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Volumes and heat capacities of binary non-aqueous mixtures.
Part 1. The systems acetonitrile–formamide and acetonitrile–*N*-methylformamide

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Abstract

The density and heat capacity of the binary mixtures acetonitrile–formamide and acetonitrile–*N*-methylformamide were measured over the entire range of compositions at 283.15–328.15 K. The excess and apparent molar volumes and heat capacities of the mixtures studied were calculated. An analysis of the experimental and calculated data was carried out. Relationships between the nature of the substances, and the temperature and composition on the thermodynamic properties of acetonitrile mixtures with formamide and *N*-methylformamide are revealed.

INTRODUCTION

Polar aprotic solvents and their mixtures have been the objects of thorough investigations [1, 2]. In earlier work [3], we measured the heat capacities of the aqueous solutions of formamide (FA) and *N*-methylformamide (MFA) at 283.15–313.15 K. Using the data on the density of these mixtures [4, 5], we calculated the heat capacity and volumetric characteristics of the water–FA and water–MFA systems. We showed [3] that the aqueous solutions of formamide were characterized by negative values of excess heat capacity C_p^E and of the change in heat capacity at dissolution of amide in water $\Delta_{soln}C_p = \bar{C}_{p2}^{\ominus} - C_{p2}^{\ominus}$, where $\bar{C}_{p2}^{\ominus}$ is the partial molar heat capacity of amide at infinite dilution in water and $C_{p2}^{\ominus}$ is the molar heat capacity of pure amide, and also by the positive initial slope of the dependence $\bar{V}_2^E = f(X_2)$ [6], where $\bar{V}_2^E$ is the excess partial molar volume of amide in water; this is connected with the hydrophilic hydration of FA molecules. It was noted that the temperature

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increase resulted in the destruction of the labile structure of the mixture formed [3]. For the water–MFA system, the appearance of the non-polar group $-CH_3$ in the MFA molecule results in positive C_p^E and $\Delta_{soln}C_p$ values and a negative initial slope for the $\bar{V}_2^E = f(X_2)$ dependence; this relates to the dominating contribution from the hydrophobic hydration. In contrast with aqueous solutions of amides, polythermal investigations for their binary mixtures with non-aqueous solvents are practically non-existent. Therefore, the aim of the present paper is to investigate the influence of temperature, substance nature and composition on the volumetric and heat capacity characteristics of FA and MFA mixtures with acetonitrile. At the same time, it is interesting to conduct a comparative analysis of the behaviour of amides in non-aqueous solvent (acetonitrile) and water.

EXPERIMENTAL

An Anton Paar DMA-60 + DMA-602 apparatus was used to measure the density of solutions. The temperature in the thermostating shell of the measuring cell was kept with ±0.005 K precision. The density of the liquid mixtures studied was measured with $\pm 8 \times 10^{-6}$ g cm^{-3} precision. This includes the errors derived from the construction of the apparatus and the faults of the thermostating system. The measuring cell was calibrated every day and at each change in the working temperature. The cell was calibrated relative to twice distilled water and dried air.

An adiabatic-shell calorimeter of container type, with automatic maintenance of the abiabatic regime, was used to measure the heat capacity [7]. The calorimetric cell was calibrated using freshly prepared twice distilled deionized water, the conductivity of which did not exceed $1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The total determination error for heat capacity was ±0.05% of the value determined. The comparison between our data and those from different authors showed good agreement: at 298.15 K, C_p (J mol^{-1} K^{-1}) for FA is 107.91 ± 0.03; 107.6 [8]; for MFA, 125.15 ± 0.04; 125.1 [9].

Acetonitrile was dried twice over P_2O_5, followed each time by distillation and selection of the medium fraction. Then the dried acetonitrile was distilled with freshly tempered K_2CO_3. The FA and MFA were stored over molecular sieves 4 Å for 48 h and then distilled in vacuo (≈133 Pa), the medium fraction being selected each time (≈60% of volume), until a final product of conductivity not worse than $1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ was obtained. The water content in the pure substances obtained was controlled by Fischer's method and was $1–2 \times 10^{-2}$% for FA and MFA and 1×10^{-2}% for AN. The solutions were prepared by the weight method in a dry box immediately before the measurements.

