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Excess enthalpies for inorganic liquids with supercritical carbon dioxide: Equation of state correlations

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Abstract

Excess enthalpies along isotherm/isobars for binary mixtures of liquid neopentane, $SnCl_4$, and $TiCl_4$, in supercritical CO_2 are correlated with two equations of state. Both equations use a Percus–Yevick hard-sphere repulsive pressure term added to an attractive term, and temperature dependent size parameters. One attractive term is empirical, the other is based on a square-well potential. Calculations for pure component enthalpies fit data better than molecular dynamics simulations, but the simulations better predict the excess enthalpies. © 1997 Elsevier Science B.V.

Keywords: Binary mixtures; Equations of state; Heats of mixing; Residual enthalpies; Supercritical CO_2

1. Introduction

Solubilities, excess enthalpies at constant temperature and pressure (H_m^E), and densities for $SnCl_4$ and $TiCl_4$, in supercritical CO_2, have been reported by Giles et al. [1], and Tolley et al. [2], respectively. Strong variations with pressure were observed for the mixings that resemble those of organic solutes in supercritical CO_2 [3]. In addition, molecular dynamics simulations that treated the solute as a spherical Lennard–Jones fluid agreed with the experiment for the inorganic solute $SnCl_4$ [1] as well as for neopentane [4].

A comparison of six equations of state (EOS) has indicated that those based on a hard-sphere pressure correlate and predict equal to or better than the conventional ones [5]. It was of interest to question how well such equations might correlate the H_m^E for inorganic solutes. In this study, the Morrison–de Santis (MDS) EOS [6] was compared with the Franck square-well (FSW) EOS [7] for the ability to correlate data for all the three solutes, $SnCl_4$, $TiCl_4$, and neopentane, in supercritical CO_2. The MDS EOS was chosen because it showed the best correlations with CO_2 data of six EOS [5]. The FSW EOS was chosen because its parameters have simple physical interpretations [7].

First, the EOS and the mixing and its combining rules will be discussed. Second, the pure component parameters for the EOS will be reported from correlations with residual enthalpies and molar volumes. Then the results of correlations and predictions of binary mixing data will be presented.

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2. Equations of state

It is convenient to express the pressure, P, of a van-der-Waals – type EOS as a sum of two terms, $P_0 + P_a$, where it is assumed that P_0 represents intermolecular repulsion, and P_a the intermolecular attraction. In this work, the EOS used the Percus–Yevick pressure for a system of hard spheres,

$$P_0 = RTV^{-1}(1 + \eta + \eta^2)/(1 - \eta)^3 \qquad (1)$$

where η symbolizes the molecular volume fraction, $b/4V$; however b was made temperature dependent as shown in Eqs. (4) and (6).

The MDS EOS reported by Morrison and McLinden [6] featured an empirically based P_a term,

$$P_a = -a_c \exp(\alpha)/(V(V + b)) \qquad (2)$$

$$\alpha = A_1(T - T_c) + A_2(T^2 - T_c^2) \qquad (3)$$

$$b = b_c[1.065655(1 - 0.12\exp(-2T_c/3T))]^3 \qquad (4)$$

A_1 and A_2 in Eq. (3) are adjustable parameters. The temperature-dependent b, in Eq. (4), represents Fermeglia's term [8], and was found to fit pure component data better [5] than the temperature-dependent b term of Morrison and McLinden [6]. It was used in Eqs. (1) and (2) to 'soften' the hard sphere. The constants a_c and b_c were derived from the critical point conditions of mechanical stability [5] that ensure an inflection point at the experimental critical temperature and pressure. The FSW EOS of Christoforakos and Franck [7] used a P_a term, derived from a square-well potential,

$$P_a = -RTb(\lambda^3 - 1)[\exp(\varepsilon/RT) - 1]/V^2 \qquad (5)$$

$$b = (2/3\pi\sigma^3)[1 - 0.12\exp(-3\varepsilon/RT)]^3 \qquad (6)$$

Here, σ is the molecular diameter, $\lambda\sigma$ the width of the well, and ε the depth of the well. As suggested by Christoforakos and Franck [7], they are used as adjustable parameters. Consequently, the inflection points of the FSW EOS depend on the adjustable parameters and occur at different critical volumes, temperatures and pressures than experimental. The temperature-dependent expression for b, Eq. (6), used with the FSW EOS was suggested by Kreglewski [9].

