Ion hydration effects in the optical absorption and molecular vibration of water

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Abstract.
Hydration occurs when some ionic species are in pure water. In this research study, optical properties of an electrolytic solution with ionic species that emulated the extracellular environment were analyzed. The attenuated total reflection ATR-FTIR spectra and Raman spectra of electrolyte solutions were measured and the vibrational spectra of pure water (type A) with electrolyte solutions in the spectral region between 2700-4000 cm^{-1} was compared. At low ionic concentrations of chloride, sodium, potassium and calcium, a weak effect on the spectrum of water was observed. We found a shifts in the absorption bands of water in IR (3286 cm^{-1} and 3492 cm^{-1}) and Raman spectra (3207 cm^{-1} and 3432 cm^{-1}), which increase with ionic concentration. This effect can be interpreted as a result of interactions between water molecules and solvated ions. This result suggests that the presence of ions in pure water modifies the optical properties of water.

1. Introduction

Biological tissue has water in the Intra and extracellular media. The extracellular medium has some ions as chloride, sodium, potassium and calcium [1]. The optical properties of water in extracellular media in the range of 2700 to 4000 cm^{-1} is strongly affected by the existence of ions [2, 3, 4]. Each ion in electrolytic solution is surrounded by water molecules i.e. ions are hydrated, and different types of intermolecular interactions can occur [5, 6, 7]. Hitherto, the presence of some ions can change the natural vibrations of water, although these free ions do not have vibrational modes in the interest region [7, 8, 9].

Raman spectroscopy and ATR-FTIR are special techniques to measure and study molecular vibrations and optical absorption in different materials, including water [5, 10, 11]. We employed these two techniques to study the alterations in optical properties of the water when these ions are added. In this paper, we report the analyze of Raman and ATR-FTIR spectra of electrolytic solutions.

2. Materials and Methods

2.1. Ionic Solution Preparation

We used KCl, $CaCl_2$, and $NaCl$ salts to prepare the electrolyte solutions. Sodium chloride ($NaCl$) (5,84 mg), potassium chloride (KCl)(7,45 mg), and calcium chloride ($CaCl_2$) (14,7 mg) were added at room temperature in $25mL$ of Milli-Q Ultrapure water type 1. The ionic

solutions were prepared under the values of level saturation for each salt. Different dilutions were arranged to study the ionic interaction with water.

2.2. FTIR and Raman measurement

The FTIR spectrometer Nicolet iS-50 was used to obtain the absorption (ATR) spectra. The interferometer mirror was moving at $0.6363\ cm^{-1}/sec$ with a resolution of $8\ cm^{-1}$ and 110 scans. The micro-Raman Horiba Evolution LabRam was used to obtain the Raman spectra. We used the excitation source of 532nm with 25mW, 10 seconds as exposure time, ten scans and a grid 600 gr/mm.

2.3. Data Analysis

After the data acquisition, the baseline correction was made with polynomial fitting. Subsequently, two Gaussian functions were used to fitting each band of spectra [12].

