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Fourier Analysis of AC Polarogaphy: Kinetic Parameters for Zn(II)-1 M NaClO$_4$ and KCl Systems

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Synopsis. The fundamental and second harmonic responses of the Zn(II)/Zn(Hg) electrode agreed with the theory with respect to the phase angle. Th ekinetic parameters of the systems were: $k_s=(2.8\pm0.3)\times10^{-3}$cm/s, $\alpha=0.30\pm0.05$ in 1 M NaClO$_4$ and $k_s=(3.3\pm0.3)\times10^{-3}$ cm/s, $\alpha=0.27\pm0.03$ in 1 M KCl.

Fourier transform AC polarography has the advantage of allowing the simultaneous measurement of the amplitude and phase angle for the components of the fundamental and higher harmonic AC current.[1-8] This opens a way to investigate the reaction at the electrode surface with different time scales, and it would probably be very useful for kinetic investigations.

The purpose of the present paper is to examine, taking the Zn(II) ion as an example, whether or not any discrepancy exists between the fundamental(1st) and second(2nd) harmonic responses under the same experimental conditions.

The apparatus and experimental procedures were the same as those of the previous paper.[8] The frequencies, f, of the applied AC potentials were 27.9, 55.8, 111.6, and 173.6 Hz, each with an amplitude, ΔE, of 5 mV. All the chemicals used were of analytical reagent grade, except for Zn(ClO$_4$)$_2$·6H$_2$O, which was prepared by the usual method.

The actual steps of the measurements were as follows: 1) The kinetic parameters were first roughly estimated, by which the computer simulation of Procedure 2) was started. 2) Simulation was continued by varying the kinetic parameters until the calculated curve for cot ϕ *vs.* $\sqrt{w}$ at peak potential, E_p, of the 1st harmonic AC polarogram coincided with the experimental curves, where ϕ is the phase angle and ω is $2\pi f$. 3) The 2nd harmonic AC polarogram was then calculated by the use of the kinetic parameters which had just been obtained by the preceding procedure, after which the polarogram was compared with the experimental curve.

1) The standard rate constants of the electrode reaction, k_s, were calculated by means of Eq. (1);

$$\cot\phi = \frac{1}{k_s}\sqrt{\frac{\omega D}{2}},$$
$$D = D_o^{1-\alpha}\cdot D_r^{\alpha} \qquad (1)$$

where ϕ is the phase angle between the 1st harmonic AC current and the applied AC potential at the reversible half-wave potential, $E^r_{1/2}$. D_o and D_r are the diffusion coefficients of the oxidized and reduced forms respectively, and α, the transfer coefficient. By plotting cot ϕ against the frequency of the AC potential, k_s is calculated from the slope of the cot ϕ *vs.* $\sqrt{\omega}$ curve, with the intercept of 1.[14] In the present case, the cathodic peak potential, $E_p{}^c$, of the 2nd harmonic AC polarogram was used as the $E^r_{1/2}$ value, and α was roughly taken as 0.3 for both systems. These values of $E^r_{1/2}$ and α were actually the averages of the values in the literatures.[9-11,16] The observed values of k_s were $(3.5\pm0.9)\times10^{-3}$ cm/s for the Zn(II)-1 M NaClO$_4$ system and $(3.7\pm0.5)\times10^{-3}$ cm/s for the Zn(II)-1 M KCl system.

2) Simulation was performed by varying the values of k_s and α, until the calculated curve (cotϕ *vs.* $\sqrt{\omega}$) coincided with the experimental curves within the limit of experimental error, where theoretical calculation was based on the expanding-plane model.[13] The experimental values of cot ϕ used in this procedure were those obtained at E_p, where the current intensity is larger than that at $E^r_{1/2}$, which improved the precision of the phase angle. The kinetic parameters thus obtained for these systems were as follows: $k_s=(2.8\pm0.3)\times10^{-3}$ cm/s and $\alpha=0.30\pm0.05$ for Zn(II)-1 M NaClO$_4$ ([H$^+$]=1 mM), and $k_s=(3.3\pm0.3)\times10^{-3}$ cm/s and $\alpha=0.27\pm0.03$ for Zn(II)-1 M KCl([H$^+$]=1 mM). In these cases, D_o was obtained experimentally, and D_r was taken from Ref. 15.

3) Using the kinetic parameters obtained from the above procedure, the theoretical curves of the 2nd harmonic AC polarogram were described (Fig. 1). The frequency dependence of the several parameters, *i.e.*, the phase angles (Fig. 2), the ratio of $I_p{}^c$ to $I_p{}^a$

