

DIRECT MEASUREMENT OF THE DOUBLE LAYER CAPACITY AT THE SILVER IODIDE-AQUEOUS ELECTROLYTE INTERFACE

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1. INTRODUCTION

In the theory of Verwey and Overbeek¹ and Deryaguin and Landau² the stability of lyophobic colloids is determined by Van der Waals attraction and electrostatic double-layer repulsion. For the calculation of this repulsion details of the double-layer structure such as κ (the reciprocal double layer thickness), ψ_s (potential at the outer Helmholtz plane) and C_{st} (the capacity of the compact double layer or Stern layer) should be known. In principle all of these quantities may be derived from the double-layer capacity.

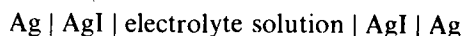
For colloidal systems the double-layer capacity has been determined indirectly by measuring the adsorption of potential-determining ions on a suspension as a function of the potential^{3–5}. This adsorption method yields the surface charge (σ) as a function of the potential (ψ) and one can calculate the differential capacity by differentiating the $\sigma(\psi)$ curves with respect to the potential.

An alternative method is the direct measurement of the capacity as has been done extensively for mercury⁶. In our laboratory it was decided to perform analogous measurements for the silver iodide–aqueous electrolyte interface and thus also to contribute to the general understanding of the stability of silver iodide sols⁷.

This study is a continuation of the work of Oomen⁸ and Engel⁹. Oomen developed the measuring technique and obtained some preliminary results on AgI electrodes. We extended both qualitatively and quantitatively the work of Engel. This was accomplished by introducing an improved purification technique in the preparation of the electrodes and the solutions and by using only pyrex glass and teflon in the cell construction. A greater variety of electrolytes in a wider range of concentrations and also several types of electrodes, including AgBr and Ag₂S, were used in our experiments. In this article we describe the experimental procedure and the results obtained for AgI electrodes in KNO₃ solutions of 5×10^{-4} to 1 M at 25°C.

2. OUTLINE OF THE METHOD

The double-layer capacity is derived from the impedance of the AgI/electrolyte solution interface, it can be determined by applying an alternating current to the cell:



The impedance of the cell can be written as:

$$\bar{Z}_{\text{cell}} = 2 \bar{Z}_{\text{Ag/AgI}} + 2 \bar{Z}_{\text{AgI}} + 2 \bar{Z}_{\text{AgI/el}} + \bar{Z}_{\text{el}} \quad (1)$$

where the complex impedance $\bar{Z} = Z' + jZ''$, with Z' as the real part and Z'' as the reactive part of \bar{Z} . The subscripts denote the Ag/AgI and AgI/electrolyte interfaces, the AgI crystal and the electrolyte solution. The equivalent circuit of the cell is represented in Fig. 1a.

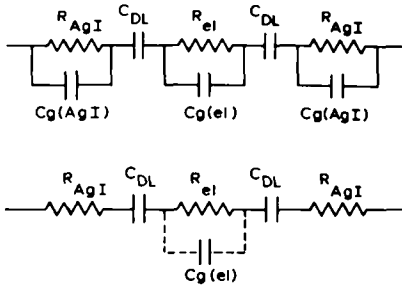


Fig. 1. (a) Equivalent circuit of the cell Ag|AgI|solution|AgI|Ag. (b) Reduced equivalent circuit. R_{AgI} = resistance of the AgI layer; $C_{\text{g(AgI)}}$ = geometrical capacitance of the AgI layer; R_{el} = resistance of the solution layer between both electrodes; $C_{\text{g(el)}}$ = geometrical capacitance of the solution layer; C_{DL} = double-layer capacitance.

To derive $\bar{Z}_{\text{AgI/el}}$ from eqn. 1 the following simplifications are introduced.

(1) Impedance measurements on the sandwich Ag/AgI/Ag showed that the impedance of the Ag/AgI interface is negligible with respect to \bar{Z}_{cell} , which is in agreement with results obtained by Armstrong *et al.*¹⁰.

