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COMPARATIVE DESCRIPTION OF THE EXTRAORDINARY PHENOMENON "THERMALLY ACTIVATED ISOBARIC PARTIAL STRUCTURE COMPACTION" OF WATER AS A SOLUTE IN SOME ALKANOLS AND ALKYLAMINES

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Abstract. *This review summarises the data available in the literature. It also includes the authors' published results of precision densimetric measurements. The research concerns with the physically unusual phenomenon of "thermally activated isobaric partial densification of the structure" (TIPCS) of dissolved water, or its so-called "negative partial molar expandability" (NPEA) in several organic solvents. They contain amphiproton hydroxyl-containing media of three alcohols: methyl alcohol (MA), tertiary butyl alcohol (TBAlcohol), and amyl or pentyl alcohol (TPA), so asprotophilic media of two amines: tert-butylamine (TBAmine) and ethylenediamine (EDA). The discussed TIPCS phenomenon, associated with a decrease in the standard (partial at infinite dilution) volume of solvated water with increasing temperature, was discovered about half a century ago in alkanol solutions of* H_2O *and recently - in water-containing media of alkylamines. However, nowadays this extraordinary effect has not yet found its physically based interpretation. It allows ones to predict the possibility of TIPCS occurrence in the binary liquid-phase system specifically selected for the study. Our comprehensive data analysis allowed us to make several inferences regarding the main characteristics of a standard solution of* H_2O *in an organic solvent. They cause extraordinary changes in the volume of the formed solvatocomplex of water under the influence of increasing temperature. Firstly, the energy parameters of the intermolecular interaction (relative affinity) water-solvent noticeably dominate over those of the solvent-solvent interaction. Those differences become more evident with increasing temperature. Secondly, a higher rate of thermal expansion of the organic solvent structure in volume (inbulk) is found than influence of temperature on structural packing of the resulting mixed molecular aggregate or water solvates complex. Thirdly, the difference in the parameters of water-solvent and solvent-solvent interactions depends not only on the proton-donor/acceptor properties of the molecules contacting in solution, but also on the configuration of the structural packing of the solvating medium. It determines the nature of steric hindrances to the formation of H-bonds. Therefore, the absolute values of the mentioned parameters*

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of relative affinity at 298.15 K increase in the series: MA << EDA ≈ TBAmine < TPAlcohol < TBAmine. It can indicate a relative strengthening of the specific interaction (mainly through the formation of hydrogen bonds) between the molecules of water and amphiprotonic or protophilic solvent in the above sequence. Indeed, difference in the solvent-solvent and water-solvent hydrogen bonding energies in the discussed liquid media of alkylamines (TBAmine and EDA) and tertiary isomeric alkanols (TBAlcohol and TPA) - with the most evident basicity - turned out to be noticeably larger than in the structural packing of water methanol solution. The ability of the components to specific interactions is quite comparable in those compounds.

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Introduction

The structural uniqueness of liquid water (or its hydrogen/oxygen isotopologue) as an individual (*unary*) solvent is based on the ability of its molecules to form a spatially coordinated continuous (continuum) three-dimensional grid of various hydrogen bonds configurations [1]. The anomalous change in the volumetric properties of the aqueous medium at low temperatures is one of the most interesting in terms of the occurrence of 3D water structure features in specific (via H-bonding) intermolecular interactions. According to it, the structure of liquid-phase water undergoes such a transformation with increasing temperature, resulting in the maximum density or minimum molar volume (V_w) of the solvent under study. Moreover, the phenomenon of decrease V_w with increasing temperature, or so-called "negative expansion" of the structural packing, for normal (protium) water is observed in a very narrow temperature range from 273.15 to 277.13 K for normal (protium) water. This temperature range becomes wider during the transition to deuterium (D_2O) and tritium (T_2O) waters, amounting to (276.97-284.34) K and (277.63-286.55) K, respectively [2-7]. The same applies to "heavy oxygen" ($-^{17}O$, $-^{18}O$) or "mixed" isotopologues of water [4, 5]. The presence of the density maximum indicates that each of the isotopologues of liquid water is not a simple one-component system. Therefore, various models of the heterogeneous structure of the aqueous medium have been actively discussed in the literature for many years [7-13]. Anomalous water properties in the currently available modeling approaches are most often associated with two forms of local structures or clusters. The *high-density* form is characterized by the presence of a noticeably less developed hydrogen bonding network than the corresponding *low-density* form. The thermally activated equilibrium between the two mentioned structural forms is a prerequisite for anomalies in the variation of both density and molar volume of water; it corresponds with correlations of hydrogen bonds characterizing the tetrahedral network, due to the tetrahedrally coordinated or *open* structure of the aqueous matrix [11-13].

The term "negative thermal expansion" (NTE) has been widely used in scientific literature since the late 80-es of the XX century [14]. Before, the discussed unusual volumetric effect was referred to as "*contraction upon heating*" one. It has been repeatedly noted in the literature that, from a purely physical point of view, the abbreviation NTE does not seem reasonable one [2, 15-17]. The process of volumetric liquid (solid) expansion at constant pressure should be formally associated with positive thermodynamic quantities $E_p = \alpha_p V = (\partial V / \partial T)_p$, where E_p and α_p are isobar molar expandability and thermal expansion coefficient, respectively. However, the NTE term is nowadays generally accepted in the scientific community for the study of compounds characterized by a decrease of both linear and bulk parameters with increasing temperature. The inner mechanisms of NTE occurrence are very specific and are overwhelmingly described for solid-phase (crystalline, hybrid, amorphous or polymeric) materials [2]. As mentioned above, liquid water has similar properties among unary solvents, but in a very narrow temperature range.

However, except for liquid protonated water (H_2O) and its isotopologues, this anomaly in the change of molar volume is also characteristic of the liquid helium isotope ^{4}He. Its density due to the phenomenon of superfluidity (in cryogenic conditions) is maximal at 2.17 K [18]. Moreover, in our previous papers on the issue [1, 2, 7, 15-17, 19, 20], we consider the NTE effects observed in binary liquid-phase systems. Such systems are exclusively only under "ordinary" conditions, i.e., at temperatures higher than $T = 273.15$ K, and atmospheric pressure (p~0.1 MPa). It is caused by the conditions of "flow" of most biochemical and technologically important processes. Indeed, the properties and state of the water component presence plays a determining role in them [1, 7, 21-25]. As we noted earlier [1], the presence (and sometimes absence) of water impurities in the reaction medium can have quite serious consequences. Water as a dissolved substance loses its characteristic or fishnet structure, and many unique properties. In this case, molecules, associates or clusters of the aqueous component exert a significant perturbing influence on the "solvate environment". It causes the emergence of a qualitatively new solvent with physicochemical and thermodynamic properties different from those of anhydrous organic medium [1, 7, 15-17, 19, 23-27].

In turn, the structural behaviour of water in the case of its extremely low content in some amphiprotic organic solvents with absence of 3D-network of hydrogen bonds typical for aqueous medium remains still understudied. It concerns the manifestation of an unusual physical effect of the decrease of the water partial molar volume or its so-called "negative partial molar volume expansion" (NPME) with increasing temperature as a dissolved substance in some solvating media. The considered phenomenon of "compression" of the standard V_2° (partial $\bar{V}_2^\infty$ or apparent $V_{\emptyset,2}^\infty$ at infinite dilution) molar volume of the dissolved substance at increasing temperature was discovered about 50 years ago during the experiments on solution of water in *tertiary* butyl alcohol (TBS), and during solution of water and urea solutions in methyl alcohol (MA) [28-31]. Further precision densimetric studies [7, 15, 19, 20, 32-40] confirmed the validity of the earlier conclusions on the atypical change in the volume taken up by a mole of water molecules being solvated in the medium of the above-mentioned alkanols. Moreover, the existence of a negative derivative $(\partial V_\mathrm{w}^\circ / \partial T)_p$ for water dissolved in tertiary amyl or *tert*-pentyl alcohol (TPA) was established [41]. However, the negative value $E_{p,\mathrm{w}}^\circ$ reflecting the NPME phenomenon is observed only in the temperature range up to $T \approx 300$ K.

