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Effects of H/D-isotope substitution and temperature on the volume characteristics of tetra-*n*-butylammonium bromide dissolved in methanol and its D-isotopomers

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Densities of $Bu^n{}_4NBr$ solutions in MeOH, MeOD, and CD_3OH were measured at salt concentrations of up to 1.5 solvomolality units (nearly $2.63 \cdot 10^{-2}$ mole fraction) at 278.15, 288.15, 298.15, 308.15, and 318.15 K. The limiting partial molar volumes of $Bu^n{}_4NBr$ dissolved in these alcohols were calculated. The isotope effects in the volume characteristics of the stoichiometric mixture of ions, $[Bu^n{}_4N^+ + Br^-]$, are mainly due to the "vibrational" changes in the solvent structure upon deuteration of different molecular fragments. Structural transformations in infinitely dilute solution of $Bu^n{}_4NBr$ in methanol are governed by non-specific solvation of the symmetrical $Bu^n{}_4N^+$ cation.

Key words: methanol, tetra-*n*-butylammonium bromide, isotope effect, volume, solvation.

Steady interest in studies of solutions of symmetrical tetraalkylammonium salts is due to peculiarities of hydration of such systems. In the case of a stoichiometric mixture of $Bu^n{}_4N^+$ and Br^- ions, $[Bu^n{}_4N^+ + Br^-]$, in aqueous solution, all features are governed by the predominant effect of hydrophobic hydration, which manifests itself in marked increase in the structuring of the solvent in the nearest environment of the bulky organic cation bearing a delocalized charge.[1,2] On the contrary, small bromide ions have a breaking effect on the structure of water (so-called "negative hydration").[3] These solvation effects are usually explained by local structuring of water (or nonaqueous solvent) through intermolecular coordination involving a system of H-bonds.[2,4] It was assumed[2] that, generally, the physical nature of solvophobic solvation not necessarily implies the formation of a three-dimensional network of H-bonds in the solvent, being at the same time dependent on the molecular properties of the solvent and on the state of the structural packing of the solvent molecules. This holds even for solutions of nonpolar substances in MeOH despite a "chain-like" (two-dimensional) molecular structure of the solvent.[5]

The role of the packing (steric) factor in the solvation of ions and neutral species becomes much more important on going from water to amphyprotic organic media.[6] Therefore, it is of interest to study methanol as a solvent, which is simultaneously similar to both water (in energy characteristics of H-bond formation) and liquid methane (in character of molecular packing).[6,7] Besides, unlike other aliphatic alcohols, the methanol molecules contain no methylene units. This provides an explanation for atypical behavior of MeOH as the solvent, which manifests itself in the so-called "boundary" solvation effects[8] and first of all in the "negative partial expansion" observed in a number of solvophilic (water,[8,9] carbamide[10]) and ionic (alkali metal halides[11]) compounds dissolved in methanol. As a result, the nature of ion solvation changes significantly upon transfer of a stoichiometric mixture $[Bu^n{}_4N^+ + Br^-]$ from water to methanol. This mainly concerns structural transformations in methanol in the solvation shell of the cation. Interpretation of the corresponding data is still rather contradictory due to the lack of reliable results of computer simulation of the system $Bu^n{}_4NBr$—MeOH using the molecular dynamics technique and quantum-chemical methods because experimental data on the thermodynamic (enthalpy,[12,13] volume,[1,4,15] *etc.*) characteristics of this system provide information only on the structure-averaged (macroscopic) properties of the solutions under study.

Earlier,[16,17] we have shown that additional information on the structural effects induced by solvation and other types of interparticle interaction in solutions can be obtained in joint studies using two non-destructive methods, densimetry and H/D-isotope substitution. The former method is suitable for evaluating those volume (packing) characteristics of the solution components, which reflect

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structural rearrangements occurring during solvation. The second method allows the role of H-bonds and other types of donor-acceptor interaction in the structure formation to be established on the molecular level.

In this work we report on a densimetry study of dilute solutions of tetra-*n*-butylammonium bromide (Bu^n_4NBr) in MeOH and its D-isotopomers (MeOD and CD_3OH) * in the temperature range 278.15—318.15 K (with an increment of 10 K). We also calculated the volume characteristics of a stoichiometric mixture of the ions of the dissolved electrolyte.

Experimental and Calculation Procedure

Experimental procedure. The materials used in our experiments were MeOH (reagent grade) and its deuterated analogs MeOD and CD_3OH (Izotop, Russia) with a deuterium content of 99.0±0.1 at.%. The alcohols were additionally purified following a known procedure[18,19] by refluxing with magnesium methoxide. Preliminary evacuation of a distillation setup followed by filling it with inert atmosphere (Ne) ensured the absence of H/D-exchange during the dehydration of MeOD and CD_3OH. The purified H/D-isotopomers of methanol contained at least 0.99982 mole fraction of the basic substance (Fischer and densimetry analyses). The stability of the isotope composition of MeOD and CD_3OH was monitored by comparing the densities of the initial alcohols and of the products of their purification following a known procedure.[20] All operations with the alcohols and their storage were performed in a dry box. Bu^n_4NBr (Sigma—Aldrich, analytical grade) used in the experiments was additionally purified by five-fold recrystallization from dehydrated ethanol.[21] In the last stage of purification, the product was precipitated in a Dewar flask filled with liquid nitrogen and decanted. The precipitate was washed with Et_2O, dried *in vacuo* at ~335 K over a period of 48 h, and stored in a vacuum desiccator over P_2O_5. The quality of the purified salt was assessed analytically, namely, based on the content of Br^- ions (argentometry) and $Bu^n_4N^+$ ions (with "Purple Benzene" reagent[22]),** and densimetrically (using reliable data[1,23] on the densities of aqueous Bu^n_4NBr solutions at 298.15 K as references).

