

The excess molar volumes of (an alkanol + a branched chain ether) at the temperature 298.15 K and the application of the ERAS model

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Abstract

The excess molar volumes V_m^E $\{x(\text{CH}_3\text{OH}$ or $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3(\text{CH}_2)_2\text{OH}$ or $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + (1 - x)\{\text{CH}_3(\text{CH}_2)_2\}_2\text{O}$ or $\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3$ or $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3\}$ have been calculated from measured values of density over the whole composition range at the temperature 298.15 K in order to investigate OH \cdots O specific interactions. The results are explained in terms of the strong self-association of the alkanols, the specific interaction between the alkanol, and the ether molecules and packing effects upon mixing. The experimental V_m^E results presented here, together with the previously reported data for the molar excess enthalpy H_m^E , has been used to test the Extended Real Associated Solution (ERAS) model. © 1997 Elsevier Science B.V.

Keywords: Excess volume; Alkanol; Ether; Binary mixtures; Molecular interactions; Association; ERAS theory

1. Introduction

In recent publications [1,2], we presented H_m^E properties for (an alkanol + an ether) mixtures and the results were explained in terms of the existence of specific interaction between the polar alkanol and the aprotic aliphatic ether. It was suggested that the degree of interaction depended on the hydrogen bonding propensity (proton donor capability) of the alkanol, and the electron acceptor capability of the ether. In continuation of these studies we have determined the V_m^E for $\{x(\text{CH}_3\text{OH}$ or $\text{CH}_3\text{CH}_2\text{OH}$ or $\text{CH}_3(\text{CH}_2)_2\text{OH}$ or $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + (1 - x) \{\text{CH}_3(\text{CH}_2)_2\}_2\text{O}$ (IPE) or $\text{CH}_3\text{C}(\text{CH}_3)_2\text{OCH}_3$ (MTBE) or $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{OCH}_3$ (TAME)}.

Alcohols are known to be self-associated through hydrogen-bonded linear chains to variable degrees of polymerization [3–7]. The degree and strength of polymerization decrease with increasing hydrocarbon chain length and also with position of the hydroxyl group in the molecule. Binary

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solutions of alkanols with nonpolar solvents generally break the three-dimensional hydrogen-bonded network of pure alkanols and give positive excess molar volumes in mixtures [8]. Treszczanowicz and Benson [9] determined the V_m^E at 298.15 K for (methanol or ethanol or *n*-propanol + heptane), and found that the excess volume is positive over the whole mole fraction range. Similar results were observed by Zielkiewicz [10] for mixtures of (propan-2-ol + heptane) at 333.15 K. These results were attributed to the dissociation of the hydrogen bonds in the alkanol molecule.

Formally, ethers can be classified as homomorphic products obtained by replacing a $-\text{CH}_2$ group in *n*-alkanes by an oxygen (O) atom. The branched chain monoethers are aprotic, possess dipole moments, but are considered essentially to be nonpolar molecules [11]. Interactions between a polar component and an ether are proposed to occur via complex formation between the two species [11]. Di-isopropyl ether has been known to participate in cross association effects with the hydrogen present in trichloromethane, and the excess molar volume has been reported as large and negative ($V_m^E(0.5) = -1.653 \text{ cm}^3 \text{ mol}^{-1}$) [11–15]. Negative excess molar volumes have also been reported for chloroform with monoethers [16]. Treszczanowicz [17] has reported positive excess molar volumes for mixtures of (methyl butyl ether or di-isopropyl + heptane) at 298.15 K with $V_m^E(0.5) = 0.239 \text{ cm}^3 \text{ mol}^{-1}$ for the (di-isopropyl ether + heptane) system. Arm and Bankay [3] have reported volume changes upon mixing for (methanol + diethyl ether) which are negative over the whole composition range with $V_m^E(0.5) = -0.80 \text{ cm}^3 \text{ mol}^{-1}$. They have discussed the results in terms of the dominance of the association between the component molecules.

The V_m^E results for the mixtures (methanol or ethanol or 2-propanol + IPE or MTBE) [18–20] have been reported in the literature. As far as we know, the V_m^E results for the other mixtures discussed here have not been reported.

2. Experimental

The alkanols: methanol (BDH, purity better than 99.8 mol%), ethanol (UnivAR, purity better than 99.9 mol%), propan-1-ol (BDH, purity better than 99.5 mol%), propan-2-ol (Janssen Chimica, purity better than 99 mol%) were dried and distilled as described elsewhere [21,22]. The ethers: di-isopropyl ether was supplied by Riedel-deHaen, 1,1-dimethylethyl methyl ether by Janssen Chimica, and 1,1-dimethylpropyl methyl ether by Aldrich Chemicals. Each of the branched ethers were distilled, dried, and degassed before use as previously described [22]. The mole fraction of water in each of the liquids were determined by Karl Fischer titration to be $< 0.01 \text{ mol}\%$. The solvents were each analysed by glc and were found to be 98.8 mol% pure in the worst case (1,1-dimethylpropyl methyl ether) and were kept in a dry box prior to use.

V_m^E 's were calculated from molar masses and densities of pure liquids and mixtures using an Anton-Paar DMA 602 vibrating-tube densimeter, thermostated at the temperature ($298.15 \pm 0.01 \text{ K}$) as previously reported [23].

