Thermodynamic Study of the N₂O + CO₂ and N₂O + CO₂ + Cyclohexane Systems in the Near-Critical and Supercritical Regions

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Carbon dioxide, CO_2, and nitrous oxide, N_2O, are fluids used in supercritical extraction. Mixtures of N_2O and CO_2 are excellent candidates to be used as supercritical fluids. In this work, excess enthalpies, H_m^E, are reported for the $N_2O + CO_2$ and $N_2O + CO_2$ + cyclohexane systems at 308.15 K and 7.64 MPa. This temperature lies between the N_2O and CO_2 critical temperatures, and the pressure is higher than the N_2O and CO_2 critical pressures. Measurements have been carried out using an isothermal high-pressure flow calorimeter. Results for the $N_2O + CO_2$ system are analyzed simultaneously with excess enthalpy data and excess volume data, V_m^E, taken from the literature, using different equations of state and mixing rules. The magnitude of the heat involved is large because of the proximity of experimental conditions to the mixture's critical locus. Experimental data for the ternary system are analyzed using different equations of state and mixing rules, and several empirical and semiempirical prediction methods are tested.

Introduction

Carbon dioxide, CO_2, is by far the fluid most frequently used in supercritical extraction processes[1]. This compound is cheap, nontoxic, and nonflammable and has relatively low critical temperature and pressure (T_c = 304.2 K, P_c = 7.38 MPa[2]). Nitrous oxide, N_2O, is a molecule very similar to carbon dioxide that has sometimes been used in supercritical extraction. N_2O and CO_2 are isoelectronic, their molecular weights are the same, and their critical constants are similar (for nitrous oxide, T_c = 309.6 K, P_c = 7.24 MPa[2]). This similitude has been considered in the literature; for instance, Cook[3] (1953) chose the $N_2O + CO_2$ system to test theories such as the theory of conformal solutions. However, N_2O has a small dipolar moment of 0.167 D, and several authors such as Chang and Huang,[4] Subra et al.,[5] and Vandana and Teja[6] have reported that N_2O is a better solvent than CO_2 for certain compounds. The explosion risk of mixtures containing N_2O and organic compounds reported by Sievers and Hansen[7] has prevented a widespread use of this fluid. Mixtures of N_2O and CO_2 may be excellent candidates to be used as supercritical fluids. For this reason, the thermodynamic properties of the $N_2O + CO_2$ and $N_2O + CO_2$ + cyclohexane systems are studied in this paper.

Cook[3] measured dew and bubble pressures for five $CO_2 + N_2O$ mixtures at temperatures from 293.15 K up to the critical point of the mixture. The vapor–liquid equilibrium data showed the mixture to be almost ideal, with small positive deviations from Raoult's law and no azeotrope. The $CO_2 + N_2O$ system was also studied extensively by Wormald and Eyears[8] who reported H_m^E and V_m^E at temperatures lower and higher than the critical temperatures of CO_2 and N_2O, respectively, and at pressures up to 12.08 MPa. These authors did not report measurements at temperatures lying between the

pure components' critical temperatures because of experimental problems. More recently, Haase and Tillmann[9] reported heat capacities of this system in the gas–liquid critical region. The measurements were carried out in a closed vessel of fixed volume, and the molar heat capacity, C_m, was derived using the Osborne and Van Dusen relationships.[10] In this work, we present H_m^E data for the $N_2O + CO_2$ system at 308.15 K and 7.64 MPa. This temperature lies between the N_2O and CO_2 critical temperatures, and the pressure is higher than the N_2O and CO_2 critical pressures.

A program is underway at our laboratory to study excess molar enthalpies, H_m^E, of N_2O + hydrocarbon mixtures at near-critical or supercritical conditions. H_m^E for the binary systems formed by N_2O and pentane, hexane, heptane, octane, cyclohexane, and toluene have been already reported[11–17] and compared with data previously obtained for the CO_2 + hydrocarbon systems. The calorimetric study is now extended to $N_2O + CO_2$ + cyclohexane mixtures, and H_m^E data for this system at 308.15 K and 7.64 MPa are also reported.

Experimental Section

The materials employed were N_2O (Air Liquide, 99.5 mol % pure), CO_2 (Air Liquide, 99.98 mol % pure), and cyclohexane (Carlo Erba, RPE-ACS, purity >99.5 mol %), and they were used without further purification.

The measurements were carried out using an isothermal high-pressure flow calorimeter (Hart Scientific model 7501) described by Christensen et al.[18] and the experimental procedure described by Castells et al.[11] The chemicals were pumped into the calorimeter at constant flow rates by two thermostated ISCO pumps (model 260D). Flow rates were selected to cover the entire concentration range with a mole fraction precision greater than ±0.001. The calorimetric cell was located in a thermostated silicon oil bath (±0.001 K). A Peltier cooling device and a pulsed heater kept the cell under isothermal conditions. A back-pressure regulator kept the pressure within ±0.01 MPa. The error of H_m^E measurements was estimated to be ±0.01H_m^E, but at least ±1 J mol⁻¹.

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Table 1. Excess Molar Enthalpy, H_m^E, for $\{xN_2O + (1 - x)CO_2\}$ at 308.15 K and 7.64 MPa

x	$H_m^E/$ J mol^{-1}	x	$H_m^E/$ J mol^{-1}	x	$H_m^E/$ J mol^{-1}	x	$H_m^E/$ J mol^{-1}
0.050	94	0.299	−275	0.584	−760	0.850	−353
0.100	142	0.349	−472	0.599	−764	0.875	−295
0.150	152	0.359	−543	0.649	−702	0.900	−244
0.190	116	0.374	−609	0.674	−655	0.925	−182
0.200	99	0.399	−676	0.724	−597	0.950	−145
0.239	9	0.424	−685	0.749	−526	0.975	−52
0.259	−44	0.449	−760	0.774	−493		
0.273	−103	0.499	−798	0.800	−428		
0.279	−153	0.549	−786	0.825	−377		

The excess enthalpies of the ternary system were measured using the pseudobinary method. Because N_2O and CO_2 are gases at ambient conditions, three syringe pumps were required, and N_2O and CO_2 were mixed dynamically before entering the calorimeter. This mixture was treated as a pure component and pumped into the calorimetric cell where it mixed with the third component, cyclohexane. Three $\{xN_2O + (1 - x)CO_2\}$ mixtures having compositions $x = 0.25$, 0.50, and 0.75 were used. Three complete sets of pseudobinary H_m^E determinations, one for each mixture, were made over the range of cyclohexane mole fraction from 0 to 1.

