Thermochimica Acta 479 (2008) 62–63

Contents lists available at ScienceDirect

Thermochimica Acta

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

Addendum

Addendum to "Effect of intramolecular cyclization on the enthalpies of solvation of tetramethylurea in water and alkanols at 298.15 K" [Thermochim. Acta 475 (2008) 72–75]

Evgeniy V. Ivanov*, Valeriy I. Smirnov, Vladimir K. Abrosimov

Laboratory of Thermodynamics of Solutions of Non-electrolytes and Biologically Active Substances,
Institute of Solution Chemistry, Russian Academy of Sciences, 1 Akademicheskaya Str., 153045 Ivanovo, Russia

ARTICLE INFO

Article history:
Received 4 September 2008
Accepted 9 September 2008
Available online 1 November 2008

Table 1
Standard enthalpies of solution, $\Delta_{sol}H^\circ$ (kJ mol^{-1}), and solvation, $\Delta_{solv}H^\circ$ (kJ mol^{-1}), for DMEU (I) and TMU (II) in H/D-isotopologues of water and methanol at 298.15 K.

Solvent	$\Delta_{sol}H^\circ$ (I)[a]	$\Delta_{sol}H^\circ$ (II)[a]	$\Delta\Delta_{sol}H^\circ$ (II → I)[a]	$\Delta_{solv}H^\circ$ (I)[b]	$\Delta_{solv}H^\circ$ (II)[b]	$\Delta\Delta_{solv}H^\circ$ (II → I)
H_2O	−17.18 ± 0.08[c]	−22.19 ± 0.05[d]	5.01 ± 0.09	−77.3	−76.2	−1.1
D_2O	−18.15 ± 0.05	−23.38 ± 0.10	5.23 ± 0.11	−78.3	−77.4	−0.9
$H_2O \rightarrow D_2O$	−0.97 ± 0.10	−1.19 ± 0.11	0.22 ± 0.14	−1.0	−1.2	0.2
MeOH	−1.50 ± 0.02[c]	−4.58 ± 0.01[d]	3.08 ± 0.02[c]	−61.6	−58.6	−3.0
MeOD	−1.75 ± 0.02	−5.01 ± 0.11	3.26 ± 0.11	−61.9	−59.0	−2.9
MeOH → MeOD	−0.25 ± 0.03	−0.43 ± 0.11	0.18 ± 0.12	−0.3	−0.4	0.1

[a] The mean-weighted $|\Delta_{sol}H^m|_{av.} = \Delta_{sol}H^\circ$ values, where m is the solution molality, were found from the results of five measurements ranging between 0.006 and 0.025 mol (kg solvent)$^{-1}$; errors represent 95% confidence interval half-with [4].

[b] The revised vaporization enthalpies, $\Delta_{vap}H^\circ$ (298.15 K), being 54.0 (±0.5) for TMU [5] and 60.1 ± (0.5) kJ mol^{-1} for DMEU [6] were used in calculations.

[c] The value from Ref. [1].

[d] The value from Ref. [7].

As it was shown in the previous report [1], the molecular cyclic analogue of 1,1,3,3-tetramethylurea (TMU), 1,3-dimethyl-2-imidazolidinone or *N*,*N*′-dimethylethyleneurea (DMEU), dissolves with a heat evolution only in water and MeOH (unlike another low-molecular alkanols). It is obvious that these exothermic ("structure-making") effects should be even more pronounced upon deuterium-substitution in the solvent molecules [2], i.e., in $H_2O \rightarrow D_2O$ and MeOH → MeOD transitions. Therefore, in addition to results reported in the "key" article [1], we present here data on the enthalpies of dissolution of TMU and DMEU in MeOD (Izotop Co., St.-Petersburg, with a deuterium content of 99.0 at.%) and D_2O (Izotop Co., 99.9 at.% D). The alcohol was additionally purified by refluxing with magnesium methoxide under inert (nitrogen) atmosphere [3]. The water content of MeOD was below 0.03 mass% (Fisher analyses). The experimental data are summarized in Table 1.

