ADVANCES IN ALTERNATING CURRENT POLAROGRAPHY AND TENSAMMETRY

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INTRODUCTION

Three years have passed since our monograph[1] was published and I felt that it might be timely to review some of the work published since that time. It is obviously impossible to review a vigorously developing field within the framework of a single lecture and I will have to limit myself to reviewing a relatively small number of papers on selected topics. In doing so I am acutely conscious of the unavoidable inadequacy and arbitrariness of my choice, a choice dictated by personal preference for certain topics and very frequently also by the availability of the necessary information. Much of the work in our field is published in journals not easily accessible and in languages not generally understood. I would like to apologize to the readers and the authors whose work has not received the attention it no doubt deserved in this review.

A.C. POLAROGRAPHY

Theory

Hung and Smith[2] have published an extensive study on the theory of a.c. polarographic processes with two-step charge transfer, i.e. processes of the type

$$O + n_1 e \rightleftarrows Y + n_2 e \rightleftarrows R$$

both for the reversible and the quasi-reversible case. They were particularly concerned with those electrode reactions where the two charge transfer steps proceed within the same potential range. The main aspects studied were: (a) the derivation of the appropriate equations; (b) predictions of the equations for the fundamental and second harmonic a.c. waves; (c) conditions under which diffusion-controlled two-step and single-step mechanisms are distinguishable; (d) the relative sensitivity of the d.c. and a.c. methods in distinguishing differences between the two-step and the single-step mechanisms; (e) methods of calculating standard potentials for the two steps from a.c. polarographic data.

One of the many interesting results is that in order to obtain two separate peaks the difference in the reversible half-step potentials of the two consecutive electrode processes must be at least $71 \cdot 2/n$ mV. With regard to the relative merits of the a.c. and d.c. methods for distinguishing differences between reversible diffusion-controlled two-step and single-step mechanisms, the authors have come to the conclusion that a.c. polarography has little

more to offer than the classical method; the real value of the a.c. method is seen in the study of quasi-reversible systems where charge-transfer kinetics play a part in the overall electrode process.

When dealing with the quasi-reversible case, Hung and Smith[2] use a method of derivation similar to that first proposed by Matsuda[3] for the analysis of the single-step quasi-reversible electrode reaction. The equation obtained for the a.c. polarographic wave is then considered with respect to: (a) the nature of the experimental results predicted for the quasi-reversible two-step process, especially with regard to the interpretation of the mechanism of the underlying electrode reaction; (b) the limiting conditions under which a quasi-reversible two-step process can still be distinguished from a single-step process; (c) the magnitudes of charge transfer rates necessary for a reversible electrode reaction.

One of the conclusions reached is that even at the lowest frequencies used in a.c. polarography ($\sim$10 c/s) and despite large values of the hetero-geneous rate constant ($\sim$10·0 cm/sec), the system does not exhibit reversible behaviour. Theory also predicts that in quasi-reversible two-step processes, at frequencies of about 8·000 c/s, resolved peaks are obtained when the half-step potentials are as little as 50 mV apart; by contrast, the minimum difference required for the resolution of a reversible two-step process (when $n_1 = n_2 = 1$) is 71 mV.

Space does not permit further discussion of the most interesting results. For all details reference should be made to the original papers, especially with regard to such topics as the influence of the difference in half-step potentials of the consecutive processes, of the charge transfer coefficients, of the rate constants, of quasi-reversible d.c. processes, distinctions between single-step and two-step mechanisms, and the evaluation of rate parameters from experimental data.

Another and to my mind very promising approach to the derivation of kinetic parameters from a.c. polarography is that by Bauer[4] who pioneered the use of second-harmonic measurements for this type of investigation. The advantage of this procedure is that the observations can be directly interpreted on the basis of the faradaic process taking place, without having to take into account double-layer effects.

Recently Bauer and Foo[5] have published an improved theoretical treat-ment and given details of the experimental technique used by them. The essential outcome of their treatment is that the ratio of the peak heights, $(i_p)_1/(i_p)_2$, (cf. *Figure 1*) is, *inter alia*, a function of the transfer coefficient, a, and of the heterogeneous rate constant, k. From the variation of the peak height ratio with frequency a and k can be inferred. It is of particular importance that the ratio of the peak heights is used in the calculations and not their absolute values; because of this the effects of a wide number of factors affecting the absolute value of the alternating current are com-pensated. The values for k and a obtained by Bauer and Foo are in very good agreement with those obtained by other authors using different methods. For details of the calculations I must refer the reader to the original publica-tion.

Other interesting results of Bauer and Foo's analysis are that the second-harmonic polarogram obtained with fast systems at low frequencies of the
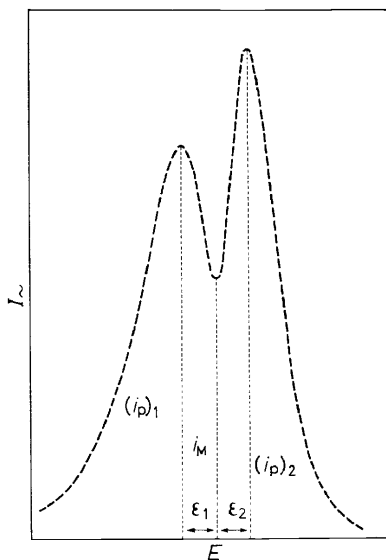
Figure 1. Second-harmonic a.c. polarogram.

alternating current is symmetrical about the d.c. polarographic half-step potential, that the second-harmonic peaks are separated by $68/n$ mV, and that the phase angle changes by $180°$ at the half-step potential. Such behaviour has been found with certain fast electrochemical reactions at low frequencies by Smith[6] and by Kooijman and Sluyters[7]. The phase angle change of $180°$ at the half-step potential has been observed by Breyer *et al.*[8] The authors foresee as useful applications of their method reversibility tests of electrode processes (symmetrical peaks separated by $68/n$ mV), the estimation of kinetic parameters, and the possibility of developing more sensitive analytical methods with experimental set-ups simpler than those currently in use.