RESULTS

Experimental data on the densities d and specific heat capacities C_p^S of the acetonitrile–formamide and acetonitrile–N-methylformamide systems at 283.15–328.15 K are given in Tables 1–4. Molar volumes V and heat capacities C_p were calculated from

$$V = (X_1M_1 + X_2M_2)/d \tag{1}$$

$$C_p = C_p^S(X_1M_1 + X_2M_2) \tag{2}$$

where X is the mole fraction and M is the molecular mass. Indices 1 and 2 refer to acetonitrile and amide, respectively.

Excess volumes V^E and heat capacities C_p^E were calculated from the

TABLE 1

Density of the AN–FA system d (g cm^{-3}) at various temperatures; X_2 is the mole fraction of FA

283.15 K		298.15 K		313.15 K		328.15 K	
X_2	d	X_2	d	X_2	d	X_2	d
0.000	0.792571	0.000	0.776618	0.000	0.760292	0.000	0.743517
0.007	0.795083	0.005	0.778455	0.004	0.761746	0.003	0.744500
0.018	0.798473	0.014	0.780984	0.018	0.765746	0.007	0.745590
0.025	0.800381	0.023	0.783877	0.032	0.770225	0.014	0.747923
0.045	0.806233	0.029	0.785502	0.065	0.780272	0.027	0.751697
0.066	0.812811	0.053	0.792840	0.177	0.815171	0.034	0.754027
0.124	0.830303	0.079	0.800555	0.285	0.850468	0.101	0.774839
0.135	0.833782	0.145	0.821192	0.350	0.872237	0.141	0.787461
0.216	0.859053	0.205	0.840065	0.475	0.915671	0.180	0.799913
0.394	0.916910	0.222	0.845361	0.601	0.961373	0.280	0.833311
0.481	0.946604	0.313	0.874849	0.635	0.973996	0.433	0.885917
0.601	0.989172	0.386	0.899512	0.783	1.030231	0.617	0.952706
0.679	1.018024	0.443	0.918862	0.880	1.068419	0.722	0.992992
0.792	1.060768	0.650	0.993141	0.948	1.095764	0.819	1.030756
0.881	1.095004	0.708	1.015058	0.966	1.103284	0.900	1.063402
0.944	1.120160	0.848	1.069025	0.977	1.107807	0.925	1.073712
0.969	1.130249	0.873	1.078820	0.989	1.112776	0.933	1.076816
0.973	1.131872	0.943	1.106822	0.992	1.114157	0.957	1.086530
0.985	1.136947	0.962	1.114447	0.995	1.115375	0.969	1.091526
0.994	1.140609	0.966	1.116355	0.998	1.116442	0.985	1.097975
0.996	1.141520	0.988	1.125294	1.000	1.117308	0.990	1.100051
0.997	1.141803	0.993	1.127299			0.994	1.101792
1.000	1.142868	0.998	1.129298			1.000	1.104231
		1.000	1.130121				

TABLE 2

Density of the AN–MFA system d (g cm^{-3}) at various temperatures; X_2 is the mole fraction of MFA

