

Excess molar enthalpies for mixtures of supercritical carbon dioxide and water + ethanol solutions

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Received 1 November 2004; received in revised form 17 March 2005; accepted 23 March 2005

Abstract

Excess molar enthalpies (H_m^E) for mixtures of supercritical CO₂ and ethanol aqueous solutions were measured at 323.15 K and 7.64 and 15.00 MPa using an isothermal high-pressure flow calorimeter. H_m^E values obtained at the lower pressure are very exothermic while those obtained at the higher pressure are moderately endothermic. H_m^E for CO₂ + H₂O mixtures at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa were also measured. These data are examined together with H_m^E data previously reported for mixtures of supercritical CO₂ and ethanol aqueous solutions, vapor–liquid equilibrium data for the ternary system CO₂ + H₂O + ethanol and the excess enthalpy data for the three related binary systems. CO₂–ethanol interactions are shown to be the main contribution to excess enthalpies when supercritical CO₂ and ethanol aqueous solutions are mixed. Ternary excess enthalpies for CO₂ + H₂O + ethanol are also obtained. Kohler's method is used for estimating these ternary data from the excess enthalpy data of the three related binary systems.

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Keywords: Supercritical carbon dioxide; Ethanol; Water; Mixtures; Excess molar enthalpies

1. Introduction

Among several supercritical fluids carbon dioxide is usually promoted as a green solvent. Supercritical fluid extraction of ethanol from the aqueous solutions produced in biochemical processes has several advantages over conventional separation methods; over the years there have been many reports on the separation process using CO₂ and/or the required phase equilibria data for the carbon dioxide + water + ethanol system at elevated pressures [1–9]. Supercritical CO₂ has been also used to extract components from hydroalcoholic mixtures. On the other hand, ethanol aqueous solutions are used as solvents of different substrates in particle design using supercritical CO₂ [10]. Calorimetric data on this kind of systems are very scarce. Depending upon their magnitude, the heat of mixing supercritical carbon dioxide and ethanol aqueous solutions could be an important

factor for the correct design and scale-up of the processes mentioned above. Recently Ochi et al. [11] pointed out the considerable amount of heat evolved when this mixing is carried out under conditions of temperature and pressure close to the CO₂ critical point ($T_c = 304.2$ K, $P_c = 7.38$ MPa). Mixtures of carbon dioxide and ethanol + water at 308.15 K show an increasingly exothermic behavior when the pressure is lowered from 8.5 to 7.5 MPa. For a given pressure, mixtures richer in ethanol are more exothermic. Excess enthalpy (H_m^E) values determined at 308.15 K exhibit minima of -3718 , -1210 and -392 J mol⁻¹ at 7.5, 8.0 and 8.5 MPa, respectively. In this paper, the calorimetric study of the CO₂ + H₂O + ethanol system is extended to other conditions of temperature and pressure: 323.15 K and 7.64 and 15.00 MPa. The ternary excess enthalpy data are interpreted in terms of vapor–liquid equilibrium (VLE) and excess enthalpy data for the three related binary systems. H_m^E data in the temperature and pressure range considered were reported by Ott et al. [12–14] for the H₂O + ethanol mixtures and by Cordray et al. [15] and Hauser et al. [16] for CO₂ + ethanol

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mixtures. H_m^E data for the $\text{CO}_2 + \text{H}_2\text{O}$ mixtures were measured by Wormald et al. [17] in the temperature range 363.4–698.2 K and at pressures up to 20.5 MPa. Excess enthalpy data for the $\text{CO}_2 + \text{H}_2\text{O}$ system in the temperature and pressure range considered (308.15–323.15 K, 7.64–15.00 MPa) are also reported in this paper.

2. Experimental

The materials employed were CO_2 (air liquid 99.98 mol% pure), ethanol absolute (PAI Panreac 99.9 mol%) and bidistilled water. Commercial materials were used without further purification.

The measurements were carried out using an isothermal high-pressure flow calorimeter (Hart Scientific model 7501) first described by Christensen et al. [18] following a procedure previously reported by Castell et al. [19]. The reactants were pumped into the calorimetric cell by two thermostated pumps (ISCO, model 260D) at constant flow rates. Flow rates were selected to cover the entire concentration range with a mole fraction precision greater than ± 0.001 . The calorimetric cell was located into a silicon bath in which temperature was controlled within ± 0.001 K. A Peltier cooling device and a pulsed heater kept the cell under isothermal conditions. A back-pressure regulator situated outside the calorimeter kept the pressure within ± 0.01 MPa. Previous results obtained with the calorimeter were reproducible to $\pm(1 + 0.01 H_m^E)$ J mol^{-1} . Reproducibility of results in the present investigation was ± 1 –2%.

