

THE INTERFACIAL TENSION OF THE MERCURY-1 M HClO₄-SOLUTION INTERFACE AT HIGH POTENTIALS; COMPARISON WITH DOUBLE-LAYER CAPACITANCE MEASUREMENTS

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INTRODUCTION

Applying the complex plane analysis method¹ to the impedance of the Hg₂²⁺/Hg electrode in 1 M HClO₄ solution we found that the differential double-layer capacitance increases steeply at potentials higher than +0.45 V vs. S.C.E.² The same result was obtained with an oscilloscopic method³.

In the potential region discussed here, the electrode reaction, $2 \text{Hg} \rightleftharpoons \text{Hg}_2^{2+} + 2e$, contributes to the cell impedance. It is essential, therefore, to make sure that the obtained capacitance values do not contain some reaction-controlled contribution that could eventually remain after subtraction of the Faraday impedance from the total cell impedance. This is possible by means of the determination of the interfacial tension, γ , which should show an abnormal decrease beyond 0.45 V in accordance with⁴

$$\frac{\partial \gamma}{\partial E} = -q(E) = -\int_0^E C_d dE \quad (1)$$

where $q(E)$ is the surface charge density and C_d the differential double-layer capacitance.

PROCEDURE AND RESULTS

Relative interfacial tension measurements were performed in an ordinary polarographic cell containing 1 M HClO₄, by means of drop-time measurements. The drop time was assumed to be proportional to the interfacial tension, without the application of further corrections⁵.

Moderately low potentials of the dropping mercury electrode were adjusted externally against a mercury pool counter electrode by means of a potentiometer. Some Hg₂(ClO₄)₂ was added to fix the potential of the counter electrode.

At high potentials, this procedure failed owing to polarization of the mercury pool electrode. In this region, the measurements were performed at various equilibrium potentials, which were adjusted by the addition of small quantities of a saturated Hg₂(ClO₄)₂ solution. This procedure has no significant influence on the composition of the cell solution except at potentials beyond 0.51 V.

The potential of the dropping mercury electrode was measured against a saturated calomel electrode with a potentiometric millivolt meter.

The plot of drop time against potential (Fig. 1) closely fits to a parabola with the electrocapillary maximum at -0.525 V vs. S.C.E. At high potentials, the expected deviation is observed*. This follows more clearly from Fig. 2, where the drop time is plotted against $(E - 0.525)^2$.

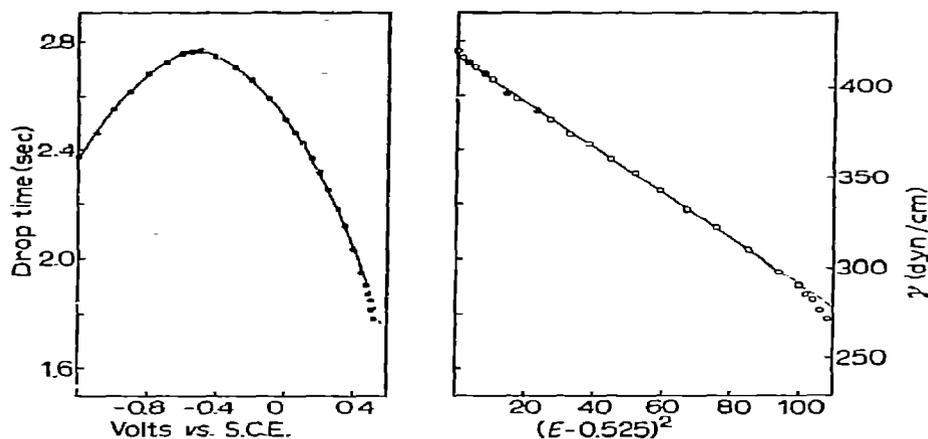


Fig. 1. Electrocapillary curve of mercury in 1 M HClO₄.

Fig. 2. Linearized electrocapillary curve of mercury in 1 M HClO₄.

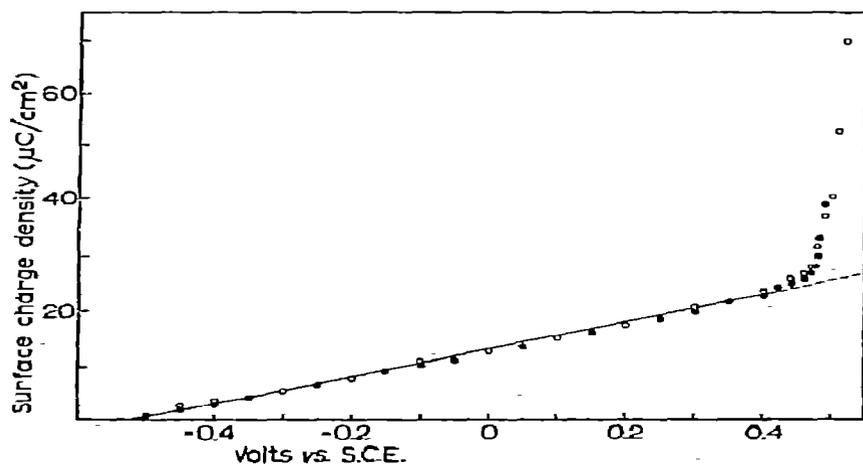


Fig. 3. Surface charge density of mercury in 1 M HClO₄: (—), calc. from Fig. 2; (O), obtained from the tangents of Fig. 1; (●), obtained by integration of capacitance data in refs. 2 and 3.