All runs were made in the steady-state fixed-composition mode. Measurements for the $N_2O + CO_2$ and $N_2O + CO_2$ + cyclohexane systems were carried out at total flow rates of 0.0056 and 0.0083 cm^3 s^{-1}, respectively. The volume flow rates were converted to molar flow rates using the densities and molar masses. For N_2O, the density at the temperature of the pump and 7.64 MPa was interpolated from the pressure−volume isotherms reported by Couch et al.[19] For CO_2, the density was calculated from the equation given in the IUPAC table.[20] The density of cyclohexane was estimated from the densities and isothermal compressibilities reported by Aicart et al.[21−22]

Results

H_m^E data for $N_2O + CO_2$ were determined at 308.15 K and 7.64 MPa over the entire composition range and are given in Table 1. Figure 1 shows a plot of H_m^E versus N_2O mole fraction for $\{xN_2O + (1 - x)CO_2\}$. Mixtures show endothermic mixing in the carbon-dioxide-rich region and exothermic mixing for $x > 0.25$. The heats measured are quite large despite the similarity between the N_2O and CO_2 molecules. H_m^E data for the binary system $N_2O + CO_2$ were fit to a Padé approximant given by

$$H_m^E = x(1 - x) \frac{\sum_{k=0}^{n} A_k(2x - 1)^k}{1 + \sum_{l=1}^{m} B_l(2x - 1)^l} \tag{1}$$

where x is the N_2O mole fraction. As was already discussed in the Experimental Section, the uncertainties in temperature, pressure, and composition are smaller than those in the excess enthalpies, and a least-squares procedure was used to minimize deviations between experimental and calculated excess enthalpies. The binary coefficients, A_k and B_l, are given in Table 2,
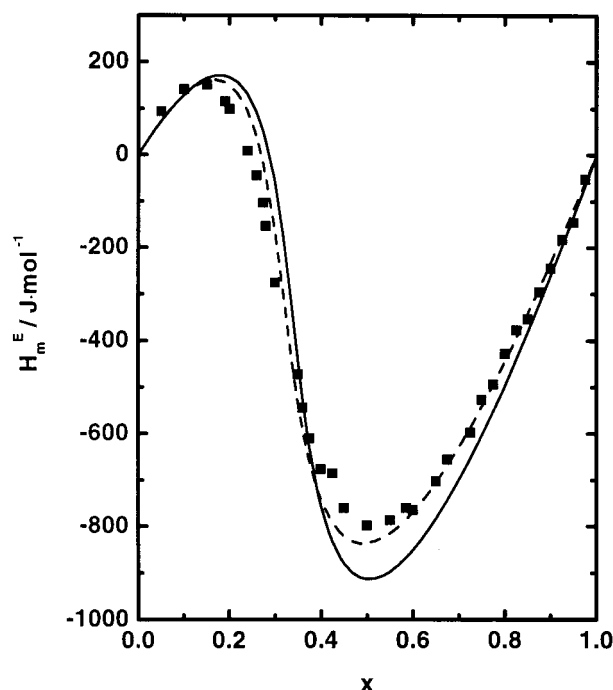
Figure 1. Excess molar enthalpies, H_m^E, of $\{xN_2O + (1 - x)CO_2\}$ at 308.15 K and 7.64 MPa. Key: ■, experimental data; —, calculated using the PR EOS and the classical 1 mixing rule; − − −, calculated using the CSRK EOS and the classical 1 mixing rule.

Table 2. Least-Squares Representation of H_m^E/J mol^{-1} for $N_2O + CO_2$, N_2O + Cyclohexane, and CO_2 + Cyclohexane at 308.15 K and 7.64 MPa: Coefficients of Equation 1, A_k and B_l; Standard Deviation between Experimental and Calculated Excess Enthalpies, σ; and Percent Ratio of the Standard Deviation and the Maximum Absolute Value of H_m^E, $\sigma/|H_{max}^E|$

coefficients	$\{xN_2O + (1 - x)CO_2\}$	$\{xN_2O + (1 - x)\text{cyclohexane}\}$	$\{xN_2O + (1 - x)\text{cyclohexane}\}^a$
A_0	−3237.6	448.43	−5917.8
A_1	−3917.7	−2445.1	−5248.8
A_2	4290.6	333.3	1111.8
A_3	−	275.68	162.24
B_1	1.0470	−0.93226	−0.96995
B_2	0.69943	−	−
B_3	−1.8663	−	−
σ	19	8.3	6.5
$\sigma/|H_{max}^E|$ (%)	2.3	2.0	0.15

[a] H_m^E data were taken at 308.15 K and 7.50 MPa. The effect of the 0.14 MPa pressure increase was taken into account using the Peng−Robinson equation of state, as described in the text.

together with standard deviations between experimental and calculated H_m^E values.

H_m^E data for $N_2O + CO_2$ + cyclohexane were determined at 308.15 K and 7.64 MPa and are given in Table 3. Equation 1 was used to evaluate the excess molar enthalpies of $\{0.25N_2O + 0.75CO_2\}$, $\{0.50N_2O + 0.50CO_2\}$, and $\{0.75N_2O + 0.25CO_2\}$, which were then added to the excess molar enthalpy of the pseudobinary system $[\{xN_2O + (1 - x)CO_2\}$ + cyclohexane], to give the ternary excess enthalpy. If the ternary system is represented as $\{x_1N_2O + x_2\text{cyclohexane} + x_3CO_2\}$, then the three series of H_m^E determinations described in the experimental procedure, are caracterized by x_1/x_3 values of $^1/_3$, 1, and 3, respectively. Figure 2 shows a plot of ternary H_m^E versus cyclohexane mole fraction for the three series of H_m^E values. Mixtures show very exo-

Table 3. Excess Molar Enthalpy, H_m^E, of $\{x_1N_2O + x_2$ cyclohexane $+ x_3CO_2\}$ at 308.15 K and 7.64 MPa for Three N_2O and CO_2 Composition Ratios, x_1/x_3

x_1	x_2	$H_m^E/$ J mol^{-1}	x_1	x_2	$H_m^E/$ J mol^{-1}	x_1	x_2	$H_m^E/$ J mol^{-1}
				$x_1/x_3 = 0.334$				
0.250	0.000	−44	0.196	0.217	−2036	0.098	0.606	−516
0.247	0.011	−1654	0.182	0.271	−1768	0.075	0.701	−285
0.244	0.023	−2255	0.175	0.300	−1609	0.066	0.734	−229
0.241	0.034	−2384	0.170	0.321	−1555	0.050	0.799	−145
0.238	0.046	−2452	0.147	0.412	−1175	0.041	0.837	−84
0.229	0.084	−2482	0.137	0.450	−971	0.031	0.876	−60
0.222	0.112	−2389	0.125	0.502	−844	0.011	0.957	9
0.208	0.169	−2222	0.118	0.529	−705			
0.201	0.195	−2081	0.111	0.557	−677			
				$x_1/x_3 = 0.996$				
0.499	0.000	−809	0.432	0.133	−1762	0.249	0.502	−509
0.494	0.010	−1277	0.411	0.178	−1533	0.230	0.538	−419
0.490	0.016	−1401	0.401	0.195	−1434	0.212	0.577	−337
0.485	0.027	−1618	0.387	0.226	−1326	0.187	0.626	−266
0.482	0.034	−1772	0.373	0.252	−1237	0.165	0.669	−186
0.472	0.053	−1830	0.361	0.280	−1146	0.142	0.714	−114
0.468	0.061	−1818	0.350	0.300	−1109	0.118	0.764	−50
0.463	0.072	−1841	0.330	0.338	−955	0.090	0.821	−31
0.461	0.076	−1829	0.316	0.366	−908	0.062	0.876	3
0.455	0.088	−1849	0.303	0.394	−818	0.047	0.906	3
0.443	0.112	−1802	0.288	0.425	−698	0.032	0.936	12
0.434	0.129	−1766	0.265	0.468	−617	0.025	0.949	7
				$x_1/x_3 = 2.998$				
0.750	0.000	−528	0.561	0.252	−804	0.292	0.610	−32
0.739	0.014	−836	0.525	0.300	−642	0.249	0.669	34
0.735	0.020	−915	0.508	0.323	−617	0.226	0.699	40
0.724	0.035	−1076	0.476	0.366	−478	0.208	0.723	59
0.713	0.049	−1103	0.451	0.398	−388	0.178	0.763	84
0.678	0.096	−1112	0.431	0.425	−360	0.146	0.806	90
0.621	0.173	−1000	0.410	0.453	−273	0.120	0.840	100
0.618	0.176	−989	0.373	0.502	−198	0.066	0.912	68
0.604	0.195	−957	0.342	0.544	−131	0.039	0.948	43
0.576	0.232	−844	0.318	0.576	−101			

