Selection of Supporting Electrolytes for Inorganic Square Wave Polarography

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As well known the choice of supporting electrolyte in the square wave a.c. polarography is much more important than that in the usual d.c. polarography, since the peak height due to the electrode reaction of depolarizer depends very prominently on the reversibility of the reaction concerned. Compared with the d.c. polarographic analysis the methodology of a.c. polarography has not yet been developed extensively. Recently Ishibashi, Fujinaga and Saito^{1,2)} studied systematically the effect of nature of supporting electrolyte on the sinucoidal wave a.c. polarographic peak height. In their pioneering works the base electrolytes examined are solutions of acid and neutral salt and also from the theoretical standpoint the reversibility of electrode processes is studied. The present author, therefore, tried to study empirically the applicability of the common supporting electrolytes to the square wave a.c. polarographic analysis.

Compositions of the supporting electrolytes examined are summarized in Table I.

Table I. List of Supporting Electrolytes.

No.	Composition*
1	1 M HCl
2	1 M H ₂ SO ₄
3	1 M HNO ₃
4	1 M NaOH
5	1 M in NH ₄ OH and 1 M in NH ₄ Cl
6	0.4 M NaF
7	0.2 M KCN
8	0.5 M CaCl ₂
9	2 M KCNS
10	0.2 M K ₂ C ₂ O ₄
11	2 M in HClO ₄ and 0.5 M in NaCl
12	Half-saturated (NH ₄) ₂ CO ₃ and 0.2 M in KOH
13	0.1 M potassium sodium tartrate
14	1 M ammonium citrate
15	0.2 M hydrazine hydrochloride
16	0.5 M in pyridine and 0.5 M in NaCl

*No surface-active agent, such as gelatin, is added.

Table II. Experimental Conditions.

Gate	2-7
Time constant	7.5
Square wave voltage	30 mv
Square wave frequency	300 c/s
Temperature	19-23°C
Depolarizer concentration	10 μ g/ml

The equipment used was the square wave polarograph manufactured by Yanagimoto Co., Kyoto, and the experimental conditions are tabulated in Table II. The mercury head was kept constant and the drop time was about 3 sec throughout the experiment. The results are summarized in Tables III-VIII, where the following abbreviations and symbols are employed. Namely,

air=In the presence of dissolved air.

N₂=The dissolved oxygen is purged by nitrogen.

RS=Recorder sensitivity in μ A/mm.

AS=Amplifier sensitivity.

E_s =Peak potential in volt *vs.* mercury pool anode.

The notations of wave form imply:

A=Well defined peak, suitable to quantitative analysis.

B=Fairly well defined peak.

Table III. Properties of Cobalt(II)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
5	air	A	-1.25	0.01	1/20	5.8
5	N ₂	A	-1.21	"	"	5.0
7	air	B	-0.92	0.004	1/20	5.2
7	N ₂	B	-0.92	0.004	1/10	5.5
9	air	A	-0.92	0.004	1/20	16.5
9	N ₂	A	-0.91	"	"	13.5
11	N ₂	B	-0.95	0.002	"	5.0
12	air	B	-1.25	0.004	1/20	5.5
12	N ₂	B	-1.25	"	"	6.0
14	air	B	-0.31	"	"	5.5
14	N ₂	B	-0.30	0.002	1/10	6.5
16	air	A	-1.15	0.004	1/20	11.0
16	N ₂	A	-1.12	"	"	10.0

Table IV. Properties of Nickel(II)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
5	air	A	-1.07	0.01	1/20	9.5
5	N ₂	A	-1.06	"	"	7.5
7	air	A	-0.86	0.004	1/50	10.0
7	N ₂	A	-0.81	"	"	5.5
9	air	A	-0.52	0.004	1/20	19.0
9	N ₂	A	-0.49	0.01	"	7.5
12	air	B	-1.02	0.004	1/20	5.0
12	N ₂	B	-1.02	"	"	4.0
16	air	A	-0.88	0.004	1/20	17.0
16	N ₂	A	-0.86	0.01	"	10.0

