Journal of Molecular Liquids 335 (2021) 116288

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Effects of different solutes on the physical chemical properties of aqueous solutions via rearrangement of hydrogen bonds in water

Nuno da Silva [a,1], Luisa A. Ferreira [b], Alexander I. Belgovskiy [b], Pedro P. Madeira [c], José A. Teixeira [a], Elizabeth K. Mann [d], J. Adin Mann Jr. [e], William V. Meyer [f], Anthony E. Smart [g], Vladimir Y. Chernyak [h], Vladimir N. Uversky [i], Boris Y. Zaslavsky [b,*]

[a] IBB—Institute for Biotechnology and Bioengineering, Centre of Biological Engineering, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[b] Cleveland Diagnostics, 3615 Superior Ave, Cleveland, OH 44114, USA
[c] Centro de Investigacao em Materiais Ceramicos e Compositos, Department of Chemistry, Aveiro, Portugal
[d] Department of Physics, Kent State University, Kent, OH, USA
[e] Department of Chemical and Biomolecular Engineering, Case Western Reserve University, Cleveland, OH, USA
[f] Scattering Solutions, Inc, Cleveland, OH, USA
[g] Scattering Solutions, Inc, Costa Mesa, CA, USA
[h] Department of Chemistry, Wayne State University, Detroit, MI, USA
[i] Department of Molecular Medicine and Byrd Alzheimer's Research Institute, Morsani College of Medicine, University of South Florida, Tampa, FL, USA

ARTICLE INFO

Article history:
Received 27 November 2020
Revised 22 March 2021
Accepted 21 April 2021
Available online 24 April 2021

Keywords:
Water
Hydrogen bonds
Water Structure
Salts
Polymers
Organic Compounds

ABSTRACT

The Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR) spectra of the OH-stretch band in aqueous solutions of inorganic salts and organic materials; Na_2SO_4, NaCl, $NaClO_4$, NaSCN, trimethylamine N-oxide, urea, poly(ethylene glycol), polyvinylpyrrolidone, and copolymer of ethylene glycol and propylene glycol (Ucon) were studied at various concentrations. The decomposition of the band into four Gaussian components peaking at 3080, 3230, 3400, and 3550 cm^{-1} fits every compound examined here with essentially flat residuals. These components were viewed as representing four different subpopulations of water with different H-bond arrangements. The experimentally estimated relative contributions of these components depend on solute type and concentration, and correlate strongly with previously reported experimentally measured solvent features of water such as solvent dipolarity/polarizability, π^*, solvent H-bond donor acidity, α, and solvent H-bond acceptor basicity, β. We suggest that water includes an ensemble of four different subpopulations of molecules with various hydrogen bond strengths, geometry, and bond defects depending on the solute. This assumption is obviously oversimplified, but for the wide range of solutes examined here we find that a given solute changes the relative amounts of these subpopulations and hence the above solvent features of water. The solvent features, π^* and α, in particular, describe a variety of physicochemical properties, such as water activity, osmotic coefficient, relative viscosity, permittivity, and surface tension, of aqueous solutions of various compounds. It follows therefore that all these physicochemical properties of aqueous solutions are determined by the relative amounts of the above subpopulations of water molecules.

1. Introduction

Physicochemical properties of aqueous solutions depend on the nature and concentration of the solute. Solubility of multiple nonionic and ionized organic compounds in water is affected by the presence of inorganic salts – the so-called salting-out and salting-in phenomena [1]. Solubility of N-acetyl ethyl esters of phenylalanine, tyrosine, and tryptophan in aqueous solutions of glucose and sucrose have been reported to differ significantly [2]. Solubilities of amino acids in aqueous solutions of ethylene glycol [3], urea [4], ethanol and dioxane [5] have also shown significant differences. As an example, water activities of aqueous solutions of Na_2SO_4 and $MgSO_4$ at the same concentrations of 1 mol/L are quite different [6] as are those in aqueous solutions of

Abbreviations: ATR-FTIR, Attenuated Total Reflection Fourier Transform Infrared.

* Corresponding author.
E-mail address: Boris.Zaslavsky@ClevelandDx.com (B.Y. Zaslavsky).
[1] DWI-Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52056 Aachen, Germany.

https://doi.org/10.1016/j.molliq.2021.116288
0167-7322/

polyethylene glycols of molecular weight 200 Da and 20,000 Da at the same concentrations of ~ 15 %wt. [7]. The osmotic coefficients for aqueous solutions of NaF, NaCl, and $MgSO_4$ at the same concentration of 0.5 mol/kg are also very different, being 0.886, 0.923, and 0.522 respectively [8]. Differences between the relative viscosity of aqueous solutions of various salts [9] or nonionic compounds, such as urea and guanidine chloride [10], and permittivity of aqueous solution of various compounds are known [11] to be quite different depending on the amount and nature of the solute. All these data imply that the solvent properties of aqueous media are changed in specific ways by the solute and its concentration.

Various solvents are commonly classified by their polarity, whose current definition represents the sum of all possible specific and non-specific interactions between the solvent and any potential solute, but excludes interactions leading to chemical transformations of the solute [12,13]. The many types of solute-solvent interactions include electrostatic, dipole-dipole, dipole-induced dipole, hydrogen bonding, and electron pair donor-acceptor. We emphasize here that the dispersion interactions that are directly dependent on the polarizability of the intervening species are commonly neglected in such considerations. Although these interactions between two induced dipole (or multipole) moments are ubiquitous, regardless of whether the interacting entities possess permanent dipole moments, they are typically ignored probably because of the lack of any suitable technique to quantify the weak effects of such solute-solvent interactions. Polarity describes the potential behavior of the solvent in a relationship with the solute, which depends on the solute structure as well as on the properties of the solvent [13]. Different polarity scales are based on different probes and spectroscopic techniques (NMR, IR, UV/Visible absorption and emission spectroscopy, etc.) [14]. According to Ab Rani *et al.* [13], measurements of polarity at different scales gives different estimates for the same solvent, and such differently described scales cannot be usefully compared. The test of an empirical polarity scale is its usefulness in explaining and/or predicting other solvent-dependent phenomena [13]. No single-parameter polarity scale can represent the many possible solute-solvent interactions. Therefore Kamlet, Taft, and co-workers developed three scales accommodating relative solvent ability to serve as a donor of hydrogen bond – hydrogen bond donor acidity (α) [15], the scale of relative solvent ability to serve as an acceptor of hydrogen bond – hydrogen bond acceptor basicity (β) [16], and the relative solvent ability to participate in dipole-dipole and dipole-induced dipole interactions – dipolarity/polarizability (π^*) [17].

