Raman Spectroscopic Study on the Acid Behavior of Aqua-Cations in Non-Aqueous Solution

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Many aqua-cations have acidic properties in solution as one of the protons of coordinated water is deprotonated. Acidic aqua-cations have recently drawn attention to the field of catalysis because of their capability to select specific sites of target molecules compared to inorganic acids.[1] Their acidity was regarded as playing an important role in activating reactions. For example, the rate of nucleophilic attack by a metal-coordinated water molecule has been found to be enhanced by 2.2×10^7 in the Cu(II)-catalyzed hydrolysis of the acetyl ester in 2-pyridinecarboxaldoxime.[2] Therefore it is important to know the characteristics of the aqua-cations from the view point of acidity to design a reaction scheme for an experiment. Although the efforts to investigate the acidity of the various kinds of aqua-cations were made, they were mostly done in aqueous media.[3] Considering the fact that a variety of organic reactions take place in non-aqueous media, it is essential to elucidate the characteristics of the aqua-cations especially in non-aqueous media.

In order to investigate the acidity of aqua-cations various kinds of methods were employed.[4] However, unfortunately none of these methods were employed in non-aqueous solutions. Brazdil *et al.*[5] found that, 4-dimethylamine-azobenzene (DMAAB) can be a good probe material in conjunction with resonance Raman spectroscopy to detect the acidity of hydroxylated ZnO_2 and TiO_2 at solid-gas interfaces. They utilized DMAAB as a Raman probe, monitoring structural change from azo to quinoid forms when the pKa value is below ~3.3. They successfully discerned whether the coordinated water molecules to metal oxides are acidic or not.

Following the approach of Brazdil *et al.*[5] we employed DMAAB to determine the acidity of aqua-cations by comparing the intensities of the Raman bands of azo form with those of quinoid form. Azo and quinoid forms have the absorption maximum at about 412 and 510 nm, respectively, as shown in Figures 1(a) and 1(b). In our experiment 632.8 nm is used as an excitation source, which is far from the absorption maximum of either form, because the intensity of non-resonance Raman scattering is linearly proportional to the concentration of molecules of interest. All the spectra were collected using a model Renishaw 2000.[6] All aqua-cations and DMAAB were dissolved in acetonitrile solvent so that the concentration was 1.0×10^{-2} M.

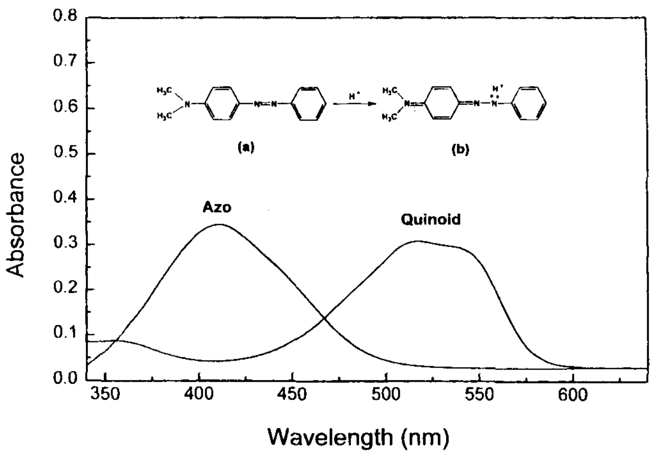

Figure 1. UV-vis absorption spectra of azo and quinoid forms of DMAAB in acetonitrile. Azo form of DMAAB (1.0×10^{-5} M) is transformed into quinoid form when acidified with HCl.

