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Solution enthalpies of 1-bromoadamantane in monoalcohols at 298.15 K

Filomena Martins[a,*], Nelson Nunes[b], M. Luísa Moita[a], Ruben Elvas Leitão[b]

[a] *Department of Chemistry and Biochemistry, Faculty of Sciences, University of Lisbon, CQB, Ed. C8, Campo Grande, 1749-016 Lisbon, Portugal*
[b] *Department of Chemical Engineering, Engineering Institute (ISEL), Polytechnic Institute of Lisbon, CQB, R. Conselheiro Emídio Navarro 1, 1950-062 Lisbon, Portugal*

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Abstract

Solution enthalpies of 1-bromoadamantane in 14 monoalcohols were measured at 298.15 K. Comparison with the solution enthalpies of 2-bromo-2-methylpropane was performed. The obtained data were discussed in terms of the effect of solute's size and solvent's structure.

Keywords: 1-Bromoadamantane; Monoalcohols; Solution enthalpy

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1. Introduction

Solution calorimetry is still one of the most important methods for studying molecular interactions in solution [1].

One of the greatest challenges of solution chemistry is the identification of the main solute–solvent effects operating in the processes under study. Linear solvation energy relationships are one of the most widely used methodologies for the identification and quantification of these effects, and have been applied to enthalpies of solution with various degrees of success [2–6]. However for solvents of the same family, the high intercorrelation between solvent descriptors does not allow a proper use of this methodology. Another approach is to gather data for a set of similar solvents and rationalize the observed behavior in terms of solvent differences. This was the procedure followed in this work.

Solution enthalpies of haloalkanes in mono- and di-alcohols and mixtures of both have been reported and discussed in the literature [2,3,7–12]. In this work we present new values for the solution enthalpies, at 298.15 K and infinite dilution, of 1-bromoadamantane (1-BrAd) in a set of 14 monoalcohols.

The solvents' set was carefully chosen in order to allow the study of the influence of several factors upon solution enthalpies, namely the increase and branching of the carbonated chain and the effect of the –OH group's position. The results are discussed and compared with published values for 2-bromo-2-methylpropane (*t*-BuBr) in the same set of alcohols (except for 1-octanol) and water [2].

2. Experimental

Measurements were carried out at 298.15 K using a Thermometric precision solution calorimeter. Experimental details have been described before [13]. This calorimeter has a resolution in temperature in the order of 1 μK, corresponding to a resolution in enthalpy of 1–4 mJ.

The calorimeter was tested for the solution process of Tris(hydroxymethyl)aminomethane (TRIS) in NaOH $0.05\ \mathrm{mol\,dm^{-3}}$ ($17.16 \pm 0.02\ \mathrm{kJ\,mol^{-1}}$ [13]) and HCl 0.1 M ($-29.73 \pm 0.04\ \mathrm{kJ\,mol^{-1}}$), showing good agreement with tabulated values (17.19 ± 0.02 and $-29.75 \pm 0.02\ \mathrm{kJ\,mol^{-1}}$, respectively [14]).

All solvents were supplied by Aldrich and Merck (min. 99.5%), with a water content below 0.1% and were used without further drying or purification. Bromoadamantane was supplied by EGA-CHEMIE (min. 99%).

Bromoadamantane was weighted on a Mettler H35 analytical balance with a precision of ±0.1 mg and its concentration ranged from 0.01 to $0.02\ \mathrm{mol\,dm^{-3}}$. Cylindrical ampoules were filled with solute and sealed. Heats of empty ampoule breaking were found to be negligible. Each enthalpy value resulted from an

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[*] Corresponding author. Tel.: +351 217500000; fax: +351 217500088.
E-mail addresses: filomena.martins@fc.ul.pt (F. Martins), nnunes@deq.isel.ipl.pt (N. Nunes), mlmoita@fc.ul.pt (M.L. Moita), rleitao@deq.isel.ipl.pt (R.E. Leitão).

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average of at least three individual experiments, with a relative standard deviation always less than 3%.

3. Results and discussion

Table 1 summarizes the experimental results for the solution enthalpies ($\Delta_{\text{sol}}H^{\infty}$) of 1-BrAd in the 14 monoalcohols and water, as well as those for *t*-BuBr taken from Ref. [2]. Since all values are positive, the solution process is endothermic in all cases.

