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Heterogeneous Exchange Processes. XXII. AgI — $^{131}I^-$ Exchange

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The dependence of the course of the heterogeneous AgI—$^{131}I^-$ exchange process on the age of the sol and on the concentration of the free iodide ion in the liquid phase was investigated in stable silver iodide sols. Generally the results obtained show a course of heterogeneous exchange in stable sols similar to that shown by the results obtained in coagulated suspensions of AgI in previous investigations.

The experiments have shown that the exchange process is sharply accelerated by adding the coagulating electrolyte. The investigations of this phenomenon allow the analysis of the change of the dispersity states and colloido-chemical characteristics of stable silver iodide sols.

INTRODUCTION

There are many papers dealing with the physical and chemical nature of the mechanisms of the exchange process, because the process of heterogeneous exchange of precipitates is convenient for obtaining information on the equilibration of the precipitates or solids in contact with the supernatant or surrounding space[1]. These investigations of heterogeneous exchange processes in AgI—$^{131}I^-$ systems have shown that the course of the exchange is influenced by different physico-chemical factors, such as colloido-chemical properties of AgI particles, the concentration of the constituent ion in the liquid phase, and the concentration and nature of the present surface active substance[1]. All these investigations have been carried out in coagulated AgI suspensions. In the present paper the same problem is studied in an analogous but stable silver iodide sol. The main aim of the present investigation is to establish in which way the constituent I^- ion is incorporated into the particles of the stable silver iodide sol. The interest is mainly directed towards the elucidation of the influence of aging conditions and the phenomenon of the acceleration of the exchange rate caused by the addition of the coagulating ion.

EXPERIMENTAL

Materials

In the experiments the analar grade BDH chemicals were used. Radioiodine ^{131}I was obtained from the »Boris Kidrič« Institute of Nuclear Sciences, Belgrade (Yugoslavia), as a solution of carrier free $^{131}I^-$ of the NaI form. Bidistilled water regularly tested for conductivity was used.

Preparation of AgI Sols

For the determination of the course of the exchange process it is necessary to separate the solid from the liquid phase at different times and to determine the distribution of radioiodide between these phases. The liquid/solid separation is carried out in two different ways: (i) an aliquote of the suspension is centrifuged, using a high-power SS-34 superspeed centrifuge, as long as a complete solid/liquid separation is obtained, or (ii) the solid/liquid separation is carried out by adding a coagulating electrolyte and by using a small-power T 20 centrifuge the solid from the liquid phase is separated. In order to obtain the quantitative coagulation it is imperative to add the coagulating electrolytes in such quantities that after the dilution in the system the coagulating electrolyte is present in the concentration higher than the critical coagulation concentration.

The following procedures are used for the silver iodide sols:

1. — In a 150 ml. Erlenmeyer flask 50.00 ml. solution of NaI (4×10^{-3} and/or 4×10^{-2} *M*) was added. In the sodium iodide solution stirred with a magnetic stirrer for 30—50 sec. 50.00 ml. of the solution of silver nitrate (2×10^{-3} and/or 2×10^{-2} *M*) was added. Then 100 ml. of a formed AgI sol was aged for t_A (= from 1 up to 100,000 minutes), labelled by means of c. f. $^{131}I^-$ (0.500 ml.), divided into 10 equal parts of circa 10 ml. and put in a 25 ml. Erlenmeyer flask with stopper. In time intervals from 7 to 30,000 minutes (= t_E, time of exchange) a concentrated $Mg(NO_3)_2$ solution was added to the samples of the system [approx. 0.6 *M* in $Mg(NO_3)_2$ was obtained in the system]. Then the suspension obtained was centrifuged by using a T 20 centrifuge (4,500 g.). 2.00 ml. of clear supernatant was used for the determination of radioactivity A_t.

The initial radioactivity A_0 was determined in the equal systems labelled in the same way, having the same material composition as the experimental system but containing no AgI.

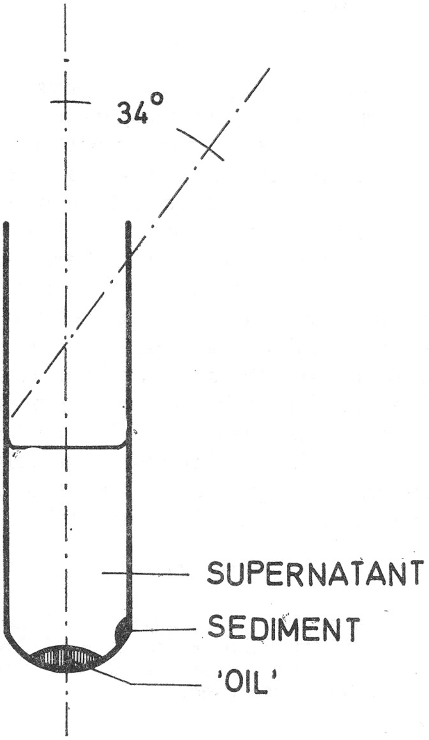

Fig. 1. After the centrifugation of AgI sol by the Servall superspeed centrifuge in the glass tube inclined by 34° in the SS-34 rotor (circa 30,000 g) (a) a clear supernatant, (b) a very concentrated sol in the form of a heavy »oil« drop and (c) a sediment strongly attached to the tube wall were obtained.

Equilibrium radioactivity A_∞ was calculated from A_0 and from analytical data on NaI and $AgNO_3$ quantities in prepared sols. The results obtained are presented in Figs. 2, 3, 5, 7, 8, partially in Figs. 4 and 13, and in Table I.

— The influence of the concentration of $Mg(NO_3)_2$ and the valency of coagulating ions (Na^+, Mg^{++}, Al^{3+}, Th^{4+}) on the measured distribution of radioactivities were examined in the same systems as described above but containing different concentrations of $Mg(NO_3)_2$ and different coagulating electrolytes. The results are given in Fig. 2 and Table I.

