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
FOLIA CHIMICA 2, 1983

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DENSIMETRIC INVESTIGATIONS OF THE TERNARY SYSTEM WATER-ACETAMIDE-NaI WITHIN THE TEMPERATURE RANGE 25-85°C

The density of NaI solutions in water-acetamide mixed solvents has been determined. The partial molal volume Φ_v^o of NaI and volume expansibility coefficient (α) has been calculated. The dependence of Φ_v^o and α coefficient of investigated solutions on the concentrations and temperature has been discussed. The conclusions about the effect of NaI and acetamide on the structure of investigated systems have been drawn.

One of the thermodynamic quantities which is used to analyse interactions among the components of a solution is the partial molal volume. The analysis of the partial molal volume of the electrolyte as a function of the concentration, temperature and composition of mixed solvent enables to draw some conclusions concerning the interactions between the solute and the solvent [1-9].

In infinitely diluted solutions, the interactions between ions and molecules of the solvent are not disturbed by the electrostatic interactions among the ions. Consequently, the partial molal volume of the electrolyte in the infinitely diluted solution ($\bar{V}_2^o$) can be very useful for the examination of the ion-solvent interactions, especially since it can be obtained relatively easy from the measurements of the density of the respective solutions.

Calorimetric [10], densimetric [11] and viscosimetric [12] investigations of the system water-acetamide have shown that the acetamide molecules can form three-dimensional structure, in which the molecules of water and acetamide are probably connected by means of hydrogen bonds. For the sake to obtain further conclusions about the water-acetamide mixed solvents measurements of the density of the NaI solutions in the discussed solvents within the temperature range 25-85°C were carried out. As we know, the melting point of acetamide is 81-82°C [13, 14] so at 85°C investigations of the whole range of miscibility could be carried out whereas at lower temperature, the range of the examinations was limited by the solubility of the solid acetamide in water.

EXPERIMENTAL

Water-acetamide mixed solvents were prepared from twice distilled water and acetamide p. a. produced by Xenon-Łódź. The method of purification of acetamide and NaI was described earlier [15]. The density of investigated solutions were carried out with the float magnetic densitometer which was built in our laboratory. The method of measurements of density was described earlier [11]. The density of the solution was calculated from the following formula:

$$d = \frac{W + w + fi}{V + w/d_{Pt}} \tag{1}$$

where:

W - the weight of the float;

w - the weight of the platinum rings on the float;

f - the solenoid constant;

i - current intensity in the measuring solenoid at the moment of departure of the float from the bottom;

V - the volume of the float;

d_{Pt} - the density of platinum at the temperature of the measurement.

The accuracy of the density measurements was $1 - 2 \cdot 10^{-5}$ g/cm^3.

RESULTS AND DISCUSSION

The results of the measurements of the density of the solutions of NaI in water-acetamide mixed solvents at the temperatures 25°, 40°, 60°, 75° and 85°C are presented in tab. 1-5.

The values of density of the investigated solutions were used to calculate the apparent molal volume of NaI in water-acetamide solvents. The apparent molal volume of the electrolyte was calculated from the formula

$$\Phi_v = \frac{1000(d_o - d)}{mdd_o} + \frac{M}{d} \tag{2}$$

where:

d - the density of the solution;
d_o - the density of the solvent;
m - the concentration of the solution;
M - the molecular weight of the electrolyte.

Table 1

Density and Φ_v NaI in water-acetamide solutions at 25°C

1.58 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.00022	-
0.0175	1.00221	36.1±0.7
0.0389	1.00464	36.1±0.5
0.0647	1.00757	36.1±0.3
0.1060	1.01223	36.2±0.2
0.1566	1.01792	36.3±0.2
0.2159	1.02456	36.3±0.1
0.2731	1.03089	36.5±0.1
0.3562	1.04006	36.6±0.1
0.4207	1.04712	36.7±0.1
0.5088	1.05676	36.7±0.1
0.6156	1.06834	36.8±0.1
0.8309	1.09100	37.3±0.1

5.10 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.00695	-
0.0104	1.00813	37.4±0.7
0.0250	1.00978	37.2±0.6
0.0364	1.01106	37.2±0.5
0.0631	1.01408	37.2±0.3
0.0896	1.01705	37.3±0.3
0.1288	1.02143	37.5±0.2
0.1625	1.02518	37.6±0.2
0.2357	1.03330	37.7±0.1
0.3159	1.04208	37.9±0.1
0.3774	1.04874	38.1±0.1
0.5364	1.06592	38.2±0.1
0.7268	1.08562	39.1±0.1

Table 1 (contd.)