The electrolyte solutions were prepared by the weighing method using components degassed by a known procedure[24] in special evacuated mixers with an error of at most $1.0 \cdot 10^{-4}$ units of $c_{sm,A}$, where $c_{sm,A}$ is the salt concentration in the solvomolality-based concentration scale.*** The use of this concentration scale is of crucial importance for interpretation of the thermodynamic functions of transfer (including H/D-isotope effects), because the ratio of the number of the solvent particles to the number of the solute particles remains constant on going from one solvent (H-isotopomer) to another (D-isotopomer).[2,17]

The solution densities, $\rho_{A,L}$, were measured on a precision hermetic magnetic float densimeter with an accuracy of $\pm 1.2 \cdot 10^{-5}$ g cm^{-3}. The temperature in the measuring unit was maintained with an accuracy of $2 \cdot 10^{-3}$ K. The apparatus design and the procedure for densimetry experiments were reported earlier.[25]

The densities of the Bu^n_4NBr solutions in MeOH, MeOD, and CD_3OH are listed in Table 1.

Processing of experimental data. The limiting partial molar volumes, $\bar{V}^{\infty}{}_A$, were calculated using a non-extrapolation procedure[25,26] based on the relation between the apparent molar volume of the dissolved electrolyte, $V_{\phi,A}$, and its concentration[14,25]:

$$V_{\phi,A} = (V_{A,L} - n_L V_L)/n_A =$$
$$= V_{\phi,A}{}^{\infty}(\equiv \bar{V}^{\infty}{}_A) + S_V n_A{}^{1/2} + b_V n_A{}^2 + ..., \quad (1)$$

where $V_{A,L} = (n_L M_L + n_A M_A)/\rho_{A,L}$ is the volume of the solution; M_L and M_A are the molecular weights of the solution components; $\rho_{A,L}$ is the solution density; S_V is the slope; and b_V is the parameter of pair ion—ion interactions. The M_L values of MeOD and CD_3OH were calculated with inclusion of incomplete H/D-exchange using the mole fraction additivity rule.

With allowance for the fact that $n_L = 55.50843$ and $n_A = c_{sm,A}$ in the solvomolality-based concentration scale, Eq. (1) can be transformed as follows

$$V_{A,L} = 55.50843 V_L + \bar{V}^{\infty}{}_A c_{sm,A} + S_V c_{sm,A}{}^{3/2} + b_V c_{sm,A}{}^2 \quad (2)$$

or rewritten in a more convenient form

$$(V_{A,L} - 55.50843 V_L)/c_{sm,A} = \bar{V}^{\infty}{}_A + S_V c_{sm,A}{}^{1/2} + b_V c_{sm,A}. \quad (3)$$

Clearly, the left side of Eq. (3) has the meaning of $V_{\phi,A}$.

The main advantages of this procedure for the determination of $\bar{V}^{\infty}{}_A$ values over conventional extrapolation technique were analyzed in detail earlier.[26] Note that, according to Eq. (2), at low concentrations of Bu^n_4NBr in methanol the experimental values of $V_{A,L}(c_{sm,A})$ lie in a narrow corridor of confidence intervals relative to the line intersecting the ordinate axis at the known point $V_{A,L} = 55.50843 V_L$. This allowed both a drastic increase in errors (so-called horn effect) in calculating $V_{\phi,A}$ at $c_{sm,A} \to 0$ and evaluation of theoretical slope* from the "limiting law" according to Debye—Hückel—Pitzer[14] to be avoided (in the latter case, one should know the derivative of the dielectric constant, ε_L, with respect to pressure and the isothermal compressibility coefficients, $\beta_{T,L}$, of the D-isotopomers of methanol at different temperatures). In this work the parameters S_V and b_V in Eq. (2) were evaluated empirically by approximating the experimental dependences of $V_{A,L}$ on $c_{sm,A}$.

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* From this point on the isotopomers of methanol (MeOH, MeOD, and CD_3OH) and Bu^n_4NBr are denoted as L_H, L_{D1}, L_{1D3}, and A, respectively.

** The content of the $Bu^n_4N^+$ and Br^- ions in the salt after purification was 99.92 and 99.85% (w/w) of their fraction in 1 mole of Bu^n_4NBr, respectively.

*** Solvomolality[2] is a dimensionless parameter of the solution composition, which expresses the concentration of the component A. Namely, $c_{sm,A} = 55.50843 n_A/n_L$, where n_A and n_L are the numbers of moles of the solute and solvent, respectively. The normalizing factor 55.50843 equals the number of H_2O moles in 1 kg of water.