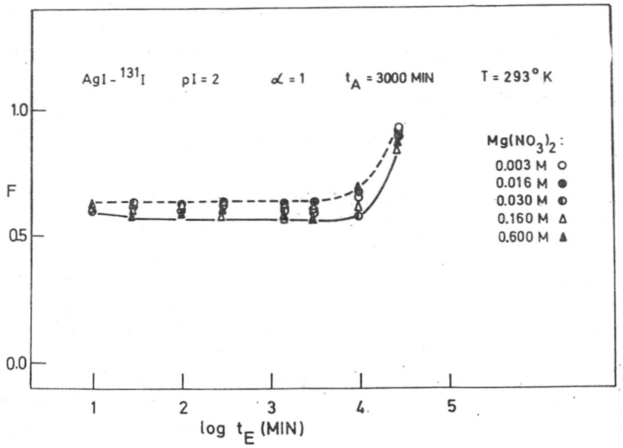

Fig. 2. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). The concentration of $Mg(NO_3)_2$ varied from 0.003 to 0.600 *M*. Prior to the exchange process of AgI — $^{131}I^-$, silver iodide was aged in the supernatant for 3000 (= t_A) minutes at $pI = 2$, $\alpha = 1$ and $T = 293^0$ K.

TABLE I

The Influence of the Valency of Coagulating Ions on the Values of Fraction Exchange F in AgI — $I^-(^{131}I^-)$ Exchange

AgI sols used were aged for $t_A = 3000$ minutes prior to exchange observation. Coagulating electrolytes were added immediately before the centrifugation of samples after exchange time t_E:

t_E minutes	F			
	0.5 *M* $NaNO_3$	0.005 *M* $Mg(NO_3)_2$	0.0005 *M* $Al(NO_3)_3$	0.00005 *M* $Th(NO_3)_4$
10	0.56	0.57	0.56	0.57
30	0.56	0.55	0.52	0.58
100	0.58	0.55	0.52	0.56
300	0.51	0.58	0.54	0.56
1500	0.53	0.57	0.54	0.57
3000	0.63	0.54	0.54	0.59
10,000	0.62	0.66	0.65	0.66
30,000	0.88	0.91	0.90	0.94

2. — Systems for the determination of A_t were prepared in the same manner as the above mentioned systems (total volume was 400 ml.), aged, labelled, one minute prior to the determined exchange time t_E, the systems were put in agitation and 4 aliquots of 8 ml. of the stable AgI sol were taken from the mixed sol, divided into 4 glass tubes and centrifuged for 10 minutes by using the SS-34 (30,000 g.) centrifuge. After centrifugation the tubes contained (see Fig. 1):

a) clear supernatant
b) heavy »oil« and
c) sediment strongly attached to the glass wall.

Radioactivities from centrifuged sols in 4 tubes were separately determined as follows:

— for the determination of radioactivity A (tube 1) 3 samples of 2.00 ml. of the clear supernatant was used,

— »oil« + supernatant (a + b) were shaken and 3 samples of 2.00 ml. of suspension counted as radioactivities B (tube 2),

— in 5 ml. of the clear supernatant 1 ml. of concn. $Mg(NO_3)_2$ solution was added. Then the coagulated sol was centrifuged using the T 20 and 2 samples of 2.00 ml. of the clear supernatant were used for the determination of radioactivity C (tube 3),

— »oil« + supernatant were shaken and in 5 ml. of the suspension obtained 1 ml. of concn. $Mg(NO_3)_2$ soln. was added, then the coagulated sol was centrifuged by the T 20 and 2 samples of 2 ml. of the clear supernatant were counted as radioactivity Q (tube 4),

— Radioactivity Z of the sediment was calculated as the difference between initial radioactivity A_0 and radioactivity B, *i. e.* $Z = A_0 — B$.

The results are presented in Figs. 10, 11, 12 and partially in Figs. 5 and 13.

3. — The distribution of the amounts of silver iodide in centrifuged systems aged for 30 to 10,000 minutes was analysed as follows: 200 ml. 2×10^{-3} and/or 2×10^{-2} *M* $AgNO_3$ were added to 200 ml. labelled 4×10^{-3} and/or 4×10^{-2} *M* NaI ($^{131}I^-$). From the aged sol in time intervals from 30 to 10,000 minutes 2 samples of 8 ml. of the sol were taken, centrifuged by the SS-34 and

— for the determination of radioactivity A_f (tube 1) 3 samples of 2.00 ml. of the clear supernatant were used. The radioactivity of »metaphase« $A_{f(x)}$ was calculated as difference $A_{f(x)} = A_f — A_\infty$. Equilibrium radioactivity A_∞ was calculated from analytical data on NaI and $AgNO_3$ quantities in prepared sols. Then the quantity of silver iodide in the »metaphase« is $f_x = n^s \cdot A_{f(x)} \cdot (A_\infty)^{-1}$, where n^S is the molar concentration of silver iodide in the system.

— »oil« + supernatant were shaken and 3 samples of 2.00 ml. of the suspension counted as radioactivities B_f (tube 2). The radioactivity of silver iodide in »oil« $A_{f(y)}$ was calculated as difference $A_{f(y)} = B_f — A_f$. Thus, the quantity of silver iodide f_y in »oil« is $f_y = n^s \cdot A_{f(y)} \cdot (A_\infty)^{-1}$,

— radioactivity of silver iodide in sediment $A_{f(z)}$ was calculated as the difference between initial radioactivity A_0 minus B_f, *i. e.* $A_{f(z)} = A_0 — B_f$. Thus, the quantity of silver iodide f_z in sediment is $f_z = n^S \cdot A_{f(z)} \cdot (A_\infty)^{-1}$. The results of the analysis of the distribution of silver iodide in centrifuged systems are shown in Figs. 6 and 9.

