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VOLUMES AND HEAT CAPACITIES OF BINARY LIQUID MIXTURES OF WATER—SULFOLANE AND WATER—HEXAMETHYLPHOSPHOTRIAMIDE

MAURIZIO CASTAGNOLO, AMERICO INGLESE, GIUSEPPE PETRELLA and ANTONIO SACCO

Istituto di Chimica Fisica, Università di Bari, Via Amendola 173, Bari (Italy)

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ABSTRACT

Density and heat capacity measurements of water—sulfolane mixtures at 303.15 K and water—hexamethylphosphotriamide mixtures at 298.15 K have been performed over the whole composition range. Molar, excess, apparent molar volumes and heat capacities were calculated for the two systems. The trends of these functions are discussed in terms of specific interactions between the components of the solvent mixtures and the changes caused by the organic solvents on the water structure.

INTRODUCTION

In previous papers [1—3] we studied the behaviour of some electrolytes in water—organic solvent mixtures by a conductrometric and calorimetric method. The results show that interpretation of the experimental data must allow for specific interactions between water and organic solvent in the aqueous binary mixture under consideration. Useful information on water—organic solvent interactions can be obtained from heat capacity measurements of binary mixtures.

Recently Desnoyers and co-workers [4] have shown that precise measurements of this function can be carried out by the LKB 8700-1 calorimetric system. This instrument, which we have in our laboratory, enables measurement of the volumetric heat capacity of a liquid sample. Thus density measurements are required in order to convert volumetric heat capacities into molar heat capacities.

This paper gives results of heat capacity and density measurements of water—sulfolane (tetrahydrothiophene-1,1-dioxide) (W—TMS) mixtures at 303.15 K and water—hexamethylphosphotriamide (W—HMPT) mixtures at 298.15 K. The latter system is particularly interesting since interactions between water and HMPT seem to be very strong [4], as reported by Gall et al. [5].

EXPERIMENTAL

Water was deionized by passage through a mixed bed ion exchange resin column and then doubly distilled in a quartz apparatus. Commercial sulfo-

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lane (Shell Co.) was purified as described by Desbarres et al. [6] and then distilled over sodium hydroxide pellets under vacuum. The water content, detected by the Karl Fisher method, was less than 0.007 wt.%. Hexamethylphosphotriamide (Fluka purum) was distilled under vacuum over sodium and triphenylmethane shortly before use.

Water—organic solvent mixtures were made up by weight. All weights were corrected to vacuum conditions and the error of the final mole fraction is estimated to be less than $\pm 5 \times 10^{-5}$. Densities were measured with an Anton Paar DMA 02C densimeter. The instrument, based on the oscillating-tube principle, was adapted to operate under flow conditions using the technical precautions described by Picker et al. [7]. The liquids studied, thermostated at experimental temperature in a water jacket mounted in the inlet section of the instrument, flowed at a flow rate of 0.5 cm^3 min^{-1} through the vibrating tube. The temperature was controlled to ± 0.002 K. The densimeter was calibrated with aqueous NaCl solutions using the equation

$$\Delta d = d - d_0 = B(\tau^2 - \tau_0^2) \tag{1}$$

where d_0 is the water density, d is the density of solution and τ and τ_0 are the oscillation period of the vibrating tube containing solution and water, respectively. The values of the constant B at 298.15 and 303.15 K were evaluated from densities of pure water [8] and of aqueous solutions of NaCl [9]. Calibration indicates that the instrument can measure differences in densities to $\pm 4 \times 10^{-6}$ g cm^{-3}.

Heat capacities were measured with an LKB 8700-1 precision calorimetric system equipped with a 100 cm^3 reaction vessel, as described by Desnoyers and co-workers [4]. Tests of the instrument have been previously reported [2]. The reproducibility of measurements indicates that the overall uncertainty in the molar heat capacities is better than 1%.

