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Thermodynamics of the solvation of non-electrolytes in C8 monofunctional organic solvents☆

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Abstract

Some results are reported concerning the enthalpies of solvation ($\Delta_{\mathrm{solv}}H^0$) of some hydrocarbons (hexane, cyclohexane), ethers (tetrahydrofuran), ketones (cyclopentanone, pentan-3-one), alcohols (butan-1-ol, butan-2-ol), and water in octan-2-ol and hexylacetate. The $\Delta_{\mathrm{solv}}H^0$ values were calculated by combining the calorimetric heats of solution here determined with the known enthalpies of vaporisation.

In the investigated solvents, the enthalpies of solvation become less negative going from alcohols to ketones to ethers and to hydrocarbons. As regards alcohols and ketones, the $\Delta_{\mathrm{solv}}H^0$ values are more differentiated in octan-2-ol than in hexylacetate. This reflects the different nature of the two solvents, amphiprotic the former and hydrogen bond acceptor the latter. The results are interpreted in terms of specific solute–solvent interactions. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Enthalpies of solution; Enthalpies of solvation; Octan-2-ol; Hexylacetate; Alcohols; Ketones; Ethers

1. Introduction

Since the pioneering work of Hansch [1] it has been assumed that the octan-1-ol/water partitioning forms a reasonably general model for the passive transport process of a molecule across a biological membrane. In particular, octanol/water partition coefficients (P_{ow}) of a lot of organic compounds have been largely investigated leading to use these quantities as a measure of the lipophilicity of the solutes. Since cell membranes exhibit different physico-chemical properties according to their nature and the physiological process they are involved in, it has been argued that the "general purpose" P_{ow}-based definition of lipophilicity could be refined to account for the different biophysical characteristics of membranes themselves. In this regard, it has recently been proposed that four types of solvent are needed to model the partitioning of solutes into membranes [2]. This so called "critical quartet" is comprised of an amphiprotic solvent, such as octan-1-ol, an inert one (n-alkane), a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA).

In recent years, we have investigated the thermodynamics of solvation of mono- and bi-functional saturated non-electrolytes in octan-1-ol (1-OCT) [3–5] by determining the Gibbs energy and enthalpy

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changes associated to this process. These quantities, combined with the corresponding ones in water, were used to calculate the standard thermodynamic functions related to the ideal transfer process from pure water to anhydrous 1-OCT in which the two solvents were considered as completely immiscible in each other. The obtained results allowed us to evaluate the relative importance of the enthalpic and entropic terms in determining the partitioning of the organic solutes between water and 1-OCT [4].

As a part of a planned study on the thermodynamics of solvation of non-electrolytes in non-aqueous C8 solvents with different HBA and HBD characteristics, we report in this paper some preliminary results concerning the enthalpies of solvation ($\Delta_{\mathrm{solv}}H^0$) of some hydrocarbons (*n*-hexane, cyclohexane), ethers (tetrahydrofuran), ketones (cyclopentanone, pentan-3-one), alcohols (butan-1-ol, butan-2-ol), and water in octan-2-ol (2-OCT) and hexylacetate (HAC), as amphiprotic or HBA solvents, respectively. 2-OCT was chosen in order to investigate the shielding effect of the functional –OH group due to the secondary position with respect to 1-OCT. The isomerism should also result in a different ability of the two alkanols to produce locally organised structure which, in turn, affect the environment experienced by the solute molecules. The HAC solvent was chosen because of its chemical stability, its low water content at saturation, and the polarity of the alkoxy group.

2. Experimental

2.1. Materials

2-OCT solvent was a Fluka commercial product of stated purity ~98%. It was refluxed and distilled over metallic sodium and stored over 4 Å molecular sieves. The purity of used samples, tested by GLC analysis, resulted >98.7% and the water content, as determined by Karl Fisher titration, was ≤0.01%. The still remaining impurities were identified by MASS-GC as isomeric alkanols (mainly octan-3-ol and octan-4-ol). Under these conditions, it was estimated that errors on the calorimetric determinations due to the impurity of the solvent did not exceed 0.1/0.2%, within the experimental uncertainty. The samples were then used without further purification.