All radioactivities were measured by an Ekco Electronics equipment with the scintillation NaI (TlI) well type counter. The investigated systems with stable sols were centrifuged by using an automatic super-speed Servall centrifuge with SS-34 rotor (circa 30,000 g). The tubes in the rotor are inclined by 34° so that after centrifugation the AgI sediment is strongly attached to the glass wall of the tubes, and the concentrated AgI suspension in the form of a drop of heavy »oil« (see Fig. 1) is at the bottom. All systems coagulated before the determination of radioactivity were preliminarily centrifuged by using a Janetzki T 20 centrifuge (*circa* 4500 g). All aged and measured systems were thermostated at 293.0 ± 0.2° K by a Haake ultrathermostate.

The fraction exchange was calculated as $F = (A_0 — A_t) / (A_0 — A_\infty)$, and the results presented as »fraction exchange«, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). The results of the analysis of the distribution of quantities of silver iodide in systems are presented as »quantity of AgI, f, (f_x, f_y, f_z and f_Σ respectively), plotted against aging time, t_A, (in minutes, logarithmic scale)« where $f_\Sigma = f_x + f_y + f_z$.

RESULTS

The results presented in Table I show that the measured values of the fraction exchange, at different times of exchange (t_E), from 10 minutes up to 30,000 minutes, do not depend on the valency of the coagulating ion, when the coagulating ion is present in the concentration higher than the critical coagulating concentration in the series Na^+, Mg^{++}, Al^{3+}, Th^{4+}. Therefore it is of no importance which coagulating electrolyte is used for the coagulation of the suspension. In the experiments described $Mg(NO_3)_2$ was used. The results of the determination of the influence of the coagulating electrolyte on the measured fraction exchange value, F, for the investigated concentration

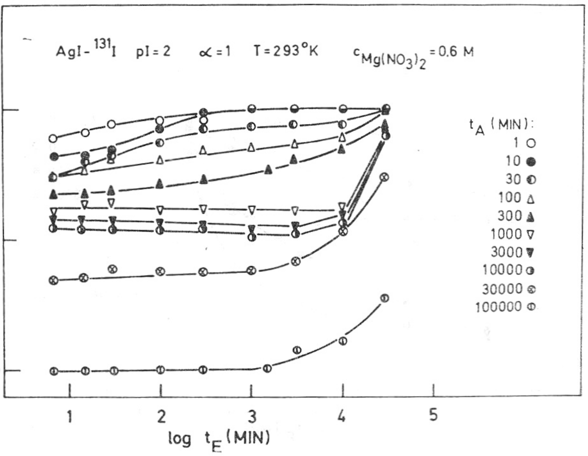

Fig. 3. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). The time of aging of AgI prior to the exchange process varied from $t_A = 1$ minute to 100,000 minutes at $pI = 2$, $\alpha = 1$, T = 293° K, and coagulated by 0.6 *M* $Mg(NO_3)_2$ before radiometric analysis.

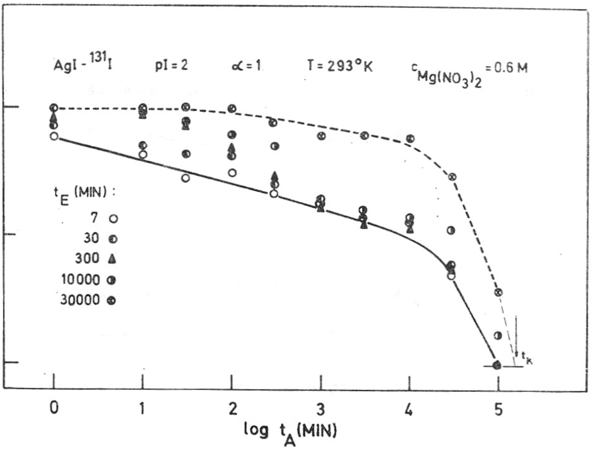

Fig. 4. Fraction exchange, F, plotted against the time of aging t_A of the AgI sol before the exchange process AgI — $^{131}I^-$. AgI was aged in the supernatant at $pI = 2$, $\alpha = 1$, T = 293° K, and coagulated by 0.600 *M* $Mg(NO_3)_2$ before radiometric analysis. t_K is the extrapolated value of the critical time at approximately 140,000 minutes.

from 0.003 M up to 0.60 M $Mg(NO_3)_2$, consequnetly in the 1 : 200 range over the critical coagulation concentration is shown in Fig. 2 and it is noted that the concentration of the coagulating electrolyte has no significant influence on F. The AgI sols aged at $pI = 2$ and $pI = 3$ show (Figs. 3—5, 7 and 8) a marked influence of the aging on the exchange course. In well-aged sols the exchange rate is small (Figs. 3, 4). In the sols of AgI aged for 10^5 minutes the fraction exchange value is significantly higher than zero only after 3000 minutes of the exchange and after 30,000 minutes the exchange has the value of $F = 0.3$. However, in the stable 1 minute aged sol, after 5 ($= t_E$) minutes, the exchange reaches value $F = 0.9$, and after 1000 minutes $F = 1.0$. In Fig. 4 the dependence of F on the time of aging, t_A, is shown for the

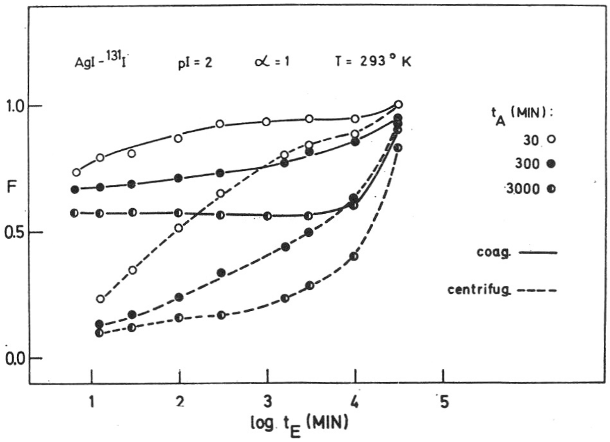

Fig. 5. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). The time of aging t_A of AgI prior to the exchange process varied from 30 to 3000 minutes. AgI—$^{131}I^-$ at $pI = 2$, $\alpha = 1$, and $T = 293^0$ K. Radiometric analysis was carried out by the coagulation of AgI (coag.) and in the equally prepared system by means of centrifugation (centrifug.) for the separation of the liquid from the solid phase.

