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Solution enthalpies of 2-chloro-2-methylpropane in the binary alcoholic mixtures methanol–1,2-ethanediol, ethanol–1,2-ethanediol and 2-methoxyethanol–1,2-ethanediol

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Abstract

The enthalpies of solution at infinite dilution of 2-chloro-2-methylpropane (*t*-BuCl) in methanol–1,2-ethanediol, ethanol–1,2-ethanediol and 2-methoxyethanol–1,2-ethanediol solvent mixtures were measured at 298 K using a calorimetric technique. These values were determined for nine different mole fractions of the alcoholic mixtures.

The preferential solvating abilities of the various solvents towards *t*-BuCl are compared and analysed in terms of the molecular structures of the alcohols.

Keywords: Alcohol; Binary system; Calorimetry; Heat of solution; Solvation

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1. Introduction

The thermodynamic functions of solution for a great number of non-polar solutes in water and aqueous solutions have been the objects of thorough investigations. Information about the functions of solution in organic solvents has also been reported and consistent interpretations have been made about the inner structure of the solvents and the molecular models for the solute–solvent–solvent interactions.

In earlier works [1–5], the solution enthalpies at infinite dilution of *tert*-butyl halides in pure monoalcohols were measured. It was noted that the structural

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nature of the solvents, namely the degree and/or type of hydrogen-bonding association, the position of the OH group, and chain branching, influenced the results [1]. However, the solution enthalpies were analysed by the method of the model solute [3] and by the method of the linear solvation energy relationships [4]. It was possible to conclude that the enthalpies of solution at infinite dilution of *tert*-butyl halides in pure hydroxylic solvents are sensitive to (i) the solute–solvent and solvent–solvent polarity effects; (ii) the ability of the solvents to act as Lewis acids; and (iii) the reorganization, observed in these network liquids, of the solvent molecules in the cybotatic region of the solute.

We continue our thermochemical studies in alcohols, presenting work on the enthalpies of solution, at infinite dilution and at 298.15 K, of 2-chloro-2-methylpropane (*tert*-butyl chloride, *t*-BuCl) in the binary liquid mixtures methanol–1,2-ethanediol, ethanol–1,2-ethanediol and 2-methoxyethanol–1,2-ethanediol. The values were determined for nine different mole fractions of the solvents, using a calorimetric technique. These data can contribute to an understanding of the solute–solvent–solvent interactions as well as of problems specifically involving solvent mixtures other than water.

2. Experimental

The three alcohols employed in this study were supplied by BDH and Merck and were subjected to no further purification other than being dried with molecular sieves. Their purity was tested by gas chromatographic and IR spectroscopic techniques. The water content was kept lower than 0.02%. The solute, *t*-BuCl, was supplied by BDH. The binary mixtures of the solvents were prepared by weight and the mole fraction purities were >99.5% for all chemical substances.

The experimental measurements were carried out using a solution calorimeter described in some detail in former papers [1,3]. The enthalpies of solution of 2-chloro-2-methylpropane were measured within the concentration range 0.01–0.03 mol l^{-1}. The enthalpies of solution were independent of concentration within the studied concentration range, which allows the solution enthalpies at infinite dilution to be obtained directly. The common procedure consists of an electrical calibration, followed by the solution process. The rate of heat evolution was linear for the first step and exponential for the second step. The Dickinson's method, described by Wadsö [6], was used.

3. Results and discussion

Several things are important to us in this work. First, we always use the same solute and a common solvent, 1,2-ethanediol, in the three binary solvent mixtures. This way we expected that more particular information on the nature of interaction effects could be obtained. Secondly, all the solvents have similar cohesive energy densities (from $\delta = 23.3$ MPa$^{1/2}$ for 2-methoxyethanol to $\delta = 29.9$ MPa$^{1/2}$ for

1,2-ethanediol) which means that they gain sufficient energy on mutual dispersion to permit mixing. This concept aims, in principle, to predict properties of the solvent binary mixtures using only the properties of its components [7]. Thirdly, two of the cosolvents are monofunctional alcohols, with considerably relatively different aliphatic chains (methanol and ethanol) and the other is a bifunctional solvent, alcohol and ether (2-methoxyethanol). Finally, the polarity of the functional groups goes in the order $OH > OCH_3 > CH_3$.

