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The Silver-Silver Iodide Electrode. II.*

M. Mirnik and R. Despotović

*Laboratory of Physical Chemistry**, Faculty of Science, University of Zagreb*
and
Institute »R. Bošković«, Zagreb, Croatia, Yugoslavia

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Electrolytically prepared Ag/AgI electrodes, fresh and aged in solutions of *p*Ag values higher than 4.3, show in the region of *p*Ag=6 to *p*I=6 negative deviations from the reversible Nernst potential. Electrodes aged in solutions of *p*Ag values lower than 4.3 show positive deviations in the same region. The zero point of the electrophoretic mobility of aged coloidal AgI and the positive stability limit of activity are equal to *p*Ag=4.3. In the region *p*I=7 to *p*Ag=7 the positive and negative deviations are practically constant and independent of *p*Ag (*p*I). The positive deviation of the electrode potentials was explained by the formation of the cubic, and the negative one by the formation of the hexagonal modification of AgI during the aging of the electrodes.

INTRODUCTION

Earlier results[1,2] on the potentiometric behaviour of the rotating electrolytically prepared silver-silver iodide electrode showed that the potential of this electrode in the region *p*I=6 — *p*Ag=6 deviates from the theoretical values of the Nernst formula. The positive and negative deviations were mostly irreproducible and the factors governing them were not established. It was shown however that the deviations were not caused by a time lag of the electrodes as the positive and negative deviations were obtained irrespectively of the direction of the activity change of I^- to Ag^+ or *vice versa*. The supposition was made that the deviations of the electrode potentials are connected with the colloidal and crystalline properties of the AgI which covers the electrodes.

This paper represents an attempt to elucidate the influence of the *p*Ag and *p*I values of the solution in which the electrodes were aged prior to the measurement of the electrode potential and the influence of the age of the electrodes, as it is known that these factors are responsible for the crystallographic modification and colloidal properties of the AgI in contact with a solution.

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A comparison of the potentials of the Ag/AgI electrodes, with the electrokinetic properties of the AgI and with the ageing and precipitation processes, should represent a contribution to the elucidation of the electrical double layer of the AgI.

The electrode potentials were measured by titrating a solution of pAg = 5 with NaI to pI = 5 using electrolytically prepared Ag/AgI electrodes.

EXPERIMENTAL

100 ml of a solution containing 10^{-5} *N* $AgNO_3$ and 10^{-3} *N* $NaNO_3$ was prepared and three equal rotating Ag/AgI electrodes and the standard electrode were immersed into this solution. From a microburette of 250 µl capacity NaI solution was added in 2.5 minutes intervals in calculated amounts causing pAg 5.0, 5.5, 6.0, 6.5, 7 and 8, respectively, and pI 7, 6.5, 6, 5.5 and 5, respectively.

In the reverse titrations $AgNO_3$ was added to NaI solutions in an analogous way.

Electrolytically prepared Ag/AgBr electrode in 0.01 *M* KBr + 1.10 *M* KNO_3 was used as reference electrode. The electrodes were obtained by electrolysing as anode 2.5 cm of a silver wire (0.5 mm dia.) melted in a glass capillary for 10 minutes (0.6 mA, 2.1 V) in a 0.02 *M* NaI solution. The electrodes were rotated axially with the aid of an electromotor.

Freshly prepared electrodes were washed with distilled water, wiped off with filter paper and left aging in a $AgNO_3$ solution of a given concentration in the dark for a given period of time. The $AgNO_3$ solutions were saturated with AgI by addition of a minute quantity of NaI solution. Before the potentiometric titration, the electrodes were washed again with distilled water, wiped off with filter paper and immersed in 10^{-5} *M* $AgNO_3$.

The potentiometric measurements were made with a compensation potentiometer (Fischer Scientific Co. Type S) using a galvanometer of 10^{-9} A per scale division as a zero instrument. The mean of the measured potentials of the three electrodes was taken as the result. The potentials were measured immediately before each next addition of the NaI solution.

RESULTS

The results of the potentiometric titrations are plotted as EMF against pI-pAg.

Fig. 1 illustrates the influence of the ageing time of the electrode in a solution of pAg 1.73 upon its potentials. The plots are curves with a nearly horizontal part in the pAg = 7 to pI = 7 range (Fig. 1.)

For fresh electrodes the horizontal part of the plots is more negative than the theoretical line with a 58 mV per pI unit slope and by ageing from 0 to 500 hours the negative deviations of the potentials become positive. Equal plots were obtained when the activity change is of the opposite direction. These results gave the evidence that the deviations are not a time lag, since the negative and positive deviations were obtained by titrations in both directions.