For 1-BrAd in the series of the *n*-alcohols, the variation of the solution enthalpy is not monotonous. The observed behavior suggests the simultaneous influence of several effects which can be divided in three different terms: a cavity term (endothermic contribution), a solvent–solute interaction term (exothermic contribution) and a third contribution due to the reorganization of solvent molecules around the solvation sphere of the solute (either endothermic/structure breaking or exothermic/structure promoting). In this series, the sum of all these contributions reaches its highest value for MeOH, the most structured of all six solvents, where the energy required for cavity formation must dominate, and its lowest value for 1-OctOH, the less structured one, where the energetic balance is quite less endothermic, as also pointed out by Litova [4]. This is probably due to a competition between inductive and steric effects in the solvent molecule which affects its interactions with the solute.

The position of the hydroxyl group also influences solution enthalpy values, as shown by the pairs (1-PrOH, 2-PrOH), (1-BuOH, 2-BuOH) and (1-PeOH, 2-PeOH). In fact, going from a primary to a secondary alcohol always leads to a higher enthalpy value. This behavior can be explained by the lesser accessibility of the –OH group of the secondary alcohols which decreases solute–solvent interactions leading to a more endothermic process.

Table 1
Infinite dilution solution enthalpies ($\Delta_{\text{sol}}H^{\infty}$) of 1-BrAd and *t*-BuBr, at 298.15 K in 14 monoalcohols and water and solvent dielectric constants

No.	Solvent	$\Delta_{\text{sol}}H^{\infty}$ (kJ mol^{-1})		ε[a]
		1-BrAd $\pm\,\sigma\Delta_{\text{sol}}H^{\infty}$	*t*-BuBr[b]	
1	Methanol	18.09 ± 0.02	2.20	32.66
2	Ethanol	16.26 ± 0.02	1.75	24.55
3	1-Propanol	15.79 ± 0.02	2.00	20.45
4	2-Propanol	18.18 ± 0.01	4.12	19.92
5	1-Butanol	15.85 ± 0.02	2.37	17.51
6	2-Butanol	19.25 ± 0.05	5.57	16.56
7	1-Pentanol	16.43 ± 0.02	2.62	13.90
8	2-Pentanol	19.08 ± 0.05	5.43	13.71[c]
9	2-Methyl-1-propanol	16.80 ± 0.06	3.36	17.93
10	2-Methyl-2-propanol	19.54[d] ± 0.02	7.26[d]	12.47
11	2-Methyl-1-butanol	17.31 ± 0.08	4.12	15.63[c]
12	2-Methyl-2-butanol	18.00 ± 0.06	5.19	5.78
13	3-Methyl-1-butanol	16.49 ± 0.07	2.95	15.19
14	Octanol	15.68 ± 0.02	–	10.34
15	Water	31.86[e] ± 0.88	1.32	78.36

[a] From Ref. [15].
[b] From Ref. [2].
[c] From Ref. [16].
[d] Values at 27 °C.
[e] From Ref. [13].

An analysis of the solution enthalpy values in the series 1-propanol, 2-methyl-1-propanol, 2-methyl-2-propanol and 1-butanol, 2-methyl-1-butanol, 2-methyl-2-butanol, shows that solution enthalpy values are higher in both series when solvents are less associated, as approximately measured by their dielectric constant, ε [15]. This is probably a result of a decrease in the amount and strength of solute–solvent interactions. This effect is particularly evident for 2-methyl-2-propanol and 2-methyl-2-butanol in which the “spherical” shape of the solvent molecules hampers full interaction with the solute, leading therefore to a higher solution enthalpy, i.e., to a more endothermic process [8,17].

In the series of isomeric alcohols (1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol, on one hand, and 1-pentanol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2-methyl-2-butanol, and 2-pentanol, on the other hand) the differences in the solution enthalpies are related to differences in the ratio of linear and cyclic intermolecular hydrogen-bond association, as reported before [8,10,11,17].

A comparison with the behavior of *t*-BuBr (also presented in Table 1) for a similar set of hydroxylic solvents, allows us to go a bit further in this analysis. Solution processes are, as expected, far more endothermic in the case of 1-BrAd, which might be a consequence of at least two factors: on one hand, the additional energy needed to destroy the crystal lattice of this solid solute and, on the other hand, the larger energy needed for breaking more solvent–solvent interactions than in the case of *t*-BuBr, given the need for a bigger solvent cavity to accommodate this larger solute molecule.

