

Influence of Sodium and Iodide Ions on the Transformation of Metaphasic Silver Iodide into the Crystalline Silver Iodide

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The influence of constitutive (AgI , I^- ions) and nonconstitutive (Na^+ ions) components of silver iodide hydrosols on the transformation rate of metaphasic silver iodide into crystalline silver iodide is studied. The simultaneous change of AgI , I^- ions, and Na^+ ions concentrations causes a complex change of the value of the constant k_x (which is proportional to the aggregation rate constant k_2). Within a certain concentration range of constitutive components, the number of primary particles n_1^0 is directly proportional to the concentration of AgI , and the size of primary particles remains unchanged. Under such conditions, the value of the constant k_x is only affected by the concentration of Na^+ ions present in the system. For relatively high ($p\text{I} = 1$) and relatively low ($p\text{I} = 4$) concentrations of I^- ions the values of the constants k_x and b exhibit a sudden decrease.

INTRODUCTION

Studies of ageing of negative stable silver iodide hydrosols by various methods (heterogeneous exchange, sedimentation analysis, electron microscopy, and light scattering) have shown that the physico-chemical properties of sol particles are changed through two different processes: a rapid process whose duration Δt_{A1} (in minutes) is approximately inversely proportional to the molar concentration C_0 of the silver iodide, and a slow process which can be traced during a long time interval after the rapid process has been completed¹⁻³. Combined electronmicroscopic³, sedimentation^{2,3}, and radiometric⁴ analyses of sols have shown that primarily formed particles (particles formed immediately after mixing of the precipitating components) are monodispersed and that they aggregate into secondary particles by a second-order kinetic process during the time interval Δt_{A1} . The radius r_1 , of primary particles determined by electron-microscopy is 8.7 and 8.4 nm for 0.01 and 0.002 molar AgI sol, respectively. The radius r_2 of secondary particles determined by the same method³ is 11.3 and 11.26 nm for 0.01 and 0.002 molar AgI sol, respectively. The size ratio r_2/r_1 is 1.3 for 0.01 molar sol and 1.34 for 0.002 molar sol. It is particularly interesting that the aggregation rates between primary and secondary particles, as well as the aggregation rate between secondary particles themselves are negligible compared with the aggregation rate between primary particles²⁻⁴. Thus, the number n_1 of primary particles can be represented as a function of the ageing time t_A :

$$n_1 = 1/(k_2 t_A + 1/n_1^0)$$

where k_2 is the rate constant of the second-order kinetic process and n_1^0 is the number of primary particles at $t_A = 0$. Secondary particles formed in the time interval Δt_A aggregate into larger particles by other mechanisms (secondary aggregation, formation of mosaic structures, recrystallization, etc.)^{1,5,6} occurring during the slow ageing process. Using various experimental techniques, such as heterogeneous exchange, electron microscopy, sedimentation analysis and light scattering, it was found that (i) the selfdiffusion coefficient of I^- ions inside primary particles is considerably higher than the selfdiffusion coefficient of I^- ions inside secondary particles, and (ii) the specific density and refractive index of secondary particles are considerably higher than the mentioned properties of primary particles. These findings are in disagreement with the suggested model of silver iodide hydrosols⁷⁻⁹ in which their basic physico-chemical properties are not changed (except particle growth and possible transformation of the hexagonal into the cubic crystallographic modification)⁹⁻¹³. In order to find a model of silver iodide hydrosols that would satisfy all experimental requirements, the concept of metaphasic silver iodide or metaphase has been suggested^{1-3,14}. According to this concept, primary particles of silver iodide are built in a new structural form — metaphasic silver iodide. Iodide and silver ions forming the metaphase are hydrated and very mobile, so that the dynamic equilibria between ions in the metaphase and the liquid phase are reached very rapidly. The metaphase transforms into crystalline silver iodide as a consequence of the collision of two primary particles. Each collision leads to the transformation of a fraction of the metaphase into the solid phase, so that the secondary particles are composed of crystalline silver iodide surrounded by the rest of untransformed metaphasic silver iodide (see scheme 2 in ref. 14). Taking into account this mechanism and the second-order kinetic process of particle aggregation, the fraction of metaphase f_m contained in the system at any ageing time t_A can be represented by the equation^{2,3,14}

$$f_m = (1 - b)/(C_0 \cdot k_\pi \cdot t_A + 1) + b \quad (1)$$

Here, C_0 is the molar concentration of silver iodide in the system, b is the fraction of metaphasic silver iodide in secondary particles, and k_π is the product of k_1 and k_2 , where $k_1 = n_1^0/C_0$. The validity of the above equation and thus the validity of the concept of metaphase was verified experimentally using the radiometric method for determining the metaphase fraction^{1-3,14}.

