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EXCESS ISOBARIC HEAT CAPACITIES AND EXCESS VOLUMES OF SOME HEXANOL + n-HEPTANE MIXTURES

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ABSTRACT

Flow microcalorimetric measurements of the excess isobaric heat capacity, and vibrating tube densimetric determinations of the excess volume were carried out over the whole concentration range for mixtures of hexan-2-ol or hexan-3-ol with n-heptane at 298.15 K. Particular attention was paid to the dilute alkanol region, where the excess heat capacity changes sign. This behavior is discussed in terms of the auto-association of the alkanol.

INTRODUCTION

The present paper continues our investigations of the heat capacities of alkanol + alkane mixtures [1,2]. Such studies are interesting from the point of view of the self-association of alkanols. We report here measurements of the excess molar isobaric heat capacities at 298.15 K for hexan-2-ol + n-heptane and hexan-3-ol + n-heptane. In the course of the investigation, the excess molar volumes of these mixtures were also determined.

EXPERIMENTAL

Hexan-2-ol and hexan-3-ol with stated minimum purities of 99 mol % were obtained from the Aldrich Chemical Co. The n-heptane was Pure Grade material from the Phillips Petroleum Co. The component liquids were used without further purification. Their densities, determined at 298.15 K, were 809.95, 814.92, and 679.62 kg m^{-3} for hexan-2-ol, hexan-3-ol, and n-heptane, respectively.

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Binary mixtures were prepared by weighing in specially designed onion cells [3]. Over most of the range of composition, the error of the mole fraction x of alkanol is estimated to be less than ± 0.00005.

Differences of the isobaric heat capacity per unit volume, $C_{p,m}/V_m$, were measured in a Picker flow microcalorimeter [4,5] using a flow rate of ~ 0.012 cm^3 s^{-1} and a temperature interval of ~ 1 K centred on 298.15 K. In most of the work, a stepwise procedure [5] was followed, however a single reference procedure was used for mixtures dilute in alkanol. In all cases the initial reference liquid was n-heptane, and 224.746 J K^{-1} mol^{-1} [6] was adopted for its molar isobaric heat capacity $C^{\star}_{p,2}$ at 298.15 K.

Excess molar volumes V^E_m were obtained from densities determined at 298.15 K in a vibrating tube densimeter (Model 02D, Sodev Inc.) operated in a static mode [3]. Samples of benzene, cyclohexane and n-heptane with known densities were used to calibrate the instrument. The error of V^E_m is estimated to be about ± 0.0003 cm^3 mol^{-1}.

Molar isobaric heat capacities $C_{p,m}$ were obtained from the volumetric heat capacities using molar volumes V_m calculated from the densities of the pure components and smoothed representations of V^E_m. For each of the two systems, several stepwise runs yielded averages of 256.31 and 269.27 J K^{-1} mol^{-1} for the molar isobaric heat capacities $C^{\star}_{p1}$ of hexan-2-ol and hexan-3-ol, respectively. The result for hexan-2-ol is comparable with the value 259.5 J K^{-1} mol^{-1} calculated from the equation given by Sriskandarajah [7] which was derived from an analysis of the heat capacities of other aliphatic alkanols.

The excess molar isobaric heat capacities $C^E_{p,m}$ were evaluated from the relation

$$C^E_{p,m} = C_{p,m} - xC^{\star}_{p,1} - (1-x)C^{\star}_{p,2} \tag{1}$$

The error of $C^E_{p,m}$ is estimated to be ± 0.02 J K^{-1} mol^{-1} for most of the range of x, and to decrease to about ± 0.005 J K^{-1} mol^{-1} for $x < 0.015$.

RESULTS AND DISCUSSION

The experimental values of V^E_m and $C^E_{p,m}$ are summarized in Tables 1 and 2, and plotted in Figs. 1 and 2. For clarity, some points at small values of x have been omitted from Figs. 1(a) and 2(a) and are shown on larger scales in Figs. 1(b) and 2(b).

