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CALORIMETRIC DETERMINATION OF PARTIAL MOLAR ENTHALPIES OF SOLUTION OF WATER AND DIMETHYLSULFOXIDE IN THEIR MIXTURES

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ABSTRACT

Values of partial molar enthalpies of solution of water and DMSO in their mixtures at various molar ratios have been calorimetrically measured; the results show no evidence for the existence of any water–DMSO stoichiometric adduct, and they allow some hypothesis to be made about the relative influence of water and DMSO upon the two solvent structures.

INTRODUCTION

The high hygroscopicity of dimethylsulfoxide (DMSO) makes practically unavoidable that small amounts of water will be absorbed during the usual handling of his solutions. If DMSO has to be used as aprotic solvent in electrochemistry, it would be rather important to know to which extent the water dissolved in DMSO retains his proton-donor behaviour.

It seems quite logical to think that the protic properties of water dissolved in an aprotic, hydrogen-bond acceptor solvent as DMSO should be less pronounced if water–solvent interactions are strong. The present research, concerning the direct calorimetric determination of partial molar enthalpies of solution of water and DMSO in their mixtures, is a contribution to the study of such interactions.

The integral enthalpy of mixing of various amounts of water and DMSO has been previously reported by Drinkard and Kivelson[1], by Lindberg and Kenttamaa[2], and by Cowie and Toporowsky[3]; the partial molar enthalpy of solution of water at infinite dilution in DMSO has been measured by Arnett and McKelvey[4]. Our research has not been restricted to water–DMSO solutions at low water content, but it covers the whole molar ratio range. Our results show no evidence for the existence of any water–DMSO stoichiometric adduct, and they allow some hypothesis to be made about the relative influence of water and DMSO upon the two solvent structures.

EXPERIMENTAL

The calorimeter cell was made from a glass dewar of about 500-ml capacity, closed by a hard nylon cover which was deeply fitted on the dewar to reduce the free volume of the cell to slightly more than 200 ml. The glass stirrer (rotating at a speed of 200 r.p.m.), the heating resistor for calibration ($R = 30.6348\ \Omega$ at 25°C, manganin wire), the glass holder for the small ampoules of water and DMSO samples, and the thermometric probe were introduced in the cell through four holes bored in the cover, and they were permanently assembled to this one.

The thermometric probe , a Fenwall glass-covered thermistor, had a resistance of 2745 Ω at 25°C; the following resistance–temperature relationship holds:

$$R_{T°C} = 2745\ [1-0.0609\ (T°C-25)]$$

which we tested from 20 to 30°C.

The thermistor was part of one leg of a resistance bridge, supplied with a voltage of 5.5 V (nickel–cadmium batteries). For heating effects of 0.1°C or less, we found that the umbalance signal of the bridge was proportional to the thermal jump in the cell according to the expression $(\mathrm{d}E/\mathrm{d}T)_{T \simeq 25°C} = -1.95 \times 10^{-2}$ V/°C.

The unbalance of the bridge was monitored by a Keithley Model 153 Electrometer, normally employed with 300 μV or 1 mV full scale range. The electrometer output was connected to a strip chart recorder, Keithley Model 370.

The cell was submerged in a water bath, whose temperature was controlled at 24 ±0.1°C with a constancy of 1×10^{-3} °C; consequently the inner-cell temperature, after the solution was continously stirred overnight, was stable on a value of 25 ±0.2°C with a linear drift less than 0.01°/h.

The cell was filled with 200 g of pure water, pure DMSO or a solution of the two components in the required molar ratio. The small samples of water or DMSO to be dissolved were introduced in the cell on sealed, thin-walled glass ampoules, easily broken at the moment of the experiment.

The heat capacity of the cell was measured just before and after each experiment by means of the heating resistor inside the cell, using a Hewlett & Packard Model 6112A constant voltage supply, an electric watch Jaquet Model 309DR, a standard resistor Officine Galileo of 1,000 Ω and a Leeds & Northrup Model 8687 potentiometer.

All the apparatus, assembled in a thermostatic room at 25 ±0.5°C, shows a reproducibility of about 1.4%. The precision was tested by several determinations of the heat of solution of crystalline KCl in water (molar ratio $KCl/H_2O = 1/27.000$) for which we obtained the average value of −4136 ±5 cal/mole, in good agreement with the value of −4146 ±1 cal/mole reported by Somsen *et al.*[5].

The commercial DMSO (Carlo Erba RP) has been distilled twice under dry nitrogen at reduced pressure after treatment with NaOH pellets for two h at 90°C; the water content, measured by Karl Fischer titration, was ~90 p.p.m.