11.55 mol. % $AcNH_2$

m NaI [mol/kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.01715	–
0.0080	1.01804	39.6±0.9
0.0293	1.02041	39.6±0.6
0.0502	1.02273	39.7±0.4
0.0835	1.02641	39.8±0.3
0.1072	1.02903	39.8±0.2
0.1347	1.03206	39.8±0.2
0.1910	1.03822	39.9±0.1
0.2441	1.04398	40.1±0.1
0.3507	1.05549	40.2±0.1
0.4420	1.06538	40.0±0.1
0.5751	1.07960	40.0±0.1
0.7283	1.09637	39.2±0.1

23.36 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.03024	–
0.0257	1.03305	42.6±0.6
0.0354	1.03410	42.5±0.5
0.0424	1.03486	42.6±0.4
0.0768	1.03860	42.8±0.3
0.1398	1.04532	43.3±0.2
0.1660	1.04812	43.3±0.2
0.1907	1.05075	43.3±0.1
0.2610	1.05814	43.6±0.1
0.3100	1.06335	43.5±0.1
0.3752	1.07011	43.7±0.1
0.4374	1.07658	43.7±0.1
0.5638	1.08978	43.5±0.1
0.6010	1.09392	43.0±0.1

Table 2

Density and Φ_v NaI in water-acetamide solutions at 40°C

1.58 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99505	–
0.0310	0.99852	37.6±0.5
0.0476	1.00036	37.7±0.4
0.0767	1.00360	37.7±0.3
0.1048	1.00672	37.8±0.2
0.1487	1.01158	37.8±0.2
0.1801	1.01504	37.8±0.2
0.2503	1.02272	38.0±0.1
0.3127	1.02955	37.9±0.1
0.4012	1.03911	38.1±0.1
0.4978	1.04951	38.1±0.1
0.6306	1.06358	38.3±0.1
0.7726	1.07853	38.3±0.1

5.10 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.00081	–
0.0104	1.00197	38.8±0.7
0.0364	1.00485	38.8±0.5
0.0651	1.00803	38.8±0.3
0.0896	1.01073	38.8±0.3
0.1312	1.01529	38.8±0.2
0.1625	1.01875	38.9±0.2
0.2357	1.02671	39.1±0.1
0.3051	1.03428	39.0±0.1
0.3774	1.04192	39.4±0.1
0.4977	1.05474	39.5±0.1
0.7268	1.07842	40.1±0.1

Table 2 (contd.)

11.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.00934	-
0.0080	1.01021	41.5±0.9
0.0196	1.01149	40.7±0.7
0.0293	1.01255	40.7±0.5
0.0885	1.01902	40.7±0.3
0.1046	1.02078	40.7±0.2
0.1251	1.02302	40.6±0.2
0.1985	1.03098	40.6±0.1
0.2441	1.03592	40.6±0.1
0.3508	1.04739	40.5±0.1
0.4420	1.05715	40.4±0.1
0.5747	1.07128	40.3±0.1
0.7283	1.08766	39.9±0.1

23.36 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.01995	-
0.0257	1.02272	43.6±0.7
0.0424	1.02450	43.6±0.5
0.0768	1.02820	43.4±0.3
0.1062	1.03134	43.4±0.2
0.1398	1.03495	43.2±0.2
0.1907	1.04039	43.1±0.2
0.2466	1.04635	43.0±0.1
0.3100	1.05303	43.0±0.1
0.4011	1.06268	42.8±0.1
0.5073	1.07366	42.9±0.1
0.5638	1.07966	42.7±0.1

41.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.02704	-
0.0129	1.02841	45.2±0.7
0.0272	1.02993	45.1±0.6
0.0612	1.03357	44.5±0.4
0.1010	1.03784	44.1±0.3
0.1506	1.04319	43.6±0.2
0.1932	1.04782	43.1±0.2
0.2471	1.05365	42.8±0.1
0.3152	1.06104	42.3±0.1
0.3833	1.06857	41.6±0.1
0.5004	1.08108	41.4±0.1
0.6294	1.09393	42.5±0.1

Table 3

Density and Φ_v NaI in water-acetamide solutions at 60°C

1.58 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.98558	-
0.0203	0.98782	38.4±0.7
0.0310	0.98900	38.6±0.6
0.0476	0.99081	38.7±0.5
0.0767	0.99400	38.7±0.3
0.1428	1.00120	38.9±0.2
0.1801	1.00525	38.9±0.2
0.2898	1.01703	39.1±0.1
0.3126	1.01949	39.1±0.1
0.4978	1.03917	39.2±0.1
0.6246	1.05242	39.3±0.1
0.7726	1.06798	39.1±0.1

5.10 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.99026	-
0.0104	0.99139	40.0±0.8
0.0189	0.99232	40.1±0.7
0.0364	0.99422	40.2±0.6
0.0896	0.99998	40.3±0.3
0.1021	1.00132	40.5±0.2
0.1625	1.00783	40.4±0.2
0.2357	1.01565	40.5±0.1
0.2632	1.01852	40.7±0.1
0.3774	1.03057	40.8±0.1
0.4035	1.03329	40.9±0.1
0.5954	1.05313	41.1±0.1
0.7268	1.06648	41.3±0.1

11.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.99697	-
0.0080	0.99783	41.9±0.9
0.0293	1.00013	41.6±0.7
0.0411	1.00142	41.4±0.5
0.0835	1.00600	41.2±0.3
0.1251	1.01048	41.2±0.2
0.1577	1.01402	40.9±0.2
0.2441	1.02335	40.5±0.1
0.3616	1.03598	40.3±0.1
0.4420	1.04462	40.0±0.1
0.5320	1.05422	39.8±0.1
0.7283	1.07550	38.8±0.1