RESULTS

Densities of water—sulfolane mixtures at 303.15 K and of water—HMPT mixtures at 298.15 K are given in Table 1 as a function of water mole fraction x_w.

Mean molar volumes V_M of solutions and excess molar volumes V^E were calculated by the equations

$$V_M = (x_w M_w + x_2 M_2)/d \tag{2}$$

and

$$V^E = V_M - x_w V_w^0 - x_2 V_2^0 \tag{3}$$

where M_W and M_2 are the molecular weights of water and of co-solvent, x_2 is the mole fraction of organic solvent, and V_w^0 and V_2^0 are the molar volumes of the pure components. Apparent molar volumes ϕ_v of the components of binary aqueous mixtures were calculated from the equations

$$\phi_{v,w} = V_w^0 + \frac{V^E}{x_w} \tag{4}$$

TABLE 1

Densities, molar volumes, excess molar volumes and apparent molar volumes of W—TMS and W—HMPT mixtures

X_w	d (g cm^{-3})	V_M (cm^3 mole^{-1})	V^E (cm^3 mole^{-1})	$\phi_{v,w}$ (cm^3 mole^{-1})	$\phi_{v,2}$ (cm^3 mole^{-1})
W—TMS; $T = 303.15$ K					
0	1.262350	95.199	0	18.7 *	95.20
0.09998	1.256150	87.538	0.047	18.57	95.25
0.19839	1.249324	79.969	0.067	18.43	95.28
0.30332	1.241165	71.858	0.046	18.25	95.27
0.40086	1.232060	64.301	0.010	18.12	95.22
0.50410	1.219807	56.301	−0.030	18.04	95.14
0.60708	1.203390	48.327	−0.064	17.99	95.04
0.70744	1.181052	40.560	−0.093	17.96	94.88
0.80763	1.147923	32.814	−0.113	17.96	94.61
0.90380	1.095701	25.412	−0.101	17.98	94.16
1	0.995651	18.095	0	18.10	93.5 *
W—HMPT; $T = 298.15$ K					
0	1.020170	175.661	0	14.4 *	175.7
0.11668	1.022477	156.870	−0.403	14.61	175.2
0.21062	1.024614	141.765	−0.704	14.73	174.8
0.29071	1.026460	128.933	−0.914	14.92	174.4
0.38269	1.028758	114.234	−1.118	15.15	173.8
0.50191	1.032606	95.198	−1.365	15.35	172.9
0.59917	1.036438	79.719	−1.517	15.54	171.9
0.70148	1.042758	63.421	−1.692	15.66	170.0
0.79743	1.045676	48.454	−1.538	16.14	168.1
0.89839	1.045130	32.908	−1.173	16.76	164.1
0.91075	1.041417	31.113	−1.022	16.95	164.2
0.91728	1.039966	30.144	−0.960	17.02	164.1
0.93022	1.036816	28.223	−0.843	17.16	163.6
0.94076	1.032517	26.696	−0.710	17.31	163.7
0.95089	1.029195	25.195	−0.614	17.42	163.2
0.96078	1.024243	23.761	−0.490	17.56	163.2
0.97025	1.018561	22.395	−0.362	17.70	162.8
0.98063	1.012729	20.872	−0.251	17.81	162.7
0.99067	1.004073	19.440	−0.101	17.97	164.8
1	0.997047	18.068	0	18.07	166 *

* Extrapolated data.

