Electrophoretic Mobility and the Isoelectric Coagulation of the Silver Iodide Sols and Suspensions*

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Electrophoretic mobility was measured on sols and suspensions of AgI aged for 4 hours and for 4 days at $6.5 > pAg > 2.8$. The electrophoretic zero-point and the electrophoretic mobility were found to be independent of the concentration of AgI in which the sols and suspensions were prepared in the region between 10^{-4} and 10^{-3} M AgI.

The zero-point of electrophoretic mobility was for 4 days old systems at pAg 5.3 and shifed after four or more days to a value of 4.3. This latter value was equal to the positive activity limit of stability. By increasing the concentration of $NaNO_3$ from 2.10^{-1} to 10^{-2} N the zero-point of a four days old sol decreased from pAg 4.7 to pAg 3.8. On the four hours old systems no influence of the $NaNO_3$ concentration could be established in the same concentration region.

By a comparison of the electrophoretic mobilities of potentials of a theoretical Ag-AgI electrode and of potentials of an electrode covered with fresh AgI with the stability regions, the conclusion could be made that the negative (positive) stability was caused by a more negative (positive) potential of the theoretical electrode than the negative (positive) electrophoretic potential of stable particles.

The isoelectric coagulation occured in the region $6.2 > pAg > 4.5$ where the potential of a theoretical Ag-AgI electrode and the electrophoretic potential of particles aged for 4 hours was more positive than the electrophoretic potential of small particles aged for 4 days which remained in suspension after shaking.

An effort was made to explain the observed regularities by introducing the dipole part of the Galvani potential.

INTRODUCTION

For further advancement of the theories of stability of lyophobic colloids it is necessary to acquire more experimental information on the interrelation between stability-instability and the measurable parameters of the double layer such as electrode and electrokinetic potentials, adsorption of constitutive ions, as well as their zero-points. It seems that the present theories had to be built on the basis of scarce experimental data and therefore necessarily many assumptions had to be made for which the probability of beeing later experimentaly confirmed was low.

The isoelectric coagulation is generally supposed to be connected with a low potential on the particles and therefore located in the vicinity of the zero-point of charge of the potential determining electrolyte. By our former investigations[1] it was established that the isoelectric coagulation is located between two limits which were called the »negative« and »positive activity limit of stability«, the isoelectric coagulation region lying between them. The aim of the present paper is to elucidate experimentally the interrelation of the electrophoretic potentials and the limits of the isoelectric coagulation.

EXPERIMENTAL

The electrophoretic measurements were made with a microelectrophoresis cell with two capillaries. According to Smith and Lisse[2] in the centre of the wider capillary the electroosmotic movement of the electrolyte is reduced to zero- if the lengths and the widths of the capillaries are in a theoretically defined ratio. The mobility of the particles was measured by microscopic observation of the amplitude of the oscillation of the particles in an alternating electric field (Frequency 1.0, 1.7 and 5.5 cycles per second 54 V/cm.).

The stability — instability relations were observed by tyndallometric measurements described elsewhere.[3] The 1 minute activity tyndallogram was used for the determination of the positive activity limit, giving practically the same results as the 10 minutes tyndallograms.

The sols were prepared in the following way: In one series of beackers of 200 ml., 50 ml. of a NaI solution were pipetted, the concentration beeing twice the desired final sol concentration. In the second series of beakers were pipetted 50.00 ml. of the AgNO$_3$ solution of the same concentration as the NaI solution. Different excesses of AgNO$_3$ were obtained by addition of different amounts of 10^{-2} N AgNO$_3$ solution with a microburette. The precipitation was performed by pouring the NaI solution into the AgNO$_3$ and back again seven times in about 15 seconds. In this way series of systems were obtained with a desired concentration of AgI and with pAg values varying between 2.8 to 6.5.

A small portion of each sol was used for measuring the pAg values potentiometrically with a rotating paraffined Ag-AgI electrode.[4]

The electrophoretic measurements were performed 3—4 hours after the preparation of the sols, and after 4 days. Immediately after the preparation the elektrophoretic mobilities were not stable enough to give reproducible values. After 4 days the values did not change any more.

The sols on which the tyndallometric measurements were performed were prepared in a similar way with a total volume of 10 ml. The tyndallometric values were measured 1 minute after the preparation of the sols.

RESULTS

The results of the electrophoretic measurements were expressed as mobilities of the particles in cm/volt. sec. and the change of the mobility with the pAg values was shown graphicaly.

