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Stefania Taniewska-Osińska, Bartłomiej Pałecz

THERMODINAMIC INVESTIGATION OF HYDROXYUREA IN WATER SOLUTIONS

The values of the relative partial molal enthalpy of water and of hydroxyurea within the temperature range 293.15-333.15 K were obtained. The course of the function of the $\bar{L}_1$, $\bar{L}_2$ and $\frac{\bar{L}_1}{T}$ vs hydroxyurea concentration and temperature is discussed.

Introduction

The aim of paper was to investigate the aqueous solution of hydroxyurea from the thermodynamic point of view. Enthalpies of solution and dilution of hydroxyurea (HU) in water [1] were determined within the temperature range 293.15-333.15 K.

Results and discussion

Our experimental enthalpies of solutions of hydroxyurea in water [1] may be described by means of the following 3rd order polynomial:

$$\Delta H_s = A_o + A_1 m + A_2 m^2 + A_3 m^3 \qquad (1)$$

where:

ΔH_s - enthalpy of solution,

m - concentration of hydroxyurea in mole/kg H_2O,

A_o, A_1, A_2, A_3 - polynomial coefficients ($A_o = \Delta H_s^{\infty}$ standard integral enthalpies of solution).

Using the function $\Delta H_s = f(m)$ determined in such a way, we

calculated the relative partial molal enthalpy of water $\bar{L}_1$ and hydroxyurea $\bar{L}_2$ using the formulas:

$$\bar{L}_1 = \frac{m^2}{55.505} \frac{d(\Delta H_d)}{dm} \tag{2}$$

$$\bar{L}_2 = -\Delta H_d - m \frac{d(\Delta H_d)}{dm} \tag{3}$$

where:

m - concentration of hydroxyurea mole/kg H_2O,

ΔH_d - integral enthalpies of dilution ($\Delta H_d = \Delta H_s^{\infty} - \Delta H_s$).

The values of the derivative $\frac{d(\Delta H_d)}{dm}$ were calculated by analytic method using an "ODRA 1304" computer.

The calculated values of $\bar{L}_1$ and $\bar{L}_2$ are presented in Tab. 1,2. It can be seen from Tab. 1 that the values of the relative partial molal enthalpy of water ($\bar{L}_1$) are positive within the investigated temperature and concentration range.

It is reasonable to assume that water particles in aqueous solutions of hydroxyurea are less firmly bound than they are in pure water, and this probably points to the disordering effect of hydroxyurea on the structure of water. The destructive effect exerted by hydroxyurea on the structure of molten water grows with increasing concentration and decreases with increasing temperature.

The destructive effect of hydroxyurea on the structure of water is confirmed by the negative values of the relative partial molal enthalpy of hydroxyurea ($\bar{L}_2$) in the whole investigated concentration and temperature range (Tab. 2).

It is known that changes in the solution structure are best shown by means of the excess of relative partial molal entropy of solvent ($\Delta\bar{S}_1^E$) changes [2, 3]:

$$\Delta\bar{S}_1^E = \frac{\bar{L}_1 - RT \ln \frac{a_1}{x_1}}{T} \tag{4}$$

In order to calculate the excess of the relative partial molal entropy of the solvent using the formula (4), the activity of

Table 1

Relative partial molal enthalpies of water ($\bar{L}_1$) in aqueous hydroxyurea sulutions

m	$\bar{L}_1$ cal/mole					
mole/kg	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.1	0.022	0.021	0.019	0.017	0.016	0.015
0.2	0.084	0.079	0.073	0.068	0.060	0.057
0.3	0.181	0.171	0.160	0.150	0.133	0.125
0.4	0.306	0.290	0.277	0.259	0.232	0.213
0.5	0.456	0.432	0.418	0.393	0.353	0.319
0.6	0.626	0.594	0.582	0.549	0.496	0.441
0.7	0.809	0.770	0.763	0.723	0.656	0.575
0.8	1.006	0.957	0.959	0.912	0.831	0.718
0.9	1.211	1.191	1.165	1.113	1.020	0.869
1.0	1.424	1.399	1.376	1.322	1.218	1.024
1.2	1.863	1.793	1.800	1.753	1.630	1.342
1.4	2.312	2.219	2.196	2.177	2.043	1.657
1.6	2.770	2.757	2.626	2.566	2.429	1.954
1.8	3.245	3.145	2.951	2.889	2.758	2.225
2.0	3.752	3.571	3.330	3.116	3.000	2.462

the solvent in the investigated solution must be known. We have not found the data on activity of hydroxyurea in water solutions in any sources. Therefore we could not count the values $\Delta\bar{S}_1^E$, in the examined systems. According to M i s h c h e n k o [4] the omission of the term R ln $\frac{a_1}{x_1}$, will not change the sing $\Delta\bar{S}_1^E$. From the considerations of authors it follows that the course of the relation $\frac{\bar{L}_1}{T} = f(m)$ illustrates the influence of the dissolved solute on the solvent structure in a similar way as the course at $\Delta\bar{S}_1^E = f(m)$ course does.

The values of $\frac{\bar{L}_1}{T}$ calculated by us (Tab. 3), were compared with those of $\frac{\bar{L}_1}{T}$ for aqueous urea [5, 6] and thiourea [7] solutions (Tab. 4).