23.36 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	1.00570	-
0.0257	1.00842	44.5±0.7
0.0354	1.00944	44.4±0.6
0.0424	1.01018	44.3±0.5
0.0768	1.01383	44.1±0.3
0.1398	1.02052	43.6±0.2
0.1660	1.02329	43.5±0.2
0.1907	1.02590	43.5±0.2
0.3100	1.03853	43.0±0.1
0.4374	1.05192	42.6±0.1
0.6010	1.06929	41.8±0.1

Table 3 (contd.)

41.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	1.01163	-
0.0129	1.01297	46.6±0.8
0.0390	1.01570	46.0±0.6
0.0612	1.01803	45.7±0.4
0.1010	1.02221	45.4±0.2
0.1506	1.02743	45.0±0.2
0.1932	1.03197	44.4±0.1
0.2312	1.03594	44.4±0.1
0.3833	1.05199	43.6±0.1
0.5052	1.06482	43.1±0.1
0.6294	1.07785	42.6±0.1
0.7284	1.08791	42.7±0.1

Table 4

Density and Φ_v NaI water-acetamide solutions at 75°C

1.58 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.97698	-
0.0203	0.97919	39.3±0.7
0.0310	0.98036	39.2±0.6
0.0476	0.98216	39.1±0.5
0.0767	0.98532	39.1±0.3
0.1428	0.99248	39.1±0.2
0.1801	0.99649	39.2±0.2
0.2898	1.00827	39.1±0.1
0.3010	1.00943	39.0±0.1
0.4978	1.03044	38.8±0.1
0.6246	1.04401	38.4±0.1
0.7726	1.06002	37.7±0.1

5.10 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.98102	-
0.0104	0.98215	40.3±0.8
0.0189	0.98306	40.6±0.7
0.0364	0.98495	40.4±0.5
0.0896	0.99065	40.3±0.3
0.1021	0.99205	40.1±0.2
0.1625	0.99855	40.0±0.2
0.2357	1.00640	[illegible].9±0.1
0.2632	1.00936	39.8±0.1
0.3774	1.02150	39.7±0.1
0.4035	1.02428	39.7±0.1
0.5954	1.04468	39.2±0.1
0.7268	1.05869	38.7±0.1

Table 4 (contd.)

11.55 mol. % $AcNH_2$

m_{NaI} [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.98726	-
0.0080	0.98811	42.5±0.9
0.0293	0.99039	42.0±0.6
0.0412	0.99167	41.7±0.5
0.0835	0.99622	41.3±0.3
0.1251	1.00071	41.0±0.2
0.1577	1.00420	40.9±0.2
0.2441	1.01348	40.6±0.1
0.3616	1.02607	40.2±0.1
0.4420	1.03472	39.8±0.1
0.5320	1.04449	39.2±0.1
0.7283	1.06581	38.2±0.1

23.36 mol. % $AcNH_2$

m_{NaI} [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99431	-
0.0258	0.99701	44.6±0.7
0.0354	0.99802	44.5±0.6
0.0424	0.99876	44.4±0.5
0.0768	1.00239	44.1±0.4
0.1398	1.00905	43.5±0.2
0.1660	1.01184	43.2±0.2
0.1907	1.01443	43.2±0.1
0.3100	1.02708	42.5±0.1
0.4374	1.04051	42.0±0.1
0.6010	1.05814	40.7±0.1

41.55 mol. % $AcNH_2$

m_{NaI} [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99960	-
0.0129	1.00092	47.5±0.8
0.0390	1.00363	46.4±0.6
0.0612	1.00594	46.0±0.4
0.1010	1.01008	45.6±0.3
0.1506	1.01529	45.0±0.2
0.1932	1.01972	44.8±0.2
0.2312	1.02376	44.3±0.1
0.3833	1.03963	43.7±0.1
0.5052	1.05250	42.9±0.1
0.6294	1.06558	42.3±0.1
0.7284	1.07563	42.3±0.1

Table 5

Density and Φ_v NaI water-acetamide solutions at 85°C

1.58 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.97055	-
0.0203	0.97275	39.3±0.6
0.0310	0.97391	39.4±0.6
0.0476	0.97570	39.3±0.5
0.0767	0.97886	39.1±0.3
0.1428	0.98601	38.9±0.2
0.1801	0.99004	38.8±0.2
0.2898	1.00183	38.6±0.1
0.3010	1.00304	38.6±0.1
0.4978	1.02408	38.2±0.1
0.6246	1.03771	37.7±0.1
0.7726	1.05356	37.2±0.1