The heat of mixing supercritical carbon dioxide and ethanol aqueous solutions may be measured using the pseudobinary method [20] to determine ternary excess enthalpies. H_2O and ethanol (EtOH) were premixed at constant composition. This mixture was treated as a pure component and pumped into the calorimetric cell. Three $[x \text{ H}_2\text{O} + (1-x) \text{ EtOH}]$ mixtures having compositions $x = 0.250$, 0.500 and 0.750 were used. A second pump was used to introduce CO_2 into the calorimetric cell. At each condition of temperature and pressure, three complete sets of pseudobinary H_m^E determinations were made over the range of CO_2 mole fraction 0–1. If the ternary system is represented as $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$, the three series of H_m^E determinations are characterized by values of $x_2/x_3 = 1/3$, 1, and 3, respectively. From here on, we will refer to the excess enthalpies of supercritical carbon dioxide and ethanol aqueous solutions as pseudobinary H_m^E data for $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$. Pseudobinary H_m^E data can be later converted to ternary data by adding to these three series of determinations the excess molar enthalpies of $[0.250 \text{ H}_2\text{O} + 0.750 \text{ EtOH}]$, $[0.500 \text{ H}_2\text{O} + 0.500 \text{ EtOH}]$, and $[0.750 \text{ H}_2\text{O} + 0.250 \text{ EtOH}]$, respectively.

All runs were made in the steady-state fixed composition mode. Measurements for $\text{CO}_2 + \text{H}_2\text{O}$ and $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ systems were carried out at total volume flow rates of 0.0028 and 0.0056 $\text{cm}^3 \text{ s}^{-1}$. The

volume flow rates were converted to molar flow rates using the densities and molar masses. CO_2 and H_2O densities at the temperature and pressure of the pumps were obtained from NIST [21]. The densities of the mixtures $\text{H}_2\text{O} + \text{ethanol}$ at the three compositions studied were obtained from Ott et al. [22] and Takiguchi et al. [23].

3. Results and discussion

3.1. $\text{CO}_2 + \text{H}_2\text{O}$ mixtures

H_m^E data for the binary system $[\text{CO}_2(x) + \text{H}_2\text{O}(1-x)]$ at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa are given in Table 1. Fig. 1 shows plots of H_m^E versus CO_2 mole fraction for the two conditions of temperature and pressure studied. With the exception of a slightly endothermic mixture at 308.15 K and 7.64 MPa for $x = 0.937$, the $\text{CO}_2 + \text{H}_2\text{O}$ mixtures show moderately exothermic mixing. Excess enthalpies exhibit minima of -231 , and -120 J mol^{-1} at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa, respectively, for mixtures very rich in water. A few data points taken at 308.15 and 323.15 K and other pressures indicate that moderately exothermic mixing may be expected at these temperatures in the pressure range 7.64–15.00 MPa.

The $\text{CO}_2 + \text{H}_2\text{O}$ system shows a wide range of immiscibility [24–26]. For a binary mixture H_m^E varies linearly with composition in the two-phase region where a gaseous and a liquid mixture of fixed composition are in equilibrium for a given temperature and pressure. The vapor and liquid-phase compositions are shown to correspond to the beginning and end of the linear sections. The plots of H_m^E versus CO_2 mole fraction for the $\text{CO}_2 + \text{H}_2\text{O}$ system show that H_m^E varies linearly with composition for most of the composition range at the two conditions of temperature and pressures studied. These linear sections connect the excess molar enthalpy of a liquid phase, mostly H_2O saturated with CO_2 , and the excess molar enthalpy of a vapor phase, mostly CO_2 saturated with H_2O . The composition of these two phases can be determined

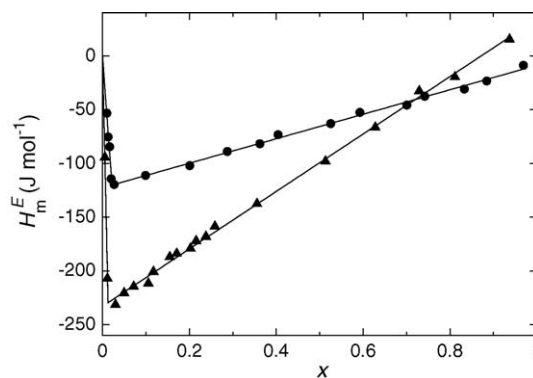


Fig. 1. Excess molar enthalpies, H_m^E , for the binary system $[\text{CO}_2(x) + \text{H}_2\text{O}(1-x)]$ vs. CO_2 mole fraction: (\blacktriangle) 308.15 K and 7.64 MPa; (\bullet) 323.15 K and 15.00 MPa; (—) calculated using Eq. (1) and coefficients given in Table 2.