The aim of this paper is to show the influence of concentration of constitutive (AgI , I^-) and nonconstitutive (Na^+) components on the kinetics and mechanism of the transformation of metaphasic silver iodide into crystalline silver iodide.

EXPERIMENTAL

The sols were prepared by the addition of 5 ml of $AgNO_3$ solutions of a given concentration into Erlenmeyer flasks containing 5 ml of NaI solutions of given concentrations. The NaI solutions contained various quantities of Na^+ ions (in the form of $NaI + NaNO_3$ mixtures). During precipitation, the solutions in flasks were stirred by a magnetic stirrer. After mixing, the molar ratio of iodide ions in the solid phase (n^s) versus iodide ions in the liquid phase (n^l) was 1 ($\alpha = n^s/n^l = 1$) for all sols. Using the method described in ref. 14, the metaphase contained in these systems was determined as a function of the ageing time t_A . During precipitation,

ageing, and determination of the metaphase fraction, the systems were thermostated at 293 K. All systems examined were prepared 9 times and the reported results represent the average values.

RESULTS AND DISCUSSION

The values of the fraction of metaphase, $*f_m$ determined by the described method, differ from the real values f_m by a constant factor Δf_m . The value of Δf_m depends on the sol concentration C_0 and on the exchange time t_E , but is independent on the ageing time of sol¹⁴. Thus, $*f_m$ vs. t_A curves obtained experimentally can be expressed by the equation

$$*f_m = f_m - \Delta f_m = (1 - b)/(C_0 \cdot k_\pi \cdot t_A + 1) + b - \Delta f_m \quad (2)$$

The solid curves in Figures 1A and 2A represent $*f_m$ as a function of t_A for 0.1 and 0.0001 molar silver iodide hydrosols. After a sufficiently long period of ageing, $*f_m$ reaches an approximately constant value; $*f_m = b - \Delta f_m = p$. The numerical value of p for a given system can be determined graphically, as represented in Figures 1A and 2A. Subtracting the value of p from the values of $*f_m$, eq. (2) can be rewritten as

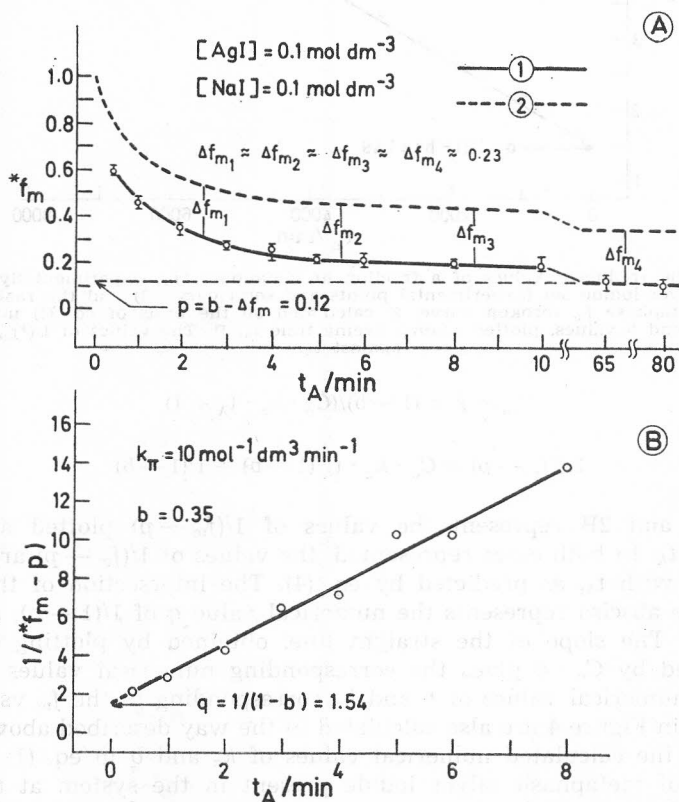


Figure 1. A. The «reduced» values of a fraction of metaphase $*f_m$, experimentally obtained in 0.1 molar silver iodide sol (experimental points and solid curve, 1) and the real values of the fraction of metaphase f_m (broken curve, 2) calculated on the basis of eq. (1) using the corresponding k_π and b values, plotted against ageing time t_A . B. The values of $1/(f_m - p)$ plotted against t_A .