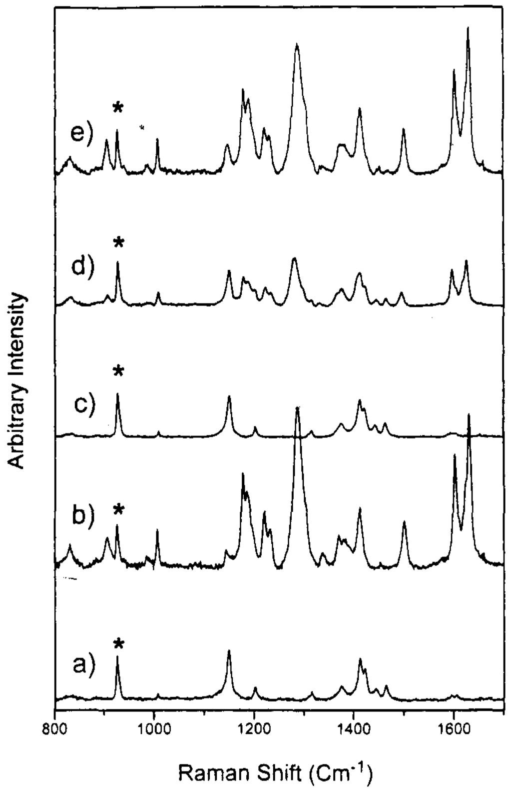

Figure 2. Raman spectra of the 1:1 mixture of DMAAB (1.0×10^{-2} M) and aqua-cations (1.0×10^{-2} M) in acetonitrile. (a) DMAAB, (b) DMAAB + HCl, (c) DMAAB + $Co(H_2O)_4Cl_2$, (d) DMAAB + $Cr(H_2O)_4Cl_2$, (e) DMAAB + $Fe(H_2O)_4Cl_2$ Asterisks represent solvent bands.

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We have illustrated the spectra of DMAAB under various conditions ranging from 800 to 1700 cm^{-1} in Figure 2. In this spectral range any of the bands attributed to aqua-cations does not exist. All the spectra are normalized by the solvent band at 926 cm^{-1}. Figures 2(a) and 2(b) represent the spectra of azo form of DMAAB and its corresponding quinoid form, respectively. The quinoid form is characterized by an intense band at 1631 cm^{-1} which is assigned to C=C stretching mode of bezene ring. Figures 2(c), 2(d), and 2(e) represent the spectra of the 1:1 mixtures of DMAAB and aqua-cations, that is, $Co(II)Cl_2(H_2O)_4$, $Cr(III)Cl_2(H_2O)_4$, and $Fe(III)Cl_2(H_2O)_4$, in acetonitrile solvent. As can be seen, each spectrum contains either azo or quinoid bands, otherwise both. The spectrum of the mixture of DMAAB and aqua-cobalt cation in Figure 2(c) is similar to that of azo form, indicating that no ionizable protons exist. On the contrary, the spectrum of the mixture of DMAAB and aqua-iron cation in Figure 2(e) is almost the same as that of quinoid form, indicating that as many ionizable protons as those of HCl exist. However, the spectrum of the mixture of DMAAB and aqua-chromium cation contains both azo and quinoid forms. This shows that the aqua-chromium cation has an intermediate acidity compared with the other two aqua-cations.

The experimental results are in good agreement with the prediction.[3] It is known that several factors such as cation charge, cation radius, geometry, and the nature of ligand affect the acidity of the aqua complexes. As a rule of thumb, aqua-cations with higher charges on the metal cations are more acidic than the ones with lower charges.[3] Since the cobalt cation has a formal charge, 2+, the aqua-cobalt cation is less acidic than the other two. Comparing the chromium cation with the iron cation, iron cation is higher in atomic number than the chromium cation, whereas both are the same in cation charge with 3+. And thus the radius of iron cation is smaller than that of chromium cation being more acidic by stabilizing the hydroxide ion.[7] As a result the intensity of the quinoid band increases in the series $Co(H_2O)_4Cl_2 < Cr(H_2O)_4Cl_2 < Fe(H_2O)_4Cl_2$. In conclusion, the Raman spectroscopic method is applied to determine the acidity of aqua-cations in non-aqueous solutions, which have not been accessible by conventional methods, and is proven to be a powerful technique to obtain information on the acidity in non-aqueous solutions on the molecular level.

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