78$ bar. C_5H_{12}: $T = 469.7$ K, $P_c = 34.15$ bar.

Table 5. Average Deviations of Excess Enthalpy by the R−K Equation and the Modified Peng−Robinson EOS

name of system	data points	data sets	R−K[a]	modified P−R[a]	R−K[b]	modified P−R[b]
carbon dioxide + methanol	174	6	1.73	2.36	75.8	91.7
carbon dioxide + ethane	59	3	1.11	1.56	19.4	27.0
carbon dioxide + ethanol	472	18	1.58	2.30	42.9	60.4
carbon dioxide + propan-1-ol	95	4	2.21	1.90	75.3	51.3
carbon dioxide + butan-1-ol	137	4	1.33	3.72	42.9	147.5
carbon dioxide + pyridine	409	15	2.20	3.44	71.6	116.3
carbon dioxide + pentane	553	21	1.59	2.11	31.6	42.6
carbon dioxide + cyclohexane	723	23	1.68	2.06	49.2	58.0
carbon dioxide + hexane	511	18	1.56	2.62	37.9	58.5
carbon dioxide + toluene	947	35	2.22	2.65	57.3	76.1
carbon dioxide + octan-1-ol	77	3	1.87	3.04	20.9	25.7
carbon dioxide + nonane	44	2	1.74	2.69	32.1	44.7
carbon dioxide + decane	365	14	1.91	2.76	36.7	53.3
total (CO_2 systems)	4566	166	1.83	2.53	47.9	67.0
ethane + methanol	137	5	2.06	5.03	11.6	26.1
ethane + ethanol	164	6	2.28	2.84	16.9	24.7
ethane + butan-1-ol	195	6	1.61	2.26	13.6	19.7
propane + methanol	83	3	0.51	2.69	7.5	40.2
propane + propan-1-ol	43	2	0.56	1.94	5.9	22.0
hexane + toluene	81	3	1.55	2.60	6.3	11.1
total (hydrocarbon systems)	703	25	1.64	3.02	11.8	23.8
chlorodifluoromethane + ethane	253	9	4.19	3.39	108.7	83.0
chlorotrifluoromethane + propane	364	12	2.62	3.57	74.2	73.8
dichlorodifluoromethane + propane	460	15	1.73	2.86	31.7	52.9
dichlorodifluoromethane + *N*,*N*-dimethylacetamide	88	4	1.21	2.40	46.4	102.3
Total (Freon systems)	1165	40	2.50	3.14	63.3	70.9
TOTAL (23 systems)	6434	231	1.92	2.69	46.7	63.0

[a] Average relative deviation = $\{\sum_{i=1}^{N}|(H^E_{cal} - H^E_{exp})_i/H^E_{(exp)max}| \times 100\%\}/N$ (%), where N is the number of data sets. [b] Average absolute deviation = $\{\sum_{i=1}^{N}|(H^E_{cal} - H^E_{exp})_i|\}N$ (J·mol^{-1}), where N is the number of data sets.

following equation

$$H^E = H^R - \sum_{i=1}^{c}(x_i H_i^R) \qquad (7)$$

where H^R is the molar residual enthalpy. The derivation of H^R from an equation of state is based on the equation shown by Lewis et al. [77-lew/mos, 85-wal]

$$H^R = RT\,(Z - 1) - \int_V^{\infty}\left\{T\left(\frac{\partial P}{\partial T}\right)_V - P\right\}\mathrm{d}V \qquad (8)$$

Substituting eq 3 into eq 8, we obtain eqs 9 and 12.

For a mixture

$$H^R = RT\left\{(Z - 1) + \left(\frac{T\left(\frac{\partial a}{\partial T}\right) - a}{2\sqrt{2}bRT}\right)\ln\left(\frac{Z + 2.414B}{Z - 0.414B}\right)\right\} \qquad (9)$$

where

$$B = bP/RT \qquad (10)$$

$$\frac{\partial a}{\partial T} = -\frac{1}{2}\sum_{i=1}^{c}\sum_{j=1}^{c}x_i x_j(1 - k_{ij})\left[m_i\sqrt{\left(\frac{a_{ci}a_j}{T_{ci}T}\right)} + m_j\sqrt{\left(\frac{a_{cj}a_j}{T_{cj}T}\right)}\right] \qquad (11)$$

For pure component i

$$H_i^R = RT\left\{(Z_i - 1) + \left(\frac{T\left(\frac{\partial a_i}{\partial T}\right) - a_i}{2\sqrt{2}b_iRT}\right)\ln\left(\frac{Z_i + 2.414B_i}{Z_i - 0.414B_i}\right)\right\} \qquad (12)$$

