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VISCOSIMETRIC INVESTIGATIONS OF WATER-ACETAMIDE SYSTEM WITHIN THE TEMPERATURE RANGE 25-85°C*

The viscosity of aqueous acetamide solutions over the whole miscibility range at temperature 25°, 40°, 60°, 75° and 85 C has been measured. The relative viscosity, temperature coefficient $\Delta\eta r/\Delta T$ and the thermodynamic function of activation for fluid flow have been calculated. The effect of dissolved acetamide on water structure has been discussed.

In recent years many works devoted to the explanations of interactions among water molecules and various amides have appeared. This problem is important due to the application of water-amide mixtures as polar solvents in many chemical processes.

One of physico-chemical properties of these solvents is viscosity. In aqueous solutions containing various types of polar molecules (alcohols, acetone, DMF) the occurence of viscosity maximum is often observed, which is interpreted in many ways by various authors [1-7]. The maximum is not observed in case of aqueous formamide solutions [8]. Some authors [9, 10] suggest that this fact points to labile structure of water-formamide mixture. Lack of data on viscosity of water-acetamide system at several temperatures made us carry do such measurements. We have measured viscosity of aqueous acetamide solutions over the whole miscibility range at temperatures: 25°, 40°, 60°, 75° and 85°C.

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Experimental

All of the reagents used in the investigations was purified by the methods described earlier [11]. The purity of acetamide was checked by melting point determination 81-82°C [12]. Viscosity measurements were made with calibrated Ubbelohde's viscometer placed in liquid thermostat preserving the required temperature with the precision ±0.05°C. Density of the investigated solutions was determined by the magnetic float densimeter [13] with the precision 2.10^{-5} g/cm^3. The error of viscosity measurements was ±0.8%.

Results

The obtained results of dynamic viscosity measurements of aqueous acetamide solutions are given in Table 1.

Table 1

The viscosity of aqueous acetamide solutions

wt % $AcNH_2$	X_{AcNH_2}	m (mole/kg)	(cP = 10^{-3} Pa·s)				
			25°C	40°C	60°C	75°C	85°C
1	2	3	4	5	6	7	8
2	0.0062	0.3455	0.924	0.675	0.481	0.388	0.342
5	0.0158	0.8910	0.978	0.710	0.503	0.404	0.354
8	0.0258	1.4721	1.035	0.745	0.527	0.419	0.366
10	0.0328	1.8810	1.076	0.773	0.543	0.430	0.374
15	0.0510	2.9875	1.186	0.848	0.589	0.461	0.399
22	0.0791	4.7749	1.365	0.957	0.662	0.511	0.441
30	0.1155	7.2553	1.614	1.122	0.757	0.579	0.500
40	0.1688	11.2360	2.028	1.386	0.899	0.685	0.587
50	0.2336	16.9291	2.606	1.694	1.094	0.831	0.703

Table 1 contd.

1	2	3	4	5	6	7	8
60	0.3137	25.3936	-	2.248	1.328	0.968	0.812
70	0.4155	39.5012	-	2.887	1.711	1.241	1.008
80	0.5493	67.7160	-	-	2.221	1.514	1.242
85	0.6333	95.9310	-	-	-	1.683	1.384
95	0.8527	321.652	-	-	-	-	1.745
100	1.	-	-	-	-	-	2.041

Table 2 contains the values of relative viscosity of the investigated systems.

According to literature [14-16] relative viscosity of non-electrolyte solutions can be described by the equation:

$$\eta/\eta_o = 1 + Bc + Cc^2 \tag{1}$$

The values of B and C coefficients of aqueous acetamide solutions estimated graphically are shown in the Table 3.

In order to determine the influence of dissolved acetamide on water the values of thermodynamic functions of activation for fluid flow were calculated.

According to Eyring's theory [17] concerning laminar flow of liquid the dynamic viscosity of the solution can be described by the equation

$$\eta = \frac{h\ N}{V} \exp \frac{\Delta G^{\ddagger}}{RT} = \frac{h\ N}{V} \exp \frac{-\Delta S^{\ddagger}}{R} \exp \frac{\Delta H^{\ddagger}}{RT} \tag{2}$$

where:

$\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ - the free energy of activation for fluid flow, enthalpy and entropy respectively

h - Planck's constant

V - molar volume of solvent

N - Avogardo number

Values of particular thermodynamic functions of activation for fluid flow were calculated from the formulae:

Table 2

The relative viscosity of aqueous acetamide solutions

wt % $AcNH_2$	25°C		40°C		60°C		75°C		85°C	
	C (mole/l)	η_r	C (mole/l)	η_r	C (mole/l)	η_r	C (mole/l)	η_r	C (mole/l)	η_r
2	0.3449	1.0382	0.3432	1.0337	0.3400	1.0309	0.3371	1.0256	0.3349	1.0224
5	0.8912	1.0988	0.8868	1.0873	0.8782	1.0780	0.8705	1.0665	0.8648	1.0583
8	1.4753	1.1629	1.4673	1.1409	1.4529	1.1294	1.4400	1.1061	1.4304	1.0942
10	1.8877	1.2090	1.8771	1.1838	1.8582	1.1637	1.8415	1.1352	1.8292	1.1181
15	3.0081	1.3326	2.9899	1.2986	2.9584	1.2623	2.9308	1.2170	2.9105	1.1928
22	4.8306	1.5337	4.7980	1.4655	4.7440	1.4188	4.6982	1.3490	4.6632	1.3184
30	7.3797	1.8135	7.3231	1.7182	7.2333	1.6224	7.1629	1.5285	7.1082	1.4947
40	11.5544	2.2786	11.4533	2.1225	11.3032	1.9267	11.1843	1.8083	11.0938	1.7548
50	17.4410	2.9281	17.2668	2.5942	17.0256	2.3446	16.8328	2.1938	16.6948	2.1016
60	-	-	26.0025	3.4426	25.6247	2.8461	25.3194	2.5554	25.1069	2.4275
70	-	-	40.5693	4.4205	39.9606	3.6669	39.4854	3.2761	39.1338	3.0134
80	-	-	-	-	68.6234	4.7600	67.7526	3.9968	67.1675	3.7130
85	-	-	-	-	-	-	96.0068	4.4430	95.1866	4.1375
95	-	-	-	-	-	-	-	-	319.0466	5.2167
100	-	-	-	-	-	-	-	-	-	6.1016

$$\Delta H^{\ddagger} = R\ d\ \ln \eta / d\left(\frac{1}{T}\right) \tag{3}$$

$$\Delta G^{\ddagger} = RT \ln (\eta V / hN) \tag{4}$$

$$\Delta S^{\ddagger} = \frac{\Delta H^{\ddagger} - \Delta G^{\ddagger}}{T} \tag{5}$$

The derivative $d \ln \eta / d\left(\frac{1}{T}\right)$ was determined numerically using the equation:

$$\ln \eta = \frac{a}{T^2} + \frac{b}{T} + C \tag{6}$$

The obtained $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ values of aqueous acetamide solutions are given in Table 4.

Table 3

The values of B and C coefficients (equation [1]) of aqueous acetamide solutions

T (^{o}C)	B (l/mole)	C (l^2/mole^2)	$\Delta B/\Delta T \cdot 10^3$
25	0.111	-0.0003	-0.7
40	0.100	-0.0004	-0.7
60	0.087	-0.0004	-0.7
75	0.077	-0.0004	-0.9
85	0.068	-0.0004	

Table 4

The enthalpy, free energy and entropy of activations for fluid flow of aqueous acetamide solutions

