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ENTHALPY OF THIOUREA AND HYDROXYUREA SOLUTION IN WATER–UREA MIXTURES

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ABSTRACT

The enthalpies of solution and dilution of thiourea (TU) and hydroxyurea (HU), in aqueous 1.0, 2.0, 3.0, 4.0 and 5.0 mol U kg^{-1} H_2O solutions of urea (U), were measured at 298.15 K. The enthalpic pair interaction coefficients of urea derivative molecule–urea molecule were determined [3], using the standard values of solution enthalpy of thiourea and hydroxyurea in water [1,2] and in aqueous solutions of urea.

INTRODUCTION

The present study is a continuation of thermodynamic investigations on aqueous urea solutions [1,2,4]. The aim of this research was to determine interactions between urea and its derivatives in aqueous solutions.

EXPERIMENTAL

Urea (puriss, POCh, Poland), thiourea (puriss, POCh, Poland) and hydroxyurea (Polfa, Poland) were crystallized twice from ethanol and dried under reduced pressure at 333 K. The calorimetric measurements were conducted in an "isoperibol" calorimeter. A heater, sunk into a 15-ohm glass jacket, was placed in a 120-cm^3 glass vessel.

The calorimetric vessel, containing two thermistors (10 kohm each) encased in stainless chrome steel, and a stainless chrome steel stirrer, was stopped with a teflon stopper. The ampoule containing the substance under study was attached to the stirrer. The thermistors were connected to an astable multivibrator system generating a rectangular wave whose frequency is a function of the temperature inside the calorimeter. Changes in the frequency of the wave were determined using a Digital Frequency meter (type PFL-21; Kabid, Poland) with a digital readout. The sensing elements were sensitive to ca. 5×10^{-5} K. The calorimeter was placed in a water thermostat whose accuracy was ca. 1×10^{-3} K.

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RESULTS AND DISCUSSION

The enthalpies of thiourea and hydroxyurea solutions, in aqueous 1.0, 2.0, 3.0, 4.0 and 5.0 mol U kg^{-1} H_2O solutions of urea in the range of urea concentrations from 0.005 to 0.1 mol kg^{-1}, were determined (Tables 1 and 2). Measurements of the enthalpies of dilution, ΔH_d, of the above systems were also made in the range of solvent concentrations from 0.1 to 2 mol (TU, HU) kg^{-1}. The plots of $\Delta H_d = f(m)$ are shown in Figs. 1 and 2. As the urea content in the solvent increases, the solution enthalpies (ΔH_d) for both urea derivatives decrease (Figs. 1 and 2). On the basis of the solution enthalpy values obtained, standard enthalpies of solution of thiourea and hydroxyurea in aqueous solutions of urea were determined graphically (Tables 1 and 2). The standard enthalpies of transfer were determined, using the standard enthalpies of solution of thiourea and hydroxyurea in water [1,2] and in water–urea mixtures.

$$\Delta H^{\infty}_{Y(W \rightarrow W+U)} = \Delta H^{\infty}_{m(W+U)} - \Delta H^{\infty}_{m(W)}$$

where Y is thiourea (TU) or hydroxyurea (HU); $\Delta H^{\infty}_{m(W)}$ are standard enthalpies of dissolution of thiourea or hydroxyurea in water [1,2]; $\Delta H^{\infty}_{m(W+U)}$ are standard enthalpies of solution of thiourea or hydroxyurea in aqueous urea solutions.

The standard enthalpies of transfer were used to obtain enthalpic pair interaction coefficients for urea molecule–urea derivative molecule [3] (Table 3)

$$\frac{\Delta H^{\infty}_{Y}}{m_U} = 2h_{U,Y} + 3h_{U,U,Y} m_U$$

where m_U molal concentration of urea (mol U kg^{-1} H_2O). Negative $h_{U,Y}$ values may be taken as indicative of strong interactions among the molecules dissolved in water.

It follows from an earlier study [2] that, contrary to what might be expected, the more negative $h_{TU,TU}$ values, in comparison with the $h_{HU,HU}$ and $h_{U,U}$ values, do not constitute proof of energetically stronger interactions between two thiourea molecules than between urea or hydroxyurea molecules. A thiourea molecule may form a smaller number of weak hydrogen bonds [5] than a urea [6] or hydroxyurea [7] molecule. For this reason, thioderivative molecules should exhibit weaker interactions with one another, as well as with molecules of a different type in the solution, than urea or hydroxyurea molecules. Smaller negative h_{xx} values for hydroxyurea and urea might be related to the weakening of the interactions among their molecules due to their entering into strong interactions with water. In the case of weak interactions between thiourea and water, interactions among thiourea molecules, regardless of their nature, are most likely in this system.