3. Results

The V_m^E results are given in Table 1 together with the deviations δV_m^E , calculated from the smoothing equation:

$$\delta V_m^E / (\text{J mol}^{-1}) = V_m^E / (\text{J mol}^{-1}) - x(1-x) \sum_{r=0}^{r=k} A_r (1-2x)^r \quad (1)$$

Table 1

Experimental excess molar volumes, V_m^E for binary mixtures of $\{xC_jH_{2j+1} + (1-x)ROR'\}$ and the deviations, δV_m^E at the temperature 298.15 K

x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$
<i>xCH₃OH + (1-x){CH₃CH(CH₃)₂O</i>								
0.009	-0.043	2.6	0.745	-0.758	-1.4	0.893	-0.407	2.9
0.109	-0.460	-3.9	0.778	-0.692	4.6	0.901	-0.378	4.5
0.349	-0.916	3.2	0.826	-0.592	1.9	0.923	-0.305	5.6
0.472	-0.987	-1.6	0.841	-0.552	5.3	0.946	-0.221	3.8
0.688	-0.848	-6.8	0.874	-0.461	4.6	0.971	-0.123	1.9
0.733	-0.781	-4.7						
<i>xCH₃OH + (1-x)CH₃C(CH₃)₂OCH₃</i>								
0.127	-0.324	-7.3	0.559	-0.639	-4.8	0.827	-0.386	3.5
0.156	-0.380	-7.4	0.611	-0.614	-2.1	0.879	-0.307	-1.0
0.188	-0.428	0.9	0.690	-0.557	-0.1	0.909	-0.233	2.2
0.220	-0.474	-0.6	0.710	-0.543	-4.5	0.914	-0.221	3.7
0.303	-0.567	0.2	0.716	-0.527	4.7	0.947	-0.141	4.9
0.334	-0.589	3.2	0.763	-0.479	0.7	0.978	-0.063	0.6
0.388	-0.622	1.7	0.783	-0.451	3.6			
0.494	0.637	7.7	0.794	-0.431	8.2			
<i>xCH₃OH + (1-x)CH₃CH₂C(CH₃)₂OCH₃</i>								
0.032	-0.078	-4.2	0.399	-0.446	6.3	0.837	-0.246	1.1
0.050	-0.113	-2.7	0.459	-0.460	-1.9	0.751	-0.216	1.2
0.099	-0.199	2.2	0.489	-0.460	-2.7	0.876	-0.214	-5.0
0.152	-0.281	-0.9	0.597	-0.435	-3.9	0.895	-0.172	1.3
0.200	-0.332	4.3	0.669	-0.392	3.1	0.923	-0.132	0.5
0.232	-0.367	-0.9	0.705	-0.369	1.9	0.937	-0.111	-0.3
0.282	-0.407	-2.4	0.745	-0.341	-0.6	0.951	-0.089	-1.2
0.335	-0.434	-1.3	0.788	-0.299	1.4	0.980	-0.039	-1.5
<i>xC₂H₅OH + (1-x){CH₃CH(CH₃)₂O</i>								
0.011	-0.047	9.1	0.513	-0.810	-3.6	0.767	-0.559	6.6
0.019	-0.097	-1.6	0.624	-0.749	4.3	0.809	-0.481	1.6
0.023	-0.114	-1.9	0.632	-0.742	4.2	0.850	-0.397	-4.3
0.043	-0.189	7.6	0.669	-0.711	-1.3	0.870	-0.348	-5.1
0.162	-0.545	0.2	0.691	-0.681	2.6	0.874	-0.338	-4.4
0.219	0.632	9.5	0.698	-0.670	3.5	0.927	-0.194	2.1
0.302	-0.728	6.5	0.727	-0.636	-3.3	0.956	-0.122	-2.9
0.407	-0.804	-7.6	0.761	-0.582	-6.5			
<i>xC₂H₅OH + (1-x)CH₃C(CH₃)₂OCH₃</i>								
0.089	-0.199	-4.0	0.529	-0.518	-1.8	0.754	-0.390	-4.8
0.161	-0.295	-1.8	0.541	-0.513	1.5	0.796	-0.338	2.2
0.246	-0.390	-2.3	0.597	-0.498	-2.0	0.805	-0.332	-1.7
0.341	-0.477	-4.1	0.617	-0.496	-9.4	0.826	-0.302	2.6
0.399	-0.500	4.0	0.652	-0.469	-1.9	0.847	-0.277	0.7
0.450	-0.510	7.2	0.671	-0.456	-1.9	0.879	-0.229	2.1
0.493	-0.515	5.4	0.682	-0.450	-3.7	0.884	-0.220	2.9
0.503	-0.514	6.3	0.712	-0.425	-1.8	0.932	-0.142	0.3
0.520	-0.518	0.2	0.733	-0.408	-3.0	0.950	-0.105	3.4

Table 1 (continued)