(2) \bar{Z}_{AgI} is real, or $\bar{Z}_{\text{AgI}} = Z'_{\text{AgI}} = R_{\text{AgI}}$ (the resistance of the AgI film). In fact \bar{Z}_{AgI} is a parallel combination of R_{AgI} and the geometrical capacitance C_{g} . It may be readily calculated that the reactive part of \bar{Z}_{AgI} can be neglected if the frequency of the alternating current is lower than $16,000 \text{ cycle s}^{-1}$ and the specific resistance of the AgI layer is less than $10^6 \Omega \text{ cm}$ (ref. 9). We used a frequency of $2,000 \text{ cycle s}^{-1}$ in our experiments. The specific resistance of the AgI layers was in the order of $10^5 \Omega \text{ cm}$, which is comparable with the results of others¹¹⁻¹⁴.

(3) $\bar{Z}_{\text{AgI/el}}$ is entirely determined by the double-layer capacitance, C_{DL} , or $\bar{Z}_{\text{AgI/el}} = (j\omega C_{\text{DL}})^{-1}$, where ω is the circle frequency. The Faraday impedance can be neglected for frequencies greater than $1,000 \text{ cycle s}^{-1}$ (ref. 9).

(4) \bar{Z}_{el} is complex. The two electrodes form a capacitor shunted by the electrolyte solution resistance. When the reactive part of \bar{Z}_{el} is small:

$$\bar{Z}_{\text{el}} = R_{\text{el}} - j\omega C_{\text{g(el)}} R_{\text{el}}^2 \quad (2)$$

where $C_{\text{g(el)}}$ is the geometrical capacity of the solution layer and R_{el} is the resistance of the solution layer.

On introducing the partial impedances subject to the above simplifications eqn. 1 reduces to:

$$\bar{Z}_{\text{cell}} = 2 Z'_{\text{AgI}} + Z'_{\text{el}} + 2 j Z''_{\text{AgI/el}} + j Z''_{\text{el}} \quad (3)$$

$$= 2 R_{\text{AgI}} + R_{\text{el}} - 2 j/\omega C_{\text{DL}} - j\omega C_{\text{g(el)}} R_{\text{el}}^2 \quad (4)$$

The reduced equivalent circuit is given in Fig. 1b. From eqn. 4 it follows that:

$$Z''_{\text{cell}} = -2/\omega C_{\text{DL}} - \omega C_{\text{g(ell)}} R_{\text{cl}}^2 \quad (5)$$

The second term on the right-hand side can be neglected for electrolyte concentrations higher than 10^{-3} M. Even for 10^{-3} M solutions its contribution to Z''_{cell} is only 4% of that of the first term.

From eqn. 5 one notes that the double-layer capacity can be determined from the measurement of the reactive part of the cell impedance. For low concentrations a correction term due to the cell geometry must be introduced.

The determination of the double-layer capacity as a function of the potential (ψ) can readily be realized for the AgI electrode by changing the concentration of the potential-determining ions Ag^+ and I^- .

3. EXPERIMENTAL

3.1. Electrical set-up

The experimental set-up for the electrical part is essentially that used by Oomen⁸ and Engel⁹; a sketch of the arrangement is given in Fig. 2. An alternating current of about $10 \mu\text{A}$ is applied to the cell. A current-limiting resistor (R_L) is connected in series with the cell. The magnitude of this resistor is about 2,000 times the cell impedance thus making the current through the cell independent of the cell impedance. The voltage across the cell is then proportional to the cell impedance and is about 5 mV.

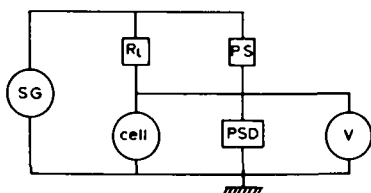


Fig. 2. Diagram of the electrical arrangement. (SG) signal generator; (R_L) current-limiting resistor; (PSD) phase sensitive detector; (PS) phase shifter; (V) voltmeter.