The form

$$X^E = x(1-x)[1-k(1-2x)]^{-1} \sum_{j=1}^{n} a_j(1-2x)^{j-1} \tag{2}$$

was fitted to the results for V^E_m (cm^3 mol^{-1}). Values of the coefficients a_j and the skewing factor k, determined by the method of least-squares with all

TABLE 1

Excess molar volumes for $xC_6H_{13}OH+(1-x)C_7H_{16}$ mixtures at 298 15 K

x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})	x	V_m^E (cm^3 mol^{-1})
Hexan-2-ol + n-heptane							
0 00263	0 0208	0 01890	0 0985	0 09544	0 2138	0 44312	0 3513
0 00480	0 0344	0 02134	0 1037	0 10597	0 2190	0 53458	0 3344
0 00485	0 0354	0 02377	0 1112	0 12787	0 2369	0 64069	0 2911
0 00593	0 0423	0 02708	0 1180	0 13350	0 2437	0 68783	0 2645
0 00606	0 0423	0 03670	0 1375	0 17391	0 2703	0 73553	0 2254
0 00707	0 0488	0 04742	0 1566	0 20751	0 2882	0 78173	0 1910
0 00849	0 0571	0 05016	0 1594	0 28422	0 3221	0 82663	0 1473
0 00961	0 0643	0 05738	0 1701	0 28485	0 3220	0 87029	0 1115
0 01204	0 0756	0 05943	0 1701	0 39076	0 3458	0 91813	0 0664
0 01421	0 0838	0 06987	0 1825	0 39093	0 3451	0 95933	0 0331
0 01472	0 0827						
Hexan-3-ol + n-heptane							
0 00223	0 0159	0 01226	0 0745	0 07354	0 2137	0 28579	0 3745
0 00259	0 0220	0 01323	0 0783	0 08295	0 2261	0 33757	0 3975
0 00259	0 0192	0 01445	0 0849	0 09322	0 2381	0 34333	0 4006
0 00462	0 0331	0 01453	0 0863	0 09415	0 2399	0 42769	0 4231
0 00474	0 0352	0 01669	0 0930	0 09617	0 2412	0 49424	0 4310
0 00560	0 0373	0 01910	0 1018	0 12646	0 2723	0 53620	0 4331
0 00571	0 0411	0 01926	0 1035	0 14222	0 2830	0 54110	0 4338
0 00588	0 0404	0 02170	0 1107	0 14955	0 2924	0 59526	0 4283
0 00701	0 0459	0 02620	0 1242	0 17369	0 3114	0 63490	0 4148
0 00720	0 0464	0 02622	0 1251	0 17426	0 3132	0 68432	0 3899
0 00736	0 0477	0 02866	0 1309	0 17504	0 3080	0 73072	0 3653
0 00827	0 0547	0 04010	0 1590	0 18857	0 3226	0 78208	0 3191
0 00928	0 0598	0 04760	0 1727	0 21244	0 3361	0 82231	0 2599
0 00938	0 0616	0 04772	0 1749	0 22831	0 3470	0 87141	0 2120
0 00953	0 0609	0 04870	0 1726	0 22870	0 3480	0 89916	0 1743
0 00979	0 0612	0 05249	0 1822	0 23111	0 3454	0 91435	0 1572
0 01171	0 0741	0 05481	0 1851	0 23123	0 3479	0 95736	0 0752

points weighted equally, are listed in Table 3 along with the standard deviations s of the representations These coefficients were used to plot the curves in Fig 1(a) and 1(b)

We were unable to find a single smoothing function to represent the results for $C_{p,m}^E$ (J K^{-1} mol^{-1}) adequately over the entire mole fraction range, and were led to consider the results for dilute alkanol mixtures separately from the main body of data Equation (2) was fitted to the points for $x > 0$ 03, and the polynomial

$$X^E = \sum_{j=1}^{n} a_j x^j \tag{3}$$

TABLE 2

Excess molar isobaric heat capacities for $x\mathrm{C_6H_{13}OH}+(1-x)\mathrm{C_7H_{16}}$ mixtures at 298.15 K

