THE INVESTIGATION OF THE STABILIZATION OF THE STRUCTURE OF AQUEOUS SOLUTIONS OF HEXAMETHYLPHOSPHORTRIAMIDE USING AN ACOUSTIC METHOD

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Measurements of the density and of ultrasonic velocity at a frequency of 15 MHz in aqueous solutions of hexamethylphosphortriamide (HMPT) over the temperature range 283.15-323.15 K for the whole concentration range are reported. On the basis of the quantities measured, the adiabatic compressibility, the deviation of the molar volume of the solution from the additive volume, the partial molar volumes and partial molar compressibilities of the components have been calculated.

The sharp extremes of the ultrasonic velocity, the adiabatic compressibility, the excess compressibility and the partial molar volumes occurring in the range of low concentrations of HMPT $(0.04(323.15 \text{ K})-0.07(283.15 \text{ K})$ molar fraction) can be attributed to the stabilization of the structure of water in the solution in consequence of the growth of clathrate structures of composition $8X \cdot 136 \text{ H}_2\text{O}$. The variations of the dependence of the partial molar compressibilities of the components on the concentration indicate a strong intramolecular interaction between the components in a solution, and in particular, over the range of low HMPT concentrations.

1. Introduction

Many papers [4, 8-10] have reported investigations of the phenomenon of the stabilization of water by dissolving molecules of non-electrolytes in it. This phenomenon lies in a decrease of the thermal agitation of the molecules and the formation of intromolecular bonds in the water, while non-electrolyte additives act on the mutual ordering of the water molecules in the same way as a decrease in temperature. The efficiency of the additives in stabilizing the structure of the water and the mechanism of their action is conditioned by the structure of the molecules of the non-electrolytes. The stabilization of the structure can be observed in the region of relatively low concentrations of the non-aqueous component: $x_2 < 0.3$ molar fraction.

The phenomenon of structure stabilization, which occurs in the solution as a result of mutual intermolecular interaction, gives rise to extrema in many physical quantities as functions of concentration.

A characteristic feature of the aqueous solutions of non-electrolytes is, among other things, the occurrence of a maximum in the ultrasonic velocity and a minimum in the adiabatic compressibility as functions of concentration. The non-electrolytes, which show this type of behaviour in their aqueous solutions, include amines (ethyldiamine and benzoamine [11], acetic acid and dioxane [1]). A maximum in the propagation velocity of ultrasonic waves has also been observed in aqueous solutions of tetrahydrofran, 1,4-dioxane and t-butyl alcohol over the concentration range 0.03 - 0.08 mole fraction [2]. The position of the maximum is attributed to the formation of structures composed of stable threedimensional clathrate compounds of 17 hydrates, i.e. $8X \cdot 136H_2O$ (X is a non-electrolyte molecule).

CHEKALIN and SHAKHPARONOV [5], on the basis of the results of the measurements of the ultrasonic velocity and of radiospectroscopic investigations, showed that the dissolving of non-electrolyte molecules in water is accompanied by a change in the composition of the hydrogen bonds between the water molecules. The clathrate compounds form themselves in a similar way to the clathrate compounds in the hydrates of ice. In the voids of these compounds there are molecules of the nonelectrolyte. This causes a decrease in the compressibility, an increase in the viscosity, and in the ultrasonic velocity etc.

However, the occurrence of a maximum in the ultrasonic velocity in solutions is not always attributed to the formation of spatial structures. The maxima that occur in the ultrasonic velocity at a concentration of approximately 0.2 molar fraction in aqueous solutions of N-methylformamide, N,N-dimethyl-formamide and N,N-dimethylacetamide were attributed by KAWAIZUMI, OHNO and MIYAHARA [13] to the formation in the solution of unbounded compounds, with the position of the maximum velocity showing the type of these compounds.

The present paper attempts, on the basis of the results of the measurements of the ultrasonic velocity in, and the density of the medium, to determine the type of structure stabilization that occurs in aqueous solutions of hexamethyl-phosphortriamide (HMPT), a compound belonging to the group of weakly associated liquids.

2. The properties of hexamethylphosphortriamide ($[N(CH_3)_2]_3PO$) and its aqueous solutions

The hexamethyltriamide of orthophosphoric acid (HMPT) is a liquid of unstable structure [14]. The structure of the liquid HMPT is characterized by a small association (there is free rotation of the molecules, and HMPT has a relatively low packing coefficient $\psi = 0.51$). However, the possibility of the existence of associates with very short lifetimes cannot be excluded. The cha-

racter of the association is different from the association occurring in water. The packing of molecules in the liquid is not dense, and its character changes relatively easily with temperature ($-dln\varrho/dT = 8.82 \cdot 10^{-4}$ deg^{-1}, where ϱ is the density and T is the temperature).

