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Short communication

Calorimetric determination of enthalpy changes for the proton ionization of *N*-tris(hydroxymethyl)methyl-4-aminobutanesulfonic acid (TABS), *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) and 3-[*N*-tris(hydroxymethyl)methylamino]-2-hyroxypropane sulfonic acid (TAPSO) in water–methanol mixtures

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ABSTRACT

Enthalpies for the two proton ionizations of the biochemical buffers *N*-tris(hydroxymethyl)methyl-4-aminobutanesulfonic acid (TABS), *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) and 3-[*N*-tris(hydroxymethyl)methylamino]-2-hyroxypropane sulfonic acid (TAPSO) were obtained in water–methanol mixtures with methanol mole fraction (X_m) from 0 to 0.360. The ionization enthalpy for the first proton (ΔH_1) of all three buffers was small and exhibited slight changes upon methanol addition. The ionization enthalpy of the second proton (ΔH_2) of TABS increased from 39.6 to 49.8 kJ mol^{-1} and for TAPS from 40.1 to 43.2 kJ mol^{-1}, with a minimum of 38.2 kJ mol^{-1} at $X_m = 0.059$. For TAPSO the increase was from 33.1 to 35.6 kJ mol^{-1} at $X_m = 0.194$, with measurements at higher X_m precluded by low solubility of TAPSO in methanol rich solvents. The solvent composition was selected so as to include the region of maximum structure enhancement of water by methanol. The results were interpreted in terms of solvent–solvent and solvent–solute interactions.

1. Introduction

Previous communications from this laboratory reported on the enthalpies of proton ionization in water–methanol solutions containing several structurally related zwitterionic buffers used in biochemistry. These were *N*,*N*-bis[2-hydroxyethyl]-2-aminoethanesulfonic acid (BES) and *N*-tris[hydroxymethyl] methyl-2-aminoethansulfonic acid (TES) [1], *N*-[2-hydroxyethyl] piperazine-*N*′-[2-ethane sulfonic acid] (HEPES) and *N*-[2-hydroxyethyl] piperazine-*N*′-[2-hydroxypropane sulfonic acid] (HEPPSO) [2], glycine, *N*,*N*-bis(2-hydroxyethyl)glycine ("bicine") and *N*-tris (hydroxymethyl)methylglycine ("tricine") [3]. This paper reports on similar studies of *N*-substituted sulfonic acid derivatives of taurine: these are *N*-tris(hydroxymethyl)methyl-4-aminobutanesulfonic acid (TABS), *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid (TAPS) and 3-[*N*-tris(hydroxymethyl) methylamino]-2-hydroxypropane sulfonic acid (TAPSO). These are useful as biochemical buffers in the physiologically important pH range. These compounds satisfy many requirements in physiological studies including stability in solution, high solubility in water and little influence of salt on buffering properties. Measurements were made in water–methanol mixtures containing up to 50% (w/w) methanol, corresponding to a methanol mole fraction (X_m) of 0.360. As stated earlier [1–3], most thermodynamic measurements on buffers in mixed solvents have determined free energies of ionization. ΔH values have been obtained from potentiometric and spectrophotometric measurements [4–12].

2. Experimental

The procedure involving the operation and calibration of the Parr 1455 solution calorimeter has already been described [1] together with the method of data analysis. TABS, TAPS and TAPSO were Sigma chemicals, dried before use. The initial solution temperature was ca. 21 °C. ΔT varied in the range 0–0.2 °C for the addition of TABS, TAPS and TAPSO to the various solutions and was precise to ±0.002 °C. The ionic strength of all solutions was maintained at 0.300 M by addition of NaCl. Due to the very low solubility of TAPSO in neutral or acidic methanol rich solutions, measurements on TAPSO were not made above $X_m = 0.2$. The method followed was