and

$$\phi_{v,2} = V_2^0 + \frac{V^E}{x_2} \tag{5}$$

V_M, V^E, $\phi_{v,w}$, $\phi_{v,2}$ values are reported in Table 1. V^E, $\phi_{v,w}$, $\phi_{v,2}$ of W—TMS and W—HMPT as a function of solvent composition are plotted in Figs. 1, 2 and 3, respectively. Mean molar heat capacities of W—TMS and W—HMPT mixtures are given in Table 2. Excess molar heat capacities C_p^E were calculated by using the equation

$$C_p^E = C_p - x_w C_{p,w}^0 - x_2 C_{p,2}^0 \tag{6}$$

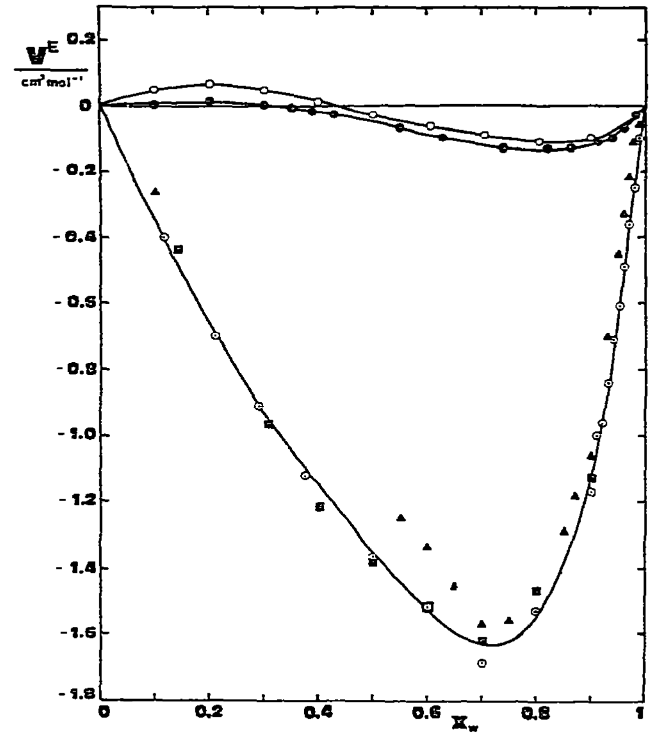

Fig. 1. Excess molar volumes of W—TMS and W—HMPT mixtures. W—TMS system: ○, present measurements; ●, Sciacovelli et al. [13]. W—HMPT system: ⊙, present measurements; ▪, Gall and Persin [14]; ▲, Kessler et al. [15].

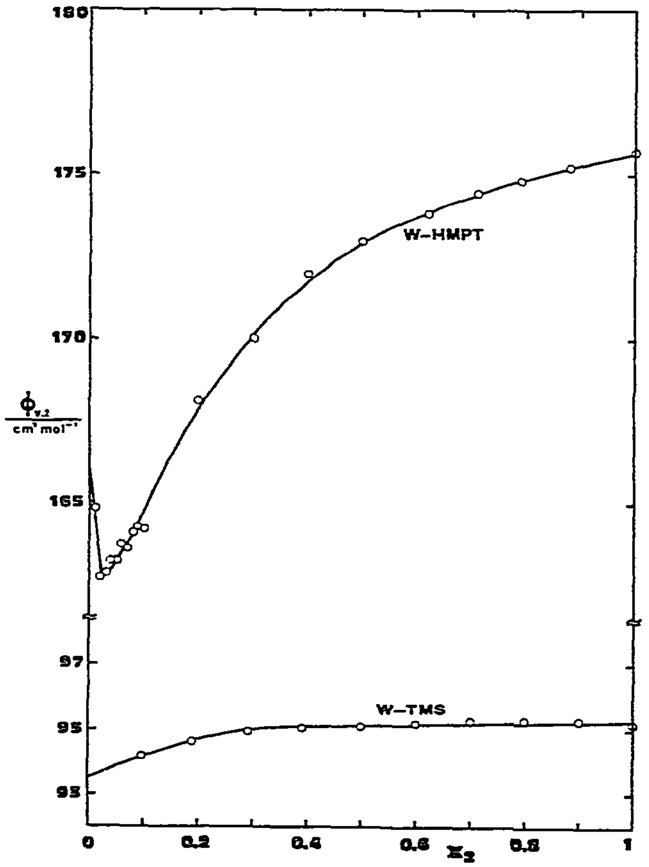

Fig. 2. Apparent molar volumes of sulfolane and HMPT in W—TMS and W—HMPT mixtures.