Mole fraction X_{AcNH_2}	25°C			40°C			60°C			75°C			85°C		
	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta G^{\ddagger}$	$\Delta S^{\ddagger}$
	$\frac{kJ}{mole}$	$\frac{kJ}{mole}$	$\frac{J}{mole \cdot K}$	$\frac{kJ}{mole}$	$\frac{kJ}{mole}$	$\frac{J}{mole \cdot K}$	$\frac{kJ}{mole}$	$\frac{kJ}{mole}$	$\frac{J}{mole \cdot K}$	$\frac{kJ}{mole}$	$\frac{kJ}{mole}$	$\frac{J}{mole \cdot K}$	$\frac{kJ}{mole}$	$\frac{kJ}{mole}$	$\frac{J}{mole \cdot K}$
0.0	16.48	9.16	24.6	15.31	8.83	20.7	13.92	8.48	16.3	12.98	8.29	13.5	12.40	8.17	11.8
0.0062	16.65	9.25	24.8	15.52	8.91	21.1	14.17	8.57	16.8	13.25	8.36	14.1	12.69	8.24	12.4
0.0158	16.88	9.39	25.1	15.79	9.04	21.6	14.50	8.69	17.4	13.62	8.47	14.8	13.08	8.34	13.2
0.0258	17.09	9.53	25.4	16.07	9.17	22.0	14.85	8.82	18.1	14.03	8.58	15.7	13.53	8.44	14.2
0.0328	17.19	9.63	25.4	16.26	9.26	22.3	15.15	8.90	18.8	14.40	8.65	16.5	13.94	8.51	15.2
0.0510	17.60	9.87	25.9	16.63	9.50	22.8	15.59	9.13	19.4	14.80	8.85	17.1	14.28	8.70	15.6
0.0791	18.13	10.22	26.6	17.27	9.82	23.8	16.18	9.45	20.2	15.41	9.15	18.0	14.91	9.00	16.5
0.1155	19.02	10.63	28.1	18.05	10.23	25.0	16.90	9.82	21.2	16.12	9.51	19.0	15.64	9.37	17.5
0.1688	20.52	11.20	31.3	19.30	10.78	27.2	17.84	10.30	22.6	17.20	10.00	20.7	16.65	9.85	19.0
0.2336	22.60	11.82	36.2	20.35	11.31	28.9	18.90	10.84	24.2	18.30	10.56	22.2	17.75	10.38	20.6
0.3137	-	-	-	21.72	12.04	30.9	20.10	11.38	26.2	19.40	11.00	24.1	18.90	10.81	22.6
0.4155	-	-	-	23.25	12.69	33.7	21.40	12.08	28.2	20.83	11.72	26.2	20.25	11.46	24.5
0.5493	-	-	-	-	-	-	23.00	12.80	30.6	22.07	12.30	28.1	21.70	12.08	26.9

Discussion

On Fig. 1 and 2 the dependences of dynamic viscosity of aqueous acetamide solutions on concentration and temperature are presented. As it is seen from Fig. 1 viscosity of water-acetamide mixtures increases monotonously with the growth of non-electrolyte contents in water over the whole investigated temperature range (25-85°C). At the temp. 85°C the dependence of viscosity of $AcNH_2-H_2O$ mixture on the composition is almost linear. The growth of temperature causes the decrease of viscosity of the solution, but the character of $\eta = f$ (mole %) function remains unchanged. From Fig. 2 it can be

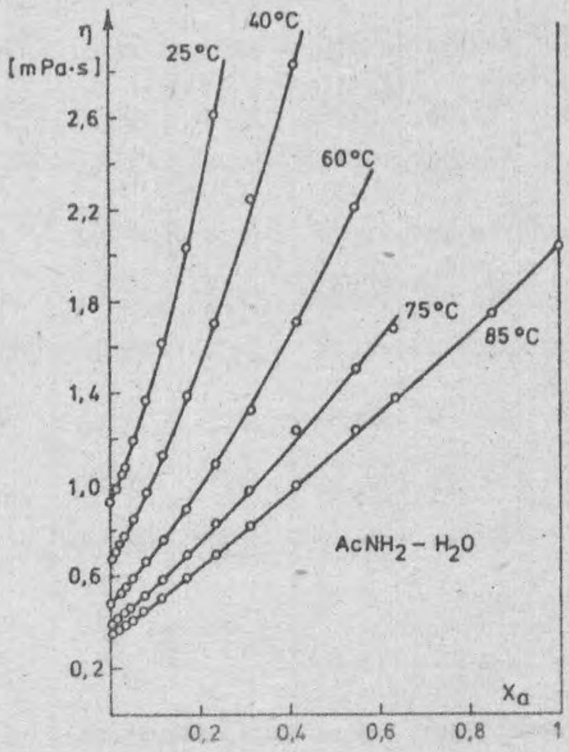

Fig. 1. Dependence of viscosity of aqueous acetamide solutions vs. composition of mixture

seen that the effect of temperature on the viscosity of investigated solutions increases with the growth of acetamide contents in water. It is connected with the fact that the viscosity of pure acetamide decreases with the growth of temperature much quicker than viscosity of water. The occurance of hydrogen bonds in mixed associates weaker than hydrogen bonds in pure water is an additional factor.

