FIG. 3. Photographs of (a) Object used for recording, (b) Reconstructed image obtained when the anayser is in perfectly crossed position, (c) Reconstructed image obtained when the analyser is slightly rotated. In this case the image possesses contrast variation which is the reverse of the image given under, (b) for reasons given in the text.
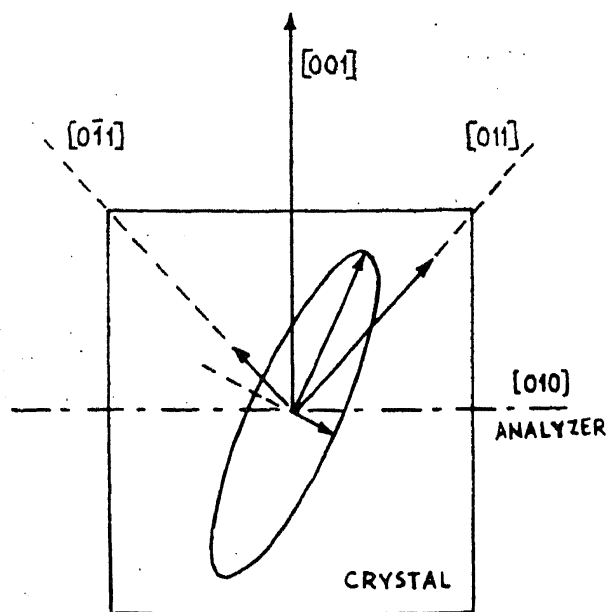

FIG. 4. Schematic diagram for explaining the phenomenon of Contrast Reversal of the retrieved image.

this rotation of the analyser should be clock-wise if the centers are preferentially aligned along [011] and anti-clockwise if they are aligned along [0$\bar{1}$1]. The observed new phenomenon of contrast reversal can be explained as follows with the aid of the schematic diagram for the analysis of light transmitted by the analyser shown in Fig. 4. When the analyser is in perfectly crossed position it absorbs all the background light which retains the state of polarisation of the light incident on the crystal; whereas the light passing through the crystal in the regions of preferential alignment comes out elliptically polarised and hence it is transmitted by the analyser. Therefore the retrieved image will possess the same contrast variation as the object used for recording. When the analyser is rotated by about two degrees in a suitable direction, depending on the direction of alignment of centers as already mentioned, it is brought into the direction of minor axis of the ellipse wherein the light transmitted by the analyser is least (for elliptically polarised light) but at the same time more background light is transmitted by the analyser and hence the effect of contrast reversal can be observed.

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ON THE SHAPES OF THE COMPLEX PLANE POLAROGRAMS

G. A. BHAT

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012

ABSTRACT

Complex plane polarograms have been obtained for Co(III)-EDTA, Cu(II)-EDTA, Cu(II)-CyDTA and m-dinitrobenzene systems. The shape of complex plane polarograms for each system is different in some respects from that of other systems. Various factors affecting the shapes, viz., frequency of measurement, reversibility of electrode processes and weak adsorption, have been discussed in detail.

INTRODUCTION

THE name "Complex Plane Polarograms" has come into existance in recent years after the work of Sluyters[1] on impedance analyses of electrochemical reactions. According to this method impedance data are plotted on a complex impedance plane having the quadrature component as Y axis and in-phase component as X axis with variation in one of the variables

viz., d.c. potential, frequency and concentration. Impedance plane plots with d.c. potential as a variable parameter is called complex plane polarograms. The main advantage of this method of analysis is that the double layer capacitance, kinetic parameters and adsorption kinetics can be calculated simultaneously even when the depolariser is present either in free state or adsorbed.