On the basis of measurements of dielectric relaxation [7] and the proton spin — lattice relaxation [14], the following conclusions were drawn in relation to the structural changes occurring with the solution of HMPT molecules in water:

— the methyl HMPT groups exist in the voids of the structure of the water without noticeably reconstructing it;

— with concentrations of HMPT up to 0.1 molar fraction, the structure of the water is relatively weakly affected, and the process of its destruction increases with a concentration of 0.5 molar fraction;

— water weakly affects the HMPT structure;

— for small amounts of solute, the HMPT molecules, which form hydrogen bonds with the water through the oxygen beside the phosphorus, do not destroy the lattice of hydrogen bonds; in

— the stability of the structure of the solution over a concentration range of 0-0.15 molar fraction of HMPT is much greater than that for pure water.

The results of the investigation of the properties of the HMPT water solutions reported in [7, 14] do not, however, give an unambiguous answer to the question of the character of the intermolecular interactions, particularly for low concentration of HMPT. It is therefore useful to conduct additional investigations using the methods of molecular acoustics.

3. The method of investigation

The measurements of the ultrasonic velocity in aqueous solutions of hexamethylphosphartriamide were performed with a pulse — phase interferometer at a frequency of 15 MHz. The measurement error did not exceed 0.1%. The medium investigated was thermostabilized with a precision of 0.05 K, while the temperature measurements were performed using copper — constantan thermocouple connected with a digital voltmeter, permitting the temperature to be read with a precision of 0.025 K. The measurements of density were performed by the pycnometric method with a precision of 0.02%. The p.f. brand HMPT of West German production and double distilled water were used in the investigations.

The ultrasonic velocity and the density of the medium. The experimental results of the measurements of the density of the medium and of the ultrasonic velocity in aqueous solutions of HMPT as functions of concentration and temperature are shown in Table 1, while. Fig. 1 shows the temperature dependence of the ultrasonic velocity for individual concentrations. It follows from these

Table 1. The measured results of the ultrasonic velocity and density in aqueous solutions of hexamethylphosphortriamide

x_2 [molar fraction]	t [K] 283.15		293.15		303.15		313.15		323.15	
	ϱ $\left[\dfrac{10^3\,\mathrm{kg}}{\mathrm{m}^3}\right]$	v [m·s^{-1}]	ϱ $\left[\dfrac{10^3\,\mathrm{kg}}{\mathrm{m}^3}\right]$	v [m·s^{-1}]	ϱ $\left[\dfrac{10^3\,\mathrm{kg}}{\mathrm{m}^3}\right]$	v [m·s^{-1}]	ϱ $\left[\dfrac{10^3\,\mathrm{kg}}{\mathrm{m}^3}\right]$	v [m·s^{-1}]	ϱ $\left[\dfrac{10^3\,\mathrm{kg}}{\mathrm{m}^3}\right]$	v [m·s^{-1}]
0.000	0.9997	1448	0.9982	1483	0.9957	1510	0.9922	1529	0.9881	1542
0.005	1.0038	1490	1.0020	1520	0.9992	1540	0.9954	1555	0.9910	1566
0.020	1.0165	1608	1.0133	1611	1.0095	1612	1.0050	1611	0.9999	1604
0.050	1.0383	1714	1.0326	1692	1.0261	1670	1.0194	1646	1.0127	1619
0.100	1.0559	1707	1.0479	1675	1.0398	1642	1.0314	1606	1.0230	1566
0.125	1.0589	1686	1.0504	1650	1.0420	1616	1.0335	1580	1.0248	1545
0.150	1.0606	1662	1.0521	1627	1.0431	1592	1.0342	1557	1.0253	1520
0.200	1.0605	1618	1.0515	1581	1.0426	1547	1.0334	1511	1.0244	1471
0.275	1.0574	1566	1.0485	1531	1.0394	1495	1.0304	1459	1.0213	1424
0.492	1.0490	1476	1.0400	1440	1.0310	1405	1.0220	1369	1.0130	1331
0.691	1.0430	1433	1.0342	1390	1.0255	1357	1.0169	1320	1.0082	1290
1.000	1.0365	1385	1.0282	1350	1.0201	1312	1.0120	1274	1.0038	1242

