Investigation of Subsystems of Colloidal AgI by Radioactive Tracer Technique*

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Stable silver iodide sols were prepared *in statu nascendi, i. e.* by direct mixing of precipitation components. The sols contained 0.0001, 0.001 or 0.01 M NaI (pI = 4, 3 or 2) and 0.0001, 0.001 or 0.01 M/l AgI at 293 K. The following subsystem fractions were separated from the stable silver iodide suspensions by radioactive tracer technique with superspeed Sorvall SS-1 centrifuge and Beckman Model L Preparative ultracentrifuge: embrional, metaphasic, and roughly dispersed silver iodide. Formation and transformation of each subsystem was examined under various conditions (pI, age of sols, addition of coagulation electrolyte Mg-nitrate). The results described reveal a number of simultaneous processes in stable silver iodide suspensions: the embrya disappear and are transformed into the metaphase and solid phase; the methoric mass also disappears turning into the solid phase, *i. e.* the silver iodide particles grow. The method employed is described in detail and the results obtained show the dependence of the silver iodide subsystem structure on its age and conditions at which it is formed.

INTRODUCTION

Stable silver iodide sols prepared *in statu nascendi* (by direct mixing of the precipitation components) represent a complex colloid system composed of polydisperse and polymorphic particles[1], whose stability depends on the activity of the potential determining ion, on the concentration of the solid phase in the suspension, on the age of the system and on the concentration and chemical nature of other components present[2]. Radiometric analysis of particle growth reveals a number of simultaneous processes in stable silver iodide sols: the embrya disappear and are transformed into the meta-phase and solid phase; the methoric mass also disappears and turns into the solid phase[1]. Silver iodide suspensions are frequently used as a model in various colloidochemical investigations, although, as a rule, the properties of their subsystems are ignored. Since the subsystems, especially in the fresh and diluted suspensions, form the main part of the system, it is of great importance to know general properties and behaviour of the subsystems of colloid silver iodide. Experiments were undertaken in order to establish the characteristic equilibria between the subsystem components. In continuation to the previous[1] investigation, new results which gave new information on the subsystems of the silver iodide sols were obtained by a minute radioanalysis of the colloid silver iodide.

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Materials

Analar grade AgNO₃ (BDH), *p. a.* grade (Merck) Mg(NO₃)₂ · 6H₂O and suprapure grade (Merck) NaI chemicals were used throughout the experiments. Silver nitrate solution was standardized by means of standard NaCl solution. NaI solution was standardized by di-iodo-dimethylfluorescein as an end point indicator. Saturated solution of $Mg(NO_3)_2$ was prepared by weighing $Mg(NO_3)_2 \cdot 6H_2O$. Water was double distilled from a two-stage Duran 50 apparatus (after Zellner, Jena-er Glass, Schott u. Gen Mainz).

Preparation of AgI Sols

All investigated sols were prepared in such a way that the liquid phase contained NaI, n^L, (1×10^{-4} M NaI corresp. to pI = 4, 1×10^{-3} M NaI corresp. to pI = 3 and 1×10^{-2} M NaI corresp. to pI = 2). Equilibrium amount of silver iodide, n^s, was always equal to equilibrium amount of NaI, *i. e.* $\alpha = n^s/n^L = 1$. For this purpose equal volumes of 2×10^{-4}, 2×10^{-3} or 2×10^{-2} M AgNO₃ were added to the 4×10^{-4}, 4×10^{-3} or 4×10^{-2} M NaI solutions (which were stirred by magnetic stirrer), containing or not radioactive ¹³¹I⁻. After precipitation sols were left to grow at 20.0 ± 0.2 °C in a Haake ultrathermostat. All examined systems were prepared 3—15 times; the results reported are average values.

