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Determination of the Ion Adsorption by the Radioactive Tracer Technique.* IV. Coagulation of Negative AgI Sols by Adding Mixtures of Different Valency Cations and the Cation Adsorption

M. J. Herak and M. Mirnik

Department of Radiochemistry, Institute »Ruđer Bošković« and Laboratory of Physical Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia, Yugoslavia

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The coagulation value of Co^{2+} for negative AgI increases with increasing concentrations of Na^+, while that of Na^+ decreases only slightly with increasing concentrations of Co^{2+}. If an ion of higher valency (Co^{+2} or Eu^{3+}) is present in concentration higher than its coagulation value, the lower valency ions (Li^+, Na^+, K^+ or Co^{2+}) exhibit a stablizing action evidenced by a minimum in turbidity curves at concentrations somewhat lower than the coagulation values of the latter ions. Electron microscope investigation shows that for prolonged time intervals the particles of the systems defined by the mentioned minima are not coagulated, while those of the systems with high turbidities are agglomerates of many primary particles. Adsorption measurements of coagulating counter ions by the radioactive tracer technique prove that the same ion exchange mechanism, which was observed earlier at concentrations higher than the coagulation value, is also valid for concentrations at which the stabilization with lower valent ions was observed. Thus the same thermodynamic equations are valid in concentrations higher and lower than the coagulation value.

INTRODUCTION

The thermodynamic parameters for ion exchange of coagulated AgI were determined by experiments in which the concentration ratio of the two exchanging ions was varied.[1] It has also been shown that the linear Schulze-Hardy rule of coagulation can be deduced applying the same thermodynamic equations which are valid for the ion exchange mechanism.[2] Since in coagulation experiments with two coagulating ions effects like additivity, sensibilisation and antagonism may be observed, it was necessary to compare the interaction of two ions during ion exchange with that in coagulation. It is therefore the purpose of the present paper to determine by light scattering measurements, the influence which a second ion may exert upon the coagulation value of the first one of different valency, and to make a comparison with the results of adsorption of the same ion pairs as measured by the radioactive tracer technique.

EXPERIMENTAL

a) Light scattering measurements

Light scattering measurements were performed in the same manner as described previously.[3] Two series of samples containing the precipitation components, were

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prepared in test tubes. One of the series had NaI with varying concentration of the coagulating ions. In the other one the concentration of $AgNO_3$ was kept constant. After mixing the components in the usual way the intensity of the scatterred light was measured at given time intervals in the Pulfrich photometer with a light scattering attachment (Trübungsmesser Zeiss, Jena).

b) Counter ion adsorption measurements

The systems were prepared as before[1] in a total volume of 100 ml. The adsorbed quantity of counter ions was determined by counting the activity of the filtered, washed and dried precipitates in a well type scintilaltion counter. The radionuclides ^{152}Eu-and^{60}Co were obtained from A. E. R. E. in Harwell.

c) Electron microscope investigation

This part of experiments was done with systems prepared in the same way as were those for the light scattering measurements. At given time intervals after the preparing of the systems by mixing of the components a drop of the sol was put on a Mowital film supported by a copper grid. Several seconds afterwards the sol was removed and the dried sample photographed in the electron microscope. (KM 4, Trüb, Täuber and Co.).