Table 6. Adjustable Parameters of the Five Models for Systems of Figure 4

		Figure					
system	parameter	4-1	4-2	4-3	4-4	4-5	4-6
modified Peng−Robinson EOS	A_1	0.620 136	0.06	0.074	0.262 954	0.060 45	0.128 651
	A_2	−0.046 49			−0.005 55	−0.006 86	−0.067 577
	A_3	−0.426 34			−0.177 43	0.003 043	0.002 024 4
	A_4	0.312 373			0.312 373	0.013 091	0.025 860 9
Redlich−Kister equation	A_1	9566.56	22 696.4	−12 717.8	16 396.5	−5 297.35	455.18
	A_2	−4063.02	11 436.6	−9 711.27	12 972.8	8 411.15	5 562.03
	A_3	2942.83	−21 115.9	−10 090.6	3 810.98	66 215.9	13 294.5
	A_4	1875.33	−1 719.93	−45 418.6	−703.22	52 116	9 183.32
	A_5	−12175.6	14 041.1	−46 496.8	71 778.1	−209 221	−892 777
	A_6	1268.97		95 352.3	77 336.5	−210 774	−12 757.9
	A_7	8143.97		102 984	−101 260	336 706	354.86
	A_8			−127 678	−111 689	281 654	3 784.84
	A_9			−119 025		−270 647	
	A_{10}					−125 410	
	A_{11}					85 379.5	
Peng−Robinson EOS	k_{ij}	0.504	0.06	0.074	0.055	0.064	0.136
NRTL	α_{12}	−0.16	0.1	0.74	−0.09	0.35	0.99
	$(g_{12} - g_{22})$	9290.63	21217.62	3479.48	9485.86	13448.04	6200.8
	$(g_{21} - g_{11})$	−3661.61	4563.1	−6149.07	−3036	2932.93	1426.13
EOS−g^E (MHV1)	α_{12}	0.11	0	0.36	0	0.71	1.98
	$(g_{12} - g_{22})$	9256.35	5789.94	19258.01	4696.92	5570.01	−66.7
	$(g_{21} - g_{11})$	3247.57	−916.92	6591.34	−3493.8	−1285.76	−1439.26

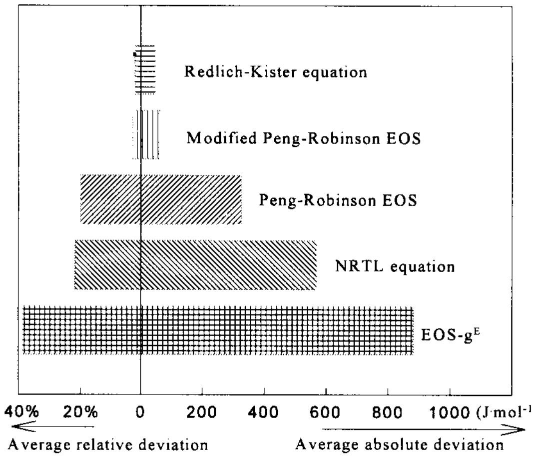

Figure 3. Overall deviations by different models.

where

$$B_i = b_i P/RT \tag{13}$$

$$\frac{\partial a_i}{\partial T} = -\frac{a_{ci} m_i}{\sqrt{T T_{ci} \alpha_i}} \tag{14}$$

$$\alpha_i = [1 + m_i(1 - \sqrt{T_{ri}})]^2 \tag{15}$$

$$m_i = 0.374\ 64 + 1.542\ 26\omega_i - 0.269\ 92\omega_i^{\ 2} \tag{16}$$

5.2. Equation for Excess Gibbs Energy. A standard form of the NRTL equation [68-ren/pra] for the excess Gibbs energy g^E was used in this work

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right] \tag{17}$$

where

$$\tau_{12} = \frac{(g_{12} - g_{22})}{RT} \tag{18}$$

$$\tau_{21} = \frac{(g_{21} - g_{11})}{RT} \quad (g_{12} = g_{21}) \tag{19}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{20}$$

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \tag{21}$$

$$\alpha_{12} = \alpha_{21} \tag{22}$$

The excess enthalpy is calculated as

$$H^E = RTx_1x_2 \frac{\tau_{21} G_{21}(x_1 + x_2 G_{21} - x_1 \alpha_{21} \tau_{21})}{(x_1 + x_2 G_{21})^2} + \frac{\tau_{12} G_{12}(x_2 + x_1 G_{12} - x_2 \alpha_{12} \tau_{12})}{(x_2 + x_1 G_{12})^2} \tag{23}$$

