

## Volumes and heat capacities of binary non-aqueous mixtures.

### Part 2. The systems acetonitrile–*N,N*-dimethylformamide and acetonitrile–hexamethylphosphoric triamide

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#### Abstract

The densities and heat capacities of binary mixtures of acetonitrile with *N,N*-dimethylformamide and hexamethylphosphoric triamide were measured between 283.15 and 328.15 K. The excess and apparent molar volumes and heat capacities of the systems studied were calculated. The influence of the nature and composition of the substance and of the temperature on the thermodynamic characteristics of acetonitrile mixtures with *N,N*-dimethylformamide and hexamethylphosphoric triamide is analysed. The thermodynamic characteristic values obtained are compared with those for the solutions of the same amides in water.

#### INTRODUCTION

Aprotic solvents and their mixtures are of great interest in experimental investigations. In particular, amides and nitriles are interesting from the theoretical point of view and are widely used in modern technologies. Among the amides *N,N*-dimethylformamide (DMFA) and hexamethylphosphoric triamide (HMPTA) are interesting because of the absence of hydrogen bonds in the pure solvents. When studying X-ray scattering by liquid DMFA, Radnai et al. [1] found a weak interaction between the molecules and a tendency to form dimers, mainly owing to dipole–dipole interaction. From measurements of the proton relaxation rate in pure HMPTA, Kessler et al. [2] observed the presence of weak self-association and did not exclude the formation of associates with short life-times. They ascribed a considerable part of the interactions between the HMPTA molecules to Van der Waals forces and to weak dipole–dipole interaction.

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As mentioned elsewhere [3, 4], pure acetonitrile (AN) is more than half associated ( $\approx 70\%$ ). The association of AN molecules is due to the interactions of N and C atoms in the nitrile group [4].

Earlier [5], we determined experimentally the heat capacities of pure HMPTA and its mixtures with water over the entire region of mixing at 283.15–298.15 K. The volumetric and heat capacity characteristics of the  $\text{H}_2\text{O}$ –HMPTA system were calculated using data on the density of this mixture [6, 7]. Analogous calculations are conducted for  $\text{H}_2\text{O}$ –DMFA mixtures at 288.15–323.15 K from data taken from refs. 8 and 9. It was shown that for aqueous solutions of DMFA and HMPTA, the values of the excess heat capacities  $C_p^E$  are high (more than  $15 \text{ J mol}^{-1} \text{ K}^{-1}$  in the water–HMPTA system at 298.15 K) and positive. The heat capacity values for dissolution of amide in water  $\Delta_{\text{soln}} C_p = \bar{C}_{p2}^\ominus - C_{p2}^\ominus$  are also high and positive ( $\bar{C}_{p2}^\ominus$  is the partial molar heat capacity of amide at infinite dilution in water and  $C_{p2}^\ominus$  is the molar capacity of pure amide [10]). All these values increase with the transition from DMFA to HMPTA. This reflects the increase in the number of non-polar groups ( $-\text{CH}_3$ ) in the amide molecules and, as a consequence, the strengthening of hydrophobic hydration [11]. The hydrophobic hydration makes a significant contribution to the values of the thermodynamic characteristics of DMFA and HMPTA mixtures with water, especially in the region of small additions of amide. It also determines the minimum in the dependences of the apparent  $\Phi_{v2}$  and partial  $\bar{V}_2$  molar volumes of amides on the mixture composition in the region which is rich in water. The depth of the minimum (or the value of the limiting initial slope of these dependences) increases from DMFA to HMPTA [7, 8]. Therefore, it is interesting to carry out a comparative analysis of the behaviour of amides in acetonitrile and in water. However, data on the densities and heat capacities of DMFA and HMPTA mixtures in AN are scarce [12, 13], and polythermal investigations of these systems are practically non-existent.

## EXPERIMENTAL

The Anton Paar DMA-60 + DMA-602 apparatus was used to measure the density of the solutions. The temperature in the thermostating shell of the measuring cell was kept to  $\pm 0.005 \text{ K}$  precision. The density of the liquid mixtures studied were measured with  $\pm 8 \times 10^{-6} \text{ g cm}^{-3}$  precision. This includes the errors owing to 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 distilled water and dried air.