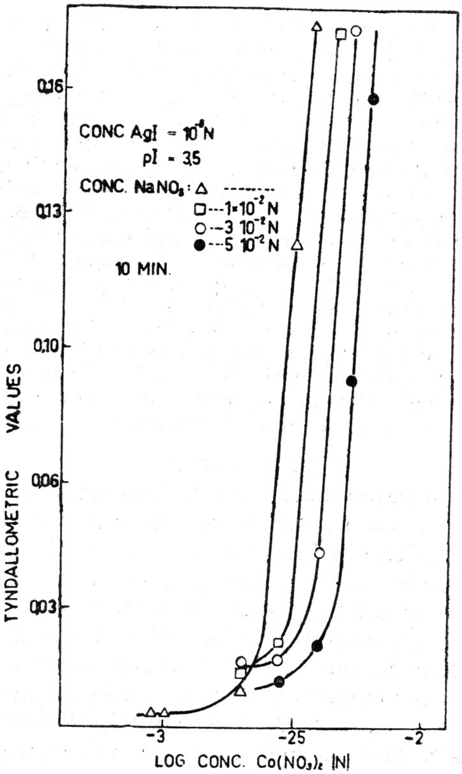

Fig. 1. Influence of the concentration of $NaNO_3$ (not added, 0.01, 0.03, and 0.05 *N*) upon the 10 minutes plot intensity of scattered light against logarithm concentration $Co(NO_3)_2$(N) of the systems AgI 0.001 *N*, pI 3.5.

RESULTS

In Fig. 1 the influence of varying concentrations of $Co(NO_3)_2$ upon the change of the intensity of scattered light for three concentrations of $NaNO_3$ is shown. The coagulation value, indicated by the steep increase of intensity with increasing concentration of Co^{2+}, shifts towards larger values on adding $1 \cdot 10^{-2}$, $3 \cdot 10^{-2}$, and $5 \cdot 10^{-2}$ *N* $NaNO_3$ respectively to the coagulating systems. The coagulation value of Co^{2+} with no other ions present amounts to $2.3 \cdot 10^{-3}$ *N*, or $\log c_{coag} = -2.64$, and is practically equal to the coagulation value of other ions with same valency.[5]

In Fig. 2 the variation of the intensity of scattered light with varying concentration of $NaNO_3$ ($4 \cdot 10^{-3}$, $5 \cdot 10^{-3}$ and $6 \cdot 10^{-3} N$ $Co(NO_3)_2$ present) is shown.

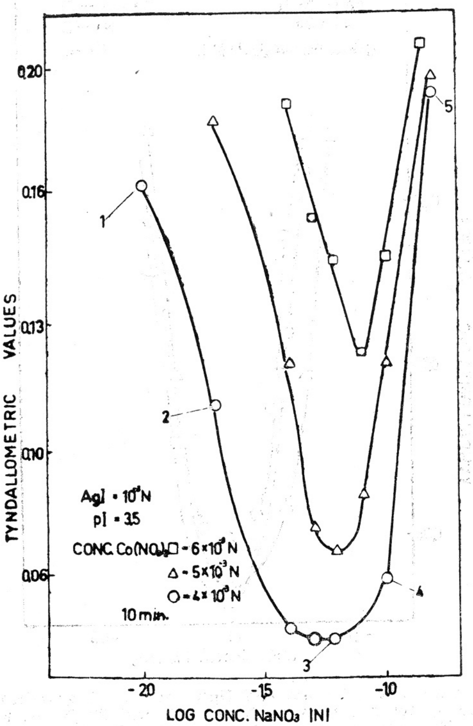

Fig. 2. Influence of the concentration of $Co(NO_3)_2$ (0.004, 0.005, and 0.006 *N*) upon the 10 minutes plot intensity of scattered light against logarithm concentration of $NaNO_3$(N) of the systems AgI 0.001 *N*, *p*I 3.5.

All concentrations of Co^{2+} are higher than its coagulation value (see Fig. 5) and therefore it should be expected that the system would be coagulated. Therefore the coagulation should be evidenced by the same high turbidity for all concentrations of Na^+. Contrary to this expectation a minimum in the turbidities appears for a Na^+-concentration of 6 to $8 \cdot 10^{-2} N$. Thus, the Na^+ ion has an apparent stabilizing effect opposing the coagulating action of Co^{2+}. When the concentration of Na^+ becomes close or equal to its coagulation value it again causes coagulation as expected. The higher the concentration of Co^{2+} the less pronounced becomes the minimum of the intensity of scattered light.

