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Electrokinetic Studies in Dispersed Systems. IV. The Influence of Surface Active Agents on the Electrokinetic Potential of AgI Precipitates*

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The influence of ionic surface active agents (SAA), represented by some aliphatic straight chain amines and acids, on the zeta-potential of AgI precipitates has been studied. It has been shown that SAA ions are zeta-potential determining in a narrow concentration region only. This region is independent of the pI of the solution. In case the sign of charge of the SAA ion is the same as that of the original precipitate there is no marked influence on the zeta-potential. Whether the sign of the zeta-potential is determined by the activity of the constituent ions in the solution or by the concentration of SAA ions, the magnitude of the zeta-potential is determined by the sign of charge and concentration of the counter ion only. The total potential difference and the zeta-potential are brought about by two different, independent processes.

The influence of surface active agents (SAA) on the electrokinetic potential of the dispersed solid phase has often been measured and interpreted¹⁻¹¹. In most of the systems there was not always a clear distinction between the influence of neutral electrolytes, potential determining ions and SAA.

Proceeding with earlier investigations of the influence of neutral electrolytes and potential determining ions on the zeta-potential of AgI precipitates¹², the influence of some simple ionic SAA on the electrokinetic potential (calculated from the streaming potential data) has been examined.

The electrokinetic potential of the system AgI-aqueous electrolyte solution is independent of pH between $pH = 5$ and $pH = 9$ ¹³ *i. e.* the concentration of H^+ and OH^- ions (or whatever their hydrated forms are). Their influence is similar to that of simple neutral electrolytes.

The influence of SAA, can be studied in a region of concentrations of neutral electrolytes and activities of potential determining ions, in which the electrokinetic potential is by these substances well defined.

As well defined electrokinetic potentials are considered those measured values which are reproducible in accordance with the discussion in the preceding paper¹². In the same paper the physical meaning ascribed to the electrokinetic potential, computed by the simple Helmholtz-Smoluchowski equation, has also been discussed.

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EXPERIMENTAL

The zeta-potentials were calculated by the simple Helmholtz-Smoluchowski equation using the data obtained by streaming potential measurements. The technique of measurement has also been described in detail earlier¹⁴.

Materials

As before, dried and fresh precipitates of AgI were used. The systems prepared with dried precipitates were always $1 \times 10^{-2} M$ in AgI. All concentrations refer to the solution before addition of AgI. After addition the precipitate was left to equilibrate in the solution for seven days. Alternatively, in some experiments, when stated so, fresh precipitates were formed in the system using the *in situ nascendi* technique¹⁵. All components of the electrolytic system and the precipitating agents were added to either $AgNO_3$ or NaI solution prior to mixing. The SAA component was always added to the NaI solution.

Aliphatic straight chain amines and straight chain monocarbonic acids (6 to 18 C-atoms in the molecule) were used as high grade purity chemicals. The amines were titrated with dilute HNO_3 in 50% ethanolic solution till $pH = 5$ (measured by a glass electrode). The precipitated salt was filtered off, recrystallized and dried at $50^\circ C$ *in vacuo*. The liquid amines were not purified further. An equal procedure was employed with carbonic acids. They were titrated to $pH = 9$ with NaOH.

All other chemicals were analytical reagent grade.

Redistilled water (conductivity less than $2 \times 10^{-6} \Omega^{-1} cm^{-1}$) was used throughout.

RESULTS

Fig. 1 shows the relationship of the zeta-potential of dried AgI precipitates versus the concentration of various amines at $pI = 5$ ($1 \times 10^{-5} N$ NaI). Fig. 2 shows the same relation for $pI = 3$.