A container-type adiabatic shell calorimeter, with automatic control of the adiabatic regime, was used to measure the heat capacity [5]. The calorimetric cell was calibrated using freshly prepared twice distilled deionized

water, the conductivity of which did not exceed  $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . The total determination error for the heat capacity was  $\pm 0.05\%$  of the value determined. A comparison between our data and those from different authors showed good agreement: at 298.15 K,  $C_p$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for DMFA is  $148.85 \pm 0.07$ ; 148.2 [8]; and for HMPTA  $321.72 \pm 0.09$ ; 322.24 [7].

The acetonitrile was dried twice over  $\text{P}_2\text{O}_5$ , followed each time by distillation and selection of the medium fraction. Then, the dried acetonitrile was distilled with freshly prepared  $\text{K}_2\text{CO}_3$ . The DMFA and HMPTA were stored over 4 Å molecular sieves for 48 h and then distilled in a vacuum ( $\approx 133 \text{ Pa}$ ), the medium fraction ( $\approx 60\%$  of the volume) being selected each time, until the final product of conductivity less than  $1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  was obtained. The water content of the pure substances obtained was monitored by Fischer's method and was  $1\text{--}2 \times 10^{-2}\%$  for DMFA and HMPTA and for  $1 \times 10^{-2}\%$  AN. The solutions were prepared immediately before the measurements using the weight method in a dry box.

## RESULTS

Experimental data on the densities  $d$  ( $\text{g cm}^{-3}$ ) and specific heat capacities  $C_p^s$  ( $\text{J g}^{-1} \text{K}^{-1}$ ) of the AN–DMFA and AN–HMPTA systems over the entire composition range at 283.15–328.15 K are given in Tables 1–4.

Over the temperature interval investigated, the  $C_p^s$  values of pure DMFA and AN increase, and that of pure HMPTA decreases with the temperature increase (see Tables 2 and 3). The result is an inversion of the  $C_p^s = f(X_2)$  dependences (where  $X_2$  is the mole fraction of DMFA or HMPTA) at various temperatures for the AN–HMPTA mixture within the temperature interval given; the inversion is observed at  $X_2 = 0.12\text{--}0.18$  and testifies to considerable rearrangements in the structure of both pure components and of the mixture itself. The destruction of rather weak, different types of associates of AN evidently begins with the first HMPTA additions [3, 4]. At the same time, changes (weakening) also occur in the weak dipole–dipole interactions of the HMPTA molecules [14]. Below  $X_2 = 0.12$ , there is an acetonitrile-like region, i.e. the solution consists of regions which preserve the structure of pure AN and of those where this structure is perturbed by the HMPTA molecules. At  $0.12 < X_2 < 0.18$ , there is a transition from an AN-like region to an HMPTA-like region. The positive sign (a characteristic of the  $C_p^s$  of pure AN) in the temperature dependence of  $C_p^s$  changes to a negative one (characteristic of the  $C_p^s$  of pure HMPTA). And furthermore, with increasing HMPTA concentration, the temperature run of the heat capacity of the mixture is determined by the temperature changes in the heat capacity of pure HMPTA.

TABLE 1

Density of the AN–DMFA system  $d$  ( $\text{g m}^{-3}$ ) at various temperatures;  $X_2$  is the mole fraction of DMFA

