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The enthalpies of solution of 2-bromo-2-methylpropane and 2-bromo-2-methylbutane in mono- and dialcohols at 298.15 K

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Abstract

A total of 29 new calorimetrically measured values for the enthalpies of solution of 2-bromo-2-methylpropane and 2-bromo-2-methylbutane in mono- and dialcohols at 298.15 K is presented. The solution enthalpies were combined with the enthalpies of vaporization of the solutes to yield the solvation enthalpies. The values are sensitive to the solvent structure and the size of the alkyl halide. Particular attention was given to the change of the hydrocarbon chain ($CH_3 \rightarrow C_2H_5$) and the halide ($Cl \rightarrow Br$) in the solute molecule. © 1998 Elsevier Science B.V.

Keywords: 2-Bromo-2-methylpropane; 2-Bromo-2-methylbutane; Mono- and dialcohols; Solution enthalpies

1. Introduction

Previous papers from our laboratory [1,2] presented the enthalpies of solution, measured at 298.15 K, of several *tert*-butyl chlorides, namely 2-chloro-2-methylpropane (*t*-BuCl) and 2-chloro-2-methylbutane (2-Cl-2-MeBu) in nine mono- and 10 dialcohols, both groups ranging from one to five carbon atoms. The present paper reports measurements for the two corresponding bromides, namely 2-bromo-2-methylpropane (*t*-BuBr) and 2-bromo-2-methylbutane (2-Br-2-MeBu) in the same solvents. The magnitude of the thermochemical parameters was studied in order to understand the influence of the number and position of the hydroxyl, methyl and methylene groups of the carbon chain in the alcohols, and also the differences obtained on replacing Cl by Br and CH_3 by C_2H_5 in the solute molecule.

2. Experimental

All solvents were the same as used in a previous work [2]. The alcohols were not subjected to any further purification after being dried with molecular sieves. The solutes employed in this study were supplied by Aldrich and Merck.

Details of the equipment, calibration, tests and operating procedure have been described previously [3,4]. In brief, the enthalpies of solution of all systems were measured in infinite dilution conditions, at 298.15 K, in a double-vessel solution calorimeter immersed in a water thermostat. The temperature stability of the thermostat was better than 0.01 K. The error in the calorimetric measurements was estimated to be $\pm 50\ \mathrm{J\ mol^{-1}}$. All the quoted calorimetric values are the mean values of at least three individual determinations.

The solubility of 2-bromo-2-methylbutane in some dialcohols is poor and the subsequent calorimetric responses irregular. In these cases, more than six

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experiments were completed to establish reasonable values for the enthalpies of solution.

3. Results and discussion

Table 1 summarizes the experimental results of the solution enthalpies (ΔH_s^∞) of 2-bromo-2-methylpropane (*t*-BuBr) and 2-bromo-2-methylbutane (2-Br-2-MeBu) in nine monoalcohols and 10 dialcohols, at 298.15 K. Table 1 also includes some data previously obtained for *t*-BuBr [1]. The enthalpies of vapourization of both solutes are, respectively, ΔH_{vap} (*t*-BuBr)= 31.81 kJ mol^{-1} and ΔH_{vap} (2-Br-2-MeBu)=37.68 kJ mol^{-1} [5]. In order to eliminate the solute–solute interactions, these values were combined to the measured enthalpies of solution to yield the solvation enthalpies, $\Delta H_{\mathrm{solv}}^\infty$. In Table 1, $\Delta H_{\mathrm{solv}}^\infty$ values are also listed.

The values of ΔH_s^∞ for the two solutes are small and positive for all alcohols, while those of $\Delta H_{\mathrm{solv}}^\infty$ are large and negative. The model underlying the solution and solvation processes were previously described [2] and our solutes behave as is generally the case for weak polar solutes in polar solvents. The strong exothermic nature of the solvation enthalpies shows that solute–solvent interaction and structure promoting effects prevail over the endothermic contributions.