As the probes for each scale, Kamlet and Taft [15–17] used various solvatochromic dyes, whose spectra change with the solvents. In this context, the dielectric constant and hydrogen bonding capacity are the most important properties of the solvent. Different solvents affect the electronic ground and excited states of the dye, with the energy gap dependent on the solvent, and change the position, intensity, and shape of the spectroscopic bands of the absorption (or emission) spectrum of the dye. When the spectroscopic band occurs in the visible part of the spectrum, solvatochromism is observed as a change of color. Each scale introduced by Kamlet and Taft [15–17] was generated using several solvatochromic dyes with strong and symmetric solvatochromic absorption spectra. As an example, for the relative dipolarity/polarizabiity π^* scale [17] the π^*-values were averaged from those obtained for seven different dyes. In total, 45 dyes were used to generate π^*-values for over 200 solvents [13]. The purpose of using multiple dyes was to avoid dye-specific π^*-value. However, Ab Rani *et al.* [13] showed that for similar solvents (a set of ionic liquids), a single dye is sufficient to measure the π^*-values to characterize the effect of the solvent on the solute species sensitive to dipole-dipole interactions.

Combinations of the above three scales describe the relative ability of a given organic solvent or water to participate in solute-solvent interactions, i.e. solvent polarity, much better than any single parameter polarity scale. The Linear Solvation Energy Relationship (LSER) model used by Kamlet, Taft, and their coworkers [18] may be described as:

$$(XYZ) = (XYZ)_o + s\pi* + a\alpha + b\beta \quad (1)$$

where (XYZ) is the solute property (solubility, reaction rate, equilibrium constant, the logarithm of a gas/solvent or solvent/solvent partition coefficient, etc.) in a given solvent; $(XYZ)_o$ is the same solute property in a reference state, e.g., in the solute-free state, s, a, and b are the solute-dependent coefficients characterizing the respective influence of the π^*, α, and β terms on the (XYZ) property under study. Once again, such important and ubiquitous intermolecular forces as dispersion forces directly depending on the polarizability of the interacting molecules are completely neglected in the LSER model. We emphasize that dispersion forces and polarizability effects likely play significant roles in all molecular interactions. While these forces and effects cannot be measured directly by existing techniques, we think that the properties that we can measure likely include their effects.

Previously, we examined the solvent properties of water in aqueous solutions of various nonionic organic compounds [19–21], amino acids [20,22], inorganic salts [20,23], polymers [20,21,24,25], and several proteins [26,27] using the solvatochromic comparison method [15–17]. The same solvatochromic dyes have been used in all our studies [19–27]. A study [23] of the influence of the Hofmeister series of sodium salts on the solvent properties of water showed that the relative effects of examined salts (Na_2SO_4, NaF, CH_3COONa, NaCl, NaBr, NaI, $NaClO_4$ and NaSCN) were strongly correlated with the linear combination of the ionic water structural entropy and anion static polarizability.

Different physicochemical properties, such as water activity, osmotic coefficient, relative viscosity, relative permittivity, surface tension, etc., of aqueous solutions of various compounds may be described in terms of the relative solvent dipolarity/polarizability, π^*, and/or relative solvent H-bond donor acidity, α, over many compounds and a large range of concentration [28]. Several examples not reported previously are shown in Supplementary Material, Figs. A.1–A.7 for water activity in solutions of NaCl and Na_2SO_4, permittivity in solutions of $NaClO_4$, relative viscosity of solutions of $NaClO_4$, NaCl, and NaSCN, and surface tension in solutions of polyvinylpyrrolidone (PVP). Note that sometimes only one or a maximum of two properties, solvent dipolarity/polarizability, π^*, and solvent H-bond donor acidity, α, are sufficient to describe important physicochemical properties of aqueous solutions of many different compounds [28].

Two solvent characteristics are typically sufficient for describing various physicochemical properties of aqueous solutions because of the linear relationship observed empirically between the three solvent characteristics [19–27]:

$$\pi*_i = k_{\pi*} + k_\alpha \alpha_i + k_\beta \beta_i \quad (2)$$

where subscript i denotes the solute concentration, and $k_{\pi*}$, k_α, and k_β are solute-specific constants.

Equation (2) was established and has so far been confirmed for aqueous solutions of over 60 individual compounds, ranging from inorganic salts and amino acids to nonionic polymers and proteins [19–27]. This empirical relationship seems to be generally applicable, and it seems to imply that dipole-dipole interactions in water depend on the hydrogen bonding. Water is known to have a permanent dipole moment 1.85 D in the gas phase, increasing to 2.9 ± 0.6 D [29] in its liquid phase. This dipole moment increase is generally attributed to polarization of water molecules induced by the hydrogen bonding in liquid water. According to Kemp and

Gordon [30] the dipole moment of a water molecule either isolated or in a cluster is derived primarily from the water lone pairs, attenuated by opposing OH dipole vectors. The increase of the dipole moment of a water molecule in the presence of other water molecules is further suggested [30] to arise predominantly from decreases in the angles between the lone pair dipole vectors. The angular decrease arises in turn from the increased participation of these lone pairs in hydrogen bonds when a water molecule is surrounded by other water molecules. Thus, it seems reasonable to suggest that all three solvent features, π^*, α, and β, in water depend on properties of hydrogen bonds, and that they already embody dispersion forces.