Kambara and Kunimatsu[9] in a very interesting paper have shown how a.c. polarography can be used to derive the activation energy of diffusion and for the testing of the reversibility of an electrode process. Their treatment is based on that introduced by Kambara and Ishii[10] who were able to show that the rate constant of the electrode process can be derived from the a.c. wave-height (Y_{AC}). Now, Kambara and Kunimatsu[9] showed theoretically and experimentally that the temperature coefficient of the a.c. peak-height decreases with increasing reversibility and that the activation energy of diffusion (Q_D) can be calculated from

$$\log(Y_{AC}\ T) = \text{const.} - Q_D/4·606\ RT$$

Hence the value of Q_D can be inferred from the slope of $\log(Y_{AC}\ T)$ against $1/T$; furthermore, it is possible to deduce whether or not the electrode process is reversible by considering the deviation of the slope from that

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predicted theoretically. The experimental results obtained with Zn(II) in 1 M potassium chloride, bromide, and iodide solutions, respectively, satisfied the theory within the temperature range, 10°–60 °C.

Suzuki et al.[11] have investigated how the a.c. wave-height changes with height of the mercury column and have come to the conclusion that the result depends on the reversibility of the electrode process. In reversible and quasi-reversible systems, such as Pb(II) in potassium chloride or oxygen in alkaline solutions, an increase in the height of the mercury column causes a slight decrease of the wave height, whilst in irreversible systems, such as Co(II) in lithium chloride, the wave height increases. When investigating the wave height vs. drop-time relationship, the authors found that in the irreversible reduction of Cr(III) to Cr(II) the results were in agreement with the Matsuda[3] equation; however, in the reversible reduction of Cd(II) the results did not agree with the theoretical predictions.

Electrode processes

An interesting contribution to the use of a.c. polarography for the study of the influence of surface films on electrode processes is that of Britz and Bauer[12].

A number of years ago we found[13] that the addition of cyclohexanol to a solution of *m*-nitrophenol produced characteristic changes in the a.c. polarogram: the d.c. step split into two, whilst the height of the a.c. wave increased (*Figure 2*). Britz and Bauer were able to elucidate the nature of the underlying electrode process, showing that a fast one-electron reaction
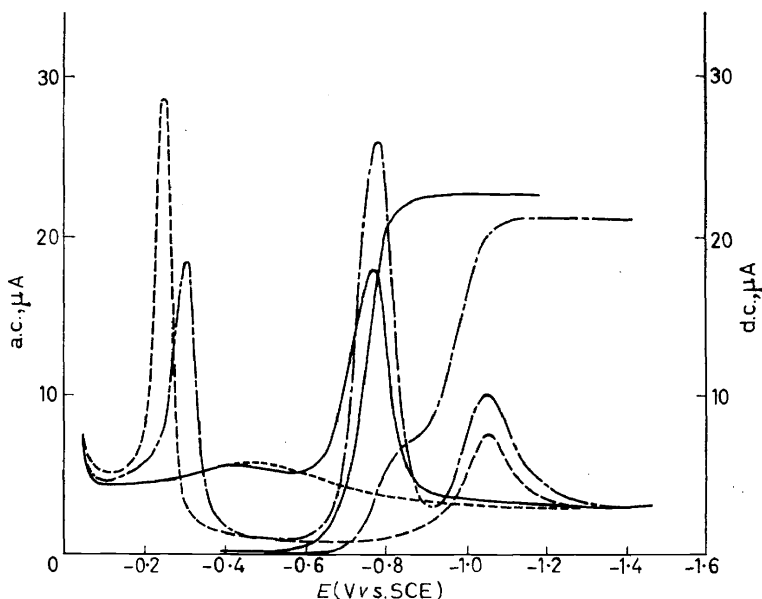
Figure 2. A.C. curves of 10⁻³M *m*-nitrophenol (——), of 3% *t*-butanol (----), and of their mixture (—·—·); Briton–Robinson buffer 0·2 M, KNO₃ 0·8 M, pH 12 (after Britz and Bauer[12]).

occurs which is followed by a regenerative dismutation and the addition of further electrons. The increase in wave height in the presence of surface films is explained by assuming that the second step in the reduction makes the first step less reversible; if surfactants impede the second step, uncoupling it from the first, the latter will become apparently more reversible.

To prove their assumption Britz and Bauer added increasing amounts of various alcohols to the nitrophenol solution; they observed that the wave height at first increased but decreased again at still higher concentrations of alcohol. In accordance with their hypothesis alcohols, even at relatively low concentrations, decrease the rate of disproportionation; above a certain alcohol concentration the addition of further electrons is completely impeded and the reaction is shifted to the desorption potential of the alcohol; finally, at still larger concentrations, alcohols decreased also the rate of the first electron transfer step.

Measurements of wave heights at progressively lower frequencies (down to 5 c/s) showed that the a.c. wave observed is in fact a composite one made up of a tensammetric contribution, due to the desorption of the alcohol, and a faradaic contribution, due to the addition of electrons to the species produced in the first electron-transfer step.

The paper also contains a number of interesting phase-angle measurements; the phase-angle which at first, quite abnormally, diminished with increasing frequency, became normal after sufficient alcohol had been added (*Figure 3*). This behaviour further supports the authors' view of the mechanism underlying the electrode reaction.

An interesting finding has been made by Tanaka and Tamamushi[14] when they examined the polarographic behaviour of In(III) in 1 M potassium
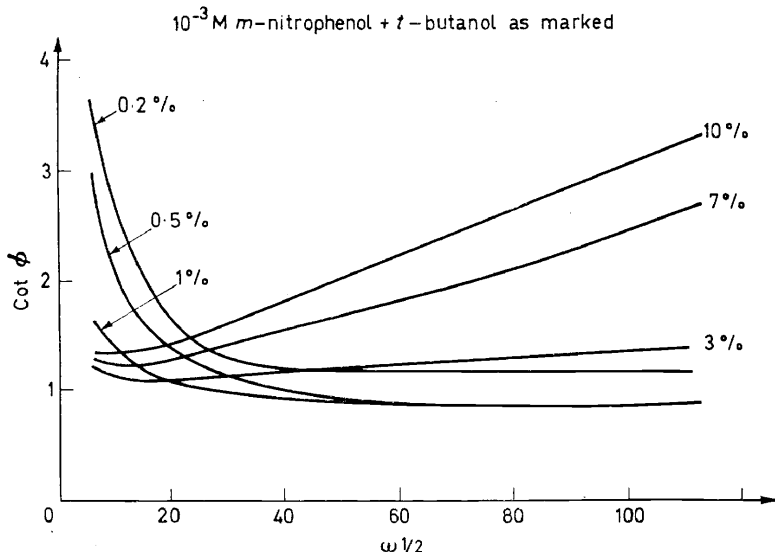