The mixing rule used for the binary mixtures was

$$A = \Sigma\Sigma x_i x_j A_{ij} \qquad (7)$$

where summations are over both components, i and j, and x is the mole fraction. The symbol A in Eq. (7) represents b in both the MDS and the FSW EOS, $\exp(\alpha)$ in Eq. (2) for the MDS EOS, and ε, λ and σ^3 for the FSW EOS. The combining rule

$$B_{ij} = (B_i + B_j)/2 \qquad (8)$$

was used for σ_{ij} and λ_{ij} in the FSW EOS, and for b_{ij} in the MDS EOS. The combining rule

$$A_{ij} = k_{ij}(A_i A_j)^{1/2} \qquad (9)$$

was used for $\exp(\alpha)_{ij}$ in Eq. (2) in the MDS EOS, and for ε_{ij} in the FSW EOS. The coefficient k_{ij} is the interaction coefficient, an adjustable parameter used for the mixtures. In order to improve the correlations for the FSW EOS, k_{ij} was made linear in mole fraction for the FSW EOS only,

$$k_{ij} = k_{ij1}x + k_{ij2} \qquad (10)$$

Kreglewski [9] considers the question of composition-dependent combining rules and suggests a further study to decide its benefit for the fitting of enthalpies.

3. Residual enthalpies

Databases were prepared of 444 single-phase liquid- and gas-like residual enthalpies and molar volumes of CO_2 [10] from 220 to 700 K and from 40 to 200 bar, 45 single-phase liquid- and gas-like residual enthalpies and molar volumes of neopentane [11] at 500 K and from 0.69 to 310 bar, 6 single-phase liquid molar volumes of $SnCl_4$ [1] at 313 and 348 K from 62.9 to 104 bar, and 6 single-phase liquid molar volumes of $TiCl_4$ [2,12] from 333 to 363 K from 1 to 125 bar. Volumes were calculated from an EOS by a combination of the half-interval, secant and Newton methods. Analytical equations were derived to calculate residual enthalpies from

$$H^* = \int_{\infty}^{V} [T(\partial P/\partial T)_V - P]\mathrm{d}V + PV - RT \qquad (11)$$

in order to compare them with the experimental data.

A simplex [13] was added to the computer program that enabled the simultaneous variation of the adjustable parameters of an EOS. The best-fit parameters were those that achieved the minimum standard deviation between calculated and experimental values of the database. The temperature derivatives of Eq. (7) were used directly to calculate H^* by Eq. (11) for the mixtures with the MDS EOS to avoid uncertain mixing and combining rules for T_c of the mixtures for Eqs. (3) and (4).

The best-fit standard deviations are displayed in Table 1. The parameters that yield those deviations are listed in Table 2 together with the critical constants predicted by each equation. From Table 1 it can be seen that the MDS EOS fits the CO_2 data better, but the two EOS are similar in fits for the other compounds. Best-fit parameters are dependent on the database. Only volume data were available for $SnCl_4$ and $TiCl_4$ and for those which were far below the critical temperature. The well-depth parameter, ε/k, reflects intermolecular attraction. The sequence of ε/k values, $CO_2 < SnCl_4 < C_5H_{12}$, matches the Lennard–Jones simulations sequence [1,4].

Figs. 1 and 2 compare experimental and calculated residual enthalpies at a supercritical temperature for CO_2, and neopentane, respectively. All the three

Table 1
Relative standard deviations for single-phase, pure component molar volumes and residual enthalpies correlated with two EOS

Substance	Number of data points	MDS	FSW
	molar volumes		
Carbon dioxide	444 [a]	0.043 [e]	0.062
Neopentane	45 [b]	0.067	0.048
Tin(IV) tetrachloride	6 [c]	0.009	0.006
Titanium(IV) tetrachloride	6 [d]	0.040	0.0002
	residual enthalpies		
Carbon dioxide	444 [a]	0.026 [e]	0.073
Neopentane	45 [b]	0.067	0.068

[a] IUPAC [10].
[b] Dawson and McKetta [11].
[c] Giles et al. [1].
[d] Giles et al. [2]; Gmelin [12].
[e] Zebolsky and Renuncio [5].

