Electrokinetic Studies in Dispersed Systems. V.
The Zeta Potential of AgI Precipitates in Mixed Solvents*

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The influence of acetone-water, dioxane-water and methanol-water solvent mixtures upon the electrokinetic potential of AgI precipitates has been studied. The same dielectric constant of the medium yields approximately the same zeta-potential only if the activity of the reversible electrode potential determining ions (constituent ions) is sufficiently large to determine a stable zeta-potential in aqueous solution of the same composition. In the iso-electric region, in the case of the theoretically balanced positive and negative potential determining ions adsorption, the influence of solvent dipoles is predominant and specific, and the dielectric constant is not a measure of the electrokinetic potential. The mechanism of the zeta-potential determining processes is manifold and any extrapolation of a single parameter of the system is insufficient to give answers of general importance.

The equation relating the electrokinetic effects and the zeta-potential always contains the dielectric constant of the medium. Whether the zeta-potential is calculated from the simple Helmholtz-Smoluchowski equation or from the numerous expressions taking into account all the corrections with regard to the surface conductance, the capillary radius or the particle size, its magnitude is primarily dependent upon the value of the dielectric constant. It has been suggested by Bikerman[1] that the value of the dielectric constant in the discussion on the zeta-potential should always be stated explicitly.

From the experimental standpoint developed in this series of papers[2-4] the need of evaluating »real« or »true« values of the zeta-potential was avoided. For that reason the values of the dielectric constant of the electrolyte solutions, commonly recorded in the literature, can be used.

It seems that the problem of the variable dielectric constant within the electric field in the electrical double layer has been settled so far by Conway, Bockris and Ammar,[5] who calculated the dielectric constant as a function of the distance from the surface of the solid phase for various ionic strengths. The statement of Overbeek[6] that water molecules may only be immobilized in that part of the electrical double layer where the field strength exceeds 5×10^5 V/cm, gives us the right to use the bulk dielectric constant for calculations of the electrokinetic potential. At least one can take advantage of the proposition given by Guggenheim[7] and express the results of the electrokinetic

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experiments in terms of the moment of the electrical double layer: M =
= $\varepsilon\zeta/4\pi$ = $\eta b\varkappa$ (b represents any particular electrokinetic function, e. g. E/P.
or V/i), making the electrokinetic data independent of any arbitrary value of
the dielectric constant. As defined, the moment is a product of three indepen-
dently measurable quantities.

An interesting problem is, however, the influence of the variable bulk
dielectric constant of the measured system upon the zeta-potential. This can
be measured experimentally by adding known quantities of a miscible polar
or nonpolar solvent to water. The most common and usual experimental
practice is to use various solvents, as for example alcohols, acetone, dioxane, etc.

Electrokinetic potentials in nonaqueous and mixed solvents have already
been measured.[8-12] Most of the results refer to nonionogenic surfaces as that
of glass. The most thorough investigation of the AgI system with respect to
double layer phenomena in water-acetone media has been made by Mackor
and Overbeek in a series of papers.[13-15] The measurements of the electrokinetic
potential were confined to the microscopic electrophoresis technique only.
By this method it was possible to measure the zero point of the electrokinetic
potential and to determine its sign at given conditions but only for stable
colloidal particles. Compared with the possibilities of the streaming potential
technique for coagulated particles, using high impedance electrometer ampli-
fiers and strip chart recorders, the ultramicroscopic electrophoresis is of poor
accuracy. Of course, it is understood that there are fundamental differences
in type and in the state of dispersion of the material subjected to measurement,
and/or inadequacies in both techniques. Nevertheless, on the basis of Mackor's
results some measurements of the zeta-potential of the AgI precipitates in
mixed solvents have been made. These results should add another argument
to the already mentioned working hypothesis, namely, that the interphase
electrical phenomena of ionogenic surfaces in electrolyte solutions are to be
investigated with respect to any single variable of the system and interpreted
in the most simple form before any attempts of a general theory can be made.