(i) In order to determine the rate of the heterogeneous exchange process between I⁻ in the liquid phase and I⁻ in the AgI particles, $[AgI]_{solid} + [I^-]_{liquid}$, stable silver iodide sols were prepared as follows: 100 ml of 2×10^{-2} M AgNO₃ solution was added by a pipette to 100.0 ml of 4×10^{-2} M NaI solution. After precipitation, the systems were aged for 30, 300, 1000 and 3000 minutes (= t_A). After aging for t_A minutes the systems were labelled with 0.1 ml of 1×10^{-3} M NaI containing ¹³¹I⁻. Immediately before the time of exchange, t_E, 10 ml of the suspension were separated from the agitated system. Then the separation of the liquid from the solid phase was carried out by the following procedures:

(i.a) by superspeed Sorvall centrifuge SS-1 (10 000 G) for 10 minutes the liquid phase was separated from the system or

(i.b) 0.2 ml of the saturated Mg(NO₃)₂ solution was added to the suspension. Although the main amount of the silver iodide was coagulated the sample was centrifuged for 5 minutes in a Janetzki T20 centrifuge (5000 G). Total separation of the liquid from the solid phase was achieved in both cases. Specol (Zeiss, Jena) was used to determine the extinction of clear supernatant, which proved to be equal to the extinction of pure Mg(NO₃)₂ solution. Radioactivities of the liquid phase at the time t_E were determined by an Ekco Electronics equipment with a well type scintillation crystal NaI(TlI) and semiautomatic scaler. The starting radioactivity A_o was determined on equally prepared systems without AgI. Equilibrium radioactivity A_∞ was determined from clear supernatant of systems prepared in the same way as for A_t determination, but by labelling a NaI solution before the precipitation. The course of the $[AgI]_{solid} + [^{131}I^-]_{liquid} \rightleftarrows [Ag^{131}I]_{solid} + [I^-]_{liquid}$ heterogeneous exchange was expressed as fraction exchange $F = (A_o - A_t)/(A_o - A_{oo})$. The results obtained are represented in Fig. 1.

(ii) In order to determine the subsystems in silver iodide suspension, experiments were carried out as follows: 100.0 ml of 2×10^{-2}, 2×10^{-3} and 2×10^{-4} M AgNO₃ solution were added by a pipette to 100.0 ml of 4×10^{-2}, 4×10^{-3} and 4×10^{-4} M NaI solutions labelled with ¹³¹I⁻. Sols prepared were thermostated at 20.0 ± 0.2 °C by Haake ultrathermostat. In time intervals of 30 minutes to 30 000 minutes (= t_A) two samples of 8 ml of the suspension were taken and centrifuged for 10 minutes by SS-1 (10 000 G). After the centrifugation three fractions, f, of the subsystems were obtained[1]: the rough dispersion of a sediment strongly attached to the tube wall, $f_{sediment}$; highly concentrated suspension in the form of a heavy »oil« drop, f_{oil}; and the embryonal silver iodide in a clear transparent supernatant, f_e. The clear supernatant from tube 1 was used for determination of the radioactivity A_f. Radioactivity corresponding to the silver iodide in the clear supernatant, *i. e.* in an embryonal form is A_{f_e} equal to $A_f - A_\infty$. The samples from tube 2 were used for determination of the radioactivity of silver iodide in the »oil« fraction. For this purpose clear supernatant with »oil« drop

of concentrated suspension was separated from the rough dispersion (attached to the tube wall): radioactivity of the sol obtained is B_f corresponding to the radioactivity of A_f and to the radioactivity of the silver iodide in the oil drop Af_{oil}. Then Af_{oil} is equal to $B_f - A_f$. In this case the radioactivity of the silver iodide in the rough dispersion $Af_{sediment}$ is equal to $A_o - B_f$. The change of the fractions f as a function of the time of aging of the suspension is shown in Fig. 2.

(iii) The efficiency of the centrifugation for the subsystem separations was examined by using Beckman Model L preparative ultracentrifuge with Type 40 rotor. Systems were prepared in the same way as for (ii) and centrifuged at 20 000 to 80 000 G. The equilibria obtained at 80 000 G indicated the presence of silver iodide in a nonsolid form of AgI, i. e. in an embryonal form. The results obtained are shown in Fig. 3.

