The Inhibitor Agent in Subramanian's Dislocation Etchant for KCl

F. Rodriguez and M. Moreno
Departamento de Física Fundamental, Facultad
de Ciencias, Universidad de Santander, Santander, Spain

Z. Naturforsch **35a**, 1419–1420 (1980);
received September 26, 1980

An optical absorption study of Subramanian's solution shows that a $[FeCl_4]^-$ complex is formed. This complex is mainly responsible for the possibility of observing dislocations in KCl using this solution as etchant.

A useful solution (10 mgr of Fe Cl_3 in 25 cc. of isopropanol plus two drops of water) for observing dislocations in KCl by the etching method has recently been reported by Subramanian [1].

The ability of solutions of this kind to selectively etch is attributed to an inhibitor effect [2, 3, 4], but little is known about the nature of the inhibitor agent. It should be kept in mind that transition-metal salts, when dissolved, may give rise to several systems, the nature of which is often difficult to determine [5, 6]. In this paper the Optical Absorption (O. A) spectrum of Subramanian's (S) solution is studied in order to elucidate the nature of the inhibitor agent in the case of KCl. The O. A. spectra were recorded using Beckman Acta CII and Cary 17.D spectrophotometers, both working in double beam mode.

We have first verified that pits formed on the KCl faces by means of fresh S-solutions are actually related to dislocations, using matched cleaved faces [3] as well as by observing the variation of the pit density under annealing and plastic deformation processes. In the latter case a relation $n = 10^{8.9}\,\varepsilon$ between the plastic deformation, ε, and the dislocation density, n, was found, as observed similarly for LiF [4].

We have noticed that the addition of water to the fresh solution inhibits progressively its ability for etching. In a 2.5 10^{-3} M solution of $FeCl_3$, when the concentration of the added water is about 2 M, the etching power of the solution disappears almost instantaneously, while lower concentrations of water induce the same phenomenon though more slowly.

In Fig. 1 (I) the O. A. spectrum of the S-solution is shown. The intensity of the three peaks at 360, 310 and 240 nm was found to increase at the same rate as the $FeCl_3$ concentration. Figure 1 also reflects the variation of the O. A. spectrum of the fresh solution due to the addition of successive amounts of water whose main effect can be seen to be the progressive destruction of the three peaks. Moreover Fig. 1 clearly exhibits an isosbestic point at $\lambda = 410$ nm pointing out the existence of a chem-

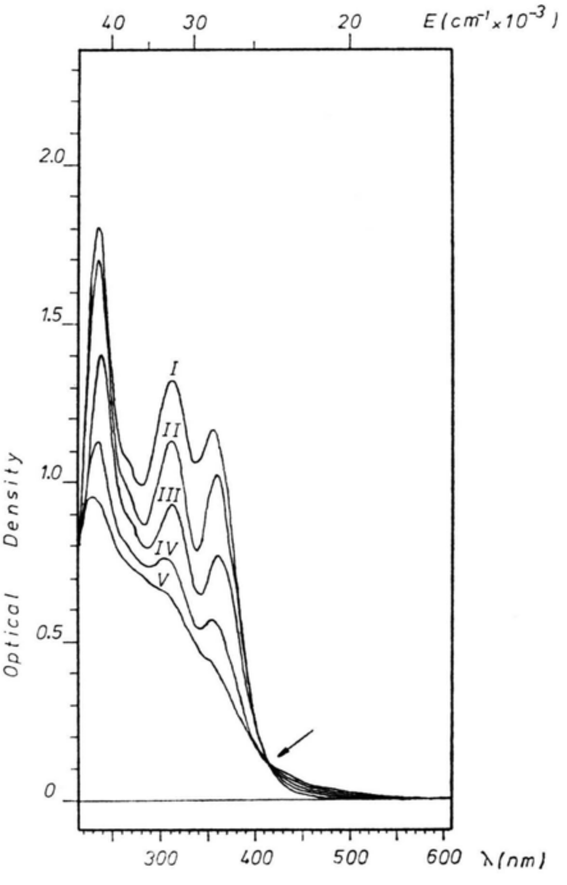

Fig. 1. Optical absorption spectra of Cl_3Fe in isopropanol ($2.2 \cdot 10^{-4}$ M). The variation of the optical absorption spectrum is obtained by the addition of H_2O. The water concentration in the solution is for (I) 0.02 M (proper of solvent); (II) 0.25 M; (III) 0.50 M; (IV) 0.75 M and (V) 1.00 M. The arrow indicates the position of the isosbestic point.