HAC was a Fluka product of stated purity ~99%. The used samples, stored over 4 Å molecular sieves, showed a GLC purity >99.3% and a water content ≤0.01%.

All other organic compounds were Fluka or Carlo Erba commercial products of the best grade available. Their GLC purity was ≥99.5% in all cases and the water content was ≤0.02%. They were used without further purification.

Water was first deionised and then distilled from alkaline $KMnO_4$.

2.2. Apparatus and measurements

The calorimetric measurements of heats of solution were performed with an *iso*-peribol calorimeter built for this purpose and already described [6]. For each compound and for each solvent at least 20 measurements were carried out with the mole fraction of the solutes ranging from 0.001 to 0.03. For all examined compounds, except water in HAC, the experimental heats of solution ($\Delta_{\mathrm{soln}}H$) showed a linear trend when plotted versus the mole fraction of the solute, X_S. This allowed us to linearly extrapolate the $\Delta_{\mathrm{soln}}H$ values in order to obtain the limiting enthalpies of solution. By evaluating all the sources of error, the maximum uncertainty affecting the experimental heats of solution and the corresponding X_S values can be estimated as large as 0.08 kJ mol^{-1} and 1×10^{-5}, respectively. However, the uncertainty of the limiting enthalpies of solution was usually lower than 0.05 kJ mol^{-1}.

In Fig. 1, the experimental $\Delta_{\mathrm{soln}}H$ values are plotted against the mole fraction X_S for all investigated organic solutes in 2-OCT and HAC. The figure also reports the fitting straight lines obtained by a least squares application.

For water in HAC only 11 measurements were carried out because of the attaining of the saturation limit ($X_S \approx 0.05$) [7]. In this case, the $\Delta_{\mathrm{soln}}H$ values sharply deviate from the linearity at $X_S > 0.025$ (see Fig. 1b). An analogous dependence of enthalpy of solution on X_S has also been found by Nilsson for water in several esters [8].

The $\Delta_{\mathrm{soln}}H$ values for tetrahydrofuran in *n*-octane (OCT) have also been determined in the range $0 < X_S < 0.035$ with the same experimental procedure, and a limiting value $\Delta_{\mathrm{soln}}H^0 = 3.12 \pm 0.01$ kJ mol^{-1} was obtained.

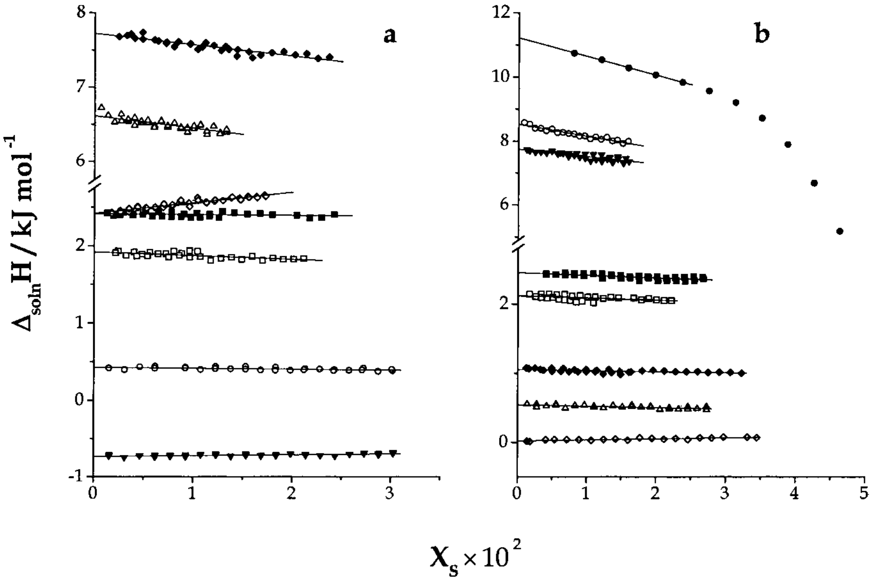

Fig. 1. Experimental $\Delta_{soln}H$ vs. the solute mole fraction X_S, in: **a**, 2-OCT; **b**, HAC. Solutes: (□) hexane; (■) cyclohexane; (◇) tetrahydrofuran; (△) pentan-3-one; (◆) cyclopentanone; (▼) butan-1-ol; (○) butan-2-ol; (●) water.