The *n*-alcohol molecules seem to participate on average in two hydrogen bonds, the hydroxyl group acting once as a proton acceptor and once as a proton donor. Several polymeric entities must be presented in neat alcohols, but linear polymers seem to be the most important [8,9]. The increase of the number of hydroxyl groups in the alcohol molecules causes the strengthening of both electron-accepting and electron-donating properties; however, the increase in the number of methyl groups in an alcohol acts oppositely [10]. In addition, 1,2-ethanediol can, in principle form three-dimensional networks, because each molecule possesses two proton donor O–H groups as well as two oxygen atoms functioning as proton acceptors in hydrogen bonds [11].

The values of the enthalpies of solution at infinite dilution and at 298.15 K, ΔH_s^∞, of 2-chloro-2-methylpropane (*t*-BuCl) in the binary solvent mixtures methanol–1,2-ethanediol, ethanol–1,2-ethanediol and 2-methoxyethanol–1,2-ethanediol are given in Table 1. These values are the average of at least five independent calorimetric measurements and the standard deviations from the mean values may reach 50 kJ mol^{-1}. One way to eliminate the term corresponding to the solute–solute interactions is by combining each ΔH_s^∞ with the enthalpy of vaporization value (28.98 ± 0.06 kJ mol^{-1} for *t*-BuCl [12]) in order to obtain the enthalpies of solvation of the gaseous solutes. This is important when different solutes are used. In our case, however, the comparative studies eliminate the solute–solute interactions, because the solute is always the same. The differences between the solution enthalpy of *t*-BuCl for each solvent composition and for pure 1,2-ethanediol, both at infinite dilution and at 298.15 K, are shown in the last column of Table 1. All values are exothermic in nature, in accordance with the high degree of structureness of the chosen reference solvent: the endothermicity of the hydrogen bond breaking (and cavity formation) prevails over the exothermicity of the solute–solvent interaction (and solvent reorganization) in the pure diol. From this point of view, the three studied systems behave in a similar way: $\delta\Delta H_s^\infty = \Delta H_s^\infty - \Delta H_s^\infty$(1,2-ethanediol) values increase monotonically from the pure monoalcohol to the pure dialcohol.

In Fig. 1, ΔH_s^∞ values are plotted as a function of solvent composition for the three systems under study. One of the principal features of the curves is the considerable difference on passing from one binary solvent mixture to another. However, using solvent mixtures of similar components (hydroxylic solvents), we may expect that bulk properties of the medium behave uniformly over a wide range of mole fraction. Then, a possible explanation for the behaviour of our solvent systems may be found by considering "selective solvation", which occurs when the composition of the solvent components in the neighbourhood of the solute molecules is different from the composition of the bulk solution.

Table 1
Solution enthalpies of *t*-BuCl (kJ mol^{-1}) at infinite dilution and at 298.15 K in alcohol–alcohol mixtures

Solvent mixture	Mole fraction [a]	ΔH_s^∞	$-\delta\Delta H_s^\infty$ [b]
Methanol–1,2-ethanediol	1	1.56	4.11
	0.955	2.09	3.58
	0.910	2.20	3.47
	0.810	2.69	2.98
	0.750	2.76	2.91
	0.500	3.62	2.05
	0.250	4.66	1.01
	0.086	5.29	0.38
	0	5.67	0
Ethanol–1,2-ethanediol	1	1.50	4.17
	0.955	1.74	3.93
	0.910	1.99	3.68
	0.810	2.20	3.47
	0.750	2.21	3.46
	0.500	2.98	2.69
	0.250	4.05	1.62
	0.086	4.79	0.88
2-Methoxyethanol–1,2-ethanediol	1	2.26	3.41
	0.955	2.37	3.30
	0.910	2.37	3.30
	0.810	2.55	3.12
	0.750	2.84	2.83
	0.500	3.39	2.28
	0.250	4.34	1.33
	0.086	5.29	0.38

