Solvent isotope effects on the solubility of argon and pair interactions in aqueous solution of hexamethylenetetramine

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The solubilities of gaseous argon in solutions of hexamethylenetetramine (hmta) in H_2O and D_2O were measured at different concentrations, at five temperatures in the range of 283—318 K, and at a partial gas pressure of 101325 Pa by microvolumetry with an accuracy of ≤0.3%. The standard Setchenov coefficients for argon solutions and the thermodynamic parameters of Ar—hmta pairwise interactions were calculated from the data on the solubility. Interactions between hydrated Ar and hmta molecules are characterized by mutual repulsions. The structural states of water in the hydration sphere of hmta and in the bulk of solution are substantially different. Due to the difference in the mechanisms of hydration of hmta and Ar, the addition of the first component leads to a decrease in the solubility of the second component.

Key words: hexamethylenetetramine, argon, solubility, isotope effects, Setchenov coefficients, pair-interaction coefficients.

Dilute solutions of nonpolar gases are of considerable interest as model systems whose parameters vary over a wide range and which can be used for quantitative estimation of structural contributions to the thermodynamic functions of hydration. It is also well known that data on the effect of isotope substitution on the solubility are informative from the viewpoint of studies of the structures of solvents and solutions.[1—5]

Investigations of solutions in which solute—solvent interactions substantially dominate over interactions between molecules of the solute are of particular importance for elucidating the nature of pair interactions in liquid systems containing hydrogen bonds. This difference in interactions is rather clearly manifested in aqueous solution of hexamethylenetetramine (hmta).[4] The hmta molecule has a perfect tetrahedral symmetry, is almost spherical in shape, and contains four centers accessible for hydrogen bonding with water molecules in the liquid state.[5] However, hmta molecules cannot form H bonds with each other due to the absence of proton-donor centers.

Studies of the properties of aqueous solutions of hmta are few in number.[4—8] The majority of studies were carried out at standard temperature, which is, apparently, one of the reasons for contradictory interpretations of the results. Based on precision data on the densities of hmta solutions in heavy and usual water at different temperatures and concentrations, the volume characteristics of hmta—water systems have been calculated.[4] Then the virial coefficients of the pairwise interactions of hmta molecules and the attraction and repulsion contributions to the Kirkwood—Baff integrals, which describe the solute—solvent and solute—dissolved compound interactions, were calculated. It was found that the attraction contribution is positive in sign and hmta molecules in solutions experience mutual repulsion. Hydration of hmta molecules increases as the temperature increases. The use of heavy water instead of usual water has the same effect.

The solubility of nonpolar gas and the thermodynamic parameters of dissolution are directly related to the structural state of the solvent and of the solution as a whole. Hence, it was of interest to measure the solubility of argon in solutions of hmta in H_2O and D_2O at different concentrations at 283—318 K.

Experimental

Argon (hereinafter A1) of high-purity grade containing 99.996 mol.% of the major component was used. Water with the natural isotope composition (L_H) was purified by deionization and double distillation using a Pyrex apparatus with the addition of $KMnO_4$ in the course of the first distillation. The conductivity of water purified according to this procedure was $\sim 2 \cdot 10^{-6}$ S cm^{-1}. In the heavy water (L_D), the deuterium content was 99.81±0.02 at.% and the conductivity was $\sim 1 \cdot 10^{-6}$ S cm^{-1}. Hexamethylenetetramine (A2) of analytical grade was purified by repeated crystallization (three times) from an aqueous solution with the use of acetone (high-purity grade)

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as a precipitating agent. Then A2 was dried *in vacuo* at 333 K for 24 h and stored in a vacuum desiccator over P_2O_5. The solutions were prepared from the deaerated components by the weight method. In the case of solutions in D_2O, a "dry" box was used. The concentration of hmta was varied over a range of 0.02—2.5 solvomolality units.* The solubility was measured by the saturation method on a precision microvolumetric setup (which has been described previously in detail[9]) with some constructional changes.[10]

Processing of experimental data. The solubility of argon was expressed in terms of coefficients of the Bunsen absorption ($\beta_{A1,L}$) of A1 gas in L solvent**:

$$\beta_{A1,L} = [\upsilon_{A1}(\text{n.c.})/\upsilon_L(T, p)]_{\text{equil}},$$

where υ_{A1}(n.c.) is the volume of the pure gas adsorbed at the experimental temperature T and pressure $p = p_{\text{tot}}$ referred to the partial pressure of 101325 Pa and brought to normal conditions (n.c.) (T = 273.15 K, p^0 = 101325 Pa), and υ_L is the volume of the deaerated solvent (or the solution) at T and p_{tot}.