5.10 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.97422	-
0.0104	0.97534	40.8±0.8
0.0364	0.97811	41.0±0.6
0.0896	0.98381	40.7±0.4
0.1021	0.98516	40.5±0.3
0.1625	0.99163	40.3±0.2
0.2357	0.99942	40.2±0.1
0.2632	1.00237	40.1±0.1
0.3774	1.01440	40.0±0.1
0.4035	1.01722	39.8±0.1
0.5954	1.03757	39.2±0.1
0.7268	1.05130	39.1±0.1

11.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.97972	-
0.0080	0.98057	42.0±0.9
0.0293	0.98284	41.8±0.6
0.0412	0.98411	41.7±0.5
0.0835	0.98863	41.4±0.3
0.1251	0.99309	41.1±0.2
0.1577	0.99661	40.7±0.2
0.2441	1.00591	40.2±0.1
0.3616	1.01848	39.8±0.1
0.4420	1.02707	39.5±0.1
0.5320	1.03664	39.3±0.1
0.7283	1.05773	38.4±0.1

23.36 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm³]	Φ_v [cm³/mol.]
0.0000	0.98616	-
0.0258	0.98884	44.9±0.7
0.0354	0.98985	44.6±0.6
0.0424	0.99058	44.6±0.5
0.0768	0.99420	44.1±0.4
0.1398	1.00086	43.3±0.3
0.1660	1.00361	43.2±0.2
0.1907	1.00625	42.8±0.2
0.3100	1.01890	42.0±0.1
0.4374	1.03228	41.7±0.1
0.6010	1.05002	40.2±0.1

Table 5 (contd.)

41.55 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99070	-
0.0129	0.99202	47.0±0.8
0.0390	0.99473	45.8±0.6
0.0612	0.99706	45.1±0.4
0.1010	1.00126	44.3±0.3
0.1506	1.00654	43.5±0.2
0.1932	1.01107	43.0±0.2
0.2312	1.01515	42.5±0.1
0.3833	1.03152	41.1±0.1
0.5052	1.04471	40.2±0.1
0.6294	1.05812	39.5±0.1
0.7284	1.06906	38.7±0.1

63.33 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99224	-
0.0251	0.99486	44.9±0.7
0.0574	0.99826	44.3±0.5
0.0844	1.00111	43.9±0.4
0.1238	1.00526	43.7±0.3
0.1637	1.00948	43.4±0.2
0.2029	1.01360	43.2±0.1
0.3127	1.02518	42.7±0.1
0.4552	1.04015	42.2±0.1
0.6203	1.05771	41.2±0.1

85.27 mol. % $AcNH_2$

m NaI [mol./kg]	d [g/cm^3]	Φ_v [cm^3/mol.]
0.0000	0.99190	-
0.0248	0.99458	41.2±0.7
0.0638	0.99876	41.6±0.5
0.1016	1.00276	42.0±0.3
0.1502	1.00786	42.5±0.2
0.1969	1.01272	42.8±0.2
0.2427	1.01746	43.0±0.1
0.3013	1.02340	43.5±0.1
0.3530	1.02870	43.6±0.1
0.4952	1.04335	43.3±0.1
0.6638	1.06107	42.3±0.1

The values Φ_v calculated for all the investigated solutions are given in tab. 1-5. Uncertainties are estimates.

It is known from literature [16, 17] that in the case of diluted solutions Φ_v depends linearly on $\sqrt{c}$ and satisfies Masson's equation:

$$\Phi_v = \Phi_v^o + A_v\sqrt{c}$$

The values A_v and Φ_v^o was calculated by Gauss-Newton's method using nonlinear estimation proposed by Swerling [18]. The values of A_v, Φ_v^o, average deviation (AVD), absolute average deviation (AAD) and standard deviation (STD) for NaI in water--acetamide solvents have been collected in tab. 6.

On fig. 1 and 2 dependence of the partial molal valume of NaI in water-acetamide solvents on the composition of the solvent and on temperature of the solution is presented.

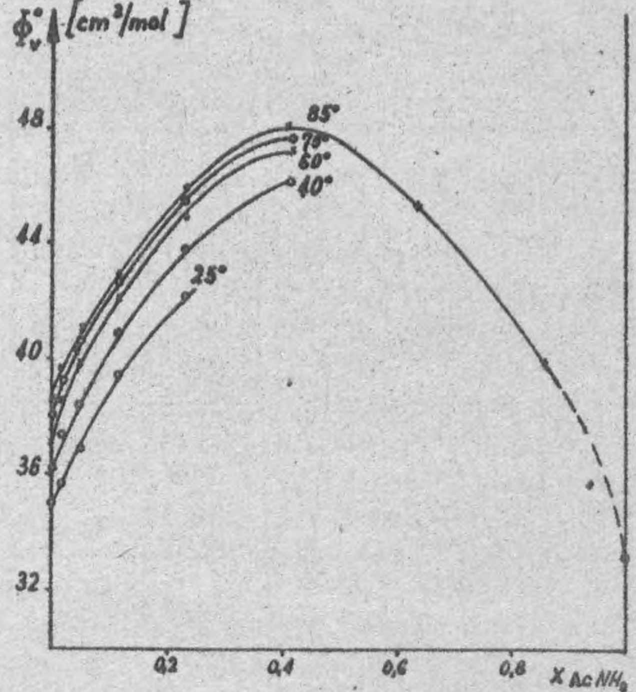


Fig. 1. Partial molal volume of NaI in water-acetamide solutions as a function of x_{AcNH_2}

