Thermochimica Acta 479 (2008) 59–61

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short communication

D_2O–H_2O solvent isotope effects on the thermodynamic properties of 1,3-dimethyl-2-imidazolidinone hydration between 288.15 and 318.15 K

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ARTICLE INFO

Article history:
Received 25 June 2008
Received in revised form 3 September 2008
Accepted 6 September 2008
Available online 16 September 2008

Keywords:
N,*N*′-Dimethylethyleneurea
Ordinary and heavy water
Enthalpies of solution

ABSTRACT

The enthalpies of solution of 1,3-dimethyl-2-imidazolidinone or *N*,*N*′-dimethylethyleneurea in H_2O and D_2O were measured at 288.15, 298.15, 308.15, and 318.15 K. Standard enthalpies, heat capacities and entropies of solution (hydration), along with D_2O–H_2O solvent isotope effects on the quantities in question, were computed. The enthalpies of the solute dissolution as well as corresponding solvent isotope effects were found to be negative and decreasing in magnitude with increasing temperature. It was concluded that, in spite of forming the “heterocomponent” H(D)-bonds in aqueous solutions of the cyclic methyl-substituted urea derivative studied, hydrophobic hydration is the predominant type of the solute hydration and it is enhanced in D_2O.

1. Introduction

1,3-Dimethyl-2-imidazolidinone or *N*,*N*′-dimethylethyleneurea (hereinafter, DMEU) is of great interest primarily as a liquid-phase molecular cyclic analogue of 1,1,3,3-tetramethylurea (TMU) [1–3]. However, the relative permittivity and molecular dipole moment of the latter: 23.06 and 3.47 [4], at 298.15 K, are appreciably lower than those for DMEU: 37.60 and 4.09 [5], respectively. Like TMU, it is an efficient dipolar aprotic medium that plays an important part in biochemical process including the manufacture of pharmaceuticals as well as in other various synthetic organic transformations [3,6,7]. Besides, in many applications, DMEU is a suitable replacement for such the carcinogenic solvent as hexamethylphosphoric triamide [8].

Interest in DMEU also stems from the desire to study the structural transformations it causes in aqueous media. The effect is largely associated with the competition between the contributions arising from the hydrophobic and hydrophilic parts of a DMEU molecule in the course of hydration and to their joint action on the structure of the surrounding solvent.[1] Having a hydrophilic >C=O group and hydrophobic $-CH_3$ and $-CH_2-CH_2-$ ones (attached to two various nitrogen atoms) in the molecular five-membered ring, DMEU can be regarded as a simplified model cyclic compound for studying the complex interaction with water.

At the same time, to the best of our knowledge, specific features of the DMEU hydration and intermolecular interactions in its aqueous solutions have not hitherto been studied. Earlier [9], it was showed that additional information on the structural effects induced by hydration and other types of interparticle interactions in aqueous solutions can be obtained with joint studies using a combination of such two experimental methods as the solution calorimetry and D_2O–H_2O solvent isotope substitution. The former method provides information about the range of enthalpic and some other energy-related characteristics of the solute (and solution as the whole), which reflect structural rearrangements occurring during hydration. The second method, due to the quantum nature of the isotope effects (hereinafter, IEs) [10], allows one to establish the role of hydrogen bonding and hydrophobic hydration in affecting structure that are manifested in the enthalpic and other thermodynamic properties.

Based on the reasoning above, we measured the molar enthalpies of solution of DMEU in H_2O and D_2O at 288.15, 298.15, 308.15 and 318.15 K. In the Discussion section below, data on thermodynamical properties of the studied systems and other (similar

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[1] In aqueous solutions, DMEU is not hydrolyzed.

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doi:10.1016/j.tca.2008.09.005

Table 1
Standard enthalpies of solution ($\Delta_{sol}H^0$, kJ mol^{-1}), of *N,N′*-dimethylethyleneurea in normal and heavy water at various temperatures (*T*, K).