Figure 3. Phase-angle *vs.* frequency relationship obtained with 10^{-3} M *m*-nitrophenol in the presence of varying concentrations of *t*-butanol (after Britz and Bauer[12]).

thiocyanate solution; the d.c. polarogram showed, within a certain negative potential range (*vs.* a mercury-pool electrode), an anomalous decrease in the cathodic current, whilst, in the same potential range, the a.c. polarogram revealed a negative admittance. Recently Tamamushi and Matsuda[15] reported that the systems In(III) in 1 M sodium bromide and Ni(II) in 1 M potassium thiocyanate also show a negative admittance; a.c. polarograms with a negative admittance have also been reported by Shirai[16] for the Ni(II) thiocyanate and the Cu(II) ammonium nitrate systems. It must be stressed that this abnormal behaviour is seen only at relatively low frequencies (< 200 c/s). To explain this finding Tanaka and Tamamushi assume the existence of a negative polarization resistance due to a decrease in the rate constant of the electrochemical process with increasing negative polarization of the electrode; they also assume that the reduction process consists of two simultaneous reactions in parallel, one going on at that part of the electrode which is covered with adsorbed thiocyanate ions, and the other proceeding at the uncovered electrode surface.

Recently, Tamamushi[17] has been able to show that the electrode systems mentioned can be used to produce undamped oscillating currents. These "electrochemical oscillators", as he calls them, represent entirely new electrochemical systems which should prove of great theoretical and practical importance in electrochemistry.

Instrumentation and methodology

The use of higher harmonics of the a.c. polarographic current for analytical purposes, as first proposed by Bauer[4], has been most ingeniously developed by Neeb[18]. He introduced a new a.c. polarographic technique which he named "double tone" or "tone-difference" polarography. The procedure
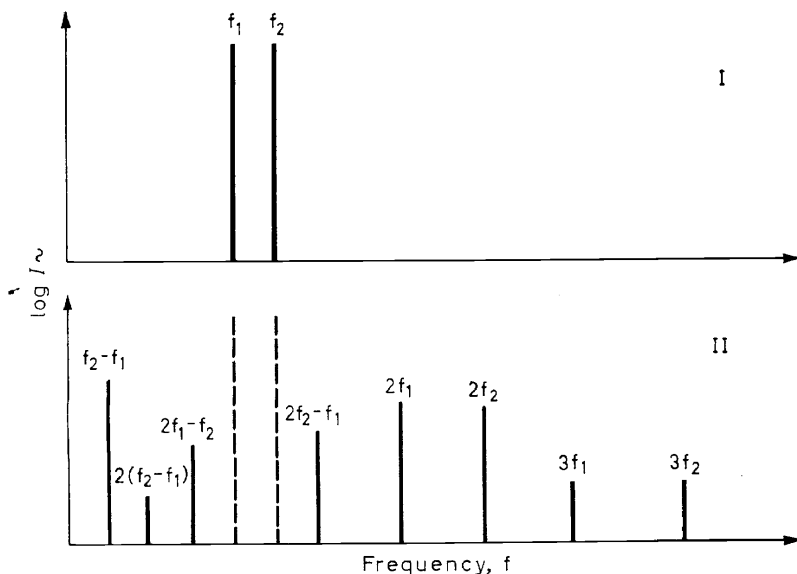

Figure 4. Frequency spectrum obtained by double-tone polarography (after Neeb[18]).

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consists in superposing onto the direct potential applied to the electrode two alternating potentials of usually the same amplitude and a small difference in frequency (f_1 and f_2) and measuring the sum of frequency combinations, such as $(f_1 - f_2)$, $2(f_1 - f_2)$, and so on. The result is a frequency spectrum such as that shown in *Figure 4*. The advantage of the method lies in the greater simplicity of the apparatus required in comparison with that used in ordinary higher-harmonics polarography.

A new way for increasing the sensitivity of a.c. polarography has been developed by Kambara and Hasebe[19] who inserted an inductance in series with the polarographic cell. By adjusting the value of the inductance, the admittance of the resulting LCR circuit can be tuned to a maximum with a corresponding increase in sensitivity. Further development of this entirely new principle will be awaited with great interest.

Kitagawa[20] has successfully used a rotating disc electrode and shown that good a.c. polarograms can be obtained with ferrocyanide in potassium nitrate solution.

Applications

Given the large number of publications in this field and the unavoidable limitations of space, it is regrettable that only a fraction of the published work can be considered here.

The method of tensammetric titrations[21] has been further developed by Breyer *et al.*[22] who showed that by using oxine, a number of metal ions, such as those of Zn(II), Cu(II), Ni(II), U(VI), Fe(III), In(III), etc., could be determined with great accuracy at high dilutions (10^{-6}—10^{-5} M). Fujinaga and his group[23] have considerably expanded the scope of tensammetric titrations by studying the a.c. polarographic and tensammetric properties of oxine derivatives, such as 8-hydroxyquinoline-5-sulphonic acid, 2-methyl-8-hydroxyquinoline and 7-iodo-8-hydroxyquinoline-5-sulphonic acid, and using them for tensammetric titrations.

A paper dealing generally with a.c. polarographic titrations has been published by Gupta and Sharma[24]. Gupta *et al.*[25] also used oxine for the titation of Zn(II), Ni(II), and Mn(II).

An interesting development of a.c. polarographic titrations which is based on changes in reversibility of the electrode process, a method originally introduced by our group[26], has been reported by Imai *et al.*[27] who found that, owing to increased reversibility, the a.c. wave of In(III) increased on the addition of halogen ions; they have successfully used the method for the quantitative estimation of iodides.

