RELAXATION OF THE SILVER/SILVER IODIDE ELECTRODE
IN AQUEOUS SOLUTION

Aan mijn ouders en schoonouders
Aan Els

K.J. Peverelli

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VOORWOORD

Het is een goede gewoonte om bij het verschijnen van een proefschrift te laten merken dat meerdere personen bij het onderzoek en de afronding daarvan hebben geholpen.

Ik dank mijn ouders die mij in staat hebben gesteld chemie te studeren en mij hebben opgevoed in het besef dat er meer is dan alleen materie.

Lieve Els, heel veel dank voor je steun in die perioden dat ik het met het schrijven somber inzag. Je zit terecht op de eerste rij.

Hooggeleerde Lyklema, beste Hans, ik dank je voor de grote vrijheid die je me bij het onderzoek hebt gegund en je geduld met een soms halsstarrige promovendus. Ook omdat de directe begeleiding van het werk niet in jouw handen lag, kon je me steeds het rechte pad van de kolloïdchemie voorhouden. Ik dank je voor de vakkennis die je met mij hebt willen delen.

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Verder wil ik alle collega's op het Van 't Hoff Laboratorium van de Rijksuniversiteit van Utrecht bedanken voor hun bereidwillige medewerking bij het lastige opdampwerk.

Tenslotte denk ik met genoegen terug aan het contact met alle collega's op het laboratorium.

STELLINGEN

I

Tijdens de interactie van deeltjes in een AgI sol blijft de lading per deeltje (inclusief die in de Sternlaag) constant. Er kan echter een locale verandering van de ladingsdichtheid optreden door ladingtransport in de vaste fase en laterale beweging van tegenionen.

> Dit proefschrift.

II

De problemen, die optreden bij het streven naar hoge waarden voor het produkt van de reciproke dubbellaagdikte en de deeltjesstraal bij het toepassen van diëlectrische meetmethoden op kolloïdale systemen, worden door Dukhin en Shilov in onvoldoende mate onderkend.

> S.S. Dukhin, V.N. Shilov, "Dielectric phenomena and the double layer in disperse systems and poly-electrolytes", Wiley and Sons, New York(1974), inleiding, hoofdstuk 2,3 en 5.
> M.M. Springer, proefschrift Wageningen(1979), hoofdstuk 1 en 2.

III

Omdat de berekening van rotatiecorrelatie tijden uit ESR metingen zeer gevoelig is voor de straal van het onderzochte molecuul, dienen Hyde en Hsia de wijze waarop deze is bepaald te vermelden.

> J.S. Hyde en L. Dalton, Chemical Physics Letters, 16,3(1972)568.
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IV

De beroepsaanduiding "logopedist" dient te worden vervangen door "communicatietherapeut".

V

Bij de beoordeling van de toxiciteit van kwik voor algen
houdt Kamp-Nielsen onvoldoende rekening met de vluchtig-
heid van metallisch kwik.

L. Kamp-Nielsen, Physiol. Plant. 24(1971)556.
J. Huisman en H.J.G. ten Hoopen, Water, Air and
Soil Pollution, 10(1978)325.
J. Huisman, H.J.G. ten Hoopen and A. Fuchs,
Environmental Pollution, (in press).

VI

Als gevolg van het niet in beschouwing nemen van dubbellaag-
effecten stellen Jagner en Árén ten onrechte dat de differentiële
vorm van potentiometrische stripping analyse voordelen biedt
boven de directe vorm. Daarnaast verdient het aanbeveling
potentiometrische stripping kurven te analyseren volgens de
procedures die in de chronopotentiometrie gebruikt worden.

D. Jagner en K. Árén, Anal. Chim. Acta, 100(1978)375.

VII

De wijze waarop Cuillel en medewerkers de specificiteit van de
in vitro reconstitutie van "brome mosaic virus" bepalen
is onjuist.

M. Cuillel, M. Herzog en L. Hirth, Virology, 95(1979)146

VIII

De Nederlandse overheid dient te bevorderen dat bij toeristische
evenementen ook aandacht wordt besteed aan de nieuwe ambachten.

Proefschrift K.J. Peverelli
"Relaxation of the silver/silver iodide electrode in aqueous
solution"
Wageningen, 2 november 1979.

CONTENTS

CHAPTER 1

GENERAL INTRODUCTION

A colloidal solution of silver iodide in water contains small particles with diameters of a few hundreds nm on which, depending on conditions, iodide ions or silver ions are adsorbed. If, for example, an excess of iodide ions is present in the solution, the particles will carry a negative electrical charge. This charge is compensated by an equal amount of positive charge in the solution around the particle. The negative charge adsorbed on the particle and the positive countercharge in the solution constitute the *electrical double layer*. The double layer can be divided into two regions: (i) the non-diffuse or Stern layer which is comprised between the particle surface and the plane of closest approach of counterions and (ii) the diffuse layer extending from the plane of closest approach of counterions to the bulk of the solution. For a more detailed description of the double layer concept and the consequences of the presence of the double layer for the dynamic properties of the interface, the reader is referred to the monograph by DELAHAY (1). The interfacial electrochemistry of silver iodide has recently been treated in a comprehensive review by BIJSTERBOSCH and LYKLEMA (2).

In the colloidal solution the particles are subjected to Brownian motion. If, due to this motion, two particles approach each other down to a distance where the diffuse double layers overlap, a *repulsive* electrostatic energy results. Furthermore, at short distance the Van der Waals forces are operative and this results in an *attractive* energy. It depends on the balance of these energies whether the particles will stay together forming aggregates which will finally lead to coagulation of the sol. A quantitative stability theory based upon the calculation of this balance as a function of the interparticle distance has been given in the DLVO theory (3, 4).

In the DLVO theory, two extreme cases are considered: (i) the charge on the particles is constant, or (ii) the potential of the particles with respect to the solution is constant. In the former case (i) the adsorption/desorption of the potential determining ions Ag^+ and/or I^- is considered to be too slow to take place during particle encounter. Thus the surface potential of the particle will increase upon approach of another sol particle. In the latter case (ii) the forementioned adsorption/desorption process is very fast and equilibrium between surface and solution is maintained during the encountering of particles. This means that now the potential is constant whereas the surface charge is decreased.

In order to directly investigate the nature and characteristics of relaxation processes like the forementioned adsorption/desorption process, a study was undertaken on the dynamic properties of the Ag/AgI *electrode* in aqueous solution. The interface of colloid chemical interest, i.e. the silver iodide/aqueous solution interface, is also part of the electrode system. Thus it is possible to study this interface using techniques known from electrode kinetics. The kinetic parameters obtained can be represented as characteristic time constants for the specific relaxation processes and then compared with the characteristic time constants of the colloid chemical system.

The coulostatic pulse method was adopted as the electrochemical technique to be used. In this method, the perturbation of the electrical double layer on the electrode is brought about by a short current impulse with a duration of about 0.5 μsec. After pulse application, the relaxation of the electrode potential is measured as a function of time. The potential/time curve is then analyzed via Laplace transformation. The main parameters to be evaluated are the exchange current density and the (differential) double layer capacitance.

In addition to the relaxation measurements, experiments were carried out to obtain characteristic information about the AgI film on the electrode. This proved to be necessary for the interpretation of the relaxation measurements in terms of charge transfer processes in the interface AgI/electrolyte solution.

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CHAPTER 2

INVESTIGATIONS OF FUNDAMENTAL PROPERTIES OF THE SILVER/ SILVER IODIDE FILM ELECTRODE

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ABSTRACT

A study is presented of the basic physicochemical properties of vacuum deposited silver/ silver iodide film electrodes. X-ray analysis and electron microscopy yield information on the crystal structure and morphology of these films. The AgI was predominantly present in the γ modification. On the AgI surface irregularities are observed with diameters of 100 nm and lower. Aged surfaces show smaller irregularities than non-aged surfaces. The total roughness factor is estimated at 1.5 with an uncertainty of at least 10%. Methods are presented to determine the average film thickness and the conductivity of the film. The films used have a thickness of about 350 nm. The specific conductivity of the AgI film is approximately 10^{-4} Ω^{-1} cm^{-1}.

INTRODUCTION

Colloidal solutions and precipitates of AgI are, among others, often used as model systems in colloid and surface chemistry [1—3]. For instance, in colloid chemistry the stability characteristics of a silver iodide sol are usually interpreted in terms of the properties of the silver iodide/aqueous solution interface. Independent means of investigating this interface have been sought for and therefore several types of experiments have been carried out on *suspensions* of AgI in addition to the classical colloidal experiments. For a survey of these matters, the reader is referred to a recent review [3].

In order to study the double layer properties of the silver iodide/aqueous solution interface, measurements have also been carried out on silver iodide *electrodes.* In that case, a layer of AgI is usually mounted on top of a silver substratum. Oomen [4] prepared his electrodes by anodizing a silver plate in an iodide solution. However, it is well known now that electrolytically prepared Ag/AgI electrodes show a high degree of roughness and porosity. From the work of Engel [5] it appeared that the AgI layers prepared by reaction of solid silver with gaseous iodine show a relatively simple geometric shape. The latter procedure was improved by Pieper and De Vooys [6]. Almost without exception, these Ag/AgI film electrodes have been used to find double layer capacitances employing impedance measurements. Although there is reasonable agreement between capacitances evaluated from surface charge measurements [3] and capacitances found directly from electrode impedance measurements [5,6],

some related problems remain unsolved. We mention: frequency dependence of capacitance, different values for roughness factors of electrode surfaces and great uncertainty as to the value of the specific conductivity of AgI. These problems are often interrelated, for instance in the sense that the evaluation of double layer capacitances from impedance measurements is affected by resistance effects down to surprisingly low frequencies [7]. It seems quite necessary to study carefully the fundamental properties of the Ag/AgI electrode.

In addition to the foregoing another point deserves attention. So far, the *static* properties of the AgI/aqueous solution interface have been the object of investigation. However, often the dynamic properties (relaxation effects in the double layer, faradaic relaxation, etc.) are important as well. As a part of our investigations concerning *both* static *and* dynamic properties of the AgI/aqueous solution interface, we have established some fundamental characteristics of the Ag/AgI film electrode. The present paper deals with the results of this study in terms of crystal structure of the AgI film, roughness of the AgI surface, thickness of the film and specific conductivity of the AgI in the film.

EXPERIMENTAL

All chemicals used were of p.a. quality (Merck) and used without further purification. In all cases the silver used was taken from "specpure" silver rods with a purity grade of 99.999%. The water used was distilled and percolated through a column containing precipitated AgI thereby removing all surface active agents. In the following, this water will be denoted as AgI-water. All glassware used in the experiments was thoroughly cleaned before use with concentrated chromic acid. After that all parts were rinsed with dilute nitric acid and AgI-water.

Preparation of the electrodes

The procedure used in making the electrodes is roughly the same as that used by Pieper and De Vooys [6]. The electrode consists of a soft glass tube with a flat bottom in which a platinum wire is fused to make electrical contact with the outer surface. The bottom of the tube was polished with the aid of a Struers polishing machine using different types of silicon carbide paper with decreasing roughness. In the final polishing stage a diamond paste was used which contained particles with an average diameter of 6 μm. In order to clean the electrode surface, the electrodes were placed in a reflux apparatus for at least 30 min containing propanol-2. A schematical drawing of the electrode is given in Fig. 1.

The Ag layer was deposited on the glass surface in a high vacuum apparatus (Edwards) at a pressure of 6.8×10^{-3} N m^{-2}. First, a thin film of chromium was deposited to improve the adhesion of the silver to the surface. By using a metal mask a circular surface was created with a surface of 0.20 cm^2 which is equal to the geometrical surface area of the electrode. The silver iodide film was prepared using a glass bulb which was connected to a flask containing iodine vapour at a pressure of about 6.8×10^3 N m^{-2}. The electrodes were allowed to react with the vapour during one minute. Films, prepared in this
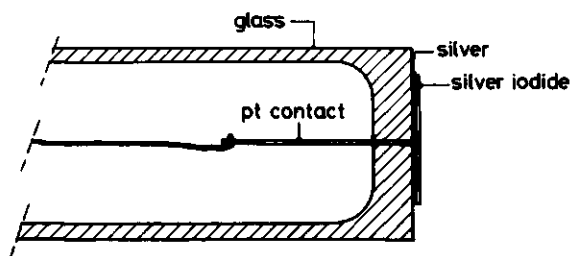
Fig. 1. Diagram of an Ag/AgI electrode with deposited layers.

way all showed an average thickness of about 3.5×10^2 nm. If the electrodes were aged, this was done in a 10^{-3} M KNO$_3$ solution at a pI of 5 for at least 6 h at a temperature of 80°C.

X-ray analysis

It was not possible to separate the film from the silver so as to collect enough material to perform direct X-ray analysis on the electrode material. Small amounts of AgI powder were therefore prepared in a way analogous to the film preparation procedure: a silver rod of 10 cm length was thoroughly cleaned and dried and then placed in the bulb. In order to obtain a sufficiently thick film, some iodine crystals were placed in the bulb to assure saturated vapour conditions. After a few hours the rod was taken from the bulb and after ageing the AgI was carefully scraped off the rod using the sharp edge of a spatula. After this, the rod was polished with silicon carbide paper and cleaned with distilled water and ethanol and dried. The procedure was then repeated until a few mg AgI were obtained.

Precipitated AgI was prepared by dropwise addition of a 0.1 mol l^{-1} solution of AgNO$_3$ to a 0.1 mol l^{-1} solution of KI. The precipitate was washed with distilled water and ethanol and dried. Thus, four powder samples were obtained: deposited and precipitated AgI, both aged and non-aged. The diffraction patterns for the four samples were measured on a Philips PW 1050 powder diffractometer using a Co X-ray tube.

Electron microscopy

The surfaces of the aged and non-aged electrodes were studied using a Philips transmission electron microscope. Replicas of the surfaces were prepared by shadowing the surfaces by a platinum and carbon beam at angles of 25° and 40°, respectively. Thereupon the surface was covered with a second layer of pure carbon by means of a beam perpendicular to the surface. The Pt-C/C layer was separated from the silver surface with a 2 mol l^{-1} HNO$_3$ solution. The separation of the AgI and the Pt-C/C layer was performed by a dilute solution of KCN or by a 2 mol l^{-1} HNO$_3$ solution. This method was also used by Engel [5].
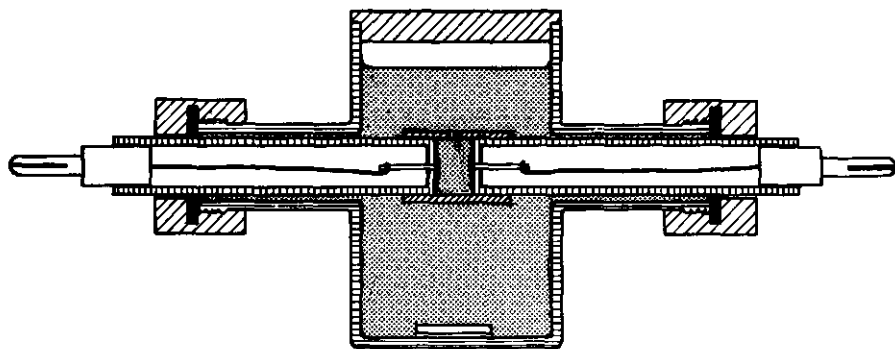
Fig. 2. Diagram of the conductivity cell. (The cell is placed in a thermostated waterbath.)

Determination of the film thickness

The amperostat used in the experimental set-up is a Metrohm coulometer E 211, other components being standard equipment. The cell contained a 0.1 mol l^{-1} solution of KI in distilled water.