However, if we correlate the solution enthalpies for 1-BrAd with those for *t*-BuBr excluding 1-octanol (for which we do not have the corresponding value for *t*-BuBr) and including water (Fig. 1) we obtain a linear relationship between them if we leave out the most structured solvents, water, methanol and ethanol. It seems therefore that the more structured the solvent, the more relevant appears to be the solute’s volume in the solution pro-

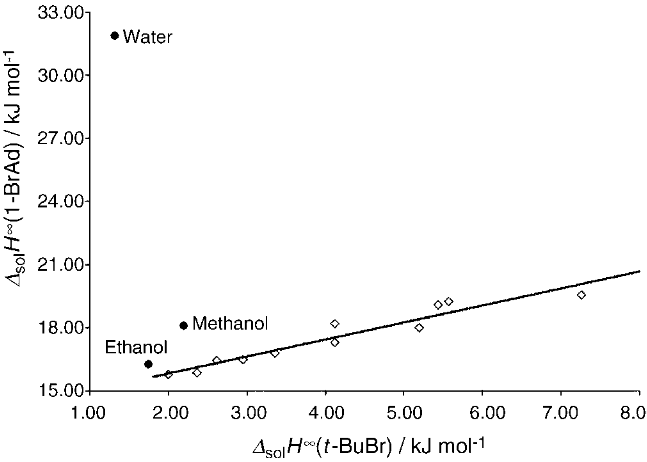

Fig. 1. Solution enthalpies at infinite dilution ($\Delta_{\text{sol}}H^{\infty}$) for 1-BrAd vs. solution enthalpies at infinite dilution ($\Delta_{\text{sol}}H^{\infty}$) for *t*-BuBr at 298.15 K.

Table 2
C values for the 14 monoalcohols and water

No.	Solvent	C^{a}
1	Methanol	0.858
2	Ethanol	0.679
3	1-Propanol	0.597
4	2-Propanol	0.560
5	1-Butanol	0.542
6	2-Butanol	0.511
7	1-Pentanol	0.501
8	2-Pentanol	0.463
9	2-Methyl-1-propanol	0.520
10	2-Methyl-2-propanol	0.467
11	2-Methyl-1-butanol	0.480
12	2-Methyl-2-butanol	0.436
13	3-Methyl-1-butanol	0.486
14	Water	2.307

[a] From Ref. [15].

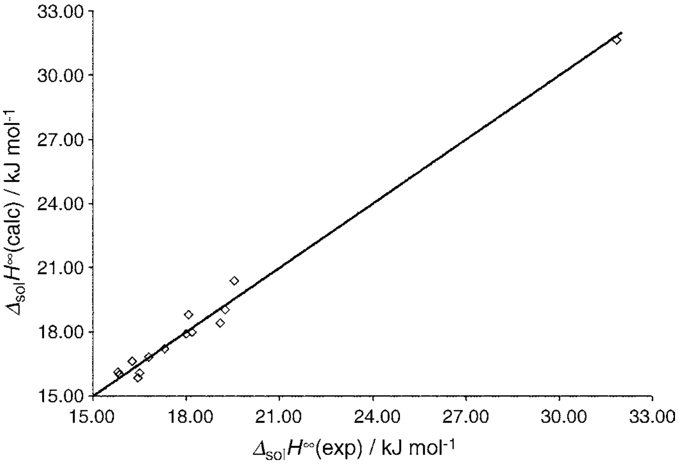

Fig. 2. Calculated vs. experimental solution enthalpies at infinite dilution ($\Delta_{sol}H^{\infty}$) for 1-BrAd at 298.15 K.

cess. Larger solutes tend to break up more solvent–solvent bonds which are present in a larger number in structured solvents.

This is further substantiated if we regress $\Delta_{sol}H^{\infty}$ (1-BrAd) versus $\Delta_{sol}H^{\infty}$ (t-BuBr) + C, where C is the cavity term, taken as a measure of the structuredness of the solvent [15] (Table 2).