Kambara *et al.*[28] have applied a.c. polarography to the estimation of phosphates. Their method consists in extracting phosphate ion as phosphomolybdate into methylisobutyl ketone and rendering the organic extract miscible with aqueous electrolyte by adding methylcellosolve, an elegant procedure first described by Fujinaga *et al.*[29, 30]. The difference between the d.c. and a.c. polarograms obtained is truly remarkable; as *Figure 5* shows, there are hardly any d.c. steps discernible, whilst the a.c. waves show sharp, well-defined peaks. I am inclined to think that this result is due to a large tensammetric component of the alternating current.
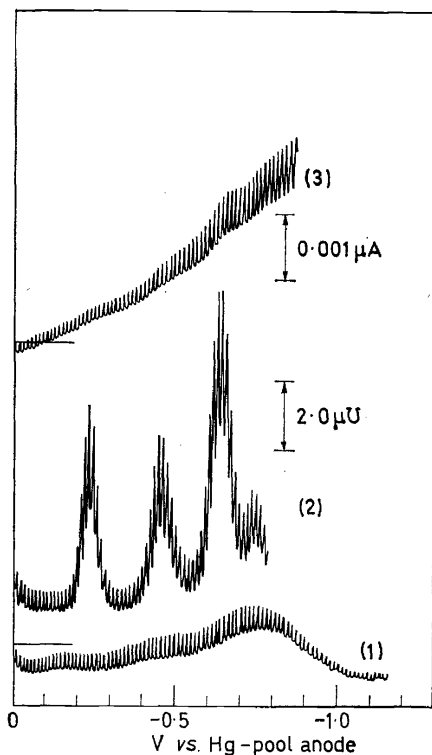
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Figure 5. Polarograms of Mo(vi) in a mixture of $HClO_4$.aq, methyl isobutyl ketone and methylcellosolve; (1) a.c. polarogram of supporting electrolyte, (2) a.c. polarogram of phosphomolybdate (31·0 p.p.m. calculated as phosphorus), (3) corresponding d.c. polarogram (from Kambara *et al.*[28]).

Musha and Ishii have applied a.c. polarography to the determination of vanadium in petroleum[31] and of metals in lubricating oils[32].

A.C. polarography is being used increasingly in the study of complexes. Thus Branica and coworkers have investigated the acetylacetonato complexes of U(vi)[33–35], Fe(iii)[36], Cu(ii)[37], In(iii)[38], and Pb(ii)[39]; they were able to show that the degree of complexation in aqueous solution could be deduced from the a.c. and the square wave (s.w.) peak-heights. Taking Cu(ii) as an example, the stability constants of the two consecutive cupric acetylacetonato (Acac) complexes is given by

$$K_1 = \frac{[CuAcac^+]}{[Cu^{2+}] \times [Acac^-]}$$

and by

$$K_2 = \frac{[CuAcac_2]}{[CuAcac^+] \times [Acac^-]}$$

The stability constants can be calculated from the shift of the half-step potentials (d.c. polarography) with pH. *Figure 6* shows how well the calculated curves of the distribution of the different complex species coincide with the a.c. waveheights.
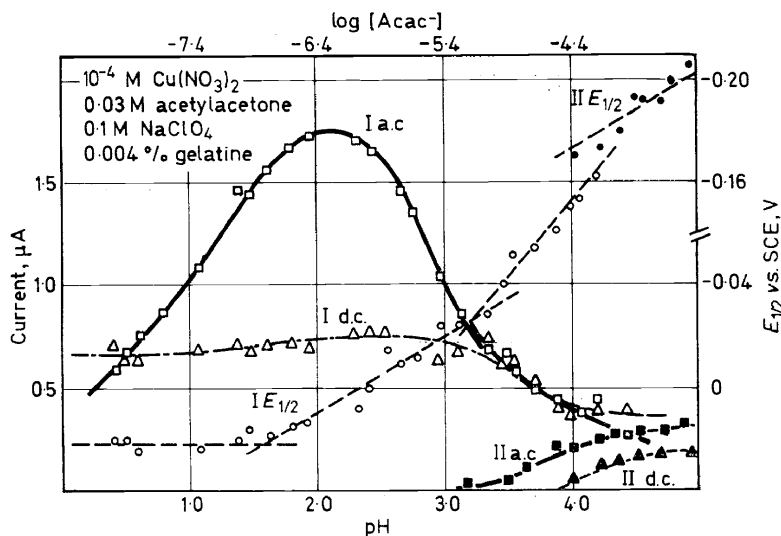
Figure 6. Distribution of various Cu-acetylacetonato complexes with changing pH (after Branica *et al.*[39]).

Branica and Jeftić[34] were also able to show how changes in the peak-height due to the presence of surfactants can be used to calculate the overall stability constants of the acetylacetonato complexes. The procedure is given in the following case in which U(vi) and Triton-X-100 are taken as an example.

Measurements are made of the influence of Triton-X-100 on the uranyl s.w. peak-height in its dependence on the free ligand concentration (pH of the solution). From the experimental curves so obtained the so-called "critical" T-X-100 concentration is determined, the critical concentration being that sufficient to reduce the original waveheight by half. If the critical concentrations are plotted against the logarithm of the concentration of free acetylacetonate ions (pH + log[HAcac]), two straight lines are obtained which intersect at a maximum point (pH_max) as shown in *Figure 7*. (At this point the UO_2Acac^+ species is present at a maximum concentration and the concentrations of the species UO_2^{2+} and $UO_2Acac_2^0$ are equal.) From a knowledge of the dissociation constant (K_a) of acetylacetone the overall dissociation constant (β_2) can be calculated using the relationship

$$\log \beta_2 = \log K_1 \times \log K_2 = 2pK_a - 2(pH_{max} + \log [HAcac])$$

In the case of In(iii) the critical concentration of T-X-100 remains constant, indicating that only one ionic species is being reduced (*Figure 7*). The authors explain the observed facts by assuming that the different ionic species present in solution penetrate the adsorbed film at the electrode surface to a different extent depending on the particular ion species.

A study of complex ions by a.c. polarography has also been made by Gupta and Chatterjee[40]; in particular Gupta *et al.* investigated complexes of Cu(ii) and Fe(iii) with dihydroxybenzoic acid[41] and of Cu(ii) with ammonia and pyridine[42].
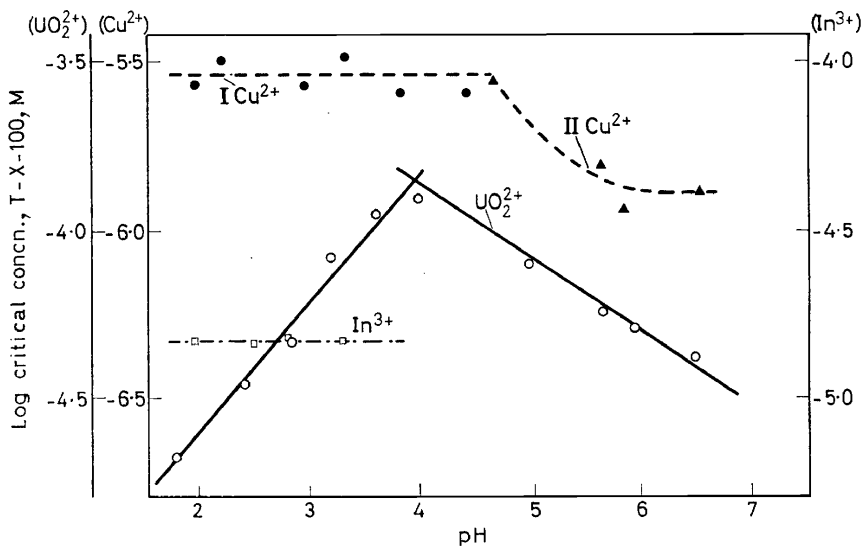
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Figure 7. U(VI) acetylacetonato complex. Plot of critical T-X-100 concentration against pH (after Jeftić and Branica[34]).

