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INTERACTIONS IN AQUEOUS SOLUTIONS OF HYDROPHILIC UREA DERIVATIVES AND NaI AT THE TEMPERATURES 293.15 AND 303.15 K

Measurements were made of the enthalpies of solution of NaI in water and in aqueous 0.1, 0.7, 1.0 and 1.5 mol ureas kg H_2O solutions of thiourea (TU) or hydroxyurea (HU) at the temperatures 293.15 and 303.15 K. Taking advantage of the standard values of solution enthalpy of electrolytes in water and in aqueous solutions of thiourea and hydroxyurea, the enthalpic pair interaction coefficients of ureas molecule-averaged ion were determined [1, 2].

Introduction

The present study is a continuation of the thermodynamic investigations on aqueous ureas solutions [3-5]. The aim of this research was to determine interactions between hydrophilic urea derivatives and electrolyt in aqueous solutions.

Experimental

Thiourea (puriss POCh Poland), Hydroxyurea (Polfa Poland) were crystallized from ethanol and dried under reduced pressure at 333 K. NaI (Merck BRD) was crystallized from a water-acetone mixture and dried under reduced pressure at 333 K.

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The measurements of the enthalpies of dissolution were performed by using an "isoperibol" calorimeter [6] accurate to 5×10^{-5}K. The calorimeter was placed in water thermostat whose temperature stability was 1×10^{-3}K.

Result and Discussion

The obtain enthalpies of solution of NaI in water and in aqueous solutions of thiourea (TU) and hydroxyurea (HU) are collected in Tables 1, 2. As can be seen, increased exothermicity of solution enthalpies. A similar increase of exothermicity is brought about by temperature increase exemplified by the NaI data. On the basis of the solution enthalpy values obtained, standard enthalpies of solution of NaI in water and aqueous solutions of ureas (TU or HU) were determined graphically (Tables 1, 2). Such a procedure was necessitated by the unavailability of the temperature derivatives of dielectric constant required for extrapolation by the Criss and Cobble method [7]. Basing on the standard enthalpies of electrolyte solution in water $\Delta H^{\infty}_{s(W)}$ and in aqueous ureas (TU or HU) solutions $\Delta H^{\infty}_{s(N)}$, standard enthalpies of electrolyte transfer from water to aqueous ureas solutions (concentration m_N) were calculated:

$$\Delta H_{E(W \to N)} = \Delta H^{\infty}_{s(N)} - \Delta H^{\infty}_{s(W)}$$

$$\Delta H_{E(W \to N)} = 2\nu h_{NE} m_N + 3\nu h_{NNE} m_N^2 + \ldots$$

where ν is the number of ions into which the electrolyte dissociates. Following that the $2\nu h_{NE}$ values were determined by putting the m_N data on the abscissa and those for $\left[\Delta H^{\infty}_{s(N)} - \Delta H^{\infty}_{s(W)}\right] \times m_N^{-1}$ on the ordimate.

The enthalpic coefficients of ureas (TU or HU) molecule-averaged ion h_{NE} interactions obtained in this way are listed in Table 3.

A view held by many authors [1, 2, 8, 9] and shared by us is that the quite large negative values of enthalpic interaction coefficients for pairs of molecules or ions of the same or different kinds are an indication of strong interactions among the dissolved molecules. The ureas molecule-averaged ion interaction coefficients

Table 1

Enthalpies of solutions (ΔH_s) of NaI in water and water-thiourea (TU) mixtures at the temperatures 293.15 K and 303.15 K (1 cal = 4.184 J).

