# **250.** *Differential Capacity Measurements in Aqueous and Methanolic Ammonium Chloride, Ammonium Fluoride, and Hydrochloric Acid in Relation to Anion Adsorption.*

By A. A. MOUSSA, H. M. SAMMOUR, and H. A. GHALY.

Differential capacities were measured in 0·1N-$NH_4Cl$ and -$NH_4F$ and in 1·0-, 0·3-, and 0·1-N-HCl, in water and methanol. For the first two electrolytes, in both solvents, earlier results were confirmed, and the method usually followed in interpreting the minimum capacity observed with increasing cathodic polarisation is discussed. In aqueous and methanolic hydrochloric acid solutions, reduction of hydrogen ions prevented extension of the measurements, and no capacity minima were observed within the cathodic potential range corresponding to ideal polarisation. The electrocapillary curves of mercury in the latter solutions were obtained. From the rate of change of the interfacial tension with the chemical potential of HCl, surface excesses of chloride ions were calculated for aqueous and methanolic 0·3N-hydrochloric acid, and the results compared.

GRAHAME[1] reported measurements of the differential capacity of the electrical double layer between mercury and methanolic salt solutions of ammonium chloride, fluoride, and nitrate. The outstanding features of the curves obtained for 0·1N-solutions are, first, the complete disappearance of the hump characteristic of the curves obtained in the corresponding aqueous solutions; secondly, the relatively low minimum capacity value, $C_{\text{min.}}$, of 9·0 μF/cm.$^2$ observed on the cathodic potential side compared with that observed in aqueous solutions, *viz.*,[2] 15·5—16·0 μF/cm.$^2$. At potentials less cathodic than that corresponding to $C_{\text{min.}}$, the curves diverged because of the specific adsorption of anions ($Cl^-$), but they coincided almost exactly at more cathodic potentials. Because of this similarity in behaviour, and by comparison with that observed in aqueous solutions, $C_{\text{min.}}$ was considered to indicate complete repulsion of any specifically adsorbed charge from the metal surface. Grahame pointed out that conclusive evidence could be obtained from the rate of change of the differential capacity with chemical potential, but the necessary data, the activity coefficient values in methanol, are lacking. From surface-tension measurements in aqueous and methanolic hydrochloric acid solutions, Parsons and Devanathan[3] had shown that anions are less readily repelled from a negatively charged mercury surface in methanol than in water. In methanol positive adsorption of the $Cl^-$ ions even at potentials corresponding to hydrogen evolution was reported, a result apparently not in accordance with Grahame's conclusion.

We measured differential capacities in 0·1N-aqueous and -methanolic ammonium chloride and fluoride under conditions differing only in minor details from those used by

---

[1] Grahame, *Z. Elektrochem.*, 1955, **59**, 740.

[2] Grahame, Poth, and Cummings, *J. Amer. Chem. Soc.*, 1952, **74**, 4422.

[3] Parsons and Devanathan, *Trans. Faraday Soc.*, 1953, **49**, 673.

Grahame. Measurements were also made in aqueous and methanolic 1·0, 0·3, and 0·1N-hydrochloric acid with a view to ascertain whether any evidence for the complete repulsion of anions from the interface could be obtained; the experimental conditions were such as to enable also the calculation of anion surface excesses.

## EXPERIMENTAL

Grahame's a.c. bridge technique of measuring the differential capacity of a spreading mercury surface [4] was used, but we adopted a simpler method of measuring area at the end of the drop time. The method has been repeatedly checked by Professor Grahame who did not find any difference between the results obtained at the end of the drop time and those obtained few tenths of a second earlier.[5] According to our procedure, in one solution and at constant polarisation, when the resistance $R$ and the capacity $C$ on the known arm of the bridge are adjusted at appropriate values, there is observed on the screen of the oscilloscope only one state of balance during the whole life of the mercury drop; $C$ and $R$ will then determine the apparent impedance corresponding to the area at that particular stage of growth at which balance occurs. By setting $R$ at a higher or a lower value and adjusting $C$, the state of balance could be made to correspond to an earlier or a later stage of growth respectively. With $R$ at its lowest possible value, $C$ is assumed to correspond to the area at the end of the drop time.

