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Calorimetric study of the solution process of tetramethylsilane in alcohols

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Abstract

Calorimetrically measured enthalpies of solution of tetramethylsilane into 16 alcohols, containing from 1 to 6 carbon atoms, are reported at 25°C and infinite dilution. These values are combined with the vaporization enthalpy of the solute to obtain standard enthalpies of gaseous tetramethylsilane and data are analysed in terms of the solvent structures.

The solution functions for tetramethylsilane (TMS) are compared with the solution functions for *tert*-butyl halides (*t*-BuX) in order to obtain information on *tert*-butyl halide–alcohol interactions. For this purpose, values of solution enthalpies are also determined for *tert*-butyl chloride, bromide and iodide in pentan-3-ol, 2-methylbutan-2-ol and hexan-1-ol.

The limitations of the use of TMS as "inert" model solute of *t*-BuX are discussed. However, the application of the Onsager reaction field theory is found to be useful in the analysis of the influence of the eccentricity factor on the interaction enthalpy and leads us to conclusions regarding the relative importance of dipolar solute–solvent interaction and solvent reorganization on the solution process of *t*-BuX in alcohols.

INTRODUCTION

Values of the thermodynamic functions of solution are known for a great number of nonpolar solutes in water. Much less work has been reported on functions of solution in organic solvents. This subject of investigation, however, is useful in the examination of the inner structure of the solvents and to fully understand a molecular model for the nature of interactions between solvent and solute. In isomeric alcohols, for example, the magnitude of the thermochemical parameters depends on

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the positions of the hydroxyl and methyl groups in the carbon chain. Differences in their behaviour are due to differences in the intermolecular association. In this context, the relative formation of linear and cyclic hydrogen-bonded chain polymers is thought to play an important role.

The thermodynamic parameters of nonpolar compounds, such as hydrocarbons and silanes, are also important in several other ways. They can provide the quantitative basis for discussion of particular solvent–solute and solvent–solvent interactions, when independent calorimetric measurements are available for polar solutes of similar structure. (In this paper we shall use the word "particular" for the "specific" (electron–donor acceptor interactions, for instance) and/or "nonspecific" (van der Waals' interactions, for instance) interactions of polar solutes which remain after comparison with nonpolar solutes of similar structure.)

In the present study, we have selected 16 pure monoalcohols as solvents and tetramethylsilane (TMS) as solute to investigate the influences due to the positions of the hydroxyl group and/or the branching in the carbon chain of the alcohols. To perform this analysis, we determined, from direct calorimetric measurements, the solution enthalpies of TMS in alcohols, at 25°C and infinite dilution.

Calorimetric studies of the solution process of *tert*-butyl halides (*t*-BuX) in several hydroxylic solvents have been reported previously [1, 2]. The results were analyzed in terms of dipole–dipole interaction forces and the energy of formation of a molecular-sized cavity to accommodate the solute. Furthermore, the influence of chain branching and the position of the –OH group in the solvent molecule were interpreted according to the values of the Kirkwood correlation factor g_k. However, much work remains to be done before we may reach a final conclusion.

Another procedure to estimate solute–solvent interactions compares the solution functions for the solutes under study with the solution functions for nonpolar solutes. If the nonpolar molecule is very similar to the polar molecule, with respect to size and shape, the deduction of the model solution functions from those of the polar solute leads to the cancellation of the cavity and common interaction contributions leaving a quantitative estimation for particular interactions between the polar solute and the solvent.

In this work we compare the solution enthalpies of TMS with the solution enthalpies of the *t*-BuX (X = Cl, Br, I) molecules, in order to obtain more information about *t*-BuX–alcohol interaction. For this purpose, values of ΔH_s^∞ of the three halides were also determined in three more alcohols: pentan-3-ol, 2-methylbutan-2-ol and hexan-2-ol.

The dipolar interactions between the *t*-BuX molecules and the solvent are evaluated using the Onsager model and the values obtained are used to discuss the relative strengths of the different types of solute–solvent interactions in those systems.

