ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 1, 1982

Stefania Taniewska-Osińska, Bartłomiej Pałecz

THERMODYNAMIC INVESTIGATION OF THIOUREA IN WATER SOLUTIONS*

Relative partial molal enthalpies of thiourea and water and excess of relative partial molal entropy of water were determined from enthalpies of solution of thiourea in water within the temperature range 293.15-333.15 K.

Introduction

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

Results and discussion

On the basis of the obtained integral enthalpies of dilution (ΔH) [1] relative partial molal enthalpies of the solvent ($\bar{L}_1$) and of the solute ($\bar{L}_2$) were calculated in Table 1.

Relation $\bar{L}_1 = f(T)$, described by a third-degree polynomial, enables us to calculate the activity of water by means of Gibbs and Helmholtz [2, 3] formula:

---

* The present work has been carried out and supported within the framework of research on Interdepartment Problem MR-I-11.

Table 1

Relative partial molal enthalpies of aqueons thiourea solutions

m	293.15 K		298.15 K		303.15 K	
	$\bar{L}_1$	$-\bar{L}_2$	$\bar{L}_1$	$-\bar{L}_2$	$\bar{L}_1$	$-\bar{L}_2$
mole/kg	J/mole					
0.1	0.2102	237.2	0.1856	208.5	0.1740	195.3
0.2	0.7885	452.4	0.7101	403.3	0.6670	378.3
0.3	1.6653	647,7	1.528	585.3	1.4382	549.9
0.4	2.7832	825.4	2.600	755.6	2.4506	710.77
0.5	4.0970	987.7	3.8911	915.0	3.6709	861.47
0.6	5.5736	1136.9	5.3712	1064.6	5.0693	1002.7
0.7	7.1912	1275.3	7.0160	1205.1	6.6200	1135.3
0.8	8.9436	1405.0	8.8060	1337.7	8.3009	1259.8
0.9	10.083	1528.3	10.726	1463.1	10.093	1376.9
1.0	12.872	1647.6	12.768	1582.5	11.983	1487.3
1.2	17.530	1882.6	17.204	1806.6	16.011	1690.9
1.4	23.286	2128.1	22.142	2017.6	20.342	1876.0
1.6			27.690	2222.9	24.990	2048.2
1.8			34.040	2430.2	30.032	2212.8
2.0					35.600	2375.5

m	313.15 K		323.15 K		333.15 K	
	$\bar{L}_1$	$-\bar{L}_2$	$\bar{L}_1$	$-\bar{L}_2$	$\bar{L}_1$	$-\bar{L}_2$
mole/kg	J/mole					
0.1	0.1534	171.6	0.1351	151.2	0.1168	130.6
0.2	0.5950	335.5	0.5229	295.2	0.4540	255.7
0.3	1.2977	491.7	1.1393	432.2	0.9929	375.6
0.4	2.2348	640.6	1.9621	562.9	1.7167	490.4
0.5	3.3808	782.0	2.9721	687.6	2.6097	600.7
0.6	4.7108	916.4	4.1523	806.7	3.6585	706.6
0.7	6.2009	1043.7	5.4881	920.9	4.8508	808.5
0.8	7.8281	1164.2	6.9675	1030.4	6.1763	906.6
0.9	9.5698	1278.0	8.5809	1135.8	7.6262	1000.3
1.0	11.405	1335.3	10.311	1237.5	9.1934	1092.9
1.2	15.273	1580.9	14.165	1431.7	12.659	1267.9
1.4	19.276	1752.1	18.493	1616.6	16.549	1434.1
1.6	24.274	1900.3	23.333	1795.7	20.865	1593.9
1.8	29.837	2026.6	28.758	1972.8	25.636	1749.7
2.0	34.991	2232.4	34.876	2151.5	30.916	1904.0
2.1			38.239	2242.6	33.771	1981.3

$$\ln a_1 = -\frac{1}{R}\int \frac{\overline{L}_1(T)}{T^2}\,dT$$

Using the values of osmotic coefficients of thiourea in water solutions at the temp. 298.15 K obtained by Bonner et al [4], the excess of relative partial molal entropy of solvent ($\Delta\overline{S}_1^E$) was calculated (Table 2, Fig. 1) over the temperature range 293.15-333.15 K.

Table 2

Excess of relative partial molal entropies of water $\Delta\overline{S}_1^E$ for aqueons thiourea and urea solutions at temperature 298.15 K

m (mole/kg)	$\Delta\overline{S}_1^E$ (J/mole deg)	
	thiourea	urea
0.1	0.00047	
0.2	0.00177	
0.3	0.00376	
0.4	0.00630	
0.5	0.00934	0.00376
0.6	0.01266	
0.7	0.01622	
0.8	0.02009	
0.9	0.02398	
1.0	0.02814	0.01381
1.2	0.03698	
1.4	0.04668	
1.5		0.02343
1.6	0.05769	
1.8	0.07048	
2.0		0.03640

