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ENTHALPY OF KNO_3 AND $CaCl_2$ SOLUTION IN WATER–HYDROPHILIC UREA DERIVATIVES MIXTURES

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ABSTRACT

Enthalpies of dissolution of KNO_3 and $CaCl_2$ in water and in aqueous 0.1, 0.7, 1.0 and 1.5 mol kg^{-1} H_2O solutions of thiourea and hydroxyurea were measured at 293.15, 298.15 and 303.15 K. The enthalpic urea derivative–electrolyte interaction coefficients were calculated using standard enthalpies of electrolyte dissolution in water and aqueous ureas solutions.

INTRODUCTION

Work on the physico-chemical properties of water solutions of urea derivatives [1,2] and aqueous solutions of electrolytes and urea derivatives [3,4] has been carried out at our laboratory for a long time.

EXPERIMENTAL

Thiourea (puriss, POCh, Poland) and hydroxyurea (Polfa, Poland) were crystallized twice from ethanol and dried under reduced pressure at 333 K (the melting temperatures being 454 K for thiourea and 413 K for hydroxyurea, given in the literature as 454 K [5] and 413–414 K [6], respectively).

KNO_3 (puriss, POCh, Poland) was crystallized from water and dried until constant weight was obtained. $CaCl_2$ (puriss, POCh, Poland) was first dried at 900 K, then in a closed apparatus over dry hydrochloride at 470 K, and finally subjected to a jet of dry argon [7]. The measurements were conducted in an isoperibol calorimeter [8] accurate to 5×10^{-5} K. The calorimeter was placed in a water thermostat with a temperature stability of 1×10^{-3} K.

RESULTS

Enthalpies of dissolution of KNO_3 and $CaCl_2$ in water and in aqueous 0.1, 0.7, 1.0 and 1.5 mol kg^{-1} H_2O solutions of thio- and hydroxyurea in the

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TABLE 1

Enthalpies of solution ΔH_m of KNO_3 in water–thiourea (TU) mixtures over the temperature range 293.15–303.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

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	ΔH_m	m	ΔH_m	m	ΔH_m	m	ΔH_m	m	ΔH_m
$T = 293.15$ K									
0.0000	35.93	0.0000	35.55	0.0000	33.70	0.0000	33.26	0.0000	32.68
0.0036	35.97	0.0034	35.59	0.0032	33.75	0.0038	33.31	0.0036	32.72
0.0059	35.98	0.0061	35.60	0.0070	33.76	0.0069	33.32	0.0065	32.74
0.0085	35.99	0.0099	35.61	0.0085	33.77	0.0092	33.33	0.0079	32.75
0.0123	35.99	0.0124	35.62	0.0119	33.77	0.0105	33.33	0.0129	32.75
0.0192	35.97	0.0149	35.61	0.0153	33.75	0.0243	33.32	0.0163	32.74
0.0243	35.95	0.0218	35.60	0.0294	33.74	0.0452	32.27	0.0242	32.73
0.0651	35.89	0.0601	35.53	0.0539	33.68	0.0711	32.17	0.0531	32.67
0.0931	35.88	0.0841	35.46	0.0900	33.58	0.0853	32.15	0.0845	32.58
0.1391	35.59	0.1253	35.33	0.1249	33.45	0.1002	32.10	0.1115	32.52
$T = 298.15$ K									
0.0000	35.09	0.0000	34.75	0.0000	33.09	0.0000	32.61	0.0000	31.96
0.0035	35.14	0.0036	34.81	0.0032	33.14	0.0037	32.66	0.0034	32.02