T	H_2O + DMEU		D_2O + DMEU	
	$10^3 \times m^a$	$-\Delta_{sol}H^{0b}$	$10^3 \times m^a$	$-\Delta_{sol}H^{0b}$
288.15	30.9–40.8	18.51 ± 0.11	31.7–39.5	19.87 ± 0.04
298.15	9.08–27.3	17.21 ± 0.09	18.6–21.5	18.28 ± 0.05
308.15	31.5–40.8	15.99 ± 0.10	21.6–25.3	16.76 ± 0.08
318.15	24.0–33.7	14.67 ± 0.13	24.3–39.4	15.13 ± 0.06

[a] Concentration (molality) ranges in which the $\Delta_{sol}H^m$ values for DMEU were averaged.

[b] Errors represent 95% confidence interval half-width [14].

to them) those have been used to reveal the specific features of the structural behavior of DMEU in water.

2. Experimental

DMEU or 1,3-dimethyl-2-imidazolidinone (Fluka, Japan, Puriss: assay <0.03% H_2O) was used without further purification. The density and refraction index of the purchased sample of the solute were 1.05223 g cm^{-3} and 1.4713, at 298.15 K (the reliable data reported in literature [5] are 1.05190 g cm^{-3} and 1.4707), respectively. Before and after measurements, the DMEU sample was stored in a vacuum dessicator over P_2O_5. Water of natural isotope composition was twice distilled in apparatus made of Pyrex glass. The electric conductivity of the prepared water was $\kappa = 1.3 \times 10^{-5}$ S m^{-1}. Heavy water (Izotop Co., St. Petersburg; $\kappa = 1.0 \times 10^{-5}$ S m^{-1}) was additionally analyzed for the content of deuterium, x_D, using a method of the precise bicapillary pycnometry [11]. With allowance for the densities of "reference" (Kell's [12]) D_2O at various temperatures, x_D corresponded to 99.92 ± 0.01 at.% D.

The experimental enthalpies of solution $\Delta_{sol}H^m$ (DMEU)[2] were measured at T = 298.15 K using an automated isoperibol (ampoule-type) calorimeter fitted with a 70 cm^3 titanium vessel and electrical calibration (before each experiment). The detection limit of the apparatus is 10 μK. The temperature instability in the bath is 1 mK in the temperature range of 278–333 K. The calorimeter setup and experimental procedure were described in detail recently [13].

3. Results

The calorimetric measurements showed that the $\Delta_{sol}H^m$ values in the high dilution region do not depend (within the experimental error) on the solute molal concentration m those ranging between 0.010 and 0.045 mol of DMEU per 1 kg of the solvent. Therefore, the $\Delta_{sol}H^0$ values (*i.e.*, the molar enthalpies of DMEU dissolution at infinite dilution) have been calculated as average values $|\Delta_{sol}H^m|_{av}$ over five measurements, according to the procedure described previously [14]. The experimental data on $\Delta_{sol}H^0$ for DMEU are listed in Table 1.

4. Discussion

According to the conclusions reached previously [15–17], heavy water is more structured than normal water and thus the properties of solutions in D_2O are more sensitive to the solvent-related changes induced by the presence of the solute. Most of these changes concern a difference between the librational/hindered translational motions of molecules in the liquid phases of H_2O and D_2O [15–18]. A decrease in the zero-point vibrational energy of water molecules caused by their deuteration brings about the formation of D-bonds in an aqueous medium that are stronger but more susceptible to destruction under the influence of the solute and temperature, compared with the similar protium bonds [10,18].

Note also that the standard (limiting) enthalpies of solution as defined do not contain the contributions from the interaction between the solute molecules. Since the energy spent to destroy the molecular packing of DMEU, $\Delta_{vap}H^0$, remains unaltered, the changes in $\Delta_{sol}H^0$ observed on going from one solvent (H_2O) to another (D_2O) are numerically equal to those in the standard hydration enthalpy, $\Delta_{hydr}H^0$, upon $H_2O \rightarrow D_2O$ isotope substitution.