dependencies that for concentration $x_2 = 0.005$ molar fraction (curve 2) the character of the change is similar to that for water, while for a concentration of 0.02 molar fraction (curve 3) the velocity is, over a certain temperature range, independent of temperature. For concentrations above 0.02 molar fraction, the character of the variation is analogous to that for pure water, which indicates a destruction of the previous structure of water (i.e. the hydrogen bonds between the water molecules have changed their distribution).
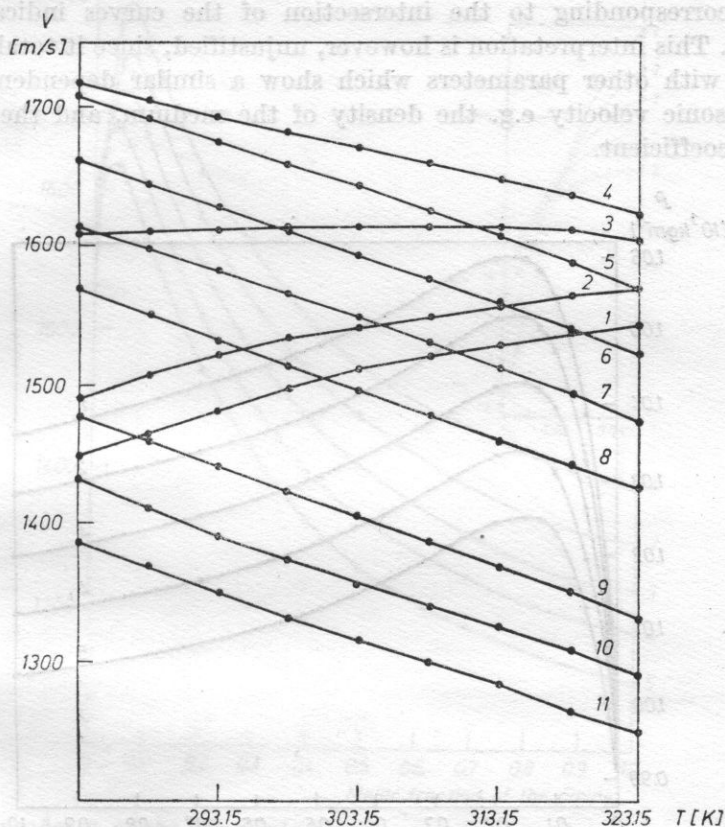
Fig. 1. The dependence of the ultrasonic velocity on temperature in aqueous solutions of HMPT

curves 1-11 corespond to concentrations of 0.000, 0.005, 0.020, 0.050, 0.100, 0.150, 0.200, 0.275, 0.492, 0.691, 1.000 molar fraction of amide

Figs. 2 and 3 show respectively the concentration dependencies of the density of the medium and the ultrasonic velocity. For both the density of the medium and ultrasonic velocity a maximum occurs at a well defined compositions of the solution. (The maximum density occurs for $x_2 \cong 0.15$ molar fraction; while a sharp maximum in the velocity occurs over the concentration range 0.04 (323.15 K)-0.07 (283.15 K) molar fraction of amide.) With an increase in the temperature this maximum thus shifts towards lower concentrations of HMPT, as for aqueous solutions of alcohols [16]. The point of intersection of

the two curves of the velocity at the different temperatures occurs for a concentration $x_2 = 0.021$ molar fraction; and the velocity does not depend on temperature (in the temperature range 283.15 - 313.15 K).

The phenomenon of the intersection of the curves of the ultrasonic velocity as a function of concentration, can be observed in many aqueous solutions of non-electrolytes [6, 16]. ENDO [6] interprets the occurrence of this phenomenon as the formation in the solution of clathrate compounds, with the concentration corresponding to the intersection of the curves indicating their composition. This interpretation is however, unjustified, since it totally neglects comparison with other parameters which show a similar dependence to that of the ultrasonic velocity e.g. the density of the medium, and the ultrasonic absorption coefficient.
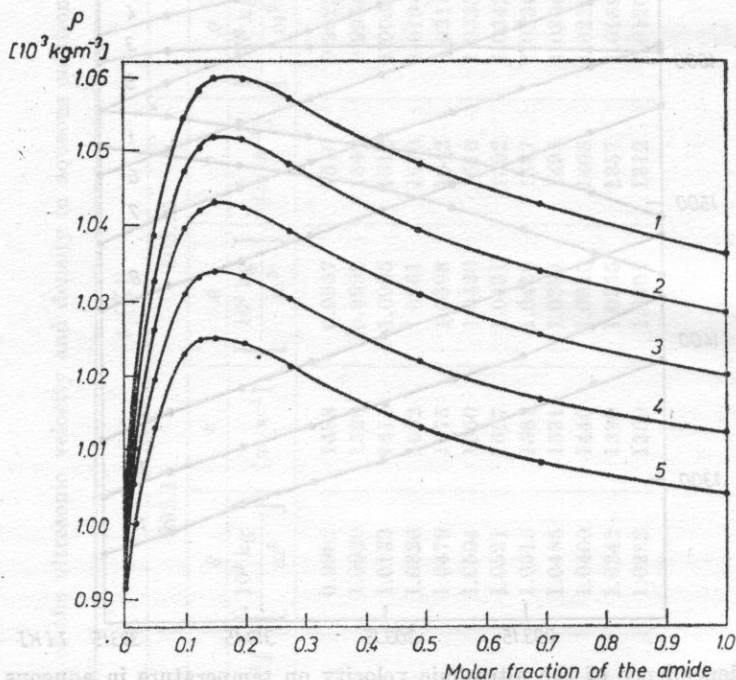

Fig. 2. The concentration dependence of the density in aqueous solutions of HMPT
curves *1-5* correspond to temperatures of 283.15, 293.15, 303.15, 313.15, 323.15 K