3. Results and discussion

In Table 1, the values of the enthalpy of solution at infinite dilution ($\Delta_{soln}H^0$) for the investigated solutes in 2-OCT and HAC are summarised with the values of the *b* slopes of the fitting straight lines. To the best of our knowledge, no comparable data of $\Delta_{soln}H^0$ are reported in literature for the examined systems.

The enthalpies of solvation of the solutes $\Delta_{solv}H^0$, calculated by combining the experimental $\Delta_{soln}H^0$ values with the corresponding standard enthalpies of vaporisation $\Delta_{vap}H^0$, are reported in Table 2. In the same table, the $\Delta_{solv}H^0$ values in 1-OCT, in OCT and in hexadecane (HDE) for the same set of compounds are also reported.

Some general features of the observed phenomenology emerge from the analysis of Fig. 2, where the values of the enthalpy of solvation and of vaporisation of Table 2 are reported. As a first remark, the $-\Delta_{vap}H^0$ values set roughly represents the lower boundary of

Table 1
Standard enthalpies of solution $\Delta_{soln}H^0$, in 2-oct and HAC and slopes of the fitting lines *b*, at 298.15 K[a]

Compound	2-OCT		HAC	
	$\Delta_{soln}H^0$	*b*	$\Delta_{soln}H^0$	*b*
Hexane	1.92 ± 0.01	−4.7 ± 0.9	2.14 ± 0.01	−3.8 ± 0.6
Cyclohexane	2.41 ± 0.01	−1.1 ± 0.8	2.45 ± 0.01	−3.8 ± 0.6
Tetrahydrofuran	2.42 ± 0.01	13.8 ± 0.8	0.022 ± 0.005	1.5 ± 0.2
Pentan-3-one	6.62 ± 0.01	−16.6 ± 1.9	0.55 ± 0.01	−2.1 ± 0.4
Cyclopentanone	7.72 ± 0.02	−15.2 ± 1.2	1.06 ± 0.01	−1.7 ± 0.4
Butan-1-ol	−0.74 ± 0.01	1.2 ± 0.2	7.74 ± 0.03	−23.6 ± 2.8
Butan-2-ol	0.43 ± 0.01	−1.3 ± 0.3	8.54 ± 0.02	−38.7 ± 2.1
Water	4.46 ± 0.01[b]	−18.7 ± 0.2[b]	11.22 ± 0.02	−58.5 ± 0.9

[a] Data in kJ mol^{-1}. From this work if not otherwise specified.
[b] Taken from [9].

Table 2
Enthalpies of vaporisation $\Delta_{\mathrm{vap}}H^0$, and of solvation $\Delta_{\mathrm{solv}}H^0$, in 2-OCT, HAC, 1-OCT, OCT, and HDE at 298.15 K[a]

Compound	$\Delta_{\mathrm{vap}}H^0$[b]	$\Delta_{\mathrm{solv}}H^0$[c]				
		2-OCT[d]	HAC[d]	1-OCT[e]	OCT[f]	HDE[g]
Hexane	31.73	−29.81	−29.59	−30.97	−31.72	−31.05
Cyclohexane	33.12	−30.71	−30.67	−31.62	−32.55	−31.51
Tetrahydrofuran	32.16	−29.74	−32.14	−28.07	−29.04	−28.53
Pentan-3-one	38.68	−32.06	−38.13	−31.76	−32.80	
Cyclopentanone	42.77	−35.05	−41.71	−34.38	−36.66	
Butan-1-ol	52.42	−53.16	−44.68	−51.96	−28.53	−28.07
Butan-2-ol	49.81	−49.38	−41.27	−49.38		
Water	44.01	−39.55	−32.79	−40.64	−33.60	−35.31

[a] Data in kJ mol^{-1}.

[b] Taken from [10].

[c] Calculated by $\Delta_{\mathrm{solv}}H^0 = \Delta_{\mathrm{soln}}H^0 - \Delta_{\mathrm{vap}}H^0$ except for HDE; $\Delta_{\mathrm{soln}}H^0$ values taken from the quoted references.