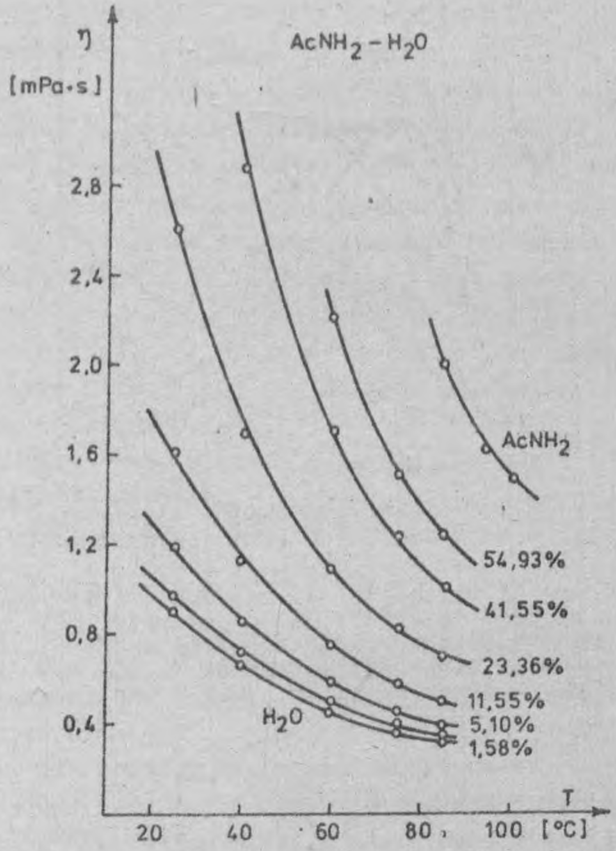

Fig. 2. Dependence of viscosity of aqueous acetamide solutions vs. temperature

In order to compare acetamide with other amides the course of relation between viscosities of water-amide mixtures and the mixed solvents composition is presented on Fig. 3.

As it is seen from the Fig. 3 in case of simple amides (F and $AcNH_2$) monotonous increase of viscosity of the mixture with the growth of amide contents can be observed.

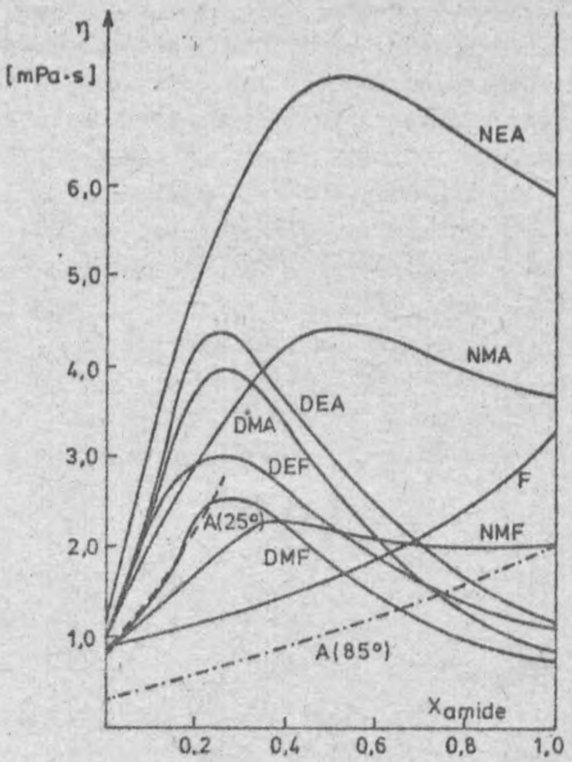

Fig. 3. Dependence of viscosity of aqueous amides solutions vs. composition of mixture at 25°C: A - acetamide, F - formamide, NMF-N-methylformamide, DMF-N,N-dimethylformamide, DEF-N,N-diethylformamide, DMA-N,N-dimethylacetamide, DEA-N,N-diethylacetamide, NMA-N-methylacetamide, NEA-N-ethylacetamide

Viscosity of water-formamide mixed solvent is smaller than viscosity of aqueous acetamide solution at the temperature 25°C. It is probably connected with greater volume of acetamide molecule in comparison with formamide molecule. A greater number of spacial hydrogen bonds in pure acetamide can also be the additional factor. Viscosity of pure amides N,N-disubstituted is much lower than that of monosubstituted (Fig. 3). It probably follows from the fact that in monosubstituted amides intermolecular hydrogen bonding occurs (chain associates) while in N,N-disubstituted amides it does not.

In case of system of N-monosubstituted amides with water the occurance of small maximum on the curve $\eta = f(x)$ of the viscosity of solution near a mole ratio 1:1 can be observed, while in aqueous solutions of N,N-disubstituted amides a pronounced maximum of viscosity of the mixture in mole relation of components 3:1 occurs. The presence of viscosity maximum of aqueous solutions of N-mono- and N,N-disubstituted amides can be explained by formation of mixed associates with precisely determined composition [3, 4] or by greater density of hydrogen bonds [19].

