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THERMOCHEMICAL INVESTIGATION OF SOLUTIONS OF SOME ELECTROLYTES IN THIOUREA-WATER MIXED SOLVENT SYSTEMS AT 313.15, 323.15 AND 333.15 K

Measurements were made of the enthalpies of solution of NaI, KNO_3 and $CaCl_2$ in water and in aqueous 0.1, 0.7 and 1.5 mole TU/ /kg H_2O solutions of thiourea in the temperature range of 313.15--333.15 K. Taking advantage of the standard values of solution enthalpy of electrolytes in water and in aqueous solutions of thiourea, the enthalpic pair interaction coefficients of thiourea molecule - averaged ion were determined [1, 2].

Introduction

The present study is a continuation of the thermodynamic investigations reported in the previous papers [3-5]. The aim of this research was to determine the standard enthalpies of electrolyte solution in water and in aqueous solutions of thiourea at concentrations of 0.1, 0.7 and 1.5 mole/kg H_2O.

Experimental

Thiourea (puriss, POCh, Poland) was crystallized from ethanol and dried under reduced pressure at 333 K. Analytically pure NaI (Merck, BRD) was crystallized from a water-acetone mixture and then dried at 333 K. KNO_3 (puriss, POCh, Poland) was crystallized from water and then dried to constant weight.

$CaCl_2$ (puriss, POCh, Poland) was dried at 470°C over dry hydrochloride and with a jet of dry argon. Amperometric determination revealed chloride content of 99.99%. The calorimetric mea-

surements were conducted in an "isoperibol" calorimeter. In the 120 ccm glass vessel was placed a heater sank into a 15 ohm glass jacket. The calorimetric vessel was stopped with a teflon stopper in which two thermistors (10 k ohm each) encased in stainless chrome steel were placed as well as a stainless chrome steel stirrer. The ampoule with the substance under study was attached to the stirrer. The thermistors were connected to an astable multivibrator system generating rectangular wave whose frequency is a function of the temperature inside the calorimeter [6]. Changes in the frequency of the wave were determined using a Digital Frequency type PFL-21 (Kabid, Poland) meter with digital readout. The sensing elements were sensitive to ca. 5 x $\times 10^{-5}$ K. The calorimeter was placed in a water thermostat whose accuracy was ca. 1 x 10^{-3} K.

Results and Discussion

The obtained enthalpies of solution of NaI, KNO_3 and $CaCl_2$ in water and in aqueous solutions of thiourea are collected in Tab. 1-3. As can be seen, increased thiourea content produces increased exothermicity of solution enthalpies. A similar increase of exothermicity is brought about by temperature increase exemplified by the NaI and KNO_3 data. On the basis of the solution enthalpy values obtained, standard enthalpies of solution of NaI, KNO_3 and $CaCl_2$ in water and in aqueous solutions of thiourea were determined graphically (Tab. 1-3). Such a procedure was necessitated by the unavailability of the temperature derivatives of dielectric constant required for extrapolation by the C r i s s and C o b b l e method [7]. Basing on the standard enthalpies of electrolyte solution in water $\Delta H^{\infty}_{S/W/}$ and in aqueous thiourea solutions $\Delta H^{\infty}_{S/N/}$, standard enthalpies of electrolyte transfer from water to aqueous thiourea solutions (concentration m_N) were calculated:

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

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

Table 1

Enthalpies of solutions (ΔH_s) of NaI in water and water-thiourea (TU) mixtures at the temperatures 313.15 K and 323.15 K