* When using molar concentrations, $c_{M,A}$, the theoretical (limiting) slope A_V equals the parameter S_V in Eq. (1) multiplied by a factor of 3/2.[14] In the solvomolality-based concentration scale, one has[16] $S_V = 1.5 A_V \rho_L{}^{0.5}[M(L_D)/M(L_H)]^{0.5}$, where $L_D \equiv L_{D1}$ or L_{1D3}.

Table 1. Densities ($\rho_{A,L}$) of Bu$^n_4$NBr solutions in MeOH, MeOD, and CD$_3$OH at different temperatures (278.15—318.15 K)

System	$c_{sm,A}$*	$\rho_{A,L}$/g cm^{-3}				
		278.15	288.15	298.15	308.15	318.15
L_H—A	0	0.80519	0.79581	0.78638	0.77691	0.76737
	0.04989	0.80723	0.79788	0.78848	0.77904	0.76953
	0.09482	0.80903	0.79970	0.79032	0.78091	0.77143
	0.1421	0.81088	0.80158	0.79223	0.78284	0.77338
	0.1771	0.81223	0.80295	0.79362	0.78425	0.77481
	0.2310	0.81428	0.80502	0.79572	0.78638	0.77697
	0.2644	0.81554	0.80629	0.79700	0.78768	0.77829
	0.2762	0.81597	0.80674	0.79745	0.78814	0.77875
	0.3613	0.81909	0.80989	0.80064	0.79138	0.78204
	0.4694	0.82295	0.81379	0.80460	0.79538	0.78611
	0.4995	0.82400	0.81485	0.80567	0.79647	0.78721
	0.9286	0.83807	0.82910	0.82008	0.81110	0.80207
	1.0016	0.84032	0.83136	0.82237	0.81341	0.80441
	1.2089	0.84644	0.83756	0.82865	0.81979	0.81087
	1.4834	0.85410	0.84530	0.83649	0.82770	0.81891
	1.5024	0.85461	0.84582	0.83702	0.82824	0.81945
L_{D1}—A	0	0.82897	0.81925	0.80949	0.79969	0.78986
	0.05859	0.83118	0.82150	0.81178	0.80202	0.79223
	0.07605	0.83183	0.82216	0.81245	0.80270	0.79292
	0.1007	0.83273	0.82308	0.81338	0.80365	0.79389
	0.1533	0.83463	0.82500	0.81535	0.80565	0.79591
	0.1971	0.83618	0.82659	0.81696	0.80728	0.79758
	0.2022	0.83637	0.82677	0.81714	0.80747	0.79777
	0.2749	0.83889	0.82933	0.81975	0.81012	0.80046
	0.3512	0.84147	0.83196	0.82240	0.81283	0.80322
	0.5008	0.84638	0.83694	0.82748	0.81797	0.80845
	1.0014	0.86142	0.85215	0.84296	0.83368	0.82446
	1.4621	0.87363	0.86455	0.85547	0.84641	0.83739
	1.5033	0.87463	0.86558	0.85652	0.84748	0.83848
L_{1D3}—A	0	0.88511	0.87470	0.86423	0.85370	0.84313
	0.04667	0.88653	0.87616	0.86573	0.85524	0.84471
	0.06983	0.88722	0.87687	0.86646	0.85599	0.84548
	0.09991	0.88811	0.87777	0.86739	0.85694	0.84646
	0.1242	0.88881	0.87850	0.86813	0.85771	0.84724
	0.1489	0.88952	0.87923	0.86888	0.85847	0.84803
	0.2008	0.89099	0.88073	0.87043	0.86006	0.84966
	0.2698	0.89290	0.88269	0.87244	0.86212	0.85178
	0.3489	0.89503	0.88487	0.87468	0.86442	0.85413
	0.5066	0.89913	0.88907	0.87898	0.86884	0.85867
	0.9917	0.91059	0.90081	0.89100	0.88116	0.87133
	1.4926	0.92089	0.91134	0.90177	0.89218	0.88263

* In the mole fraction scale, one has $x_A = c_{sm,A}/(55.50843 + c_{sm,A})$.

The volume characteristics of the Bu$^n_4$NBr solutions in MeOH, MeOD, and CD$_3$OH calculated using Eq. (3) are listed in Table 2. For comparison, Table 3 includes the most reliable published data on the $\bar{V}^{\infty}{}_A$ values and on the partial volumes of the constituent ions for the salt under study in MeOH at the standard temperature.

Results and Discussion

The data listed in Tables 2 and 3 point to good agreement between the results of our experiments and the published data despite a rather large scatter of the latter data set relative to the arithmetic mean values of $\bar{V}^{\infty}{}_A$(MeOH) at 298.15 K.