Adiabatic compressibility and the excess compressibility of solutions. On the basis of the measured values of the ultrasonic velocity in, and the density of the medium, the adiabatic compressibility of the solutions β_s was calculated. Two facts should be noted in the analysis of the concentration dependence of β_s shown in Fig. 4; the occurrence of the minimum; and the point of the intersection of the curves, which is independent of time. The former corresponds with the occurrence of the maxima in the ultrasonic velocity and in the density;

while the latter, corresponds with the occurrence of the intersection of the curves of ultrasonic velocity at different temperatures. The minimum in the adiabatic compressibility in aqueous solutions of HMPT (Fig. 4) occurs over the same concentration range as the maximum velocity (Fig. 3).
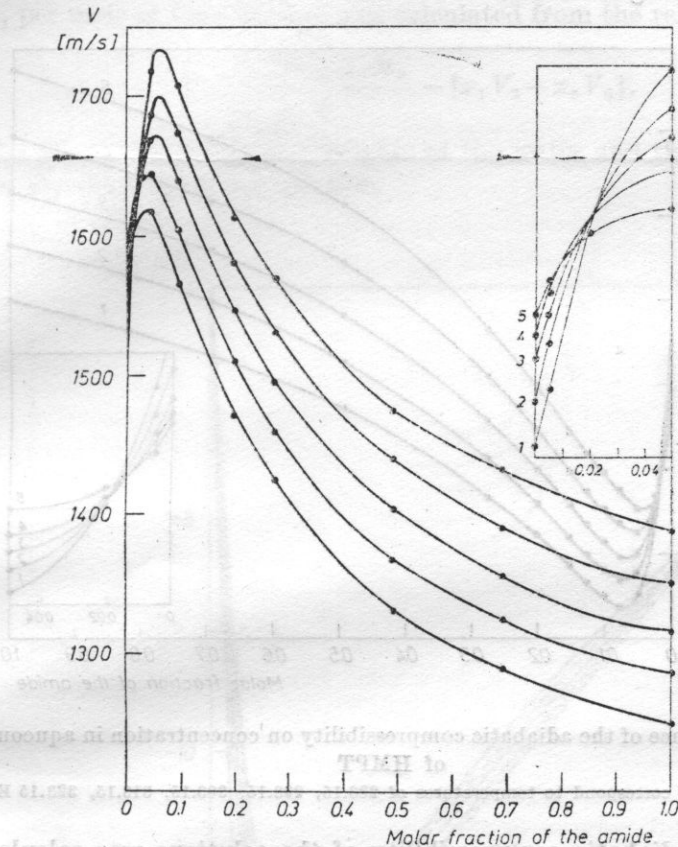

Fig. 3. The dependence of the ultrasonic velocity on concentratio in aqueous solutions of HMPT

curves 1-5 correspond to temperatures of 283.15, 293.15, 303.15, 313.15, 323.15 K

The sharp extrema of the adiabatic compressibility and the ultrasonic velocity occurring over the concentration ranges of 0.04 (323.15 K)-0.07 (283.15 K) molar fraction indicate that the greatest structural stability is achieved over this concentration range. It is thus most likely that the clathrate compounds $8X \cdot 136H_2O$ will form in the solution, where the molecules of HMPT enter the voids of the hexadecahedra formed by the water molecules. The formation of the clathrate compounds causes a decrease in the adiabatic compressibility and an increase in the ultrasonic velocity in the solution, which proceeds until the voids are totally filled. Further increase in the compressibility is conditioned by the occurrence in the solution of additional molecules of amide,

which do not enter the voids of the clathrate compounds. The destruction of the clathrate compounds is indicated by the occurrence for $x_2 \cong 0.15$ molar fraction of a maximum in the density of the medium, where the structure is most densely packed, and for which the water molecules are linked to the amide molecules by hydrogene bonds.
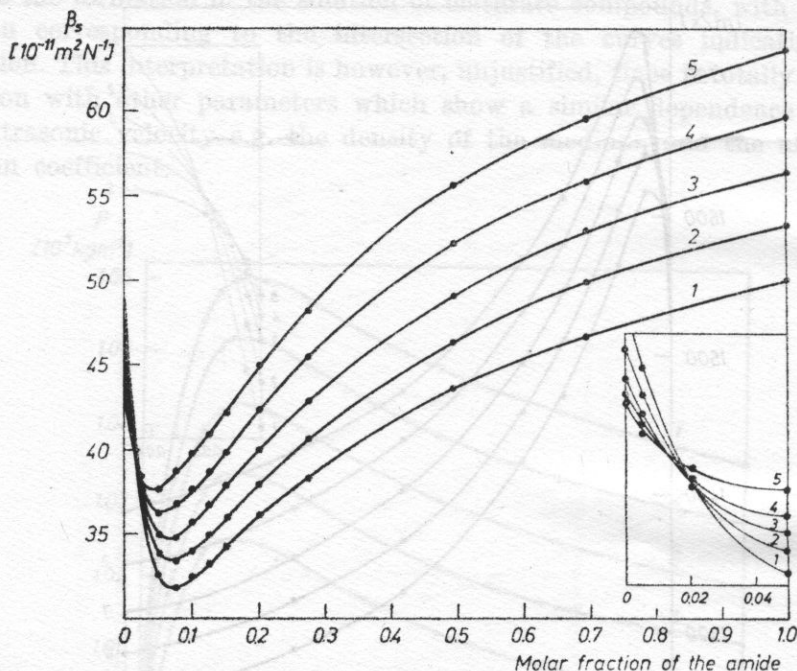

