Thermochimica Acta, 6 (1973) 369–374

CALORIMETRIC MEASUREMENT OF THE WATER IONIZATION ENTHALPY IN DIMETHYLSULFOXIDE–WATER MIXTURES AT 25°C

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(Received 4 December 1972)

ABSTRACT

The $\overline{\Delta H}_{\text{ion}}$ of the process $2H_2O_X \rightarrow H_3O_X^+ + OH_X^-$ has been calorimetrically measured in dimethylsulfoxide (DMSO)–water solutions for X_{DMSO} molar ratios ranging between 0 and 0.8 at $T = 25$°C. The $\overline{\Delta H}_{\text{ion}}$ values show a well-pronounced minimum at $X_{\text{DMSO}} = 0.5$, for which composition the ionization reaction is 4.28 kcal/mole less endothermic than in pure water. The combination of the $\overline{\Delta H}_{\text{ion}}$ data with the existing $pK_{a/i}$ values reveals several features of DMSO–water mixtures with regard to the ionic solvating power and the mixed solvent structure.

INTRODUCTION

The ionization of weak acids in dimethylsulfoxide (DMSO)–water mixtures has received recently a good deal of interest[1–3], particularly for the dependence of the dissociation on the ionic solvation and the solvent structure. Generally, unless the anionic solvation is not exhanced, oxyacids are less dissociated in the mixtures than in pure water, in spite of the fact that the DMSO is known to be a stronger base than water[4]. It is also known[5,6] that the ionic product of water shows a rapid decrease with increasing DMSO content of the mixture; this can be related to a drastic reduction of the water activity when mixed with DMSO, but it could be connected as well to some structural modification which can act against the ionization process.

In view of the fact that structural modifications and ionic solvation effects cannot be well detected from free energy measurements only, we found it significant to determine experimentally by direct calorimetry the enthalpy change related to the ionization process of water in DMSO–water mixtures. These heats of ionization can also be useful for subsequent calorimetric investigation of ionization of acids in these solvent mixtures. Our measurements ranged from pure water up to 0.8 molar ratio of DMSO, and have been performed at $t = 25 \pm 0.01$ °C. The average thermal jump into the cell during the experiments was about 0.2°C.

EXPERIMENTAL

The calorimetric apparatus, fitted with a 25-ml reaction vessel, has been described previously[7,8]; DMSO (Carlo Erba RP) has been purified according to Butler[9]. Aqueous solutions of HCl and NaOH of suitable concentrations (see later) were prepared from standard 1.00 F solutions by dilution with CO_2-free distilled water, and their concentrations checked by potentiometric titration. DMSO–water mixtures of known molar ratio, containing a known amount of HCl or not, have been prepared by weight.

PROCEDURE

19.39 g of a DMSO–water solution at a known molar ratio X', containing also $1.37 \cdot 10^{-4}$ moles of HCl were introduced in the calorimetric cell, together with a sealed glass ampoule containing 0.55 g of a NaOH aqueous solution with $1.40 \cdot 10^{-4}$ moles of base. As soon as the thermal equilibrium was reached, the glass ampoule was broken and the reaction

$$\mathrm{Na}^+_{aq} + \mathrm{OH}^-_{aq} + \mathrm{H_3O}^+_{X'} + \mathrm{Cl}^-_{X'} \rightarrow \mathrm{Na}^+_X + \mathrm{Cl}^-_X + 2\mathrm{H_2O}_X \tag{1}$$

took place. In the reaction (1) the subscripts X' and X refer to the DMSO molar ratio in the solutions before and after the mixing, respectively. The solvated hydrogen ion has been written as $\mathrm{H_3O^+}$ because it seems probable[5,10,11] that in a medium as DMSO–water in the range of concentrations we used the DMSO does not show any tendency to substitute water for the primary solvation of the proton. The values of $[\mathrm{Na}^+_X]$ and $[\mathrm{Cl}^-_X]$ are of the order of $7 \cdot 10^{-3}$ F. The molar ratio X' was chosen in such a way as to lead to a round number (0.1, 0.2 etc.) for the final value of X after the mixing with the aqueous NaOH solution.