Reprint requests to Dr. M. Moreno, Departamento de Física Fundamental, Facultad de Ciencias, Universidad de Santander, Santander, Spain.

0340-4811 / 80 / 1200-1419 $ 01.00/0. — Please order a reprint rather than making your own copy.

ical reaction induced by the addition of water. Comparing these results with the loss of etching power induced by water it is reasonable to assume that the three peaks in Fig. 1 are actually associated with the system responsible for the inhibitor effect of the S-solution.

The intensity and the position of the O. A. bands suggests that such a system could be a complex of Fe^{3+}, the three bands of Fig. 1 being related to charge transfer processes. However, the O. A. results indicate that in such a complex Fe^{3+} is not bonded directly to solvent molecules through the OH group. In fact, assuming a spin-pairing correction $8/3\ D \simeq 1.3$ eV for Fe^{3+} [7], Jørgensen's equation [8] predicts that the position of the first π-charge transfer transition would be around 4,30 eV for a ferric complex with oxygen as ligand, which is about 0.8 eV larger than the position of the first charge-transfer peak observed in the present case. In this way the first π-charge transfer band for $Fe^{3+}:MgO$ and $Fe^{3+}:Al_2O_3$ is found at 4.35 and 4.78 eV, respectively [9, 10].

By contrast the position of the first peak agrees well with that expected for a ferric complex with chlorine as ligand in view of the lower value of the optical electronegativity of chlorine (3.0 for chlorine; 3.2 for oxygen). Furthermore, the position and the relative intensities of the three peaks, as well as the position of the shoulder shown in Fig. 1, are essentially the same as those found for organic salts of $[FeCl_4]^-$ in dichloromethane [11]. From all this it can reasonably be concluded that $[FeCl_4]^-$ is formed by solving Cl_3Fe in isopropanol, such a complex being the inhibitor agent for the S-solution.

It is clear that, if $[FeCl_4]^-$ is formed from $FeCl_3$, not all the ferric ions introduced into the solution can give rise to $[FeCl_4]^-$ complexes. In this way accepting the molar extinction coefficients reported by Day and Jørgensen [11] for $[FeCl_4]^-$ we have estimated from Fig. 1 (I) that no more of 75% of ferric ions are present as $[FeCl_4]^-$ complexes in the solution. Moreover, this figure should be considered as an upper limit due to the likely contribution of the other ferric systems to the background of Figure 1.

A parallel ESR investigation has been started for a further insight into the S-solution. The first experiments support the present interpretation.

Acknowledgements

We would like to thank to the "Departamento de Optica y Estructura de la Materia (U. A. M.)" for the facilities given for using the Cary 17-D spectrophotometer.

[1] K. N. Subramanian, J. Amer. Cer. Soc. **59**, 456 (1976).
[2] J. J. Gilman, W. G. Johnston, and G. W. Sears, J. Appl. Phys. **29**, 747 (1958).
[3] S. Amelinckx, The Direct Observation of Dislocations, Academic Press, New York **1964**.
[4] J. J. Gilman and W. G. Johnston, Solid State Physics **13**, 147 (1962).
[5] A. Vertes, J. Nagy-Czako, and K. Burger, J. Phys. Chem. **82**, 13 (1978).
[6] D. R. Sandstrom, J. Chem. Phys. **71**, 2381 (1979).
[7] A. G. Coutts and P. Day, Phys. Stat. Sol. (b) **88**, 767 (1978).
[8] C. K. Jørgensen, Progr. Inorg. Chem. **12**, 101 (1970).
[9] F. A. Modine, E. Sonder, and R. A. Weeks, J. Appl. Phys. **48**, 8 (1977).
[10] H. H. Tippins, Phys. Rev. **B1**, 126 (1970).
[11] P. Day and C. D. K. Jørgensen, J. Chem. Soc. **1964**, 6226.