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Solvation of cobalt(II) and trifluoromethanesulfonate ions in N,N-dimethylformamide–methanol mixed solvent studied by means of FT-IR spectroscopy

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Abstract

FT-IR spectra of $Co(CF_3SO_3)_2$–N,N-dimethylformamide (DMF)–methanol (MeOH) solutions have been measured over the whole range of solvent composition. The data together with the obtained previously spectra of DMF–MeOH mixtures have been analyzed using the difference spectra method in the region of CO and OH stretching bands. The number of DMF and MeOH molecules in the first solvation sphere of Co(II) ion versus solvent composition has been determined. The second solvation sphere has been revealed and characterized quantitatively. Solvation of trifluoromethanesulfonate (triflate) ion as well as ion association in DMF solution have been also studied.
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1. Introduction

FT-IR spectra, as very sensitive for changes in hydrogen bonds, were recently used for studying intermolecular complex in DMF–MeOH mixtures, providing comprehensive information about its concentration and structure [1]. The modern methods of quantitative analysis of the spectra, factor analysis and difference spectra method, were applied, giving complementary results. In the present work, changes in FT-IR spectra of $Co(CF_3SO_3)_2$–DMF–MeOH solutions compared with those of DMF–MeOH mixtures were analyzed to find the effect of ions on hydrogen bonds in the solvent and thus interactions between solvent molecules and ions. An excellent tool for studying the solvation phenomena is the difference spectra method in a version presented by one of us [2]. It was applied to the solvent groups participating in solvation of ions, i.e. carbonyl group from DMF and hydroxylic group from MeOH, and provided the solute-affected spectra of solvent molecules. Analysis of the shape and position of these spectra allowed to draw a detailed picture of solvation spheres of both ions. Simultaneously, the numbers of DMF and MeOH molecules influenced by one ion

in particular spheres were obtained and related to the respective solvation numbers.

With regard to Co(II) ion, analysis of the affected spectra showed undoubtedly the presence of the second solvation sphere including molecules of both solvent components. In the light of our results, vibrational studies which ignore this state of solvent molecules around the bivalent and trivalent metal ions employ too simple a model of solution [3,4].

Solvation of ions in mixed solvents was investigated in our laboratory also by thermodynamic method, using enthalpies of transfer of ions from pure solvent to mixtures [5]. From these data the mean composition of the solvation sphere of Co(II) ion in several aqueous-organic as well as organic mixed solvents could be derived on the basis of the preferential solvation theory [6]. As the spectroscopy studies presented in this paper provide the same kind of information concerning Co(II) ion, it will be interesting to compare the results with those from the thermodynamic studies of $Co(CF_3SO_3)_2$–DMF–MeOH system, which are in progress now.

2. Experimental

2.1. Chemicals and solutions

Methanol (Aldrich, HPLC grade, 99.9+%) and N,N-dimethylformamide (Aldrich, HPLC grade, 99.9+%) were

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stored over 3 Å molecular sieves (Aldrich) in a dry-box. Methanol was distilled using a Vigreux column prior to use. No traces of water were found in IR spectra of DMF.

Co(CF$_3$SO$_3$)$_2$ was obtained by dissolving cobalt(II) carbonate in trifluoromethanesulfonic acid (Fluka, purum, ≥98.0%) and purified by triple crystallization from redistilled water. The crystals were dried in vacuo at 383 K and their composition was checked by standard EDTA titration of cobalt.

Co(CF$_3$SO$_3$)$_2$ solutions in mixtures of methanol and *N,N*-dimethylformamide were prepared by weighing, their densities were measured using Anton Paar DMA 5000 densimeter at 25.0 ± 0.001 °C. The methanol mole fractions in the solutions were changing of about 0.1; the salt concentration was equal to 0.470 ± 0.0007 mol dm^{-3}.

2.2. IR measurements

FT-IR spectra were recorded on an IFS 66 Bruker spectrometer. A cell with CaF$_2$ windows of regulated width of the order of 1 μm was used. The accurate path length for each solution was calculated basing on the height of the bands at 1260 and 2500 cm^{-1}, measured also in a cell of constant width (29.98 μm, as determined interferometrically). One hundred and twenty-eight scans were collected and averaged for each spectrum at a selected resolution of 2 cm^{-1}. The temperature was kept at 25.0 ± 0.1 °C by circulating thermostated water through the mounting plates of the cell. The temperature was monitored by a thermocouple inside the cell. All spectra were baseline corrected before analysis.

