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Interactions in aqueous solutions of alkylthioureas. Excess enthalpies at 298.15 K [1]

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Abstract

The enthalpies of dilution in water of five alkylthioureas were determined at 298.15 K. Comparison of the concentration coefficients of the excess enthalpies with those of alkylureas in water makes possible an identification of similar behaviours, determined by weak and comparable interactions, mediated or assisted by the solvent. A preliminary application of the Savage–Wood additivity of group method gave results supporting the validity of the model assumed for these interactions in preceding papers.

INTRODUCTION

Studies on diluted or moderately concentrated aqueous solutions of non-electrolytes provide information about molecular interactions in mixtures of polar compounds. Alkylthioureas, like the related families of ureas, amides etc. are simple non-electrolytes with two kinds of functional group that perturb water in different ways and generate distinct interactions. In the present paper, we report the enthalpies of dilution in water at 298.15 K of five alkylthioureas: monomethylthiourea (MMTU), monoethylthiourea (METU), 1,3-dimethylthiourea (1,3-DMTU), 1,3-diethylthiourea (1,3-DETU) and 1,1,3,3-tetramethylthiourea (TMTU). Interactions in the dilute solutions of thiourea and alkylureas have been discussed in our preceding papers [1–12]. Enthalpies of solution and phase transitions of alkylthioureas have been also recently reported [13,14].

For the aqueous solutions of these organic solutes, solute–solute, solute–solvent and solvent–solvent interactions have similar intensities, time

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scales and probabilities of occurring. For the alkylthioureas, however, the occurrence of solute–solute hydrogen bonds in water can be practically excluded. The properties of their aqueous solutions can thus provide a new check of the soundness of the interaction model proposed by us for the aqueous solutions of ureas [10–12] and uncharged peptides [15–18]. In this model, the formation of stable solute–solute dimers is rejected and the thermodynamic excess properties are rationalized as being due to the coalescence of the hydration cospheres.

EXPERIMENTAL

The alkylthioureas (Aldrich Chemie products) were crystallized from water–ethanol mixtures and dried in vacuo. Purity tests by DSC gave values of about 99%. All the solutions were freshly prepared by weight, using bidistilled and degassed water. Calorimetric measurements were carried out using a LKB 10700-1 standard flow microcalorimeter at 298.15 ± 0.01 K.

The excess enthalpies of binary non-symmetrical solutions can be reported, in the molality scale, as a power series expansion

$$H^{E}(m) = h(xx)m^2 + h(xxx)m^3 + \dots \qquad (1)$$

where the coefficients $h(xx)$, $h(xxx)$ etc. are the enthalpic contribution to the corresponding virial coefficients of the excess Gibbs energy, $g(xx)$, $g(xxx)$

$$g(xx) = h(xx) - Ts(xx) \qquad (2)$$

$$g(xxx) = h(xxx) - Ts(xxx) \qquad (3)$$

The coefficients in eqn. (1) are obtained by fitting the experimental enthalpies of dilution according to eqn. (4), where m' and m are the initial and final molalities of each experiment

$$\Delta_{\text{dil}}H(m' \rightarrow m) = h(xx)m(m - m') + h(xxx)m(m^2 - m'^2) + \dots \qquad (4)$$

RESULTS AND DISCUSSION

In the case of non-electrolyte solutions, the coefficients of eqns. (1)–(4) take into account both solute–solute interactions and changes of the solute–solvent and solvent–solvent interactions with respect to the infinitely diluted reference solutions [19–22].

Preliminary values of the second and third enthalpic virial coefficients for the five studied alkylthioureas and (for comparison) for the corresponding set of alkylureas are given in Table 1.