Previously,[11] it has been demonstrated that if the measurement error for υ_{A1} is $\leq 0.4\%$, it is necessary to apply a correction for the imperfect behavior of the gas, which can be expressed in terms of the compressibility coefficient $z(T, p)$:

$$z(T, p) = p\upsilon_{n,A1}(T, p)/(RT), \quad (1)$$

where $\upsilon_{n,A1}$ is the molar volume of the gas at T and p.

By multiplying both sides of Eq. (1) by n_{A1} (the amount of gas dissolved) we obtain the following equation:

$$z_{A1}(T, p)n_{A1} = p\upsilon_{A1}(T, p)/(RT). \quad (2)$$

Under normal conditions,

$$z_{A1}(\text{n.c.})n_{A1} = p^0\upsilon_{A1}(\text{n.c.})/(RT^0). \quad (3)$$

From Eqs. (2) and (3) it follows:

$$p^0\upsilon_{A1}(\text{n.c.})/[z_{A1}(\text{n.c.})RT^0] = p\upsilon_{A1}(T, p)/[z_{A1}(T, p)RT]. \quad (4)$$

Taking into account that $p = p^0$ (according to the definition of $\beta_{A1,L}$), the following equation can be obtained:

$$\upsilon_{A1}(\text{n.c.}) = [z_{A1}(\text{n.c.})/z_{A1}(T, p)](T^0/T)\upsilon_{A1}(T, p).$$

Therefore, the Bunsen absorption coefficient corrected for the imperfect behavior ($\beta^*_{A1,L}$) can be calculated according to the following formula:

$$\beta^*_{A1,L} = \upsilon_{A1}(T, p)\cdot 273.15z_{A1}(\text{n.c.})/[\upsilon_L(T, p)Tz_{A1}(T, p)] =$$

$$= \upsilon_{A1}(\text{n.c.})z_{A1}(\text{n.c.})/[\upsilon_L(T, p)z_{A1}(T, p)].$$

The compressibility coefficients were calculated according to Lee-Kessler's method.[12]

To check the accuracy and reliability of the data, we measured the solubility of argon in pure H_2O and D_2O and compared the results with the most reliable values available in the literature.[6] Our results and the published data[13—19] were summarized in the single selection for each system (Table 1) and were processed by the least-squares method using the following model:

$$\ln\beta^*_{A1,L} = A_0 + A_1/T + A_2\ln T. \quad (5)$$

The data in Table 1 indicate that there is no systematic error in our measurements. Repeated measurements of $\beta^*_{A1,L}$ at different temperatures revealed a rather high (at a level of about 0.2—0.3%) convergence of the values obtained.

The results of measurements of the solubility of argon in solutions of hmta in H_2O and D_2O are given in Table 2. The concentrations of argon and hmta are given in the solvomolality

Table 1. The Bunsen absorption coefficients $\beta^*_{A1,L}$[a] for argon in H_2O and D_2O