Table V. Properties of Iron(III)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
10	air	A	-0.48	0.04	1/20	11.0
10	N ₂	A	-0.46	"	"	14.0
12	air	A	-0.27	0.004	1/20	15.0
12	N ₂	A	-0.27	0.01	"	15.5
14	air	A	-0.33	0.01	1/50	12.5
14	N ₂	A	-0.30	"	"	10.5

Table VI. Properties of Iron(II)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
3	air	A	-0.77	0.004	1/50	11.0
3	N ₂	B	?	"	"	—
10	air	A	-0.36	0.04	1/20	14.0
10	N ₂	A	-0.30	0.04	1/20	14.0
12	air	A	-0.20	0.01	1/50	6.5
12	N ₂	A	-0.21	"	"	7.0
14	air	A	-0.25	0.01	1/50	11.0
14	N ₂	A	-0.26	"	"	10.5

Table VII. Properties of Tin(II)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
1	air	A	-0.50	0.01	1/50	14.0
1	N ₂	A	-0.50	"	"	12.0
8	air	A	-0.49	0.004	1/20	6.5
8	N ₂	A	-0.46	0.002	1/10	7.0
9	air	A	-0.32	0.01	1/50	12.5
9	N ₂	A	-0.29	"	"	13.0
10	N ₂	B	-0.41	0.002	1/10	7.0
15	air	A	-0.50	0.01	1/50	15.0
15	N ₂	A	-0.50	"	"	14.0

Table VIII. Properties of Arsenic(III)-Peak.

No. of supporting electrolyte	Atmosphere	Wave form	E_s	RS	AS	Peak height in cm
1	air	A(1st wave)	-0.48	0.01	1/20	5.5
	"	A(2nd wave)	-0.67	"	"	9.5
1	N ₂	A(1st wave)	-0.47	"	"	6.5
	"	A(2nd wave)	-0.66	"	"	6.0
2	air	A	-1.03	0.01	1/20	9.5
2	N ₂	A	-0.95	"	"	6.5
3	air	A	-1.04	0.01	1/20	8.5
3	N ₂	A	-1.01	"	"	6.5
12	air	B(1st wave)	-1.36	0.004	1/50	3.0
	"	B(2nd wave)	-1.44	"	"	3.0
12	N ₂	B(1st wave)	-1.36	"	"	3.0
	"	B(2nd wave)	-1.44	"	"	3.0
15	air	B(1st wave)	-0.49	0.004	1/50	4.5
	"	A(2nd wave)	-0.71	"	"	10.0
	"	A(3rd wave)	-0.91	"	"	9.0
15	N ₂	B(1st wave)	-0.49	"	"	4.5
	"	A(2nd wave)	-0.71	"	"	9.0
	"	A(3rd wave)	-0.92	"	"	6.5

Analogous measurements were carried out with lead, cadmium, zinc and copper ions in the concentration of 1 μ g/ml. The supporting electrolytes to be recommended are as follows.

For Pb(II): 1 M HCl; 0.5 M in ammonium acetate and 0.1 M in tartaric acid; 2 M in HClO₄ and 0.5 M in NaCl; 0.2 M hydrazine hydrochloride.

Cd(II): 1 M HCl; 1 M in NH₃ and 1 M in NH₄OH; 0.1 M KCl.

Zn(II): 0.1 M in ammonium acetate and 0.025 M KCNS; 1 M in NH₃ and 1 M in NH₄Cl; 0.5 M in pyridine and 0.5 M in NaCl.

Cu(II): 0.5 M in ammonium acetate and 0.1 M in tartaric acid; 1 M HCl.

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Elucidation of Electrode Processes by the Use of A.C. Polarography⁽¹⁾

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SUMMARY

The types of results obtained in a.c. polarographic work are discussed in terms of the underlying electrode processes. Thus, it is shown how the technique may be used as a means of elucidating and establishing the mechanisms of polarographic reactions.

A.c. polarography consists in the superposition of a small, sinusoidal alternating voltage upon the direct potential applied to a dropping mercury electrode. By plotting the measured alternating current against the applied direct potential, wave-shaped a.c. polarograms are obtained. The a.c. polarographic technique has been described in detail in a number of review articles (1, 2, 3).