Table 1

Excess molar enthalpy, H_m^E , for the binary system $[\text{CO}_2(x) + \text{H}_2\text{O}(1-x)]$ at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa

x	H_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)	x	H_m^E (J mol ⁻¹)
308.15 K and 7.64 MPa					
0.006	-94	0.155	-187	0.356	-137
0.011	-207	0.171	-184	0.513	-98
0.030	-231	0.202	-179	0.628	-67
0.050	-220	0.216	-172	0.729	-33
0.072	-215	0.238	-168	0.812	-20
0.105	-212	0.259	-159	0.937	15
0.117	-201				
323.15 K and 15.00 MPa					
0.017	-85	0.201	-102	0.701	-46
0.010	-53	0.288	-89	0.742	-38
0.013	-75	0.362	-82	0.834	-31
0.020	-114	0.404	-73	0.885	-23
0.027	-120	0.525	-63	0.969	-9
0.099	-111	0.593	-53		

from the solubility data of $[\text{CO}_2(x) + \text{H}_2\text{O}(1-x)]$ reported by Wiebe [24]. At 308.15 K and 7.64 MPa, x values of 0.022 and 0.997 are obtained for the liquid and vapor phases, respectively. At 323.15 K and 15.00 MPa, x values of 0.022 and 0.994 are obtained for the liquid phase and vapor phases, respectively. These values are in agreement with those corresponding to the beginning of the linear sections shown in Fig. 1; the end of these sections cannot be established from the plots.

H_m^E data for $[\text{CO}_2(x) + \text{H}_2\text{O}(1-x)]$ were fitted to a (n, m) Pade function given by

$$H_m^E = x(1-x) \frac{\sum_{i=0}^n A_i (2x-1)^i}{1 + \sum_{j=1}^m B_j (2x-1)^j} \quad (1)$$

where A_i and B_j are adjustable coefficients. A least-square procedure was used to minimize deviations between experimental and calculated excess enthalpies. At each condition of temperature and pressure two different sets of coefficients have been used to represent data in the two-phase and one-phase region, respectively. In the linear sections, a $(1, 2)$ Pade function with fixed values for the denominator coefficients, $B_1 = 0$ and $B_2 = -1$, may be used in order to keep the weight factor $x(1-x)$. This results in a first-degree polynomial in the composition variable; the slope is $A_1/2$ and the zero intercept is $(A_0 - A_1)/4$. The H_m^E representation using Eq. (1) is shown in Fig. 1. Table 2 lists values for the coefficients A_i and B_j and the standard deviation between experimental and calculated H_m^E values.

3.2. $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ mixtures

Pseudobinary H_m^E data for $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$ at 323.15 K and 7.64 and 15.00 MPa are given in Tables 3 and 4. Figs. 2 and 3 show plots of H_m^E versus CO_2 mole fraction for these mixtures. Excess enthalpies at 323.15 K and 7.64 MPa are considerably exothermic for ethanol-rich mixtures ($x_2/x_3 = 1/3$) and become less exothermic when the amount of ethanol decreases. Excess

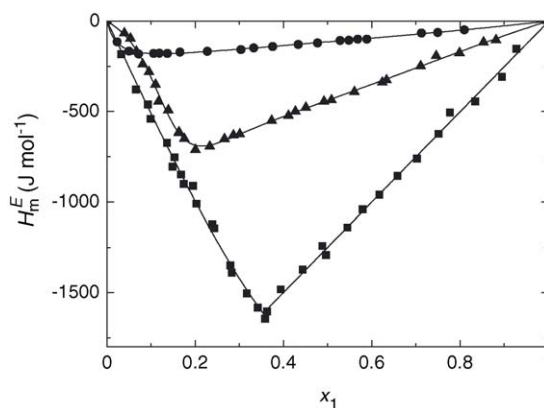


Fig. 2. Excess molar enthalpies, H_m^E , of $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$ at 323.15 K and 7.64 MPa vs. CO_2 mole fraction for three H_2O and EtOH composition ratios: (■) $x_2/x_3 = 1/3$; (▲) $x_2/x_3 = 1$; (●) $x_2/x_3 = 3$; (—) calculated using Eq. (1) and coefficients given in Table 5.

