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Electrokinetic Studies in Dispersed Systems. III. Electrokinetic Potentials of the Silver Iodide by the Streaming Potential and Electroosmotic Method

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The zero point of the ζ -potential (streaming potential and electroosmosis) on AgI coagulated with a neutral electrolyte lies in the region between pAg 5.1 and 6.2 in which region it is irreproducible. The shift of the zero point towards lower pAg values is smallest for the 3-valent and highest for the monovalent cations. The ζ -potential is independent of the pI value between 3 and 9. The change in concentration of the neutral electrolyte from 10^{-4} to $10^{-2} N$ lowers the ζ -potential for a factor of 3 to 4. The relation between the ζ -potential and the coagulation with neutral electrolyte and the isoelectric coagulation is discussed.

INTRODUCTION

The electrode potentials, electrophoretic and electroosmotic mobilities as well as streaming and centrifugation potentials have to serve as the basis for any theory of the stability of colloids based on the concept of the electrical double layer. For the purpose of the development of a general theory of stability reliable measurements of the cited electrical entities should be collected and correlated with the stability-instability relations of suitable colloidal systems.

Following this idea a discussion was started by the senior author¹ based on some early results on electrokinetic potentials of the AgI system of different investigators, on results of adsorption of potential determining ions, and on potentiometric measurements on Ag/AgI electrode. In a previous paper² an attempt to elucidate the electrophoretic behaviour of the AgI system was made. The present paper should contribute to the same discussion some results on streaming potentials and electroosmotic mobilities of the AgI system.

EXPERIMENTAL

The precipitates »in statu nascendi«

The precipitations were performed by mixing 500 ml. of each precipitation component (NaI and AgNO₃) giving sols $10^{-3} M$ in AgI. The activity of potential determining ions was controlled potentiometrically by means of a reversible paraffined Ag/AgI electrode³. The potentiometric measurements were made immediately

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after the precipitations and the activities adjusted to the required value by additions of NaI or AgNO₃ solutions from a microburet. The precipitates were left standing for seven days in the mother liquor before measurements of the streaming potential or electroosmosis were made.

The »dried« precipitates

The dried precipitates were prepared following an idea of Lange and Crane⁴ by mixing 0.16 *N* solutions of NaI and AgNO₃ under vigorous stirring at room temperature. The precipitates were filtered off and washed with warm and cold redistilled water, till the filtrate showed constant values of conductivity, dried at room temperature, ground in an agate mortar and stored dry till use. 1 gram of the precipitate was stirred in 1 liter of solutions of various electrolytes with different *pI* or *pAg* values, obtained by the addition of NaI or AgNO₃ solutions, and controlled potentiometrically. They were also left standing for 7 days.

All solutions were prepared by dissolution of weighed amounts of analytical grade salts in redistilled water (conductivity less than $2 \times 10^{-6} \Omega^{-1} \text{cm.}^{-1}$). The concentration of NaI was determined by potentiometric titration with AgNO₃. The streaming potential apparatus was described in a previous paper⁵. The suspension of AgI in the mother liquor was poured onto the disc in the plug tube in small portions and compressed by suction. The precipitate was never allowed to come out of the mother liquor. After the last portion was added and the plug formed, suction was continued for 5 minutes. This treatment was found satisfactory to obtain reproducible results. Some characteristics of such plugs are given in the following figures, which are mean values of seven precipitates, with *pAg* varying from 6 to 9, and whose ζ -potentials varied from -13 to $+7$ mV.

Height of the plug in the tube	2.7 ± 0.2 [cm.]
Inner diameter of the tube	0.5 ± 0.05 [cm.]
Apparent density of AgI in the tube, d_{app}	0.36 ± 0.06 [g.cm. ⁻³]
Density of the solid AgI ⁶	5.67 [g.cm. ⁻³]
Porosity = $1 - d_{\text{app}}/d_{\text{real}}$	0.94 ± 0.01
Hydrodynamic coefficient, <i>D</i>	$(1.2 \pm 0.2) \times 10^{-7}$ [cm. ² sec.g. ⁻¹]
Mean pore radius (theoretical), <i>r</i>	1.7 ± 0.6 [μ]

The hydrodynamic coefficient is defined as the volume of liquid transported in unit time through unit area under unit pressure⁷:

$$D = V/PtF \times 13.6 \times 981 \quad [\text{cm.}^2 \text{sec. g.}^{-1}]$$

(*D* = hydrodynamic coefficient, *V* = volume in cm³, *P* = pressure in cm. of mercury, *t* = time in seconds, *F* = area of cross section of the plug in cm.², 13.6 = the specific gravity of mercury, 981 = the gravitational force acceleration). The mean pore radius can be computed from the following expression⁷ for a system consisting of spheres:

$$r = \sqrt{8 dD\eta/W} \quad [\text{cm.}]$$

(*r* = mean pore radius, *d* height of the plug, η = viscosity of the liquid, *D* and *W* as above).

