A C T A U N I V E R S I T A T I S L O D Z I E N S I S
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ACTIVITY OF WATER IN AQUEOUS ACETAMIDE SOLUTIONS WITHIN THE TEMPERATURE RANGE 298.15-358.15 K

On the basis of our values of the relative partial molal enthalpy of water in aqueous acetamide solutions activity, a_1, and activity coefficient, f_1, of water and pressure of water vapour over the aqueous acetamide solutions and the osmotic pressure of these solutions have been calculated. From the analysis of changes of these functions on the concentration of acetamide in solution and temperature the conclusion that acetamide has a small disordering effect on water structure has been drawn.

From densimetric [1], viscosimetric [2] and thermochemical [3] investigations it follows that the molecules of acetamide have little disordering effect on water structure. This effect increases with the rise of the concentration of acetamide in the solution and decreases when the temperature increases. In the present paper we have examined the interactions among water and acetamide molecules on the basis of the dependence of activity coefficient of water in aqueous acetamide solutions on the concentration of solution and temperature. Utilizing the values of activity of water in the aqueous acetamide solutions the pressure of water vapour over the investigated solutions and their osmotic pressure in the concentration range of $AcNH_2$ 0-4 $mole.kg^{-1}$ of water within the temperature range 298.15-358.15 K have been calculated.

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Experimental

The method of purification of acetamide and the procedure of the measurements of enthalpy of solution of acetamide in water have been described previously [3].

Results

It is known that the activity of solvent at given temperature one can calculate from equation

$$\ln a_{1(T)} = \ln a_{1(298.15)} - \frac{1}{R} \int_{298.15}^{T} \frac{\bar{L}_{1(T)}\, dT}{T^2} \qquad (1)$$

where

$a_{1(298.15)}$ is the activity of solvent in the solution at 298.15 K; R is the gas constant;

T is the temperature in Kelvin;

$\bar{L}_{1(T)}$ is the dependence of the relative partial molal enthalpy of solvent in the solution on the temperature; in case of aqueous acetamide solutions the values of $\bar{L}_1$ were taken from literature [3] and they have been described by equation:

$$\bar{L}_{1(T)} = A_1 + A_2\, m + A_3\, m^2 \qquad (2)$$

where m is molal concentration of acetamide in the solution.

The values of the coefficients A_1, A_2 and A_3 have been calculated by the least squares method using Odra 1305 computer and they are given in Table 1. Using the values of coefficients A_1, A_2 and A_3 the values of $\bar{L}_1$ in the concentration range 0.2-4.0 mole of $AcNH_2$ on kg of water for selected concentrations of acetamide were calculated. The values of $\bar{L}_1$ of water in aqueous acetamide solutions as a function of temperature were described by equation

$$\bar{L}_{1(T)} = D_1 + D_2 T + D_3\, T^2 \qquad (3)$$

The values of the coefficients D_1, D_2 and D_3 calculated by the least squares method using Odra 1305 computer are given in Table 2.

Substituting equation 3 in equation 1 and using the values of activity of water in aqueous acetamide solutions at 298.15 K from literature data [4] the values of activity of water, a_1, in aqueous

Table 1

Coefficients A_1, A_2 and A_3 for equation 2 for aqueous acetamide solutions

T(K)	A_1	A_2	A_3
298.15	-0.062338	0.680322	0.378984
313.15	-0.048507	0.583972	0.338384
323.15	-0.049266	0.548746	0.306544
333.15	-0.031007	0.432441	0.292990
343.15	-0.028754	0.378647	0.218645

Table 2

Coefficients D_1, D_2 and D_3 for equation 3 for aqueous acetamide solutions

m / mol.kg^{-1}	D_1	D_2	D_3
0.2	-0.415699	0.003798	-0.000007
0.4	-0.933705	0.009714	-0.000019
0.6	-1.682395	0.017495	-0.000034
0.8	-2.661771	0.027140	-0.000053
1.0	-3.871830	0.038650	-0.000075
1.2	-5.312575	0.052025	-0.000100
1.4	-6.984005	0.067265	-0.000129
1.6	-8.886119	0.084370	-0.000161
1.8	-11.018919	0.103340	-0.000196
2.0	-13.382403	0.124174	-0.000234
3.0	-28.660096	0.256320	-0.000477
4.0	-49.704909	0.435087	-0.000803

Table 3

Activity of water in aqueous acetamide solutions within the temperature range 298.15-358.15 K

m mol.kg^{-1}	x_1	298.15	313.15	323.15	333.15	343.15	348.15	358.15
0.2	0.9964	0.9966	0.9966	0.9966	0.9966	0.9966	0.9966	0.9966
0.4	0.9929	0.9933	0.9933	0.9933	0.9933	0.9933	0.9932	0.9932
0.6	0.9893	0.9899	0.9899	0.9898	0.9898	0.9898	0.9898	0.9898
0.8	0.9858	0.9865	0.9864	0.9864	0.9864	0.9864	0.9864	0.9863
1.0	0.9823	0.9830	0.9829	0.9829	0.9828	0.9828	0.9828	0.9828
1.2	0.9789	0.9798	0.9797	0.9796	0.9796	0.9796	0.9796	0.9795
1.4	0.9754	0.9766	0.9765	0.9764	0.9764	0.9763	0.9763	0.9763
1.6	0.9720	0.9734	0.9733	0.9732	0.9731	0.9730	0.9730	0.9730
1.8	0.9686	0.9702	0.9700	0.9699	0.9698	0.9698	0.9698	0.9697
2.0	0.9652	0.9670	0.9668	0.9667	0.9666	0.9665	0.9665	0.9664
3.0	0.9488	0.9518	0.9514	0.9512	0.9510	0.9509	0.9508	0.9507
4.0	0.9328	0.9374	0.9368	0.9364	0.9361	0.9359	0.9358	0.9357