H_2O		0.1 mol TU		0.7 mol TU		1.5 mol TU	
m(NaI) mole/kg	$-\Delta H_s$ cal/mole	m(NaI) mole/kg	$-\Delta H_s$ cal/mole	m(NaI) mole/kg	$-\Delta H_s$ cal/mole	m(NaI) mole/kg	$-\Delta H_s$ cal/mole
				313.15 K			
0.0000	2225	0.0000	2254	0.0000	2392	0.0000	2560
0.0089	2166	0.0075	2220	0.0069	2361	0.0062	2540
0.0111	2160	0.0098	2211	0.0092	2356	0.0095	2526
0.0154	2156	0.0141	2202	0.0123	2344	0.0101	2522
0.0298	2146	0.0199	2190	0.0245	2317	0.0208	2501
0.0542	2122	0.0254	2180	0.0321	2306	0.0254	2495
0.0899	2100	0.0325	2172	0.0654	2270	0.0543	2460
0.1089	2093	0.0680	2132	0.0895	2252	0.0794	2440
				323.15 K			
0.0000	2449	0.0000	2474	0.0000	2600	0.0000	2772
0.0119	2400	0.0069	2455	0.0069	2583	0.0079	2748
0.0153	2399	0.0121	2436	0.0091	2574	0.0125	2733
0.0245	2396	0.0252	2415	0.0199	2552	0.0219	2720
0.0532	2382	0.0489	2390	0.0302	2540	0.0435	2700
0.0793	2370	0.0651	2371	0.0452	2521	0.0510	2691
0.1005	2360	0.0801	2368	0.0729	2300	0.0795	2676

Table 2

Enthalpies of solution (ΔH_s) of KNO_3 in water and water-thiourea (TU) mixtures over the temperature range 313.15 to 333.15 K

H_2O		0.1 mole TU		0.7 mole TU		1.5 mole TU	
m mole/kg	ΔH_s cal/mole	m mole/kg	ΔH_s cal/mole	m mole/kg	ΔH_s cal/mole	m mole/kg	ΔH_s cal/mole
			313.15 K				
0.0000	7980	0.0000	7881	0.0000	7571	0.0000	7385
0.0082	7956	0.0112	7845	0.0131	7528	0.0138	7357
0.0092	7957	0.0148	7846	0.0152	7528	0.0185	7358
0.0142	7961	0.0298	7844	0.0310	7522	0.0342	7355
0.0169	7960	0.0456	7827	0.0533	7504	0.0695	7340
0.0259	7958	0.0899	7796	0.0912	7474	0.1025	7320
0.0431	7949						
0.0911	7908						
			323.15 K				
0.0000	7772	0.0000	7663	0.0000	7457	0.0000	7310
0.0085	7738	0.0090	7622	0.0099	7424	0.0089	7271
0.0099	7740	0.0112	7624	0.0123	7424	0.0115	7273
0.0123	7741	0.0195	7633	0.0451	7405	0.0342	7251
0.0242	7736	0.0317	7608	0.0745	7387	0.0651	7225
0.0438	7719	0.0683	7586	0.0954	7373	0.0954	7204
0.0835	7681	0.0921	7568				

Table 2 (cont.)

1	2	3	4	5	6	7	8
			333.15 K				
0.0000	7533	0.0000	7502	0.0000	7360	0.0000	7186
0.0085	7535	0.0092	7475	0.0083	7313	0.0093	7148
0.0094	7537	0.0153	7476	0.0211	7314	0.0149	7149
0.0121	7539	0.0321	7473	0.0423	7297	0.0315	7133
0.0159	7540	0.0651	7450	0.0732	7265	0.0853	7096
0.0251	7538	0.0911	7424	0.0992	7250	0.1001	7082
0.0498	7529						
0.0799	7510						

Table 3

Enthalpies of solutions (ΔH_s) of $CaCl_2$ in water and water-thiourea (TU) mixtures in temperature 323.15 K