TABLE 2

Molar, excess molar and apparent molar heat capacities of W—TMS and W—HMPT mixtures

x_w	C_p (J K^{-1} mole^{-1})	C_p^E (J K^{-1} mole^{-1})	$\phi_{c,w}$ (J K^{-1} mole^{-1})	$\phi_{c,2}$ (J K^{-1} mole^{-1})
W—TMS; T = 303.15 K				
0	178.05	0	91 *	178.0
0.09998	169.36	1.59	91.14	179.8
0.19839	160.27	2.61	88.44	181.3
0.30332	150.87	3.99	88.44	183.8
0.40086	142.13	5.82	88.45	186.9
0.50410	131.87	5.63	86.44	189.4
0.60708	121.48	5.82	84.87	192.9
0.70744	110.58	5.23	82.68	195.9
0.80763	99.27	4.22	80.50	200.0
0.90380	87.96	2.80	78.37	207.1
1	75.28	0	75.28	220 *
W—HMPT; T = 298.15 K				
0	322.24	0	75 *	322.2
0.11668	294.00	0.58	80.21	322.9
0.21062	272.07	1.85	84.06	324.6
0.29071	254.04	3.59	87.63	327.3
0.38269	232.84	5.11	88.66	330.5
0.50191	205.33	7.04	89.32	336.4
0.59917	183.12	8.84	90.06	344.3
0.70148	158.99	9.97	89.51	355.6
0.79743	137.37	12.04	90.40	381.7
0.89839	114.04	13.65	90.49	456.6
0.91075	110.98	13.64	90.28	475.1
0.91728	109.68	13.96	90.52	491.0
0.93022	106.47	13.95	90.29	522.1
0.94076	103.75	13.82	89.99	555.5
0.95089	99.24	11.82	87.73	562.8
0.96078	95.29	10.30	86.02	584.9
0.97025	91.45	8.80	83.91	618.1
0.98063	85.86	5.78	81.20	620.7
0.99067	80.24	2.64	77.96	604.7
1	75.30	0	75.30	590 *

* Extrapolated data.

where $C^0_{p,w}$ and $C^0_{p,2}$ are the molar heat capacities of water and of organic solvent. $C^0_{p,w}$ values at 298.15 and 303.15 K were taken from the literature [10]. Apparent molar heat capacities were calculated from

$$\phi_{c,w} = C^0_{p,w} + \frac{C_p^E}{x_w} \tag{7}$$

and

$$\phi_{c,2} = C^0_{p,2} + \frac{C_p^E}{x_2} \tag{8}$$

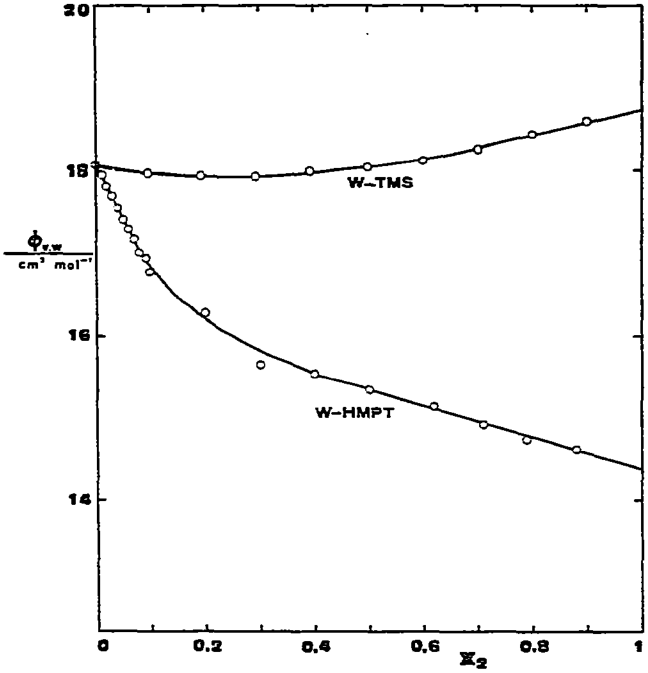

Fig. 3. Apparent molar volumes of water in W—TMS and W—HMPT mixtures.