The object of this article is to show how a.c. polarography can be used with advantage for the elucidation of electrode reactions. More specifically, the aim of the present communication is to discuss the types of observations made in a.c. polarography and their interpretation in terms of the underlying electrode reactions.

The three main variables studied in a.c. polarography are the magnitudes of the a.c. polarographic current and of the a.c. base current and the value of the summit potential of the a.c. polarographic wave. In order to apply a.c. polarography to the elucidation of electrode reactions, the dependence of these three variables on various factors—such as the frequency and amplitude of the alternating voltage, the nature and concentration of the supporting electrolyte—is studied. In the following, we shall discuss in detail how these variables change with the experimental conditions in different types of processes. It should be made clear from the outset that a.c. polarographic observations can be satisfactorily interpreted only in conjunction with the corresponding d.c. polarograms.

I. FACTORS INFLUENCING THE A.C. POLAROGRAPHIC WAVE

A number of equations have been derived, intended to describe the a.c. polarographic wave in terms of the various parameters which influence the electrode reaction. We shall give here only two of these equations, one of which has been fully substan-

(1) The authors wish to dedicate this paper to Professor J. Heyrovsky in honour of his seventieth birthday.

tiated experimentally, and the other which appears to be the most general equation which can be written at the moment. These equations are (4, 5)

$$\Delta i_{(E)} = \frac{nFA(\omega D)^{\frac{1}{2}} C_B [\exp(nFV/RT) - 1]}{\sqrt{2} [\exp(nFV/RT) + \exp(nF[\Delta E + V]/RT) + \exp(-nF\Delta E/RT) + 1]} \quad (1)$$

$$\Delta i_{(E)} = \frac{\sqrt{2} n^2 F^2 A V C_B k}{RT[Z^2 + 2Z + 2]^{\frac{1}{2}}} \frac{\exp[(1 - \alpha)nF\Delta E/RT]}{1 + \exp[nF\Delta E/RT]} \quad (2)$$

where $Z = k(2/\omega D_R)^{\frac{1}{2}} \left[\left(\frac{D_R}{D_O} \right)^{\frac{1}{2}} + \exp(nF\Delta E/RT) \right] \exp(-\alpha nF\Delta E/RT)$

and where $\Delta i_{(E)}$ is the r.m.s. value of the a.c. polarographic current, V the amplitude of the superposed alternating voltage, ΔE the direct potential relative to the standard potential of the redox system, ω the angular frequency (radians/sec) of the alternating voltage, C_B the total bulk concentration of depolarizer, D_O and D_R the diffusion coefficients of the oxidized and reduced forms respectively (assumed in equation (1) to be both equal to D), k the heterogeneous rate constant of the electron-transfer reaction, α the transfer coefficient, n the number of electrons involved per molecule of depolarizer, A the area of the electrode, T the absolute temperature, F the Faraday and R the gas constant.

Equation (1) has been derived under the assumption that the diffusion coefficients of the oxidized and reduced species are equal and that the frequency is low and/or the rate constant very large. This equation has been substantiated experimentally (4) and found to describe accurately the shape and height of the a.c. polarographic wave in the case of simple reversible processes at low frequencies.

Equation (2) has been derived without the assumptions that the diffusion coefficients of the oxidized and reduced forms are equal and also for all values of the frequency for a finite rate constant. On the other hand, this equation is valid only for amplitudes of the alternating voltage no greater than 7 millivolts (5), whereas equation (1) has been found to be valid for amplitudes up to about 30 millivolts.

In discussing the theoretical dependence of the a.c. wave on various parameters, we shall use whichever of the above equations is best suited for the particular case: thus for instance, we shall use equation (1) when discussing the influence of the amplitude of the alternating voltage, but equation (2) when discussing the influence of the heterogeneous rate constant.

Influence of n . Equation (2) shows that, at small amplitudes of the alternating voltage, the height of the a.c. wave varies as the square of the number of electrons involved. Use of equation (1) has shown that the a.c. polarographic wave becomes narrower with increasing n ; this has also been confirmed experimentally (4).

