The structure of diluted binary solutions of amides according to the heat capacity data

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The specific heat capacities of hexamethylphosphoric triamide, diethylpropionamide, their aqueous solutions, and mixtures of hexamethylphosphoric triamide with formamide were measured in the temperature range from 288.15 to 318.15 K. The dependences of the partial molar heat capacity of aqueous solutions of amides on the composition of the mixture have maxima in the region of 0.02—0.04 molar fractions of amide. The maximum on a similar dependence for solutions of hexamethylphosphoric triamide corresponds to the concentration of 0.01 molar fractions. The conclusion on the formation of solvates (hydrates) in the systems studied was made. The heat capacity coefficients of pair and triple interactions were calculated in terms of the McMillan—Mayer theory. A change in the heat capacity characteristics with the temperature change was analyzed.

Key words: heat capacity, water, hexamethylphosphoric triamide, diethylpropionamide, formamide, coefficients of interaction, microheterogeinity, hydrophobic substances, temperature.

Heat capacity characteristics reflect the state of a solution, because they are very sensitive to structural rearrangements in the solution when the ratio of its components changes.

For many substances, an increase in their concentration in an aqueous solution results in a monotonic decrease in the apparent molar heat capacity (Φ_{Cp2}) from the value of partial molar heat capacity at infinite dilution ($\bar{C}^0_{p2}$) to the heat capacity of the neat substance (C^0_{p2}).[1] For *tert*-butyl alcohol (Bu^tOH),[2] 2-*n*-butoxyethanol,[3] piperidine,[4] *tert*-butyl acetate (TBA),[5] and several other substances,[6] the dependences of Φ_{Cp2} and $\bar{C}^0_{p2}$ on the composition of their aqueous solutions have an extreme character. In the opinion of several authors,[7—9] a maximum on these dependences within the range of the molar fraction of the non-aqueous component $0.01 < X_2 < 0.07$ is evidence for the microheterogeneous state of the system due to micelle formation.[9] At the same time, the presence of the maximum on these dependences cannot be related unambiguously to the micelle formation process, since the formation of micelles is not always accompanied by the extreme dependence of the heat capacity on the composition.[6] In addition, there are no grounds to speak about micelle formation in the case of a solution containing no surfactants.

The extreme shape of the dependences $\Phi_{Cp2} = f(X_2)$ and $\bar{C}_{p2} = f(X_2)$ is mainly characteristic of aqueous solutions of strongly hydrophobic substances. It can be assumed that the character of these dependences in the region of small additives of the dissolved substance is determined to a considerable extent by hydrophobic effects.

However, aggregation of molecules is not characteristic of aqueous systems only. It can take place in other solvents with a developed network of hydrogen bonds and a high degree of self-association (hydrazine, formamide, ethylene glycol, glycerol, and others).[10]

From this viewpoint, it is of interest to study the heat capacity of diluted solutions of typically hydrophobic substances of similar chemical nature, but with different structures in water and non-aqueous solvents with a high degree of self-association (for example, in formamide), and to reveal the temperature effect on changing the heat capacity characteristics.

Experimental

In the region of compositions of 0.00—0.10 molar fractions of the dissolved substance, we determined the specific heat capacities ($C_p{}^s$/J g^{-1} K^{-1}) of hexamethylphosphoric triamide (HMPA), diethylpropionamide (DEP), their aqueous solutions, and mixtures of HMPA with formamide (FA). Measurements were carried out on a container-type adiabatic calorimeter with automatic maintenance of the adiabatic regime[1] in the 288.15—318.15 K temperature range. Total error of determination of the specific heat capacity was ±0.05%. The results obtained agree well with the data of other authors: at 298.15 K, the molar heat capacity ($C_p{}^m$/J mol^{-1} K^{-1}) is 107.91±0.03 for FA (our data) and 107.8 [11]; and 321.72±0.09 (our data) and 322.24 [12] for HMPA. The substances used were purified according to the procedures recommended previously

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2479—2483, December, 1998.

for HMPA and FA [1] as well as for DEP [13]. The residual content of water in purified amides determined by the Fischer method was $(1-3) \cdot 10^{-2}$ %. Water was a freshly prepared bidistillate with a specific electroconductivity not higher than $1 \cdot 10^{-6}$ Ohm^{-1} cm^{-1}.

Results and Discussion

The experimental values of the specific heat capacities $C_p{}^s$ obtained are presented in Table 1.