The standard molar expandability of water dissolved in TPA changes its sign from negative to positive above this value. The recent results of densimetric study of water solutions in protophilic solvating media of two alkylamines, *tertiary* butyl amine (TBA) and ethylenediamine (EDA) are of particular interest [17, 42, 43]. Indeed, E. V. Ivanov, E. Yu. Lebedeva, A. A. Pakina, N. G. Ivanova, G.I. Egorov, and researchers from the Institute of Chemical Research of the Russian Academy of Sciences, Ivanovo, Russia [17, 43] contribute into the establishment and interpretation of this unusual phenomenon in water-containing alkylamines. The following sections of this paper concern detected NPME phenomenon. It also considers behavior of water dissolved in TBAmine and EDA; it shows the most pronounced "loss" of volume, reaching more than 9 $cm^3 \cdot mol^{-1}$ at T> 290 K {in the case of the system (TBAmine + H_2O) [17]}.

However, study of the state and solvation of water molecules in the liquid alkanols and alkylamines, the nature of the effect of the water component in micro quantities on the structural packing and thermodynamic characteristics of the surrounding solvent is an urgent task of both solution physicochemistry. The modern technologies concerning non-aqueous systems include technological processes of separation and extraction of liquid systems aimed at obtaining especially pure compounds. In terms of biochemistry and physiology, the NPME presents in standard solutions of urea (M) in the same organic media (water-containing systems) [2, 16, 28, 44, 45]. It confirms research results (see [46-54]) on the high degree of complementarity of the M structures formed in aqueous solutions. On the other hand, it indicates the indispensability of M as the major metabolite in physiologically important processes occurring in the living organisms. Nevertheless, we do not consider this issue; it is quite complicate and requires special attention.

Indeed, available in the literature data on the volumetric properties and structural state of infinitely dilute (standard) solutions of water in methanol, *tert*-butanol, *tert*-pentanol, and alkylamine media allow us to dwell on the fundamentally important problem of terminological description of the phenomenon under study. The term "negative partial molar expandability" with the corresponding abbreviation NPME was introduced by E.V. Ivanov, E.Y. Lebedeva, and V.K. Abrosimov [15]. Notwithstanding, they [15] believed this term is formal; it should be used with a sufficient degree of caution, "quoted" in the absence of other, more physically reasonable definition of the considered volumetric effect. According to it, replacing of the unary solvent with the OTR effect (see above) by a binary solution infinitely diluted to one of its components causes controversial effect. In such a (two-component) system, only the partial or apparent molar volume of the dissolved substance $\bar{V}_{\mathrm{w}}^{\infty} = V_{\emptyset,\mathrm{w}}^{\infty} (\equiv V_{\mathrm{w}}^{\circ})$ shows a tendency to decrease with increasing temperature. In other words, the volume occupied by one mole of dissolved water (as a structural unit of the solution) under the condition of complete exclusion of interaction between H_2O molecules should hypothetically decrease against the background of thermally expanding solvating medium *inbulk* (in the solvent volume). It constitutes a certain "absurdity" of the term OPMR [2, 55].

Therefore, we attempted to change this situation [2, 16, 17, 45, 56] in accordance with ideas of normal (i.e., positive in sign) isobaric thermal expandability of solution itself and its components, using known thermodynamic and semiempirical model approximations

[7, 57-59]. Moreover, we found that the main reason for the decrease V_{w}° with increasing temperature (or the presence of a negative sign at $E_{p,\mathrm{w}}^{\circ}$) is the difference in the rate of volumetric expansion of the amphiprotic solvent structural packing in the solvate environment of the dissolved substance and in the volume of the formed standard solution. As a consequence, the effect of relative "compression" or, more precisely, compaction of the local mixed aggregate structure (solvatocomplex of water) against the background of thermoactivated "loosening" of the molecular packing of the *bulk* solvent appears. Therefore, we will use the term - *thermoactivated isobaric partial compaction of the structure* of the formed solvate complex (abbreviated as TIPCS).

Discussion of the study results on the TIPCS phenomenon in standard water solutions

We believe, it is impossible to analyse structural and energetic transformations accompanying the TIPCS phenomenon, occurring in the liquid amphiprotic organic solvent under the influence of water molecules dissolved (solvated) in it without consideration of physicochemical and thermodynamic properties of formed standard binary solution and its components.According to the IUPAC recommendations [60-62], the *standard state* postulates the hypothetical existence of the dissolved substance molecules (in our case, water) surrounded by an infinitely large number of solvent molecules exclusively in monomeric form. Obviously, there are no concentration-dependent water-water interactions in this solution. All the volumetric (structural) changes take place only in the surrounding solvating medium under the influence of the force field of the solute molecule. This solute molecule should remainvirtually incompressible. This assumption greatly facilitates the interpretation of structural and thermodynamic effects induced by interactions in a water-containing organic medium [1, 7, 37, 38, 63]. Since the process of water "depolymerization" is directly related to the chemical nature of the solvent (or solvating) organic medium. Its molecular structure and ability to donor-acceptor and/or other interactions, allows us to consider the main characteristics of the selected amphiprotic solvents in which the TIPCS effect is observed.

Comparative analysis of amphiprotic organic solvents characterized by the presence of the TIPCS or "negative partial molar expansion" effect of the solvated aqueous component

According to the generally accepted classification [64, 65] based on the Lewis acid-base theory and the Brønsted-Lowry protolytic theory, the *amphiproton* solvents we consider are conditionally divided into *amphiproton hydroxyl-containing solvents* (MA, TBAlcohol, and TPA), including water, and *protophilic H-bond donors* (TBAmine and EDA). The amphiprotonic acidic and basic media include subgroups of solvents with high dielectric constant ε^* (water and MS) and low dielectric constant ε^* (TBA and TPA). Predominantly basic protophilic liquid media of amines (TBAmine and EDA) are also characterized by very low values ε^* (Table 1).

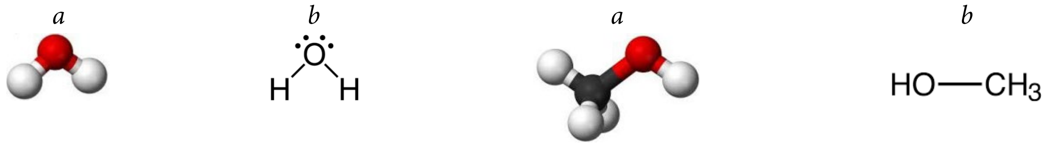
Table 1. Basic properties of the considered amphiprotic solvents at T = 298.15 K, p = 101325 Pa

