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THERMOCHEMICAL INVESTIGATIONS OF AQUEOUS ACETAMIDE SOLUTIONS WITHIN THE TEMPERATURE RANGE 25-70°C

Heat of solution ΔH_m of acetamide in water at 25°, 40°, 50°, 60° and 70°C over the concentration range 0-2 mole $AcNH_2$/kg H_2O was measured. Using these values the relative partial molal enthalpies of both the components of solutions, activity of water a_1 and the values of the excess relative partial molal entropy ΔS_1^E for water of investigated solutions have been calculated.

The analysis of the mentioned thermodynamic functions in relation to the concentration and temperature has shown that the acetamide molecules introduced to water slightly disturb water structure.

Thermodynamic investigations of acetamide $CaCl_2$, KNO_3, CsI and NaI solutions made it possible to observe certain similarity of properties of thermodynamic solutions in molten acetamide and in water [1]. Basing on the analysis of results of thermodynamic investigations of electrolyte solutions in different solvents [2-5] it may be assumed that the similarity of thermodynamic salt solutions in molten acetamide and in water is caused by the remainings three-dimentional hydrogen bond network in liquid state occuring both in solid acetamide [6-8] and in ice [9].

It seemed interesting to examine the binary water-acetamide system in order to attempt the explanation of mutual interactions among the molecules of these substances.

Experimental

Reagents

For the heat of solution measurements twice distilled water and p.a. acetamide produced by Xenon-Łódź crystallized from 95% ethanol were used [10]. The melting temperature of acetamide was 81-82°C [11, 12].

Apparatus

The heat of solution of acetamide in water was measured in the improved nonizothermic - nonadiabatic calorimeter of Vrewski type [13]. Dewar vessel with 220 cm^3 capacity was used. Temperature sensitivity was 0.002°C. The error of measurements was estimated to be ±1.5%.

Results

The obtained results of integral heat of solution ΔH_m of acetamide in water within the concentration range 0-2 mole of $AcNH_2$/kg of water at the temp. 25°, 40°, 50°, 60° and 70°C are given in Table 1. The izotherms $\Delta H_m = f(m)$ are described by the equation $\Delta H_m = a + p\sqrt{x}$, and a, p coefficient were calculated by the least squares method using Odra 1305 computer. Using the values of the obtained a and p coefficients the integral heat of dillution ΔH^o_m and the derivative $d(\Delta H^o_m)/d\sqrt{m}$ were calculated.

The values of relative partial molal enthalpy of water $\overline{L}_1$ and acetamide $\overline{L}_2$ were determined using the known dependencies

$$\overline{L}_1 = \frac{m\sqrt{m}}{2 \cdot \frac{1000}{M}} \cdot \frac{d(\Delta H^o_m)}{d\sqrt{m}} \quad (1)$$

Table 1

Heat of solution ΔH_m of acetamide in water (kcal/mole)

25°C		40°C		50°C		60°C		70°C	
m	ΔH_m	m	ΔH_m	m	ΔH_m	m	ΔH_m	m	ΔH_m
0.0208	2.38	0.0202	2.68	0.0200	2.86	0.0202	3.02	0.0203	3.14
0.0406	2.37	0.0404	2.67	0.0403	2.86	0.0405	3.01	0.0405	3.13
0.0883	2.36	0.0999	2.66	0.0821	2.85	0.0553	3.01	0.0701	3.13
0.1212	2.35	0.1049	2.66	0.1110	2.84	0.0888	3.00	0.0993	3.13
0.1509	2.35	0.1478	2.65	0.1673	2.84	0.1181	3.00	0.1081	3.13
0.2103	2.34	0.2185	2.64	0.2455	2.83	0.1475	2.99	0.1299	3.12
0.3222	2.33	0.2717	2.63	0.3714	2.81	0.2223	2.98	0.2517	3.11
0.4849	2.32	0.3527	2.62	0.5203	2.80	0.3770	2.97	0.3453	3.10
0.6325	2.30	0.4980	2.61	0.6977	2.79	0.5089	2.96	0.3988	3.10
0.7853	2.29	0.6345	2.61	0.8513	2.79	0.6557	2.95	0.4754	3.10
0.9471	2.28	0.7847	2.60	1.0110	2.78	0.8403	2.95	0.6064	3.10
1.1544	2.27	0.9202	2.60	1.1735	2.78	1.0022	2.94	0.7827	3.09
1.3514	2.26	1.0192	2.59	1.3672	2.77	1.2066	2.94	0.9012	3.09
1.5132	2,26	1.2835	2.58	1.5514	2.76	1.4667	2.94	1.1173	3.08
1.6959	2.25	1.5350	2.57	1.7379	2.76	1.6232	2.93	1.3031	3.08
1.8841	2,24	1.7894	2.57	1.9203	2.75	1.8472	2.93	1.6072	3.07
2.0489	2,24	1.9000	2.56	2.0945	2.75	2.0200	2.92	1.8918	3.07
2.1002	2,23	2.0720	2.56			2.100	2.92	2.0001	3.06
		2.100	2.55					2.1065	3.06