The solution enthalpies for 2-Br-2-MeBu are, in general, greater than the corresponding values for *t*-BuBr, showing an endothermic size effect, which is related to the break of the solvent structure in order to obtain a suitable cavity to accommodate the solute molecules during the solution process. The exceptions, solvents Nos. 4, 8, 10, 13 and 17 in Table 1, only show small differences in ΔH_s^∞ ($\leq$0.13 kJ mol^{-1}).

The biggest ΔH_s^∞ values for both solutes in this set of results are observed for ethane-1,2-diol and the smallest values for pentane-1,5-diol. Ethane-1,2-diol is an example of a solvent with competing hydrogen bonds. Its molecules are associated not only through intermolecular but also through strong intramolecular hydrogen bonds. The gauche-trans equilibrium in the pure liquid has been already studied [6,7]. On account of the vicinal polar groups, this diol is a solvent with possible intramolecular bonds and it was found that

Table 1
Solution enthalpies (ΔH_s^∞) and solvation enthalpies ($\Delta H_{\mathrm{solv}}^\infty$) of 2-bromo-2-methylpropane (*t*-BuBr) and 2-bromo-2-methylbutane (2-Br-2-MeBu) in mono- and dialcohols at 298.15 K

No.	Solvent	ΔH_s^∞/ (kJ mol^{-1})		$-\Delta H_{\mathrm{solv}}^\infty$/(kJ mol^{-1})	
		t-BuBr	2-Br-2-MeBu	*t*-BuBr	2-Br-2-MeBu
1	Methanol	2.20 [a]	3.12	29.61	34.56
2	Ethanol	1.75 [a]	2.20	30.06	35.48
3	Propan-1-ol	2.00 [a]	2.13	29.81	35.55
4	Propan-2-ol	4.12 [a]	4.09	27.69	33.59
5	Butan-1-ol	2.37 [a]	2.40	29.44	35.28
6	Butan-2-ol	5.57 [a]	5.65	26.24	32.03
7	2-Methylpropan-1-ol	3.36 [a]	3.71	28.45	33.97
8	Pentan-1-ol	2.62 [a]	2.50	29.19	35.18
9	2-Methylbutan-1-ol	4.12 [a]	4.25	27.69	33.43
10	Ethane-1,2-diol	6.07	5.94	25.74	31.74
11	Propane-1,2-diol	4.81	5.32	27.00	32.36
12	Propane-1,3-diol	2.67	2.74	29.14	34.94
13	Butane-1,2-diol	4.22	4.10	27.59	33.58
14	Butane-1,3-diol	4.78	5.12	27.03	32.56
15	Butane-1,4-diol	1.54	2.26	30.27	35.42
16	Butane-2,3-diol	4.31	4.35	27.50	33.33
17	Pentane-1,5-diol	0.91	0.80	30.90	36.88
18	Diethylene glycol	2.26	3.22	29.55	34.46
19	Triethylene glycol	4.04	5.06	27.77	32.62

[a] Values from Ref. [1].

the formation of an internal hydrogen bond determines the gauche conformation to be more stable. The more ordered structure of the solvent results in a decrease in the solvent–solute interactions. Conversely, intramolecular hydrogen bonds are totally absent in pentane-1,5-diol [8]. Therefore, the exothermic establishment of various solute–solvent interactions is most favourable for pentane-1,5-diol and unfavourable for ethane-1,2-diol.

