Reversibility of the L-Cysteine/L-Cystine redox couple at physiological pH on graphite electrodes modified with coenzyme B_{12} and vitamin B_{12}

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Vitamin B_{12}, when confined on electrode surfaces exhibits catalytic activity in several electron transfer reactions including the reduction of molecular oxygen (1,2), of alkyl halides (3-6) and in the oxidation of L-cysteine, Glutathione, (7,8) hydrazine (9-11) and in the oxidation and reduction of nitric oxide (12). In this fashion it behaves similarly to inorganic complexes like cobalt phthalocyanines and porphyrins, which are well known to catalyze the reactions described above. In this work we investigate the catalytic activity of B_{12} co-enzyme and vitamin B_{12}, which have similar structures, for the redox chemistry of the L-cysteine/L-cystine system in a wide pH range. The main difference between these two molecules is the presence of an adenosyl group in the coenzyme, that is bound to the cobalt center. Graphite modified with vitamin B_{12} exhibit two well-defined reversible redox processes corresponding to the Co(II)/Co(I) and Co(III)/Co(II) transitions. In contrast, a graphite electrode freshly modified with B_{12} coenzyme shows no redox processes and this is attributed to the adenosyl group that forms a C-Co bond. This bond is broken upon the electroreduction of the coenzyme, when the modified electrode is polarized at potentials below -1.1 V vs SCE. Following this reduction, the cyclic voltammograms of the electrode modified with the co-enzyme are similar to those obtained with vitamin B_{12}
We have compared the behavior of graphite electrodes modified with both vitamin B_{12} and B_{12} coenzyme for the oxidation of L-cysteine at different pH. At pH values higher than 7.4, the oxidation waves are quite irreversible on both systems. However, at pH 7.4, a well-defined oxidation peak is observed which is assigned to the oxidation of L-cysteine to L-cystine and a reduction wave is observed during the reverse scan. The separation between the oxidation wave and the reduction wave is minimum at pH 7.4. For pH values lower than 7.4 the process again becomes very irreversible in both systems.

Fig.1 compares the catalytic response of graphite modified with both B_{12} coenzyme and vitamin B_{12}. It is clear in the Figure that the electrode modified with the coenzyme is more active than that modified with the vitamin B_{12}. This result may appear surprising since the coenzyme, upon its reduction, is probably structurally identical to vitamin B_{12}. The difference in the reactivity may then be explained by a preferred orientation of the supported coenzyme for approach of the thiol to the presumed active cobalt site. Also, it should be noted that an electrode modified with B_{12} coenzyme that has not been reduced at -1.1 V is inactive for L-cysteine oxidation. This demonstrates that the Co center is the active site for the reaction since in the case of the coenzyme, it is blocked by the adenosyl group.

Tafel plots constructed from data obtained with a graphite rotating disk modified with B_{12} coenzyme show straight lines with slopes close to 0.12 V/decade indicating that a first-one electron transfer is rate determining.

The higher reversibility observed at pH 7.4 for the oxidation of L-cysteine has not been observed previously with electrodes modified with cobalt phthalocyanines.

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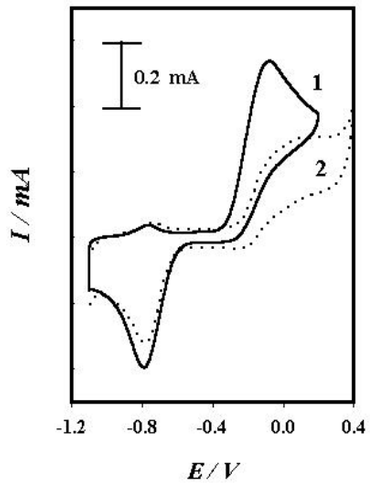

Fig.1. Comparison of the response of B_{12} coenzyme (1) and vitamin B_{12} (2) at pH 7.4 for the oxidation of L-cysteine.