Surface Enhanced Raman Spectroscopic (SERS) and electrochemical study of some hydroxamic acid derivatives as perspective inhibitors of copper corrosion in neutral solutions

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Recently some benzohydroxamic acid (BHA) derivatives were reported as a new class of copper corrosion inhibitors [1]. The experimental characterisation was done using the quartz-microbalance method. It was demonstrated that the chemical nature of the substitute and its benzene ring position have a critical role for the grade of the inhibiting action. In this work we continue the investigation on the applicability of various benzohydroxamic acids as possible corrosion inhibitors by studying their effect on the metal's electrochemical behavior. Besides, we aim to provide some insight about the mechanism of the copper-organic molecule interaction. The clarification of the later is especially important in the light of the fact that the inhibition process usually comprises an adsorption as one of its most important steps.

The characterisation of the copper electrochemical behavior was done by a ±10 mV linear polarization around the steady state potential in solutions of 0.005M (*p*-chloro-, *p*-methoxy-, and *p*-nitro-) BHA+0.5M NaCl at 25°C. The results are shown in Fig. 1. According to them, instead of inhibiting, the presence of BHA slightly accelerates the corrosion rate of copper.

The problem about the bonding coordination of the investigated molecules on the metal surface was addressed by means of Surface Enhanced Raman Spectroscopy. SERS is actively developed and used as one out of a limited number of techniques able to investigate adsorption processes *in-situ* [2,3]. It proves that all of the studied benzohydroxamic acids in the form of their 0.005M aqueous solutions, with and without the presence of chloride and sulphate ions, provide a strong SERS effect on a copper substrate. The spectra for *p*-nitro BHA are presented in Fig.2. The experimental data show that the group frequencies belonging to the benzene ring, such as, for example, 1598, 1504, 1452, 1397, 1212, and 1184 cm^{-1} are significantly enhanced, but not shifted from their positions in the crystal compounds for all the investigated molecules. This fact suggests that the benzene group is not involved in the adsorption process and its plane is perpendicular to the copper surface. In this case, the bonding interaction is most probably realized through the hydroxamic and *p*-substituting functional groups. In the particular case of the *p*-nitro BHA the asymmetric stretch of the nitro group at 1351 cm^{-1} has a varying intensity, and thus, it could be assumed that *p*-nitro BHA adsorbs via both its hydroxamic and nitro groups.

The joint application of electrochemical and SERS methods shows that a significant interaction exists between the copper surface and the BHA. It leads, however, to accelerated instead of lowered corrosion. Currently, the reason for this behavior is investigated.

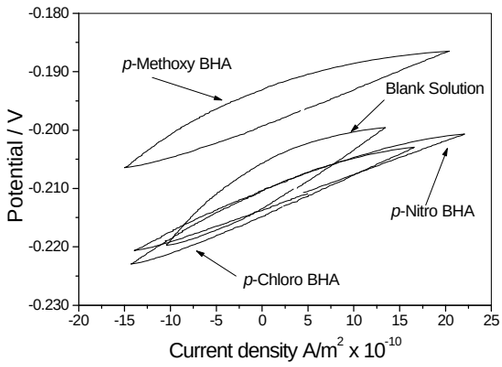

Fig.1 Polarization curves of Cu in BHA+NaCl solutions. Polarization rate=0.1 mV/sec.

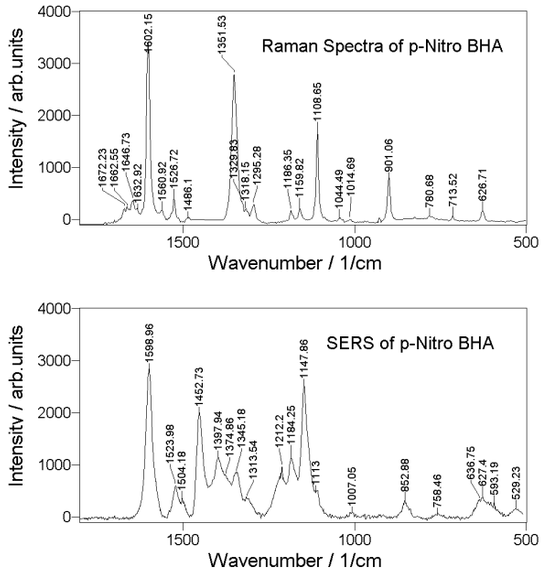

Fig.2 Raman (up) and SERS (down) results for *p*-Nitro BHA.

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