After having recorded the thermal effect of reaction (1), indicated as ΔH_r, a second experiment was performed by introducing in the cell 19.39 g of the same DMSO–water mixture of X' molar ratio, not containing HCl, and dissolving in this mixture 0.55 g of the same aqueous NaOH solution. The thermal effect of the dilution reaction.

$$\mathrm{Na}^+_{aq} + \mathrm{OH}^-_{aq} \rightarrow \mathrm{Na}^+_X + \mathrm{OH}^-_X \tag{2}$$

indicated as ΔH_{dil} was recorded; the two values ΔH_{dil} and ΔH_r were algebrically subtracted so that $\Delta H_{dil} - \Delta H_r = \Delta H_{ion}$ is the thermal effect related to the process

$$2\mathrm{H_2O}_X + \mathrm{Cl}^-_X \rightarrow \mathrm{H_3O}^+_{X'} + \mathrm{OH}^-_X + \mathrm{Cl}^-_{X'} \tag{3}$$

ΔH_{ion} value, referred to 1 mole of $\mathrm{H_3O^+}$ and 1 mole of $\mathrm{OH^-}$ and indicated as $\overline{\Delta H}_{ion}$, can be considered very similar to the thermal effect of the process

$$2\mathrm{H_2O}_X \rightarrow \mathrm{H_3O}^+_X + \mathrm{OH}^-_X \tag{4}$$

which represents the molar dissociation of water in the mixed solvent X as initial and final state. In fact the molar enthalpy of process (4) should be obtained by adding to $\overline{\Delta H}_{ion}$ values the molar transfer enthalpy of HCl (at infinite dilution) from solvent X' to solvent X

$$\mathrm{H_3O}^+_{X'} + \mathrm{Cl}^-_{X'} \rightarrow \mathrm{H_3O}^+_X + \mathrm{Cl}^-_X \tag{5}$$

process (4) being the sum of processes (3) and (5). We notice, however, that for each X'–X couple, the difference of composition results to be small (about 0.07 when the DMSO final molar ratio is $X = 0.8$, which is the most unfavourable case) and that it is known from the literature[12] that the molar enthalpy of transfer of HCl from/to DMSO–water solutions of different composition is also quite small (of the order of 0.085 kcal/mole for a change 10→20% w/o DMSO content). We think therefore that the error made by neglecting the thermal effect of process (5) in our experimental conditions is included in the limit of precision of our measurements, which is not better than ±0.5%, and we take the $\overline{\Delta H}_{\text{ion}}$ of reaction (3) as the molar enthalpy of dissociation of water dissolved in DMSO–water solution at 25°C. We did not extend our measurements beyond $X_{\text{DMSO}} = 0.8$ mainly because the difference between X' and X should have been too large for the above mentioned approximation. Furthermore the difference between ΔH_r and ΔH_{dil} values becomes too near to the experimental precision limit if aqueous NaOH solution is dissolved in a DMSO–water solution containing a large amount of the organic component.

EXPERIMENTAL RESULTS

In Table 1, the results obtained for $\overline{\Delta H}_{\text{ion}}$ in various DMSO–water solutions at the indicated DMSO molar ratios are reported. Each result is the difference between the average values obtained from at least 4 reaction experiments (process (1)) and 4 dilution experiments (process (2)); average deviations are indicated near the tabulated values.

TABLE 1

MOLAR IONIZATION ENTHALPY OF WATER IN DMSO–WATER SOLUTIONS AT VARIOUS MOLAR RATIOS AT 25°C

X_{DMSO}	$\overline{\Delta H}_{\text{ion}}$ (kcal/mole)	$\Delta H^{\circ}_{\text{ion}}$ (kcal/mole)
0	13.37±0.05	13.37±0.05
0.1	14.78±0.07	14.54±0.07
0.2	12.46±0.07	11.88±0.07
0.3	11.33±0.06	10.36±0.06
0.4	11.04±0.07	9.31±0.07
0.5	9.09±0.11	6.86±0.11
0.6	11.09±0.11	8.55±0.11
0.7	15.45±0.09	12.75±0.09
0.8	18.68±0.08	15.96±0.08

$\overline{\Delta H}_{\text{ion}}$ reported in Table 1 are referred to process (4), in which *the initial state is water dissolved in the mixed solvent X.* If we take into account the partial molar enthalpy of solution ($\overline{\Delta H}^{\text{sol}}_{H_2O}$ of pure water in DMSO–water solutions at X_{DMSO} molar ratio, which we previously measured[7], we can calculate the standard molar enthalpy of the process

$$2H_2O_w \rightarrow H_3O^+_X + OH^-_X \qquad (6)$$

for which $\overline{\Delta H}^{\circ}_{\text{ion}} = \overline{\Delta H}_{\text{ion}} + 2\overline{\Delta H}^{\text{sol}}_{\text{H}_2\text{O}}$.