Determination of the resistance of the film

In order to obtain a value for the resistance of the film the electrodes were placed in the cell sketched in Fig. 2. The electrode surfaces are held in a fixed position to each other by means of a small perspex cylinder. This set-up was used before by Pieper and De Vooys who measured the capacitance of the system by means of an impedance bridge [6]. Using this set-up a conductivity cell of known geometry is created which permits the estimation of the solution part of the total cell resistance. The two electrodes are connected to the cell by means of two Sovirel screwcaps with inner teflon rings. The temperature of the complete cell was maintained at 25.0 ± 0.1°C. To be able to measure the resistance of the film which is expected to be in the range of 1 to 100 Ω, a high conductivity in the solution is established by using a 1 mol l^{-1} KNO$_3$ solution [8,9]. No nitrogen is led through as this had no effect on the measured values for the cell resistance.

A Wayne Kerr Universal Bridge B 224 was used which measured the cell capacitance C_p and resistance R_p in a parallel arrangement. A Rohde Schwarz SUB EN 408070 wave generator was used. This instrument also served as zero indicator, being more sensitive than the indicator of the bridge system itself.

RESULTS AND DISCUSSION

X-ray analysis

The study of the crystal structure of precipitated AgI has been the subject of several investigations [2,8,10]. At room temperature and normal pressure two stable modifications are found: the cubic or zinc blende type and the hexagonal or wurtzite type. These two modifications are denoted as γ-AgI and

β-AgI, respectively. The influence of various precipitation conditions like pH, temperature, activity of potential determining ions and rate of coagulation were investigated by Despotović [2]. The precipitation of AgI from a solution containing excess silver ions, gives rise to formation of almost pure γ-AgI. If iodide ions are in excess, the β modification precipitates [2,10].

X-ray analysis was performed on four different powder samples which were prepared as described in the experimental section. The diffraction pattern measured for the aged silver iodide which was grown on silver by vapour phase reaction is given in Fig. 3. The numbers of reflections and their relative intensities were compared with the NBS standard diffraction data for the γ and β modification [11]. Apart from the first peak at about 13°, all reflections are either characteristic for γ-AgI or common to both modifications. Specific reflections for β are not present except the one at 13°. The diffraction pattern of the non-aged *deposited* sample did not show pronounced differences with the one given in Fig. 3. The diffraction pattern measured for the *precipitated* sample is given in Fig. 4. The aged and non-aged samples which were prepared from precipitated silver iodide show all reflections of both modifications indicative of a mixture of γ and β. This is in agreement with the results of Lyklema [10] and Despotović et al. [2]. As with the deposited AgI, no influence of the aging on the diffraction was found.

As a further confirmation of the emerging picture, all four AgI samples were photographed using an optical microscope. The precipitated silver iodide particles show a considerable increase in micro crystal size when the material is aged. No such effect could be observed in the case of deposited silver iodide. This is due to the method of preparation: on the photographs it could be seen
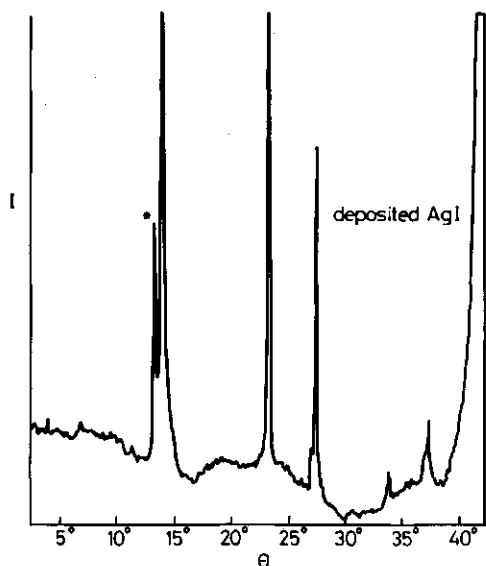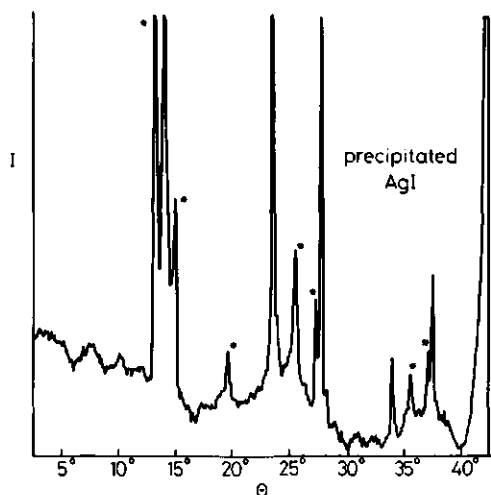

Fig. 3. X-ray diffraction pattern of deposited AgI.

Fig. 4. X-ray diffraction pattern of precipitated AgI. Reference to the symbol * is made in the text

that the particles are in fact fragments of the layer scraped off by the spatula.

From the results we conclude that in silver iodide films formed on silver by reaction with iodine vapour under reduced pressure, the cubic or γ modification strongly prevails.

Surface characterization — electron microscopy

Investigations of thin silver iodide films using electron microscopy have been carried out by several authors [5,12,13]. The process of ageing and the conditions under which the film is formed strongly influence the shapes and distribution of the micro-crystals [12]. Engel used electron micrographs to estimate the roughness of the surface [5]. He studied films grown on polished silver plates.

In order to compare our AgI surface with these earlier results, electron micrographs were made of the surfaces of the silver layer and of the AgI film. Because the films are destroyed by making the replicas it is not possible to study the same part of the surface before and after aging. The pictures shown therefore refer to different electrodes but this is not a serious drawback, since the systematic differences between the three types of surface are easily recognized. Figure 5 shows the polished glass surface covered with deposited Ag. The scratches are caused by the final polishing stage and are still clearly visible although less pronounced than on Engel's electrodes where polished silver was used [5]. The small grains which are uniformly distributed on the surface might be attributed to condensation of clusters of atomic silver e.g. a special type of growing of the silver lattice [12]. However, it is clear from the electron micrographs that these grains are no longer present on the AgI surface.

Micrographs of the surfaces of non-aged and aged AgI films are shown in Figs. 6 and 7, respectively. The black regions on the micrographs are probably due to traces of silver iodide which were not removed during the processing of the replica. One of the most pronounced differences between the two surfaces is the more crystalline character of the aged surface. Anyway we have to do with a net growth of large crystals at the expense of smaller ones, i.e. with Ostwald ripening. Still, on the aged crystals small hummocks are visible which were also observed by Engel [5]. He suggested that they are due to slow recrystallization during the aging process after the fast growth of the underlying crystals during the reaction of the iodine molecules with the surface. However, our findings are that the non-aged surface (Fig. 6) shows rounded structures with vague contours of crystals. In this case the hummocks seem to be even bigger which rules out the possibility that they originate during the ageing. A more probable explanation is that during aging, mass transfer takes place from these hummocks to the underlying crystalline surface. These crystals grow and take a more pronounced shape while the hummocks decrease to the residual ones in Fig. 7. Engel suggested that the hummocks were caused by the ageing and they would not be present at the non-aged surface [5]. However, his pictures of these surfaces are rather vague and white spots on it might possibly be small hummocks. Furthermore, our findings are in accordance with earlier observations of Ostwald ripening [12] and with the results of direct measurements of the double layer capacitances of both the aged and the non-
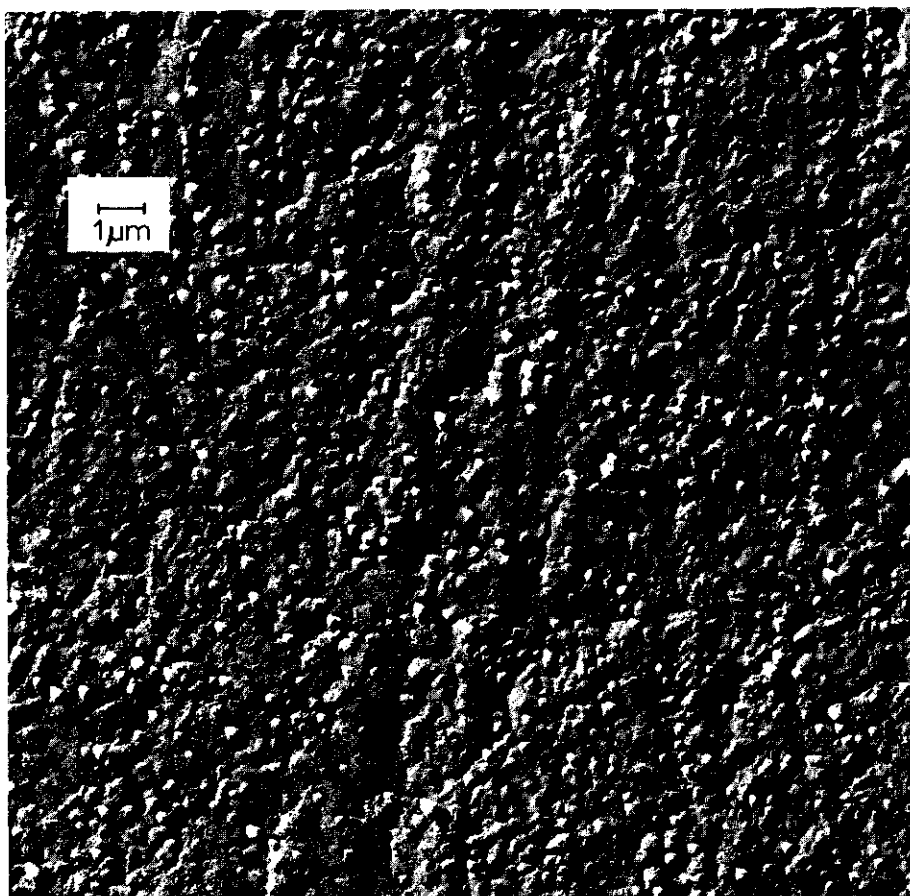
Fig. 5. Electron micrograph of the surface of a silver layer deposited on polished glass. Magnification is 70,000 for all three micrographs.

aged AgI electrodes in aqueous solution [14]. In these measurements it appears that the ageing process is accompanied by a considerable decrease of the double layer capacitance.

On the basis of the present data and in view of earlier attempts [5], a decision has to be made about the relation between the real area and the geometric area of the AgI surface. Before we do so, it has to be pointed out that the frequently used term "roughness factor" does not always have the same unambiguous meaning. Let us for instance suppose that irregularities with an order of magnitude of 2.5 nm are present on the surface of an AgI electrode. Looking at the electrical double layer at the electrode/solution interface, the compact Stern layer would have a thickness of about 0.5 nm and the diffuse double layer thickness in the case of a 10^{-3} mol l^{-1} solution of a 1-1 salt would be of the order of 10 nm. In this example the Stern layer would "follow" the micro surface including the irregularities, whereas the diffuse double layer mainly "sees" the geometric surface. Consequently, the Stern layer capacitance is related to the total micro surface area (= geometric surface × roughness factor
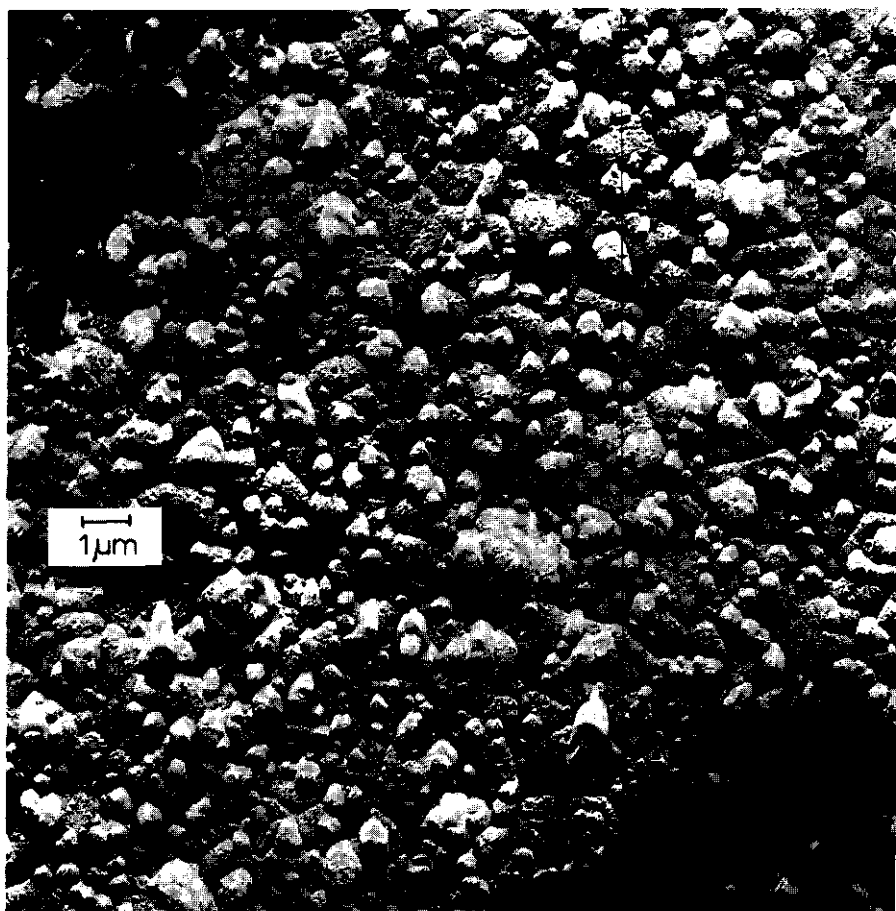
Fig. 6. Electron micrograph of the surface of a non-aged AgI film covering the silver layer.

accounting for the irregularities), and the diffuse layer capacitance is not. Of course, the situation can even be more complicated in the sense that also irregularities with higher dimensions are present. A rigorous treatment in such a case would require some functional relationship between the effective roughness factor and the characteristic length of the feature studied. For instance, in applying more than one roughness factor for one and the same surface. Especially in applying relaxation techniques to solid electrodes with a certain degree of roughness one should be aware of the fact that a "growing" diffusion layer "sees" a gradually diminishing surface area.

