Journal of Thermal Analysis and Calorimetry, Vol. 61 (2000) 637–647

EXCESS MOLAR ENTHALPIES AND EXCESS MOLAR VOLUMES OF (WATER+OCTAN-1-OL OR +OCTAN-2-OL) AT 298.15 K

L. Bernazzani, S. Cabani, G. Conti and V. Mollica[*]

Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa
Via Risorgimento 35 – 56126 Pisa, Italy

Abstract

The excess molar enthalpies and volumes have been determined for the binary system (water+octan-1-ol or +octan-2-ol) by means of direct calorimetric and densimetric measurements in the miscibility range. The experimental data were described through a Redlich–Kister type equation. For excess enthalpies a sigmoidal shape is predicted, while excess volumes are negative except for a little positive queue observed for (water+octan-1-ol) system at very low water content. Also the partial molar enthalpies of solution and the partial molar volumes of water in the two isomeric octanols at infinite dilution have been evaluated and discussed. A comparison is made between excess enthalpies and excess free energies calculated by the UNIFAC method.

Keywords: binary mixtures, excess enthalpies, excess volumes, octan-1-ol, octan-2-ol, water

Introduction

In the frame of a systematic investigation concerning the thermodynamic aspects of the partition process of organic compounds between water and octan-1-ol, we specifically investigated the role of water as cosolvent in the organic phase, by realising how dissolved water modulates the extracting ability of octan-1-ol [1, 2].

Moreover the results of previous studies allowed to recognize that the knowledge of the structure of water-saturated octanol solvent is fundamental to rationalize the complex phenomenology. In particular, calorimetric determinations of the limiting enthalpies of solution of several organic non-electrolytes in water/octanol mixtures at various composition enabled us to observe that a critical structural reorganization of the solvent has to occur at water mole fraction of about 0.08 [3, 4]. At lower concentration dissolved water is prevailingly in monomeric form, whereas beyond this value the water molecules aggregate to form clusters with high local organization.

In order to get further insight about this topic and to allow the development of a more realistic modellistic approach it is very important to achieve an accurate thermodynamic characterisation of the water+octan-1-ol binary mixture in the whole composition

---

[*] Author for correspondence. e-mail: vince@dcci.unipi.it

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

range. We report here excess molar enthalpies, H^E, and volumes, V^E, at 298.15 K for the systems water+octan-1-ol (1-OCT) and water+octan-2-ol (2-OCT), which has been investigated to get a term of comparison. Both the investigated binary mixtures show a very extended miscibility gap at 298.15 K, and namely from X_W=0.2633 [2] to nearly pure water (X_W=0.999926) [5] for W+1-OCT mixture, and from X_W=0.22 [6] again to nearly pure water (X_W=0.9994) [6] for W+2-OCT mixture. Only the alcohol rich region has obviously been investigated in present work. The values of the partial molar enthalpy of solution and partial molar volume of water in the isomeric alkanols are also reported. The experimental H^E data are discussed in relation to excess free energies obtained by the UNIFAC method.

Experimental

Materials

The solvents, octan-1-ol and racemic (±)-octan-2-ol, were Fluka products of purissimum grade (>99.5%). The used samples showed a GLC purity better than 99.7% and a water content <0.01%, determined by Karl Fischer titration; they were then stored over molecular sieves and used as such. Water was first deionised and then distilled from alkaline $KMnO_4$.