Fig. 1 shows that in the region of low concentration of the AgI (from 10^{-4} to 10^{-3} M) and with 10^{-3} N NaNO$_3$ present the concentration of the AgI does not influence the electrophoretic mobility. The zero-point of the electrophoretic mobility shifts from pAg 5.2 with sols aged for 4 hours to 4.3 with those aged for 4 days. In the region from pAg 6.2 to 4.3 the electrophoretic mobility shifts towards negative values in the period between 4 hours and 4 days.

On the basis of Fig. 2 the conclusion can be made that the zero-point of the electrophoretic mobility of the sols aged for 4 days with 10^{-4} to 10^{-3} M AgI is equal to the positive activity limit of stability, given as the inter-

section point of the tangent on the steepest part of the one minute activity tyndallogram with the axis of abscissa.

The influence of the concentration of $NaNO_3$ on the zero-point of the electrophoretic mobilities of sols aged for 4 days and prepared with a concentration of 2.10^{-4} M AgI at the positive activity limit of stability is shown
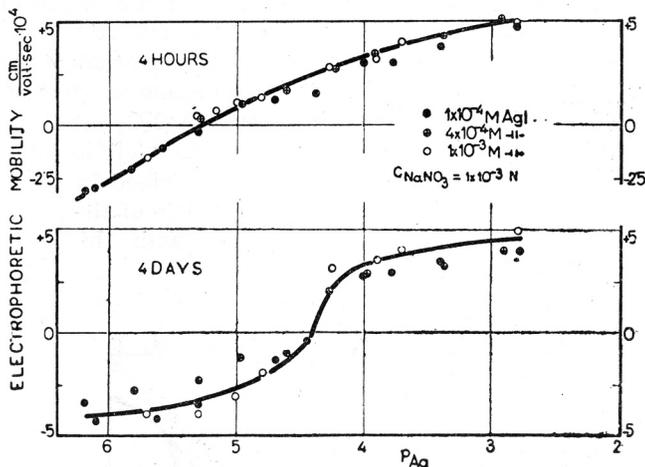

Fig. 1. The electrophoretic mobility of sol particles aged for 4 hours and 4 days against the pAg. Sol concentration: 1.0×10^{-4}, 4.0×10^{-4}, $1.0 \cdot 10^{-3}$ M AgI and $1.0 \cdot 10^{-3}$ N $NaNO_3$.
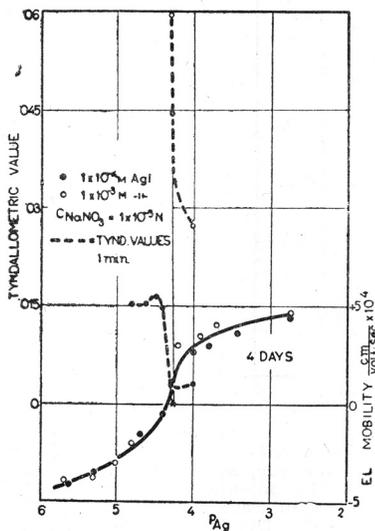

Fig. 2.

Fig. 3.

Fig. 2. The electrophoretic mobility of sol particles aged for 4 days and the tyndallometric value of sols aged for 1 minute against the pAg.
Sol concentration: $2.0 \cdot 10^{-4}$ M AgI and $2.0 \cdot 10^{-4}$,
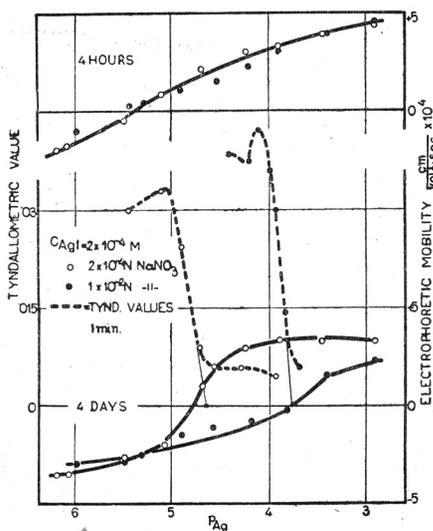$1.0 \cdot 10^{-2}$ N $NaNO_3$

Fig. 3. The influence of the concentration of $NaNO_3$ on the plots: Electrophoretic mobility of sol particles aged for 4 hours and for 4 days and the tyndallometric value of sols aged for 1 minute against the pAg.
Sol concentration: $2.0 \cdot 10^{-4}$ M AgI and $2.0 \cdot 10^{-4}$, $1.0 \cdot 10^{-2}$ N $NaNO_3$

in Fig. 3. The zero-point and the stability limit shift when the concentration
of NaNO$_3$ increases from 2.10^{-4} to 1.10^{-2} N, from pAg 4.7 to 3.8. The mobility
of the particles aged for 4 hours is independent of the concentration of NaNO$_3$.

