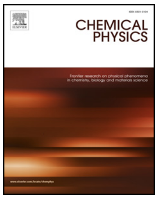
Chemical Physics 513 (2018) 266–272

Contents lists available at ScienceDirect

Chemical Physics

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



ATR-FTIR study of the isosbestic point in water solution of electrolytes

A. De Ninno[a,*], M. De Francesco[b]

[a] ENEA UTAPRAD-DIM, C.R. Frascati, Via Enrico Fermi, 45 00044 Frascati (Roma), Italy
[b] ENEA UT-RINN C.R. Casaccia, Via Anguillarese 301, S. Maria di Galeria 00123 (Roma), Italy

ARTICLE INFO

Keywords:
Water
Vibrational spectroscopy
Electrolytes
Isosbestic point
Dipole moment

ABSTRACT

Here we report an ATR-FTIR study on aqueous electrolytic solutions aimed to investigate the nature of the isosbestic point observed in the stretching mode broad band. This feature reveals that the properties of the system are described by the superposition of two components at equilibrium whose relative abundance depends on the running parameter. Here we show that the OH intramolecular bond length changes differently in the two components. It has been observed that, surprisingly, the OH bond length of highly correlated water molecules decreases with the concentration of the solute. On the opposite, it expands in molecules belonging to small cluster. As the shortening of the OH bond shows that the water-water interaction prevails on water-ion interaction, we make the hypothesis that the decrease of the bond length is due to a collective behaviour of the water molecules replacing the classic concept of H-bond in water.

1. Introduction

Classical theories of electrolytes are based on the picture of a fully ionised gas [1] because it is assumed that, during the solution, they are completely dissociated in ions. In fact, all the thermodynamic properties can be obtained from the statistic integral $\int e^{-F(p,q)/T}dpdq$, where $F(p,q)$ is the free energy of the solvent plus the ions. As it is well known from classical electrodynamics, the free energy of a system of charged particles in a medium (with fixed volume and temperature) is obtained by dividing the energy of the charges in vacuum by the dielectric constant of the medium. However, this assumption is based on the hypothesis that the distances among the ions are much greater than the molecular dimensions. Since the solution overall is neutral i.e. $\sum_a z_a n_a = 0$, wheren_a and$z_a$are, respectively, the number of ions of a-type and their charges, the energy related to the Coulombic attraction must be much lower than the kinetic energy of the ions, hence the density must be lower than: $\frac{n}{V} \ll \left(\frac{\varepsilon T}{z^2}\right)^3$ [2]. Such a constrain makes these theories fully working up to concentrations of approximately c ≤ 0.1 M. Below that limit, the Debye-Hückel model predicts a charge distribution around a positive ion placed at the origin of a three-dimensional cage and the interaction between the ions in solution and the water molecules is discussed in the framework of classical electrostatics. At much higher concentration the number of water molecules strongly bound to each solute became insufficient to shield. Ions, unshielded, fall back to their initial, stable configuration of crystal. How and how many water molecules are seized by the solute is actually object of debate. The terms hydration number, coordination number and solvation number are often used interchangeably since they all refer to the ability of ions to tight bind water. However, this definition is based on an unsolved question: how tight is tight enough? The answer affect the results of the measures: many different kinds of hydration numbers can be obtained by different experimental techniques [3]. The confusion suggest that a convincing model of aqueous solution at high concentration is still lacking.

Actually, the right question to be asked for is about the super-molecular structure of liquid water: assuming that liquid water structure is provided by a three dimensional network of continuously evolving hydrogen bonds, the only parameter able to account for changes of the macroscopic parameters (such as viscosity, entropy of solvation, etc.) is, as a matter of fact, the strength of the H-bond. However, the concept of H-bond turns out to be merely phenomenological: the calculated electronic ground state of the water molecules has a smooth structure without the highly directional charge densities required to form H-bonds. In order to explain the existence of the H-bond it is mandatory to assume that the molecules in the condensed state are in a ground state which differs from the ground state of the isolated molecule and provides the required feature of highly directional charge density. A two fluids picture is thus expected from this simple consideration [4].