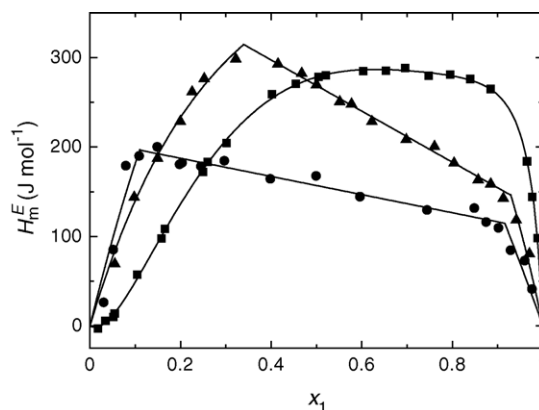


Fig. 3. Excess molar enthalpies, H_m^E , of $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$ at 323.15 K and 15.00 MPa vs. CO_2 mole fraction for three H_2O and EtOH composition ratios: (■) $x_2/x_3 = 1/3$; (▲) $x_2/x_3 = 1$; (●) $x_2/x_3 = 3$; (—) calculated using Eq. (1) and coefficients given in Table 5.

Table 2

Coefficients A_i and B_j and standard deviation, σ , for least-squares representation of H_m^E (J mol⁻¹) for [CO₂ (x) + H₂O (1 - x)] at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa

Interval	308.15 K and 7.64 MPa		323.15 K and 15.00 MPa	
	$0 \leq x \leq 0.022$	$0.022 \leq x \leq 0.997$	$0 \leq x \leq 0.022$	$0.022 \leq x \leq 0.994$
A_0	18190	-397.48	-5613.3	-262.67
A_1	-	534.33	-	227.72
B_1	-	0	-	0
B_2	-	-1	-	-1
σ	5	4	4	2

enthalpies at 323.15 K and 15.00 MPa are moderately endothermic with the exception of a slightly exothermic mixture ($x_1=0.017$, $x_2=0.246$, $x_3=0.737$), which is the mixture richest in ethanol.

Lim et al. [9] reported phase equilibria for CO₂ + H₂O + EtOH and CO₂ + EtOH at 323.15 K and pressures up to 18.50 MPa. Fig. 4 shows data obtained at pressures (9.05 and 11.80 MPa) close to those used in this study, together with composition lines for the three series of H_m^E determinations carried out at 7.64 and 15.00 MPa. A plait point exists at 323.15 K and 11.80 MPa. At 9.05 MPa, the plait point disappears; an indication of VLE in the binary system CO₂ + EtOH for mixtures in the CO₂ mole fraction range (0.750–0.963). The same happens at 7.64 MPa.

The beginning of the two-phase region for CO₂ + EtOH at 323.15 K and 7.64 and 9.05 MPa and phase equilibria for CO₂ + H₂O + EtOH inferred from calorimetric data at 323.15 K and 7.64 and 15.00 MPa are also indicated in Fig. 4. It may be observed in the H_m^E versus x_1 plots of Figs. 2 and 3 a change in the curvature within the two-phase region of the ternary mixtures. When the tie-lines and the composition lines of the three series of H_m^E determinations are coincident or almost coincident, H_m^E varies linearly with x_1 in the two-phase regions and it is possible to obtain from calorimetric data the composition coordinates of a gaseous and a liquid mixture, not necessarily in equilibrium, but belonging to the binodal curve. In the case of CO₂ + H₂O + EtOH tie-lines and composition lines are almost coincident for

Table 3

Excess molar enthalpy, H_m^E , of [CO₂(x_1) + {H₂O(x_2) + EtOH(x_3)}] at 323.15 K and 7.64 MPa for three H₂O and EtOH composition ratios, x_2/x_3