Influence of concentration. In simple reversible cases, to which the above equations refer, the height of the a.c. wave is a linear function of bulk concentration. In both the above equations, the current has been derived initially as a function of the interface concentrations of the oxidized and reduced species; hence, the height of the wave is directly proportional to the bulk concentration only then, when the interface concentration is directly proportional to the bulk concentration. Where this is not so, the

wave height might be either larger or smaller than that calculated from the above equations, a fact which can be valuable in the interpretation of electrode processes.

Influence of capillary characteristics. Both equations (1) and (2) show that the alternating current is proportional to the surface area of the drop at the instant at which the current is measured, that is to $m^{2/3} t^{2/3}$ where m is the rate of flow of mercury and t the time after the beginning of the life of a drop. This shows the important distinction that the alternating current is limited by the available surface area, while the direct polarographic current depends on the rate of diffusion of depolarizer from the bulk of the solution to the electrode and is proportional to $m^{2/3} t^{1/6}$. It is evident, therefore, that the height of the a.c. polarographic wave should be independent of the height of the mercury reservoir, a fact which has also been experimentally confirmed by Okuda and Tachi (6). The position here is thus the same as that encountered with kinetic d.c. polarographic currents, whose magnitude is limited by a surface reaction occurring at the electrode.

Influence of diffusion. Equation (1) shows that the height of the wave depends on the square root of the diffusion coefficient. It should be remembered that in equation (1) it is assumed that the diffusion coefficients of the oxidized and reduced forms are equal; in cases where this is not so, it is theoretically more correct to use, not the diffusion coefficient of either form separately, but their geometric mean (7).

Although the d.c. polarographic current also varies as the square root of the diffusion coefficient, the diffusion processes involved in the two cases are quite different. In the case of the a.c. process, the diffusion processes involved are *periodic* ones, producing a so-called "concentration wave" which extends only to a very small distance from the electrode, as already shown by Warburg (8); in fact, the amplitude of the concentration wave decreases exponentially with distance from the electrode surface. The diffusion process which limits the d.c. polarographic current is a quite different one, since it involves *continuous* transport of depolarizer to and from the electrode. The space in which the d.c. diffusion occurs is orders of magnitude larger than that within which the a.c. diffusion takes place; the latter has been graphically described as "micro-diffusion" by Koutecky (9).

Influence of temperature. Equation (1) shows that the effect of temperature on the height of the a.c. wave is governed by the magnitude of the temperature change itself and by the change of the diffusion coefficient with temperature. It can be seen that at the summit potential and for small amplitudes of the alternating voltage, the temperature coefficient of the a.c. wave will be equal to the temperature coefficient of $D^{1/2}$, less approximately $\frac{1}{3}\%$ due to the effect of the "T" term. Since the temperature coefficient of the d.c. polarographic current is governed mainly by the increase of the diffusion coefficient with temperature, it follows that the temperature coefficient of the a.c. wave will be about $\frac{1}{3}\%$ per degree less than that of the d.c. polarographic step. Experimental data available up to the present (10) tend to confirm this prediction, but a

detailed study of the influence of temperature on the a.c. polarographic wave is still lacking.

The above argument refers to reversible processes. Equation (2) shows that for partly reversible processes, where the magnitude of the rate constant k is a limiting factor in the height of the a.c. wave, the effect of the temperature will be complicated by the dependence of the rate constant on temperature change.

Influence of the superposed alternating voltage. It has been shown experimentally (11) that equation (1) accurately describes the variation of the alternating current with amplitude of the superposed alternating voltage up to amplitudes of the order of 30 millivolts. At the summit potential, the alternating current varies as $\tanh (nFV/2RT)$, the latter term being directly proportional to V for amplitudes up to a few millivolts, i.e. amplitudes for which equation (2) is also valid.

The effect of frequency on the alternating current remains a matter of some doubt at the present time. Two equations have been derived (7, 12) to express the influence of higher frequencies, and these equations differ in the sign of one of the terms in the denominator; experimental evidence has shown that in different cases, one or the other of these equations may be valid (13). However, both equations reduce to the same form, similar to that of equation (1), at sufficiently low frequencies.