283.15 K		298.15 K		313.15 K		328.15 K	
X_2	d	X_2	d	X_2	d	X_2	d
0.000	0.792571	0.000	0.776618	0.000	0.760292	0.000	0.743517
0.003	0.793879	0.007	0.778932	0.002	0.761000	0.003	0.744529
0.011	0.796553	0.013	0.780983	0.002	0.761029	0.006	0.745469
0.018	0.798407	0.031	0.785809	0.006	0.762055	0.015	0.747891
0.047	0.806266	0.049	0.790744	0.011	0.763476	0.021	0.749705
0.062	0.810030	0.065	0.795102	0.021	0.766275	0.038	0.754430
0.136	0.829440	0.083	0.799828	0.029	0.768525	0.044	0.756036
0.234	0.853770	0.115	0.808230	0.038	0.771095	0.058	0.759786
0.324	0.875168	0.117	0.808655	0.094	0.786254	0.217	0.802158
0.456	0.905367	0.252	0.842382	0.190	0.811248	0.257	0.812420
0.552	0.926077	0.327	0.860320	0.255	0.827731	0.306	0.824563
0.608	0.937927	0.409	0.879330	0.407	0.864294	0.501	0.871190
0.662	0.949060	0.412	0.879880	0.536	0.893354	0.686	0.911737
0.703	0.957021	0.538	0.908320	0.634	0.914350	0.718	0.917837
0.795	0.974593	0.676	0.937463	0.748	0.937902	0.842	0.942764
0.858	0.986516	0.733	0.949183	0.853	0.958201	0.903	0.954216
0.874	0.989338	0.845	0.970787	0.894	0.966018	0.937	0.960525
0.905	0.995027	0.895	0.980036	0.899	0.966966	0.972	0.966967
0.933	1.000011	0.929	0.986282	0.937	0.973951	0.977	0.967856
0.961	1.004809	0.941	0.988345	0.965	0.979045	0.986	0.969662
0.975	1.007298	0.954	0.990746	0.982	0.982019	0.989	0.970232
0.990	1.009818	0.974	0.994300	0.988	0.983119	0.999	0.971893
0.993	1.010235	0.985	0.996118	0.992	0.983853	1.000	0.971981
1.000	1.011311	0.988	0.996706	1.000	0.985199		
		1.000	0.998522				

experimental data. The calculations were performed using

$$V^{\mathrm{E}} = V - (X_1 V_1^{\ominus} + X_2 V_2^{\ominus}) \tag{3}$$

$$C_p^{\mathrm{E}} = C_p - (X_1 C_{p1}^{\ominus} + X_2 C_{p2}^{\ominus}) \tag{4}$$

where $V_{1,2}^{\ominus}$ and $C_{p1,2}^{\ominus}$ are the molar volumes and heat capacities of the pure components of the mixture.

The values of V^{E} and C_p^{E} are shown plotted against the mole fraction of amide in Figs. 1 and 2. The V^{E} values (Fig. 1) are negative over the entire composition range and at all the temperatures studied; this indicates that the formation of acetonitrile mixtures with FA and MFA occurs with compression. The value of the compression is greater than 1%; this assumes a considerable interaction between the mixture components. At the same time, the values of the volumetric effect of mixing show that the

TABLE 3

Specific heat capacities C_p^S (J g^{-1} K^{-1}) of the AN–FA system at various temperatures; X_2 is the mole fraction of FA

X_2	283.15 K	298.15 K	313.15 K	328 15 K
0.000	2.2228	2.2335	2.2462	2.2609
0.012	2.2224	2.2333	2.2467	2.2620
0.026	2.2218	2.2331	2.2472	2.2633
0.042	2.2209	2.2329	2.2478	2.2648
0.064	2.2201	2.2332	2.2487	2.2672
0.082	2.2195	2.2333	2.2498	2.2688
0.095	2.2198	2.2340	2.2508	2.2703
0.122	2.2200	2.2349	2.2522	2.2728
0.198	2.2242	2.2393	2.2580	2.2810
0.297	2.2382	2.2529	2.2721	2.2976
0.414	2.2581	2.2730	2.2932	2.3208
0.515	2.2763	2.2914	2.3117	2.3406
0.604	2.2928	2.3080	2.3283	2.3580
0.702	2.3119	2.3267	2.3472	2.3774
0.798	2.3311	2.3461	2.3667	2.3982
0.842	2.3402	2.3553	2.3760	2.4080
0.892	2.3514	2.3665	2.3876	2.4204
0.912	2.3558	2.3713	2.3925	2.4250
0.932	2.3608	2.3762	2.3976	2.4311
0.948	2.3652	2.3805	2.4019	2.4354
0.966	2.3701	2.3854	2.4066	2.4402
0.988	2.3769	2.3919	2.4129	2.4462
1.000	2.3808	2.3954	2.4162	2.4494

interaction in the AN–FA mixture is stronger than in AN–MFA. The minimum in the $V^E = f(X_2)$ dependence for both systems occurs at equimolal ratio between the components. The increase in the deviation from additivity of the mole volumes with the temperature increase is evidently connected with a stronger influence of temperature on the associative equilibria in individual components than on the equilibria of the formation of molecular complexes of acetonitrile with amides. It is also noteworthy that, at the same time, the change in temperature does not influence the position of the extreme in the dependence of V^E on the mixture composition.