The lack of extremum on curve $\eta = f(x)$ of water-formamide systems substanciates probably the labile structure of the above mentioned mixtures [9, 10]. According to Nomoto and Endo [20] in F-H_2O system hydrates of clathrate type occur, in which amide molecules are built in water structure. It can be supposed, that a similar phenomenon occurs in case of water-acetamide mixtures. The above statement is in agreement with the results of measurements of dielectric permittivity of aqueous acetamide mixtures [21-23]. Gonczarov et al. [23] suggest that acetamide molecule can built in water structure forming hydrogen bonds with water molecules. These bonds are slightly weaker than hydrogen bonds in pure water.

Using the data from Table 2 the temperature coefficients $\Delta\eta_r/\Delta T$ of aqueous acetamide solutions were calculated (Table 5).

Table 5

The values of temperature coefficient $\Delta\eta_r/\Delta T$ of aqueous acetamide solutions

X	25-40°C	40-60°C	60-75°C	75-85°C
0.05	-0.002	-0.002	-0.002	-0.002
0.10	-0.006	-0.005	-0.004	-0.003
0.15	-0.010	-0.009	-0.007	-0.005
0.20	-0.017	-0.012	-0.010	-0.009
0.30	-	-0.029	-0.019	-0.012
0.40	-	-0.032	-0.025	-0.022
0.50	-	-	-0.044	-0.025
0.60	-	-	-	-0.029

Table 6

The coefficient $\Delta\eta_r/\Delta T$ of some nonelectrolyte solutions in water

	Formamide [19]	Acetamide	Urea [24]	Thiourea [24]	Ethyl-urea [24]	1,3-diethyl-urea [24]	N,N-Dimethylformamide [19]
$\Delta\eta_r/\Delta T$	+	-	+	+	-	-	-

For the sake of comparison the sign of coefficient $\Delta\eta_r/\Delta T$ of some nonelectrolyte solutions in water was given in Table 6.

From the data in Table 6 it follows that temperature coefficient $\Delta\eta_r/\Delta T$ is positive in case of aqueous solutions of formamide, urea and thiourea and negative for acetamide, DMF and ethyl-urea derivative solutions. If we conclude in the same way as in case of electrolyte solutions, we can suppose that DMF, ethyl - and diethylurea order water structure, while formamide, urea and thiourea have breaking effect.

The values of B coefficient of equation (1) (Table 3) of acetamide in water are positive and they decrease with the temperature growth. Thus, $\Delta B/\Delta T$ coefficient is negative, alike $\Delta\eta_r/\Delta T$. As it is seen from Table 7 the values of B coefficient of amides increase with the growth of ammount of hydrophobic methyl groups, which is connected with the growth of volume of their molecules and probably with the growth of interactions between amide and water (hydrophobic hydration). Similar changes can be observed in case of C coefficient of equation (1) (Table 7) relating to interactions among dissolved amide molecules. The decrease of value of B coefficient of acetamide in water with temperature growth is probably caused by smaller contribution of hydrophobic hydration.

From the works of Good [25] and Nightingale [26] it follows that in case of water structure ordering substances both enthalpy and entropy of activation for fluid flow grow with the increase of solution concentration. The growth of temperature of the solution causes the decrease of values of these functions, because the structure of solution is more and more disturbed by thermal motions of molecules.

Table 7

The values of B and C coefficients (equation 1) of amides in water at 25°C

Amides	B	C
Formamide	0.019	-0.001
Acetamide	0.111	-0.0003
Propionamide	0.188	0.004
n-Butyramide	0.264	0.013
N,N-Dimethylformamide	0.171	0.001
N,N-Dimethylacetamide	0.267	0.007

As it is seen from Table 4 in case of aqueous acetamide solutions both enthalpy and entropy of activation for fluid flow grow with the increase of acetamide concentration in water. From this fact it follows that viscous flow of aqueous acetamide solution deserves more energy in comparison to water. It seems probable that it is connected with greater packing of molecules in water-$AcNH_2$ system than in pure water. Intermolecular distances grow with the increase of temperature, which fascilitates the viscous flow of the solution. Enthalpy and entropy of activation for fluid flow of the discussed system decrease and the effect of the solution concentration on their values also decreases.

Alike in water-acetamide system enthalpy of activation for fluid flow of water-DMF system grows within the range 0 ~ 20 mole % of DMF, while in case of aqueous formamide solutions the discussed function decreases within the range 0 ~ 30 mole % of formamide (Fig. 4). From the comparison of the discussed amides it can be supposed that formamide breaks water structure, DMF orders it forming mixed associates of precisely determined composition while acetamide forms network of hydrogen bonds with water molecules, slightly disturbing primary water structure.