Returning to the AgI surfaces of Figs. 6 and 7 we recall that it has been established that the largest irregularities are of the order of 100 nm for a non-aged surface and clearly smaller for aged surfaces. Especially in the case of the aged surface we see that the irregularities have very different dimensions, anyway down to about 2.5 nm which corresponds with the resolution limit of the electron microscope. Quite *arbitrarily* we denote the roughness in the range 100 nm to 2.5 nm as the primary roughness. The corresponding primary rough-
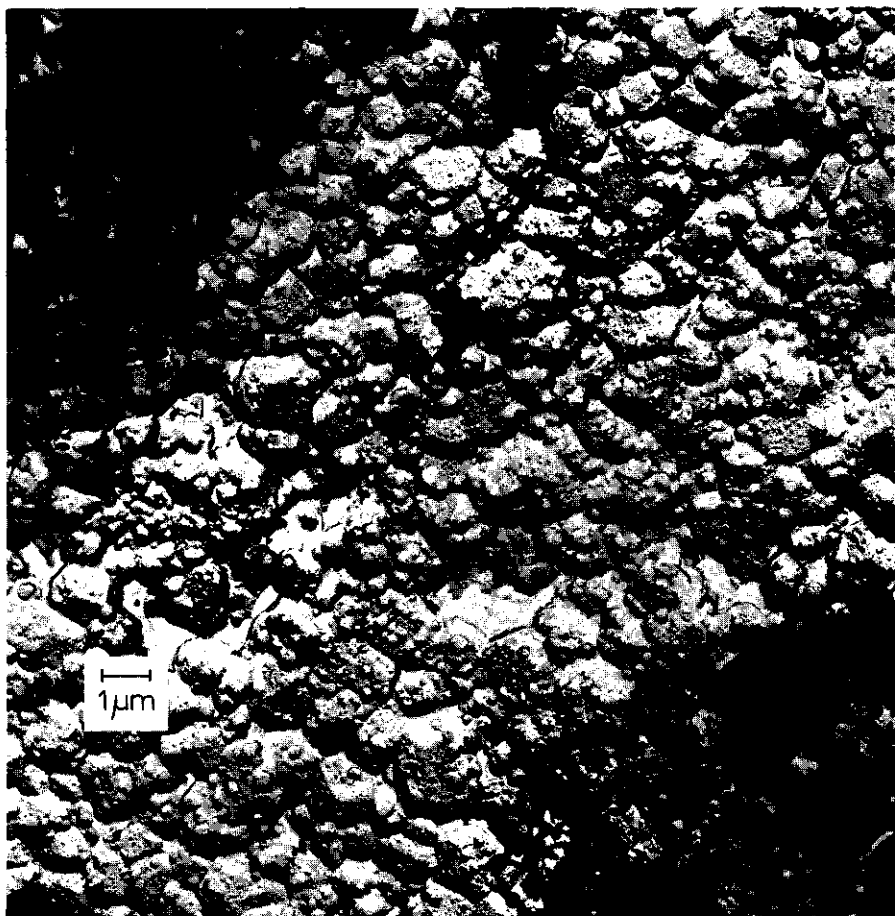
Fig. 7. Electron micrograph of the surface of a similar AgI film after ageing.

ness factor r_1 is defined as the ratio between the total surface area including microareas with a diameter down to 2.5 nm and the geometric surface area. By stereoscopic analysis and counting of hummocks on completely comparable aged AgI surfaces a value of 1.42 was found for r_1 [5]. The analysis by De Vooys and Pieper [15] will not be followed here because the surfaces obtained by these authors seem to possess a considerably higher degree of roughness. Because of the fact that the hummocks were considered to be hemispheres [5] it seems to us that the value mentioned is a high estimate. We will therefore adopt a value for r_1 of 1.4, keeping in mind that the uncertainty of this figure is considerable, probably at least 5%. It has been put forward [5] that some secondary roughness is present on the aged AgI surface. The electron micrograph is in principle not conclusive in this respect. However, some observations with relevance to a possible secondary roughness can be made:

(a) the irregularities included in r_1 have diameters down to the resolution of the observation technique; it is more than likely that there are smaller irregularities as well,

(b) the primary roughness factor r_1 does not change much on ageing the AgI surface (compare Figs. 6 and 7); however, capacitance measurements indicate a considerable decrease in microsurface area [14],

(c) the smaller the irregularities on the surface are, the smaller their relative contributions to the roughness factor: considering the small irregularities as hemispheres is clearly overdone. Taking all these points together, it seems justified to conclude that the secondary roughness factor r_2 (accounting for irregularities from about 2.5 nm down to atomic dimensions) will not be higher than 1.1. Evidence in support of this figure could possibly be found from capacitance measurements on electrodes which have been aged during different periods. In conclusion, the figures mentioned can be combined to a total roughness factor r which represents the ratio between the real surface area and the geometric surface area. The value of this r equals $r_1 \cdot r_2$ and should be taken as 1.5 with an uncertainty of at least 10%.

Determination of the film thickness

In a previous investigation, Engel [5] measured the thickness of an AgI film on polished Ag by means of an optical method: polarization interferometry according to Nomarski and Weill [16]. We measured the film thickness with an electrochemical method i.e. coulometry at constant current. The silver iodide electrode (WE) carries a constant cathodic current i which is generated by the coulometer and flows back through a platinum counter electrode (CE). The potential of WE is measured against a saturated calomel electrode (SCE) as a function of time. A typical example of such a potential-time curve is given in Fig. 8. Apart from the threshold in the first part, the potential is nearly constant in time indicative of a single electrode process. The cathodic current reduces the AgI from the lattice in the film to metallic silver while iodide ions diffuse into the solution. During the experiment the solution was stirred. It turned out not to be necessary to remove oxygen. Obviously, there was no need to keep the temperature constant. When the reduction is almost complete,
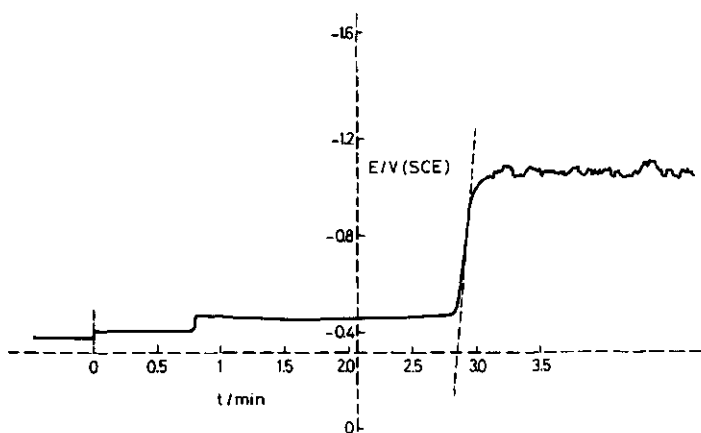

Fig. 8. Typical potential/time curve for a stripping experiment. The switching-on of the current is indicated by a small increase in overpotential at $t = 0$. The potential variations at about -1.0 V (SCE) are due to hydrogen evolution.

the potential of WE increases to the level where the solvent is reduced. The time that corresponds to the total reduction of the film is obtained as an extrapolation of the steep, almost linear part. The corresponding charge is equivalent to the AgI content of the film. The current density used in the experiment which is given by Fig. 8 was 0.5 mA cm^{-2} and the transition time was 2.85 min. This corresponds with a charge of 1.71×10^{-2} C. Using the density of γ-AgI equal to 5.67 g cm^{-3} [17], the average film thickness can be calculated to be 3.79×10^2 nm. The accuracy of the coulometric film thickness determination method can be estimated from test experiments using AgI film electrodes prepared by controlled electrolysis. In this way we found that the inaccuracy is less than 1%. In general, the stripping current should not be chosen too high if reliable thickness values are to be ascertained.

For all electrodes which were prepared by reaction with molecular iodine at reduced pressure, the time of exposure was 1 min. The film thickness of these electrodes turned out to be always between 3×10^2 and 4×10^2 nm. This is illustrative of the fact that experimental conditions like exposure time, iodine content of the vapour and surface condition of the electrode are difficult to reproduce, making a thickness determination as described above the more necessary.

All potential-time curves showed a small but distinct increase after about 1/4 of the transition time. This intriguing phenomenon might be related to some second stable phase in the film or anyway as a second kind of overall reduction process. Some discussion on this point is given in the concluding remarks.

Determination of the resistance of the silver iodide film

Regarding the experimental set-up which was used for the resistance measurement (Fig. 2), we can write for the total cell resistance R_t:

$$R_t = 2R_f + R_s + 2R_i \tag{1}$$

R_f denotes the AgI film resistance, R_s the resistance of the electrolyte solution whithin the perspex cylinder and R_i the sum of the resistive components of the interfacial impedances of the Ag/AgI and AgI/solution interfaces [5]:

$$R_i = Z_i'(\text{Ag/AgI}) + Z_i'(\text{AgI/soln.}) \tag{2}$$

The purification method which we used as described in the experimental section implies that the cell solution contains Ag$^+$ and I$^-$ ions whose activities are determined by the solubility product of AgI. This is the reason why the electrodes cannot be considered as ideally polarizable and the R_i term should be included in eqn. (1). In the case of an Ag/AgI electrode there are two interfaces per electrode: Ag/AgI and AgI/solution, both contributing to R_i. By using Randles' equivalent circuit for the two interfaces [18], we can set up the equivalent circuit for the complete electrode, which is given in Fig. 9. It should be noted that, strictly speaking, classical Warburg behaviour is not possible when there is only one mobile species in the simple case of an ideal solid electrolyte [19,20]. For the sake of explaining the approximation $R_i \ll R_f$ we have included a Warburg-like impedance in our equivalent circuit. This is thought to
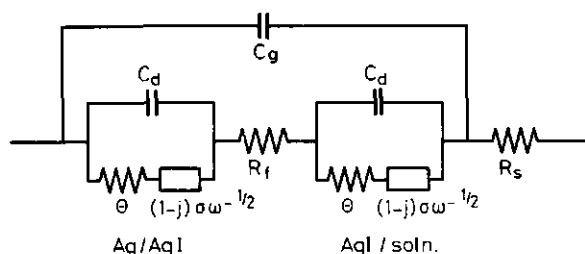
Fig. 9. Randles equivalent circuit for an Ag/AgI film electrode. Reference to the symbols is made in the text.

be connected with a distribution of relaxation times as is found for real solid electrolytes [21]. Coulostatic pulse measurements are indicative of a corresponding impedance in our case. This point will be discussed in more detail elsewhere [14]. It is now possible to estimate Z_i' for the two interfaces using eqn. (3) [5]:

$$Z_i' = (\theta + \sigma\omega^{-1/2})/\{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2(\theta + \sigma\omega^{-1/2})^2\} \tag{3}$$

assuming reasonable values for the differential capacitances C_d of the two interfaces, for the charge transfer resistance θ and for the Warburg coefficient σ, respectively. These values are given in Table 1. They are based on experimental results for the charge transfer kinetics of the Ag/AgI electrode which we will publish in forthcoming papers. The results of these calculations are summarized in Table 2. It turns out that at not too low frequencies R_i has a negligible value compared with R_s, which is on the order of 10 Ω as calculated with standard data for the equivalent conductivity of KNO_3 solutions [17]. The angular frequency used in our measurements is 1.88×10^5 s^{-1}. It appeared from the dielectric constant and the specific conductivity of cubic AgI that at this frequency the contribution of the *geometrical* capacitance C_g to the real component of the impedance R_i is completely negligible [24,25]: the time constant for the dielectric relaxation is on the order of 10^{-8} s, corresponding to angular frequencies much higher than 2×10^5 s^{-1}. For this reason the influence of C_g can be neglected in the computation of R_i. In principle, R_s can be obtained from eqn. (1) by measuring the total cell resistance as a function of the distance d between the electrode surfaces. For not too small values theory predicts a linear relationship between R_s and d and this is indeed found [22]. In Fig. 10, the total cell resistance R_s is given as a function of d as measured for one pair of electrodes at three different surface states. It was verified that at the used frequency R_i had become negligible for all three surfaces: for $\omega \geqslant 2 \times$

TABLE 1

Values for the parameters which characterize the electrode kinetics of the Ag/AgI electrode, used in the estimation of R_i (pAg$_{soln.}$ = 7)

Interface	θ/Ω cm^2	σ/Ω cm^2 s$^{-1/2}$	C_d/μF cm^{-2}
Ag/AgI	5×10^{-2}	2×10^2	3
AgI/soln.	$5 \times 10^{+3}$	5×10^5	20

TABLE 2

Results of calculations on the resistive part of the interfacial impedances of the Ag/AgI electrode

ω/s^{-1}	$Z'_i(Ag/AgI)/\Omega\ cm^2$	$Z'_i(AgI/soln.)/\Omega\ cm^2$
1.88×10^3	4.7	2.9×10^{-2}
1.88×10^4	1.2	7.0×10^{-4}
1.88×10^5	2.9×10^{-1}	1.1×10^{-5}
1.88×10^6	4.4×10^{-2}	1.5×10^{-7}

TABLE 3

Comparison of different values for the specific resistance of γ-AgI (the values marked with * are taken from diagrams)

Authors name	$R_{sp}/\Omega cm$	Ref. No.
Takahashi et al.	$\pm 1.2 \times 10^4$ *	8
Armstrong et al.	7.7×10^3	24
Our measurements	1.2×10^4	—
Hoshino and Shimoji	$\pm 1.0 \times 10^5$ *	29

10^5 s^{-1}, R_t no longer showed any frequency dispersion. This is in agreement with the conclusions from Table 2. Curve 1 was measured for two electrodes covered with a vacuum deposited silver layer. After the experiment the electrodes were thoroughly rinsed with distilled water and ethanol and dried with warm air. After preparation of the silver iodide film the resistance measurement was repeated before and after the ageing process. This gave rise to an increase in R_s as indicated by curves 2 and 3, respectively. The resistance of the aged film was calculated as the difference between 1 and 3 which corresponds to the average experimental difference. This value is 2.1 ± 0.1 Ω per film.
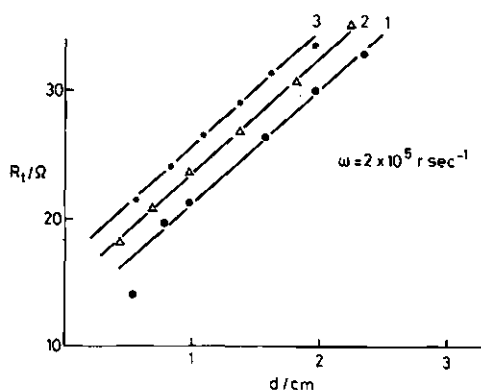

Fig. 10. Plot of the total cell resistance R_t at a frequency of 2×10^5 s^{-1} against electrode distance. ($\bullet$) refers to the silver film and ($\triangle$) and (*) to the non-aged and aged AgI film, respectively. R_{AgI} equals the difference between lines 1 and 3.

After this experiment the thickness of both films was measured as described in the previous section. The average thickness turned out to be 3.48×10^2 nm. From the geometrical surface area, the measured thickness and resistance, the specific resistance of the deposited aged AgI was calculated to be 1.2×10^4 Ω cm. Results of other authors are mentioned in Table 3. Comparing the difference between the results it should be kept in mind that the conductivity is greatly influenced by the method of preparation and, in the case of pellets, also by the pressure that is exerted on the samples [23]. The smaller values for the film resistance which were found in the case of the non-aged films (Fig. 10, curve 2) can be explained by the higher number of imperfections in the crystal structure. It clearly follows from the electron micrographs that the crystal lattice rearranges upon aging to more a perfect structure which is accompanied by an increase in resistance.

CONCLUDING REMARKS

A recent review by Kennedy [26] on thin solid film research points out that such properties of thin silver iodide films as conductivity and crystal structure strongly depend on the conditions under which they are formed. For example, Cochrane [27] found that when silver iodide was deposited on mica the β form was present but when glass was used both the β and γ modification developed. Sieg [28] studied the sublimation of silver iodide at room temperature and found only the γ modification but did not specify the kind of substratum he used. Takahashi et al. [8] measured the specific conductivity of AgI pellets and investigated their structure by X-ray analysis. Starting from pure γ-AgI, he accomplished a $\gamma \rightarrow \beta$ transition by a procedure of repeated heating and cooling. After each cycle the conductivity was measured as a function of temperature and the crystal structure was established by X-ray diffraction.

The value we measured for the specific conductivity of our films (8.3×10^{-5} Ω^{-1} cm^{-1}) is in excellent agreement with the value found by Takahashi et al. for γ-AgI. Furthermore, our analysis rules out the possibility that the film we measured consists of β-AgI doped with impurities which could increase the conductivity. The appearance of the "unknown" peak in Fig. 3 is difficult to explain because as a β-AgI reflection it is not consistent with the complete absence of all other specific β reflections. It is not possible that this is caused by the presence of small amounts of silver which could be scraped off the rod during the preparation of the powder samples: it is known that metallic silver shows no reflections at that angle [11]. In addition to this, the small threshold which is observed in the overpotential/time curve during the stripping of the film could be correlated with non-homogeneity in the film i.e. the presence of other species than γ, for example β-AgI films. In order to get a sufficient amount of powder for the X-ray experiment films were grown on the rod which were much thicker than the evaporated ones. This may introduce some uncertainty as to which extent these powder samples represent the film material. However, taking into account that the powders consisted of almost pure γ-AgI it is very probable that this is also true in case of the film. Thus, the small effect in the potential/time curve for the stripping of an AgI film is likely to have a different cause and it would certainly be worthwhile to undertake a separate study on this point.