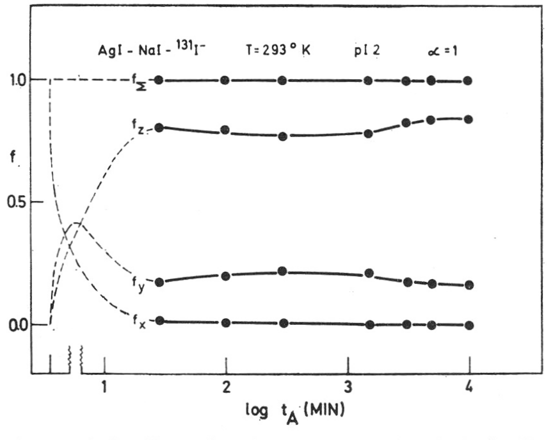

Fig. 6. The quantity of AgI, f, (in the solid phase of the AgI sol, f_z, in the concentrated heavy »oil« drop of suspension f_y, and in the clear supernatant f_x) plotted against the time of aging t_A of AgI sol at $pI = 2$, $\alpha = 1$, and $T = 293^0$ K. The total quantity of AgI f_Σ in the system is $f_\Sigma = f_x + f_y + f_z$.

exchange time $t_E = 7$, 30, 300, 10,000, 30,000 minutes. By extrapolation over measured F values for the AgI sol ($t_A = 10^5$ minutes) the value of critical exchange time $t_K = 140{,}000$ minutes is obtained. The results described were obtained by measuring the change of radioactivity of the liquid phase separated from the solid phase by adding $Mg(NO_3)_2$ in the sample and then centrifuged by the T 20. When the liquid/solid separation is carried out only by means of a high-power superspeed SS-34 centrifuge, the course of the exchange process during the time is different (Fig. 5) than the course of exchange in coagulated sols. In these systems there is a dependence of the exchange rate on the age of the AgI sol. After 30,000 minutes of the exchange, the difference between the fraction exchange value, obtained by separation

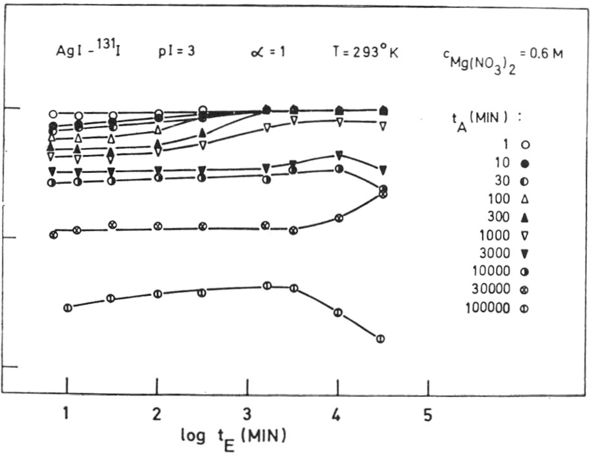

Fig. 7. Fraction exchange, F, plotted against the exchange time, t_E (in minutes, logarithmic scale). The time of aging t_A of AgI prior to the exchange process varied from 1 to 100,000 minutes at $pI = 3$, $\alpha = 1$, $T = 293^0$ K, and coagulated by $Mg(NO_3)_2$ before radiometric analysis.

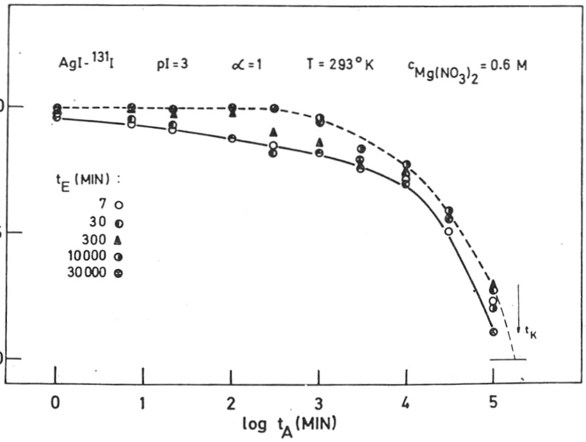

Fig. 8. Fraction exchange, F, plotted against the time of aging, t_A, of the AgI sol before the exchange process AgI—$^{131}I^-$. AgI was aged in the supernatant at $pI = 3$, $\alpha = 1$, $T = 293^0$ K, and coagulated by $Mg(NO_3)_2$ before radiometric analysis. t_K is the extrapolated value of the critical

with coagulation, is small. Therefore the collateral results in Fig. 5 show a marked effect of the coagulating ion on the measured fraction exchange values F. The explanation of this effect was obtained by the analysis of the distribution of the amount of AgI in each phase after centrifugation by the SS-34.