0.0062	35.15	0.0079	34.85	0.0085	33.16	0.0082	32.68	0.0069	32.04
0.0099	35.16	0.0098	34.84	0.0102	33.17	0.0105	32.69	0.0081	32.05
0.0121	35.17	0.0152	34.83	0.0119	33.16	0.0129	32.69	0.0131	32.04
0.0396	35.15	0.0249	34.82	0.0298	33.15	0.0312	32.67	0.0425	31.99
0.0702	35.03	0.0439	34.77	0.0513	33.08	0.0595	32.59	0.0923	31.84
0.1098	34.90	0.0851	34.64	0.0949	32.96	0.0852	32.50	0.1179	31.75
0.1125	34.86	0.1234	34.50	0.1189	32.87	0.1089	32.41	0.1339	31.67
$T = 303.15$ K									
0.0000	34.46	0.0000	34.15	0.0000	32.56	0.0000	32.22	0.0000	31.69
0.0034	34.51	0.0035	34.21	0.0034	32.62	0.0038	32.28	0.0037	31.74
0.0063	34.52	0.0068	34.22	0.0062	32.64	0.0057	32.29	0.0062	31.75
0.0082	34.53	0.0093	34.24	0.0095	32.65	0.0100	32.31	0.0089	31.77
0.0101	34.55	0.0125	34.25	0.0112	32.66	0.0123	32.32	0.0101	31.78
0.0195	34.55	0.0425	34.16	0.0153	32.64	0.0242	32.29	0.0159	31.78
0.0245	34.53	0.0553	34.13	0.0293	32.63	0.0438	32.23	0.0249	32.76
0.0452	34.47	0.0850	34.05	0.0531	32.55	0.0592	32.20	0.0415	31.70
0.0835	34.35	0.0985	34.02	0.0931	32.44	0.0795	32.13	0.0785	31.59
0.1125	34.25	0.1231	33.92	0.1231	32.31	0.0998	32.04	0.1002	31.50

TABLE 2

Enthalpies of solution ΔH_m of KNO_3 in water–hydroxyurea (HU) mixtures over the temperature range 293.15–303.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

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	ΔH_m	m	ΔH_m	m	ΔH_m	m	ΔH_m
$T = 293.15$ K							
0.0000	35.58	0.0000	33.82	0.0000	33.48	0.0000	32.80
0.0034	35.62	0.0032	33.86	0.0036	33.51	0.0034	32.83
0.0062	35.63	0.0069	33.87	0.0071	33.52	0.0065	32.84
0.0089	35.64	0.0073	33.89	0.0095	33.53	0.0079	32.85
0.0112	35.65	0.0099	33.89	0.0102	33.55	0.0101	32.86
0.0198	35.64	0.0153	33.88	0.0341	33.52	0.0243	32.83
0.0341	35.62	0.0323	33.85	0.0625	33.46	0.0522	32.78
0.0554	35.57	0.0732	33.80	0.0721	33.37	0.0843	32.70
0.0921	35.45	0.1251	33.69	0.0953	33.29	0.1009	32.61
$T = 298.15$ K							
0.0000	34.77	0.0000	33.23	0.0000	32.85	0.0000	32.25
0.0038	34.81	0.0032	32.27	0.0035	32.89	0.0034	32.30
0.0082	34.83	0.0079	33.28	0.0081	32.90	0.0089	32.31
0.0134	34.85	0.0099	33.30	0.0099	32.92	0.0112	32.33
0.0189	34.84	0.0132	33.31	0.0129	32.93	0.0199	32.38
0.0349	34.75	0.0201	33.30	0.0245	32.91	0.0399	32.29
0.0940	34.65	0.0596	33.20	0.0653	32.81	0.0651	32.22
0.1249	34.53	0.0999	33.03	0.0922	32.74	0.0901	38.12
$T = 303.15$ K							
0.0000	34.18	0.0000	32.77	0.0000	32.46	0.0000	31.71
0.0040	34.24	0.0038	32.82	0.0035	32.52	0.0038	31.76
0.0091	34.26	0.0081	32.84	0.0085	32.54	0.0089	31.78
0.0108	34.27	0.0095	32.85	0.0103	32.55	0.0101	31.79
0.0115	34.28	0.0185	32.85	0.0111	32.55	0.0118	31.80
0.0189	34.26	0.0311	32.83	0.0351	32.50	0.0251	31.77
0.0495	34.18	0.0751	32.66	0.0540	32.46	0.0589	31.69
0.0853	34.08	0.1025	32.60	0.0621	32.42	0.0821	31.60
0.1089	33.99	0.1345	32.50	0.1011	32.26	0.1234	31.49

