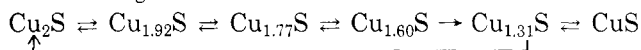


Figure 4. Current-voltage curve of: (a) $\text{Cu}_{1.92}\text{S}$ (0.25 mg), (b) $\text{Cu}_{1.77}\text{S}$ (0.25 mg), and (c) $\text{Cu}_{1.31}\text{S}$ (0.25 mg) included in a carbon paste electrode; H_2SO_4 1 M (40 mg); carbon (50 mg); scan rate: $10^{-4} \text{ V}\cdot\text{s}^{-1}$

current densities occurs via the formation of different intermediate compounds. The oxidation may be explained by the following scheme:



Some of these sulfides are known as minerals: $\text{Cu}_{1.92}\text{S}$ (djurleite), $\text{Cu}_{1.77}\text{S}$ (digenite), $\text{Cu}_{1.60}\text{S}$ (anilite); Koch and McIntyre have recently prepared a new phase ($\text{Cu}_{1.40}\text{S}$ – $\text{Cu}_{1.35}\text{S}$) by anodic oxidation of thin films of cuprous sulfide evaporated onto glass (8).

Considering the difference in experimental technique and method of preparation of the sulfides, the agreement between our results ($\text{Cu}_{1.31}\text{S}$) and the work of Koch and McIntyre (8) is reasonable.

We have also shown that, under certain conditions, carbon paste electrodes can be very useful for the study of sparingly soluble electroactive compounds such as minerals (sulfides or oxides). The preparation of such electrodes does not require specialized equipment, no pretreatment is needed. They give reproducible results with a precision of 5% and can be employed for quantitative and qualitative analyses of insoluble species.

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RECEIVED for review November 30, 1978. Accepted March 12, 1979.

Complications in the Interpretation of Pulse Polarographic Data on Complexation of Heavy Metals with Natural Polyelectrolytes

Sir: At present, the interest for characterization of the interactions between heavy metal ions and natural polyelectrolytes by electrochemical techniques is growing strongly. Recent work by a. o. Stevenson (1, 2) and Buffle et al. (3, 4) indicates that both the static method of potentiometry using suitable ion-selective electrodes and dynamic methods involving different types of pulse polarography can provide useful information on the natural systems. In a study of copper(II)/fulvic acids solutions, Bresnahan et al. (5) compared results obtained from experiments with a solid state copper ion-selective electrode with differential pulse polarographic results. However, the two methods did not seem to yield consistent data. The authors (5) concluded that differential pulse polarography (DPP) is an "unreliable" method with respect to the system studied, and they put all their confidence in the results originating from potentiometric measurements.

The question now arises whether it is justified to use DPP as it was often used, that is: based on the supposition that DPP peak current is directly proportional to free metal ion concentration, the complexes with natural polyelectrolytes being assumed to be fully inert. Working with natural systems, at least three types of possibly complicating phenomena deserve our attention: (i) formation of fully labile complexes, (ii) kinetic effects due to limited rates of association/dissociation of the metal/polyelectrolyte complex, and (iii) adsorption of the polyelectrolyte on the mercury electrode, thereby inducing adsorption of the metal as well. A test for the presence of these effects is preferentially carried out using normal pulse polarography (NPP) with varying pulse duration. It has been described how kinetic effects influence the shapes of pulse polarograms and the corresponding relationships between limiting current and pulse duration (6, 7).

Experimentally obtained NP polarograms (see Figure 1) indicate that the Cd^{2+} /fulvic acids system is not affected by kinetic effects when experiments are carried out on the usual time scale for pulse polarography (typically 1–100 ms). However, the shape of the NP polarogram and more specifically its dependence on the effective pulse duration unambiguously shows the characteristics of reactant adsorption. As far as the shape of the polarogram is concerned, the characteristics of induced metal ion adsorption have been indicated by Barker and Bolzan (8) and Flanagan et al. (9). Experimental demonstrations were limited to systems with inorganic ligands like bromide and iodide, although Wolff and Nürnberg (10) observed analogous phenomena in NP polarograms of aromatic nitro compounds.

In fact, it is not very surprising that strong effects of induced reactant adsorption are exhibited in pulse polarograms of systems with natural polyelectrolytes. It is well known that these polyelectrolytes are adsorbed on the Hg electrode in quite a wide potential range (11). Normal pulse polarograms can therefore be expected to show the corresponding characteristics which are (i) a maximum at the beginning of the wave, the height of the maximum being strongly dependent on the pulse duration; (ii) decreased limiting currents, resulting from the depletion effect connected with the adsorption of the reactant; and (iii) a marked dependence of the shape of the wave on the initial potential chosen, in accordance with the potential dependence of the adsorption. The data given in Figures 1 and 2 are meant to illustrate that these qualitative characteristics are easily recognized in the normal pulse polarogram.