Table 4

Activity coefficient of water in aqueous acetamide solution within the temperature range 298.15-358.15 K

m mol.kg^{-1}	x_1	298.15	313.15	323.15	333.15	343.15	348.15	358.15
0.2	0.9964	1.0002	1.0002	1.0002	1.0002	1.0002	1.0002	1.0002
0.4	0.9929	1.0004	1.0004	1.0004	1.0004	1.0004	1.0003	1.0003
0.6	0.9893	1.0006	1.0006	1.0005	1.0005	1.0005	1.0005	1.0005
0.8	0.9858	1.0007	1.0006	1.0006	1.0006	1.0006	1.0006	1.0005
1.0	0.9823	1.0007	1.0006	1.0006	1.0005	1.0005	1.0005	1.0005
1.2	0.9789	1.0009	1.0008	1.0007	1.0007	1.0007	1.0007	1.0006
1.4	0.9754	1.0012	1.0011	1.0010	1.0010	1.0009	1.0009	1.0009
1.6	0.9720	1.0014	1.0013	1.0012	1.0011	1.0010	1.0010	1.0010
1.8	0.9686	1.0016	1.0014	1.0013	1.0012	1.0012	1.0012	1.0011
2.0	0.9652	1.0019	1.0017	1.0016	1.0015	1.0013	1.0013	1.0012
3.0	0.9488	1.0032	1.0027	1.0025	1.0023	1.0022	1.0021	1.0020
4.0	0.9328	1.0049	1.0043	1.0039	1.0035	1.0033	1.0032	1.0031

acetamide solutions for selected concentrations of $AcNH_2$ at 298.15, 313.15, 323.15, 333.15, 343.15, 348.15 and 358.15 K have been calculated. The results are given in Table 3. In Table 4 the values of activity coefficient of water, f_1, in aqueous acetamide solutions calculated from known relation

$$f_1 = \frac{a_1}{x_1} \tag{4}$$

where x_1 is the mole fraction of water in the solution are presented. The analysis of the experimental errors and the approximations using in the calculations permits to estimate the error in activity (activity coefficient) of water as $\pm$ 0.001. The pressure of water vapour over aqueous acetamide solutions was calculated from the equation

$$p_1 = p_o \cdot a_1 \tag{5}$$

where p_o is the pressure of water vapour over pure water. In the calculations following values of p_o were used: 31.672, 73.759, 123.337, 199.157, 311.574, 385.435 and 578.086 hPa at 298.15, 313.15, 323.15, 333.15, 343.15, 348.15 and 358.15 K [5] respectively. For the purpose to observe the deviation of water-acetamide system from Raoult's law the values $\Delta p = p_1 - p_o \cdot x_1$ were also calculated. The results of the calculations of p_1 and Δp for aqueous acetamide solutions are presented in Table 5. The values of osmotic pressure of aqueous acetamide solutions were calculated from relation

$$\Pi = -\frac{RT}{\bar{V}_1} \ln a_1 \tag{6}$$

where $\bar{V}_1$ is the partial molal volume of water. With regard for the small dependence of the partial molal volume of water in aqueous acetamide solutions on concentration in the calculations the values $\bar{V}_1$ equal to molal volume of water at given temperature were taken. The obtained values of osmotic pressure of aqueous acetamide solutions are given in Table 6.

Table 5

The pressure of water vapour over the aqueous acetamide solutions within the temperature range 258.15-358.15 K [hPa]

m mol.kg^{-1}	298.15		313.15		323.15		333.15	
	p_1	Δp	p_1	Δp	p_1	Δp	p_1	Δp
0.2	31.56	0.00	73.51	0.02	122.92	0.03	198.48	0.04
0.4	31.46	0.01	73.26	0.02	122.51	0.05	197.81	0.07
0.6	31.35	0.02	73.01	0.04	122.08	0.06	197.13	0.10
0.8	31.24	0.02	72.76	0.05	121.66	0.07	196.45	0.12
1.0	31.13	0.02	72.50	0.05	121.23	0.08	195.74	0.11
1.2	31.03	0.03	72.26	0.06	120.83	0.10	195.09	0.14
1.4	30.93	0.04	72.02	0.08	120.43	0.13	194.45	0.19
1.6	30.83	0.04	71.79	0.10	120.03	0.15	193.80	0.22
1.8	30.73	0.05	71.55	0.11	119.63	0.17	193.15	0.25
2.0	30.63	0.06	71.31	0.12	119.23	0.19	192.50	0.27
3.0	30.15	0.10	70.18	0.20	117.32	0.30	189.40	0.44
4.0	29.69	0.15	69.10	0.30	115.50	0.45	186.44	0.67