Table 2

Values of thermodynamic functions for $AcNH_2$-H_2O system at 25°C

m (mole/kg)	$\bar{L}_1$ (cal/mole)	$\bar{L}_2$ (cal/mole)	a_1	$\Delta\bar{S}_1^E$ (10^3cal/mole · deg)
0	0	0		0
0.0208	0.003	23.5	0.9997	0
0.0406	0.008	33.2	0.9994	0
0.0883	0.026	49.4	0.9984	0
0.1212	0.042	57.9	0.9978	0.1
0.1509	0.058	64.6	0.9973	0.2
0.2103	0.096	76.2	0.9962	0.4
0.3222	0.182	94.3	0.9942	0.6
0.4849	0.337	115.7	0.9914	1.1
0.6325	0.501	132.2	0.9890	1.2
0.7853	0.694	147.3	0.9864	1.5
0.9471	0.919	161.7	0.9838	2.0
1.1544	1.237	178.5	0.9805	2.5
1.3514	1.566	193.2	0.9774	3.0
1.5132	1.856	204.4	0.9748	3.4
1.6959	2.202	216.4	0.9720	4.0
1.8841	2.579	228.1	0.9691	4.7
2.0489	2.924	237.9	0.9667	5.2
2.100	3.034	240.8	0.9659	5.4

Table 3

Values of thermodynamic functions for $AcNH_2$-H_2O system at 40°C

m (mole/kg)	$\bar{L}_1$ (cal/mole)	$\bar{L}_2$ (cal/mole)	a_1	$\Delta\bar{S}_1^E$ (10^3cal/mole · deg)
0	0	0	1	0
0.0202	0.002	20.0	0.9997	0
0.0404	0.007	28.3	0.9994	0
0.0999	0.027	44.7	0.9982	0
0.1049	0.029	45.8	0.9981	0.1
0.1478	0.048	54.3	0.9973	0.2
0.2185	0.087	66.1	0.9961	0.3
0.2717	0.120	73.7	0.9951	0.5
0.3527	0.178	84.0	0.9937	0.6
0.4980	0.298	99.8	0.9911	0.9
0.6345	0.429	112.6	0.9889	1.0
0.7847	0.590	125.2	0.9864	1.2
0.9202	0.749	135.6	0.9841	1.5
1.0192	0.873	142.7	0.9826	1.5
1.2835	1.233	160.2	0.9783	2.1
1.5350	1.613	175.1	0.9744	2.6
1.7894	2.030	189.1	0.9704	3.2
1.9000	2.221	194.9	0.9687	3.4
2.0720	2.530	203.5	0.9661	3.8
2.100	2.581	204.9	0.9657	3.9

Table 4

Values of thermodynamic functions for $AcNH_2$-H_2O system at 50°C

m (mole/kg)	$\bar{L}_1$ (cal/mole)	$\bar{L}_2$ (cal/mole)	a_1	$\Delta\bar{S}_1^E$ (10^3cal/mole · deg)
0	0	0	1	0
0.0200	0.002	19.5	0.9997	0
0.0403	0.007	27.6	0.9994	0
0.0821	0.020	39.6	0.9986	0
0.1110	0.031	46.0	0.9980	0.1
0.1673	0.057	56.5	0.9970	0.2
0.2455	0.101	68.5	0.9956	0.4
0.3714	0.188	84.2	0.9934	0.6
0.5203	0.311	99.7	0.9907	0.9
0.6977	0.483	115.4	0.9879	0.9
0.8513	0.651	127.5	0.9852	1.3
1.0110	0.843	138.9	0.9827	1.4
1.1735	1.054	149.7	0.9800	1.9
1.3672	1.325	161.6	0.9769	2.2
1.5514	1.602	172.1	0.9740	2.5
1.7379	1.900	182.2	0.9711	2.9
1.9203	2.206	191.5	0.9683	3.3
2.0945	2.513	200.0	0.9656	3.7