Based on the experimental data, we calculated by Eqs. (1)—(3) the excess molar capacities ($C_p{}^E$) of the mixtures and apparent (Φ_{Cp2}) and partial ($\bar{C}_{p2}$) molar capacities of the dissolved substances:

$$C_p{}^E = C_p{}^m - (X_1 \cdot C^0{}_{p1} + X_2 \cdot C^0{}_{p2}), \quad (1)$$

$$\Phi_{Cp2} = (C_p{}^m - X_1 \cdot C^0{}_{p1})/X_2, \quad (2)$$

$$\bar{C}_{p2} = \Phi_{Cp2} + X_2 \cdot (d\Phi_{Cp2}/dX_2), \quad (3)$$

where X is the molar fraction; $C^0{}_p$ is the molar heat capacity of the neat component; 1 and 2 are indices attributed to the solvent and dissolved substance, respectively.

The dependences of the values obtained on the composition of the mixtures are presented in Figs. 1—3.

The dependences of the excess heat capacities of the mixtures studied on their composition are presented in Fig. 1. The $C_p{}^E$ values of mixtures of water with HMPA and DEP in the concentration range studied are positive, which is characteristic of solutions of liquids that are not associated through the H bond, and they increase as the content of amide in the mixture increases. This is due to the high degree of structure formation in the mixture as compared to neat components. In this composition region, hydrophobic effects play a predominant role in the intermolecular interaction. HMPA is a more hydrophobic substance, *i.e.*, it possesses a

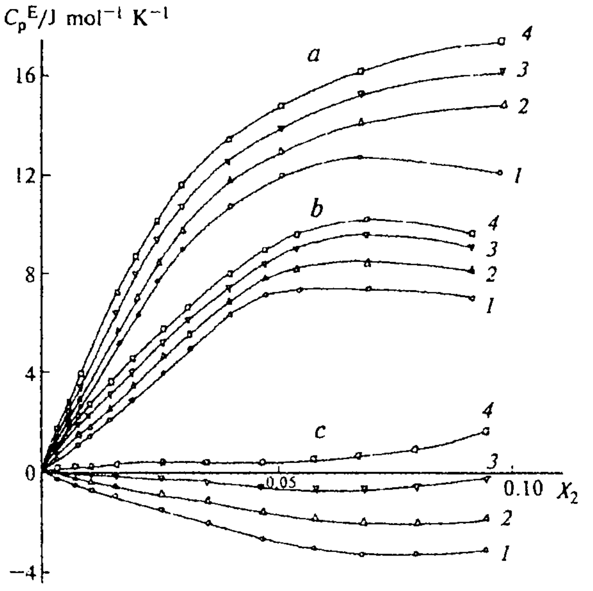

Fig. 1. Excess heat capacities ($C_p{}^E$) of the H_2O—HMPA (*a*), H_2O—DEP (*b*), and FA—HMPA (*c*) systems at 288.15 (*1*), 298.15 (*2*), 308.15 (*3*), and 318.15 (*4*) K.

Table 1. $C_p{}^s$ values of binary mixtures at different temperatures (T/K = 298.15—318.5)

X_2*	$C_p{}^s$/J g^{-1} K^{-1}			
	288.15	298.15	308.15	318.15
		H_2O—HMPA		
0.0000	4.1860	4.1793	4.1779	4.1792
0.0020	4.1719	4.1735	4.1799	4.1869
0.0040	4.1577	4.1660	4.1783	4.1926
0.0060	4.1424	4.1564	4.1672	4.1797
0.0080	4.1283	4.1451	4.1677	4.1909
0.0160	4.0944	4.1195	4.1466	4.1866
0.0202	4.0745	4.0954	4.1365	4.1691
0.0249	4.0516	4.0792	4.1081	4.1419
0.0302	4.0146	4.0397	4.0740	4.1090
0.0403	3.9251	3.9569	3.9793	4.0105
0.0513	3.8089	3.8371	3.8630	3.8895
0.0686	3.6185	3.6572	3.6827	3.7087
0.0997	3.2975	3.3666	3.3919	3.4185
1.0000	1.8126	1.7953	1.7728	1.7532
		H_2O—DEP		
0.0000	4.1864	4.1793	4.1779	4.1792
0.0040	4.1580	4.1680	4.1780	4.1915
0.0080	4.1289	4.1451	4.1685	4.1896
0.0102	4.1175	4.1348	4.1601	4.1821
0.0148	4.0982	4.1117	4.1475	4.1696
0.0194	4.0798	4.1003	4.1352	4.1600
0.0261	4.0508	4.0803	4.1089	4.1416
0.0318	4.0361	4.0575	4.0878	4.1204
0.0404	4.0007	4.0273	4.0526	4.0887
0.0482	3.9601	3.9883	4.0188	4.0523
0.0550	3.8909	3.9356	3.9791	4.0088
0.0705	3.7589	3.8103	3.8623	3.8975
0.0933	3.5759	3.6245	3.6703	3.6937
1.0000	2.1628	2.1951	2.2292	2.2649
		FA—HMPA		
0.0000	2.3854	2.3954	2.4080	2.4254
0.0015	2.3788	2.3900	2.4035	2.4213
0.0039	2.3695	2.3824	2.3970	2.4154
0.0074	2.3578	2.3722	2.3880	2.4071
0.0109	2.3458	2.3625	2.3794	2.3990
0.0163	2.3285	2.3477	2.3658	2.3873
0.0266	2.2969	2.3182	2.3400	2.3648
0.0363	2.2673	2.2926	2.3157	2.3433
0.0479	2.2348	2.2630	2.2889	2.3200
0.0590	2.2112	2.2405	2.2684	2.2992
0.0692	2.1918	2.2219	2.2517	2.2836
0.0811	2.1774	2.2043	2.2326	2.2670
0.0964	2.1609	2.1861	2.2152	2.2535
1.0000	1.8126	1.7953	1.7728	1.7532