DISCUSSION

According to Gorochowsky[5] the concentration of sols in the nascent state
influences the value of the electrophoretic zero-point. At the concentration
of 2.5. 10^{-3} M AgI the zero-point was at pAg 5.5 and at the concentration 5.
10^{-5} it was at pAg 3.5. Applying the same technique of preparation of the
sols by pipeting the NaI solution into the stirred AgNO$_3$ solution the authors
obtained a similar influence on the zero-point as well as on the positive
stability limit. When the sols were prepared as described in the experimental
part by direct mixing of the components the influence of the sol concentration
was eliminated. Therefore the results obtained with this technique were
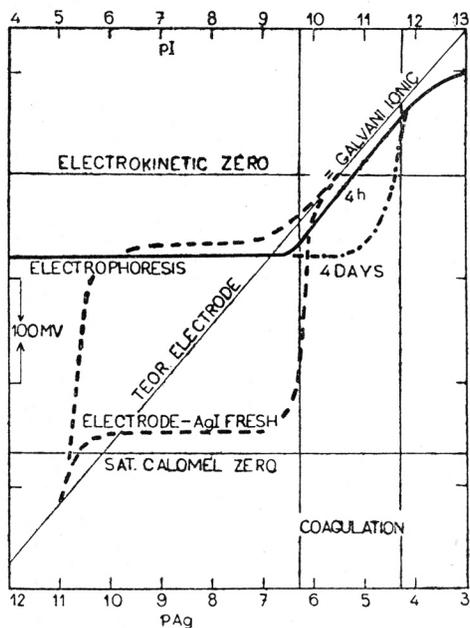considered as representative.

Fig. 4. A comparison of the electrode potentials and the electrokinetic potentials with the
isoelectric coagulation region of the AgI system. pAg = 5.5 the supposed zero-point of the
ionic part of the Galvani potential (thin line) measured as the potential of a reversible
electrode. Thick dashed line: potential of an electrode covered with fresh colloidal AgI. Thick
line: Electrophoretic potentials of sols aged for 4 hours and 4 days. The isoelectric coagulation
region between the negative and positive stability limit.

Gorochowsky[5] observed that the change of the zero-point of the electro-
phoretic mobility is connected with »the shift of the domain of the minimum
stability of the sols«. Fig. 3 confirms this observation by the shift of the
stability limit and of the zero-point of particles aged for 4 days, when the
concentration of NaNO$_3$ was changed.

There was an apparent disagreement between the results of Gorochowsky and those of Basinski[5] (Fig. 3). The zero-point of electrophoresis on fresh sols in the nascent state obtained by Gorochowsky was at $pAg = 5.5$ and the zero-point obtained by Basinski was at 4.5 on sols with no data as to their age given in the cited paper. Our results explain the divergence as an aging effect. Certainly, Basinski worked with aged sols.

From the fact that the concentration of $NaNO_3$ does not influence the electrophoretic mobility of the particles aged for 4 hours (Fig. 3) the conclusion may be made that in the early stages the process of the formation of the primary particles, i. e. the nucleation, is in a broad region of the concentration of neutral electrolytes indepedent of their concentration. The secondary process of formation of coagulated particles by the isoelectric coagulation is, however, dependent on the concentration of the neutral electrolyte which is evidenced by the shift of the electrophoretic zero-point of the aged particles and of the positive stability limit to a lower pAg value with the increasing concentration of $NaNO_3$. This may be taken as a confirmation of the correctness of the assumption that the sols in the nascent state are suitable for the observation and measurement of the coagulation phenomena with the neutral electrolytes, because the nucleation is independent of the varying concentrations of the neutral electrolytes, present at the beginning of the sol formation.

There are no direct methods for the measurement of the constants and parameters of the electrical double layer. If any measurable quantities can give some data for the elucidation of the structure of the double layer, then electrophoretic and electroosmotic potentials, potentials of electrodes prepared in different ways, adsorption of potential-determining ions and stability — instability relations can certainly be used for this purpose.

The change of the potential of a Ag-AgI electrode with a theoretical slope of 58 mV certainly represents the change of the ionic part of the Galvani-potential[6].