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
0.004	0.793610	0.002	0.777242	0.001	0.760667	0.007	0.745468
0.007	0.794605	0.003	0.777536	0.006	0.761993	0.010	0.746212
0.011	0.795431	0.010	0.779354	0.013	0.763665	0.014	0.747261
0.026	0.799348	0.020	0.781887	0.021	0.765642	0.022	0.749341
0.032	0.800957	0.029	0.783998	0.032	0.768437	0.026	0.750353
0.043	0.803410	0.033	0.784965	0.038	0.770003	0.046	0.755480
0.052	0.805732	0.063	0.792435	0.052	0.773434	0.062	0.759321
0.065	0.808654	0.073	0.794566	0.061	0.775711	0.064	0.759749
0.093	0.815282	0.078	0.795824	0.105	0.786048	0.090	0.766208
0.138	0.825323	0.128	0.807316	0.147	0.795645	0.104	0.769647
0.194	0.837371	0.152	0.812643	0.233	0.814357	0.169	0.784500
0.239	0.846424	0.234	0.830075	0.275	0.822764	0.308	0.813789
0.288	0.856203	0.317	0.846379	0.402	0.846783	0.347	0.821331
0.331	0.864225	0.426	0.865799	0.560	0.873151	0.446	0.839321
0.392	0.875162	0.485	0.875679	0.651	0.886808	0.594	0.863279
0.454	0.885755	0.542	0.884790	0.731	0.897937	0.678	0.875805
0.592	0.907219	0.639	0.899180	0.749	0.900469	0.765	0.887800
0.646	0.914962	0.765	0.916287	0.850	0.913440	0.850	0.898700
0.753	0.929478	0.844	0.926264	0.899	0.919339	0.904	0.905497
0.843	0.940682	0.897	0.932526	0.917	0.921567	0.924	0.907913
0.893	0.946524	0.922	0.935453	0.945	0.924860	0.937	0.909471
0.920	0.949643	0.949	0.938545	0.962	0.926746	0.955	0.911429
0.941	0.952033	0.960	0.939782	0.974	0.928089	0.963	0.912433
0.965	0.954717	0.971	0.941025	0.979	0.928688	0.983	0.914754
0.983	0.956606	0.986	0.942666	0.990	0.929922	0.990	0.915596
0.990	0.957325	0.991	0.943188	0.995	0.930437	0.992	0.915824
0.991	0.957325	1.000	0.944181	0.996	0.930641	1.000	0.916676
1.000	0.958424			1.000	0.931024		

The molar volumes  $V$  and heat capacities  $C_p$  were calculated from

$$V = (X_1 M_1 + X_2 M_2) / d \quad (1)$$

$$C_p = C_p^s (X_1 M_1 + X_2 M_2) \quad (2)$$

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

Excess volume  $V^E$  and heat capacities  $C_p^E$  were calculated from the experimental data using

$$Y^E = Y - X_1 Y_1^\ominus - X_2 Y_2^\ominus \quad (3)$$

TABLE 2

Density of the AN–HMPTA system  $d$  ( $\text{g m}^{-3}$ ) at various temperatures;  $X_2$  is the mole fraction of HMPTA

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	0.798611	0.003	0.779173	0.006	0.764990	0.005	0.747566
0.014	0.803798	0.005	0.780541	0.008	0.767108	0.009	0.751423
0.018	0.806925	0.008	0.783295	0.018	0.774702	0.014	0.755513
0.036	0.820508	0.011	0.785886	0.028	0.782342	0.024	0.762831
0.041	0.823830	0.017	0.790310	0.032	0.785142	0.024	0.763191
0.055	0.833138	0.019	0.791703	0.032	0.785402	0.030	0.767270
0.068	0.841372	0.026	0.797430	0.033	0.786090	0.037	0.772450
0.078	0.847404	0.031	0.800564	0.050	0.797994	0.041	0.775298
0.085	0.851230	0.044	0.809668	0.060	0.804515	0.042	0.776126
0.095	0.857268	0.055	0.817131	0.071	0.811221	0.052	0.782741
0.119	0.869917	0.096	0.841851	0.171	0.862928	0.082	0.801941
0.251	0.922958	0.123	0.856150	0.240	0.889426	0.201	0.860390
0.411	0.963912	0.200	0.890163	0.313	0.912087	0.250	0.878560
0.533	0.985740	0.351	0.936307	0.452	0.944118	0.388	0.916880
0.572	0.991615	0.520	0.969908	0.524	0.956744	0.457	0.931573
0.622	0.998380	0.548	0.974252	0.663	0.976239	0.539	0.945473
0.669	1.004043	0.674	0.991158	0.741	0.985093	0.611	0.956064
0.766	1.014296	0.705	0.994672	0.811	0.991965	0.698	0.966882
0.873	1.023802	0.792	1.003403	0.888	0.998608	0.802	0.977859
0.909	1.026554	0.865	1.009820	0.918	1.000950	0.864	0.983476
0.923	1.027617	0.904	1.013016	0.921	1.001243	0.893	0.985927
0.927	1.027897	0.928	1.014818	0.923	1.001377	0.918	0.987968
0.928	1.028008	0.941	1.015745	0.939	1.002609	0.932	0.989061
0.950	1.029579	0.957	1.016944	0.948	1.003275	0.942	0.989846
0.953	1.029754	0.963	1.017305	0.952	1.003539	0.960	0.991187
0.965	1.030573	0.992	1.019292	0.972	1.004985	0.976	0.992389
0.981	1.031693	0.996	1.019621	0.981	1.005622	0.989	0.993276
0.994	1.032518	1.000	1.019847	0.989	1.006165	0.993	0.993584
1.000	1.032863			1.000	1.006883	0.997	0.993856
						1.000	0.994038