x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$
<i>x</i> C ₂ H ₅ OH + (1 - <i>x</i>)CH ₃ CH ₂ C(CH ₃) ₂ OCH ₃								
0.038	-0.054	-0.1	0.399	-0.316	-3.7	0.734	-0.266	1.4
0.158	-0.184	1.7	0.406	-0.317	-3.5	0.769	-0.245	2.9
0.169	-0.193	1.8	0.460	-0.328	-5.9	0.802	-0.222	3.7
0.234	-0.240	2.3	0.559	-0.323	-2.0	0.847	-0.194	-4.9
0.257	-0.249	7.5	0.639	-0.301	4.3	0.931	-0.105	-5.3
0.269	-0.258	5.2	0.710	-0.279	0.6			
<i>x</i> C ₃ H ₇ OH + (1 - <i>x</i>)(CH ₃ CH(CH ₃)) ₂ O								
0.036	-0.177	-3.7	0.350	-0.961	-6.6	0.757	-0.775	-4.5
0.046	-0.220	-8.0	0.423	-1.012	-2.2	0.807	-0.657	0.6
0.094	-0.410	-8.3	0.517	-1.038	-1.3	0.843	-0.561	-0.4
0.119	-0.490	-4.9	0.637	-0.948	3.7	0.873	-0.478	-2.8
0.159	-0.603	2.1	0.675	-0.906	2.6	0.902	-0.384	-3.4
0.219	-0.735	1.5	0.748	-0.779	9.1	0.964	-0.153	-3.3
<i>x</i> C ₃ H ₇ OH + (1 - <i>x</i>)CH ₃ C(CH ₃) ₂ OCH ₃								
0.022	-0.065	-1.5	0.419	-0.647	-0.4	0.759	-0.482	-1.0
0.061	-0.169	-0.7	0.427	-0.647	1.5	0.798	-0.424	0.6
0.099	-0.260	-1.4	0.489	-0.662	-4.9	0.849	-0.341	0.2
0.170	-0.399	-0.1	0.530	-0.654	-1.1	0.881	-0.279	0.6
0.228	-0.487	1.5	0.586	-0.635	-0.6	0.893	-0.257	-0.6
0.281	-0.551	0.8	0.632	-0.606	1.5	0.908	-0.224	-0.6
0.332	-0.598	1.5	0.691	-0.558	1.5	0.957	-0.113	-2.8
<i>x</i> C ₃ H ₇ OH + (1 - <i>x</i>)CH ₃ CH ₂ C(CH ₃) ₂ OCH ₃								
0.147	-0.315	1.3	0.614	-0.453	6.5	0.839	-0.260	2.1
0.232	-0.382	2.7	0.669	-0.416	3.1	0.859	-0.231	3.3
0.302	-0.446	1.8	0.687	-0.406	2.8	0.885	-0.202	-4.3
0.374	-0.476	-8.2	0.720	-0.380	4.9	0.968	-0.064	-5.2
0.429	-0.484	-9.2	0.745	-0.361	2.2			
0.526	-0.491	-2.1						
<i>x</i> CH ₃ CH(CH ₃)OH + (1 - <i>x</i>)(CH ₃ CH(CH ₃)) ₂ O								
0.041	-0.091	9.1	0.464	-0.485	-3.6	0.788	-0.364	6.6
0.076	-0.169	-1.6	0.547	-0.486	4.3	0.841	-0.299	1.6
0.104	-0.218	-1.9	0.621	-0.472	4.2	0.872	-0.257	-4.3
0.150	-0.280	7.6	0.671	-0.450	-1.3	0.895	-0.219	-5.1
0.234	-0.274	0.2	0.702	-0.420	2.6	0.923	-0.176	-4.4
0.275	-0.422	9.5	0.742	-0.401	3.5	0.949	-0.123	2.1
0.350	-0.457	6.5	0.754	-0.392	-3.3			
<i>x</i> CH ₃ CH(CH ₃)OH + (1 - <i>x</i>)CH ₃ C(CH ₃) ₂ OCH ₃								
0.044	-0.058	-9.6	0.391	-0.244	4.9	0.773	-0.189	-1.1
0.088	-0.099	-6.9	0.515	-0.259	-0.7	0.803	-0.172	-0.7
0.160	-0.158	-9.0	0.627	-0.242	0.7	0.832	-0.147	6.1
0.200	-0.179	-3.4	0.648	-0.233	3.9	0.871	-0.125	0.4
0.310	-0.228	-4.4	0.727	-0.211	-1.2	0.909	-0.094	0.6
0.385	-0.249	-0.7	0.737	-0.213	-7.9	0.944	-0.062	-0.4

Table 1 (continued)

x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$	x	V_m^E (cm ³ mol ⁻¹)	$\delta V_m^E \times 10^3$
$xCH_3CH(CH_3)OH + (1-x)CH_3CH_2C(CH_3)_2OCH_3$								
0.019	-0.009	-2.8	0.513	-0.145	-2.9	0.731	-0.130	0.8
0.055	-0.025	5.7	0.541	-0.143	-5.1	0.778	-0.117	-1.7
0.124	-0.067	1.3	0.608	-0.145	-0.7	0.809	-0.113	3.4
0.214	-0.106	4.6	0.680	-0.143	4.7	0.866	-0.087	0.1
0.309	-0.125	-1.5	0.694	-0.137	0.6	0.914	-0.060	-2.3
0.393	-0.143	2.9	0.716	-0.133	0.6	0.948	-0.037	-4.3

Table 2

Coefficients A_r and standard deviations σ for an alkanol (1)+a branched chain ether (2) at the temperature 298.15 K by Eq. (1)

Branched chain ether	A_0	A_1	A_2	$\sigma \times 10^3$ (cm ³ mol ⁻¹)
<i>Methanol</i>				
IPE	-3.917	0.276	-0.869	4.5
MTBE	-2.570	0.096	-0.479	4.4
TAME	-1.851	0.290	-0.143	3.9
<i>Ethanol</i>				
IPE	-3.278	0.523	-0.490	13.7
MTBE	-2.066	0.060	-0.226	4.7
TAME	-1.302	-0.048	-0.225	4.3
<i>Propan-1-ol</i>				
IPE	-4.114	0.193	-0.612	8.3
MTBE	-2.629	0.131	-0.247	1.6
TAME	-1.941	0.299	-0.428	7.8
<i>Propan-2-ol</i>				
IPE	-1.952	-0.014	-0.607	4.7
MTBE	-1.026	0.038	-0.232	3.7
TAME	-0.599	-0.068	-0.097	10.5

The values of the parameters A_r have been determined using the method of least squares and are given in Table 2.