Qualitative data	Water	MA	TBAlcohol	TPA	TBAmine	EDA
Molecular gross formula	H_2O	CH_4O	$C_4H_{10}O$	$C_5H_{12}O$	$C_4H_{11}N$	$C_2H_8N_2$
Molar mass M^*, g·mol^{-1}	18.015	32.042	74.123	88.150	73.138	60.099
Melting temperature $T^*_{\mathrm{m.p}}$, K	273.15	175.5	298.8	264.2	206.2	284.3
Boiling temperature $T^*_{\mathrm{b.p}}$, K	373.15	337.8	355.5	375.2	317.6	391.2
Molar volume V^*_m, cm^3·mol^{-1}	18.069	40.747	95.103	109.62	106.47	67.376
Van der Waals volume V_{vdw}, cm^3·mol^{-1}	12.4	21.7	52.3	62.6	54.3	41.5
Relative packing of molecules, V_{vdw}/V^*_m	0.686	0.533	0.550	0.571	0.510	0.616
Volume expansion coefficient$10^3\alpha^*_p$, K^{-1}	0.2571	1.132	1.299	1.059	1.556	1.054
Isothermal compressibility coefficient $10^{10}\beta^*_T$, Pa^{-1}	4.524	12.48	12.45	11.12	16.69	5.08
Enthalpy of evaporation $\Delta_{\mathrm{vap}}H^{*,\circ}_m$, kJ·mol^{-1}	43.99	37.43	46.94	50.30	29.71	46.00
Isobaric heat capacity $C^*_{p,m}$, J-mol^{-1}·K^{-1}	75.299	80.35	221.88	248.86	191.71	172.59
Relative dielectric permittivity ε^*	78.30	32.63	12.20	5.82	4.13	12.60
Dipole moment of the molecule μ^*, D	1.84	2.87	1.66	1.70	1.29	1.90
Electrostatic factor, $\varepsilon^*\mu^*$, D	144.1	93.65	20.25	9.89	5.33	23.94
Index of Refraction, n^*_D	1.3325	1.3266	1.3852	1.4049	1.3776	1.4540
Molecular polarizability $10^{24}\alpha^*_0$, cm^3	1.465	3.26	8.82	10.64	9.69	7.21
Donor number (according to Gutman) *DN*, kcal·mol^{-1}	18.0	19.0	38.0	44.0	57.0	55.0
Acceptor number (according to Gutmann) *AN*	54.8	41.3	27.1	22.2	(6,70)	20.9
Parameter of "structurability" (according to Otaki) S_{p}	19.3	8.6	~ 0	1.7	(-3.5)	2.2
Specific interaction energy, kJ·mol^{-1}	38.45	23.93	14.78	16.70	(-2.36)	1.84
Non-specific interaction energy, kJ·mol^{-1}	3.06	11.02	29.68	31.13	29.59	41.68

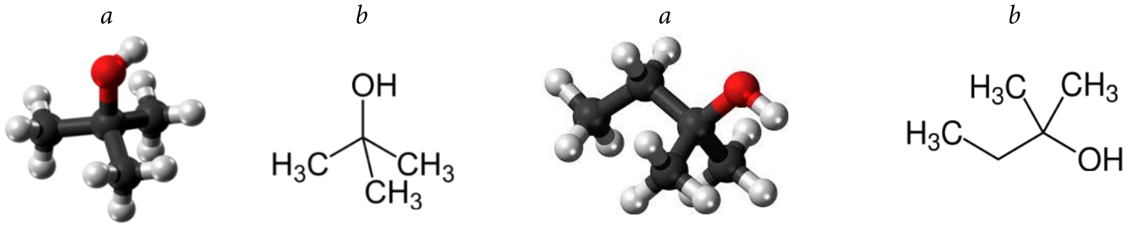
Notice. Data for TBAlcohol are given at T = 299.15 K. 1 Debye (D) = 3.33564×10^{-30} Coulomb (C)·m

Table 1 presents the main physicochemical and thermodynamic properties of the considered organic solvents. They include those directly related to the ability to interact with the molecules of water dissolved in them. In addition, Figure 1 demonstrates the specific features of the molecular structure comprising the structural packing of each of the liquid media listed in the table.

Water **Methanol (MA)**



***tert*-Butanol (TBAlcohol)** ***tert*-Pentanol (TPA)**



***tert*-Butylamine (TBAmine)** **Ethylenediamine (EDA)**

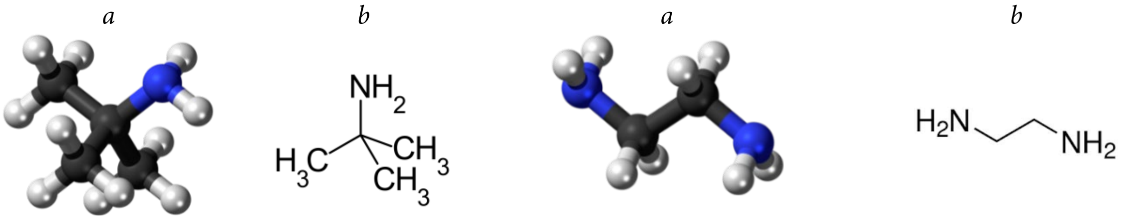


Fig. 1. 3D (***a***) and 2D (***b***) structural representations of the considered amphiprotic solvents molecules including water

According to Table 2, the numerical values presented are the "weighted averages" based on the systematization of compiled literature data for each of the listed solvent characteristics [7, 16, 17, 19, 24, 31-33, 38-43, 45, 64-71]. The table also includes semiempirical parameters based on various modelling approaches or formally evaluating scales along with experimentally determined properties. These include donor-acceptor numbers of solvents (AN and $DN_{(\mathrm{SbCl_5})}$), *structurization parameters* (S_p), and energy characteristics of intermolecular interactions of different nature. Further, Table 1 presents the energies of specific interaction U_sp (through strong dipole-dipole contacts or hydrogen bonds) and nonspecific contacts U_nsp (through *universal* or van der Waals forces). This principle of total energy of intermolecular interaction separation $U_\mathrm{tot} = U_\mathrm{sp} + U_\mathrm{nsp}$ in a unary fluid is based on the concept of Dack [70]. According to the conclusions of [70], p_coh, where $U_\mathrm{tot} \equiv p_\mathrm{coh} V_m^* = \Delta_\mathrm{vap} H_m^{*,\circ} - RT$ is the cohesion energy density. One of the fundamental thermodynamic relations of Maxwell, linking the internal pressure of a liquidU_tot with its internal energy p_intU, *is used to express the nonspecific component* of the quantity: $p_\mathrm{int} = (\partial U/\partial V)_T = T(\partial p/\partial T)_V - p \approx \alpha_p^* T/\beta_T^*$, where p is the external pressure at $p_\mathrm{int} \gg p$. Hence, $U_\mathrm{sp} = \Delta_\mathrm{vap} H_m^{*,\circ} - RT - (V_m^* \alpha_p^* T/\beta_T^*)[\equiv U_\mathrm{nsp}]$ (see Table 1). The dimensionless *structurization* S_p parameter in Table 1 proposed by Otaki [71] is treated quite differently. The concept of [71] supposes the value $\Delta_\mathrm{vap} H_m^{*,\circ}$consists of the donor-acceptor interaction energies *DA*. They can be assessed through the Gutmann numbers (*AN* and *DN* in Table 1), and other interactions related to van der Waals interactions - *VDW*. In addition, the contribution of the *STR* interaction energy due to the spatially three-dimensional ordering of molecules in the structural packing of the liquid is also taken into account. The values of *DA*/(kJ·mol^{-1}) are postulated as corresponding to the expression: 4.18×10^{-2} ·f_{DA}·*DN*·*AN*, where the parameter f_{DA} is assumed to be 0.5 for water and 0.6 for the other amphiprot solvents. The values of VDW/(kJ·mol^{-1}) are assessed by assuming that this contribution S_p is identical to the value of 0.222V_m^*/(cm^3), which is proportional to the enthalpy of vaporization (in kJ·mol^{-1}) of the corresponding (by molar volume) *n*-alkane at T = 298.15 K. In this case, $S_\mathrm{p} \equiv STR/(\mathrm{kJ \cdot mol^{-1}}) = \Delta_\mathrm{vap} H_m^{*,\circ} - 0{,}0418 \cdot f_{DA}(AN \times DN) - 0{,}222 V_m^*$ [71].