thermic mixing except for a few cases in the cyclohexane-rich region.

The numerical treatment of H_m^E data for the ternary system is based on expressing this property as the sum of a binary contribution, $(H_m^E)^{bin}$, and a ternary contribution, $(H_m^E)^{ter}$.

$$H_m^E = (H_m^E)^{bin} + (H_m^E)^{ter} \quad (2)$$

The binary contribution is calculated from the H_m^E values of the three related binary systems. When the ternary contribution is omitted, eq 2 provides a prediction. H_m^E data for $\{xN_2O + (1 − x)$cyclohexane$\}$ at 308.15 K and 7.64 MPa have been already reported and correlated using eq 1 by Cabañas et al.[14] The binary coefficients obtained are given in Table 2. No two-phase region was observed for these mixtures. H_m^E data for $\{xCO_2 + (1 − x)$cyclohexane$\}$ were measured at 308.15 K and 7.5 MPa by Christensen et al.,[23] and a two-phase region was reported for $x > 0.95$. At these conditions of temperature and pressure, the effect on the excess enthalpy of this small increment in pressure is not negligeable. H_m^E data for $\{xCO_2 + (1 − x)$cyclohexane$\}$ at 308.15 K and 7.5 MPa were correlated using the Peng−Robinson equation of state (EOS)[24] and the classical mixing rule with two adjustable binary parameters. Using these parameters, H_m^E data for this system at the same temperature and 7.64 MPa were calculated. The values thus obtained for $\{xCO_2 + (1 − x)$cyclohexane$\}$ were correlated using eq 1, and the binary coefficients obtained are given in Table 2. The
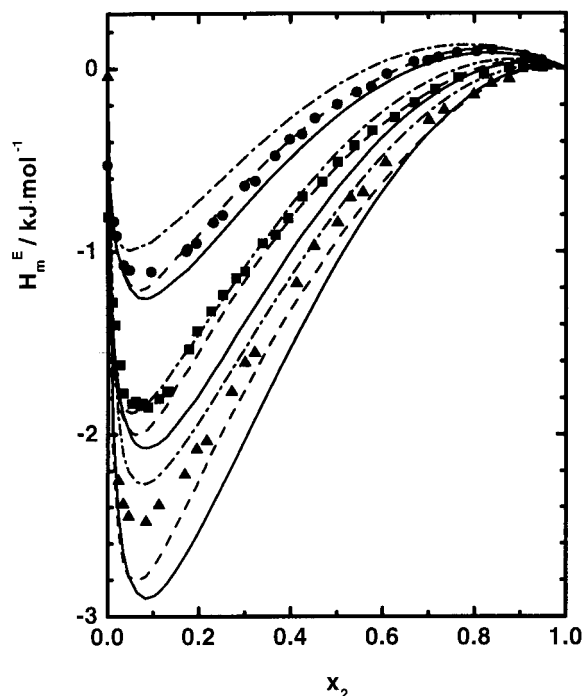
Figure 2. Excess molar enthalpies, H_m^E, of $\{x_1N_2O + x_2$cyclohexane $+ x_3CO_2\}$ versus cyclohexane mole fraction at 308.15 K and 7.64 MPa. Key: ■, $x_1/x_3 = 1$; ●, $x_1/x_3 = 3$; ▲, $x_1/x_3 = 1/3$; —, predicted using the PRSV EOS and the classical 2 mixing rule; − − −, predicted using the PRSV EOS and the Wong−Sandler−NRTL mixing rule; −·−·−, predicted using Kholer's method.

H_m^E mimimum value increases by 11% as a consequence of the pressure increment.

The different empirical methods to estimate the binary contribution $(H_m^E)^{bin}$ to the ternary excess enthalpy have been reviewed by Pando et al.[25] In this work, Kholer's method[26] is used. This is a symmetrical method that gives the same weight to the three related binary systems. The binary contribution to ternary H_m^E is given by

$$(H_m^E)^{bin} = \sum_{i<j} x_i x_j \frac{\sum_{k=0}^{n} A_k \left(\frac{x_i - x_j}{x_i + x_j}\right)^k}{1 + \sum_{l=1}^{m} B_l \left(\frac{x_i - x_j}{x_i + x_j}\right)^l} \quad (3)$$

where A_k and B_l are the coefficients of eq 1 for each of the three binary systems. The ternary contribution of the system was correlated using a differential Padé approximant, DPA, introduced by Pando et al.[25] This approximant is given by

$$\frac{(H_m^E)^{ter}}{x_1 x_2 x_3} =$$
$$\frac{\sum_{k=0}^{n_1} C_k(x_1 - x_3)^k + \sum_{l=1}^{n_2} C_l'(x_2 - x_3)^l + \sum_{k=1}^{n_1}\sum_{l=1}^{n_2} C_{kl}(x_1 - x_3)^k(x_2 - x_3)^l}{1 + \sum_{k=1}^{m_1} D_k(x_1 - x_3)^k + \sum_{l=1}^{m_2} D_l'(x_2 - x_3)^l + \sum_{k=1}^{m_1}\sum_{l=1}^{m_2} D_{kl}(x_1 - x_3)^k(x_2 - x_3)^l} \quad (4)$$

where C_k, C_l', C_{kl}, D_k, D_l' and D_{kl} are the ternary coefficients and n_1, n_2, m_1, and m_2 are the orders of

Table 4. Prediction (Kholer Equation and PRSV EOS) and Correlation (Kholer Equation + Differential Padé Aproximant) of H_m^E for $\{x_1 N_2O + x_2 \text{cyclohexane} + x_3 CO_2$ at 308.15 K and 7.64 MPa: Coefficients of Equation 4; Standard Deviation between Experimental and Calculated Excess Enthalpies, σ (J mol^{-1}); and Percent Ratio of the Standard Deviation and the Maximum Absolute Value of H_m^E, $\sigma\% = 100\ \sigma/|H_{max}^E|$