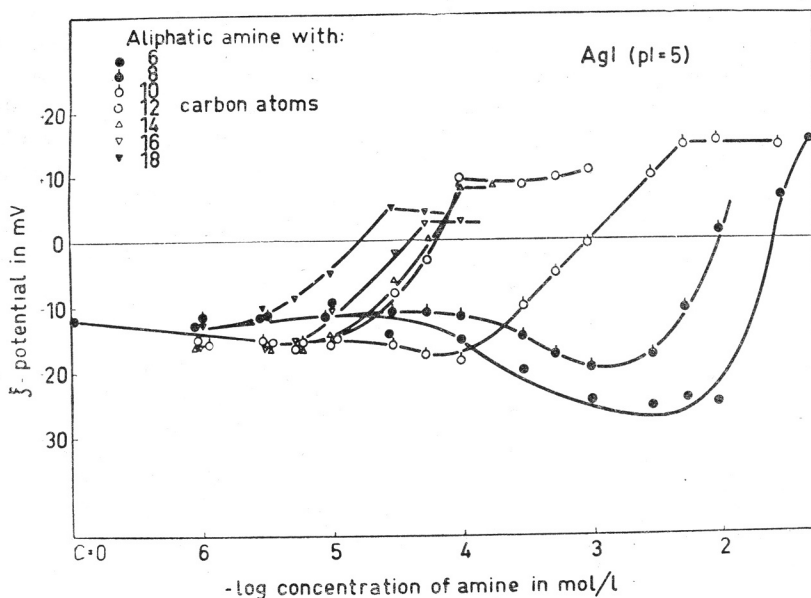


Fig. 1. The zeta-potential of negative AgI precipitates at $pI = 5$ as the function of the concentration of various aliphatic amines (positive surface active ions).

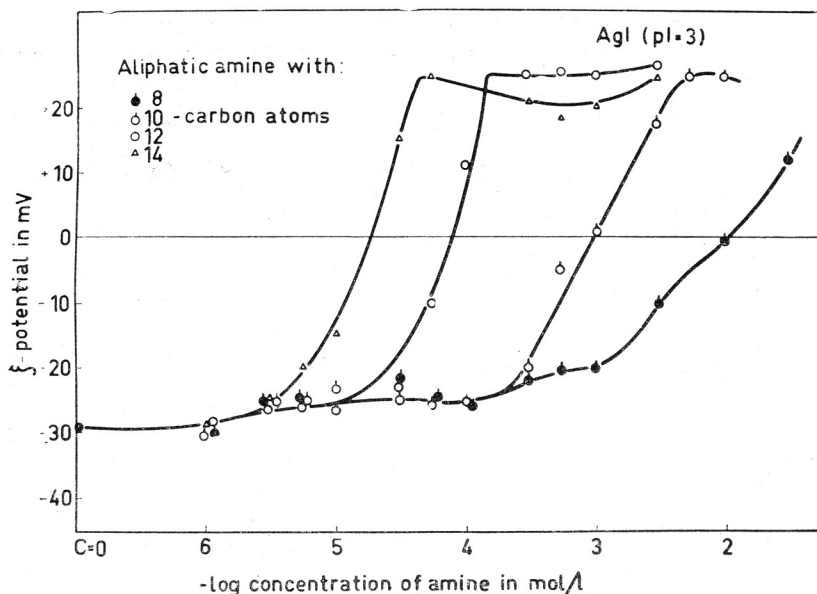


Fig. 2. The zeta-potential of negative AgI precipitates at $pI = 3$ as the function of the concentration of various aliphatic amines (positive surface active ions).

Both pI values gave well defined zeta-potentials of AgI precipitates in aqueous solutions of neutral electrolytes¹². The difference in magnitude of the measured zeta-potential between $pI = 5$ and $pI = 3$ solutions is caused by the increased concentration of the Na^+ counter ion from NaI. The shapes of the curves are the same in both figures.

In Fig. 3 the zeta-potential of AgI precipitates at $pAg = 4$ (positive precipitates in a pure aqueous solution) is shown against the concentration gradient of Na-soaps of several aliphatic carbonic acids. In general the curves show the same shape as in Figs. 1 and 2.

All curves in the mentioned figures are characterized by (I) an initial portion, in which the concentration of SAA is low and does not influence the zeta-potential of the precipitate. The SAA ion is not a zeta-potential determining component of the electrolytic solution. Next to this region of concentrations is (II) a relatively narrow region in which the sign of the zeta-potential is reversed; the SAA ion is a potential determining component in this concentration region. The slope, $d\zeta/d\log c$, can be as large as 30 mV in this region. The AgI precipitate-solution systems for which the zeta-potential is near zero are extremely sensitive to experimental conditions. No system has been found as yet which would not give a measurable streaming potential. Mostly the systems were either slightly negative in the first few seconds of streaming and then changed swiftly to positive or *vice versa*.

Finally there is (III) again a region of concentrations of SAA in which no influence on the zeta-potential of opposite sign is exhibited. This region of high concentrations was only observed with amines with more than 10 C-atoms in

the molecule. The SAA ions are again not potential determining. There are experimental difficulties in the use of higher concentrations of SAA caused by their insolubility.