For $\alpha = 1$ the quantity of AgI in any form in the system is $f_n = n^S \cdot A_{f(n)} \cdot (A_\infty)^{-1}$, and $f = f_x + f_y + f_z = n^S$. The results show ($f_x$, f_y, f_z) that at *p*I = 2 the AgI sols prepared and aged under the same conditions changed very slightly in all investigated time intervals (from $t_A = 30$ up to 10,000 mi-

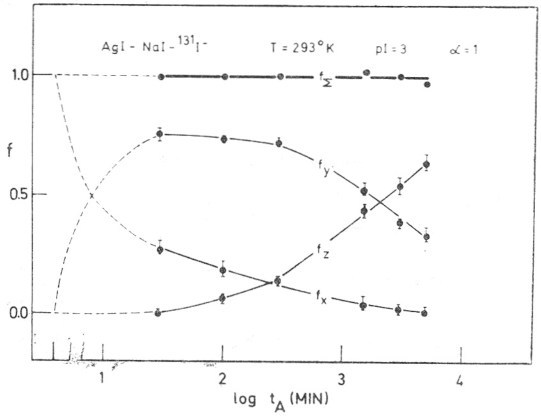

Fig. 9. The quantity of AgI, f, (in the clear supernatant, f_x, in the concentrated heavy »oil« drop of suspension f_y and in the »solid phase« of AgI sol, f_z) plotted against the time of aging, t_A, (in minutes, logarithmic scale) of AgI sol at pI = 3, $\alpha = 1$, and T = 293° K. The total quantity of AgI, f, in the system is $f_\Sigma = f_x + f_y + f_z$.

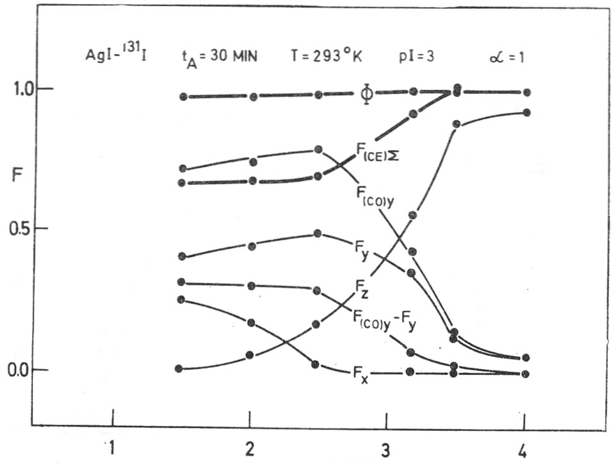

Fig. 10. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). For different meanings of F values see description in Results. AgI was aged in the supernatant before the beginning of the exchange process for 30 minutes at pI = 3, $\alpha = 1$, and T = 293° K.

nutes) and that $f_{\Sigma} = 1.0$. Comparing the results in Figs. 3—6 with those in Figs. 7—9, and 13, we can see that with the increase of the *p*I value from 2 to 3 the exchange rate increases in the systems, except for *p*I in the same way. In systems at $pI = 3$ the critical aging time is $t_K = 180{,}000$ minutes. The influence of the coagulating electrolytes on the measured fraction exchange values is higher at $pI = 3$ than at $pI = 2$ (Fig. 13). The distribution of AgI in the tube layers after centrifugation by the SS-34 is shown in Fig 9. Contrary to the constancy at $pI = 2$ (Fig. 6) the time dependence on the amount of AgI at $pI = 3$ is evident (Fig. 9). The amount f_z of the AgI sediment grows

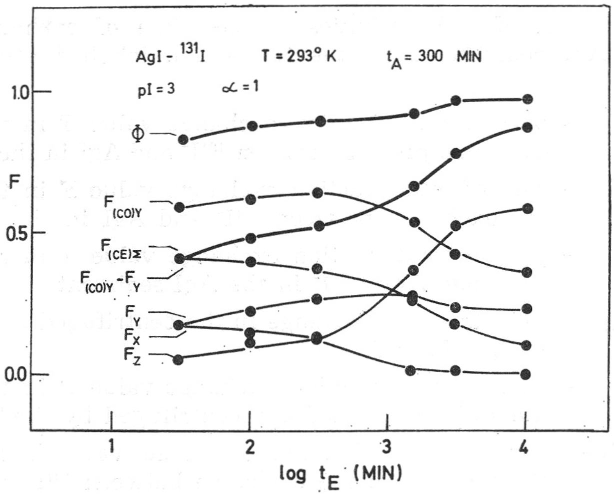

Fig. 11. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). For different meanings of F values see description in Results. AgI was aged in the supernatant before the beginning of the exchange process for 300 minutes at $pI = 3$, $\alpha = 1$, and $T = 293^{\circ}$ K.

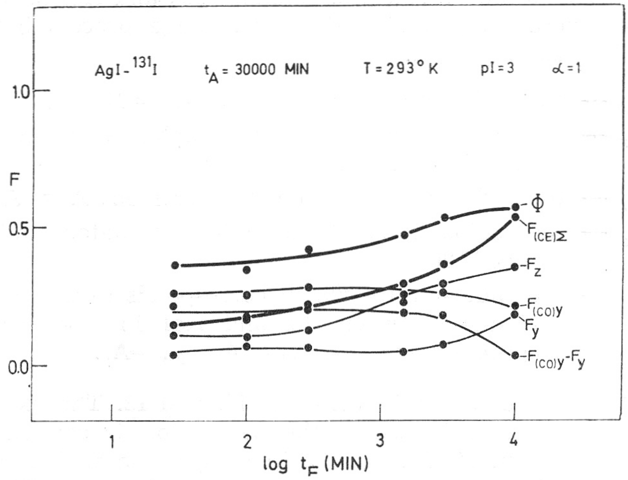

Fig. 12. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). For different meanings of F values see description in Results. AgI was aged in the supernatant before the beginning of the exchange process for 3000 minutes at $pI = 3$, $\alpha = 1$, and $T = 293^{\circ}$ K.

continuously from a fresh to a well aged AgI sol at the aging time $t_A = 30$ minutes $f_z = 0.01$, and $t_A = 4500$ minutes $f_z = 0.64$. At higher t_A values the sediment cannot be precisely separated from the »oil« and for this reason the distribution is not calculated. The amount of AgI in the »oil«, f_y, decreases with the aging of the AgI sol. Simultaneously the amount of f_x is decreased. The total amount of AgI in the system, based on the radiometric analysis, is in very good agreement with $f_\Sigma = 1$. Measuring the radioactivity of each phase at different times t_E, the exchange fraction parts for each phase are determined during the observation of the exchange process in the following way:

The distribution of radioactivities at the time of exchange t_E in the suspension of AgI centrifuged by the SS-34 and labelled after aging time t_A is:

F_x — part of total fraction exchange value F in relation to the exchange process between $^{131}I^-$ and AgI in the »metaphase«.