Fig. 4. The dependence of the adiabatic compressibility on concentration in aqueous solutions of HMPT

curves 1-5 correspond to temperatures of 283.15, 293.15, 303.15, 313.15, 323.15 K

The excess adiabatic compressibility of the solutions was calculated from relation

$$\beta_s^D = \beta_s - \frac{1}{V}\,[x_1 V_1 \beta_{s,1} + x_2 V_2 \beta_{s,2}], \tag{1}$$

where x_1, x_2 are the molar fractions of water and amide respectively; $V = x_1 V_1 + x_2 V_2$ is the volume of a mole of the solution calculated in an additive manner; V_1, V_2 are the molar volumes of water and amide, respectively; $\beta_{s,1}, \beta_{s,2}$ respectively, the adiabatic compressibilities of the water and the amide.

It follows from the results shown in Fig. 5 that the values of β_s^D are always negative, i.e. the β_s are lower than those of the compressibility calculated in an additive manner. The solution of HMPT in water causes a decrease in the excess compressibility of the solution to a particular concentration

(0.07 (283.15 K) - 0.125 (323.15 K) molar fraction, beyond which further addition of the amide causes an increase.

The additional molar volume of the solutions and the partial molar volumes of the components in the solution. The change in the volume of the solution prepared, per mole of the solution, was calculated from the relation

$$\Delta V = \frac{x_1 M_1 + x_2 M_2}{\varrho} - [x_1 V_1 + x_2 V_2], \qquad (2)$$

where M_1, M_2 are the molecular weights of the water and the amide, respectively; ϱ is the density of the solution.
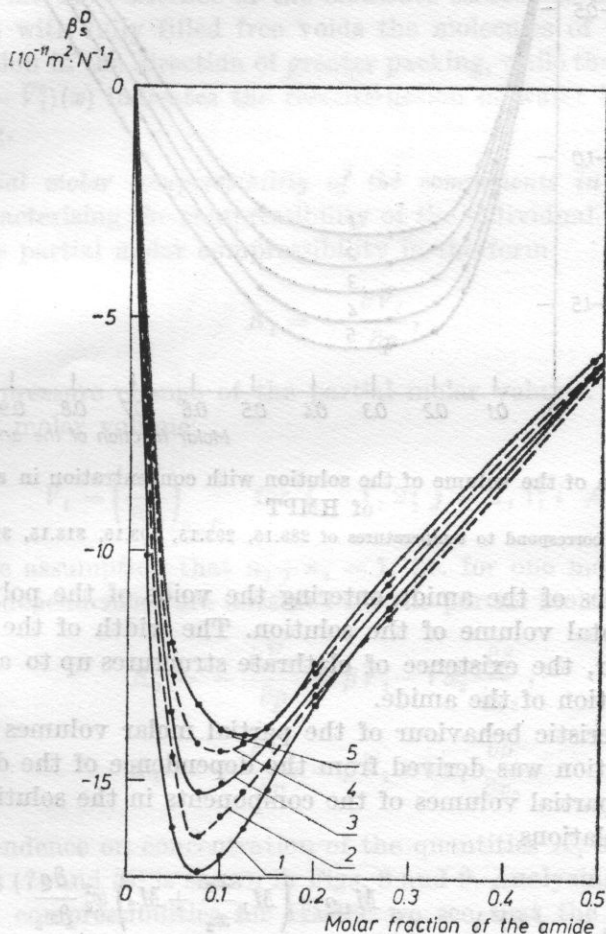

Fig. 5. The dependence of the excess adiabatic compressibility on concentration in aqueous solutions of HMPT

curves 1-5 correspond to temperatures of 283.15, 293.15, 303.15, 313.15, 323.15 K

The deviation of the volume of the solution from the simple additive volume as a function of concentration is shown in Fig. 6. A decrease in the