T/K	Ar—H_2O	Ar—D_2O
278.15	46.812,[b] 47.12[c]	—
278.163	47.205[d]	—
283.15	41.655,[b] 41.88,[c] 41.80[e]	46.16[f]
283.157	42.023[d]	—
283.22	41.84,[g] 41.82[h]	45.12,[g] 45.94[h]
288.15	37.478,[b] 38.27[c]	41.54,[c] 41.21[e]
288.165	37.699[d]	—
288.17	37.62,[g] 37.63[h]	41.33,[g] 41.03[h]
288.30	—	41.09[i]
293.15	34.16[e]	37.28,[c] 36.69[f]
298.01	—	33.78[i]
298.15	31.258,[b] 31.21,[c] 31.412[d]	33.80,[c] 33.10[j]
298.15	31.19,[g] 31.30[h]	33.44,[g] 33.61[h]
303.15	28.87[e]	31.51[f]
308.15	26.912,[b] 26.81[c]	29.13,[i] 30.19[j]
308.159	27.075[d]	—
308.25	26.85,[g] 26.90[h]	28.22,[g] 28.46[h]
313.15	25.20[e]	26.40[f]
318.15	23.93,[b] 23.73,[c] 24.099[d]	26.99[i]
318.17	24.01,[g] 24.01[h]	24.97,[g] 24.97[h]

[a] υ_{A1}/cm^3 and υ_L/dm^3 were used.
[b] See Ref. 13.
[c] See Ref. 14.
[d] See Ref. 15.
[e] See Ref. 16.
[f] See Ref. 19.
[g] Determined experimentally by us.
[h] Calculated according to Eq. (5).
[i] See Ref. 17.
[j] See Ref. 18.

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* In this work, a unitary concentration scale, *viz.*, the solvomolality c_{sm}, was used. The solvomolality is a nondimensional rational parameter that characterizes the composition of the solution and is numerically equal to the amount of solute contained in 55.5084 mol of the solvent. This value is expressed as $(n_i/n_L)\cdot 55.5084$, where n_i and n_L are the amounts of the solute and the solvent, respectively. The normalizing factor 55.5084 (numerically equal to the amount of H_2O in 1 kg of water) was introduced in order that c_{sm} and the molality c_m in aqueous solutions be numerically equal. The use of different concentration scales in the thermodynamics of solutions has been considered in detail in Ref. 2, where it has been demonstrated that it is advantageous to use the c_{sm} scale for calculations of the transfer function (including isotope effects) because this makes it possible to compare the thermodynamic functions of dissolution and solvation in different solvents with retention of the ratio between the number of particles of the solute and the solvent.

** By the solvent is meant not only L_H and L_D but also the A2 — $[L_{H(D)} + A2]$ solution.

Table 2. Solubility of argon ($c_{\mathrm{sm.A}}$) at 101325 Pa and at different temperatures in hmta—$H_2O(D_2O)$ systems

T/K	$c_{\mathrm{sm.A2}}$		$c_{\mathrm{sm.A1}} \cdot 10^3$	
	H_2O	D_2O	H_2O	D_2O
283.22	0	0	1.86884	2.02515
	0.057	0.032	1.8481	2.0072
	0.135	0.218	1.8299	1.9396
	0.238	0.257	1.7976	1.9285
	0.353	0.553	1.7683	1.8196
	0.628	1.034	1.6968	1.7107
	0.887	1.388	1.6524	1.6593
	1.164	1.601	1.6143	1.6365
	1.593	2.134	1.5580	1.6102
	2.274	2.294	1.5161	1.6047
288.17	0	0	1.68135	1.85524
	0.059	0.075	1.6682	1.8308
	0.237	0.244	1.6335	1.7702
	0.368	0.392	1.6127	1.7352
	0.750	0.591	1.5484	1.6807
	0.983	0.928	1.5257	1.6039
	1.261	1.073	1.5007	1.9828
	1.587	1.433	1.4767	1.5342
	1.979	1.851	1.4611	1.5044
	2.239	2.282	1.4568	1.4905
298.15	0	0	1.39908	1.50301
	0.071	0.064	1.3874	1.4887
	0.223	0.186	1.3685	1.4699
	0.328	0.321	1.3554	1.4450
	0.462	0.597	1.3401	1.4111
	0.733	0.872	1.3093	1.3798
	1.035	1.305	1.2780	1.3485
	1.446	1.536	1.2442	1.3423
	2.005	2.012	1.2088	1.3320
	2.394	2.183	1.1881	1.3324
308.25	0	0	1.20616	1.27155
	0.050	0.071	1.1995	1.2638
	0.269	0.172	1.1850	1.2543
	0.270	0.392	1.1868	1.2311
	0.360	0.681	1.1777	1.2065
	0.501	0.996	1.1696	1.1883
	0.794	1.266	1.1490	1.1735
	1.384	1.555	1.1253	1.1612
	1.742	2.069	1.1040	1.1497
	2.412	2.394	1.0841	1.1494
318.17	0	0	1.08270	1.12897
	0.119	0.018	1.0788	1.1266
	0.405	0.135	1.0722	1.1200
	0.711	0.194	1.0650	1.1154
	0.864	0.392	1.0632	1.1053
	1.093	0.530	1.0593	1.0980
	1.620	0.925	1.0522	1.0847
	1.678	1.184	1.0529	1.0721
	2.031	1.767	1.0491	1.0567
	2.390	2.452	1.0476	1.0498