It disappears for concentration higher than $7 \cdot 10^{-3}$ *N*. The coagulation value of Co^{2+} amounts to $2 \cdot 10^{-3}$ *N* or log $c_{coag} = -2.7$. Electron microscope photographs were taken for the particles in the systems with $4 \cdot 10^{-3}$ *N* Co^{2+} and $1 \cdot 10^{-2}$, $2 \cdot 10^{-2}$, $5 \cdot 10^{-2}$ and $1.6 \cdot 10^{-1}$ *N* Na^+. These micrographs (Fig. 3) show that the particles of a system defined by the minimum were neither aggregated nor do they form coagula. The particles of the systems with low, as well as those with higher concentrations of Na^+ are coagula formed from the primary particles. The smallest particles forming the coagula seem to be larger than the elementary, noncoagulated, particles. This may be due to the melting of several aggregated primary particles in the electron beam, or to a recrystallisation process observed usually in concentrations somewhat lower than the coagulation value. The particles will settle to the bottom in all the systems after long enough periods of time. It may be concluded that for conditions at the minimum of Fig. 2. the speed of coagulation was slowed down and the pure process of coagulation replaced by a process of ageing. This is partly a very slow coagulation and partly a recrystallisation of primary into coarser secondary particles forming the coagulated aggregates.

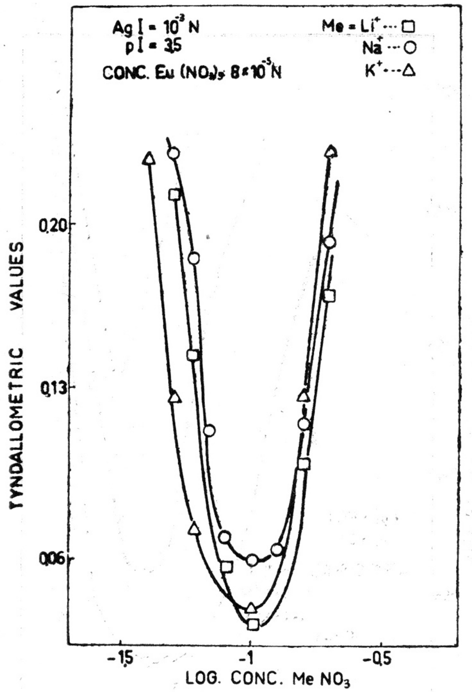

Fig. 4. Plots (10 minutes) intensity of scattered light against logarithm concentration $MeNO_3$: (Me = Li^+, Na^+, K^+) of the systems AgI 0.001 *N*, pI 3.5 and $Eu(NO_3)_3$ 8.10^{-5} *N*. Left hand plot $Eu(NO_3)_3$ — concentration tyndallogram.

The stabilizing action of ions of lower valencies against the coagulating action of those of the higher ones is demonstrated by Figs. 2., 4. and 5. In Figs. 2. and 4. the stabilization caused by Li^+, Na^+ and K^+ and opposing the coagulating action of Co^{2+} and Eu^{3+} is evidenced by a minimum in turbidities in