x_1	x_3	H_m^E (J mol ⁻¹)	x_1	x_3	H_m^E (J mol ⁻¹)	x_1	x_3	H_m^E (J mol ⁻¹)
$x_2/x_3 = 1/3$								
0.033	0.725	-184	0.238	0.572	-1122	0.496	0.378	-1293
0.065	0.701	-379	0.243	0.568	-1144	0.544	0.342	-1140
0.092	0.681	-461	0.280	0.540	-1349	0.579	0.316	-1041
0.099	0.676	-541	0.282	0.539	-1389	0.617	0.287	-961
0.136	0.648	-674	0.317	0.512	-1504	0.658	0.257	-856
0.149	0.638	-805	0.342	0.494	-1582	0.703	0.223	-761
0.153	0.635	-754	0.358	0.482	-1645	0.751	0.187	-624
0.168	0.624	-849	0.362	0.479	-1604	0.777	0.167	-506
0.173	0.620	-901	0.394	0.455	-1482	0.834	0.125	-444
0.195	0.604	-912	0.443	0.418	-1373	0.895	0.079	-308
0.203	0.598	-1010	0.488	0.384	-1242	0.928	0.054	-154
$x_2/x_3 = 1$								
0.040	0.480	-67	0.175	0.413	-650	0.492	0.254	-444
0.053	0.474	-96	0.201	0.400	-711	0.509	0.246	-437
0.067	0.467	-167	0.233	0.384	-694	0.560	0.220	-392
0.081	0.460	-239	0.266	0.367	-651	0.624	0.188	-339
0.095	0.453	-281	0.287	0.357	-631	0.633	0.184	-326
0.110	0.445	-351	0.301	0.350	-625	0.711	0.145	-248
0.117	0.442	-445	0.373	0.314	-551	0.746	0.127	-192
0.139	0.431	-493	0.411	0.295	-524	0.798	0.101	-176
0.163	0.419	-613	0.427	0.287	-500	0.853	0.074	-117
0.163	0.419	-619	0.451	0.275	-478	0.881	0.060	-104
$x_2/x_3 = 3$								
0.023	0.244	-114	0.227	0.193	-167	0.548	0.113	-106
0.050	0.238	-166	0.303	0.174	-158	0.568	0.108	-99
0.071	0.232	-182	0.332	0.167	-148	0.589	0.103	-100
0.106	0.224	-179	0.375	0.156	-142	0.712	0.072	-66
0.119	0.220	-178	0.433	0.142	-130	0.749	0.063	-63
0.137	0.216	-179	0.477	0.131	-122	0.809	0.048	-48
0.166	0.209	-171	0.528	0.118	-107	-	-	-

Table 4

Excess molar enthalpy, H_m^E , of $[\text{CO}_2(x_1) + \{\text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)\}]$ at 323.15 K and 15.00 MPa for three H_2O and EtOH composition ratios, x_2/x_3

x_1	x_3	H_m^E (J mol ⁻¹)	x_1	x_3	H_m^E (J mol ⁻¹)	x_1	x_3	H_m^E (J mol ⁻¹)
$x_2/x_3 = 1/3$								
0.017	0.737	-3	0.347	0.490	241	0.796	0.153	281
0.034	0.725	6	0.402	0.449	259	0.840	0.120	276
0.052	0.711	10	0.454	0.410	271	0.885	0.086	265
0.054	0.710	14	0.505	0.371	279	0.908	0.069	237
0.104	0.672	57	0.521	0.359	280	0.930	0.053	224
0.158	0.632	98	0.603	0.298	285	0.953	0.035	185
0.165	0.626	108	0.653	0.260	285	0.965	0.026	184
0.249	0.563	172	0.696	0.228	288	0.977	0.017	144
0.260	0.555	184	0.747	0.190	280	0.988	0.009	98
0.302	0.524	204						
$x_2/x_3 = 1$								
0.055	0.473	69	0.415	0.293	293	0.761	0.120	201
0.098	0.451	144	0.467	0.267	282	0.804	0.098	182
0.149	0.426	187	0.500	0.250	270	0.857	0.072	163
0.200	0.400	229	0.551	0.225	251	0.885	0.058	159
0.226	0.387	262	0.578	0.211	248	0.913	0.044	142
0.252	0.374	277	0.623	0.189	228	0.941	0.030	119
0.322	0.339	298	0.698	0.151	208	0.970	0.015	81
$x_2/x_3 = 3$								
0.030	0.243	26	0.245	0.189	179	0.848	0.038	132
0.051	0.237	85	0.296	0.176	185	0.875	0.031	116
0.079	0.230	179	0.398	0.151	164	0.902	0.025	110
0.109	0.223	190	0.499	0.125	168	0.928	0.018	85
0.149	0.213	200	0.596	0.101	144	0.960	0.010	73
0.198	0.201	181	0.744	0.064	130	0.976	0.006	41
0.203	0.199	183						

mixtures poor in CO_2 and the composition of the liquid mixture may be obtained. At very high CO_2 concentrations, however, the slope of the tie lines changes very fast and it is difficult to estimate the composition of the CO_2 -rich gaseous mixture. Only the points corresponding to CO_2 -poor liquid mixtures are shown in Fig. 4. There is a good agreement between phase equilibria previously reported at 323.15 K and 9.05 and 11.80 MPa and phase equilibria inferred from calorimetric data at 323.15 K and 7.64 and 15.00 MPa; the point for $x_2/x_3 = 1/3$ and 7.64 MPa indicates the inflection

in the binodal curve due to the existence of VLE in the $\text{CO}_2 + \text{EtOH}$ system.