Consequently, the liquid-phase media of water and MA appear to be the most structured (in terms of the spatial distribution of molecules and the strength of the hydrogen bonds formed). In these solvents, a clear dominance of the contribution U_sp with high values of the electrostatic factor $\varepsilon^* \mu^*$ is observed (see Table 1). On the other hand, *tert*-alkanols (TBAlcohol and TPA) are comparable in ratio $U_\mathrm{sp}/U_\mathrm{nsp}$ and magnitude S_p with similar characteristics for aprotonic dipolar media of organic nature [1]. The corresponding results for alkylamines (TBAmine and EDA) indicate the problematic use of the above models (see table 1). Apparently, this is due both to difficulties in determining the acceptor and donor numbers [66, 67], and to the presence of a noticeable scatter in the available literature values of the "force" (energy) characteristics, especially for the liquid-phase TBAmine medium [64-69].

In this context, a comparative analysis of both individual properties (as presented in Table 1) and their totality for the amphiprotic solvents discussed seems more propriate. According to [72, 73], considering the "isothermal bulk compression modulus "$K_T = 1/\beta_T^*$ as a measure of the elasticity of the spatial H-bond grid, allows us to conclude that the molecular packages forming the liquid media of water and EDA are similar ones (see Table 1). Formally, a necessary condition for the emergence of a three-dimensional (tetrahedrally coordinated) hydrogen bonding network is the presence of two electron-donor and two electron-acceptor centers in the solvent molecule [72]. H_2O and EDA molecules, unlike molecules of other solvents in Table 1, satisfy these requirements. This largely predetermines the "water-like" behaviour of the indicated diamine in a number of properties, such as $\Delta_{\text{vap}}H_m^{*,\circ}$, V_{vdw}/V_m^*,μ^*, specific heat capacity $c_p = C_{p,m}^*/M^*$, the relatively low value α_p^*, and rather high electrostatic factor (see Table 1). In contrast, the structure of *tert*-butyl monoamine appears rather loose with a low electrostatic field around the molecules. It indicates a predominantly universal character of the intermolecular interactions in the TBA liquid medium. According to Table 1, molecules of methanol and *tertiary* isomeric alcohols (TBAlcohol and TBP) form strong hydrogen bonds with their surroundings. However, in the first case (MA) this ability is very evident; in the second case the so-called *steric factor* is evident (especially in the case of TBAlcohol). It is due to structural-packaging mismatches for the realization of directed (specific) intermolecular contacts.

These inferences are largely confirmed by the results of computer modelling and structural (spectroscopic) studies of the solvents under study. According to the simple *grid model* [74], the local orientational ordering of molecules in liquid methanol corresponds to association in zigzag chain clusters. The cluster shape in TBAlcohol represents a large variety of branched structural formations, including cyclic structure (up to hexamers) [75]. Therefore, the isobaric heat capacity of TBAlcohol shows a markedly more evident variability with temperature than that observed for unbranched MA [75, 76]. The transition from TBAlcohol to TPA entails an increase in steric effects due to the greater number of possible structural conformations in the liquid medium of the latter alkanols (based on the results of calculations using *density functional theory*) [77] in spite of insignificant differences in their basic thermodynamic properties (see Table 1). Meanwhile, TPA remains liquid up to temperatures below T = 273.15 K. It makes this alcohol a useful alternative to *tert*-butanol in the study of water solvation effects. As in the case of TBAlcohol and TPA, *gosh* conformational interactions play an important role in the energetic stabilization of the liquid EDA structure [78-80]. The possibility of formation of two strong and two weak hydrogen bonds through each nitrogen atom predicted in [78, 79] confirms the above assumption on the presence of a three-dimensional branched network of H-bonds in diamine liquid medium. Meanwhile, it is less pronounced one than in water [80]. In turn, the steric factor causes a marked decrease in the basicity (electron-donating ability) of TBAmine, as compared to isomeric *n*- and *2*-butylamines [81]. It is one of the most probable reasons for insignificant specific component in the total interaction energy between its molecules in the condensed state (see Table 1).

Results of densimetric study of water volumetric properties as a dissolved substance in amphiprotic organic media with experimentally determined TIPCS effect

The structural and thermodynamic properties of amphiprotic organic solvents (see Table 1) are directly related to their characteristics in extremely dilute (or standard) relative to water solutions [7, 15, 17, 19-25, 31-43, 70, 82]. As mentioned above, the considered solvating media are used in a number of technological processes and experimental devices, which are associated with the presence of traces of water in them (often in the form of atmospheric moisture). As a result, obtaining reliable information on the thermodynamic and structural properties of such (binary) liquid systems is a prerequisite for the successful realization of the practical and theoretical tasks. In accordance with Table 1, the intensity and direction of structural changes and intermolecular interactions in each amphiprot medium under the influence of dissolved water molecules depend on the donor-acceptor, electrostatic properties of the solvate environment, and largely on the structure (packing) of the latter. Table 2 shows results of the densimetric study of water solutions in the organic solvating media.

Table 2. Available information in the literature on standard (partial) molar volumes of water (V_w°, cm^3·mol^{-1}) in the studied amphiprot solvents at different temperatures (T) and p= 0.1 MPa

T, K	MA	TBAlcohol	TPA	TBAmine	EDA
278.15	*14.72 ± 0.02* [15], 14.54 ± 0.02 [19, 20], 14.55 ± 0.03 [31], 14.73 ± 0.03 [32], 14.71 ± 0.04 [34]	-	*15.24 ± 0.05* [41]	*9.41 ± 0.02* [17]	13.14 ± 0.03 [43] (extrapolation $\bar{V}_w$ from mixtures to "pure" EDA)
283.15	-	-	-	*9.27 ± 0.02* [17]	-
288.15	*14.59 ± 0.02* [15], 14.43 ± 0.03 [19, 20], 14.44 ± 0.06 [31], 14.67 ± 0.03 [32]	17.73 ± 0.05 [36] (extrapolation $\bar{V}_w$ from mixtures to "pure" TBAlcohol)	*14.68 ± 0.05* [41]	*9.08 ± 0.02* [17], 5.06 ± 0.05 [36]	*12.43 ± 0.03* [43], 11.81 ± 0.10 [42]
293.15	-	-	-	*8.96 ± 0.02* [17], 4.75 ± 0.05 [36]	11.16 ± 0.10 [42]
298.15	*14.47± 0.02* [15], 14.35 ± 0.02 [19, 20], 14.41 ± 0.02 [31], 14.48 ± 0.03 [32], 14.49 ± 0.07 [34]	16.87 ± 0.05 [36] (extrapolation $\bar{V}_w$ from mixtures to "pure" TBAlcohol)	*14.56 ± 0.05* [41]	*8.82 ± 0.02* [17], 4.53 ± 0.05 [36]	*12.30 ± 0.03* [43], 11.50 ± 0.10 [42]
299.15	-	*17.06 ± 0.02* [15], 17.07 ± 0.03 [33], 16.61 ± 0.03 [39]	-	-	-
303.15	-	*16.85 ± 0.02* [15], 16.80 ± 0.03 [33], 16.31 ± 0.03 [39]	-	*8.68 ± 0.02* [17], 4.48 ± 0.05 [36]	11.75 ± 0.10 [42]
308.15	*14.34± 0.02* [15], 14.24 ± 0.02 [19, 20], 14.34 ± 0.03 [31], 14.29 ± 0.03 [32]	*16.58 ± 0.02* [15], 16.56 ± 0.03 [33], 16.60 ± 0.05 [36], 15.63 ± 0.03 [39]	*14.61 ± 0.05* [41]	4.34 ± 0.05 [36]	*12.24 ± 0.03* [43], 11.72 ± 0.10 [42]
313.15	-	*16.32 ± 0.02* [15], 16.30 ± 0.03 [33], 15.44 ± 0.03 [39]	-	-	11.71 ± 0.10 [42]
318.15	*14.21± 0.02* [15], 14.14 ± 0.03 [19, 20], 14.23 ± 0.02 [31], 14.19 ± 0.03 [32], 14.20 ± 0.04 [34]	*16.05 ± 0.02* [15], 16.05 ± 0.03 [33], 16.17 ± 0.05 [36], 15.16 ± 0.03 [39]	*14.70 ± 0.05* [41]	-	11.69 ± 0.10 [42]
323.15	-	14.58 ± 0.03 [39]	-	-	*12.13 ± 0.03* [43], 11.73 ± 0.10 [42]
328.15	-	-	-	-	11.72 ± 0.10 [42]
333.15	-	13.95 ± 0.03 [39]	-	-	*12.03 ± 0.03* [43], 11.73 ± 0.10 [42]