(iv) The systems prepared for the determination of the methoric mass were as follows: 10.0 ml of 2×10^{-2}, 2×10^{-3} and 2×10^{-4} M AgNO$_3$ solutions were added to 10.0 ml of 4×10^{-2}, 4×10^{-3} and 4×10^{-4} M NaI solutions. The precipitated systems were aged for various aging times t_A from 1 minute to 100 000 minutes. Fifteen seconds before t_A was reached, the system was strongly agitated and labelled with 0.1 ml ^{131}I$^-$, and the sol was coagulated at the time t_A by adding 0.2 ml of saturated Mg(NO$_3$)$_2$. Immediately after the coagulation the sample was centrifuged with T20. Clear supernatant was used for determination of the radioactivity of the liquid phase A^L. The standard of the initial radioactivity A_o was prepared as before. Equilibrium radioactivity was calculated as $A_\infty = A_o/(1 + \alpha)$.

<div align="center">RESULTS AND DISCUSSION</div>

The exchange rate of the constitutive ions between the solution and the solid phase depends on the properties of both phases and on the interface or methoric layer[1,2]. If a change of properties of one of the phases or metaphases is caused by the experimental procedure, the exchange rate of the constitutive ions must change too[1]. One such experimental procedure is coagulation of a stable sol, which changes the properties of the methoric layer, and very probably also the characteristics of the solid phase. The heterogeneous exchange process (Fig. 1) shows that the coagulation process causes an increase of the exchange rate in silver iodide suspension. Fraction exchange, F, at the time t_E
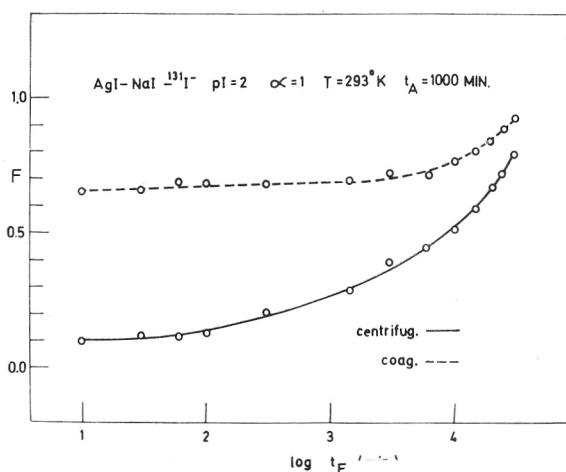

Fig. 1. Fraction exchange F measured at 293° K as a function of the exchange time t_E (minutes). Radiometric analysis was carried out in equally prepared systems by centrifugation (solid line) and by coagulation (dashed line).

is much higher on identically prepared systems if the separation of the liquid phase from the solid phase has been carried out via coagulation as compared with the separation by centrifugation. Differences are higher at the beginning of the exchange and decrease with the aging of the sol, so that after $t_E = 30\,000$ minutes the differences are negligible. Three subsystems can be obtained by SS-1 (10 000 G) as shown in Fig. 2: a clear supernatant with the
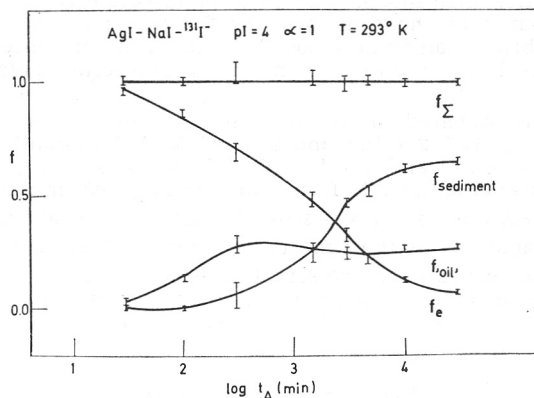

Fig. 2. Quantity of silver iodide subsystem fractions f represented as function of aging time t_A (minutes) for systems prepared at pI = 4, 0.0001 M/l AgI: fraction of embryonal AgI f_e, fraction of AgI in »oil drop« f_{oil} and fraction of AgI in a sediment $f_{sediment}$. In the systems $f_\Sigma = f_e + f_{oil} + f_{sediment}$.

embryonal silver iodide, f_e; a rough dispersion of a settled silver iodide strongly attached to the tube wall, $f_{sediment}$; and a highly concentrated suspension in the form of a heavy »oil« drop, f_{oil}. The fractions of the silver iodide subsystems, f, for sols prepared as described under (ii), can be determined by radiometry as follows:

The total amount of silver iodide present in the system is n^S, and expressed as the sum of subsystems it is

$$f_\Sigma = f_e + f_{oil} + f_{sediment} = n^s \qquad (1)$$

and since the radioactivity A of each subsystem fraction is proportional to its total amounts, f, we can write

$$\alpha = n^s/n^L = A^s/A_\infty = (A_{f_e} + A_{f_{oil}} + A_{f_{sediment}})/A_\infty \qquad (2)$$

or in the form

$$n^s = (A_{f_e} \cdot n^L)/A_\infty + (A_{f_{oil}} \cdot n^L)/A_\infty + (A_{f_{sediment}} \cdot n^L)/A_\infty \qquad (3)$$

where each of the three factors in equation (3) corresponds to the amount of silver iodide in one of the subsystem fractions, i. e.

$$f_e = (A_{f_e} \cdot n^L)/A_\infty; \ f_{oil} = (A_{f_{oil}} \cdot n^L)/A_\infty; \ f_{sediment} = (A_{f_{sed}} \cdot n^L)/A_\infty \qquad (4)$$

The changes of the fractions f as a function of time t_A are shown in Fig. 2. In the represented case fraction f_e is of great importance. Although after the centrifugation supernatant liquor is optically transparent and totally clear, it contains greater amounts of silver iodide up to $t_A = 1000$ minutes. The complex solubility of AgI at pI = 4 is so small that it cannot play any role[3].

The results obtained by ultracentrifuge (Fig. 3) indicate that after saturation acceleration (70 000—80 000 G) there remains about 9—10% of silver iodide in the system. Undoubtedly, this denotes that the silver iodide is present in the observed suspension in a form different from that in the solid phase. The smaller amount of embryonal AgI obtained by ultracentrifuge as compared with SS-1 is certainly the consequence of a strong mechanical coagulation during the centrifugation. The results are very interesting regardless of the fine structure of the silver iodide in an »embryonal« fraction.
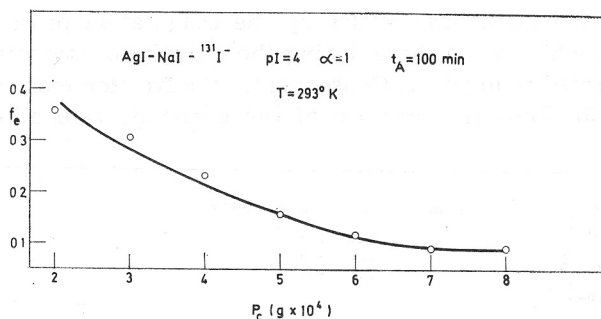

Fig. 3. Fraction of silver iodide remaining in supernatant after centrifugation f_e measured as a function of acceleration G. Before centrifugation the system was aged for $t_A = 100$ minutes.

The analysis of the influence of coagulation on the silver iodide in the sediment and »oil« drop shows the dependence of the fractions f on the coagulation effect (Fig. 4). Intensity of the coagulation effect depends on the age of the system. Hence it follows that aging changes that part of the silver iodide on which coagulation effect depends. It can be embryonal silver iodide or colloid particles of the silver iodide composed of the structurally defined solid phase surrounded by metaphasic silver iodide (which is a remainder of embryoanal structure). Metaphasic silver iodide has not the properties of
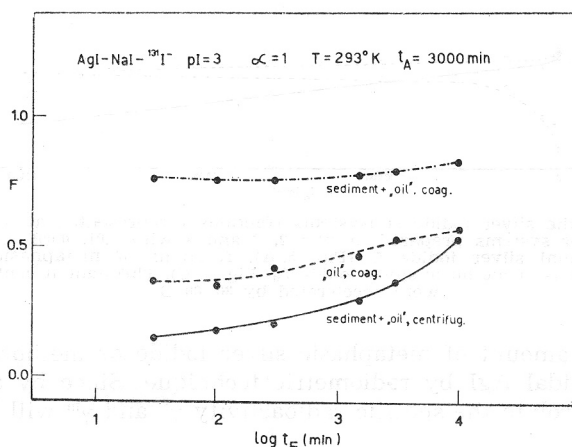