The alternating current of the signal generator (SG) is split into two parts, a reference signal through a phase shifter (PS) and a signal to R_L and the cell. The phase of the reference signal can be altered by the PS. Both signals are introduced in a phase-sensitive detector (PSD) whose output is proportional to the cell voltage and the reference signal if both are in phase. The phase is adjusted by substituting a non-reactive decade resistor (Sullivan type AC 440) for the cell, so that variation of the resistance does not change the output signal of the PSD. This procedure eliminates the contribution of Z'_{cell} to \bar{Z}_{cell} and thus only Z''_{cell} is measured. The value of Z''_{cell} was determined by substituting a reference capacitor of $3 \mu\text{F}$ (Sullivan C 1891) for the cell. The SG, PS and PSD are all incorporated in the same instrument, a lock-in amplifier model 220 from Princeton Applied Research.

The advantages of this set-up when compared with the alternating current bridge technique are the simplicity of the measurement and the rapid response

which makes it possible to follow the time dependence of the double-layer capacity. A disadvantage is the reduced accuracy of measurements in solutions of low concentration because of the large solution resistance in series with the double-layer capacity. As a check, the double-layer capacity was occasionally also determined with an a.c. bridge, the results of both methods being in good agreement.

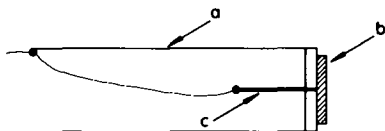


Fig. 3. The Ag/AgI electrode. (a) glass tube (2 cm diameter) with polished bottom; (b) deposited layers (Ag and AgI); (c) platinum wire.

3.2. The Ag/AgI electrode (see Fig. 3)

The Ag electrodes were prepared by evaporating silver (Drijfhout, 99.999% pure) in high vacuum. This method reduces contamination which could be introduced by the method of Oomen⁸ and Engel⁹ of polishing solid silver plates.

In a flat bottomed soft-glass tube a platinum wire was fused for electrical contact. After polishing the surface the tube was placed in a reflux-apparatus with isopropanol for about one h. At a pressure of 10^{-5} Torr a thin layer of chromium (about 100 Å) was deposited on the glass bottom, followed by a thicker non-transparent layer of silver (about 10,000 Å). The chromium layer was introduced to improve the adhesion of the silver to the glass surface. It appeared from electron photo-micrographs that the surface of this silver layer was flatter than that of polished silver plates.

The silver surface was allowed to react with iodine vapour, at room temperature and a reduced pressure of about 50 Torr, to yield a AgI layer about 1500 Å thick. This method was used because electrolytical preparation of the AgI layer produces an irregular coverage of the silver and considerable roughness of the AgI surface.

The electrodes were aged for six h at 80°C in the cell in a 10^{-3} M KNO₃ solution containing also 10^{-5} M KI.

3.3. The cell (see Fig. 4)

The cell consists of a pyrex-glass beaker (instead of the perspex used in ref. 9) with two side tubes for the electrodes and a lid with inlets for N₂ gas, the thermometer, the salt bridge with Van Laar¹⁵ capillary and for filling. The electrodes are held in place by teflon O-rings and screwcaps (Sovirel).

The position of the electrodes was controlled by a teflon tube, in which a flat ring was fixed. This construction was introduced because it produces a well-defined solution compartment between both electrodes so that there was no boundary effect and the geometrical correction (*cf.* eqn. 2) could easily be made. A further advantage is that it extends the life of the electrodes. The electrodes were not firmly pressed against the teflon ring to avoid damage of the AgI surface and to favour the stirring of the solution between them.

The temperature in the cell was kept constant at about 0.1°C by circulating water from a thermostat through the water-mantle.

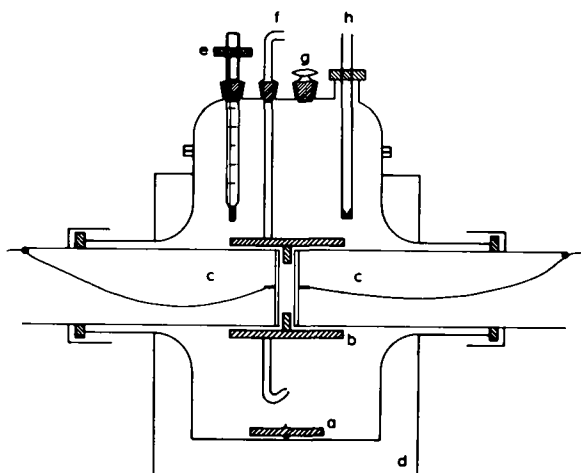


Fig. 4. Cell construction. (a) magnetic stirrer with teflon coating; (b) teflon tube with teflon ring; (c) two identical electrodes; (d) water mantle; (e) thermometer in teflon holder; (f) gas-inlet tube; (g) filling opening; (h) "Van Laar" capillary (connected to a salt bridge).