4. Discussion

All of the V_m^E curves are negative and symmetrical at $x = 0.5$. For each of the alkanols, the V_m^E data increase in the following order: IPE < MTBE < TAME. This trend would seem to indicate (a) a more organised packing effect and (b) stronger specific interactions for systems containing IPE than MTBE or TAME. This can be explained by considering the structural implications of the three branched ethers. IPE is less sterically hindered than MTBE or TAME where the latter two molecules

Table 3
Characteristic parameters of pure components for the ERAS model at 298.15 K

Component	V_{mol} (cm ³ mol ⁻¹)	V^* (cm ³ mol ⁻¹)	T^* (K)	P^* (J cm ⁻³)	V
Methanol	40.74	31.70	4776	469.2	1.285
Ethanol	58.68	46.31	4980	454.9	1.267
Propan-1-ol	75.15	60.06	5183	471.8	1.251
Propan-2-ol	76.96	61.09	5069	443.9	1.260
IPE	142.2	326.4	4853	326.4	1.278
MTBE	119.9	94.39	4946	346.8	1.270
TAME	133.4	107.5	5332	226.5	1.241

experience greater intramolecular congestion arising from the packing of three methyl groups around a common C (carbon) group. This leads to a strained structure and decreased availability of the O atom in the ether to interact with the OH group of the alkanol. This effect is enhanced as the degree of branching increases. At equimolar concentrations for each of the ethers, all of the systems exhibit a similar trend in V_{m}^{E} when increasing the chain length of the alkanol, e.g., for the IPE systems, V_{m}^{E} is less negative for ethanol than methanol, -0.99 cm³ mol⁻¹ and -0.82 cm³ mol⁻¹, respectively, while 1-propanol is more negative than either ethanol or methanol, i.e., -1.02 cm³ mol⁻¹. The lack of discernment in any trends displayed by the $V_{\text{m}}^{\text{E}}(x = 0.5)$ value is indicative of the significant role molecular packing effects play in determining the excess molar volume. This result is to be expected if the large differences in the molar volumes of the different components in each mixture are considered. V_{m}^{E} for the mixtures (2-propanol + IPE or MTBE or TAME) show the least negative behaviour, and this is probably attributable to the shielding effect on the alkanol hydroxy group by the two adjacent methyl groups, thus limiting association between the alkanol and the ether species.

The V_{m}^{E} results for the mixtures discussed here have not been reported in the literature except for (methanol or ethanol or 2-propanol + IPE or MTBE) [18–20]. Blanco et al. [18] recently reported the V_{m}^{E} at 298.15 K for (methanol or ethanol or 2-propanol + IPE or MTBE), and showed that V_{m}^{E} was negative over the whole mole fraction range. Our $V_{\text{m}}^{\text{E}}(x = 0.5)$ results compare well with those reported by Blanco et al. and deviate by $\pm 2\%$ in the worst case. Blanco et al. [18] have also reported positive V_{m}^{E} for branched hydrocarbon analogous of the branched chain ether with methanol or ethanol or 2-propanol. A comparison of these results with those reported indicate that the negative volumetric behaviour exhibited here is most likely due to the association between the proton of the alkanol hydroxy group and the ethereal oxygen. Nakashini et al. [19] have reported $V_{\text{m}}^{\text{E}}(x = 0.5)$ for (methanol + IPE) at 298.15 K of -1.015 cm³ mol⁻¹ and Farkova [20] have recently reported $V_{\text{m}}^{\text{E}}(x = 0.5)$ for (methanol + IPE or MTBE) at 298.15 K of -0.9821 and -0.6506 cm³ mol⁻¹, respectively. The reported results deviate slightly from those presented here by approximately $\pm 2\%$ (Table 3).

5. The ERAS model

A quantitative treatment that accounts for the competing effects present in alkanol mixtures and for the change in free volume upon mixing is offered by the ERAS [24–26] models.

The ERAS model combines the real associated solution model with a free volume contribution using Flory's equation of state [24–31]. The version of the ERAS model used here has been described

Table 4
Pure component properties for the alkanols at 298.15 K used in the ERAS model

Component	Δh^* (kJ mol ⁻¹)	Δv^* (cm ³ mol ⁻¹)	K_{298}
Methanol	-25.1 ^a	-5.6 ^a	986 ^a
Ethanol	-25.1 ^a	-9.3 ^b	317 ^a
Propan-1-ol	-25.1 ^a	-7.6 ^c	197 ^a
Propan-2-ol	-25.1 ^a	-5.6 ^a	131 ^a

^aFrom Ref. [29].

^bFrom Ref. [30].

^cFrom Ref. [32].