*X_2 is the molar fraction of HMPA or DEP in the mixture.

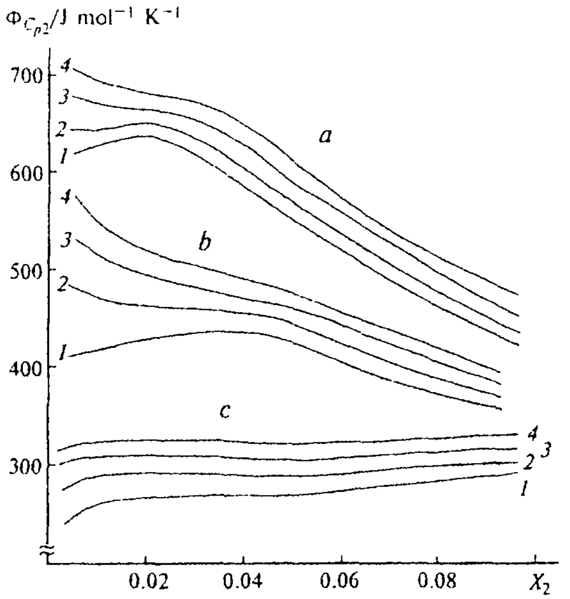

Fig. 2. Apparent molar heat capacities of the H_2O—HMPA (*a*), H_2O—DEP (*b*), and FA—HMPA (*c*) systems at 288.15 (*1*), 298.15 (*2*), 308.15 (*3*), and 318.15 (*4*) K.

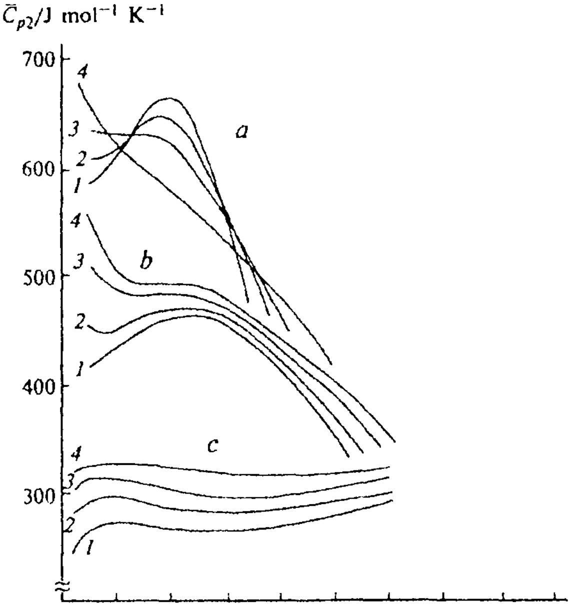

Fig. 3. Partial molar heat capacities of the H_2O—HMPA (*a*), H_2O—DEP (*b*), and FA—HMPA (*c*) systems at 288.15 (*1*), 298.15 (*2*), 308.15 (*3*), and 318.15 (*4*) K.

larger effective surface of contact of nonpolar groups with the aqueous environment than DEP,[10] which explains the higher values of $C_p{}^E$ in the H_2O—HMPA system than those in the H_2O—DEP system. In addition, the HMPA molecule forms two hydrogen bonds with water molecules through the oxygen atom,[14] which favors an additional stabilization of the structure of the mixture. It is known[15] that the system reaches the maximum degree of structure formation at $X = 0.09$ molar fractions of HMPA. For the FA—HMPA system in the concentration range studied, $C_p{}^E$ are negative (except for $C_p{}^E$ at 318.15 K), which can be explained by the decomposition of the formamide structure when HMPA is added and intermolecular associates with a weaker bond are formed.