3.4. Materials

Twice-distilled water was used. After the first distillation (in a Barnstead, Model E.M.O. 5, still) the water was fed through a column of activated charcoal (Norit, R.O.W. 0.8 Sw speciaal) to remove surface-active agents, whereupon it was distilled in an all-quartz apparatus (Quartz et Silice, Model P.B.-15). After degassing by nitrogen the conductivity of the water was $10^{-7} \Omega^{-1} \text{cm}^{-1}$.

The chemicals used were all p.a. quality (B.D.H., Merck). Before use they were heated to a temperature just below their melting point or temperature of decomposition to remove surface active materials. The solutions were heated with a AgI suspension at 80°C to remove materials which otherwise may adsorb at the electrode surface.

The nitrogen was led over a B.T.S. catalyst (B.A.S.F.) and a molecular sieve (B.D.H., type 5A) to remove O_2 and CO_2 and through a suspension of AgI in water to remove surface active impurities.

3.5. Experimental procedure

Before use the cell was rinsed with a 5% HF solution and twice-distilled water and then heated with a AgI suspension for one day to remove impurities. Before the installation of the electrodes the cell was carefully rinsed. After filling the cell with a fresh solution the electrodes were allowed to come into equilibrium for several hours.

The concentration of potential determining ions (p.d.i.) was varied by dropwise addition of a 10^{-3} M KI or 10^{-3} M AgNO_3 solution with the same inert electrolyte concentration as used in the cell.

The p.d.i. concentration was determined by measuring the e.m.f. between the AgI electrode and a saturated calomel electrode (SCE) which was connected to the cell by means of a salt bridge. As the concentration of the Ag^+ and I^- ions is always much smaller than the inert electrolyte concentration the cell e.m.f. (E)

can be written as:

$$E = E''_{0,Ag} - (RT/F)pAg = E''_{0,I} + (RT/F)pI \quad (6)$$

where: E''_0 = standard potential including activity coefficients and diffusion potentials. pAg ; pI = the negative logarithm of the Ag^+ or I^- concentration. At a given inert electrolyte concentration and temperature the values of $E''_{0,Ag}$ and $E''_{0,I}$ were evaluated by measuring the e.m.f. of cells with solutions of known Ag^+ and I^- concentrations.

After each addition of p.d.i. the Z''_{cell} was measured after a constant e.m.f. was reached. At the same time the phase angle adjustment and the calibration with the $3 \mu F$ reference capacitor were successively checked. The phase angle proved to be very stable (within 0.02°).

4. RESULTS AND DISCUSSION

The experimental procedure described in the preceding sections yields Z''_{cell} as a function of the cell e.m.f., E . In order to derive the double-layer capacity per unit of surface area, C_{DL} , as a function of the potential ψ two additional quantities have to be known, namely the surface area of the AgI electrode and the pAg (or E , see eqn. 6) at the point of zero charge (p.z.c.).

Electron photo-micrographs showed that the AgI surface is rough on a microscopic scale. The roughness factor R_f , defined as the ratio between the microscopic and geometrical surface area, was estimated by using the assumption, introduced by Mackor⁴, that at the p.z.c. the double-layer capacity of the interface AgI/ $10^{-3} M KNO_3$ is equal to $6.0 \mu F cm^{-2}$ as measured for the Hg/ $10^{-3} M KNO_3$ system. A roughness factor of 2.0 was found, in close agreement with the value of 1.9 estimated by Engel from electron photo-micrographs.