[a] Mole fraction of the first component of the solvent mixture. [b] $\delta\Delta H_s^\infty = \Delta H_s^\infty - \Delta H_s^\infty$(1,2-ethanediol).

3.1. Preferential solvation

A comparative study of the preferential solvating abilities of solvents towards *t*-BuCl is possible and it may be observed in Fig. 1. If both solvents of each alcoholic mixture have the same solvating ability, the plot should be a straight line going from the characteristic ΔH_s^∞ value of one solvent to that of the other. Conversely, preferential solvation of the solute by one of the solvents would result in a curvature of ΔH_s^∞ against the mole fraction of the solvent.

In Fig. 1, where the ideal behaviour is represented by a dashed line, we may distinguish between the three solution processes of *t*-BuCl in the binary mixtures. In the measurements with methanol–1,2-ethanediol, the position of the experimental points indicates that, for mole fraction values of methanol higher than 0.75, 1,2-ethanediol is a better solvating solvent than methanol, which is perfectly in

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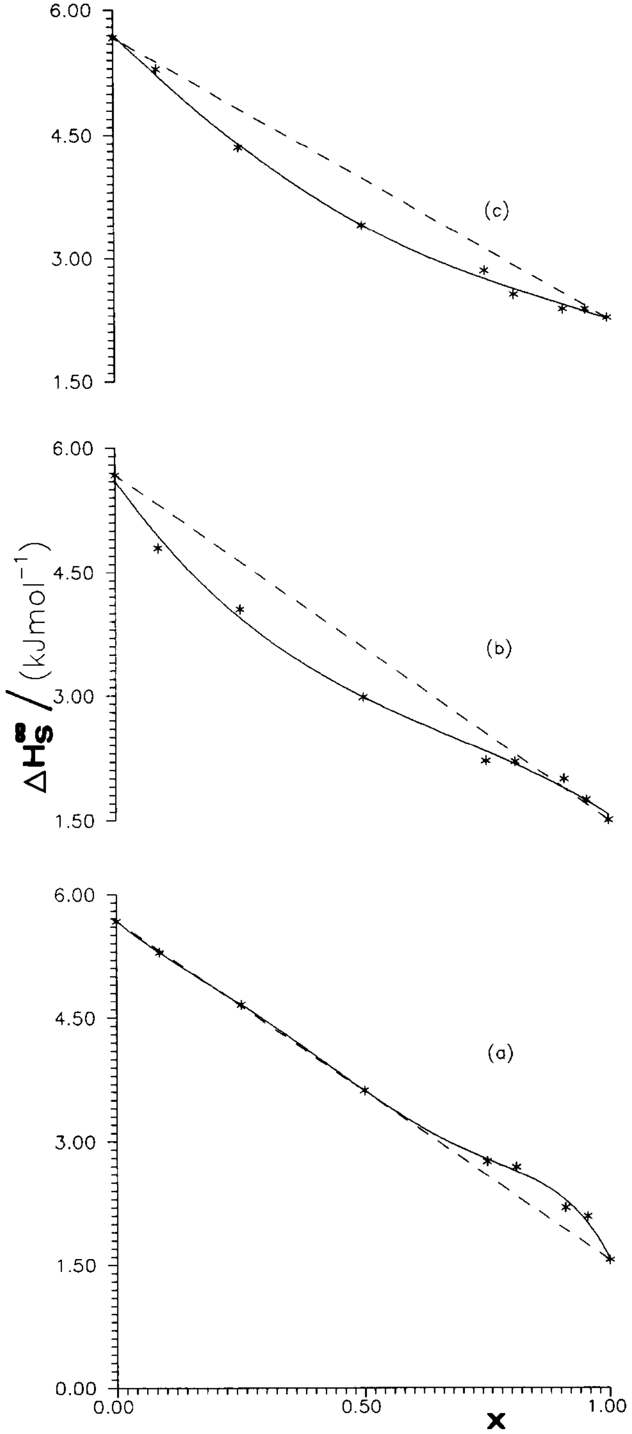
Fig. 1. Solution enthalpies of *t*-BuCl at infinite dilution against the mole fraction. (a) Methanol–1,2-ethanediol; (b) ethanol–1,2-ethanediol; (c) 2-methoxyethanol–1,2-ethanediol.