					PRSV			
					classical 2		Wong−Sandler −NRTL	
	Kholer		Kholer+DPA[a]					
x_1/x_3	σ	$\sigma\%$	σ	$\sigma\%$	σ	$\sigma\%$	σ	$\sigma\%$
$^1/_3$	150	6.0	82	3.3	290	12	200	8.1
1	91	4.9	85	4.6	200	11	110	5.9
3	130	11	27	2.4	71	6.4	33	3.0
total	120	4.8	70	2.8	202	8.1	130	5.2

[a] Coefficients for least-squares representation of $H_m^E/$J mol^{-1} using Kholer's equation for the binary contribution and a (2, 1, 0, 0) approximant for the ternary contribution: $C_0 = -799.94$, $C_1 = -6811.0$, $C_2 = -31127$, $C_1' = -7101.9$, $C_{11} = -1964.6$, and $C_{21} = 124920$

polynomials in numerator and denominator. The approximant can be represented by indicating the values adopted by n_1, n_2, m_1, and m_2 as (n_1, n_2, m_1, m_2). The (2, 1, 0, 0) approximant was found to describe adequately the ternary contribution to $N_2O + CO_2 +$ cyclohexane. Deviations between experimental and calculated excess enthalpies obtained for the three series of H_m^E determinations using Kholer's equation (eq 3) and Kholer's equation plus the (2, 1, 0, 0) approximant are given in Table 4. Values for the coefficients of this approximant are also given in Table 4. Results from H_m^E predictions using Kholer's equation are shown in Figure 2. Predicted values are always less exothermic than experimental values, and relative deviations between both values are higher for ternary mixtures with $x_1/x_3 = 3$. Values for the relative deviations between experimental and correlated H_m^E for the three series of determinations are similar.

The values observed for H_m^E of $N_2O + CO_2$ and $N_2O + CO_2 +$ cyclohexane and their changes with composition can be discussed in terms of the proximity of the experimental conditions to the N_2O and CO_2 critical points and the mixtures' critical loci. To illustrate this, the pressure−temperature projections of the phase diagrams are shown together with the experimental conditions in Figure 3. The $N_2O + CO_2$ critical locus is based on data reported by Cook[3] and Rowlinson et al.[27] The vapor−liquid equilibrium curves of CO_2 and N_2O are based on data from Couch et al.[19] and the IUPAC table,[20] respectively. The $N_2O + CO_2$ critical locus goes continuously from the CO_2 to the N_2O critical points, according to a type I diagram in the classification of Scott and Van Kronynenburg.[28] For $CO_2 +$ cyclohexane, the critical locus was taken from Krichevski and Sorina.[29] The locus for $NO_2 +$ cyclohexane was estimated using the procedure described by Heidemann and Kahlil[30] and the Peng and Robinson equation of state[24] and the classical mixing rule as described in the Equation of State and Mixing Rules section of this paper. No binary parameter was considered as the critical locus close to the experimental (P, T) conditions does not seem to be sensitive to the value of the binary parameter k_{ij}. The $CO_2 +$ cyclohexane and $NO_2 +$ cyclohexane critical loci are also type I. These loci run parallel to each other in the section of the $P-T$ diagram shown in Figure 3, although they exhibit a maximum pressure instead of
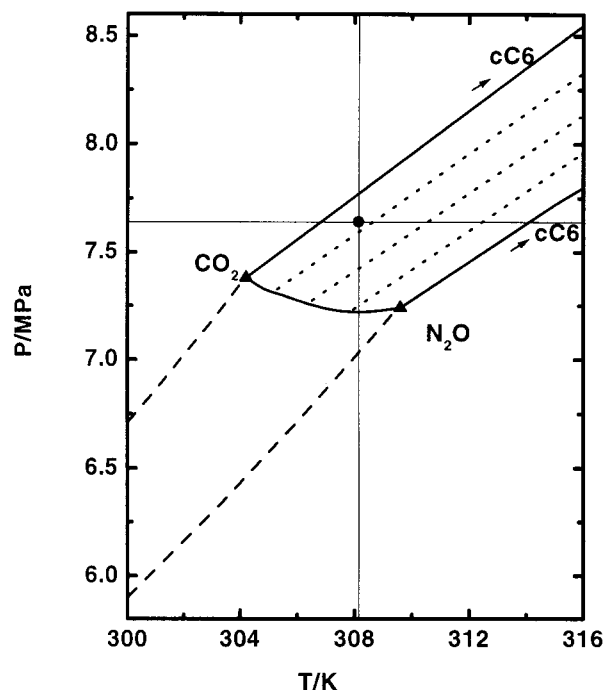
Figure 3. Plot of P against T for $N_2O + CO_2 +$ cyclohexane showing the vapor−liquid equilibrium curves (− − −) and critical points (▲) of carbon dioxide and nitrous oxide, the critical locus (−) for the three related binary mixtures, the critical locus (- - -) of $\{x_1 N_2O + x_2 \text{cyclohexane} + x_3 CO_2\}$ for $x_1/x_3 = 1$, 3, and $^1/_3$, and (T, P) coordinates (●) where experimental measurements were made.

the minimum pressure of the $N_2O + CO_2$ critical locus. The critical mole fraction data for $N_2O + CO_2$[3,27] enable us to locate on the critical locus the mixtures with x_{NO_2}/x_{CO_2} values of $^1/_3$, 1, and 3 and to draw by interpolation the approximate loci for the three pseudobinary mixtures also shown in Figure 3.

As can be readily seen in Figure 3, at 308.15 K and 7.64 MPa, the temperature is between the critical temperatures of CO_2 and N_2O, and the pressure is higher than the critical pressures of both components. Therefore, CO_2 is a supercritical fluid with a density of 284 kg m^{-3}, similar to a gas,[20] while N_2O is a liquid with a much higher density,[19] 710 kg m^{-3}. The $N_2O + CO_2$ mixtures can be supercritical fluid or liquid, depending on the composition. For N_2O mole fractions lower than approximately 0.8, mixtures are supercritical.[3,27] At higher N_2O concentrations, mixtures are liquid. The most exothermic value is observed for a N_2O mole fraction of 0.499. At this composition, H_m^E reaches a mimimum value of -798 J mol^{-1} because of the condensation of the low-density CO_2 in a mixture of higher density, similar to a liquid. The transition between a liquid and a fluid mixture is continuous. The heats measured are quite large, despite the similarity between the N_2O and CO_2 molecules, as a consequence of the great differences in the densities of the pure components and their mixtures at these conditions of temperature and pressure.