Extensive application of this method has been found in recent years for the study of electrode kinetics having frequency or concentration as variable parameters[1]. Information with regard to d.c. potential as a variable, *i.e.*, complex plane polarograms and particularly about their various shapes, seems to be lacking. This communication attempts to throw some light on the shapes of the complex plane polarograms and the various factors that influence the shapes from our study as well as on the work of others.
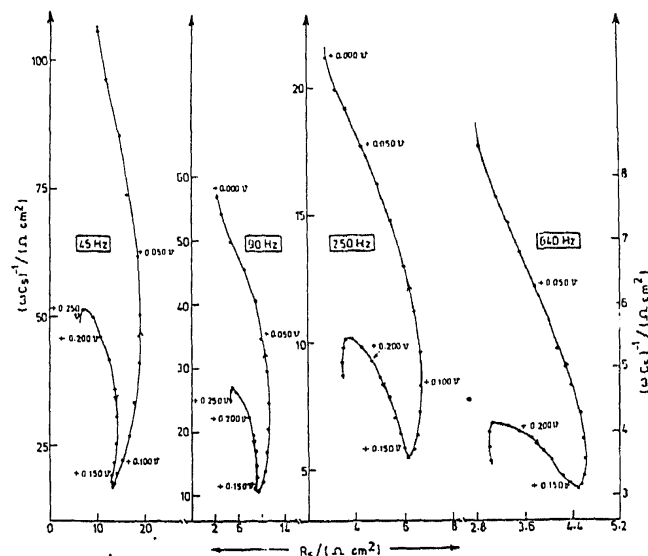
EXPERIMENTAL

The cell impedance is obtained either by means of phase sensitive a.c. polarograph or an a.c. impedance bridge. From the measured cell impedance, the real and imaginary components are evaluated. The details of the calculation are given in reference 1. The systems selected for illustrating the objective are Co(III)-EDTA complex[2], Cu(II)-CyDTA complex[2] (CyDTA- trans-1,2 cyclohexanediamine tetraacetic acid), Cu(II)-EDTA complex[2] and *m*-dinitrobenzene[3]. The details of experimental procedure and conditions are given elsewhere[2]. The frequency range of measurements is from 22 Hz to 2000 Hz and reference to ' higher or lower frequencies ' in this text is with respect to this frequency domain.

RESULTS AND DISCUSSION

Figure 1 represents the complex plane polarograms for the reduction of Co(III)-EDTA complex at dropping mercury electrode at different frequencies. This is a reversible electrochemical reduction (k_s = 0·28 cm. sec^{-1})[2]. Essentially all the polarograms start from the base line,* deviate from it when the electrochemical reaction begins, transverse to a minimum in the direction of concentration variation plot, rise again covering the path above the concentration variation plots and finally return to the base line. Measurements at several frequencies show that these polarograms have a crest-like shape. At lower frequencies the polarograms are steep and well defined and they become broad at higher frequencies. This change in shape at higher frequencies is due to the poor response of the system

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* Base line is formed by the locus of the points on impedance plane in absence of the depolarizer[4]. Contribution to cell impedance in such cases comes from the cell resistance and double layer capacitance.

to the rapid oscillations of a.c. signal at higher cycles, rendering the system more irreversible. The small width of the complex plane polarograms at lower frequencies is due to the variation in the double layer capacitance as well as the phase angle with d.c. potential[5].

FIG. 1. Complex plane polarograms of Co(III)-EDTA complex. Co-EDTA—1·0 mM; acetate buffer—0·1 M; NaNO—0·9 M; Polyoxyethylene laury ether—3·0 μM.

FIG. 2. Complex plane polarograms of Cu(II)-EDTA complex. Cu-EDTA—2·0mM; acetate buffer—0·1 M; KNO$_3$—0·4 M; polyoxyethylene lauryl ether (LEO)—3·0 μM.

Figure 2 represents the complex plane polarograms of Cu(II)-EDTA complex which belong to the quasi-reversible case. In this case, all the complex plane polarograms are broad at all measured frequencies and the peaks are not so well defined even at lower frequencies. The peaks are not observed at higher frequencies, the diminishing of peaks being gradual from lower frequencies to higher frequencies. In addition, portion of the polarograms before and after the peak potential lie in a position different from that

in Fig. 1. Consequently, the shapes are like loops (the arrow shows the applied d.c. potential increasing cathodically). The peak potentials of the individual polarograms shift to more cathodic region with increase in measured frequency.