RESULTS AND DISCUSSION

In our experiments the samples of pure water or pure DMSO dissolved in 200 g of H_2O–DMSO solutions were ranging from 60 to 120 mg. Indicating with $X_{H_2O} = a$ the water molar ratio in the 200 g of solution in the cell, and with q_1 and q_2 the amounts of heat evolved by addition of respectively n_1 moles of water and n_2 moles of DMSO, the partial molar enthalpies of solution of water and DMSO will be

$$(\overline{\Delta H}^{\text{sol}}_{H_2O})_{X_{H_2O}=a} = -\frac{q_1}{n_1}\,; \quad (\overline{\Delta H}^{\text{sol}}_{\text{DMSO}})_{X_{H_2O}=a} = -\frac{q_2}{n_2} \tag{1}$$

Expressions (1) are valid if:

(*i*) for both the components one assumes the standard state as a reference state, *i.e.* $H^0_{H_2O} = 0$ and $H^0_{\text{DMSO}} = 0$ for pure H_2O and DMSO at 1 atm and 25°C, respectively;

(*ii*) the composition of the solution in the cell does not change on adding the small amounts of water and DMSO used for the solution experiments.

This last requirement is not strictly observed in our experiments, but we noticed that for 4 or 5 additions of small amounts of the same component to the same solution, the differences between the values of the evolved heat per mole were largely included in the experimental errors limits.

In Table I are reported the results obtained for $\overline{\Delta H}^{\text{sol}}_{H_2O}$ and $\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$ in various H_2O–DMSO solutions at the indicated molar ratios. Each result is the average value of at least six measurements made in two distinct solutions of the same molar ratio (average deviations are indicated near the tabulated values).

TABLE I

PARTIAL MOLAR ENTHALPIES OF SOLUTION OF WATER ($\overline{\Delta H}^{\text{sol}}_{H_2O}$) AND DMSO ($\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$) IN H_2O–DMSO SOLUTIONS AT VARIOUS COMPOSITIONS (T = 25 ±0.2°C)

X_{H_2O}	$\overline{\Delta H}^{\text{sol}}_{H_2O}$ (*cal/mole*)	$\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$ (*cal/mole*)
0	−1280 ±14	0
0.05	−1322 ±8	−21.7 ±1.5
0.10	−1357 ±24	−35.0 ±2.5
0.20	−1360 ±3	−38.5 ±3
0.30	−1347 ±24	−61.0 ±1
0.40	−1263 ±4	−70.0 ±1
0.50	−1114 ±22	−221 ±9
0.60	−865 ±2	−532 ±7
0.65	−686 ±20	−760 ±7
0.72	−486 ±6	−1378 ±6
0.80	−292 ±6	−2146 ±21
0.90	−121 ±6	−3334 ±11
1	0	−4328 ±16

The same results are plotted in Fig. 1, *vs.* the molar ratio of H_2O. Using the expression

$$(\overline{\Delta H}_{\text{mix}})_{X_{H_2O}=a} = a(\overline{\Delta H}^{\text{sol}}_{H_2O})_{X_{H_2O}=a} + (1-a)(\overline{\Delta H}^{\text{sol}}_{\text{DMSO}})_{X_{H_2O}=a} \qquad (2)$$

we calculated the values of the enthalpies of mixing H_2O–DMSO per mole of solution

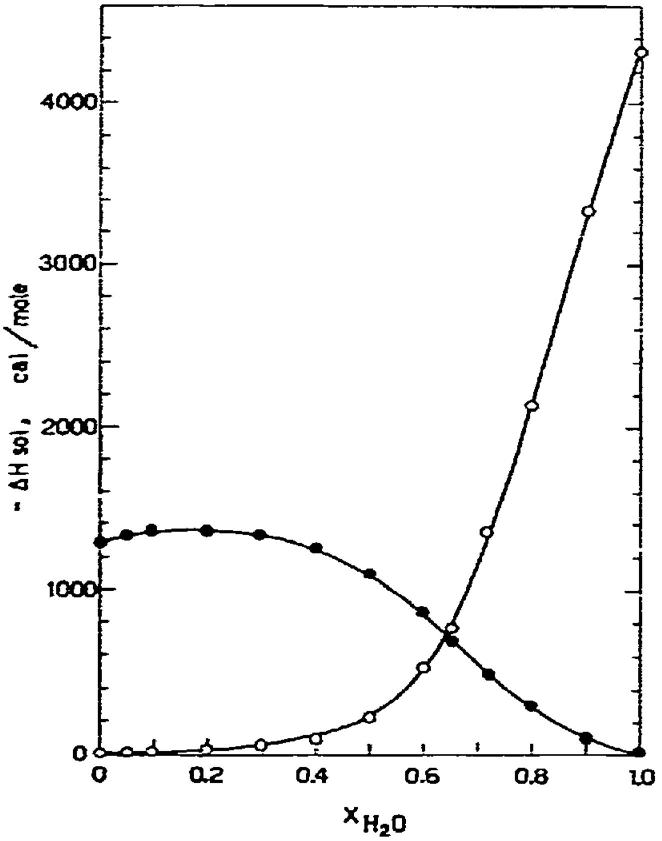

Fig. 1. $\overline{\Delta H}^{\text{sol}}_{H_2O}$, (●), and $\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$, (○), values in H_2O-DMSO solutions of various water molar ratio ($T = 25° \pm 0.2°C$).

at the various molar ratios. Those values are plotted in Fig. 2, together the results reported by Lindberg[6] and by Cowie[3].

