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The enthalpies of solution of 2-chloro-2-methylpropane, 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in mono- and dialcohols at 298.15 K

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Abstract

The enthalpies of solution at infinite dilution of 2-chloro-2-methylpropane in 9 dialcohols and of 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in 19 mono- and dialcohols, at 298.15 K, were measured using a solution calorimeter. These values are discussed in terms of solute–solvent interactions. Together with previous data, this information provides a thermodynamic picture of the effect of the size of the alkyl chlorides and the structure of the alcohols.

Keywords: Alkyl chlorides; Calorimetry; Heat of solution; Mono- and dialcohols

1. Introduction

Recent decades have seen enormous progress in the experimental and theoretical treatment of molecular interactions in solution [1,2]. We shall focus our attention on the information provided by the experimental functions of solution on aspects of the interactions of solvents with solute molecules.

In previous papers from our laboratory, solution enthalpy measurements of *tert*-butyl halides in pure monoalcohols and in several binary mono/dialcohol mixtures were reported [3–7]. These results suggest that the structural nature of the alcoholic solvents (the degree and/or type of hydrogen-bonding association, the position of the

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hydroxylic groups and chain branching) and the size of the alkyl group of the solute influenced the results.

To achieve a more complete description of the solute–solvent interactions which take place in these systems, new calorimetric data were determined.

In the present study, we measured the solution enthalpies, at 298.15 K and infinite dilution, of 2-chloro-2-methylpropane in 9 dialcohols and of 2-chloro-2-methylbutane and 3-chloro-3-methylpentane in 19 mono- and dialcohols, by means of a calorimetric technique (direct method). Solvation enthalpies are calculated from these values and from heats of vapourization of the monohalogen compounds [8].

The results presented here allow conclusions to be drawn concerning the size of the solute, the number and position of the hydroxyl groups and the carbon chain length of the alcohols, and the particular structures of the diols.

2. Experimental

The calorimeter used in the heat of solution measurements is similar to that described before and the experimental procedure has also been described in earlier publications [5,7]. It comprises a double-glass-walled cylindrical vessel (400 cm^3) submerged in a high precision thermostat. Spherical ampoules (< 1 cm^3) were filled with the solute and sealed by flame. The electrical calibration of the calorimeter was performed just before each measurement using a constantan heater resistor connected to a convenient power supply and an ammeter. The temperature was regulated using a platinum resistor (Tinsley 5187SA) and a resistance bridge (Tinsley 5840).

The enthalpies of solution for the systems under study were obtained by direct measurements and the total uncertainty is about ± 50 J mol^{-1}.

The alcohols we studied were from BDH and Merck and were only submitted to drying processes. The solutes were supplied by BDH, Merck and Aldrich and were used without further purification.

3. Results and discussion

The experimental results of the solution enthalpies (ΔH_S^∞) of 2-chloro-2-methylpropane (*t*-BuCl), 2-chloro-2-methylbutane (2-Cl-2-MeBu) and 3-chloro-3-methylpentane (3-Cl-3-MePe) in mono- and dialcohols are presented in Table 1. Table 1 also includes previous values obtained for the first solute. All values refer to a standard state of infinite dilution.

Our enthalpy data for the solution of the three alkyl chlorides have positive values which correspond to endothermic processes. From a direct comparison of the second with the third and fourth column in Table 1, the results indicate that, for monoalcohols, the solutions of 2-Cl-2-MeBu and 3-Cl-3-MePe require higher energies for the same solvent. The solution enthalpies for 2-Cl-2-MeBu in dialcohols are, in general, smaller than the corresponding values for *t*-BuCl, except for ethane-1,2-diol, propane-1,2-diol and butane-1,2-diol; however, the same tendency is not followed by 3-Cl-3-MePe. Size

Table 1
Solution enthalpies of 2-chloro-2-methylpropane (*t*-BuCl), 2-chloro-2-methylbutane (2-Cl-2-MeBu) and 3-chloro-3-methylpentane (3-Cl-3-MePe) at infinite dilution (ΔH_s^∞) in mono- and dialcohols, at 298.15 K