EXPERIMENTAL

The calorimetric experiments were carried out in an apparatus described in some detail in former papers [1, 2]. Special care was taken to fill with TMS and seal the spherical ampoules, due to the low value of the solute boiling point ($T_e = 26.5$°C).

The rate of the heat evolution was linear during the electrical calibration, which was performed before each measurement, and exponential during the solution process. Dickinson's method was used as described by Wadsö [3].

The values of the solution enthalpies were independent of concentration in the measurement range from 0.01 to about 0.03 mol l^{-1}.

The results presented in this paper are the mean values of at least five calorimetric experiments. Standard deviations from the mean value may reach 50 J mol^{-1}. Heats of empty ampoule breaking were found to be negligible and corrections for condensation of solute vapour were performed in all cases.

The alcohols, from BDH and Merck, were dried over molecular sieves and their purity was tested by gas-chromatographic and IR spectroscopic techniques. The water content was kept lower than 0.02%. TMS (>99.5%) and the *tert*-butyl halides (>99.5%) were from BDH and Fluka. *t*-BuI was distilled under reduced pressure and copper wire was added to stabilize the material during storage in dark flasks at temperatures below 5°C.

RESULTS AND DISCUSSION

The enthalpy values for the solution of tetramethylsilane into the alcohols, at 25°C and infinite dilution, are listed in Table 1. The enthalpy of vaporization of TMS, at 25°C, is $\Delta H_{vap} = 24.7$ kJ mol^{-1} [4]. Our enthalpies of solution, ΔH_s^∞, of liquid TMS were combined with that value to yield the solvation enthalpy, ΔH_{solv}^∞, of gaseous TMS. These values are also listed in Table 1. Enthalpies of solution and of solvation of *t*-BuX in pentanols and hexan-1-ol obtained in this work are given in Table 2. The vaporization enthalpies of the three halides, chloride, bromide and iodide, used in the calculations are, respectively, 28.98, 31.81 and 35.41 kJ mol^{-1}, at 25°C [5].

The solution process of TMS

The model underlying a solution process can be envisaged as being composed of several stages: a cavity of suitable size to accommodate the solute molecule is created in the solvent, solvent molecules are reorganized around the cavity and then the solute is introduced into the cavity and various solvent–solute interactions are set up. The change of the

TABLE 1

Enthalpies of solution of liquid (ΔH_s^∞) and of gaseous (ΔH_{solv}^∞) tetramethylsilane, at 25°C and infinite dilution (kJ mol^{-1})

Solvent	ΔH_s^∞	$-\Delta H_{solv}^\infty$
Methanol	3.81	20.9
Ethanol	2.51	22.2
Propan-1-ol	1.71	23.0
Butan-1-ol	1.43	23.3
Pentan-1-ol	1.55	23.2
Hexan-1-ol	1.36	23.3
Propan-2-ol	2.53	22.2
Butan-2-ol	3.11	21.6
Pentan-2-ol	2.90	21.8
Pentan-3-ol	3.96	20.7
2-Methylpropan-1-ol	1.68	23.0
2-Methylbutan-1-ol	1.90	22.8
2-Methylpropan-2-ol	4.54 [a]	20.2
2-Methylbutan-2-ol	2.58	22.1
3-Methylbutan-1-ol	1.43	23.3
3-Methylbutan-2-ol	3.67	21.0

[a] Value obtained at 27°C.

solvent structure around the solute molecule is frequently neglected. For structured or network solvents as alcohols, however, it can only be neglected when the Gibbs energy is under investigation, since the solute cosphere is in equilibrium with the bulk [6]. In other words, and using Grunwald's language, the Gibbs energy is a pure isodelphic property [7].

In general, two different kinds of solvent–solute interactions should be considered: those arising from long-range intermolecular forces, the so-called nonspecific solvent–solute interactions, and the specific solvation interactions arising from localized and directed in space donor–acceptor bonds.