Pseudobinary H_m^E data for each of the three series of determinations were fitted to a (n, m) Pade function given by Eq. (1) where x is CO_2 mole fraction. In some cases the experimental data for the entire CO_2 mole fraction range are described using a single set of coefficients in Eq. (1). If necessary, two different sets of coefficients have been used to represent the two-phase and one-phase regions, respectively. For linear sections, a $(1, 2)$ Pade function with fixed values for

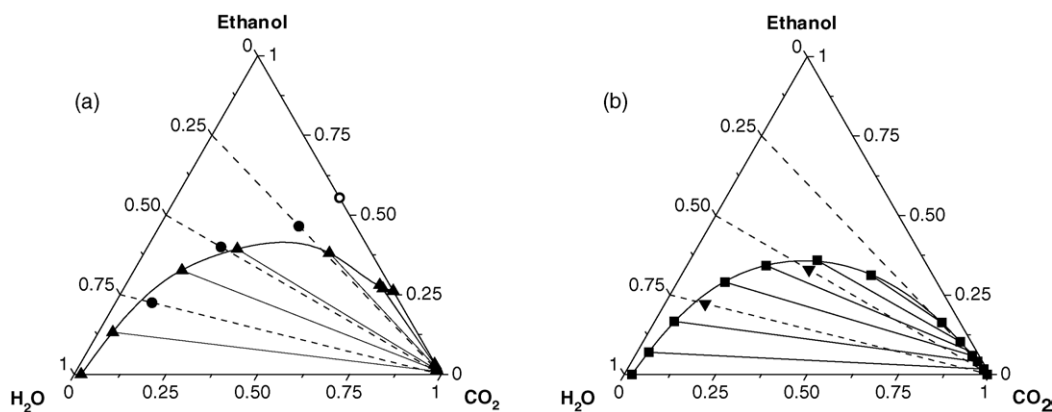


Fig. 4. Phase equilibria and path of the three series of H_m^E determinations (---) for the $[\text{CO}_2(x_1) + \text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)]$ system at 323.15 K. (a) (●) 7.64 MPa, this paper; (○) 7.64 MPa [7]; (▲) 9.05 MPa [7]. (b) (■) 11.80 MPa [7]; (▼) 15.00 MPa, this paper.

Table 5

Coefficients A_i and B_j and standard deviation, σ , for least-squares representation of H_m^E (J mol⁻¹) for [CO₂(x_1) + {H₂O(x_2) + EtOH(x_3)}] at 323.15 K for three H₂O and EtOH composition ratios, x_2/x_3

x_2/x_3	(n, m)	Interval	A_0	A_1	A_2	A_3	B_1	B_2	σ
<i>P</i> = 7.64 MPa									
1/3	(1, 0)	$0 \leq x_1 \leq 0.354$	-7853.0	-2705.1	-	-	-	-	34
	(1, 2)	$0.354 \leq x_1 \leq 1$	-4997.5	4986.7	-	-	0	-1	30
1	(3, 2)	$0 \leq x_1 \leq 1$	-1754.2	-2580.9	-346.27	775.08	2.4758	1.6704	15
3	(2, 1)	$0 \leq x_1 \leq 1$	-459.44	-28.158	-58.822	-	0.95285	-	4
<i>P</i> = 15.00 MPa									
1/3	(3, 2)	$0 \leq x_1 \leq 1$	1112.8	102.75	-521.00	618.26	-0.17897	-0.69761	3
1	(2, 0)	$0 \leq x_1 \leq 0.339$	1457.9	366.22	611.04	-	-	-	11
		$0.929 \leq x_1 \leq 1$	-	-	-	-	-	-	-
	(1, 2)	$0.339 \leq x_1 \leq 0.929$	1075.2	-571.37	-	-	0	-1	7
3	(1, 0)	$0 \leq x_1 \leq 0.110$	1758.6	-326.24	-	-	-	-	20
		$0.916 \leq x_1 \leq 1$	-	-	-	-	-	-	-
	(1, 2)	$0.110 \leq x_1 \leq 0.916$	628.55	-203.48	-	-	0	-1	7

the denominator coefficients, $B_1 = 0$ and $B_2 = -1$, was used. The H_m^E representation using Eq. (1) is shown in Figs. 2 and 3. Table 5 lists values for the coefficients A_i and B_j and the standard deviation between experimental and calculated H_m^E values.

