

The Influence of Water Addition on Solutions of FeCl₃ in Isopropanol

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By means of Optical Absorption, EPR and Mössbauer techniques it is demonstrated that the addition of small amounts of water to solutions of FeCl₃ in isopropanol enhances the concentration of [FeCl₄][−] complexes, this addition leading also to the formation of ferric dimers involving two Fe³⁺–OH[−] bridges. An explanation of this fact based on the disproportionation of FeCl₃ and water hydrolysis is reported.

Recently it has been established that in isopropanol solutions of FeCl₃ containing H₂O a significant fraction of the ferric ions (around 50%) can be in the form of [FeCl₄][−] complexes [1, 2], this fraction being larger than that observed with methanol [3] or ethanol [4]. In order to further elucidate the role of water in isopropanol solutions of FeCl₃ we have used Optical Absorption (OA), EPR and Mössbauer techniques. The solutions have been prepared from Merck anhydrous FeCl₃ and Merck isopropanol containing 0.02 M H₂O nominally.

Figure 1 shows that in the OA spectrum of a 2.5 · 10^{−4} M solution of FeCl₃ in isopropanol the three charge transfer peaks at 360, 310 and 237 nm characteristic of [FeCl₄][−] complexes [4, 5] become more and more prominent upon water addition. It must be noted that the relative intensity of the peaks at 360 and 310 nm [4, 5] is affected by the presence of other ferric species in the solution [1] whose nature is clarified later.

Qualitative agreement with the results above is obtained by EPR measurements at room temperature which are sensitive only to [FeCl₄][−] complexes [2, 6]. The measured intensities indicate about twice the concentration of [FeCl₄][−] in a 0.018 M FeCl₃ solution containing 0.2 M H₂O compared to the initial one with 0.02 M H₂O. If all ferric species are converted to [FeCl₄][−] by adding enough HCl the signal intensity again about doubles.

Figure 2 shows that on addition of KOH the OA spectrum of a 2.5 · 10^{−4} M solution of FeCl₃ in isopropanol evolves in a similar way as that shown in Figure 1. On further addition of H₂O or KOH the [FeCl₄][−] complexes

are destroyed [1]; they have practically disappeared when [H₂O] ≈ 1 M or [KOH] ≈ 2 · 10^{−3} M.

Our experimental results can be understood as follows. In pure isopropanol the solvation is mainly governed by the disproportionation reaction [3, 6, 7]



(S = solvent) which implies the presence of at least three different ferric species in the solution. Though similar but more involved processes have been postulated [3, 7] leading to the formation of other octahedral species (such as [FeClS₅]²⁺) we shall ignore them for simplicity.

As [FeCl₄][−] is rather stable we suppose that the introduction of water mostly affects the octahedral species [FeCl₂S₄]⁺ leading to the formation of new ferric species which should likely involve OH[−] ions rather than H₂O molecules in view of the similarities of the results shown in Figs. 1 and 2. The increase in the [FeCl₄][−] signal can then be explained by Cl[−] ions resulting from the destruction of [FeCl₂S₄]⁺ and being trapped by FeCl₃ to give [FeCl₄][−].

As regards the nature of ferric species containing OH[−] ions as ligands in isopropanol solutions with 0.2 M H₂O recent magnetic measurements [2] suggest the formation of ferric dimers.

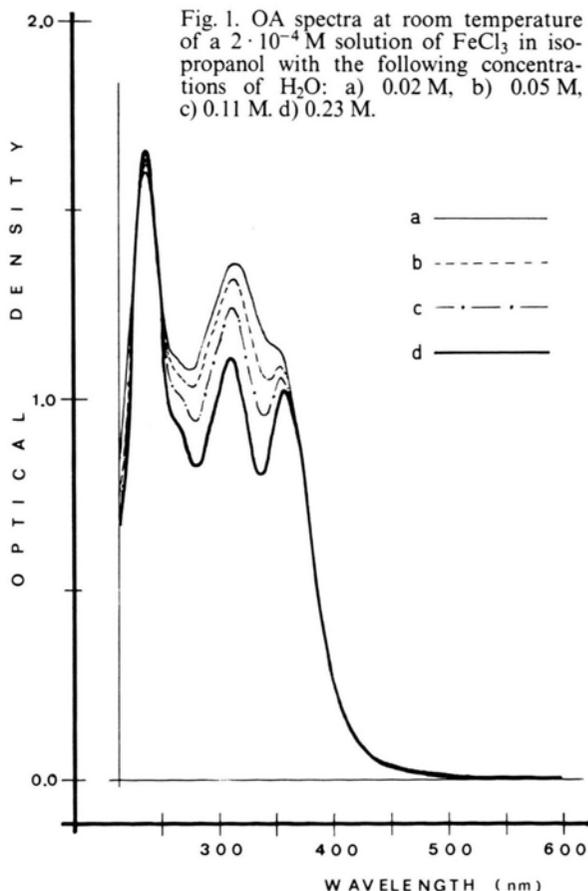


Fig. 1. OA spectra at room temperature of a 2 · 10^{−4} M solution of FeCl₃ in isopropanol with the following concentrations of H₂O: a) 0.02 M, b) 0.05 M, c) 0.11 M, d) 0.23 M.