Table 5
Physical properties at 298.15 K: thermal expansion coefficient α , isothermal compressibilities κ_T and densities ρ for the pure compounds used in the ERAS model

Compound	$\alpha \times 10^4$ (K ⁻¹)	Reference	$\kappa_T \times 10^4$ (MPa ⁻¹)	Reference	ρ (kg m ⁻³)
Methanol	11.89	[29]	12.48	[29]	786.52
Ethanol	10.93	[33]	11.49	[34]	785.12
Propan-1-ol	9.95	[33]	10.26	[34]	799.74
Propan-2-ol	10.64	[35]	11.42	[34]	780.92
IPE	14.50	[36]	17.19	[37]	718.39
MTBE	14.20	[36]	15.39	[37]	735.43
TAME	9.66	[37]	19.58	[37]	765.99

Table 6
ERAS model parameters characterising mixture properties of {an alkanol + branched chain ether} at 298.15 K

Mixture	X_{AB} (J cm ⁻³)	$-\Delta h_{AB}^*$ (kJ mol ⁻¹)	$-\Delta v_{AB}^*$ (cm ³ mol ⁻¹)	K_{AB}
<i>Methanol</i>				
+ IPE	7.8	24.5	9.6	350
+ MTBE	11.8	23.7	8.4	350
+ TAME	11.8	23.3	9.8	350
<i>Ethanol</i>				
+ IPE	2.8	21.9	11.0	220
+ MTBE	5.0	21.0	10.7	128
+ TAME	15.0	21.0	14.7	38
<i>Propan-1-ol</i>				
+ IPE	5.0	21.6	10.0	108
+ MTBE	3.0	20.2	9.1	80
+ TAME	2.0	19.6	10.0	50
<i>Propan-2-ol</i>				
+ IPE	5.0	19.5	6.7	60
+ MTBE	2.8	18.1	6.0	45
+ TAME	3.8	18.4	6.9	40

by Funke et al. [25] relating to mixtures consisting of two associating components. This model has been simplified and the equations have been described in an earlier publication [26]. Together with the previously reported H_m^E data, the ERAS parameters h_{AB}^* , v_{AB}^* , K_{AB} and X_{AB} were adjusted simultaneously to the experimental V_m^E and H_m^E data. In all the systems studied here, the ether was assumed to be an inert component without self association ($K_B = 0$), but cross-association was possible ($K_{AB} \neq 0$). For all the alcohols an average value of -25 J mol^{-1} for the enthalpy of hydrogen bonding h_A^* was assumed [29]. The value of v_A^* and K_A for each of the four alkanols was used from literature sources given in Tables 4 and 5. The pure component properties are listed in Table 4 and the adjustable parameters for all the binary systems are listed in Table 6. Fig. 1a and Figs. 2–4c compare the experimental results with values calculated from the ERAS model and show the chemical and physical contributions to V_m^E .

For the {methanol + (IPE or MTBE or TAME)} mixtures, the calculated V_m^E curves agree well with the experimental data. The largest deviation between the predicted and experimental results ($\pm 0.09 \text{ cm}^3 \text{ mol}^{-1}$) is observed for the {methanol + TAME} system. The chemical contribution seems to largely affect the symmetry of the predicted V_m^E curves. The predicted H_m^E curves for {methanol + (IPE or MTBE or TAME)} are qualitatively reproduced, i.e., the exothermic behaviour of the experimental curves in the alkanol-rich region is adequately predicted. However, the magnitude of the predicted exothermic behaviour was larger than those experimentally determined for all the systems investigated. The ERAS model correctly predicts the endothermic H_m^E behaviour up to alkanol mole fraction of $x = 0.65$.

For the {(ethanol or 1-propanol or 2-propanol) + (IPE or MTBE or TAME)}, the calculated V_m^E and H_m^E curves are of the same sign as the experimental curves as shown in Figs. 2–4. However, large

Fig. 1. (a) V_m^E and H_m^E ERAS model description of x methanol + (1 - x) IPE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (b) V_m^E and H_m^E ERAS model description of x methanol + (1 - x) MTBE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (c) V_m^E and H_m^E ERAS model description of x methanol + (1 - x) TAME at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution.

Fig. 2. (a) V_m^E and H_m^E ERAS model description of x ethanol + (1 - x) IPE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (b) V_m^E and H_m^E ERAS model description of x ethanol + (1 - x) MTBE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (c) V_m^E and H_m^E ERAS model description of x ethanol + (1 - x) TAME at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution.

Fig. 3. (a) V_m^E and H_m^E ERAS model description of x propan-1-ol + (1 - x) IPE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (b) V_m^E and H_m^E ERAS model description of x propan-1-ol + (1 - x) MTBE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (c) V_m^E and H_m^E ERAS model description of x propan-1-ol + (1 - x) TAME at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution.

Fig. 4. V_m^E and H_m^E ERAS model description of x propan-2-ol + (1 - x) IPE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (b) V_m^E and H_m^E ERAS model description of x propan-2-ol + (1 - x) MTBE at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution; (c) V_m^E and H_m^E ERAS model description of x propan-2-ol + (1 - x) TAME at 298.15 K: \diamond , experimental data; —, ERAS model; \cdot , chemical contribution; — —, physical contribution.