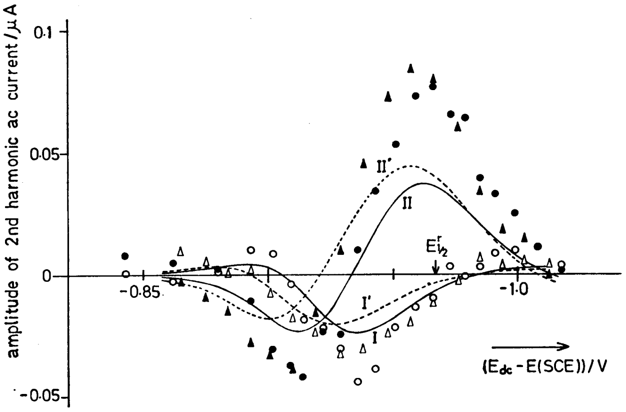

Fig. 1. 2nd harmonic AC polarogram of Zn(II)-1 M NaClO$_4$ ([H$^+$]=1 mM) system.
f=27.9 Hz; ○—in-phase component
●—quadrature component
f=111.6 Hz; △—in-phase component
▲—quadrature component
simulation curves for $k_s=2.8\times10^{-3}$ cm/s and $\alpha=0.30$
f=27.9 Hz (——), f=111.6 Hz (- - -)
I,I'=in-phase component
II,II'=quadrature component
ΔE=5 mV, n=2, [Zn(II)]=1.01 mM, $D_o=0.71\times10^{-5}$ cm^2/s, $D_r=1.70\times10^{-5}$ cm^2/s, drop time=3.58 s, electrode area=0.015 cm^2.

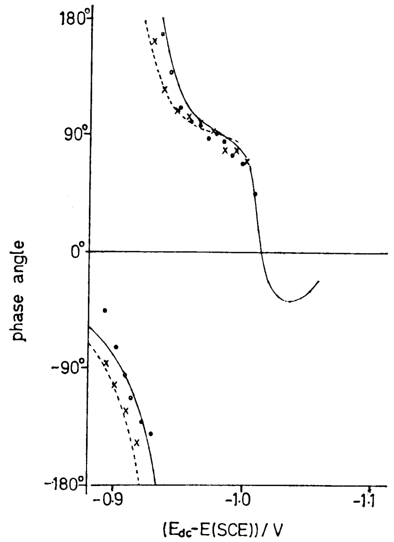

Fig. 2. Phase angle of the 2nd harmonic AC polarogram of Zn(II)-1 M $NaClO_4$($[H^+]=1$ mM) system.
o: $f=27.9$ Hz, x: $f=111.6$ Hz
simulation curves
$f=27.9$ Hz (——), $f=111.6$ Hz (----)
same parameters as Fig. 1.

(cathodic and anodic peak currents respectively), and the separation between E_p^c and E_p^a (the anodic peak potential), were consistent with the theoretical predictions. However, the amplitude of the experimental curve was considerably (about twice) larger than that of the theoretical one in both systems. To confirm that the discrepancy was larger than the experimental error, the D_o of Zn(II) (for the case of 1 M KCl solution) was measured by using different starting materials ($ZnCl_2$ and zinc metal). The D_o found after four measurements was $(0.73\pm0.02)\times10^{-5}$ cm^2/s; its error gave only an error of less than 2% in the amplitude.

In conclusion, the results for the 1st and 2nd harmonic AC polarograms for the present systems agree with each other with respect to the phase angle. The kinetic parameters obtained from the phase angle of the 1st and 2nd harmonic responses are in good agreement with those previously reported.[9–11,16]

The observed amplitude, which was larger than the theoretical one, is assumed to be due to the effect of the spherical diffusion. In the present systems, the departure of the measured amplitude from the theoretical amplitudes was larger than in the cadmium system.[8] This may be qualitatively interpreted in terms of the fact that the spherical diffusion influences both the surface concentration and the deviation from the electrochemical equilibrium.[17]

References

1) H. Kojima and S. Fujiwara, This Bulletin, **44**, 2158 (1971).

2) S. C. Creason and D. E. Smith, *J. Electroanal. Chem.*, **36**, A1 (1972).

3) *ibid.*, **40**, A1 (1972).

4) B. J. Huebert and D. E. Smith, *Anal. Chem.*, **44**, 1179 (1972).

5) S. C. Creason and D. E. Smith, *J. Electroanal. Chem.*, **47**, 9 (1973).

6) D. E. Glover and D. E. Smith, *Anal. Chem.*, **45**, 1869 (1973).

7) S. C. Creason and D. E. Smith, *ibid.*, **45**, 2401 (1973).

8) M. Hirota, Y. Umezawa, H. Kojima, and S. Fujiwara, This Bulletin, **47**, 2486 (1974).

9) T. G. McCord and D. E. Smith, *Anal. Chem.*, **42**, 126 (1970).

10) J. H. Sluyters and J. J. C. Oomen, *Rec. Trav. Chim. Pays-Bas*, **79**, 1101 (1960).

11) P. Teppema, M. Sluyters-Rehbach, and J. H. Sluyters, *J. Electroanal. Chem.*, **16**, 165 (1968).

12) D. E. Smith and A. J. Bard "Electroanalytical Chemistry," M. Dekker, New York, N. Y. (1966).

13) T. G. McCord and D. E. Smith, *Anal. Chem.*, **40**, 289 (1968).

14) J. K. Frischman and A. Timnick, *ibid.*, **39**, 507 (1967).

15) N. H. Furman and W. C. Cooper, *J. Amer. Chem. Soc.*, **72**, 5667 (1950).

16) P. J. Lingane and J. H. Christie, *J. Electroanal. Chem.*, **10**, 284 (1965).

17) J. R. Delmastro and D. E. Smith, *Anal. Chem.*, **38**, 169 (1966).