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Thermochemistry of 1-bromoadamantane in binary mixtures of water–aprotic solvent

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Abstract

Solution enthalpies of 1-bromoadamantane in the mixed solvents water–*N*,*N*-dimetylformamide, water–*N*,*N*-dimethylacetamide and water–acetone were determined at 298.15 K, within the range of solubility of 1-bromoadamantane (1-BrAd) in the mixed solvents. The solution enthalpy of 1-bromoadamantane in water was determined based on extrapolation from the three mixtures. Enthalpies of transfer from the mixed solvents to cyclohexane were calculated. The effect of the composition of the mixtures on the thermochemical values obtained was also investigated.

Keywords: 1-Bromoadamantane; Mixtures; Water; Solution enthalpy

1. Introduction

Solvents exert a profound influence on chemical systems, influencing solubility and partition, chemical equilibrium, spectroscopic and electrochemical properties and reaction rates [1]. The study of the interactions of solute molecules with the surrounding medium remains one of the less understood aspects in this field. In the case of solvent mixtures, the complexity is considerably enhanced due to the number and types of solvent interactions among different components of the mixture and because solutes can suffer preferential solvation by one of the co-solvents.

Study of the solvation of electrolytes and non-electrolytes in aqueous, non-aqueous and mixed solvents can be done by several techniques. Our approach involves solution calorimetry that, in combination with cavity solution theories, can provide a sound picture of the solution process by identifying the main solute–solvent–solvent interactions [2–5].

Recent studies have shown that adamantyl compounds and their derivatives might have antibacterial, antiviral, antitumor and anti-inflammatory activity [6,7]. A pre-requisite to proceed with the use of any new compound found to be of pharmaceutical interest is to have as much knowledge of its physicochemical properties as possible. In this work we intend to determine the enthalpy of solution at infinite dilution, $\Delta_{\text{sol}}H^{\infty}$, of 1-bromoadamantane (1-BrAd) in water at 298.15 K (Fig. 1).

Since 1-bromoadamantane is insoluble in water, its solution enthalpy cannot be measured directly. Total dissolution of 1-bromoadamantane is only achieved in aqueous mixtures at high mole fractions of the organic co-solvent. Thus, one has to work with a set of water poor mixtures from which the desired value can be obtained by extrapolation. Piekarsky has recently reported a monotonous variation of the solution enthalpies for various species in H_2O/DMF mixtures and other aqueous mixtures with non-polar organic co-solvents within the whole range of the mixed solvent composition [5]. Based on this assumption, we chose to make our first estimate of $\Delta_{\text{sol}}H^{\infty}$ of 1-BrAd in water in H_2O/DMF mixtures.

Given the potential uncertainties, the values obtained by extrapolation must be confirmed through independent measurements in other mixtures. The choice of the additional organic co-solvents can be rationalized on the basis of an appropriate set of solvent descriptors, such as those provided by the TAKA model [8]. The TAKA model involves the solvatochromic

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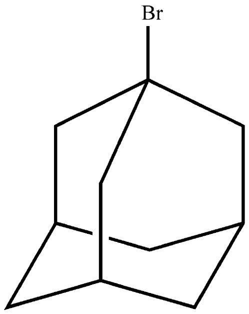

Fig. 1. 1-Bromoadamantane.

Table 1
Solvatochromic parameters for the three organic solvents

Organic solvent	π^*	α	β
N,*N*-dimethylformamide	0.88	0.00	0.69
N,*N*-dimethylacetamide	0.85	0.00	0.76
Acetone	0.62	0.08	0.48

parameters π^*, α and β, which reflect dipolarity/polarizability, and Lewis acidity and basicity.

Following this approach and taking also into consideration Piekarski's findings, *N*,*N*-dimethylacetamide and acetone were selected as co-solvents to prepare two extra aqueous binary mixtures. The closeness of the solvatochromic parameters' values for these three solvents (Table 1), suggests a similarity of the physicochemical properties described by these parameters.

2. Experimental

Experimental measurements were carried out at 298.15 K using a Thermometric precision solution calorimeter. The calorimeter is a 100 mL Pyrex glass vessel fitted with a thermistor for sensing temperature and a heater for calibration and equilibration. This equipment 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 in NaOH 0.05 mol dm^{-3}, showing good agreement with tabulated values (17.16 ± 0.02 versus 17.19 ± 0.02 [9]).