A discussion similar to that provided for the $N_2O + CO_2$ system can be followed for the ternary system $N_2O + CO_2 +$ cyclohexane. For this system, the contribution of the binary system $N_2O + CO_2$ to the ternary enthalpy is relatively small, and qualitatively, the behavior of the pseudobinary and ternary systems are essentially the same. Therefore, the ternary system $N_2O + CO_2 +$ cyclohexane can be discussed in terms of the mixtures

formed by $\{0.25N_2O + 0.75CO_2\}$, $\{0.50N_2O + 0.50CO_2\}$, or $\{0.75N_2O + 0.25CO_2\}$ and cyclohexane. As can be seen in Figure 3, at 308.15 K and 7.64 MPa, these three $N_2O + CO_2$ mixtures are supercritical because the temperature and pressure of the measurements are greater than the critical conditions of the mixture. The values of density for these fluid mixtures can be estimated using any EOS and may be low (mixtures with $x_1/x_3 = 1$ and $x_1/x_3 = 1/3$) or intermediate ($x_1/x_3 = 3$). Cyclohexane ($T_c = 553.5$ K, $P_c = 4.10$ MPa[2]) is a liquid, because the temperature of measurements is lower than its critical temperature and the pressure is greater than its critical pressure. As before, depending on the composition, the mixture of the three components can be a supercritical fluid or a liquid. In this case, the fluid region is restricted to a very narrow range at low concentration of cyclohexane, and the density of the mixture is quite large. Based on the behavior of the CO_2 + cyclohexane and N_2O + cyclohexane systems and the position of (P, T) coordinates with respect to the pseudo-binary critical locus, we could expect to cross a two-phase boundary for ternary mixtures with $x_1/x_3 = 1/3$. Given the extremely low values of x_2 (less than 0.04), it is difficult to establish whether two or three experimental points are taken in the two-phase region. The condensation of the low-density binary mixture of N_2O and CO_2 in the cyclohexane liquid is very exothermic. The most exothermic values are observed at $x_1/x_3 = 1/3$, with a maximum close to -2500 J mol^{-1} as a consequence of the lower density of the fluid mixture $N_2O + CO_2$ at this composition. This is in agreement with the values observed for the three binaries related to $N_2O + CO_2$ + cyclohexane. At 308.15 K and 7.64 MPa, both the $N_2O + CO_2$ and N_2O + cyclohexane mixtures show moderately endothermic mixing in the cyclohexane-rich region and exothermic mixing in the nitrous-oxide-rich region, reaching minimum values of -798 and -414 J mol^{-1}, respectively.[14] The CO_2 + cyclohexane mixtures,[23] however, are always very exothermic and exhibit a minimum value for a CO_2 mole fraction value of 0.91. Thus, in the case of $N_2O + CO_2$ + cyclohexane, very exothermic values can be expected for the mixtures with higher values of the CO_2 mole fraction.

Equation of States and Mixing Rules

The experimental results were correlated using different EOSs and mixing rules. The equations used were those proposed by Soave[31] (SRK), Peng and Robinson[24] (PR), Patel and Teja[32,33] (PT), and Kubic,[34] and the modification of the PR equation proposed by Strijek and Vera[35] (PRSV). All of these equations have the repulsive term of the van der Waals EOS. The Carnahan–Starling–van der Waals (CSVdW) and Carnahan–Starling–Redlich–Kwong (CSRK) EOSs that have the hard-sphere repulsive term proposed by Carnahan and Starling[36] were also used. A cubic modification of the chain of rotators EOS (CCOR) proposed by Lin and co-workers[37,38] was also tested. The constants a, b, c, d, and c^R that appear in these equations were calculated using the critical constants and acentric factors taken from Reid et al.[2] according to the expressions given in the original papers.

Mixing rules are required to extend the equations of state to mixtures. The mixing rules used were the one-fluid van der Waals or classical mixing rule and the rule proposed by Wong and Sandler.[39] The classical mixing rule evaluates a constant for the mixture, θ, in terms

of those of pure components and the composition according to the expression

$$\theta = \sum_i \sum_j x_i x_j \theta_{ij} \tag{5}$$

The expression used to evaluate θ_{ij} ($i \neq j$) depends on the meaning of the constant. If the constant has dimensions of energy, then θ_{ij} is given by eq 6, and if the constant has dimensions of volume, then θ_{ij} is given by eq 7.

$$\theta_{ij} = \sqrt{\theta_{ii}\theta_{jj}}(1 - k_{ij}) \tag{6}$$

$$\theta_{ij} = \frac{1}{2}(\theta_{ii} + \theta_{jj})(1 - \delta_{ij}) \tag{7}$$

where $k_{ij} = k_{ji}$ and $\delta_{ij} = \delta_{ji}$ are binary parameters that are optimized to minimize the differences between the experimental and calculated values. In this work, up to two adjustable parameters have been used to describe the constants of the EOS. We will refer to this mixing rule as classical 1 when only one binary parameter in the constant a is considered. We will refer to this mixing rule as classical 2 when two binary parameters in the constants a and b are considered. With the exception of the CCOR EOS, the Wong–Sandler mixing rule was also used for the cubic equations. This mixing rule combines information of an excess Gibbs energy model, G_m^E, with the EOS. The essential assumption is to equate the excess Helmholtz energy calculated using the EOS in the limit of infinite pressure, A_m^E ($P \rightarrow \infty$), and the excess Gibbs energy of any thermodynamic model at low pressure, G_m^E (low P). On the basis of this assumption, it can be easily shown that the constants a and b of the EOS are related through

$$a = b\left[\sum_i x_i \frac{a_i}{b_i}\left(\frac{C_i}{C}\right) + \frac{G_m^E}{C}\right] \tag{8}$$

For the SRK, PR, and PRSV EOSs, $C = C_i$ are numerical constants with values given by eqs 9 and 10, while for the PT and Kubic EOSs, C and C_i ($C \neq C_i$) are functions of b and c and b_i and c_i, respectively, given by eqs 11–13

SRK $\qquad\qquad C = -\ln 2 \tag{9}$

PR and PRSV $\qquad C = \dfrac{\ln(\sqrt{2} - 1)}{\sqrt{2}} \tag{10}$

Kubic $\qquad\qquad C = -\dfrac{b}{b + c} \tag{11}$

PT $\qquad\qquad C = \dfrac{b}{2N} \ln\left|\dfrac{M + b}{Q + b}\right| \tag{12}$

where

$$N = \sqrt{bc + (b + c)^2/4} = \sqrt{b^2 + c^2 + 6bc}/2$$
$$M = (b + c)/2 - N \tag{13}$$
$$Q = M + 2N = (b + c)/2 + N$$

As a second condition, a quadratic dependence of the second virial coefficient of the mixture, $B(T)$, with composition is imposed.

$$B(T) = \left(b - \frac{a}{RT}\right) = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \quad (14)$$

The expression for the virial coefficient cross-term introduces an additional binary parameter k_{ij}.

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right](1 - k_{ij}) \quad (15)$$

Both the Wilson equation[40] and the NRTL model[41] with $\alpha = 0.3$ were used in eq 8 as G_m^E models. The parameters of these models, A_{12} and A_{21}, are usually obtained from vapor−liquid equilibrium data. Because these data are not avalailable for mixtures involving N_2O and hydrocarbons, values for the parameter of the Wong−Sandler mixing rule are obtained by comparing experimental and calculated H_m^E and V_m^E values.