EXPERIMENTAL

The streaming potential experimental technique was applied as described in an
earlier paper.[2] Streaming potentials developed across two unpolarizable Ag/AgI
electrodes were measured on a vibrating reed electrometer and recorded on a
strip chart recorder. Regression coefficients of the streaming potential upon the
applied pressure were used in calculations. Conductivity measurements were per-
formed on a 1000 cycle conductivity bridge for conductances down to 3×10^{-6} Ohms^{-1}.
Lower conductances were measured using a high resistance Wheatstone bridge. The
standard error of conductivities measured with the A. C. bridge was estimated to be
about $3^0/o^2$. The standard error of three repeated measurements at 10^{-8} Ohms^{-1} or
lower was about $20^0/o$.

All measurements were performed at 20 ± 0.5^0 C. The silver iodide precipitates
used were prepared as »dried« precipitates.[4] The pI or pAg values were achieved
by adding known quantities of NaI or AgNO$_3$ solutions to the system. All precipi-
tates were left for 7 days to equilibrate in solutions which were then submitted to
measurement. Precipitates in solutions with an excess of NaI were shielded from
direct light during this period. Those with an excess of AgNO$_3$ were kept in total
darkness to prevent the reduction of silver ions. The solvents used were acetone,
1,4-dioxane and methanol. Chemically pure solvents were dried and distilled twice
discarding about $20^0/o$ both of the first distillate and of the residue.

This procedure of purification proved satisfactory as mixtures with fairly large
proportions of water were mostly used.

The mixtures of water with acetone were the same as Mackor's,[13] and the cited values of the dielectric constant were used in computations. For all other mixtures the dielectric constants were taken or interpolated from a compilation of data by Conway.[16] The mixtures were chosen so as to obtain isodielectric media with dielectric constants of approximately 75, 68, 55, 39 with any of the three solvents and water. The compositions used in this work are listed in the Table.

TABLE

Component mixed with water	mole-%	dielectric constant	mean dipole moment
acetone	2.65	74.3	1.89
	7.25	67.6	1.93
	18.7	54.1	2.03
	42.0	38.7	2.23
methanol	6.49	75.6	1.86
	19.4	67.3	1.84
	40.7	55.6	1.80
	83.5	39.1	1.73
dioxane (1,4)	1.52	74.1	1.85
	2.96	68.7	1.83
	7.69	54.2	1.76
	14.9	38.8	1.65
	29.4	20.7	1.45

The water used was distilled three times, the third time from a silica still. Its conductance never exceeded 2×10^{-6} Ω^{-1} cm^{-1}.

All other chemicals were analytical reagent grade. The solutions were prepared by weight from dried chemicals.

RESULTS

The zeta-potential against pI relationship of AgI precipitates in aqueous solutions has been established in the preceding papers.[4]

In Fig. 1 the same relationship is given for a 7.3 mol % acetone water solvent mixture. The points above the unmarked abscissa in this and the
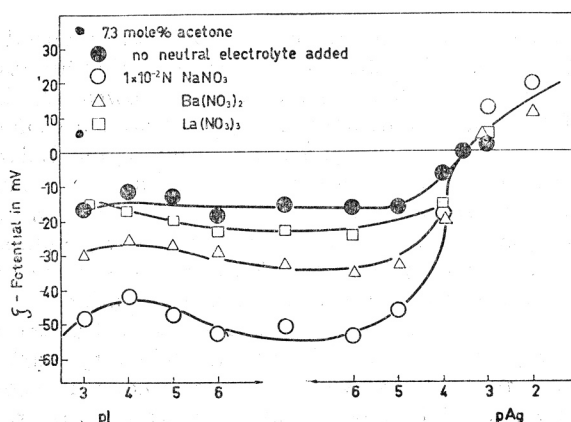

Fig. 1. The zeta-potential of AgI precipitates in 7.3 mol% acetone media versus $pI(pAg)$ in the absence of neutral electrolytes (full points) and in 1×10^{-2} normal solutions of Na (circles), Ba (triangles) and La (squares) nitrates. The unmarked abscissa refers to solutions with no NaI or AgNO$_3$ added.

subsequent Figs. 2 and 3, represent AgI precipitates in solutions of some neutral electrolyte, but with no potential determining ions added in the form of NaI or AgNO$_3$.