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CHAPTER 3

A KINETIC STUDY OF THE SILVER/SILVER IODIDE FILM ELECTRODE IN AQUEOUS SOLUTION USING THE COULOSTATIC PULSE TECHNIQUE

I. PROPERTIES IN 0.1 M KNO$_3$ SOLUTION

ABSTRACT

A study is presented of the kinetics of the Ag/AgI film electrode in 0.1 M KNO$_3$ solution. After applying a charge impulse (coulostatic pulse), the overpotential/time curve is measured and Laplace transformed into an impedance/frequency function. Using an iterative procedure and Randles' construction method, the double layer capacitance, the exchange current density and the Warburg coefficient are calculated. Two distinct relaxation phenomena take place: a fast one which proceeds on the order of μsec and a slower one in the msec range. They are connected with transfer processes in the Ag/AgI and AgI/solution interfaces respectively. The evaluated capacitances compare rather well with values obtained by the classical potentiometric titration technique. Standard exchange current densities for the two interfaces are measured as a function of electrode potential and the transfer coefficient of the AgI/solution transfer process is calculated. It also appeared that aging of the electrode simply results into a decrease of the surface roughness.

INTRODUCTION

The stability of lyophobic colloids is a phenomenon which has drawn the attention of many investigators in colloid chemistry. Silver iodide sols were often used as model systems in their studies (1). In a review on recent developments in the theory of lyophobic stability, OVERBEEK (2) has pointed out that much of the work done was directed towards the thermodynamics and only to a very modest extent to the kinetic aspects of the stability phenomenon. He considered the time needed for a collision between two particles which are subject to Brownian motion. This time is defined as the time during which there is overlap of the electrical double layers of the two colloidal particles. OVERBEEK (2) estimated the collision time between 10^{-5} and 10^{-7} sec. He also pointed out that the real collision time can be considerably longer than this Brownian collision time. OVERBEEK(2), PIEPER *et al.* (3) and HONIG *et al.* (4) evaluated several effects which are able to account for a prolonged collision time, like hydrodynamic interaction and electrostatic repulsion during approach. An estimation of the real

collision time based on the overall picture has not been given so far.

If, in the case of a silver iodide sol, the rate of adsorption/desorption of the potential determining Ag^+/I^- ions is too low to maintain equilibrium with the solution during a collison, i.e. to maintain a constant potential, then the constant charge approach is valid. The total charge on the particle would be constant and there would be no need for kinetic considerations. However, other relaxation mechanisms in addition to charge desorption may be operative as well. *Diffuse* double layer relaxation in the solution (relaxation time τ_d) according to DEBYE is known to be very fast compared with the collision time in not too low salt concentrations. During the desorption/adsorption process, ions have to move through the *non-diffuse* or Stern part of the double layer. The rate of this process can be expressed by the non-diffuse double layer relaxation time τ_c. Migration of charge along the particle surface may also play a role (1-3). Thus, to evaluate the constant charge/constant potential problem, one has to consider several relaxation times. Tentative experiments on the rate of the desorption/adsorption process (τ_c) were done by FRENS *et al.* (5) and DE VOOYS (6).

The process of adsorption/desorption of p.d. ions is equivalent with the process that takes place in the silver iodide/solution interface of an Ag/AgI electrode when it carries an electrical current. Investigation of the electrode kinetics of such an electrode i.e. determination of its exchange current density, will - under certain conditions - yield information on the forementioned process (τ_c). We therefore started investigations of the kinetics of the Ag/AgI film electrode transfer process, using a technique which is both fast and relatively insensitive to ohmic drop effects, originating from the solution and from the AgI film. The coulostatic pulse method, which had been used in several electrode kinetic studies, seems to be quite suitable.

In a previous paper (7), we discussed the fundamental properties of the Ag/AgI film electrode which was used in the present investigation. Looking at the results of these preparative studies in terms of the specific resistance of the AgI film on the electrode and taking into account the potentialities of the coulostatic technique, it seems to be possible to explore the time region down to about 10^{-6} sec. The present paper deals with the application of the coulostatic pulse method to the Ag/AgI film electrode. Results are interpreted in terms of the exchange current density, the non-diffuse double layer relaxation time τ_c and its dependence on the (equilibrium) electrode potential and the composition of the aqueous solution.

ANALYSIS OF COULOSTATIC TRANSIENTS

The use of very short current pulses in electrode kinetics was suggested by
BARKER (9) and developed further by DELAHAY (10) and REINMUTH (11). A critical
review of the characteristic features and possibilities was recently given by one
of us (8).

In the coulostatic experiment, the double layer is charged by a current
pulse of very short duration, usually less than 1 μsec. After cessation of the
pulse, the double layer discharges through the faradaic impedance and the resul-
ting potential/time decay curve contains information about the kinetics of the
interfacial charge transfer process. One of the advantages of this technique is
that no net current flows through the cell during the actual measurement. This
means that the ohmic drop is eliminated. The analysis of the coulostatic transient
may be carried out either directly, i.e. in the time domain, or after transfor-
mation of the signal into the frequency domain, using the well-known Laplace
transform procedure (12). In order to obtain maximum information, especially in
the short time range, we choosed to use the latter procedure.

From a coulostatic transient, one obtains the real and imaginary components
of the electrode impedance $Z(\omega)$ by (13):

$$Z(\omega) = \frac{\bar{\eta}(\omega)}{\bar{i}(\omega)} \tag{1}$$

where $\bar{\eta}(\omega)$ and $\bar{i}(\omega)$ represent the Laplace transformed overvoltage and current re-
spectively. As it has been indicated (12), the Laplace operator has taken the
value $j\omega$, where ω is the angular frequency and j the imaginary unit. In principle,
the coulostatic impulse technique has the advantage that the transform of the
current function takes a very simple form (12):

$$\bar{i}(\omega) = \int_0^\infty i(t) \exp(-j\omega t)\, dt = \int_0^\infty q\, \delta(t) \exp(-j\omega t)\, dt = q \tag{2}$$

where $\delta(t)$ is the Dirac delta function and q is the total amount of charge used
in charging the double layer. The function $\eta(t)$ is transformed by describing it
with a set of trial functions, the Laplace transforms of which are mathematically
known (12):

$$\eta(t) = \sum_{i=1}^{n} c_i\, f_i(t) \tag{3}$$

After the evaluation of the coefficients, the transform is also known because Laplace transformation is a linear operation:

$$\bar{\eta}(\omega) = \sum_{i=1}^{n} c_i \, \bar{f}_i(\omega) \tag{4}$$

The impedance spectrum is obtained by separating the real and imaginary components of the impedance expression. The frequency range to be used is related to the original time range covered by the aperiodic experiment:

$$\omega_{max} \approx 1/t_{min} \qquad \omega_{min} \approx 1/t_{max} \tag{5}$$

In our calculations concerning the Ag/AgI film electrode, three exponential functions and three error functions were used as trial functions. The time constants of these functions were choosen by an iterative procedure, included in the computer program for complete data handling.

In order to analyze the impedance data, the well-known equivalent circuit of RANDLES (14) was used, representing the electrode/solution interface of an electrode were both charge transfer polarization and diffusional mass transfer polarization are accounted for. The differential capacitance C_d of the interface is also included in the scheme.
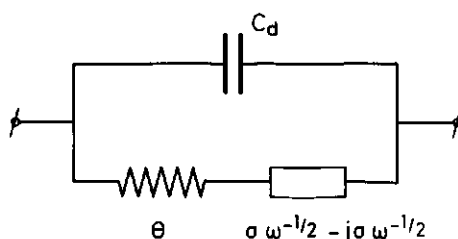

Fig. l   Randles' equivalent circuit for the electrode/solution interface.

The ohmic resistance is left out because, in principle, the coulostatic experiment is insensitive to this. The resulting scheme is given by Fig. 1. The double layer capacitance is shunted by the faradaic impedance Z_F, which can be written as:

$$Z_F = Z_F' - j\, Z_F'' = \theta + (1-j)\sigma\, \omega^{-\frac{1}{2}} \tag{6}$$

where θ and σ are the charge transfer resistance and the Warburg coefficient respectively. One can easily derive Z_F' and Z_F'' as functions of the components of the electrode impedance Z_{el}' and Z_{el}'', ω and C_d, using the scheme in Fig. 1:

$$Z_F' = Z_{el}' / \{1 - 2\,\omega C_d\, Z_{el}'' + \omega^2 C_d^2 (Z_{el}'^2 + Z_{el}''^2)\} \tag{7}$$

$$Z_F'' = \{Z_{el}'' - \omega C_d (Z_{el}'^2 + Z_{el}''^2)\} / \{1 - 2\,\omega C_d Z_{el}'' + \omega^2 C_d^2 (Z_{el}'^2 + Z_{el}''^2)\} \tag{8}$$

After calculation, Z_F' and Z_F'' can be plotted against $\omega^{-\frac{1}{2}}$, according to eqn. (6). Then θ is obtained as the intercept of $Z_F'(\omega^{-\frac{1}{2}})$ and σ as the slope of both $Z_F'(\omega^{-\frac{1}{2}})$ and $Z_F''(\omega^{-\frac{1}{2}})$. To calculate Z_F' and Z_F'' from Z_{el}' and Z_{el}'', a value for C_d is needed. On the other hand, one can calculate C_d using:

$$C_d = \omega^{-1} \{Z_{el}'' / (Z_{el}'^2 + Z_{el}''^2) - Z_F'' Z_{el}' / Z_F' (Z_{el}'^2 + Z_{el}''^2)\} \tag{9}$$

Apparently, the frequency dependence of Z_F should be utilized in evaluating both C_d and the kinetic parameters θ and σ. An iterative procedure was used which started with an approximated value for C_d using only the first term on the right hand side of eqn. (9). The set of Z_F' and Z_F'' values which were then calculated using eqns. (7) and (8), were used to calculate the slope and intercept of $Z_F'(\omega^{-\frac{1}{2}})$ and $Z_F''(\omega^{-\frac{1}{2}})$. Using the highest value for ω again, eqn. (9) can be applied to give a new capacitance value, somewhat smaller than the first one. This procedure converged almost always after three or four cycles. The linearity of the $Z_F'(\omega^{-\frac{1}{2}})$ and $Z_F''(\omega^{-\frac{1}{2}})$ plots improved as well and this fact provides evidence for the applicability of the Randles' concept in the case of the AgI/aqueous solution interface. Values for the exchange current density i_o were calculated using the well-known relationship that holds in the case of small amplitudes:

$$i_o = RT/nF\theta \tag{10}$$

For a correct calculation of real interfacial capacitances and exchange current densities, information is required on the roughness of the AgI electrode surface. This point has been treated in a previous paper (7). The roughness factor, which is the ratio between the real, microscopic surface area and the geometrical surface area, turned out to be approximately 1.5 for our AgI film electrodes. All

values given for C_d and i_o have been calculated using this roughness factor and thus refer to the real surface area.

EXPERIMENTAL

The measuring system

The experimental set-up used in the coulostatic pulse experiment is given in Fig. 2. Two identical electrodes are used, this has the advantages that first--order deviations from linearity in the current voltage relation are eliminated (15-17) and that amplitudes up to 10 mV are allowed using the simple picture of Randles' equivalent circuit.
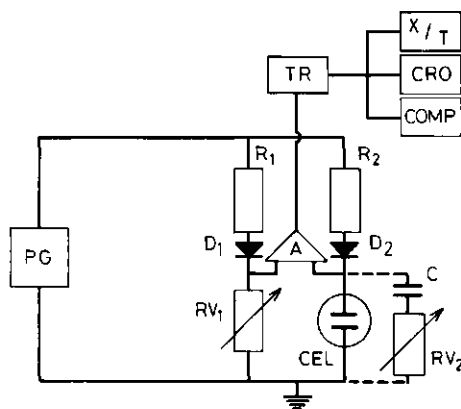

Fig. 2   Experimental set-up for coulostatic impulse measurements. Reference to the symbols is made in the text.

Although the ohmic resistance of the cell is principally uneffective during the measurement, the variable resistance RV_1 is used to roughly compensate for it during application of the pulse, avoiding in this way overload effects in the amplifier. R_1 and R_2 are 10 KΩ resistances which are much higher than the ohmic resistance of the cell. PG is a Hewlett Packard 214 A pulse generator, A a fast differential amplifier (Analog type 46 K) with a risetime well below 1 μsec.

Leakage of charge back into the pulse generator is prevented by the two diodes D_1 and D_2. The amount of applied charge is measured by replacing the cell by a known capacitance in series with a variable resistance RV_2. The latter is given a value equal to RV_1 so that the ohmic resistances of the two branches are always the same. The overpotential/time curve is registrated by a Datalab DL 905 transient recorder TR which stores the signal in a 1024 word memory with 8 bit resolution (better than 0.25%). The curve can be read out using a simple x,t-recorder or a paper tape puncher to facilitate computer handling of the data. It can be observed continuously by using an oscilloscope. With this set-up it is possible to study relaxation curves in various ways after application of only one single pulse. This improves the lifetime of the electrodes and undesired memory effects are avoided.

The cell

A double wall, all pyrex cell was used. The temperature was maintained at $25.0^{\circ} \pm 0.1^{\circ}C$. A sketch of the cell is given in Fig. 3. Nitrogen was purified before use by leading it through a BTS catalyst and a molecular sieve (MS, 4A, 1/16). Before each experiment, nitrogen was lead through the solution; during the measurement a nitrogen atmosphere was maintained.
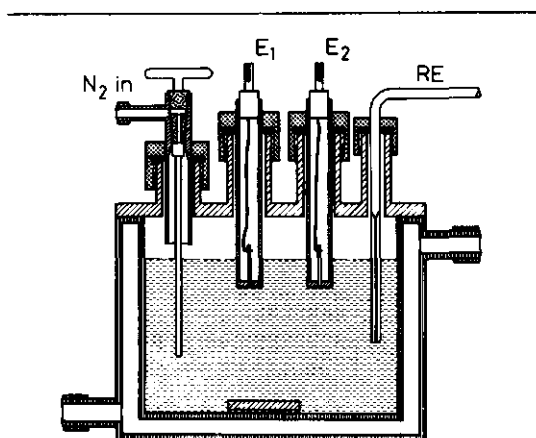

Fig. 3   The cell. A short description is given in the text.

All probes were mounted on top of the cell using Sovirel screw caps with inner teflon rings.

E_1 and E_2 are the two identical electrodes. The preparation method and the characteristic properties of these electrodes were described in detail earlier (7). They consist of two soft glass tubes with a diameter of 12 mm and a flat bottom of 3 mm thickness in which a platinum wire is fused to ensure electrical contact. After polishing with silicon carbide paper (Struers) with decreasing roughness and diamond paste containing particles with a diameter of 0.4 μ, a silver layer is deposited by vacuum deposition. After that the silver electrode is allowed to react with iodine vapor under reduced pressure ($\pm$ 1 cm. Hg). A reaction time of 1 minute resulted into a thickness of the silver iodide layer of about 350 nm. The thickness was measured by a coulometric stripping experiment (7). For electrodes prepared in the described way the roughness factor, defined as the ratio between the real and the geometric surface area, was estimated to be approximately 1.5. It should be kept in mind that the uncertainty of this figure is considerable, i.e. at least 10%.

The equilibrium potential of the electrodes in the cell solution was varied by adding small amounts of KI or $AgNO_3$ solution. Inert electrolyte was always present in excess thus keeping the ionic strength constant. The electrode potentials were measured against a satured calomel reference electrode which was brought in electrical contact with the cell by means of a capillary bridge (RE in Fig. 3) according to VAN LAAR (18,19). pAg or pI was calculated from the cell emf after determination of the standard potential which includes activity coefficients and liquid junction potentials (19). Before use the cell and all glass parts were thoroughly cleaned by using concentrated chromic acid, diluted nitric acid and distilled water which had been brought into contact with AgI suspension. After that, the cell was filled with an AgI suspension and stirred during at least 12 hours.