ATR-FTIR is one of the most readily available experimental methods for analysis of rearrangement of H-bonds in aqueous solutions of various compounds [31–33]. The results of the exploratory study [34] also corroborate that the solvent features of water in the solutions are controlled by the arrangement of H-bonds.

The main purpose of this study was to explore rearrangements of hydrogen bonds in aqueous solutions of several compounds using ATR-FTIR spectroscopy. By comparing the relationship of different components of the OH stretching band with previously reported solvent features of water we have confirmed that such relationships may describe the origin of the solute effects on the solvent properties of water.

2. Materials

Polyethylene glycol (PEG-4000, Lot#BCBG9026V) with molecular weight (Mw) of 4000 Da was purchased from Fluka Analytical, and polyvinylpyrrolidone 40 (PVP-40, Batch#094 K0100) with Mw of 40,000 Da was obtained from Sigma-Aldrich (St. Louis, MO, USA). Ucon 50-HB-5100 (Ucon-4000), a random copolymer of 50% ethylene oxide and 50% propylene oxide, Lot#SJ1955S3D2, with Mw 3930, was purchased from Dow-Chemical (Midland, MI, USA). Trimethylamine N-oxide (TMAO) and urea were obtained from Sigma-Aldrich and used without further purification. Sodium chloride, sodium sulfate, sodium perchlorate, and sodium thiocyanate of analytical reagent grade were purchased from Sigma-Aldrich and used without further purification. HPLC grade water was used for preparation of all solutions.

3. Methods

3.1. ATR-FTIR measurements

ATR-FTIR spectra for each sample were measured in two separately prepared solutions using an Alpha II FT-IR spectrometer (Bruker) equipped with diamond ATR (platinum T Diamond, Bruker). All measurements were performed at about 25 °C using 20 scans for each sample, 24 scans for background in the spectral range of 4000–1000 cm^{-1} with resolution of 4 cm^{-1}. The spectra were reproducible to within ± 1 cm^{-1}.

3.2. Analysis of spectra

ATR-FTIR spectra were analyzed with custom software written in Wolfram Mathematica (version 9). The software performed peak analysis by fitting the data using 'NonlinearModelFit' function, the model function being a sum of two, three, four, and five Gaussians with floated central frequencies. We found that the best and most reliable fits are obtained with four Gaussians with peak locations close to the values from literature [33] (3080 cm^{-1}, 3230 cm^{-1}, 3400 cm^{-1}, and 3550 cm^{-1}). The program displays the results graphically (raw data, model function fit, and individual Gaussians), and reports the calculated parameter values for each individual peak with metrics of each fit quality.

4. Results

Fig. 1 shows typical examples of ATR-FTIR spectra of OH stretching bands in pure water and aqueous solutions of 2.0 M TMAO and 2.0 M NaSCN. The OH stretching band is typically made up of several components, each assigned to water molecules existing in different H-bonded environments (see Supplementary Material, Table A.1). All the assignments in the literature shown in Table A.1 are based on rather questionable models of water structure. The assignment of the Gaussian components to water structures is ambiguous. Components at lower optical frequencies are generally assigned to water molecules forming strong, ice-like, hydrogen bonds, while those at higher frequencies are assigned to water molecules in an environment with weaker and/or distorted hydrogen bonds. Fitting the OH stretching band in water and all the aqueous solutions of various compounds with one, two, three, four, and five Gaussian components showed that the satisfactory fit was always obtained with exactly four components positioned at 3080 cm^{-1}, 3230 cm^{-1}, 3400 cm^{-1}, and 3550 cm^{-1} in agreement with the data obtained by Kitadai, *et al.* [31]. From analysis of different assignments of these and other differently positioned components used in the literature (see Table A.1) we suggest assigning these components as: (I) 3080 cm^{-1} - water molecules with four tetrahedrally arranged hydrogen bonds, (II) 3230 cm^{-1} – water molecules with four distorted hydrogen bonds, (III) 3400 cm^{-1}- water molecules with loosely arranged four and three hydrogen bonds, and (IV) 3500 cm^{-1} – water molecules with three, two and single hydrogen bonds. This assignment is only a rough approximation of the complex hydrogen-bond network existing in water [35], plausibly based on the internally consistent empirical measurements. We conjecture that these subpopulations or clusters of water with different properties may be distributed throughout, and the ratio of these subpopulations/clusters, which exist in pure water, may vary in solutions of different solutes.

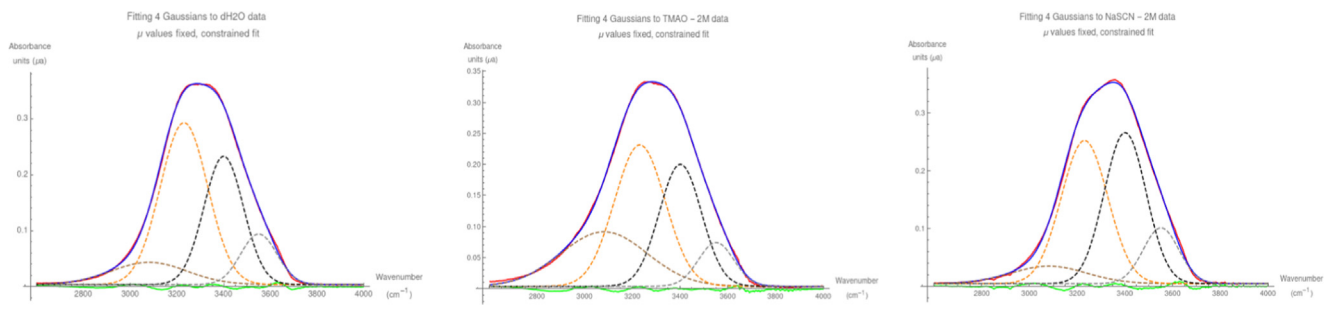

Fig. 1. ATR-FTIR spectra of water, 2 M TMAO and 2 M NaSCN.

