Communication to the Editor

Negative AC Polarographic Waves—Phase-selective Polarograms

In an earlier publication¹⁾, we drew attention to and explained the phenomena of “negative” ac polarographic waves and of complex-shaped waves with both negative and positive portions. These, as was shown, need not be due to particular electrochemical properties of the relevant system under scrutiny (or even to instrumental errors), but may arise simply from the vectorial combination of the various impedances that make up an electrochemical cell. In that publication, we dealt only with normal, total-component ac polarographic curves. Since then, we have built an ac/dc potentiostatic polarograph²⁾ based on the paper of Brown, Smith and Booman³⁾ and in using it have found that, when recording phase-selective polarograms, one obtains markedly negative waves for the 90°-phase component at far lower frequencies than in normal, total-component polarography. We have investigated this with some computer calculations and report the results here. Negative waves as described are likely to be encountered more and more frequently in view of the increasing use of phase-selective ac instruments.

Calculations

We took again the model system used in the previous work (ref. 1, Fig. 6) with the following parameter values: $n=2$ (no. of electrons transferred), $A=5.10^{-2}$ cm² (dme area), $d=1$ (ratio of diffusion coefficients of reduced to oxidised species), $D=10^{-5}$ cm² sec⁻¹ (diffusion coefficient), $\alpha=0.5$ (transfer coefficient), $T=300$ K°, $C_{ox}=1$ mM (bulk concentration of oxidised species) $V=15$ mV rms (applied ac voltage), $R_s=100$ Ω (series resistance), $C=0.5$ μ F (double-layer capacitance), $k=0.03$ cm sec⁻¹ (heterogeneous rate constant).

Total currents and phase angles at some frequencies and potentials were computed according to the equations given by Breyer and Bauer⁴⁾, and these were resolved into their 0° and 90° component currents and computer-plotted. Fig. 1 shows the two sets of curves thus obtained, which correspond to Fig. 6 in ref. 1. We note that the 0° component shows negative portions only at very high frequencies (here 6 kHz), but the 90° component becomes dented at the “summit” potential at frequencies as low as 60 Hz, and fully negative at above 600 Hz, which is about one order of magnitude below that for the total-component polarograms¹⁾. The difference between the two phase components is not surprising—at, say, 600 Hz and the summit potential, the faradaic admittance is predominantly resistive for this system and this makes the whole cell impedance more resistive, or less capacitive. One would also expect the negative-wave effect to be enhanced by increased concentration of the electroactive species where again the cell impedance becomes more resistive; Fig. 2 shows this to be true, for the same system at 600 Hz, with concentrations varying from 0.1 to 100 mM. We see that the in-phase waves remain positive, but the out-of-phase waves

Fig. 1. (a) In-phase and (b) out-of-phase polarograms for a range of frequencies (marked, in Hz) for $k=0.03$, $\alpha=0.5$, $d=1$, concentration = 1 mM (for full list of parameters, see text).

Fig. 2. (a) In-phase and (b) out-of-phase polarograms for the same system as in Fig. 1, at the constant frequency 600 Hz, and a range of concentrations (marked, in mM).

become markedly more and more negative (though showing also some positive portions). The limit to this decrease, of course, lies at zero out-of-phase current since at infinite concentration the faradaic impedance would be a short-circuit across the double-layer capacity, leaving only the series resistance, which has no 90° component.

Modern potentiostatic polarographs provide for iR compensation (i.e. instrumental compensation for the internal series resistance of the cell); the effects of varying degrees of compensation (expressed in %) are shown in Fig. 3. Again we see no negative effects on the 0° waves, but there is a transition from purely negative to purely positive waves in the 90° component as we go from 0 to 100% compensation. This is equivalent to reducing the series resistance from its full value (here 100Ω) to zero, where any capacitive components of the faradaic admittance would add simply to the capacitive double-layer admittance.

Fig. 3. (a) In-phase and (b) out-of-phase polarograms for the same system as in Fig. 1, at constant frequency 1000 Hz, and concentration 1 mM, for a range of iR compensation (marked, in %),

Fig. 4. Out-of-phase polarograms over a range of frequencies (marked, in Hz), for 1 mM Cu (II) in 1 M LiNO₃, 15 mV rms ac applied, no iR compensation; currents plotted against the summit potential, $E_s = 0.005$ V vs. SCE.

Fig. 5. Computer-simulated out-of-phase polarograms over a range of frequencies (marked, in Hz), corresponding to the system in Fig. 4 (for list of calculated parameters, see text).

Experimental

A set of experimental out-of-phase polarograms was recorded for the system 1 mM Cu(II) in 1 M LiNO₃ at 25°C. 15 mV rms ac voltage were applied to the cell and no iR compensation was used. Fig. 4 shows the resulting curves, which range from purely positive, at low frequencies, to purely negative at high frequencies. These

curves were then computer-simulated, using the experimentally obtained parameters $R_s=127\ \Omega$, $C=0.208\ \mu\text{F}$, $D_{ox}=0.859\times 10^{-5}\text{ cm}^2\text{ sec}^{-1}$, $D_{red}=1.064\times 10^{-5}\text{ cm}^2\text{ sec}^{-1}$ (*i.e.* $d=1.24$), $\alpha=0.695$, $A=0.0089\text{ cm}^2$, $k=0.049\text{ cm sec}^{-1}$, and concentration 1 mM . The computer simulation, for the sake of simplicity, assumed a potential-independent double-layer capacity—the experimental value at the summit potential—and this accounts for the fact that the generated curves shown in Fig. 5 lie on a “base” current of constant magnitude with respect to potential. With due regard to this qualification, however, Fig. 5 is a close simulation of the experimentally derived Fig. 4.

Discussion

One can now set down the conditions favourable to the appearance of these negative waves. They are: large series resistance—increasing iR compensation will eliminate negative waves—; large depolariser concentrations; small heterogeneous rate constant and increasing frequency, though, as mentioned, we note negative effects on the 90° component at lower frequencies than in the total component.

In the previous work¹⁾, we calculated the maximum possible decrease below the base current (a decrease of 13.4%); here the situation is simpler: the 90° component may become close to zero for large concentrations of depolariser, at iR compensation less than 100%.

Again we emphasise that such negative waves are not due to instrumental errors; the currents measured will produce, within the usual experimental errors, meaningful results in subsequent calculations. It is perhaps worth mentioning that negative waves are also observed in phase-selective tensammetric studies.

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