Materials

All chemicals used were of p.a. quality (Merck and Baker). The surface area of the AgI electrodes is very small as compared with the surface area of AgI suspensions (0.20 cm^2 per electrode). It therefore is of utmost importance to remove compounds which can adsorb on the electrode surface. To this aim the distilled water used was percolated through a column containing precipitated AgI which was renewed at regular intervals. In the following, water treated like this will be denoted as "AgI-water".

KNO$_3$ was used as the inert electrolyte. To prepare an "adsorbate free" 0.1 M KNO$_3$ solution 1 mol of the salt was diluted in a concentrated AgI suspension and stirred during at least one night at a temperature of about 80°C. After separation of the AgI from the solution, AgI-water was added to obtain a 1.0 M KNO$_3$ solution. Tenfold dilution of this stock solution with AgI-water gave a 0.10 M KNO$_3$ solution, sufficiently free of adsorbable compounds.

RESULTS AND DISCUSSION

Experiments in 0.10 M KNO$_3$ solution

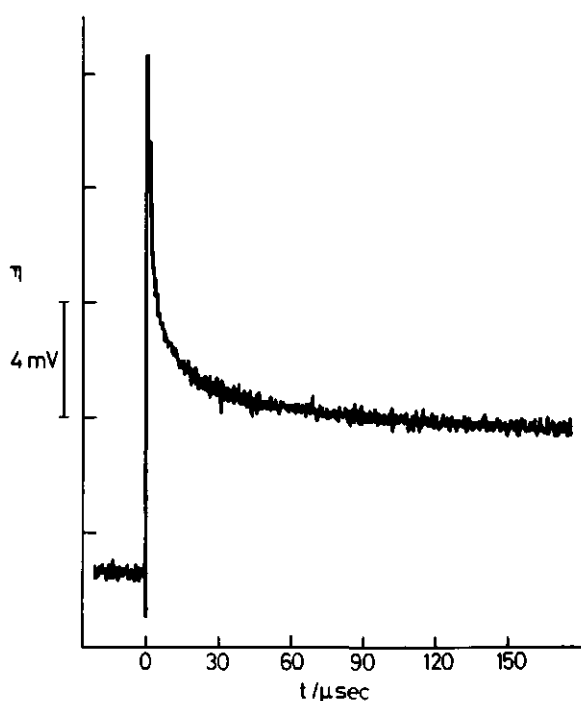An Ag/AgI electrode has two interfaces through which charge transfer takes

Fig. 4   Overpotential/time decay curve for the Ag/AgI film electrode in the microsecond time range. The pI=5.85; inert electrolyte: 0.10 M KNO$_3$. Δq=8.14x10^{-9}C. The sum of the overpotentials of the two electrodes is registrated.
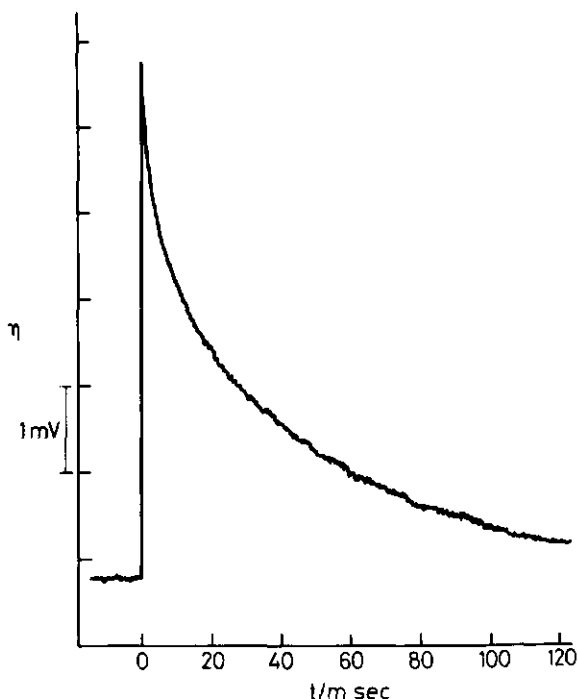
Fig. 5   The same decay curve as in Fig. 4 in the millisecond time range.
$\Delta q = 8.20 \times 10^{-9} C$.

place: the Ag/AgI interface and the AgI/electrolyte solution interface. This could complicate the analysis of the relaxation curve and it is therefore desirable to separate the two relaxation effects. In a previous paper (7) we reported on some fundamental properties of the AgI film. These properties are important with respect to possible relaxation effects connected with the AgI phase. Conductivity measurements were carried out on the electrodes used and an X-ray analysis was performed of the isolated AgI. These experiments resulted into strong indications of the presence of the cubic or γ-type AgI phase in the film. The specific conductivity of the AgI layer on the electrodes appeared to be $8.3 \times 10^{-5} \Omega^{-1} cm^{-1}$ which is in excellent agreement with the value found by

TAKAHASHI *et al.* (20). The electrical conductivity is related to the motion of interstitial silver ions in the crystal lattice, their transport number being estimated by several investigators to be very close to 1 (21-24).

The coulostatic experiments were carried out in 0.10 M KNO_3 solutions with varying concentrations of Ag^+ and I^-ions. Figs. 4 and 5 give typical overpotential--time curves measured in the µsec and msec range respectively. The pI was choosen to be 5.85 as most stability experiments with AgI sols are carried out at negative charge (1).

The relaxation behaviour seems to be governed by two phenomena, one occuring in the microsecond region and one occuring in the millisecond region. In the following, the two will be distinguished by denoting them as the fast relaxation and the slow relaxation respectively. It was verified from experiments with simulative RC-circuits that the measured decay on the microsecond range was a real electrode effect and that decay from overload in the amplifier or transient recorder did not play a role. Unlike the slow relaxation, the fast one was not influenced by the activity of electro-active ions. Therefore it is likely that the fast relaxation has to be connected with the solid phase AgI and/or the interface Ag/AgI. For a more quantitative analysis and to test this hypothesis, we have to start with the complete equivalent circuit for the Ag/AgI electrode
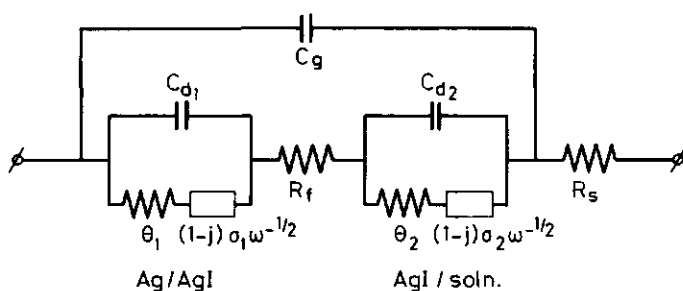

Fig. 6   Equivalent circuit for an Ag/AgI film electrode. Reference to the symbols is made in the text.

and this is given by Fig. 6 (7). C_g is the geometrical capacitance of the AgI film, which is determined by the relative dielectric constant ϵ_r of γ-AgI and the film dimensions. From analysis of the infrared vibrational spectrum of γ-AgI, BOTTGER and GEDDES calculated ϵ_r to be 7.0 (25). R_f and R_s are the ohmic resistances of the AgI-film and the solution between the two electrodes respectively. C_d, θ and σ are the usual symbols for the electrode kinetic parameters: differential double layer capacitance, transfer resistance and Warburg coefficient (or diffusion polarisation) respectively for the two interfaces. As the time constant of the geometrical relaxation of γ-AgI is only 10^{-8} sec (7), C_g can be neglected in the analysis of the relaxation curves because the duration of the current pulse is 0.5 - 1 microsec. The discharge of C_g across R_f can be considered to be exponential. If the following values are assumed: $C_g = 10^{-9}$ F, $R_f = 10$ Ω and using the type of calculation given for double layer relaxation (11) (which is essentially the same thing), it can be demonstrated that contributions to the measured overvoltage can be neglected at times beyond 0.2 μsec. The possibility that the fast relaxation can be interpreted as a tail of this bulk AgI relaxation effect, seems to be ruled out. An additional argument could be the fact that the fast relaxation does not correspond with an exponential decay. Effects related to a redistribution of initially inhomogeneously distributed charge on the irregular AgI surface could be responsible for deviations from the purely exponential type of decay. However, the observed surface properties do not allow explanations in terms of charge density homogenization on the microsecond range.

The effects of the two ohmic resistances R_f and R_s are eliminated by the use of coulostatic pulses: after the charging of C_{d1} and C_{d2} the cell carries no current and the two capacitors are discharged through the faradaic impedances. Looking at the fast relaxation in Fig. 4, it is clear that it is complete on the 10^{-2} sec. range where the slow relaxation is operative. In terms of the equivalent circuit this can be put as follows: the discharges of C_{d1} and C_{d2} are fully separated. Obviously, this facilitates the analysis: we have to do with two different electrochemical interfaces in series, each with their own, rather different time constants for relaxation.

In Fig. 7 a plot of the real and imaginary components of the faradaic impedance against the inverse square root of frequency is given for the slow relaxation of Fig. 5. This plot was obtained by the iterative procedure described before. In this way, C_d was calculated to be 15.9 μF cm^{-2} (referring to the real surface area). θ and σ are obtained from the intercept and slopes (averaged between Z_F' and Z_F'') according to eq. 8. Using eq. 10, the exchange current den-
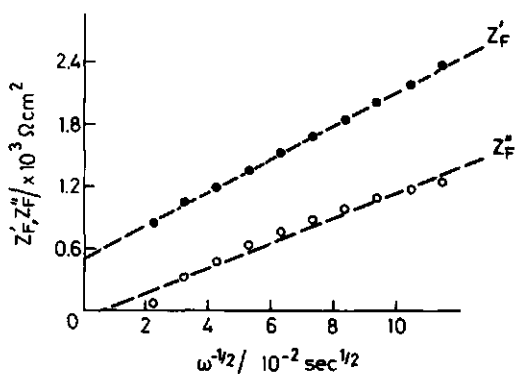
Fig. 7   Randles' construction method to obtain θ and σ from Z_F', $Z_F''/\omega^{-\frac{1}{2}}$ plots. Plotted impedance values refer to the experiment in Fig. 5.

sity i_o was calculated to be 5.2 x 10^{-5}Acm^{-2}. The fast relaxation was analyzed in the same way although we found that the linearity of the plot was often less than for the slow relaxation. An explanation for this can be found in a more detailed analysis of the processes which occur in the AgI film. The matter will
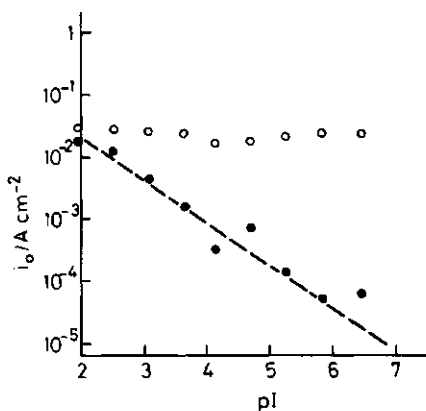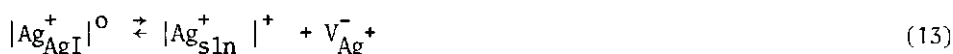

Fig. 8   Logarithmic plot of i_o values against pI. o = fast relaxation (Ag/AgI int.), ● = slow relaxation (AgI/sln. int.).

be more fully discussed later on in this paper. In Fig. 8 log i_o for the fast (open circles) and slow relaxation (black circles) is plotted against pI. It is clear that $(i_o)_{fast}$ is not influenced by pI and that there is a linear relationship between log $(i_o)_{slow}$ and pI. This is in accordance with the assumptions that the fast relaxation take place in the interface Ag/AgI and the slow relaxation in the interface AgI/sln. A quantitative representation of the results is given by:

$$\log\ (i_o)_{slow}\ =\ \log\ k_s^{\ast}\ -\ \alpha\ pI \tag{11}$$

Obviously, there is an analogy between eq. 11 and the well-known expression for the exchange current density at an interface where electron transfer takes place, i.e. the usual situation in electrode kinetic studies. This analogy can be described in more detail by representing the adsorption/desorption equilibrium by eqs. (12) and (13) (6, 26):

$$V_{Ag^+}^-\ +\ |I_{AgI}^-\ |^O\ \overset{\rightarrow}{\leftarrow}\ |I_{sln}^-\ |^- \tag{12}$$

$$|Ag_{AgI}^+|^O\ \overset{\rightarrow}{\leftarrow}\ |Ag_{sln}^+\ |^+\ +\ V_{Ag^+}^- \tag{13}$$

$V_{Ag^+}^-$ is a silver ion vacancy in the crystal lattice and can be compared with the electron in the reaction OX + e $\overset{\rightarrow}{\leftarrow}$ RED. In eq. (11) $k_s^{\ast}$ represents an over-all rate constant which equals $(i_o)_{slow}$ at pI = 0. α is the transfer coefficient for I^- ions. The dotted line in Fig. 8 represents the interpretation in terms of eq. (11) and is calculated by means of a linear regression procedure. The results are collected in table I. The errors in α and log $k_s^{\ast}$ (= log $(i_o)_{slow}^{st}$) are the calculated standard deviations of the slope and intercept.

Table I

Data for the ion transfer kinetics of the interface AgI/sln. Log $(i_o)_{slow}^{st}$ refers to pI/pAg = 0. τ represents the time constant for transfer.

ion	α	$\log(i_o)_{slow}^{st}/_{Acm^{-2}}$	$\tau/_{10^{-3}sec.}$	$\log(i_o)_{slow}^{st}/_{Acm^{-2}}$
I^-	0.68 $\pm$ 0.04	−0.35 $\pm$ 0.18	1.4	−2.68 (6)
Ag^+	0.61 + 0.06	−0.48 $\pm$ 0.29	1.5	−1.42 (6)

The dependences on pI of the mass transfer polarization coefficient σ for the fast and slow relaxations are given in Fig. 9. The dotted line represents the Warburg coefficient σ as a function of pI corresponding with the diffusional mass transport of I^- ions in the aqueous solution, calculated with eq. 14 (27, 28):

$$\log \sigma_{sln} = \log \{RT/F^2 \sqrt{2D_i}\} + pI \tag{14}$$

The deviation of the experimental values for σ_{slow} from these σ_{sln} values can be explained by the following reasoning: as the slow relaxation proceeds, a concentration gradient is built up on the solution side (σ_{sln}) as well as on the AgI side (σ_{AgI}). It can be considered as a gradient in silver ion vacancies which changes due to the motion of interstitial silver ions. For low values of pI, σ_{sln} is very small and σ_{AgI} becomes the determining factor: σ_{fast} and σ_{slow} approach each other in this region. This is expressed by:

$$\sigma_{slow} = \sigma_{sln} + \sigma_{AgI} \tag{15}$$

$$\sigma_{fast} = \sigma_{AgI} \tag{16}$$

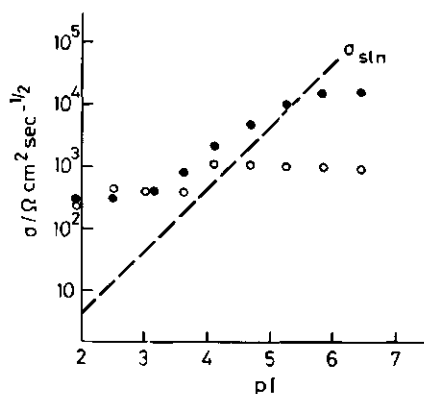An average value for σ_{AgI}, calculated from Fig. 9, is given in Table II. Eq. 16

Fig. 9   Logarithmic plot of Warburg coefficients (diffusion polarization) against pI. Symbols have the same meaning as in Fig. 8.

only contains a term which accounts for polarization in the AgI film because
during the fast relaxation there is no build-up of a concentration gradient of
electrons on the silver side of the Ag/AgI interface. In connection with the
tentative explanations given, it should be recalled that, strictly speaking,
Warburg behaviour in the AgI film is not possible (7).
It is not to be expected that conditions for linear diffusion are fulfilled in
the thin AgI film. Moreover, the interstitial silver ions move not only in a
concentration gradient but also migrate according to the potential gradient in
the film. Nevertheless, it proved to be useful to adopt the Warburg concept, as

Table II

Values for several parameters which characterize the AgI film.