Each measurement of the streaming potential was made at seven different pressures and the measurement taken as reliable if a linear dependence of the measured potential against pressure was obtained.

The electroosmotic apparatus was described in a previous paper⁸. The suspension of AgI was brought into the plug tube by a dropper and the filled tube centrifuged (at 2000 r.p.m., *l* = 9 cm.) for 10 minutes. The applied current was as low as possible. A current of 1 mA for 30 sec. was the upper limit. The volume transports were recorded for 3 different currents, each two times, and the measurement taken as reliable if a linear dependence of the volume transport per unit time against current was obtained.

Conductances were measured in the streaming potential cell by the bridge method as described⁵. As the majority of the precipitates was in the mother liquor of 10^{-3} *N* in electrolytes, no attempts were made to make corrections for the surface conductance.

The results are expressed in terms of the ζ -potential computed by the expression

$$\zeta = (4 \pi \eta / \epsilon) \kappa \times b$$

(the symbols have their usual meaning^{5,8}. b is the regression coefficient of the streaming potential upon pressure for streaming potential measurements, or the volume transport per unit time upon current strength for the electroosmotic measurements. The transformation of constants results in the following formulas:

a) for the streaming potential:

$$\zeta = 1.05 \times 10^5 b \kappa \quad [\text{mV}] \quad \text{and}$$

b) for the electroosmosis:

$$\zeta = 1.42 \times 10^5 b \kappa \quad [\text{mV}]$$

In Fig. 1 different plots of streaming potentials against pressure illustrate the range of experimental conditions encountered in AgI systems of different conductivity and ζ -potential.

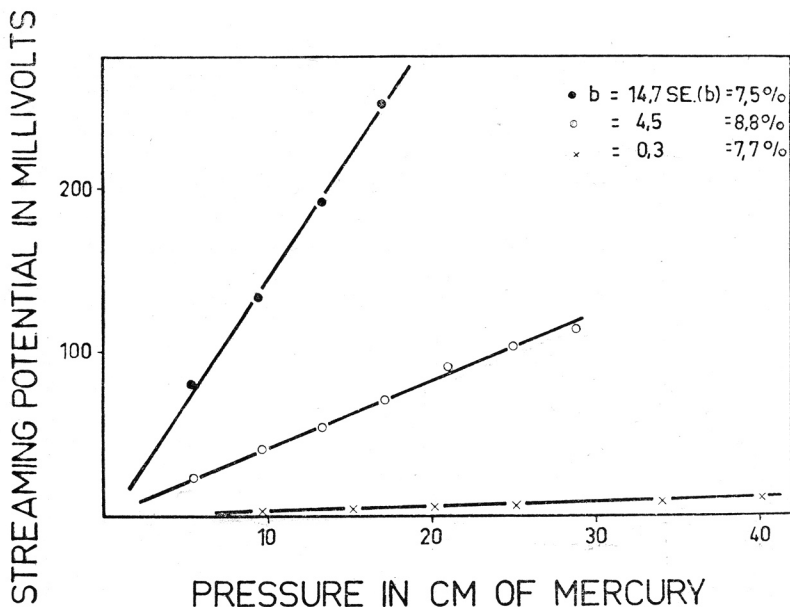


Fig. 1. Streaming potential versus pressure for different concentrations of electrolyte: $1 \times 10^{-4} N$ (full points), $1 \times 10^{-3} N$ (circles) and $1 \times 10^{-2} N$ (crosses).

Fig. 2. shows the general relationship of the ζ -potential against the activity of potential determining ions and the 95% confidence limits for AgI precipitates coagulated by $\text{La}(\text{NO}_3)_3$ using the »in statu nascendi« technique. In the region of $pI > 8$ and $pAg < 4$ the reproducibility of the ζ -potentials is fair and the potentials are almost constant and independent of pI (see also Figs.

4 and 5). In the isoelectric coagulation region the potentials are irreproducible and the values are randomly distributed having plus or minus signs at the same pAg . The region of dispersed ζ -potentials spreads over more than one pAg unit, which shifts from electrolyte to electrolyte.