Bromoadamantane was supplied by Sigma–Aldrich (minimum 99%). All the aprotic solvents were supplied by Sigma–Aldrich (minimum 99.5%), and were used without further drying or purification. The water used was ultrapure water (Millipore, 18.2 mΩ cm resistivity), freshly prepared.

The concentration of 1-BrAd ranged from 0.01 to 0.02 mol dm^{-3}. Cylindrical ampoules were filled with solute and sealed. The heat associated with breaking empty ampoules was found to be negligible. Each value of enthalpy resulted from the average of at least three individual experiments, with a relative standard deviation always less than 3%.

The binary mixtures were prepared by mass on a Mettler H35 analytical balance with a precision of ±0.1 mg.

3. Results

Experimental data obtained in this work are presented in Table 2.

Based on these results, which are also presented in Fig. 2, and given the linear trend observed, values for water were estimated by simple linear regression for each of the binary mixtures. Extrapolated values of 31.97 ± 0.24 kJ mol^{-1} for water–*N*,*N*-dimethylformamide, 31.90 ± 0.53 kJ mol^{-1} for water–*N*,*N*-dimethylacetamide and 30.29 ± 0.88 kJ mol^{-1} for water–acetone were determined. Combining the three results and their uncertainties, s_i, and making a weighted average ($w_i = s_i^{-2}/(\Sigma s_i^{-2}/3)$), we obtain for the enthalpy of solution of 1-bromoadamantane in water the value of 31.86 ± 0.88 kJ mol^{-1}. The reported uncertainty corresponds to a 95% confidence interval, σ, calculated as $\sigma = t \times s/\sqrt{3}$, where t is the appropriate Student's t value and s is the weighted standard deviation. From the same linear regressions, we can also evaluate, for each mixture, the enthalpy of solution when $x = 1$, that is, for the pure co-solvent. The values obtained are 17.65 ± 0.14 kJ mol^{-1} for *N*,*N*-dimethylformamide, 16.77 ± 0.25 kJ mol^{-1} for *N*,*N*-dimethylacetamide and 16.75 ± 0.62 kJ mol^{-1} for acetone, respectively, which agree within experimental uncertainty with the directly measured values [10].

The results show that all enthalpy values are endothermic. As the amount of water in the mixtures increases, the enthalpy for the solution process also increases.

The enthalpies of transfer from a solvent, S, or a mixture, M, to a reference solvent, S_{ref}, can be calculated by Eq. (1),

$$\Delta_{\text{tr}}H^{\infty} = \Delta_{\text{sol}}H^{\infty}(\text{S or M}) - \Delta_{\text{sol}}H^{\infty}(\text{S}_{\text{ref}}) \qquad (1)$$

The solution enthalpy at infinite dilution of 1-BrAd in cyclohexane was previously reported by us [10] as 13.19 ± 0.04 kJ mol^{-1}. From this value, we calculated the corresponding $\Delta_{\text{tr}}H^{\infty}$ for our systems, as shown in Table 3.

The magnitude of $\Delta_{\text{tr}}H^{\infty}$ increases with water content in the mixtures, indicating that the specific solute(s)/solvent inter-

Table 2
Solution enthalpies ($\Delta_{\text{sol}}H^{\infty}$) of 1-bromoadamantane, at 298.15 K and infinite dilution, for different mole fractions of aqueous mixtures of aprotic solvents and corresponding standard deviations

	Organic solvent	$x_{\text{organic solvent}}$	x_{water}	$\Delta_{\text{sol}}H^{\infty} \pm \sigma\Delta_{\text{sol}}H^{\infty}$ (kJ mol^{-1})
N,*N*-dimethylformamide	0.70	0.30	21.98	0.26
	0.65	0.35	22.62	0.26
	0.60	0.40	23.37	0.08
	0.55	0.45	24.11	0.02
N,*N*-dimethylacetamide	0.80	0.20	19.82	0.40
	0.75	0.25	20.43	0.16
	0.65	0.35	22.23	0.09
	0.54	0.46	23.66	0.13
Acetone	0.70	0.30	20.91	0.08
	0.65	0.35	21.52	0.11
	0.55	0.45	22.53	0.05
	0.46	0.54	24.26	0.16

