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Enthalpies of solution of trimethylurea in water and in *N*,*N*-dimethylformamide [1]

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Abstract

Enthalpies of solution of trimethylurea in water at 296.84 and 316.95 K and in *N*,*N*-dimethylformamide at 298.15 K were measured with a Tian–Calvet type rotating calorimeter. The results, combined with literature values on other methyl-substituted urea compounds, show that the solvation of methyl-substituted ureas comprises additive contributions from the methyl groups.

INTRODUCTION

Recently, in one of our laboratories (Amsterdam), partial molar enthalpies of solution were determined for urea and several methyl-substituted ureas in the solvents water and *N*,*N*-dimethylformamide (DMF) [1]. The results strongly suggested group additivity in the enthalpies of solvation of the compounds in the two solvents. However, the investigation did not include trimethylurea. Enthalpies of solution of this compound in the two solvents mentioned above can serve as a final check on the assumed additivity. Therefore we present in this paper the results of a calorimetric investigation on the enthalpies of solution of trimethylurea in water and in DMF.

EXPERIMENTAL

Trimethylurea (molar mass 102.14 g mol^{-1}) was obtained from Alfa Products with an indicated purity of 97 mol.%. It was recrystallized twice

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[1] This paper is dedicated to Professor Loren G. Hepler on the occasion of his retirement.

from ethyl acetate. The product used in the experiments had a purity better than 99 mol.%.

Enthalpies of solution were measured with a Tian–Calvet type rotating calorimeter manufactured by Setaram (Lyon, France) and equipped with a mixing cell of 100 cm^3. Solute samples of 0.04–0.12 g were contained in glass ampoules and dissolved in about 50 cm^3 of solvent. The usual procedure was followed [2]. The calorimeter was tested by measuring the enthalpy of solution of urea in water at 298.15 K. The result, $\Delta_{sol}H_m^\infty = (15.27 \pm 0.17)$ kJ mol^{-1}, is in good agreement with literature values (ranging from 15.27 to 15.40 kJ mol^{-1}) [3–6]. The measured enthalpies of solution of trimethylurea in water refer to temperatures of 296.84 and 316.95 K and those in DMF to 298.15 K.

RESULTS AND DISCUSSION

Molar enthalpies of solution, $\Delta_{sol}H_m$, of trimethylurea in water are presented in Table 1. The final molalities of the solutions range from 0.2×10^{-2} to 1.8×10^{-2} mol kg^{-1}. No significant dependence on concentration can be observed and consequently the mean value of $\Delta_{sol}H_m$ at each temperature is considered to be that at infinite dilution, $\Delta_{sol}H_m^\infty$. By interpolation we obtained $\Delta_{sol}H_m^\infty = -(1.67 \pm 0.13)$ kJ mol^{-1} at 298.15 K. Using not further purified trimethylurea, Spencer and Hovick [7] obtained $\Delta_{sol}H_m^\infty = -(3.18 \pm 0.13)$ kJ mol^{-1}.

The values of $\Delta_{sol}H_m^\infty$ at 296.84 and 316.95 K show that the temperature coefficient of the enthalpy of solution of trimethylurea in water is large and positive. This is characteristic for aqueous solutions of compounds contain-

TABLE 1

Molar enthalpies of solution of trimethylurea in water at 296.84 and 316.95 K

Solute mass (mg)	Solvent mass (g)	10^2 m (mol kg^{-1})	Corrected heat (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$T = 296.84$ K				
52.43	50.4	1.018	−1.061	−2.07
58.46	49.7	1.152	−1.146	−2.00
59.11	49.3	1.174	−1.022	−1.77
90.81	51.4	1.730	−1.629	−1.83
92.60	52.9	1.714	−1.622	−1.79
$T = 316.95$ K				
71.77	49.7	1.414	1.064	1.51
72.94	48.7	1.466	1.045	1.46
86.14	49.6	1.700	1.324	1.57
114.44	50.7	2.210	1.606	1.43
111.55	48.0	2.275	1.722	1.58