where  $Y$  is  $V$  or  $C_p$ , respectively and  $Y^\ominus$  is the  $V$  or  $C_p$  value for the pure components.

The excess values obtained are shown in Fig. 1 plotted against the amide mole fraction. The  $V^E$  values are negative over the entire composition region and at all the temperatures studied. This suggests that the process of the formation of AN–DMFA and AN–HMPTA mixtures proceeds with compression; this assumes a significant interaction between the mixture components. It can be seen that this interaction is considerably smaller in the AN–DMFA system than in AN–HMPTA.

TABLE 3

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

$X_2$	283.15 K	293.15 K	298.15 K	303.15 K	313.15 K	323.15 K
0.000	2.2225	2.2303	2.2335	2.2372	2.2462	2.2259
0.010	2.2193	2.2280	2.2314	2.2360	2.2454	2.2561
0.020	2.2156	2.2254	2.2293	2.2338	2.2439	2.2552
0.029	2.2128	2.2235	2.2276	2.2323	2.2430	2.2547
0.040	2.2092	2.2205	2.2248	2.2300	2.2408	2.2529
0.050	2.2060	2.2175	2.2222	2.2276	2.2389	2.2518
0.060	2.2026	2.2147	2.2194	2.2250	2.2368	2.2503
0.069	2.1998	2.2121	2.2169	2.2227	2.2350	2.2486
0.079	2.1964	2.2090	2.2141	2.2198	2.2327	2.2462
0.089	2.1932	2.2057	2.2112	2.2171	2.2301	2.2440
0.097	2.1907	2.2036	2.2090	2.2151	2.2283	2.2426
0.148	2.1734	2.1878	2.1940	2.2003	2.2145	2.2293
0.219	2.1523	2.1662	2.1729	2.1793	2.1941	2.2091
0.293	2.1319	2.1464	2.1529	2.1597	2.1745	2.1898
0.416	2.1016	2.1167	2.1235	2.1305	2.1455	2.1610
0.490	2.0852	2.1006	2.1076	2.1147	2.1298	2.1455
0.601	2.0633	2.0792	2.0865	2.0934	2.1088	2.1249
0.695	2.0466	2.0627	2.0701	2.0774	2.0929	2.1090
0.793	2.0309	2.0473	2.0550	2.0620	2.0778	2.0941
0.836	2.0245	2.0410	2.0488	2.0560	2.0717	2.0882
0.887	2.0170	2.0336	2.0415	2.0488	2.0647	2.0811
0.909	2.0141	2.0308	2.0388	2.0460	2.0618	2.0782
0.919	2.0126	2.0292	2.0373	2.0445	2.0603	2.0769
0.930	2.0113	2.0279	2.0359	2.0432	2.0590	2.0755
0.938	2.0101	2.0268	2.0349	2.0422	2.0579	2.0745
0.948	2.0087	2.0255	2.0335	2.0409	2.0566	2.0731
0.955	2.0078	2.0245	2.0326	2.0400	2.0558	2.0723
0.970	2.0060	2.0227	2.0306	2.0381	2.0539	2.0704
0.979	2.0048	2.0215	2.0296	2.0370	2.0529	2.0693
0.987	2.0037	2.0206	2.0286	2.0364	2.0519	2.0684
1.000	2.0021	2.0189	2.0270	2.0344	2.0502	2.0668

The temperature increase results in more negative  $V^E$  values in both systems. The temperature increase influences the associative equilibria in the pure components more than in the mixtures. It is noteworthy that the temperature changes does not influence the position of the minimum in the dependence of  $V^E$  on the mixture composition.

The excess heat capacities  $C_p^E$  are insignificant in absolute value (little more than  $2 J mol^{-1} K^{-1}$ ), being positive for the AN–DMFA system and negative for AN–HMPTA (Fig. 1).