From Fig. 1 it can be seen that in such a solvent the zeta-potential is almost constant and again independent of pI (or pAg) in a broad region from pI = 3 to pAg = 4. There is a shift of the zero point of the zeta-potential from about 5.5 in aqueous solutions to about 3.5 in 7.3 mol % acetone. This fact has already been observed and interpreted by Mackor.[13] It can also be seen that in solutions to which no neutral electrolyte has been added the zeta-potential has a low value. In the pI gradient the ionic strength changes, because NaI represents the only ionic component of the solution. But in large regions of pI this does not influence the measured electrokinetic potential. At high and constant concentrations (1 × 10^{-2} N) of Na, Ba and La nitrates the zeta-potential is markedly higher.

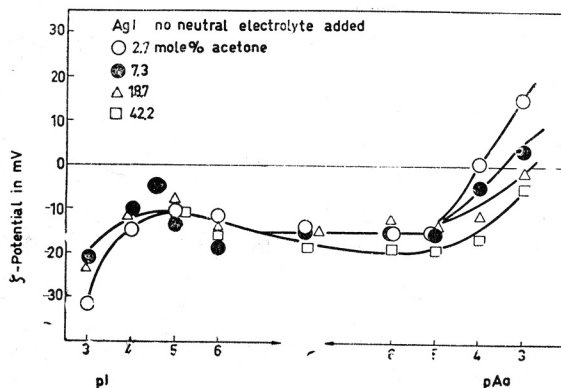Fig. 2. The zeta-potential of AgI precipitates in media of various acetone content versus pI(pAg). No neutral electrolyte added. The unmarked abscissa refers to solutions with no NaI or AgNO$_3$ added.

It can be seen that the dependence of the zeta-potential on the counter ion valence is preserved: the Na ion determines the highest zeta-potential in this series, Ba the intermediate, and La the lowest. In Fig. 2 the zeta-potential of AgI precipitates in solutions of variable acetone mole fractions is shown as a function of pI (pAg). In the large region between pI = 4 and pAg = 5 the zeta-potential is independent of the solvent composition from 0 to 42 mole %, and, as in aqueous solutions, almost constant. At pI = 3 the zeta-potential increases up to the value determined by higher concentrations of the Na ion. In the region pAg = 4 to 3 the zeta-potential changes sign, the zero point being dependent on the acetone concentration.

In Fig. 3 the electrokinetic potential is represented as the »moment of the electrical double layer« (discussed in the introductory part of this paper), and plotted against pI (pAg) for various acetone concentrations and 1 × 10^{-2} N NaNO$_3$ Thus the data should be independent of the arbitrary value of the dielectric constant. If the dielectric constant were low owing to dielectric saturation, there should be no systematic change in the computed moment for the change in the bulk value. In Fig. 3, however, it can be seen that this

moment decreases continuously by an increase in the acetone content. In fact no significant change was observed from zero up to 18.7 mol % of acetone ($\varepsilon = 54$). As the activity of sodium nitrate actually decreases according to the Debye-Hückel expression, the $\varepsilon \zeta / 4 \pi$ function should increase.
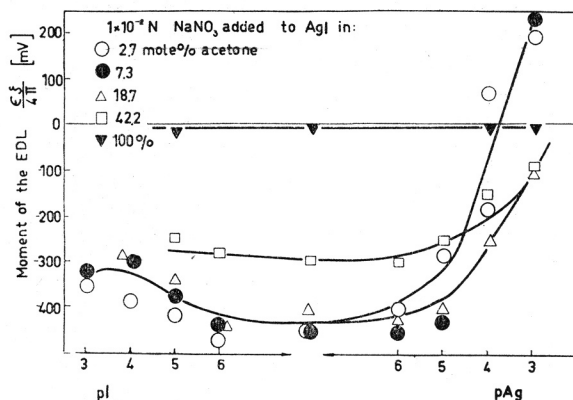