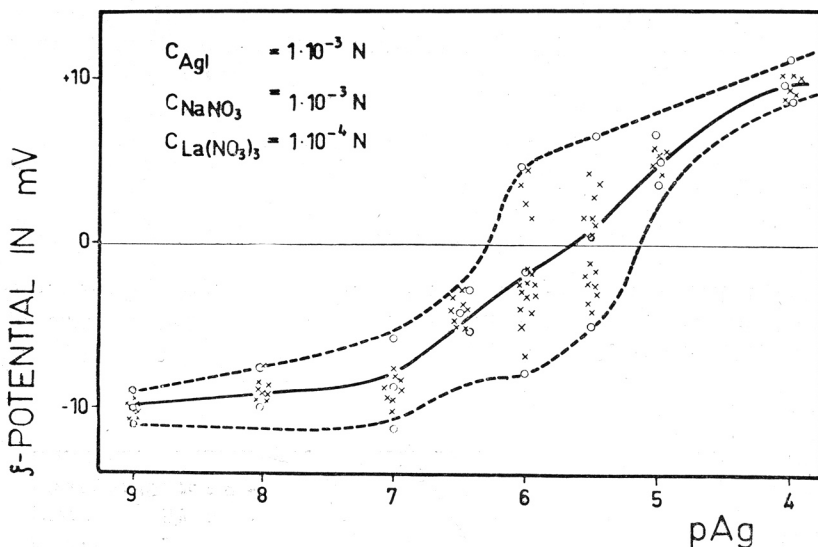


Fig. 2. The ζ -potential of AgI precipitates in statu nascendi versus the activity of potential determining ions and the 95% confidence limits.

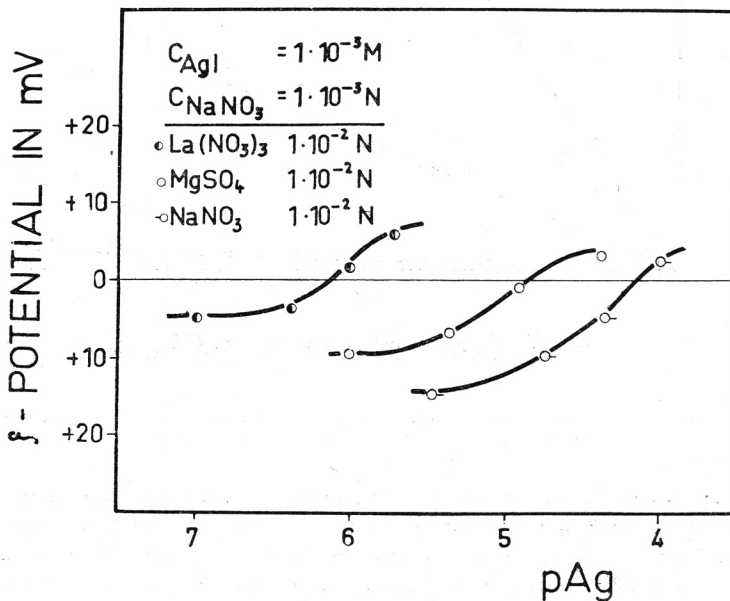


Fig. 3. The zero point of the ζ -potential electroosmosis of AgI precipitates »in statu nascendi« in $10^{-2} N$ solutions of $La(NO_3)_3$, $MgSO_4$ and $NaNO_3$.

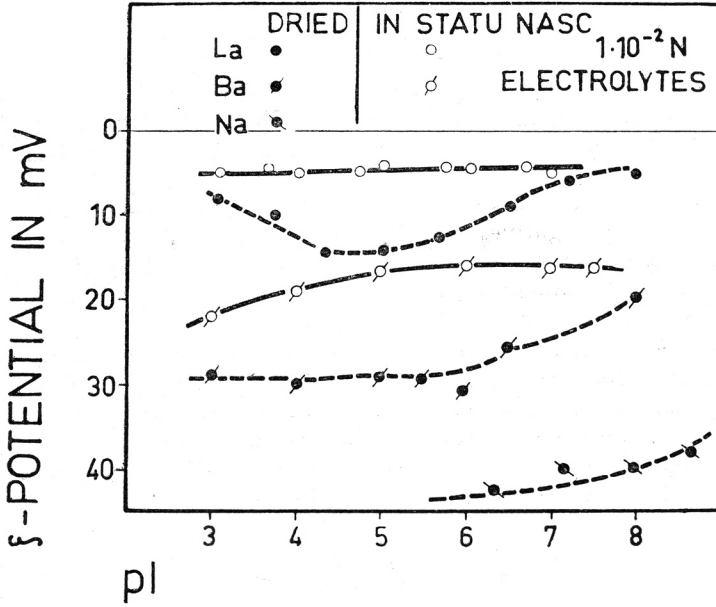


Fig. 4. The influence of the valency of the counter ions upon the ζ -potential streaming potential of AgI precipitates »in statu nascendi« (circles) and »dried« (full points)