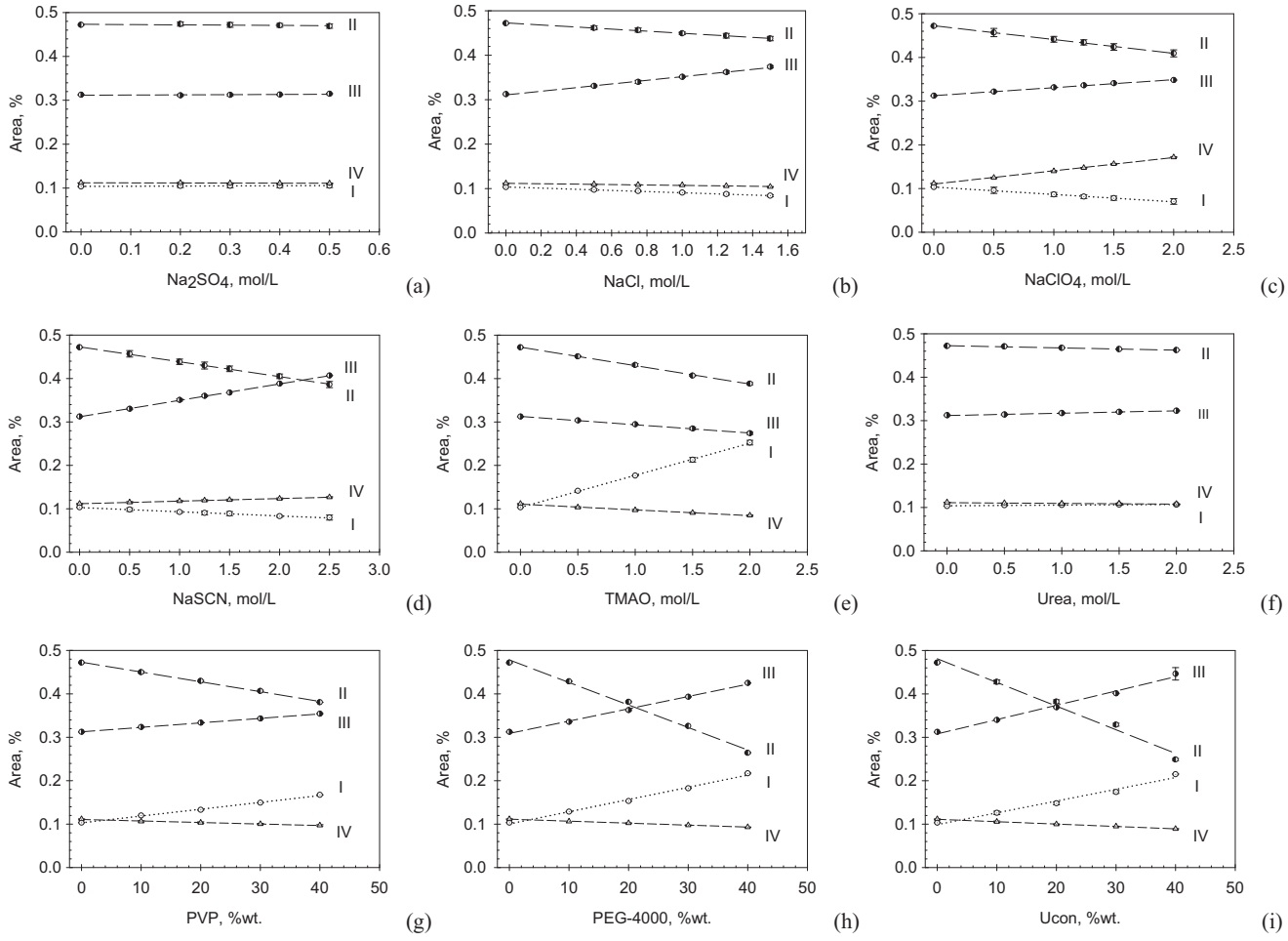

Fig. 2. Contribution of each Gaussian component of water into overall ATR-FTIR spectra of OH-stretch band for the solutes examined as a function of the solute concentration. (I (3080 cm^{-1}), II (3230 cm^{-1}), III (3400 cm^{-1}) and IV (3550 cm^{-1})).

Analysis of the OH stretching band in aqueous solutions was continued by decomposition of the spectral band into four Gaussian components, and the estimates of the relative percentage area for each component as the function of the solute concentration. These estimates are plotted as functions of the solute concentration in Fig. 2 a-i (see Supplementary Material, Table A.2). The data obtained for Na_2SO_4 and NaCl agree with those published by Kutadai *et al.* [31].

These dependencies in Fig. 2 are shown in more detail in Figs. A.8-A.15, where the trends are quite convincing. The relative intensities of the component I (3080 cm^{-1}) decrease with the solute concentration in solutions of NaCl, $NaClO_4$ and NaSCN, but increase for all the other compounds, including Na_2SO_4. The relative intensities of the component II (3230 cm^{-1}) decrease with the solute concentration in solutions of all examined compounds. The relative intensities of the component III (3400 cm^{-1}) decrease with the solute concentration only in solutions of Na_2SO_4 (slightly) and TMAO (significantly), but increase with the solute concentration for all other examined compounds. The relative intensities of the component IV (3550 cm^{-1}) increase with the solute concentration in solutions of $NaClO_4$ and NaSCN, and decrease in solutions of all other examined compounds. The area sum of all four Gaussian distributions is normalized to unity to better indicate their relative contributions.