Fig. 3. The electrokinetic potential of AgI precipitates (expressed as the »moment of the electrical double layer«) in 1×10^{-2} N NaNO₃ solutions of various acetone content versus the pI (pAg) gradient. The unmarked abscissa refers to solutions with no NaI or AgNO₃ added.

The next step in the elucidation of the problem of the influence of the dielectric constant of the medium upon the electrokinetic potential of AgI was the preparation of isodielectric mixtures of some other solvents with water.
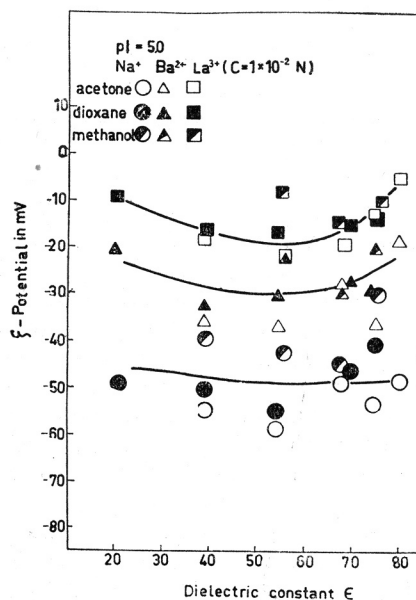

Fig. 4. The electrokinetic potential of AgI precipitates at pI = 5.0., and 1×10^{-2} N solutions of Na (points), Ba (triangles) and La (squares) nitrates versus the dielectric constant of the solvent mixture: acetone-water (hollow markings), dioxane-water (full markings) and methanol-water (semi-hollow markings).

As a suitable characterization the $pI = 5$ section in Figs. 1, 2 and 3 was chosen. In Fig. 4 the zeta-potential of AgI precipitates in $10^{-2} N$ solutions of Na, Ba, and La nitrates, at constant $pI = 5$ is shown against the dielectric constant of the solvent mixture.

The dispersion of the measured values is large, but it may be concluded that isodielectric mixtures cause the same zeta-potential with the same counter-ion in solution. The valency and concentration of the counter-ion is still the most important factor governing the value of the zeta-potential. The equal electrokinetic potential for isodielectric mixtures has been stated by Mukherjee and Chaterjee[17] for glass capillaries in methanol and ethanol. This statement is confined to the relatively high ionic strength of the solutions examined. By taking mean values for each solvent separately, it follows that the values for methanol are the lowest, for dioxane intermediate, and for acetone the highest. To establish the difference between the solvents explicitly,
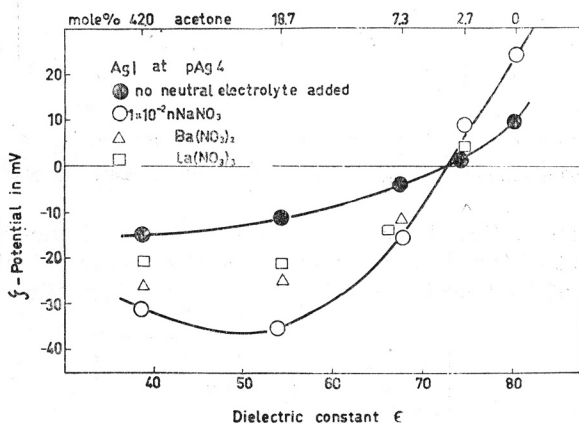

Fig. 5. The electrokinetic potential of AgI precipitates at $pAg = 4$ and in $1 \times 10^{-2} N$ solutions of Na (circles), Ba (triangles) and La (squares) nitrates versus the dielectric constant of the acetone-water solvent mixture.

the AgI precipitate-solution systems were chosen in the vicinity of the zero-point of the zeta-potential. The vicinity of this point is a critical region, where the influence of the surface-dipole interactions should be most emphasized.