Table 5

Values of thermodynamic functions for $AcNH_2$-H_2O system at 70 °C

m (mole/kg)	$\bar{L}_1$ (cal/mole)	$\bar{L}_2$ (cal/mole)	a_1	$\Delta\bar{S}_1^E$ (10^3cal/mole · deg)
0	0	0	1	0
0.0202	0.002	16.6	0.9997	0
0.0405	0.006	23.5	0.9994	0
0.0553	0.009	27.6	0.9991	0
0.0888	0.019	35.0	0.9984	0
0.1181	0.029	40.3	0.9979	0.1
0.1475	0.040	45.1	0.9973	0.2
0.2223	0.074	55.3	0.9960	0.3
0.3770	0.163	72.1	0.9933	0.5
0.5089	0.256	83.7	0.9909	0.8
0.6557	0.374	95.1	0.9885	0.7
0.8403	0.543	107.6	0.9854	1.0
1.0022	0.707	117.5	0.9828	1.0
1.2066	0.934	128.9	0.9794	1.5
1.4667	1.251	142.2	0.9753	1.7
1.6232	1.457	149.6	0.9728	1.9
1.8472	1.768	159.5	0.9693	2.2
2.0200	2.022	166.8	0.9667	2.4
2.1000	2.143	170.1	0.9655	2.6

Table 6

Values of thermodynamic functions for $AcNH_2$-H_2O system at 70°C

m (mole/kg)	$\bar{L}_1$ (cal/mole)	$\bar{L}_2$ (cal/mole)	a_1	$\Delta\bar{S}_1^E$ (10^3cal/mole · deg)
0	0	0	1	0
0.0203	0.002	13.3	0.9997	0
0.0405	0.005	18.8	0.9994	0
0.0701	0.010	24.9	0.9988	0
0.0993	0.018	29.7	0.9982	0
0.1081	0.020	30.9	0.9980	0
0.1299	0.026	33.9	0.9977	0.1
0.2517	0.071	47.2	0.9954	0.3
0.3453	0.115	55.3	0.9938	0.4
0.3988	0.142	59.4	0.9929	0.4
0.4754	0.185	64.9	0.9915	0.6
0.6064	0.267	73.3	0.9893	0.6
0.7827	0.391	83.3	0.9864	0.6
0.9012	0.483	89.3	0.9843	0.8
1.1173	0.667	99.5	0.9808	0.8
1.3031	0.840	107.4	0.9778	0.9
1.6072	1.151	119.3	0.9730	1.0
1.8918	1.469	129.5	0.9686	1.2
2.0001	1.597	133.1	0.9669	1.2
2.1065	1.726	136.6	0.9653	1.3

$$\bar{L}_2 = -\Delta H_m^o - \frac{\sqrt{m}}{2} \cdot \frac{d(\Delta H_m^o)}{d\sqrt{m}} \qquad (2)$$

The values of excess of relative partial molal entropy of water of the investigated solutions were calculated from the equation

$$\Delta \bar{S}_1^E = \frac{\bar{L}_1 - RT \ln a_1/N_1}{T} \qquad (3)$$

N_1 - mole fraction of solvent

a_1 - activity of solvent

Water activity (a_1) occuring in equation (3) was calculated from the equation:

$$\ln a_1 = -\frac{1}{R} \int_{298}^{T} \frac{\bar{L}_1(T)}{T^2} \, dT \qquad (4)$$

The function $\bar{L}_1(T)$ was expressed by the equation $\bar{L}_1(T) = a + bT + cT^2$ and the values a_1 corresponding to the temperature 25°C (298°K) was calculated using the data on vapour pressure of acetamide solutions obtained by Kangro and Groeneveld [14]. All calculated by us values of thermodynamic functions of aqueous acetamide solutions are presented in tables 2-6.