TABLE 2

Enthalpies of solution of liquid (ΔH_s^∞) and of gaseous (ΔH_{solv}^∞) *tert*-butyl halides, at 25°C and infinite dilution (kJ mol^{-1})

Solvent	*t*-BuCl		*t*-BuBr		*t*-BuI	
	ΔH_s^∞	$-\Delta H_{solv}^\infty$	ΔH_s^∞	$-\Delta H_{solv}^\infty$	ΔH_s^∞	$-\Delta H_{solv}^\infty$
Hexan-1-ol	2.70	26.28	2.84	28.97	2.63	32.78
Pentan-3-ol	6.76	22.22	7.30	24.51	7.12	28.29
3-Methylbutan-2-ol	6.46	22.52	7.27	24.54	7.52	27.89

TMS, as regards specific solvent–solute interactions, may be visualized as an inert solute. Thus, the enthalpy of solvation values in the second column of Table 1 represent the sum of three different terms, one of which is always endothermic (the cavity contribution), another is always exothermic (the solute–solvent interaction contribution) and the other one, the contribution from the reorganization of the solvent in the cosphere of the solute, can be either exothermic (structure promoting effect) or endothermic (structure breaking effect).

Data in Table 1 may also be analysed from the point of view of the solvent molecular structures: the carbon chain length, the chain branching and the position of the –OH group in the solvent molecule.

It is generally accepted that alcohols are self-associated structures, stabilized by hydrogen bonds consisting of linear and/or cyclic polymers.

Along the set of normal alcohols, the aliphatic group size increases and the concentration associated with linear hydrogen-bonded chain polymers over the alcohol gross concentration, also increases. (For normal alcohols higher than hexan-1-ol, that concentration decreases with increasing alkyl chain length.) Dielectric relation studies suggest that 60–75% of the *n*-alcohol molecules are linear polymers, the other 40–25% being related to the number of monomers, hydrogen-bonded short linear chains and nonpolar cyclic species [8].

As stated before, this structural nature of the alcohols (predominantly linear association) allows the introduction of the solute into the solvents without an extensive hydrogen-bond disruption [1]. The energetics of cavity formation, however, also depend on the relation between the solute and the solvent size and shape [9, 10]. In this context, the more endothermic enthalpies of the solute cavity formation would correspond to the solution of TMS ("large" solute) in the alcohols of smaller size molecules (methanol and ethanol). This effect accounts for the ΔH_s^∞ (or ΔH_{solv}^∞) sequence for the lower normal alcohols, as shown in Table 1. It can also be seen in Table 1 that ΔH_s^∞ for pentan-1-ol is greater than that expected. This peculiar feature presumably indicates a different degree and/or type of association.

The influence of the positions of the –OH group and chain branching in the solvent molecule, which is particularly relevant for butanols and pentanols, was also examined.

The enthalpies of solution for isomeric alcohols follow the order alkane-1- < 2- < 3-ol. This series shows that ΔH_s^∞ (and ΔH_{solv}^∞) increases as the hydroxyl group approaches the centre of a molecule. This is strongly related to the amount of shielding of the hydroxyl group in the hydrocarbon chain. Shinomiya [8] estimated, for instance, that the percentages of C_1 for the isomeric pentanols are about 68% for pentan-1-ol, 50% for pentan-2-ol and 18% for pentan-3-ol (only 18% of the gross concentration for pentan-3-ol is associated with the formation of linear hydrogen-bonded chain polymers which the primary dispersion region originates) [8].

The sequence presented above is also observed for other properties of isomeric alcohols, for instance the boiling temperature. These properties are all connected with the ratio of linear and cyclic intermolecular hydrogen-bond degrees of association.

As can be noted, solution enthalpies of alkane-2-ol do not depend markedly on the length of the alkyl group, but instead on the chain branching.

For normal alcohols, solution enthalpies are similar for the same position of the branching with respect to the –OH group, irrespective of the length of the alkyl chain; conversely, when the branching moves from the vicinity of the –OH group, solution enthalpies tend to decrease.