A rigorous analysis, taking into quantitative account the effects of induced adsorption, seems to be feasible (9, 12). In the case of normal pulse polarography, the vital part of this

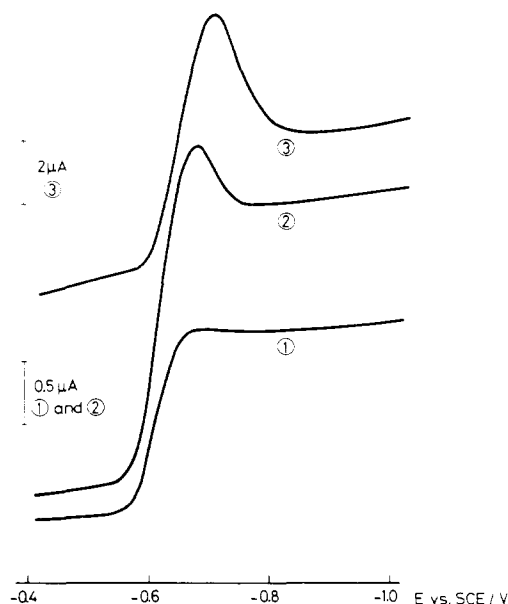


Figure 1. Normal pulse polarograms for an aqueous solution of $\text{Cd}(\text{NO}_3)_2$: 2×10^{-4} M; fulvic acids: 57.3×10^{-3} g TOC/L; KNO_3 : 10^{-1} M. The pH was 7.6. Initial potential: 0.0 V vs. SCE, droptime 2 s, mercury flow rate 1.56 mg/s, effective pulse duration t_p : 168 ms (1), 47.8 ms (2), 10.0 ms (3)

analysis could be the quantitative inspection of the relationship between limiting current and pulse duration. A first approach to this relationship has been put forward (13) and results in estimations of surface excess of reactant, surface concentration of reactant, and effective diffusion coefficients. For the data shown in Figures 1 and 2, it follows that the adsorption coefficient is of the order of 10^{-2} cm which does not seem to be an unreasonable value for the system considered. Furthermore, it should be noted that the slope of the $i_l - t_p^{-1/2}$ plot as given in Figure 2 is much lower than expected, mainly because of the depletion effect mentioned. A more extensive treatment of these matters is in preparation.

In differential pulse polarography, the situation is much less obvious. In a great many cases the shape of the DPP wave does not cause suspicion because there is *only* an enlargement of the peak. Following the calculations by Flanagan et al. (14), it can be concluded that peak currents obtained for the copper/fulvic acids system (5) easily exceed the values obtained in the absence of adsorption by a factor of 5 or more! This is the first reason why the interpretation of DPP data should not start from the assumption that peak currents are directly related to the bulk concentration of the hydrated metal ion. Especially in titrations, where the metal/polyelectrolyte ratio is varied, dramatic misinterpretations can result. A second point which must be mentioned in this context is the consideration of the lability characteristics of the metal/polyelectrolyte complex(es). There are clear indications (3,13) that these complexes are labile, which means that a lowering of DPP peak currents is due only to a decrease of the average diffusion coefficient. Thus the measured DPP peak current should not be interpreted as indicative for the "free" metal concentration. Information on this parameter should be obtained from a careful consideration of peak potentials. The best comparison with solid-state ion-selective electrode experiments can be made if potentiometric measurements are also carried out with an amalgam electrode. In that way both static and dynamic information are obtained from one and the same electrode; subsequently the static data

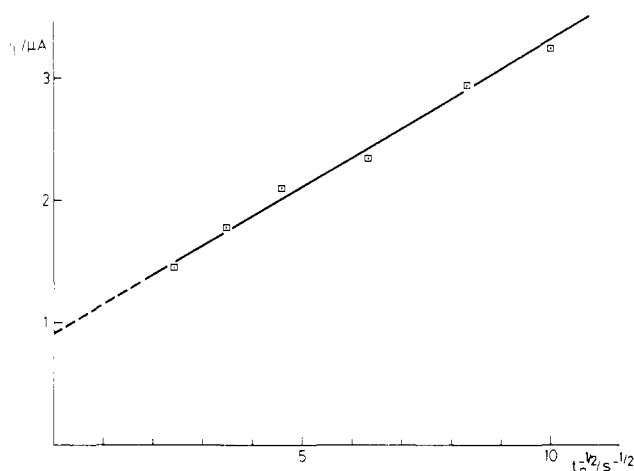


Figure 2. Plot of NPP limiting current against $t_p^{-1/2}$ for the solution as described in Figure 1

can be compared with the static data obtained with a different electrode.

In conclusion it can be emphasized that in case of induced reactant adsorption, normal pulse polarograms show some characteristic features whereas differential pulse polarograms are often in no way indicative of the complications involved. It is therefore justified to preferentially use normal pulse polarography at least in first orientational stages of investigations on systems where the effects could occur. If necessary, model experiments should be carried out in order to define the electrochemical properties of the system. The most effective approach is to measure normal pulse polarograms as a function of pulse duration. In the author's opinion, this should become a routine procedure as it also reveals information on the lability characteristics of the metal complexes involved (7).

ACKNOWLEDGMENT

The author is grateful to Jacques Buffle of the University of Geneva, Switzerland, who sent him the manuscripts indicated by References 3 and 4 prior to publication.

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RECEIVED for review January 3, 1979. Accepted March 12, 1979.