Due to the large contribution of the diffuse double-layer capacity to the measured capacity, the p.z.c. and the minimum in the capacity curves occur at the same potential (corresponding to a pAg of 5.10) for low KNO_3 concentrations (less than $10^{-2} M$). Our value of 5.10 is lower than those reported in the literature^{5,9,14}. Based on the results of Lyklema⁵ that the pAg at the p.z.c. is independent of the KNO_3 concentration for concentrations exceeding $10^{-2} M$ (except for 1 M), the pAg at the p.z.c. was also taken equal to 5.10.

In Fig. 5 the double-layer capacity per square cm (C_{DL} in $\mu F cm^{-2}$) vs. the potential relative to the p.z.c. is plotted for 0.0005, 0.001, 0.003, 0.01, 0.05, 0.1 and 1 M solutions of KNO_3 . The values of the capacity for different pairs of electrodes agreed to within 10–15%. For one and the same pair of electrodes the reproducibility is much better (1–2%).

A comparison of our results with the curves determined by Engel⁹ for KNO_3 concentrations higher than $3 \times 10^{-3} M$ shows agreement within the range of deviation for different pairs of electrodes. From an integration of the capacity vs. potential curves the surface charge (σ) vs. potential (ψ) curves, shown in Fig. 6, are obtained. These curves can be compared with those obtained from adsorption measurements on AgI suspensions⁵. Agreement was found to within 10–20%. In the adsorption measurements the surface area of the suspension was estimated by means of positive adsorption of dyes and by negative adsorption of counter-ions.

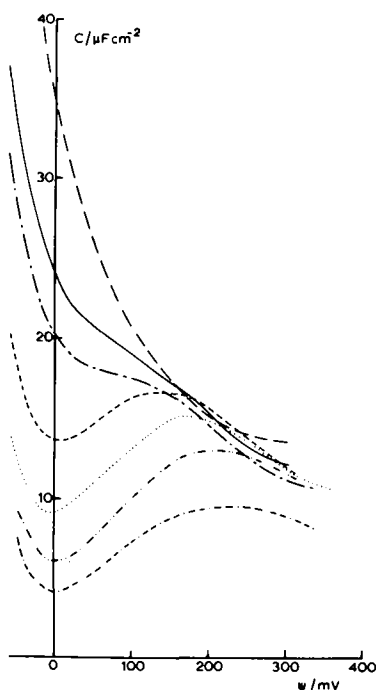


Fig. 5. The double layer capacitance (C_{DL}) as a function of the potential (ψ). (---) 5×10^{-4} M, (···) 10^{-3} M, (- · -) 3×10^{-3} M, (- - -) 10^{-2} M, (- · ·) 5×10^{-2} M, (- -) 10^{-1} M, (—) 1 M.

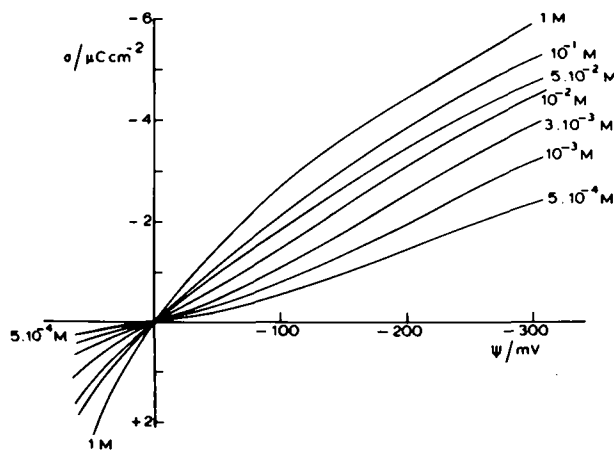


Fig. 6. The surface charge density (σ) as a function of the potential (ψ), obtained by integrating the curves of Fig. 5.

Summarizing, we conclude that different methods of determination of the capacities and the surface area yield the same results within the experimental accuracy.

To interpret our experiments we use the model of Gouy and Chapman as modified by Stern and assume the absence of specific adsorption^{6,7}.