Solvent	ΔH_s^∞ (kJ mol^{-1})		
	t-BuCl	2-Cl-2-MeBu	3-Cl-3-MePe
Methanol	1.56[a]	2.54	3.12
Ethanol	1.50[a]	1.90	2.12
Propan-1-ol	1.62[a]	2.07	2.28
Propan-2-ol	3.57[a]	3.83	4.08
Butan-1-ol	2.10[a]	2.28	2.34
Butan-2-ol	5.11[a]	5.53	5.62
2-Methylpropan-1-ol	3.09[a]	3.33	3.59
Pentan-1-ol	2.56[a]	2.55	2.60
2-Methylbutan-1-ol	3.78[a]	3.85	3.96
Ethane-1,2-diol	5.67[a]	5.83	6.07
Propane-1,2-diol	4.72	5.17	5.50
Propane-1,3-diol	5.19	2.90	3.18
Butane-1,2-diol	3.80	4.10	4.49
Butane-1,3-diol	5.59	4.85	5.69
Butane-1,4-diol	3.24	2.84	2.45
Butane-2,3-diol	4.27	3.96	4.58
Pentane-1,5-diol	2.46	1.45	1.14
Diethylene glycol	3.06	2.81	4.09
Triethylene glycol	4.26	3.39	5.37

[a] Values from Ref. [3].

effects, the number and position of –OH groups, as well as hydrogen-bonding association in the alcohols should be considered.

Another way to compare the experimental data is illustrated in Fig. 1(a) and (b), where ΔH_S^∞ for 2-Cl-2-MeBu and 3-Cl-3-MePe are plotted against ΔH_S^∞ for *t*-BuCl, and in Fig. 1(c), where ΔH_S^∞ for 3-Cl-3-MePe is plotted as a function of ΔH_S^∞ for 2-Cl-2-MeBu.

If the solvents propane-1,3-diol and pentane-1,5-diol are excluded from Fig. 1(a) and (b), good linear relationships are obtained. The behaviour of solution enthalpies in these dialcohols may be related to the particular structures of the solvents: as can be noted, both alcohol molecules are of the type $HO-(CH_2)_n-OH$ (ω-alkanediols); in addition, inspection of Fig. 1(b) shows that the experimental point for butane-1,4-diol also lies far from the mentioned linear relationship.

Fig. 1(c) shows that diethylene glycol and triethylene glycol are the exceptions to the normal behaviour of the represented systems. Again, a good straight line is obtained if these two solvents are excluded from the plot. In the three figures, the solid lines represent the best equations fitting the data ($N = 17$) using least squares analysis and the broken lines are the bisectors of the quadrant.

In order to obtain more information concerning the interaction mechanisms acting during the solution process of the studied compounds, we need to eliminate the term