Calorimetric apparatus and procedure

Owing to the limited miscibility of the investigated systems and the very slow solubilisation which occurs even at very low water content, it is not possible to obtain direct measurements of the heats of mixing by means of a flow or a batch calorimeter. We then performed calorimetric dissolution experiments at 298.15 K with an isoperibol calorimeter already described [2], and equipped with a Hamilton automatic dispenser which allows consecutive injection of small amount of water in the vessel containing the organic solvent until the saturation is reached. With this procedure the thermal effect, q_i, measured for each water addition step allowed simultaneously to calculate the enthalpies of solution of water in the organic solvent, $\Delta_{soln}H$, as a function of the water concentration as well as the excess enthalpies of the binary water+organic solvent mixture:

$$\Delta_{soln}H=\frac{q_i}{n_{W,i}} \tag{1}$$

$$H^E=\frac{\sum_i q_i}{n_j+\sum_i n_{W,i}} \tag{2}$$

where n_j and $n_{W,i}$ are the moles of the solvent j and of water added during the i-th step, respectively. Because of the instrumental features and the way the determinations were performed, it was possible to estimate the maximum error on q_i quantity as high as 0.05 to 0.1 J which gave in the experimental conditions a maximum uncertainty of about 1% on both $\Delta_{soln}H$ and H^E. However, by considering the dispersion of the experimental points with respect to fitting curves, it is reasonable to assume the uncertainty of each point generally does not exceed 0.5%.

Density apparatus and procedure

Density measurements were carried out by means of an A. Paar vibrating-tube densimeter (Mod. 60/602) operating in the static mode at 298.15 K. Its precision is estimated to be better than $3\cdot10^{-3}$ kg m^{-3}. Temperature control inside the oscillating chamber, calibration, test of the apparatus, as well as measurements procedure were described in detail elsewhere [7, 8]. All mixtures, which were not degassed, were prepared by weighing. The uncertainty in the mole fraction of water, X_W, was estimated less than 0.0001. The apparent molar volumes of water, Φ_V, were calculated from the experimental density values of the binary mixtures, ρ, by the equation:

$$\Phi_V = \frac{M_W}{\rho} + \frac{(\rho_j - \rho)M_j}{\rho\rho_j}\,\frac{(1-X_W)}{X_W} \tag{3}$$

where M_W and M_j are the molecular masses of water and j solvent, respectively, and ρ_j is the density of the pure solvent. The excess molar volumes, V^E, of the binary mixtures were obtained by the equation:

$$V^E = \frac{X_W M_W + (1-X_W)M_j}{\rho} - \frac{X_W M_W}{\rho_W} - \frac{(1-X_W)M_j}{\rho_j} \tag{4}$$

where ρ_W is the density of pure water. The overall uncertainties in Φ_V and V^E due to density or mole fraction error were estimated to be less than 0.05 and 0.005 cm^3 mol^{-1}, respectively.

The densities of pure alkanols measured at 298.15 K were 0.82169 g cm^{-3} for octan-1-ol and 0.81633 g cm^{-3} for octan-2-ol.

Results and discussion

Experimental $\Delta_{soln}H$ values for dissolution of water in the isomeric alkanols as well as the corresponding H^E values are collected in Table 1. Both data series cover the whole miscibility range. In Fig. 1 the $\Delta_{soln}H$ values are plotted *vs.* the mole fraction of water. As it can be observed the trends are monotonically decreasing and are linear up to X_W=0.17 and X_W=0.1 in 1-OCT and 2-OCT, respectively.

By fitting our data to a linear equation as a function of X_W [$\Delta_{soln}H=\Delta_{soln}H°+bX_W$] in the linearity range, we find for octan-1-ol the values $\Delta_{soln}H°$(1-OCT)= 3.37±0.01 kJ mol^{-1} and $b=-13.1\pm0.1$ kJ mol^{-1}, and for octan-2-ol $\Delta_{soln}H°$(2-OCT)= 4.46±0.01 kJ mol^{-1} and $b=-18.7\pm0.2$ kJ mol^{-1}, where $\Delta_{soln}H°$ represents the limiting enthalpy of solution of water in the two solvents. Nilsson [9] reported the partial molar enthalpy of solution of water in octan-1-ol in the range $0.008<X_W<0.08$ showing that linearity was held in the explored field; he found the values $\Delta_{soln}H°$(1-OCT)=3.31±0.05 kJ mol^{-1} and $b=-12.1\pm0.5$ kJ mol^{-1}

which agree well with our results. No values have been found in literature for the W+2-OCT mixture; H^E data are also lacking for both investigated systems. The higher $\Delta_{soln}H°$ and H^E values found for W+2-OCT system with respect to W+1-OCT are however consistent with the literature excess enthalpies concerning binary mixtures of water+isomeric alkanols as, *f. i.*, 1- and 2- propanol or 1- and 2-butanol [9, 10].