[d] $\Delta_{\mathrm{soln}}H^0$ from Table 1.

[e] $\Delta_{\mathrm{soln}}H^0$ from [5] except for cyclopentanone [4] and water [9].

[f] $\Delta_{\mathrm{soln}}H^0$ values calculated as $\lim_{x\to 0} H^E/x(x-1)$ except for tetrahydrofuran ($\Delta_{\mathrm{soln}}H^0 = 3.12 \pm 0.01$ kJ mol^{-1} this work) and water [11]; excess enthalpies taken from [12,13].

[g] Taken from [14].

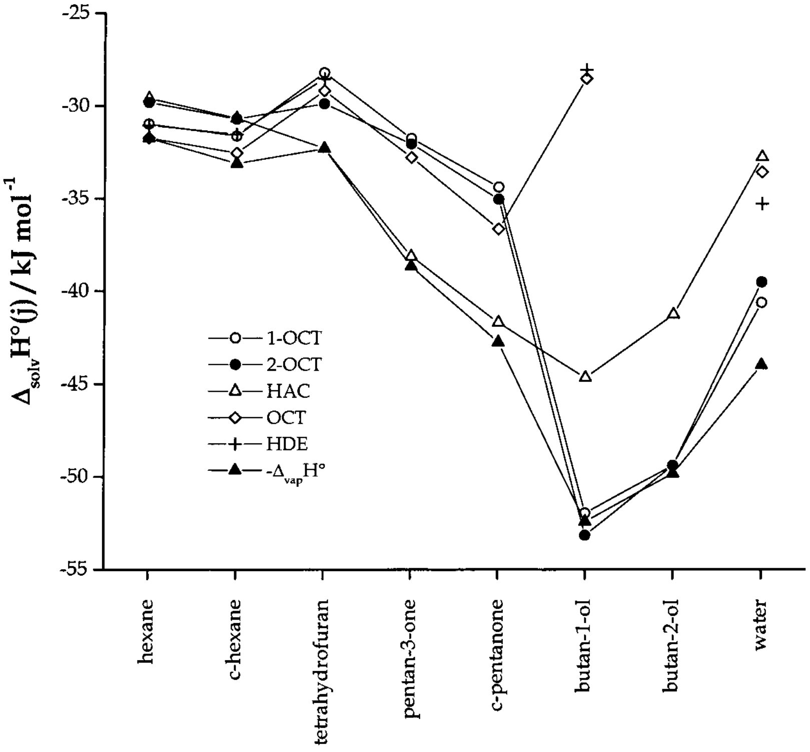

Fig. 2. Enthalpies of vaporisation $\Delta_{\mathrm{vap}}H^0$, and of solvation $\Delta_{\mathrm{solv}}H^0$(j), of the investigated solutes in 1-OCT, 2-OCT, HAC, OCT, and HDE.

the plotted data: this means in practice the solute molecules interact with the solvent more weakly than (or at most as well as) they do with themselves in the state of pure liquid. In the series of investigated compounds, the enthalpies of solvation in 1-OCT and 2-OCT show nearly overlapping values with differences not exceeding 1.7 kJ mol^{-1}. Furthermore, the $\Delta_{\mathrm{solv}}H^0$ values in the completely apolar solvents OCT and HDE are very close to those in the isomeric octanols for all solutes except the hydrogen bond donor ones (water, butan-1-ol, butan-2-ol). On the contrary, HAC shows specific enthalpic effects depending on the polarity and the nature of the functional group of the solutes. In other words, while the isomeric octanols behave towards the solutes like an alkane, HAC is the most effective, among the examined solvents, in recognising the non-HBD solutes. In particular, the enthalpies of solvation in HAC of tetrahydrofuran, pentan-3-one and cyclopentanone nearly coincide with the corresponding $-\Delta_{\mathrm{vap}}H^0$ values, thus indicating that these solutes in HAC are involved in a framework of interactions equivalent to that in their pure liquid.

