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Effect of intramolecular cyclization on the enthalpies of solvation of tetramethylurea in water and alkanols at 298.15 K

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ABSTRACT

The enthalpies of solution of *N*,*N*′-dimethylethyleneurea (1,3-dimethyl-2-imidazolidinone) in water, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and *t*-butanol (2-methyl-2-propanol) were measured calorimetrically at 298.15 K. For comparison purposes, the previous data on enthalpic effects of 1,1,3,3-tetramethylurea dissolution (solvation) in the same solvents were analyzed. It has been concluded that the intramolecular cyclization of tetramethylurea, to form dimethylethyleneurea, results in strengthening of the solute solvation and this tendency is more pronounced in a non-aqueous (alcoholic) medium.

1. Introduction

In continuation of previous thermochemical studies [1–4] on solvation peculiarities of methyl-substituted ureas in aqueous and alcoholic media, we report in this paper the standard enthalpies of solution, $\Delta_{sol}H^\circ$, of 1,3-dimethyl-2-imidazolidinone (*N*,*N*′-dimethylethyleneurea or DMEU) in water and alkanols (C_1–C_4), with a view to gaining information on energy-related changes in the structural packing of the solvent under the influence of the intramolecular cyclization in 1,1,3,3-tetramethylurea (TMU) molecules.

Indeed, a DMEU molecule (Fig. 1) can be regarded as a cyclic analogue of a TMU molecule, in which two *N*,*N*′-*trans*-sited (relative to >C=O) methyl groups are replaced by $-CH_2-CH_2-$ grouping between nitrogen atoms. Like TMU, DMEU is a highly effective dipolar aprotic medium acting only as a hydrogen bond acceptor without any ability as a proton donor [5,6]. At the same time, the specified cyclic derivative has larger polarity with a molecular dipole moment, μ, of *ca.* 4.09*D* at 298.15 K [5] as compared to $\mu \approx 3.47D$ for its acyclic analogue [7,8]. In addition, the static dielectric constant, ε, of DMEU is almost twice as high as that for TMU (37.60 [5] and 23.06 [8], respectively).

Since TMU is a strongly hydrophobic solute and steric-controlled (configurational) effects play a perceptible role in the process of its solvation [2,4,9], we would expect a similar behaviour for the dissolved DMEU, too, although both "non-polar" (cyclic and acyclic) and carbonyl groups of the molecules compared interact probably in a different way with surrounding water or alcohol molecules. In view of this, we have focused here our attention on comparison of the enthalpic effects of DMEU dissolution in water, methanol (MeOH), ethanol (EtOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), 1-butanol (1-BuOH), and 2-methyl-2-propanol or *tert*-butanol (*t*-BuOH) with the values of $\Delta_{sol}H^\circ$ obtained recently [4] for TMU in the same solvating media at 298.15 K.

2. Experimental

DMEU (Fluka, Puriss: assay <0.03% H_2O) was used without any further purification. The density (ρ) and refraction index (n_D) of the "net" solute were 1.05225 and 1.4712 g cm^{-3}, respectively, at 298.15 K (the data reported in the literature [5] are 1.05190 g cm^{-3} for ρ and 1.4707 g cm^{-3} for n_D). Water was twice distilled to reach a specific electrical conductivity of *ca.* 1.3×10^{-5} S m^{-1}. Guaranteed-HPLC-grade alkanols (with a purity of no worse than 99.8 mol%) were purchased from Sigma–Aldrich Co. except for EtOH (Merck) and used without any further purification. The water content of these solvents, determined with a Karl Fisher titration, was below 0.05 mass%. Prior to experiments, all alcohols were stored in brown glass bottles under air-tight conditions.

The experimental enthalpies of DMEU dissolution, $\Delta_{sol}H^m$, were measured at $T = (298.15 \pm 0.005)$ K using an isoperibol ampoule-type calorimeter fitted with a 60 cm^3 reaction vessel and electrical

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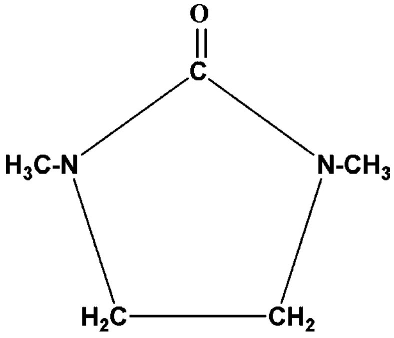

Fig. 1. *N,N′*-Dimethylethyleneurea molecule.

calibration. The thermometric and thermal sensitivities of the apparatus were, respectively, 10^{-5} K and 2×10^{-3} J/mm of the recording scale. The relative random error of measurements did not exceed 0.5%. The calorimeter was tested by measuring (in a series of 10 experiments) the enthalpies of solution of KCl and 1-PrOH in water at 298.15 K being 17.23 ± 0.07 and -10.17 ± 0.04 kJ mol^{-1}, respectively. The agreement between our and the most reliable literature $\Delta_{sol}H^\circ$ values (17.22 ± 0.04 kJ mol^{-1} for KCl [10] and -10.18 ± 0.03 kJ mol^{-1} for 1-PrOH [11]) is seen to be excellent. The calorimeter setup and experimental procedure were described in detail previously [2,4,12].