In Fig. 5 the influence of the variable dielectric constant of acetone-water mixtures on the zeta-potential of AgI precipitates at $pAg = 4$ is shown. The zeta-potential of the AgI precipitate at $pAg = 4$ in an aqueous solution is stable and reproducibly positive, as it is shown by a single point for Na as counter-ion. This figure shows that this potential is reversed by addition of acetone. In the presence of $Ba(NO_3)_2$ the reversal of sign is accomplished at lower acetone concentrations than with $NaNO_3$ or $La(NO_3)_3$, or in the absence of neutral electrolytes.

Fig. 6 gives the zeta-potential of AgI precipitates at $pAg = 3$, and in $1 \times 10^{-2} N$ Na nitrate solution vs. the dielectric constant of the solvent. The three curves represent this relationship for methanol, dioxane and acetone. The reversal of sign of the zeta-potential is accomplished with acetone only. Dioxane has a distinct quantitative effect on the zeta-potential but down to

$\varepsilon = 38$, the limit of the range studied, does not reverse the sign. In the same range, i. e. up to 83.5 mol %, methanol does not influence the zeta-potential at all. Thus the lowering of the dielectric constant of the medium cannot be taken as a cause for the reversal of the sign in the case of acetone. The reversal has to be ascribed to the oriented dipole adsorption, if the dipole moment of the adsorbate is markedly different from the value for water.
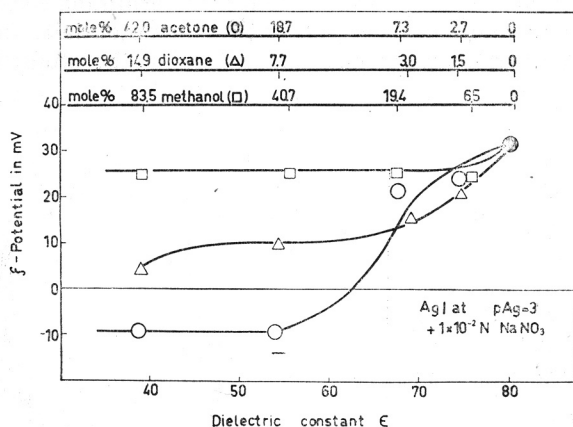

Fig. 6. The electrokinetic potential of AgI precipitates at pAg = 3 and in 1×10^{-2} N solutions of NaNO₃ as a function of the dielectric constant of the solvent mixture: acetone-water (points), dioxane-water (triangles) and methanol-water (squares).

To elucidate the phenomenon of charge reversal by solvent molecules other than water, the experimental results were represented in the coordinates of the zeta-potential vs. the relative change in the hypothetic mean dipole moment of the solvent mixture. The hypothetic mean dipole moment has been computed as

$$m \, \hat{\delta}_s + (1 - m) \, \hat{\delta}_w = \hat{\delta}_m \qquad \qquad (1)$$

where $\hat{\delta}_m$, $\hat{\delta}_s$, $\hat{\delta}_w$ are the mean dipole moment, the dipole moment of the solvent molecule, and the dipole moment of the water molecule, respectively. m Is the mole fraction of the solvent component other than water in the mixture. The relative change in % of the mean dipole moment with respect to water is defined as:

$$\Delta \hat{\delta} \% = \frac{\hat{\delta}_m - \hat{\delta}_w}{\hat{\delta}_w} \times 100 \qquad \qquad (2)$$

In Fig. 7 the relative change of the mean dipole moment of the solution for AgI precipitates at pAg = 4 is shown. μ Indicates the ionic strength to which the results refer. In Fig. 8 the same is shown for pAg = 3 solutions. Now from both figures it can be seen that this characterization is better for elucidation of the influence of the solvent. Dioxane lowers the mean dipole moment of the mixture, being a nonpolar solvent. Acetone, owing to the high dipole moment of its molecules, increases it.