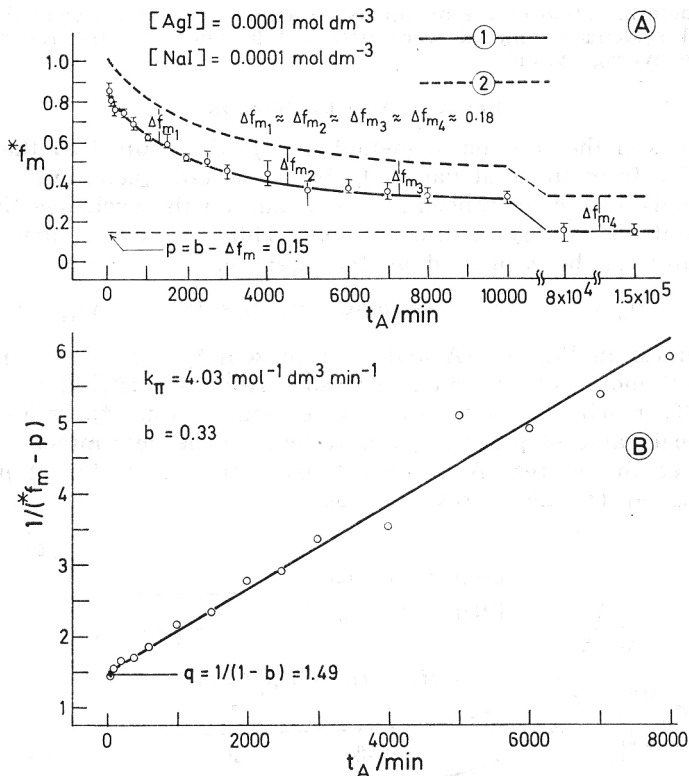


Figure 2. A. The »reduced« values of a fraction of metaphase $*f_m$, experimentally obtained in 0.0001 molar silver iodide sol (experimental points and solid curve, 1) and the real values of a fraction of metaphase f_m (broken curve, 2) calculated on the basis of eq. (1) using the corresponding k_π and b values, plotted against ageing time t_A . B. The values of $1/(f_m - p)$ plotted against t_A .

$$*f_m - p = (1 - b)/(C_o \cdot k_\pi \cdot t_A + 1) \quad (3)$$

and hence

$$1/(f_m - p) = C_o \cdot k_\pi \cdot t_A/(1 - b) + 1/(1 - b) \quad (4)$$

Figures 1B and 2B represent the values of $1/(f_m - p)$ plotted against the ageing time t_A . In both cases represented, the values of $1/(f_m - p)$ are in linear relationship with t_A , as predicted by eq. (4). The intersection of the straight line with the abscissa represents the numerical value q of $1/(1 - b)$, and hence, $b = 1 - 1/q$. The slope of the straight line, obtained by plotting $1/(f_m - p)$ vs. t_A divided by $C_o \cdot q$ gives the corresponding numerical values of k_π (see eq. 4). The numerical values of b and k_π corresponding to the f_m vs. t_A curves represented in Figure 4 are also calculated in the way described above. Finally, substituting the calculated numerical values of k_π and b in eq. (1) yields the fraction f_m of metaphasic silver iodide present in the system at t_A . Figures 1A and 2A show the real values $*f_m$ for 0.1 and 0.0001 molar AgI sols (broken curves). Figure 3 shows the values of k_π (solid curve) and b (broken curve) as functions of the molar concentration of silver iodide, $C_o = [\text{AgI}]$. In the concentration range from $C_o \approx 0.0005$ to $C_o \approx 0.05$ mol dm $^{-3}$ the constant b