The excess heat capacities C_p^E of the AN–FA and AN–MFA systems are insignificant in absolute value (not more than 1.5 J mol^{-1} K^{-1}), unlike the analogous values for the solutions of these amides in water, where for the water–MFA mixture, C_p^E values are more than one order higher [9]. This is because for the mixtures of amides with AN, the contribution from physical (mainly dipole–dipole) interactions to the properties of the solution is significant [10]. Specific interactions in these systems, unlike in

TABLE 4

Specific heat capacities C_p^S (J g^{-1} K^{-1}) of the AN–MFA system at various temperatures; X_2 is the mole fraction of MFA

X_2	283.15 K	298.15 K	313.15 K	328.15 K
0.000	2.2228	2.2335	2.2462	2.2609
0.022	2.2184	2.2302	2.2439	2.2595
0.051	2.2128	2.2261	2.2410	2.2578
0.072	2.2089	2.2232	2.2388	2.2566
0.094	2.2046	2.2199	2.2365	2.2550
0.135	2.1971	2.2142	2.2322	2.2522
0.183	2.1885	2.2074	2.2270	2.2487
0.283	2.1710	2.1935	2.2159	2.2403
0.372	2.1566	2.1818	2.2064	2.2331
0.446	2.1455	2.1728	2.1993	2.2278
0.539	2.1321	2.1621	2.1907	2.2214
0.618	2.1216	2.1537	2.1839	2.2163
0.703	2.1109	2.1452	2.1771	2.2113
0.792	2.1003	2.1367	2.1704	2.2063
0.838	2.0951	2.1326	2.1671	2.2038
0.884	2.0900	2.1285	2.1639	2.2014
0.920	2.0861	2.1254	2.1614	2.1996
0.954	2.0826	2.1226	2.1592	2.1979
0.973	2.0805	2.1209	2.1578	2.1969
1.000	2.0778	2.1188	2.1561	2.1956

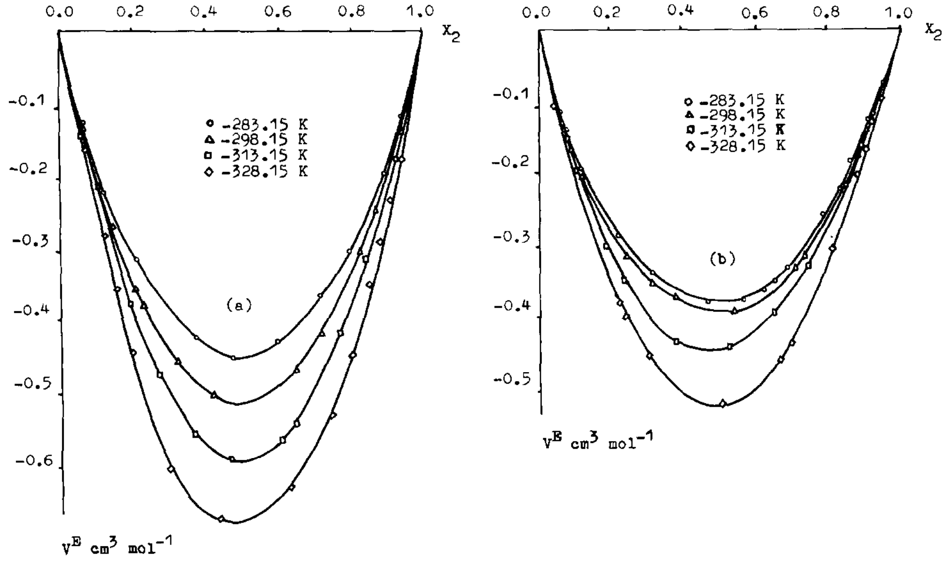

Fig. 1. Excess molar volumes V^E of the systems AN–FA (a) and AN–MFA (b) at various temperatures. X_2 is the mole fraction of amide.