The $h(xx)$ coefficient values are much more negative (or less positive for TMTU) for the sulphur-containing solutes. The behaviour of MMU is

TABLE 1

Coefficients of the excess enthalpies of aqueous solutions of thioureas in comparison with ureas at 298.15 K

	$h(xx)$ [a]	$h(xxx)$ [b]		$h(xx)$ [a]	$h(xxx)$ [b]
TU	−970(14)	70(11)	U	−351(3)	21(6)
MMTU	−800(14)	–	MMU	−85(2)	21(2)
1,3-DMTU	−914(24)	303(28)	1,3-DMU	35(14)	78(16)
METU	−473(43)	186(91)	MEU	160(14)	37(6)
1,3-DETU	−286(37)	817(94)	1,3-DEU	1011(78)	139(34)
TMTU	527(13)	–	TMU	2032(80)	−139(20)

Units: [a] J kg mol^{-2}; [b] J $\text{kg}^2\text{mol}^{-3}$. The 95% confidence limits are given in parentheses.

known to be intermediate between that of urea-like solutes and the present hydrophobic set of solutes. The first four alkylthioureas seem to behave like MMU, displaying also (except for MMTU) positive values for the third coefficients $h(xxx)$. TMTU instead resembles more nearly the other alkylureas.

The data can be rationalized by assuming that in these dilute aqueous solutions, as in those of ureas, three kinds of comparable group interactions are present: those between two hydrated polar frameworks of solute molecules, those between two hydrophobic hydrated groups, and cross-interactions. The first kind is promoted by a resettlement of the hydration water, which pushes back the perturbation induced by the structure-breaking attitude of the thiourea [10–21]. The second one is the well-known hydrophobic effect (the theory of which, however, has still to be refined). For thiourea aqueous solutions, only the first effect occurs. For the solutions of the first alkylthioureas, coalescence of the hydrophilic cospheres is still the prevailing effect, even in the presence hydrophobic and cross-interactions. For TMTU, the hydrophobic interactions seem to predominate. The behaviour of TMU and of *t*-butylurea seems also to be due to prevailing hydrophobic interactions, but the data are not in conflict with the formation of stable dimers [8].

As for some of the solutions of alkylureas, an additive group approach, such as that of Savage and Wood [22], is approximately operative, probably on account of compensation between different effects. Preliminary evaluation of the group contributions to the $h(xx)$ coefficients, according to this approach, is reported in Table 2. The $h(xy)$ coefficients are decomposed into the contributions due to each pair of hydrated groups i and j

$$h(xy) = \sum_{ij} n_i^x n_j^y H(ij) \tag{5}$$

In the absence of sufficient data, $H(\text{TU–TU})$ and $H(\text{CH}_2\text{–CH}_2)$ contributions are assumed as fixed values, choosing respectively the experimental

TABLE 2

Group contributions $H(ij)$ to the second coefficients of the excess enthalpies for alkylureas and alkylthioureas at 298.15 K

i	j	$H(ij)$	i	j	$H(ij)$
TU	TU	−970 [a]	U	U	−350 [a]
CH_2	CH_2	24 [a]	CH_2	CH_2	24(5)
TU	CH_2	30(13)	U	CH_2	74(10)
	$\sigma = \pm 235$			$\sigma = \pm 128$	

Units: J kg mol^{-2}.

[a] Fixed values; for TU–TU and U–U, the experimental $h(xx)$ values were used, taken without uncertainty. For CH_2–CH_2 the value calculated for alkylureas was assumed. Data for alkylureas from ref. 9.

intermolecular h(TU–TU) value and the value of $H(CH_2–CH_2)$ calculated for the alkylureas. When H(TU–TU) only was fixed, a value of 40(18) J kg mol^{-2} was calculated for $H(CH_2–CH_2)$. However, the $H(TU–CH_2)$ value obtained in this way falls within its own uncertainty range.

The fact that the signs and orders of magnitude of these coefficient values are similar to those for alkylureas, amides and uncharged amino acid and peptide derivatives confirms, in our opinion, that the models chosen to rationalize the properties of these aqueous solutions are valid.

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