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Original Scientific Paper

Heterogeneous Exchange of Precipitates. XI. Influence of Concentration of the Coagulating Co^{2+} Ion on the $\text{AgI} - \text{I}^-$ Exchange*

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In previous investigation it was shown that the heterogeneous $\text{AgI} - \text{I}^-$ exchange process depends on the colloido-chemical characteristics of the system. In the present paper the course of heterogeneous $\text{AgI} - \text{I}^-$ exchange process at various $\text{Co}(\text{NO}_3)_2$ concentration has been investigated by measuring the progress of the exchange process using the radioactive tracer technique (carrier free ^{131}I).

The used AgI was coagulated by the *in statu nascendi* method or by *isoelectric* precipitation. The concentrations of $\text{Co}(\text{NO}_3)_2$ was from 0.00010 M to 1.0 M, the concentration of the constituent I^- ion was 0.0010 M (*pI* 3). In *in statu nascendi* AgI was aged in the mother liquor for $t_A = 100$ and 30.000 minutes prior to exchange reaction and the dried *isoelectric* AgI was for 10 minutes ($= t_G$) kept in contact with the solution in which the exchange was observed.

The results showed that the kinetics of the exchange process depends, in different way on the Co^{2+} concentration for differently prepared AgI particles. The exchange rate for *in statu nascendi* AgI aged for $t_A = 100$ minutes increased when the Co^{2+} concentration was increasing from 0.010 to 0.10 M and decreased with the Co^{2+} concentration was increasing from 0.10 to 1.0 M. In the case of AgI aged for $t_A = 30.000$ minutes the increase of the Co^{2+} concentration from 0.0010 M to 0.010 M caused an increase of the exchange rate, while a decrease of the exchange rate occurred when the concentration of the solutions was increased from 0.010 M to 1.0 M Co^{2+} . It is evident that the exchange rate on the *isoelectric* AgI precipitates does not depend on the Co^{2+} concentration. These results were explained by the effect of the $\text{Co}(\text{NO}_3)_2$ concentration on the rate of the coagulation and of aging of the AgI particles.

In the preceding papers of this series some of the most characteristic features of the exchange process in the silver halide systems were established. Among others the influence of an excess of the constituent ions on the $\text{AgI} - \text{I}^-$ and $\text{AgI} - \text{Ag}^+$ exchange, the influence of the valency of the coagulating ions present in high concentrations, the influence of some surface active substances, as well as the method of preparation of the AgI (*in statu nascendi*, *dried*, *aged*, or *isoelectric*) precipitates were investigated¹⁻⁵.

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In the present paper the influence of the concentration of the coagulating counter ion Co^{2+} on the $\text{AgI} - \text{I}^-$ exchange will be systematically studied on the fresh ($\text{AgI}_{in situ}$) or on the isoelectric (AgI_{isoe}) forms of the AgI precipitates.

EXPERIMENTAL

The results were expressed as fraction exchange $F = (A_0 - A_t) / (A_0 - A_\infty)$ dependent on various parameters (concentration of coagulating ion, aging of precipitate, pretreatment of precipitate). Radioactivities (A) of the systems at time of exchange $t_E = 0$ ($A = A_0$) and $t_E = t$ ($A = A_t$) were measured as radioactivities of the aliquots x of the total starting volume V ($V = 100$ ml) of the system. The equilibrium value A_∞ was obtained by the formula⁶

$$A_{(\infty)i} = [A_0 - (x/V) \sum_1^{i-1} A_{(t)i}] [1 + \alpha - (x/V) (i - 1)]^{-1}$$

where $\alpha = n^s/n^l$: the ratio of the amounts of the exchanging ion (I^-) in the solid and liquid phase respectively.

The general experimental method was described in previous papers.^{1,3,5} The *statu nascendi* systems (*in situ*) were obtained by adding 50.0 ml 0.0020 M AgNO_3 solution to 50.0 ml of stirred 0.0040 M NaI solution containing $\text{Co}(\text{NO}_3)_2$ 0.0020 M, 0.020 M, 0.20 M, and 2.0 M, respectively. After the aging time $t_A = 100$