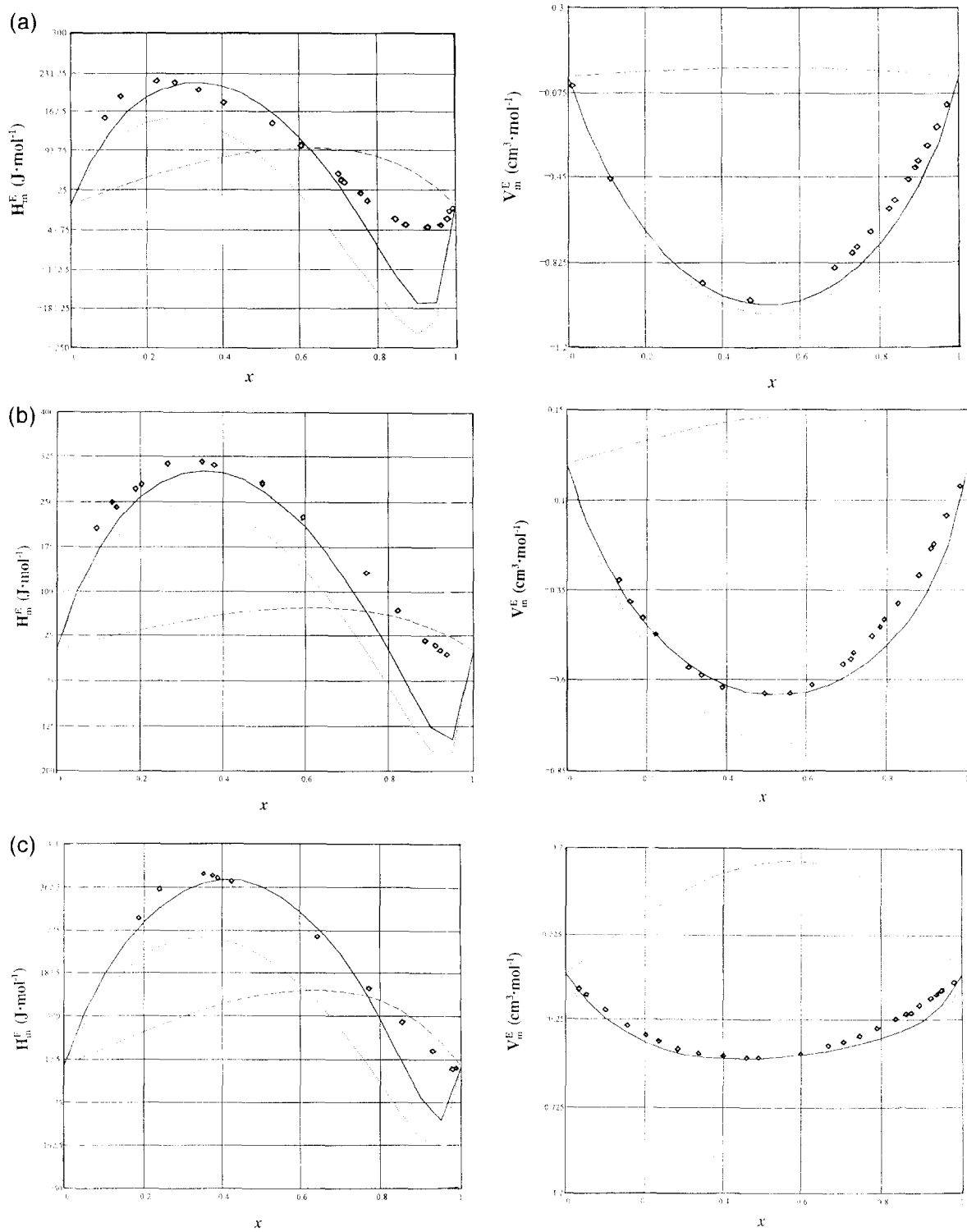


Fig. 1.