Process (6) represents the formation of one mole of solvated protons and one mole of solvated OH^- ions in the mixed solvent X, *from the ionization of water in the pure state, i.e. at unit activity*. $\overline{\Delta H}^{\circ}_{\text{ion}}$ values are also listed in Table 1.

DISCUSSION

The main feature of the data reported in Table 1 is the minimum exhibited by $\overline{\Delta H}_{\text{ion}}$ and $\overline{\Delta H}^{\circ}_{\text{ion}}$ values for $X_{\text{DMSO}} = 0.5$. This is a rather peculiar behaviour of DMSO–water mixtures. In fact in other water–polar organic solvent mixtures as water–ethanol[13], water–ethylene glycol[14] the $\overline{\Delta H}_{\text{ion}}$ of water shows a continous decrease with the increasing content of the organic component. The minimum is present both in $\overline{\Delta H}_{\text{ion}}$ and in $\overline{\Delta H}^{\circ}_{\text{ion}}$ values, so it can't be linked to some difference of enthalpy at the initial state of the ionization process, since for the $\overline{\Delta H}^{\circ}_{\text{ion}}$ values the initial state is always pure H_2O (process (6)).

The reason why the water ionization is less endothermic in DMSO–water mixtures at $X_{\text{DMSO}} = 0.5$ than in pure water can therefore be related to one of these two facts: (i) the ions are more strongly solvated in the mixture; (ii) the mixed solvent possesses a structure which is more favourable, with respect to the pure water structure, to the ions solvation.

It is clear that every further step in the discussion can be done only with the help of entropy data. In the literature[5] are reported the values of $\text{p}K_{a/1}$ for the process (4) at 20°C. From these data, we calculate the $\text{p}K_{a/1}$ values at 25°C using the well-known equation

$$\text{p}K_{20\,^{\circ}\text{C}} = \text{p}K_{25\,^{\circ}\text{C}} + \frac{\overline{\Delta H}_{\text{ion}}}{1.987} \times \frac{\Delta T}{T_1 \cdot T_2 \cdot 2.303} \tag{7}$$

The calculations of eqn (7) have been made using $\overline{\Delta H}_{\text{ion}}$ values of Table 1, and not $\overline{\Delta H}^{\circ}_{\text{ion}}$ values, because the $\text{p}K_{a/1}$ found in the literature take *the water dissolved in the mixed solvent as initial standard state* for every DMSO–water mixture.

From $\text{p}K_{25\,^{\circ}\text{C}}$ it is easy to calculate $\overline{\Delta G}_{\text{ion}}$ for the process (4), and then, using the Gibbs–Helmholtz equations, the $\overline{\Delta S}_{\text{ion}}$ values.

For a comparison purpose, it is convenient to express $\overline{\Delta G}$, $\overline{\Delta H}$ and $T\overline{\Delta S}$ of the water ionization in terms of differences between the value related to the mixed solvent of X_{DMSO} molar ratio and that of the pure water[15] so that

$$\overline{\Delta G}_{\text{ion}_X} - \overline{\Delta G}_{\text{ion}_w} = \delta\overline{\Delta G}_{\text{ion}}$$

In the same way $\delta\overline{\Delta H}_{\text{ion}}$ and $\delta T\overline{\Delta S}_{\text{ion}}$ can be defined and calculated. These "transfer" enthalpy, entropy and free energy values of ionization of water in the various mixed solvents are listed in Table 2 and plotted versus δ_{DMSO} in Fig. 1. From the plots reported in Fig. 1 it is clearly noticeable that the ionization process is more difficult in the DMSO–water mixtures than in pure water, as $\delta\overline{\Delta G}_{\text{ion}}$ values are always posi-