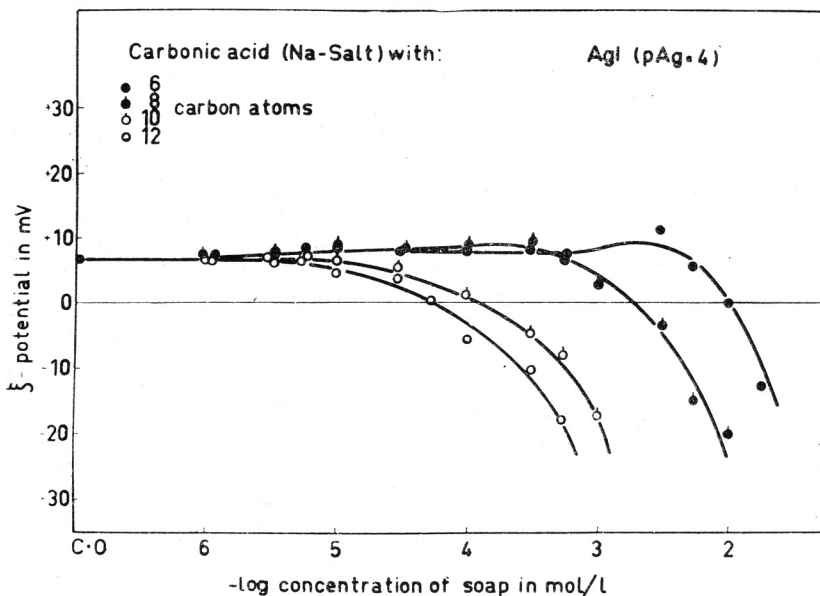


Fig. 3. The zeta-potential of positive AgI precipitates at $pAg = 4$ as the function of the concentration of various aliphatic monocarboxylic acids (sodium soaps) (negative surface active ions).

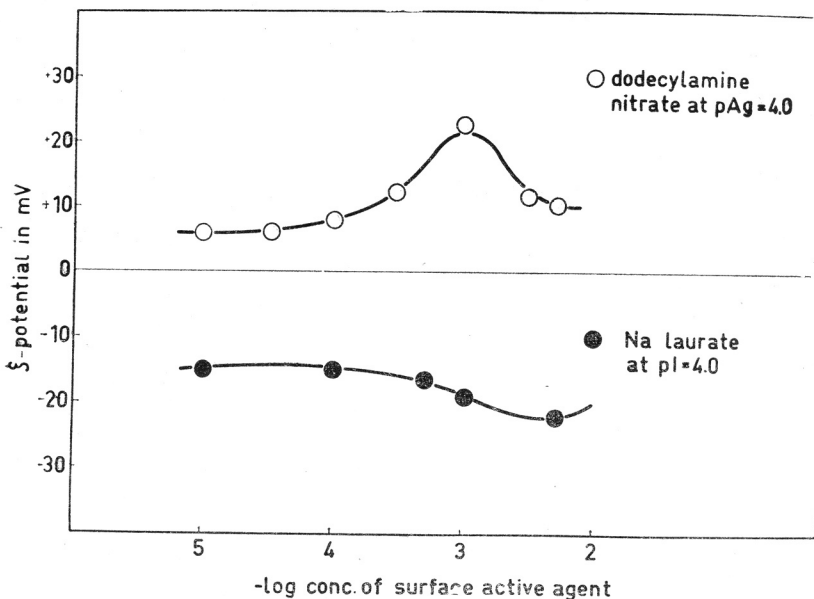


Fig. 4. The zeta-potential of positive AgI precipitates as the function of the concentration of positive surface active ions, and vice versa.

