SHORT COMMUNICATIONS

A New Method for Determining the Potential of the Electrocapillary Maximum by the Vibrated Dropping Mercury Electrode

Hideo Imai, Senkichi Inouye and Shōkichi Chaki

(Received May 15, 1958)

The current-voltage curve of the mercuric ion was recorded with a conventional polarograph, using the vibrated dropping mercury electrode (VDME), to which an a. c. electric field is applied (cf. Fig. 1).

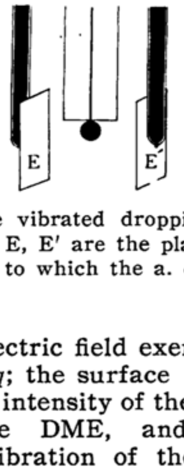

Fig. 1. The vibrated dropping mercury electrode: E, E' are the platinum plate electrodes to which the a. c. voltage is applied.

The a. c. electric field exerts a force as great as qE (q; the surface charge of the DME, E; the intensity of the a. c. electric field) on the DME, and causes the mechanical vibration of the DME. The vibration results in the increase of the limiting current of the electrolytic reduction of the mercuric ion, the convection current being superinduced on the diffusion-controlled one.

In the region of the positive polarization, the vibration gradually retards as the applied potential is shifted toward more negative potentials, corresponding to the decrease of the surface charge, and accordingly, the convection current gradually decreases. At the potential of zero charge, that is, the potential of the electrocapillary maximum, the vibration entirely ceases, and the limiting current is solely controlled by the diffusion. In the region of the negative polarization, the limiting current reincreases as the applied potential is shifted toward more negative potentials, corresponding to the increase of the surface charge. Thus, one can obtain the current-voltage curve which gives a minimum at the potential of the electrocapillary maximum, as is illustrated in Fig. 2. The more intensified is the electric field, the sharper is the "cut-in" of the minimum (cf. Fig. 2 A and B).

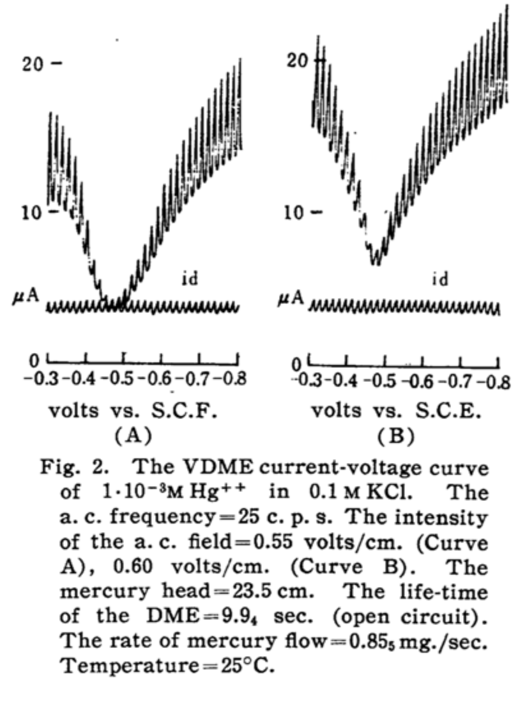

Fig. 2. The VDME current-voltage curve of $1\cdot10^{-3}$M Hg^{++} in 0.1 M KCl. The a. c. frequency=25 c. p. s. The intensity of the a. c. field=0.55 volts/cm. (Curve A), 0.60 volts/cm. (Curve B). The mercury head=23.5 cm. The life-time of the DME=9.9_4 sec. (open circuit). The rate of mercury flow=0.85_5 mg./sec. Temperature=25°C.

The potential of the electrocapillary maximum in various solutions was evaluated by this method, and the data gave a good agreement with those given by D. C. Grahame[1]. Among the various methods of measuring the potential of the electrocapillary maximum[2], this VDME method seems to be most promising in point of the ease and rapidness of the recording, of its good reproducibility and

1) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

2) D. C. Grahame, R. P. Larson and M. A. Poth, *J. Am. Chem. Soc.*, **71**, 2978 (1949). T. I. Popova and T. A. Kryukova, *J. physik. Chem.*, **25**, 283 (1951). J. A. V. Butler, "*Electrocapillarity*", Methuen Co. Ltd., London, (1940), p. 56.

accuracy. Moreover, this technique has the potentiality for the sensitization of the polarographic analysis as the rotated dropping mercury electrode[3] is the case.

Laboratory of Chemistry
Minami College
Hiroshima University
Hiroshima

3) G. Charlot, "*Modern Electroanalytical Methods*", Elsevier Pub. Co., Amsterdam, (1958), I. M. Kolthoff and Y. Okinaka, p. 83 and N. Tanaka et al., p. 97.