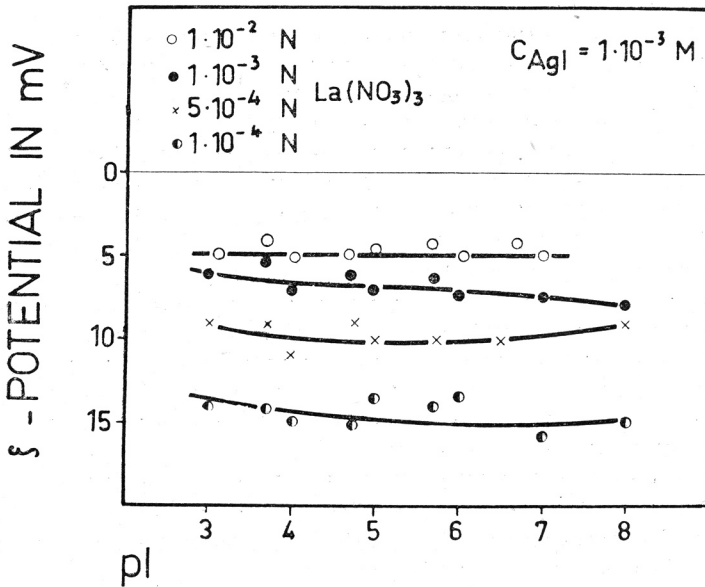


Fig. 5. The influence of various concentrations of $\text{La}(\text{NO}_3)_3$ upon the ζ -potential streaming potential of AgI precipitates »in statu nascendi«.

Even after 14 days of ageing of the precipitates in the mother liquor no improvement of the reproducibility was obtained. In the positive stability region the ζ -potentials are again reproducible, positive, and exhibit a tendency towards constant values at $pAg = 4$.

In Fig. 3 the variation of the position of the zero point of the ζ -potential with various neutral (i. e. non potential determining) electrolytes is shown. The zero point lies at $pAg = 4.2, 4.9$ and 6.1 for Na^+ , Mg^{++} , and La^{+++} in concentrations of $10^{-2}N$, respectively.

The influence of the neutral electrolytes upon the values of the electrokinetic potential of negative AgI precipitates both »in statu nascendi« and »dried« is shown in Fig. 4. The curves represent mean values of three repeated measurements. The values show a distinct decrease of negative potentials with increasing valency of the counter ions.

In Fig. 5 the influence of the concentration of $La(NO_3)_3$ on the ζ -potential of the »in statu nascendi« precipitates is shown. A tri-valent ion was chosen because its coagulation value is low, giving a broad region of concentrations in which the coagulated form is most probably in equilibrium with its mother liquor. The figure shows the constancy of the ζ -potential with pI and the decrease of the ζ -potential with the increasing concentration of the neutral electrolyte.

DISCUSSION

One of the aims of the present paper was to establish the role of the measured electrokinetic potentials (streaming potential and electroosmosis) in the isoelectric coagulation region and in the coagulation with neutral electrolytes, and to give some data on the electrokinetic properties of the AgI system in general.

The streaming potential and electroosmotic mobility can be measured on coarse particles only i. e. on particles which are not colloidal dispersed and which can be pressed into plugs. Outside the isoelectric coagulation region (i. e. outside of $pAg = 4.5$ to 6.2) the ζ -potentials could be measured only if some coagulating agent was added, in our case $La(NO_3)_3$, in excess of the coagulation concentration (see Fig. 5). Without the added $La(NO_3)_3$ the measured values inside the isoelectric coagulation region show a similar irreproducibility of the zero point and of the magnitude of the ζ -potential between $pAg = 5.1$ and $pAg = 6.2$.

In a previous paper² it was established that the pAg value of the positive stability limit coincides with the zero point value of the electrophoretic mobility of the particles which remain colloidal dispersed after some days. The interrelation of the negative stability limit at $pAg = 6.2$ and the mobility could not be established. It may be accidental that this irreproducible region of the ζ -potentials of the coarse particles lies between the zero point of mobility of the coagulating, but still colloidal dispersed particles at $pAg = 5.1$ (ref. 2 Fig. 1) and the negative stability limit at $pAg = 6.2$. Most probably in this region the measurement itself affects the value of the ζ -potential shifting it towards positive or negative values.