The number of applications of the a.c. method in biological research is steadily growing. Thus Berg and his group use it extensively for the investigation of biopolymers. The biopolymers investigated were dextrans, proteins, and nucleic acids. With dextrans it was found that their power to suppress the base current is a function of the molecular weight[43].

The proteins studied comprised ribonuclease, lysozyme, trypsin, chymotrypsin, and serum albumin. It was found that they are desorbed at negative potentials, shortly before the final current-rise. According to Berg[44] this desorption is also the cause of the splitting of d.c. steps in the Brdička (Cocomplex) protein reaction. Alternating current polarography indicated clearly first the adsorption of the protein–cobalt complex, followed by its desorption and the discharge of further quantities of the complex on the now uncovered electrode surface.

The work of Berg *et al.* on nucleic acids[45, 46] shows that the a.c. method is particularly useful for the study of denaturation processes. Nucleic acids in their native state yield a rounded tensammetric wave at negative potentials; after denaturation (by heat, light, or pH changes) a sharp peak at more negative potentials develops *(Figure 8)*. This behaviour is typical of the helix–coil transition during denaturation. If the denaturation process involves only splitting of the molecule without helix changes (e.g. when using ultrasonic degradation) the height of the rounded wave increases but no sharp peak appears. Berg and coworkers have used the a.c. method with great success for kinetic studies of the denaturation process.

A new method for the investigation and analysis of proteins has recently been developed by Breyer and Sato[47]. Whereas Berg[44] was mainly concerned with the a.c. polarographic behaviour of proteins at negative polarizations
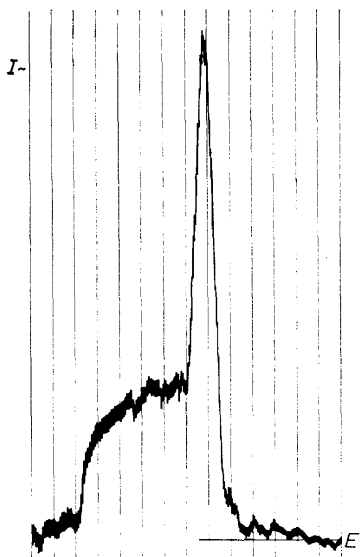
Figure 8. A.C. curve obtained with heat-denatured DNA (Berg, private communication).

of the dropping mercury electrode, Breyer and Sato investigated the potential region extending from about the electrocapillary maximum to the extreme positive region limited by mercury dissolution. In preliminary experiments they had found that in a number of electrolytes (e.g. sulphates, nitrates) at high positive polarizations there appears a new type of a.c. wave which they called "predissolution wave" because it occurs at potentials close to the beginning of the anodic dissolution of mercury; they showed that the wave is due to the solubility product of the mercurous salts formed at the electrode surface being exceeded as a consequence of the electrode reaction, in a manner completely analogous to the well known mechanism by which the a.c. waves of, say, halogen ions are formed. Now, on addition of proteins the predissolution wave shifts to more positive potentials and markedly increases in height due to complex formation between the protein and mercurous ions (*Figure 9*). This increase in waveheight was used for protein analysis in the concentration range, 20 to 200 p.p.m. For the estimation of smaller concentrations (2 to 20 p.p.m.) the lowering of the base-current by protein addition at about — 0·1 V was measured. The calibration curves are shown in *Figure 10*.

In the same communication, Breyer and Sato also report that the growth of micro-organisms, in particular moulds, in either distilled water or in salt solutions, produced typical changes in the anodic a.c. polarogram. As seen in *Figure 11* a hump appeared on the curve at about + 0·2 V, and this was first discernible about 16 h after infection of the solution with a few mould cells. With the passing of time the hump gradually increased. As expected no change was seen in a sterile control solution. The changes in the a.c. polarogram became visible about 1–2 weeks before any growth could be detected macroscopically, a useful fact if one remembers how profoundly experimental results can be affected by infection of the distilled water used.
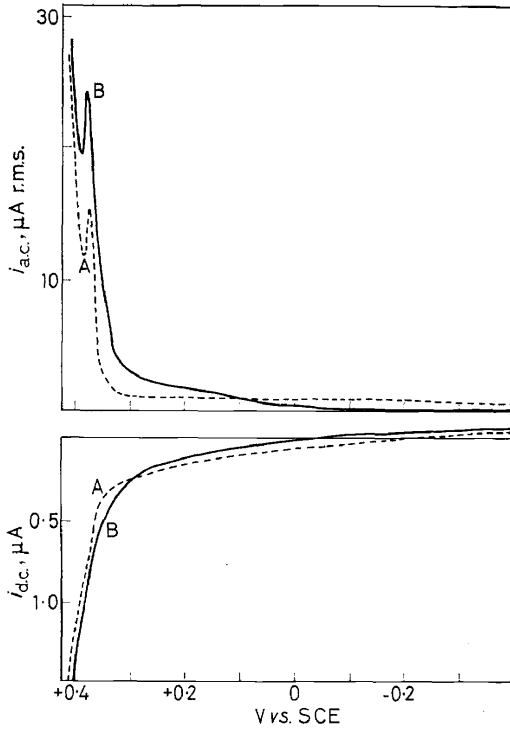
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Figure 9. Effect of serum albumin addition on a.c. and d.c. polarograms of sodium sulphate: (A) 1 м sodium sulphate; (B) same +0·02% serum albumin (after Breyer and Sato[47]).
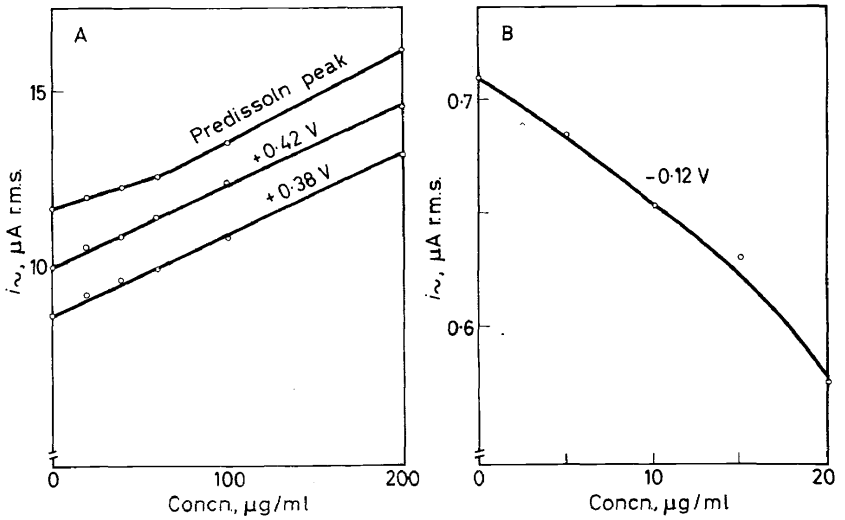