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In order to check this we have looked at the Mössbauer spectrum of a 0.10 M solution of FeCl_3 in isopropanol containing 0.2 M H_2O , frozen at 77 K. This is because ferric dimers exhibit a rather narrow Mössbauer spectrum arising from a short spin-spin relaxation time which avoids the development of magnetic hyperfine structure but allows the existence of quadrupolar doublets produced by the axial symmetry of the dimer [8].

In isopropanol solutions containing *only* $[\text{FeCl}_4]^-$ complexes, the Mössbauer spectrum at 77 K is a very broad band covering the ± 10 mm/sec range. The spectrum shown in Fig. 3 consisting of a doublet centered at $\delta = +0.48$ mm/sec (referred to metallic iron) with a separation

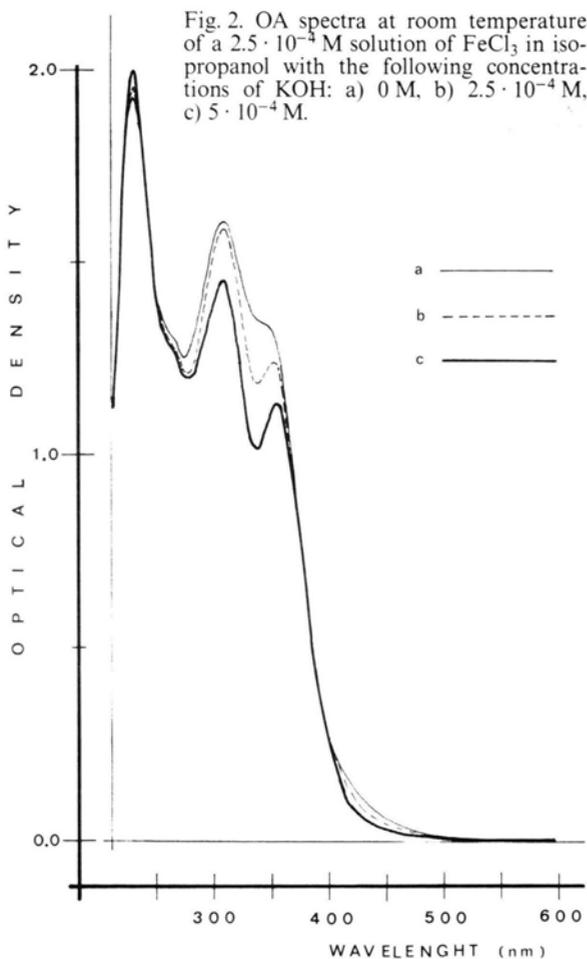


Fig. 2. OA spectra at room temperature of a $2.5 \cdot 10^{-4}$ M solution of FeCl_3 in isopropanol with the following concentrations of KOH: a) 0 M, b) $2.5 \cdot 10^{-4}$ M, c) $5 \cdot 10^{-4}$ M.

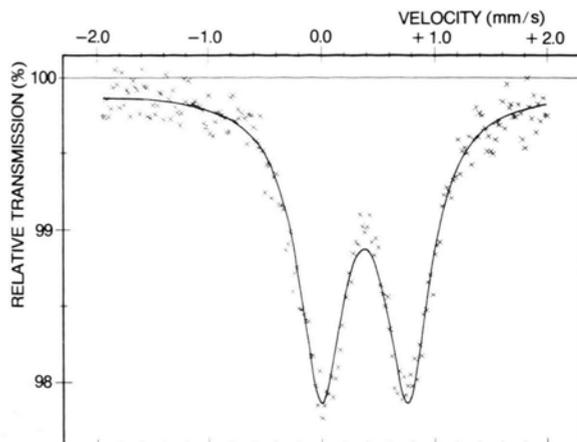


Fig. 3. Mössbauer spectrum of a 0.10 M solution of FeCl_3 in isopropanol containing 0.2 M of water frozen at 77 K. Note the velocity scale of the drawing. No other Mössbauer peaks were observed in the full range of velocities, $+10$ to -10 mm/sec.

$\Delta E = 0.77$ mm/sec between the peaks can reasonably be ascribed to the presence of ferric dimers with two $\text{Fe}^{3+}-\text{OH}^-$ bridges in the solution. In fact similar Mössbauer spectra have been observed in aqueous solutions of ferric salts with a pH near 2.3 and have been assigned to the presence of ferric dimers involving two $\text{Fe}^{3+}-\text{OH}^-$ bridges [8].

In conclusion, the present work supports the idea that the enhancement of the $[\text{FeCl}_4]^-$ concentration in FeCl_3 solutions in isopropanol on addition of water is related to a significant hydrolysis of water and the instability of $[\text{FeCl}_2\text{S}_4]^-$. This instability could be explained by the position of the OH group in isopropanol making the Fe-S bond weaker than methanol or ethanol.

Similar results have recently been reported [9] for solutions of BeCl_2 in acetonitrile. However in this case the enhancement of the $[\text{BeCl}_4]^-$ NMR signal upon addition of water has not been ascribed to water hydrolysis [9].

The formation of ferric dimers involving OH^- ions in isopropanol solutions of FeCl_3 upon addition of water indicates that these solutions can become acid, which could be related with their efficiency for etching [1]. Further work along this line is currently in progress.

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