scale. Calculations were carried out according to the following equation:

$$c_{\mathrm{sm.A1}} = \beta^*_{\mathrm{A1.L}}(55.5084 \cdot M_{\mathrm{A1}} + c_{\mathrm{sm.A2}} M_{\mathrm{A2}})/(\upsilon^*_{\mathrm{n.A1}} \rho_{\mathrm{A2.L}}),$$

where M_{A1} and M_{A2} are the molecular masses of the solvents (L_H or L_D) and the solute (A2), respectively, $\upsilon^*_{\mathrm{n.A1}}$ (22395 cm^3 mol^{-1}) is the real molar volume of the gas[11] in normal conditions, and $\rho_{\mathrm{A2.L}}$ is the density of the solution of A2 in $L_{\mathrm{H(D)}}$ solvent. We used the densities published previously.[4]

The dependence of $c_{\mathrm{sm.A1}}$ on $c_{\mathrm{sm.A2}}$ was approximated (to attain the minimum rms deviation) using the following mathematical model:

$$\ln c_{\mathrm{sm.A1}} - \ln c^*_{\mathrm{sm.A1}} = \sum_{i=1}^{n} a_i c^i_{\mathrm{sm.A2}}\,, \qquad (6)$$

where $c^*_{\mathrm{sm.A1}}$ is the solubility of argon in $L_{\mathrm{H(D)}}$. The regression analysis demonstrated that the concentration dependences of $c_{\mathrm{sm.A1}}$ are adequately reproduced at $n = 2$ with the rms approximation error $\sigma_{0.95} \le 0.002$.

The a_i coefficients for Eq. (6) are given in Table 3.

Calculation of parameters of pairwise interactions. A change in the solubility of nonelectrolyte A1 upon addition of compound A2 to solvent L is generally described by the following equation:

$$k_s = [\ln(c^*_{\mathrm{A1}}/c_{\mathrm{A1}})] \cdot c_{\mathrm{A2}}^{-1}, \qquad (7)$$

which is analogous to the empirical equation proposed initially[20] for solutions of nonelectrolytes in aqueous-salt systems. Here, c^*_{A1} is the solubility of A1 in L, c_{A1} is the solubility of A1 in [L + A2] solution with a concentration equal to c_{A2}, and k_s is the Setchenov coefficient (parameter). Previously,[21] the necessity of changing the sign of the left-hand side of Eq. (7) to the opposite has been substantiated. This makes it possible to put the effect of A2 on the solubility of A1 (a decrease or an increase in the solubility) into one-to-one correspondence with the sign of k_s (the minus or plus sign, respectively).

It has been demonstrated[22–24] that the differential form of Eq. (7) is thermodynamically reasonable and, hence, is more suited for calculations:

$$k_s = (\partial \ln c_{\mathrm{A1}}/\partial c_{\mathrm{A2}})_{\mu_{\mathrm{A1}}},$$

where μ_{A1} is the chemical potential of A1.