F_y — part of total fraction exchange value F in the relation to the exchange between $^{131}I^-$ and AgI in the »oil«.

F_z — part of total fraction exchange value F in relation to the exchange AgI—$^{131}I^-$ in the AgI sediment

$F_{(CE)\Sigma}$ — total fraction exchange in the centrifuged system $F_{(CE)\Sigma} = F_x + F_y + F_z$

$F_{(CO)y}$ — part of total fraction exchange value F in the relation to the »oil« coagulated and centrifuged by the T 20

$F_{(CO)y} — F_y = F_d$ — part of total fraction exchange value F in relation to the increase of the exchange between $^{131}I^-$ and AgI in the »oil« caused by the coagulation process.

$$F = F_{(CE)} + F_d = \Phi$$

By adding $Mg(NO_3)_2$ to the system, the »metaphase« and AgI surrounded with the »metaphase« were coagulated and the exchange process between $Na^{131}I$ and AgI in »oil« was prolonged.

A_y — the radioactivity of the »oil« $A_y = B — A$

A_x — the radioactivity of the »metaphase« in the clear supernatant $A_x = A — C$

A_z — the radioactivity of the AgI sediment $A_z = A_0 — B$

$A_{(coag)y}$ — the radioactivity of the »oil« coagulated and centrifuged by the T 20

A_d — the radioactivity which corresponds to the increase of the exchange between ^{131}I and AgI in »oil« caused by the coagulation process, $A_d = A_{(coag)y} — A_y$.

The results obtained are shown in Figs. 10, 11, and 12. The exchange values are higher in the systems in which the separation is carried out by the coagulation method (Figs. 10, 11, and 12 in comparison with Figs. 5 and 13) and they are in good agreement with the results shown in Figs. 5 and 13. In all cases (Figs. 10—12) the values Φ, $F_{(CE)\Sigma}$, and F_z reach their maximum at the end of the exchange process and the values $F_{(CO)y}$, F_y, F_d, and F_x decrease.

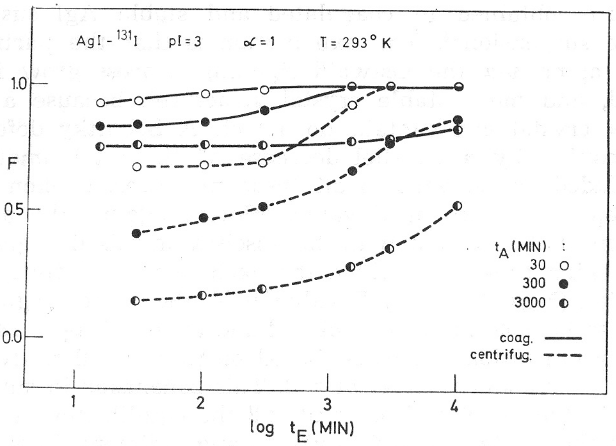

Fig. 13. Fraction exchange, F, plotted against the exchange time, t_E, (in minutes, logarithmic scale). The time of aging, t_A, of AgI prior to the exchange process. AgI—$^{131}I^-$ at pI = 3, α = 1, and T = 293° K. Radiometric analysis was carried out by the coagulation of AgI (coag.) and in the equally prepared system by means of centrifugation (centrifug.) for the separation of the liquid from the solid phase.

The analysis of the results in Fig. 10 is qualitatively equal to the analysis of the results shown in Figs. 10—12. For this reason, by the aging of the AgI sols their exchange rate decreases and all measured values were lower for the aged sols (Figs. 10—12).

DISCUSSION

The aim of the present paper was to find out to what extent (i) the concentration of the constituent I^- ion, (ii) the time of the aging of systems, and (iii) the mode of the liquid-solid separation influence the fraction exchange value, F, of the AgI—$^{131}I^-$ systems in stable silver iodide sols.