6.00
4.50
3.00
1.50
(c)
6.00
4.50
3.00
1.50
(b)
ΔH_s^{∞} / (kJmol^{-1})
6.00
4.50
3.00
1.50
0.00
(a)
0.00
0.50
1.00
x

accordance with the dipolarity and HBD properties of both solvents [13]. In the case of ethanol–1,2-ethanediol, ethanol shows preferential solvation in relation to 1,2-ethanediol, for mole fraction values of ethanol lower than 0.75. A possible explanation can be found assuming that the molecules of this component are more "free" to interact with the lone electron pairs of the solute than those of the dialcohol. In spite of the observation that hydrophobic effects are not dominant in these intermolecular processes, it is also possible that the introduction of the solute into the solvent induces stronger ethanol–ethanol affinity; in fact, ethanol compared with methanol always shows a stronger alcohol–alcohol affinity due to its longer aliphatic chain [14]. Data for the binary alcoholic mixture 2-methoxyethanol–1,2-ethanediol reflect, all along the solvent concentration range, that 2-methoxyethanol has the stronger solvating ability. An analysis of conformational isomerism and of intra- and intermolecular interaction in 1,2-ethanediol and 2-methoxyethanol shows that the two compounds possess similar sets of rotamers, but intramolecular hydrogen bonding is greatly reduced in 2-methoxyethanol, there being a higher contribution from the trans form [11]; 2-methoxyethanol is classified as "moderate" in terms of hydrogen bonding capability, while methanol, ethanol and 1,2-ethanediol are classified as "strong" [7]. These reasons and the other structural properties described before lead us to conclude that 2-methoxyethanol molecules are more "free" to interact with the solute than 1,2-ethanediol.

It appears that a fairly delicate balance exists between the breaking and forming of hydrogen bonds in the binary solvents in the neighbourhood of the solute species and the polarity effects between solute and solvent. In this case, the understanding of solute–solvent–solvent interactions assumes an additional degree of complexity, at least in quantitative terms: one of the most serious elements of uncertainty introduced is the influence of the cavity enthalpic term.

During recent years, there have been many solution calorimetric studies, which have provided us with a fair knowledge about aqueous enthalpies and heat capacities of solution of binary solvent mixtures. We think that it is also important to study other hydroxylic mixtures. The case of mixtures involving 1,2-ethanediol is particularly relevant because it has some properties in common with water and may lead to comparative studies and to a better understanding of the unusual thermodynamic properties of water [15]. We suggest that the solution of *t*-BuCl in binary alcoholic mixtures seems to induce "preferential solvation". The replacement of one apolar position of an *n*-alcohol (CH_3 group) by another of longer aliphatic chain (CH_3CH_2 group) and the introduction of another polar group (OCH_3) in a monoalcohol yield significant differences in the various intermolecular affinities, solvent–solvent and solute–solvent. However, deviations from ideality may also be a consequence of the change in molecular configuration of the solvent, and, hence, in the shape of the alcohol molecules, due to the formation of alcohol–alcohol complexes, mixed associates at specific compositions of the solvent, which interact with solute molecules in a different way than the pure alcohols.

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