For a comparison of the electrokinetic measurements with the electrode potential measurements, a knowledge of the relative difference between the zero-points of the different potentials is necessary[7]. One possible criterion is to ascribe a value of zero to the ionic part of the Galvani potential at the zero-point of charge. The zero-point of charge can be considered as equal to the zero-point of adsorption of the potential-determining ions. Several workers have obtained the zero-point of adsorption in the vicinity of pAg 5.5 to 6[8]. Therefore the zero-point in Fig. 4 was supposed to be at pAg 5.5.

The potential of a rotating Ag-AgI electrode covered with fresh electrolyticaly prepared colloidal AgI increases in the region pI 5.5 to 6.5 faster than a reversible electrode to become in the region pI 6.5 to pAg 6.0 practically constant. The plots of e. m. f. against pI (pAg) are independent of the direction of the activity change. The upper and the lower type of plots (dashed lines) and plots lying between them may be obtained in both directions by repeated titrations. Among others these facts indicate that a simple time lag or nonreversibility could not explain these characteristics of the electrodes.[4, 9]

The electrophoretic potentials were calculated from the measured mobility by aid of Smolychowsky's resp. Henry's equation using a factor of 6π[10]. Plots calculated with a factor 4π are leading to the same conclusions.

Applying the above assumption, the relative positions of the electrophoretic and electrode potential plots against the logarithm of the activity of the potential — determining electrolyte are presented in Fig. 4.

The main conclusion is that in the negative stability region ($pAg > 6.2$) the potential-determining process at the electrode covered with fresh colloidal AgI is not the same as the process at a reversible (theoretical) electrode in the region $pI = 6$ to $pAg = 6$. The electrophoretic potential is in the same region also independent of the pI values. From this the conclusion can be drawn that the process causing the electrophoretic mobility and the process causing the irreversible behaviour of the Ag-electrodes covered with colloidal AgI are the same and different from the process causing the adsoption of the potential determining ions and thus causing the rise of the ionic part of the Galvani potential.

Lange and Schuecker[11] calculated the change of the electrode potential in a system in which the quantity of the potential determining ions was insufficient to build up — by ionic adsorption — the ionic part of the Galvani potential so that the dipole part was prevailing. The curve obtained was analogous to the lower curve measured with fresh electrodes. From this analogy the conclusion can be made that the potential determining process on colloidal AgI particles in the low activities of the potential determining ions is the orientation of the H_2O dipoles, causing the rise of the dipole part of the Galvani potential. The suface of the particles with the adjoining layer into which the potential determining ions can not diffuse because of their too low concentration (less than $10^{-6} N$) represents a system analogous to the system considered by Lange and Schuecker.

Equal electrophoretic mobilities of particles in the region of $pAg \cong 6.5$ to $pI \cong 5$ can hardly be explained by the ionic part of the Galvany potential. When the particles are formed in a concentration $10^{-2} M$ AgI at $pAg > 6.5$ (stable region) and supposing that they contain about 1000 AgI molecules, the adsorbed quantity[12] of the potential determining iodide ions can not be higher than one ion per particle (Adsorption capacity 1 part per thousand, zero-point of adsorption pAg 5.5). It is highly unprobable that the particle of 23000—10000 times higher mass than the counter ion (a. e. N^+, Na^+) would be moving electrophoretically, especially when at the same time the counter ion is located in a medium of low viscosity such as water. It is much more probable that the ion will move in the opposite direction. At 10 pI units from the zero-point of adsorption the relative mass of the particles would be smaller for only a factor of 10.

If the measured potentials have any bearing on the stability of colloids the conclusion has to be made that the negative stability of AgI particles is effectuated by a more negative potential of the theoretical (reversible) electrode than the electrophoretic potential of the stable particles. In terms of the theoretical potentials the negative stability is caused by the ionic part of the Galvani potential that is more negative as the negative dipole part.

In the isoelectric coagulation region the primary particles start to coagulate immediately after their formation. The increasing tyndallometric values 1 minute after the mixing of the precipitation components indicate this. After 4 hours the particles are coagulated and start to sediment. ([1] II. Fig. 5., IV.

Fig. 1). After their sedimentation they will form visible flocks after shaking. On such coagulated but still homogeneously dispersed particles the 4 hours electrophoretic mobilities were measured. If on the sediments the electroosmotic mobilities were measured after several days a curve analogous to the 4 hours electrophoresis curve was obtained ([9] p. 208, Fig. 1). Four or more days later, after shaking the sediments, few very small particles remained dispersed; by measuring their electrophoretic mobility the 4 days electrophoretic curve was obtained. In times shorter than 1 or 2 hours it was possible to observe particles moving with different velocities, occasionally in opposite direction.