5.3. Combined EOS−g^E Model. Recently, new mixing models were developed that combine equations of state with excess Gibbs energy models using different standard states [95-kol, 95-kur/koj]. The mixing rules relate mixture parameters *a* and *b* of a cubic equation of state to an activity coefficient model. In this work we calculated excess enthalpy using a model that combines the Peng−Robinson EOS and the NRTL equation. The MHV1 mixing rule by Michelsen [90-mic] has the following form

$$a = \alpha bRT \tag{24}$$

$$\alpha = \sum_{i=1}^{c} x_i \alpha_i + \frac{1}{q}\left[\frac{g^{E(NRTL)}}{RT} + \sum_{i=1}^{c} x_i \ln\left(\frac{b}{b_i}\right)\right] \tag{25}$$

$$q = -0.53 \tag{26}$$

The temperature derivation of the combined parameter α

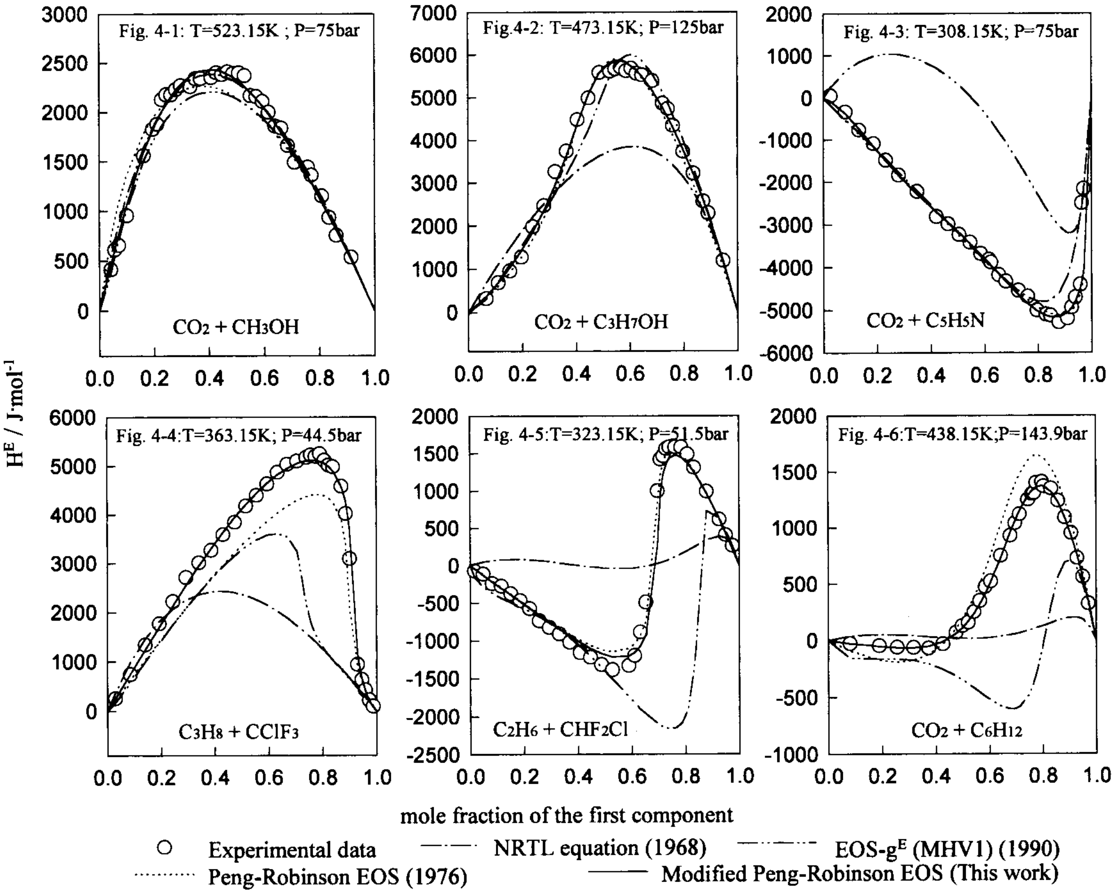

Figure 4. Some results of data correlation by some models.