Although the abscissa is not exactly proportional to the concentration relations, the specific influence of acetone is distinguishable: the reversal of charge brought about by acetone is accomplished at lower differences of the mean dipole moment and the value of the reversed potential is larger. The conclusion can be made that the charge reversal can be caused by the presence of different solvent molecules irrespectively whether they cause an increase or decrease of the hypothetic mean dipole moment of the solvent. The increase in activity of the reversible electrode potential determining ions from $pAg = 4$ to $pAg = 3$, renders more positive electrokinetic potentials. In this case the reversal of sign with dioxane is not emphasized in the studied concentration range.
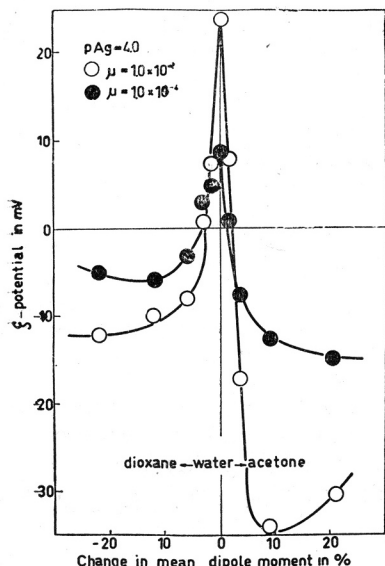

Fig. 7. The electrokinetic potential of AgI precipitates at $pAg = 4$ versus the hypothetic mean dipole moment change (in %) of the solvent. μ is the ionic strenght of the solution to which the results refer.
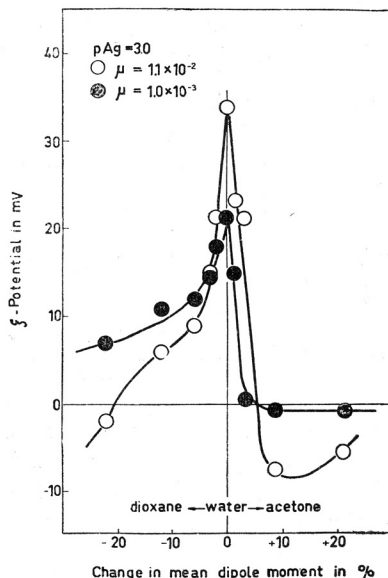
Fig. 8. The electrokinetic potential of AgI precipitates at $pAg = 3$ versus the hypothetic mean dipole moment change (in %) of the solvent. μ is the ionic strength of the solution to which the results refer.

DISCUSSION

The influence of the dielectric constant of the medium upon the electrokinetic phenomena seems at present not to be established definitely. If the electrical double layer, as represented by the Gouy-Stern-Grahame model, should have been a dielectrically saturated structure, there should be a pronounced independence in the computed value of the electrokinetic potential owing to changes in the solvent composition. From the results of Fig. 5 and 6 it is evident that it is not simple to obtain an explicit answer. The dielectric state in the outer part of the electrical double layer cannot even be described by the concentration of a neutral electrolyte only. Any general conclusion upon the experimental data should take the following points into consideration:

a) the type of the surface: ionogenic or adsorption type;

b) the ionic contents (strength) of the solution, but with a differentiation between potential determining components and neutral electrolyte ions;

c) the dipoles in the outer part of the electrical double layer as the principal components in the isoelectric region; the dipoles of the specific adsorption character in all regions of concentrations where they are present next to simple ions (potential determining or neutral).