In Fig. 4 the relationship of the zeta-potential and the concentration of the SAA ions of the same sign of charge as that of the zeta-potential of the AgI precipitate determined by the pI (or pAg) values is given. There is no influence

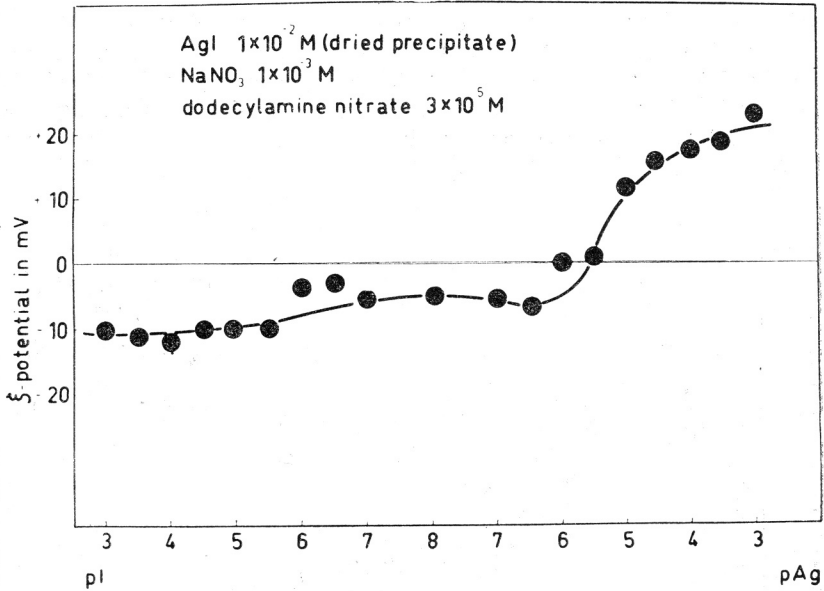


Fig. 5. The zeta-potential of dried AgI precipitates at a constant concentration of dodecylamine as the function of pI (pAg) of the solution.

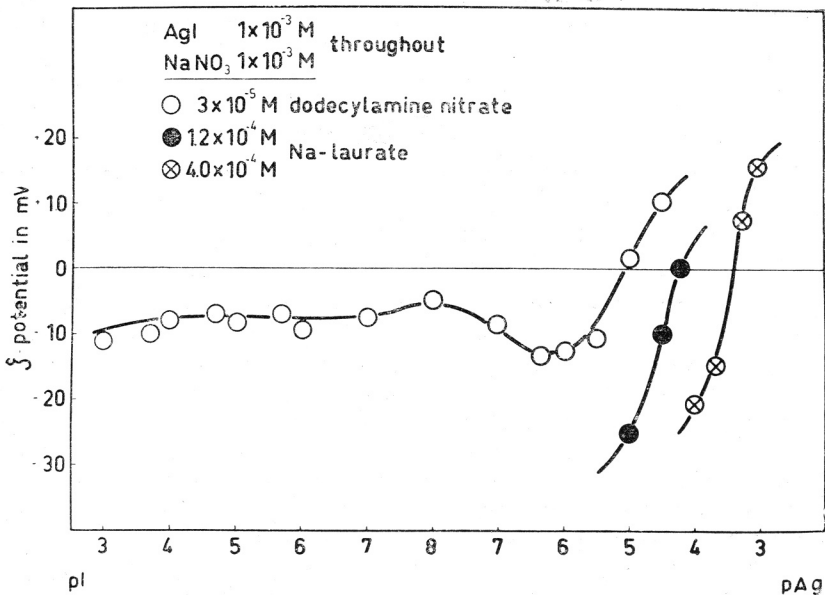


Fig. 6. The zeta-potential of AgI precipitates *in statu nascendi* at a constant concentration of dodecylamine or sodium laurate as the function of pI (pAg) of the solution.

on the zeta-potential, except for a slight maximum (minimum) at higher concentrations.

In Fig. 5 it is shown that at a fixed concentration of dodecylamine there is no influence of the pI of the solution on the zeta-potential in a broad region, from $pI = 3$ to $pAg = 7$. Even the zero point of the zeta-potential in the pI gradient remains the same as for monovalent counter ions. The results of Fig. 5 refer to the dried precipitates. In Fig. 6 the same is shown for precipitates *in statu nascendi*. There is a shift in the zero point of the zeta-potential from $pAg = 5$ to $pAg = 3$, approximately, due to increase in concentration of Nalaurate from $1.2 \times 10^{-4} M$ to $4.0 \times 10^{-4} M$.

