

The elimination of the hyperfine structure in the electron paramagnetic resonance spectrum of the PS-manganese (II) system could result from a reduction in the electron spin lattice relaxation time, or to dipolar or exchange effects. The absence of hyperfine structure in the spectra of the sodium oleate-manganese (II) system, together with the observation that the electron paramagnetic resonance line-width (~ 300 gauss) is less than the overall hyperfine splitting (~ 500 gauss for manganese (II) ions), makes it fairly certain that here exchange narrowing is involved³.

The model would lead one to expect, by virtue of the proximity of the metal cations to one another, that dipolar and exchange effects might occur for the water in oil conformation, and it is suggested that the spectra shown in Fig. 1a and b demonstrate this. It would also predict the disappearance of these effects in the presence of ATP as is observed in Fig. 2a for PS, and also would account for the reappearance of the hyperfine structure in the manganese (II)-oleate system on addition of ATP.

The spin lattice relaxation times (T_1) of the water protons in the water-in-oil complex will depend on whether the binding sites of the PS for the added metal ion are interior or exterior sites⁴. The formation of a ternary complex with ATP is expected to modify the T_1 's of the water protons. Using a broad line NMR spectrometer, and measuring T_1 by the spin echo technique, a drop in T_1 from 338.6 msec for the sodium oleate-manganese (II) emulsion to 25.1 msec on the addition of ATP was observed. No attempt to degass the sample was made in this experiment. No such clear cut effect on T_1 was observed, however, with PS, but further studies are in progress.

It is concluded that electron paramagnetic resonance observations substantiate the water in oil colloid conformation suggested¹, and also the view that it is disrupted by ATP. They also support the view that this concept may also apply to oleate-manganese (II) systems. The nuclear magnetic resonance measurements and the narrowness of the electron paramagnetic resonance line in the oleate-manganese (II) suggest that it has a somewhat tighter packing than the PS-manganese (II) system.

As has already been suggested¹, these effects of bivalent metal cation on the colloidal properties of PS may well be relevant to certain membrane processes.

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Estimation of Electrochemical Activity of Carbon using a Paste Electrode

THE carbon paste electrode recommended by Adams^{1,2} for polarographic oxidation of various organic substances is also suitable for estimating the activity of carbon samples with respect to the reduction of oxygen and hydrogen peroxide.

The paste used for filling the electrode was a mixture of powdered spectral graphite with grains smaller than 60μ (SU 103, Elektrokarbon Topolčany) and of the active carbon (10-30 weight per cent according to the activity of the sample) bound together with paraffin oil (25-35 weight per cent). Polarographic curves of current against voltage were recorded using the voltage scan 0.8 volts per min. The electrolysed solutions were either

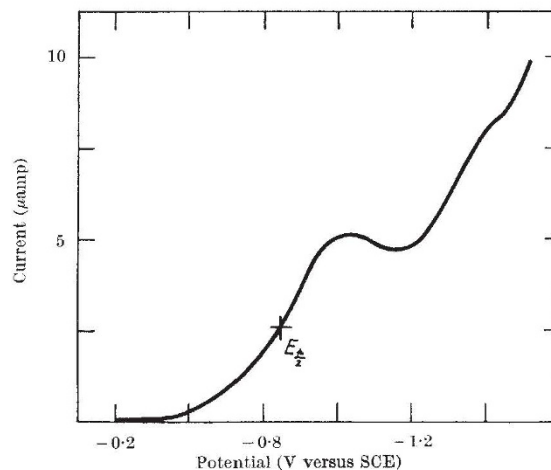


Fig. 1. Reduction of oxygen and hydrogen peroxide at carbon paste electrode in 0.1 M sodium acetate buffer solution pH 4.7 (saturated with air oxygen).

0.1 M sodium acetate buffer solution of pH = 4.7 or 0.1 M potassium hydroxide; they were saturated with air oxygen.

The measure of the activity of the carbon is the decrease of the overvoltage of oxygen reduction compared with the value obtained with a standard paste electrode prepared from powdered graphite and paraffin oil alone. The decrease of the overvoltage was determined by the change of the electrode potential corresponding to the half of the current peak (Fig. 1). If the active carbon is catalytically active with respect to decomposition of hydrogen peroxide, the current peak of oxygen increases while that of hydrogen peroxide decreases.

Experience with samples of more than 30 kinds of active carbon has shown that the carbon activity increases with increasing surface per unit weight and with the degree of granulation. Various catalysts which increase the catalytic activity of carbon, especially those containing silver, have been examined. In some cases the decomposition of hydrogen peroxide is so rapid that the oxygen reduction could be observed only in the more positive current peak.

The results obtained with the paste electrode coincided with the estimation of carbon samples for the oxygen electrode of the fuel cell based on polarization curves of porous electrodes³. The addition of active carbon to a paste electrode also decreases the overvoltage of reduction of cobalt (II) and nickel (II); anodic peaks of ionization of the deposits of these metals could also be observed at an electrode potential 0.4-0.5 volts more positive than that of the cathodic process.

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Occurrence of a Double Azeotrope in the Binary System Hexafluorobenzene + Benzene

RECENTLY there has been much interest in the thermodynamic properties of binary mixtures of aromatic fluorocarbons and aromatic hydrocarbons. Experimental studies of the phase diagrams^{1,2}, excess volumes³ and excess enthalpies⁴ of mixing can be interpreted by assuming that intermolecular complexing exists between the