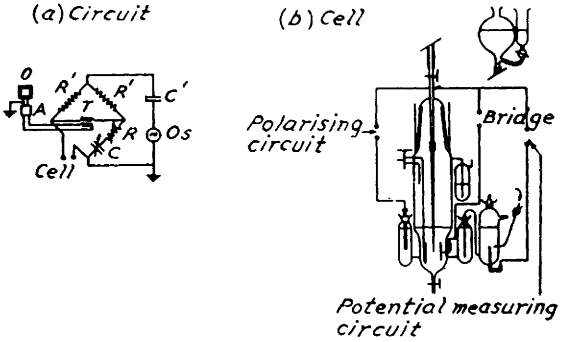

FIG. 1.

*O, Cossor-type oscilloscope.*
*A, Two-stage audio-amplifier.*
*R'*, 1000 *Ohm non-inductive resistances.*
*R*, 11,111 *Ohm standard resistance box.*
*C, Decadic condenser,* 0·0001—3·0 $\mu$F.
*Os, R.C. Oscillator.*
*C'*, 0·1$\mu$F *Condenser.*
*T, Audio-transformer.*

The various components of the bridge used, and the cell in which measurements were performed were as shown in Fig. **1**(*a*) and (*b*), respectively. The input to the bridge was 5 mv, and measurements were all made at 1000 cycles/sec. In aqueous hydrochloric acid the potential of the dropping-mercury cathode was varied with respect to a mercury anode in the same solution, an ordinary potentiometer being used in series with a mirror Onwood micro-ammeter. The potentiometer readings served only to indicate extent of polarisation. In the methanolic acid solutions the potential of the cathode was varied with respect to an auxilliary graphite electrode. In both solutions the potential of the mercury cathode against a hydrogen electrode in the same solution was registered on a valve circuit. In aqueous and methanolic ammonium chloride the mercury cathode was polarised directly against a decinormal calomel electrode in water. A filter-paper plug was used to minimise mixing of solvents. In ammonium fluoride solutions it was essential, with the type of cell used, to replace the calomel electrode by a mercury–mercurous sulphate electrode in aqueous 0·2M-sodium sulphate so as to eliminate the effect of $Cl^-$ ions.

The rate of flow of mercury was determined in each solution under exactly the same conditions as were subsequently followed during the measurements, from the mass and drop time of one hundred drops collected at open circuit. At each polarisation the time necessary for five drops to form was measured accurately to 0·1 sec. and an area factor was computed.

*Materials.*—Mercury (" Carlo Erba ") was purified by standard methods, then thrice distilled under vacuum. Methanol (Merck's " pro analysi ") was distilled once before use. A stock solution of hydrogen chloride in methanol was diluted as required. The aqueous acid solutions were prepared from a twice-distilled constant-boiling mixture. Ammonium chloride and fluoride (" AnalaR ") were used as supplied.

---

[4] Grahame, *J. Amer. Chem. Soc.*, 1941, **63**, 1207.
[5] *Idem*, personal communication.

The cell and its accessories, including the mercury reservoir, were all accommodated in an air thermostat provided with a sliding-front glass door. Measurements were all made at 25° ± 0·5°.

## RESULTS AND DISCUSSION

For the aqueous and methanolic ammonium salt solutions our results agree excellently with Grahame's.[1,2] Well-defined minimum capacities amounting, respectively, to 16·1 and 15·6 μF/cm.$^2$ in water and to 9·0 μF/cm.$^2$ for both electrolytes in methanol, were obtained. The corresponding potentials, with respect to the unpolarisable reference electrodes used, were −1·20 and −1·45 v in the aqueous solutions, and −0·90 and −1·15 v in the methanolic ones. For electrolytes which exhibit specific anion adsorption, $C_{\text{min.}}$ is usually considered to indicate complete repulsion of any specifically adsorbed charge, and according to Grahame,[6] the relation

$$1/C_{\text{min.}} = 1/C^0 + 1/C^d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

holds, $C^0$ being the differential capacity of the charge-free space between the mercury surface and the electrolyte, and $C^d$ that of the diffuse part of the electrical double layer. In 0·1N-solutions of uni-univalent electrolytes at 25°, the latter is given (in μF/cm.$^2$) by