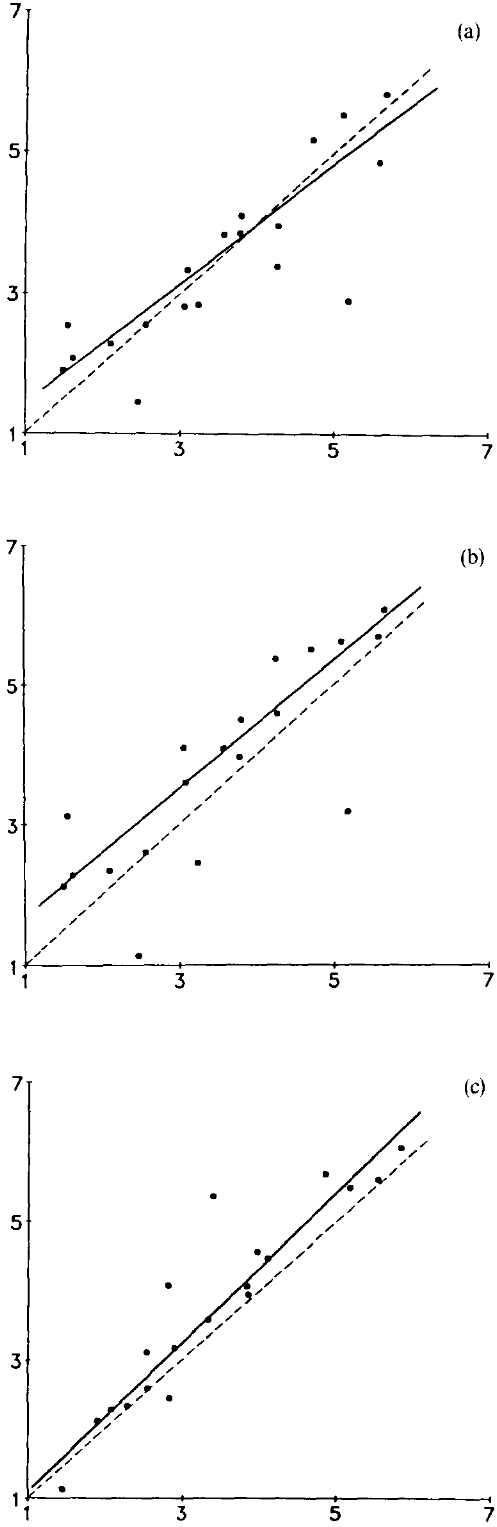

Fig. 1 Solution enthalpies at infinite dilution (kJ mol^{-1}) in mono- and dialcohols. (a) ΔH_S^∞ (2-Cl-2-MeBu) vs. ΔH_S^∞ (*t*-BuCl). (b) ΔH_S^∞ (3-Cl-3-MePe) vs. ΔH_S^∞ (*t*-BuCl). (c) ΔH_S^∞ (3-Cl-3-MePe) vs. ΔH_s (2-Cl-2-MeBu).

due to solute–solute interactions. This is important because different solutes are used in this work. To do so, we combined ΔH^{∞}_{S} with the enthalpy of vapourization values: 28.98 kJ mol^{-1} for *t*-BuCl, 34.64 kJ mol^{-1} for 2-Cl-2-MeBu and 39.90 kJ mol^{-1} for 3-Cl-3-MePe. The value for *t*-BuCl is an experimental value reported in the literature, and the other vapourization enthalpies were obtained as described by Wädso [8]. As expected, solvation enthalpies ($\Delta H^{\infty}_{\text{solv}}$) are highly exothermic in nature (Table 2), and always follow the order:

$$t\text{-BuCl} > 2\text{-Cl-2-MeBu} > 3\text{-Cl-3-MePe}$$

The size of the solute (molar volume $V = 111$ cm^3 mol^{-1} for *t*-BuCl, 123 cm^3 mol^{-1} for 2-Cl-2-MeBu and 136 cm^3 mol^{-1} for 3-Cl-3-MePe) is an important factor in these thermodynamic properties: the larger the molecule, the more exothermic the solvation process, as is generally the case for non-polar (and weakly polar) solutes in strongly polar solvents [3,9].

Several stages can be envisaged as comprising the model underlying the process of transferring a gas phase solute molecule to a solvent: first, breaking the hydrogen bonds of a solvent structure to obtain a suitable cavity to accommodate the solute (which cannot be neglected in the case of network solvents such as alcohols); second, the introduction of the solute into the cavity; third, the reorganization of solvent molecules around the solute and the establishment of various solute–solvent interactions. Thus,

Table 2
Solvation enthalpies of 2-chloro-2-methylpropane (*t*-BuCl), 2-chloro-2-methylbutane (2-Cl-2-MeBu) and 3-chloro-3-methylpentane (3-Cl-3-MePe) at infinite dilution ($\Delta H^{\infty}_{\text{solv}}$) in mono- and dialcohols, at 298.15 K

Solvent	$-\Delta H^{\infty}_{\text{solv}}$ (kJ mol^{-1})		
	t-BuCl	2-Cl-2-MeBu	3-Cl-3-MePe
Methanol	27.42	32.10	36.78
Ethanol	27.48	32.74	37.78
Propan-1-ol	27.36	32.57	37.62
Propan-2-ol	25.41	30.81	35.82
Butan-1-ol	26.88	32.36	37.56
Butan-2-ol	23.87	29.11	34.28
2-Methylpropan-1-ol	25.89	31.31	36.31
Pentan-1-ol	26.42	32.09	37.30
2-Methylbutan-1-ol	25.50	30.79	35.94
Ethane-1,2-diol	23.31	28.81	33.83
Propane-1,2-diol	24.26	29.47	34.40
Propane-1,3-diol	23.79	31.74	36.72
Butane-1,2-diol	25.18	30.54	35.41
Butane-1,3-diol	23.39	29.79	34.21
Butane-1,4-diol	25.74	31.80	37.45
Butane-2,3-diol	24.71	30.68	35.32
Pentane-1,5-diol	26.52	33.19	38.76
Diethylene glycol	35.92	31.83	35.81
Triethylene glycol	24.72	31.25	34.53