$\sigma_{AgI}/\Omega cm^2 sec^{-\frac{1}{2}}$	$R_{sp}^{-1}/\Omega^{-1} cm^{-1}$	$|Ag_i^+|/mol cm^{-3}$	$D_i/cm^2 sec^{-1}$	$\bar{D}_{Ag^+}/cm^2 sec^{-1}$	$\bar{D}_{Ag^+}/cm^2 sec^{-1}$
6.5×10^2	8.3×10^{-5}	3.8×10^{-9}	5.8×10^{-3}	9.3×10^{-10}	2.8×10^{-10} (31)

analysis of Z_F' and Z_F'' for the fast relaxation indicates a Warburg-type behaviour
of the Ag/AgI interface. In a study of the impedance of the silver/solid electro-
lyte interface using powdered β - AgI, ARMSTRONG et al. (29) contribute a distor-
tion of the geometric semicircle in the complex impedance plane at MHz frequen-
cies to "inductive effects". Our analysis of the fast relaxation gives evidence
for interference by a charge transfer through the silver/solid electrolyte inter-
face. The deviation of σ_{slow} at high values of pI is probably related to instru-
mental shortcomings: at these low ion activities sweep times of 1 sec. or more
were necessary. If accurate inspection of this region is desired, it could proof
useful to simplify the electronic set-up such that it is more directed at the
long time region, i.e. it has a much higher series resistance R in combination
with longer pulse durations.
      Both σ_{AgI} and the specific conductivity R_{sp}^{-1} are determined by the concen-
trations of charge carriers and their diffusion coefficients:

$$\sigma_{AgI} = RT/F^2 |Ag_i^+| (2 D_i)^{\frac{1}{2}} \qquad (17)$$

$$R_{sp}^{-1} = F^2 |Ag_i^+| D_i/RT \qquad (18)$$

Eqn. (18) is the well known NERNST-EINSTEIN relation for an ionic conducting solid (30). From the two equations $|Ag_i^+|$ and D_i, the concentration and the diffusion coefficient of interstitial silver ions can be calculated. σ_{AgI} is calculated as the average of the values given in Fig. 9, resulting into the value 6.46 x 10^2 $\Omega cm^2 sec^{-\frac{1}{2}}$. R_{sp}^{-1} was reported in an earlier paper to be 8.33 x 10^{-5} $\Omega^{-1} cm^{-1}$ (7). The results are summarized in Table II. The fraction f_i, of the total number of Ag^+ ions which are interstitial, is calculated as the ratio of $|Ag_i^+|$ and the total number of Ag^+ ions in the AgI lattice and equals 1.6 x 10^{-7}. The *average* diffusion coefficient is calculated with the aid of (26):

$$\bar{D}_{Ag^+} = f_i \times D_i \qquad (19)$$

Table II compares the value thus obtained for $\bar{D}_{Ag^+}$ with the one measured by JORDAN and POCHON for γ-AgI, who used a tracer method (31). Despite the questionable validity of the diffusion concept in the AgI film there is surprisingly good agreement (within the order of magnitude) with their value. The *average* diffusion coefficient is very low due to the fact that the only species which are able to move in the lattice are the interstitial silver ions. Related to the diffusing interstitial silver ions only, the diffusion coefficient is quite high, but this can be expected for such a system. It is in accordance with the crystal structure of γ-AgI which is favourable for very fast ion diffusion: after an in-
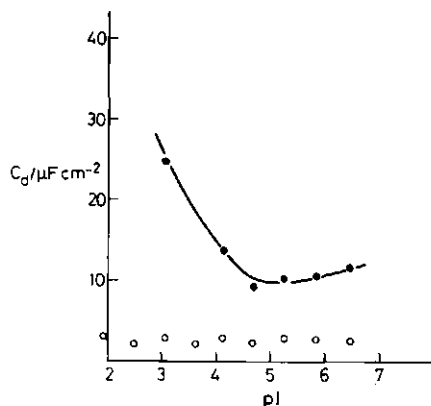

Fig. 10   Capacitance vs. potential curve in the pI region. For meaning of symbols see Fig. 8.

terstitial ion has formed, it moves through an empty chain of facesharing poly-
hedra (32).

Fig. 10 gives the capacitance values for the two interfaces. Again there is
no influence of pI on the fast relaxation capacitance. It compares rather well
(at least with respect to the order of magnitude) with an estimated value for the
diffuse double layer capacitance in the AgI solid based on the relative dielectric
constant and the values for $|Ag_i^+|$ and D_i mentioned in Table II.
The $(Cd)_{slow}$ values at not too low pI are in good agreement with the results of
direct double layer capacitance measurements by DE VOOYS (6). The capacitance
behaviour at low pI is probably related to complex formation on the electrode
surface.

Fig. 11, 12 and 13 give the corresponding results for varying Ag^+ concen-
trations. In Fig. 13 the results of PIEPER and DE VOOYS (3) and LYKLEMA and
OVERBEEK (33) are also given, obtained with direct capacitance measurements and
potentiometric titrations of AgI suspensions respectively. There is reasonable
agreement between the three methods when the rather great uncertainty in the de-
termination of the roughness factor is taken into account. The results of linear
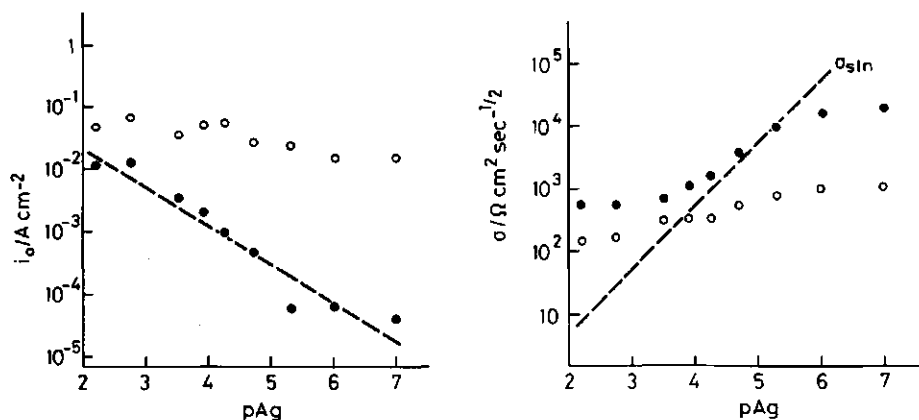regression analysis on the $(i_o)_{slow}$/pAg data are shown in Table I. In contrast to

Fig. 11 and 12. The same parameters as in Fig. 8 and 9 versus pAg.

the experiments in which pI was varied there seems to be a slight increase of
$(i_o)_{fast}$ with $|Ag^+|$. This may be explained by the fact that the slow relaxation
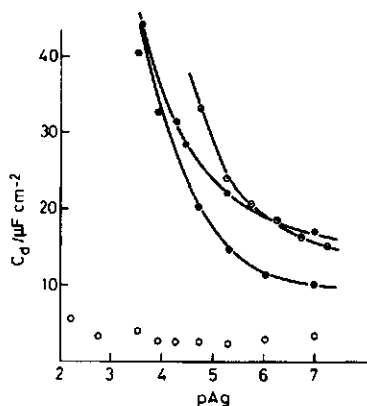
,Fig. 13   Capacitance vs. potential curves in the pAg region. ⊙ = Pieper and
De Vooys (3), ✳ = Lyklema and Overbeek (33), ● = our results for the
slow relaxation; o = fast relaxation.

becomes faster as pAg decreases which means that the separation of the two re-
laxations becomes more and more difficult. Another possibility is that the
amount of adsorbed Ag^+ influences the interstitial ion activity, hence increasing
$(i_o)_{slow}$ according to eq. 11 (pAg in stead of pI). However, the diffuse double
layer thickness within the AgI phase is quite low (7) which means that the in-
fluence on bulk properties cannot be significant. Table I compares the standard
values of $(i_o)_{slow}$ (= k_s^* acc. to eqn. (11)) with the ones found by DE VOOYS (6).
He did not measure $(i_o)_{slow}$ directly but calculated it by adapting theoretical
values for the interfacial impedance AgI/sln to experimental ones. However, no
account was made for effects connected with the solid phase AgI and the inter-
face Ag/AgI which makes the values less reliable.

Combining the values for $(i_o)_{slow}$ and $(C_d)_{slow}$ as given by Fig. 8 - 13 it
is possible to calculate the *relaxation time* τ_c for ion transfer through the
AgI/sln interface using eqn. (10):

$$\tau_c = \theta \times C_d \tag{20}$$

The results for pAg = 5 and pI = 5 are given in Table I. A rather striking fact

is the resemblance between the Ag^+ and I side of the potential axis for both α and k_s^* (eqn. (11), Table I). This possibly indicates a common rate determining step in the desorption/adsorption process of Ag^+ and I^- which is apparently independent of the nature of the potential determining ion, i.e. located on the AgI side of the AgI/sln interface. The influence of variation in the concentration of the inert electrolyte as well as its nature (various mono- and divalent cations) on the double layer capacitances and the exchange current densities was also studied. We will report on this in a forthcoming paper.

The effect of aging

All electrodes used in this study were aged by keeping them after preparation in a dilute electrolyte solution at a temperature of $80^{\circ}C$ during at least 10 hours. We reported on some differences between aged and non-aged electrodes in a previous paper (7). Electron micrographs suggested a decrease in roughness of the AgI surface upon aging. To confirm this effect, capitance measurements were carried out on aged and non-aged electrodes in a 1.0 M KNO_3 solution. In Fig. 14
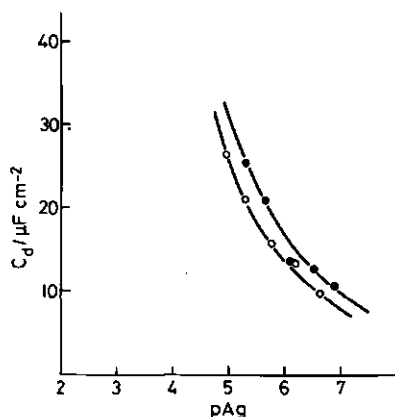

Fig. 14   The effect of aging on capacitance vs. potential as measured in *1.0 M* KNO_3 solution. $\bullet$ = before aging, $\circ$ = after aging.

the C_d/pAg curves are given for the slow relaxation before and after aging. From these curves an average reduction of $18 \pm 2\%$ is deduced, so that the roughness factor decreases with the same percentage. It appeared that aging does not affect

the kinetic parameters of the electrode, provided they are referred to the real surface area. These results are in contradiction with the picture given by ENGEL (28) who suggested that the roughness factor would increase upon aging.

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CHAPTER 4

A KINETIC STUDY OF THE SILVER/SILVER IODIDE FILM ELECTRODE IN AQUEOUS SOLUTION USING THE COULOSTATIC PULSE TECHNIQUE

II. INFLUENCE OF THE NATURE AND CONCENTRATION OF THE INERT ELECTROLYTE

ABSTRACT

The results are presented of a systematic study on the influence of the inert electrolyte on the kinetics of the Ag/AgI film electrode. The coulostatic pulse method was used as measuring technique. Analysis of the relaxation data was carried out after Laplace transformation of the decay curves measured. Both the double layer capacitance and the kinetic parameters of the AgI/aqueous solution interface were evaluated. Particular attention was paid to the influence of the nature and concentration of the indifferent electrolyte on the various kinetic parameters. The main conclusion is that the exchange current density and the transfer relaxation time seem to be almost independent of the inert electrolyte. Both the concentration and the nature of the cation of the electrolyte are unimportant factors with respect to the dynamic properties of the electrode.

INTRODUCTION

In a recent paper (1), we reported on the kinetic properties of the Ag/AgI electrode in 0.1 M KNO_3 solution. The exchange current density i_o at pI = 5 appeared to be 1.8 x 10^{-4} Acm^{-2}. From this, the relaxation time τ_c for ion transfer through the interface was calculated to be 1.4 msec. In fact, the transfer of potential determining ions through the interface is one of the possible relaxation mechanisms which are operative after a sudden change in the amount of charge in the interface AgI/electrolyte solution. Others are diffuse double layer relaxation (on both sides of the interface) and relaxation by transport of charge through the Stern layer parallel to the surface of an AgI electrode or particle (1-3). In the previous paper (1) it was outlined that the aim of this study is to gain information on relaxation processes in the electrode/solution interface in relation with the stability of AgI-sols. The charge transfer relaxation which is directly accessible by means of the coulostatic pulse technique takes place through the non-diffuse or Stern part of the electrical double layer on AgI. As the structure of the double layer is influenced by the nature of the inert electrolyte, the kinetics of the charge transfer were now studied in various

concentrations of KNO_3 and in 0.1 M solutions of the nitrates of Li^+, Cs^+, Mg^{2+}, Ca^{2+} and Ba^{2+}. This paper deals with the results of these experiments. One of the results of the experiments in 0.1 M KNO_3 was that there was a fast relaxation on the µsec. scale which was not influenced by the concentration of the potential determining ions (1). This was one of the reasons to propose that the fast relaxation takes place in the interface Ag/AgI. The independency of the fast relaxation of the solution composition was also found in the present study. Because no new information concerning the fast relaxation was found, this paper only deals with the results of the analysis of the slow relaxation.

EXPERIMENTAL PROCEDURE

The use of coulostatic pulses in electrode kinetics and the analysis of the potential/time decay curve were described in the first paper of this series (1). Analysis of the slow relaxation yields C_d, the differential capacitance of the AgI/solution interface and i_o, the exchange current density. These parameters were measured as functions of the potential of the electrode (expressed as pAg or pI). From the dependence of $\log(i_o)$ on pAg(pI) α, the transfer coefficient of the corresponding electrode reaction, is obtained (1).

The experimental set-up used in the coulostatic pulse experiments, the construction of the cell and the preparation of the Ag/AgI electrodes were described before (1, 4). Measurements were made in 0.1 M solutions of KNO_3, $LiNO_3$, $CsNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Ba(NO_3)_2$. All chemicals used were of p.a. quality (Merck or Baker). To prepare 0.1 M solutions which were free of surface active compounds, 0.1 mol of the salt was diluted in about 300 ml AgI-water (1) which also contained precipitated AgI. This solution was stirred at $80^{\circ}C$ during at least one night. After cooling and separation of the AgI from the solution, AgI-water was added to obtain a 0.1 M solution.