Table 6

Partial molal volume of NaI in water-acetamide solutions $[cm^3/mol.]$

Temperature °C	Mol. % $AcNH_2$	A_v	Φ_v^o	AVD	AAD	STD
25	0.00 [19]	-	35.0	-	-	-
	1.58	1.107535	35.94	0.00047	0.074	0.25
	5.10	1.606257	36.95	0.00087	0.097	0.32
	11.55	1.049767	39.48	0.00024	0.050	0.17
	23.36	2.776644	42.09	0.00026	0.081	0.27
40	0.00 [19]	-	36.1	-	-	-
	1.58	0.900160	37.46	0.00013	0.029	0.10
	5.10	1.126276	38.55	0.00087	0.115	0.38
	11.55	-0.463497	40.82	0.00009	0.029	0.09
	23.36	-1.402206	43.78	0.00027	0.078	0.26
	41.55	-6.997564	46.22	0.00088	0.105	0.35
60	0.00 [19]	-	37.2	-	-	-
	1.58	1.275229	38.36	0.00018	0.051	0.16
	5.10	1.468765	39.90	0.00026	0.053	0.18
	11.55	-3.198569	42.15	0.00032	0.055	0.18
	23.36	-4.109054	45.19	0.00051	0.068	0.23
	41.55	-5.865616	47.20	0.00037	0.049	0.16
75	0.00 [19]	-	38.0	-	-	-
	1.58	-0.789445	39.37	0.00014	0.089	0.30
	5.10	-1.509170	40.63	0.00032	0.053	0.18
	11.55	-4.632418	42.77	0.00105	0.108	0.36
	23.36	-5.912258	45.64	0.00148	0.114	0.38
	41.55	-7.123480	47.93	0.00146	0.136	0.45
85	0.00 [19]	-	38.5	-	-	-
	1.58	-2.366759	39.79	0.00056	0.079	0.26
	5.10	-2.401355	41.31	0.00093	0.113	0.38
	11.55	-4.639369	42.61	0.00019	0.080	0.27
	23.36	-7.221746	46.04	0.00092	0.105	0.35
	41.55	-10.837112	47.89	0.00122	0.137	0.46
	63.33	-5.473913	45.66	0.00130	0.103	0.33
	85.27	2.915267	41.18	0.01417	0.443	1.48
	100.0 [20]	-	33.0	-	-	-

Table 7

Partial molal volume of some elektrolytes in several solvents at 25°C [cm³/mol.]

pure solvents

Electrolyte	Water [19] D = 78.5	Methanol D = 32 [24]	Ethylene glycol D = 37.7 [30]	Formamide D = 111 [31]	DMF [33] D = 36.7 [31]	NMA 35° D = 179 [34]
NaCl	16.62	-3.3 [25]	-	21.1 [32]	-	26.0 [2]
NaBr	23.50	5.1 [26]	27.3 [27]	28.0 [32]	12.05	32.6 [2]
NaI	35.01	12.8 [27]	38.4 [27]	39.85 [32]	21.00	42.0 [2]
KI	45.24	21.5 [28]	47.2 [27]	50.75 [32]	35.60	45.9 [35]
$NaNO_3$	27.79	-	-	33.85 [32]	24.05	35.0 [2]
NH_4Br	42.57	20.8 [29]	-	44.05 [32]	32.20	44.7 [2]

mixed solvents $CH_3OH - H_2O$ [36]

Electrolyte	9.47 wt% D = 74.36	19.84 wt% D = 69.28	34.48 wt% D = 62.19	41.20 wt% D = 58.61
NH_4Cl	34.75	34.35	34.00	33.65
NH_4Br	42.95	42.75	42.35	42.00
NH_4I	96.95	96.75	96.60	96.50

As we can see from fig. 1, at 85°C the partial molal volume of NaI in the investigated solutions increases with the growth of acetamide concentration in the mixed solvent up to 40 mol. % $AcNH_2$ and then decreases to reach the value Φ_v^o NaI in pure acetamide.

At lower temperatures investigations in the full range were imposible because of the limited solublity of solid acetamide in water, however from fig. 1 we can see that the course of the discussed dependence at lower temperatures is similar.

The dielectric constant as a function of the composition of the mixture water-acetamide changes analogically, reaching the maximum value of dielectric constant in the solution containing about 40 mol. % acetamide [21]. The authors of the paper [21] assume that the acetamide molecules are built-in via H. Bonding into the water structure and vice versa. The increase in the dielectric constant should be the result of a more parallel ordering of the individual dipoles in the mixtures, resulting from the planar structure of the amide molecules.