Discussion

The course of dependence of integral heat of solution ΔH_m of acetamide in water on concentration and temperature is presented on Fig. 1. As it can be seen the $\Delta H_m = f(m)$ isotherms show monotonous course. The exotermicity of the acetamide in water dissolution process increases with the growth of the concentration of the solution and decreases with the temperature growth. The slope of $\Delta H_m = f(m)$ curves decreases with the solution concentration and temperature growth.

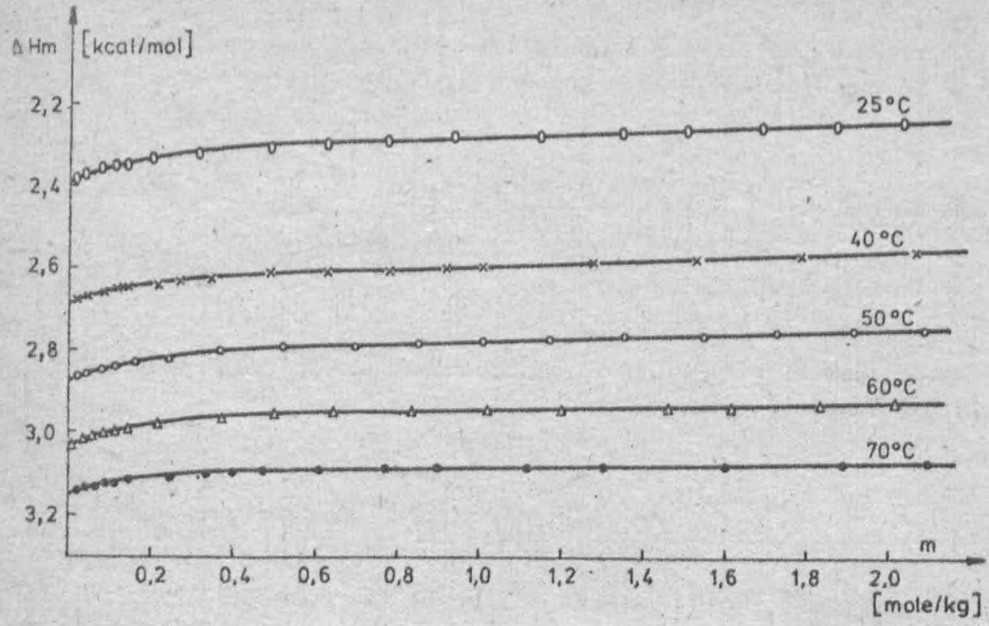

Fig. 1. Dependence of heat of solution ΔH_m of acetamide in water vs concentration at various temperatures

The conclusions about the influence of solute on solvent can be drawn from the analysis of the course of concentration and temperature dependence of relative partial molal enthalpies of the solution components and esspecially from the course of the function $\Delta\bar{S}_1^E = f(m, T)$. The values of the discussed thermodynamic functions of acetamide solutions in water (Tables 2-6) calculated by us are presented on Fig. 2-4 as curves $\bar{L}_1 = f(m)$, $\bar{L}_2 = f(m)$ and $\Delta\bar{S}_1^E = f(m)$ corresponding to the temp. 25°, 40°, 50°, 60° and 70°C (Fig. 2-4). As it is seen from Fig. 2 the dependence of relative partial molal enthalpy of water $\bar{L}_1$ the investigated solutions on concentration and temperature is similar to that in case of aqueous urea solutions [15] and water structure breaking electrolytes. Thus the conclusion on breaking primary water structure by acetamide molecules can be drawn.