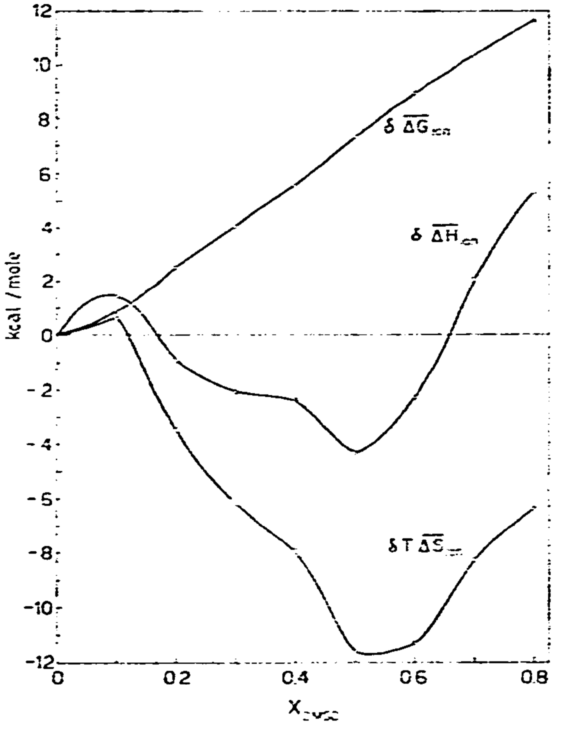

Fig. 1. Thermodynamic quantities for ionization of water in DMSO–H_2O mixtures at $t = 25$ °C.

TABLE 2

TRANSFER ENTHALPY, ENTROPY AND FREE ENERGY VALUES OF WATER IONIZATION IN DMSO–WATER MIXTURES AT THE INDICATED MOLAR RATIO AT 25 °C

X_{DMSO}	$\delta\overline{\Delta H}_{ion}$ (*kcal/mole*)	$\delta\overline{\Delta G}_{ion}$ (*kcal/mole*)	$\delta T\overline{\Delta S}_{ion}$ (*kcal/mole*)
0.1	1.41	0.85	0.56
0.2	−0.91	2.52	−3.43
0.3	−2.04	4.11	−6.15
0.4	−2.33	5.59	−7.92
0.5	−4.28	7.33	−11.61
0.6	−2.28	8.97	−11.25
0.7	2.08	10.33	−8.25
0.8	5.31	11.65	−6.34

tive and they increase with increasing concentration of the organic component. However, this increased difficulty of the process must be attributed to different effects, according to the composition of the solvent, *i.e.*:

(*a*) $0 < X_{DMSO} \lesssim 0.15$; the ionization enthalpy is more positive in the mixtures than in pure water. The term $\delta T\overline{\Delta S}$ is also positive, but not so large as to compensate the $\delta\overline{\Delta H}_{ion}$ term. In this range of concentrations the ions are solvated almost exclusively by water[10] and it is logical that with the decreasing of the water concentration, the hydration energy decreases too. The water ionization is certainly a "order-forming" process, and for DMSO–water mixtures at low DMSO content it is less anti-entropic than in water ($\delta T\Delta S_{ion} > 0$); this is in favour of the hypothesis that these mixtures are more ordered than pure water; in other words, the presence of small amounts of DMSO strengthens the water structure[1,7].

(*b*) $0.15 \lesssim X_{DMSO} \lesssim 0.50$; the enthalpy term is favourable to the ions solvation in the mixtures with respect to water, but the entropy term is contrary. With the increased DMSO content, the solvation bonds formation is more exothermic; the main cause of this it is probably the solvation of the proton, which could be bound now also to DMSO molecules[1,10]. However, the solvent structure becomes more and more disorganized, reaching the maximum disorder at $X_{DMSO} \cong 0.5$, and this entropy effect, which is against the dissociation process, always prevails over the better solvation of the protons.

(*c*) $X_{DMSO} \gtrsim 0.5$; with the increase of the organic component in the mixtures the ion solvation becomes less exothermic. This can be related to the drastic reduction of the hydration of OH^- ion, which in DMSO–water mixtures is always very little solvated by DMSO molecules[6]. On the other hand the entropy term increases, due to the large percentage of DMSO, by itself highly associated. The increase of the $\delta T\overline{\Delta S}_{ion}$ is nevertheless always lower than the $\delta\overline{\Delta H}_{ion}$ increase, so the overall dissociation is more hindered with the increase in DMSO content.

We reach so the conclusions that even with respect to the reaction of ionization of water, the DMSO–water mixtures can be divided in three zones[16]: one from 0 to about 15 mole %, with a structure favourable to the dissociation but a lower solvating power than pure water; one from 15 to about 50 mole %, with a higher solvating power but a disordered structure, and finally one after 50 mole %, with a reinforced structure but a rapid lowering of the solvating ability.

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