Information on the volume effects caused by solvation of the 1 : 1 electrolyte under study can also be obtained[14] from the differences ($\bar{V}^{\infty}{}_A - \bar{V}^{\infty}{}_{in,A}$), where $\bar{V}^{\infty}{}_{in,A} = (4/3)\pi(r_+ + r_-)^3N_0$ is the intrinsic volume of Bu$^n_4$NBr in solution (N_0 is the Avogadro constant). The crystallographic radii, $r_{i,\pm}$, of the Bu$^n_4$N$^+$ and Br$^-$ ions are respectively 0.494 nm (according to Stokes) and 0.196 nm (ac-

Table 2. Parameters of Eq. (3) for $\mathrm{Bu^n{}_4NBr}$ solutions in MeOH, MeOD, and $\mathrm{CD_3OH}$ at 278.15—318.15 K

System	T/K	$\bar{V}^\infty{}_\mathrm{A}$	S_V	$-b_\mathrm{V}$
		cm^3 mol^{-1}		
$\mathrm{L_H}$—A	278.15	286.2±0.2	6.8±0.5	1.7±0.3
	288.15	286.4±0.2	7.7±0.5	1.8±0.3
	298.15	286.6±0.3	8.1±0.6	1.8±0.3
	308.15	286.9±0.3	8.6±0.8	1.8±0.4
	318.15	287.1±0.4	8.9±0.8	1.7±0.5
$\mathrm{L_{D1}}$—A	278.15	286.3±0.4	6.2±1.0	1.4±0.6
	288.15	286.4±0.4	7.2±0.9	1.5±0.5
	298.15	286.6±0.5	7.3±1.1	1.4±0.6
	308.15	286.6±0.3	7.9±0.6	1.6±0.3
	318.15	286.9±0.5	8.3±1.1	1.4±0.6
$\mathrm{L_{1D3}}$—A	278.15	287.2±0.3	6.0±0.6	1.1±0.3
	288.15	287.5±0.3	6.5±0.8	1.1±0.5
	298.15	287.6±0.3	7.3±0.7	1.2±0.4
	308.15	287.9±0.4	7.7±1.0	1.0±0.6
	318.15	287.9±0.3	7.7±0.8	1.0±0.4

Table 3. Partial volumes ($\bar{V}^\infty{}_\mathrm{A}$/cm^3 mol^{-1}) and the volumes of the constituent ions $\bar{V}^\infty{}_+$ and $\bar{V}^\infty{}_-$* for $\mathrm{Bu^n{}_4NBr}$ solutions in MeOH at 298.15 K

$\bar{V}^\infty{}_\mathrm{A}$	$\bar{V}^\infty{}_+$	$\bar{V}^\infty{}_-$	Reference
285.6	263.6	22.0	27
286.2	267.9	18.3	28
285.3	265.6	19.7	29
286.5	267.9	18.6	30
290.0	270.2	19.8	31
287.0	—	—	32
286.2	—	—	33
*286.7***	*267.0***	*19.7***	

* The volumes were determined with an error of at most ±1 cm^3 mol^{-1}; $\bar{V}^\infty{}_+ \equiv \bar{V}^\infty(\mathrm{Bu^n{}_4N^+})$ and $\bar{V}^\infty{}_- \equiv \bar{V}^\infty(\mathrm{Br^-})$.

** Averaged value.

cording to Pauling).[14] This gives for the intrinsic volumes of the ions in solution $\bar{V}^\infty{}_\mathrm{in,+} = 304.10$ and $\bar{V}^\infty{}_\mathrm{in,-} = 18.99$ cm^3 mol^{-1}; hence, $\bar{V}^\infty{}_\mathrm{in,A} \approx 323.1$ cm^3 mol^{-1}.

A comparison of these values with the volumes of the constituent ions (components of the parameter $\bar{V}^\infty{}_\mathrm{A}$, see Table 3) suggests that the formation of a $\mathrm{Bu^n{}_4NBr}$ solution in MeOH is governed by the changes in the solvent structure within the solvation shell of the cation. This is confirmed by the fact that $\bar{V}^\infty{}_\mathrm{in,A}$ approximately equals the molar volume, V_A, of the crystalline salt ($V_\mathrm{A} \approx 323\pm2$ cm^3 mol^{-1} at 298.15 K [15]) and that $\bar{V}^\infty{}_\mathrm{in,-}$ nearly equals $\bar{V}^\infty{}_-$. The latter is most probably due to superposition of several mutually cancelling volume effects, first of all the electrostriction induced contraction of the MeOH structure ($\bar{V}^\infty{}_\mathrm{el,-}$) and structure loosening due to steric unmatching in the molecular packing of the solvent ($\bar{V}^\infty{}_\mathrm{str,-}$) in the nearest environment of the anion.[14] The results of *ab initio* calculations[34] and Monte Carlo simulation[35] suggest that the $\bar{V}^\infty{}_\mathrm{str,-}$ value, or the "structural" contribution to $\bar{V}^\infty{}_-$, is related to "packing"-dependent changes in the mutual orientation of Me groups of the alcohol molecules upon the formation of H-bonded complexes (clusters) $\mathrm{Br^-}$...H—OMe.

The ability of $\mathrm{Br^-}$ ion to be involved in these interactions with the solvent seems to be a reason for the negative temperature coefficient of the parameter $\bar{V}^\infty(\mathrm{Br^-})$ in alcohols.[14] * With allowance for this fact, the observed increase in $\bar{V}^\infty{}_\mathrm{A}$ in the temperature range studied in this work (see Table 2) can be considered as an argument in favor of correctness of the conclusion about the predominant role of structural transformations in the nearest environment of the $\mathrm{Bu^n{}_4N^+}$ ion (see above). This also suggests that in the case of $\mathrm{Bu^n{}_4NBr}$ solutions in MeOH the nature of ion solvation is basically different from that observed for solutions of alkali metal bromides in methanol (here, the electrolyte parameter $\bar{V}^\infty$ decreases as temperature increases[11,15]).