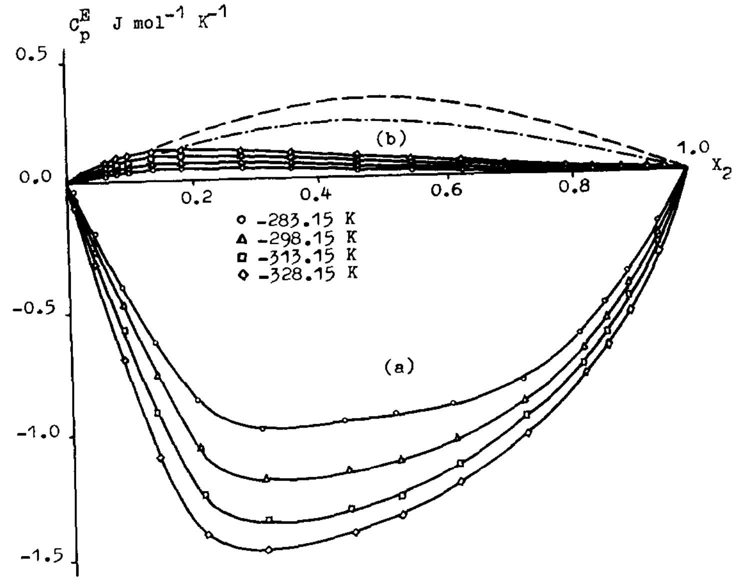

Fig. 2. Excess heat capacities of the systems AN–FA (a) and AN–MFA (b). X_2 is the mole fraction of amide. Broken lines show C_p^E values calculated using the models of associated solutions: ---, AN–FA; -·-·-, AN–MFA at 298.15 K.

aqueous ones, are considerably weaker. It is the specific interactions that play the basic role in the formation of the intermolecular associates and complexes in the aqueous systems. Hydrophobic effects also play an essential role in the interactions of amides with water, especially in the region of small additions of amides [4, 9]. A definition of the effects obtained, i.e. an assignment of the contributions to heat capacity to one or other type of interaction in solution, is rather difficult. Therefore, we have calculated C_p^E using the athermal (AAS) and non-athermal (NAS) associated solution models. The calculations were based on the method proposed earlier [11] for the calculation of the excess heat capacity of non-electrolyte solutions using a complex relationship between the parameters of the associative equilibria for the mixtures of AN with FA and MFA; these parameters were obtained from ^{1}H NMR data [12]. Calculations of C_p^E values according to this method showed that universal interactions did not predominate in AN–MFA systems, and that the course of the C_p^E dependences was controlled completely by the processes of association (the AAS and NAS models yielded practically coincident results). The structure of pure associated components is destroyed with the first addition of amide to acetonitrile. The amide–amide and AN–AN bonds are partially destroyed and replaced by amide–AN bonds. However, it is difficult in this case to distinguish between the contributions to C_p^E from the various type of interactions. The C_p^E values assume negative magnitudes for the AN–FA mixture (Fig. 2). The differences between the experimental C_p^E values and those obtained from the calculations according to the AAS and NAS models should evidently be explained by the insufficiently adequate quantitative description of association in this system with respect to the values that are obtained using double differentiation on temperature [11]. The AN–FA system is characterized by a higher degree of association than the AN–MFA system [12]. A broad minimum in the dependence of C_p^E on composition at $X_2 = 0.25$–0.40 testifies to the existence of a series of associates in the AN–FA system. The associative equilibria move towards lower contents of amide in the mixture with an increase in temperature. This is also confirmed by the decrease in the numerical values of the associative equilibria constants with increasing temperature [12]. For the AN–MFA system, C_p^E values are positive but very small ($C_p^E < 0.166\ \mathrm{J\,mol^{-1}\,K^{-1}}$ at 328.15 K); this seems rather unusual taking into account the high dielectric permeability of pure MFA ($\varepsilon = 182.4$ at 298.15 K [13]). This is probably because the positive contribution to C_p^E from the formation bonds between AN and MFA is compensated for to a considerable degree, owing to the destruction of the chain structure of pure MFA [14]. The temperature increase results in the appearance of a small extreme, which can be connected with the thermal destruction of the structures of the mixture components and with the formation of associates with definite compositions. For both systems, $\mathrm{d}C_p^E/\mathrm{d}T > 0$ is observed.