Values of pseudobinary H_m^E data for the three series of determinations at 323.15 K and 7.64 MPa are intermediate between those reported by Ochi et al. [11] at 308.15 K for analogous series of determinations at 7.5 and 8.0 MPa. When the pressure is raised to 15.00 MPa, the mixing of supercritical CO₂ and ethanol aqueous solutions becomes endothermic. Very exothermic mixing may be avoided at both temperatures by raising the pressure of the experiments. To a good approximation the heat evolved when supercritical CO₂ and ethanol aqueous solutions are mixed at constant temperature and pressure is the sum of two binary contributions: H_m^E for CO₂ + H₂O and H_m^E for CO₂ + EtOH. As shown earlier in this paper, CO₂ + H₂O mixtures at 308.15 and 323.15 K and pressures from 7.64 to 15.00 MPa exhibit moderately exothermic mixing; H_m^E values do not change much with pressure. However, CO₂ + ethanol mixtures at 308.15 K change from very exothermic mixing at 7.50 MPa to partially exothermic and partially endothermic mixing at 10.00 and 12.5 MPa [15,16]. At 325.15 K, CO₂ + ethanol mixtures change from very exothermic mixing for most of CO₂ mole fraction at 5.00, 7.50 and 10.00 MPa to moderately exothermic mixing at 12.5 MPa [15]. Thus, the variation of H_m^E for CO₂ + ethanol with temperature and pressure follows the same trends as that of H_m^E for [CO₂(x_1) + {H₂O(x_2) + EtOH(x_3)}]. CO₂-ethanol interactions substantially change with pressure and represent the main contribution to excess enthalpies when supercritical CO₂ and ethanol solutions are mixed.

Ternary excess enthalpies for [CO₂(x_1) + H₂O(x_2) + EtOH(x_3)], $H_m^E(x_1)^{ter}$, may be obtained from the pseudobinary excess enthalpies $H_m^E(x_1)^{pseu}$ reported in Tables 3 and 4 by adding the corresponding enthalpy for the [x H₂O + (1 - x)

EtOH] mixtures, $H_m^E(x)^{bin}$:

$$H_m^E(x_1)^{ter} = (1 - x_1)H_m^E(x)^{bin} + H_m^E(x_1)^{pseu} \quad (2)$$

where $x = 0.250, 0.500$ and 0.750 . Ott et al. [12–14] have reported excess enthalpies for H₂O + EtOH at several temperatures and pressures in the 298.15–473.15 K and 0.40–15.00 MPa intervals. Mixtures at 298.15 and 323.15 K show exothermic mixing; at a given temperature, $H_m^E(x)$ varies slightly with pressure. Values of -387, -146 and -76 J mol⁻¹ are obtained for $H_m^E(0.750)^{bin}$, $H_m^E(0.500)^{bin}$, $H_m^E(0.250)^{bin}$, respectively, at 323.15 K and 15.00 MPa.

Due to the time and effort required to obtain a meaningful set of ternary excess enthalpy data, there has been considerable interest in developing reliable equations for estimating ternary data from the excess enthalpy data of the three related binary systems. Equations of state, group contribution methods and empirical equations may be used to this end. The first two methods have limited applicability in the case of phase-splitting mixtures. For this reason, the empirical method proposed by Kohler [27] was used to calculate ternary excess enthalpies for [CO₂(x_1) + H₂O(x_2) + EtOH(x_3)] at 323.15 K and 7.64 and 15.00 MPa from the H_m^E values of the three related binary systems. This is a symmetrical method that gives the same weight to the three related binary systems. The ternary H_m^E is given by,

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

where A_k and B_l are the coefficients of Eq. (1) for the three binary systems. Values for these coefficients are given in Table 6. Binary H_m^E data fitted using Eq. (1) were as follows: H_m^E data of CO₂ + H₂O are reported in this work at 323.15 K and 15.00 MPa; excess enthalpies for this system do not change much with pressure and these binary data were

Table 6

Correlation of binary H_m^E data at 323.15 K related to the ternary system $[\text{CO}_2(x_1) + \text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)]$ using Eq. (1): coefficients A_i and B_j and standard deviation between experimental and calculated excess enthalpies, σ (J mol^{-1})

	$\text{CO}_2 + \text{H}_2\text{O}$ 7.64 and 15.00 MPa	$\text{H}_2\text{O} + \text{EtOH}$ 7.64 and 15.00 MPa	$\text{CO}_2 + \text{EtOH}$ 7.64 MPa	$\text{CO}_2 + \text{EtOH}$ 15.00 MPa
(m, n)	(1, 2)	(3, 2)	(3, 3)	(3, 2)
A_0	-262.71	-584.13	-8538.6	426.89
A_1	227.79	-1444.5	-2878.7	1396.6
A_2	-	-2351.4	-28682	-2161.0
A_3	-	-1299.7	49439	3986.9
B_1	0	0.28992	1.5248	-1.5511
B_2	-1	-0.59188	5.8301	2.3422
B_3	-	-	-8.1448	-
σ	2	5	30	1.5