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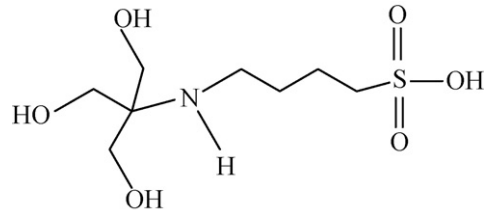
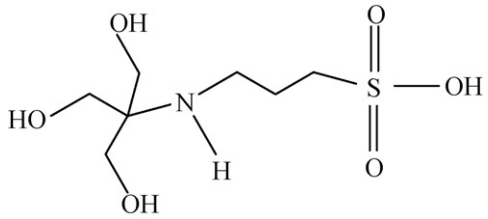
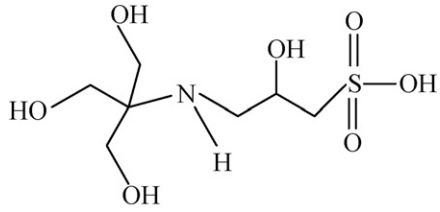
similar to that described by Ramette [13] for enthalpy determinations of the proton ionizations of glycine in water. Reliable data at X_m above 0.273 for TAPSO in the presence of 0.300 M HCl and 0.300 M NaCl could not be obtained due to the low solubility of TAPSO in these solutions.

The starting materials were the zwitterionic forms ($HB^{\pm}$) of TABS, TAPS and TAPSO:







Enthalpy changes were measured for

$$HB^{\pm}(c) + H^+ \rightarrow H_2B^+(soln.) \quad \Delta H_A \tag{1}$$

$$HB^{\pm}(c) \rightarrow HB^{\pm}(soln.) \quad \Delta H_B \tag{2}$$

and

$$HB^{\pm}(c) + OH^- \rightarrow B^-(soln.) + H_2O \quad \Delta H_C \tag{3}$$

The enthalpy of ionization of the first proton is given by

$$H_2B^+(soln.) \rightarrow H^+ + HB \pm (soln.) \quad \Delta H_1 = \Delta H_B - \Delta H_A \tag{4}$$

and ΔH_2 for the ionization of the second proton is given by

$$\Delta H_2 = \Delta H_C - \Delta H_B - \Delta H_N \tag{5}$$

where ΔH_N is the enthalpy change for the neutralization reaction $H^+ + OH^- \rightarrow H_2O$ (soln.). Values for ΔH_N at each solvent composition and ionic strength of 0.300 M have been reported earlier [1].

3. Results and discussion

Table 1 lists values of ΔH_A, ΔH_B, ΔH_C, ΔH_1 and ΔH_2 for TABS, TAPS and TAPSO.

For TABS and TAPS, methanol addition is accompanied by an increasing trend in the enthalpy of reactions (1), (2) and (3), respectively. This trend is similar to that observed in previous studies on *N*-substituted biochemical buffers [1–3] and has been attributed to less favorable solvation of H_2B^+, HB± and B^- as the dielectric constant of the medium is decreased by methanol addition ($\varepsilon_{H_2O} = 78.3$; $\varepsilon_{methanol} = 32.6$, at 25.0 °C). On purely electrostatic grounds, a drop in the dielectric constant of the medium is expected to hinder both proton dissociation and zwitterion solvation. This is reflected in ΔH_A, ΔH_B and ΔH_C of the three buffers, all of which exhibit dramatic increases with methanol addition.

Table 1 also shows that ΔH_1 for TABS, TAPS and TAPSO is small and exhibits little dependence on methanol. Similar small changes in ΔH_1 have been observed for BES and TES [1]. Reported values of apparent proton dissociation constants of $-SO_3H$ groups in compounds that bear structural similarity to TABS and TAPS are in the range 1.5–2.0 [14]. For example, pK_{a1} for 2-aminoethane sulfonic acid is 1.5 at 25 °C [14]. For TAPSO, potentiometric titration curves indicate that pK_{a1} at 25 °C in water is ca. 3.0 and is little affected by methanol addition [15]. It is interesting to compare ΔH_1 for TABS, TAPS and TAPSO in water with those for HEPES and HEPPSO [2]. For HEPES ΔH_1 is 8.47 kJ mol^{-1} and for HEPPSO, which has a –OH proximal to the sulfonate, ΔH_1 is16.7 kJ mol^{-1}. The relatively large ΔH_1 in HEPES and HEPPSO can be attributed to the attachment of the sulfonate proton to the piperazine nitrogen [16].

