The Influence of Water Addition on Solutions of $FeCl_3$ in Isopropanol

F. Rodríguez and M. Moreno
Departamento de Optica y Estructura de la Materia,
Facultad de Ciencias, Universidad de Santander,
Santander, Spain

J. C. Fayet
Laboratoire de Spectroscopie de Solide, ERA 682,
Faculté des Sciences du Mans,
72017 Le Mans Cedex, France

F. Varret
Laboratoire de Spectrométrie Mössbauer, ERA 682,
Faculté des Sciences du Mans,
72017 Le Mans Cedex, France

Z. Naturforsch. **38 a,** 701 – 702 (1983);
received December 29, 1982

By means of Optical Absorption, EPR and Mössbauer techniques it is demonstrated that the addition of small amounts of water to solutions of $FeCl_3$ in isopropanol enhances the concentration of $[FeCl_4]^-$ complexes, this addition leading also to the formation of ferric dimers involving two Fe^{3+}–OH^- bridges. An explanation of this fact based on the disproportionation of $FeCl_3$ and water hydrolysis is reported.

Recently it has been established that in isopropanol solutions of $FeCl_3$ containing H_2O a significant fraction of the ferric ions (around 50%) can be in the form of $[FeCl_4]^-$ 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 $FeCl_3$ we have used Optical Absorption (OA), EPR and Mössbauer techniques. The solutions have been prepared from Merck anhydrous $FeCl_3$ and Merck isopropanol containing 0.02 M H_2O nominally.

Figure 1 shows that in the OA spectrum of a $2.5 \cdot 10^{-4}$ M solution of $FeCl_3$ in isopropanol the three charge transfer peaks at 360, 310 and 237 nm characteristic of $[FeCl_4]^-$ 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 $[FeCl_4]^-$ complexes [2, 6]. The measured intensities indicate about twice the concentration of $[FeCl_4]^-$ in a 0.018 M $FeCl_3$ solution containing 0.2 M H_2O compared to the initial one with 0.02 M H_2O. If all ferric species are converted to $[FeCl_4]^-$ by adding enough HCl the signal intensity again about doubles.

Figure 2 shows that on addition of KOH the OA spectrum of a $2.5 \cdot 10^{-4}$ M solution of $FeCl_3$ in isopropanol evolves in a similar way as that shown in Figure 1. On further addition of H_2O or KOH the $[FeCl_4]^-$ complexes are destroyed [1]; they have practically disappeared when $[H_2O] \simeq 1$ M or $[KOH] \simeq 2 \cdot 10^{-3}$ M.

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

$$2\,FeCl_3 + 4\,S \rightleftharpoons [FeCl_2S_4]^+ + [FeCl_4]^- \qquad (1)$$

(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 $[FeClS_5]^{2+}$) we shall ignore them for simplicity.

As $[FeCl_4]^-$ is rather stable we suppose that the introduction of water mostly affects the octahedral species $[FeCl_2S_4]^+$ leading to the formation of new ferric species which should likely involve OH^- ions rather than H_2O molecules in view of the similarities of the results shown in Figs. 1 and 2. The increase in the $[FeCl_4]^-$ signal can then be explained by Cl^- ions resulting from the destruction of $[FeCl_2S_4]^+$ and being trapped by $FeCl_3$ to give $[FeCl_4]^-$.

As regards the nature of ferric species containing OH^- ions as ligands in isopropanol solutions with 0.2 M H_2O recent magnetic measurements [2] suggest the formation of ferric dimers.

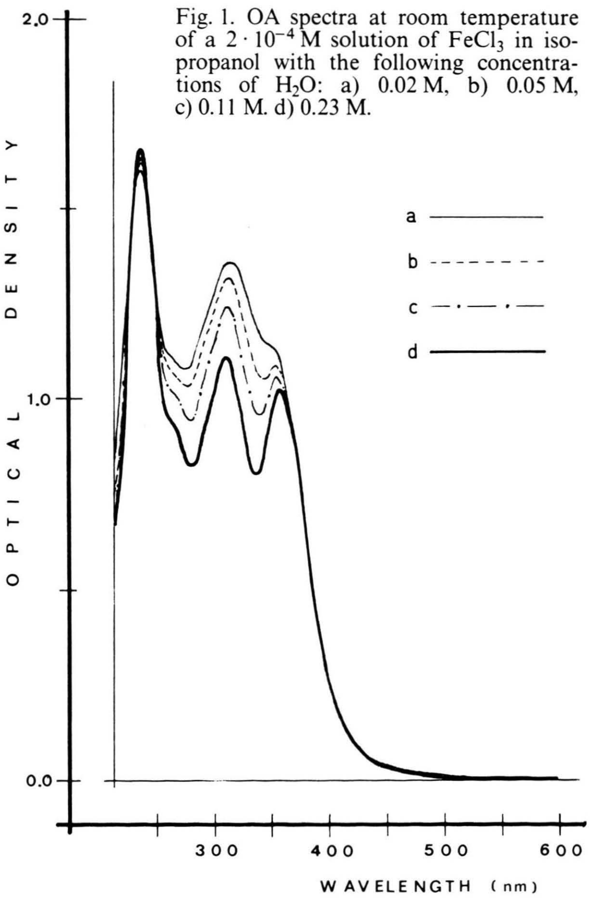

Fig. 1. OA spectra at room temperature of a $2 \cdot 10^{-4}$ M solution of $FeCl_3$ in isopropanol with the following concentrations of H_2O: a) 0.02 M, b) 0.05 M, c) 0.11 M. d) 0.23 M.