Table 1 Partial molar enthalpies of solution of water, $\Delta_{soln}H$, and excess molar enthalpies, H^E, at 298.15 K

X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}	X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}	X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}
Water+octan-1-ol								
0.0040	3.29	13.1	0.1038	1.97	274.6	0.1855	0.99	381.2
0.0079	3.26	26.0	0.1070	2.00	280.7	0.1882	0.92	382.9
0.0118	3.25	38.7	0.1102	1.91	286.5	0.1908	0.95	384.8
0.0157	3.12	50.8	0.1134	1.84	292.0	0.1934	0.86	386.3
0.0196	3.14	62.9	0.1165	1.76	297.2	0.1971	0.86	388.1
0.0234	3.10	74.8	0.1196	1.79	302.4	0.1997	0.85	389.6
0.0272	3.04	86.3	0.1227	1.80	307.7	0.2024	0.81	391.0
0.0310	2.93	97.3	0.1258	1.66	312.4	0.2049	0.78	392.3
0.0347	2.92	108.2	0.1288	1.71	317.3	0.2075	0.77	393.5
0.0384	2.86	118.8	0.1318	1.64	321.9	0.2101	0.73	394.6
0.0421	2.81	129.1	0.1348	1.61	326.3	0.2126	0.71	395.6
0.0458	2.80	139.3	0.1378	1.60	330.7	0.2151	0.69	396.6
0.0494	2.70	149.0	0.1408	1.50	334.7	0.2177	0.64	397.3
0.0530	2.69	158.6	0.1437	1.51	338.7	0.2201	0.63	398.1
0.0565	2.65	168.0	0.1466	1.47	342.6	0.2226	0.63	398.8
0.0601	2.60	177.2	0.1495	1.37	346.1	0.2251	0.58	399.4
0.0636	2.54	186.0	0.1524	1.40	349.7	0.2275	0.56	399.9
0.0671	2.49	194.6	0.1553	1.37	353.1	0.2300	0.56	400.4
0.0706	2.48	203.0	0.1581	1.30	356.3	0.2324	0.55	400.9
0.0740	2.32	210.9	0.1609	1.28	359.4	0.2348	0.52	401.2
0.0774	2.40	219.0	0.1637	1.23	362.3	0.2372	0.47	401.4
0.0808	2.31	226.6	0.1665	1.18	365.0	0.2395	0.43	401.5
0.0842	2.30	234.2	0.1693	1.20	367.8	0.2419	0.43	401.6
0.0875	2.21	241.4	0.1720	1.12	370.3	0.2442	0.40	401.6
0.0908	2.20	248.5	0.1748	1.08	372.6	0.2465	0.37	401.5
0.0941	2.16	255.5	0.1775	1.07	374.9	0.2489	0.35	399.9
0.0974	2.07	262.0	0.1802	1.03	377.1	0.2512	0.35	399.8
0.1006	2.06	268.5	0.1828	1.03	379.2	0.2534	0.33	399.6

