INFRARED STUDY OF LOW CONCENTRATION AQUEOUS IONIC SALT SOLU-TIONS: PURE AND MIX SALTS

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In a previous infrared (IR) study[a] of nine alkali halide salts in aqueous solution in the concentration range from 0.2 M up to the saturation limit we arrived at the conclusion that the solutions were made up of two type of waters: pure water and salt solvated water. These salts are completely ionized but form mono species pairs that do not absorb IR but perturb the surrounding water molecules whose signature could be followed with the concentration variations. The attenuated total reflection (ATR) technique was used to acquire the spectra. Factor analysis (FA) was used to separate the principal spectra and determine the species abundances. For this presentation we have analyzed two binary salts, Na^+-Cl^- and Na^+-I^-, from 1.0 M down to 2 mM and found that the situation was similar to that at higher concentrations with 5.0 and 4.0 water molecules solvated to the Na^+-Cl^- and Na^+-I^- ion pairs, respectively. Pushing the analysis further, we studied mixtures of NaI and CsCl from 1.0 M to 50 mM that revealed the formation of Na^+-Cl^- and Cs^+I^- ion pairs solvated with 10 water molecules (5 each ion pairs). These were compared to the original NaI and CsCl ion pairs that are solvated with 4 and 3 water molecules, respectively. The study of salt mixtures confirms our previous findings. These results shed a new light on "simple" aqueous systems whose molecular organization is still a matter of debate.

[a] J. Chem. Phys. **1**15, 2664 (2001)