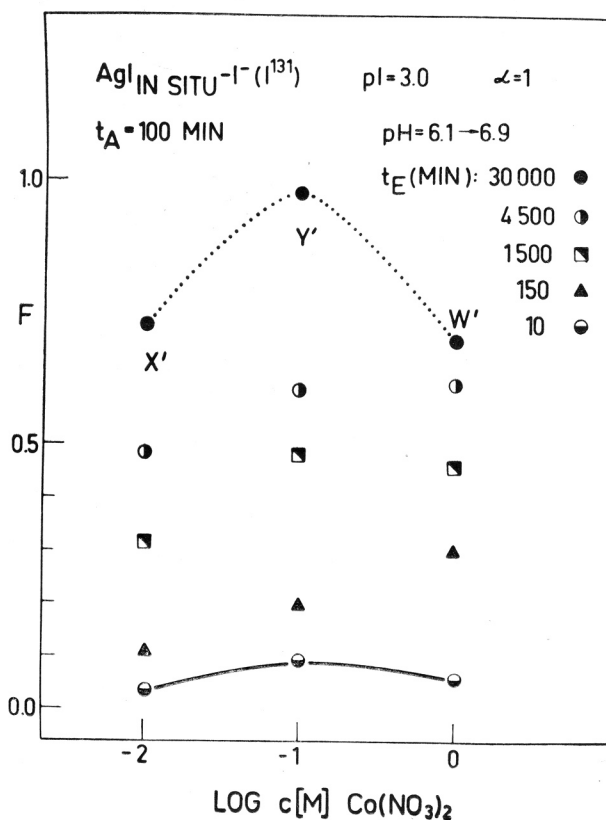


Fig. 1. Fraction exchange F (ordinate) against the logarithm of molar concentration ($\text{LOG } c [\text{M}]$) of Co-nitrate (abscissa). System: $\text{AgI} - \text{I}^-$ (¹³¹I). *In situ nascendi* formed AgI was aged in mother liquor for $t_A = 100$ minutes prior to exchange reaction. Exchange time $t_E = 10, 150, 1,500, 4,500, 30,000$ minutes, $c_{\text{NaI}} = 0.0010$ M ($=n^l$), $c_{\text{AgI}} = 0.0010$ M/l ($=n^s$), $\alpha = n^s/n^l = 1.0$, $\text{pH} = 6.1$ to 6.9

and 30 000 minutes respectively the system was labelled with the carrier free radio-nuclide ^{131}I . Samples of clear supernatant liquor (volume x) were taken at determined time intervals t_E and radioactivity A_t was determined by a scintillation counter. Initial radioactivity A_0 was determined on equally marked systems which did not contain AgI.

The isoelectric AgI was prepared in the same way as in ref. 4. by coagulation of $p\text{Ag}$ values in the region $6.2 > p\text{Ag} > 4.5$ and subsequently washed with four times distilled water until a constant conductivity of water after rinsing was attained. The precipitate was decanted and dried in vacuum.

In the systems with dried isoelectric AgI (AgI_{isoe}) the precipitate was brought in contact with 0.0010 M NaI solution containing $\text{Co}(\text{NO}_3)_2$ 0.00010 M, 0.0010 M, 0.010 M, 0.10 M, and 1.0 M respectively. After aging time t_A the system was labelled with the carrier free ^{131}I solution. Radioactivity A_t , A_0 and A_∞ was obtained as above.

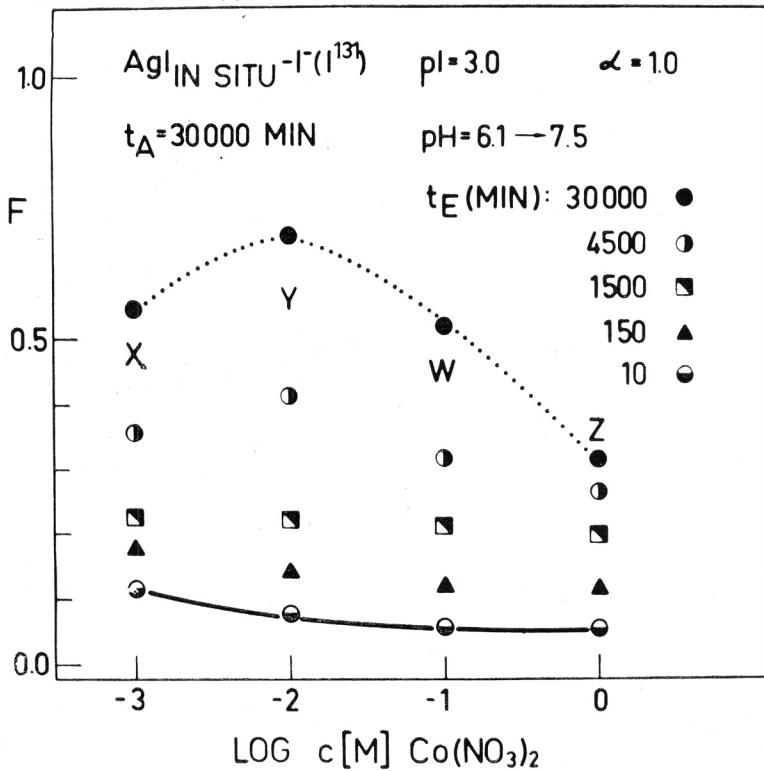


Fig. 2. Fraction exchange F (ordinate) against the logarithm of molar concentration ($\text{LOG } c [\text{M}]$) of Co-nitrate (abscissa). System: $\text{AgI} - \text{I}^- (^{131}\text{I})$. In situ nascendi formed AgI was aged in mother liquor for $t_A = 30,000$ minutes prior to exchange reaction. Exchange time $t_E = 10, 150, 1500, 4500,$ and $30,000$ minutes, $c_{\text{NaI}} = 0.0010 \text{ M} (= n^L), c_{\text{AgI}} = 0.0010 \text{ M/l} (= n^S), \alpha = n^S/n^L = 1.0, \text{pH} = 6.1 \text{ to } 7.5.$

RESULTS

The results were given as plots of fraction exchange (F) against logarithm of $\text{Co} (\text{NO}_3)_2$ concentration. In all cases pI was 3.0, $\alpha = 1.0$, and pH between 6.1 to 7.8.