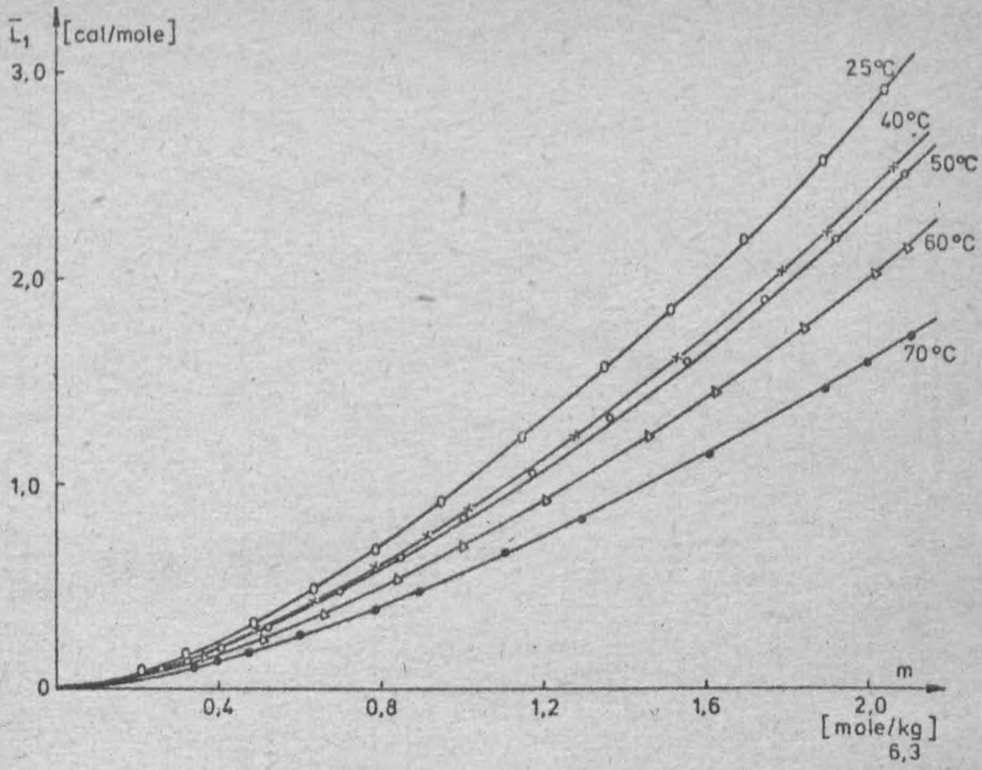

Fig. 2. Dependence of $\bar{L}_1$ of acetamide-water system vs concentration at various temperatures

It is also known, that positive $\bar{L}_1$ values point to the fact that molal enthalpy of evaporation of solvent from solution is smaller than molal enthalpy of evaporation of pure solvent. It follows that in aqueous acetamide solutions water molecules are bonded weaker than in pure water. Thus a conclusion can be drawn about the disturbance of water structure by introducing acetamide molecules to it. The above conclusion is also supported by the course of concentration and temperature dependence of relative partial molal enthalpy of acetamide $\bar{L}_1$ in the investigated solutions (Fig. 3). The decrease of the absolute values $\bar{L}_1$ and $\bar{L}_2$ with temperature growth can be explained by previous disturbance of primary water structure by thermal motions of its molecules, the intensity of which grows with the temperature growth.

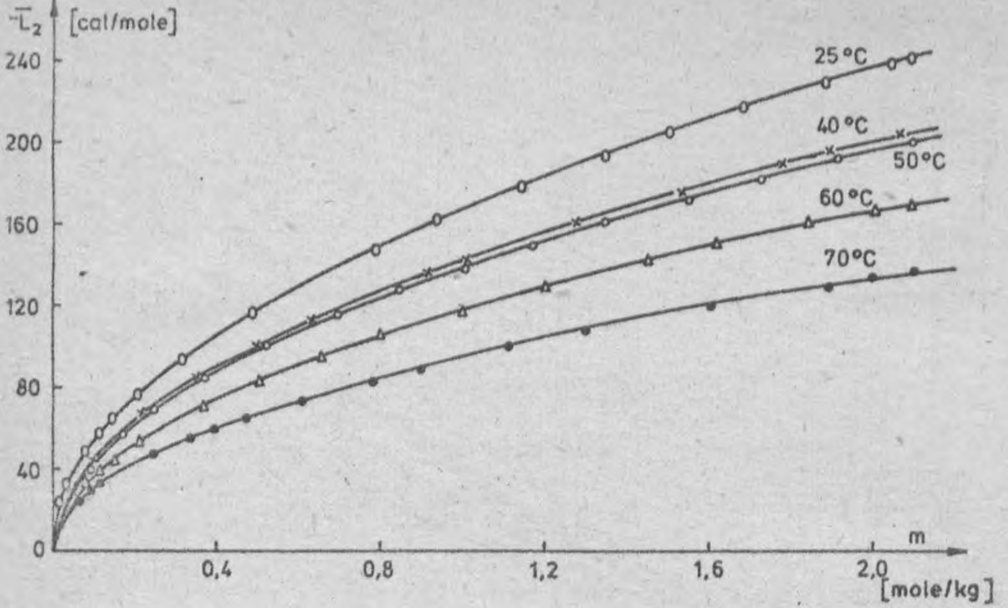

Fig. 3. Dependence of $\bar{L}_2$ of acetamide-water system vs. concentration at various temperatures