It was of substantial interest to determine the standard values of the Setchenov parameter $k_s^{\varnothing}$. An interpolation-extrapolation procedure has been proposed[21] for these calculations. In this case, the transfer of one mole of A1 from a *standard** solution in pure L to a [L + A2] solution standard relative to the state of each of the components is considered:

$$k_s^{\varnothing} = \lim_{(c_{\mathrm{A1}} \to c_{\mathrm{A1}} = 1,\ \mathrm{hyp})} \ \lim_{(c_{\mathrm{A2}} \to c_{\mathrm{A2}} = 1,\ \mathrm{hyp})} (\partial \ln c_{\mathrm{A1}}/\partial c_{\mathrm{A2}})_{\mu_{\mathrm{A1}}^{\varnothing}},$$

where $\mu_{\mathrm{A1}}^{\varnothing}$ is the chemical potential of A1 in the standard solution.

The $k_s^{\varnothing}$ values calculated under these conditions do not contain contributions of the interactions between the solute, due to which these values are convenient to use in studies of the effect of changes in the structural state of L, induced by the presence of A2, on the solubility of A1.

To study the interactions between dissolved A1 and A2 particles, it is necessary to change the conditions of standardization and to consider the transfer of one mole of A1 from a

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* The hypothetical solution with a unit concentration possessing the properties of an infinitely dilute (ideal) solution is taken to mean the standard solution.[25]

Table 3. Coefficients of the approximate equation (6) and rms errors of approximation (σ)

T/K	$-a_1$		a_2		$\sigma \cdot 10^3$	
	H_2O	D_2O	H_2O	D_2O	H_2O	D_2O
283.22	0.1681(0.005)	0.2124(0.006)	0.0336(0.003)	0.0488(0.003)	2	2
288.17	0.1269(0.004)	0.1944(0.004)	0.0282(0.002)	0.0433(0.002)	1	2
298.15	0.1009(0.002)	0.1250(0.005)	0.0137(0.001)	0.0323(0.002)	1	2
308.25	0.0654(0.005)	0.0881(0.002)	0.0088(0.002)	0.0191(0.001)	2	1
318.17	0.0256(0.001)	0.0562(0.003)	0.0050(0.001)	0.0108(0.002)	1	1

Note. The numerical confidence intervals are given in parentheses.

standard solution in pure L to a [L + A2] solution standard with respect to the state of A1:

$$k_s^{\varnothing} = \lim_{(c_{A1} \to c_{A1}=1,\ \mathrm{hyp})} (\partial \ln c_{A1}/\partial c_{A2})_{\mu_{A1}^{\varnothing}}.$$

The major thermodynamic relationships for calculations of the thermodynamic parameters of pairwise interactions in a ternary nonelectrolyte—binary solution system have been analyzed in detail previously.[26] In particular, it has been demonstrated that in the case of transfer of one mole of nonelectrolyte A1 from standard (ideally dilute) solution in pure L to standard (with respect to the state of A1) solution of A2 in L (the amount of compound L remains the same) with the concentration $c_{\mathrm{sm,A1}}$, the change in the Gibbs energy is described by the following equation:

$$\Delta_{\mathrm{tr}}G^{\varnothing}(\mathrm{A1,L{\to}L{+}A2}) = -RT\ln(c_{A1}/c^{\bullet}_{A1}) = -RTk_s^{\varnothing}c_{\mathrm{sm,A2}}.$$

Taking into account Eq. (6), it can be written:

$$\Delta_{\mathrm{tr}}G^{\varnothing}(\mathrm{A1,L{\to}L{+}A2}) = -RT\sum_{i=1}^{n} a_i c^{i}_{\mathrm{sm,A2}}.$$

At small $c_{\mathrm{sm,A2}}$,

$$\Delta_{\mathrm{tr}}G^{\varnothing}(\mathrm{A1,L{\to}L{+}A2}) = -RTa_1c^{i}_{\mathrm{sm,A2}}. \qquad (8)$$

According to the results reported previously,[26—28] the concentration dependence of $\Delta_{\mathrm{tr}}G$ can be expressed as an expansion in terms of $c_{\mathrm{sm,A2}}$:

$$\Delta_{\mathrm{tr}}G = 2c_{\mathrm{sm,A2}}g_{\mathrm{A1A2}} + 6c_{\mathrm{sm,A1}}c_{\mathrm{sm,A2}}g_{\mathrm{A1A1A2}} + \ldots, \qquad (9)$$

where g_{A1A2}, g_{A1A1A2}, ... are parameters of pair, three-particle, and higher-order interactions between the solutes. For the standard state, the higher terms of expansion (9) approach zero; hence,

$$\Delta_{\mathrm{tr}}G^{\varnothing} = 2c_{\mathrm{sm,A2}}g_{\mathrm{A1A2}}. \qquad (10)$$