For aqueous solutions of HMPA, the temperature dependence of $C_p{}^E$ is complex. It is known[1] that in the 288.15—298.15 K temperature range, the $dC_p{}^E/dT$ derivative in the whole composition region changes its sign two times. This is associated with the extreme temperature dependence of the heat capacity of neat water in the 288.15—318.15 K range and the negative temperature run of $C_p{}^E$ for pure HMPA, which is observed rather rarely for heat capacities of organic substances. The positive temperature run of the $C_p{}^E$ values is observed for all three mixtures in the composition range studied. The composition dependences of Φ_{Cp2} and $\bar{C}_{p2}$ are presented in Figs. 2 and 3. In the H_2O—HMPA mixture, the $\bar{C}_{p2} = f(X_2)$ dependence at 288.15 K exhibits a maximum in the composition region with $X_2 = 0.02$ molar fractions. A maximum at the same composition of this mixture, but at $T = 298.15$ K, has been observed previously.[12] This extreme is evidence of structural changes in the mixture due to the rearrangement of structures of components and their mutual influence. It is assumed[6] that the presence of the extreme is related to microlamination of the mixture and the existence in the solution of regions with the structure of neat components. No extremes are observed on the $\Phi_{Cp2} = f(X_2)$ dependences published[10,16] for the H_2O—HMPA system; it was concluded that no lamination occurred in this system. As the temperature increases, the value of the maximum decreases, and at 318.15 K, the $\bar{C}_{p2} = f(X_2)$ dependence is monotonically descending (see Fig. 3). A temperature increase results in the destruction of structures of the components of the mixture.

The $\bar{C}_{p2} = f(X_2)$ dependence for the H_2O—DEP mixture is also extreme. In this case, however, the maximum is flattened and situated in the composition range of $0.02 < X_2 < 0.03$ molar fractions of DEP, *i.e.*, the composition range in which the region of possible lamination is observed in this mixture is somewhat broader than in the case of the H_2O—HMPA mixture. As the temperature increases, the height of the maxima decreases. In this system, they are observed at 318.15 K as well, which indicates that this structure is retained at higher temperatures, as compared to aqueous solutions of HMPA. There are no grounds for drawing conclusions about the micelle formation in these mixtures, since HMPA and DEP are not surfactants.

It is too early to draw conclusions about similar structures of formamide solutions of HMPA from the behavior of the dependences of Φ_{Cp2} and $\bar{C}_{p2}$, because this system is insufficiently studied. The values of apparent and partial molar heat capacities in the FA—HMPA mixture increase as the HMPA content increases. An insignificant maximum is observed on the $\bar{C}_{p2} = f(X_2)$ curve at X_2 = 0.01 molar fractions of HMPA. Perhaps, this system also contains regions where structures of neat components exist; however, this is observed at a lower concentration of HMPA than in the case of its aqueous solution. As the temperature increases, the Φ_{Cp2} and $\bar{C}_{p2}$ values increase.

The possibility of existence of the regions of structures of neat components at a low content of the dissolved substance in the mixture is determined by the properties of the dissolved substance (strongly hydrophobic or surfactant) and the properties of the solvent as well. For this purpose, the solvent should contain a highly organized structure (most likely, due to H bonds). For non-associated solvents or solvents associated according to the type of universal interactions, for example, for the acetonitrile—HMPA system, the $\bar{C}_{p2} = f(X_2)$ dependences are monotonic.[17]

Analysis of the experimental data allowed researchers[6] to conclude that the extreme character of the $\bar{C}_{p2} = f(X_2)$ and $\Phi_{Cp2} = f(X_2)$ functions for binary mixtures at low concentrations of the dissolved substance is not related to the lamination regions. It has been concluded[10] that the existence of a maximum on such curves for aqueous solutions of substances is the result of the pair interaction (C_{22}) and the fact that for the majority of hydrophobic substances, the heat capacity coefficient of triple interactions (C_{222}) is positive. The heat capacity characteristics of the systems under study calculated from the experimental data are presented in Table 2. The C_{22} and C_{222} coefficients were calculated in terms of the McMillan—Mayer theory using the equation

$$\Phi_{Cp2} = \bar{C}^0{}_{p2} + C_{22}\cdot m + C_{222}\cdot m^2, \qquad (4)$$

where m is the molar concentration of the dissolved substance (mol kg^{-1} of solvent).