Finally, for 2-methylpropan-2-ol (globular shape), where the hydroxyl group is in the middle of the carbon chain and there is also a branching at that point, ΔH_s^∞ reaches its highest value.

Several other studies on butanols and pentanols have shown that the isomeric structure of alcohols has a significant effect. This is the case of the recent reports on the solution thermodynamics of *t*-BuX [1] and on the excess volumes of mixing for isomeric butanol/acetone systems [11]. From a comparative analysis of the results presented here with those quoted in the literature we note that the same tendency is observed in passing from one isomer to another.

Comparison of the solution process of TMS and t-*BuX*

One approach to carry out the analysis of solvent effects on the solution processes makes use of model solutes. The solution functions of the solutes under examination are compared with the solution functions of nonpolar "inert" solutes with approximately the same molar volumes and shapes. In general, experimental data may be analyzed by means of the expression

$$Z = \delta\Delta H_s^\infty - \delta\Delta H_{sep}^\infty = \delta\Delta \mathrm{H}_{solv}^\infty = \delta\Delta H_{int}^\infty + \delta\Delta \mathrm{H}_{reorg}^\infty \qquad (1)$$

where the symbol δ represents the difference between the value of the function ΔH for the solute and for the model solute. ΔH_{sep}^∞ refers to the enthalpy involved in the separation of the pure solute molecules and is taken as the vaporization enthalpy, ΔH_{int}^∞ is the solvent–solute interaction enthalpy and ΔH_{reorg}^∞ is the term used to describe the change of the solvent structure in the cybotactic region of the solute.

Taking into account the structure of *tert*-butyl halides, we decided to compare the solution enthalpies of these solutes to that of TMS, used as a "reference" apolar molecule. We must point out that TMS is not, in fact, a "model" solute for *t*-BuX since its molar volume ($136\ \mathrm{cm^3\,mol^{-1}}$) is somewhat larger than the molar volume of *t*-BuCl (110 $cm^3 mol^{-1}$), *t*-BuBr (113 $cm^3 mol^{-1}$) and *t*-BuI (120 $cm^3 mol^{-1}$). A better model solute would be 2,2-dimethylpropane but unfortunately its boiling point is too low to allow liquid state experiments at room temperature.

The limitations of the use of TMS, however, can be discussed and the results allow us to interpret solute–solvent interactions at the molecular level, as we shall discuss later.

In eqn. (1), the quantities $\delta\Delta H_s^\infty$ and $\delta\Delta H_{sep}^\infty$ are obtained from the experimentally determined data. Some results used in the calculations have already been published in the literature [2, 5]. In the case of *t*-BuX and TMS, Z values do not correspond rigorously to $\delta\Delta H_{int}^\infty + \delta\Delta H_{reorg}^\infty$, since the molar volumes are not equal and, consequently, the cavity term and the general dispersive interaction term do not cancel each other when we subtract the solvation enthalpies for both solutes. Nevertheless, a very reasonable estimation of the involved error can be made. If we calculate the enthalpy of a spherical cavity of 110 $cm^3 mol^{-1}$ (*t*-BuCl) and that of a cavity of 136 $cm^3 mol^{-1}$ (TMS) in isomeric alcohols the difference is of the order of 6 $kJ mol^{-1}$ and this value is very similar for all the isomeric alcohols. However, the difference between the energy of the *t*-BuI cavity and that of the model solute is 3.5 $kJ mol^{-1}$. As regards the solute–solvent dispersive interactions, again they will not be the same for *t*-BuX and TMS: they will be stronger in the case of the bigger solute (higher

TABLE 3

Values of Z and Z' for *t*-BuX, using TMS as reference solute ($kJ mol^{-1}$)