3. Results and discussions

The vibrational modes and optical absorption peaks of aqueous electrolytic solution have a slightly different behavior than water. To analyze how many vibrational and absorption peaks are present in Raman, and IR spectra of water, a decomposition of spectra in two or more peaks could be performed to obtain the best fit to experimental data [13, 14, 15]. In Figure 1 (a), (c) and (e) are shown the Raman spectra for pure water (in black) and four concentrations (4, 3, 2 and 1 M of $CaCl_2$, KCl, and NaCl) of the electrolytic solutions (in color), at room temperature. In Figure 1 (b), (d), and (f), two Gaussian functions were used to describe each experimental band. In a similar way, Figure 2 shown experimental IR spectra. The Gaussian function parameters values are in Tables 1 and 2.
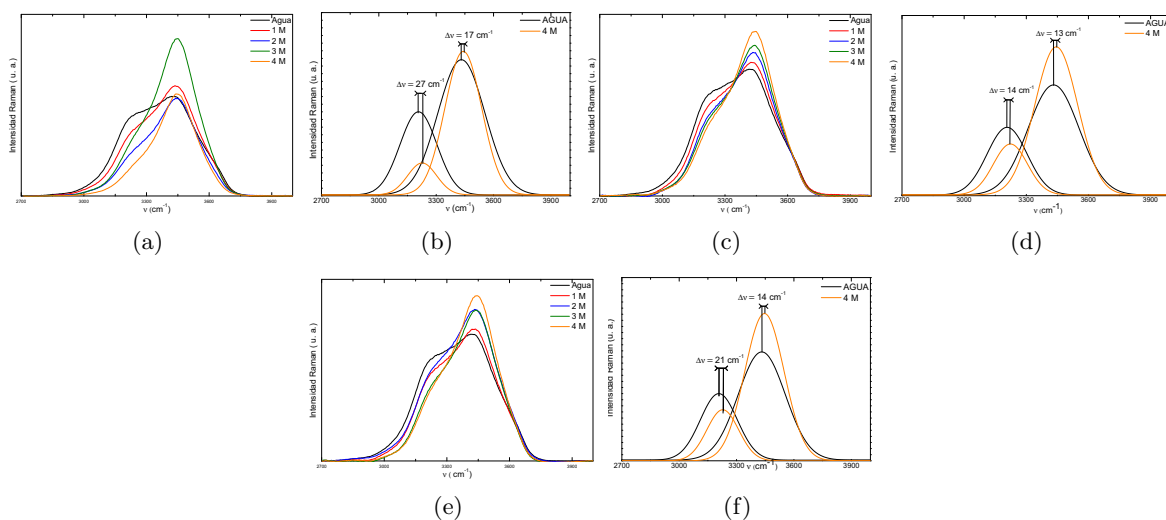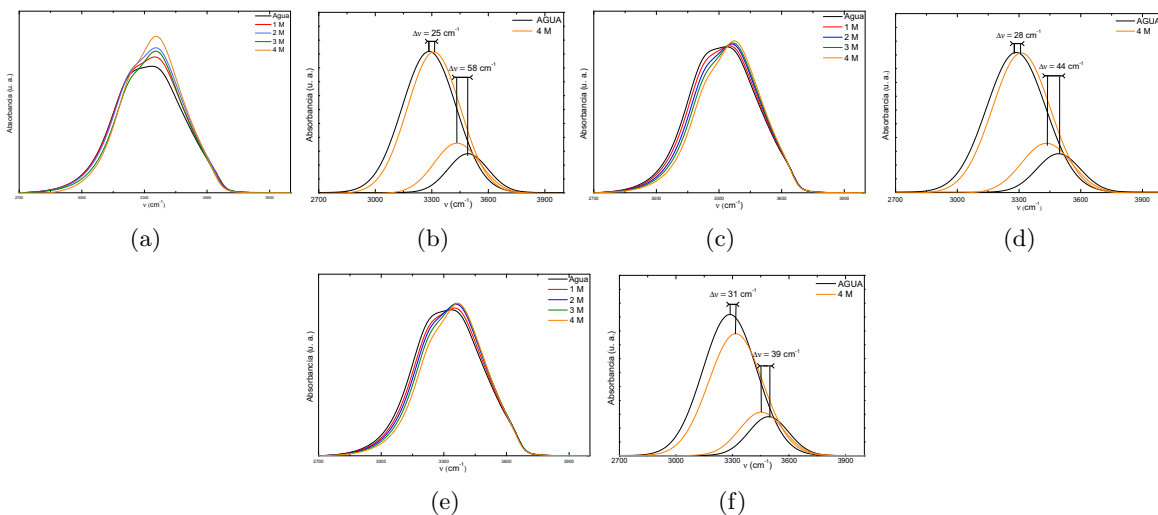

Figure 1. Raman spectra of water (in black) and aquous electrolytic solution (in color) of $(a)CaCl_2$, $(c)KCl$, $(e)\ NaCl$ and two-peak Gaussian fitting to (b) $CaCl_2$, (d) KCl, (f) $NaCl$.