Figures 2a, 2b, and 2c show that by allowing the electrodes to age in the solutions of pAg 1.7, 2.4, and 4.0 respectivelly the time necessary for the deviations to become positive increases from 1 to over 7 days. In the solution of pAg 4.8 (Fig. 2d) the deviation of the electrodes remained negative even after 22 days. The titrations in the opposite direction gave practically identical curves. (Fig. 2a, 2b, 2c and 2d)

In Fig. 3 the potential measured at the assumed $pAg = pI = 8$ was plotted against the electrode ageing time in solutions of different pAg. This figure as well as the preceding one show that pAg 4 to 4.8 is a transition region where

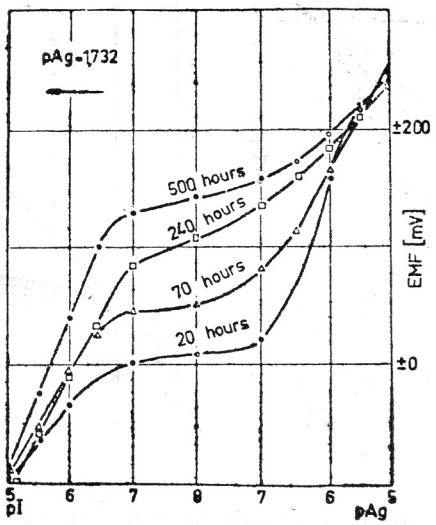


Fig. 1. Influence of the aging time on the electrode potentials. Apscissa: pI—pAg; Ordinate: EMF of the cell Ag/AgI—(I⁻, Ag′)—(0.01 *M* KBr)—AgBr/Ag. Ag/AgI electrodes aged for 20, 70, 240 and 500 hours in saturated solutions of pAg 1.73.

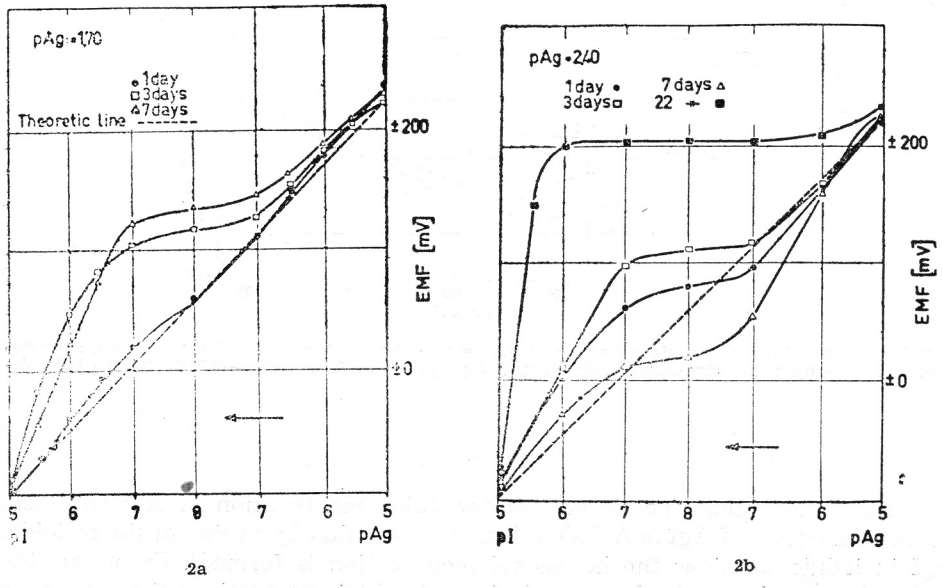
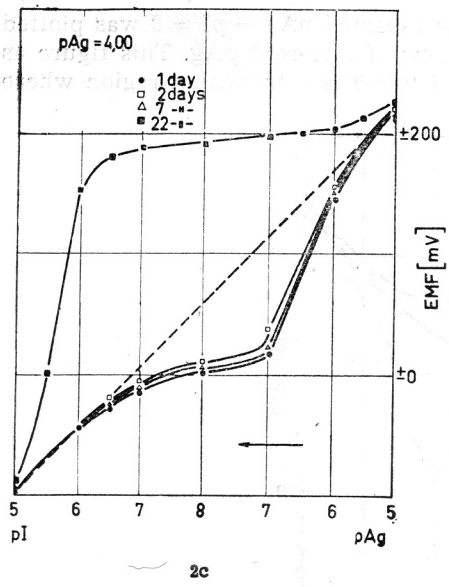
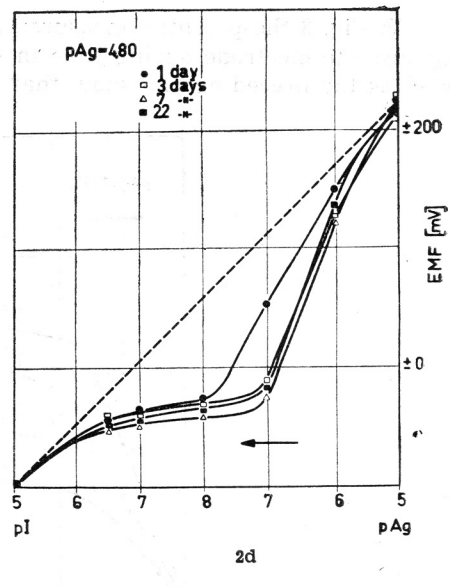