In this model the surface charge σ is equal and opposite to that of the diffuse double layer ($\sigma = -\sigma_{diff}$). From the σ - ψ curves (see Fig. 6) the potential at the Outer Helmholtz Plane (o.h.p.), ψ_δ , and the diffuse double-layer capacity, C_{diff} , can be calculated from the relations:

$$\sigma_{diff} = (2RT\epsilon c_s/\pi)^{1/2} \sinh(zF\psi_\delta/2RT) \quad (7)$$

$$C_{diff} = (\epsilon c_s/2\pi RT)^{1/2} \cosh(zF\psi_\delta/2RT) \quad (8)$$

where c_s = electrolyte concentration, ϵ = permittivity, z = valency of the ions including sign, F = faraday constant, R = gas constant, T = absolute temperature.

The electrical equivalent of the double layer is represented by a series connection of the Stern or compact double-layer capacity (C_{St}) and C_{diff} to give the total capacity:

$$1/C_{DL} = 1/C_{diff} + 1/C_{St} \quad (9)$$

From the calculated C_{diff} and the measured C_{DL} , C_{St} may be determined. The accuracy of this determination depends on the magnitude of C_{diff} and C_{DL} .

For low KNO_3 concentrations where $C_{\text{DL}} \approx C_{\text{diff}}$ (especially near the p.z.c.) the values of C_{St} are less accurate.

It appeared from the measurements of Grahame¹⁶ on mercury that C_{St} is only a function of the surface charge and not of the electrolyte concentration. For AgI the same results are obtained for concentrations greater than $10^{-3} M$ (see Fig. 7). In the $10^{-3} M$ and $5 \times 10^{-4} M$ solutions however fluctuations in C_{St} exceed the limit of accuracy. For the Hg/HClO_4 and Hg/NaClO_4 systems analogous results were derived from the capacity *vs.* potential curves for concentrations below $10^{-4} M$, as determined in ref. 17. A possible explanation for this effect could be a lower hydrated ion density in the Stern layer.

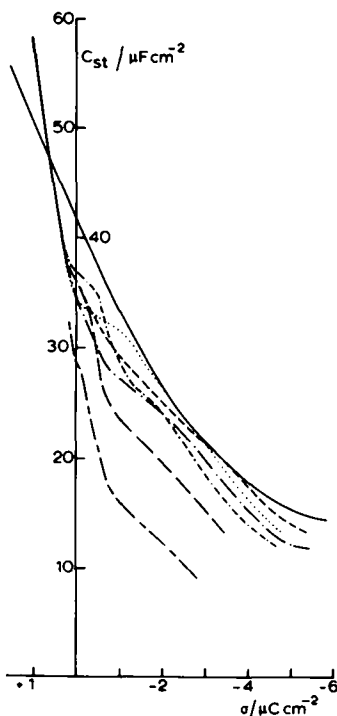


Fig. 7. The Stern layer capacitance (C_{St}) as a function of the surface charge density (σ). (—) $5 \times 10^{-4} M$, (— —) $10^{-3} M$, (— — —) $3 \times 10^{-3} M$, (— · —) $10^{-2} M$, (·····) $5 \times 10^{-2} M$, (— — —) $10^{-1} M$, (—) $1 M$.

The model used here may also be tested by an alternate method. Following Honig¹⁸ we write at the p.z.c. (see eqn. 9):