H_2O		0,1 mole TU		0,7 mole TU		1,5 mole TU	
m mole/kg	$-\Delta H_s$ kcal/mole	m mole/kg	$-\Delta H_s$ kcal/mole	m mole/kg	$-\Delta H_s$ kcal/mole	m mole/kg	$-\Delta H_s$ kcal/mole
323.15 K							
0.0000	21.21	0.0000	21.30	0.0000	21.56	0.0000	21.75
0.0068	21.17	0.0078	21.29	0.0071	21.49	0.0069	21.68
0.0075	21.08	0.0099	21.23	0.0089	21.44	0.0079	21.63
0.0095	21.08	0.0125	21.19	0.0119	21.39	0.0101	21.62
0.0104	21.05	0.0248	21.15	0.0201	21.36	0.0249	21.53
0.0220	21.01	0.0529	21.09	0.0509	21.18	0.0641	21.43
0.0434	20.96	0.0899	21.00	0.0939	21.09	0.0842	21.38
0.0695	20.89					0.1011	21.35
0.0941	20.82						

where ν is the number of ions onto 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 ordinate.

The enthalpic coefficients of thiourea molecule-averaged ion h_{NE} interactions obtained in this way are listed in Tab. 4. A view held by many authors [1, 2, 8, 9] and shared by us is that

Table 4

Enthalpic pair interaction coefficients of electrolyte - thiourea (TU) in water solutions

T/K	$-h_{NE}$/cal kg mole^{-2}		
	TU-NaJ	TU-KNO_3	TU-$CaCl_2$
313.15	72	225	
323.15	64	200	150
333.15		150	

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 thiourea molecule-averaged ion interaction coefficients obtained for all the salts under study have negative values (Tab. 4) which may be due to strong interactions between the molecules of urea derivative and the electrolyte present in the solution. As the temperature increases, the absolute h_{NE} values decrease (Tab. 4) which may be related to weakened interactions between thiourea molecules and ions, brought about by increased intensity of thermal motions in the solution.

References

[1] Cassel R. B., Wood R. H., J. Phys. Chem., 78, 2465 (1974).

[2] Perron G., Joly D., Desnoyers J. E., Avedikian L., Morel J. P., Can. J. Chem., 56, 552 (1978).

[3] Taniewska-Osińska S., Pałecz B., J. Chem. Thermodynamics, 12, 775 (1980).
[4] Taniewska-Osińska S., Pałecz B., J. Chem. Thermodynamics, 14, 11 (1982).
[5] Taniewska-Osińska S., Pałecz B., Acta Uniw. Lodz. Folia Chim., 1, 77 (1982).
[6] Jadczak J., Metrologia - czynnik postępu w nauce i technice, Wrocław (1979), p. 137.
[7] Criss C. M., Cobble J. W., J. Am. Chem. Soc., 83, 3223 (1961).
[8] Fuchs R., Hagen C. P., J. Phys. Chem., 77, 179 (1973).
[9] Piekarski H., Can. J. Chem., 61, 2203 (1983).

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TERMOCHEMICZNE BADANIA ROZTWORÓW PEWNYCH ELEKTROLITÓW W MIESZANINACH WODA-TIOMOCZNIK

Zmierzono całkowitą entalpię rozpuszczania NaI, KNO_3 i $CaCl_2$ w zakresie stężeń 0,005-0,1 mol/kg roztworu w wodzie i mieszaninach zawierających 0,1, 0,7 i 1,5 mol TU/kg H_2O w przedziale temperatur 313,15-333,15 K. Wykorzystując wartości entalpii rozpuszczania obliczono standardowe entalpie rozpuszczania i entalpowe współczynniki oddziaływania par cząsteczka tiomocznika elektrolit.

Стефания Таневска-Осиньска, Бартломией Палэч

ТЕРМОХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ РАСТВОРОВ ЭЛЕКТРОЛИТОВ В СМЕСЯХ ВОДА-ТИОМОЧЕВИНА

Измерена интегральная энтальпия растворения NaI, KNO_3, $CaCl_2$ в диапазоне концентраций 0.005-01 мол/кг раств. в воде и смесях содержащих 01, 07 и 15 мол Т /кг H_2O в интервале температур 31315-33315 К. Пользуясь значениями энтальпии растворения рассчитаны стандартные энтальпии растворения и энтальпийные коэффициенты взаимодействия пар молекула тиомочевины электролит.