range 0.004–0.1 mol kg^{-1} electrolyte concentration at temperatures ranging from 293.15 to 303.15 K (Tables 1–4). As can be seen, an increase in the thiourea (TU) and hydroxyurea (HU) content is followed by an increase in the exothermicity of the electrolyte increased temperature.

On the basis of the solution enthalpy values obtained, standard enthalpies of solution of electrolyte in aqueous solutions of thiourea and hydroxyurea were determined graphically (Tables 1–4). Such a procedure was necessitated because of the unavailability of the temperature derivatives of dielectric constant required for extrapolation by the Criss and Cobble method [9].

TABLE 3

Enthalpies of solution ΔH_m of $CaCl_2$ in water–thiourea (TU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

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	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	80.87	0.0000	81.15	0.0000	82.59	0.0000	83.13	0.0000	83.88
0.0036	80.71	0.0038	80.93	0.0035	82.38	0.0033	82.91	0.0036	83.64
0.0064	80.54	0.0050	80.81	0.0063	82.26	0.0059	82.79	0.0043	83.55
0.0085	80.46	0.0081	80.69	0.0081	82.13	0.0078	82.71	0.0086	83.39
0.0105	80.33	0.0099	80.64	0.0097	82.09	0.0091	82.67	0.0104	83.30
0.0219	80.12	0.0201	80.14	0.0225	81.79	0.0149	82.52	0.0251	82.63
0.0398	79.83	0.0401	80.02	0.0501	81.55	0.0401	82.03	0.0452	82.47
0.0552	79.66	0.0759	79.72	0.0801	81.25	0.0752	81.75	0.0989	82.21
0.0897	79.41	0.1349	79.31	0.1201	80.96	0.0912	81.65	0.1198	82.05
0.1221	79.20	0.1649	79.14	0.1709	80.83	0.1205	81.52	0.1579	81.84

TABLE 4

Enthalpies of solution ΔH_m of $CaCl_2$ in water–hydroxyurea (HU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

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	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	81.12	0.0000	82.43	0.0000	82.99	0.0000	83.72
0.0037	80.83	0.0039	82.26	0.0038	82.79	0.0037	83.39
0.0049	80.75	0.0050	82.13	0.0054	82.71	0.0063	83.26
0.0084	80.58	0.0099	81.88	0.0089	82.59	0.0097	83.14
0.0104	80.50	0.0223	81.63	0.0212	82.28	0.0220	82.80
0.0425	79.91	0.0521	81.29	0.0489	81.82	0.0649	82.22
0.0901	79.45	0.0928	81.00	0.0901	81.56	0.0896	82.05
0.1305	79.24	0.1203	80.83	0.0998	81.52	0.1149	81.88
0.1852	79.00	0.1531	80.67	0.1112	81.44	0.1653	81.63

DISCUSSION

Using the standard enthalpies of electrolyte solution in water $\Delta H^{\infty}_{m_{\mathrm{W}}}$ and in aqueous solutions of urea derivatives $\Delta H^{\infty}_{m_{\mathrm{W+N}}}$ (Tables 1–4), the standard enthalpies of electrolyte transfer from water to aqueous urea solutions (urea content m_{N}) were calculated

$$\Delta H_{\mathrm{E_{W \rightarrow W+N}}} = \Delta H^{\infty}_{m_{\mathrm{W+N}}} - \Delta H^{\infty}_{m_{\mathrm{W}}}$$

$$\Delta H_{\mathrm{E_{W \rightarrow W+N}}} = 2\nu h_{\mathrm{NE}} m_{\mathrm{N}} + 3\nu h_{\mathrm{NNE}} m_{\mathrm{N}}^2 + \ldots$$

where ν is the number of ions into which the electrolyte dissociates. A plot of the dependence under discussion was made by putting the m_{N} values on the abscissa and the $(\Delta H^{\infty}_{m_{\mathrm{W+N}}} - \Delta H^{\infty}_{m_{\mathrm{W}}})m_{\mathrm{N}}^{-1}$ on the ordinate and extrapolating to zero non-electrolyte content.