Table 1 Continued

X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}	X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}	X_W	$\Delta_{soln}H$/ kJ mol^{-1}	H^E/ J mol^{-1}
Water+octan-2-ol								
0.0039	4.41	17.4	0.0862	2.86	312.4	0.1570	1.92	468.3
0.0078	4.34	34.4	0.0895	2.84	321.5	0.1599	1.87	473.0
0.0117	4.26	50.9	0.0928	2.77	330.3	0.1627	1.84	477.5
0.0155	4.17	67.0	0.0960	2.71	338.8	0.1655	1.78	481.8
0.0193	4.10	82.7	0.0992	2.66	347.0	0.1683	1.74	486.0
0.0230	4.01	97.9	0.1024	2.60	355.0	0.1711	1.69	489.9
0.0268	3.95	112.7	0.1055	2.58	362.9	0.1739	1.67	493.8
0.0305	3.87	127.1	0.1087	2.51	370.5	0.1766	1.59	497.4
0.0342	3.81	141.2	0.1118	2.49	378.0	0.1793	1.57	500.9
0.0378	3.72	154.8	0.1150	2.44	385.2	0.1820	1.50	504.1
0.0415	3.65	168.1	0.1181	2.43	392.3	0.1847	1.46	507.2
0.0451	3.61	181.1	0.1213	2.40	399.3	0.1874	1.41	510.1
0.0486	3.55	193.8	0.1244	2.37	406.1	0.1900	1.39	512.9
0.0522	3.46	206.1	0.1274	2.34	412.8	0.1926	1.31	515.5
0.0557	3.43	218.1	0.1305	2.28	419.2	0.1953	1.22	517.7
0.0592	3.36	229.8	0.1335	2.21	425.4	0.1979	1.21	519.9
0.0627	3.28	241.1	0.1365	2.17	431.3	0.2004	1.14	521.9
0.0661	3.23	252.2	0.1395	2.12	437.1	0.2030	1.08	523.7
0.0695	3.19	263.0	0.1425	2.08	442.7	0.2056	1.02	525.2
0.0729	3.11	273.4	0.1454	2.06	448.1	0.2081	0.95	526.6
0.0763	3.06	283.6	0.1484	2.01	453.4	0.2106	0.88	527.7
0.0796	3.00	293.5	0.1513	1.98	458.5	0.2131	0.81	528.6
0.0829	2.94	303.1	0.1542	1.93	463.5			

Table 2 reports the Φ_V and V^E values of water in octan-1-ol and octan-2-ol determined in the composition range from pure alcohol to nearly saturated solution. Plots of Φ_V values *vs*. X_W are shown in Fig. 2. In both cases the apparent molar volumes show a linear decreasing (more pronounced for 1-OCT) with increasing water mole fraction up to $X_W \approx 0.05$. A linear extrapolation by a simple least-squares method gives values of partial molar volume at infinite dilution of water, in octan-1-ol $\bar{V}_W^{o}$=18.58 cm^3 mol^{-1}, and in octan-2-ol $\bar{V}_W^{o}$=18.06 cm^3 mol^{-1}. The former value agrees very well with the result by Berti *et al.* [8], while no literature data have been found for water in octan-2-ol. The smaller $\bar{V}_W^{o}$ values for water in secondary with respect to normal octanol agrees with similar results showed in 2-methylpropan-2-ol [11] with respect to isomeric butan-1-ol [12]. At higher water mole fraction the curves show a

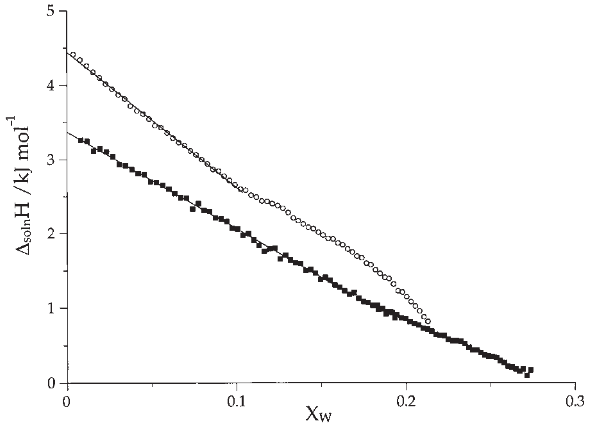

Fig. 1 Enthalpies of solution, $\Delta_{soln}H$, of water in octan-1-ol (■) and in octan-2-ol (o) *vs.* the mole fraction of water, X_W. Lines calculated by linear regression in the linearity ranges

variation of the slope much more sharp for 1-OCT, in which a plateau is attained at $\Phi_V \cong 18$ cm^3 mol^{-1}, very close to molar volume of pure water. This feature and the results of a X-ray diffraction analysis by Franck *et al.* [13] strongly support the hypothesis that water aggregates in clusters involving the –OH groups of octan-1-ol molecules, when X_W rises to over 0.05.