The apparent molar volumes ($\Phi_{V1,2}$) and heat capacities ($\Phi_{C_p1,2}$) of the components of the studied systems were calculated from the experimental data (Tables 1–4). The calculations were performed using

$$\Phi_{V1} = \frac{(d_2 - d)X_2M_2}{X_1dd_2} + \frac{M_1}{d} \tag{5}$$

$$\Phi_{V2} = \frac{(d_1 - d)X_1M_1}{X_2dd_1} + \frac{M_2}{d} \tag{6}$$

$$\Phi_{C_p1} = \frac{(C_p - X_1C_{p1}^{\ominus})}{X_2} \tag{7}$$

$$\Phi_{C_p2} = \frac{(C_p - X_2C_{p2}^{\ominus})}{X_1} \tag{8}$$

The results obtained are shown in Figs. 3–6 as dependences on composition.

It is noticeable that the $\Phi_{V2} = f(X_2)$ dependences are linear and change monotonously with the mixture composition, and that their values are close to those of the mole volumes of the pure components of the mixtures at the respective temperatures. The interaction in the AN–FA system is probably similar to that observed in the water–FA mixture [6].

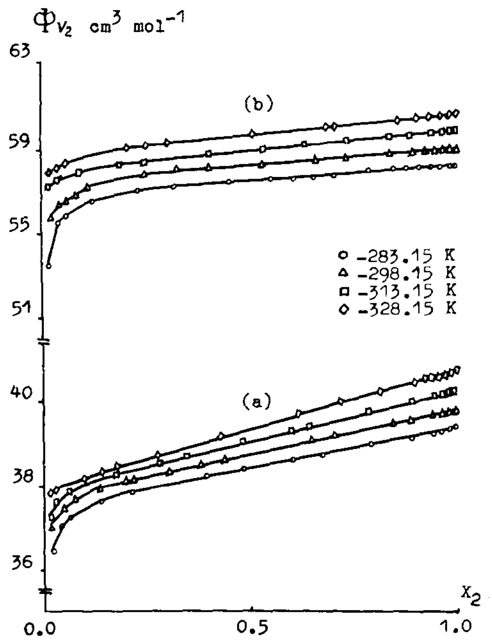

Fig. 3. Apparent molar volumes of FA (a) and MFA (b) in the mixtures with AN. X_2 is the mole fraction of amide.

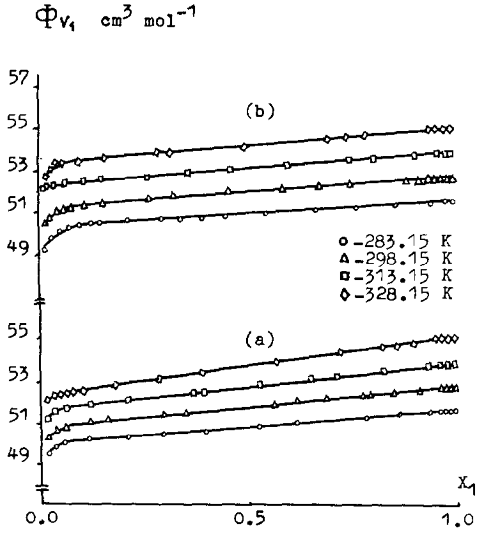

Fig. 4. Apparent molar volumes of AN in the mixtures with FA (a) and MFA (b). X_1 is the mole fraction of AN.