$$C^d = 19{\cdot}47(q_M{}^2 + 0{\cdot}174D)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $q_M$ is the total surface charge density in μcoul./cm.$^2$, and $D$ is the dimensionless dielectric constant of the solvent. From our results in aqueous solutions, although equations (1) and (2) yielded a $C^0$ value of 17·1 μF/cm.$^2$ in agreement with values previously reported,[7] yet this was not so, *e.g.*, in methanolic solutions. For $C^0$ in methanol Grahame reported 9·2 μF/cm.$^2$, but when this is combined with the value for $C_{\text{min.}}$ of 9·0 μF/cm.$^2$, eqn. (1) gives $C^d = 414$ μF/cm.$^2$, a physically unacceptable value since from eqn. (2), $D$ for methanol being taken as 32·5, $q_M$ would be about 20 μcoul./cm.$^2$. The value experimentally obtained, however, was 5·7 ± 0·5 μcoul./cm.$^2$. Two consequences follow. By substituting the experimental $q_M$ value in eqn. (2), and combining the result with the observed value of $C_{\text{min.}}$, which is the procedure usually followed, $C^0$ will be found to be 9·8 μF/cm.$^2$, a value which is higher than that reported by Grahame. Alternatively, if $C^d$ as obtained from eqn. (2), by using the presumably accurate $q_M$ value of 5·7 μcoul./cm.$^2$, is combined with Grahame's value of 9·2 μF/cm.$^2$ for $C^0$, $C_{\text{min.}}$ would then be $\simeq$ 8·7 μF/cm.$^2$ as compared with the experimentally observed value of 9·0 μF/cm.$^2$: the difference is believed to be outside the limits of experimental error even with our relatively simple technique. However, it is possible that Grahame's theory does not apply strictly in solvents other than water.

The results of the differential capacity measurements in the aqueous and methanolic hydrochloric acid are shown in Fig. 2. On the cathodic side, measurements were extended only to those potential values indicated. Over the potential range used, the mercury-solution interface was believed to be ideally polarised. At more cathodic potentials a sudden rise in the charging d.c. current occurred, and the resistance values which gave balance showed simultaneously a marked increase. With the sort of a.c. bridge used, the above observations simply indicate leakage through the electrical double layer condenser as a result of a continuous discharge of $H_3O^+$ ions.[8] It was therefore considered unjustifiable to extend the measurements to more negative potentials under conditions which would limit the applicability of equations (1) and (2). Parsons and Devanathan [3] extended their surface-tension measurements to potentials as negative as −0·950 v. This, however, was intended by the authors for comparing the results of measurements of the rate of an electrode reaction with those derived from measurements at an approximately ideal polarised electrode. As judged from the present measurements, the differential

---

[6] Grahame, *Chem. Rev.*, 1947, **41**, 441.

[7] Devanathan, *Trans. Faraday Soc.*, 1954, **50**, 373.

[8] Frumkin, *Acta Physicochim. U.R.S.S.*, 1940, **13**, 799.

capacity curves for the various acid concentrations used tend to converge on the negative potential side, in both water and methanol, to a low common capacity value, but no well-defined minima which would indicate complete repulsion of the specifically adsorbed charge are observed over the potential range corresponding to ideal polarisation. Since in these solutions, measurements were made with respect to an electrode which is reversible to cations in the same solution, and the data for the activity coefficients in both solvents are available, the surface excess of the $Cl^-$ ions, $\Gamma$, may be readily obtained [9] from

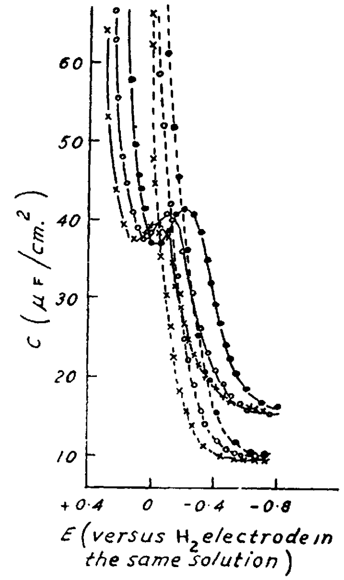

FIG. 2. *Differential capacity in the solutions: full lines, aqueous; broken lines, methanolic solution.*
×, 0·1N-HCl; ○, 0·3N-HCl; ●, 1·0N-HCl.

FIG. 3*a*.

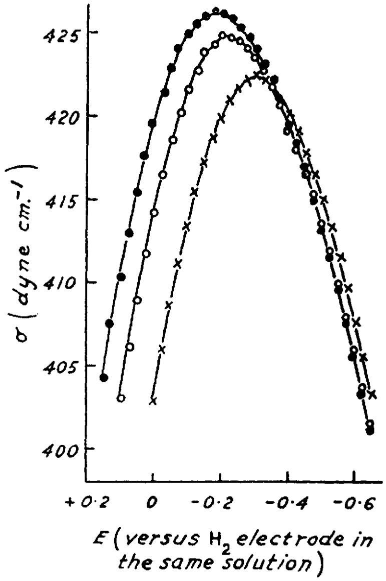

FIG. 3*b*.