Reprint requests to Dr. M. Moreno, Departamento de Optica y Estructura de la Materia, Facultad de Ciencias, Universidad de Santander, Santander/Spanien.

0340-4811 / 83 / 0600-0701 $ 01.3 0/0. – Please order a reprint rather than making your own copy.

Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung") beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

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* $[FeCl_4]^-$ 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 $\Delta E = 0.77$ mm/sec between the peaks can reasonably be ascribed to the presence of ferric dimers with two $Fe^{3+}-OH^-$ 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 $Fe^{3+}-OH^-$ bridges [8].

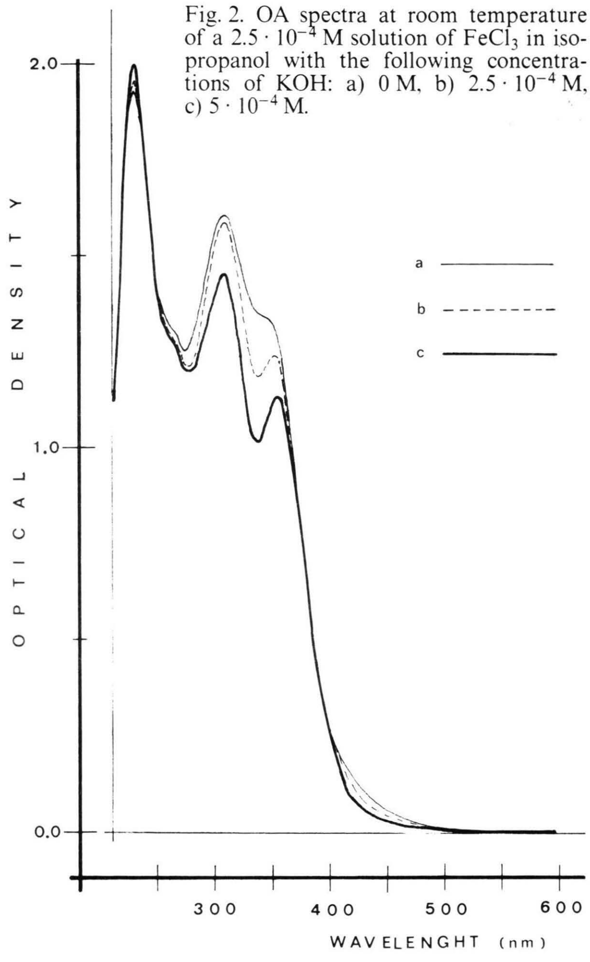

Fig. 2. OA spectra at room temperature of a $2.5 \cdot 10^{-4}$ M solution of $FeCl_3$ in isopropanol with the following concentrations of KOH: a) 0 M, b) $2.5 \cdot 10^{-4}$ M, c) $5 \cdot 10^{-4}$ M.

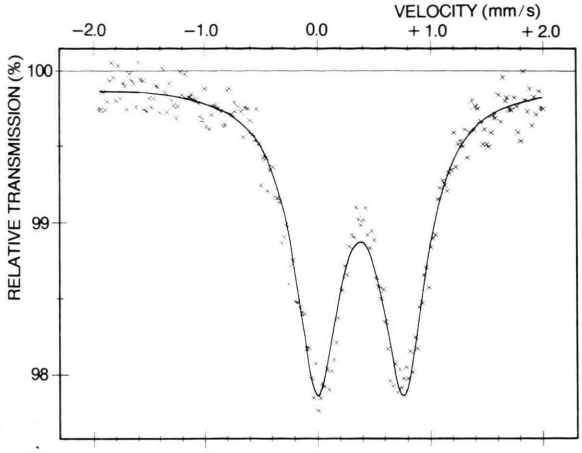

Fig. 3. Mössbauer spectrum of a 0.10 M solution of $FeCl_3$ in isopropanol containing 0.2 M of water frozen at 77 K. Note the velocity scale of the drawing. No other Mössbauer peaks were observed in the full range of velocities, +10 to −10 mm/sec.

In conclusion, the present work supports the idea that the enhancement of the $[FeCl_4]^-$ concentration in $FeCl_3$ solutions in isopropanol on addition of water is related to a significant hydrolysis of water and the instability of $[FeCl_2S_4]^+$. 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 $[BeCl_4]^-$ 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.

Acknowledgements

Useful correspondance with Prof. C. K. Jørgensen, Prof. A. Vertes and Dr. F. Wehrli is gratefully acknowledged. Two of us (F. Rodríguez and M. Moreno) would like to thank to the "Comisión Asesora para la Investigación Científica y Técnica" for financial support.

[1] F. Rodríguez and M. Moreno, Z. Naturforsch. **35a**, 1419 (1980).
[2] F. Rodríguez and M. Moreno, unpublished results.
[3] R. S. Drago, D. Hart, and R. L. Carlson, J. Amer. Chem. Soc. **87**, 1900 (1965).
[4] G. Brealey and N. Uri, J. Chem. Phys. **20**, 257 (1952).
[5] B. D. Bird and P. Day, J. Chem. Phys. **49**, 392 (1968).
[6] T. B. Swanson and V. W. Laurie, J. Phys. Chem. **69**, 244 (1965).
[7] A. Vertes, J. Nagy-Czako, and K. Burger, J. Phys. Chem. **82**, 13 (1978).
[8] A. Vertes, L. Korecz, and K. Burger, Mössbauer Spectroscopy, Elsevier, Amsterdam 1979, p. 295.
[9] F. W. Wehrli and S. L. Wehrli, J. Magn. Reson. **47**, 151 (1982).