Solvation effects in aqueous solutions investigated by FTIR-ATR spectroscopy

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Introduction
Spectroscopic measurements in the mid-infrared of aqueous solutions are strongly influenced by broad absorption bands covering nearly the whole spectral range. The fundamental asymmetric and symmetric stretching vibrations of H₂O are located between 2650 cm⁻¹ and 2500 cm⁻¹. At 1440 cm⁻¹ the bending mode of the H₂O appears and between 2100 cm⁻¹ and 2000 cm⁻¹ there are weak vibrations due to the inherent structure of water. Strong absorbances below 1200 cm⁻¹ are due to the restricted rotational motions of the water molecules. Each solute disturbs the structure of the liquid water leading to changes in the vibrations of the H₂O clusters and therefore to alterations in the infrared spectra of aqueous solutions. Since water is a strong infrared absorber and remains in an excess amount as solvent, care have to be taken when pure water is used as reference in IR spectroscopy. Beside the changing of the water absorption bands due to the hydration shell of the solute, a change of the water density have to be taken into account. Despite of this interference it is possible to get relevant IR spectroscopic information on the hydration effects by means of adequate tools such as the measurement of quasi simultaneous sample and reference spectra (single beam sample reference SBSR spectra). In order to quantify the influences of ions, acid and bases, respectively, we measured FTIR-ATR absorbance spectra of aqueous solutions of NaCl, KCl, CaCl₂, as well as of HCl and NaOH. The influence of HCl and NaOH on lysine spectra and their compensation will be shown as an example.

SSBR spectra of 1M solutions of NaCl, KCl and CaCl₂ are shown in Figure 2. All exhibit a characteristic s-shaped band in the OH stretching region, which is quite similar for NaCl and KCl, but differ from the band of CaCl₂. All salts solutions exhibit an increased absorbance of the H₂O bending band at 1640 cm⁻¹ as well as a strong decreasing edge of a band in the librational region below 1000 cm⁻¹. These pattern include density changes of water upon solvation of salts, too. A detailed view of the continuum and bending region of water is given in Figure 3. The peak maximum of the additional absorbance of the H₂O bending band of the NaCl solution is shifted to 1637 cm⁻¹, that of the KCl solution to 1632 cm⁻¹, whereas the maximum of the CaCl₂ band absorbtion at 1641 cm⁻¹ near the pure water bending vibration. Characteristic deviations from this HO-Spectrum are found in the region between 2500 cm⁻¹ and 2000 cm⁻¹. Again the changes of CaCl₂ are different from that of the other chlorides. This results in the recently published extensive study on hydrated alkali halide solutions. The D spectrum (1) of 1M CaCl₂ exhibits a pronounced deviation from the baseline in the bending region (Figure 4). This may indicate an enriched concentration of Ca⁺ near the Ge-plate. Bands occurring in the OH stretching region of all salts, probably due to exceeding the limit of the weak absorber approximation. In the spectra of solvated HCl and NaOH a high offset of the absorbance below 3100 cm⁻¹ is characteristic. These bands are presumably due to the additional vibrations of H₂O and OH and the close cluster of HO molecules around the proton and hydroxide ion that build up distinct water complexes. In Figure 5 the spectra of 0.77M HCl and 0.68M NaOH solutions are shown, whereas traces in Figure 6 reflect the corresponding dichroic difference spectra of the integrated absorbance of the spectra of solvated ions fulfill the Lorentz-Lorentz law (Figure 7). This indicates, that the solvation effects of the different ions in a model solution could be treated additively. An example is shown in Figure 8. A NaOH solution with pH 12.6 was set to pH 10 by adding HCl (Figure 8A). From this spectrum we subtract a NaCl solvation spectrum (Figure 8B) that equals D spectrum (1) of 1M CaCl₂ (Figure 8C) that is equal to a independently measured spectrum of aqueous HCl with pH 0.2 (Figure 8D).

Experimental
All Fourier transformed infrared attenuated total reflection (FTIR-ATR) measurements were performed at 22°C on a Bruker IFS 66/s spectrometer equipped with a variable polarizer and a 20° SBSR mirror attachment (angle of incidence = 45°). Optimized Ge plate thickness was 50µm. The spectra were recorded at 4 cm⁻¹ spectral resolution through the upper and lower half of the internal reflection element (IRE) with very short interframe delay time. One half of the IRE is then used for the sample the other one for reference. 50 interferograms per spectrum were averaged by long time baseline drifts and by peaks of gassy water and carbon dioxide. All spectra were scanned at 6 cm⁻¹ resolution. The mean number of active internal reflections were 13.5. Solutions of salts, HCl and NaOH were measured with pure H₂O as reference. The general measurement procedure is exemplified in Figure 1. In the limit of the weak absorbed approximation and for an angle of incidence ~45° one can calculate the dichroic difference spectra D according to equation (1) with R = 2 for isotropic bulk samples (Figure 4). Deviations of a flat line show anisotropic behavior. This result from an imprints process of or from exceeding the limit of the weak absorber approximation.

Solvation effects of salts, HCl and NaOH

Depending on the concentration of H₂O the absorption bands of L-lysine exhibit strong alterations. From this behavior we get information of the confirmation of aqueous lysine (Schwarzott et al. in prep.). At low and high pH values clear offsets appear in the spectra of solvated lysine (Figures 9A, 10A). The difference of the lysine spectra measured at the lowest and highest pH values (pH=0.2 and pH=12.8) reflect the pattern of solvated HCl and NaOH, respectively (Figures 9C, 10C). Therefore we corrected the SSBR spectra of the amino acid by a probe solution subtracted base spectra to get rid of the spectral offset (Figures 9B, 10B). The remaining sigmoidal band shape of the OH stretching region mainly shows effects of hydration of lysine. However, lysine is acting as a buffer during the titration process and thus leading to excess concentrations of chloride and sodium. Probably this is the reason of the small deviations between the difference of the lysine spectra and the spectra of the scaled solutions of HCl and NaOH (see Figures 9D, 10D).