had been outlined by Kurihara et al. [95-kur/koj]

$$\left(\frac{\partial \alpha}{\partial T}\right)_{x_i} = \sum_{i=1}^{c} x_i\left(\frac{d\alpha_i}{dT}\right) + \frac{1}{q}\left[\frac{\partial(g^{E(NRTL)}/(RT))}{\partial T}\right]_{x_i} \qquad (27)$$

Substituting eqs 17 and 27 into eq 24, we obtain eq 28.

$$\frac{\partial a}{\partial T} = \frac{bx_1x_2}{qT}\left[\frac{(g_{21}-g_{11})(3\alpha_{21}x_2t_{21}G_{21})}{(x_1+x_2G_{21})^2} + \frac{(g_{12}-g_{22})(3\alpha_{12}x_1\tau_{12}G_{12})}{(x_2+x_1G_{12})^2}\right] \qquad (28)$$

Using eqs 3–16, where of those eq 11 is replaced with eq 28, we can calculate the excess enthalpy by the combined EOS–g^E model.

5.4. Modified Peng–Robinson EOS. We modified the Peng–Robinson EOS by expressing k_{ij} as a function of composition. The composition dependent k_{ij} is similar to the Redlich–Kister expansion:

$$k_{ij} = \sum_{i=1}^{5} A_i(2x-1)^{i-1} \qquad (29)$$

where A_i is are adjustable parameters and x is the mole fraction of the first component.

Using eqs 3–16, where of those k_{ij} in eq 6 are replaced with eq 29, we can calculate the excess enthalpy by the modified Peng–Robinson EOS.

For the two-phase regions (vapor–liquid equilibrium), we use eq 30 to calculate the excess enthalpy.

$$H^E = A_1 + A_2x \qquad (30)$$

where $A_{1,2}$ are adjustable parameters.

6. Results and Discussion

The results of data correlation by the different models are shown in Figure 3. The maximum number of adjustable parameters used in the Redlich–Kister equation is 11. On the other hand, fewer parameters are necessary for correlation with the modified Peng–Robinson EOS than with the Redlich–Kister equation, that is at most five. The average deviations of correlating excess enthalpy data by the modified Peng–Robinson EOS and the Redlich–Kister equation are summarized in Table 5.

In cases when excess enthalpies are not very big (<3000 J/mol) and H^E–x curves are symmetric, all tested models are able to fit the experimental data with good accuracy (Figure 4-1). Among them, the NRTL equation provides the best fit for such systems. However, when excess enthalpy values are very large (Figure 4-2) or the excess enthalpy curve is highly asymmetric, the NRTL model is no longer able to fit the data. The MHV1 model has higher flexibility than the NRTL equation. Nevertheless, the MHV1 model also fails for highly skewed systems (Figure 4-3, 4-4). Among the tested models, only the modified Peng–Robinson EOS is capable of describing systems with changing sign of the excess enthalpy (S-shaped H^E curves, Figure 4-5, 4-6). The adjustable parameters of the five models for systems of Figure 4 are shown in Table 6.

7. Conclusions

In the vicinity of the critical point, the excess enthalpy shows strong variations with temperature, pressure, and composition. Excess enthalpy curves can exhibit large negative or positive values and S-shaped transitions of these extrema. At normal conditions, excess enthalpy data can be correlated well using standard thermodynamic models, such as the NRTL equation. However, as shown in this work, these model often fail to correctly describe the large and asymmetric changes of excess enthalpy at high pressures and temperatures.

The present study provides the following conclusions:

I. All data sets in the excess enthalpy database could be correlated to within the experimental accuracy with the Redlich−Kister equation. Depending on complexity of the system, the number of adjustable parameters of the equation varied from 4 to 11.

II. Among the standard thermodynamic models tested (Peng−Robinson EOS, NRTL, and MHV1 models), the modified Peng−Robinson EOS gave the best correlation of the excess enthalpy data in the database. For symmetric hydrocarbon + hydrocarbon systems, the NRTL equation provided better results than the Peng−Robinson EOS.

III. When correlating the excess enthalpy data with the Peng−Robinson EOS, the optimized values of the parameter k_{ij} were found to vary strongly with temperature and weakly with pressure. When the parameter k_{ij} was assumed to be independent of temperature and pressure, simultaneous fitting all excess enthalpy data of one system gave a poor fit for most mixtures.

IV. Good correlation of the individual data sets could be obtained using a modified Peng−Robinson EOS with a composition dependent k_{ij} that is given by a Redlich−Kister type function. Using this model, the number of parameters necessary to fit the individual datasets is only one to five.

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