In the molar ratio range, $0.45 < X_{H_2O} < 0.8$, the values reported by Cowie are sensibly lower than ours and Lindberg's data. It is our opinion that this difference arises because Cowie's values have been obtained by mixing relatively large amounts of the two liquids; this causes a big temperature raising and a consequent increase of the thermal capacity of the solutions[2] during the measurements.

The plot in Fig. 2 concerning our calculated values shows that $-\overline{\Delta H}_{\text{mix}}$ attains his maximum value of +750 cal/mole for $X_{H_2O} \cong 0.66$; this is in good agreement with the fact that the experimentally measured values of $\overline{\Delta H}^{\text{sol}}_{H_2O}$ and $\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$ have the same value of −730 cal/mole for $X_{H_2O} = 0.64$ (Fig. 1).

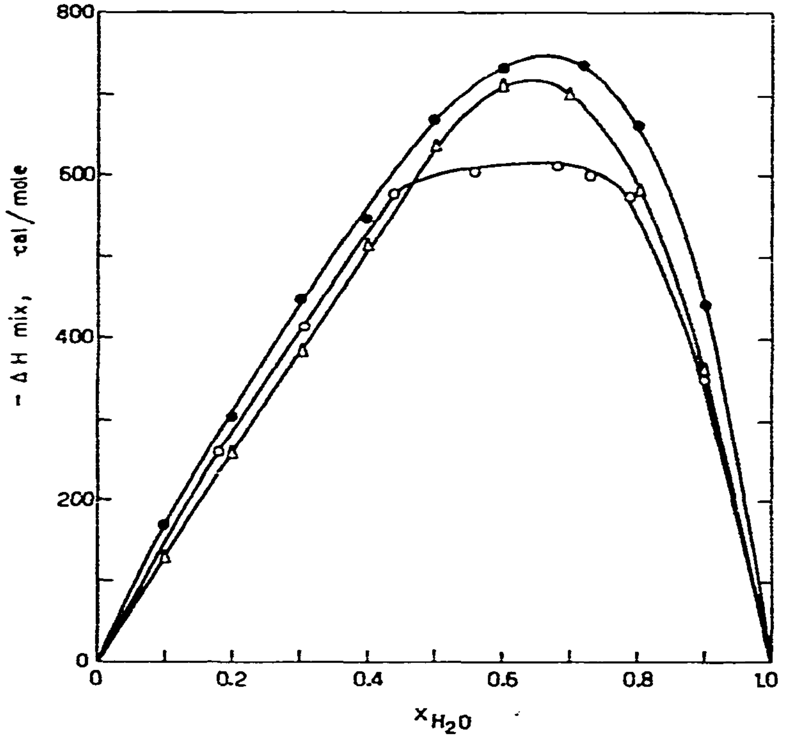

Fig. 2. Enthalpies of mixing H_2O–DMSO per mole of solution at various molar ratio; (○) from Ref. 3; (△) from Ref. 6; (●) from our experimental values (Table I and Eqn. 2).

Our experimental value of $(\overline{\Delta H}^{\text{sol}}_{H_2O})_{x_{DMSO}\to 1} = -1{,}280 \pm 14$ cal/mole is in very good agreement with the result of Arnett and McKelvey[4] ($-1{,}280 \pm 30$ cal/mole, direct measurement) and with the value obtainable by a plot reported by Drinkard and Kivelson[1]. The value of $-4{,}328 \pm 16$ cal/mole we measured for $(\overline{\Delta H}^{\text{sol}}_{DMSO})_{x_{H_2O}\to 1}$ does not seem to us previously reported in the literature.

Taking into account the values of the molar enthalpies of vaporization of water and DMSO at 25°C $\overline{\Delta H}^{\text{vap}}_{H_2O} = 10{,}450$ cal/mole[7] and $\overline{\Delta H}^{\text{vap}}_{DMSO} = 12{,}650$ cal/mole[8] we obtained the following values for the molar enthalpies of solvation of water and DMSO at infinite dilution in DMSO and water, respectively

$$(\overline{\Delta H}^{\text{solvat.}}_{H_2O})_{x_{DMSO}\to 1} = -11{,}730 \text{ cal/mole}$$

$$(\overline{\Delta H}^{\text{solvat.}}_{DMSO})_{x_{H_2O}\to 1} = -16{,}980 \text{ cal/mole}$$

The ratio between the values of the two solvation enthalpies is about 2/3, and this could suggest that, at infinite dilution for both the solutes, one water molecule should be solvated by two DMSO molecules and one DMSO molecule by three of water (this implies that the bonds formed between a large amount of DMSO and a few water molecules are qualitatively of the same kind of those formed between a large amount of water and a few DMSO molecules).