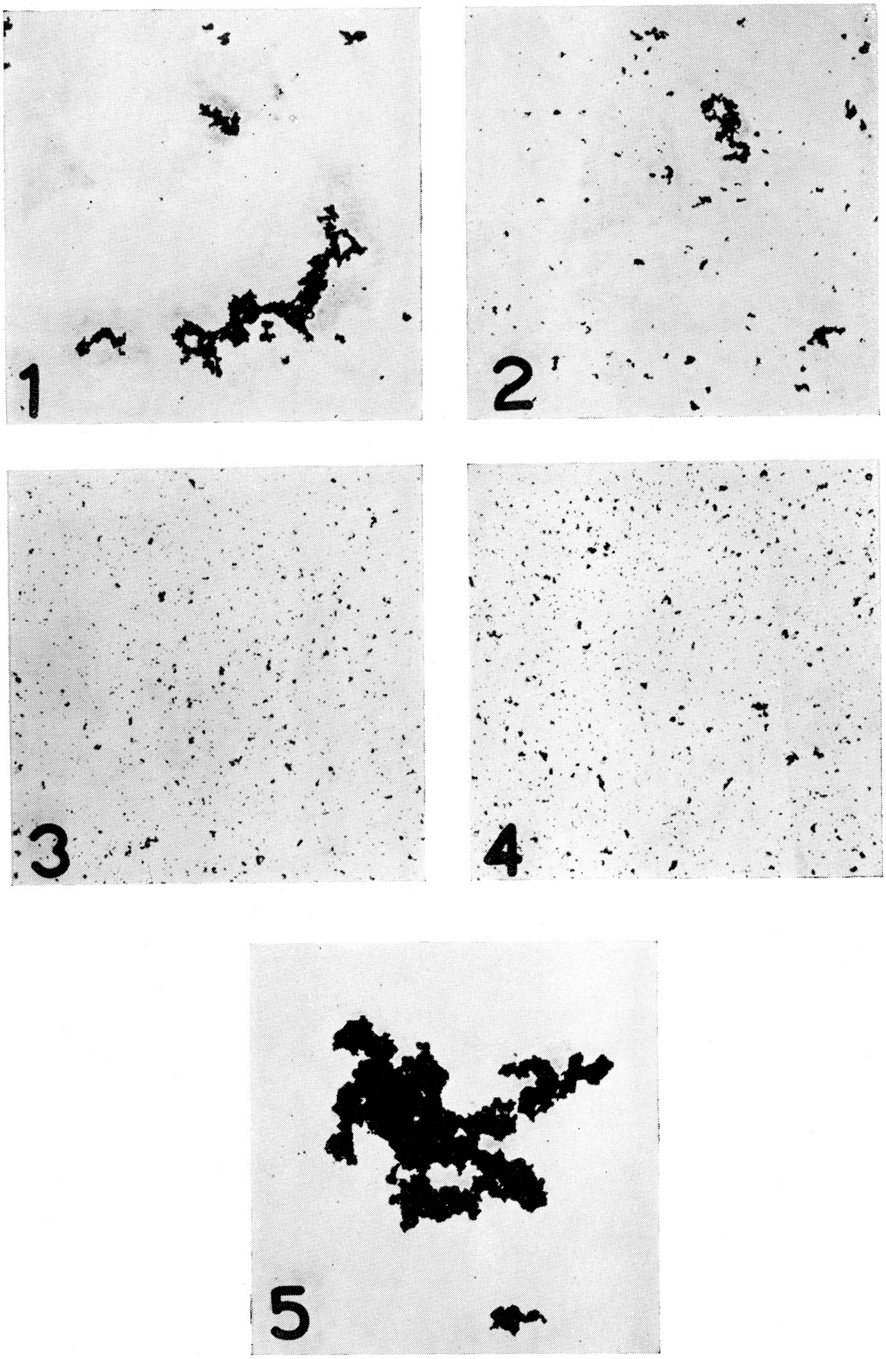

Fig. 3. Electron microscope photographs Nos. 1, 2, 3, 4. and 5 (×10.500, 10 minutes) of the systems AgI 0.001 *N* *p*I 3.5 $Co(NO_3)_2$ 0.004 and $NaNO_3$ 0.01, 0.02, 0.05, 0.1 and 0.16 *N*.

concentrations close to 0.1 *N* concentrations of monovalent ions. A similar but pronounced minimum appears for 10^{-4} *N* Co^{2+} with $8 \cdot 10^{-5}$*N* Eu^{3+} and is shown in Fig. 5. In all these cases the concentrations of ions with higher valency were greater than their coagulation values.

Measurements of the adsorbed quantities of the coagulating ions Eu^{3+} and Co^{2-} in the same concentration region are shown in Fig. 6. The measurements were performed 16 hours after the precipitation in systems showing high turbidities. Those with low turbidities in the minima have not settled by this time and could not have been measured without centrifugation. It follows from Figure 6. that the sum of the adsorbed quantities of both ions is constant and independent of their concentration even in case the concentration of one of the ions is lower than its coagulation value. This was shown earlier to be valid for concentrations higher than the coagulation value. As expected, with increasing concentration of Co^{2+} its adsorbed quantity increases while at the same time the amount of adsorbed Eu^{3+} decreases.