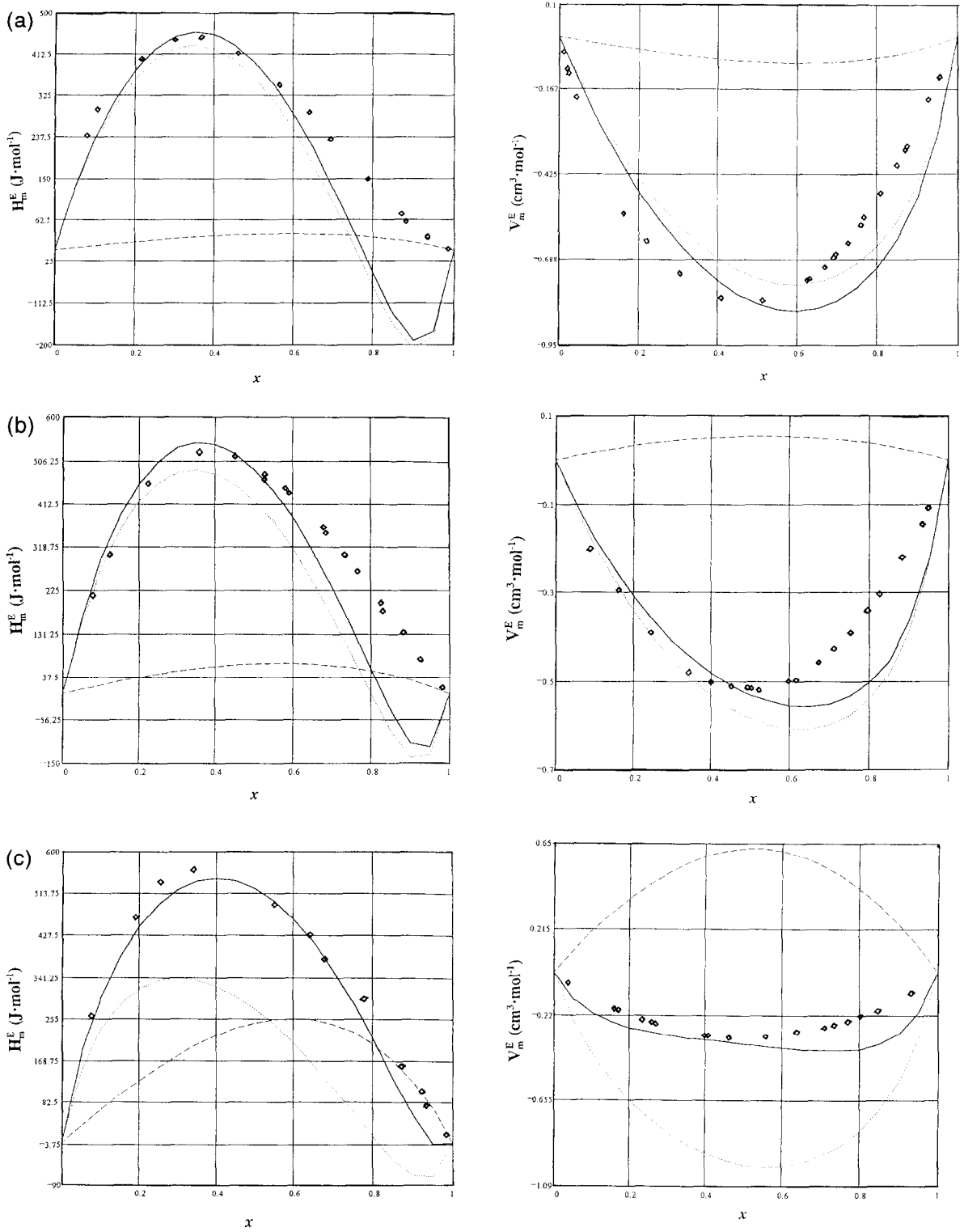


Fig. 2 (see p. 214 for caption).

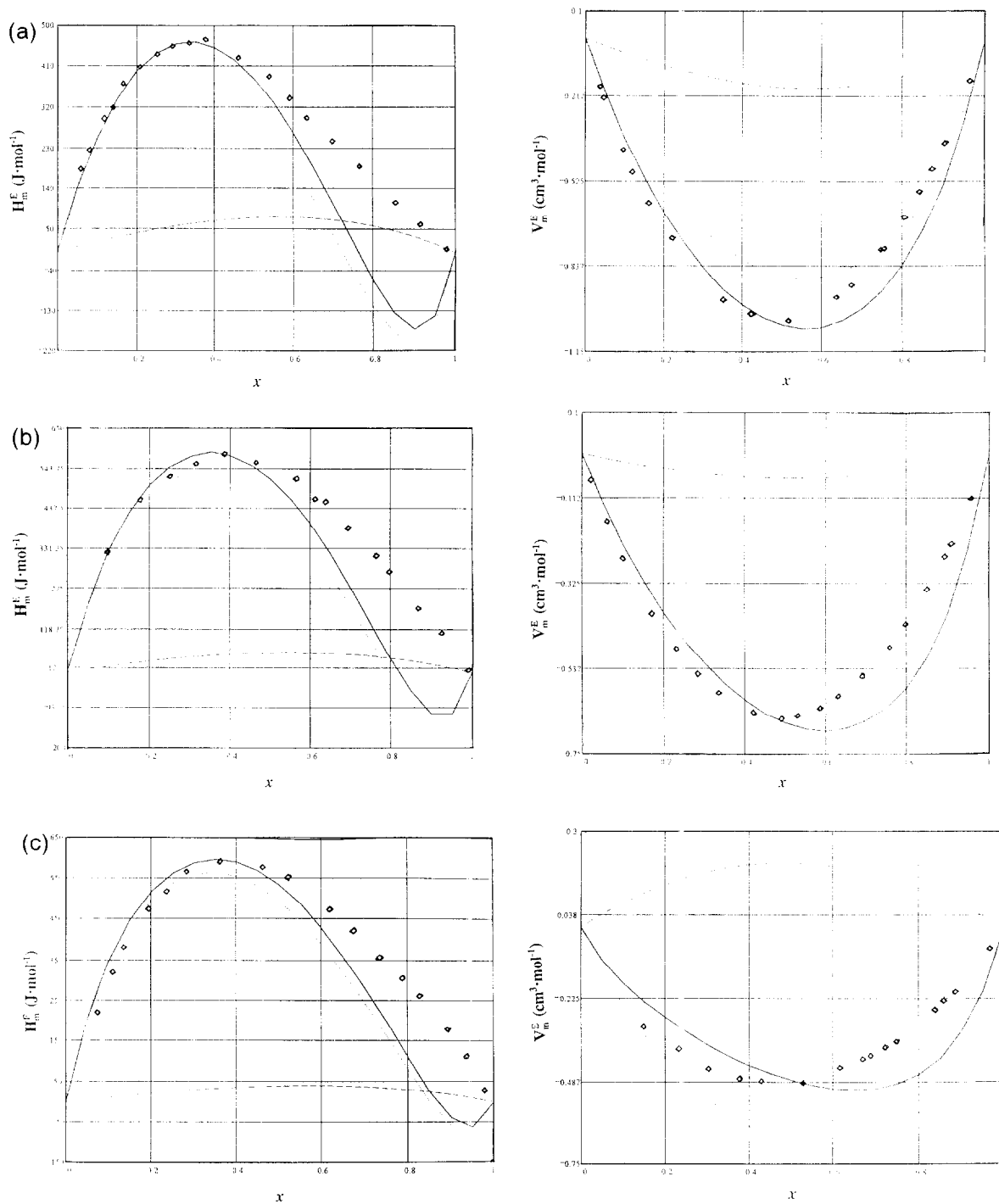


Fig. 3 (see p. 214 for caption).