m mol kg^{-1}	343.15		348.15		358.15	
	p_1	Δp	p_1	Δp	p_1	Δp
0.2	310.51	0.06	384.12	0.07	576.11	0.11
0.4	309.47	0.11	382.83	0.13	574.18	0.20
0.6	308.40	0.16	381.51	0.20	572.19	0.29
0.8	307.33	0.18	380.18	0.22	570.19	0.31
1.0	306.22	0.16	378.81	0.20	568.15	0.30
1.2	305.21	0.21	377.55	0.25	566.25	0.36
1.4	304.19	0.28	376.30	0.35	564.36	0.49
1.6	303.18	0.33	375.04	0.40	562.47	0.57
1.8	302.16	0.37	373.78	0.45	560.58	0.65
2.0	301.14	0.41	372.51	0.49	558.68	0.71
3.0	296.26	0.64	366.47	0.77	549.59	1.10
4.0	291.60	0.96	360.69	1.16	540.89	1.65

Table 6

The osmotic pressure of aqueous acetamide solution within the temperature range 298.15-358.15 K [kPa]

m mol kg^{-1}	298.15	313.15	323.15	333.15	343.15	348.15	358.15
0.2	467	489	504	517	530	537	549
0.4	922	967	995	1 022	1 048	1 062	1 086
0.6	1 392	1 461	1 504	1 545	1 585	1 606	1 643
0.8	1 863	1 957	2 014	2 071	2 124	2 152	2 202
1.0	2 351	2 469	2 543	2 612	2 681	2 718	2 780
1.2	2 798	2 940	3 029	3 111	3 194	3 237	3 313
1.4	3 246	3 413	3 516	3 614	3 709	3 760	3 848
1.6	3 696	3 887	4 006	4 121	4 227	4 286	4 386
1.8	4 148	4 364	4 498	4 627	4 748	4 814	4 927
2.0	4 601	4 842	4 992	5 137	5 272	5 345	5 471
3.0	6 273	7 142	7 371	7 591	7 796	7 907	8 097
4.0	8 863	9 364	9 676	9 973	10 250	10 399	10 653

Discussion

As it is seen from Table 3 the values of activity of water, a_1, in aqueous acetamide solutions decrease with the increase of the concentration of acetamide in solution. The activity of water in solutions containing less than 1 mole of acetamide in 1 kg of water does not depend on the temperature and it decreases a small as the temperature increases for more concentrated solutions. Moreover, the activity of water differs a little from the molar fraction of water in the solution. These changes are more visible in case of the activity coefficient of water, f_1. For all investigated solutions the values of activity coefficient of water are larger than unity. From this it follows that the molecules of water in aqueous acetamide solutions are more free than they are in pure water. Hence, one conclude that acetamide weakly disorders water structure. This disordering effect of acetamide on the structure of water de-

creases a little with the increase of temperature. It is known that the activity coefficient can serve as a measure of deviation of a given solution from the behaviour of ideal solution. As it is seen from Table 4 the aqueous acetamide solutions show small positive deviation from ideal solution which decreases with the increase of temperature. Similar conclusion it follows from the analysis of results in Table 5. All investigated aqueous acetamide solutions show positive deviation from the Rauolt's law. It confirms that acetamide has small disordering effect on water structure which decreases a little with the increase of temperature. Finally, it is interesting to compare the activity coefficient of water in the solutions containing other nonelectrolytes with similar nature and dimension of molecules as acetamide. The nonelectrolyte chosen for this purpose is urea. The values of activity coefficient of water in aqueous urea solutions were calculated from L o g v i n i e n k o's thermochemical data [6] and the osmotic coefficients from literature data [7, 8]. The results are given in Table 7. As it is seen from Table 7 the values of activity coefficient of water in aqueous acetamide and urea solutions within the experimental error are identical. Thus, it can conclude that the interactions water - acetamide and water - urea are similar.

T a b l e 7

Activity coefficients of water
in aqueous nonelectrolytes solutions at 298.15 K

m / mole kg^{-1}	Acetamide	Urea
0.5	1.0005	1.0000
1.0	1.0007	1.0007
1.5	1.0013	1.0013
2.0	1.0019	1.0018
2.5	1.0025	1.0022
3.0	1.0032	1.0034
4.0	1.0049	1.0045

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AKTYWNOŚĆ WODY W WODNYCH ROZTWORACH ACETAMIDU
W ZAKRESIE TEMPERATURY 298.15-358.15 K

Na podstawie własnych wartości względnej cząstkowej molowej entalpii wody w wodnych roztworach acetamidu obliczono aktywność a_1 i współczynnik aktywności f_1 wody, prężność pary wodnej nad wodnymi roztworami acetamidu oraz ich ciśnienie osmotyczne. Z analizy zależności tych funkcji od stężenia acetamidu i temperatury wysnuto wniosek o niewielkim niszczącym wpływie acetamidu na strukturę wody.