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 0.0090 and 0.0186 mol of DMEU per 1 kg of the solvent. Therefore, the $\Delta_{sol}H^\circ$ values (i.e., the molar enthalpies of DMEU dissolution at infinite dilution) have been calculated as average quantities $|\Delta_{sol}H^m|_{av}$ over six measurements, according to the procedure described recently [4,13]. The experimental data on $\Delta_{sol}H^\circ$ for DMEU in the above-enumerated solvents, along with those for TMU taken from our previous work [4], are presented in Table 1.

4. Discussion

It is known that the analysis of partial thermodynamic characteristics of a solute at its hypothetical (standard [14]) state of the infinite or limiting dilution with a solvent allows us to exclude fully the possibility of intermolecular solute–solute interactions in a binary liquid system under study. Such an analysis gives the most detailed information when physically grounded correlations between standard thermodynamic characteristics of a solute and structure-related properties of solvating media in a homologues series of solvents are considered [4,15].

We have previously [2,4] shown that the experimentally (from calorimetry data) observed pattern of TMU solvation changes appreciably between aqueous and alkanolic media. Herewith the structural features of each alkanol (compared to water) play an important role in these changes. In particular, the dissolution of TMU in low-molecular alkanols (C_1–C_4) except for 2-PrOH and 1-BuOH is accompanied by heat evolution (see Table 1). In other words, the enthalpic effects of transfer, $\Delta_{tr}H^\circ$ ($\equiv\delta\Delta_{sol(v)}H^\circ$), caused by branching of the alkanol molecules, 1-PrOH → 2-PrOH and 1-BuOH → *t*-BuOH, are opposite in sign and dominated by the configurational (steric) changes in the solvation environment of the solute. Most interesting, however, is the fact that the $\Delta_{sol}H^\circ$ value for TMU in *t*-BuOH is close to that in MeOH although the solute molecules interact in a different way with surrounding molecules of alcohols compared. It should be noted here that *t*-BuOH can be considered as a molecular isomer of MeOH, in which all alkyl hydrogen atoms are replaced with the methyl groups (i.e., it is trimethylmethanol). EtOH and 2-PrOH are intermediate units of such replacement (or methanolic mono- and dimethyl-substituted derivatives, respectively), forming the limiting series of structure-isomeric “non-linear” alkanols: $H_3COH \to H_2(CH_3)COH \to H(CH_3)COH \to (CH_3)_3COH$.

Considering the results presented in Table 1 from this point of view led us to the conclusion that solutions of DMEU in water and normal and branched alkanols (C_1–C_4) have a number of characteristic features. To begin with, when TMU is replaced with DMEU, the increase in endothermicity of dissolution of the solute becomes more pronounced in water than in each of alcohols considered. Experimentally the difference in $\Delta_{sol}H^\circ$ for DMEU and TMU in H_2O is found to be 5.01 kJ mol^{-1}, whereas the change in $\Delta_{tr}H^\circ$ ($H_2O \to ROH$) caused by a cyclization of a solute molecule is -1.93 kJ mol^{-1} for R≡Me and decreases in magnitude with increasing the alkyl-group molecular weight or size (at a side R-branching), on the whole, except for R≡2-Pr (see Table 1).

Furthermore, unlike TMU, the cyclic analogue under comparison dissolves with the exothermic effect only in water and MeOH. That is, the cyclization of a TMU molecule, to form a DMEU molecule, results in a change of sign (to the positive one) of the $\Delta_{sol}H^\circ$ value in the cases of dissolution in EtOH, 1-PrOH and *t*-BuOH. Herewith the endothermicity of the specified process for DMEU in *t*-BuOH is substantially lower than that in other alkanols (C_2–C_4) studied. This partially confirms our previous [3,4,15–17] inferences about specific features (caused by the so-called “boundary effects”)[1] of solvation of the acyclic and bicyclic methyl-substituted ureas, as well as water, in MeOH and *t*-BuOH.