Solvent	*t*-BuCl		*t*-BuBr		*t*-BuI	
	$-Z$	$-Z'$	$-Z$	$-Z'$	$-Z$	$-Z'$
Methanol	6.5	12.5	8.7	14.2	11.9	15.4
Ethanol	5.3	11.3	7.9	13.4	11.4	14.9
Propan-1-ol	4.4	10.4	6.8	12.3	10.4	13.9
Butan-1-ol	3.6	9.2	6.1	11.6	9.6	13.1
Pentan-1-ol	3.3	9.3	6.1	11.6	9.7	13.2
Hexan-1-ol	3.0	9.0	5.7	11.2	9.5	13.0
Propan-2-ol	3.2	9.2	5.5	11.0	8.8	12.3
Butan-2-ol	2.3	8.3	4.6	10.1	8.0	11.5
Pentan-2-ol	1.9	7.9	4.6	10.1	7.8	11.3
Pentan-3-ol	1.5	7.5	3.8	9.3	7.6	11.1
2-Methylpropan-1-ol	2.9	8.9	5.5	11.0	9.0	12.5
2-Methylbutan-1-ol	2.4	8.4	4.9	10.4	8.6	12.1
2-Methylpropan-2-ol	2.5	8.5	4.4	9.9	4.1	7.6
2-Methylbutan-2-ol	2.1	8.1	4.5	10.0	7.7	11.2
3-Methylbutan-1-ol	2.9	8.9	5.6	11.1	9.0	12.5
3-Methylbutan-2-ol	1.5	7.5	3.5	9.0	6.9	10.4

polarizability). Since the interaction term is about twice the cavity term and since they have opposite signs, we can conclude that the Z values presented in Table 3 are less exothermic by about 6 kJ mol^{-1} for t-BuCl, 5.5 kJ mol^{-1} for t-BuBr and 3.5 kJ mol^{-1} for t-BuI [12, 13]. The corrected values Z^{-} are also presented in Table 3.

Solute dipole–solvent interaction energy: application of the Onsager theory

The values of Z presented in Table 3 reflect some well identified solute–solvent interactions, namely those involving the solute dipole and the solvent reorganization effect arising from the presence of the solute in the bulk. The Onsager reaction field theory, which allows the calculation of the interaction of a dipole with a dielectric continuum, can be useful in order to quantify the dipolar interaction and to have an insight into the intensity of the reorganization effect which is difficult to arrive at by other methods. It is true that the solvents we are dealing with are associated solvents which cannot be accurately described as a dielectric continuum. Nevertheless it is known that the hydrogen bonds in an associated liquid are disrupted as the temperature rises, so that at temperatures near the boiling point the associated liquid behaves as a normal liquid since the liquid network has been destroyed by the thermal energy. In other words, at those temperatures, the dielectric constant of the liquid does not contain contributions from solvent association. To estimate the interaction of the solute dipole with the alcoholic solvents we can thus use the Onsager theory attributing to the solvent its dielectric constant at (or near) the boiling point. Alternatively we can estimate the interaction of the dipole with solvents which have identical polarity but are not network liquids (ketones, for example).

Following the Onsager theory [14], the interaction of a point dipole μ with a dielectric continuum ε, is given by (in c.g.s. units)

$$\omega = -R\mu N_A/2 \tag{2}$$

where N_A is the Avogadro's constant and R, the so-called reaction field, can be given by different equations according to the shape of the dipole cavity, the position of the dipole inside its cavity or the polarizability of the dipole. For a polarizable point dipole not centred in its spherical cavity, R is given by

$$R = \frac{4\pi N_A}{3V}\,\frac{(\varepsilon-1)(2\varepsilon-1)}{2\varepsilon+n_D^2}\,\frac{n_D^2+2}{3}\,\mu\sum_{n=0}^{\infty}\frac{n^2(n+1)}{n+n\varepsilon+\varepsilon}\left(\frac{s}{a}\right)^{(2n-2)} \tag{3}$$

where V is the molar volume of the solute cavity, n_D is the solute refractive index, ε is the dielectric constant of the solvent, s is the distance from the dipole to the cavity centre and a is the radius of the spherical cavity.

We must point out that ω in eqn. (2) is a Gibbs energy since it represents the electrical work done by transferring the dipole from a medium of $\varepsilon = 1$ to a dielectric of permittivity ε at constant temperature and pressure.