Calculations of  $C_p^E$  using the athermal (AAS) and non-athermal (NAS) models of associated solutions were carried out on the basis of the method

TABLE 4

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

$X_2$	283.15 K	298.15 K	313.15 K	328.15 K
0.000	2.2228	2.2335	2.2462	2.2609
0.012	2.1922	2.2038	2.2161	2.2303
0.038	2.1378	2.1514	2.1615	2.1740
0.056	2.1054	2.1181	2.1292	2.1406
0.088	2.0675	2.0714	2.0774	2.0851
0.169	2.0096	2.0043	1.9997	1.9987
0.210	1.9891	1.9797	1.9708	1.9659
0.270	1.9656	1.9498	1.9366	1.9271
0.325	1.9463	1.9267	1.9102	1.8975
0.418	1.9203	1.8956	1.8742	1.8578
0.495	1.9030	1.8747	1.8505	1.8319
0.572	1.8882	1.8572	1.8308	1.8104
0.600	1.8833	1.8515	1.8243	1.8034
0.698	1.8678	1.8338	1.8048	1.7821
0.741	1.8617	1.8270	1.7972	1.7739
0.702	1.8552	1.8196	1.7890	1.7650
0.835	1.8501	1.8139	1.7828	1.7583
0.895	1.8434	1.8065	1.7747	1.7494
0.917	1.8412	1.8041	1.7720	1.7466
0.952	1.8378	1.8002	1.7677	1.7420
0.977	1.8354	1.7976	1.7649	1.7389
1.000	1.8334	1.7953	1.7624	1.7363

proposed earlier [15] whereby the excess heat capacity of a non-electrolyte is calculated using a complex set of the parameters of the associative equilibria for the mixtures of AN with DMFA and HMPTA, obtained from  $^1H$ NMR data [16]. The calculation of  $C_p^E$  values using this method showed that for the AN–HMPTA system, the NAS model yields good agreement with experiment, whereas the AAS model does not. It is vital to take into account the universal interactions (NAS model) when considering the thermodynamic properties of these systems, because association in AN mixtures with DMFA and HMPTA is relatively weak. It has been stated [1] that only dipole–dipole interaction with anti-parallel orientation of the dipoles is observed between AN and DMFA molecules. The maximum in the  $C_p^E = f(X_2)$  dependence at  $X_2 = 0.1–0.2$  also testifies to the existence of a set of associates of the type  $DMFA \cdot nAN$  ( $n = 2–3$ ). The increase in the positive contribution to  $C_p^E$  with increasing temperature relates to the weakening of the AN–AN bonds, to the formation of DMFA–AN associates of different compositions, and to the energy expended in the change in the thermal stability of the associates formed and in the number of molecules in them. As mentioned above, in

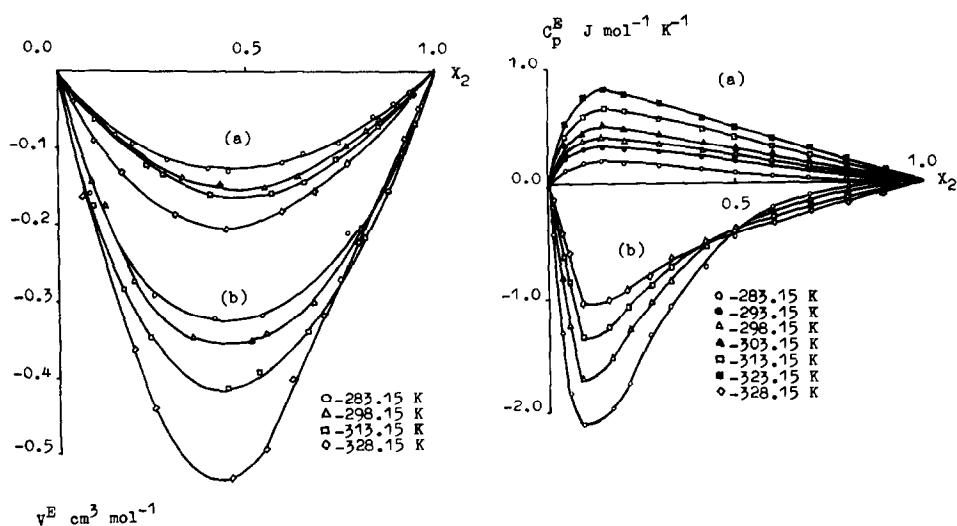


Fig. 1. Excess molar volume  $V^E$  and heat capacities  $C_p^E$  of mixtures AN-DMFA (a) and AN-HMPTA (b) at various temperatures.  $X_2$  is the mole fraction of amide.