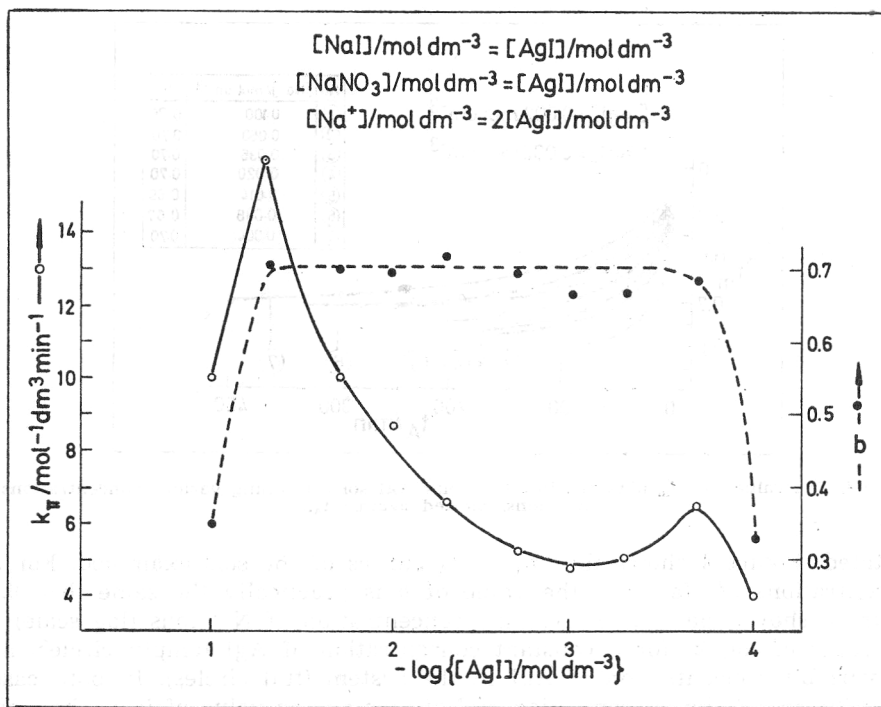


Figure 3. The influence of a simultaneous change of the AgI, I^- ions, and Na^+ ions concentration (log scale) on the value of k_π (empty circles, solid curve) and b (full circles, broken curve).

does not depend on C_0 , and its value is approximately 0.7. This means that about 70% of the metaphasic silver iodide remains untransformed in each collision between two primary particles^{1-3,14}. Thus, secondary sol particles are composed of 70% of metaphasic silver iodide and 30% of solid, crystallographically well-defined silver iodide. In the concentration range $C_0 \approx 0.001$ mol dm^{-3} to 0.05 mol dm^{-3} the constant k_π increases with increasing concentration of silver iodide. In the range from $C_0 = 0.001$ mol dm^{-3} to $C_0 = 0.0005$ mol dm^{-3} , the values of k_π increase with decreasing concentration of silver iodide, and for $C_0 = 0.1$ mol dm^{-3} and $C_0 = 0.0001$ mol dm^{-3} , the values of k_π suddenly decrease. The decrease of k_π values at the boundary concentrations of silver iodide is followed by the decrease of the values of b . It is interesting that the concentrations of silver iodide (and thus the concentrations of iodide ions in the liquid phase) for which the values of k_π and b suddenly decrease, correspond approximately to the concentrations of iodide ions characteristic of the coagulation maximum (pI 1) and of the boundary of maximal stability (pI 4) of silver iodide hydrosols. The complex change of k_π values with the change of sol concentration (and the simultaneous change of Na^+ and I^- ions concentration) is probably caused by the simultaneous but opposite influence of stabilizing I^- and coagulating Na^+ ions. In order to find the functional dependence between the concentration of coagulating ions and the value of k_π , a series of 0.002 molar AgI sols with constant I^- ions concentration ($[I^-] = 0.002$ mol dm^{-3}) and various Na^+ ions concentrations was pre-

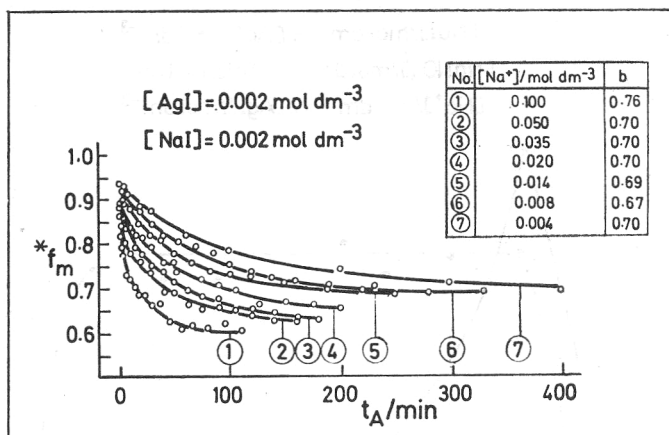


Figure 4. The values of $*f_m$ obtained in 0.002 molar AgI sol containing various concentrations of Na^+ ions, plotted against t_A .