5. Discussion

The relative contributions of the four components estimated from analysis of ATR-FTIR spectra and the solvent features of aqueous solutions under consideration show that these features are strongly correlated with the relative intensities of certain solute-specific FTIR determined water components. Each correlation may be described in the general form as:

$$SF(\pi*_i, \alpha_i, \beta_i) = k_o + k_1 I_i^N + k_2 I_i^M \quad (3)$$

where SF is a solvent feature (dipolarity/polarizability, π^*, solvent H-bond donor acidity, α, solvent H-bond acceptor basicity, β); I^N and I^M are relative intensities of water components N and M (I, II, III, or IV) correspondingly, subscript i denotes the solute concentration; and k_o, k_1, and k_2 are constants. While the relative contributions of Gaussian components may not be totally independent, an analysis of the cross-terms in the covariance matrix suggests that this set of four appears to be both necessary and sufficient, and is demonstrated to be superior to a fit with either three or five Gaussian components.

The observed correlations described by Eq. (3) imply that the water components assigned to particular subpopulations or clusters cannot be localized within the hydration layer of a solute because solvatochromic probes are too big to fit in such a layer.

The only other reasonable explanation seems to be that the relative amounts of the water subpopulations/clusters in bulk water change in the presence of a solute.

Note that typically all three solvent features for solutions of a given solute may be described by Eq. (3) with both I_i^N and I_i^M, or with either I_i^N or I_i^M. As an example, the solvent dipolarity/polarizability, π^*, in aqueous solutions of TMAO is correlated with the relative intensity of component IV (3550 cm^{-1}) as:

$$\pi*_i = 1.106_{\pm 0.002} - 0.09_{\pm 0.02} I_i^{3550} \quad (3a)$$

where I^{3550} is the relative intensity of water component IV; subscript i denoted the TMAO concentration.

The solvent hydrogen bond donor acidity, α, in the TMAO solutions is correlated with the relative intensities of component III (3400 cm^{-1}) and component IV (3550 cm^{-1}) as:

$$\alpha_i = 0.65_{\pm 0.02} + 0.99_{\pm 0.09} I_i^{3400} + 2.51_{\pm 0.08} I_i^{3550} \quad (3b)$$

as well as the solvent hydrogen bond acceptor basicity, β:

$$\beta_i = 0.98_{\pm 0.01} - 0.55_{\pm 0.04} I_i^{3400} - 1.89_{\pm 0.04} I_i^{3550} \quad (3c)$$

where I^{3400} is the relative intensity of water component III; all other parameters are as defined above.

Qualitatively similar relationships were observed for all the compounds examined here. Several examples of the correlations described by Eq. (3) are illustrated graphically in Fig. 3 i–iii. The coefficients of Eq. (3) describing the relationships between different solvent features and relative contributions of water components I, II, III, or IV for aqueous solutions of various compounds examined here are presented in Table 1 together with all statistical characteristics of the observed relationships.

Analysis of the data in Table 1 shows, first, that the relative intensities of different water components control the observed relationships for various solutes. Second, the same water component(s) correlate with all solvent features for a given solute (see in Table 1, e.g., for Na_2SO_4, urea and Ucon). When two water components are involved, one component may be common to all three features, whereas the other component may affect only some of the solvent features (see, e.g., in Table 1 for NaCl, $NaClO_4$, NaSCN and TMAO). The two components III and IV are found in correlations for most of the solutes examined here. As an example, component IV (3550 cm^{-1}) representing the water subpopulation/cluster with the least number of H-bonds affects 17 out of 27 relationships, and component III (3400 cm^{-1}) representing subpopulation/cluster of water molecules with three and four hydrogen bonds affects 14 relationships out of the 27 relationships.

From our measurements we conjecture that water comprises four different subpopulations/clusters of water molecules with various strength, geometry, and defects of hydrogen bonds, the contributions of which are affected by the solute. This assumption is oversimplified (see e.g., in [35]) but in this case, it seems that the three solvent features of water respond in the aqueous solutions of a given solute to changes in the relative amounts of the subpopulations. The solvent features, π^* and α, in particular, describe a variety of physicochemical properties, such as water activity, osmotic coefficient, relative viscosity, permittivity, and surface tension, of aqueous solution of various compounds. Therefore, all these physicochemical properties of aqueous solutions are governed by the relative amounts of the subpopulations of water molecules.

Questions remain as to which structural features of solutes govern the solvent properties of water. While it is known that shape,