Influence of the transfer coefficient and the heterogeneous rate constant. Alternating current polarography has been used to measure both the transfer coefficient and the heterogeneous rate constant (cf. e.g. 7, 11, 12, 14, 15); these measurements, however, are subject to the uncertainty mentioned above since they involve observations over a wide range of frequencies.

The summit potential. In the simplest case, the summit potential coincides with the half-step potential. Differences of these potentials might be due, *inter alia*, to differences in the diffusion coefficients of the oxidized and reduced species, to values of the transfer coefficient appreciably different from 0.5 (5), and to amplitudes of the alternating voltage which are too large (16). However, under the usual experimental conditions (frequencies of 50 or 60 c.p.s.; amplitudes ≤ 15 mv.), differences between the summit and half-step potentials due to the above causes will generally be only a few millivolts.

Interpretation of appreciable differences between the summit and half-step potentials is based on the premise that the summit potential corresponds to equality of surface concentrations of the oxidized and reduced species.

We can now proceed to discuss how departures from the theory outlined above can be used for the interpretation of electrode reactions.

II. DEPARTURES IN WAVE HEIGHT

(a) *The Wave is Too Small.*

One of the most important experimental conditions, which must be satisfied when measuring the height of the a.c. wave, is that the series resistances in the circuit should

be kept sufficiently small. Normally, it is sufficient to keep the series resistances below about 100 ohms. Owing to the small interface impedance produced by the a.c. process, higher series resistances will cause the a.c. wave to be smaller than theoretically expected; this has been fully discussed elsewhere (17). It has been pointed out (18) that because the base current and the a.c. polarographic current have different phase angles, the height of the a.c. wave should be computed vectorially; however, at low frequencies, the difference produced by using a scalar calculation is not important.

There are in the main two reasons why the observed a.c. wave height may differ from the calculated one. In the first instance, the theoretical calculation may be invalid because of the use of an incorrect magnitude for one of the parameters present in the equation; the other possible reason is that there may be a factor influencing the electrode process, for which no allowance has been made in the theory and the equations derived from it. The most important factor of the first kind is the concentration, since the interface concentration might not depend linearly on the bulk concentration, as has been assumed in the derivation of equations (1) and (2).

Where the wave is too small, without there being any reason to suspect that the values of the parameters used in calculating the theoretical wave height are incorrect, differences in wave height are ascribed to changes in reversibility of the electrode process.

Interface concentration. Departures from the theoretical wave height due to differences in interface concentration from the expected one are mostly due to adsorption processes. Thus, it is a common experience with organic depolarizers that the calibration curves show a limiting form (19), in contradistinction to the linear calibration curves obtained with inorganic depolarizers; in other words, in the presence of higher concentrations of organic depolarizers, the a.c. wave is lower than expected. The limiting value of the current obtained in these cases gives an indication of the surface requirement of the depolarizer molecules.

Another type of process, where the interface concentrations of the electroactive species may be smaller than expected, is where these species take part in side reactions at the interface. An example of this type of reaction is given by the reduction of U(VI) ion. It has been shown by numerous authors (e.g. 20, 21, 22) that in acid media a dismutation of the U(V) produced at the electrode takes place according to

In d.c. polarography, this dismutation is accompanied by an increase in the stepheight, whereas in a.c. polarography the wave height is lowered. This is due to the fact that a.c. polarography shows only the reversible reduction $\text{U(VI)} \rightleftharpoons \text{U(V)}$ and, accordingly, the a.c. polarographic wave is lowered to the extent by which the U(V) concentration at the interface diminishes due to dismutation (23).

Reversibility. In cases where there is no reason to suspect that the values of the parameters used in calculating the theoretical wave height are in error, and yet the wave is smaller than expected, we assume that the main reason for such an effect is

a lower reversibility of the electrode process. Accordingly, the a.c. criterion of reversibility, ρ , has been defined (24) as the ratio of the observed to the theoretical wave height.

