Bartłomiej Pałecz*

ENTHALPY OF NaI DISSOLUTION IN AQUEOUS HYDROPHYLIC UREA DERIVATIVES SOLUTIONS AT 298.15 K**

Enthalpies of dissolution of NaI in aqueous solutions of thiourea and hydroxyurea have been measured at 298.15 K. The enthalpic pair interaction coefficients of urea derivatives molecule - NaI have been determined using standard enthalpies of NaI in water and aqueous solutions of ureas.

INTRODUCTION

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

EXPERIMENTAL

Thiourea ("puriss" P.O.Ch. Poland) and hydroxyurea (Polfa Poland) were crystalized twice from ethanol and dried under reduced pressure at 333 K (the melting temperature were 454 K for thiourea and 413 K for hydroxyurea, while the literature data being 454 K for thiourea [5] and 413-414 K for hydroxyurea [6]. NaI (Merck, BRD) was crystallized from a 1 : 1 water-acetone mixture and dried under reduced pressure at 333 K.

* Department of Physical Chemistry, Institute of Chemistry University of Łódź, Poland.

[19]

The measurements were conducted in an isoperibol calorimeter [7] accurate to 5×10^{-5} K. The calorimeter was placed in a water thermostat whose temperature stability was 1×10^{-3} K.

RESULTS

Enthalpies of NaI dissolution in water and aqueous 0.1, 0.7, 1.0, 1.5 mol·kg^{-1} H$_2$O solutions of thiourea (TU) and hydroxyurea (HU) in the range of electrolyte concentrations of 0.002 - 0.05 mol·kg^{-1} at 298.15 K (Tab. 1, 2).

Table 1

Enthalpies of solution (ΔH_s) of NaI in water-thiourea (TU) mixtures at 298.15 K

(units: m in mol kg^{-1}, ΔH_s in kJ mol^{-1})

0.1 mol TU/kg H$_2$O		0.5 mol TU/kg H$_2$O		0.7 mol TU/kg H$_2$O	
m	- ΔH_s	m	- ΔH_s	m	- ΔH_s
0.0000	7 785	0.0000	8 410	0.0000	8 700
0.0034	7 705	0.0029	8 350	0.0026	8 650
0.0071	7 655	0.0085	8 295	0.0091	8 550
0.0149	7 575	0.0121	8 260	0.0151	8 485
0.0289	7 455	0.0225	8 175	0.0249	8 395
0.0349	7 365	0.0251	8 160	0.0389	8 310
0.0481	7 385	0.0485	8 025	0.0499	8 250
0.0501	7 365	0.0501	8 010	0.0558	8 235

1.0 mol TU/kg H$_2$O		1.5 mol TU/kg H$_2$O	
m	- ΔH_s	m	- ΔH_s
0.0000	9 120	0.0000	9 790
0.0026	9 070	0.0033	9 725
0.0079	8 995	0.0063	9 680
0.0132	8 930	0.0113	9 630
0.0295	8 795	0.0298	9 470
0.0311	8 785	0.0351	9 425
0.0419	8 725	0.0432	9 390
0.0511	8 670	0.0508	9 355

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 (Tab. 1, 2). Such a procedure was necessitated by the unavailability of the tempera-

ture derivatives of dielectric constant required for extrapolation by the Criss and Cóbble method [8].

Enthalpies of solution (ΔH_s) of NaI in water-hydroxyurea (HU) mixtures at 298.15 K
(units: m in mol·kg^{-1}, ΔH_s in kJ·mol^{-1})

0.1 mol HU/kg H$_2$O		0.5 mol HU/kg H$_2$O		0.7 mol HU/kg H$_2$O	
m	$-\Delta H_s$	m	$-\Delta H_s$	m	$-\Delta H_s$
0.0000	7 760	0.0000	8 325	0.0000	8 580
0.0029	7 700	0.0031	8 270	0.0028	8 520
0.0069	7 635	0.0062	8 245	0.0072	8 450
0.0098	7 590	0.0092	8 200	0.0101	8 415
0.0189	7 510	0.0154	8 140	0.0195	8 320
0.0251	7 460	0.0321	8 025	0.0298	8 225
0.0401	7 370	0.0451	7 960	0.0352	8 190
0.0498	7 330	0.0539	7 935	0.0509	8 100