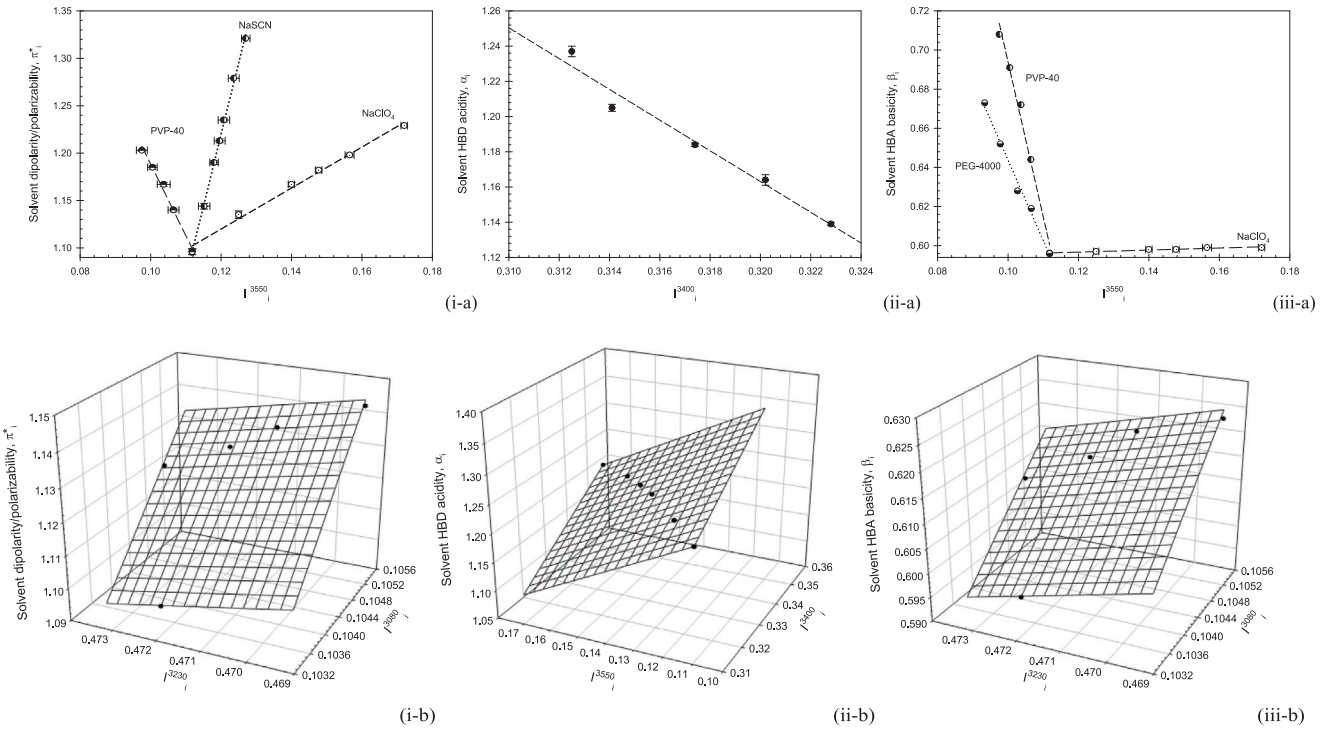

Fig. 3. Examples of linear relationships (Eq. (3)) between relative contributions of Gaussian water components and solvent features of water in aqueous solutions of different compounds: (i) solvent dipolarity/polarizability, π^*, as a function of (a) relative contributions of water Gaussian component IV in solutions of $NaClO_4$, NaSCN, and PVP-40; (b) relative contributions of water Gaussian components I and II in solutions of Na_2SO_4; (ii) solvent hydrogen bonding donor acidity, α, as a function of (a) relative contributions of water Gaussian component III in solutions of urea; (b) relative contributions of water Gaussian components III and IV in solutions of $NaClO_4$; (iii) solvent hydrogen bonding acceptor basicity, β, as a function of (a) relative contribution of water Gaussian component IV in solutions of $NaClO_4$, PVP-40, and PEG-4000; (b) relative contributions of water Gaussian components I and II in solutions of Na_2SO_4.

Table 1
Coefficients and statistical characteristics of Eq. (3) (N – number of experimental points; r^2 – correlation coefficient; SD – standard deviation; F – variation ratio).

Solute	Solvent feature	k_0	k_1	I_1	k_2	I_2	N	r^2	SD	F
Na_2SO_4	π*	n/a	$23.7_{\pm1.7}$	3080	$-2.3_{\pm0.7}$	3230	5	0.9932	0.002	146.1
	α	$3.6_{\pm0.1}$	$-27.9_{\pm0.5}$	3080	$1.1_{\pm0.2}$	3230	5	0.9995	0.0006	2161
	β	n/a	$13.2_{\pm1.8}$	3080	$-2.0_{\pm0.7}$	3230	5	0.9788	0.002	46.3
NaCl	π*	$0.69_{\pm0.04}$	$1.3_{\pm0.1}$	3400	n/a	n/a	6	0.9651	0.006	110.6
	α	$2.6_{\pm0.9}$	$-1.6_{\pm0.7}$	3400	$-8.3_{\pm5.9}$	3550	6	0.9755	0.001	59.8
	β	$0.626_{\pm0.001}$	$-0.097_{\pm0.003}$	3400	n/a	n/a	6	0.9969	0.0001	1278
$NaClO_4$	π*	$0.86_{\pm0.01}$	$2.2_{\pm0.1}$	3550	n/a	n/a	6	0.9921	0.005	500.2
	α	$0.4_{\pm0.1}$	$3.5_{\pm0.5}$	3400	$-2.4_{\pm0.3}$	3550	6	0.9832	0.001	87.7
	β	$0.569_{\pm0.003}$	$0.088_{\pm0.009}$	3400	n/a	n/a	6	0.9564	0.0003	87.7
NaSCN	π*	$2.34_{\pm0.03}$	$-2.62_{\pm0.06}$	3230	n/a	n/a	7	0.9975	0.004	1973
	α	$25.1_{\pm5.7}$	$-19.8_{\pm5.2}$	3230	$-130.2_{\pm29.1}$	3550	7	0.9901	0.006	199
	β	$0.48_{\pm0.01}$	$1.08_{\pm0.08}$	3550	n/a	n/a	7	0.9709	0.001	167
TMAO	π*	$1.119_{\pm0.003}$	$-0.074_{\pm0.009}$	3400	n/a	n/a	5	0.9018	0.0005	18.4
	α	$0.42_{\pm0.01}$	$2.6_{\pm0.04}$	3400	n/a	n/a	5	0.9996	0.001	1324
	β	$1.17_{\pm0.02}$	$-1.85_{\pm0.07}$	3400	n/a	n/a	5	0.9998	0.0007	2712
Urea	π*	$-1.1_{\pm0.2}$	$7.1_{\pm0.7}$	3400	n/a	n/a	5	0.9702	0.006	97.6
	α	$4.0_{\pm0.3}$	$-8.7_{\pm0.9}$	3400	n/a	n/a	5	0.9693	0.008	94.8
	β	n/a	$2.0_{\pm0.2}$	3400	n/a	n/a	5	0.9740	0.002	112.4
PVP-40000	π*	$1.94_{\pm0.05}$	$-7.5_{\pm0.4}$	3550	n/a	n/a	5	0.9896	0.005	286.6
	α	$-5.1_{\pm0.7}$	$5.4_{\pm1.3}$	3080	$51.5_{\pm5.5}$	3550	5	0.9993	0.002	1452
	β	$1.49_{\pm0.06}$	$-7.9_{\pm0.6}$	3550	n/a	n/a	5	0.9857	0.006	206.7
Ucon-3930	π*	$2.8_{\pm0.3}$	$-1.2_{\pm0.3}$	3400	$-11.7_{\pm2.0}$	3550	5	0.9954	0.004	218.3
	α	$-6.3_{\pm1.2}$	$5.7_{\pm1.3}$	3400	$51.8_{\pm7.5}$	3550	5	0.9980	0.004	507.6
	β	$2.5_{\pm0.4}$	$-1.4_{\pm0.4}$	3400	$-13.2_{\pm2.2}$	3550	5	0.9948	0.004	191.6
PEG-4000	π*	$1.8_{\pm0.1}$	$-0.5_{\pm0.1}$	3400	$-4.7_{\pm0.6}$	3550	5	0.9974	0.0008	384.2
	α	$-1.6_{\pm0.2}$	$25_{\pm1.7}$	3550	n/a	n/a	5	0.9866	0.024	220.5
	β	$1.06_{\pm0.03}$	$-4.2_{\pm0.3}$	3550	n/a	n/a	4[†]	0.9924	0.004	261.9