x	$C^E_{p,m}$ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$ (J K^{-1} mol^{-1})
Hexan-2-ol + n-heptane							
0.00247	−0.029	0.01472	2.41	0.09544	9.79	0.46502	8.44
0.00263	−0.065	0.01890	3.49	0.09963	9.89	0.53458	7.69
0.00263	−0.071	0.02134	3.97	0.10597	10.02	0.54378	7.36
0.00480	0.052	0.02377	4.47	0.12787	10.63	0.58159	6.88
0.00480	0.033	0.02415	4.53	0.13350	10.47	0.64069	6.44
0.00485	0.043	0.02708	5.02	0.16225	10.88	0.64151	6.25
0.00593	0.183	0.03670	6.25	0.17391	10.91	0.68783	5.80
0.00606	0.197	0.04177	6.85	0.20751	11.17	0.73165	5.37
0.00606	0.195	0.04742	7.36	0.22956	10.99	0.73553	5.49
0.00707	0.395	0.04963	7.53	0.28422	10.80	0.78173	4.81
0.00849	0.726	0.05016	7.51	0.28485	10.62	0.82663	4.28
0.00961	1.024	0.05738	8.00	0.39039	9.48	0.87029	3.39
0.01204	1.711	0.05943	8.18	0.39093	9.58	0.91813	2.40
0.01421	2.32	0.06871	8.72	0.44312	8.71	0.95933	1.23
Hexan-3-ol + n-heptane							
0.00223	−0.052	0.01323	1.198	0.09415	11.02	0.49424	9.38
0.00259	−0.114	0.01445	1.50	0.09617	10.93	0.49434	9.30
0.00259	−0.087	0.01453	1.61	0.14222	12.27	0.49552	9.54
0.00462	−0.117	0.01669	2.04	0.14955	12.69	0.59526	6.88
0.00474	−0.112	0.01926	2.68	0.17392	12.74	0.64250	5.85
0.00560	−0.076	0.02170	3.22	0.18857	13.18	0.64404	5.82
0.00571	−0.060	0.02620	4.41	0.21244	13.15	0.68432	4.75
0.00588	−0.064	0.02622	4.23	0.23103	12.97	0.69066	4.58
0.00701	0.052	0.02866	4.69	0.23111	13.17	0.78208	2.86
0.00720	0.081	0.04010	6.55	0.28410	12.85	0.78223	2.95
0.00736	0.054	0.04772	7.54	0.28489	12.69	0.81231	2.42
0.00928	0.353	0.04845	7.46	0.28579	12.95	0.82789	2.39
0.00938	0.414	0.04870	7.61	0.33973	12.35	0.86466	1.64
0.00953	0.404	0.05249	8.00	0.34333	12.43	0.87141	1.68
0.00979	0.437	0.07354	9.71	0.39286	11.35	0.91435	1.27
0.01171	0.899	0.08293	10.15	0.39836	11.40	0.95736	0.69
0.01226	0.969	0.08295	10.43	0.44145	10.68		

was adjusted to fit the points for $x < 0.06$. The results of these analyses are also listed in Table 3. Use of eqns (2) and (3) with the transition between the two forms occurring at $x = 0.045$ provides reasonable representations of $C^E_{p,m}$ as shown in Fig. 2(a) and 2(b).

The excess volumes for both of the present systems are positive at all mole fractions. It can be seen from Fig. 1 that the curve for hexan-2-ol falls below that for hexan-3-ol over most of the range, and is more skewed toward $x = 0$. At high dilutions of alkanol ($x < 0.01$) the curves are very