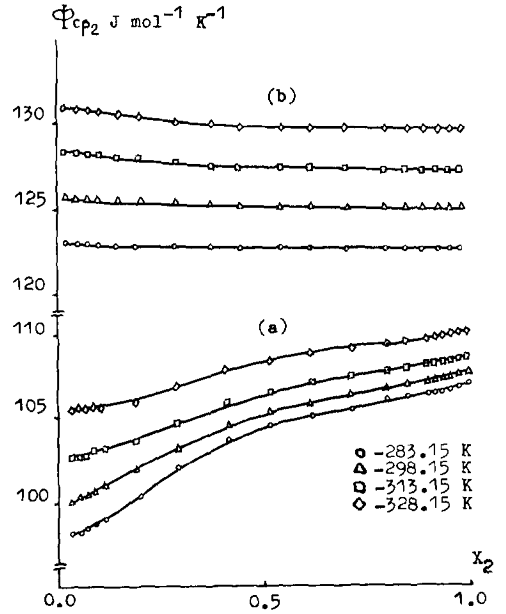

Fig. 5. Apparent molar heat capacities of amides Φ_{C_p2} in the systems AN–FA (a) and AN–MFA (b). X_2 is the mole fraction of amide.

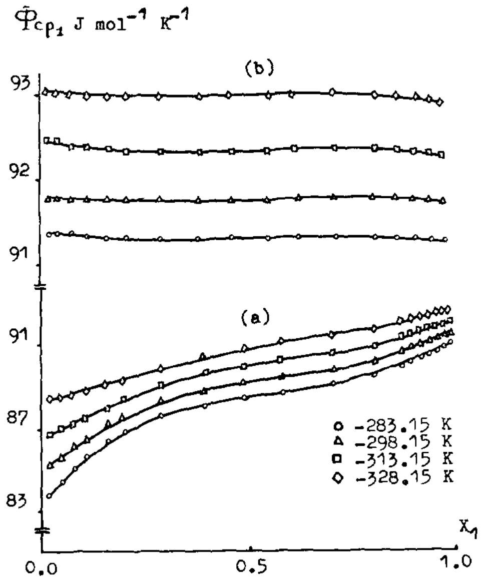

Fig. 6. Apparent molar heat capacities of AN Φ_{C_p1} in the mixtures with FA (a) and MFA (b). X_1 is the mole fraction of AN.

The monotonous increase of Φ_{V2} up to $V_2^{\ominus}$ which is observed in both systems while X_2 changes from 0 to 1 relates, as mentioned above, to the destruction of the structure of the mixture components when FA is first added to the solvent, and to the formation of H-bonds between FA and the solvent molecules. Here, a vacant space which is suitable for accommodation of FA molecules is not formed within the solvent structure. Therefore there is a monotonous change in Φ_{V2} with increasing X_2. Similar intermolecular interactions are also observed for the AN–MFA system, although they differ significantly from those observed for the water–MFA system [9] where the $\Phi_{V2}=f(X_2)$ dependence in the $X_2=0.05$ region goes through a minimum, the depth of which decreases with increasing temperature. De Visser et al. [9] relate this minimum to the hydrophobic hydration, i.e. to the strengthening of the water–water interaction in the region of small MFA concentrations. This results in the increasing free volume within the structure which is available for accommodation of the non-electrolyte molecules. With increasing MFA concentration, this effect is changed by the destruction of quasi-clathrate formations, and the volume which is occupied by the non-electrolyte molecules in solution begins to grow. The absence of extremes in the $\Phi_{V2}=f(X_2)$ dependence for the AN–MFA system in the region of small additions of MFA, suggests that the effects occurring in the aqueous solutions of MFA are absence in this system. These conclusions are also confirmed by an analysis of the $\Phi_{C_p2}=f(X_2)$ dependences (Fig. 5).

The apparent molar volumes Φ_{V1} of AN in FA and MFA are practically identical (Fig. 4). This reflects the practically equal values of the enthalpies of formation of H-bonds between the molecules of AN and amides, and the virtually equal associative equilibria constants of the molecular complexes in the mixtures of FA and MFA with AN [12].

A positive temperature course, i.e. $d\Phi_{i,j}/dT>0$, is observed for all apparent molar values.

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