cipitated. Figure 4 shows the $*f_m$ vs. t_A curves of the sols examined. For all concentrations of Na^+ ions, the value of b is practically the same ($b \approx 0.7$). Figure 5 shows the influence of the concentration of Na^+ ions (\log scale) on the value of $\log k_\pi$ for a constant concentration of AgI (empty circles) and for variable concentration of AgI in the system (full circles). In both cases, the influence of the concentration of Na^+ ions on the value of k_π is the same. It is interesting that in the concentration region from $[Na^+] = 0.002\ mol\ dm^{-3}$

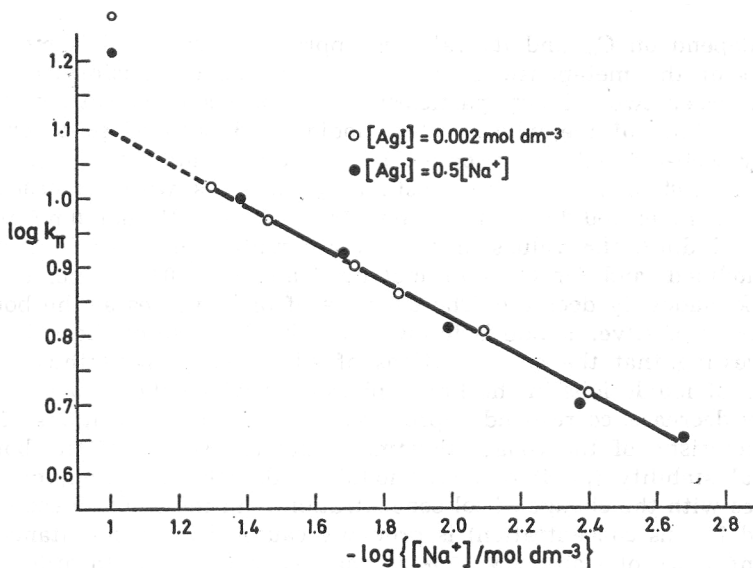


Figure 5. The dependence of values of $\log k_\pi$ on the concentration (\log scale) of Na^+ ions present in the liquid phase. The values marked by empty circles correspond to systems with constant concentration of silver iodide ($[AgI] = 0.002\ mol\ dm^{-3}$) and the values marked by full circles correspond to the systems with various AgI concentrations.

to $[\text{Na}^+] = 0.05 \text{ mol dm}^{-3}$, $\log k_\pi$ is a linear function of $-\log [\text{Na}^+]$. Hence, the change of k_π with the concentration of Na^+ ions, inside the mentioned concentration region, can be expressed by the simple relation $k_\pi = k_\pi^0 [\text{Na}^+]^m$, where k_π^0 and m are constants. From the results represented in Figure 5 it is possible to draw the following conclusions:

First, the change of Γ^- ions concentration in the concentration range from $[\Gamma^-] = [\text{AgI}] = 0.001 \text{ mol dm}^{-3}$ to $[\Gamma^-] = [\text{AgI}] = 0.1 \text{ mol dm}^{-3}$ does not affect the value of k_π . This is in accordance of Γ^- ions concentration on the electrokinetic phenomena of AgI sols^{15,16}.

Secondly, for a given concentration of Na^+ ions, the value of k_π does not depend on the concentration of AgI in the system. Hence

$$k_\pi = k_2 \cdot n_1^0 / C_0 = \text{constant} \quad (5)$$

where eq. (5) follows directly from the definitions for k_π and k_1 . It is evident that eq. (5) is valid only in the case when the change of C_0 is followed by a proportional change of the product $n_1^0 k_2$. This can be attained under two conditions:

1. $n_1^0 = \text{constant}$, $k_2 = K \cdot C_0$, where K is the proportionality constant. Hence

$$k_\pi = K \cdot n_1^0 \quad (6)$$

Under such conditions ($n_1^0 = \text{constant}$), the value of k_2 changes as a consequence of the particle size r_1 of primary particles, caused by the change of the AgI molar concentration C_0 :

$$r_1 = P \cdot C_0^{1/3} \quad (7)$$

where P is a proportionality constant. Since the particles of stable sols are electrically charged, the rate constant k_2 of aggregation of primary particles to the secondary ones can be expressed as

$$k_2 = k_d / W \quad (8)$$

where $k_d = 8 RT/3N = \text{constant}$ is the rate constant of the diffusion-controlled coagulation process of monodispersed particles^{17,19}, and W is the stability factor. For a constant concentration of Na^+ and Γ^- ions in the system, and at constant temperature, the Verwey-Overbeek approximation of the stability factor¹⁸ can be expressed as a function of r_1 only:

$$W = a_1^{-0.5 + a_2 r_1} a_3^{-a_4 r_1} a_5^{-0.5 + a_4 r_1} / 4 r_1^2 \quad (9)$$

By combining eq. (6) with eq. (9) it is very easy to show that k_2 is not a linear function of C_0 , and that the condition $k_\pi = \text{constant}$ for $n_1^0 = \text{constant}$ is not satisfied. The case $n_1^0 = f(C_0)$, $k_2 = f'(C_0)$ is not taken into consideration, because the analysis similar to that described above has shown that for this case the product $n_{01} \cdot k_2$ is not a linear function of C_0 .

2. $k_2 = \text{constant}$, $n_1^0 = k_1 \cdot C_0$, where k_1 is the proportionality constant. Hence

$$k_\pi = k_1 \cdot k_2 \quad (10)$$

In this case, the number of primary particles n_1^0 , is directly proportional to the concentration of silver iodide in the system and their size does not depend

on the sol concentration C_0 . This conclusion is in accordance with experimental data obtained by electron microscopy³ and the radiometric method for the characterization of particulate processes⁴ in identically prepared systems. Thus, the rate constant k_2 of aggergation of primary particles into the secondary ones does not depend on AgI and I^- ions concentrations, but only on the concentration of Na^+ ions inside the concentration regions examined ($[AgI] = 0.001$ to 0.05 mol dm^{-3} , $[I^-] = 0.001$ to 0.05 mol dm^{-3} , $[Na^+] = 0.002$ to 0.1 mol dm^{-3}).

CONCLUSION

The change of concentrations of constitutive (AgI , I^- ions) and nonconstitutive (Na^+ ions) components of silver iodide hydrosols affects the rate of transformation of the metaphasic silver iodide to the crystalline silver iodide. However, inside the wide concentration range of constitutive components ($[I^-] = [AgI] = 0.001$ to 0.02 mol dm^{-3}) the value of the constant k_π and thus the value of the constant k_2 depend only on the concentration of Na^+ ions. For a constant concentration of Na^+ ions, the values of the constants k_π and k_2 do not depend on the concentration of AgI in the system, because the change of AgI concentration is followed by a proportional change in the number of primary particles. Inside the concentration range of $[Na^+] = 0.002$ to 0.05 mol dm^{-3} , the change of k_π can be expressed by the simple relation $k_\pi = k_\pi^0 [Na^+]^m$. The value of b is constant under the same concentration conditions. The values of k_π and b suddenly decrease at I^- ions concentrations corresponding to the concentration of I^- ions which are characteristic for the coagulation maximum and for the boundary of maximal stability. The cause of these effects will be subject of further investigations.

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SAŽETAK

Utjecaj natrij- i jodid-iona na prijelaz metafaznog srebro-jodida u kristalinični srebro-jodid

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U radu je proučavan utjecaj konstitucijskih (AgI , I^-) i nekonstitucijskih (Na^+) komponenata hidrosolova srebrnog jodida na brzinu transformacije metafaznog srebrnog jodida u kristalni srebrni jodid. Istovremena promjena koncentracija AgI , te iona I^- i Na^+ uzrokuju složenu promjenu vrijednosti konstante k_π proporcionalne konstanti brzine agregacije k_2 . U stanovitom koncentracijskom području konstitucijskih komponenata broj primarnih čestica sola n_1^0 upravo je proporcionalan koncentraciji AgI , a veličina primarnih čestica ostaje konstantna. Unutar takvih uvjeta, na vrijednost konstante k_π utječe samo koncentracija iona Na^+ nazočnih u sistemu. Za relativno visoke ($p\text{I} = 1$) i relativno niske ($p\text{I} = 4$) koncentracije iona I^- , vrijednosti konstanti k_π i b naglo se smanjuju.

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