It is important to emphasize the difference between the a.c. reversibility and the d.c. polarographic reversibility. The latter, measured by the slope of the log-plot, depends directly on the value of the heterogeneous rate constant; thus, the log-plot becomes non-ideal when the value of k becomes appreciably smaller than 10^{-2} cm sec⁻¹(25). On the other hand, the a.c. reversibility is not directly determined by the value of the heterogeneous rate constant; this can be understood by remembering that in calculating ρ , the influence of the heterogeneous rate constant has already been allowed for according to the relation of equation (2); moreover, ρ does not depend on the frequency of the alternating voltage (24).

The a.c. efficiency, ρ , was introduced as an empirical quantity and it is not possible, at this stage, to give an unequivocal theoretical explanation for it. It must be remembered that a number of assumptions were made in deriving equations (1) and (2), such as the applicability of Fick's diffusion law, the assumption that the transfer coefficient does not depend on the electrode potential, and, moreover, possible effects due to double-layer structure have not been considered. Deviations of ρ from the theoretical value of unity may be due to any of the above factors, perhaps to the thermodynamic reversibility of the electron-transfer reaction itself, as well as to other factors as yet unknown.

Without enquiring into the causes of reversibility in any particular process, it is noteworthy that changes in reversibility can be detected much more readily by changes in the a.c. wave height than by measurement of the d.c. polarographic log-plot. For instance, it has been found (24) that ρ changes in some cases by a factor of 3 without any corresponding observable change in the log-plot; in other cases, it has been observed (26) that at an overvoltage of the d.c. polarographic step as small as a few millivolts, the a.c. wave disappears completely. It should be remembered, however, that it is unsafe to use the a.c. method exclusively as a criterion of reversibility, a fact which we shall discuss more fully later.

(b) *The Wave is Too Large.*

The most common reason why the a.c. polarographic wave is larger than expected from theory, is the presence of adsorption processes at the electrode/solution interface. The reason why the wave in these cases is too large is in the main a twofold one: firstly, there is an excess surface concentration of depolarizer present at the electrode and secondly, the adsorption/desorption equilibria established at the interface themselves contribute to the alternating current; this latter factor will be discussed in one of the following sections. The sum of electron-transfer and adsorption/desorption current has been termed "re-arrangement current" (19).

Even when no adsorption in the common meaning of the word is present, the concentration of depolarizer in parts of the double layer may be larger than it is in the

Table I
Variation of Temperature Coefficient with
Concentration of Adsorbed Depolarizer

Concentration	Alternating 3°C	Current 20°C	Temperature Coefficient
$5 \times 10^{-5} \text{M}$	6.6 μA	4.0 μA	-2.9%
$1 \times 10^{-4} \text{M}$	9.3	6.8	-1.8
3	12.8	12.8	0.0
6	14.1	16.4	+0.9
1×10^{-3}	14.7	18.5	+1.4

due to the fact that the surface concentration is greater than the bulk concentration. However, the temperature coefficient of the wave under these conditions is abnormal; as the temperature is increased, the height of the a.c. wave often decreases due to decreased adsorption. In other words, the excess surface concentration—and hence also the height of the a.c. wave—decreases with temperature, even though the wave may still be larger than in the total absence of adsorption.

To make this clearer, consider the results in Table I for the quinone/hydroquinone system (29). It can be seen that at high bulk concentrations, where the a.c. wave height is limited by the available surface area and the surface is fully covered by adsorbed depolarizer molecules, the temperature coefficient of the wave is positive and of the same order of magnitude as expected in cases where no adsorption is present. This is due to the fact that even at the higher temperature, the surface remains fully covered and the increase in a.c. wave height reflects only the increase in the diffusion coefficients with temperature. At low concentrations, the temperature affects the alternating current not only in the usual way, i.e. due to an increase in the diffusion coefficients, but also by decreasing the excess surface concentration of depolarizer. At the very lowest concentrations, the effect of temperature on the adsorption process outweighs the increase in diffusion, so that the temperature coefficient of the a.c. wave is even negative. At the concentration where the two effects counterbalance one another, the temperature coefficient of the a.c. wave becomes zero.

(c) *Altered Shape of Wave.*

It has been observed (30, 31) in a number of cases that, depending on the concentration and/or the nature of the depolarizer, broad "humps" are obtained instead of well-defined a.c. polarographic waves. We are inclined to attribute this particular phenomenon to a low reversibility of the electrode process.