From the aforesaid it follows that large negative values of the difference ($\bar{V}^\infty{}_\mathrm{A} - \bar{V}^\infty{}_\mathrm{in,A}$) in MeOH depend on the sum of the contributions $\bar{V}^\infty{}_\mathrm{el,+}$ and $\bar{V}^\infty{}_\mathrm{str,+}$ determining the structural state of the solvated $\mathrm{Bu^n{}_4N^+}$ ion. Since the surface density of the electric charge on the cation is low, the contribution $\bar{V}^\infty{}_\mathrm{el,-}$ must be rather small and therefore weakly dependent on temperature. The volume effect, $\bar{V}^\infty{}_\mathrm{str,+}$, is to a great extent determined by steric features of the cation arrangement in the structural matrix of MeOH. These features are most often explained assuming that the solvent molecules can penetrate into the inner coordination sphere of the tetraalkylammonium ion with a tracery structure.[14,36–38] However, we believe that a better explanation is provided by yet another approach,[39] according to which the decrease in the effective radius of the $\mathrm{Bu^n{}_4N^+}$ ion is due to rolling up elastic alkyl chains in the nonaqueous medium. On the contrary, in aqueous solution these chains readily form structural voids in the solvent and, as a consequence, lose the ability to roll up.

This is confirmed by the published data[29,40] and by the results obtained in this work (see Table 2). Indeed, transfer of a mole of stoichiometric mixture of ions [$\mathrm{Bu^n{}_4N^+ + Br^-}$] from water to MeOH is accompanied by the formation of structures characterized by closer packing and higher thermal stability. In particular, published data for a $\mathrm{Bu^n{}_4NBr}$ solution in $\mathrm{H_2O}$ are as follows: $\bar{V}^\infty{}_\mathrm{A} = 300.40$ cm^3 mol^{-1} and $(\partial/\bar{V}^\infty{}_\mathrm{A}/\partial T)_p = 0.2694$ cm^3 mol^{-1} K^{-1} at 298.15 K [40] (*cf.* $(\partial/\bar{V}^\infty{}_\mathrm{A}/\partial T)_p \approx 0.023$ cm^3 mol^{-1} K^{-1} for $\mathrm{Bu^n{}_4NBr}$ in MeOH**).

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* Yet another possible reason for "negative partial expansion" of the solvation complex $\mathrm{Br^-}$—MeOH is a decrease in the dielectric constant of the solvent on raising the temperature.[14]

** Obtained by processing the data listed in Table 2 using the equation $\bar{V}^\infty{}_\mathrm{A} = \bar{V}^\infty{}_\mathrm{A}(T_0) + a_1(T - T_0)$ at $T_0 = 298.15$ K.

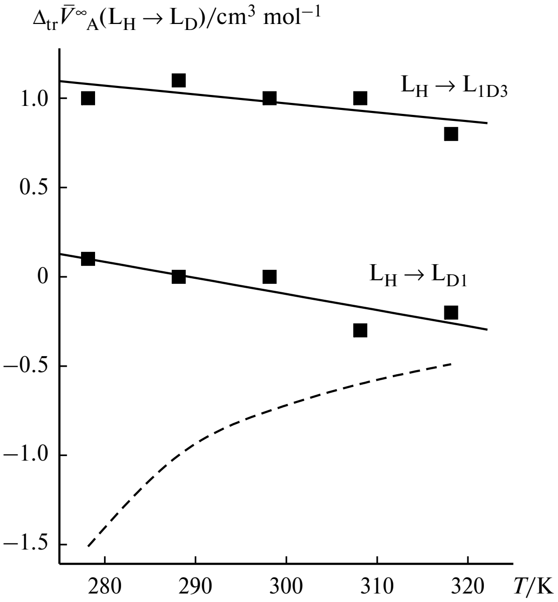

Fig. 1. Temperature dependences of isotope effects in the limiting partial molar volume of $Bu^n{}_4NBr$ in MeOH (solid lines) and H_2O (dashed line).

A comparison of the volume characteristics of solvation of $Bu^n{}_4NBr$ in MeOH and H_2O suggests the following. Structure-forming effects caused by solvophobic solvation (hydration) of the cation are much less pronounced for MeOH than for water. The presence of terminal Me groups in the MeOH molecules significantly changes the nature of cation—solvent interactions. This manifests itself not only in steric features of the packing (see above) of the solvation complex $Bu^n{}_4N^+$—MeOH * but also in that the limiting partial molar expansion $\bar{E}^{\infty}{}_{A} = (\partial/\bar{V}^{\infty}{}_{A}/\partial T)_p$ of $Bu^n{}_4N^+$ in MeOH at T = 298.15 K is much less than the molar expansion of the solvent E_L (this is opposite to the case of aqueous solution).