The concentration of the constituent I^- ion expressed as *pI* values shows a marked influence on the AgI—$^{131}I^-$ exchange process (Figs. 3—6 as compared with 7, 8, 9, and 13) in stable silver iodide sols, similar to that in coagulated silver iodide sols[1]. A higher exchange rate at *p*I = 3 as compared with the results at *p*I = 2 is probably caused by a higher particle dispersity in a higher total iodide dilution in the liquid phase[3]. The Ostwald ripening process (compare Figs. 6 and 9) in which the metastable colloid form AgI is transferred into a more stable one is different at *p*I = 2 and *p*I = 3: at first approximation it is not important what the »metaphase« really is (a very high by dispersed AgI which cannot be separated by the SS-34 or a molecular AgI) but what is essential is that the transformation from the »metaphase« via the »oil« phase to the solid sediment of AgI is a process different at *p*I = 2 than at *p*I = 3. Coagulating ions with a different valency and different concentrations higher than the critical coagulation concentration exhibit the same influence on the measured values of the fraction exchange, F, of AgI—$^{131}I^-$ exchange process only at the same *p*I (Fig. 2, Table I). The influence of *p*I on F values is significant (compare Figs. 5 and 13). The variation of the time of aging, t_A, of stable AgI sols, exhibits a marked influence on the AgI—$^{131}I^-$ exchange process. A fast exchange takes place in the suspension having a short aging time, t_A (Figs. 3, 4, and 7—13) which is in good agreement with the results obtained in coagulated and stable AgI suspensions[1] and silver bromide suspensions[2]. The explanation is that the particles of silver iodide during aging *via* the Ostwald ripening process grow into a higher, better ordered, and more stable crystal structure[4], because a high ordered »perfect ideal« crystal can contain no defect. A Schottky defect which can change the position by a parallel decrease of the total amount of crystal defects is included as relevant in all these processes. Broken lines (Figs. 4 and 8) represent the maximal F values plotted against the aging time, t_A. The intersection of the tangent with the abscissa on this line gives the critical value for the aging time after which the exchange is relatively insignificant. By extrapolation (Figs. 4 and 8) F value to 0, the critical aging time, t_K, is obtained as $t_K = 140{,}000$ minutes at $pI = 2$ and at $pI = 3$ $t_K = 180{,}000$ minutes. The main recrystallization processes, based on these results, are completed in the systems at $pI = 2$ and then at $pI = 3$. This conclusion in supported by the results shown in Figures 6 and 9. At $pI = 2$ the equilibrium of the amount of silver iodide in the »metaphase«, f_x, »oil«, f_y, and sediment, f_z, is reached in the time shorter than 30 minutes as compared with systems at $pI = 3$ in which it is not obtained even after 4500 minutes. In the light of the results obtained previously[3] these differences in the speed of reaching the equilibrium of dispersity and in the course of the exchange process also depend on the chemical composition of the liquid phase, with which the solid phase is in contact during the aging and during the exchange process. The addition of the coagulating electrolyte immediately before the end of the exchange process causes a sudden change in F (Figs. 5 and 13). We suppose that the phenomenon observed could be explained in the following way (Figs. 14 and 15): by adding a solution of $AgNO_3$ to the solution of NaI the supersaturated solution of AgI is formed. The time of the beginning of the precipitation process is t_0. The subcritical particles, that is the embryo, are formed after a very short induction (a slightly inclined part of curve x). A sharply inclined part of curve X shows that the rate of formation of the embryo is very high. The end of this process is at time t_x. The quantity of the subcritical particles, *i. e.* embryos (I. in Fig. 15), M_x from $(M_x)_{t_0} = 0$ at the

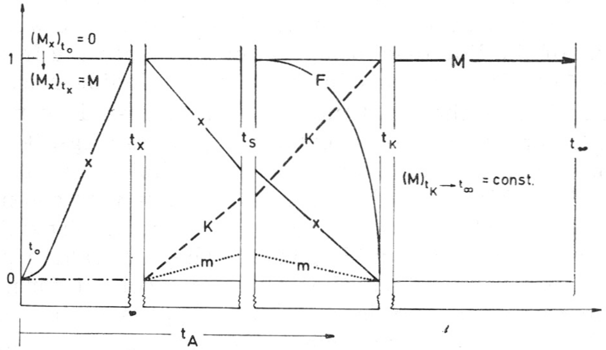

Fig. 14. The process of the ideal crystal growth from the embryo via nucleus and secondary particle structures is represented schematically. The ordinate represents relative values *e. g.*: the number or the quantity of the mass of the embryo or the quantity of the nucleus, M_x, the mass of the solid phase, K, the mass of methoric silver iodide, m, and the total quantity of the solid phase, *M*, in the shape of an ideal crystal. The abscissa is the time base from cca milliseconds up to years per unit of scale.

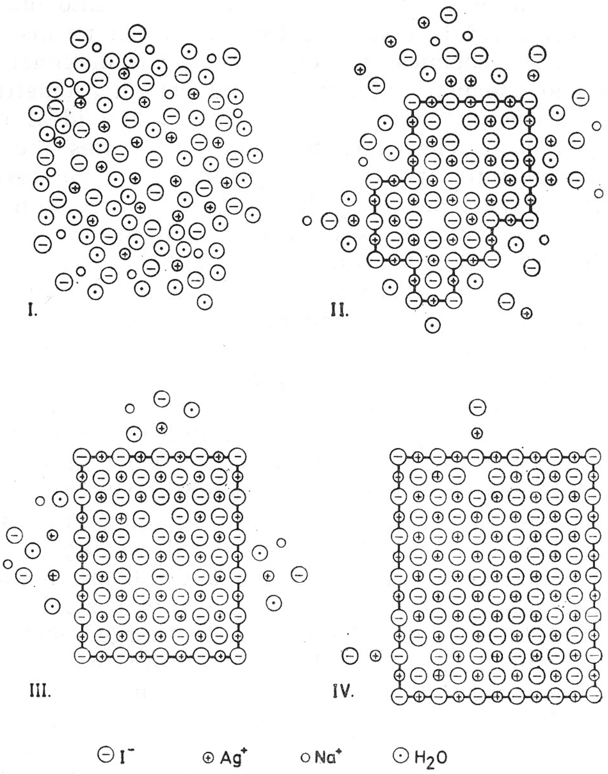

Fig. 15. Schematic picture of the crystal growth from the embryo (I.) via nucleus (II.) to secondary particles (III., IV).