AN-HMPTA mixture the values of  $C_p^E$  are negative over the entire composition range. The difference in the donor-acceptor properties (HMPTA is a strong donor, and AN an acceptor) leads to the assumption of the formation of hydrogen bonds between the AN and HMPTA molecules, as occurs in the aqueous solution of HMPTA, where its molecule forms two H bonds with water molecules [17]. The maximum in the dependence of  $C_p^E$  on the composition of the  $H_2O$ -HMPTA mixture at  $X_2 = 0.09$  is associated with the cooperative interactions (hydrophobic hydration, formation of H bonds, etc.) [5]. The minimum in the  $C_p^E = f(X_2)$  dependence for the AN-HMPTA mixture (Fig. 1) is also obtained at  $X_2 = 0.09$ . However,  $^1H$ NMR investigations have shown [16] that strong intermolecular interactions of H-bond type are absent in this system and this extreme relates exclusively to the pair-wise interactions. A good agreement between the experimental  $C_p^E$  values and those calculated from the NAS model also testifies to the predominant role of dipole-dipole interactions in this mixture. The  $C_p^E$  dependences on composition experience the inversion within the  $0.35 < X_2 < 0.60$  interval. Up to  $X_2 = 0.35$ ,  $dC_p^E/dT > 0$ . After  $X_2 = 0.60$ , the dependence of the excess heat capacity on temperature becomes negative. The apparent molar volumes and heat capacities of the components of the mixtures studied were calculated from the experimental data (Tables 1–4) using the equations

$$\Phi_{V1} = \frac{(d_2 - d)X_2M_2}{X_1dd_2} + \frac{M_1}{d} \quad (4)$$



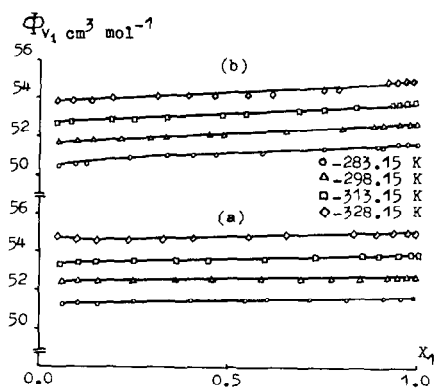


Fig. 2. Apparent molar volumes  $\Phi_{V1}$  of AN in the mixtures with DMFA (a) and HMPTA (b).  $X_1$  is the mole fraction of AN.

$$\Phi_{V2} = \frac{(d_1 - d)X_1M_1}{X_2dd_1} + \frac{M_2}{d} \quad (5)$$

$$\Phi_{cp1} = (C_p - X_1C_{p1}^\ominus)/X_2 \quad (6)$$

$$\Phi_{cp2} = (C_p - X_2C_{p2}^\ominus)/X_1 \quad (7)$$

The results obtained are plotted against the mixture composition in Figs. 2–5.

The functions  $\Phi_{V1,2} = f(X_{1,2})$  are linear and increase monotonously in the dependence on the composition of the mixtures (Figs. 2 and 3). The  $\Phi_{V1,2}$  values are close in magnitude to the values of the molar volumes of the components of the mixtures at corresponding temperatures. The absence of the minima in the  $\Phi_{V2} = f(X_2)$  dependences in the region of

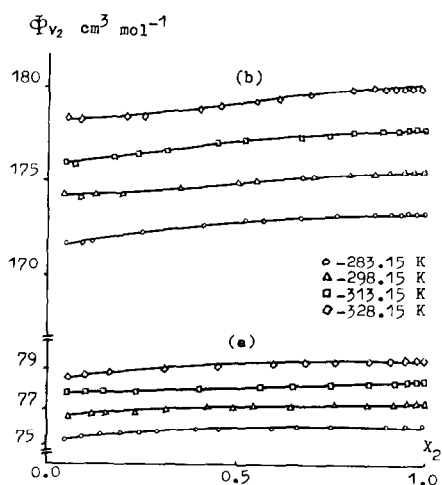


Fig. 3. Apparent molar volumes  $\Phi_{V2}$  of DMFA (a) and HMPTA (b) in the mixtures with AN.  $X_2$  is the mole fraction of amide.

