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THERMOCHEMICAL INVESTIGATION OF THE SOLUTIONS OF SEVERAL SALTS IN MOLTEN UREA AT 413.15 K

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ABSTRACT

Enthalpies of solution ΔH_s of NaCl, KCl, NH_4Cl, $NaNO_3$, KNO_3, NH_4NO_3 and $CaCl_2$ in molten urea at 413.15 were measured. The amount of biuret formed as a result of the thermal decomposition of urea during the calorimetric experiments were determined spectroscopically.

INTRODUCTION

The solutions of nitrates and chlorides of potassium, sodium, ammonium and calcium in molten urea were investigated. The choice of electrolytes was governed by the various effects on the water structure exerted by some groups of salts [1–4]: KNO_3, $NaNO_3$, NH_4NO_3, NaCl and KCl are structure-breaking; NH_4Cl does not notably change the water structure; whereas $CaCl_2$ is considered to be structure-making at room temperature. A comparison of the solution enthalpies of these electrolytes on water and in urea, and their dependences on concentration at temperatures near the melting points of both solvents, may elucidate the effect of the salts on the structure of urea.

EXPERIMENTAL

The salts used (P.O.Ch. Gliwice, Poland, pro analysi) were dried at 373.15 K. Anhydrous $CaCl_2$ was dried in a stream of HCl then stored under P_2O_5. Urea (P.O.Ch., pro analysi) was dried under reduced pressure at 333.15 K. Measurements of the enthalpy of solution were performed in an isoperibol calorimeter. A 150 ml Dewar flask was used as the calorimetric vessel. The temperature inside the calorimeter was determined by means of a quartz thermometer (Hewlett–Packard) of sensitivity ±0.001 K. The experimental precision was about ±0.1 kJ mol^{-1}.

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RESULTS AND DISCUSSION

Under the experimental conditions urea underwent a decomposition, forming biuret [5]. The concentration of biuret was determined by means of ultraviolet spectroscopy. The biuret content did not exceed 2.5 wt.% in the solutions under discussion. Figure 1 shows the dependence of the wt.% (w) of biuret versus time (t) of decomposition of urea, $w = f(t)$; an example is shown in Table 1. It was considered important to determine whether the highest content of 2.5 wt.% of biuret in solution, which occurs at $t = 20$ min, the time of the experiments performed, affects the measured enthalpy of dissolution of a salt in urea to a perceptible degree. Therefore, the enthalpies of solution of the salts were measured in urea with increasing biuret content up to 4 wt.%. No effect was observed. The obtained enthalpies of solution (ΔH_s) of electrolytes as a function of concentration (m) in fused urea are given in Tables 2 and 3. Figures 2 and 3 show the dependence of ΔH_s on concentration (m) of the investigated salts in urea and in water taken from literature data.

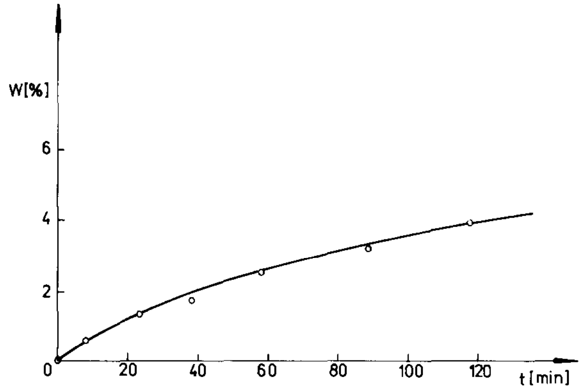

Fig. 1. Biuret content (w) vs. time (t) of urea decomposition in the presence of NH_4Cl ($m = 1.4998$ mol kg^{-1}, w in wt.%, t in min).

TABLE 1

Biuret content vs. time (t) of urea decomposition in NH_4Cl solution ($m = 1.4998$ mol kg^{-1})

w (wt.%)	t (min)
0	0
0.66	7.5
1.36	23
1.75	38
2.53	58
3.26	88
3.59	118

TABLE 2

Enthalpies of solution (ΔH_s) of salts in urea at 413.15 K (ΔH_s in kJ mol^{-1}, m in mol kg^{-1})

KCl		NaCl		NH_4Cl		$CaCl_2$	
m	ΔH_s	m	ΔH_s	m	ΔH_s	m	ΔH_s
0.0044	15.61	0.0010	3.16	0.0048	−18.65	0.0020	−99.02
0.0164	14.28	0.0231	2.77	0.0098	−16.20	0.0030	−97.13
0.0290	13.14	0.0465	2.41	0.0113	−15.24	0.0050	−96.34
0.0675	12.02	0.0610	2.13	0.0129	−14.83	0.0101	−92.86
0.0775	11.82	0.1320	1.63	0.0130	−14.65	0.0250	−90.44
0.1450	11.64	0.1450	1.57	0.0163	−13.21	0.0580	−90.06
0.2320	11.52	0.1690	1.43	0.0175	−12.49	0.0800	−88.76
0.2655	11.35	0.2130	1.36	0.0476	−10.62	0.1300	−88.43
		0.3530	0.98	0.0575	−10.06	0.1800	−88.41
		0.4280	0.88	0.0592	−10.02	0.2310	−87.92
		0.4820	0.75	0.0860	−8.71	0.301	−87.71
				0.1050	−8.22	0.4101	−87.50
				0.1070	−8.22		
				0.2530	−3.79		
				0.3744	−1.97		
				0.4558	−0.92		
				0.5250	−0.69		