It is seen from the data in Table 2 that the C_{22} coefficients for aqueous solutions of HMPA and DEP are negative and decrease with a temperature increase, and C_{222} are positive and also decrease with a temperature increase. These changes in the coefficients are characteristic of the majority of aqueous solutions of hydrophobic substances.[10] At $T \leq 298.15$ K, the appearance of a maximum on the $\bar{C}_{p2} = f(X_2)$ curve is related[10] first of all to different signs of coefficients of pair and triple interactions and, correspondingly, to their different contributions to the $\bar{C}_{p2}$ value. When the temperature increases, the decrease in the height of maxima and their shift to lower X_2 values are related to the increase in the negative C_{22} values and the decrease in the positive values of C_{222}, as well as, probably, a change in their sign (see Fig. 3, H_2O—HMPA system, T = 318.15 K).

Table 2. Heat capacity characteristics of binary mixtures at different temperatures

T/K	$\bar{C}^0{}_{p2}$[a]	$C^0{}_{p2}$[b]	$\Delta C^0{}_{p2}$[c]	C_{22}[d]	C_{222}[e]
	J mol^{-1} K^{-1}				
			H_2O—HMPA		
288.15	682.6	324.8	357.8	−41.5	9.62
298.15	698.0	321.7	376.3	−46.9	3.99
308.15	761.9	317.7	444.2	−51.5	2.72
318.15	818.8	314.2	504.6	−58.5	1.63
			H_2O—DEP		
288.15	404.5	279.4	125.1	−1.05	0.62
298.15	444.7	283.6	161.1	−1.17	0.43
308.15	502.0	288.0	214.0	−2.53	0.16
318.15	557.2	292.6	264.6	−3.34	0.08
			FA—HMPA		
288.15	243.8	324.8	−81.0	3.52	−0.41
298.15	278.8	321.7	−42.9	2.86	−0.12
308.15	304.2	317.7	−13.5	1.20	0.37
318.15	318.3	314.2	4.1	0.26	1.64

[a] $\bar{C}^0{}_{p2}$ is the partial molar heat capacity of the dissolved substance at infinite dilution.

[b] $C^0{}_{p2}$ is the molar heat capacity of the neat substance.

[c] $\Delta C^0{}_{p2} = \bar{C}^0{}_{p2} - C^0{}_{p2}$ (the change in heat capacity upon dilution).

[d] C_{22} is the heat capacity coefficient of pair interaction (J kg mol^{-2} K^{-1}).

[e] C_{222} is the heat capacity coefficient of triple interaction (J kg^2 mol^{-3} K^{-1}).

The C_{22} and C_{222} coefficients in the FA—HMPA system, as in many non-aqueous mixtures, have the same order but opposite signs to the corresponding coefficients for aqueous solutions of HMPA. When the temperature increases, the C_{22} values decrease as in water, and the C_{222} values increase, unlike those for aqueous solutions. For this system, it is difficult to explain the behavior of the $\bar{C}_{p2} = f(X_2)$ functions by the signs of the corresponding coefficients. The $\Delta C^0{}_{p2}$ value, which along with $\bar{C}^0{}_{p2}$ is one of the criteria of hydrophobicity,[18] is negative in this mixture, which, by analogy to aqueous solutions, indicates the hydrophilic character of the dissolved substance. Strictly speaking, it is invalid to extend the criteria used for aqueous solutions to non-aqueous systems. However, it is difficult to find other procedures and methods of analysis of thermodynamic parameters of non-aqueous solutions.

The results presented show that the extreme character of the $\bar{C}_{p2} = f(X_2)$ dependences can hardly be interpreted unambiguously. In our opinion, this behavior of thermodynamic functions is related to the formation by the dissolved substance (if it is not a surfactant) of a set of solvates (hydrates) with large sizes of the solvate (hydrate) shell and their transformations. In the case of strongly hydrophobic substances, the formation of the hydrophobic sphere plays an important role. It is associated with the ability of water to choose the optimum geometry of arrangement of molecules as applied to the individual characteristics of the molecule of the dissolved substance.[19]

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33642a).

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Received October 27, 1997;
in revised form February 17, 1998