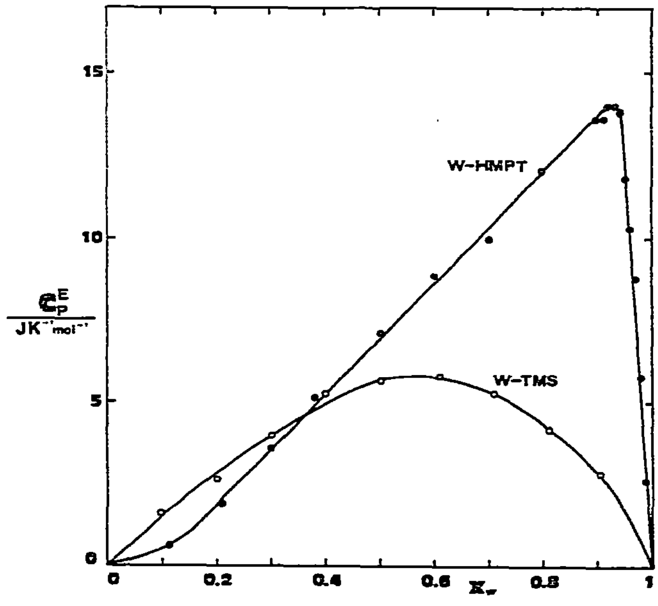

Fig. 4. Excess molar heat capacities of W—TMS and W—HMPT mixtures.

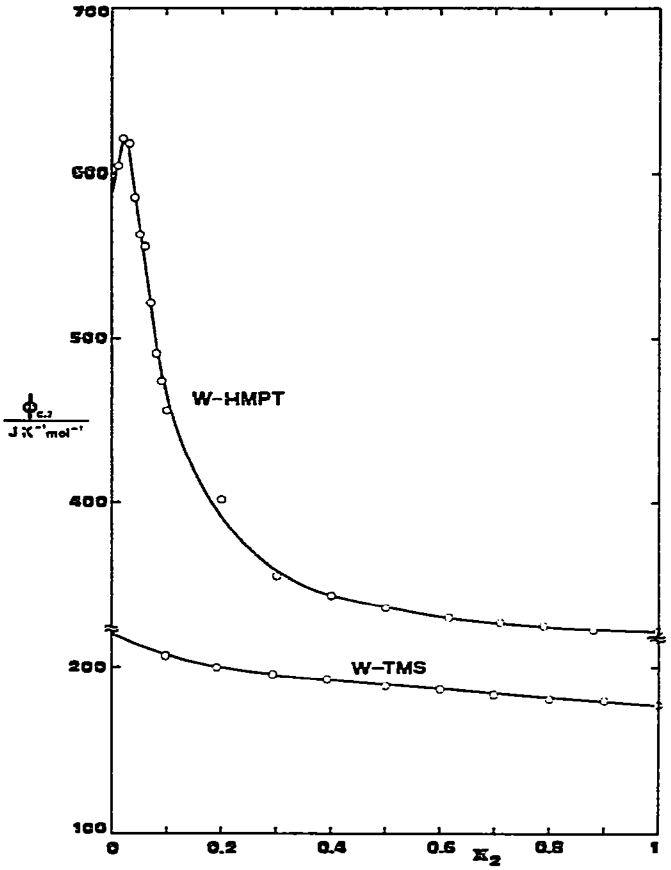

Fig. 5. Apparent molar heat capacities of sulfolane and HMPT in W—TMS and W—HMPT mixtures.