A completely different situation emerges when HBD solutes are considered. Butan-1-ol appears to be the most effective solute in recognising the chemical environment surrounding it, with enthalpic values ranging from approximately -28 kJ mol^{-1} for solvation in alkanes to -52.42 kJ mol^{-1} for vaporisation and to -53.16 kJ mol^{-1} for solvation in 2-OCT. As a matter of fact, isomeric butanols show enthalpy changes connected with the solvation process in both 1-OCT and 2-OCT that roughly match the corresponding $-\Delta_{\mathrm{vap}}H^0$ values, while in the alkanes, the solvation effect is nearly a half. Actually, the $\Delta_{\mathrm{solv}}H^0$ values of butan-2-ol in OCT and HDE are lacking, but the corresponding ones in both *n*-hexane and *n*-heptane are about -26 kJ mol^{-1}, thus supporting the previous observation. The comparison of the enthalpies of solvation of butan-1-ol and butan-2-ol in the isomeric octanols suggests that only the isomerism of the solute molecule is significant.

The behaviour of water is noteworthy. As it can be observed the values of the enthalpy of solvation of water in all compared solvents are fairly well distinguished. It is well known that water is a very effective solvent in recognising the solutes according to their functional group [15]. The plotted data show that water is still effective in recognising the polar groups when is present in low concentration, i.e. when is considered as a solute.

The so far developed comparisons sketch a merely qualitative rationale of the observed phenomenology and any further interpretation of the data set should account at least for the different sizes of the solute molecules. At this regard, we can assume that the solvation process can be divided in two steps reflecting (a) the formation in the solvent of a cavity with a suitable size to host the solute molecule and (b) the switching on of the solute–solvent interactions. It can be easily argued that, from an enthalpic point of view, solute–solvent interactions for completely apolar solutes are mainly related to dispersive interactions with the hydrocarbon portion of the solvent. Therefore, the interaction effect should be nearly the same in all considered hydrocarbon–solvent systems. If this hypothesis is correct, the enthalpies of solvation of hydrocarbons in different solvents should be mainly related to the different cavitation enthalpies, and hence to the different cohesive energies of each solvent. However, the hydrocarbons (*n*-hexane and cyclohexane) show $\Delta_{\mathrm{solv}}H^0$ values lying at about -30 kJ mol^{-1} in all compared solvents independently on their nature leading to the conclusion that also the cavitation term should be nearly the same. In other words, the difference between the enthalpies of solvation of a monofunctional compound in different solvents reflects the difference of specific interactions involving the polar centres of both solute and solvent.

In order to evaluate the enthalpic effect connected to these interactions, we subtract out from the experimental $\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ value of each solute in the j solvent, the corresponding value of $\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ for a hypothetical hydrocarbon of the same structure (cyclic or acyclic) and intrinsic volume of the solute itself. The so calculated quantities $\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ have the advantage to be independent of the size of the solute and of the cohesive energies of the solvent. Obviously, this is a quite rough model and an accurate study of the enthalpies of solvation in homologous series of compounds and in each solvent would be necessary. Fig. 3 shows the $\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ values for the investigated monofunctional solutes in OCT, HAC, 1-OCT and 2-OCT.

As it can be observed the examined solvents show different abilities in discriminating solutes belonging

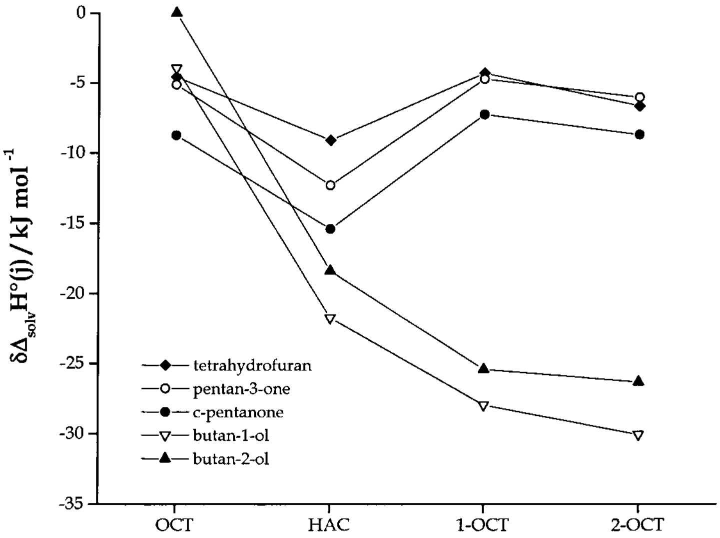

Fig. 3. $\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ quantities (see text) for monofunctional solutes in OCT, HAC, 1-OCT, and 2-OCT.