The enthalpy of interaction of the dipole with the dielectric can therefore be obtained by calculating the temperature derivative of eqn. (2) and using the Gibbs–Helmholtz relationship

$$\Delta H_{\text{int}} = -\frac{2\pi N_A^2}{3V}\mu^2(2\varepsilon+1)\left\{AS\left[(1+\alpha T) - TB\frac{\mathrm{d}\varepsilon}{\mathrm{d}T} - TC\frac{\mathrm{d}n_D}{\mathrm{d}T}\right] - TA\frac{\mathrm{d}S}{\mathrm{d}T}\right\} \tag{4}$$

where A, B and C are given by

$$A = \frac{\varepsilon - 1}{2\varepsilon + n_D^2}\,\frac{n_D^2 + 2}{3} \tag{5}$$

$$B = \frac{2}{2\varepsilon + 1} + \frac{n_D^2 + 2}{(2\varepsilon + n_D^2)(\varepsilon - 1)} \tag{6}$$

$$C = \frac{4n_D(\varepsilon - 1)}{(2\varepsilon + n_D^2)(n_D^2 + 2)} \tag{7}$$

α is the isobaric thermal expansion coefficient of the solute and S is the summation in eqn. (3). The eccentricity parameter, s/a, is temperature dependent. Although it seems fair to neglect the effect of temperature on the distance from the dipole to the cavity centre s, because it is an intramolecular parameter, the radius of the Onsager cavity a is related to the partial molar volume of the solute which is temperature dependent. $\mathrm{d}S/\mathrm{d}T$ in eqn. (4) is thus calculated by

$$\begin{aligned}\frac{\mathrm{d}S}{\mathrm{d}T} = & -\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\sum_{n=0}^{\infty}\left[\frac{n^2(n+1)^2}{(n+n\varepsilon+\varepsilon)^2}\left(\frac{s}{a}\right)^{(2n-2)}\right] \\ & -\frac{\alpha}{3}\sum_{n=0}^{\infty}\left[\frac{n^2(n+1)(2n-2)}{n+n\varepsilon+\varepsilon}\left(\frac{s}{a}\right)^{(2n-2)}\right]\end{aligned} \tag{8}$$

For a dipole centred in the spherical cavity, eqn. (4) becomes

$$\Delta H_{\text{int}} = -\frac{4\pi N_A^2}{3V}\mu^2\left[A'(1+T\alpha) - T\left(B'\frac{\mathrm{d}n_B}{\mathrm{d}T} + C'\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}\right)\right] \tag{9}$$

where $A' = A$, given by eqn. (5), and B' and C' are given by

$$B' = \frac{4}{3}n_D\left(\frac{\varepsilon - 1}{2\varepsilon + n_D^2}\right)^2 \tag{10}$$

$$C' = \frac{1}{3}\left(\frac{n_D^2 + 2}{2\varepsilon + n_D^2}\right)^2 \tag{11}$$

TABLE 4

Properties (at 25°C) of *tert*-butyl halides used in the calculations of the dipolar interactions with different solvent media

	μ [a] (D)	V [b] ($cm^3\ mol^{-1}$)	n_D [c]	dn_D/dT (K^{-1})	α [d] (K^{-1})
t-BuCl	2.14	110.6	1.3824	-5.8×10^{-4}	1.2×10^{-3}
t-BuBr	2.21	113.1	1.4249	-5.8×10^{-4}	1.6×10^{-3}
t-BuI	2.20	120.3	1.4889	-5.8×10^{-4}	2.0×10^{-3}

[a] Dipole moment. [b] Molar volume. [c] Refractive index. [d] Isobaric thermal expansion coefficient.

In both, eqns. (4) and (9), c.g.s. units must be used, but if we replace the parameter $4\pi N_A^2/3$ by the factor 151.955, which contains constants and conversion factors, the result will be in kilojoules per mole if V and μ are taken, respectively, in $cm^3\ mol^{-1}$ and Debye units.