Equations which allow one to calculate g_{A1A2} and $k_s^{\varnothing}$ directly from the data on solubility can be obtained from Eqs. (8) and (10) if the concentration dependences of these values are approximated by a model of type (6):

$$g_{\mathrm{A1A2}} = -RTa_1/2 \quad \text{and} \quad k_s^{\varnothing} = a_1/2.$$

By approximating the dependence of g_{A1A2} on T by the equation

$$g_{\mathrm{A1A2}} = \sum_{j=0}^{2} b_j\,(T - 298.15)^j$$

and using the known thermodynamic relations, the enthalpy (h_{A1A2}) and entropy (S_{A1A2}, Ts_{A1A2}) coefficients of interactions can be readily calculated.

Results and Discussion

The temperature dependences of the coefficients of A1—A2 pairwise interactions for hmta—Ar—$H_2O(D_2O)$ systems are given in Fig. 1. The corresponding values at 298.15 K are given below.

	g_{A1A2}	h_{A1A2}	s_{A1A2}	Ts_{A1A2}
	J mol^{-1}		/J mol^{-1} K^{-1}	/J mol^{-1}
H_2O	125	1480	4.5	1340
D_2O	155	1800	4.5	1640

It can be seen that the g_{A1A2} values are positive throughout the temperature range under study. This indicates that mutual repulsions between the hydrated Ar atoms and hmta molecules prevail and the transfer of Ar from $L_{H(D)}$ to [L + A2] is thermodynamically unfavorable. The g_{A1A2} values decrease as the temperature increases. The use of D_2O instead of H_2O leads to an increase in g_{A1A2}, *i.e.*, the effect of a decrease in the solubility under the effect of hmta additives is enhanced in D_2O.

The systems under consideration have a number of characteristic features. First, the concentrations of A1 both in pure L and in a solution of A2 in L are very low, which allows one to ignore change in the interaction

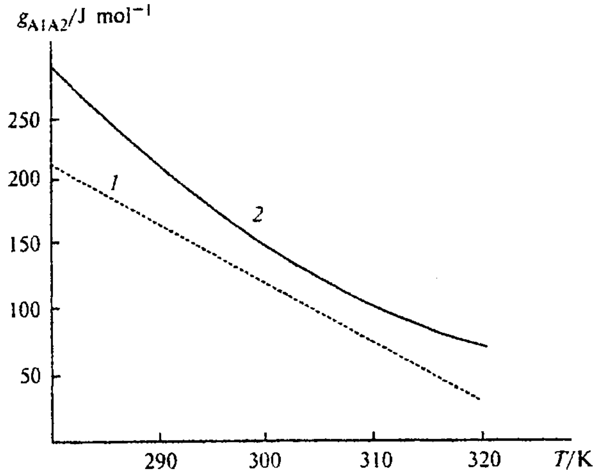

Fig. 1. Temperature dependence of the coefficients of Ar—hmta pairwise interactions g_{A1A2} in H_2O (*1*) and D_2O (*2*).

between A2 and the solvent under the effect of A1. This fact makes it possible to use the thermodynamic parameters of the solubility for identification and qualitative interpretation of the structural rearrangements of the solvent upon changes in the temperature and the composition of the solution.[2,29] Second, the Ar atoms and hmta molecules are hydrated according to the hydrophobic and hydrophilic mechanisms, respectively. This gave grounds to interpret the results with predominant allowance for the structural orientation.