Joint analysis of the results obtained in this work and of the published data[41,42] on weak solvation of $Bu^n{}_4N^+$ and $Bu^n{}_4NBr$ in MeOH suggests that non-specific interparticle interactions play the predominant role in the formation of molecular packing of the system under study. These interactions are strongly dependent on the size and rovibrational characteristics of the contacting molecules and ions, which manifests itself on the macroscopic level as the volume effects of $Bu^n{}_4NBr$ solvation upon H/D-isotope substitution in the Me and OH groups of the solvent molecules (Fig. 1).

The plots in Fig. 1 show that selective deuteration of methanol leads to considerably different magnitudes of the volume contributions to $\bar{V}^{\infty}{}_{A}(T)$. If the contribution $\Delta_{tr}\bar{V}^{\infty}{}_{A}(T, L_H \to L_{1D3})$* on going from MeOH to CD_3OH is positive (on the average, about 1 $cm^3\ mol^{-1}$), replacement of MeOH by MeOD leaves the $\bar{V}^{\infty}{}_{A}(T)$ value unchanged within the limits of experimental error (see Table 2). Yet another salient feature of the plots in Fig. 1 is that they are directed oppositely compared to the aqueous $Bu^n{}_4NBr$ solution. What is more, the stoichiometric mixture of the ions under study is characterized by negative $\Delta_{tr}\bar{V}^{\infty}(H_2O \to D_2O)$ values which dramatically increase in the low-temperature region (up to nearly $-1.5\ cm^3\ mol^{-1}$ at 278.15 K).

As mentioned above, large "packing"-related changes in the system $Bu^n{}_4NBr$—H_2O caused by H/D-isotope substitution and temperature are due to the joint effects of hydrophobic hydration of the cation and negative hydration of the anion and to the ability of the anion to form stronger D-bonds with the solvent molecules.[2,16] All the isotope effects give negative contributions to the $\bar{V}^{\infty}{}_{A}$ value.[14,40] Taking into account the fact that transfer of a mole of $Bu^n{}_4NBr$ from light water to heavy water is an exothermic process,[2,43] the contribution $\Delta_{tr}\bar{V}^{\infty}{}_{+}(H_2O \to D_2O) \approx \Delta_{tr}\bar{V}^{\infty}{}_{str,+}(H_2O \to D_2O)$** plays the determining role. Raising the temperature levels the structural differences between light and heavy water, which results in the observed decrease in $\Delta_{tr}\bar{V}^{\infty}{}_{A}(H_2O \to D_2O)$.

Basically different shapes of the temperature dependences of the isotope effects, $\Delta_{tr}\bar{V}^{\infty}{}_{A}(L_H \to L_D)$, confirm that the structure-forming effects intrinsic in aqueous $Bu^n{}_4NBr$ solutions do not play the key role in the methanol environment of the $Bu^n{}_4N^+$ cation. This is also indicated by positive values of the isotope effects in the enthalpy characteristics of solvation of the stoichiometric mixture of ions under study on going from MeOH to MeOD.[43,44] According to published data,[43] $\Delta_{tr}H^{\infty}{}_{A}(L_H \to L_{D1}, 298.15\ K) \approx 1.1 \pm 0.3\ kJ\ mol^{-1}$, while the contributions of the constituent ions to this value depend on the calculation procedure and lie between 0.6 and 0.8 $kJ\ mol^{-1}$ for $Bu^n{}_4N^+$ and between 0.3 and 0.5 $kJ\ mol^{-1}$ for Br^-.

Endothermicity of transfer of Br^- ion from MeOH to MeOD (medium characterized by higher electron-acceptor (or proton-donor) ability[45]) should indicate[14–16] a densification of the structure of the solvation complex Br^-—methanol formed involving stronger Br^-...D—OMe bonds. However, the isotope effect, $\Delta_{tr}\bar{V}^{\infty}{}_{A}(L_H \to L_{D1})$, is nearly zero and weakly depends on temperature (see Table 2 and Fig. 1). This is in excellent agreement with the assumption of predominant role of non-specific inter-

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* According to published data,[14,27] the $\bar{V}^{\infty}{}_{+}$ value for this ion in methanol solution (at the standard temperature) is the lowest among all organic solvents.

* The isotope effect, $\Delta_{tr}\bar{V}^{\infty}{}_{A}(L_H \to L_D)$, is the difference $\bar{V}^{\infty}{}_{A}(L_D) - \bar{V}^{\infty}{}_{A}(L_H)$.

** The isotope effects in $\bar{V}^{\infty}{}_{A}$ were analyzed assuming $\Delta_{tr}\bar{V}^{\infty}{}_{in,i} \approx 0$ and $\Delta_{tr}\bar{V}^{\infty}{}_{el,i} \approx 0$.[15] Then, $\Delta_{tr}\bar{V}^{\infty}{}_{A} \approx \Delta_{tr}\bar{V}^{\infty}{}_{str,+} + \Delta_{tr}\bar{V}^{\infty}{}_{str,-} \approx \Delta_{tr}\bar{V}^{\infty}{}_{str,A}$.

particle interactions in the $Bu^n{}_4NBr$—methanol system (see above).