Equations (4) and (9) were used to calculate the enthalpy of interaction, at 25°C, of the *tert*-butyl halides dipole with different solvent media. For alcoholic solvents we estimated, as previously discussed, the interaction of the dipole with a hypothetical medium whose dielectric constant at 25°C would be the same as that of the alcohols at the boiling point. This hypothetical medium will be referred as non-associated (n.a.) alcohol. We also chose, for comparison, the solvents acetone and pentane. The solute and solvent properties used in the calculations are presented in Tables 4 and 5.

First, we should like to analyse the influence of the eccentricity factor on the calculated interaction enthalpy, ΔH_{int}. From the results in Table 6,

TABLE 5

Solvent properties (at 25°C) used in the calculation of the dipolar interactions with different solvent media

Solvent	ε [a]	$-d\varepsilon/dT$
Pentane	1.836	0.0016
Acetone	20.70	0.09771
n.a. Methanol	26.50	0.1535
n.a. Ethanol	17.20	0.1180
n.a. Propan-1-ol	11.53	0.1035
n.a. Butan-1-ol	8.0	0.080
n.a. Propan-2-ol	11.82	0.110
n.a. Butan-2-ol	7.4	0.075
n.a. 2-Methylpropan-1-ol	8.5	0.090
n.a. 2-Methylpropan-2-ol	6.22	0.070

[a] Dielectric constant.

TABLE 6

Interaction enthalpy, ΔH_{int} (kJ mol^{-1}) of the *t*-BuCl dipole with different media as a function of the eccentricity parameter s/a

Solvent	ΔH_{int} (kJ mol^{-1}) when s/a is			
	0	0.05	0.1	0.2
Pentane	−2.20	−2.23	−2.30	−2.62
Acetone	−5.98	−6.05	−6.26	−7.20
n.a. Methanol	−6.09	−6.16	−6.38	−7.33
n.a. Ethanol	−6.22	−6.30	−6.52	−7.48

where ΔH_{int} calculated values are presented for *t*-BuCl solute in different media as a function of s/a, we can conclude that, in the range of small s/a values, the influence of the eccentricity is negligible. This is clearly a consequence of the molecular geometry (globular shape) of *tert*-butyl halides, and so the dipole must be located very near the molecular centre ($s/a < 0.1$). In the discussion which follows we will thus use eqn. (9) to calculate the dipolar interactions. We can also conclude from the results in Table 6 that the dipolar interaction with acetone (a non-network solvent) is very similar to that with the so-called n.a. alcohols. This is a good indication that the enthalpy we are calculating is, in fact, the dipolar part of the solute–solvent interaction.

In Table 7 we report the results, obtained using eqn. (9), for the dipolar interaction of the three *tert*-butyl halide solutes with different media and these values are compared with the Z' values, obtained from the experimental solution enthalpies after correction to take into consideration the volume difference of TMS and *t*-BuX, as discussed earlier.

TABLE 7

Dipolar interaction enthalpies (kJ mol^{-1}) of *t*-BuX with different media; comparison with Z' values, corrected for the volume difference between *t*-BuX and TMS

Solvent	*t*-BuCl		*t*-BuBr		*t*-BuI	
	$-Z'$	$-\Delta H_{\text{int}}$	$-Z'$	$-\Delta H_{\text{int}}$	$-Z'$	$-\Delta H_{\text{int}}$
Methanol	12.5	6.1	14.2	7.0	15.4	7.3
Ethanol	11.3	6.2	13.4	7.2	14.9	7.4
Propan-1-ol	10.4	6.6	12.3	7.6	13.9	7.8
Butan-1-ol	9.6	7.0	11.6	8.0	13.1	8.2
Propan-2-ol	9.2	6.7	11.0	7.6	12.3	7.9
Butan-2-ol	8.3	7.1	10.1	8.1	11.5	8.3
2-Methylpropan-1-ol	8.9	7.1	11.0	8.1	12.5	8.3
2-Methylpropan-2-ol	8.5	7.6	9.9	8.5	7.6	8.7