Notice. The italicized values are those we used for further analysis. MolarvolumesofwaterV_w^* (cm^3·mol^{-1}) [5, 7, 24]: 18.016 (278.15 K); 18.021 (283.15 K); 18.031 (288.15 K); 18.048 (293.15 K); 18.069 (298.15 K); 18.094 (303.15 K); 18.123 (308.15 K); 18.157 (313.15 K); 18.193 (318.15 K); 18.233 (323.15 K); 18.276 (328.15 K) and 18.323 (333.15 K).

The values V_{w}° in most of the literature sources cited in Table 2 were calculated using the traditional procedure of extrapolation of the concentration dependence of the apparent molar volume $V_{\emptyset,\mathrm{w}}$ to the state of infinite dilution of the solution aqueous component. We use the procedure of either linear or polynomial MNC regression analysis. It allows us to describe (recover) the experimentally obtained functions $V_{\emptyset,\mathrm{w}} - m$, where m is the molality of the solution. At the same time, the existing limitations for accurate determination $V_{\emptyset,\mathrm{w}}(m)$ by the densimetric method in the region of compositions with extremely low dissolved matter content are known to cause negative consequences [83, 84]. Specifically, $V_{\emptyset,\mathrm{w}} \to \pm\infty$ at $m \to 0$. In other words, there is the so-called "gramophone tube" effect of estimation errors $V_{\emptyset,\mathrm{w}}(m)$ due to a sharp increase in the statistical weight of this quantity in the high dilution region with respect to the dissolved component [84].

According to Table 2, only the values V_{w}° for MA and TBAlcohol correspond quite well, perhaps, except for the results borrowed from [19, 20, 39]. The corresponding values for the system (TPAlcohol + H_2O) are known to date only due to a single publication by Sakurai [41]. The same applies to the authors [43] study on the volumetric properties of water solutions in EDA, considering the absence of regularity in the temperature-dependent change V_{w}° in the above diamine according to Waltz et al. [42]. As for the available values $V_{\mathrm{w}}^{\circ}(T)$ in *tert*-butyl amine, the results of the authors [36] seem to be absurd because of unrealistically large losses in the molar volume of water (V_{w}^{*}) during its dissolution in TBAmine (see Table 2). Thus, according to [36], these losses, which are about 13 $\mathrm{cm^3 \cdot mol^{-1}}$ at T = 288 K, increase to ~ 13.8 $\mathrm{cm^3 \cdot mol^{-1}}$ when the temperature increases to 308 K (see Table 2). The reason for the "detection" of such significant volume effects in [36] obviously is due to the authors' insufficient control of residual water in the TBAmine medium. This causes noticeable decrease in the calculated values $V_{\emptyset,\mathrm{w}}(m)$ and, as a consequence, a significant underestimation of the extrapolated value (V_{w}°). The experimental procedure of density measurement related to both the sensitivity of the densimeter and the reproducibility of the obtained data [83, 84].

It is important to take concern the conditions ensuring the reliability of obtaining V_{w}° amphiprotic organic media of different nature in the experimental study when performing a comparative analysis of the volumetric effects of water dissolution. We will consider (italicized in Table 2) the results of [41, 43] for the systems (TPA + H_2O) and (EDA + H_2O), and data of some researches [15, 17]. Those were obtained for water solutions in highly purified MA, TBAlcohol and TBAmine using a rational procedure of calculation V_{w}°. The latter is based on the use of the solvomolar concentration scale sm [15-17, 45, 83-86] as a reference value in calculating $V_{\emptyset,\mathrm{w}}$the *total* volume of solution V_{s}:

$$V_{\mathrm{s}}(sm) = (55{,}50843M_{\mathrm{a}}^{*} + smM_{\mathrm{w}}^{*})\rho_{\mathrm{s}}^{-1} = V_{\mathrm{s}}^{\circ} + V_{\emptyset,\mathrm{w}}sm, \tag{1}$$

where M_{w}^{*} and M_{a}^{*} are the molar masses of water (w) and amphiprotic organic solvent (a), respectively; ρ_{s} is the density of the solution; $V_{\mathrm{s}}^{\circ} = 55{,}50843V_{\mathrm{a}}^{*}$ is the total volume of the solution at $sm \to 0$ (here $V_{\mathrm{a}}^{*} = M_{\mathrm{a}}^{*}/\rho_{\mathrm{a}}^{*}$, the total volume of the solvent). Notably, unlike the "traditional" way of calculating the value $V_{\emptyset,\mathrm{w}}\{= M_{\mathrm{w}}^{*}/\rho_{\mathrm{s}} - 10^3(\rho_{\mathrm{s}} - \rho_{\mathrm{a}}^{*})/(m\rho_{\mathrm{s}}\rho_{\mathrm{a}}^{*})\}$ [84], the experimental value ρ_{s} in equation (1) is used once. The normalizing multiplier 55.50843, equal to the number of moles of H_2O in 1 kg of water, is used so that *in the dimensionless* (by definition) scale sm the ratio of the dissolved substance quantity (n_{w} mole) to the solvent quantity (n_a mole) remains the same as in aqueous solution, where the concentrations m and sm numerically coincide [83, 84, 86].

We applied the relation [16, 17, 85], which expresses the excess molar volume of the water solution in the selected amphiprotic solvent V_s^E relative to 55.50843 moles of the latter one, for the calculation V_w° within the considered following procedure:

$$V_\mathrm{s}^\mathrm{E}(sm) = V_\mathrm{s}(sm) - V_\mathrm{s}^\circ - V_\mathrm{w}^\circ sm = (V_{\emptyset,\mathrm{w}} - V_\mathrm{w}^\circ)sm. \tag{2}$$

The value V_s^E in dilute solutions can be replaced by a virial series expansion in powers sm [85, 87]:

$$V_\mathrm{s}^\mathrm{E}(sm) = v_\mathrm{ww} sm + v_\mathrm{www} sm^2 + \ldots \tag{3}$$

Transforming equations (2) and (3) with respect to $V_{\emptyset,\mathrm{w}}(sm)$ in equation (1) provides a relatively simple relation for determining V_w°:

$$V_\mathrm{s}(sm) - V_\mathrm{s}^\circ = V_{\emptyset,\mathrm{w}} sm = V_\mathrm{w}^\circ sm + v_\mathrm{ww} sm^2 + v_\mathrm{www} sm^3 + \ldots \tag{4}$$

The coefficients v_ww and v_www, within the "formalism" of the Macmillan-Mayer solution theory [85, 87], represent the bulk contributions to the value $V_{\emptyset,\mathrm{w}}$ {equation (4)} from solvent-induced pairwise and ternary (crossing) w-w interactions. Considering the densimetric studies, we used rather dilute water solutions compiled in Table 2. Moreover, we calculated the values V_w° mainly (except for the methanol water solution) according to equation (4) without taking into account the negligibly small (according to the criterion evaluation results) parameter v_www.