Peculiarities of solvation of the bulky $Bu^n{}_4N^+$ ion bearing a strongly delocalized charge in methanol allow the observed volume (packing-related) effects to be interpreted as manifestation of the "isotope" differences in the nature of the cation—solvent dispersion interaction*. This assumption seems to be quite substantiated because, first, the polarizability of the $Bu^n{}_4N^+$ ion is nearly an order of magnitude higher than that of the MeOH molecule ($31.51 \cdot 10^{-24}$ *vs.* $3.26 \cdot 10^{-24}$ cm^3, see Refs. 27 and 15, respectively) and, second, the key role in such interactions is played by the difference between the corresponding molecular parameters (*e.g.*, polarizability and size) of the solvent isotopomers.

H/D-Isotope substitution in methanol mainly leads to a decrease in the energy (frequency) of zero-point molecular vibrations and, as a consequence, to a decrease in the molecular size and polarizability in the following order: MeOH > MeOD > CD_3OH.[17,46—48] The polarizability and "hard-sphere volume" of the alcohol molecules decrease by 0.15% only upon deuterarion of the OH group and by nearly 1% on going from MeOH to CD_3OH. If we formally assume that the type of molecular packing of the solvation complex $Bu^n{}_4N^+$—MeOH remains "qualitatively" unchanged upon H/D-isotope substitution, weakening of the ion—solvent dispersion interactions in the second case causes the formation of looser structures.

We believe that this provides the best explanation for both the observation of positive isotope effect, $\Delta_{tr}\bar{V}^{\infty}{}_A(L_H \to L_{1D3})$, and the absence of this effect in the corridor of confidence intervals for $\bar{V}^{\infty}{}_A$ in the case of MeOH → MeOD substitution (see Fig. 1).

Thus, we can state that structural changes in an infinitely dilute solution of $Bu^n{}_4NBr$ in methanol are governed by non-specific solvation of symmetrical $Bu^n{}_4N^+$ cation interacting with the solvent molecules through dispersion forces.

References

1. P. R. Philip and J. E. Desnoyers, *J. Solut. Chem.*, 1972, **1**, 353.
2. *Sovremennye problemy khimii rastvorov* [*Modern Problems of Solution Chemistry*], Ed. B. D. Berezin, Nauka, Moscow, 1986, 264 pp. (in Russian).
3. O. Ya. Samoilov, *Struktura vodnykh rastvorov elektrolitov i gidratatsiya ionov* [*The Structure of Aqueous Electrolyte Solutions and Ion Hydration*], Izd. Akad. Nauk SSSR, Moscow, 1957, 185 pp. (in Russian).
4. G. A. Krestov, *Termodinamika ionnykh protsessov v rastvorakh* [*Thermodynamics of Ionic Processes in Solutions*], Leningrad, Khimiya, 1984, 272 pp. (in Russian).
5. E. V. Ivanov, V. K. Abrosimov, N. G. Ivanova, and E. Yu. Lebedeva, *Dokl. Akad. Nauk*, 2002, **386**, 636 [*Dokl. Phys. Chem.*, 2002 (Engl. Transl.)].
6. Yu. G. Bushuev, D. Sc. (Chem.) Thesis, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2001, 345 pp. (in Russian).
7. Yu. G. Bushuev and T. A. Dubinkina, *Zh. Fiz. Khim.*, 1996, **70**, 1628 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
8. V. G. Grasin, Ph. D. (Chem.) Thesis, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2002, 175 pp. (in Russian).
9. M. Sakurai and T. Nakagawa, *J. Chem. Thermodyn.*, 1984, **16**, 171.
10. E. V. Ivanov and V. K. Abrosimov, *Zh. Fiz. Khim.*, 1997, **71**, 70 [*Russ. J. Phys. Chem.*, 1997, **71** (Engl. Transl.)].
11. N. Takenaka, T. Takemura, and M. Sakurai, *J. Chem. Eng. Data*, 1994, **39**, 207; 796; 802.
12. C. Chin and C. M. Criss, *J. Solut. Chem.*, 1978, **7**, 205.
13. A. V. Kustov, E. Yu. Lebedeva, and V. P. Korolev, *Zh. Fiz. Khim.*, 1998, **72**, 374 [*Russ. J. Phys. Chem.*, 1998, **72** (Engl. Transl.)].
14. A. M. Kolker and L. P. Safonova, in *Ionnaya sol′vatatsiya* [*The Ion Solvation*], Ed. G. A. Krestov, Nauka, Moscow, 1987, p. 199 (in Russian).
15. N. G. Ivanova, Ph. D. (Chem.) Thesis, Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2002, 167 pp. (in Russian).
16. E. V. Ivanov and V. K. Abrosimov, *Zh. Neorg. Khim.*, 2000, **45**, 1074 [*Russ. J. Inorg. Chem.*, 2000, **45**, 968 (Engl. Transl.)].
17. E. V. Ivanov, N. G. Ivanova, V. K. Abrosimov, E. Yu. Lebedeva, and L. S. Efremova, in *Problemy khimii rastvorov i tekhnologii zhidkofaznykh materialov* [*Problems of Solution Chemistry and Technology of Liquid-Phase Materials*], Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 2001, p. 135 (in Russian).
18. C. Mann, in *Electroanalytical Chemistry*, Marcel Dekker, New York, 1969, **3**, p. 57.
19. E. V. Ivanov, N. G. Ivanova, V. K. Abrosimov, and E. Yu. Lebedeva, *Izv. Akad. Nauk. Ser. Khim.*, 2001, 2252 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2360].
20. E. V. Ivanov, A. N. Strakhov, and V. K. Abrosimov, *Ob"emnye svoistva metanolov razlichnogo deiterozameshcheniya* [*The Volume Characteristics of Differently Deuterated Methanols*], Deposited in and available from VINITI, No. 5099-B87 (16.07.87), Ivanovo, 1987, 26 pp. (in Russian).
21. J. Thomas and D. F. Evans, *J. Phys. Chem.*, 1970, **74**, 3812.
22. R. L. Shriner, R. C. Fuson, D. Y. Curtin, and T. C. Morrill, *The Systematic Identification of Organic Compounds: A Laboratory Manual*, Wiley, New York, 1980.
23. P. Picker, E. Trambley, and C. Jolicoeur, *J. Solut. Chem.*, 1974, **3**, 377.
24. A. N. Strakhov and G. A. Krestov, *Zh. Fiz. Khim.*, 1972, **46**, 2666 [*Russ. J. Phys. Chem.*, 1972, **46** (Engl. Transl.)].
25. V. K. Abrosimov and V. V. Korolev, in *Eksperimental′nye metody khimii rastvorov: Densimetriya, viskozimetriya i drugie metody* [*Experimental Methods of Solution Chemistry. Densimetry, Viscosimetry, and Other Methods*], Ed. A. M. Kutepov, Nauka, Moscow, 1997, p. 5 (in Russian).
26. V. K. Abrosimov, *Zh. Fiz. Khim.*, 1988, **62**, 1913 [*Russ. J. Phys. Chem.*, 1988, **62** (Engl. Transl.)].