The behaviour of ΔH_s^∞ along the *n*-alcohols follows the order:

2-Br-2-MeBu: MeOH>EtOH<1-PrOH<1-BuOH<1-PeOH

t-BuBr: MeOH>EtOH>1-PrOH<1-BuOH<1-PeOH

Furthermore, ΔH_s^∞ for 2-Br-2-MeBu shows the biggest value for methanol, while *t*-BuBr for butanol and pentanol are still bigger than for methanol. The observed differences are, no doubt, a consequence of a competition between inductive and steric effects in the alcohol molecules (the inversion takes place in EtOH or 1-PrOH) which affect the exothermic interaction with solute molecules. In this context, the differences in the molar volumes, V_M, of the solute molecules also play an important role: V_M (2-Br-2-MeBu)=128 cm^3 mol^{-1}, V_M (*t*-BuBr)=113 cm^3 mol^{-1} and V_M (2-Cl-2-MeBu)=123 cm^3 mol^{-1}. This kind of behaviour slightly differs from that observed in our previous investigations, in which alkyl chlorides were used instead of alkyl bromides [2].

The influence of the position of the hydroxyl group in the solvent is clearly seen, for the solution of both solutes in monoalcohols, for the pairs (1-PrOH, 2-PrOH) and (1-BuOH, 2-BuOH), where the solution enthalpies for the secondary alcohols are twice the value or even more of the solution enthalpies for primary alcohols, in accordance with earlier observations concerning the alkyl chlorides. The amount of shielding of the –OH group and the ratio of linear and cyclic intermolecular hydrogen-bond degrees of association support this behaviour [9,10]. The same kind of explanation can be envisaged for the butanediols 1,4 and 2,3.

For diols with the –OH groups attached to the ends of the alkyl chain, ΔH_s^∞ decreases with the lengthening of the carbon chain, in accordance with previous observations on thermochemical properties [2,8].

Bromides in butanediols follow exactly the pattern observed for chlorides. The reasons for this were already advanced.

In the present study, we investigated two different influences concerning the change of the hydrocarbon chain ($CH_3 \rightarrow C_2H_5$), and the halide (Cl→Br) in the solute molecule.

In Fig. 1(a), the values of ΔH_s^∞ for 2-Br-2-MeBu are plotted against the corresponding results for *t*-BuBr. A similar plot for 2-Br-2-MeBu vs. 2-Cl-2-MeBu is shown in Fig. 1(b). The values used in this plot for 2-Cl-2-MeBu are from our previously published data [2]. It is evident from these figures that the representations of the experimental results are nearly linear. In the figures, the dashed lines are derived from linear correlation analysis ($y=a_0+a_1x$). The values of the coefficients a_i were adjusted by the least-squares method:

(a) ΔH_s^∞ (2-Br-2-MeBu)=0.476+0.940 ΔH_s^∞ (*t*-BuBr) (N=19; r=0.96; σ=0.39)
(b) ΔH_s^∞ (2-Br-2-MeBu) = −0.002+1.065 ΔH_s^∞ (2-Cl-2-MeBu) (N=19; r=0.94; σ=0.48)

In these equations, N represents the number of pairs of points, and r and σ the correlation coefficient and the standard deviation of the fit were represented, respectively. The broken lines, also shown in the same figures, represent the bisectors of the quadrant.

In the first plot, Fig. 1(a), none of the points shows a big deviation from the straight line. Conversely, in the second plot, Fig. 1(b), deviation is the greatest for the solvent triethylene glycol. It is difficult to give a clear explanation for the highly positive ΔH_s^∞ value for this solvent and, in fact, the kind of dominant interaction in this case has not yet been clarified. If triethylene glycol is excluded from the linear calculations, an excellent straight line is obtained (a_0=−0.114; a_1=1.067; r=0.98; σ=0.32). However, the general conclusions are not sensitive to this difference.