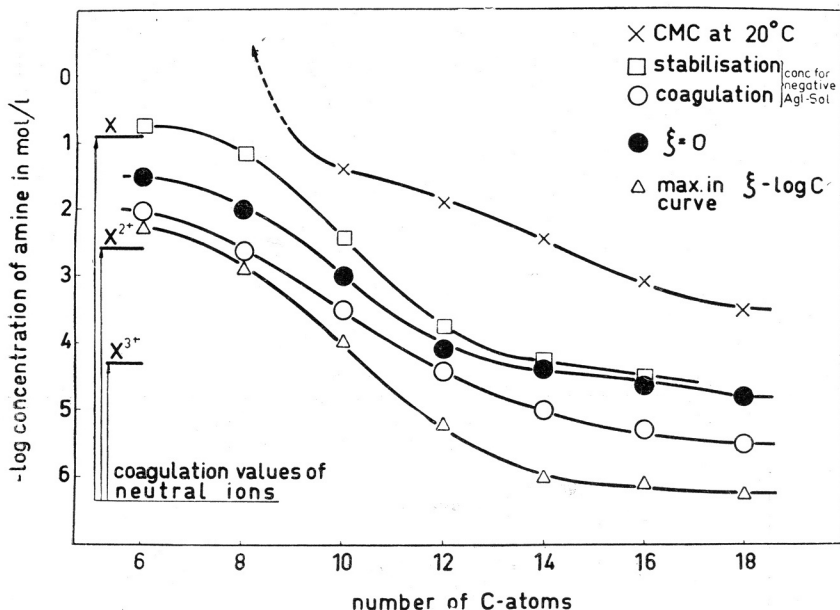


Fig. 7. The characteristic concentrations for the minima in negative zeta-potentials of AgI precipitates (triangles), for the coagulation concentrations (circles) and stabilization concentration (squares) of a negative AgI sol ($1 \times 10^{-3} M$) at $pI = 5$, for the interpolated zero point of electrokinetic potential (full circles) and for bulk micelle formation (according to Ralston l. c.) (crosses) as the function of the number of C-atoms in the molecule of the aliphatic straight chain amine.

In Figs. 7 and 8 some critical concentrations of various SAA ions are given, by the order of increasing number of C-atoms in the molecule.

The critical concentrations in Fig. 7 which refer to positive SAA ions and negative AgI precipitates are: 1) the concentration in which a minimum appears in the zeta-potential — SAA concentration curve; 2) the critical concentration for the coagulation of a stable AgI sol ($1 \times 10^{-3} M$ at $pI = 5$); 3) the critical concentration for which the interpolated value of the zeta-potential is zero; 4) the critical concentration which stabilizes the same AgI sol coagulated by the SAA in concentration mentioned under 2); 5) the critical concentration for bulk micelle formation according to Ralston¹⁶. The last data were added in order to show that the phenomena measured in this paper refer to concentrations lower for one or two orders of magnitude.

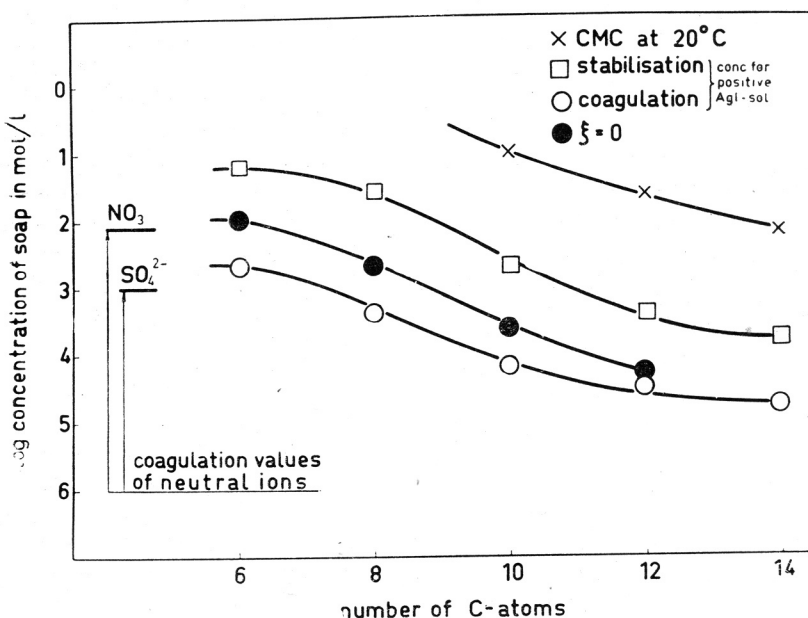


Fig. 8. The characteristic concentrations for the coagulation (coagulation value) (circles) and stabilisation (squares) of a positive AgI sol ($1 \times 10^{-3} M$) at $pAg = 4$, for the interpolated zero points of the electrokinetic potential of a positive AgI precipitate (full circles), and for micelle formation (according to Ralston, l. c.) (crosses), as the function of the number of C-atoms in the molecule of the aliphatic straight chain carbonic acid (sodium soap).