The main advantage *of a rational* approach to estimation V_w° based on equation (4) and the solvomolar concentration scale is the replacement of the extrapolation procedure by an interpolation one. The values $V_{\emptyset,\mathrm{w}}(sm)$ in the region of sufficiently high dilutions are within a narrow confidence interval with respect to the line crossing the ordinate axis at a known point: $V_\mathrm{s}^\circ = 55{,}50843 V_\mathrm{a}^*$, which is set in advance. This fact practically eliminates the influence of the "gramophone pipe" effect mentioned above, caused by the catastrophic increase in determination errors $V_{\emptyset,\mathrm{w}}$ at $sm \to 0$.

Influence of the amphiproton or protophilic solvent nature and temperature on the volumetric effects of water dissolution, related to the TIPCS phenomenon

We will analyze the above equation (4) to realise the negative sign of $E_{p,\mathrm{w}}^\circ = (\partial V_\mathrm{w}^\circ / \partial T)_p$ or the TIPCS phenomenon. Having differentiated all its parts by temperature, the following inequalities can be compiled for the limiting case ($sm \to 0$):

$$(\partial V_\mathrm{w}^\circ / \partial T)_p > 0 \text{ at } (\partial V_\mathrm{s} / \partial T)_p - (\partial V_\mathrm{s}^\circ / \partial T)_p > 0, \tag{5}$$

on the other side,

$$(\partial V_\mathrm{w}^\circ / \partial T)_p < 0 \text{ at } (\partial V_\mathrm{s} / \partial T)_p - (\partial V_\mathrm{s}^\circ / \partial T)_p < 0. \tag{6}$$

The above conclusion were made on the basis of thermodynamic inequality (6). It possesses the structural packages of amphiprotic organic solvents given in Tables 1 and 2 in the presence of water molecules dissolved in them become less expandable under the influence of increasing temperature. However, this particular research concerns the local structural aggregates or solvatocomplexes formed by water molecules in the medium of a particular solvent under the condition of infinite dilution.

A similar conclusion is suggested in the case of detailing one of the most famous thermodynamic Maxwell's cross-ratios [17, 35]:

$$-(\partial V_\mathrm{w}^\circ/\partial T)_p = -E_{p,\mathrm{w}}^\circ = (\partial S_\mathrm{w}^\circ/\partial p)_T, \tag{7}$$

where S_w° is the standard (partial) molar entropy of the solvated substance. The negative sign at $E_{p,\mathrm{w}}^\circ$ should correspond to the increase in S_w°. It is due to the structurization of the amphiprotic solvent surrounding the water molecule under the influence of increasing pressure, as follows from equation (7). Therefore, the water-solvent bonds formed in the standard solution should be stronger than those in the *inbulk* solvent.

Table 3 contains the values $E_{p,\mathrm{w}}^\circ$ for the compared organic media.

Table 3. Standard (partial) molar expandabilities of water ($E_{p,\mathrm{w}}^\circ$, $\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$) in amphiprotic solvents, estimated for the corresponding temperature intervals (see Table 2), at p = 0.1 MPa

T, K	MA	TBAlcohol	TPA	TBAmine	EDA
278.15	-0.0127 ± 0.0003	–	-0.1120 ± 0.0030	-0.0241 ± 0.0023	–
288.15		–	-0.0241 ± 0.0030		-0.0084 ± 0.0018
298.15		-0.0531 ± 0.0006	-0.0017 ± 0.0030		
308.15			0.0075± 0.0030		
318.15			0.0123± 0.0030	–	

Notice. Values of expandability of water in TBAlcohol are given at temperatures from 299.15 K. For the system (TBAmine + H_2O) the temperature range is limited to 303.15 K, and for the system (EDA + H_2O) to 333.15 K.

We approximated the predominantly linear functions $V_\mathrm{w}^\circ - T$ (italicized in Table 2) with a first-order regression equation to find $E_{p,\mathrm{w}}^\circ$:

$$V_\mathrm{w}^\circ(T) = V_\mathrm{w}^\circ(\theta) + [\partial\, V_\mathrm{w}^\circ(T)/\partial\,(T-\theta)]_p (T-\theta), \tag{8}$$

where θ is the "average weighted" temperature (of comparison). The values $E_{p,\mathrm{w}}^\circ$ for the system (TPA + H_2O) were obtained by selecting a mathematical model reconstructing the temperature dependence V_w° in the corresponding temperature range (see Table 2), followed by the procedure of differentiation by $(T-\theta)$.

If we approximate the temperature dependence $E_{p,\mathrm{w}}^\circ(T)$ for a standard solution of water in TPA (see Table 2) by the linear equation (8), abstracting from the chosen model for estimating the values V_w° in Table 3, we obtain the derivative $[\partial\, V_\mathrm{w}^\circ(T)/\partial\,(T-\theta)]_p$ = -(0.0115±0.0075) $\mathrm{cm^3 \cdot mol^{-1} \cdot K^{-1}}$. Solvents can be arranged according to the expression of the TIPCS phenomenon with respect to dissolved water in a series: EDA < (TPA) < MA << MA << TBAmine << TBAlcohol, taking into account the absolute values of $E_{p,\mathrm{w}}^\circ$, presented in Table 3. Naturally, the above sequence should undergo changes with respect to the *tert*-pentanol water solution in the area of low temperatures (see Table 3). This sharp occurrence of the TIPCS effect in the system (TPS + H_2O) at T = (278.15-288.15) K has not yet been found a reasonable enough explanation. This is probably due to both difficulties in preparing this alkanol for the experiments and inaccuracies in the determination procedure $V_\mathrm{w}^\circ(T)$. It justifies the need for a thorough verification of the data [41] on the density of water solutions in TPA. Accordingly, we will further adhere to the interpretation based on the above proposed sequence in the change $E^{\circ}_{p,\mathrm{w}}$ (298.15 K) in the transition from one water-containing amphiprotic system to another.

Fig. 2 illustrates the tendencies of change with increasing temperature of the *standard excess* (partial) molar volumes of water $V_{\mathrm{w}}^{\circ,\mathrm{E}} = V_{\mathrm{w}}^{\circ} - V_{\mathrm{w}}^{*}$ in the solvents (see Tables 1, 2). According to the definition [7, 63, 88], the value in its physical meaning $V_{\mathrm{w}}^{\circ,\mathrm{E}}$ is identical to the change in the volume of one mole of dissolved water in the isobaric-isothermal process of replacing the structural packing. The features of the aqueous medium surrounding the H_2O molecule in the environment of the solvating medium molecules $V_{\mathrm{w}}^{\circ,\mathrm{E}}$ can be considered in this context as the *volumetric effect of water dissolution* [63]. Data of Table 2 were used for calculation $V_{\mathrm{w}}^{\circ,\mathrm{E}}(T)$ by $V_{\mathrm{w}}^{*}(T)$.

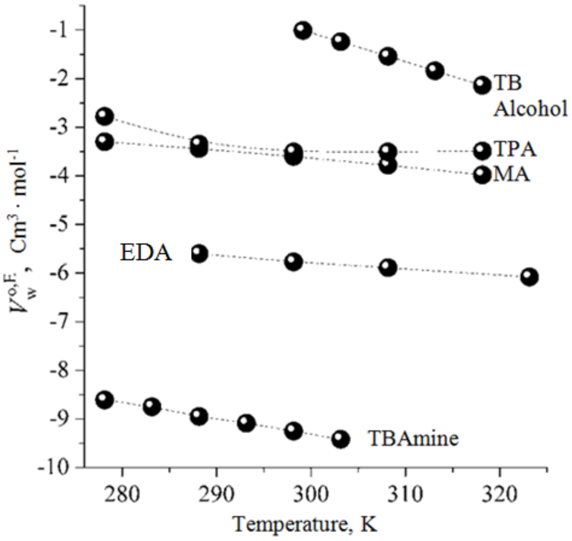


Fig. 2. Temperature dependences of water dissolution volume effects in amphiprotic organic solvents with experimentally revealed TIPCS phenomenon

There are two general conclusions in terms of volume effects $V_{\mathrm{w}}^{\circ,\mathrm{E}}$ evolution with increasing temperature shown in Fig. 2.