According to many authors [16-20] the best measure of either destructive or ordering influence of the solute on solvent are the values $\Delta\bar{S}_1^E$ of the excess of relative partial molal entropy of the solvent. This value is negative in case of substances ordering the structure of solvent and positive for those disturbing it.

The course of dependence of the values of the excess relative partial molal entropy of water $\Delta\bar{S}_1^E$ for aqueous acetamide solutions on the concentration and the temperature are presented on Fig. 4.

For the sake of comparison the discussed relation for aqueous urea solutions at the temp. 25°C has also been showed [26]. As it is seen from Fig. 4 the values $\Delta\bar{S}_1^E$ of aqueous acetamide solutions are positive and they decrease with the growth of concentration of the solution. So it is possible to draw a conclusion about distructing the water structure by acetamide.

With the temperature growth the values $\Delta\bar{S}_1^E$ decrease and approach to zero. This implies that the disordering influence of acetamide on water decreases with the temperature growth which seems obvious if consider the growing disturbance of water structure by more intensive thermal motions of molecules in higher temperature.

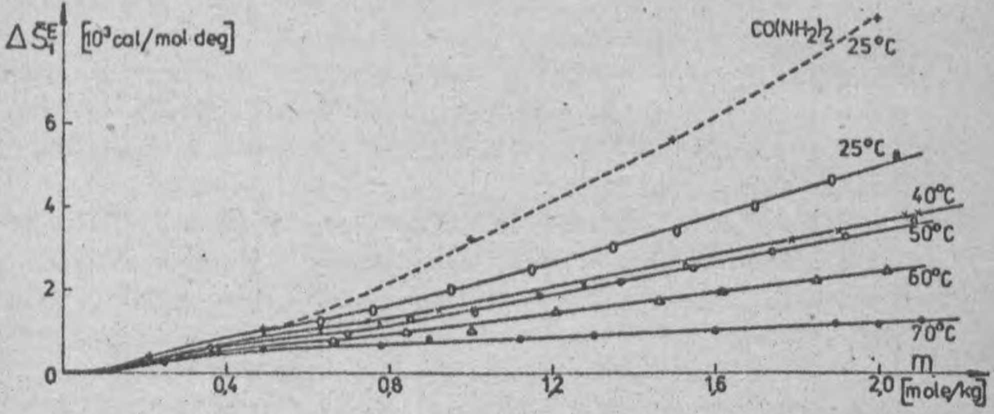

Fig. 4. The excess of relative partial molal entropy $\Delta\bar{S}_1^E$ of water-acetamide system

Very small $\Delta\bar{S}_1^E$ values of aqueous acetamide solutions allow to suppose that acetamide molecules introduced to water while building in the ice-like water structure slightly disturb it and probably form mixed agregates of molecules bound with hydrogen bonds. The conclusion drawn from the course of dependence of $\Delta\bar{S}_1^E$ of the solutions investigated by us is confirmed by densimetric [21], viscosimetric [22] and dielectric [23-25] investigations of aqueous acetamide solutions.

As it is seen from plot 4 the values $\Delta\bar{S}_1^E$ of aqueous urea solutions are also positive [26] but they are bigger in comparison to those obtained for aqueous acetamide solutions. It points to a stronger disturbance of primary water structure by urea than by acetamide.

REFERENCES

[1] Taniewska-Osińska S., Woldan M., Rocz. Chem., 51, 1933 (1977).

[2] Mishchenko K. P., Klujeva M. L., Teoret. Eksp. Khim., 1, 201 (1965).

[3] Mishchenko K. P., Subbotina W. W., Krumgalz B. S., Teoret. Eksp. Khim., 5, 268 (1969).