the exothermic nature of the enthalpies of solvation values shows that the solute–solvent interaction and structure-promoting (reorganization of the solvent in the cosphere of the solute) effects should prevail over the cavity contribution and structure-breaking effects, which are always endothermic [5].

According to the structural nature of the solutes and solvents, two different kinds of solute–solvent interactions should be considered in this work: long-range, non-specific intermolecular forces of dipole–dipole type and specific solvation interactions arising from localized and directed in space donor–acceptor bonds.

Attending to previous conclusions [3–7], it is now important to investigate not only the influences of the positions of the hydroxyl group and/or the branching in the carbon chain of the alcohols, but also the influences of the number of –OH groups and the particular structures of the dialcohols.

The ability of the hydroxyl group to take part in hydrogen bonding is responsible for the distinctive properties of alcohols. In fact, alcohols are stabilized by hydrogen bonds consisting of linear and/or cyclic polymers. Monoalcohols present intermolecular association, but some dialcohols are associated through inter- and intramolecular bonds.

The solvation enthalpies of the three chlorides in monoalcohols tend to increase with increasing size of the aliphatic group (except for the step methanol → ethanol), as observed before [3]. A comparative study of dialcohol behaviour shows that with the lengthening of the carbon chain between the positions of the –OH groups, $\Delta H^{\infty}_{\text{solv}}$ values are always shifted to smaller (more exothermic) values:

ethane-1,2- > propane-1,3- > butane-1,4- > pentane-1,5-diol

This regularity is in accordance with the behaviour of other thermochemical quantities [10]. These facts suggest a competitive effect between the size of the aliphatic group and the number of –OH groups in the alcohol.

$\Delta H^{\infty}_{\text{solv}}$ values for the three solutes in isomeric monoalcohols always show the sequence: alkane-1-ol < alkane-2-ol; this is a consequence of the amount of shielding of the hydroxyl group in the hydrocarbon chain which is related to the ratio of the linear and cyclic intermolecular hydrogen-bond degrees of association [11,12]. A similar feature can be envisaged for diols if both –OH groups move from the end to the middle of the carbon chain (butane-1,4-diol < butane-2,3-diol).

The analysis of solvation enthalpies for primary monoalcohols and for the corresponding ω-alkanediols indicates that contributions of structural effects also depend on the solute: the smaller the carbon chain of the alcohol, the greater the $\Delta H^{\infty}_{\text{solv}}$ difference for *t*-BuCl; for 2-Cl-2-MeBu and 3-Cl-3-MePe, however, no marked differences are apparent, except when passing from ethane-1,2-diol to propane-1,3-diol.

Another interesting feature concerns the behaviour of butanediols. The solvation processes for butane-1,2-, butane-1,3- and butane-2,3-diol are less exothermic than those for butane-1,4-diol. There are several reasons for this. If we assume that (i) in butane-1,2- and butane-2,3-diol, where the two hydroxyl groups are situated in adjacent positions, a strong intramolecular interaction exists, weakening the intermolecular cohesion; (ii) the intramolecular interaction between the hydroxyl groups also exists in butane-1,3-diol, the difference between butane-1,2-diol and ω-isomers being rather small, as for propanediols; and that (iii) the intramolecular hydrogen bonding is greatly reduced in butane-1,4-diol (and absent in pentane-1,5-diol) [13], we may conclude, as discussed before for the pair ethane-1,2-diol/2-methoxyethanol [7], that alcohol molecules without extensive intramolecular association are more free to interact with the solute and, consequently, show more exothermic heats of solvation.

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