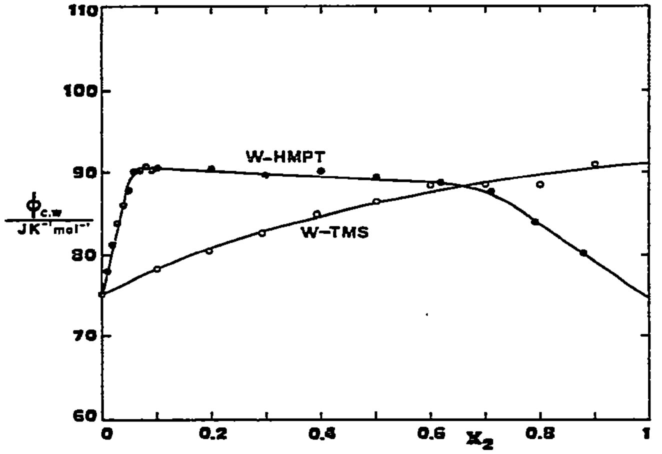

Fig. 6. Apparent molar heat capacities of water in W—TMS and W—HMPT mixtures.

C_p^E, $\phi_{c,w}$ and $\phi_{c,2}$ values are also given in Table 2 and plotted as a function of solvent composition in Figs. 4, 5 and 6, respectively.

DISCUSSION

Density measurements

The densities of pure sulfolane at 303.15 K and pure HMPT at 298.15 K can be favourably compared with the values 1.26227 [11] and 1.02009 [12] g cm^{-3} previously reported. Molar excess volumes calculated from density measurements of W—TMS mixtures at 303.15 K and W—HMPT mixtures at 298.15 K reported by other authors [13—15] are shown in Fig. 1 together with our data. V^E values for the W—TMS system are small, negative in water rich mixtures and positive in non-aqueous regions. The W—HMPT system shows V^E 10 times bigger than that of W—TMS and negative over the whole composition range, with a maximum at $x_w \sim 0.7$.

The experimental results were fitted by the polynomial form of the Redlich—Kister type

$$V^E = x_1 x_2 \sum_{j=1}^{n} A_j Z^{j-1} \tag{9}$$

with

$$Z = x_1^{1/2} \tag{10}$$

for water (1)—HMPT (2) mixtures, and

$$Z = x_1 - x_2 \tag{11}$$

for water(1)—TMS(2) mixtures.

The A_j values determined by the least-squares method are listed in Table 3 together with the standard deviation σ defined by

$$\sigma = [\Sigma(V^E_{\text{calc.}} - V^E_{\text{exp.}})^2/(N-n)]^{1/2} \tag{12}$$

where N is the number of points and n the number of coefficients of eqn. (9).

TABLE 3

Values of the least-squares parameters A_j in eqn. (9) and standard deviation σ of the molar excess heat capacities and of the molar excess volumes of the W—TMS and W—HMPT mixtures

System	Function	A_1	A_2	A_3	A_4	A_5	σ
W—TMS	V^E	−0.1145	−0.750	−0.200	−0.470	−0.781	0.001
W—TMS	C_p^E	23.74	7.231	−15.05	3.207	25.93	0.064
W—HMPT	V^E	0.7409	−22.72	24.46	19.91	−37.39	0.032

V^E trends in Fig. 1 show that interactions between water and HMPT are much stronger than those between water and sulfolane. However, as shown by Somsen and co-workers [16], better information on interactions in binary aqueous mixtures can be deduced from the shape of apparent molar volumes against solvent composition curves. As may be seen in Fig. 2, $\phi_{v,2}$ values for the W—HMPT system show a pronounced decrease starting from the value in pure HMPT with an accentuated minimum in the $0 \leqslant x_2 \leqslant 0.1$ range. $\phi_{v,2}$ values for the W—TMS system are almost constant around the pure TMS value and show a slight decrease in water-rich mixtures. $\phi^0_{v,2}$ values for HMPT and TMS, equal to 166 and 93.5 cm^3 mole^{-1}, respectively, have been calculated by extrapolation.