TABLE 2

Molar enthalpies of solution of trimethylurea in dimethylformamide at 298.15 K

Solute mass (mg)	Solvent mass (g)	$10^2\ m$ (mol kg^{-1})	Corrected heat (J)	$\Delta_{sol}H_m$ (kJ mol^{-1})
40.22	47.2	0.834	6.210	15.77
54.77	52.4	1.023	8.377	15.62
65.09	47.7	1.336	10.002	15.69
88.03	48.0	1.795	13.510	15.67

ing alkyl groups. An approximate value for the change in heat capacity ΔC_p^∞ in going from the pure component to an infinitely dilute solution can be obtained from

$$\Delta C_p^\infty = \frac{\Delta(\Delta_{sol}H_m^\infty)}{\Delta T} \qquad (1)$$

With the present results we obtained $\Delta C_p^\infty = (169 \pm 7)$ J K^{-1} mol^{-1}. This value may be compared with those presented by Konicek and Wadsö [8] on substituted amides with three methyl(ene) groups. They found for *N*-ethylacetamide, $\Delta C_p^\infty = (163 \pm 4)$ J K^{-1} mol^{-1} and for *N*-methylpropionamide, $\Delta C_p^\infty = (155 \pm 3)$ J K^{-1} mol^{-1}.

Table 2 gives the enthalpies of solution of trimethylurea in DMF obtained at 298.15 K. Again, a significant dependence on concentration is absent and consequently the mean value is considered to be that at infinite dilution: $\Delta_{sol}H_m^\infty = (15.69 \pm 0.06)$ kJ mol^{-1}. The agreement with the value reported by Spencer and Hovick [7], $\Delta_{sol}H_m^\infty = (15.23 \pm 0.17)$ kJ mol^{-1}, is reasonable.

The partial molar enthalpies of transfer at infinite dilution from water to DMF defined by

$$\Delta_{tr}H_m^\infty(\mathrm{H_2O\ to\ DMF}) = \Delta_{sol}H_m^\infty(\mathrm{DMF}) - \Delta_{sol}H_m^\infty(\mathrm{H_2O}) \qquad (2)$$

reflect the changes in the enthalpy of solvation when a solute is transferred from an aqueous environment, where it may be hydrophobically hydrated to some extent, to an aprotic medium. The present results and the enthalpies of solution of urea and methyl-substituted ureas in water and DMF reported previously [1,4] are compiled in Table 3, together with the corresponding partial molar enthalpies of transfer.

Table 3 shows that in urea the introduction of one methyl group, to form methylurea, causes a shift in $\Delta_{tr}H_m^\infty(\mathrm{H_2O}$ to DMF) of (9.67 ± 0.06) kJ mol^{-1}. Addition of a second methyl group at the same N atom, to give 1,1-dimethylurea, results in a change of (7.31 ± 0.08) kJ mol^{-1}. When the second methyl group is introduced at the other N atom, so that 1,3-dimethylurea is formed, the shift in $\Delta_{tr}H_m^\infty(\mathrm{H_2O}$ to DMF) is (9.88 ± 0.06) kJ mol^{-1}, a value close to that for the first methyl group. It may indicate that

TABLE 3

Enthalpies of solution in water and dimethylformamide and the corresponding partial molar enthalpies of transfer for urea and its methyl-substituted derivatives at 298.15 K

Compound	$\Delta_{sol}H_m(H_2O)$ (kJ mol^{-1})	$\Delta_{sol}H_m(DMF)$ (kJ mol^{-1})	$\Delta_{tr}H_m$(H_2O to DMF) (kJ mol^{-1})
Urea	15.28 ± 0.04	5.85 ± 0.03	−9.43 ± 0.05
Methylurea	11.19 ± 0.01	11.43 ± 0.04	0.24 ± 0.04
1,1-Dimethylurea	12.01 ± 0.05	19.56 ± 0.05	7.55 ± 0.07
1,3-Dimethylurea	1.05 ± 0.03	11.17 ± 0.02	10.12 ± 0.04
Trimethylurea	−1.67 ± 0.13	15.69 ± 0.06	17.36 ± 0.14
Tetramethylurea	−24.53 ± 0.01	0.17 ± 0.02	24.70 ± 0.02