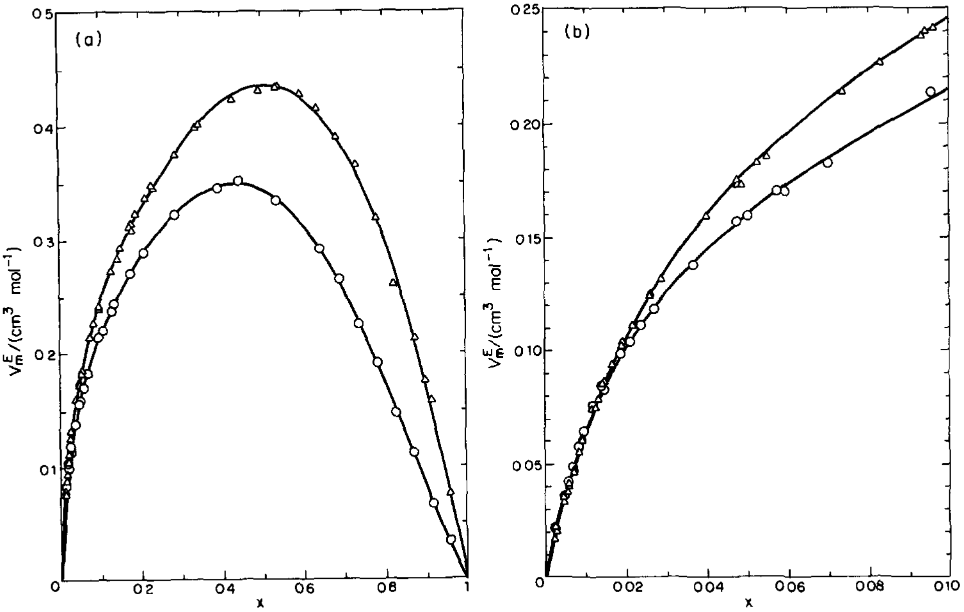

Fig 1 Excess molar volumes for $xC_6H_{13}OH+(1-x)C_7H_{16}$ at 298 15 K (○) Hexan-2-ol, (△) hexan-3-ol, (———) least-squares representations by eqn (2)

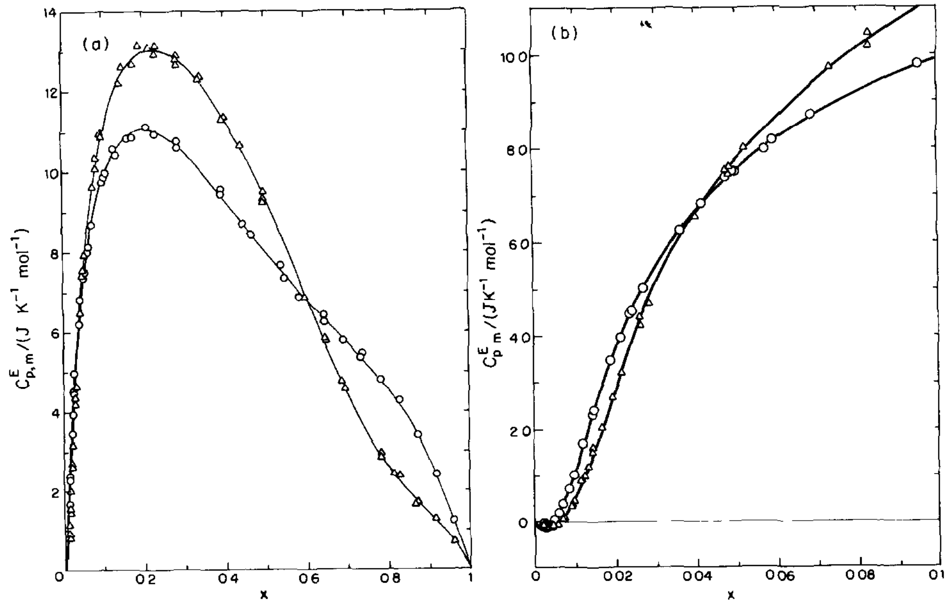

Fig 2 Excess molar isobaric heat capacities for $xC_6H_{13}OH+(1-x)C_7H_{16}$ at 298 15 K (○) Hexan-2-ol, (△) hexan-3-ol, (———) least-squares representations by eqn (2) for $x > 0\ 045$ and by eqn (3) for $x < 0\ 045$

TABLE 3

Coefficients a_j, skewing factors k and standard deviations s for least-squares representations of V_m^E by eqn (2) and $C_{p m}^E$ by eqns (2) and (3) for $x C_6H_{13}OH + (1 - x)C_7H_{16}$ mixtures at 298 15 K

	Hexan-2-ol + *n*-heptane			Hexan-3-ol + *n*-heptane		
	V_m^E (cm^3 mol^{-1}) eqn (2) $0 < x < 1$	$C_{p m}^E$ (J K^{-1} mol^{-1})		V_m^E (cm^3 mol^{-1}) eqn (2) $0 < x < 1$	$C_{p m}^E$ (J K^{-1} mol^{-1})	
		eqn (2) $0 045 < x < 1$	eqn (3) $0 < x < 0 045$		eqn (2) $0 045 < x < 1$	eqn (3) $0 < x < 0 045$
a_1	1 37178	32 0339	$-1 6116 \times 10^2$	1 74161	37 2033	$-1 1934 \times 10^2$
a_2	−0 96441	−4 1169	$4 4732 \times 10^4$	−1 67363	22 1968	$2 2452 \times 10^4$
a_3	−0 31769	15 2878	$-2 1580 \times 10^6$	0 44065	−14 7503	$-5 6014 \times 10^5$
a_4	0 44970	−19 4875	$4 9498 \times 10^7$		−1 3412	$4 4098 \times 10^6$
a_5	−0 18761		$-5 6002 \times 10^8$		31 4844	
a_6			$2 5067 \times 10^9$			
k	0 96192	0 9249		0 93637	0 6673	
s	0 0016	0 089	0 051	0 0028	0 110	0 067