Consequently, the h_{xx} values for thiourea in water [2] are larger on the

TABLE 1

Enthalpies of solution, ΔH_m, of thiourea (TU) in water–urea (U) mixtures at 298.15 K

1 mol U kg^{-1} H_2O		2 mol U kg^{-1} H_2O		3 mol U kg^{-1} H_2O		4 mol U kg^{-1} H_2O		5 mol U kg^{-1} H_2O	
$m_{(TU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(TU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(TU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(TU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(TU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})
0.0000	21340	0.0000	20300	0.0000	19410	0.0000	18670	0.0000	17960
0.0051	21338	0.0061	20300	0.0050	19422	0.0048	18674	0.0058	17966
0.0068	21344	0.0065	20302	0.0062	19406	0.0054	18642	0.0061	17942
0.0089	21334	0.0079	20290	0.0079	19417	0.0085	18660	0.0094	17920
0.0095	21321	0.0083	20298	0.0081	19403	0.0091	18670	0.0096	17955
0.0122	21325	0.0098	20290	0.0091	19409	0.0102	18665	0.0098	17932
0.0185	21224	0.0131	20285	0.0151	19405	0.0199	18652	0.0142	17906
0.0215	21321	0.0209	20275	0.0243	19392	0.0215	18669	0.0254	17908
0.0314	21309	0.0299	20270	0.0329	19380	0.0327	18640	0.0354	17865
0.0795	21267	0.0410	20250	0.0379	19384	0.0541	18610	0.0691	17870
0.0815	21260	0.0625	20230	0.0685	19352	0.0843	18581	0.0899	17857
0.1252	21225	0.0995	20210	0.1025	19338	0.0995	18550	0.1011	17824

TABLE 2

Enthalpies of solution, ΔH_m, of hydroxyurea (HU) in water–urea (U) mixtures at 298.15 K

1 mol U kg^{-1} H$_2$O		2 mol U kg^{-1} H$_2$O		3 mol U kg^{-1} H$_2$O		4 mol U kg^{-1} H$_2$O		5 mol U kg^{-1} H$_2$O	
$m_{(HU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(HU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(HU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(HU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})	$m_{(HU)}$ (mol kg^{-1})	ΔH_m (J mol^{-1})
0.0000	21320	0.0000	20700	0.0000	20210	0.0000	19750	0.0000	19380
0.0054	21325	0.0048	20705	0.0048	20222	0.0050	19765	0.0053	19399
0.0068	21301	0.0052	20708	0.0063	20200	0.0061	19744	0.0064	19362
0.0069	21314	0.0071	20692	0.0072	20215	0.0068	19760	0.0074	19375
0.0080	21318	0.0083	20688	0.0085	20193	0.0078	19731	0.0085	19358
0.0099	21310	0.0085	20696	0.0098	20208	0.0075	19758	0.0089	19376
0.0113	21304	0.0104	20678	0.0125	20198	0.0101	19729	0.0109	19390
0.0242	21312	0.0199	20665	0.0201	20189	0.0192	19742	0.0211	19355
0.0295	21308	0.0242	20660	0.0245	20205	0.0311	19753	0.0243	19368
0.0421	21282	0.0351	20640	0.0381	20200	0.0395	19724	0.0451	19352
0.0695	21260	0.0524	20639	0.0642	20165	0.0492	19752	0.0711	19375
0.1021	21210	0.0981	20614	0.0898	20115	0.0911	19700	0.1125	19350