Figure 10. Calibration curves of serum albumin; (A) in 0·1 м sodium sulphate; (B) in half-saturated magnesium sulphate (after Breyer and Sato[47]).
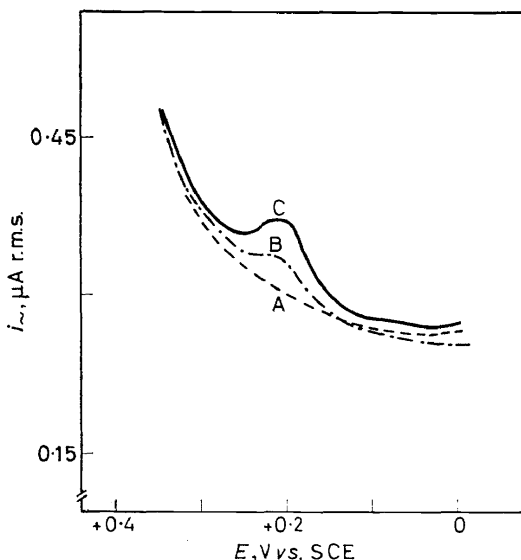
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Figure 11. Effect of growing moulds on anodic a.c. polarogram of $0 \cdot 3$ M sodium nitrate; (A) control; (B) 16 h after infection; (C) 64 h after infection (after Breyer and Sato[47]).

TENSAMMETRY

The first really comprehensive study of tensammetry has been made by Jehring[48]. His work contains both theoretical treatment of the adsorption process and new applications of the method. He has studied a great variety of compounds, such as various alcohols, ketones, organophosphates and phosphinoxides, amines, pyridinium derivatives, alkyl- and arylsulphonates, organotin compounds, hydrocarbons, methyl cellulose, and so on. The quantities evaluated were: (a) the wave-height as a function of concentration of tenside; (b) the suppresion of the base-current as a function of concentration; (c) the adsorption coefficient; (d) the degree of coverage of the electrode surface; (e) the thickness and dielectric constant of the film; (f) the desorption potentials as a function of concentration; (g) the time-dependence of the adsorption (diffusion) equilibrium.

Jehring was able to show that the lowering of the base-current and the drop-time, t, are connected by the expression.

$$\Delta \bar{\imath} / \bar{\imath}_0 = Kct^{1/2}$$

where $\bar{\imath}$ is the alternating current (averaged over the drop-life) in the presence of surfactant, $\bar{\imath}_0$ is the same in the absence of surfactant, c is the concentration and K is a constant which includes also the diffusion coefficient of the tenside. Numerous investigations comprising cationic, anionic, and uncharged species confirmed the dependence of the capacity-current (i.e base-current) lowering effect on the square root of the drop time. As little as 1 p.p.m. of surfactant could be estimated; using slow-dropping capillaries ($t > 40$ sec) the sensitivity could be improved to $0 \cdot 1$ p.p.m. The same square-

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root dependence on the drop-time was also found in the inhibition of faradaic processes by surface films[48-54].

An interesting application of tensammetry is that of Jehring for the measurement of the degree of polymerization of polyethylene glycol; he was able to show that with increasing average molecular weight the tensammetric peak-potential moves to progressively more negative values and that it is a linear function of the reciprocal average molecular weight[48, 53, 55]. Other findings were that separate tensammetric peaks are obtained with polyethylene glycols of different molecular weight when the peak-potentials differ by as little as 15 mV[54] and that polyethylene-glycol ethers yield up to four a.c. waves within their adsorption range; these waves could be due to stepwise desorption, re-orientation of molecules, formation of polylayers, or similar processes[48, 49].

When studying organo-tin compounds Jehring found that these substances are strongly adsorbed even from organic solvents. They give rise also to faradaic currents so that the a.c. method is particularly suitable for their analysis. It permits the detection of as little as 0·1 per cent of the toxic triorgano-tin compound contained as impurity in the diorgano-tin compound[56]; the latter is widely used as a stabilizer in the plastics industry. Jehring has also used graphite-paste electrodes in the study of a.c. processes in the presence of surface films[57].

Another group of compounds studied by Jehring comprises the organo-phosphates, -thiophosphates, -phosphonates, and -phosphinoxides. He found that the range of potentials within which these compounds are adsorbed increases with the size of the organic part of the molecule and that, as usual, the peak-potential is a linear function of the logarithm of the concentration. It is interesting to note that a substitution of sulphur for oxygen causes a shift of the adsorption range to more positive potentials, a finding interpreted by Jehring as chemisorption at the positively-charged electrode and orientation of the S-atom towards the electrode surface[48, 53].

A particularly valuable finding of Jehring's seems to me to be the fact that two tensides present simultaneously in a mixture can be estimated singly by using different drop times of the electrode. The condition required is that the two surfactants reach diffusion equilibrium at sufficiently different rates. Then, if the drop rate is high, the tenside prevalently adsorbed will be that which establishes diffusion equilibrium quickly and the tensammetric wave will be mainly due to its adsorption/desorption. Conversely, at slow drop rates and assuming that the slower tenside is more strongly adsorbed (which generally is the case), the slower tenside will be able to reach the surface of the electrode and will displace the faster one, so that now the tensammetric process will be governed mainly by the slow tenside. An example of this "separation tensammetry" is shown in *Figure 12*. Details will be found in Jehring's original work[50].