The isoelectric coagulation region of AgI (pAg between 4.5 and 6.2) can therefore be defined as the region where the measured electrokinetic effects

can be positive or negative depending on the age and/or the size of the particles, on the influence of the measurement on the ζ -potential and on the method of measurement. The positive activity limit of stability is defined by the electrophoretic zero point of particles remaining colloidal dispersed after some days.

The zero point of the ζ -potential of coagulated particles pressed into plugs could not be made reproducible as yet, but the value of the negative stability limit at $pAg = 6.2$ could be taken as the highest pAg value at which positive electrokinetic values were ever observed.

The problem of the dependence of the ζ -potential upon the activity of the potential determining ions is of major importance for the theory of stability of hydrophobic colloids and of the electrical double layer. In the negative stability region the electrophoretic mobility could not be measured for the particles are too small to be visible. With the streaming potential and electroosmotic technique the measurements are possible providing the particles are coagulated by a neutral electrolyte. Fig. 4 shows that over 4 or 5 pI units the ζ -potential of precipitates »in statu nascendi« remains constant. The accuracy of measurements is insufficient to establish the inclination precisely for tri-valent ions (La^{+++}). The ζ -potentials for bi-valent ions (Ba^{++}) indicate a slight increase in the negative values with the decrease in pI values. Rutgers and Nagels⁹ (Fig. 4) in a recent paper obtained a similar result for the centrifugation potential technique on dialysed sols in the region $pI = 2$ to 3. In the case of addition of KI the ζ -potential decreased while the ϵ -potential increased (i. e. proportional to pI).

In the case of the »dried« precipitates (Fig. 4) the curves show a similar trend in general, namely constancy or a slight inclination, La^{+++} excepted, where a maximum in the negative potential can be observed.

Fig. 5 shows the influence of tri-valent electrolyte upon the ζ -potential and that this influence is very pronounced. The neutral electrolyte, or more precisely its counter ion is ζ -potential determining, while the ϵ -potential determining ion (I^-) at the same time is not ζ -potential determining. The decrease in the negative values of the ζ -potential is large with the increasing concentration of the counter ion in low concentrations, somewhat smaller in high concentrations. The possibility exists that this change is a logarithmic one. For the centrifugation potential technique on dialysed sols Rutgers and Nagels (ref. 9. Figs. 2, 3 and 4) obtained the same result, for the corrected as for the uncorrected values of the ζ -potential.

In the experimental elucidation of the role of the ζ -potentials in the coagulation with neutral electrolytes the major problem, to our concern, is the impossibility of the application of the same technique of measurement in the stable and in the coagulation region, namely below and above the coagulation concentration of the neutral electrolyte. The similarity of the dependence of the ζ -potential upon the concentration of neutral electrolyte for the dialysed sols (ref. 9 Figs. 2 and 4) and the coagulated precipitates (Fig. 5) favours the supposition that there is an analogy between the functions of both. The absolute values differ largely probably due to the inadequate methods of calculation available.

For the electrophoretic mobility it was possible to show that the increase of the concentration of the monovalent neutral electrolyte causes a shift of

the positive stability limit and the zero mobility towards lower pAg values. Fig. 3 of the present paper shows the same for the ζ -potential of coagulated particles. In both cases the concentration of the Na^+ ion present was below its coagulation value. Unexpected is only the fact that this shift for bi-valent ion is smaller and even negligible for the tri-valent ion.

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IZVOD

Elektrokinetičke studije u disperznim sistemima. III. Elektrokinetički potencijali srebrnog jodida

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Mjerenjem potencijala strujanja i elektroosmotskog transporta na srebrnom jodidu, koji je koaguliran neutralnim elektrolitom, utvrđena je nul točka ζ -potencijala između pAg 5.1 i 6.2. ζ -potencijal je u tom području ireproducibilan. Pomak nul točke ζ -potencijala prema nižim pAg vrijednostima malen je za trovalentne, veći za dvo, a najveći za jednovalentne protuione. ζ -potencijal je neovisan o pI vrijednostima u području između $pI = 3$ i $pI = 9$. Promjena u koncentraciji neutralnog elektrolita od $10^{-4} N$ na $10^{-2} N$ smanjuje ζ -potencijal za faktor 3—4. Diskutira se o odnosu između ζ -potencijala s jedne strane i koagulacije neutralnim elektrolitom, odnosno izoelektrične koagulacije s druge strane.

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