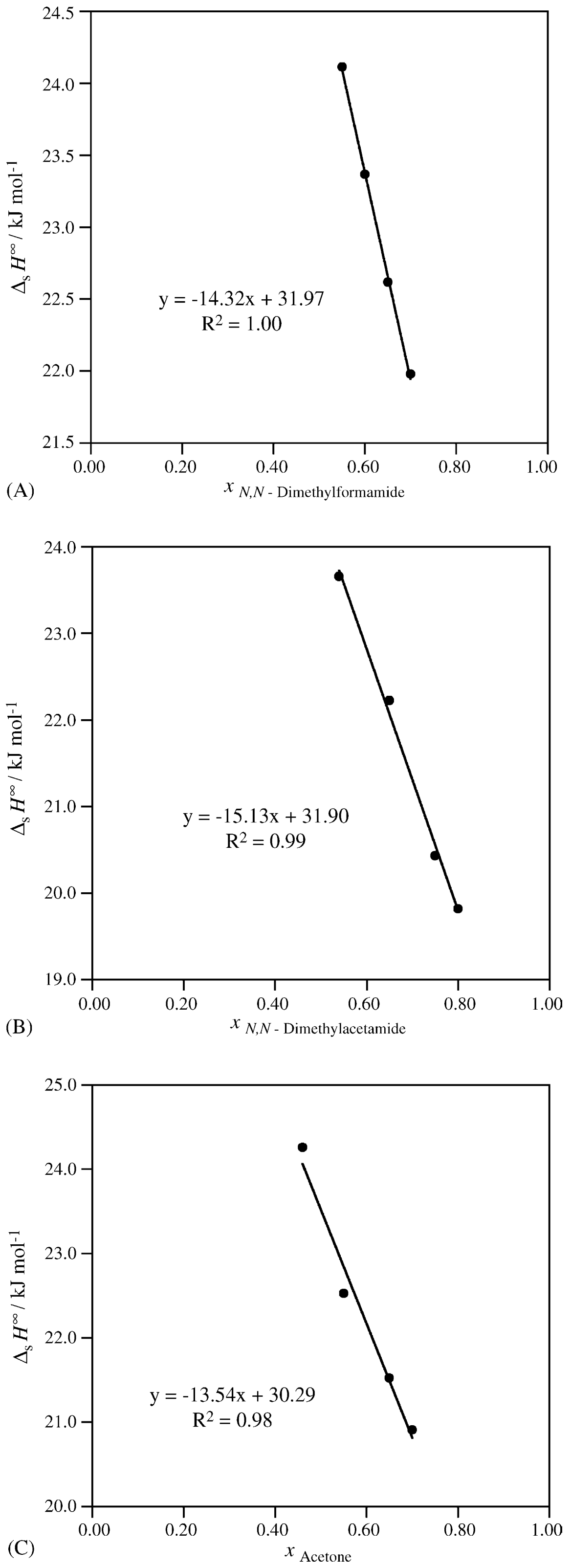

Fig. 2. $\Delta_{sol}H^{\infty}$ vs. mole fraction of organic solvent: (A) water–*N*,*N*-dimethylformamide, (B) water–*N*,*N*-dimethylacetamide and (C) water–acetone.

Table 3
Enthalpies of transfer of 1-bromoadamantane ($\Delta_{tr}H^{\infty}$), at 298.15 K and infinite dilution, from aqueous mixtures of aprotic solvents to cyclohexane

Organic solvent	$x_{\text{organic solvent}}$	x_{water}	$\Delta_{tr}H^{\infty}$ (kJ mol^{-1})
N,*N*-dimethylformamide	0.70	0.30	8.79
	0.65	0.35	9.43
	0.60	0.40	10.18
	0.55	0.45	10.92
N,*N*-dimethylacetamide	0.80	0.20	6.63
	0.75	0.25	7.24
	0.65	0.35	9.04
	0.54	0.46	10.47
Acetone	0.70	0.30	7.72
	0.65	0.35	8.33
	0.55	0.45	9.34
	0.46	0.54	11.07

actions, which are exothermic in nature, must be diminishing. In fact, at each mole fraction, the system behaves as a ternary system with two solutes. At lower water content, these specific interactions are due to co-solvent–water and co-solvent–1-BrAd interactions. At higher water content, they result from water–co-solvent and water–1-BrAd interactions. The observed trend should therefore be attributable to a large hydrophobic behaviour of 1-BrAd, which prevents this solute molecule from interacting with water molecules. Moreover, this effect overcomes the exothermic contributions resulting from either the specific interactions co-solvent–1-BrAd or water–co-solvent, depending on the mole fraction value.

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