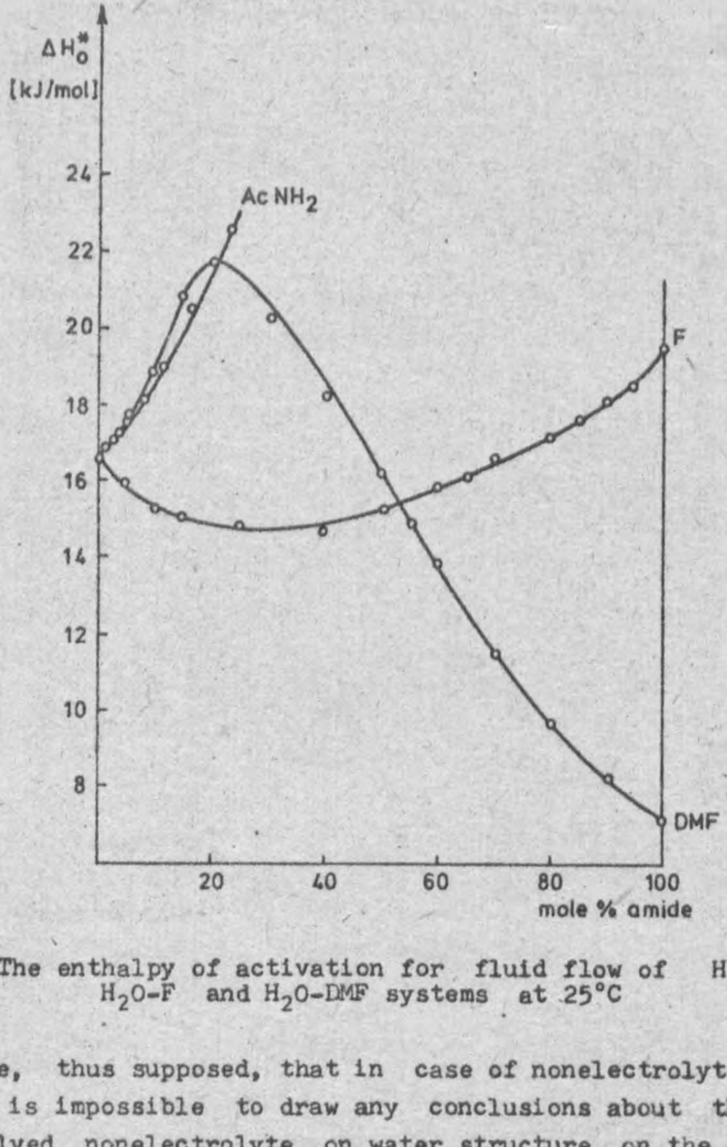

Fig. 4. The enthalpy of activation for fluid flow of H_2O-$AcNH_2$, H_2O-F and H_2O-DMF systems at 25°C

It can be, thus supposed, that in case of nonelectrolyte solutions it is impossible to draw any conclusions about the effect of dissolved nonelectrolyte on water structure on the base of the sign of temperature coefficients $\Delta B/\Delta T$ or $\Delta\eta_r/\Delta T$. Different signs of these coefficients of the discussed water-formamide, water-acetamide and water-DMF systems substantiate only the different structure of aqueous amide solutions.

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BADANIA WISKOZYMETRYCZNE UKŁADU WODA-ACETAMID W ZAKRESIE TEMPERATURY 25-80°C

Zmierzono lepkość mieszanin woda-acetamid w całym zakresie mieszalności w temperaturze 25°, 40°, 60°, 75°, 85°C. Obliczono lepkość względną, współczynnik temperaturowy $\Delta\eta_r/\Delta T$ oraz funkcje termodynamiczne aktywacji lepkiego przepływu. Przedyskutowano wpływ rozpuszczonego acetamidu na strukturę wody.

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ВИССКОЗИМЕТРИЧЕСКИЕ ИССЛЕДОВАНИЯ СИСТЕМЫ ВОДА-АЦЕТАМИД В ИНТЕРВАЛЕ ТЕМПЕРАТУРЫ 25-85°С

Определена вязкость системы вода-ацетамид в интервале температуры 25-85°С. Рассчитано относительную вязкость, температурный коэффициент $\Delta\eta_r/\Delta T$ и термодинамические функции активации вязкого течения. Анализ полученных данных в зависимости от концентрации и температуры позволил сделать вывод о влиянии ацетамида на структуру воды.