Based on the data on self-diffusion coefficients for molecules in hmta solutions, it has been demonstrated[5] that of two possible types of arrangement of hmta molecules in the tetrahedral water structure, giving rise to a closed (clathrate) or "open" structure, the second type, which is associated with the formation of four hydrogen bonds between water molecules and nitrogen atoms of hmta molecules in the framework, is realized. This leads to the rearrangement of the water structure such that it is equal to structure destruction, *i.e.*, to a decrease in the overall ordering of the system. Based on the analysis of the volume properties of hmta solutions in H_2O and D_2O, we also found[4] that hmta molecules destroy the inherent water structure, thus forming new, highly ordered (lace-like) structures. When D_2O is used instead of H_2O, the hydration spheres about hmta become more compact due to strengthening of the hydrogen bonds. This is also evidenced by data[7] on the enthalpy characteristics of the isotope effects of dissolution of hmta. These conclusions do not contradict the inference[6] that hmta is a structure-forming compound because the structural states of water in the hydrate sphere of hmta and in the bulk of solution are substantially different. Hence, according to the classification reported previously,[1] hmta should be classified as a hydrophilically hydrated compound, *viz.*, a compound destroying the water structure.

The parameters f_{A1A2} ($f = g$, h, and s) represent contributions to the corresponding thermodynamic functions F ($F = G$, H, and S) associated with the fact that the solvated A1 and A2 molecules are brought closer together from an infinitely large distance to a particular critical distance. These parameters take into account new sources of imperfections that appear in the ternary system due to weakening of the L—A1 and L—A2 interactions under the effect of newly formed interactions between A1 and A2.

Impressive progress in the qualitative interpretation of the effects of changes in the solubility of nonelectrolytes under the influence of the third component of the system was achieved by employing notions based on the concepts of structural salting-in—salting-out and overlapping of the Gurney hydration *cospheres*.[30] As mentioned above, Ar atoms are hydrated according to the hydrophobic mechanism, resulting in stabilization of the water structure. In this case, the more ordered the initial structure of the solvent, the more noticeable the stabilization effect. The hydrophilic hydration of hmta is associated with the rearrangement of the water structure; as a result of which this structure in the nearest environment of hmta molecules becomes "inconvenient" for participation in hydrophobic hydration of argon. This competition leads to weakening of hydrophobic hydration of Ar atoms, and their stabilizing action is attended by the additional expenditure of energy. Hence, the plus signs of the g_{A1A2} contributions may be associated with the changes in the solvent—solvent interactions under the influence of hmta. As a result, argon is forced out of the solution. An analogous conclusion follows from the results of the study[31] in which it was demonstrated that overlapping of the hydration *cospheres* of hydrophobic and hydrophilic species leads to a decrease in the solubility of the nonelectrolyte ($k_s^{\varnothing} < 0$).

The replacement of H_2O by the more structured D_2O and an increase in the temperature lead to strengthening of hydration of hmta molecules.[4,7] At first glance, this should lead to an increase in g_{A1A2} (a decrease in $k_s^{\varnothing}$). It can be seen from Fig. 1 that $g_{A1A2}(D_2O) < g_{A1A2}(H_2O)$, but g_{A1A2} decreases rather rapidly (approaching zero) as the temperature increases. We believe that in this case two effects, *viz.*, strengthening of hydration of hmta and thermal predestruction of the water structure, are in competition, resulting in weakening of hydrophobic hydration of argon and, as a consequence, in a decrease in its solubility. Apparently, the second effect prevails. Hence, $c_{A1}(T) \to c^{*}_{A1}(T)$, whereas g_{A1A2} and $k_s^{\varnothing}$ approach zero as the temperature increases.

The portion of a more destroyed (than in the bulk of solution) water structure increases also, due to overlapping of the hydration spheres of argon and hmta of differing nature. The validity of this suggestion is supported by the plus signs of the entropy coefficient Ts_{A1A2} and the isotope effect involved in this parameter. A comparison of the coefficients of pairwise interactions (see above) demonstrated that, as in the pure solvent, dissolution of argon in hmta solutions is controlled by the entropy and enthalpy effects.

The results obtained in this work provide rather strong evidence that the use of the isotope substitution method has considerable utility in improving the reliability of interpretation of data on structure-thermodynamic characteristics of dissolution and hydration of compounds.

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