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* Induction interactions Bu_4N^+—MeOH can be neglected because the corresponding isotope difference in the solvent is nearly zero.[46]

27. Y. Marcus, G. Hefter, and T.-S. Pang, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 1899.
28. F. Kawaizumi and R. Zana, *J. Phys. Chem.*, 1974, **78**, 627.
29. B. E. Conway, D. M. Novak, and L. Laliberte, *J. Solut. Chem.*, 1974, **3**, 683.
30. B. E. Conway, *J. Solut. Chem.*, 1978, **7**, 721.
31. R. N. French and C. M. Criss, *J. Solut. Chem.*, 1982, **11**, 625.
32. C. M. Criss and A. J. Pasztor, *J. Solut. Chem.*, 1978, **7**, 27.
33. J. Padova and I. Abrahamer, *J. Phys. Chem.*, 1967, **71**, 2112.
34. R. Ayala, J. M. Martinez, R. R. Pappalardo, and E. S. Marcos, *J. Phys. Chem. A.*, 2000, **104**, 2799.
35. Yu. G. Bushuev and T. A. Dubinkina, *Zh. Fiz. Khim.*, 1996, **70**, 1971 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
36. M. Krell, M. C. R. Symons, and J. Barthel, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3419.
37. L. I. Krishtalik, N. M. Alpatova, and E. V. Ovsyannikova, *Elektrokhimiya*, 1990, **26**, 429 [*Sov. Electrochem.*, 1990, **26** (Engl. Transl.)].
38. J. Barthel, L. Klein, W. Kunz, P. Calmetters, and P. Turq, *J. Solut. Chem.*, 1994, **23**, 955.
39. A. G. Novikov, N. M. Rodnikova, J. Bartel, and O. V. Sobolev, *Zh. Neorg. Khim.*, 2003, **48**, 481 [*Russ. J. Inorg. Chem.*, 2003, **48** (Engl. Transl.)].
40. G. Perron, N. Desrosiers, and J. E. Desnoyers, *Can. J. Chem.*, 1976, **54**, 2165.
41. N. G. Manin and V. P. Korolev, *Zh. Fiz. Khim.*, 2002, **76**, 246 [*Russ. J. Phys. Chem.*, 2002, **76** (Engl. Transl.)].
42. M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 2146.
43. V. P. Korolev, N. G. Manin, and G. A. Krestov, *Zh. Fiz. Khim.*, 1987, **61**, 1976 [*Russ. J. Phys. Chem.*, 1987, **61** (Engl. Transl.)].
44. C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, 1971, **75**, 388.
45. G. A. Krestov, V. P. Korolev, and D. V. Batov, *Dokl. Akad. Nauk SSSR*, 1987, **293**, 882 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
46. I. B. Rabinovich, *Vliyanie izotopii na fiziko-khimicheskie svoistva zhidkostei* [*The Effect of Isotopism on the Physicochemical Properties of Liquids*], Nauka, Moscow, 1968, 308 pp. (in Russian).
47. M. F. Smith and W. A. Van Hook, *Z. Naturforsch.*, 1989, **44a**, 371.
48. S. A. Wieczorek, A. Uranczyk, and W. A. van Hook, *J. Chem. Thermodyn.*, 1996, **28**, 987.

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