H_2O		0.1 mol TU/kg H_2O		0.7 mol TU/kg H_2O		1.0 mol TU/kg H_2O		1.5 mol TU/kg H_2O	
m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol
293.15 K									
0.0000	1680	0.0000	1722	0.0000	1950	0.0000	2050	0.0000	2220
0.0042	1663	0.0051	1700	0.0035	1925	0.0049	2020	0.0051	2200
0.0089	1650	0.0072	1694	0.0081	1904	0.0079	2004	0.0099	2184
0.0125	1640	0.0158	1669	0.0110	1896	0.0105	1996	0.0145	2173
0.0320	1603	0.0290	1644	0.0325	1850	0.0199	1974	0.0321	2149
0.0452	1588	0.0542	1612	0.0521	1820	0.0311	1954	0.0542	2121
0.0748	1560	0.0698	1597	0.0685	1805	0.0528	1928	0.0701	2105
303.15 K									
0.0000	2005	0.0000	2045	0.0000	2260	0.0000	2360	0.0000	2510
0.0040	1978	0.0059	2015	0.0041	2238	0.0039	2336	0.0049	2486
0.0091	1957	0.0079	2004	0.0092	2220	0.0079	2320	0.0089	2476
0.0185	1931	0.0124	1991	0.0180	2195	0.0109	2315	0.0158	2460
0.0341	1910	0.0295	1955	0.0279	2177	0.0199	2297	0.0301	2436
0.0502	1892	0.0389	1944	0.0411	2160	0.0311	2275	0.0448	2416
0.0692	1875	0.0521	1928	0.0599	2140	0.0551	2244	0.0647	2391

Table 2

Enthalpies of solutions (ΔH_S) of NaI in water-hydroxyurea (HU) mixtures at the temperatures 293.15 K and 303.15 K (1 cal = 4.184 J)

0.1 mol HU/kg H_2O		0.7 mol HU/kg H_2O		1.0 mol HU/kg H_2O		1.5 mol HU/kg H_2O	
m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol	m(NaI) mol/kg	$-\Delta H_s$ cal/mol
293.15 K							
0.0000	1720	0.0000	1925	0.0000	2015	0.0000	2170
0.0052	1697	0.0049	1896	0.0062	1986	0.0059	2146
0.0085	1685	0.0099	1878	0.0083	1978	0.0078	2137
0.0145	1671	0.0198	1853	0.0198	1950	0.0110	2128
0.0259	1648	0.0245	1844	0.0221	1946	0.0291	2090
0.0421	1624	0.0388	1823	0.0432	1916	0.0421	2070
0.0625	1600	0.0592	1798	0.0651	1894	0.0599	2050
303.15 K							
0.0000	2040	0.0000	2235	0.0000	2325	0.0000	2465
0.0049	2016	0.0069	2208	0.0049	2303	0.0059	2448
0.0078	2000	0.0089	2196	0.0079	2292	0.0098	2437
0.0151	1980	0.0149	2180	0.0151	2270	0.0148	2425
0.0329	1950	0.0251	2160	0.0321	2241	0.0241	2412
0.0501	1930	0.0401	2142	0.0502	2217	0.0301	2400
0.0689	1908	0.0552	2125	0.0649	2204	0.0549	2375

Table 3

Enthalpic pair interaction coefficients of NaI - urea derivatives in water solutions

T/K	$-h_{NE}$/cal kg mol^{-2}	
	TU-NaI	HU-NaI
293.15	105	95
303.15	98	90

obtained have negative values (Table 3), which may be due to strong interactions between the molecules of hydrophilic urea derivatives (TU, HU) and the electrolyte present in the solution. As the temperature increases, the absolute h_{NE} values decrease (Table 3) which may be related to weakened interactions between ureas molecules (TU, HU) and ions (Na^+I^-), brought about by increased intensity of thermal motions in the solution.

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ODDZIAŁYWANIA POMIĘDZY HYDROFILOWYMI POCHODNYMI MOCZNIKA I NaI W WODNYCH ROZTWORACH W TEMPERATURACH 293.15 i 303.15 K

Zmierzono entalpię rozpuszczania NaI (w zakresie stężeń 0.004--0.1 mol NaI/kg rozpuszczalnika) w wodzie i wodnych roztworach hydrofilowych pochodnych mocznika (tiomocznika i hydroksymocznika) zawierających 0.1, 0.7, 1.0 i 1.5 mol (TU, HU)/kg H_2O. Pomiary były wykonane w temperaturach 293.15 i 303.15 K. Wykorzystując wartości entalpii rozpuszczania obliczono standardowe entalpie rozpuszczania i entalpowe współczynniki oddziaływania par cząsteczka pochodnej mocznika - uśredniony jon $(Na^+ J^-)$.