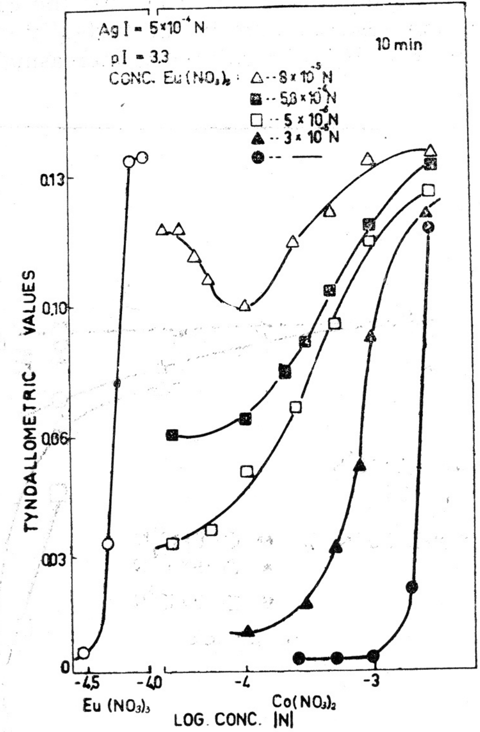

Fig. 5. Influence of the concentration of $Eu(NO_3)_3$ $3 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, $5.8 \cdot 10^{-5}$ and $8 \cdot 10^{-5}$ *N* upon the 10 minutes plots intensity of scattered light — logarithm concentration of $Co(NO_3)_2(N)$ of the systems AgI $5 \cdot 10^{-4}$ *N*, pI 3.3.

DISCUSSION

The phenomenon of antagonism is revealed in Fig. 1. Namely, the higher the concentration of Na^+ the larger is the coagulation value of Co^{2+}, instead of becoming smaller as should be expected if the process of coagulation was determined by additivity. The concentrations of Na^+ are however lower than the corresponding coagulation value.[3]

The effect of Co^{2+} upon the coagulation value of Na^+ is according to expectation. Namely, the higher the concentration of Co^{2+} the lower is the coagulation value of Na^+ (Fig. 2). It should be stressed that the concentrations of Co^{2+} are larger here than the coagulation value of this ion.

The principle of additivity requires that in all systems in which the concentration of an ion is greater than its coagulation value, the coagulation should occur with the same speed irrespective of the second ion concentration. On the other hand, the results in Figs. 1., 2., 4., and 5. demonstrate, that ions of lower valency exhibit a stabilizing action against the coagulating tendency of the higher valency ions. A minimum in the turbidity curve appears when the concentration of the ion of lower valency is increasing towards its coagulation value.