[†] Data for 0.5 M concentration was not used in the regression analysis.

anisotropy, charge delocalization, polarizability, etc. of a solute do significantly affect the microscopic properties of water in solutions, it remains unknown why some solutes influence certain solvent features of water more strongly than others. This is a subject for further research.

6. Conclusions

Analysis of the ATR-FTIR spectra of the OH-stretch band in aqueous solutions of different compounds at various concentrations shows that the decomposition of the band into four Gaussian components at 3080, 3230, 3400, and 3550 cm^{-1} provides highly satisfactory fits for all compounds examined here. These components represented four different subpopulations/clusters of water with different H-bond arrangements from water molecules with four tetrahedrally arranged hydrogen bonds to water molecules with two and single hydrogen bonds. The experimentally estimated relative contributions of these components appear to depend on solute type and concentration. Comparison of these differences in the relative intensity of the water components with changes in the experimentally measured solvent features of water (solvent dipolarity/polarizability, π*, solvent H-bond donor acidity, α, and solvent H-bond acceptor basicity, β) reported previously shows a strong solute-specific correlation between each solvent feature and the relative contribution(s) of either one or two different components. A theoretical model explaining the relationships established between two independently estimated empirical properties of water is currently under development.

Author contributions

B.Y.Z. conceived the idea and coordinated the research. E.K.M., J. A.M., W.V.M., A.E.S., J.A.T., V.Y.C. and V.N.U. contributed to conceptualization. B.Y.Z., E.E.K., W.V.M., and A.E.S. contributed to the design of the experiments. N.DS., P.P.M. and L.A.F. conducted experiments. W.V.M. and A.I.B. developed software for data analysis. E.K.M., J.A.M., J.A.T., A.I.B., W.V.M., A.E.S., V.N.U., and B.Y.Z participated in data analysis and model development. All authors participated in writing and discussions of the paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

N.DS. and J.A.T. were supported by the Portuguese Foundation for Science and Technology(FCT) under the scope of the strategic funding of UIDB/04469/2020 unit and BioTecNorte operation (NORTE-01-0145-FEDER-000004) funded by the European Regional Development Fund under the scope of Norte2020 - Programa Operacional Regional do Norte. P.P.M. was supported within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 & UIDP/50011/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES.

P.P.M acknowledges University of Aveiro for funding in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of August 29, changed by Law 57/2017, of July 19.

EKM acknowledges partial support by NSF-1709985; this work was completed while serving at the National Science Foundation.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2021.116288.