Considering the results presented in Table 1 and Fig. 1 from this point of view led us to the following. To begin with, the dissolution of DMEU in the H/D isotopologues of water is accompanied by a considerable heat evolution over the whole temperature range studied. Herewith the $\Delta_{sol}H^0$ values decrease in magnitude (*i.e.*, the DMEU dissolution becomes less exothermic) as the temperature increases and also when H_2O replaces D_2O. A change in the isotope composition of the aqueous medium has a rather slight influence on $\Delta_{sol}H^0$, varying this temperature-dependent quantity on (3–7)% when the solvent molecules are deuterated. As a comparison, the incertainity in the $\Delta_{sol}H^0$ determination is no more than 0.5% in the case in question (see above).

Like our data, the large and negative $\Delta_{sol}H^0$ (T) values have been also observed earlier [19–22] for a number of solutes and, particularly when accompanied by a positive temperature slope, $(\partial\Delta_{sol}H^0/\partial T)_p$, are indicative of a predominantly hydrophobic hydration. The higher $|\Delta_{sol}H^0|$ values and more positive slope for the deuterium-substituted solvent (Table 1 and Fig. 1) indicate that this type of DMEU hydration is enhanced in D_2O.

Furthermore, one can see from Fig. 1 that the D_2O–H_2O solvent IE on $\Delta_{hydr}H^0$ becomes zero about 335 K, taking on a positive (by sign) value at higher temperatures. We believe that the revealed sign inversion is mainly caused by the isotopic distinction in the rate of thermal predestruction of the water structure. Indeed, as the temperature increases, the structural (vibration-energy-

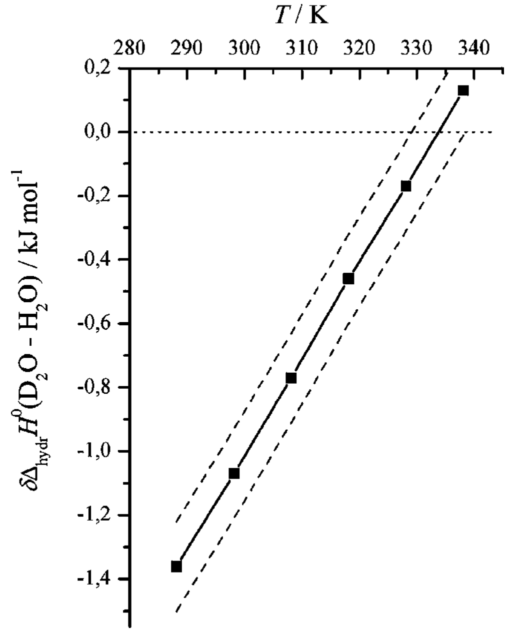

Fig. 1. D_2O–H_2O Solvent isotope effects on the enthalpy of DMEU dissolution (hydration) in the aqueous medium as a function of temperature. The dashed lines limit the half-width of the confidence interval (±ζ) for quantities considered.

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[2] Here m is the solution molality [moles of the solute (DMEU) per 1 kg of the solvent (H_2O or D_2O)].

related) differences between H_2O and D_2O become less pronounced [10,16–18] and the rising positive enthalpy-isotope contribution caused by a faster destruction of the spatial hydrogen-bond network of heavy water (compared to H_2O) result in weakening of the negative enthalpy-isotope effect of DMEU hydrophobic hydration.

Note that a similar inversion of the sign of the $\delta\Delta_{\text{hydr}}H^0$ ($H_2O \rightarrow D_2O$) value at $T \approx 318$ K was discovered previously [23] for the tetramethyl-*bis*-urea (TM*b*U, or 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octan-3,7-dione) that can be regarded as a bicyclic analogue of DMEU. However, unlike the latter case, the “predominantly hydrophilic-hydrated” TM*b*U dissolves in water with an endothermic effect being $\sim$3.7 kJ mol^{-1} at 298.15 K [23]. Herewith, within the temperature range lying under an inversion point, the $\delta\Delta_{\text{hydr}}H^0$ (TM*b*U; $H_2O \rightarrow D_2O$) values are positive and smaller by a factor of five, compared with those for DMEU.