Thus the following explanation could be given for the process of the isoelectric coagulation. Immediately after the mixing of the precipitation components all AgI is in the form of the primary particles with negative electrokinetic potentials. As the adsorption of the potential determining ions in the vicinity of the zero-point of adsorption becomes to small to contribute 1 adsorbed ion per primary particle, the ionic part of the Galvani potential can arise only by coalescence of some of the particles into one agregate. After this has been accomplished (in about 4 hours) the electrophoretic potential indicates the rise of the ionic part of the Galvani potential by its slope and by its zero-point. The electrophoretic zero-point can be considered as equal to the supposed zero-point of adsorption. After 4 days there are some primary particles left in the suspension, their concentration beeing to small to lead to a sufficient number of collisions causing coagulation. After 4 hours the remaining primary particles could not be observed among the great number of the coagulated particles.

Therefore the isoelectric coagulation is caused by the more positive electrophoretic potential of the coagulated particles and a negative potential of the primary particles.

In terms of the theoretical potentials the isoelectric coagulation could be explained as caused by the more positive ionic part of the Galvani potential of the coagulated particles and a negative dipole part of the primary particles.

The positive stability could be explained by a more positive theoretical (ionic Galvani) potential of the Ag-AgI electrode and the less positive electrophoretic potential. In terms of the theoretical potentials the positive stability is caused by the ionic part of the Galvani potential that is more positive than its positive dipole part.

The position of the isoelectric coagulation on the side of excess Ag-ion activities and the negative potential of the primary particles in the isoelectric coagulation region can be explained by the specific orientation (or/and adsorption) of the water dipoles on the AgI surface.

There is one more indication that the process causing the negative stability is not directly or solely connected with the double layer structure arising from the adsorption of the potential determining ions. The negative stability limit is equal for all three silver halides[13]. Thus, it may be concluded that the coagulation induced at the negative activity limit is caused by the destruction of the double layer causing stability and by the subsequent formation of the layer in which the equilibrium with the Ag-activities is established. Thus the layer causing stability should be in all three cases equal.

It would be difficult to explain the equality of the double layers if they were formed by the adsorption of different halide ions. In all three cases the water dipoles remain equal.

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IZVOD

Elektroforetska pokretljivost i izoelektrična koagulacija solova i suspenzija argentum jodida

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Izvršena su elektroforetska mjerenja na 4 sata i 4 dana starim AgI solovima i suspenzijama u području $6.5 > pAg > 2.8$. Utvrđeno je, da su nultočka elektroforetske gibljivosti i elektroforetska gibljivost neovisni o koncentraciji, u kojoj su solovi i suspenzije pripremani u granicama između 10^{-4} do 10^{-3} M AgI. (Sl. 1.) Nultočka elektroforetske gibljivosti nalazi se kod 4 sata starih sistema kod pAg 5.3, te se nakon 4 ili više dana pomiče na vrijednost 4.3. Ova potonja vrijednost jednaka je pozitivnoj granici stabiliteta. (Sl. 2.) Kod povećanja koncentracije neutralnog elektrolita $NaNO_3$ od 2.10^{-4} N na 10^{-2} N pomiče se nultočka 4 dana starog sola od vrijednosti pAg 4.7 na vrijednost 3.8. $NaNO_3$ u istim koncentracijama ne utječe međutim na vrijednosti elektroforetskih nultočaka 4 sata starih sistema. (Sl. 3.)

Uspoređujući elektroforetske gibljivosti s potencijalima teoretske Ag-AgI elektrode i elektroda pokrivenih svježe pripremljenim AgI dolazimo do zaključka, da je negativni (pozitivni) stabilitet uzrokovan negativnijim (pozitivnijim) potencijalom teoretske elektrode od negativnog (pozitivnog) elektroforetskog potencijala stabilnih čestica. (Sl. 4.)

Izoelektrična koagulacija nastaje kod 1.10^{-3} N $NaNO_3$ u području $6.2 > pAg > 4.5$, a ovdje je potencijal teoretske Ag-AgI elektrode i elektroferetski potencijal 4 sata starih čestica pozitivniji od elektroforetskog potencijala 4 dana starih sitnih čestica, koje zaostaju nesedimentirane nakon mućkanja suspenzija.

Opisan je pokušaj razjašnjivanja ovih pojava s pomoću dipolnog i ionskog dijela Galvanijeva potencijala.