In the opinions of the authors of refs. 1–4, KNO_3, $NaNO_3$, KCl and NaCl have a structure-breaking effect on water. The positive values of ΔH_s, which decrease with increasing electrolyte concentration, suggest an analogous influence on the structure of urea. The large negative values of ΔH_s for $CaCl_2$ which increase with the salt concentration in fused urea, suggest that

TABLE 3

Enthalpies of solution (ΔH_s) of salts in urea at 413.15 K (ΔH_s in kJ mol^{-1}, m in mol kg^{-1})

KNO_3		$NaNO_3$		NH_4NO_3	
m	ΔH_s	m	ΔH_s	m	ΔH_s
0.0055	23.49	0.0030	18.00	0.0124	−16.94
0.0135	23.46	0.0050	17.17	0.0220	−15.56
0.0215	21.42	0.1000	16.25	0.0490	−12.51
0.0350	20.52	0.0130	15.91	0.0567	−11.96
0.0400	19.78	0.0200	15.49	0.1005	−9.79
0.0652	19.47	0.0350	15.07	0.1500	−8.96
0.1010	19.05	0.0600	14.57	0.1900	−8.58
0.1615	18.76	0.1040	14.07	0.2600	−8.37
0.1960	18.51	0.1550	13.65		
0.02201	18.42	0.1900	13.50		
0.2603	18.17	0.2200	13.39		
0.3110	17.88				

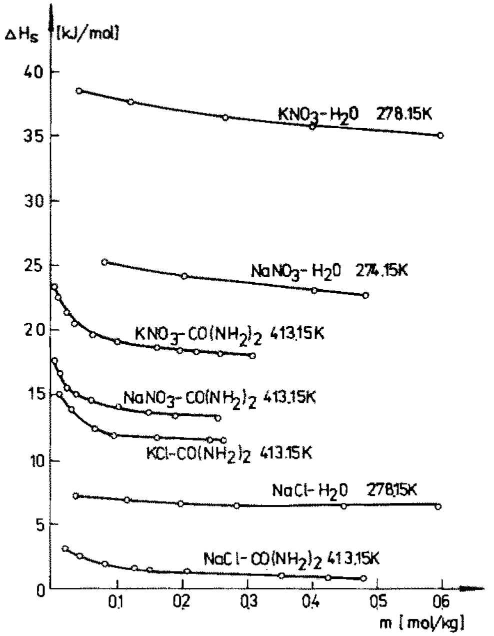

Fig. 2. The concentration dependence of ΔH_s of electrolytes in fused urea and in water (taken from ref. 2): ΔH_s in kJ mol^{-1}; m in mol kg^{-1}.

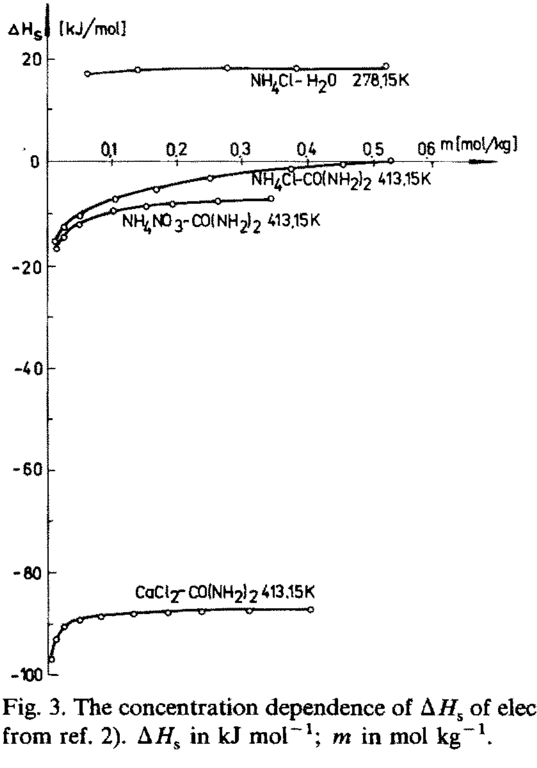

Fig. 3. The concentration dependence of ΔH_s of electrolytes in fused urea and in water (taken from ref. 2). ΔH_s in kJ mol^{-1}; m in mol kg^{-1}.

this salt is "structure-making". A similar conclusion has been drawn from the thermodynamic and viscosimetric characteristics of aqueous solutions of $CaCl_2$ [6,7].

The similar behaviour of the salts in solutions of urea and water may be attributed to the three-dimensional network of H-bonds present on ice and urea crystals which is partially preserved in the liquid states achieved near the melting temperatures.

Electrolytes NH_4Cl and NH_4NO_3 show different thermochemical behaviours in the two solvents. In urea solutions, ΔH_s values for NH_4Cl and NH_4NO_3 are negative and decrease with an increase in concentration. This behaviour is similar to that of $CaCl_2$ which is considered a "structure-making" salt. In water, both show "structure-breaking" effects, with positive ΔH_s values. This different behaviour of the ammonium salts in urea may be connected with a specific interaction of the NH_4^+ ion with the urea molecules resulting in the formation of clathrates or complexes. No description of this interaction could be found in the literature.

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