Fig. 4. Fraction exchange F represented as function of exchange time t_E (minutes) for coagulated »oil« (dashed line), coagulated sediment + »oil« (dotted and dashed line) and centrifuged sediment + »oil« (hard line). Systems were prepared at pI = 3, 0.001 M/L AgI and 3000 minutes (= t_A) before centrifugation.

the solid phase, and ions in it are very mobile. Since the sol is prepared with iodide ions in excess, the metaphasic part of colloid particles has negative electrostatic sign (caused by adsorption) and the transfer of I^- ions between the solid and the liquid phase is relatively slight. This causes a relatively slow exchange rate (hard line in Fig. 4). When the negative sign of colloid particles is compensated, the exchange of I^- ions between the liquid phase and methoric mass is not prevented. The consequence is very fast equilibration of the specific radioactivities of the liquid phase, γ^L, and metaphase, γ^m. At the same time, the metaphase settles by the coagulation process, so that the radioactive ions which were there during the coagulation process remain fixed in the newly formed solid phase. Consequently the fraction exchange, F, rapidly increases (Fig. 5). Thus the increase of the exchange rate allows the deter-
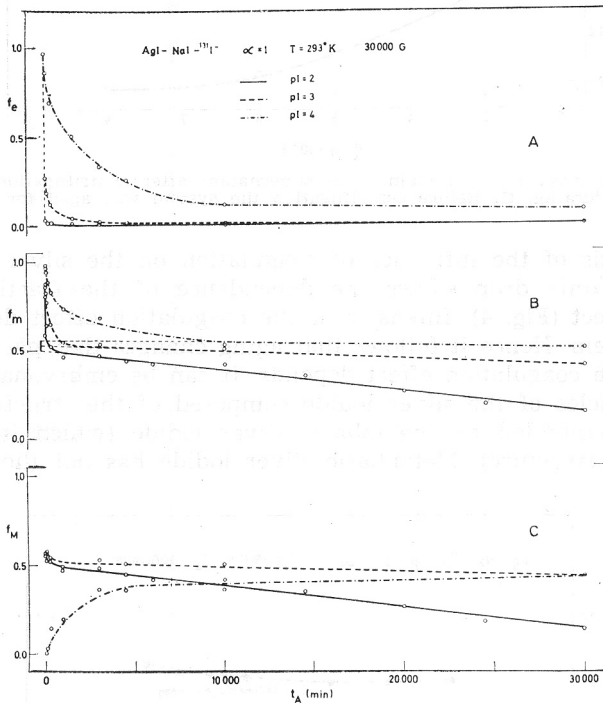

Fig. 5. Quantity of the silver iodide subsystems fractions f represented as a function of aging time t_A (minutes) for systems prepared at pI = 2, 3 and 4 with 0.01, 0.001 and 0.0001 M/L AgI: fractions of embryonal silver iodide f_e (Fig. 5. A), fractions of metaphasic silver iodide f_m (Fig. 5. B) and fractions of methoric silver iodide f_M (Fig. 5. C). Throughout centrifugation systems were accelerated by 30 000 G.

mination of the amount of metaphasic silver iodide or methoric mass of AgI in a stable colloidal AgI by radiometric technique. Since by addition of the coagulation electrolyte the specific radioactivity γ^L and γ^m will be equilibrated we can write

$$\gamma^L = \gamma^m \qquad (5)$$

owing to

$$\gamma^L = A^L/n^L \qquad (6)$$

where A^L is the radioactivity of the liquid phase after the coagulation. If the radioactivity of methoric mass is A^m and n^m, the total amount of I^- in the methoric mass is as follows

$$\gamma^m = A^m/n^m = (A_0 - A^L)/n^m \qquad (7)$$

The radioactivity of methoric mass

$$A^m = A_0 - A^L \qquad (8)$$

In the short time of coagulation process, the radioactive $^{131}I^-$ cannot penetrate the solid phase as the diffusion coefficient is very small[4]. In such a case the complete $^{131}I^-$ is exchanged in the methoric mass and the following equation is valid

$$A^L/n^L = (A_0 - A^L)/n^m \qquad (9)$$

If the total amount of I^- present in the form of silver iodide is $f_\Sigma = 1$ (solid phase + methoric mass), $n^L = 1/\alpha$ and