used to estimate ternary enthalpies at 7.64 and 15.00 MPa. H_m^E data of $\text{H}_2\text{O} + \text{EtOH}$ were taken from Ott et al. [13] as described earlier in this paper. H_m^E data of $\text{CO}_2 + \text{EtOH}$ have been measured by Cordray et al. [15] at 325.15 K at 7.5, 10.0 and 12.50 MPa. The small difference in temperature was ignored. Excess enthalpies for this system change considerably with pressure. The Peng–Robinson equation of state [28] together with the Wong–Sandler mixing rule [29] and the non-random two liquid model (NRTL) for the excess Gibbs energy [30] were used to describe this pressure effect. The interaction parameters obtained from the simultaneous fit of H_m^E at 325.15 K and 10.0 and 12.5 MPa ($k_{12} = 0.4363$, $A_{12} = 7176 \text{ J mol}^{-1}$ and $A_{21} = -53.18 \text{ J mol}^{-1}$) were used to calculate H_m^E at 323.15 K at 15.00 MPa.

Values for the standard deviations, σ , between experimental ternary excess enthalpies and those predicted using Kohler's method for the three series of determinations are given in Table 7. These values are of similar magnitude for the two pressures studied and should be compared to ternary H_m^E values. To this end, values for the percent ratio of σ and the maximum absolute value of H_m^E , $\sigma\% = 100\sigma/|H_m^E|_{\max}$, are also included in Table 7. Predictions of the very exothermic values obtained at the lower pressure are much more accurate than those of the smaller enthalpies obtained at the higher pressure. The same may be said for the H_m^E versus x_1 plots for the three series of determinations. These poor predictions at 323.15 K and 15.00 MPa stress out the importance of measurements in the ternary system.

Table 7

Prediction of H_m^E for $[\text{CO}_2(x_1) + \text{H}_2\text{O}(x_2) + \text{EtOH}(x_3)]$ at 323.15 K and 7.64 and 15.00 MPa using Kohler's method for three H_2O and EtOH composition ratios, x_2/x_3 : standard deviation between experimental and calculated excess enthalpies, σ , and percent ratio of σ and the maximum absolute value of H_m^E , $\sigma\% = 100\sigma/|H_m^E|_{\max}$

	7.64 MPa			15.00 MPa		
x_2/x_3	1/3	1	3	1/3	1	3
σ (J mol^{-1})	90	195	100	140	155	120
$\sigma\%$	5	24	19	52	75	31

4. Conclusions

Excess enthalpies for mixtures of supercritical CO_2 and ethanol aqueous solutions were measured at 323.15 K and 7.64 and 15.00 MPa. H_m^E values obtained at the lower pressure are very exothermic while those obtained at the higher pressure are moderately endothermic. These data are examined together with data previously reported at 308.15 K and 7.5, 8.0 and 8.5 MPa taking into account VLE data for the ternary system $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ and the excess enthalpy data for the three related binary systems. Excess enthalpies for $\text{CO}_2 + \text{H}_2\text{O}$ were only available at higher temperatures. For this reason, H_m^E for this system at 308.15 K and 7.64 MPa and 323.15 K and 15.00 MPa were also measured. Moderately exothermic enthalpies are obtained in both cases. The $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ and $\text{CO}_2 + \text{H}_2\text{O}$ systems present immiscibility at the temperature and pressure conditions of this study. The vapor and liquid compositions obtained from calorimetric data are found to be in agreement with previously reported VLE data.

CO_2 -ethanol interactions are shown to be the main contribution to excess enthalpies when supercritical CO_2 and ethanol solutions are mixed. Very exothermic mixing at 308.15 or 323.15 K may be avoided by raising the pressure of the experiments.

Ternary excess enthalpies for $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ are obtained from the pseudobinary excess enthalpies of $\text{CO}_2 + \text{ethanol}$ solutions by adding the term corresponding to $\text{H}_2\text{O} + \text{ethanol}$ mixing. An empirical method for estimating ternary data from the excess enthalpy data of the three related binary systems is used to predict ternary excess enthalpies for $\text{CO}_2 + \text{H}_2\text{O} + \text{ethanol}$ at 323.15 K and 7.64 and 15.00 MPa. Predictions at the lower pressure are satisfactory but those at the higher pressure are poor. These results point out the importance of measurements in the ternary system.

Acknowledgements

We gratefully acknowledge the financial support of the Spanish Ministry of Science and Technology (MCyT) and

the Universidad Complutense de Madrid (UCM), research projects PPQ2003-04143-C02-02 and PR3/04-12375. A.C. thanks MCyT for its support through a “Ramón y Cajal” contract. E.P.V. thanks UCM for financial support through a FPI predoctoral grant. Y.S.V. thanks MCyT for financial support through a FPI predoctoral grant.

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