RESULTS AND DISCUSSIONS

A. INFLUENCE OF THE KNO_3 CONCENTRATION

The double layer capacitance

The analysis of the relaxation curve using Laplace transformation and a plot of the real and imaginary components of the Faradaic impedance versus $\omega^{-\frac{1}{2}}$ yield a.o. C_d, the differential double layer capacitance of the interface AgI/electrolyte solution (1). Thus, as a by-product of the kinetic experiments,

capacitance/potential curves were obtained for various KNO_3 concentrations. A
comparison of these results with capacitance values obtained by direct techniques
(direct capacitance measurements (5) and potentiometric titrations of AgI sus-
pensions (2,6)) could indicate the correctness of the use of the simple equiva-
lent circuit of Randles (7) to represent the AgI/electrolyte solution interface.
Thus it can also be a support for the validity of the i_o and τ_c values obtained
using this circuit.
The reproducibility of the capacitance values obtained was also studied. Series of
five identical experiments were carried out at different values of pAg and pI
and in different KNO_3 concentrations. All capacitance values agreed within 15%
(averaged over all series using the same pair of electrodes). In judging this
rather poor figure it should be kept in mind that the capacitance value is ob-
tained as the result of an iterative procedure.
Figs. 1 and 2 give the capacitance values as a function of pAg resp. pI for five
KNO_3 concentrations. In the previous paper (1), a satisfactory agreement was
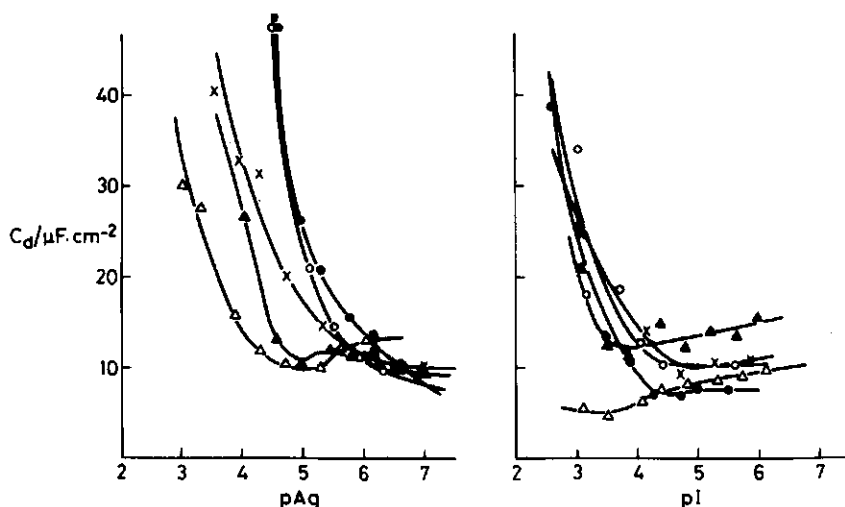

Fig. 1   The differential capacitance C_d of the AgI/solution interface as a
          function of pAg in various KNO_3 concentrations: • = 1.00 M; o = 0.30 M;
          x = 0.10 M; ▲ = 0.03 M; ∆ = 0.01 M.
Fig. 2   The same plot as in Fig. 1 for the pI region studied.

found in the case of 0.1 M KNO_3 (C_d vs. pAg) between our results and direct meas-
urements of double layer capacitance on the same type of electrodes (5), as well
as results derived from potentiometric titrations of AgI suspensions (6). Although
the C_d/pAg curves for the other KNO_3 concentrations are not precise replications
of the direct capacitance measurements (5), the over-all shape of the curves mat-
ches very well. In the case of 0.03 and 0.01 M KNO_3 a distinct minimum is found
at pAg = 5.0. This is in agreement with the results of PIEPER and DE VOOYS (5)
and ENGEL (8). It is an interesting phenomenon that this minimum (the point of
zero charge) is always found at a higher pAg, i.e. about 5.6, in the case of AgI
suspensions (2). The increase in capacitance at low values of pI in Fig. 2 is
probably caused by complex formation at the electrode surface (1). It is not like-
ly that this is a real capacitance effect connected with a second point of zero
charge of the electrode. The effect seems to be less at 0.03 M KNO_3 and it is
absent at 0.01 M KNO_3. It will not be considered further as it is of no impor-
tance in our kinetic studies. The correctness of the evaluated capacitances jus-
tifies the model used (Randles' circuit) and makes the interpretation of the
measurements in terms of exchange current densities more reliable.

The exchange current density and the transfer coefficient

It was shown in the previous paper (1) that the slow relaxation on the msec time
scale could be attributed to the desorption/adsorption of potential determining
ions between the solution and the AgI surface. The corresponding exchange current
density $(i_o)_{slow}$ expresses the rate at which this equilibrium restores itself
after bringing about a sudden change in charge density on the electrode. From
the experiments in 0.1 M KNO_3 solution at various Ag^+ and I^- concentrations, it
appeared that there is a linear relationship between $\log(i_o)_{slow}$ and pI/pAg (1):

$$\log(i_o)_{slow} = \log k_s^* - \alpha \; pI(pAg) \tag{1}$$

From a linear regression analysis on the $\log(i_o)_{slow}$/pI data, the standard devi-
ation in the slope α and the intercept $\log k_s^*$ could be calculated. α is the well
known transfer coefficient with a value between zero and one, k_s^* the over-all
rate constant of the desorption/adsorption process. This procedure was followed
for the five KNO_3 concentrations studied. The results of the experiments are
given in Figs. 3 and 4.
From the slope and intercept i_o was recalculated for pI = 5. This corresponds

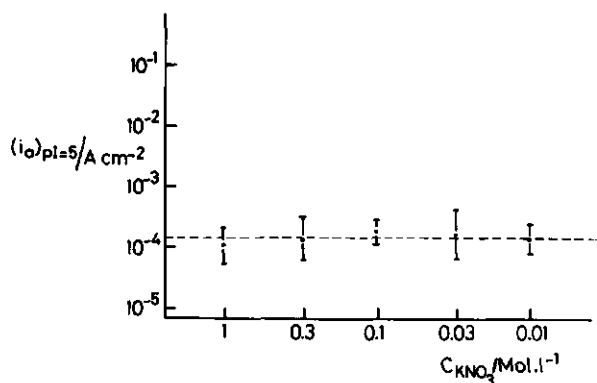.Fig. 3   Logarithmic plot of the exchange current density i_o at about pI = 5
for various KNO_3 concentrations.

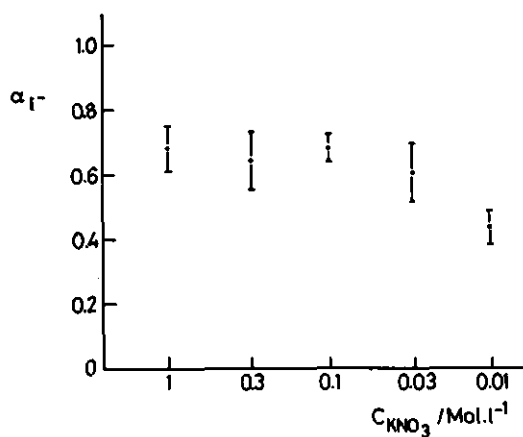Fig. 4   The transfer coefficient α of the I⁻ ion for various KNO_3 concentra-
tions.

with a rather low value for the activity of the electroactive species, but it
was chosen as most of the experiments on the stability of AgI sols are carried

out at this pI value or close to it (2). The indicated error intervals were calculated from the standard deviations in α and log k_s^*. The dotted curve is the average value of the five $\log(i_o)_{slow}$ values and corresponds to $- 3.86 \pm 0.29$. ($\sim 1.4 \times 10^{-4}$ Acm^{-2}). The relaxation times for ion transfer τ_c were calculated from these i_o values and the capacitance data from Fig. 2 by using:

$$\tau_c = (RT/F) \frac{C_d}{(i_o)_{slow}} \qquad (2)$$

This equation gives the relaxation time of a parallel combination of the capacitor C_d and the resistance θ. The latter is the ion transfer resistance, which equals $(RT/F)/(i_o)_{slow}$ (1).

The results for pI = 5 are shown in Table I. In this table, the upper and lower figures are calculated from the standard deviation intervals in $(i_o)_{slow}$ using

Table I

Relaxation times τ_c for Ag^+/I^- ion transfer through the AgI/solution interface at various KNO_3 concentrations. The upper and lower limits for τ_c are also given.

KNO_3 conc.	1.00		0.30		0.10		0.03		0.01	
		0.2		0.4		0.8		0.1		0.5
τ_c(pAg = 5)	0.6		1.2		1.5		0.3		0.5	
$/$ 10^{-3} sec		2.5		3.9		2.9		0.8		0.6
		0.9		0.9		0.9		0.9		0.9
τ_c(pI = 5)	1.8		2.0		1.4		2.3		1.5	
$/$ 10^{-3} sec		3.6		4.3		2.2		4.6		2.6

eqn. (2). The intervals around τ_c are not symmetrical because the linear regression analysis was performed on logarithmic $(i_o)_{slow}$ values. It is clear from Table I that at pI = 5, τ_c is not influenced by the inert electrolyte concentration. This indicates that the rate determining step in the adsorption/desorption process of I^- ions is located very close to or at the AgI surface. Except for the value for 0.01 M KNO_3, the α_I- values in Fig. 4 are pointing in the same direction. A confrontation of these results with the potential profile at the interface could proof useful.

The corresponding results for pAg = 5 are given in Figs. 5 and 6. The behaviour of $(i_o)_{slow}$ is almost the same as before and the average value given by
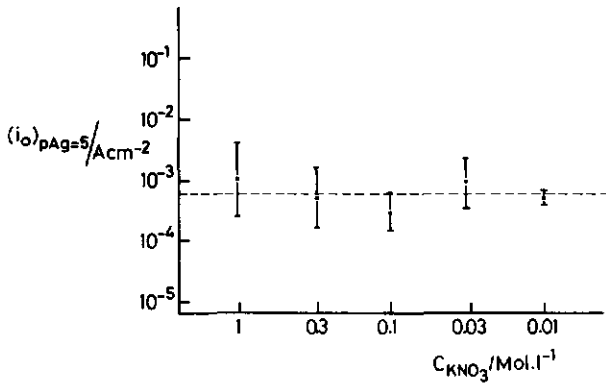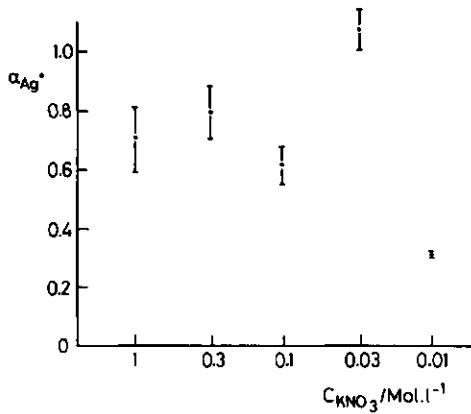
Fig. 5   The same plot as in Fig. 3 for pAg = 5.

Fig. 6   The same plot as in Fig. 4 for the Ag^+ion.

the dotted line in Fig. 5 corresponds to 5.8×10^{-4} $A.cm^{-2}$. The large scatter in α values in Fig. 6 is probably not a real electrode effect in view of the constantness of the $(i_o)_{slow}$ values. The corresponding relaxation times are given

in Table I. It is to be noted that τ_c is almost the same for ion transfer at positive potentials as it is at negative potentials. It seems that there is one fundamental step in the adsorption/desorption processes which is rate determining, irrespective of the type of potential determining ion present in the solution.

B. INFLUENCE OF THE NATURE OF THE CATION

The double layer capacitance

Experiments were also carried out in solutions containing 0.1 M $X(NO_3)_n$ with n = 1 and X = Li^+, K^+ and Cs^+ and with n = 2 and X = Mg^{2+}, Ca^{2+} and Ba^{2+}. It is well known that both the valence and the nature of the cation influence the coagulation concentration of negative AgI sols (2).
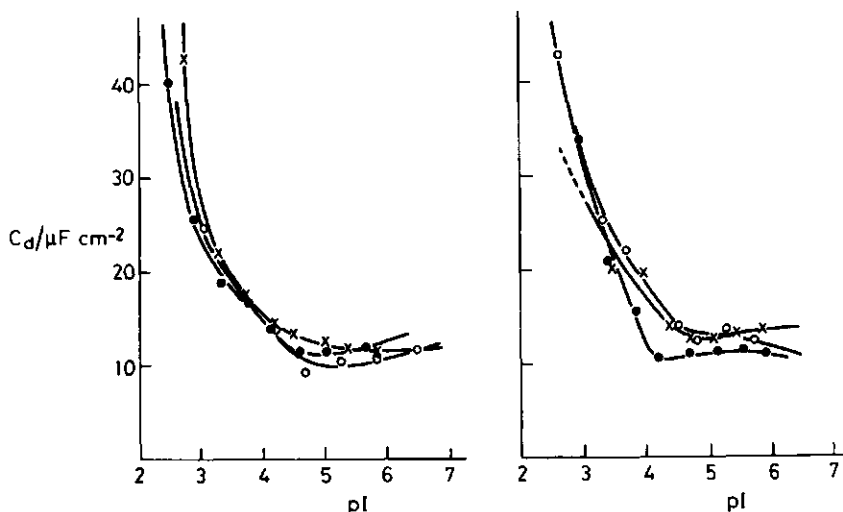In Figs. 7 and 8 the results of the capacitance evaluations are shown for the

Fig. 7   The differential capacitance C_d of the AgI/solution interface as a function of pI for three different inert electrolytes. $\bullet$ = 0.10 M $LiNO_3$; o = 0.10 M KNO_3; x = 0.10 M $CsNO_3$.

Fig. 8   The same plot as in Fig. 7 for three divalent cations. $\bullet$ = 0.10 M $Mg(NO_3)_2$; o = 0.10 M $Ca(NO_3)_2$; x = 0.10 M $Ba(NO_3)_2$.

monovalent and the divalent cations respectively. Particularly, the negative potential region was investigated because it can be expected that changes take place on the negatively charged electrode where the Stern part of the double layer is mainly constituted by cations.

The C_d/pI dependency is in qualitative agreement with the direct capacitance measurements by PIEPER (9). The capacitance values for $Mg(NO_3)_2$ solutions are significantly lower than for $Ca(NO_3)_2$ solutions. This result is in agreement with Pieper's findings for 1, 0.01 and 0.001 M solutions. Again we may conclude that for the present purposes the results for the capacitance values are quite satisfactory.

The exchange current density and the transfer coefficient

The results of the kinetic experiments with variations of pI for the six cations investigated are shown in Figs. 9 and 10. Both the recalculated value for i_o at
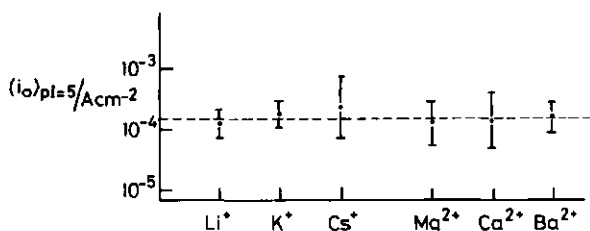
Fig. 9   Logarithmic plot of the exchange current density i_o at pI = 5 for 0.1 M *solutions of the nitrates of six different cations.*

pI = 5 and the transfer coefficient α seem to be insensitive to the nature and the valency of the cation. The effects of (KNO_3) concentration variation and cation variation seem to be similar: α lies between 0.6 and 0.8; $(i_o)_{pI=5}$ lies between 10^{-3} and 10^{-4} A cm^{-2}. The results for the region around pAg = 5 do not differ much from those in Figs. 9 and 10. The average value for $(i_o)_{pAg=5}$ is only somewhat higher than the corresponding value for pI = 5.
The resulting relaxation times are given in Table II.

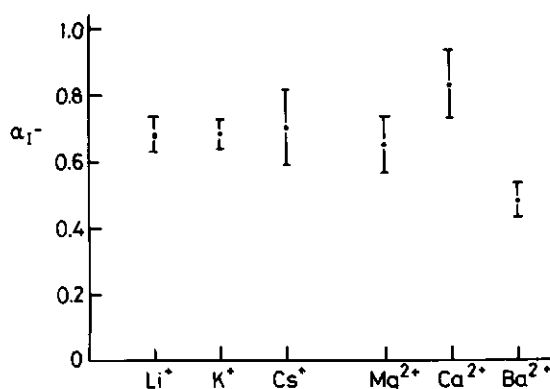Fig. 10   The transfer coefficient α of the I^- ion for 0.1 M solutions of the nitrates of six different cations.

Table II

Relaxation times τ_c for Ag^+/I^- transfer through the AgI/solution interface for various nitrates as indifferent electrolyte. The upper and lower limits for τ_c are also given.