The change of the discussed relation $\frac{\bar{L}_1}{T}$ describes the character of the course and the sign of concentrational dependence

Table 2

Relative partial molal enthalpies of hydroxyurea ($\bar{L}_2$) in aqueous hydroxyurea solutions

m	$\bar{L}_2$ cal/mole					
mole/kg	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
0.1	24.9	23.3	21.2	19.7	17.4	16.8
0.2	48.1	45.1	41.4	38.7	34.1	32.7
0.3	69.9	65.4	60.8	56.8	50.4	47.7
0.4	89.6	84.3	79.3	74.2	66.0	61.7
0.5	108	102	96.8	90.7	81.0	74.9
0.6	125	118	113	106	95.3	87.2
0.7	140	133	128	121	109	98.6
0.8	155	147	143	135	122	109
0.9	168	159	156	148	134	119
1.0	181	171	169	160	146	128
1.2	203	191	190	182	166	144
1.4	222	207	207	200	184	157
1.6	239	220	219	215	198	168
1.8	255	229	227	225	209	177
2.0	270	236	229	232	216	184

of the excess of relative partial molal entropy of water ($\Delta\bar{S}_1^E$) (to confirm our supposition concentrational relations of $\frac{\bar{L}_1}{T}$ and $\Delta\bar{S}_1^E$ changes of water - urea and water - thiourea systems are presented in Tab. 4).

The positive values of $\frac{\bar{L}_1}{T}$ (tab. 3) confirms our supposition about the breaking effect of hydroxyurea on water structure. They also suggest that the effect of thiourea and urea molecules on water structure is more destructive than the effect of hydroxyurea molecules (Tab. 4).

Table 3

The values of $\frac{\Gamma_1}{T}$ for aqueous hydroxyurea solutions

m	$\Gamma_{1/T}$ cal/mole deg.					
mole/kg	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K	333.15 K
-	-	-	-	-	-	-
0.2	0.0003	0.0002	0.0002	0.0002	0.0002	0.0001
0.3	0.0006	0.0006	0.0005	0.0005	0.0004	0.0003
0.4	0.0011	0.0010	0.0009	0.0008	0.0007	0.0006
0.5	0.0015	0.0014	0.0014	0.0013	0.0011	0.0009
0.6	0.0021	0.0020	0.0019	0.0018	0.0015	0.0013
0.7	0.0027	0.0026	0.0025	0.0023	0.0020	0.0017
0.8	0.0034	0.0032	0.0032	0.0029	0.0026	0.0022
0.9	0.0041	0.0040	0.0038	0.0036	0.0032	0.0026
1.0	0.0048	0.0047	0.0045	0.0042	0.0038	0.0031
1.2	0.0063	0.0060	0.0059	0.0056	0.0050	0.0040
1.4	0.0079	0.0074	0.0072	0.0070	0.0063	0.0050
1.6	0.0094	0.0092	0.0087	0.0082	0.0075	0.0059
1.8	0.0111	0.0105	0.0097	0.0092	0.0085	0.0067
2.0	0.0128	0.0120	0.0110	0.0100	0.0093	0.0074

Table 4

Excess of relative partial molal entropies of water $\Delta\bar{S}_1^E$ and $\frac{\Gamma_1}{T}$ for at aqueous urea, thiourea and hydroxyurea solutions

m	Urea		Thiourea [7]		Hydro-xyurea
mole/kg	$\frac{\Gamma_1}{T}$ $\left[\frac{\text{cal}}{\text{mole deg}}\right]$	$\Delta\bar{S}_1^E$ [5] $\left[\frac{\text{cal}}{\text{mole deg}}\right]$	$\frac{\Gamma_1}{T}$ $\left[\frac{\text{cal}}{\text{mole deg}}\right]$	$\Delta\bar{S}_1^E$ $\left[\frac{\text{cal}}{\text{mole deg}}\right]$	$\frac{\Gamma_1}{T}$ $\left[\frac{\text{cal}}{\text{mole deg}}\right]$
0.2	0.0003 [5]	0.0001	0.0005	0.0004	0.0002
0.5	0.0014 [5]	0.0009	0.0031	0.0023	0.0014
0.8	0.0031 [5]		0.0071	0.0048	0.0032
1.0	0.0044 [6]	0.0033	0.0102	0.0068	0.0047
1.5	0.0081 [5]	0.0056	0.0187	0.0184	0.0083
2.0	0.0156 [6]	0.0087			0.0119

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Department of Physical Chemistry
Institute of Chemistry
University of Łódź

Stefania Taniewska-Osińska, Bartłomiej Pałecz

BADANIA TERMODYNAMICZNE ROZTWORÓW HYDROKSYMOCZNIK-WODA

Wykorzystując uzyskane w poprzednich pracach wartości entalpi rozpuszczania hydroksymocznika w wodzie, obliczono względną cząstkową molową entalpię obydwu składników roztworu oraz $\frac{L_1}{T}$ w przedziale temperatur 293,15-333,15 K. Przeprowadzona analiza wspomnianych funkcji termodynamicznych w zależności od stężenia i temperatury roztworu wskazuje na podobieństwo wpływu hydroksymocznika do mocznika i tiomocznika na strukturę wody.

Стефания Таневска-Осиньска, Бартломей Палеч

ТЕРМОДИНАМИЧЕСКИЕ ИССЛЕДОВАНИЯ РАСТВОРОВ ГИДРОКСИМОЧЕВИНА-ВОДА

Пользуясь ранее определенными значениями теплоты растворения гидроксимочевины в воде расечитана относительной парциальной моляльной энтальпией обоих компонентов раствора L_1, L_2 а также $\frac{L}{M}$ в интервале температуры 293.15-333.15 К. Проведенный анализ упомянутых термодинамических функций в зависимости от концентрации и температуры указывает на сходство влияния гидроксимочевины, мочевины и тиомочевины на структуру воды.