This simple hypothesis is supported by the fact that in dilute solutions of water in DMSO, the excess molar volume of water is constant and negative for water molar ratios ranging from zero to about 0.35, and in dilute solutions of DMSO in water the excess molar volume of DMSO is constant and negative for DMSO molar ratios ranging[2] from zero to about 0.25.

Several opinions can be found in the literature about the kind of bonds which are established between water and DMSO, as the formation of a stoichiometric adduct $(H_2O)_2 \cdot DMSO$[3], the presence of non-specific dipole–dipole or ionic-type bonds[9], or mixed hydrogen and dipolar bonding[1,10]. From our calorimetric measurements it can be inferred only that the water–DMSO interactions do not lead to stoichiometric compounds. In fact the flexus points in the curves reported in Fig. 1 are not so evident to justify the formation of any adduct with a definite molar ratio.

The value of $-\overline{\Delta H}^{\text{sol}}_{\text{H}_2\text{O}}$ shows a slight increase in the molar ratio range $0 < X_{\text{H}_2\text{O}} < 0.2$; after that it decreases slowly until $X_{\text{H}_2\text{O}} \cong 0.35$, and quite rapidly for $X_{\text{H}_2\text{O}} \gtrsim 0.35$. Therefore the solvation of water in DMSO is basically of the same kind until the water content of the solutions does not exceed $X_{\text{H}_2\text{O}} \cong 0.35$. Hence it is quite reasonable that small amounts of water are almost completely bonded in the solvent structure; this agrees with the results reported previously[10] about the NMR behaviour of small amounts of water dissolved in DMSO.

The maximum value shown by $-\overline{\Delta H}^{\text{sol}}_{\text{H}_2\text{O}}$ at a water molar ratio $X_{\text{H}_2\text{O}} \cong 0.2$ can be explained by an effect of water–water interaction, but it could also suggest the hypothesis that a water–DMSO solution with $X_{\text{H}_2\text{O}} \cong 0.2$ solvates water molecules slightly better than pure DMSO. It has been already pointed out[11,12] that a proton donor substance in DMSO can break the cyclic structure of the solvent, forming some linear aggregates. In such a way, DMSO containing some water should present a less ordered structure than pure DMSO, becoming more available for the solvation of a subsequent small amount of water added on it.

According to this hypothesis, water behaves toward DMSO as a structure breaker, and DMSO added in small amount to water shows the properties of a strong structure maker (see the behaviour of $\overline{\Delta H}^{\text{sol}}_{\text{DMSO}}$ in Fig. 1 for water-rich solutions). This last statement is in agreement with the results of a very recent study[13] about the modifications caused by small amounts of DMSO on the water structure.

REFERENCES

1 W. Drinkard and D. Kivelson, *J. Phys. Chem.*, 62 (1968) 1494.
2 J. Kenttamaa and J. J. Lindberg, *Suom. Kemistilehti B*, 33 (1960) 32.
3 J. M. G. Cowie and P. M. Toporowski, *Can J. Chem.*, 39 (1961) 2240.
4 E. M. Arnett and D. K. McKelvey, *J. Amer. Chem. Soc.*, 88 (1966) 2598.
5 G. Somsen, J. Coops, and M. W. Tolk, *Rec. Trav. Chim. Pays Bas*, 82 (1963) 231.
6 J. Kenttamaa and J. J. Lindberg, *Suom. Kemistilehti B*, 33 (1960) 98.
7 M. Randall (Ed.), *Int. Crit. Tab.*, Vol. VII, McGraw-Hill, New York, 1930, p. 232.
8 H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, 72 (1960) 618.
9 J. J. Lindberg and C. Maiani, *Acta Chem. Scand.*, 17 (1963) 1477.
10 J. R. Holmes, D. Kivelson, and W. C. Drinkard, *J. Amer. Chem. Soc.*, (1962) 4677.
11 A. J. Parker, *Quart. Rev. Chem. Soc.*, 16 (1962) 163.
12 J. J. Lindberg and J. Kenttamaa, *Suom. Kemistilehti B*, 33 (1960) 104.
13 G. J. Safford, P. C. Schaffer, P. S. Leung, G. F. Doebbler, G. W. Brady, and E. F. X. Lyden, *J. Chem. Phys.*, 50 (1969) 2140.