4. Conclusion

The present investigation permitted the acquisition of solution enthalpy values of alkyl bromides in mono- and dialcohols. The collected data from calorimeter and the consequent discussion and effective comparison of these values with other alkyl halides, assayed

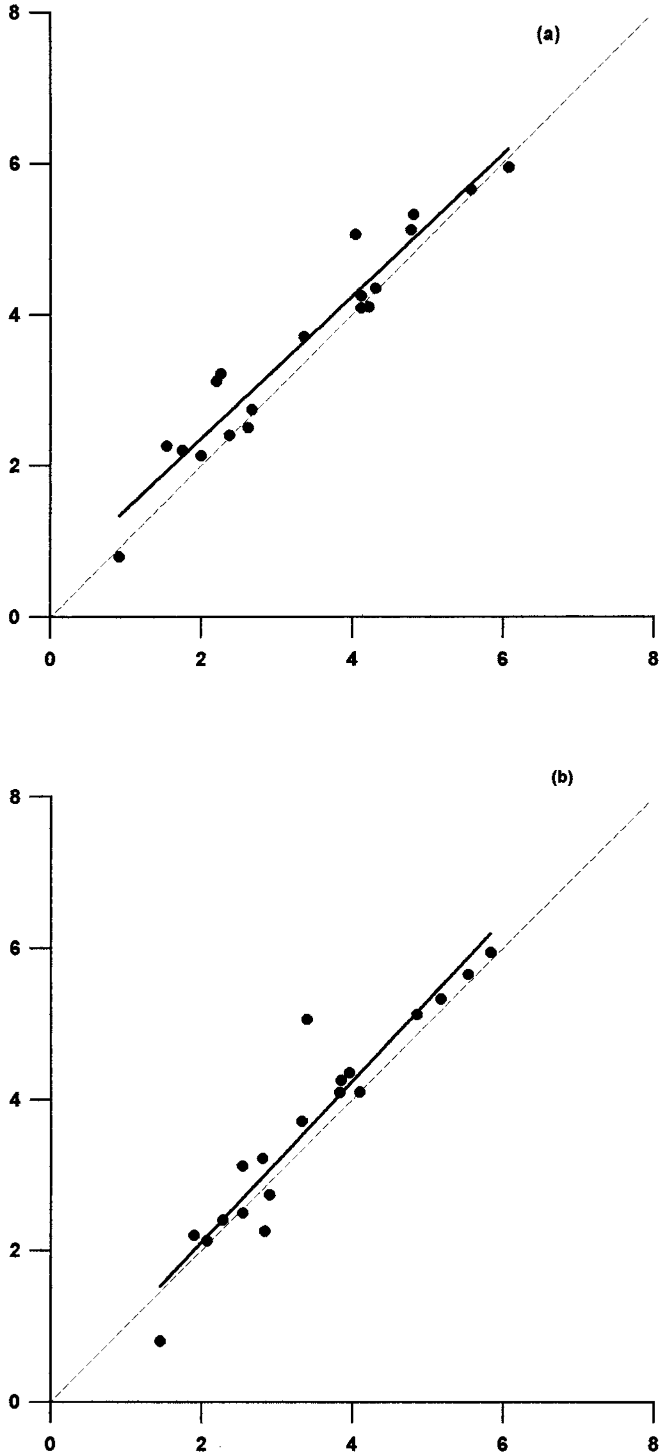

Fig. 1. Solution enthalpies at infinite dilution (kJ mol^{-1}) in mono- and dialcohols. (a) ΔH_s^∞ (2-Br-2-MeBu) vs. ΔH_s^∞ (*t*-BuBr). (b) ΔH_s^∞ (2-Br-2-MeBu) vs. ΔH_s^∞ (2-Cl-2-MeBu).

in identical experimental conditions, were relevant to the understanding of the contribution of solvent structure, and the change of the hydrocarbon chain ($CH_3 \rightarrow C_2H_5$) and the halide ($Cl \rightarrow Br$) in the solute molecule. The characteristics of the ΔH_s^∞ (2-Br-2-MeBu) vs. ΔH_s^∞ (*t*-BuBr) and ΔH_s^∞ (2-Br-2-MeBu) vs. ΔH_s^∞ (2-Cl-2-MeBu) diagrams are very similar. In addition, these plots are similar to those for the corresponding solutions of alkyl chlorides in mono- and dialcohols, although their ΔH_s^∞ values are different.

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