volume of the solution, which takes its extreme value over the concentration range 0.2-0.5 molar fraction, can be observed for the whole concentration range. A decrease in the molar volume of the solution accompanying the solution of the amide in water also confirms the formation of the clathrate structures,
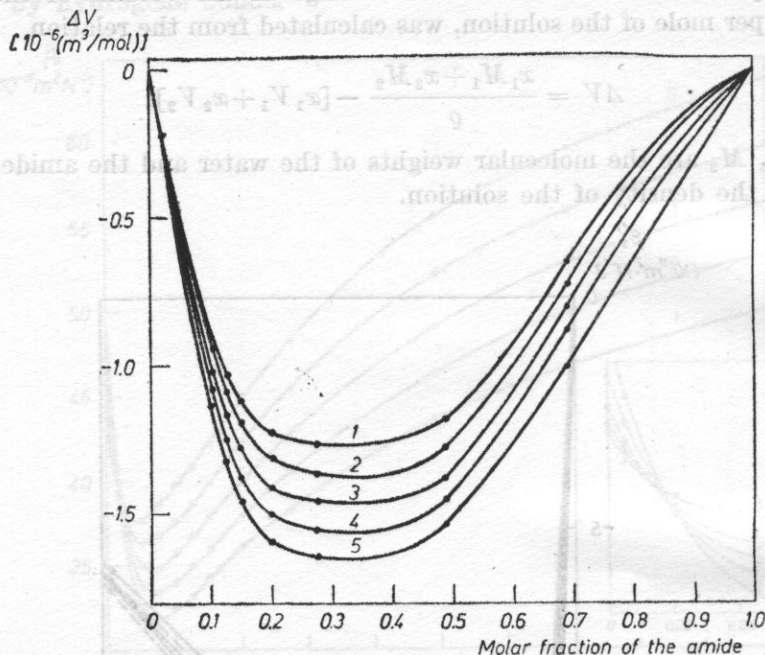

Fig. 6. The variation of the volume of the solution with concentration in aqueous solutions of HMPT

curves *1-5* correspond to temperatures of 283.15, 293.15, 303.15, 313.15, 323.15 K

with the molecules of the amide entering the voids of the polyhedrons, thus decreasing the total volume of the solution. The width of the minimum ΔV suggests, however, the existence of clathrate structures up to a concentration of 0.5 molar fraction of the amide.

The characteristic behaviour of the partial molar volumes of the components in the solution was derived from the dependence of the density on concentration. The partial volumes of the components in the solution were calculated from the relations

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2, T} = \frac{M_1\varrho + \left(M_1\dfrac{x_1}{x_2} + M_2\right)x_2^2\dfrac{\partial\varrho}{\partial x_2}}{\varrho^2}, \tag{3}$$

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1, T} = \frac{M_2 - \left(M_1 + \dfrac{x_2}{x_1}M_2\right)x_1^2\dfrac{\partial\varrho}{\partial x_2}}{\varrho^2}, \tag{4}$$

while Fig. 7 shows the dependence on concentration of the difference of the molar volumes of the components in the solution (V_1 and V_2) and the molar volumes for an infinite dilution ($\overline{V}_1^0$ and $\overline{V}_2$). It follows from the curves that a decrease in the molar volume of the amide occurs in the solution, reaching its extreme value for $x_2 \cong 0.05$ molar fraction, beyond which it rapidly increases up to a concentration of 0.2 molar fraction. Contrary to the behaviour of the molar volume of HMPT in the solution, an increase in the molar volume occurs at a concentration of 0.05 molar fraction.

The character of the curves for the aqueous solutions of HMPT shown in Fig. 7 is analogous to that of the aqueous solutions of alcohols [15] and amines [12]. The sharp minimum of the function $(\overline{V}_2 - \overline{V}_2^0)(x)$ for $x_2 = 0.05$ molar fraction confirms the existence of the clathrate structures in the solution and indicates that with fully filled free voids the molecules of the amide change their distribution in the direction of greater packing, while the maximum of the function $(\overline{V}_1 - \overline{V}_1^0)(x)$ indicates the reconstruction of water in the direction of lower packing.

The partial molar compressibility of the components in the solution. The quantity characterizing the compressibility of the individual components in the solution is the partial molar compressibility in the form

$$K_i = -\frac{\partial \overline{V}_i}{\partial p}, \qquad (5)$$

which is the pressure change of the partial molar volume. By differentiation of the partial molar volume

$$\overline{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{n_j, T} \quad \text{for } i = 1, 2; \; j = 2, 1; \; i \neq j, \qquad (6)$$

and under the assumption that $n_1 + n_2 = 1$, i.e. for one mole of the solution, the following dependencies are obtained for the partial molar compressibilities:

$$K_1 = -\frac{\partial \overline{V}_1}{\partial p} \equiv \beta \overline{V}_1 - V x_2 \frac{\partial \beta}{\partial x_2}, \qquad (7)$$

$$K_2 = -\frac{\partial \overline{V}_2}{\partial p} = \beta \overline{V}_2 + V x_1 \frac{\partial \beta}{\partial x_2}. \qquad (8)$$