2.3. Analysis of spectral data

The solute-affected solvent spectrum, ε_a, was extracted from the spectral data according to the difference spectra method in a version described in Ref. [2]. The spectrum of a solvent component in its molar absorptivity scale is defined for each wavenumber as:

$$\varepsilon_a = \frac{1}{NMm}(\varepsilon - \varepsilon_b) + \varepsilon_b \tag{1}$$

where ε is the spectrum of this component in solution at molality m (mol kg^{-1}), ε_b the spectrum of the considered component of "bulk" type, identical with the spectrum of the component in mixed solvent of given composition, N the affected number that denotes the number of moles of the solvent component affected by 1 mol of a solute, and M is molecular weight of this component (kg mol^{-1}).

The both unknowns, ε_a and N, were determined simultaneously by the computer simulation procedure presented in Ref. [7]. Gaussian peak function and the sum of Gaussian and Lorentzian peak functions were found as the best for fitting the experimental difference spectra.

The spectra were handled and analyzed using the commercial PC programs GRAMS/32 (Galactic Industries Corporation, Salem) and RAZOR (Spectrum Square Associates, Ithaca) run under GRAMS/32.

3. Results and discussion

3.1. Affected spectra

Fig. 1 presents FT-IR spectra in the carbonyl group absorption region measured in Co(CF$_3$SO$_3$)$_2$–DMF–MeOH solutions (a) and in DMF–MeOH mixtures (b) as well as their difference (c). The spectra converted to the molar absorption coefficient scale of DMF were interpolated for methanol mole fractions changing of 0.1. The analogous spectra in the hydroxylic group region are presented in Fig. 2.

The difference spectra method applied to the spectral data provided the spectra of both solvent components affected by the salt and N values denoting the mean number of DMF or MeOH molecules influenced by one molecule of Co(CF$_3$SO$_3$)$_2$. The analysis was performed in the whole range of solvent composition for x_{MeOH} step equal to 0.1. The salt concentration, the same in all solutions, was high enough to ensure sufficient
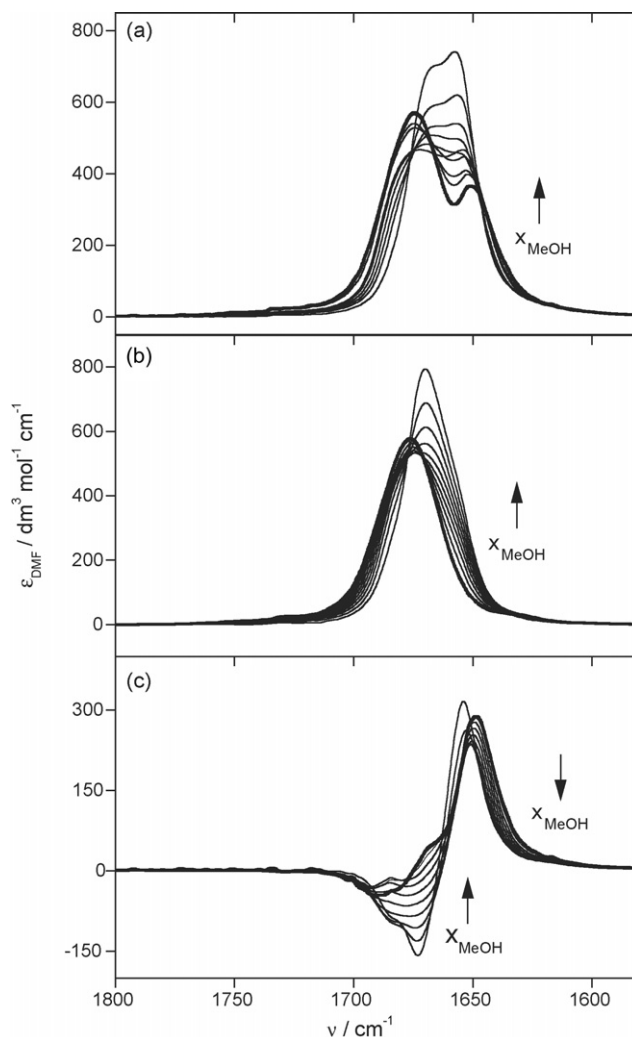

Fig. 1. FT-IR spectra measured in the CO absorption region, interpolated for methanol mole fractions in the solvent changing of 0.1 step. (a) Co(CF$_3$SO$_3$)$_2$–DMF–MeOH solutions, salt concentration 0.470 ± 0.0007 mol dm^{-3}. (b) DMF–MeOH mixtures. (c) The difference of the spectra from (a) and (b). Increase of methanol mole fraction is shown by arrows.