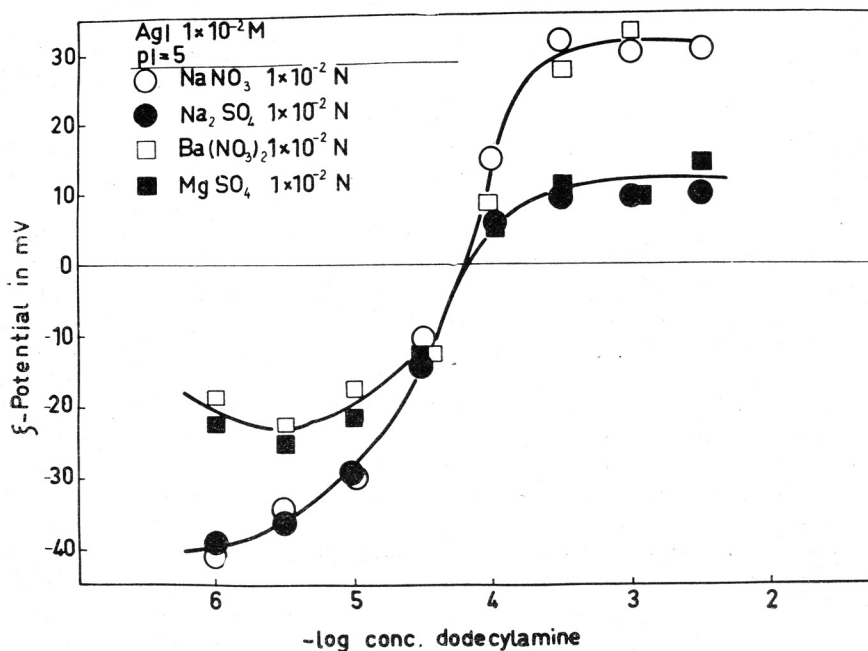


Fig. 9. The magnitude and the sign of the zeta-potential of a typical negative AgI precipitate as the function of the charge of the counter ion and the concentration of dodecylamine.

From the figure it can be seen that the larger the molecule of the SAA the lower the critical concentrations. It follows that amines with more than 12 C atoms, in comparison with coagulation values for simple neutral ions¹⁷, given at the left-hand side of the figure, behave like trivalent ions.

In Fig. 8 the analogous critical concentrations are given for negative SAA ions and positive AgI precipitates. There are given: 1) the coagulation concentration for a positive AgI sol ($1 \times 10^{-3} M$ at $pAg = 4$); 2) the critical concentration for which the interpolated zeta-potential is zero; 3) the *stabilization* concentration and 4) the critical concentration for bulk micelle formation. Compared once again with the coagulation concentrations for simple neutral ions it follows that soap ions with more than 8 C atoms in the molecule behave as neutral ions with a charge higher than two. This figure is not so complete as Fig. 7, because of experimental difficulties.

Fig. 9 shows that the zeta-potential of an AgI precipitate at $pI = 5$ is influenced by SAA ions and neutral electrolyte ions in two different manners. At low concentrations of the SAA the zeta-potential of an AgI precipitate at $pI = 5$ is negative. The magnitude of this zeta-potential is determined by the valency of the counter ion, positive in sign. If the concentration of the neutral electrolyte is held constant, say $1 \times 10^{-2} N$, and the concentration of the SAA increased, the sign of the zeta-potential is reversed. For this positive precipitate the counter ions are the anions of the neutral electrolyte, despite of the fact that the pI value of the solution has remained unchanged. It can be seen from the figure that Na_2SO_4 , a 1—2 electrolyte determined a relatively large value of the zeta-potential by its Na^+ ion on the left-hand negative branch of the curve, and a lower value on the right-hand positive branch, due to the double charged SO_4^{2-} ion. The contrary is true with $Ba(NO_3)_2$, a 2—1 electrolyte. $NaNO_3$ (1—1) and $MgSO_4$ (2—2) electrolytes show symmetrical behaviour on both sides of the S-shaped curve.