The inclusion of C leads to an excellent regression (Fig. 2), for which the figures of merit are:

$$\Delta_{sol}H^{\infty}(\text{1-BrAd}) = (8.38 \pm 0.48) + (1.04 \pm 0.09)\Delta_{sol}H^{\infty}(t\text{-BuBr}) + (9.50 \pm 0.32)C$$

$$N = 14;\quad \text{S.D.} = 0.48;\quad R = 0.9939;\quad F = 450$$

where N is the number of solvents, S.D. the standard deviation of the fit, R, the correlation coefficient and F the Fisher–Snedecor statistics. This result is even more significant if compared with the poorer quality of the uniparametric regressions $\Delta_{sol}H^{\infty}$ (t-BuBr) versus C (r = 0.49; S.D. = 1.59) and $\Delta_{sol}H^{\infty}$(1-BrAd) versus C (r = 0.91; S.D. = 1.72).

The decrease of relevance of the solute's volume in less structured solvents, on the other hand, can be pin-pointed if we analyze the differences between the solution enthalpies for both solutes in the pairs (1-PrOH, 2-PrOH), (1-BuOH, 2-BuOH) and (1-PeOH, 2-PeOH). In fact, the magnitude of the difference for each pair is the same for the two solutes, within experimental uncertainty. It seems therefore that for these pairs of solvents the solute's size does not influence significantly the enthalpy of solution.

4. Conclusions

From the results presented in this work, we can conclude that the volume of 1-BrAd is a major factor in the solution process in highly structured solvents, for which the disruption of solvent–solvent bonds and the creation of cavities require more energy than for less structured solvents.

For the sub-set of less structured solvents, the differences among solution enthalpies seem to be connected not so much to the breaking of solvent–solvent bonds but to the setting up of solute–solvent interactions and the formation of new solvent–solvent bonds.

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References

[1] H. Piekarski, Thermochim. Acta 420 (2004) 13–18.
[2] R.M.C. Gonçalves, L.M.P.C. Albuquerque, A.M.N. Simões, Portugaliae Electrochim. Acta 9 (1991) 487–499.
[3] R.M.C. Gonçalves, L.M.P.C. Albuquerque, F.E.L. Martins, A.M.N. Simões, J.J.M. Ramos, J. Phys. Org. Chem. 5 (1992) 93–100.
[4] N.A. Litova, V.P. Korolev, Russ. J. Gen. Chem. 71 (2001) 702–706.
[5] B.N. Solomonov, V.N. Novikov, A.B. Solomonov, Russ. J. Gen. Chem. 72 (2002) 854–863.
[6] N.G. Manin, S.Yu. Belichenko, V.P. Korolev, Russ. J. Gen. Chem. 73 (2003) 9–16.
[7] R.M.C. Gonçalves, A.M.N. Simões, J. Solution Chem. 16 (1987) 39–43.
[8] R.M.C. Gonçalves, A.M.N. Simões, J. Solution Chem. 19 (1990) 315–320.
[9] R.M.C. Gonçalves, L.M.P.C. Albuquerque, A.M.N. Simões, Thermochim. Acta 247 (1994) 265–271.
[10] L.M.P.C. Albuquerque, M.L.C.J. Moita, A.M.N. Simões, R.M.C. Gonçalves, Thermochim. Acta 275 (1996) 67–73.
[11] L.M.P.C. Albuquerque, M.L.C.J. Moita, A.M.N. Simões, R.M.C. Gonçalves, Thermochim. Acta 322 (1998) 57–61.
[12] M.D. Borisover, A.A. Stolov, F.D. Baitolov, A.I. Morozov, B.D. Solomonov, Thermochim. Acta 285 (1996) 199–209.
[13] N. Nunes, F. Martins, R.E. Leitão, Thermochim. Acta 441 (2006) 27–29.
[14] A.J. Head, R. Sabbah, in: K.N. Marsh (Ed.), IUPAC Recommended Reference Materials for the Realization of Physicochemical Properties, Blackwell, Oxford, 1987 (Chapter 9).
[15] Y. Marcus, The Properties of Solvents, Wiley, Chichester, 1999, p.140.
[16] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, 4th ed., John Wiley & Sons, New York, 1986, pp. 207–208, 210–211.
[17] R.M.C. Gonçalves, L.M.P.C. Albuquerque, A.M.N. Simões, J.J.M. Ramos, Thermochim. Acta 209 (1992) 63–75.