It is known that the partial molal volume of the electrolyte in the infinitely diluted solution is a sum of the own volume of the electrolyte and the changes of the volume taking place in the solvent as a result of the presence of ions. According to Gurney's [22] and Frank-Wen's [23] multilayer model of solvation, the partial molal volume of the ion in the infinitely diluted solution $\bar{V}^o_{ion}$ can be written as the sum of the following components:

$$\bar{V}^o_{ion} = \bar{V}^o_{cryst} + \bar{V}^o_{elect} + \bar{V}^o_{disord} + \bar{V}^o_{caged}$$

where:

$\bar{V}^o_{cryst}$ - the partial molal volume of the ion in a crystal;

$\bar{V}^o_{elect}$ - the change in the partial molal volume caused by the electrostriction of the solvent;

$\bar{V}^o_{disord}$ - the change in the partial molal volume caused by the disturbance of the structure of the solvent;

$\bar{V}^o_{caged}$ - the change in the partial molal volume caused by the ordering of the structure of the solvent.

In the case of NaI solutions in water-acetamide solvents the analogical course of the functions $\Phi_v{}^o = f(x)$ and $D = f(x)$ (D - dielectric constant) may indicate that among the components of the partial molal volume (which have been listed above) probably $\bar{V}^o_{elect}$ is the most important in this case. Changes in the structure of the mixed solvent caused by the electrolyte (the components $\bar{V}^o_{disord}$ and $\bar{V}^o_{caged}$) are probably small in comparison with $\bar{V}^o_{elect}$.

Figure 2 shows moreover that the course of the dependence Φ^o_v NaI on the temperature is also the same for all investigated mixed solvents and corresponds to the course of the dependence $\bar{V}^o_{elect} = f(T)$ in water solutions.

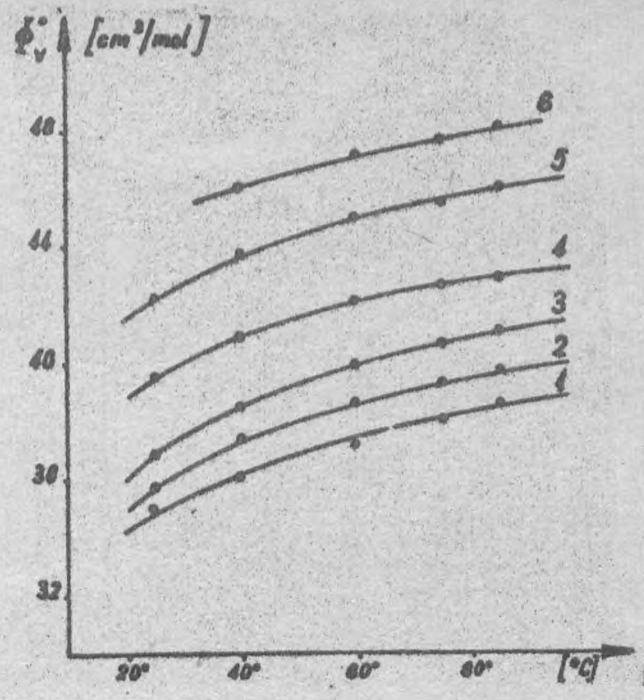
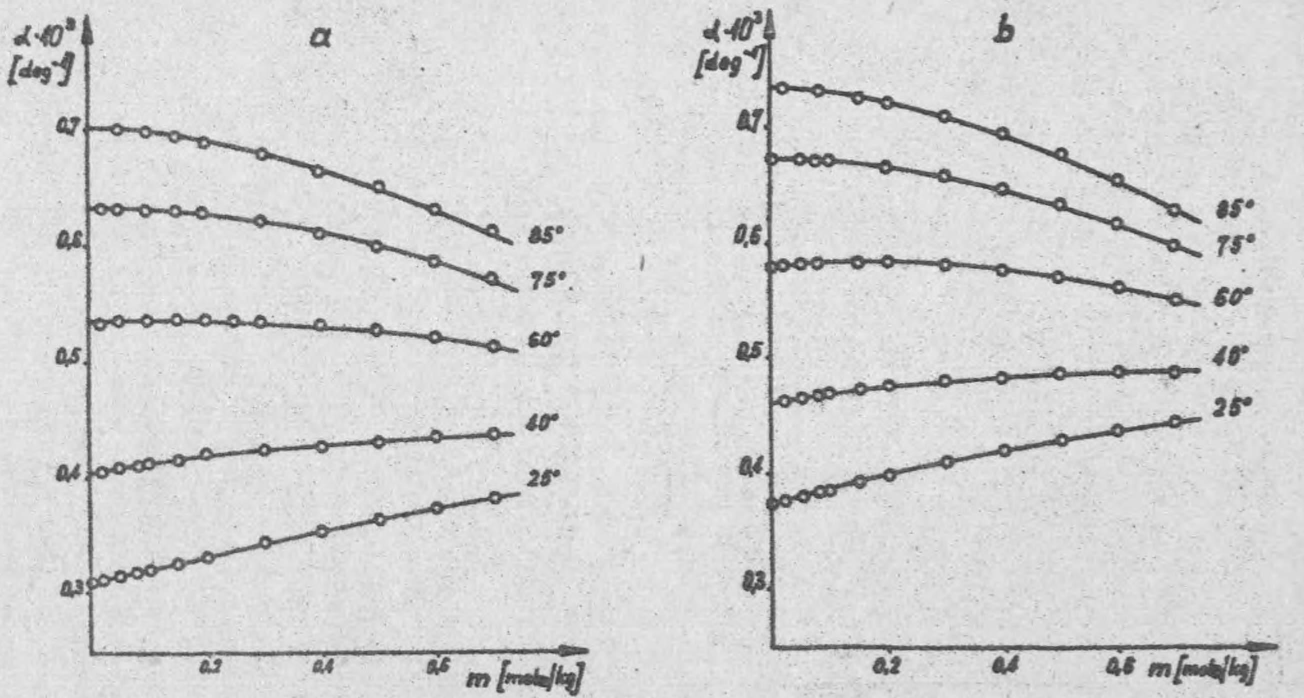