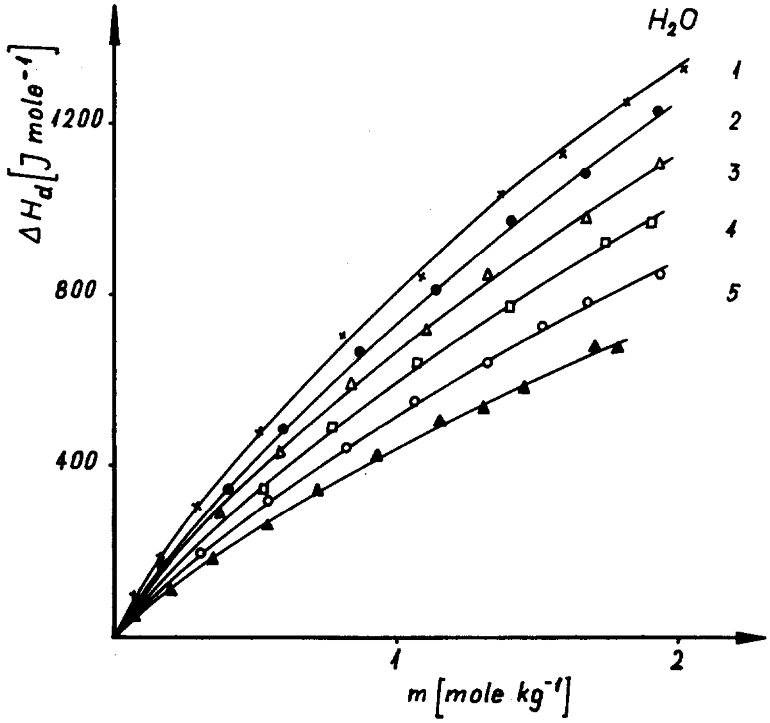

Fig. 1. Enthalpies of dilution of thiourea, ΔH_d, in water and aqueous urea solutions. H_2O [1], (1) 1, (2) 2, (3) 3, (4) 4, and (5) 5 mol U kg^{-1} H_2O.

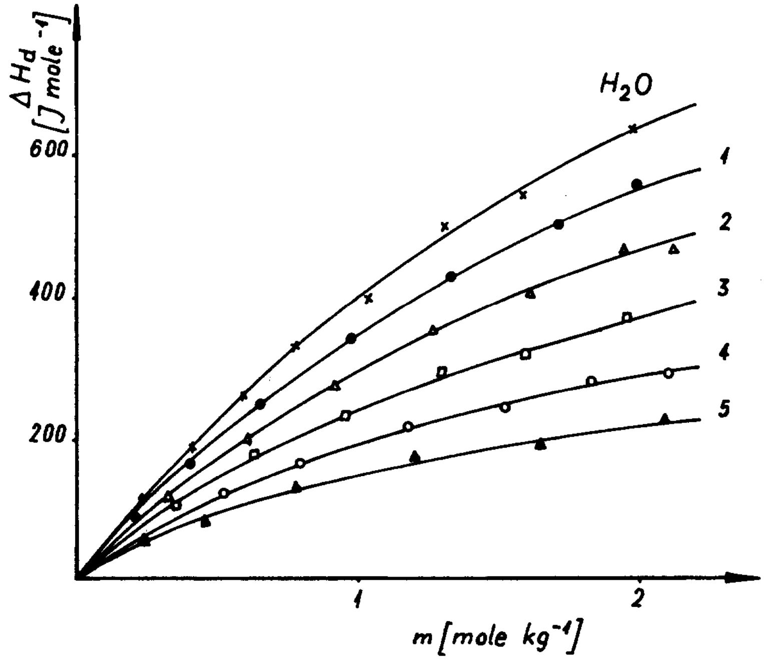

Fig. 2. Enthalpies of dilution of hydroxyurea, ΔH_d, in water and aqueous urea solutions. H_2O [2], (1) 1, (2) 2, (3) 3, (4) 4, and (5) 5 mol U kg^{-1} H_2O.

TABLE 3

Experimental and calculated enthalpic pair interaction for urea–urea derivative in water solution at 298.15 K

Solute water–urea	$h_{U,Y}$ (J kg mol^{-2})	$h_{U,Y}^{calc}$ (J kg mol^{-2})
Thiourea (TU)	−650	−615
Hydroxyurea (HU)	−390	−419

negative side than those for hydroxyurea [2] or urea [8]. This, however, does not indicate that the interactions among thioderivative molecules are stronger than those among urea or hydroxyurea molecules.

The larger negative values of enthalpic pair interaction coefficients for hydroxyurea, in comparison with urea, may be due to energetically stronger interactions among hydroxyurea molecules [8,9].

In three-component systems, the more negative values of the coefficients $h_{U,TU}$ indicate stronger interactions between thiourea than between hydroxyurea and urea. Possibly, in the case of systems containing hydroxyurea, competitive interactions among hydroxyurea water molecules take place. This is suggested by the smaller negative values of the enthalpic pair interaction coefficients for $h_{U,HU}$ in comparison with those for $h_{U,TU}$.

Using the assumption of Barone et al. [9] we calculated the enthalpic pair interaction coefficients, $h_{U,Y}$, on the basis of the enthalpic pair interaction coefficients for molecules of the same substance ($h_{U,U} = -350$ J kg mol^{-2} [8], $h_{TU,TU} = -1078$ J kg mol^{-2} [2], $h_{HU,HU} = 503$ J kg mol^{-2} [2])

$$h_{U,Y}^{calc} = \left[h_{U,U} h_{Y,Y}\right]^{1/2}$$

The calculated values of $h_{U,Y}$ are in good agreement with those obtained in this study (Table 3).

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