Finally, Jehring reported that the application of phase-shift detection methods, as well as higher-harmonics and square-wave polarography, improve the sensitivity of tensammetric estimations up to ten times[54]. It seems surprising that phase-shift methods should give an improved performance in view of the fact that the phase angle changes only very little during tensammetric processes[58].
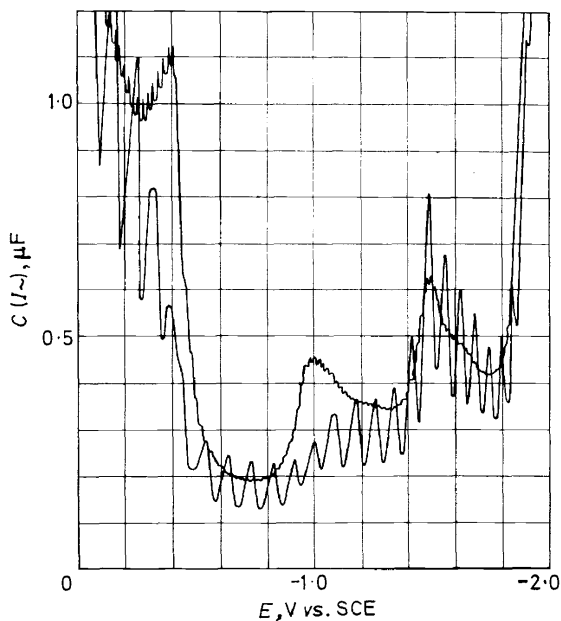
Figure 12. Separation tensammetry of a mixture of 1.6×10^{-3} M triethyl phosphate and 2.0×10^{-5} M antarox (nonylphenolpolyglycol ether) in 1 M potassium chloride; the triethyl phosphate peak at -1.0 V, seen at fast drop rates ($t = 1.4$ sec), vanishes at slow drop rates ($t = 7.5$ sec) (after Jehring[50])

An extensive study of tensammetric processes has also been carried out by Narayan[59]. He studied mainly the tensammetry of aromatic hydrocarbons, of lauryl sulphate, and of thiourea. With regard to the latter substance he found that, in contradistinction to the other compounds studied, the a.c. base-current was not depressed but enhanced. To explain this finding, Narayan suggested that thiourea exists in the double-layer as a tautomeric anion and thus causes an increase in the double-layer capacitance, just as other specifically-adsorbed anions do.

Further conclusions reached by Narayan include the view that squeezing-out type of forces are more important in the adsorption process than are electrostatic forces. This conclusion is reached from studies of the behaviour of lauryl sulphate, and similar anionic detergents, which are desorbed cathodically only at relatively high negative potentials; that is, these compounds remain at the interface in spite of strong electrical repulsion forces. It is my feeling that this view cannot be of general validity. As always in surface processes the surface behaviour of a compound depends on the balance of van der Waals and electrostatic forces, so that the conditions will change with the nature of the individual compound; however, in the case of lauryl sulphate and other anionic detergents, Narayan's conclusions seem completely justified.

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With regard to the desorption mechanism, Narayan thinks that the displacement of organic molecules from the interface by oriented water dipoles plays a major part and that the displacing effect of unspecific ion adsorption is relatively small. The desorption process is regarded as leading from a highly condensed or micellar film over a less condensed (liquid?) film to a gaseous state and finally to desorption. At times the single transition stages might appear as separate peaks; alternatively, if the desorption proceeds gradually, only a hump may be seen. These ideas so far seem to be purely qualitative; in the abstract of the thesis, made available to me by the kindness of Professor K. S. G. Doss (Central Electrochemical Research Institute, Karaikudi, India), I could find no supporting evidence for the views expressed. However, many of the assumptions seem reasonable, even if alternative mechanisms, such as molecular rearrangement, polylayer formation, change in structure of the adsorbed molecules (e.g. of complexes), change in bond type, etc., are equally responsible for the multiple peaks observed.

An important point made by Narayan is that the charge density is a better criterion of the desorption process than is the value of the desorption potential; he was able to show that the desorption of simple organic molecules takes place at the same surface-charge density on either side of the electrocapillary zero. Investigating the frequency dependence of tensammetric waves, Narayan made the most interesting finding that the cathodic peak-heights rapidly decreased with increasing frequency, whereas the height of the anodic peaks (e.g. of lauryl sulphate) seemed unaffected by frequency changes (the frequency range used is not stated in the abstract).

Much work has also been done in the field of tensammetry by Gupta and coworkers[60, 61] who have studied systems similar to those investigated by Jehring. As would be expected, the conclusions reached are essentially the same as those of Jehring and I refer readers who require details to the literature quoted. Other studies of Gupta and coworkers concern the influence of tensammetric waves on reduction peaks due to the reduction of inorganic cations and *vice versa*[62] and the investigation of complexes of pyridine with *o*-cresol and alcohol in aqueous media[63].

Of great interest is the work of Neeb[64] who has applied his double-tone polarography to the study of tensammetric processes. He investigated *n*-octanol, oxine, camphor, and pyridine and found, as already inferred by the work of Biegler[65], that the content in higher harmonics of tensammetric processes exceeds that associated with faradaic currents. There were also distinct differences in the frequency spectra of octanol and pyridine on the one hand, and of oxine and camphor on the other (*Figure 13*), differences which according to Neeb might be explained by the varying velocity of adsorption and/or of diffusion of the tensides. From the analytical point of view it is of great interest that Neeb's method increases the sensitivity of tensammetric analysis 5–10 fold. The remarkable improvement of the waveform is seen in *Figure 14*.