Calculation of the Excess Molar Enthalpies and Excess Molar Volumes

The excess molar enthalpy of a mixture is given by

$$H_m^E = H_m^R(\text{mixture}) - \sum_i x_i H_{m,i}^R \quad (16)$$

where H_m^R is the residual molar enthalpy of the mixture and $H_{m,i}^R$ is that of pure components. The residual molar enthalpy can be calculated using any EOS by

$$H_m^R = RT(z - 1) + \int_\infty^V \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \quad (17)$$

where z is the compressibility factor. This expression is valid both for the pure components and for the mixture. The excess molar volumes are given by an expression similar to eq 16

$$V_m^E = V_m(\text{mixture}) - \sum_i x_i V_{m,i} \quad (18)$$

where $V_m(\text{mixture})$ and $V_{m,i}$ are the molar volumes of the mixture and the pure components, respectively. Values of H_m^E for $N_2O + CO_2 +$ cyclohexane and the three related binary systems at 308.15 K and 7.64 MPa and of H_m^E and V_m^E for $N_2O + CO_2$ at 262.4, 298.8, 312.6, and 324.7 K, and pressures ranging from 3.48 to 12.08 MPa[8] were calculated using the EOS and mixing rules described before. The uncertainties in temperature, pressure, and composition are also smaller than those in the excess volumes, and a least-squares procedure was used to minimize differences between experimental and calculated H_m^E and V_m^E values. The mixing rules' binary parameters were adjusted to give the best fit to experimental values using a Gauss nonlinear method as follows.

$N_2O + CO_2$. The results of the calculation of H_m^E for $N_2O + CO_2$ at 308.15 K and 7.64 MPa are shown in Table 5. Similar results are obtained when the Wilson and NRTL models are used with the Wong−Sandler mixing rule and only those obtained using the NRTL model are given in Table 5. The deviations obtained using a particular mixing rule and the PR, PRSV, SRK, PT, and Kubic EOSs are essentially the same, because of the similar description of the fluid pure properties achieved with any of these EOSs. As for the noncubic EOS, it should be noted that the CSRK EOS is able to

Table 5. Correlation of H_m^E for $N_2O + CO_2$ at 308.15 K and 7.64 MPa Using Different EOSs and Mixing Rules: Values for the Binary Parameters; Standard Deviation between Experimental and Calculated Excess Enthalpies, σ; and Percent Ratio of the Standard Deviation and the Maximum Absolute Value of H_m^E, $\sigma\% = 100\ \sigma/|H_{max}^E|$

EOS	mixing rule	parameters			σ^a	$\sigma\%$
SRK	classical 1	$k_{12} = -0.003\ 376$			89	11
	classical 2	$k_{12} = -0.020\ 71$	$\delta_{12} = -0.024\ 71$		28	3.5
	Wong−Sandler NRTL	$k_{12} = -0.055\ 78$	$A_{12} = 46.800^a$	$A_{21} = 50\ 900^a$	24	3.0
PR	classical 1	$k_{12} = -0.003\ 686$			91	11
	classical 2	$k_{12} = -0.022\ 42$	$\delta_{12} = -0.025\ 74$		29	3.6
	Wong−Sandler NRTL	$k_{12} = -0.039\ 26$	$A_{12} = 49.382^a$	$A_{21} = 59\ 025^a$	22	2.7
PRSV	classical 1	$k_{12} = -0.003\ 382$			90	11
	classical 2	$k_{12} = -0.021\ 72$	$\delta_{12} = -0.025\ 19$		28	3.6
	Wong−Sandler NRTL	$k_{12} = -0.038\ 92$	$A_{12} = 51.354^a$	$A_{21} = 58\ 813^a$	21	2.6
PT	classical 1	$k_{12} = -0.003\ 455$			94	12
	classical 2	$k_{12} = -0.021\ 08$	$\delta_{12} = -0.028\ 48$		28	3.6
	Wong−Sandler NRTL	$k_{12} = -0.035\ 45$	$A_{12} = 80.376^a$	$A_{21} = 56\ 838^a$	21	2.6
Kubic	classical 1	$k_{12} = -0.003\ 668$			100	13
	classical 2	$k_{12} = -0.023\ 96$	$\delta_{12} = -0.065\ 03$		28	3.5
	Wong−Sandler NRTL	$k_{12} = -0.030\ 12$	$A_{12} = 41.094^a$	$A_{21} = 57\ 483^a$	21	2.6
CCOR	classical 1	$k_{12} = 0.000\ 160\ 9$			88	11
	classical 2	$k_{12} = -0.016\ 74$	$\delta_{12} = -0.029\ 53$		40	5.0
CSVdW	classical 1	$k_{12} = 0.000\ 263\ 4$			140	18
	classical 2	$k_{12} = 0.029\ 18$	$\delta_{12} = 0.037\ 65$		68	8.5
CSRK	classical 1	$k_{12} = -0.002\ 868$			50	6.3
	classical 2	$k_{12} = -0.011\ 16$	$\delta_{12} = -0.011\ 18$		31	3.9

^{a} Values are in J mol^{-1}.

describe adequately the excess enthalpies using only one binary parameter (the standard deviation is 50 J mol^{-1}). These results are shown in Figure 1, together with those obtained for the PR EOS and the classical 1 mixing rule. The best results are obtained when the PR, PRSV, SRK, PT, or Kubic EOS is used in conjunction with the Wong−Sandler mixing rule; standard deviations range from 21 to 24 J mol^{-1}.

For the $N_2O + CO_2$ system, the H_m^E and V_m^E values reported by Wormald and Eyears[8] have been correlated simultaneously using the PR, CSVdW, and CSRK EOSs. Results of these correlations are presented in Table 6. The sum of the squares of the relative deviations was taken as the objective function. Results for the PR and CSRK EOSs are similar. Figure 4 shows plots of H_m^E and V_m^E data at 312.5 and 324.7 K as functions of pressure, for a N_2O molar fraction of 0.495, together with correlations obtained using the PR EOS and the classical 2 and Wong−Sandler mixing rules. Correlations can be considered satisfactory given the large temperature (262−325 K) and pressure (3.5−12 MPa) intervals covered by these data. For this system, the prediction of H_m^E at 308.15 K and 7.64 MPa using several EOSs and the binary parameters obtained from the simultaneous correlation of H_m^E and V_m^E data given in Table 6 has been also attempted. Deviations between experimental and calculated H_m^E values obtained from the PR, CSVdW, and CSRK EOSs and the different mixing rules are also given in Table 6. Predictions are poor; the lowest deviations correspond to the PR EOS and the Wong−Sandler−Wilson mixing rule. The best simultaneous description of all of the data is that provided by the PR EOS and the Wong−Sandler−Wilson mixing rule.