In addition, it is noteworthy the fact that, like aqueous solutions of TMU, the large negative $\Delta_{sol}H^\circ$ value for DMEU in water (see Table 1) points to the predominantly hydrophobic type of the solute hydration. However, in the case of a cyclic analogue, this hydration (“structure-making”) effect is less pronounced. The results in Table 1, along with the above-marked data on “electrostatic factor” ($\mu\varepsilon$) of DMEU and TMU, account for the given inference. These results support also our previous conclusion [2–4] that the structuring effects typical of aqueous solutions (i.e., totally associated to hydrophobic hydration) of aprotic methyl-substituted ureas play a minor role in their alkanolic media. On the other hand, it is possible that the more polar (relative to TMU) molecules of DMEU are responsible for the higher hydrogen-bond-accepting ability of the latter. This inference indirectly proves to be true by the fact of a perceptible increase of Gutmann's donor number (DN) on going from TMU (DN = 29.6 [8]) to its cyclic derivative *N,N′*-dimethylpropyleneurea or DMPU (DN ≅ 34 [18]). Unfortunately, the literature data on DN for DMEU, which could confirm the given assumption, are lacking.

Note that, by definition, $\Delta_{sol}H^\circ = \Delta_{solv}H^\circ - \Delta_{cond}H^\circ(\equiv -\Delta_{vap}H^\circ)$, where $\Delta_{solv}H^\circ$ and $\Delta_{cond}H^\circ(\Delta_{vap}H^\circ)$ are the standard molar enthalpies of solvation and condensation (vaporization) of the solute, respectively [15]. That is, a positive/negative sign at the $\Delta_{sol}H^\circ$ value suggests that the solute–solvent interaction is weaker/stronger than the interaction between molecules in their own liquid medium of DMEU or TMU, because the solvation of a solute can be identified with the condensation of 1 mol of its

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[1] It is associated with the unique molecular structure of each of these alcohols, i.e., with the absence of hydrocarbon chain units (“intermediate” methylene groups) in their molecules. This manifests itself in deviations of the standard (partial) thermodynamic properties of a solute in MeOH or *t*-BuOH from the tendencies of their variations in the above-mentioned series of alkanols [16].

Table 1
Standard enthalpies of solution of *N*,*N′*-dimethylethyleneurea (I) and tetramethylurea (II) in water and normal and branched alkanols (C_1–C_4) at 298.15 K

Solvent	$10^3 \times m$ (I)[a] (mol (kg solvent^{-1}))	$\Delta_{sol}H^\circ$ (I)[b] (kJ mol^{-1})	$\Delta_{sol}H^\circ$ (II)[b] (kJ mol^{-1})	$\Delta\Delta_{sol}H^\circ$ (II → I)[b] (kJ mol^{-1})
Water	9.08–16.5	−17.18 ± 0.08	−22.19 ± 0.05[c]	5.01 ± 0.09
Methanol	11.2–17.9	−1.50 ± 0.02	−4.58 ± 0.01[c]	3.08 ± 0.02
Ethanol	11.7–17.5	2.01 ± 0.01	−1.30 ± 0.06[d]	3.31 ± 0.06
1-Propanol	10.9–18.6	2.98 ± 0.01	−0.35 ± 0.03[d]	3.33 ± 0.03
2-Propanol	12.4–18.1	4.56 ± 0.03	1.39 ± 0.04[d]	3.17 ± 0.05
1-Butanol	11.4–17.4	3.78 ± 0.02	0.33 ± 0.02[d]	3.45 ± 0.03
t-Butanol	11.1–16.8	0.98 ± 0.01[e]	−2.42 ± 0.10[e,d]	3.40 ± 0.11[e]

[a] Concentration ranges in which the $\Delta_{sol}H^m$ values for DMEU (I) were averaged.
[b] Errors represent 95% confidence interval half-with [4,13].
[c] Value from Ref. [2].
[d] Value from Ref. [4].
[e] T = 299.15 K.