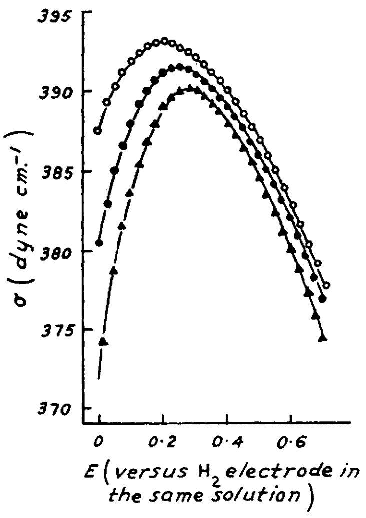

FIG. 3. *Electrocapillary curves in* (a) *aqueous solutions*: ●, 0·1N-HCl; ○ 0·3N-HCl; ×, 1·0N-HCl; *and* (b) *methanolic solutions*: ○, 0·1N-HCl;] ●, 0·3N-HCl; ▲, 1·0N-HCl.

$$-(d\sigma/du)_E = \Gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

[9] Ref. 6, p. 458.

where $u$ is the chemical potential of HCl,$\sigma$ is the interfacial tension, and $E$ is the measured potential. The $\sigma$ values as a function of $E$ were derived on the basis of the well-known thermodynamic relations:

$$-\,d^2\sigma/dE^2 = dq_M/dE = C \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

or

$$\iint_{E_{\text{e.c.m.}}}^{E} C\,.\,d^2E = \int_{E_{\text{e.c.m.}}}^{E} q_M\,.\,dE = \Delta\sigma \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

The values chosen for the co-ordinates of the electrocapillary maxima were those of Parsons and Devanathan. The electrocapillary curves obtained for the aqueous and methanolic solutions are presented graphically in Figs. 3(*a*) and (*b*). Direct comparison with previous results is not possible since in this case the $\Delta\sigma$ values are in fact the quantities that need to be compared. However, for the methanolic solutions, for example, the absolute $\sigma$ values over almost the whole potential range used scarcely differ from those obtained by Parsons and Devanathan by more than 0·5 dyne, which is the limit of accuracy with which the values can be read from their curves. The agreement is considered highly satisfactory for two sets of results obtained from two basically different methods of measurement.

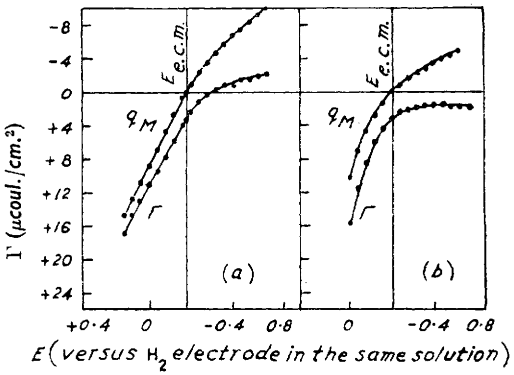

FIG. 4. *Surface excess,* Γ, *in* 0·3N-HCl: (*a*) *aqueous,* (*b*) *methanolic.*

From the rate of change of the interfacial tension with the chemical potential as given by equation (3), Γ values at 50 mv intervals were obtained for aqueous and methanolic 0·3N-hydrochloric acid. The activity coefficient values for the aqueous solutions were computed from Harned and Ehlers's data at 25°.[10] For 1·0, 0·3, and 0·1N-hydrochloric acid the values used were 0·809, 0·755, and 0·796 respectively. Those for the methanolic solutions were computed from Nonhebel and Hartley's data,[11] the corresponding values being 0·319, 0·343, and 0·437 respectively. In Fig. 4(*a*) and (*b*), the Γ values obtained are shown plotted against the polarising potential $E$. On the same figure the corresponding $q_M$ values are also shown. As can be seen from these results, Parsons and Devanathan's conclusion that chloride ions are less readily repelled from a negatively charged mercury surface in the methanolic than in the aqueous solution is further confirmed. If the positive adsorption observed in the methanolic solutions is to be ascribed to undissociated hydrogen chloride molecules rather than chloride ions, as suggested by Grahame,[12] this probably would have had its effect also at the uncharged mercury surface, which can hardly be deduced from the results of the present measurements.

FACULTY OF SCIENCE,
UNIVERSITY OF CAIRO.

[*Received, July 8th,* 1957.]

---

[10] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 2179.
[11] Conway, " Electrochemical Data," Elsevier Publishing Co., London, 1952, p. 94.
[12] Grahame, *Ann. Rev. Phys. Chem.*, 1955, **6**, 352.