Values of H_m^E and V_m^E for the different conditions of temperature and pressure were also predicted using

Table 6. Values for the Binary Parameters and Relative Standard Deviation, $100 \sigma_r$, for the Correlation of the H_m^E and V_m^E Data Reported by Wormald and Eyears[8] for N_2O + CO_2 and Results for the Prediction of H_m^E at 308.15 K and 7.64 MPa Using These Binary Parameters: Standard Deviation between Experimental and Calculated Excess Enthalpies, σ; and Percent Ratio of the Standard Deviation and the Maximum Absolute Value of H_m^E, $\sigma\% = 100 \sigma/|H_{max}^E|$

EOS	mixing rule	parameters	H_m^E and V_m^E correlation $100\sigma_r$	H_m^E prediction σ^a	$\sigma\%$
PR	classical 1	$k_{12} = 0.006973$	73	570	71
	classical 2	$k_{12} = 0.003095$	65	530	66
		$\delta_{12} = -0.004573$			
	Wong−Sandler−Wilson	$k_{12} = -0.0009802$	66	230	29
		$A_{12} = 862.8^a$			
		$A_{21} = -653.4^a$			
CSVdW	classical 1	$k_{12} = 0.004735$	81	300	38
	classical 2	$k_{12} = 0.003566$	81	290	36
		$\delta_{12} = -0.001162$			
CSRK	classical 1	$k_{12} = 0.005782$	76	490	62
	classical 2	$k_{12} = 0.002006$	66	450	57
		$\delta_{12} = -0.004271$			

[a] Values are in J mol^{-1}.
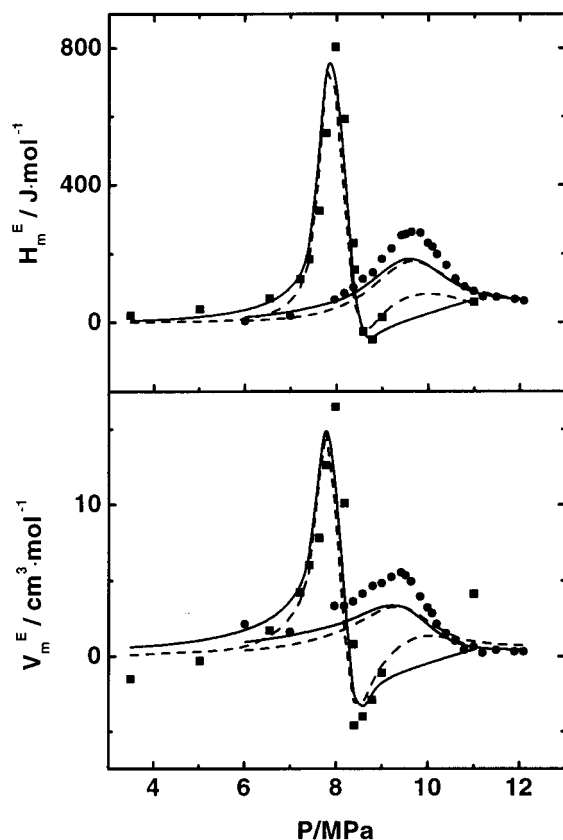
Figure 4. Plot of H_m^E and V_m^E versus pressure for {0.495N_2O + 0.505CO_2}. Key: ■, 312.15 K; ●, 324.7 K;[8] −, correlated using the PR EOS and the classical 2 mixing rule; − − −, correlated using the PR EOS and the Wong−Sandler−Wilson mixing rule.

several EOSs and the binary parameters given in Table 5. As an example, Figure 5 shows plots of H_m^E and V_m^E at 312.5 and 324.7 K as functions of pressure for a N_2O molar fraction of 0.495. Lines arethe results obtained using the PRSV and CSRK EOSs and the classical 1 mixing rule. Differences between experimental and calculated values are considerable, and in some cases, the sign of the predicted excess function is opposite to that of experimental data. From a qualitative point of
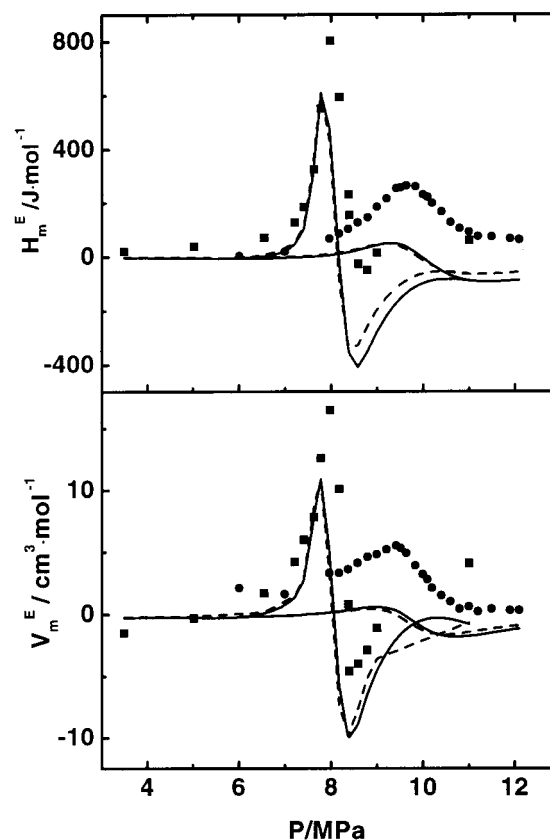
Figure 5. Plot of H_m^E and V_m^E versus pressure for {0.495N_2O + 0.505CO_2}. Key: ■, 312.15 K; ●, 324.7 K;[8] −, predicted using the PR EOS and the classical 1 mixing rule; − − −, predicted using the CSRK EOS and the classical 1 mixing rule.

view, however, the predictions can be considered accurate, and the maxima and minima appear at the right pressure.

N_2O + CO_2 + Cyclohexane. As was already mentioned, the excess enthalpies of the binary systems N_2O + CO_2, N_2O + cyclohexane, and CO_2 + cyclohexane at 308.15 K and 7.64 MPa are available, and these data can be used to predict H_m^E of the ternary system using different EOSs and mixing rules. The mixing rules described in the preceding section do not consider a ternary contribution, and only binary parameters are used. The Wong−Sandler mixing rule has already been used to predict properties of ternary mixtures. Wong and Sandler[39] used the PRSV EOS to predict from binary parameters vapor−liquid equilibrium data for the systems cyclohexane + benzene + H_2O, ethanol + benzene + H_2O, and CO_2 + propane + H_2O. Recently, Ohta[42] (1997) used the PRSV EOS and the Wong−Sandler mixing rule to predict satisfactory H_m^E values for the ternary system ethanol + 2-butanone + benzene from binary H_m^E data.

The SRK, PR, PRSV, and PT EOSs were used to predict H_m^E for the ternary system. These EOSs are those that better describe H_m^E for the three related binary systems. Values for the parameters and deviations obtained in the correlation of H_m^E for N_2O + cyclohexane and CO_2 + cyclohexane are shown in Table 7, while those for N_2O + CO_2 were already given in Table 5. When the Wong−Sandler mixing rule is used, values for the k_{12} parameter are higher than the values obtained for N_2O + CO_2. Similar k_{12} values for this rule were already reported for CO_2 + 1-propanol mixtures

Table 7. Correlation of H_m^E for N₂O + Cyclohexane at 308.15 K and 7.64 MPa and CO₂ + Cyclohexane at 308.15 K and 7.5 MPa Using Several EOSs and Mixing Rules: Values for the Binary Parameters; Standard Deviation between Experimental and Calculated Excess Enthalpies, σ; and Percent Ratio of the Standard Deviation and the maximum absolute value of H_m^E, $\sigma\% = 100\ \sigma/|H_{max}^E|$