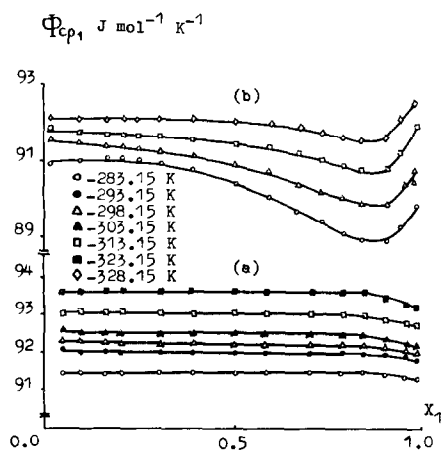


Fig. 4. Apparent molar heat capacities  $\Phi_{Cp1}$  of AN in the mixtures with DMFA (a) and HMPTA (b).  $X_1$  is the mole fraction of AN.

small additions of DMFA and HMPTA to AN, which are characteristic of the aqueous solutions of these amides [7, 8], leads to the conclusion that the interaction of amides with AN is quite different from that of their interaction with water. When an amide molecule is in aqueous surroundings, hydrophobic hydrations play an important role, as does the formation of H bonds (more than one in the case of HMPTA [17]). In the water structure, the non-polar  $\text{CH}_3$  groups of the amide molecules favour the strengthening of water–water interactions; as a result, the free volume in the water structures which is accessible for accommodation of the amide molecules increases [18]. This is what determines the appearance of the minima in the dependences of  $\Phi_{V2}$  on the mixture composition in the

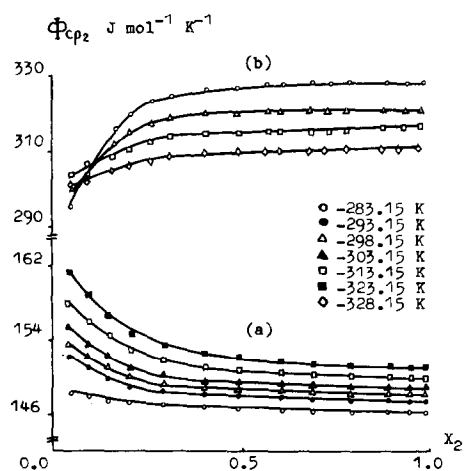


Fig. 5. Apparent molar heat capacities  $\Phi_{Cp2}$  of DMFA (a) and HMPTA (b) in the mixtures with AN.  $X_2$  is the mole fraction of amide.

region of small additions of hydrophobic substances such as DMFA and HMPTA [11]. In addition, with increasing amide concentration the effect of the hydrophobic hydration is replaced by the effect of the destruction of quasi-clathrate formations. The volume occupied by the amide molecule in water begins to grow, which is reflected in the increase of  $\Phi_{V2}$  values. For solutions of DMFA and HMPTA in AN, the monotonous increase of  $\Phi_{V2}$  with increasing concentration of amides in the mixture relates only to the destruction of the structures of the mixture components when they are added to each other. This conclusion is also confirmed by the shape of the  $\Phi_{cp2} = f(X_2)$  dependence for the AN–HMPTA mixture (Fig. 5).