1.0 mol HU/kg H$_2$O		1.5 mol HU/kg H$_2$O	
m	$-\Delta H_s$	m	$-\Delta H_s$
0.0000	8 975	0.0000	9 580
0.0037	8 910	0.0033	9 530
0.0070	8 870	0.0062	9 490
0.0100	8 845	0.0098	9 455
0.0175	8 775	0.0164	9 405
0.0299	8 680	0.0312	9 300
0.0432	8 620	0.0422	9 245
0.0510	8 580	0.0521	9 205

DISCUSSION

The plots of enthalpy of dissolution of NaI in the aqueous solutions of ureas exhibit the increase of exothermic effect of dissolution along with the content of the organic component [4]. More evident increase of the exothermic effect of NaI dissolution in due to the increase of the thiourea and hydroxyurea concentration (Tab. 1, 2).

Using the standard enthalpies of solutions ΔH_s^∞(NaI) determined in this work the enthalpic pair interaction coefficents nonelectrolyte - electrolyte (h_{NE}) were calculated [3] (Tab. 3). The h_{NE} values for the solution of urea and hydrophilic urea derivatives is negative unlike those for alkylureas [4].

T a b l e   3

Enthalpic pair interaction coefficients h_{NE} for
urea derivatives - averaged ion (Na^+I^-) in water
solutions at 298.15 K

Nonelectrolit (Na^+I^-)	$-h_{NE}$ $J \cdot kg \cdot mol^{-1}$
U - NaI*	310 ± 20
HU - NaI	370 ± 20
TU - NaI	420 ± 20

* Ref. [4].

As has alreddy been mentioned, in the case of the threecompo-
nent systems with hydrophilic urea derivatives, thiourea solutions
exhibit larger negative values of the enthalpic nonelectrolyte -
averaged ion interaction coefficients than hydroxyurea solutions
(Tab. 3). 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 com-
petitive process in which hydroxyurea molecules enter into strong
interactions with water.

REFERENCES

[1] S. T a n i e w s k a-O s i ń s k a, B. P a ł e c z, J. Chem.
Thermodynamics, 12, 775 (1980).
[2] S. T a n i e w s k a-O s i ń s k a, B. P a ł e c z, J. Chem.
Thermodynamics, 14, 11 (1982).
[3] B. P a ł e c z, S. T a n i e w s k a-O s i ń s k a, Thermo-
chimica Acta, 116, 349 (1987).
[4] B. P a ł e c z, S. T a n i e w s k a-O s i ń s k a, Thermo-
chimica Acta, (1989) in press.
[5] K. B. J a c i m i r s k i, W. P. W a s i l i e w, Instabi-
lity Constants of Complex Compounds, Oxford 1960.
[6] I. K. L a r s e n, B. J e r s l e v, Acta Chem. Scand., 20,
983 (1966).

[7] B. P a ł e c z, S. T a n i e w s k a-O s i ń s k a, Thermo-
chimica Acta, 79, 299 (1984).

[8] C. M. C r i s s, J. W. C o b b l e, J. Am. Chem. Soc., 83,
3223 (1961).

Bartłomiej Pałecz

ENTALPIE ROZPUSZCZANIA NaI W WODNYCH ROZTWORACH HYDROFILOWYCH
POCHODNYCH MOCZNIKA W TEMPERATURZE 298,15 K

Zmierzono całkowitą entalpię rozpuszczania NaI w zakresie stę-
żeń 0,002-0,05 mol(NaI)kg (rozpuszczalnika) w wodzie i wodnych
roztworach zawierających 0,1, 0,7, 1,0 i 1,5 mol TU lub HU/kg H$_2$O.
Wyznaczono entalpowe współczynniki oddziaływania cząsteczka pochod-
nej mocznika - uśredniony jon NaI w roztworze wodnym i porównano z
analogicznymi wartościami odnoszącymi się do mocznika i jego hydro-
fobowych pochodnych.