We ventured to convert the drop times to interfacial tensions, supposing the maximum value of γ to be 420 dyn cm⁻¹ (see *e.g.* ref. 6). The surface-charge density was calculated as a function of potential by graphical differentiation of the curve in Fig. 1. The results are represented in Fig. 3. It is easily verified that in the potential

* In view of the accuracy of the drop-time measurements (*ca.* 0.01 sec), this deviation is significant at potentials beyond 0.45 V.

region where the interfacial tension values fit to the parabola, this plot should be a straight line, the slope of which is twice the negative slope of the line in Fig. 2.

The surface charge density was also obtained by integration of the double-layer capacitance data published previously^{2,3}, taking the potential of zero charge at -0.525 V. Obviously, the results are in accordance with the electrocapillary data; this provides the desired further proof of the steep increase of the double-layer capacitance at high potentials.

DISCUSSION

Dr. R. PARSONS has kindly pointed out that a thoughtless application of the Lippmann equation is not allowed if an appreciable amount of potential-determining ions is present. For in this case the electrode is not completely polarized and, if the electrode reaction is sufficiently fast, the Gibb's equation for a completely reversible electrode should be considered:

$$-d\gamma = \sum \Gamma_i d\mu_i + \Gamma_{\text{Hg}_2^{2+}} d\mu_{\text{Hg}_2^{2+}} + \Gamma_e d\mu_e$$

in which μ is the chemical potential, Γ the surface excess, and i refers to all components except Hg_2^{2+} ions and electrons⁷. The chemical potentials of these species can be related to the potential difference across the interface by

$$dE = \frac{d\mu_{\text{Hg}_2^{2+}}}{2F} = -\frac{d\mu_e}{F}$$

Since it may be assumed that all other μ_i 's are virtually independent of potential, it follows that the derivative of the electrocapillary curve gives

$$-\frac{\partial\gamma}{\partial E} = F(2\Gamma_{\text{Hg}_2^{2+}} - \Gamma_e)$$

in which $\Gamma_{\text{Hg}_2^{2+}}$ is the sum of the surface excess, $\Gamma_{\text{Hg}_2^{2+}}(\text{M})$, on the metal side of the double layer and the surface excess, $\Gamma_{\text{Hg}_2^{2+}}(\text{S})$, on the solution side. This means that $-\partial\gamma/\partial E$ is not equal to the charge q on the electrode, but

$$-\frac{\partial\gamma}{\partial E} = q + 2F\Gamma_{\text{Hg}_2^{2+}}(\text{S})$$

If, however, the excess of Hg_2^{2+} in the solution exists only in the diffuse layer (no specific adsorption, which seems reasonable to assume as the electrode has a strongly positive charge) the correction will be negligibly small, since most of the excess of counter ions will be formed by the indifferent electrolyte, *i.e.*, H^+ and ClO_4^- ions, which are present in a much higher concentration.

These considerations are analogous to those given by OVERBEEK for a Ag/AgI electrode⁷.

The question arises, whether the quantity, obtained by integrating the capacitance-potential curve in the case of a perfectly non-polarized electrode, contains a similar correction or not. In our opinion, the capacitance, measured by an a.c. method in accordance with the equivalent circuit, represents only the charge supplied to the electrode, which does not pass the interface by a faradaic process but serves to increase or decrease the surface charge of the electrode. This implies that the second equality in (1) is still correct.

Consequently, the agreement between the integrated capacitance data and differentiated electrocapillary data might suggest that, in fact, $2F\Gamma_{\text{H}_2\text{S}_2^{2+}}$ (S) is negligible with respect to q in the potential region of our measurements.

SUMMARY

Interfacial tension values have been measured in order to calculate the electrical charge density as a function of potential. The results are in accordance with those obtained from double-layer capacitance data reported earlier^{2,3}, also at highly positive potentials.

REFERENCES

- 1 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, 82 (1963) 525.
 - 2 M. SLUYTERS-REHBACH AND J. H. SLUYTERS, *Rec. Trav. Chim.*, 83 (1964) 217, 967.
 - 3 J. H. SLUYTERS AND R. DE LEEUWE, *Rec. Trav. Chim.*, 83 (1964) 657.
 - 4 D. C. GRAHAM, *Chem. Rev.*, 41 (1947) 441.
 - 5 P. CORBUSIER AND L. GIERST, *Anal. Chim. Acta*, 15 (1956) 254.
 - 6 A. FRUMKIN, Transactions of the Symposium on Electrode Processes, Wiley, New York, 1961, p. 1.
 - 7 J. TH. G. OVERBEEK, *Colloid Science*, edited by KRUYT, Elsevier, Amsterdam, 1952, ch. IV.
- J. Electroanal. Chem.*, 13 (1967) 31-34