Table 2
Standard enthalpies of solvation of DMEU (I) and TMEU (II), $\Delta_{solv}H^\circ$ (kJ mol^{-1}), in water and alkanols at 298.15 K

Property[a]	H_2O	MeOH	EtOH	1-PrOH	2-PrOH	1-BuOH	*t*-BuOH[b]
$-\Delta_{solv}H^\circ$ (I)	69.2	53.5	50.0	49.0	47.4	48.2	51.0
$-\Delta_{solv}H^\circ$ (II)	67.7	50.1	46.8	45.9	44.1	45.2	47.9
$-\Delta\Delta_{solv}H^\circ$ (II → I)	1.5	3.4	3.2	3.1	3.3	3.0	3.1

[a] Values are determined with an error no more than ±1 kJ mol^{-1}.
[b] T = 299.15 K.

gaseous molecules in an infinitely large amount of a solvent. However, the quantity considered does not provide a complete information on the energy changes in the solvent structure induced by the solvation of DMEU and TMU molecules. To compare the solvation effects of two solutes in question, the energy spent to destroy the structure packing of each of them (i.e., the $\Delta_{vap}H^\circ$ values) must be taken into account. In view of this, we have estimated data on $\Delta_{solv}H^\circ$ using the $\Delta_{vap}H^\circ$ values, which are (45.5 ± 0.5) kJ mol^{-1} for TMU [8] and (52 ± 1) kJ mol^{-1} for DMEU[2] at 298 K. The results are listed in Table 2, where the $\Delta\Delta_{solv}H^\circ$ values relating to the replacement of TMU with DMEU in the solvating media under study are also included.

The analysis of data presented in Table 2 leads us to the following. Firstly, in all cases considered, the change in $\Delta_{solv}H^\circ$ caused by a substitution of DMEU for TMU points to strengthening of the solute solvation. Herewith, if the enthalpic effect of the solute hydration increases only by *ca.* 1.5 kJ mol^{-1} (i.e., within the experimental error of $\Delta_{vap}H^\circ$ determining), the $\Delta\Delta_{solv}H^\circ$ (TMU → DMEU) value for each alkanol in question grows more than twice in magnitude. Secondly, the change in $\Delta_{solv}H^\circ$ caused by the cyclization of a TMU molecule are found to be weak depending on the nature of linear or lateral branching in an alkanol (C_1–C_4) molecule, amounting to *ca.* −3.2 kJ mol^{-1}, on the average. It means that all features of TMU solvation in the alcoholic media studied are characteristic of the same solutions of DMEU too. However, as it has been already mentioned above, the solvation enthalpic effect (and, as a consequence, a solute–solvent affinity) is higher in the latter case.

It is clear that such an appreciable difference in $\Delta\Delta_{solv}H^\circ$ (TMU → DMEU) between water and alkanols in question (see Table 2) is defined not only by the solute capability to be built into the "parent" structure matrix of the solvent, but also by the nature of association of both DMEU and TMU with the surrounding solvating medium through hydrogen bonding. As it is known [4,19,20], a low-molecular alkanol is a stronger proton donor than water and this capacity decreases, on the whole, from MeOH to 1-BuOH, and in a sequence primary ROH > secondary ROH > tertiary ROH (R≡propyl or butyl) as well. Hence the tendency to weakening of the DMEU solvation caused by an increase in the alkanol R-size (Table 2) can be explained generally by a decrease in the acidity (proton-donating capacity) of the solvent. A similar conclusion holds true for enthalpic effects of the TMU solvation in the alcoholic media studied, too.

Since the energy spent to destroy the net solute structure increases appreciably when a TMU molecule is cyclized ($\Delta\Delta_{vap}H^\circ \cong 6.5$ kJ mol^{-1}), the enthalpic contribution in $\Delta\Delta_{solv}H^\circ$ (TMU → DMEU) due to the formation of H bonds probably is the main factor that determines the negative sign of the molar thermodynamic characteristic considered. At the same time the changes both in $\Delta_{sol(v)}H^\circ$ and in $\Delta\Delta_{sol(v)}H^\circ$ induced by 1-PrOH → 2-PrOH → 1-BuOH → *t*-BuOH replacements (see Tables 1 and 2) show that the ability of DMEU or TMU to participate in >C=O···HOR interactions with the surroundings is caused by the presence (or absence) of additional steric hindrances for H-bonding in the alkanol medium. As regards the aqueous solutions compared, for which the $-\Delta\Delta_{solv}H^\circ$ value is minimal (Table 2), the contribution of energy-packing effects connected with the creating of the solvation cavity (or "caging process") and the hydrophobic hydration of TMU and DMEU molecules seems to be more pronounced here.

5. Summary

Thus, one can conclude that the intramolecular cyclization of TMU, to form DMEU, results in strengthening of the solute solvation and this tendency is found to be the most pronounced in alkanols. The formation of "heterocomponent" H bonds in the alcoholic media under study is the main factor that determines the negative sign of the difference in enthalpies solvation for DMEU and TMU. However, the latter inference should be substantiated by performing additional experimental and theoretical studies.

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[2] Data on vaporization latent heat taken from [http://www.mitsuichemicals.com/dmi.htm], allowing for that the DMEU vapor pressure is weakly and linearly depending on temperature.

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