nearly the same, and accordingly lead to limiting excess partial molar volumes $V_1^{E,\infty}$ for the alkanols at infinite dilution in n-heptane which are equal within their estimated uncertainties (9 2 ± 1 5 cm^3 mol^{-1} for hexan-2-ol and 8 0 ± 0 4 cm^3 mol^{-1} for hexan-3-ol)

The excess isobaric heat capacities are predominately positive, but both systems have a region near $x = 0$ where $C_{p,m}^E$ takes on small negative values In Fig 2, the curves for both alkanols have a maximum near $x = 0 2$, the maximum for hexan-3-ol exceeding that for hexan-2-ol by about 2 J K^{-1} mol^{-1}. However, the curve for hexan-2-ol is broader than that for hexan-3-ol and hence the curves cross twice, once near $x = 0 045$, and again near $x = 0 6$

We are not aware of any directly comparable studies of the present systems However, V_m^E [8] and $C_{p,m}^E$ [1] have been reported for hexan-1-ol + n-heptane mixtures at 298 15 K The curve of V_m^E for that system is sigmoid and very different in shape from the curves in Fig 1 The excess volumes of alkanol + alkane mixtures have been interpreted on the basis of the auto-association of the alkanol to form multimers, and a balance between chemical, physical and structural contributions [9] Qualitatively, positive contributions to V_m^E arise from the chemical effects of breaking H-bonds, and from the disruption of non-specific physical interactions between the true molecular species Negative contributions result from changes in free volume, and from packing effects such as the accommodation of molecules within the multimer structure For hexan-1-ol + n-heptane mixtures, the structural contributions are dominant for $x > 0 5$, and V_m^E is negative in that region This is not the case for the present mixtures, suggesting that the fitting of n-heptane molecules into the multimer structure of the secondary alkanols is sterically hindered

The $C_{p,m}^E$ curves in Fig 2 resemble the curve reported for hexan-1-ol + n-heptane [1], which also has negative values of $C_{p,m}^E$ occurring for mixtures dilute in alkanol ($x < 0\ 003$) However, the curve for hexan-1-ol is broader and flatter and does not have a point of inflexion in the region $x > 0\ 5$ Similar differences were noted by Bravo et al [10] who found that the shapes of the $C_{p,m}^E$ curves for a number of branched hexanol + n-alkane mixtures depended upon whether the alkanol was primary, secondary, or tertiary

The most interesting feature of the present results is the occurrence of negative $C_{p,m}^E$ at small alkanol mole fractions Analogous behavior has been observed for a number of other alkanol + n-alkane mixtures [1,2,11–15], and also for small mole fractions of benzonitrile in benzonitrile + cyclohexane mixtures [16] In the case of alkanol + n-alkane mixtures, Costas and Patterson [15] have discussed this behavior in terms of changes in the self-association of the alkanol when the mixture is formed Assuming that such changes are of primary importance at small alkanol mole fractions, they showed that $C_{p,m}^E$ for several alkanol + alkane mixtures could be interpreted quite well in that region on the basis of a slightly modified form of the simple association theory of Kehiaian and Treszczanowicz [17] Rather surprisingly, it was found that the concentration of tetramers was relatively high even at low mole fractions of the alkanol, where one would expect dimers to predominate This finding is supported by our recent analyses of $C_{p,m}^E$ for some C_5-alkanol + n-heptane mixtures [2]

In applying the association model [15] to the present systems, the notation is the same as in our earlier work [2] It can be shown that

$$C_{p,m}^E/x = \Phi(\phi_A, \phi_1) - \Phi(\phi_A^\star, 1) \tag{4}$$

where

$$\Phi(\phi_A, \phi_1) = \left(\Delta H_m^\ominus/T\right)^2 \{R\phi_1 S_2(\phi_A)\}^{-1} \times \sum_{i=2}^{\infty} (i-1) K_i^{(\phi)} \phi_A^i \{S_1(\phi_A) - S_2(\phi_A)/i\} \tag{5}$$

with

$$S_1(\phi_A) = 1 + \sum_{j=2}^{\infty} K_j^{(\phi)} \phi_A^{j-1} \tag{6}$$

and

$$S_2(\phi_A) = 1 + \sum_{j=2}^{\infty} j K_j^{(\phi)} \phi_A^{j-1} \tag{7}$$

In these equations, $\Delta H_m^\ominus$ is the standard enthalpy of H-bond formation, T is