Cation	Li^+	K^+	Cs^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
τ_c (pAg = 5) $/\ 10^{-3}$sec	0.5 *1.5* 5.2	0.8 *1.5* 2.9	0.3 *1.0* 2.8	0.05 *0.6* 8.3	0.5 *2.3* 10.3	0.6 *2.0* 7.3
τ_c (pI = 5) $/\ 10^{-3}$sec	1.5 *2.5* 4.2	1.0 *1.5* 2.2	0.5 *1.4* 4.5	1.1 *2.3* 5.0	0.9 *2.4* 6.5	1.2 *2.0* 3.6

The following conclusions can be drawn:

1. It was indicated earlier (1) that the adsorption equilibrium between Ag^+ and I^- ions in the solution and the AgI electrode may be represented by:

$$V_{Ag^+}^- \ + \ |I_{AgI}^-|^0 \ \rightleftarrows \ |I_{sln}^-|^- \tag{3}$$

$$|Ag_{AgI}^+|^0 \ \rightleftarrows \ |Ag_{sln}^+|^+ \ + \ V_{Ag^+}^- \tag{4}$$

$V_{Ag}^-{}^+$ is a silver ion vacancy in the AgI crystal lattice. The independency of the kinetics for both reactions of the composition of the solution (and hence of the double layer composition) provides an indication that there is a rate determining step which takes place very close to or just at the electrode surface;

2. The similarity in the kinetics of the two apparently independent electrode reactions possibly indicates that this step is a *common* one. As the common species in eqns. 3 and 4 is the silver ion vacancy it is probable that this common step is the recombination of $V_{Ag}^-{}^+$ with an adsorbed Ag^+ ion or an I^- ion which is on a lattice point in the AgI structure.

3. Within the limits of accuracy, as indicated by the standard deviation in $(i_o)_{slow}$, the relaxation time for charge transfer is of the order of 10^{-3} sec for pAg, pI = 5. Furthermore, it is almost independent of the indifferent electrolyte in solution.

A further investigation of the influence of a.o. the specific properties of the AgI film and the temperature on the dynamic properties of the AgI electrode should be very useful. In particular the incorporation of certain divalent ions in the AgI lattice could strongly alter the concentration of silver ion vacancies. Thus, the present results and conclusions can be checked.

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CHAPTER 5

THE SIGNIFICANCE OF RELAXATION EFFECTS FOR COLLOID STABILITY

INTRODUCTION

The experiments on the kinetics of the Ag/AgI film electrode, which were described in the preceding chapters, have a colloid chemical background. One of the reasons to study this particular electrode is the possibility to gain information on relaxation processes in the interface AgI/electrolyte solution. It is the purpose of this final chapter to consider the consequences of the relaxation data for the stability theory of AgI sols systematically. A first attempt will be made by comparing the electrode relaxation effects measured with some similar processes for a colloidal AgI particle as mentioned by other investigators (1-4).

ELECTRIC RELAXATION EFFECTS CONNECTED WITH AgI SOL PARTICLES

In Fig. 1, a schematic picture is given of two negatively charged colloid AgI
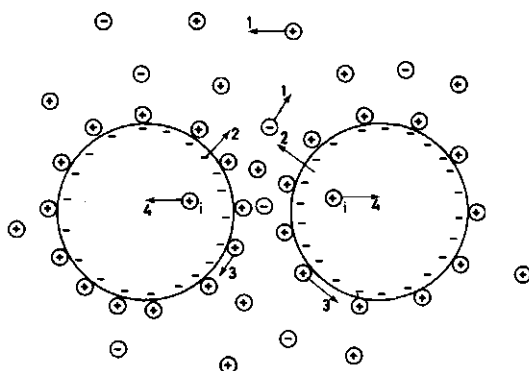

Fig. 1   Two approaching AgI particles in Brownian motion in 0.1 M KNO_3 solution. The negatively charged particles are surrounded by cations (K^+). The diffuse double layer consists of K^+ and NO_3^- ions. The numbered arrows correspond to the four described relaxation processes. $\theta = K^+$, $\theta = NO_3^-$, $- = I^-$, $\theta_i = $ interstitial Ag^+.

particles with a diameter of a few hundred Angstroms, subjected to Brownian motion and moving towards each other. When their mutual distance is of the order of the diffuse double layer thickness (which is about one nm. under coagulation conditions), the overlap of the diffuse double layers will cause a charge injection in the double layer in the region of approach. The repulsive electrostatic energy increases as the interparticle distance decreases. The opposite, attractive v/d Waals energy also increases in magnitude. The balance of these two will determine if the particles stick together or not. A calculation of the balance of these energies as a function of the interparticle distance has been given by the DLVO theory (5).

As outlined in the introduction of chapter 3, it depends on the posibility of the several processes to relax on the timescale of a Brownian collison, whether the charge on the particle has to be treated in a static way or in a dynamic way. The time needed for a Brownian collison was calculated by FRENS (1) and OVERBEEK (4) to be 10^{-5} to 10^{-7} sec, depending on the particle radius and the electrolyte concentration (via the double layer thickness). However, if the particles come close together, electrostatic repulsion and hydrodynamic interaction increase the collison time (HONIG, ROEBERSEN and WIERSEMA (6)). Under coagulation conditions, a collision, or interaction time of 10^{-5} to 10^{-4} sec or more seems realistic.

The time scales of the following processes that may lead to a decrease of charge in the region of interaction must be compared with the particle interaction time:

1. *diffuse double layer relaxation*

This process is fast compared to 10^{-4} sec. For instance, it is 10^{-8} sec in a 0.1 M KNO_3 solution (1, 7). However, its contribution to the discharging is negligible: under coagulation conditions more than 95% of the charge is located in the non-diffuse or Stern-layer (3).

2. *compact double layer or Stern-layer relaxation*

Because almost all of the particle charge is located in the compact double layer under coagulation conditions, it is to be expected that a relaxation process in this layer will have a large effect on the total charge on the particle. In, for example, a discharging process, the potential determining ions (Ag^+ or I^-) have to move through this layer to reach the solution.

3. *relaxation through migration of charge along the surface of the particle*

The extra amount of charge is only injected at the region of approach. Possibly, counterions are able to move away from this region by surface conduction and "spread" over the particle.

4. *relaxation by transport of charge through the interior of the particle*

Inside the particle, interstitial silver ions are the charge carriers (chapter 3). Movement of silver interstitials to or from the region of contact (depending on the sign of the particle charge) would effectively contribute to a decrease in the electrostatic repulsion.

The time scales on which the relaxations 2 and 4 may proceed can be estimated from the electrode relaxation measurements described in the foregoing chapters. The four types of charge transport which correspond with the described relaxation processes are indicated in Fig. 1.

RELAXATION OF THE Ag/AgI ELECTRODE

On the timescale covered by the technique used (μsec and higher), two distinct relaxations were measured, one in the μsec timerange and one in the msec time-range. In chapter 3 it was explained that the fast relaxation is to be attributed to ion transfer processes in the solid/solid Ag/AgI interface. As the fastest processes that could be measured with the technique used are on the μsec time-scale, relaxation of the diffuse double layer on the solution side cannot be held responsible for the fast relaxation step. It was shown in chapter 3 and supported by the capacitance measurements in various electrolytes reported in chapter 4 that the slow relaxation on the msec timescale is connected with the transfer of ions through the AgI/electrolyte solution interface.

The relaxation time of the slow process appeared to be approximately 1 msec for coagulation conditions and no significant influence of the inert electrolyte variation could be detected within the limits of accuracy.

SIMILARITIES AND DIFFERENCES IN THE RELAXATION BEHAVIOUR OF SOL PARTICLES AND ELECTRODES

The electrodes which were used in this study are very flat with a roughness factor of about 1.5 (8). Here, one encounters one of the main differences between an electrode and an AgI sol particle: it is well known that these particles do not have a flat surface (9) and the small channels and cavities will cause diffusion processes to be slower than in the case of a flat electrode surface.

The Ag/AgI interface which played a role in the fast electrode relaxation, is not present in a sol particle; only the slow or Stern relaxation is common to both. As the electrode is uniformly polarized (from the macroscopic point of view), migration of charge along the electrode surface will not occur in this

case. From the resistance measurements reported in chapter 2 it was concluded that the geometrical relaxation time of the electrode (transport of charge through the interior of the particle) is on the order of 10^{-8} sec. It has to be noted that the silver iodide film on the electrode consisted of γ-AgI and that most sols on which experiments are done consist of β-AgI. This means that, as the specific resistance of β-AgI is about 100 times that of γ-AgI, the geometric relaxation time of sol particles will be on the order of 10^{-6} sec.

The main conclusions that can be drawn from the results of this study, are:
1. the Stern-layer relaxation of AgI particles is experimentally accessible by electrode kinetic studies of Ag/AgI electrodes;
2. this Stern-layer relaxation appears to be a rather constant phenomenon, not influenced by the concentration and nature of the inert electrolyte;
3. compared with the interaction time of sol particles (up to 10^{-4} sec.), the Stern relaxation is relatively slow (appr. 10^{-3} sec).
From this, it may be deduced that during interaction between sol particles, the total amount of charge on the particle is constant. However, migration of charge along the surface and/or through the interior of the particle could very well be responsible for a decrease of the local charge density in the region of short distance between the particles.

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SUMMARY

The aim of this study is to detect and characterize relaxation processes on silver/silver iodide *electrodes* in aqueous electrolyte solution. The information obtained is to be used for an estimation of the consequences of similar processes on colloidal AgI *particles* during encounter.

In chapter 1 a general introduction is given. It is explained how electrode kinetic data can be used to obtain insight in the dynamic aspects of the stability of the lyophobic colloids.

Some fundamental properties of the Ag/AgI film electrode which are important in the interpretation of the relaxation measurements are described in chapter 2. The preparation of the electrode, the silver layer and the AgI film is described. The specific resistance of the AgI film was obtained from measurement of the electrode resistance and the thickness of the AgI film. An estimation of the roughness factor of the AgI surface is made using electron micrographs and results of other investigators who worked with the same type of electrodes.

In chapter 3 the relaxation behaviour of the Ag/AgI electrode in 0.1 M KNO_3 solution is described. The used pulse technique, the experimental set-up and the method of analysis are treated. It is shown that there are two relaxation processes: a fast one on the µsec scale and a slower one on the msec scale. They are probably connected with charge transfer processes in the Ag/AgI and AgI/electrolyte solution interface respectively. The standard exchange current density and the transfer coefficient for the slow relaxation of both the Ag^+ and the I^- reaction are calculated. The double layer capacitances are also obtained and their values agree with the results of other studies.

Relaxation measurements in various KNO_3 concentrations and various types of inert electrolyte are reported in chapter 4. One of the main conclusions is that the slow relaxation is not influenced by the concentration and nature of the inert electrolyte.

In chapter 5 an attempt is made to interpret the results obtained with the electrodes in terms of relaxation processes occurring at interacting AgI sol particles. It is indicated that some of the possible relaxation processes are fast as compared with the process of encountering of two colloid particles.

Diffuse double layer relaxation in the aqueous solution and migration of inter-
stitial silver ions in the solid are examples of such fast processes. On the other
hand, the transfer of potential determining ions (silver or iodide ions) through
the Stern layer is a rather slow process with a time constant which is lower than
the particle encountering time by a factor of about ten. Thus, in the case of
silver iodide sols, exchange of charge between particle and solution will not
occur. However, redistribution of charge in the region of short distance between
the interacting particles is possible via the fast relaxation processes. Thus,
the silver iodide colloid appears to be intermediate between the constant charge
case and the constant potential case.

SAMENVATTING

Het doel van dit onderzoek is het meten van relaxatieprocessen aan zilver/ zilverjodide *elektroden* in waterige elektrolytoplossingen. Met de verkregen informatie wordt nagegaan wat de consequenties zijn van soortgelijke processen tijdens de ontmoeting van deeltjes van een zilverjodide *kolloïd*.

In hoofdstuk 1 wordt een algemene inleiding gegeven. Beschreven wordt hoe elektrodekinetische gegevens kunnen worden gebruikt om inzicht te verkrijgen in de dynamische aspecten van de stabiliteit van lyofobe kolloïden.

Enkele basiseigenschappen van de Ag/AgI elektrode die van belang zijn voor de interpretatie van de relaxatiemetingen worden in hoofdstuk 2 beschreven. Een beschrijving wordt gegeven van de bereiding van de elektrode, de zilverlaag en de AgI film. De specifieke weerstand van de AgI film werd verkregen na meting van de weerstand van de elektrode en de dikte van de AgI film. Een schatting van de ruwheidsfactor van het AgI-oppervlak wordt gemaakt door gebruik te maken van elektronenmicroscoopopnamen en resultaten van andere onderzoekers die met een zelfde type elektrode hebben gewerkt.

In hoofdstuk 3 wordt het relaxatiegedrag van de Ag/AgI elektrode in 0.1 M KNO_3 beschreven. De gebruikte pulstechniek, de proefopstelling en de analysemethode worden behandeld. Aangetoond wordt dat er sprake is van twee relaxatieprocessen: een snel proces op de µsec. tijdschaal en een langzamer proces dat zich afspeelt op de msec. tijdschaal. Zij hangen waarschijnlijk samen met ladingoverdrachtsprocessen in respectievelijk het grensvlak Ag/AgI en het grensvlak AgI/elektrolytoplossing. Een berekening wordt gegeven van de standaard uitwisselingsstroomdichtheid en de overdrachtscoëfficiënt voor de langzame relaxatie van de Ag^+ en de I^- reactie. De dubbellaag capaciteiten worden ook verkregen en de waarden stemmen overeen met de resultaten van andere onderzoekingen.

In hoofdstuk 4 worden de resultaten gegeven van de relaxatiemetingen in verschillende KNO_3 concentraties en verscheidene inerte elektrolyten. Eén van de hoofdconclusies luidt dat de langzame relaxatie niet wordt beïnvloed door de concentratie en de aard van het inerte elektrolyt.

In hoofdstuk 5 wordt een poging gedaan om de resultaten die behaald zijn met de elektroden te interpreteren in termen van relaxatieprocessen aan AgI soldeeltjes. Aangegeven wordt dat sommige relaxatieprocessen volledig verlopen zijn tijdens de ontmoeting van twee kolloïdale deeltjes. Diffuse dubbellaagrelaxatie

in de oplossing en migratie van interstitiële zilverionen in de vaste fase zijn voorbeelden van zulke processen. De overdracht van potentiaalbepalende ionen (zilver en jodide) door de Sternlaag is echter een relatief langzaam proces. De tijdconstante hiervoor is ongeveer tien maal groter dan de ontmoetingstijd van de deeltjes. In het geval van zilverjodide solen zal uitwisseling van lading tussen deeltje en oplossing derhalve niet plaatsvinden. Echter, daar waar de deeltjes elkaar naderen is herverdeling van lading mogelijk d.m.v. de snelle relaxatieprocessen. Het zilverjodide kolloïd blijkt zodoende intermediair te zijn tussen het constante lading geval en het constante potentiaal geval.

CURRICULUM VITAE

Ik ben geboren op 25 februari 1950 te Koog a/d Zaan.
Van 1962 tot 1968 volgde ik het onderwijs aan het Reformatorisch College
Blaise Pascal te Zaandam waar ik in juni 1968 het HBS-B diploma mocht behalen.
In september 1968 werd een aanvang gemaakt met de scheikundestudie aan de Vrije
Universiteit te Amsterdam. Het kandidaatsexamen S3 (scheikunde en natuurkunde
met wiskunde) werd behaald in december 1971. Het doctoraalexamen werd afgelegd
in juni 1975 met als hoofdvak Analytische Chemie (in het bijzonder de Elektro-
analyse), eerste bijvak Fysische Chemie en tweede bijvak Bedrijfseconomie.
Van 1 oktober 1975 tot 1 oktober 1978 ben ik als wetenschappelijk assistent in
dienst geweest van de Landbouwhogeschool bij de vakgroep Fysische en Kolloïd-
chemie. In die periode mocht ik het onderzoek uitvoeren dat in dit boekje is
beschreven.
Vanaf 19 februari 1979 ben ik werkzaam als programmeur/systeemontwerper bij
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