The trend of $\phi_{v,2}$ values for HMPT is very similar to that observed for strongly hydrophobic solutes like *t*-butylalcohol [17] and alkoxyethanols [18]. Thus increased water—water interactions at very low HMPT concentrations and strong water—HMPT interactions with a maximum at $x_w \sim 0.7$ can explain the $\phi_{v,2}$ and V^E trends for the W—HMPT system. On the contrary, the regular trend of $\phi_{v,2}$ for the W—TMS system, as the one seen for water—formamide [16] and water—acetonitrile mixtures [16], indicates that TMS gradually breaks down the water structure. Heats of mixing, very exothermic for W—HMPT [19] and endothermic for W—TMS [20], are in agreement with the interpretation of our results. It is also interesting to observe $\phi_{v,w}$ trends in the two systems under consideration. As can be seen in Fig. 3, $\phi_{v,w}$ decreases in W—HMPT up to the extrapolated value of 14.4 cm^3 mole^{-1}, while in W—TMS $\phi_{v,w}$ slightly increases to a value of 18.7 cm^3 mole^{-1}.

Somsen and co-workers [16], by taking into account the aqueous binary mixtures as a simple packing of molecules considered as hard spheres, have demonstrated that there exists a relation between $\phi^0_{v,w}$ values and the molar volume of the organic co-solvent. Thus water molecules strongly depolymerized in non-aqueous regions should be favourably inserted in the holes between the molecules of organic solvents with high molar volumes causing low $\phi^0_{v,w}$ values. In this light, the low $\phi^0_{v,w}$ value in W—HMPT seems reasonable, while the value observed in W—TMS seems abnormal, considering that the TMS molar volume (95.2 cm^3 mole^{-1}) is high.

Heat capacities measurements

As can be seen in Fig. 4, the trend of C_p^E as a function of water composition for the W—HMPT system, is characterized by a very accentuated maximum at $x_w \sim 0.9$. On the contrary, the C_p^E trend for the W—TMS system seems more regular. The "fitting" of the curves with a smoothing function as eqn. (9) did not give a satisfactory result for C_p^E of W—HMPT mixtures taking into account a reasonable number of coefficients. The coefficients of the fitting of C_p^E for W—TMS mixtures by eqns. (9) and (10) are reported in Table 3.

Calorimetric results (Fig. 4), as well as those from densimetry, indicate that W—HMPT interactions are much stronger than W—TMS interactions, as shown by higher C_p^E values for the former system than for the latter, and by the strong asymmetry of the curve which shows a maximum strongly shifted towards water-richer mixtures in the case of the W—HMPT system. The maximum in the $\phi_{c,2}$ curve in Fig. 5 in the water-rich region confirms that HMPT behaves like a strongly hydrophobic solute. As in the case of $\phi_{v,2}$ curves, $\phi_{c,2}$ curves show that TMS behaves in a much more regular manner than HMPT. In fact the $\phi_{c,2}$ curve for TMS increases regularly from 178 J K^{-1} $mole^{-1}$ in pure TMS to a value a little larger than 220 J K^{-1} $mole^{-1}$ in pure water obtained by extrapolation.

Unlike what is shown by the W—TMS system, the $\phi_{c,w}$ trend for the W—HMPT system also appears very irregular: $\phi_{c,w}$ increases suddenly in the $0 \leqslant x_2 \leqslant 0.1$ range, then it becomes nearly constant around 90 J K^{-1} $mole^{-1}$, to then decrease from $x_2 \sim 0.7$ up to the extrapolated value of about 75 J K^{-1} $mole^{-1}$ in pure water. $\phi_{c,w}$ values observed by us for our systems are very high and comparable to those of pure water, as has already been observed for other water—organic solvent systems [16].

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