[4] Tungusov W. M., Mishchenko K. P., Zhur. Strukt. Khim., 8, 1005 (1967).

[5] Bogdanov W. G., Klujeva M. L., Mishchenko K. P., Zhur. Obshch. Khim., 40, 721 (1970).

[6] Senti F., Harker D., J. Am. Chem. Soc., 62, 2008 (1940).

[7] Hamilton W. C., Acta Cryst., 18, 866 (1965).

[8] Denne W. A., Small R. W. H., Acta Cryst., B27, 1094 (1971).

[9] Kavanau J. L., Water and Solute-Water Interactions, (San Francisco) (1964).

[10] Christoffers H. J., Kegeles G., J. Am. Chem. Soc., 85, 2562 (1963).

[11] Singh D., Singh N. P., Bahadur Lal., Indian J. Chem., 13, 1177 (1975).

[12] Sprawocznik chimiká, t. II, Leningrad (1963), 452.

[13] Woldan M., Doctoral Dissertation, University, Łódź (1973).

[14] Kangro W., Groeneveld A., J. Phisik Chem. Neuve Folge 32, 110 (1962).

[15] Łogwinienko R., Taniewska-Osińska S., Pluta M., Acta Chimica 18, 25-30 (1973).

[16] Mishchenko K. P., Połtorackij G. M., Voprosy tiermodinamiki i stroyenija vodnykh i nevodnykh rastvorov elektrolitov, Khimija, Leningrad (1968).

[17] Mishchenko K. P., Jakówlev J. F., Zhur. Obshch. Khim., 29, 1761 (1959).

[18] Mishchenko K. P., Podgornaja E. A., Zhur. Obshch. Khim., 31, 1743 (1961).

[19] Frank H. S., Robinson A. L., J. Chem. Phys. 8, 933 (1940).

[20] Mishchenko K. P., Ponomarieva A. M., Zhur. Obshch. Khim., 26, 1296 (1958).

[21] Woldan M., Taniewska-Osińska S., J. Pol. Chem., in press.

[22] Woldan M., Taniewska-Osińska S., in prepared.

[23] Rohdewald P., Moldner M., J. Phys. Chem., 77, 373 (1973).

[24] Gonczarov W. S., Jastremskij P. S., Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Tekhnol., 19, (4) 602 (1976).

[25] Gonczarov W. S., Ljaszczenko A. K., Jastremskij P. S., Zhur. Strukt. Khim., 17, 4, 662 (1976).

[26] Taniewska-Osińska S., Łogwinienko R., Rocz. Chem., 50, 151 (1976).

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TERMOCHEMICZNE BADANIA WODNYCH ROZTWORÓW ACETAMIDU W ZAKRESIE TEMP. 25-70°C

Przeprowadzono pomiary ciepła rozpuszczania ΔH_m acetamidu w wodzie w temperaturze 25°, 40°, 50°, 60° i 70°C w zakresie stężeń 0-2 moli $AcNH_2$/kg wody. Korzystając z otrzymanych wartości ΔH_m obliczono względną cząstkową molową entalpię wody $\bar{L}_1$ i acetamidu $\bar{L}_2$ oraz aktywność wody a_1 i wartości nadmiaru względnej cząstkowej molowej entropii wody $\Delta\bar{S}_1^E$ badanych roztworów. Na podstawie analizy zależności wymienionych funkcji termodynamicznych od stężenia i temperatury roztworu wysnuto wniosek, że acetamid wprowadzony do wody powoduje nieznaczne zakłócenie jej struktury.

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ТЕРМОХИМИЧЕСКИЕ ИССЛЕДОВАНИЯ ВОДНЫХ РАСТВОРОВ АЦЕТАМИДА ПРИ 25-70°С

Проведено измерения теплоты растворения ΔHм ацетамида в воде при 25°, 40°, 50°, 60° и 70°С в интервале концентрации 0-2 м $AcNH_2$/кг H_2O. Пользуясь значениями ΔHм рассчитано: относительную парциальную моляльную энтальпию обоих компонентов раствора, активность воды и избыточную относительную парциальную моляльную энтропию воды $\Delta\bar{S}_1^E$ исследованых растворов. На основе анализа зависимости упомянутых термодинамических функции от концентрации и температуры раствора сделан вывод, что ацетамид слабо разрушает структуру воды.