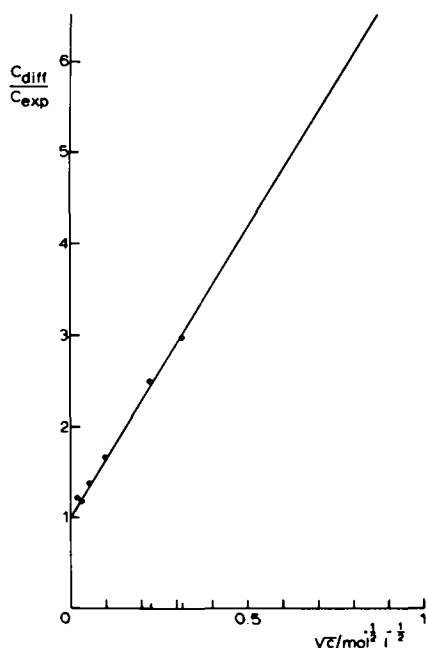
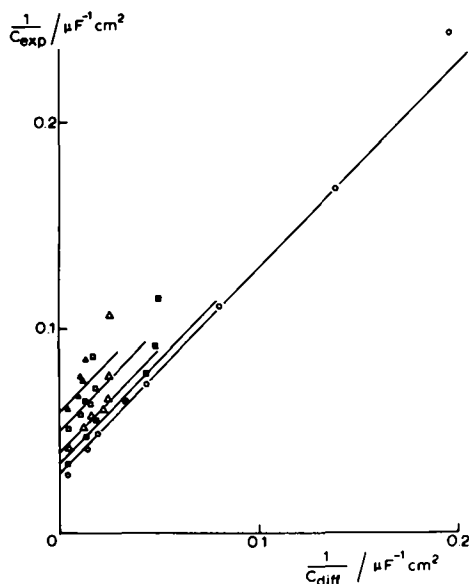
$$(1/C_{\text{DL}})_{\text{p.z.c.}} = (1/fC_{\text{diff}})_{\text{p.z.c.}} + (1/fC_{\text{St}})_{\text{p.z.c.}} \quad (10)$$

$$(C_{\text{diff}}/C_{\text{DL}})_{\text{p.z.c.}} = (1/f) + (C_{\text{diff}}/fC_{\text{St}})_{\text{p.z.c.}} \quad (11)$$

on using eqn. 8, C_{diff} can directly be calculated at the p.z.c. where $\psi_{\delta} = 0$. For KNO_3 solutions in water at 25°C , eqn. 11 can be written as:

$$(C_{\text{diff}}/C_{\text{DL}})_{\text{p.z.c.}} = (1/f) + (228.5 c_s^{\frac{1}{2}}/fC_{\text{St}})_{\text{p.z.c.}} \quad (12)$$

In eqns. 10–12 f represents a multiplication factor which should equal 1 if the estimate of the microscopic surface area is correct. According to eqn. 12 $(C_{\text{diff}}/C_{\text{St}})_{\text{p.z.c.}}$ when

Fig. 8. Plot of $(C_{diff}/C_{exp})_{p.z.c.}$ against \sqrt{c} .Fig. 9. Plot of $(C_{exp})^{-1}$ against $(C_{diff})^{-1}$, for $\sigma = 0$ (○), -1 (■), -2 (△), -3 (□), -4 (▲) $\mu C \text{ cm}^{-2}$.

plotted against $\sqrt{c_s}$ should yield a straight line with an intercept of $1/f$, such a plot of our data is shown in Fig. 8. The value of $1/f$ derived from the intercept equals 1.01 ± 0.05 , thus confirming the correctness of the normalization procedure and the justification for the applicability of the Gouy-Chapman-Stern model at the p.z.c.

Another way of comparing experiments directly with this theory was proposed by De Levie and Parsons⁶. They applied eqn. 9 at constant charge and plotted $1/C_{DL}$ against $1/C_{diff}$. A straight line with unit slope must be obtained for each value of the surface charge. The intercept is $(C_{st})^{-1}$ (see Fig. 9). As could already be expected by considering Fig. 7, deviations from linearity at low electrolyte concentrations are also apparent here.

5. CONCLUSION

With the present set-up the double-layer capacity at the AgI/electrolyte solution interface for concentrations greater than $10^{-4} M$ can be accurately measured.

At low concentrations the correction due to the cell geometry (see eqn. 5) increases rapidly with decreasing concentration. The results then become less reliable.

The reproducibility of the results with different pairs of electrodes is 10–15% and for one and the same pair 1–2%, which is better than can be achieved by the adsorption method.

The model of Gouy, Chapman and Stern without specific adsorption gives a satisfactory explanation of the experimental results, except at solution con-

centrations below 3×10^{-3} M. However it does not rule out the possibility that a small amount of specific adsorption does occur.

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SUMMARY

The double layer capacity at the AgI/KNO₃ solution interface was determined directly with the aid of an alternating current in the concentration range of 5×10^{-4} to 1 M.

To avoid contamination of the electrode surface a new cell construction was developed and the preparation of the electrodes and solutions was improved.

The results were interpreted in terms of the Gouy, Chapman, Stern theory.

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