Firstly, the most significant "losses" of water volume (per mole H_2O) are observed at its dissolution in alkylamines. Moreover, the volume of the solvate complex formed by the incorporation of the water component molecules into the structural matrix of TBAmine is less than half of the molar volume of water at $T < 293$ K (V_{w}^{*}). Such a significant compaction of the structure surrounded by a water molecule is obviously due to both the most significant protonation ability of TBAmine, and the smallest compactness of the structural packing of this amine compared to other solvents in Table 1. It implies the presence of voids in the structural packing of TBAmine suitable for accommodating monomeric H_2O molecules. According to [89], it can cause the compression of the water solvato-complex structure, which increases in the case of strong water-amide hydrogen bonds. The embedding of a water molecule in the EDA structural matrix (see Table 1), which is more densely packed than in TBAmine, MA or *tert*-alkanols, is accompanied by the formation of a solvate cavity of the corresponding size [42, 73, 80, 89]. However, the structure of the formed H_2O-EDA solvato-complex also undergoes a noticeable compaction due to the presence of two unsubstituted amino groups in the solvent molecule. These groups are capable of forming stronger hydrogen bonds with water than in unary or alcoholic media.

Secondly, Fig. 2 and Table 3 show that the most "suitable" for the unusual volume effect (TIPCS) discussed here are the "related" (in structure) amphiprotic media of *tertiary* butanol and butylamine, despite significant differences in the structural organization of infinitely dilute (standard) water solutions. It is partly true for the *tert*-pentanol medium in the low-temperature region (see Fig. 2) [41]. The mentioned above solvents have comparable values of the molar volume (V_a^*) and the density of the spatial distribution of molecules in the structural packing ($V_{w,a}/V_a^*$). The small difference in molecular polarizabilities ($\alpha_{0,a}^*$) determines the similarity of the nonspecific interaction energy values in the liquid media of TBAlcohol, TBAmine, and TPA (see Table 1). At the same time, the steric factor mentioned above prevents the formation of a strong structure in *tert*-butyl amine. It makes more compressible and expandable compared to that in TBA or TPA. This conclusion is supported by the very low enthalpy of TBAmine vaporization (see Table 1). Hence, the incorporation of water molecules into the most adapted initial matrix of TBAmine has a pronounced structurising effect due to the formation of strong heterocomponent H-bonds. Perhaps, dissolved water (in the monomeric state) creates a structure similar to a tetrahedrally coordinated packing of solvating medium molecules. According to Table 3 and Fig. 2, this tendency, apparently, should increase with increasing temperature and weaken in the transition from TBAmine to TBAlcohol and further to MA (TPA) and EDA.

Hence, it shows the TIPCS phenomenon is based on both the balance of energy characteristics of interaction between the solution components and the structural and packing features of the solvating medium. Since the considered state of infinite dilution excludes the interaction between dissolved water molecules, perhaps the most important task in the thermodynamic analysis of the TIPCS phenomenon is to establish the relationship between the *parameters of molecular affinity* water-solvent and solvent-solvent.

Parameters of "relative affinity" between molecules of interacting components in standard water solutions characterized by the presence of the TIPCS phenomenon

Partially, the solution to the problem can be achieved through the semiempirical approach proposed by Ben-Naim and Marcus [57-59]. According to this approach, the energy *parameter of relative affinity* $\Delta G^{*,\circ}$ associated with the volume effects in solution can be represented as a following ratio:

$$\Delta G^{(*),\circ} = kT\rho_a^{(*)}(V_w^\circ - V_a^*) = RT(V_w^\circ - V_a^*)(V_a^*)^{-1}, \qquad (9)$$

where k is Boltzmann constant, $\rho_a^{(*)} = N_A/V_a^*$ is *number density* parameter. Table 4 shows the $\Delta G^{(*),\circ}$ molar volume values $V_a^* = M_a^*/\rho_a^*$ of the organic solvating media necessary for the calculations.

Taking into account the limiting expressions of Kirkwood-Buff (KB) theory for molar volumes, the value V_w° can be interpreted as [57, 58]:

$$V_w^\circ = \left[1 - \rho_a^{(*)}(G_{aa}^\circ - G_{aw}^\circ)\right]\left(\rho_a^{(*)}\right)^{-1}, \qquad (10)$$

where G_{aa}° and G_{aw}° are the volume-effect related KB integrals referring to solvent-solvent and solvent-water interactions, respectively.

Table 4. Numerical values of molar volumes (V_a^*, cm^3·mol^{-1}) and extensibilities ($E_{p,\mathrm{a}}^*$, cm^3·mol^{-1}·K^{-1}, given in parentheses) of amphiprotic organic solvents at different temperatures (T) and p = 0.1 MPa

T, K	MA [19, 20]	TBAlcohol [33]	TPA [41]	TBAmine [17]	EDA [43]
278.15	39.796 (0.04611)	–	107.19 (0.1161)	103.27 (0.1557)	–
283.15	–	–	–	104.04 (0.1582)	–
288.15	40.265 (0.04756)	–	108.39 (0.1215)	104.88 (0.1608)	66.683 (0.06871)
293.15	–	–	–	105.64 (0.1633)	–
298.15	40.747 (0.04902)	94.980* (0.1229)*	109.62 (0.1269)	106.47 (0.1658)	67.383 (0.07089)
299.15	–	95.103 (0.1237)	–	–	–
303.15	–	95.604 (0.1267)	–	107.33 (0.1684)	–
308.15	41.245 (0.05048)	96.247 (0.1305)	110.91 (0.1323)	–	68.102 (0.07306)
313.15	–	96.909 (0.1343)	–	–	–
318.15	41.747 (0.05193)	97.590 (0.1381)	112.27 (0.1377)	–	–
323.15	–	–	–	–	69.220 (0.07632)
333.15	–	–	–	–	69.997 (0.07850)

Notice. The selected temperatures for each solvent correspond to those for the standard water solutions in Table 2 (values in italics). (*) - Approximated value

The equation (9) can be transformed into the following form:

$$\Delta G^{(*),\circ} = RT(G_\mathrm{aa}^\circ - G_\mathrm{aw}^\circ)(V_\mathrm{a}^*)^{-1}. \tag{11}$$

As it follows from equations (9) and (11), the value $V_\mathrm{a}^*\Delta G^{(*),\circ}/RT$ can be viewed as a measure of the relative affinity of the molecules in the solvent and the resulting binary system:

$$G_\mathrm{aa}^\circ - G_\mathrm{aw}^\circ = V_\mathrm{w}^\circ - V_\mathrm{a}^*, \tag{12}$$

Temperature-dependent data on $G_\mathrm{aa}^\circ - G_\mathrm{aw}^\circ$ or $V_\mathrm{w}^\circ - V_\mathrm{a}^*$ for water solutions in the compared solvating media are given in Table 5. The temperature-dependent values $\Delta G^{(*),\circ}$ are shown in Fig. 3. According to their results, $\Delta G^{(*),\circ} < 0$, since $G_\mathrm{aa}^\circ < G_\mathrm{aw}^\circ$. This fact allows us to conclude the affinity of dissolved water molecules to the molecules of the amphiprotic organic solvent of the series considered (Tables 1-5). It generally prevails over the affinity of the molecules to each other.