Fig. 2. Partial molal volume of NaI in water-acetamide solutions as a function of temperature. 1 - H_2O; 2 - 1.58 mol. % (5 wt %) $AcNH_2$; 3 - 5.10 mol. % (15 wt %) $AcNH_2$; 4 - 11.55 mol. % (30 wt %) $AcNH_2$; 5 - 23.36 mol. % (50 wt %) $AcNH_2$; 6 - 41.55 mol. 2 (70 wt %) $AcNH_2$

Having compared the values $\bar{V}_2^o$ of electrolytes in various solvents we infer that the partial molal volume of the electrolyte increases with the growth of the dielectric constant of the solvent, which would agree with the course of the dependence $\Phi_v^o = f(D)$ of the water-acetamide solvents investigated by us. The influence of the structure of the solvent on the value $\bar{V}_{ion}^o$ can be easily observed when we compare CH_3OH, DMF and ethylene glycol (all the solvents have a similar dielectric constant). The partial molal volume of electrolytes in ethylene glycol is considerably higher than in CH_3OH or DMF, which is connected with the strong association of ethylene glycol with the participation of the hydrogen bonds. The increase in the value Φ_v^o NaI in water-acetamide solvents caused by the growth of the contents of acetamide may be therefore also partly caus-


a
b
α·10³ [deg⁻¹]
0,7
0,6
0,5
0,4
0,3
0,2
0,4
0,6
m [mole/kg]
85°
75°
60°
40°
25°

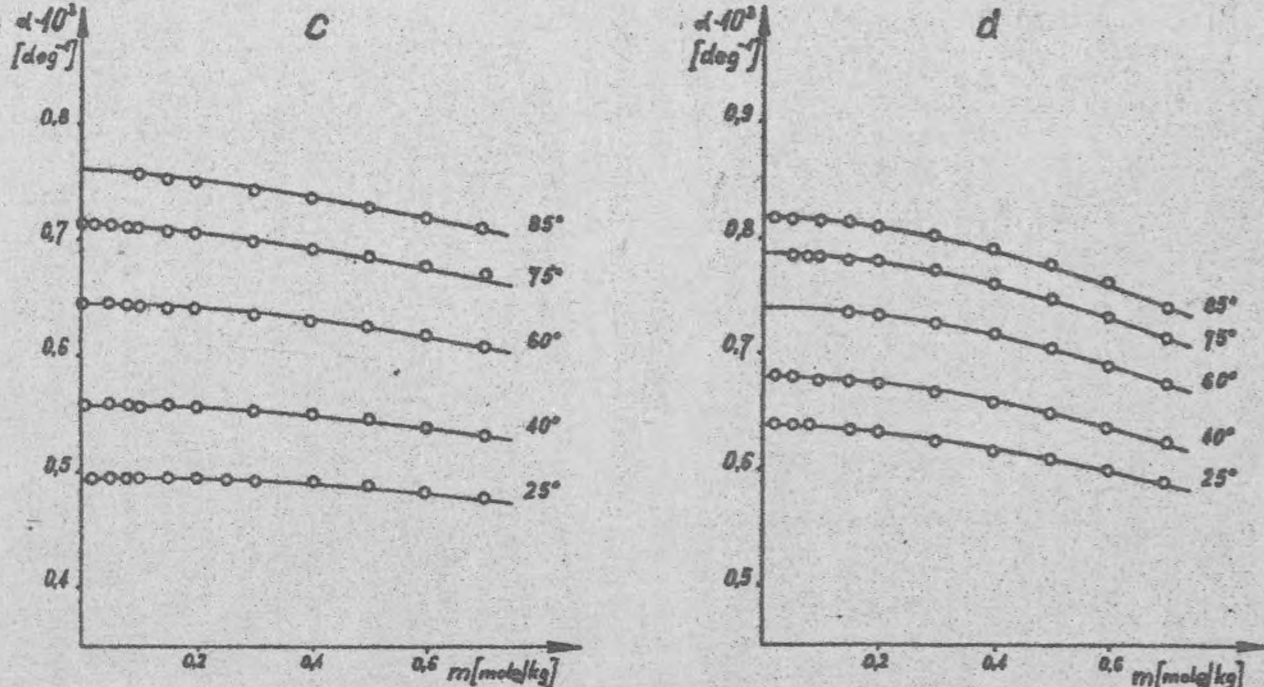


Fig. 3. The volume expansibility coefficient (α) of NaI in water-acetamide solutions. a - 1.58 mol. % (5 wt %) $AcNH_2$; b - 5.10 mol. % (15 wt %) $AcNH_2$; c - 11.55 mol. % (30 wt %) $AcNH_2$; d - 23.36 mol. % (50 wt %) $AcNH_2$

ed by the increase in number of the hydrogen bonds between water and acetamide molecules.