Table 2
Best-fit parameters and critical constants for two EOS

EOS		CO_2	C_5H_{12}	$SnCl_4$	$TiCl_4$
MDS	A_1, $\times 10^{-3}$	−3.122 [a]	2.684	0.6489	2.662
	A_2, $\times 10^{-6}$	1.693 [a]	−4.247	−0.5328	−2.348
	V_c, cc mol^{-1}	108 [a]	356	415	360
	V_c, experimental	94.0 [b]	311 [c]	351 [d]	339 [d]
FSW	λ	1.79	1.54	1.874	2.274
	σ, Å	3.73	5.46	5.840	5.835
	ε/k, K	140	318	266.5	172.0
	V_c, cc mol^{-1}	116	382	479	402
	T_c, K	314	457	683	777
	T_c, experimental	304 [b]	434 [c]	592 [d]	638 [d]
	P_c, bar	81.2	35.9	42.1	57.1
	P_c, experimental	73.8 [b]	32.0 [c]	37.5 [d]	46.6 [d]

[a] Zebolsky and Renuncio [5].
[b] IUPAC [10].
[c] Dawson et al. [14].
[d] Dean [15].

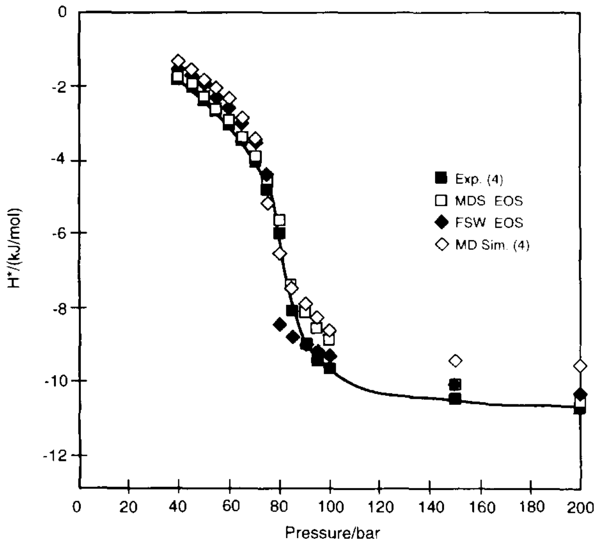

Fig. 1. Residual enthalpy, H^*, against pressure for CO_2 at 310 K. The solid line connects experimental data.

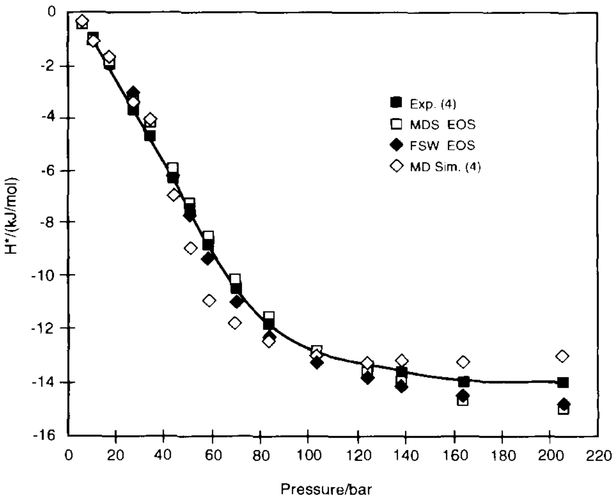

Fig. 2. Residual enthalpy, H^*, against pressure for neopentane at 500 K. The solid line connects experimental data.

calculations show a large increase in absolute values – from small negative gas-like values at low pressures to large negative liquid-like values at high pressures. The values for the molecular dynamics simulations were from the graphs of Rowley et al. [4]. It can be seen in Fig. 1, for CO_2, that the MDS EOS fits the residual enthalpies better at most pressures than the FSW EOS or the MD simulation [4]. Both of the EOS remain closer to experimental enthalpies at high pressures than the simulation which levels at values less negative than experimental. From Table 1, it is seen that both of the EOS for neopentane fit equally well in Fig. 2, on an average, within 7%. The MD simulations mimic the psuedo-phase changes over lower pressure intervals than in the experiment and show lesser enthalpy change values than in the experiment or the EOS.