Inspection of Table 7 shows that the ΔH_{int} values are similar to Z' values for the alcohols with more carbon atoms. This is an indication that in those high molecular weight monoalcohols the structural effects are negligible. However for lower molecular weight monoalcohols, and particularly for methanol, ethanol and propan-1-ol, there is a significant difference between ΔH_{int} and Z' values showing the presence of a reorganizational term (structural effect) in those solvents. The fact that Z' values are more exothermic than ΔH_{int} values indicates that the solutes under consideration induce in those alcohols a structure promoting effect, a conclusion which was reached, from a different approach, by Grunwald [7, 15]. Since the difference between Z' and ΔH_{int} values is larger for *t*-BuI, the results in Table 7 also suggest that this solute has a stronger structural influence in alcoholic media.

CONCLUSION

In this investigation we measured, by calorimetry, the enthalpy of solution at infinite dilution and at 25°C of tetramethylsilane (TMS) in a series of alcohols. It was found that these solution enthalpies show the influence of the aliphatic group size of the solvent as well as that of the position of the hydroxyl group and/or the branching of the alkyl chain on the structure of isomeric alcohols.

However the comparison of the solution process of TMS to that of *tert*-butyl halides (*t*-BuX) in the same alcohols allows one to obtain information about the solute–solvent interactions in the *t*-BuX/alcohol systems. The difference between the solvation enthalpy of the *t*-BuX solutes and that of the TMS solute is a complex quantity which reflects a measure of interactions arising from the solute permanent dipole, the eventual specific solute–solvent interactions (hydrogen bonding, change transfer interactions), and also the reorganization, observed in network liquids, of the solvent molecules in the cybotactic region of the solute. Making use of the commonly accepted hypothesis of the cavity theory of solution, that difference was corrected in order to estimate the quantity $Z' = \delta\Delta H_{\text{int}} + \delta\Delta H_{\text{reorg}}$.

The interaction enthalpy of the dipoles of *t*-BuX solutes with a dielectric continuum was calculated using Onsager's reaction field theory and compared with Z'. From this comparison it was suggested that the lower molecular weight alcohols are network liquids whose structure is reinforced when *t*-BuX solutes are dissolved therein.

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REFERENCES

1 R.M.C. Gonçalves and A.M.N. Simões, J. Solut. Chem., 16 (1987) 39; 19 (1990) 315; Can. J. Chem., 65 (1987) 1474.
2 R.M.C. Gonçalves, L.M.P.C. Albuquerque, F.E.L. Martins, A.M.N. Simões and J.J. Moura Ramos, J. Phys. Org. Chem., 5 (1992) 93.
3 I. Wadsö, Sci. Tools, 13 (1966) 33.
4 W.V. Steele, J. Chem. Thermodyn., 15 (1983) 595.
5 I. Wadsö, Acta Chem. Scand., 22 (1968) 2438.
6 H.L. Friedman, Chem. Br., 9 (1973) 300.
7 E. Grunwald, J. Am. Chem. Soc., 108 (1986) 5726.
8 T. Shinomiya, Bull. Chem. Soc. Jpn., 62 (1989) 908.
9 J.J. Moura Ramos, M.S. Dionísio, R.M.C. Gonçalves and H.P. Diogo, Can. J. Chem., 66 (1988) 2894.
10 J.J. Moura Ramos, J. Solut. Chem., 18 (1989) 957.
11 K.R. Patil, G. Pathak and S.D. Pradhan, Thermochim. Acta, 177 (1991) 143.
12 M.S. Dionísio, J.J. Moura Ramos and R.M.C. Gonçalves, Can. J. Chem., 68 (1990) 1937.
13 J.J. Moura Ramos and R.M.C. Gonçalves, Thermochim. Acta, 190 (1991) 225.
14 C.J.S. Böttcher, The Theory of Electric Polarization, Vol. 1, Elsevier, Amsterdam, 1973.
15 E. Grunwald, J. Am. Chem. Soc., 106 (1984) 5414.