Some informations concerning the influence of the dissolved electrolyte on the solvent structure can be also obtained from analysis of the dependence of the volume expansibility coefficient (α) on the concentration of the solution and temperature. From the papers of K r u m g a l z [37, 38] and B a r o n [39] it follows that electrolytes ordering the structure of the solvent cause a lowering of the volume expansibility coefficient value (α), wheras electrolytes break the structure of the solvent, increase its value.

The value of the coefficient α increases with the growth of temperature, because the structure of the solution is gradually disturbed by the more intensive thermal motions of the molecules and the dependence of the discussed coefficient v. s. concentration of electrolyte decreases. There is a temperature at which the coefficient α does not depend on the concentration of the salt, so probably it is a proof of the compensation of the effect of the disordering of the solvent structure with the effect of its ordering in the process of ionic solvation. Quite obviously the temperature depends on the kind of electrolyte and solvent. The volume expansibility coefficient of the solutions of NaI in water-acetamide solvents was calculated from the formula

$$\alpha = - \frac{1}{d} \left(\frac{\partial d}{\partial T} \right)_{x,m}$$

The derivative $(\partial d/\partial T)_{x,m}$ was calculated analytically from the determined values of the coefficients of the equation $d = a + bT + cT^2$ describing the dependence of the density of the investigated solution on the temperature. The values of the coefficient α of NaI solutions are presented on fig. 3. The error of the calculations was 0.2%.

As we can see from fig. 3 the coefficient α of the investigated solutions increases with the growth of acetamide contents in the mixed solvent and the temperature of the solution. It can be also observed that the discussed coefficient α in mixed water-acetamide solvents containing 5 wt % and 15 wt %

$AcNH_2$ at lower temperatures (25°; $40^\circ C$) increases with the growth in concentration of NaI and decreases when the temperature is higher than $40^\circ C$.

In mixed solvents containing larger amounts of acetamide the coefficient α decreases with the increase of the concentration of the salt in the solution in the whole range of investigated temperature. The increase of the value of the coefficient α proves that solutions expand more than a pure solvent. It can be therefore infered that the growth of acetamide contents in a water solutions of NaI cause the increase of disordering effect of the introduced acetamide on water structure. In a similar destructive way the structure of the investigated solutions is affected by increase of temperature.

In mixed solvents containing small amounts of acetamide (5 wt % and 15 wt %) NaI initially (up to $40^\circ C$) destroys the structure of the mixed solvents (α increases), and then at higher temperatures the effect of ordering of the structure by the introduced ions caused by the solvation prevails (α decreases). In solvents containing 30 wt % of acetamide and more, NaI orders the structure of the mixed solvents in the whole examined range of temperature. The change of the influence of NaI on the mixed water-acetamide solvents is probably connected with the fact that the hydrogen bonds in mixed associates are weaker than the hydrogen bonds in water. The above conclusion is in agreement with opinion arising from the investigations of the volume expansibility of water-acetamide mixture [11] from which follow that the mixtures expand more than pure water.

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DENSYMETRYCZNE BADANIE UKŁADU TRÓJSKŁADNIKOWEGO WODA-ACETAMID-NaI W ZAKRESIE TEMPERATURY 25-85°C

Zmierzono gęstość roztworów w rozpuszczalniku mieszanym woda-acetamid w zakresie temperatury 25-85°C. Wykorzystując otrzymane dane gęstości obliczono cząstkową molową objętość Φ_v^o NaI oraz współczynnik rozszerzalności objętościowej α. Przedyskutowano zależność Φ_v^o NaI i współczynnika α badanych roztworów od stężenia elektrolitu i temperatury oraz wysnuto wnioski dotyczące wpływu NaI i acetamidu na strukturę badanych układów.

Марян Вольдан

ДЕНСИТОМЕТРИЧЕСКИЕ ИССЛЕДОВАНИЯ СИСТЕМЫ H_2O-$AcNH_2$-NaI В ИНТЕРВАЛЕ ТЕМПЕРАТУРЫ 25-85°С

Определена плотность растворов NaI в смешанным растворителе вода-ацетамид. Рассчитано парциальный мольный обьём $\bar{V}_2^o$ и коэффициент термического расширения α электролита в растворах.

Проведен анализ зависимости $\bar{V}_2^o$ и коэффицента α от концентрации и температуры. Сделано вывод о влиянии NaI и ацетамида на структуру исследованых растворов.