The destruction of the AN structure proceeds up to  $X_2 = 0.4$ . This effect increases with decreasing temperature. The isotherms of the  $\Phi_{cp2} = f(X_2)$  dependences experience the inversion at  $0.0 < X_2 < 0.1$ . The change in the sign of the  $d\Phi_{cp2}/dT$  derivative from positive to negative occurs in this composition region. After  $X_2 > 0.4$ , the  $\Phi_{cp2}$  values are practically independent of the mixture composition; this confirms that the effects of the destruction of the structures are compensated for by the effects of the formation of intermolecular associates. For AN–DMFA,  $\Phi_{cp2}$  values decrease with increasing amide content in the mixture. This change in the dependence suggests a certain strengthening of the solution structure; it relates to the destruction of weak AN–AN bonds by DMFA molecules and to the formation of stronger AN–DMFA bonds [1]. The subsequent course of the  $\Phi_{cp2} = f(X_2)$  dependence ( $X_2 > 0.3$ ) suggests the mutual compensation between the effects of destruction and the formation of various associates. The  $\Phi_{V1}$  and  $\Phi_{cp1}$  values are close to the values of molar volumes and heat capacities of pure AN at corresponding temperatures. They are practically linearly dependent on composition and temperature (except for  $\Phi_{cp1}$  for HMPTA). All the characteristic parameters obtained for AN–DMFA increase with temperature. One cannot conclude unambiguously on the influence of temperature on the heat capacity characteristics of the AN–HMPTA system. As noted above, this relates to a different dependence of the heat capacity of pure HMPTA (Table 4) which seems unusual, because for the majority of organic solvents the heat capacity increases with temperature. Evidently, for many liquids, as for water, the temperature dependence of the heat capacity (and not only the heat capacity) can be of extremal character [19]. Therefore, the final result depends on the temperature interval of the measurements.

## REFERENCES

- 1 T. Radnai, S. Itoh and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, 61 (1988) 3845.
- 2 Yu.M. Kessler, M.G. Fomichev, N.M. Alpatova and V.P. Emelin, *Russ. J. Struct. Chem.*, 13 (1972) 517.
- 3 M.F. Vux, *Russ. J. Struct. Chem.*, 12 (1971) 3.

- 4 M.I. Shakhparonov, Introduction to Modern Solution Theory, Vysshaya shkola, Moscow, 1976.
- 5 A.M. Kolker, M.V. Kulikov and G.A. Krestov, *Izv. Vuzov. Khim. Khim. Tekhnol. (Russ.)*, 78 (1985) 11.
- 6 H. Chebib, C. Jambon and J.-C. Merlin, *J. Chim Phys. Phys.-Chim. Biol.*, 78 (1981) 607.
- 7 M. Castagnolo, A. Inglese, G. Petrella and A. Sacco, *Thermochim. Acta*, 44 (1981) 67.
- 8 G. Visser, G. Perron, J.E. Desnoyers, W.J.M. Heuvelsland and G. Somsen, *J. Chem. Eng. Data*, 22 (1977) 74.
- 9 G.M. Poltoratskii (Ed.), *Thermodynamic Characteristics of Non-Aqueous Solutions of Electrolytes Khimiya, Leningrad*, 1984.
- 10 M.V. Kulikov, A.M. Kolker, L.P. Safonova and A.I.G. Krestov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 52 (1990) 2532.
- 11 Yu.M. Kessler and N.A. Abakumova, *Izv. Vuzov. Khim. Khim. Tekhnol. (Russ.)* 25 (1982) 162.
- 12 Z.V. Pachuliya, N.I. Zheleznyak, G.N. Dushina, Yu.G. Bushuyev and G.A. Krestov, *Izv. Vuzov. Khim. Khim. Tekhnol. (Russ.)*, 27 (1983) 1523.
- 13 G. Visser and G. Somsen, *J. Solution Chem.*, 8 (1979) 593.
- 14 Yu.M. Kessler, V.P. Emelin, A.I. Mishustin and P.S. Yastremskii, *Russ. J. Struct. Chem.*, 16 (1975) 797.
- 15 M.Yu. Nikiforov, G.A. Alper and G.A. Krestov, *Russ. J. Phys. Chem.*, 59 (1985) 585.
- 16 A.I.G. Krestov, M.Yu. Nikiforov, G.A. Kerokosyan, G.A. Alper and A.M. Kolker, *Russ. J. Phys. Chem.*, 65 (1991) 358.
- 17 V.P. Belousov and M.Yu. Panov, *Thermodynamics of Aqueous Solutions of Non-Electrolytes, Khimiya, Leningrad*, 1983.
- 18 C. Visser, W.J.M. Heuvelsland, L.A. Dunn and G. Somsen, *J. Chem. Soc. Faraday Trans. 1*, 74 (1978) 1159.
- 19 R. Reed, J. Prausnitz and K. Sherwood, *Properties of Gases and Liquids, Khimiya, Leningrad*, 1970.