Table 1. Gaussian function parameters values to Raman spectra of water and electrolytic solutions.

salt	Concentration (M)	Peak 1 (cm^{-1})	$\Delta\nu$ (cm^{-1})	Peak 2 (cm^{-1})	$\Delta\nu$ (cm^{-1})	COD R^2
Water	-	3207 $\pm$1	-	3432 $\pm$1	-	0,997
$CaCl_2$	1	3224 $\pm$1	14	3448 $\pm$1	16	0,998
	2	3227 $\pm$1	17	3449 $\pm$1	17	0,999
	3	3232 $\pm$1	22	3449 $\pm$1	17	0,999
	4	3234 $\pm$1	27	3449 $\pm$1	17	0,998
KCl	1	3207 $\pm$1	0	3432 $\pm$1	0	0,998
	2	3215 $\pm$1	8	3438 $\pm$1	6	0,999
	3	3219 $\pm$1	12	3443 $\pm$1	11	0,999
	4	3224 $\pm$1	14	3445 $\pm$1	13	0,998
$NaCl$	1	3214 $\pm$1	7	3436 $\pm$1	4	0,998
	2	3222 $\pm$1	15	3444 $\pm$1	12	0,998
	3	3223 $\pm$1	16	3443 $\pm$1	11	0,999
	4	3228 $\pm$1	21	3446 $\pm$1	14	0,999

The study of distances between ion and water molecules can be used to understand the ion-water interaction. The cations Na^{1+} and K^{1+} have a minor distance with the water molecules in the first shell of hydration, $3.3\mathring{A}$ and $3.7\mathring{A}$ respectively, whereas the distance of ion-water is $4.5\mathring{A}$ for Cl^{1-} [16]. The distance ion-water molecule influences the diffusion process of the ion through the cellular membrane. In particular, the concentration of ions sodium in the extracellular media increases according to the degree of malignancy of cervical cancer [17]. These differences between the Na^{1+}-water distances could explain why the membrane channel distinguishes explicit ions in solution such as Na^{1+} and why the shift frequency over Raman spectra is stronger for sodium more than potassium.

Figure 2. Absorption spectra of water (in black) and aquous electrolytic solution (in color) of (a)$CaCl_2$, (c)KCl, (e) $NaCl$ and two-peak Gaussian fitting to (b) $CaCl_2$, (d) KCl, (f) $NaCl$.

The two values of normal vibration of water obtained by optical absorption were $3286\pm8cm^{-1}$ and $3492\pm8cm^{-1}$, see Table 2. The experimental results to Na^{1+}, K^{1+} and Cl^{1-} are similar

to reported previously i.e. these ions alter the normal frequency of water at high-frequency [4, 8, 10, 12, 14, 18, 19]. In this study, different concentrations were compared. The absorption spectrum of water for the natural vibration $3286 \pm 8 cm^{-1}$ was shifted to the higher frequency and the $3492 \pm 8 cm^{-1}$ natural vibrations, to the lower frequency with the increase of salts concentration.

Table 2. Gaussian function parameters values to absorption spectra of water and electrolytic solutions.

salt	Concentration (M)	Peak 1 (cm^{-1})	$\Delta\nu$ (cm^{-1})	Peak 2 (cm^{-1})	$\Delta\nu$ (cm^{-1})	COD R^2
Water	-	3286 $\pm$8	-	3492 $\pm$8	-	0,998
$CaCl_2$	1	3295 $\pm$8	9	3479 $\pm$8	13	0,998
	2	3301 $\pm$8	15	3462 $\pm$8	30	0,998
	3	3308 $\pm$8	22	3443 $\pm$8	49	0,998
	4	3311 $\pm$8	25	3434 $\pm$8	58	0,998
KCl	1	3297 $\pm$8	11	3488 $\pm$8	4	0,998
	2	3307 $\pm$8	21	3479 $\pm$8	13	0,998
	3	3311 $\pm$8	25	3467 $\pm$8	32	0,998
	4	3314 $\pm$8	28	3448 $\pm$8	44	0,998
$NaCl$	1	3298 $\pm$8	12	3488 $\pm$8	4	0,998
	2	3306 $\pm$8	20	3480 $\pm$8	12	0,998
	3	3313 $\pm$8	27	3472 $\pm$8	20	0,998
	4	3317 $\pm$8	31	3453 $\pm$8	39	0,998

4. Conclusions

The main ion hydration effect in the optical properties and molecular vibration is the shift in vibrational modes by the presence of ions. A substantial shift in the vibrational modes was observed with increasing salts concentration. The change in the frequency of vibration evidence ion induces alterations in the normal vibrations of the water since electrostatic interaction between ions and counterions in water molecules to affect the frequency of vibration. FTIR-ATR and Raman spectra show a similar effect. However, these spectra differ in the second sub-band, which corresponds to the antisymmetric stretching.

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