The dependence on concentration of the quantities K_1 and K_2 determined from relations (7) and (8) is shown in Figs. 8 and 9. Analyzing the curve for the partial molar compressibilities for HMPT we see that the compressibility of an amide molecule in the solution is low for dilute solutions (Fig. 9), with a subsequent increase up to an concentration of 0.075 molar fraction. There is a characteristic point of inflexion at a concentration of 0.05 molar fraction, beyond which the increase in K_2 is very rapid. Contrary to the behaviour of the adiabatic
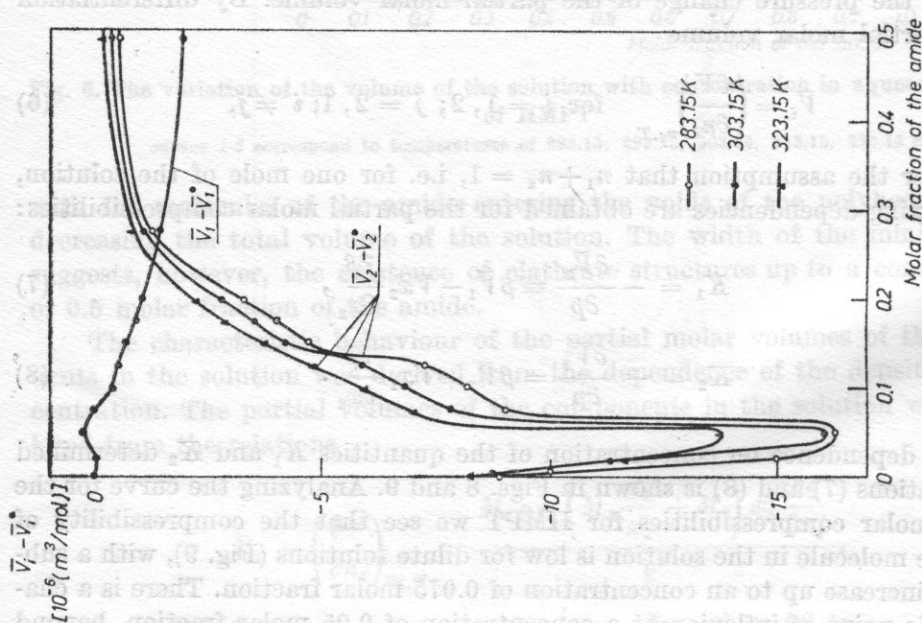
while Fig. 7 shows the dependence on concentration of the difference of the molar volumes of the components in the solution $(\bar{V}_1 - \bar{V}_1^0)$ and $(\bar{V}_2 - \bar{V}_2^0)$. It follows from the curves that a change in the molar volume of the amide occurs in the region reaching its extreme value x_a, ≈ 0.05 molar fraction, beyond which it rapidly increases up to a concentration of 0.3 molar fraction. Contrary to the behaviour of the molar volume of HMPT in the solution, an increase in the molar volume occurs at a concentration of 0.05 molar fraction.

The character of the curves for the aqueous solutions of HMPT shown in Fig. 7 is analogous to that of the aqueous solutions of alcohols [15] and amines [ ]. The sharp minimum of the function $(\bar{V}_2 - \bar{V}_2^0)(x)$ for $x_a = 0.05$ molar fraction confirms the existence of the clathrate structures in the solution and indicates that with fully free voids filled the molecules of the amide change their distribution in the direction of greater packing. While the maximum of the function $(\bar{V}_1 - \bar{V}_1^0)(x)$ indicates the reconstruction of water in the direction of lower packing.

The partial molar compressibility of the components in the solution. The quantity characterizing the compressibility of the individual components in the solution is the partial molar compressibility in the form

$$\bar{K}_i = -\frac{\partial \bar{V}_i}{\partial p},$$ (5)

which is the pressure change of the partial molar volume. By differentiation of the partial molar volume:

$$\frac{1}{n_i RT} K_T^0; \; \; \bar{V}_i^0; \; \; \text{if } i = 2, \text{ if } i = \bar{V}_i$$

under the assumption that $n_i + n_w = 1$, i.e. for one mole of the solution, the pressure dependence we obtain for the partial molar compressibility:

$$\bar{K}_i = -\frac{\partial \bar{V}_i}{\partial p}$$

The characteristic behaviour of the partial molar volumes of the amide results in the solution is connected with the dependence of the density on the concentration. The partial volumes of the components in the solution were determined. The dependence on concentration of the quantities $\bar{K}_i^0$ and $\bar{K}_2^0$ determined from the densities (μ_i^0) is shown in Figs. 7 and 8. Analyzing the curve of the partial molar compressibility for HMPT, we see that the compressibility of the amide molecule in the solution is low for dilute solutions (Fig. 7), with a slight increase up to an concentration of 0.075 molar fraction. There is a characteristic point of inflexion at a concentration of 0.06 molar fraction, beyond which the increase in $\bar{K}_i$ is very rapid. Contrary to the behaviour of the adiabatic

Fig. 8. The variation of the partial adiabatic compressibility of water with concentration in aqueous solutions of HMPT