In addition, it is noteworthy that the D_2O–H_2O solvent IE on $\Delta_{\text{hydr}}H^0$ (Table 1) is roughly equal to the IE on the energy of water–water hydrogen bond, which amounts to $-(1.0 \pm 0.1)$ kJ mol^{-1} at 298.15 K [10,24]. This indicates that DMEU molecules are capable of forming the strong hydrogen (H- or D-) bonds in aqueous media.

The results obtained in the present work made it possible to calculate a heat capacity of DMEU dissolution and the corresponding IE of its hydration. The temperature dependence of $\Delta_{\text{sol}}H^0$ was approximated by the equation [21]:

$$\Delta_{\text{sol}}H^0(T) = \Delta_{\text{sol}}H^0(\theta) + \Delta_{\text{sol}}C_p^0\theta\left(\frac{T}{\theta} - 1\right),$$

where $\Delta_{\text{sol}}H^0$ (T) and T (current temperature, K) are variables, $\Delta_{\text{sol}}H^0$ (θ) and $\Delta_{\text{sol}}C_p^0$ are the enthalpy and heat capacity parameters desired at a reference temperature θ (K), respectively. The form of equation assumes that the heat capacity of solution, $\Delta_{\text{sol}}C_p^0$, does not depend on temperature. The results of approximation by the equation show that $\Delta_{\text{sol}}C_p^0$ (T) values being (127.4 ± 3) and (157.4 ± 3) J mol^{-1} K^{-1} for (H_2O + DMEU) and (D_2O + DMEU), respectively, are positive and large as observed usually for hydrophobic-hydrated solutes [20–22,25,26] and become more positive at replacement of H_2O with D_2O. Since $\Delta_{\text{sol}}C_p^0$ reflects the structural changes in the solvent and intensity of the solvent–solute interactions [27], it can be suggested that the effect of hydrophobic hydration is more pronounced in the deuterated aqueous medium. From the equation, one can obtain the more accurate-predicted value of temperature at the inversion point (see Fig. 1), $T_{\text{inv}} = (334 \pm 3)$ K, that are in a good agreement with the above-made conclusions.

Also, the $\Delta_{\text{sol}}C_p^0$ values and the heat capacity of a “pure” liquid DMEU ($C_p^* = 205.8$ J mol^{-1} K^{-1} at 293.15 K)[3] allowed us to calculate the standard or limiting partial molar heat capacities of the specified solute in H_2O and D_2O, $\bar{C}_p^0 (\equiv \bar{C}_p^\infty) = C_p^* + \Delta_{\text{sol}}C_p^0$, which are equal, respectively, to 333 and 363 J mol^{-1} K^{-1} at 293.15 K.

5. Summary

Thus, one can conclude that, in spite of forming the strong “heterocomponent” hydrogen bonds in aqueous (H_2O or D_2O) solutions of the cyclic methyl-substituted urea derivative studied, hydrophobic hydration is the predominant type of the solute hydration and it is enhanced in heavy (deuterated) water. Also, one can infer that the negative-to-positive sign inversion of the solvent isotope effect on $\Delta_{\text{hydr}}H^0$ (DMEU) at $T = (334 \pm 3)$ K is most likely due to distinction in the rate of thermal predestruction of H_2O and D_2O structures. Meanwhile, to derive more detailed conclusions, it should be performed the additional experimental and theoretical studies.

Acknowledgment

This work was financially supported by the Russian Foundation for Basic Research (project no. 04-03-32957).

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[3] This value has been borrowed from the table sited in http://www.mitsuichemicals. com/dmi.htm. We remind also that, according to Eq. (1), the $\bar{C}_p^0$ value is taken to be temperature-independent.