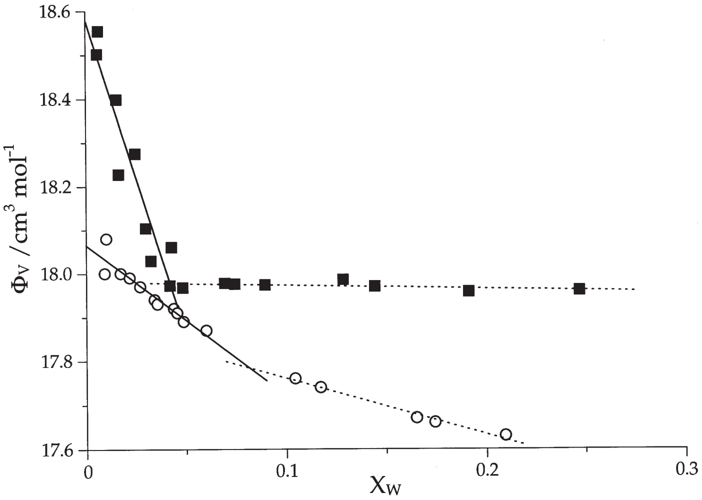

Fig. 2 Apparent molar volumes, Φ_V, of water in octan-1-ol (■) and in octan-2-ol (o) *vs.* the mole fraction of water, X_W. Solid lines calculated by least-squares fitting

Table 2 Apparent molar volumes of water, Φ_V, and excess molar volumes, V^E, at 298.15 K[a]

X_W	Φ_V	V^E	X_W	Φ_V	V^E	X_W	Φ_V	V^E
Water+octan-1-ol								
0.0058	18.50	0.0025	0.0324	18.03	–0.0013	0.0744	17.98	–0.0069
0.0064	18.55	0.0031	0.0419	17.97	–0.0040	0.0894	17.97	–0.0085
0.0154	18.40	0.0051	0.0427	18.06	–0.0003	0.1285	17.99	–0.0107
0.0163	18.23	0.0026	0.0484	17.97	–0.0049	0.1444	17.97	–0.0142
0.0246	18.27	0.0051	0.0552	18.05	–0.0011	0.1913	17.96	–0.0212
0.0298	18.10	0.0011	0.0693	17.98	–0.0063	0.2468	17.96	–0.0265
Water+octan-2-ol								
0.0092	18.00	–0.0007	0.0355	17.93	–0.0048	0.1171	17.74	–0.0385
0.0101	18.08	0.0001	0.0438	17.92	–0.0066	0.1651	17.67	–0.0658
0.0171	18.00	–0.0012	0.0455	17.91	–0.0071	0.1743	17.66	–0.0707
0.0217	17.99	–0.0017	0.0487	17.89	–0.0087	0.2094	17.63	–0.0916
0.0269	17.97	–0.0025	0.0600	17.87	–0.0120			
0.0341	17.94	–0.0044	0.1043	17.76	–0.0318			