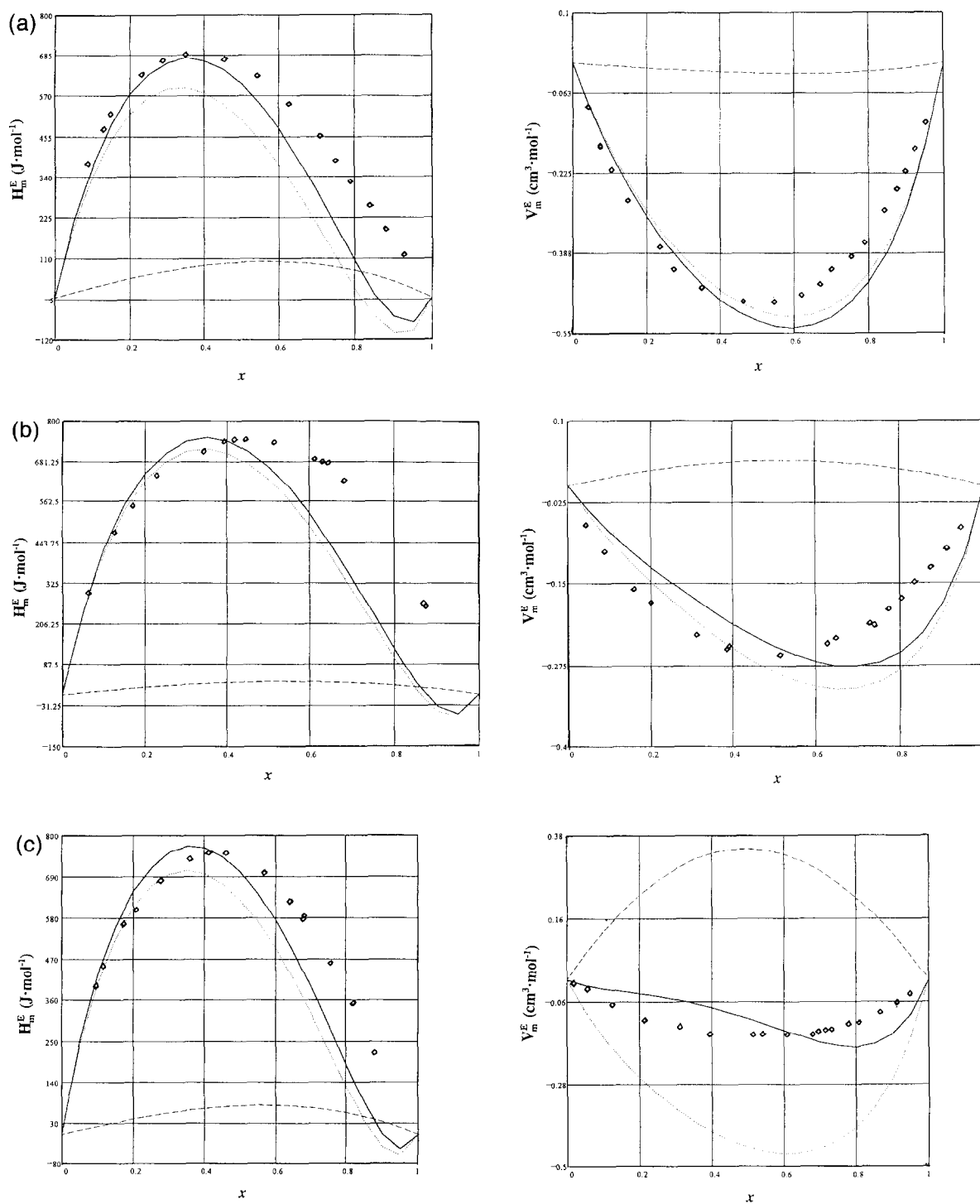


Fig. 4 (see p. 214 for caption).

deviations in the symmetry of the predicted V_m^E curves are observed. A comparison of the systems tested here shows that the {(ethanol or 2-propanol) + TAME} mixtures exhibit the worst V_m^E prediction with the shape, size and symmetry of the predicted curve in disagreement with the experimental V_m^E curves. For all the {(ethanol or 1-propanol or 2-propanol) + a branched chain ether} systems the ERAS model predicts accurately the endothermic H_m^E behaviour of the systems up to an $x = 0.6$ alkanol mole fraction. At $x > 0.7$, the calculated H_m^E curves indicate small exothermic behaviour that is in disagreement with the experimental H_m^E . Consequently, deviations between calculated and experimental H_m^E curves are as large as 190 J mol^{-1} in some cases.

6. List of symbols

A_r	Coefficient from Redlich Kister expansion
H_m^E	Molar excess enthalpy (J mol^{-1})
Δh_A^*	Self-association enthalpy of component A (kJ mol^{-1})
Δh_{AB}^*	Cross-association enthalpy of component A with component B (kJ mol^{-1})
K_A	Self-association constants of component A
X_{12}	Binary van der waals interaction parameter (J cm^{-3})
K_{AB}	Association constant of component A with component B
P_i^*	Characteristic parameter of component i for pressure (J cm^{-3})
T_i^*	Characteristic parameter of component i for temperature (K)
Δv_A^*	Self-association volume of component A ($\text{cm}^3 \text{ mol}^{-1}$)
Δv_{AB}^*	Cross-association volume of component A with B ($\text{cm}^3 \text{ mol}^{-1}$)
V_m^E	Molar excess volume ($\text{cm}^3 \text{ mol}^{-1}$)
V_i^*	Molar hard core volume of component i ($\text{cm}^3 \text{ mol}^{-1}$)
V_{mol}	Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
x_j	Mole fraction of component i
\bar{V}_i	Reduced volume of component i

Greek letters

δ	Deviations between calculated and experimental value
κ_T	Compressibility coefficient (10^{-4} MPa^{-1})
X_{AB}	Binary van der Waals interaction parameter (J cm^{-3})
θ_i	Surface fraction of component i
ψ_i	Contact energy fraction of component i

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