the NH_2 and $NHCH_3$ groups on either side of the molecules are solvated independently, which should imply that the enthalpy of transfer for trimethylurea will be larger than that for urea by (9.67 + 7.31 + 9.88 = 26.86 ± 0.12) kJ mol^{-1}. Experimentally the difference in the enthalpies of transfer of urea and trimethylurea is found to be (26.79 ± 0.15) kJ mol^{-1}, in excellent agreement with the predicted value. In addition, the difference in $\Delta_{tr}H_m^{\infty}(H_2O$ to DMF) between trimethylurea and tetramethylurea, (7.34 ± 0.14) kJ mol^{-1}, is within uncertainty limits equal to the same difference between 1,1-dimethylurea and methylurea. Consequently, the assumption of independent solvation of both sides of the urea molecules [1,7] is further substantiated by these results.

Additivity in the solvation of methyl-substituted urea compounds means that it is possible to describe their partial molar enthalpies of transfer in terms of $\Delta_{tr}H_m^{\infty}$ of the parent compound urea and the group contributions for primary and secondary methyl groups. The equation

$$\begin{aligned}\Delta\Delta_{tr}H_m &= \Delta_{tr}H_m^{\infty}(\text{methyl-substituted urea}) - \Delta_{tr}H_m^{\infty}(\text{urea})\\ &= n\ \Delta H(\text{prim}) + m\ \Delta H(\text{sec}) \qquad (3)\end{aligned}$$

TABLE 4

Calculated and observed increments relative to urea in the partial molar enthalpies of transfer of methyl-substituted ureas from water to dimethylformamide

Compound	n	m	$\Delta\Delta_{tr}H_m$(calc) (kJ mol^{-1})	$\Delta\Delta_{tr}H_m$(obs) (kJ mol^{-1})
Methylurea	1	0	9.77 ± 0.14	9.67 ± 0.06
1,1-Dimethylurea	0	1	17.04 ± 0.16	16.98 ± 0.09
1,3-Dimethylurea	2	0	19.54 ± 0.19	19.55 ± 0.06
Trimethylurea	1	1	26.81 ± 0.21	26.79 ± 0.15
Tetramethylurea	0	2	34.08 ± 0.22	34.13 ± 0.05

relates the difference in the enthalpy of transfer of a methyl-substituted urea compound and that of unsubstituted urea to the numbers n of primary and m of secondary methyl-substituted groups and their enthalpic contributions, $\Delta H(\mathrm{prim})$ and $\Delta H(\mathrm{sec})$ respectively. A least-squares analysis of the experimental data in terms of eqn. (3) yields $\Delta H(\mathrm{prim}) = (9.77 \pm 0.14)$ kJ mol^{-1} and $\Delta H(\mathrm{sec}) = (17.04 \pm 0.16)$ kJ mol^{-1}. Values of $\Delta\Delta_{\mathrm{tr}}H_{\mathrm{m}}$ calculated with eqn. (3) are presented in Table 4, together with the observed values. In view of the uncertainties, the agreement is quite satisfactory.

REFERENCES

1 A. Rouw and G. Somsen, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 3397.
2 G. Della Gatta, L. Stradella and P. Venturello, J. Solution Chem., 10 (1981) 209.
3 E.P. Egan and B.B. Luff, J. Chem. Eng. Data, 11 (1966) 192.
4 C. de Visser, H.J.M. Grünbauer and G. Somsen, Z. Phys. Chem. N.F., 97 (1975) 69.
5 S. Taniewska-Osinska and B. Palecz, J. Chem. Thermodyn., 14 (1982) 11.
6 H. Piekarski and G. Somsen, Can. J. Chem., 64 (1986) 1721.
7 J.N. Spencer and J.W. Hovick, Can. J. Chem., 66 (1988) 562.
8 J. Konicek and I. Wadsö, Acta Chem. Scand., 25 (1971) 1541.