4. Excess enthalpies

The two EOS with the best-fit parameters in Table 2 were used to fit excess enthalpies for the three binary mixtures. Databases were prepared of 112 single-phase H^E_m for liquid neopentane mixed with supercritical CO_2 at 310 and 313 K from 62.9 to 104 bar [4], 149 single-phase H^E_m and V^E_m for liquid $SnCl_4$ mixed with supercritical CO_2 at 313 and 348 K from 62.9 to 125 bar [1], and 27 single-phase H^E_m and V^E_m for liquid $TiCl_4$ mixed with supercritical CO_2 at 348 K at 62.9 and 125 bar [2].

Table 3 shows the standard deviations between experimental and calculated values of H^E_m for each of the mixtures and the corresponding EOS. The values of the interaction parameter, k_{ij}, are shown under each H^E_m deviation. From Table 3 it can be seen that the MDS EOS correlates the H^E_m better and the FSW EOS correlates the V^E_m better.

Figs. 3 and 4 present comparisons of the calculations of H^E_m with experiment at 310 K from 62.9 to 104 bar, respectively, for CO_2 and neopentane mixtures. The molecular dynamics simulation fits data better at the lower pressure (see Fig. 3) than either of the EOS. Simulation data were from the graphs of Rowley et al. [4]. The FSW EOS predicts excessively negative H^E_m in Fig. 3 near the phase change. All calculations show the slight endothermic values that result in Fig. 4 as the pressure increases to 104 bar. Only the FSW EOS predicts the change to exothermic H^E_m at high concentrations of CO_2 shown by the data, but the EOS calculations are excessively negative.

The same pattern is shown in Figs. 5 and 6 for the excess enthalpies of $SnCl_4$ mixed with CO_2 at 313 K from 62.9 to 125 bar, respectively. The pressure change causes a rise in the H^E_m comparable to that

Table 3

Absolute standard deviations between experimental and calculated single-phase enthalpies (H^E_m) and volumes (V^E_m) of mixing for three binary mixtures. Interaction parameters, k_{ij}, are shown below each pair

Mixture	Maximum and minimum H^E_m and V^E_m		Standard deviations	
			MDS	FSW
$CO_2+C_5H_{12}$ [a]	H^E_m/(J mol^{-1})			
310, 313 K	493	−4300	303	715
62.9–104 bar			k_{ij} values	
112 data			0.956	1.021
CO_2+SnCl_4 [b]	V^E_m/(cm^3 mol^{-1})			
313, 348 K	36.7	−146	15.3	10.8
62.9–125 bar	H^E_m/(J mol^{-1})			
149 data	110	−4760	347	532
			k_{ij} values	
			0.995	$1.162+0.115X$ [d]
CO_2+TiCl_4 [c]	V^E_m/(cm^3 mol^{-1})			
348 K	8.0	−104	11.2	9.4 [e]
62.9, 125 bar	H^E_m/(J mol^{-1})			
27 data	150	−1660	228	403 [e]
			k_{ij} values	
			0.855	$1.108+0.101X$ [d]

[a] Rowley et al. [4].

[b] Giles et al. [1].

[c] Tolley et al. [2].

[d] These k_{ij} values were set linear in X, the mole fraction of CO_2.

[e] Deletion of poorly fitting values at X=0.94 from the correlation changes the deviations to 6.7 cm^3 mol^{-1} and 141 J mol^{-1}.