to different classes. This evidence clearly emerges if we compare the behaviour of HBD and non-HBD solutes. In fact, while the isomeric octanols are the most effective in differentiating these two classes of solutes ($\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ values for alkanols are as larger as four times the corresponding ones for ketones or tetrahydrofuran), this ability reduces in HAC and practically disappears in OCT. This behaviour also reflects the ability of isomeric octanols to act as hydrogen bond donors as well as acceptors towards –OH group of the solute molecule. On the other hand, HAC shows the highest affinity towards carbonyl group and is the only solvent able to differentiate all considered solutes, with $\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ values fairly equally spaced. The comparison between the $\delta\Delta_{\mathrm{solv}}H^0(\mathrm{j})$ values of butan-1-ol and butan-2-ol as well as of pentan-3-one and cyclopentanone in each solvent shows that the entity of the interaction is strongly influenced by the accessibility of the functional group of both solute and solvent. In fact, the cyclic and primary structures allow stronger interactions than acyclic and secondary ones, respectively.

The whole set of enthalpic data seems to indicate that the phenomenology of the solvation process is determined by the hydrocarbon unit–solvent interactions and by the polar group–solvent interactions, the former being of the same entity for all the studied solvents, the latter depending on the nature of the functional groups of the two components and on their mutual accessibility. Obviously, the entropy changes associated to this process should be also taken into account. An analogous investigation carried out in 1-OCT showed that significant enthalpy–entropy compensation occurs [4]. A thorough analysis of the enthalpic and entropic effects will be done as soon as the Gibbs energies of solvation in 2-OCT and HAC are available.

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References

[1] C. Hansch, Acc. Chem. Res. 2 (1969) 232.
[2] D.E. Leahy, J.J. Morris, P.J. Taylor, A.R. Wait, J. Chem. Soc., Perkin Trans. 2 (1992) 723.
[3] S. Cabani, G. Conti, V. Mollica, P. Berti, Thermochim. Acta 162 (1990) 195.
[4] S. Cabani, G. Conti, V. Mollica, L. Bernazzani, J. Chem. Soc., Faraday Trans. 87 (1991) 2433.
[5] L. Bernazzani, S. Cabani, G. Conti, V. Mollica, J. Chem. Soc., Faraday Trans. 91 (1995) 649.

[6] L. Bernazzani, S. Cabani, G. Conti, V. Mollica, Thermochim. Acta 269/270 (1995) 361.
[7] R. Stephenson, J. Stuart, J. Chem. Eng. Data 31 (1986) 56.
[8] S.O. Nilsson, J. Chem. Thermodyn. 18 (1986) 1115.
[9] L. Bernazzani, S. Cabani, G. Conti, V. Mollica, J. Therm. Anal. Cal. 61 (2000) 637.
[10] V. Majer, V. Svoboda, Enthalpies of Vaporisation of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series, Blackwell, Oxford, 1985.
[11] S.O. Nilsson, J. Chem. Thermodyn. 18 (1986) 877.
[12] C. Christensen, J. Gmehling, P. Rasmussen, U. Weidlich, Heat of Mixing Data Collection, Binary and Multicomponent Systems, DECHEMA Chemistry Data Series, Vol. III, Part 2, Frankfurt, 1984.
[13] J. Gmehling, T. Holderbaum, Heat of Mixing Data Collection, Binary and Multicomponent Systems, DECHEMA Chemistry Data Series, Vol. III, Suppl. 1, Part 3, Frankfurt, 1989.
[14] M.H. Abraham, G.S. Whiting, R. Fuchs, E.J. Chambers, J. Chem. Soc., Perkin Trans. 2 (1990) 291.
[15] S. Cabani, P. Gianni, V. Mollica, L. Lepori, J. Solution Chem. 10 (1981) 563.