

Fourier transform near infrared study of aqueous solutions of simple salts: from molecular spectroscopic study to chemometrics

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Introduction

Studies of the structure and physical properties of aqueous solutions of simple salts such as NaCl and CaCl₂ are very important from the point of view of basic research as well as practical applications. Near infrared (NIR) spectroscopy has long been employed for investigating aqueous solutions because the technique is very sensitive to structural changes in water due to hydrogen-bonding and hydration. The purpose of the present study is to provide new insights into the effects of hydration on the structure of aqueous solutions by using both molecular spectroscopic techniques and chemometrics.

Experimental

Twenty-one LiCl, NaCl and CaCl₂ solutions were prepared with concentrations from 0 to 5.0 M at an increment of 0.25 M. Fourier transform (FT) NIR spectra of the solutions were measured at 8 cm⁻¹ resolution with a JEOL JRS-6500N FT-Raman spectrophotometer equipped with a TGS detector. Quartz cells of 0.1 cm thickness (for the 7800–5900 cm⁻¹ region) and 1 cm thickness (for the 11,100–9330 cm⁻¹ region) were employed for the NIR measurements. The spectra obtained were subjected to numerical curve fitting (modified Marquard's nonlinear least-squares method); the band shapes were approximated by a Gaussian function. Principal component analysis (PCA) was performed by Unscrambler using the 7800–5900 cm⁻¹ region.

Results and discussion

Figure 1 shows NIR spectra in the 7800–5900 cm⁻¹ region of 5.0 M LiCl (a), NaCl (b) and CaCl₂ (c) solutions and the results of curve fitting. A feature appearing in the 7500–5900 cm⁻¹ region is largely due to a $\nu_1 + \nu_3$ mode of water but it includes a very weak shoulder near 7400

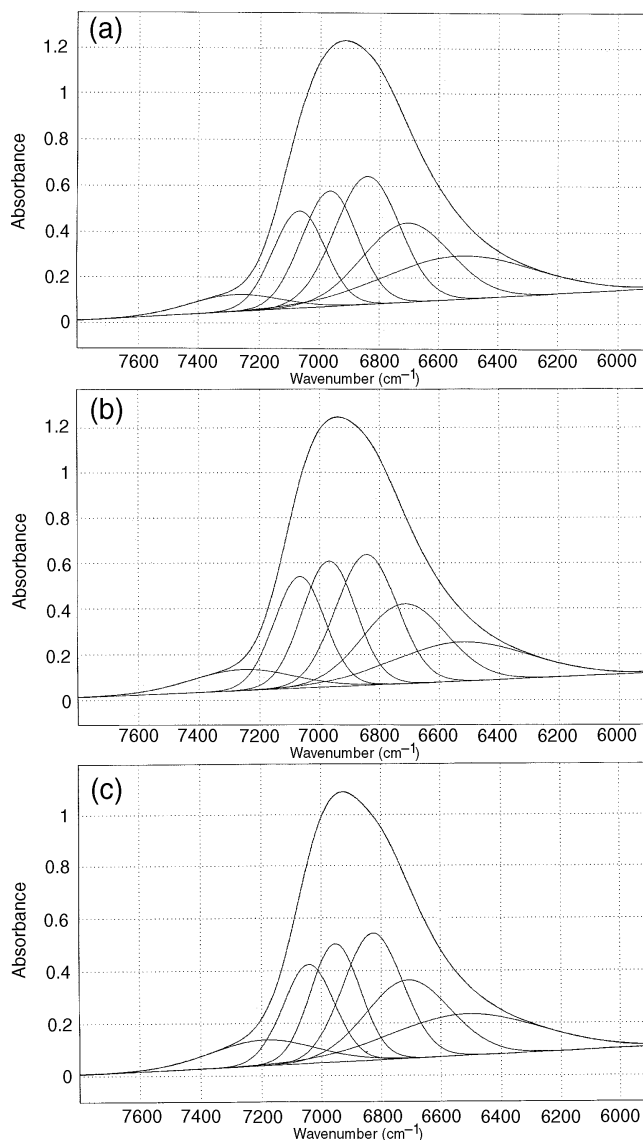


Figure 1. Results of curve fitting for the 7800–5900 cm^{-1} region of NIR spectra of 5.0 M LiCl (a), NaCl (b) and CaCl_2 (c) solutions.

cm^{-1} assigned to the $\nu_1 + \nu_2 + \nu$ mode (ν ; rotational mode).¹ For the curve fitting it was assumed that the feature consists of six bands; one is due to the $\nu_1 + \nu_2 + \nu$ mode and the other five arise from the $\nu_1 + \nu_3$ mode. Evidence for the presence of the five bands comes from the second derivatives of the NIR spectra shown in Figure 1. The second derivatives show five bands in the 7200–6000 cm^{-1} region. Peak maxima in the second derivatives nearly correspond to those of the band components of the curve fitting. We refer to the five components as S_0 , S_1 , S_2 , S_3 and S_4 .

Probably, S_0 , S_1 , S_2 , S_3 and S_4 species are ascribed to water molecules with no, one, two, three and four hydrogen bondings, respectively.² We have compared the fractions of the five species in the LiCl, NaCl and CaCl₂ solutions with those in pure water. It has turned out that for all the solutions the fractions of S_1 and S_2 species decrease while those of S_0 and S_3 increase with the increase in concentration. The hydration breaks down the equilibrium among the five species. The amount of S_0 species increase with hydration but the S_0 species in aqueous solutions are significantly different from S_0 species in pure water because the band frequencies of the two kinds of S_0 species are different. Probably, most of the S_0 species in aqueous solutions are not pure S_0 species but are those interacted with cation or anion.

We performed PCA for the above solutions using the 7800–5900 cm⁻¹ region. The loading coefficient spectra of principal factor 1 for the three solutions suggest that the absorption wavelengths corresponding to S_0 , S_2 and S_3 species contribute largely to the first principal factor.

References

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