References

[1] P.K. Grover, R.L. Ryall, Critical appraisal of salting-out and its implications for chemical and biological sciences, Chem. Rev. 105 (2005) 1–10.
[2] T.S. Lakshmi, P.K. Nandi, Effects of Sugar Solutions on the Activity Coefficients of Aromatic Amino Acids and Their N-Acetyl Ethyl Esters, J. Phys. Chem. 80 (1976) 249–252.
[3] Y. Nozaki, C. Tanford, The solubility of amino acids and related compounds in aqueous ethylene glycol solutions, J. Biol. Chem. 240 (1965) 3568–3573.
[4] P.L. Whitney, C. Tanford, Solubility of Amino Acids in Aqueous Urea Solutions and Its Implications for the Denaturation of Proteins by Urea, J. Biol. Chem. 237 (1962) 1735–1737.
[5] Y. Nozaki, C. Tanford, The solubility of amino acids and two glycine peptides in Aqueous Ethanol and Dioxane Solutions. Establishment of a hydrophobicity scale, J. Biol. Chem. 246 (1971) 2211–2217.
[6] M. El Guendouzi, A. Mounir, A. Dinane, Water activity, osmotic and activity coefficients of aqueous solutions of Li_2SO_4, Na2SO4, K_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at T = 298.15 K, J. Chem. Thermodyn. 35 (2003) 209–2200.
[7] L. Ninni, M.S. Camargo, A.J.A. Meirelles, Water activity in poly(ethylene glycol) aqueous solutions, Thermochim. Acta 328 (1999) 169–176.
[8] R.A. Robinson, R.H. Stokes, Tables of osmotic and activity coefficients of electrolytes in aqueous solution at 25 °C, Trans. Faraday Soc. 45 (1949) 612–624.
[9] G.J. Janz, B.G. Oliver, G.R. Lakshminarayanan, G.B. Mayer, Electrical conductance, diffusion, viscosity, and density of sodium nitrate, sodium perchlorate, and sodium thiocyanate in concentrated aqueous solutions, J. Phys. Chem. 74 (1970) 1285–1289.
[10] K. Kawahara, C. Tanford, Viscosity and density of aqueous solutions of urea and guanidine hydrochloride, J. Biol. Chem. 241 (1956) 3228–3232.
[11] A. Saito, O. Miyawaki, K. Nakamura, Dielectric relaxation of aqueous solutions with low molecular weight nonelectrolytes and its relationship with solution structure, Biosci. Biotech. Bioch. 61 (1997) 1831–1835.
[12] C. Reichardt, T. Welton, Solvents and Solvent Effects in Organic Chemistry, Wiley-VCH, Weinheim, 2010.
[13] M.A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N.H. Hassan, R. Wilding, Understanding the polarity of ionic liquids, Phys. Chem. Chem. Phys. 13 (2011) 16831–16840.
[14] R. Cabot, C.A. Hunter, Molecular probes of solvation phenomena, Chem. Soc. Rev. 41 (2012) 3485–3492.
[15] R.W. Taft, M.J. Kamlet, The solvatochromic comparison method. 2. The. alpha.-scale of solvent hydrogen-bond donor (HBD) acidities, J. Am. Chem. Soc. 98 (1976) 2886–2894.
[16] M.J. Kamlet, R.W. Taft, The solvatochromic comparison method. I. The. beta.-scale of solvent hydrogen-bond acceptor (HBA) basicities, J. Am. Chem. Soc. 98 (1976) 377–383.
[17] M.J. Kamlet, J.L. Abboud, R.W. Taft, The solvatochromic comparison method. 6. The pi* scale of solvent polarities, J. Am. Chem. Soc. 99 (1977) 6027–6038.
[18] R.W. Taft, J.L.M. Abboud, M.J. Kamlet, M.H. Abraham, Linear solvation energy relations, J. Solution Chem. 14 (1985) 153–186.
[19] L.A. Ferreira, L. Breydo, C. Reichardt, V.N. Uversky, B.Y. Zaslavsky, Effects of osmolytes on solvent features of water in aqueous solutions, J. Biomol. Struct. Dyn. 35 (2017) 1055–1068.
[20] L.A. Ferreira, V.N. Uversky, B.Y. Zaslavsky, Role of solvent properties of water in crowding effects induced by macromolecular agents and osmolytes, Mol. BioSystems 13 (2017) 2551–2563.
[21] L.A. Ferreira, V.N. Uversky, B.Y. Zaslavsky, Phase equilibria, solvent properties, and protein partitioning in aqueous polyethylene glycol-600-trimethylamine N-oxide and polyethylene glycol-600-choline chloride two-phase systems, J. Chromatogr. A 1535 (2018) 154–161.
[22] L.A. Ferreira, V.N. Uversky, B.Y. Zaslavsky, Effects of amino acids on solvent properties of water, J. Mol. Liquids 277 (2019) 123–131.
[23] L.A. Ferreira, V.N. Uversky, B.Y. Zaslavsky, Effects of Hofmeister series of sodium salts on the solvent properties of water, Phys. Chem. Chem. Phys. 19 (2017) 5254–5261.
[24] L.A. Ferreira, P.P. Madeira, L. Breydo, C. Reichardt, V.N. Uversky, B.Y. Zaslavsky, Role of solvent properties of aqueous media in macromolecular crowding effects, J. Biomol. Struct. Dynam. 34 (2016) 92–103.
[25] L.A. Ferreira, J.T. Cole, C. Reichardt, V.N. Uversky, N.B. Holland, B.Y. Zaslavsky, Solvent properties of media in aqueous solutions of elastin-like polypeptide, Int. J. Mol. Sci. 116 (2015) 13528–13547.
[26] L.A. Ferreira, N.B. Gusev, V.N. Uversky, B.Y. Zaslavsky, Effect of human heat shock protein HspB6 on the solvent features of water in aqueous solutions, J. Biomol. Struct. Dyn. 36 (2018) 1520–1528.
[27] L.A. Ferreira, A.W. Mooradally, B. Zaslavsky, V. Uversky, S. Graether, Effect of an intrinsically disordered plant stress proteins on the properties of water, Biophys. J. 115 (2018) 1696–1706.
[28] L.A. Ferreira, J.A. Loureiro, J. Gomes, V.N. Uversky, P.P. Madeira, B.Y. Zaslavsky, Why physicochemical properties of aqueous solutions of various compounds are linearly interrelated, J. Mol. Liquids 221 (2016) 116–123.
[29] Y.S. Badayal, M.-L. Saboungi, D.L. Price, S.D. Shastri, D.R. Haeffner, A.K. Soper, Electron distribution in water, J. Chem. Phys. 112 (2000) 92069208.
[30] D.D. Kemp, M.S. Gordon, An interpretation of the enhancement of the water dipole moment due to the presence of other water molecules, J. Phys. Chem. A 112 (2008) 4885–4894.
[31] K. Masuda, T. Haramaki, S. Nakashima, B. Habert, I. Martinez, S. Kashiwabara, Structural change of water with solutes and temperature up to 100 oC in aqueous solutions as revealed by attenuated total reflectance infrared spectroscopy, Appl. Spectrosc. 57 (2003) 274–281.
[32] Y. Chen, Y.-H. Zhang, L.-J. Zhao, ATR-FTIR spectroscopic studies on aqueous LiClO4, NaClO4, and Mg(ClO4)2 solutions, Phys. Chem. Chem. Phys. 6 (2004) 537–542.
[33] N. Kitadai, T. Sawai, R. Tonoue, S. Nakashima, M. Katsura, K. Fukushi, Effects of ions on the OH stretching band of water as revealed by ATR-IR spectroscopy, J. Solution Chem. 43 (2014) 1055–1077.
[34] J. Pavelec, D. Di Guiseppi, B.Y. Zaslavsky, V.N. Uversky, R. Schweitzer-Stenner, Perturbation of water structure by water-polymer interactions probed by FTIR and polarized Raman spectroscopy, J. Mol. Liquids 275 (2019) 463–473.
[35] E. Brini, C.J. Fennell, M. Fernandez-Serra, B. Hribar-Lee, M. Luksic, K.A. Dill, How water properties are encoded in its molecular structure and energies, Chem. Rev. 117 (2017) 12385–12414.