$$n^m = (A_0 - A^L)/\alpha \cdot A^L = f_m \qquad (10)$$

The results of the change of the methoric mass f_m in silver iodide suspensions with $\alpha = 1$ at $pI = 2$, 3 and 4 for the time interval from $t_A = 1$ minute to 100 000 minutes are shown in Fig. 5. In all cases the amounts of methoric mass desrease exponentially at the beginning. The time interval of the exponential decrease of f_m is inversely proportional to the concentration of sol. Comparing the results in Fig. 5. A with 5 B we can see that exponential change of f_m lies in the time interval at which fraction f_e falls to $f_e = 0$ (ca $t_A = 100$ minutes at $pI = 2$, $t_A = 1000$ minutes at $pI = 3$ and $t_A = 10\,000$ minutes at $pI = 4$). The consequence of the collision of embrya is the formation of solid phase surrounded with embryonal remainders. Those are real colloid particles of the stable negative silver iodide in suspension. In such a system the ratio of the solid phase and the embryonal remainder or metaphasic mass is responsible for the stability of colloid particles. Fig. 5. C shows changes of embryonal or metaphasic remainder versus time for metaphasic remainder bound on the solid phase f_M which is equal to the differences between f_m and f_e. In all cases f_M reaches its maximum between 0.5 and 0.6. This maximum probably represents the equilibrium between the rate of formation of the colloid particles and the rate of transformation of embryonal remainder into the solid phase. In this way the linear parts of the curves in Figs. 5. B and 5. C correspond to the rate of change from the embryonal, metaphasic part of colloid particle into the solid phase. Then the intersections of f_m or f_M lines with the t_A-axis correspond to the critical aging time[5] ($f_m = 0$) at which the sol completely loses its colloid stability. Such a model of the formation and aging of the colloidal silver iodide is in very good agreement with Težak's precipitation scheme[6]. It is important to point out that in stable negative silver iodide sols, embrya remain in the suspension for a long aging time, depending on the sol concentration[1]. Except for this fact, each colloid particle of the stable negative silver iodide is composed of the solid crystallographically definite silver iodide and methoric AgI, which represents the embryonal remainder and which often represents the greatest amount of silver iodide particles in the stable colloid suspension.

The present considerations of the results obtained by radioactive tracer technique will help in the study of the colloidal subsystems. They indicate that the properties of this system are only a sum of the partial properties of the subsystem components. Investigations of these partial characteristics of this complex system can help to elucidate various behaviour patterns of such colloid systems.

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IZVOD

Istraživanje subsistema koloidnog AgJ tehnikom radioaktivnog obilježivača

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Solovi stabilnog srebrnog jodida koji je pripreman *in statu nascendi* (direktnim miješanjem taložnih komponenata) predstavljaju kompleksan koloidni sistem jer je sastavljen iz polimorfnih i polidisperznih čestica. Nastajanje takvog sistema, nakon stavljanja u kontakt precipitacionih komponenata, odvija se putem uravnotežavanja, nastajanja i nestajanja koloidnih subsistema. Za istraživanja su pripremani solovi s 0.0001, 0,001 i 0,01 M NaJ (pJ = 4, 3 i 2) i 0,0001, 0,001 te 0,01 M/1 AgJ na 293 K. Primjenom tehnike radioaktivnog indikatora, a pomoću superbrze Sorvall SS/1 centrifuge i Beckman Model L preparativne ultracentrifuge (upotrebljen je rotor Type 40), u solovima srebrnog jodida identificirane su tri grupe subsistema: embrionalni, metafazni i grubodisperzni AgJ. Nastajanje i transformiranje ovih subsistema istraživano je pod različitim uvjetima (pJ, starost sola i koncentracija koagulacionog elektrolita Mg-nitrata). Rezultati pokazuju istovremenost različitih procesa: embriji nestaju transformirajući se u metafazu i čvrstu fazu, metorička masa nestaje prelazeći u čvrstu fazu, tj. čestice srebrnog jodida rastu. Primijenjena metoda opisana je detaljno, a dobiveni rezultati pokazuju ovisnost strukture subsistema o njegovoj starosti i uvjetima u kojima je subsistem nastao.