Less drastic alterations in wave shape have been observed in cases where adsorption of the electroactive species occurs. Thus, for instance, in the case of the quinone/hydroquinone system, the wave becomes progressively broader at concentrations where the height of the wave has reached its limiting value (29).

The wave shape may also be altered in the direction of increased steepness. For instance, halogen ions produce needle-sharp, asymmetric a.c. waves whose summit

bulk of the solution; this view was introduced by Frumkin (27) to explain anomalous anion reductions, and its general application has been discussed by Delahay (28).

In the presence of adsorption processes, peculiar temperature effects are observed. Thus, for instance, at low bulk concentrations, the observed a.c. wave height is larger than expected,

potential differs quite appreciably from the half-step potential of the corresponding d.c. polarographic step. It has been shown that these waves are due to adsorption/desorption processes involving the mercurous halides formed at the electrode surface in virtue of the electrode process.

III. SIGNIFICANCE OF THE SUMMIT POTENTIAL

It has been mentioned that differences between the summit potential and the half-step potential can be due to too large an amplitude of the alternating voltage, to unequal diffusion coefficients of the oxidized and reduced species, and to values of the transfer coefficient different from 0.5. Equation (2) shows that for small values of the alternating voltage, at low frequencies

$$E_s - E_{\frac{1}{2}} = RT/nF \ln (D_O/D_R)^{\frac{1}{4}} \quad (3)$$

and at high frequencies

$$E_s - E_{\frac{1}{2}} = RT/nF \ln [(1-\alpha)D_O^{\frac{1}{2}}/\alpha D_R^{\frac{1}{2}}] \quad (4)$$

Equation (4) shows that there can be an appreciable difference between the summit and half-step potentials at high frequencies when the value of the transfer coefficient is sufficiently different from 0.5. For the present purpose, we are more interested in the low frequencies, where equation (3) shows that the difference between the summit and half-step potentials depends on the fourth root of the ratio D_O/D_R ; hence for all practical purposes, this difference will be negligible.

The half-step potential has thermodynamic significance only for reversible processes, while in partly reversible processes, it appears that the summit potential has thermodynamic significance. In cases where the summit and half-step potentials differ appreciably and where the d.c. polarographic step is not of the reversible shape, the summit potential indicates the nearest approach to reversibility achievable under the particular experimental conditions; the smallness of the a.c. wave in such cases shows that the reversibility of the process is not complete. An example of this type of behaviour is found in the reduction of bismuth ion in the presence of increasing concentrations of chloride ions (24). Table II shows that in the absence of chloride ion, when the process is known to be irreversible from the d.c. polarographic point of view, the summit and half-step potentials differ considerably; with increasing chloride concentration, the summit potential shifts continuously towards more negative values, presumably due to

Table II
Effect of Chloride on the Reduction of Bi (III)

	Total chloride concentration $\times 10^3 M$					
	0.0	2.2	6.2	18	60	180
$E_{\frac{1}{2}}$ (V vs. satd. mercurous sulphate half-cell)	-0.44	-0.41	-0.41	-0.42	-0.44	-0.47
E_s	-0.40	-0.41	-0.41	-0.43	-0.45	-0.49
A.c. efficiency	0.06	0.20	0.38	0.64	1.06	0.98
Log-plot (mV)	40	23	23	23	21	20

increasing complexation of the bismuth ion by chloride; the half-step potential, on the other hand, shifts first to more positive potentials and then to more negative values. The conclusion follows naturally, that the summit potential measures the reversible potential—or rather that potential at which the process is most nearly reversible—and that the difference between the summit and half-step potentials in the absence of chloride ions is due to the fact that under these conditions, the half-step potential has no thermodynamic significance. The progressive change of the a.c. efficiency with increasing chloride concentration, even when the summit and half-step potentials coincide, shows that the a.c. reversibility is a much more sensitive criterion than the log-plot (Table II).