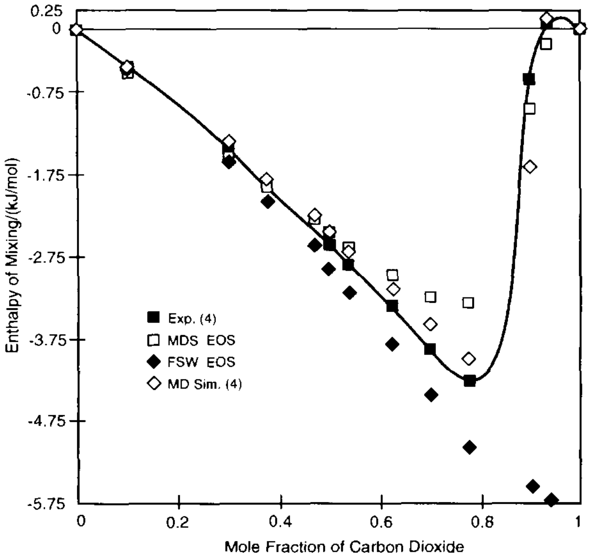

Fig. 3. Enthalpies of mixing for CO_2 and neopentane at 310 K and 62.9 bar. The solid line connects experimental data.

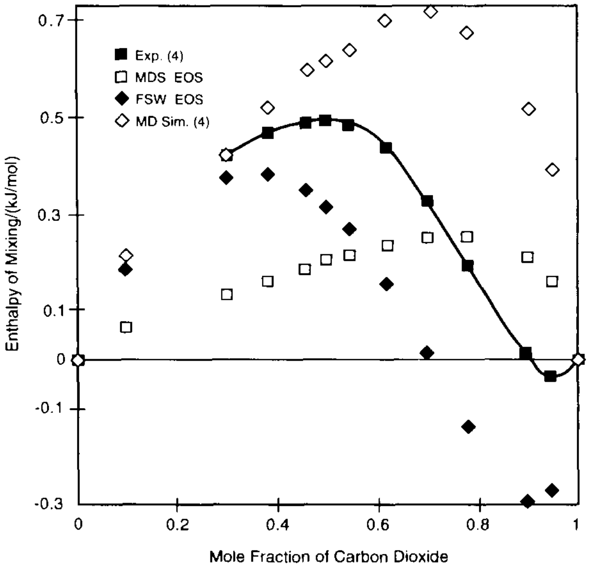

Fig. 4. Enthalpies of mixing for CO_2 and neopentane at 310 K and 104 bar. The solid line connects experimental data.

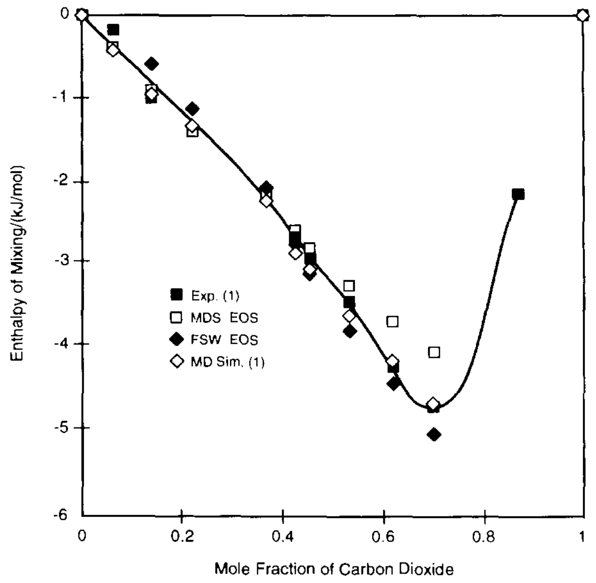

Fig. 5. Enthalpies of mixing for CO_2 and tin(IV) chloride at 313 K and 62.9 bar. The solid line connects experimental data.

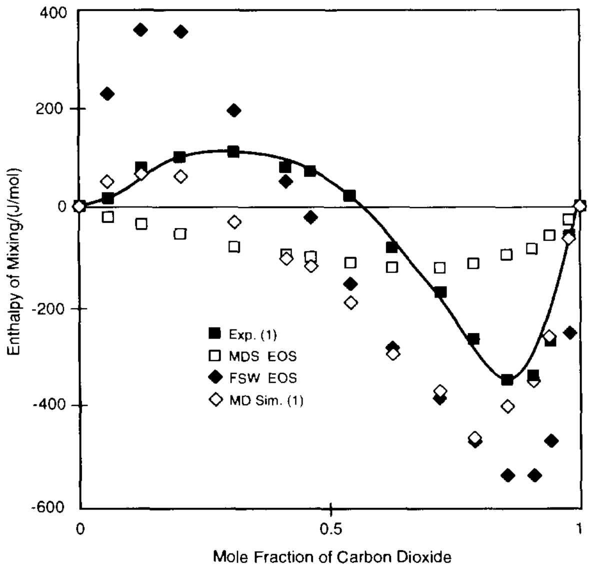

Fig. 6. Enthalpies of mixing for CO_2 and tin(IV) chloride at 313 K and 125 bar. The solid line connects experimental data.