initial time of the precipitation process ($t_A = 0$), reaches its maximum $(M_x)_{t_x} = M$ at time $t_A = t_x$. The embryo — nucleus equilibrium probably started in the time interval from t_0 and t_x, in all probability after the induction period. At time $t_A = t_x$ the main quantity of the subcritical particles are transformed into critical particles. This is the moment of the start of the generation of supercritical particles of the single mass $K = m_K + m$, where m_K is the mass of solid silver iodide, and m the mass of the methoric silver iodide surrounding the solid phase centre (II. in Fig. 15). Mass m reaches its maximum at $t_A = t_S$ and decreases to $m = 0$ at time $t_A = t_K$. In the time interval from t_x to t_S the number and mass of K increase at the expense of critical particles, x, and methoric silver iodide, m, in the time interval from t_S to t_K (III. in Fig. 15). At critical time t_K the quantities of masses x and m are approximately equal to 0. The rest of mass m, although very small, is proportional to the dispersity of the solid phase at critical time t_K. During the time of t_K to t_∞ the rest of m is transformed into the crystal solid $(m)_{t_K \rightarrow t_\infty} \rightarrow M$, where M is the total mass of crystal silver iodide (IV. in Fig. 15). Since the total quantity of m at critical time t_K is so small, the total mass of the solid phase, M, is practically constant in the time interval from t_K to t_∞, that is $(M)_{t_K \leftarrow t_\infty} = \text{const.}$ If all the mass of silver iodide is at the equilibrium time, t_{∞}, transformed into only one crystal, then an »ideal« silver iodide crystal is formed, which means such a crystal structure in which the chemical and crystal order is maximal, based on the thermodinamics and chemistry of crystals and not on geometrical formality. In all these schematic pictures of the process of the ideal crystal growth from the embryos *via* nucleus and secondary structures the Scheme II in Fig. 15 is of special interest for the explanation of the results shown in Figs. 5 and 13: the particles of stable colloid AgI contain many crystal defects in crystal space which causes a negative charge in the crystal surface layer in the light of the Grimley-Mott theory and in agreement with Honig's experiments and their interpretations[5]. In this time interval the capacity of this charge is the consequence of the mode of crystal growth and of the chemical conditions in the liquid phase. In this charged layer AgI is incorporated into a fixed position[6] as a complexoid[7] surrounded by molecules of water and NaI and AgI of different structures[3,4] from which the methorical layer with its negative charge is formed. In this way the transport of the iodide ion (in the same form as radioiodide) is slow in the high negative charged methorical layer and fast in the slightly negative charged colloid silver iodide particles. At the same time, by the aging process in the silver iodide sols with $pI = 2$ the crystalite sizes of AgI are bigger than at $pI = 3$ and F-values obtained in all cases (Figs. 5 and 13) are higher in systems with $pI = 3$ than $pI = 2$. If in the system with a stable colloid AgI a coagulating electrolyte is added, the negatively charged methorical layer is neutralized and at this moment, in this very mobile mass of methoric AgI, the exchange process very quickly reaches an equilibrium for this part of the solid phase. The jump in the exchange process is important for the explanation of the increase of F-values and is in connection with the quantity of silver iodide in the layer. Immediately after addition of the coagulating electrolyte, the structure shown as Scheme II is transformed into the structure shown as Scheme III in Fig. 15. It is the model of a standard silver iodide particle of the coagulated suspension with certain crystal defects and with corresponding adsorption capacities which decrease to the minimum by aging (IV. Fig. 15). In all these schemes we supposed an adsportion of iodide ions on the crystal surface in the complexoid form[5,7], in which the fixed position is fixed inasmuch as the defects are fixed in the crystal. By displacing the crystal defects the position of the fixed adsorbed complexoid is moving but always located. The analysis of the transfer of the mass of silver iodide between sediment, »oil« and »metaphase« is in good agreement with the previous exchange results, showing that a certain dispersity equilibrium is reached earlier in systems at $pI = 2$ (Fig. 6) than at $pI = 3$ (Fig. 9). In each part of this colloid substructure of silver iodide the exchange process was observed during the period of 10,000 minutes (Figs. 10—12). Taking into account the change of the total mass of AgI in each mass fraction (f-values in Fig. 9), F_x and F_y fraction exchange values decrease with the time as the quantity of f_x and f_y decreases, while F_z increases as f_z. Between all colloid substructures of present silver iodide in the observed time interval complex equilibria exist (in dispersity and in the exchange process). For this reason (with the technique applied) we could not precisely determine the rate of transfer of iodide ion in each colloid substructure of silver iodide. Meanwhile, as may be seen the total fraction exchange values in centrifuged systems,

$F_{(CE)\Sigma}$ increase with the time. The total fraction exchange values decrease with the aging of the system. On the basis of the results obtained we can conclude that the course of the exchange process in the systems containing stable silver iodide sols is generally very similar to the course in silver iodide suspensions[1]. Especially interesting in these systems is the fact that the addition of coagulating ions causes an acceleration in the exchange process. On the basis of this phenomenon the present results show the role of the investigated factors in surface processes, in the crystal growth, and in the connection between crystal space and colloid phenomena, as revealed by heterogeneous exchange processes.

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IZVOD

Procesi heterogene zamjene. XXII. AgJ — $^{131}J^-$ zamjene

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Na stabilnim solovima srebrnog jodida istraživana je ovisnost toka procesa heterogene AgJ — $^{131}J^-$ zamjene o starosti sola i koncentraciji slobodnog jodidnog iona u tekućoj fazi. Dobiveni rezultati pokazuju sumarno sličan tok procesa heterogene zamjene na stabilnim solovima s rezultatima dobivenim u prethodnim istraživanjima na koaguliranim suspenzijama AgJ. U svrhu radiometrijske analize primijenjene su dvije metode separacije radionuklida $^{131}J^-$; odvajanje centrifugiranjem i odvajanje tekuće od krute faze dodatkom koagulacionog elektrolita. Paralelni eksperimenti pokazali su da se dodatkom koagulacionog elektrolita naglo ubrzava proces zamjene. Istraživanja tog fenomena pružaju mogućnost šireg objašnjenja transporta jodidnog iona u krutu fazu i omogućuju analizu promjene disperzitetnih stanja i koloidno kemijskih karakteristika ispitivanih stabilnih solova srebrnog jodida.

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