[a] Φ_V and V^E in cm^3 mol^{-1}

Both H^E and V^E excess properties were fitted to a polynomial Redlich–Kister (R–K) equation:

$$Y^E = X_W(1-X_W)\sum_{k=0}^{n} A_k(1-2X_W)^k \quad (Y=H,\ V) \tag{5}$$

Equation (5) furnishes the corresponding excess property in the whole composition range and hence also inside the miscibility gap where it has no significance. Furthermore, some difficulties arise in setting up the fitting procedure when data at disposal refer to a small composition range. Nevertheless when data are fitted to Eq. (5) an important constraint condition can be imposed regarding the limiting excess property when $X_W \to 1$. In fact we have from the relation between limiting enthalpy of solution and excess enthalpy:

$$\Delta_{\mathrm{soln}}H^{\mathrm{o}}(\mathrm{w}) = \lim_{X_W \to 1}\frac{H^E}{(1-X_W)} = \sum_{k=0}^{n} A_k(-1)^k \tag{6}$$

where $\Delta_{\mathrm{soln}}H^{\circ}(\mathrm{w})$ is the enthalpy of solution at infinite dilution of the alkanol in water. In similar way we obtain for the relation between limiting partial molar volume and excess volume:

$$\overline{V}_j^{\mathrm{o}} - V_j^{\mathrm{o}} = \sum_{k=0}^{n} A_k(-1)^k \tag{7}$$

where $\overline{V}_j^o$ and V_j^o are the partial molar volume at infinite dilution of the alkanol in water and its molar volume, respectively. The condition (6) and (7) can be introduced in the least-squares procedure as a linear constraint by means of the undetermined multipliers method by Lagrange. Experimental values of $\Delta_{soln}H°(w)$ for 1-OCT and 2-OCT, as well as $\overline{V}_j^o$ for 2-OCT, are unfortunately lacking, but they can be estimated with good accuracy by the group contributions method to the thermodynamic properties in water by Cabani *et al*. [14] whose reliability has been widely shown. Limiting enthalpies of solution in water can then be calculated by: $\Delta_{soln}H°(w)= \Delta_{solv}H°(w)+ \Delta_{vap}H°$, where limiting enthalpies of solvation in water, $\Delta_{solv}H°(w)$, are calculated according to the group contributions by Cabani, and the vaporisation enthalpies, $\Delta_{vap}H°$, are taken from literature sources or calculated by the Ducros method [15]. Data used for calculation of fitting constraints are summarised in Table 3.

Table 3 Values used to set up the constraint conditions of Eqs (6) and (7)

	$\Delta_{soln}H°(w)$[a]	$\overline{V}_j^o - V_j^o$[b]
octan-1-ol	–4.34[c]	–9.39[e]
octan-2-ol	–4.33[d]	–9.93[f]

[a] $\Delta_{soln}H°(w)=\Delta_{solv}H°(w)+\Delta_{vap}H°$

[b] V_j^o calculated from the experimental densities of pure solvents

[c] $\Delta_{solv}H°(w)$ value (–75.32 kJ mol^{-1}) calculated by group contributions ([14]); $\Delta_{vap}H°$=70.98 kJ mol^{-1} from [16]

[d] $\Delta_{solv}H°(w)$ value (–74.3 kJ mol^{-1}) calculated by group contributions ([14]); $\Delta_{vap}H°$=69.97 kJ mol^{-1} calculated by group contributions by Ducros [15]

[e] $\overline{V}^o_{1-OCT}$=149.1 cm^3 mol^{-1} from [17]; V^o_{1-OCT}=158.49 cm^3 mol^{-1}

[f] $\overline{V}^o_{2-OCT}$=149.6 cm^3 mol^{-1} calculated by group contributions ([14]); V^o_{2-OCT}=159.53 cm^3 mol^{-1}

Table 4 Parameters of Eq. (5) for excess enthalpies and volumes of water+C8-alkanols mixtures

Property	Mixture	A_0	A_1	A_2	A_3	σ[a]
H^E/J mol^{-1}	1-oct+w	420.28	3885.0	–875.32		0.98
	2-oct+w	949.56	4384.8	–894.78		0.90
V^E/cm^3 mol^{-1}	1-oct+w	–0.6009	2.3563	–4.0586	2.3742	0.0027
	2-oct+w	–1.3932	2.7755	–3.5666	2.1957	0.0003

[a] Standard deviation of the fit

Table 4 reports the regression parameters of fittings to Eq. (5) for the examined systems of both considered excess properties. As regards the enthalpies, a three-parameter R–K equation was sufficient in order to get a reliable description of experimental data. In fact a F-test procedure applied to the fittings to either three or four parameters R–K equation gave similar results for both 1-OCT and 2-OCT. On the contrary, for the excess volumes four parameters were required in order to adequately fit the data. In Fig. 3 experimental H^E values plotted *vs*. the mole fraction of water are compared with trends calculated according to Eq. (5). In Fig. 4 the same comparison is made for excess volumes, V^E.