TABLE 4

Size ratios r, association constants $K_i^{(\phi)}$ ($i = 3$, 4) and standard molar enthalpies $\Delta H_m^{\ominus}$ of H-bond formation for $xC_6H_{13}OH+(1-x)C_7H_{16}$ mixtures at 298 15 K

Alkanol	r	$10^{-3}\,K_3^{(\phi)}$	$10^{-4}\,K_4^{(\phi)}$	$-\Delta H_m^{\ominus}$ (kJ mol^{-1})
Hexan-2-ol	1 08	0 68	14 99	25 9
Hexan-3-ol	1 08	0 57	4 43	25 7

the temperature, R is the gas constant, and ϕ_1 is the nominal volume fraction of alkanol defined by

$$\phi_1 = x/\{x + r(1-x)\} \tag{8}$$

where r is the (alkane/alkanol) ratio of hard core molecular volumes $K_i^{(\phi)}$ is the i-mer classical association constant expressed in volume fractions ϕ_A, the volume fraction of alkanol monomer in the mixture (assuming no volume change on mixing) is identified with the smallest positive root of the conservation equation

$$\phi_A S_1(\phi_A) = \phi_1 \tag{9}$$

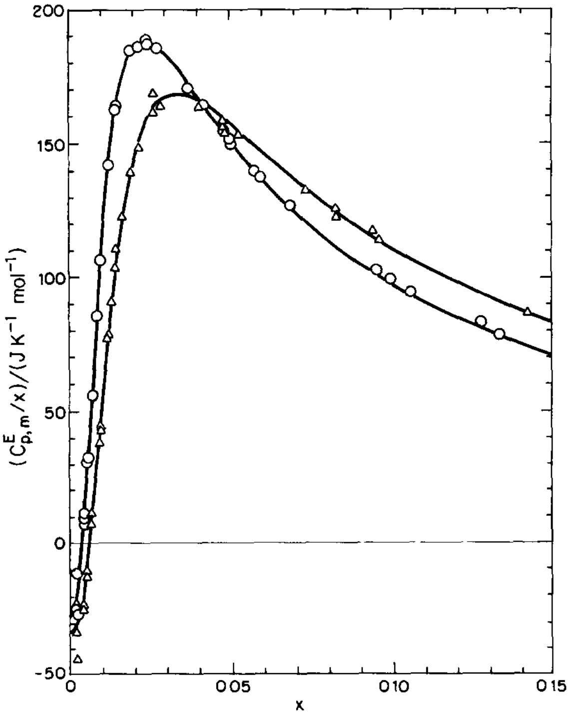

Fig 3 Plot of $C^E_{p\,m}/x$ for $xC_6H_{13}OH+(1-x)C_7H_{16}$ at 298 15 K (○) Hexan-2-ol, (△) hexan-3-ol, (———) calculated from eqn (4) with parameters from Table 4

The solution of this equation for the special case when $\phi_1 = 1$ is denoted by $\phi_A^\star$, and corresponds to the volume fraction of monomer in the pure alkanol

Equation (4) was fitted to each set of experimental results for $x < 0.15$. The group volumes proposed by Bondi [18] were used to estimate r The values of $\Delta H_m^\ominus$ and the association constants were determined by least-squares analyses The treatment was limited to dimers, trimers, and tetramers. For both systems the best fit was obtained when only trimers and tetramers were considered (i.e $K_2^{(\phi)} = 0$) The results are given in Table 4 Curves of $C_{p,m}^E/x$ calculated from eqn. (4) are shown in Fig 3, where the experimental values are plotted for comparison The theory reproduces the maxima of $C_{p,m}^E/x$ very well Some deviations from the experimental results occur for $x < 0.01$ These may be due to the simplified form of the theoretical treatment However, extension of the analyses to include dimers did not lead to improved fits in this region.

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