Complex plane polarograms of Cu(II)-CyDTA complex, the reduction of which is very much irreversible, are given in Fig. 3. In this system different types of behaviour have been observed at different frequency range. At low frequencies the shapes of the polarograms are similar to those of Cu-EDTA complex and at high frequencies (frequency > 110 Hz) the polarograms are like Co-EDTA system. At intermediate frequencies the loop-shaped polarograms found at low frequencies gradually shrink and finally get converted into crest-like shape. At 600 Hz and above the polarograms are almost straight lines rising vertically upwards. The straight line pattern indicates that the system being irreversible is incapable of responding to a.c. signal of high frequencies and the contribution to the total cell impedance comes from the double layer capacitance and the cell resistance.

m-Dinitrobenzene exhibits two d.c. polarographic waves at about pH 4 and above and the corresponding complex plane polarograms[3] for this system are given in Fig. 4. There are two interesting aspects to be noted here, the first being the difference in shapes of the two polarograms at a given pH and the second is the effect of pH on their shapes. At any pH values the complex plane polarograms corresponding to first d.c. main wave have crest-like shape whereas the second set of polarograms corresponding to second d.c. main wave have loop-like shape. At low pH values the shape is that of an irreversible system and at high pH values, the shape is that of a reversible system. The reason for the above type of behaviour is given elsewhere[3].

From the above observations with regard to the complex plane polarograms of the above four typical systems, the following conclusions can be drawn on the shapes of complex plane polarograms. The influencing factors that affect the shapes are usually the reversible-irreversible nature, the frequency of measurements and the nature of the electrode reaction, *viz.*, simple electron transfer or electron transfer coupled with adsorption, side reactions, etc. The influence of frequency in the increasing order is to broaden the complex plane polarograms as evidenced from Figs. 1, 2 and 3. Also, it could be seen that the steepness of the polarograms reduces with the increase in the measured frequency. This is due to the fact that at high frequencies the response of the system to the alternating signal becomes poorer and consequently the variation of the impedance with potential near the peak is much smaller. The dependance of the shapes

on reversibility of the system can be understood from the first three figures where the reversibility of the system is in the decreasing order[2]. It is obvious that at a given frequency the steep and well defined polarograms are exhibited by reversible systems and polarograms tend to broaden and become less steep as the reversibility of the systems decreases.
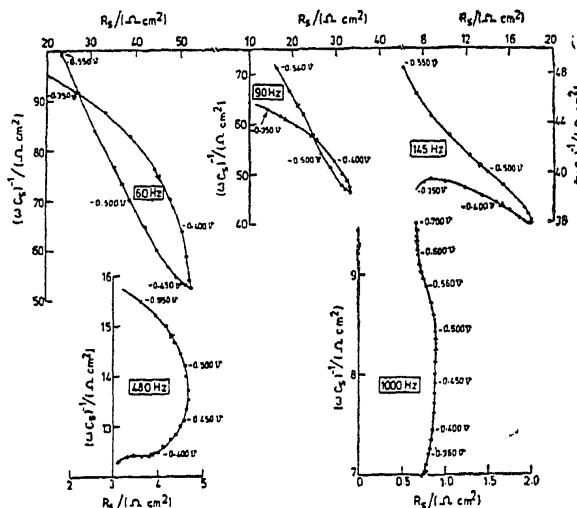

FIG. 3. Complex plane polarograms of Cu(II)-CyDTA complex. Cu-CyDTA—2·0 mM; acetate buffer—0·1 M; KNO₃—0·4 M; LEO—3·0 μM.
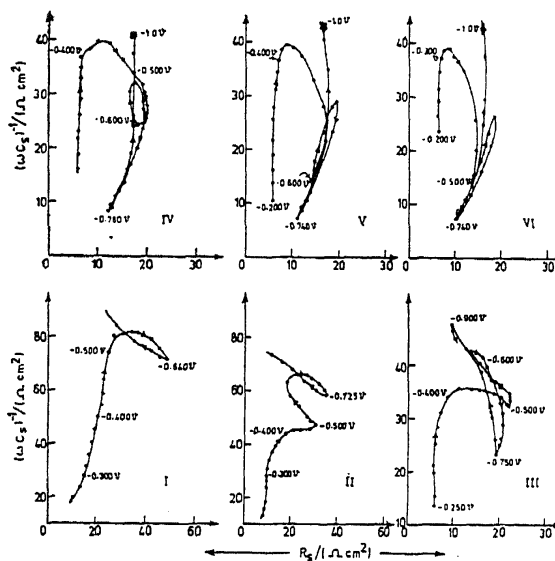

FIG. 4. Complex plane polarograms of *m*-dinitrobenzene at 400 Hz. All polarograms refer to the solutions containing 1·0 mM of *m*-dinitrobenzene, 0·8 M KCl, 45% ethanol, 0·005% methyl cellulose, and either citrate buffer or phosphate buffer of appropriate pH. (I) pH–4·1, (II) pH–6·0, (III) pH–7·1 (IV) pH–8·2, (V) pH–9·0, (VI) pH–12.