Table 1
ΔH_A, ΔH_B, ΔH_c, ΔH_1 and ΔH_2 for TABS, TAPS and TAPSO in water–methanol mixtures

X_m	ΔH_A (±0.2 kJ mol^{-1})	ΔH_B (±0.2 kJ mol^{-1})	ΔH_C (±0.2 kJ mol^{-1})	ΔH_1 (±0.2 kJ mol^{-1})	ΔH_2 (±0.2 kJ mol^{-1})
TABS					
0	7.8	7.5	−10.7	−0.3	39.6
0.059	13.1	12.4	1.8	−0.7	41.3
0.123	14.9	15.2	11.4	0.3	43.4
0.194	15.2	16.6	21.2	1.5	48.5
0.273	18.0	17.7	24.5	−0.4	48.2
0.360	18.3	15.1	25.9	−3.2	49.8
TAPS					
0	16.9	15.9	−1.7	−1.0	40.1
0.059	21.4	21.0	7.3	−0.4	38.2
0.123	22.4	22.9	16.1	0.5	40.4
0.194	24.3	22.1	21.5	−2.2	43.3
0.273	24.4	24.2	24.6	−0.2	41.8
0.360	25.5	23.0	27.0	−2.8	43.2
TAPSO					
0	22.0	20.2	−4.4	−1.8	33.1
0.059	24.8	23.9	5.9	−1.0	33.9
0.123	26.9	29.1	14.5	2.2	32.6
0.194	29.6	27.5	19.2	−2.1	35.6
0.273	–	–	21.5	–	–
0.360	–	–	24.8	–	–

Notwithstanding the low value of pK_{a1}, reaction (1) can be considered essentially complete because of the large excess of HCl used (0.300 M HCl vs. ~0.02 M for the three buffers).

Table 1 lists the following ΔH_2 changes starting from water: for TABS, an increase from 39.6 to 49.8 kJ mol^{-1}; for TAPS, from 40.1 to 43.2 kJ mol^{-1} with a maximum of 43.3 kJ mol^{-1} at $X_m = 0.194$; for TAPSO from 33.1 to 35.6 kJ mol^{-1} (at $X_m = 0.194$). Reported values in water, based on electrochemical measurements, are: for TABS, 35.4 kJ mol^{-1} ($I = 0.05$) as estimated from pK-T data in Ref. [4]; for TAPS, 41.49 kJ mol^{-1} ($I = 0.1$ M) [5]; for TAPSO, 39.1 kJ mol^{-1} ($I = 0$) [6].

Reported pKa_2 values at 25.0 °C are 8.672 ($I = 0.05$ M) for TABS [4], 8.38 ($I = 0.1$ M) for TAPS [5] and 7.6347 ($I = 0$) for TAPSO [6]. The lower ΔH_2 for TAPSO, as compared to TABS and TAPS, is in agreement with compilations [17–19] that show that within a given series of amines, enthalpies of ionization of the *N*-bound proton decrease with increasing acid strength.

As has been stated in the previous communications, it is important to note that ΔH trends are much more difficult to interpret than those in free energy, ΔG. This is because enthalpy changes arise from electrostatic contributions as well as structural and steric factors and it is often difficult to assess their relative contributions [20]. On the other hand, free energy changes can be understood in electrostatic and nonelectrostatic terms. Accumulation of more data on proton ionization enthalpies in amphiprotic solvents will contribute to understanding the factors involved in the ionization and solvation processes.

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