One can see from the table that the H/D-isotope substitution in all cases considered induces an increase in exothermicity of the enthalpy of a solute dissolution. For aqueous solutions, this structuring effect is the substantially more pronounced, supporting the conclusion [1] that hydrophobic hydration is the predominant type of DMEU hydration. However, like values of $\Delta\Delta_{sol}H^\circ$ (TMU → DMEU) in aqueous and methanolic media, $H_2O \rightarrow D_2O$ and MeOH → MeOD isotope effects on the specified quantity of transfer are positive, too (Table 1). That is, the cyclization of a TMU molecule result in weakening of its structure-making effect and solvation, as a whole. It is noteworthy that the solvent isotope effects on $\Delta_{sol(v)}H^\circ$ for both solutes compared (see the table) are roughly equal to the isotope effects on the energy of water–water and methanol–methanol hydrogen bonds being, respectively, *ca.* −1.0 kJ mol^{-1} [8,9] and *ca.* −0.4 kJ mol^{-1} [8] at 298.15 K. This indicates that DMEU and TMU are capable of forming *exactly* hydrogen

---

DOI of original article: 10.1016/j.tca.2008.07.001.

* Corresponding author. Tel.: +7 4932 351859; fax: +7 4932 336246.
E-mail address: evi@isc-ras.ru (E.V. Ivanov).

0040-6031/$ – see front matter
doi:10.1016/j.tca.2008.09.004

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)	77.3	61.6	58.1	57.1	55.5	56.3	59.1
$-\Delta_{solv}H^\circ$ (II)	76.2	58.6	55.3	54.4	52.6	53.7	56.4
$-\Delta\Delta_{solv}H^\circ$ (II → I)	1.1	3.0	2.8	2.7	2.9	2.6	2.7

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

bonds both with aqueous and methanolic surroundings. In the deuterated solvation complexes, these bonds are more stable than those in the protiated analogues. Herewith, a negative sign at the $\Delta\Delta_{solv}H^\circ$ (TMU → DMEU) values and their increasing in magnitude on going from water H/D-isotopologues to methanol ones can serve as the corroboration of the conclusion [1] that the more polar molecules of TMU cyclic analogue are responsible for the higher hydrogen-bond-accepting ability.

Appendix A. Erratum

In conclusion, we should correct the mistakes which have involuntarily slipped in Table 2 of the key article [1]. These inaccuracies are related to the wrong-established enthalpies of a solute vaporization, $\Delta_{vap}H^\circ$, namely, *ca.* 52.0 kJ mol^{-1} for DMEU and *ca.* 45.5 kJ mol^{-1} for TMU at 298.15 K. As a consequence, the solvation enthalpies for these solutes in aqueous and alkanolic media have been incorrectly estimated, too. At the same time the difference in the revised $\Delta_{vap}H^\circ$ between DMEU and TMU (see the note b under Table 1 of this work) is found to be practically unaltered being (6 ± 1) kJ mol^{-1}. Therefore, all conclusions made on the basis of $\Delta_{solv}H^\circ$ (DMEU → TMU) values in the previous (key) article [1] remain in force. The corrected values of $\Delta_{solv}H^\circ$ for DMEU and TMU in water and alkanols (MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, and *t*-BuOH) are listed below in Table 2.

References

[1] E.V. Ivanov, V.I. Smirnov, V.K. Abrosimov, Thermochim. Acta 475 (2008) 72–75.
[2] M. Nakamura, K. Tamura, S. Murakami, Thermochim. Acta 253 (1995) 127–136.
[3] C. Mann, in: A.J. Bard (Ed.), Electrochemical Chemistry, vol. 3, Marcel Dekker Inc., New York, 1969, p. 57.
[4] E.V. Ivanov, V.K. Abrosimov, V.I. Smirnov, Thermochim. Acta 463 (2007) 27–31.
[5] P. Kneisl, J.W. Zondlo, J. Chem. Eng. Data 32 (1987) 11–13.
[6] R.F. de Farias, Quím. Nova 22 (1999) 509–511.
[7] E.V. Ivanov, V.K. Abrosimov, V.I. Smirnov, Thermochim. Acta 449 (2006) 90–92.
[8] I.B. Rabinovich, Influence of Isotopy on the Physicochemical Properties of Liquids, Consultant Bureau, New York, 1970.
[9] A. Ben-Naim, A Solvation Thermodynamics, Plenum Press, New York, 1987.