Thus, experiments should be designed so as to take into account every single variable mentioned above. The results of this and the preceding papers indicate that there are always regions of concentrations in which a component proves to be determinant, as well as other regions in which its influence is limited or even negligible. Neither has a general conclusion any value if the whole problem is not surveyed in the described sense. Another conclusion which can be made on the basis of the described results can be summarized as follows: it is insufficient and often difficult to extrapolate a single parameter of the studied system and interpret the electrokinetic data as its dependent variable. In the present paper this becomes evident from the results plotted in Fig. 4. Hence, it can be concluded that the dielectric constant of the medium is not a critical parameter, except at extreme values. This statement applies only to such an ionic state of the solution which determines a stable and reproducible electrokinetic potential in an aqueous solution of the same ionic composition (as the reference system). From Figs. 5 and 6 it can be concluded that the dielectric constant is once again not a critical quantity, but that the phenomena should be better interpreted in terms of specific interactions of solvent dipoles and the surface. The character of this specific interaction cannot be understood from electrokinetic data. It has been confirmed by experiments that there is always a trend towards more negative electrokinetic potentials. The region in which these results were obtained is understood as the isoelectric region. Here the ionic influence on the electrokinetic potential is not defined, i. e. the measured values in the corresponding isoelectric region in an aqueous solution render irreproducible and unstable potentials. At $pAg = 4$ in an aqueous solution the surface state is stabilized and the electrokinetic potential is positive. By addition of acetone, and similarly of dioxane, this stability is »broken«. The same value of the positive electrokinetic potential is achieved at higher concentrations of potential determining ions.

The results of this and the preceding papers indicate that the solid surface electrolyte solution systems have a definite limited number of typical structures. The dependence of the magnitude of the electrokinetic potential on the counter-ion valence is preserved under various circumstances. The potential determining ion independence of the electrokinetic potential is evident in aqueous as well as in mixed solvent solutions. The isoelectric region is not a property of the solid phase only, but also of the composition of the solvent, and in both cases it is characterized by poorly defined, unstable electrokinetic potentials. The apparently stable structure of the system in regions which have been called stability regions, resists to influences such as additions of electrolytes or solvents. The breaking-down of this structure is sudden with respect to the successive additions of the critical component. The structure which remained stable for several logarithmic concentration units breaks down in this critical region within one logarithmic unit of change in concen-

tration. Further additions of the critical component lead to the build-up of a new structure with the same resistant properties. Therefore, it is very probable that the complex situation of two-phase boundaries could be hardly, if ever, solved by extrapolation of any single parameter as the independent variable.

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IZVOD

**Elektrokinetičke studije u disperznim sistemima. V.
Elektrokinetički potencijal taloga AgJ u miješanim otapalima**

V. Pravdić i M. Mirnik

Promatran je utjecaj smjesa otapala (aceton-voda, dioksan-voda i metanol-voda) na elektrokinetički potencijal taloga AgJ. Ustanovljeno je, da ista dielektrička konstanta medija određuje isti elektrokinetički potencijal samo u području pI = 3 do pAg 5 (tj. aktiviteta potencijalno determinantnih iona), gdje je elektrokinetički potencijal i u vodenim otopinama jednoznačno definiran i stabilan. U izoelektričkom području, gdje je utjecaj pozitivnih i negativnih potencijalno determiniranih iona izbalansiran, narav otapala bez obzira na dielektričku konstantu smjese određuje elektrokinetički potencijal. Najizrazitije je utjecaj otapala na elektrokinetički potencijal izražen ako se promatra kao funkcija diferencije u hipotetičkom srednjem dipolnom momentu otapala. Ukazuje se na mnogostrukost utjecaja raznih parametara sistema na električki potencijal granica faza kao i na nemogućnost, da se ekstrapolacijom samo jedne varijable dođe do opće važećih zaključaka.

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