Fig. 2. Influence of the pAg and of the ageing time on the electrode potentials. Apscissa: pI—pAg; Ordinate: EMF of the cell Ag/AgI—(I⁻, Ag+)—(0.01 *M* KBr)—AgBr/Ag. Ageing in saturated AgI solutions of p Ag: a) 1.7, b) 2.4, c) 4.0, d) 4.8



2c



2d

the positive deviations of the electrode potential at low pAg change into the negative deviation at high pAg. (Fig. 3)

Freshly prepared electrodes and electrodes which aged in solutions of pAg values higher than 4.8 retained their negative deviations of the electrode potential.

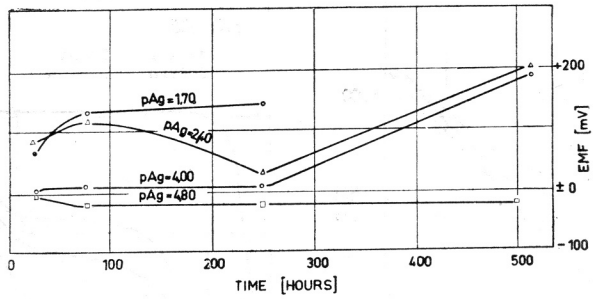


Fig. 3. Change of the electrode potential at $pAg = pI = 8$ with the ageing time of the electrodes. Abscissa: ageing time, Ordinate: EMF of the Ag/AgI—(10^{-8} *M*, I^-, Ag^+)—(0.01 *M* KBr)—AgBr/Ag.

DISCUSSION

It is known that the amount of the cubic modification of AgI increases during the ageing of AgI in $AgNO_3$ solutions[6,7] and that by ageing of the colloidal AgI in iodide solutions the hexagonal modification is formed[3]. From this the conclusion can be made that in solution with high pAg values the well aged AgI of the electrodes is of a hexagonal modification and that at low activities

of the I^- ($10 < pAg < 7$) the potential of the electrode covered with the hexagonal modification is negative compared with the reversible Nernst values and is practically independent of the pI values.

Similarly in solutions of low pAg most probably the cubic modification of AgI is formed on the electrodes during the ageing and that the cubic modification determines the positive deviation of the $pAg = 6$ to 11 region. The deviations between the extremely positive and negative values correspond probably to mixtures of both modifications, caused by different ages and different ion activities. The turning point seems to occur at pAg 4.3. This value is equal to the positive stability limit of activity and to the zero point of the electrophoretic mobility of aged colloidal AgI[4].

Carmody[5] investigated the influence of light on the potentials of silver halide electrodes. The effects were smaller than 1 mV and hence, this influence must be neglected in our measurements, since the reproducibility was 1—5 mV at higher activities, and at lower activities ($pAg = 6$ to $pI = 6$) it was 20 mV only.

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IZVOD

Elektroda srebro - srebreni jodid. II

M. Mirnik i R. Despotović

Elektrolitički pripremane Ag/AgI elektrode, svježe i starene, u otopinama sa pAg vrijednostima većim od 4,3, pokazuju u intervalu od $pAg = 6$ do $pI = 6$ negativna odstupanja od reverzibilnog Nernstova potencijala. Elektrode starene u otopinama sa pAg vrijednostima manjim od 4,3 pokazuju pozitivna odstupanja u istom intervalu. Nul točka elektroforetske pokretljivosti starenoga koloidnog AgI i pozitivna aktivitetna granica stabilnosti je kod vrijednosti $pAg = 4{,}3$. U intervalu od $pI = 7$ do $pAg = 7$ pozitivna i negativna odstupanja su praktično konstantna i neovisna o pAg vrijednostima većim od 4,3, pokazuju u intervalu od $pAg = 6$ do $pI = 6$ negativna kubične, a negativno odstupanje formiranjem heksagonalne modifikacije AgI, starenjem elektroda.

FIZIČKO-KEMIJSKI INSTITUT
PRIRODOSLOVNO-MATEMATIČKOG FAKULTETA
I
INSTITUT »RUĐER BOŠKOVIĆ«

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