DISCUSSION

It has been known that highly charged ions, macromolecules and surface active agents can reverse the sign of the electrokinetic potential of a surface. For a simple ionogenic surface, as that of an AgI precipitate, in pure aqueous solution of some simple inorganic salt, the sign of the electrokinetic potential is determined by the activity of the constituent ions, Ag^+ and I^- . The magnitude of this potential is determined by the valency and the concentration of the counter ion, *i. e.* the ion with the sign of charge opposite to the sign of the electrokinetic potential. This has been established in a previous paper¹². In Figs. 1, 2, 3 and 9 it is shown that the SAA exhibit an influence only upon the sign of the zeta-potential, this influence being restricted to a narrow concentration region. The width of this region and the effective concentrations vary with the specific character of the SAA. Outside this region there is no influence of the SAA of the type studied on the zeta-potential of AgI precipitates.

There is an equality of the role of the constituent (or potential determining) ions and the SAA ions; as it has been shown in a previous paper¹² (Figs. 4 and 5) there are broad concentration regions of constituent ions, from $pI = 3$ to $pI = 8$, in which there is no influence of these ions on the electrokinetic potential. From Figs. 1 and 2 it can be concluded that *e. g.* octylamine does not

influence the zeta-potential in the concentrations between $10^{-6}M$ to $10^{-3}M$. The same can be seen for octanoic acid from Fig. 3. The influence exhibited, *i. e.* the reversal of the sign of the zeta-potential is accomplished in less than one log concentration unit. Similarly such a narrow region can be found as the isoelectric region in the zeta-potential — pAg diagram in Fig. 2 of a previous paper¹².

In numerous textbooks and papers the electrokinetic or zeta potential has been explained as a functionally dependent part of the total double layer potential. The experimental results described in the previous paper¹² show the constancy of the zeta potential with increasing reversible electrode potential (*i. e.* pI or pAg value of the solution). Now the second aspect of this problem is shown, that with constant reversible electrode potential of the system (*i. e.* constant pI or pAg) the zeta potential can be markedly changed or even reversed by addition of a critical quantity of a substance such as a long-chain amine or soap. The conclusion is near, that the reversible electrode potential and the zeta potential are determined probably by two different independent processes. This conclusion certainly applies to the systems measured in the present paper.

The fact that the critical concentrations of the SAA decrease with increasing chain length leads to the probable explanation that all the specific influences are directly related to the molecular (or ionic) size. Combining this statement with the results of Fig. 9, which show that only the simple counter ions determine the magnitude of the zeta-potential, there is a strong indication that large SAA ion enter the inner part of the double layer, the smaller, hydrated Na^+ , Ba^{2+} , Mg^{2+} , NO_3^- or SO_4^{2-} ions forming only the outer part of it.

As in preceding papers, in the present paper too, the discussion is not based on the quantitative data in the zeta-potentials. At present it seems quite unnecessary to define any relation to some *true* or *real* zeta-potentials.

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IZVOD

**Elektrokinetičke studije u disperznim sistemima. IV.
Utjecaj površinsko-aktivnih supstanci na elektrokinetički potencijal
taloga AgJ***V. Pravdić i M. Mirnik*

Promatran je utjecaj ionskih površinsko aktivnih supstanci (PAS) (alifatskih ravno lančastih amina i masnih kiselina) na zeta-potencijal taloga AgJ. Utvrđeno je, da PAS-e imaju bitan utjecaj na elektrokinetički potencijal samo u određenom, vrlo uskom, području koncentracija. To je područje neovisno o aktivitetu konstitucionih iona u otopini (pJ ili pAg). Kada ion PAS-e ima isti predznak kao i prvobitni talog AgJ, specifičnog utjecaja PAS-e nema. Utvrđeno je, da je veličina elektrokinetičkog potencijala određena isključivo nabojem i koncentracijom protuiona, bez obzira na to, da li je predznak naboja površine određen aktivitetom konstitucionih iona ili koncentracijom iona PAS-e. Izvodi se zaključak, da moraju postojati dva različita neovisna elektrokemijska procesa, kojima se uspostavljaju reverzibilni (elektrodni, termodinamički) potencijal i elektrokinetički (zeta) potencijal.

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