Fig. 7. The variation of the partial molar volumes $(\bar{V}_1 - \bar{V}_1^0)$ of the water and $(\bar{V}_2 - \bar{V}_2^0)$ of the amide as functions of concentration in aqueous solution of HMPT
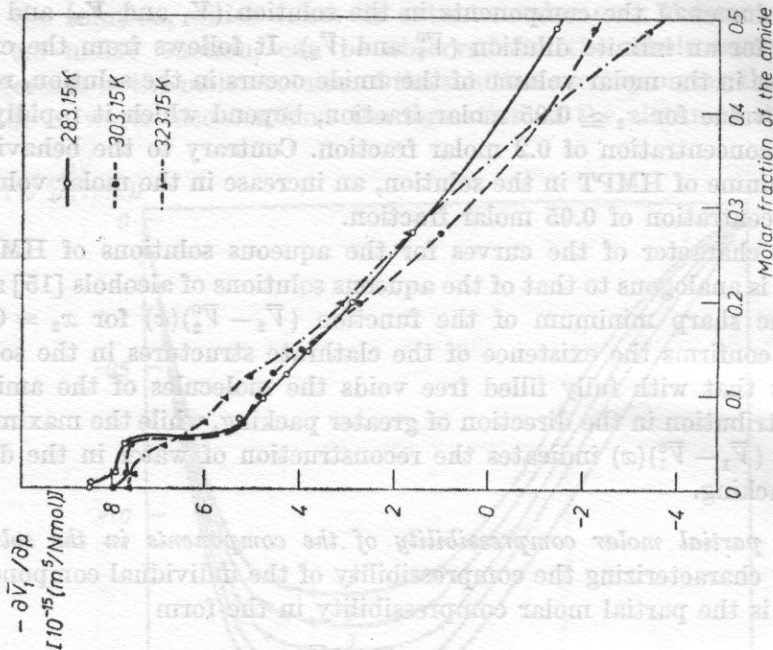
compressibility of the amide in the solution, the partial molar compressibility
of the water, K_1, decreases with increasing concentration of the amide (Fig. 8).
Up to a concentration of 0.05 molar fraction, K_1 is almost independent of con-
centration, and subsequently decreases rapidly up to a concentration of 0.075
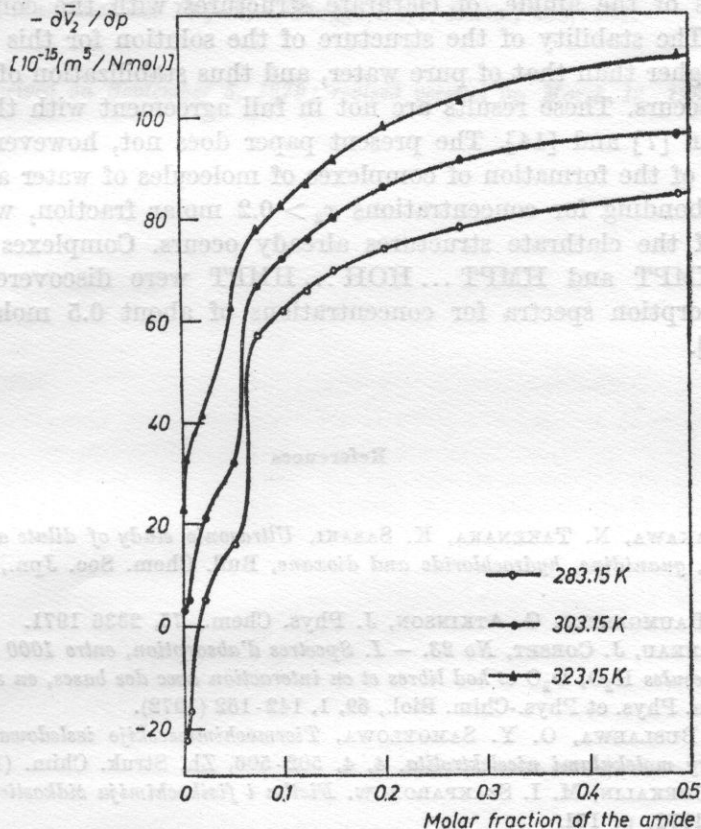

Fig. 9. The variation of the partial adiabatic compressibility of the amide with concentration
in aqueous solutions of HMPT

molar fraction. The decrease in the compressibility of water for $x_2 \cong 0.02$ is
caused by the lower compressibility of the clathrate structures, while the sta-
bility of K_1 over the range 0.02 - 0.05 molar fraction indicates that the mole-
cules of HMPT enter the voids formed by the clathrate structure of water.
The occurrence of additional amide molecules, which do not enter the voids
of the clathrate compounds caused an increase in K_2 and a decrease in the com-
pressibility of the water, K_1. The relationship of $K_1(x)$ and $K_2(x)$ indicates
a strong intermolecular interaction between the components in the solution,
particularly over the lower range of concentrations.

5. Final conclusions

Ultrasonic and volumetric investigations of the structure of aqueous solutions of hexamethylphosphortriamide indicate the occurrence, at low concentrations of the amide, of clathrate structures with the composition $8X \cdot 136H_2O$. The stability of the structure of the solution for this concentration is much higher than that of pure water, and thus stabilization of the structure of water occurs. These results are not in full agreement with the conclusions proposed in [7] and [14]. The present paper does not, however, exclude the possibility of the formation of complexes of molecules of water and HMPT by hydrogen bonding for concentrations $x_2 > 0.2$ molar fraction, where the destruction of the clathrate structures already occurs. Complexes of the types HOH ... HMPT and HMPT ... HOH ... HMPT were discovered in the infrared absorption spectra for concentrations of about 0.5 molar fraction of HMPT [3].

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