Table 5. Numerical values of parameters $\{(G^{\circ}_{\mathrm{aa}} - G^{\circ}_{\mathrm{aw}}) = (V^{\circ}_{\mathrm{w}} - V^{*}_{\mathrm{a}})$, $\mathrm{cm^3 \cdot mol^{-1}}\}$ for the studied liquid-phase systems (amphiprotic solvent + water) at different temperatures (T) and p = 0.1 MPa

T, K	MA [15,19,20]	TBAlcohol [15,33]	TPA [41]	TBAmine [17]	EDA [43]
278.15	-25.08	-	-91.95	-93.86	-
283.15	-	-	-	-94.77	-
288.15	-25.68	-	-93.71	-95.80	-54.25
293.15	-	-	-	-96.68	-
298.15	-26.28	-77.98*	-95.06	-97.65	-55.08
299.15	-	-78.04	-	-	-
303.15	-	-78.75	-	-98.65	-
308.15	-26.91	-79.66	-96.30	-	-55.86
313.15	-	-80.59	-	-	-
318.15	-27.54	-81.54	-97.57	-	-
323.15	-	-	-	-	-57.09
333.15	-	-	-	-	-57.97

Notice. The selected temperatures for each solvent correspond to those in Tables 2-4. (*) - Approximated value

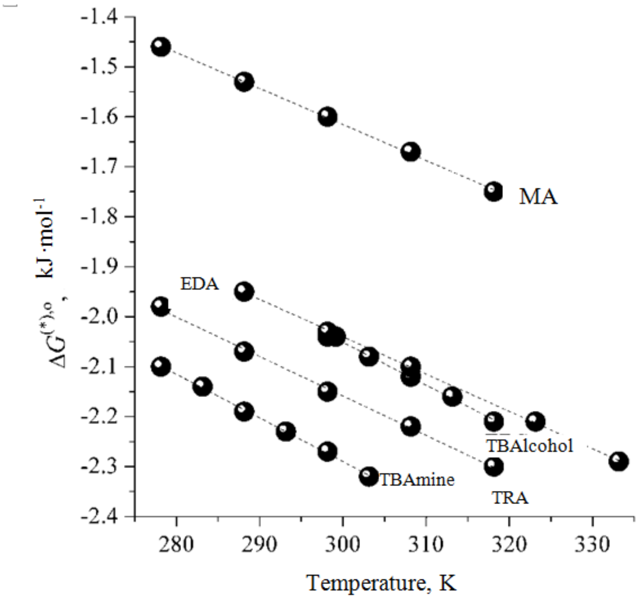


Fig. 3. Temperature dependences of "relative affinity" parameters in standard solutions of water in amphiprotic organic solvents with experimentally established TIPCS phenomenon

According to dependences presented in Fig. 3, the exception of water solution in MA, and the difference in the parameters $\Delta G^{(*),\circ}$ are generally insignificant ones. However, the results of the TIPCS phenomenon for the compared liquid systems research refer (for the reasons mentioned above) to different temperature intervals. The only temperature at which it is possible to compare our data on $\Delta G^{(*),\circ}$, is T = 298.15 K {in the case of the system (TBAmine + H_2O) the required value is estimated by interpolation}. At this temperature, the values $\Delta G^{(*),\circ}$ (in kJ × $\mathrm{mol^{-1}}$) form a series: MA (1.60) << EDA (2.03) ≈ TBAlcohol (2.04) < TPA (2.15) < TBAmine (2.19). In our opinion, the sequence reflects the specific interaction (mainly through the formation of hydrogen bonds) between water molecules and amphiprotonic or protophilic solvent. The difference in the solvent-solvent and water-solvent hydrogen bonding energies found in liquid media with the most pronounced basicity (see Table 1) - alkylamines (TBAmine and EDA) and *tertiary* isomeric alkanols (TBAlcohol and TPA) - was found to be noticeably larger than in the structural packing of an extremely dilute solution of water in methanol. Moreover, the ability of the components to specific interactions is quite comparable one.

Obviously, water molecules, penetrating into the structural packing of amphiprotic organic solvent, form H-bonded solvate complexes, energetically much more stable compared to molecular aggregates in solvating *inbulk* medium. This difference is minimal in methanol solution and most pronounced in *tert*-butylamine medium. At the same time, the relative strengthening of heterocomponent H-bonding is not always associated with the thermoactivated increase in the compactness of molecular packing of the formed solvato-complex (see Table 2). The trends of the values $\Delta G^{(*),\circ}$ with increasing temperature are different from the character of their distribution at T = 298.15 K. Fig. 3 shows the values of relative affinity for the system (TBAmine + H_2O) undergo the most noticeable evolution. They change a standard water solution in MA. These results confirm our assumptions on the dependence of the value $\Delta G^{(*),\circ}$ on the donor-acceptor properties of the molecules contacting in solution, and on the configuration of the structural packing of the solvating medium. It determines the nature of steric hindrances to the formation of hydrogen bonds. These reasons indicate the character of the change in the values $\left|\Delta G^{(*),\circ}\right|$ and $\left|V_{\mathrm{w}}^{\circ,\mathrm{E}}\right|$ with increasing temperature (see Figs. 2, 3). It also is consistent with the conclusions [2, 15-17] on the influence of the amphiprotic medium nature on the difference in the rate of the solvent structural packing volumetric expansion in the solvate environment of the dissolved substance and in the volume of the formed standard solution.

Hence, partial replacement of solvent-solvent bonds by water-solvent bonds causes increased contribution of specific interactions via -OH or $-NH_2$ groups in the molecules. It is confirmed by the formation of a more compact molecule packing in the solvate shell compared to the initial (*balk*) amphiprotic solvent at increasing temperature (see Fig. 2). Taking into account equations (11) and (12), the observed increase $\left|\Delta G^{(*),\circ}\right|$ with increasing temperature (see Fig. 3) is due to a more marked decrease of the component $|G_{\mathrm{aa}}^{\circ}|$ compared to $|G_{\mathrm{aw}}^{\circ}|$ due to the lower stability of the solvent-solvent bonds.

Brief conclusion

Our analysis of TIPCS phenomenon concerning a decrease in the standard (partial at infinite dilution) molar volume of water in some amphiprotic organic solvents allowed us to formulate a number of basic conclusions.

Firstly, the energy parameters of the intermolecular interaction (relative affinity) water-solvent noticeably dominate over those of the solvent-solvent interaction. These differences become evident with increasing the temperature.

Secondly, these differences result in a higher rate of thermal expansion of the organic solvent structure in volume (*inbulk*) than is the case with the effect of increasing temperature on the structural packing of the resulting mixed molecular aggregate or water solvatocomplex.

Thirdly, the difference in the parameters of water-solvent and solvent-solvent interactions depends on the proton-donor/acceptor properties of the molecules contacting in solution, and on the configuration of the structural packing of the solvating medium. It determines the nature of steric hindrances to the formation of H-bonds.

Hence, we found the absolute values of the mentioned parameters of relative affinity at 298.15 K increase in the series: MA << EDA ≈ TBAmine < TPAlcohol < TBAmine. It may indicate a relative strengthening of the specific interaction (mainly through the formation of hydrogen bonds) between the molecules of water and amphiprotonic or protophilic solvent in the above sequence. Moreover, in the liquid media of alkylamines (TBAmine and EDA) and tertiary isomeric alkanols (TBAlcohol and TPA) under study - with the most pronounced basicity - the above-mentioned difference in the solvent-solvent and water-solvent hydrogen bonding energies appeared to be significantly larger than in the structural packing of methanol solution of water, where the ability of components to specific interactions is quite comparable.

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