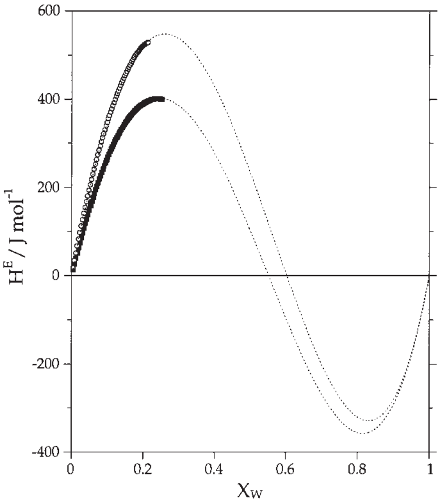

Fig. 3 H^E plots for the binary systems W+1-OCT (■) and W+2-OCT (o). Lines represent best-fitting curves

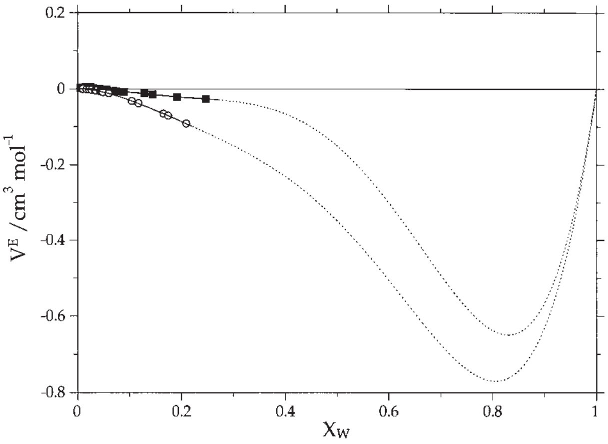

Fig. 4 V^E plots for the binary systems W+1-OCT (■) and W+2-OCT (o). Lins represent best-fitting curves

An attempt to interpret the complex phenomenology which leads to phase demixing in the two systems can be developed by comparing the trends of the excess enthalpies with those of the excess free energies and by calculating the entropic contribution. The experimental excess free energies are only available for W+1-OCT system in the range $0.02<X_W<0.14$ by processing the VLE data by Berti *et al.* [18], but a reliable estimation can be achieved by applying one of the well known group contributions methods like UNIFAC. In Fig. 5 the excess thermodynamic functions G^E, H^E, and TS^E for W+1-OCT or 2-OCT are plotted *vs.* X_W. The G^E functions are cal-

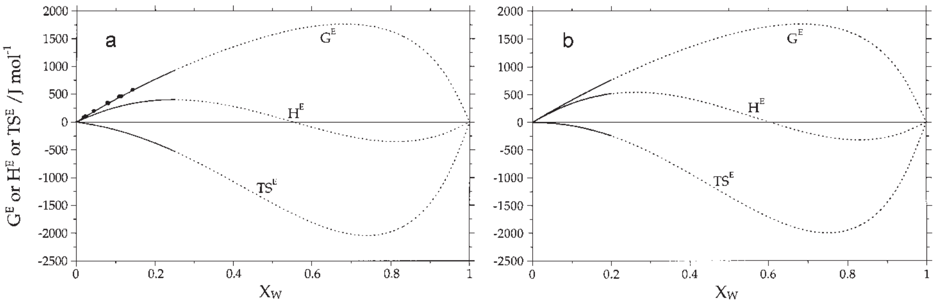

Fig. 5 Excess thermodynamic properties for the binary systems W+1-OCT (a) and W+2-OCT (b). (•) G^E values calculated from [18]