From the point at which the plot intersected the axis of the ordinate we obtained the value corresponding to $2\nu h_{\mathrm{NE}}$ [10]. The enthalpic coefficients of non-electrolyte molecule–averaged ion (h_{NE}) interactions are collected in

TABLE 5

Enthalpic pair interaction coefficients for molecule of urea derivatives–averaged ion in water solutions at various temperatures

T (K)	h_{NE} (J kg mol^{-2})			
	TU–KNO_3	HU–KNO_3	TU–$CaCl_2$	HU–$CaCl_2$
293.15	975	900		
298.15	880	805	485	435
303.15	800	710		

Table 5. All the h_{NE} values for systems with thio- and hydroxyurea are negative and they decrease, in absolute terms, with increasing temperature (KNO_3, Table 5).

It follows from the work of several authors [10–12] that enthalpic interaction coefficients for pairs of the same or different kind of molecules of the dissolved substances which exhibit hydrophilic or ionic properties have negative values.

The h_{NE} values obtained from the three-component systems under discussion (Table 5) are negative, which may reflect relatively strong interactions taking place between urea derivative molecules and the electrolyte in the solution.

An increase in the temperature brings about a decrease of the absolute h_{NE} values (Table 5) which is probably due to a weakening of the interactions between non-electrolyte molecule and ions accompanying the increased intensity of thermal motions.

As has already been mentioned, in the case of the three-component systems with hydrophilic urea derivatives, thiourea solutions exhibit larger negative values of the enthalpic non-electrolyte–averaged ion interaction coefficients than do hydroxyurea solutions (Table 5). The smaller negative h_{NE} values for aqueous hydroxyurea solutions with electrolytes are most probably due to the weakening of the hydroxyurea molecule–ion interactions related to the competitive process in which hydroxyurea molecules enter into strong interactions with water [6,13].

REFERENCES

1 S. Taniewska-Osińska and B. Pałecz, J. Chem. Thermodyn., 12 (1980) 775.
2 S. Taniewska-Osińska and B. Pałecz, J. Chem. Thermodyn., 14 (1982) 11.
3 B. Pałecz, Doctoral thesis, University of Lodz, Poland, 1982.
4 S. Taniewska-Osińska and B. Pałecz, Acta Univ. Łodz, Folia Chim. Ser. II, 5 (1985) 123.
5 K.B. Jacimirskii and W.P. Wasiliew, Instability Constants of Complex Compounds, Oxford University Press, Oxford, 1960.
6 I.K. Larsen and B. Jerslev, Acta Chem. Scand., 20 (1966) 983.
7 A. Finch, P.J. Gardner and C.J. Steadman, J. Phys. Chem., 75 (1971) 2325.
8 B. Pałecz and S. Taniewska-Osińska, Thermochim. Acta, 79 (1984) 299.
9 C.M. Criss and J.W. Cobble, J. Am. Chem. Soc., 83 (1961) 3223.
10 H. Piekarski, Can. J. Chem., 61 (1983) 2203.
11 S. Taniewska-Osińska and A. Piekarska, Bull. Acad. Pol. Sci., Ser. Sci. Chim., 26 (1978) 612.
12 R.H. Wood and L.H. Hiltzik, J. Solution Chem., 9 (1980) 45.
13 J.E. Steward, J. Chem. Phys., 26 (1957) 248.