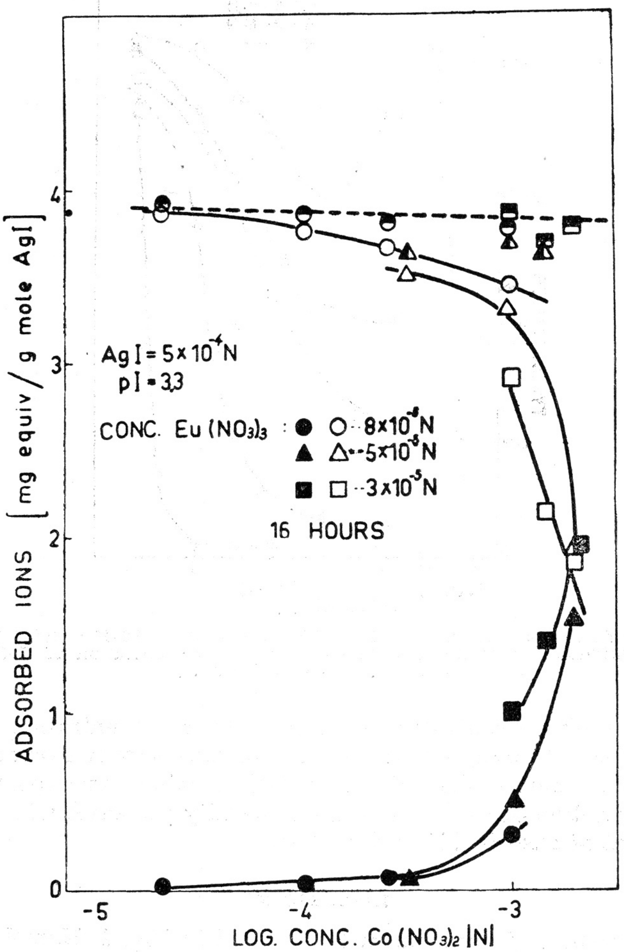

Fig. 6. The 16 hours plots adsorbed quantity of Eu^{3+} and Co^{2+} (gramequivalents) and the sum of the adsorbed quantities of Eu^{3+} and Co^{2+} against logarithm concentration of $Co(NO_3)_2$ (*N*) of the systems AgI $5 \cdot 10^{-4}$, pI 3.3 and $Eu(NO_3)_3$ $3 \cdot 10^{-5}$, $5 \cdot 10^{-5}$, and $8 \cdot 10^{-5}$ *N*.

The adsorption measurements of Fig. 6. show that the total amount of the adsorbed counter ions is constant and equal to the adsorbed quantity for concentrations above the coagulation value. It might be concluded by extrapolation to the region of minima that this is the case there too. We may therefore conclude that coagulation is a kinetic phenomenon. Namely, the same adsorption equilibrium as evidenced by constant maximum amount of adsorbed counter ions (measured on coagulated and stabilized systems) does not prove unequivocally that the coagulation occurs at the same rate. In systems at the minima of turbidity curves part of the adsorbed ion of higher valency will be replaced by lower valency ions. Most probably the establishment of this adsorption equilibrium is delayed as compared with the establishment of the equilibrium of only one ion and as a consequence the coagulation process is delayed or slowed down too. Figure 6. may also be considered as evidence that the thermodynamics which is valid for the counter ion adsorption in the coagulation region must be valid in the stability region as well. Thus the analogous adsorption isotherms which are valid in the stability region are valid in the coagulation region too. The results of Fig. 6. justify the application of the same counter ion exchange isotherms which were obtained for coagulated particles to be valid for stable ones too. Namely, the check of the validity of the ion exchange theory of coagulation in respect to the explanation of the critical coagulation concentration[5] was based upon the following assumption: the adsorption isotherms for the solid of a stable and coagulated state differ only in the constants which determine them, while the terms defining the influence of the counter ion concentration and valency remain the same in both cases.

It was shown (Fig. 6.) that the sum of the adsorbed quantities of two coagulating ions in concentrations lower than the coagulation value is constant and equal to the adsorbed quantity in concentrations higher than the coagulation value. It may be concluded that the above assumption was therefore justified and that the thermodynamically requested additivity of the adsorbed quantities is valid also in the stability region.

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IZVOD

Određivanje adsorpcije iona tehnikom radioaktivnih tracera. IV. Koagulacija negativnih solova srebrnog jodida smjesama kationa različitih valencija

M. J. Herak i M. Mirnik

Koagulaciona vrijednost Co^{2+} povećava se s rastućom koncentracijom Na^+. Koagulaciona vrijednost Na^+ smanjuje se samo neznatno s rastućom koncentracijom Co^{2+}, koja je viša od njegove koagulacione vrijednosti. U slučaju prisutnosti iona više

valencije (Co^{2+} odnosno Eu^{3+}) u koncentraciji višoj od njegove koagulacione vrijednosti, ion niže valencije (Li^{+}, Na^{+}, K^{+} odnosno Co^{2+}) djeluje stabilizaciono, što se očituje u sniženim tindalometrijskim vrijednostima, odnosno s minimumom tih vrijednosti u koncentraciji nešto nižoj od koagulacione vrijednosti iona niže valencije. Elektronsko mikroskopske snimke pokazuju, da su čestice sistema u minimumu nekoagulirane primarne čestice, dok su one visokih tindalometrijskih vrijednosti aglomerati sastavljeni iz velikoga broja primarnih čestica. Mjerenja adsorpsije protuiona metodom radioaktivnih indikatora pokazala su, da isti mehanizam ionske izmjene, koji je utvrđen u koncentracijama iona višim od koagulacione vrijednosti, vrijedi i u koncentracijama, u kojima se pojavljuje stabilizacija s niževalentnim ionima. Prema tome je opravdana primjena istih termodinamskih jednadžbi i u području koncentracija koje su niže od koagulacionih vrijednosti.

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