culated with the UNIFAC method (Dortmund form) according to Tiegs *et al.* [19] The reliability of the method is confirmed by comparing the calculated trend with the experimental data of Berti for the W+1-OCT mixture [18]. The H^E functions represent the experimental data fitted to Eq. (5), and, finally, TS^E are the entropic terms. In both cases the G^E functions are always positive showing a pronounced maximum at $X_W \cong 0.7$. However, if the free energy of mixing is calculated by adding to G^E the ideal term, a binodal curve is obtained which presents two minima, at $X_W \cong 0.2$ and $X_W > 0.99$, corresponding to the boundaries of the miscibility gap. The comparison between H^E and TS^E functions for each system shows that the entropic term rules the phase demixing. In particular for the W+1-OCT mixture the H^E term reaches the maximum value at $X_W \cong 0.25$, *i. e.*, slightly below the solubility limit. The entropic term is always negative and the more it decreases the higher is the water content in the mixture. This result is strictly consistent with our hypothesis that the structural organization of the mixture increases with the water content up to saturation. A similar behaviour is also showed by the W+2-OCT mixture where a more significant unfavourable enthalpic effect is recognizable.

* * *

This work has been supported by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Cofin97 MURST CFSIB) and by Consiglio Nazionale delle Ricerche (C.N.R. Roma).

References

1 S. Cabani, G. Conti, V. Mollica and L. Bernazzani, J. Chem. Soc., Faraday Trans., 87 (1991) 2433.
2 L. Bernazzani, S. Cabani, G. Conti and V. Mollica, J. Chem. Soc., Faraday Trans., 91 (1995) 649.
3 L. Bernazzani, S. Cabani, G. Conti and V. Mollica, Thermochim. Acta, 269/270 (1995) 361.
4 L. Bernazzani, S. Cabani, G. Conti and V. Mollica, J. Solution Chem., 29 (2000) 389.
5 A. Apelblat, Ber. Bunsenges. Phys. Chem., 87 (1983) 2.
6 A. F. M. Barton, Solubility Data Series, IUPAC, Pergamon Press, Oxford, 1984, Vol. 15.

7 L. Lepori, M. Mengheri and V. Mollica, J. Phys. Chem., 87 (1983) 3520.
8 P. Berti, S. Cabani and V. Mollica, Fluid Phase Equil., 32 (1987) 195.
9 S.-O. Nilsson, J. Chem. Thermodynamics, 18 (1986) 1115.
10 J. Christensen, J. Gmehling, P. Rasmussen and J. Weidlich, Heats of Mixing, Data Collection, Binary Systems, Chemistry Data Series, Vol. III, Part 1, Schön and Wetzel, Frankfurt/Main 1984.
11 L. A. K. Staveley and B. Spice, J. Chem. Soc., (1952) 406.
12 A. D'Aprano, I. D. Donato, E. Caponetti and V. Agrigento, Gazz. Chim. Ital., 108 (1978) 601.
13 N. P. Franks, M. H. Abraham and W. R. Lieb, J. Pharm. Sci., 82 (1993) 466.
14 S. Cabani, P. Gianni, V. Mollica and L. Lepori, J. Solution Chem., 10 (1981) 563.
15 M. Ducros, J. F. Gruson, H. Sannier and J. Velasco, Thermochim. Acta, 44 (1981) 131.
16 V. Majer and V. Svoboda, Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series, Blackwell, Oxford, 1985.
17 Y. Kita and K. W. Miller, Biochemistry, 21 (1982) 2840.
18 P. Berti, S. Cabani, G. Conti and V. Mollica, J. Chem. Soc. Faraday Trans. I, 82 (1986) 2547.
19 D. Tiegs, J. Gmehling, P. Rasmussen and A. Fredenslund, Ind. Eng. Chem. Res., 26 (1987) 159.