Maruyama and Okabe[66] made the interesting observation that cholic and desoxycholic acids give two tensammetric waves at potentials more negative than the electrocapillary maximum. Like Narayan, they attribute the appearance of two waves to different states of the adsorption layer, this being gaseous at less negative and condensed at higher negative potentials.
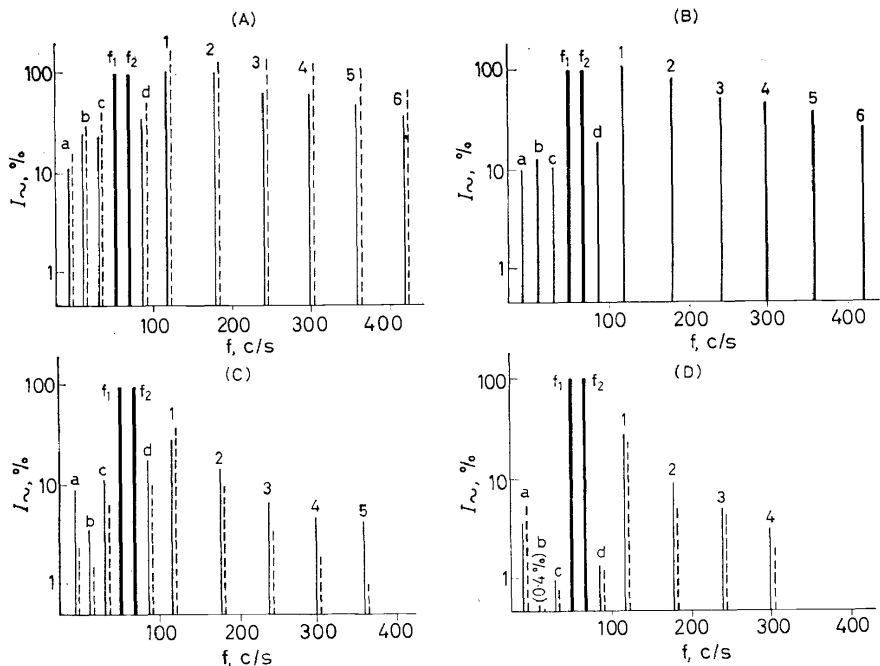
Figure 13. Tensammetric current frequency spectra of octanol, pyridine, oxine, and camphor (after Neeb[64]) (A) 10^{-3} M octanol (0·5 M Na_2SO_4); (B) 0·1 M pyridine (0·5 M] Na_2SO_4); (C) 10^{-3} M oxine (0·2 M ammonium acetate); (D) 10^{-3} M camphor (0·5 M Na_2SO_4).
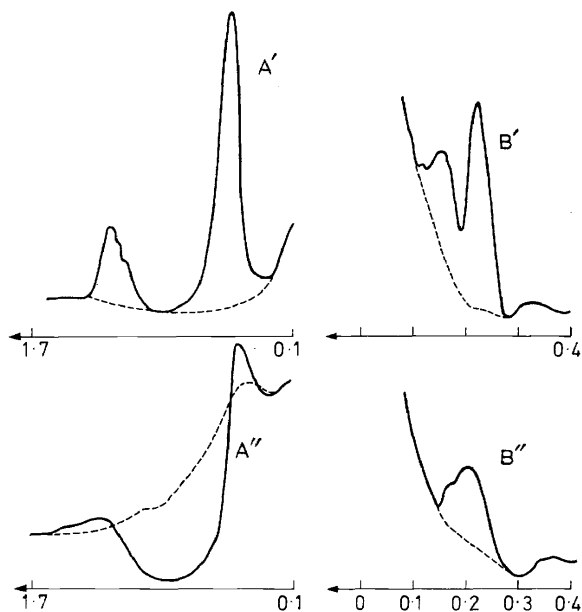

Figure 14. Tensammetric waves at fundamental and second-harmonic frequencies: (A) 10^{-4} M *n*-octanol in 0·5 M sodium sulphate; (B) 4×10^{-6} M oxine in 0·2 M ammonium acetate; A′, B′, 70 c/s; A″, B″, 35 c/s; (------) base current (after Neeb[64]).
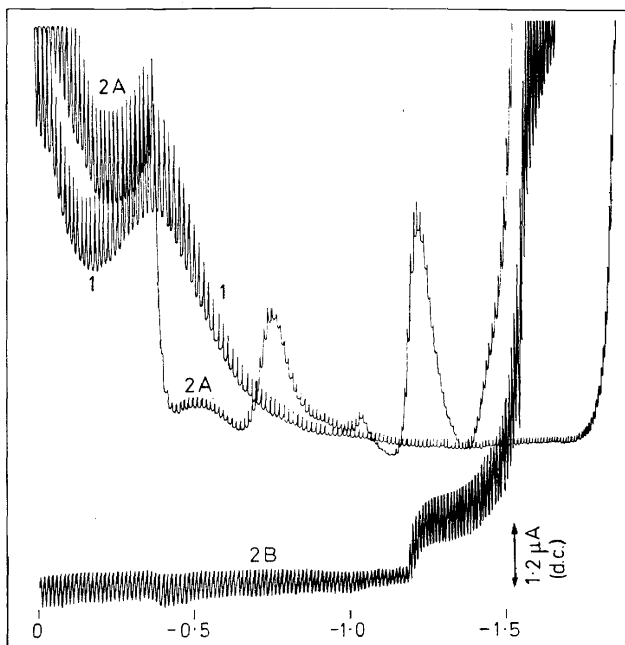
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Figure 15. Polarograms of tridipyridyl-cobalt complex: (1) a.c. polarogram of supporting electrolyte (0·5 M NaCl); (2A) a.c. polarogram after addition of 10^{-3} mole/litre of [Co (dipyridyl)$_3$] (ClO$_4$)$_3$.3H$_2$O; (2B) corresponding d.c. polarogram (after Vlček[69]).

Finally, I should like to give an example of the great usefulness of the a.c. method in the study of the electrochemical behaviour of complexes. Recently Vlček[69] has discussed the electrochemistry of Co(dipyridyl)$_3$$^{3+}$ complexes and I am greatly indebted to Dr. Vlček for permission to reproduce here the polarograms obtained in his institute. I believe that the graph reproduced in *Figure 15* shows very clearly the wealth of information that can be gained by applying the a.c. method. My interpretation of the electrode process is that the complex is adsorbed at about $-0·4$ V (suppression of the base current) and rearranged (ligand rearrangement?) at about $-0·75$ V (purely tensammetric current), the re-formed complex is adsorbed again at about $-1·05$ V (small tensammetric peak after which the current falls below the base-current), it is reduced at about $-1·25$ V (faradaic current shown by d.c. polarogram), and finally the reduced form is desorbed at about $-1·35$ V (the current after the peak and the base-current coincide).

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