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Note

INTERACTIONS IN AQUEOUS SOLUTIONS OF UREA DERIVATIVES AND NaI AT 298.15 K

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ABSTRACT

Enthalpies of dissolution of NaI in aqueous solutions of urea, monomethylurea, monoethylurea, 1,3-dimethylurea and 1,3-diethylurea have been measured at 298.15 K. The enthalpic pair interaction coefficients of urea derivative molecule–NaI are determined using standard solution enthalpies of NaI in water and aqueous solutions of ureas.

INTRODUCTION

Investigations on the physicochemical properties of aqueous solutions of urea and urea derivatives [1–3] and of electrolytes in aqueous solutions of urea derivatives [4,5] have been carried out in our laboratory for a long time.

EXPERIMENTAL

Urea (U), monomethylurea (MMU), monoethylurea (MEU), 1,3-dimethylurea (DMU) and 1,3-diethylurea (DEU) (Fluka, puriss) were crystallized twice from ethanol and dried under reduced pressure at 333 K.

NaI (Merck, puriss) was crystallized from a 1 : 1 water–acetone mixture and dried under reduced pressure at 333 K.

The calorimeter measurements were conducted in an "isoperibol" calorimeter accurate to 5×10^5 K [3].

RESULTS

Enthalpies of dissolution of NaI in water and aqueous solutions of ureas from 0.1 to 2.0 mol urea (kg water)$^{-1}$ in the range of electrolyte concentrations of 0.004–0.1 mol NaI (kg solvent)$^{-1}$ were measured at 298.15 K (Tables 1–5). On the basis of the solution enthalpy values obtained, stan-

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TABLE 1

Enthalpies of solution ΔH_m of NaI in water–urea (U) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

H_2O		0.5 mol U (kg H_2O)$^{-1}$		0.7 mol U (kg H_2O)$^{-1}$		1.0 mol U (kg H_2O)$^{-1}$		1.5 mol U (kg H_2O)$^{-1}$		2.0 mol U (kg H_2O)$^{-1}$	
m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	7615	0.0000	8220	0.0000	8450	0.0000	8810	0.0000	9370	0.0000	9875
0.0025	7570	0.0026	8175	0.0030	8390	0.0023	8765	0.0031	9305	0.0030	9810
0.0061	7530	0.0079	8090	0.0065	8350	0.0059	8710	0.0061	9270	0.0072	9740
0.0125	7455	0.0121	8050	0.0099	8290	0.0089	8670	0.0091	9235	0.0098	9705
0.0198	7390	0.0252	7930	0.0149	8245	0.0159	8560	0.0148	9185	0.0151	9650
0.0285	7320	0.0411	7830	0.0311	8135	0.0298	8495	0.0301	9060	0.0298	9540
0.0406	7260	0.0521	7780	0.0498	8035	0.0479	8410	0.0511	8955	0.0489	9435

TABLE 2

Enthalpies of solution ΔH_m of NaI in water–monomethylourea (MMU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

0.5 mol MMU (kg H_2O)$^{-1}$		0.7 mol MMU (kg H_2O)$^{-1}$		1.0 mol MMU (kg H_2O)$^{-1}$		1.5 mol MMU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	7910	0.0000	8010	0.0000	8160	0.0000	8410
0.0022	7855	0.0035	7960	0.0041	8075	0.0025	8350
0.0052	7825	0.0059	7905	0.0059	8035	0.0043	8325
0.0069	7780	0.0079	7875	0.0079	8000	0.0062	8285
0.0089	7740	0.0123	7805	0.0098	7975	0.0083	8240
0.0198	7625	0.0292	7680	0.0149	7910	0.0199	8140
0.0389	7505	0.0412	7615	0.0299	7780	0.0213	8115
0.0501	7445	0.0514	7510	0.0492	7615	0.0405	7990

TABLE 3

Enthalpies of solution ΔH_m of NaI in water–monoethylourea (MEU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

0.5 mol MEU (kg H_2O)$^{-1}$		1.0 mol MEU (kg H_2O)$^{-1}$		1.5 mol MEU (kg H_2O)$^{-1}$		2.0 mol MEU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	7510	0.0000	7425	0.0000	7345	0.0000	7260
0.0026	7475	0.0028	7385	0.0026	7315	0.0030	7215
0.0042	7450	0.0045	7365	0.0044	7290	0.0048	7185
0.0065	7425	0.0072	7330	0.0062	7270	0.0052	7180
0.0092	7380	0.0099	7305	0.0085	7245	0.0078	7155
0.0199	7300	0.0211	7215	0.0195	7135	0.0111	7130
0.0408	7155	0.0398	7115	0.0325	7080	0.0251	7030
0.0515	7130	0.0499	7070	0.0481	6995	0.0451	6900