observed for neopentane mixed with CO_2. Simulation data were obtained from the graphs given by Giles et al. [1]. The simulations produce the best fit to the data at both pressures. The MDS EOS has small

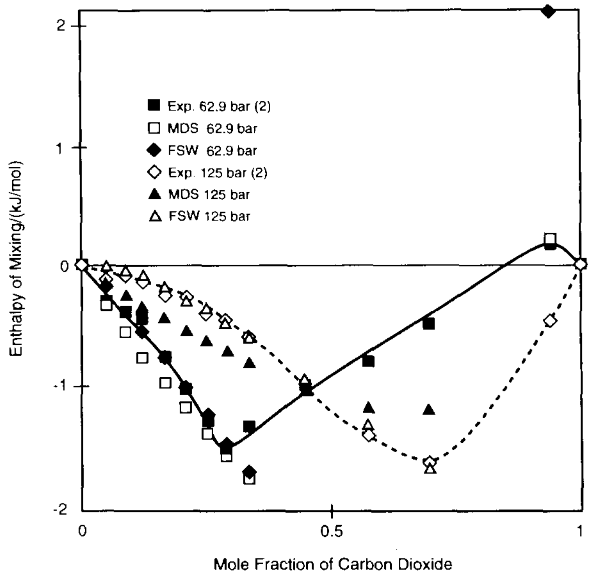

Fig. 7. Enthalpies of mixing for CO_2 and titanium(IV) chloride at 348 K. The solid line connects experimental data at 62.9 bar; the broken line connects experimental data at 125 bar.

negative values in Fig. 6, where the data is small and positive. The FSW EOS shows positive, and then negative H_m^E as the mole fraction of CO_2 increases, but the extrema are excessive.

The mixing results of $TiCl_4$ with CO_2 are given in Fig. 7. Here, calculations from the two EOS are compared with experimental H_m^E at 348 K, at 62.9 and 125 bar. Fig. 7 shows the FSW EOS fits experiment better than the MDS EOS, except at the lowest and highest mole fractions of CO_2. If the one endothermic value is removed from the correlation at the highest mole fraction, the standard deviation improves from 403 J mol^{-1} given in Table 3 for the FSW EOS to 141 J mol^{-1}.

The molecular dynamics simulations [1,4] measured the cross interaction parameter, ε_{12}, by correlation with one or two values near the minimum in H_m^E. When this is done with the EOS interaction parameter, k_{ij}, the change to endothermic values with an increase in pressure occurs at too high a pressure. Some H_m^E values at the high pressure are required together with the low pressure ones to regress the best interaction parameter. Nevertheless, there is some predictive value in the EOS. Parameters are held constant throughout the range of experimental conditions once obtained. Only six densities were used for the correlation of the pure metal chlorides. Yet, the equations were useful in estimating $H_{\mathrm{m}}^{\mathrm{E}}$.

The composition-dependent interaction parameter, used here for the mixtures of the metal chlorides with supercritical CO_2 was helpful in lowering the standard deviations between experimental and calculated $H_{\mathrm{m}}^{\mathrm{E}}$ for the FSW EOS. It is reasonable to expect nearest-neighbor environment to change with concentration, and the concept is reflected here. No improvement was observed in the mixing of CO_2 with neopentane from such a mixing rule, nor for the MDS EOS.

5. Conclusions

It has been shown that EOS can provide useful estimates of excess enthalpies for mixtures even when there is a paucity of enthalpy data for the pure components. Molecular dynamics simulations fit the $H_{\mathrm{m}}^{\mathrm{E}}$ data better than the EOS and use more physically meaningful parameters. The EOS fit the pure component residual enthalpies better than molecular simulations. The usefulness of the EOS can be extended to the mixtures of an inorganic solute with supercritical CO_2.

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