Even weak adsorption of reactants, products or intermediates seem to have profound effects on the shapes of the complex plane polarograms. Normally the complex plane polarograms are crest-like when the electrode processes involve only electron transfer. Such examples are found with electrochemical reduction of Co-EDTA complex (Fig. 1) and of zinc ion

reduction[6] in KCl. If there is a weak adsorption of any one of the reactants, products or intermediates, the shapes are found to be loop-like[7] (Figs. 2 and 3). However, d.c. and a.c. polarograms of these systems are S-shaped and bell-shaped respectively and these shapes do not indicate the presence of weak adsorption. The effect of weak adsorption is very much evident from Fig. 3, where the loop-like shape at lower frequencies changes to crest-like shape at higher frequencies. The reason for such a change is that there exists an adsorption-desorption equilibrium at low frequencies and with increase in frequency such an equilibrium is not possible for this system owing to the rapid oscillations of a.c. signal compared to the rates of adsorption and desorption. Consequently, the effect due to adsorption on complex plane polarograms is not felt at higher frequencies. The above conclusions are valid for the reduction of *m*-dinitrobenzene also. The effect of the increase in pH is to reduce the role of protonation in the reduction process and at higher pH, the reduction of unprotonated species occurs which is more reversible.

In general, it can be said that the shapes of the complex plane polarograms are greately influenced by the frequency of measurements, reversible-irreversible nature of the systems and other phenomina like adsorption, side reactions, etc. Many a time, from the appearance of the complex plane polarograms, a qualitative idea about the behaviour of the system at electrode interface can be conceived.

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THE PHYLOGENETIC AND ECOLOGICAL IMPLICATIONS OF THE HAEMOLYMPH PROTEINS IN CRUSTACEA

M. A. ALIKHAN AND S. AKHTAR*

Laurentian University, Sudbury, Ontario, Canada P3E 2C6

ABSTRACT

Haemolymph protein patterns have been studied in three crustacean species: the terrestrial herbivorous woodlouse, *Porcellio laevis* (Isopoda), the terrestrial carnivorous pillbug, *Armadillidium vulgare* (Isopoda) and the commonest southern Ontario crayfish, *Orconectes propinquus* (Decapoda).

The studies revealed that the haemolymph protein patterns were more or less identical in *Armadillidium* and *Orconectes*. When the differences due to age, physiological status, sex, diet and season are eliminated, the residual differences, it is postulated, are due to the phylogenetic status of the species.

THE study of naturally occurring haemolymph compounds provides valuable information in the understanding of relationships of one animal to another of the same or different species. Most of the investigations of the crustacean haemolymph proteins have been concerned with the changes occurring in the single species because of its developmental or moulting cycle[1], diet[3], sex[1] and season[6]. Recently, Jazdzewski *et al*[8] reported that, haemolymph protein constituents may be influenced in a species by its habitat. The present investigations, which entails a comparison of the haemo-

lymph protein concentration of three crustacean species should provide valuable information in understanding some aspects of the evolution of these species.

Two isopod species, *Procellio laevis* and *Armadillidium vulgare*, and one decapod species, *Orconectes propinquus*, were used in the study. Haemolymph proteins were separated by polyacrylamide gel electrophoresis method of Davis[5], as modified by Alikhan and Lysenko[1].

Whenever required, the peaks of individual proteins were measured from densitometric tracings of the polyacrylamide gels by means of a polar planimeter. These units were converted to the percentage of the total number of the units for the entire protein pattern,

* Present Address: David Kaunda Technical School, Private Bag 13X, Ridgeway, Lausaka, Zambia.