TABLE 4

Enthalpies of solution ΔH_m of NaI in water–1,3-dimethylurea (DMU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

0.5 mol DMU (kg H_2O)$^{-1}$		1.0 mol DMU (kg H_2O)$^{-1}$		1.5 mol DMU (kg H_2O)$^{-1}$		2.0 mol DMU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	7490	0.0000	7405	0.0000	7320	0.0000	7240
0.0025	7455	0.0031	7355	0.0023	7280	0.0029	7180
0.0059	7405	0.0061	7320	0.0059	7245	0.0065	7135
0.0078	7385	0.0069	7315	0.0081	7230	0.0079	7115
0.0092	7370	0.0089	7280	0.0099	7215	0.0101	7100
0.0195	7280	0.0149	7230	0.0212	7135	0.0205	7020
0.0408	7145	0.0395	7060	0.0432	6985	0.0389	6895
0.0505	7110	0.0509	7000	0.0505	6965	0.0521	6850

TABLE 5

Enthalpies of solution ΔH_m of NaI in water–1,3-diethylurea (DEU) mixtures at 298.15 K (units: m in mol kg^{-1}, ΔH_m in kJ mol^{-1})

0.5 mol DEU (kg H_2O)$^{-1}$		0.7 mol DEU (kg H_2O)$^{-1}$		1.0 mol DEU (kg H_2O)$^{-1}$		1.5 mol DEU (kg H_2O)$^{-1}$		2.0 mol DEU (kg H_2O)$^{-1}$	
m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$	m	$-\Delta H_m$
0.0000	7155	0.0000	6990	0.0000	6735	0.0000	6320	0.0000	5940
0.0026	7105	0.0032	6935	0.0033	6675	0.0031	6275	0.0025	5880
0.0052	7070	0.0062	6905	0.0062	6645	0.0069	6250	0.0072	5840
0.0092	7030	0.0078	6885	0.0087	6610	0.0099	6235	0.0120	5795
0.0115	6995	0.0132	6820	0.0103	6600	0.0151	6175	0.0198	5730
0.0152	6960	0.0182	6780	0.0172	6525	0.0253	6125	0.0311	5655
0.0201	6930	0.0231	6735	0.0198	6510	0.0398	6085	0.0401	5605
0.0310	6855	0.0349	6675	0.0411	6475	0.0455	6065	0.0452	5580

TABLE 6

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

Nonelectrolyte	h_{NE} (J kg mol^{-2})
U	-310 ± 10
MMU	-150 ± 5
MEU	55 ± 5
DMU	60 ± 5
DEU	235 ± 10

dard enthalpies of solution of electrolyte in aqueous solutions of urea derivatives were determined graphically (Tables 1–5). Such a procedure was necessitated by the unavailability of the temperature derivatives of dielectric constant required for extrapolation by the Criss and Cobble method [6].

DISCUSSION

The plots of enthalpy of dissolution of NaI in the aqueous solutions of ureas (Table 1) exhibit an increase of exothermic effect of dissolution along with the content of the organic component.

The replacement of a hydrogen atom in the urea molecule by a methyl group (monomethylurea, MMU) results in a much smaller increase in the exothermic effect of NaI dissolution in comparison with urea solutions (Tables 1 and 2). The substitution of urea hydrogen atoms by a larger alkyl radical (e.g. monoethylurea, MEU) or by a larger number of radicals (e.g. 1,3-dimethylurea, DMU and 1,3-diethylurea, DEU) diminishes exothermic ΔH_m^∞ (NaI) due to an increase of hydrophobic hydration (Tables 3–5).

Using the standard enthalpies of solutions ΔH_m^∞ (NaI) determined in this work the enthalpic pair interaction coefficients nonelectrolyte–electrolyte (h_{NE}) were calculated [5,7] (Table 6). The h_{NE} values for the solution of urea are negative unlike those for alkylureas. The exception is monomethylurea whose the enthalpic pair interaction coefficient is negative (Table 6).

Replacement of a hydrogen atom in the urea molecule by an alkyl group leads to a diminished share of hydrophilic properties of the particle of substituted urea, which is reflected both in enthalpies of NaI in aqueous urea solutions (Tables 2–5) and in positive values of the enthalpic pair interaction coefficients alkylurea–NaI (Table 6). The hydrophobic character of urea alkyl derivatives increases with increase in the amount of radicals and their size in the order MMU < MEU < DMU < DEU.

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