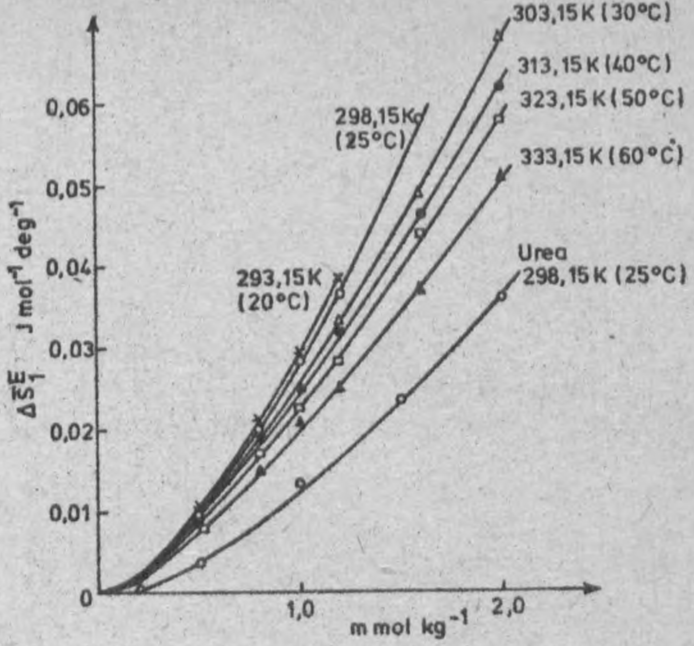

Fig. 1. Excess of relative partial molal entropy of solvent $\Delta\bar{S}_1^E$ as a function of concentration of thiourea in water

The values of $\Delta\bar{S}_1^E$ calculated by us for thiourea solutions in temperature range under investigation show the structure-breaking character of thiourea. The obtained values of excess of relative partial molal entropy of water at the temperature 298.15 K are more positive than the values of this function for urea solutions [5, 6] (see Table 2). It suggests more destructive effect of thiourea molecules on water structure than that of urea molecules.

On the basis of heat capacity and small changes in the water proton signal, Subramanian et al [7] reached the same conlusion about the destructive effect of urea and thiourea on the structure water, the effect of thiourea being stronger.

The more destructive effect of thiourea on specific water structure is caused by the replacement of oxygen atom in a urea molecule by a sulphur atom [8, 9] which has weaker proton accepting ability. A planar thiourea molecule being bigger than that of urea, does not have enough room in the hydrogen bond lattice of water structure [10].

REFERENCES

[1] Taniewska-Osińska S., Pałecz B., J. Chem. Thermodynamics 12, 775 (1980).

[2] Izmailov N. A., Elektrokhimia rastvorov, p. 112. Izd. Khark. Univ. Kharkov (1959).

[3] Robinson R. A., Stokes R. M., Electrolytes Solutions, London (1955).

[4] Bonner O. D., Jordan C. F., Arisman R. K., Bednarek J. M., J. Chem. Thermodynamics, 8, 1173 (1976).

[5] Łogwinienko R., Doctoral thesis, Łódź University 1972.

[6] Barone G., Elia V., Rizzo E., IV Intern. Conf. Calorimetry and Thermodynamics, Montpellier, France (1975).

[7] Subramanian S., Sarma T. S., Balasubramanian D., Ahluwalia J. C., J. Phys. Chem., 75, 815 (1971).

[8] Stewart J. E., J. Chem. Phys., 26, 248 (1957).

[9] Penkala T., Zarys krystalochemii, t. 2, Warszawa (1968), s. 145.

[10] Stępień A., University of Łódź. Personal communication.

Department of Physical Chemistry
Institute of Chemistry
University of Łódź

Stefania Taniewska-Osińska, Bartłomiej Pałecz

BADANIA TERMODYNAMICZNE ROZTWORÓW TIOMOCZNIK-WODA

Na podstawie pomiarów całkowitego ciepła rozpuszczania tiomocznika w wodzie [1] w przedziale temperatur 293.15-333.15 K wyliczono wartości względnych cząstkowych molowych entalpii wody $(\bar{L}_1)$ i tiomocznika $(\bar{L}_2)$. Korzystając z wartości $(\bar{L}_1)$ oraz aktywności wody w tych mieszaninach wyznaczono nadmiar względnej cząstkowej molowej entropii rozpuszczalnika $(\Delta\bar{S}_1^E)$. Przeprowadzona analiza wspomnianych funkcji termodynamicznych w zależności od stężenia i temperatury wskazuje na silniej niszczący wpływ tiomocznika niż mocznika na strukturę wody.

Стефания Таневска-Осиньска, Бартломией Палэч

ТЕРМОДИНАМИЧЕСКИЕ ИССЛЕДОВАНИЯ РАСТВОРОВ ТИОМОЧЕВИНА-ВОДА

Пользуясь калориметрически измеренной интегралной теплотой растворения тиомочевины в воде в пределе температур 293.15--333.15 K, определено относительные парциальные моляльные энтальпии воды (L_1) и тиомочевины $(\bar{L}_2)$. Исхоца из значений $(\bar{L}_1)$ и активности воды в этих растворах определена избыточная о.п.м. энтропия воды $(\Delta\bar{S}_1^E)$. Проведенный анализ упомянутых термодинамических функций в зависимости от концентрации и температуры указывает на более сильное разупорядочивающее влияние тиомочевины чем мочевины на структуру воды.