What happen to the water molecules at concentration ≥ 0.01 M ? We tried to answer to this question by studying the deformation induced on the OH stretching band up to the solubility limit of several chloride salts. The OH stretching band width is attributed to water

---

[*] Corresponding author.
E-mail address: antonella.deninno@enea.it (A. De Ninno).

https://doi.org/10.1016/j.chemphys.2018.08.018
Received 21 June 2018; Accepted 8 August 2018
Available online 09 August 2018
0301-0104/ © 2018 Elsevier B.V. All rights reserved.

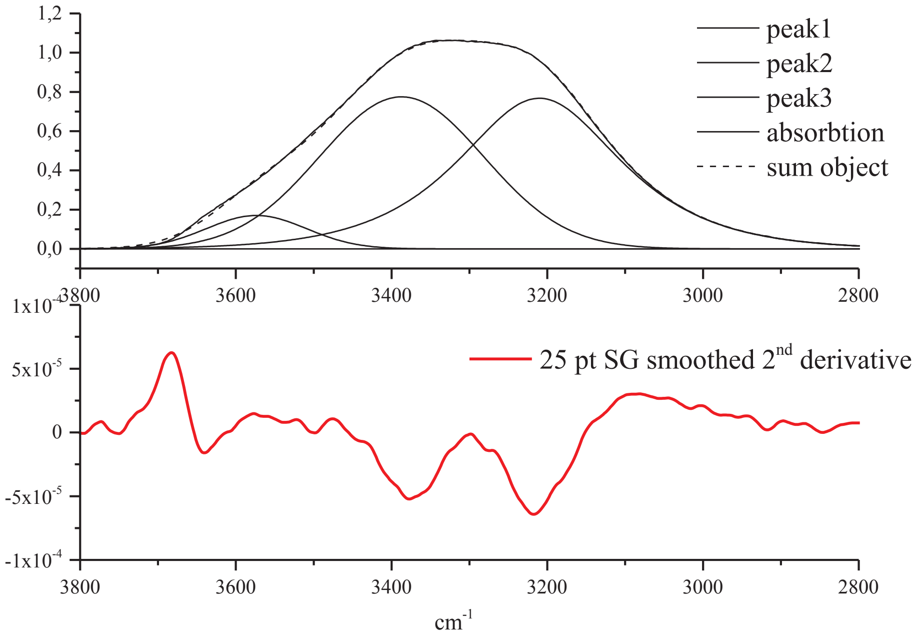


Fig. 1. OH stretching band (NaCl 0.1 M) and deconvolution sub-bands. The second derivative of the signal is shown in the bottom panel: three main minima are clearly visible thus revealing the position of the minimum number of Gauss*Lorentz (Voigt) peak type sub-bands used for the signal reconstruction (the Savitzy-Golay smoothing slightly shift the minimum in the bottom panel with respect to the position of the sub-bands maxima). The error between the sum and the measured signal is < 10^{-6}.

molecules involved in different hydrogen bonding. Low-energy vibrations are related to molecules forming larger or stronger H-bonds, high-energy vibration and on the opposite, are attributed to water molecules involved in almost nothing water-water correlation. Larger clusters, ice-like components, have been located at about 3200 cm^{-1}, smaller clusters at about 3400 cm^{-1}, and monomeric water molecules, gas-like components, at about 3600 cm^{-1} [5]. Moreover, it is apparent that in vapour, where molecules can be assumed to be independent, the peaks at ≈3200 and ≈3400 cm^{-1}, observed in condensed water are absent, whereas, in vapour, we can observe a number of peaks whose position is slightly higher than 3600 cm^{-1}. On the contrary in ice the dominant feature is the peak at ≈ 3200 cm^{-1} while the other features fade away by decreasing temperature.