In cases where adsorption of the electroactive species is known to occur, the summit potential is often found to differ appreciably from the half-step potential, while the d.c. polarographic step has a non-reversible shape. By analogy with the case discussed above, we assume that in such cases the summit potential corresponds to equality of the concentrations of the oxidized and reduced forms at the electrode surface, while the half-step potential has no thermodynamic significance. Equations based on this premise (32, 33) enable calculation of the relative adsorption coefficients of the oxidized and reduced species.

In all the foregoing discussion, it has been assumed that the a.c. wave is an outcome of a more or less reversible electron-transfer reaction. The case where the alternating current is not predominantly due to electron-transfer, but to adsorption/desorption processes will be discussed in Section V.

IV. A.C. BASE CURRENT

The relative magnitude of the base current in the presence and absence of depolarizer can give valuable information about adsorption processes. At potentials where no electron-transfer processes take place, the alternating current measures the capacity of the double layer (34). In the presence of adsorption, especially of organic molecular species which have a significantly lower dielectric constant than water, the interface capacity is lowered and hence the alternating current is smaller also. Consequently, by comparing a.c. polarograms in the presence and absence of depolarizer, it can easily be seen whether the adsorption process concerns the oxidized, the reduced, or both forms (Fig. 1). If the adsorption has occurred in the oxidized form, the base current is lowered before the a.c. polarographic wave; if it has occurred in the reduced form, the lowering is seen after the a.c. polarographic wave; finally, if both forms are adsorbed, the base current is lowered on both sides of the a.c. wave. Thus the a.c. polarogram provides direct information about adsorption which otherwise must be obtained, more laboriously and less accurately, from electrocapillary curves; in some cases the electrocapillary curves may not show the presence of adsorption at all, while the phenomenon is clearly visible on the corresponding a.c. polarograms (36).

D.c. polarography gives a clear indication of adsorption processes only then, when the d.c. polarographic step has a small step preceding or following the main one, as

Fig. 1. Schematic a.c. polarograms.

- (1) Oxidant adsorbed; (2) Reductant adsorbed;
 (3) Oxidant and reductant adsorbed. (From Breyer et al. (35.))

has first been described by Brdicka (37); this behaviour is observed only in those cases where the reduced form is much more strongly adsorbed than the oxidized form or *vice versa*. In cases where the oxidized and reduced forms are adsorbed to comparable extents, the d.c. polarogram will show only a single step, even though the strength of adsorption of both forms may be quite high; in such cases, the depression of the a.c. base current shows clearly whether or not adsorption processes are present.

V. A.C. WAVES IN ABSENCE OF ELECTRON TRANSFER

It has been repeatedly mentioned that adsorption/desorption processes can contribute to the production of a.c. waves. Waves which are entirely due to adsorption/desorption processes, i.e. where no electron transfer takes place, have been called tensammetric waves (34). Tensammetric waves are observed at potentials where the structure of the double layer changes suddenly due to adsorption. At such potentials, application of a small alternating voltage produces periodic adsorption/desorption processes which result in high a.c. waves; these can be readily distinguished from a.c. waves due to electron-transfer reactions by the fact that there is no d.c. polarographic step of corresponding magnitude at potentials where the tensammetric wave occurs.

The fact that a.c. waves are obtained also in the complete absence of electron transfer should be constantly borne in mind when the a.c. method is used as a test for reversibility of an electrode process. There is always the danger that the presence of an a.c. wave might be attributed to a reversible electron-transfer reaction, when in fact the reversible process concerns adsorption/desorption equilibria. This point is especially important in cases where organic solvents are added to the electrolyte. Such addition can in itself cause the production of a.c. waves for a number of reasons:

(i) The solvent molecules themselves might be adsorbable and give rise to purely tensammetric waves; this case can be easily distinguished by the fact that there is no corresponding direct current of comparable magnitude.

(ii) The presence of organic solvent might tend to equalize the adsorption of oxidized and reduced forms and thereby contribute to the production of an a.c. wave, due to an increased reversibility of the adsorption/desorption process.

(iii) Finally, there is the possibility of interchange at the interface between oxidized and/or reduced molecular species and added solvent molecules in a reversible manner, a process which could also produce an a.c. wave.

It is the hope of the authors that this article might contribute to the realization of the many potential uses of the a.c. method in the interpretation of electrode processes.

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