EOS	mixing rule	system	parameters			σ^a	$\sigma\%$
SRK	classical 1	N₂O + cyclohexane	$k_{12} = 0.1601$			58	14
		CO₂ + cyclohexane	$k_{12} = 0.1630$			320	7.6
	classical 2	N₂O + cyclohexane	$k_{12} = 0.1282$	$\delta_{12} = -0.02840$		26	6.4
		CO₂ + cyclohexane	$k_{12} = 0.01285$	$\delta_{12} = -0.1511$		110	2.6
PR	classical 1	N₂O + cyclohexane	$k_{12} = 0.1568$			69	17
		CO₂ + cyclohexane	$k_{12} = 0.1558$			350	8.3
	classical 2	N₂O + cyclohexane	$k_{12} = 0.1154$	$\delta_{12} = -0.03712$		20	4.8
		CO₂ + cyclohexane	$k_{12} = -0.01231$	$\delta_{12} = -0.1700$		120	2.8
PRSV	classical 1	N₂O + cyclohexane	$k_{12} = 0.1535$			66	16
		CO₂ + cyclohexane	$k_{12} = 0.1536$			340	8.1
	classical 2	N₂O + cyclohexane	$k_{12} = 0.1157$	$\delta_{12} = -0.03363$		23	5.5
		CO₂ + cyclohexane	$k_{12} = -0.004439$	$\delta_{12} = -0.1588$		110	2.7
	Wong−Sandler−NRTL	N₂O + cyclohexane	$k_{12} = 0.6953$	$A_{12} = 4426^a$		13	3.0
				$A_{21} = 2951^a$			
		CO₂ + cyclohexane	$k_{12} = -0.2506$	$A_{12} = 5088^a$		46	1.1
				$A_{21} = 4388^a$			
PT	classical 1	N₂O + cyclohexane	$k_{12} = 0.1570$			68	16
		CO₂ + cyclohexane	$k_{12} = 0.1595$			340	8.0
	classical 2	N₂O + cyclohexane	$k_{12} = 0.1180$	$\delta_{12} = -0.03815$		21	5.1
		CO₂ + cyclohexane	$k_{12} = 0.007404$	$\delta_{12} = -0.1710$		110	2.6

^{a} Values are in J mol⁻¹.

by Vandana and Teja[43] and for *tert*-amyl alcohol + *tert*-amyl methyl ether by Semar et al.[44] As was already observed for N₂O + CO₂, the deviations obtained using a particular mixing rule and the SRK, PR, PRSV, and PT EOSs are essentially the same, and for the sake of brevity, results for the Wong−Sandler−NRTL mixing rule are shown only for the PRSV EOS. The PRSV EOS used in conjunction with the Wong−Sandler mixing rule provides the best description of H_m^E for N₂O + cyclohexane and CO₂ + cyclohexane. Deviation values are low, and relative deviations are similar to those obtained for N₂O + CO₂. Table 4 and Figure 2 show results of predictions for the three series of ternary H_m^E determinations using the PRSV EOS and the classical 2 and Wong−Sandler mixing rules. As can be observed in Figure 2, the excess enthalpies predicted using the Wong−Sandler mixing rule are more exothermic than the experimental values. These predictions are more accurate than those obtained using the classical mixing rule and of similar accuracy to those obtained using the totally empirical method proposed by Kholer.[25] In this case, however, the number of binary parameters required is much larger. On the other hand, relative deviations obtained using the PRSV EOS and the Wong−Sandler mixing rule for the three series of H_m^E determinations are more similar to each other than those obtained using Kholer's equation.

Conclusions

The excess molar enthalpies H_m^E of N₂O + CO₂ and N₂O + CO₂ + cyclohexane were measured at 308.15 K and 7.64 MPa. H_m^E values for N₂O + CO₂ are moderately positive in the carbon-dioxide-rich region and considerably negative in the nitrous-oxide-rich region. H_m^E values for N₂O + CO₂ + cyclohexane are very exothermic except for a few mixtures in the cyclohexane-rich region. The values observed for H_m^E of N₂O + CO₂ and N₂O + CO₂ + cyclohexane and their changes with composition can be explained in terms of the proximity of the experimental conditions to the N₂O and CO₂ critical points; the densities of N₂O, CO₂, and cyclohex-

ane; and the mixtures' critical loci. The large negative values of H_m^E seem to be a consequence of the nitrous oxide or carbon dioxide change of state from that of a low-density fluid to that of a liquid-mixture component. H_m^E for the ternary mixtures also can be described in terms of the excess entahlpies for the three related binaries.

The SRK, PR, PT, and PRSV equations of state used in conjunction with the Wong−Sandler mixing rule reproduce well the excess enthalpies of N₂O + cyclohexane, CO₂ + cyclohexane, and N₂O + CO₂ at 308.15 K and 7.64 MPa. Ternary excess enthalpies can be predicted using the binary parameters values obtained for three related binaries. These equations of state and this mixing rule are also able to correlate the extensive sets of H_m^E and V_m^E data reported by Wormald and Eyears[8] for N₂O + CO₂. The expressions required to evaluate the numerical constants of the Wong−Sandler mixing rule for several equations of state are provided. The Wong−Sandler mixing rule is shown to have good predictive and correlating capabilities for the SRK, PR, PT, and PRSV equations of state. Similar results are obtained when any of these four equations is used in combination with the Wong−Sandler mixing rule.

The Padé approximant correlations of binary H_m^E data used in conjunction with the empirical method of Kholer provide a good prediction of ternary H_m^E data. An accurate description of these data is obtained by adding a ternary contribution term given by a differential Padé approximant. Padé approximants provide a good modeling of binary and ternary H_m^E data but have the disavantage of not being useful to simultaneously describe V_m^E data.

Acknowledgment

Nomenclature

A = Helmholtz energy
A_{ij} = Wilson and NRTL equations coefficients
A_l = correlation equation coefficient
a = equation of state constant
b = equation of state constant
B_k = correlation equation coefficient
$B(T)$ = second virial coefficient
C_k, C_l, C_{kl} = coefficients in the correlation equation for a ternary term
C = equation of state numerical constant
c, c^R = equation of state constants
D = Debye
D_k, D_l and D_{kl} = coefficients in the correlation equation for a ternary term
d = equation of state constant
G = Gibbs energy
H = enthalpy
J = joule
K = Kelvin
k = binary parameter
N, M, Q = equation of state numerical constants
P = pressure
MPa = 10^6 Pascal
R = gas constant
T = temperature
V = volume
x = mole fraction
z = compressibility factor

Greek Letters

α = parameter in the NRTL equation
θ = equation of state constant
δ = binary parameter
σ = standard deviation

Superscripts

E = excess property
bin = binary
ter = ternary
R = residual

Subscripts

c = critical property
m = molar
i, j = molecular species
max = maximum

Acronyms

CCOR = cubic modification of the chain of rotators
CSVdW = Carnahan−Starling−van der Waals
CSRK = Carnahan−Starling−Redlich−Kwong
EOS = equation of state
NRTL = Non-random-two-liquids
PT = Patel-Teja
PR = Peng−Robinson
PRSV = Peng−Robinson−Stryjek−Vera
SRK = Soave−Redlich−Kwong

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