We propose to make the deconvolution of the wide band between 2800 and 3800 cm^{-1} by using three sub-bands peaked at (about) 3200, 3400 and 3600 cm^{-1} [6]. This is, actually, the minimum number of sub-bands that allows a univocal deconvolution of the peak as can be obtained by the second derivative of the spectrum drawn in Fig. 1. The assignment of these sub-bands matches the above description.

2. Results and discussion

We used ATR-FTIR spectroscopy to study chloride solutions of monovalent ions Li^+, Na^+, K^+, Cs^+ and divalent ions: Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Zn^{++} and Cd^{++}. To prepare the solutions in bi-distilled water the salts have been purchased by Sigma-Aldrich. We used a Shimadzu-IR Affinity-1S equipped with a single reflection ATR diamond cell. Measurements were made at room temperature. For each spectrum 45 scans were recorded at resolution of 4 cm^{-1}. The preliminary reduction of the IR spectral data (ATR penetration depth compensation, baseline subtraction, normalisation,) and the fitting were performed using the Labsolution Shimadzu spectral analysis software, such as the bands deconvolution routine. The deconvolution has been done by using Gaussian·Lorentzian peak sub-bands.

Stretching broad band of aqueous solutions, located in the range 2800–3800 cm^{-1}, is strongly affected both by the type and by the concentration of the solutes. It has been observed that an isosbestic (equal absorption) point appears when increasing the molar concentration of the monovalent ions, see Fig. 2 and for three on six divalent ions, Fig. 3.

These observations rule out the hypothesis that the isosbestic point only occur because of the changes in the solvation shell around the cations and/or because of the variations of the H-bond network of water. Molecular Dynamics (MD) simulations suggest that changes in H-bond network occurs with the aim of increasing the size of the hydration cage and decreasing charge density of the cation [7] but such an hypothesis is not confirmed by the experiment. Actually ions that have the larger charge density do not show the isosbestic point.

In Table 1 is shown the list of ionic radii, charge densities, isosbestic points and Pauling electronegativities of the cations investigated. As it can be seen in Fig. 4, only cations with electronegativity ≤ 1 show the isosbestic point pointing to a threshold in the attracting force between the ionic charge and the electron cloud of water molecules. Even though electronegativity has been considered as an intrinsic property of atoms, it seems also it depends on the chemical environment (valence state and coordination number) [8]. Since each ion is surrounded by a certain number of opposite charges in order to maintain the electroneutrality, electronegativity can be defined in terms of effective ion potential $\varphi = Z^*/r_i$, where Z^* is the effective nuclear charge and r_i is the ionic radius also depending on the coordination number. Ions potentials are related to Pauling electronegativities by a linear regression [9]. A deeper discussion about the isosbestic point occurrence and the electrons clouds shape of the solutes should be done in the future. Here we underline that electronegativity and not the charge density has to be considered in order to correctly understand the isosbestic point formation. In facts, the attraction between cations and electrons also depends on the electrons cloud shape while the charge density is a space-averaged quantity.

On increasing the concentration, OH stretching spectrum shows a blue shift of the 3200 cm^{-1} centred peak and, and on the opposite, a red-shift of the 3600 cm^{-1} centred peak. Greater red-shift that have been observed for $CaCl_2$, $MgCl_2$ and LiCl at concentration ≥3 M, also showing a dragging effect on the intermediate peak, which is almost unaffected in the other salts, see Fig. 5. In table 2 the shift values for the three components are shown both for monovalent and divalent ions at fixed concentration in order to have a quantitative comparison among homogeneous molarities.

The variation of the OH bond length Δl can be evaluated by the shift of the centre-band frequencies from the relationship: $\Delta\omega/\omega = -\Delta l/2l$. We assumed that the pure water, zero concentration, lengths coincide, respectively, with $l_{ice} = 1.024$ Å [10] for high correlation molecules, $l_{vapour} = 0.9724$Å [11,12] for non-correlated molecules and an average

Download English Version:

https://daneshyari.com/en/article/7837104

Download Persian Version:

https://daneshyari.com/article/7837104

Daneshyari.com