The aging of the *in situ nascendi* precipitate decreases the exchange rate. The fraction exchange of the precipitate aged for 100 minutes (Fig. 1) becomes

after 30,000 minutes close to $F = 1$ in 0.10 M $\text{Co}(\text{NO}_3)_2$ solution. In more (1.0 M) and in less (0.010 M) concentrated solutions the exchange is lower.

The fraction exchange of the precipitate aged for 30,000 minutes (Fig. 2) is highest in 0.010 M Co^{2+} solution, but even after 30,000 minutes of exchange its value is not higher than 0.7 while in 1.0 M solution its value is as low as 0.3 approximately.

On dried precipitate (Fig. 3) the maximum is hardly observable and the exchange rate is low in all measured $\text{Co}(\text{NO}_3)_2$ concentrations between 0.00010 M to 1.0 M. In times up to 30,000 minutes in the region from 0.00010 to 1.0 M of Co^{2+} concentration the fraction exchange does not increase above $F = 0.35$.

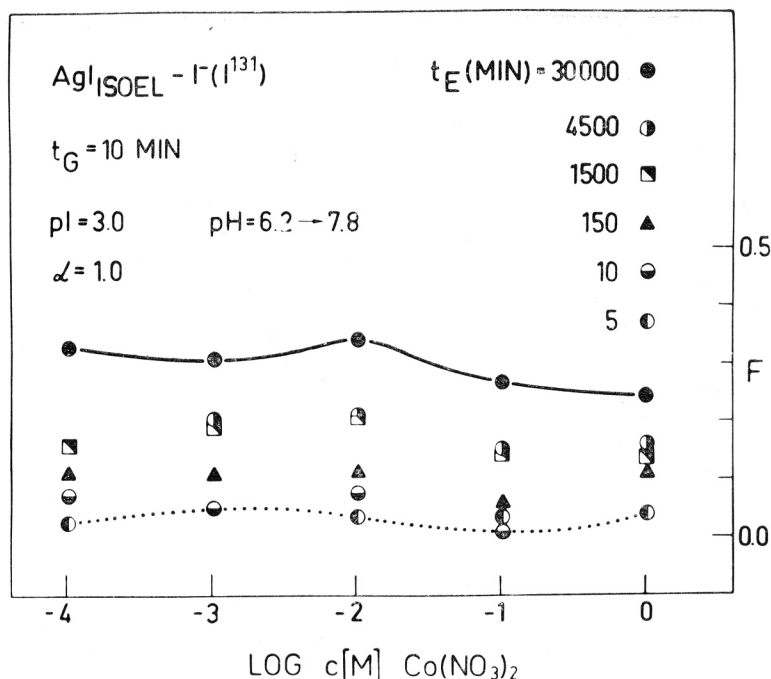


Fig. 3. Fraction exchange F (ordinate) against the logarithm of molar concentration ($\text{LOG } c$ [M]) of Co-nitrate (abscissa). System: $\text{AgI} - \text{I}^-$ (^{131}I). Dried (isoelectric) AgI precipitate was in contact with the prepared mother liquor for $t_G = 10$ minutes prior to exchange process, $c_{\text{NaI}} = 0.0010$ M ($= n^L$), $c_{\text{AgI}} = 0.0010$ M/l ($= n^S$), $\alpha = n^S/n^L = 1.0$, $pH = 6.2$ to 7.8 .

DISCUSSION

It follows from Figs. 1 and 2 that by decreasing the time of aging of the systems the characteristic maximum in the exchange rate is shifted from higher concentrations of the coagulating ion (0.10 M Co^{2+} , $t_A = 100$ minutes) toward lower concentrations (0.010 M Co^{2+} , $t_A = 30,000$ minutes). This shift could probably be attributed to the coagulating action of this ion and to the state of this ion and to the state of coagulation of the precipitate. The exchange of the fresh precipitate ($t_A = 100$ minutes) as compared with the aged one ($t_A = 30,000$ minutes) is faster because of the less advanced aggregation of the coagula. The

decrease of the exchange rate with the concentration may be attributed to more advanced aggregation caused by the higher concentrations. On the other side the slower exchange in lower concentration may be connected with the relative stability of the stable primary particles forming the solid phase. These were secondary structures formed by aging and coarsening and not by coagulation as in the higher concentrations. Of course the transition from the typical limiting cases is gradual of courses.

A contribution to these views is the relative insensitivity of the exchange process on the isoelectric precipitate (Fig. 3). In all concentrations of Co-nitrate the introduced precipitate had the same dispersity and the particles of the precipitate were very coarse. It is known that the reprecipitation depends primarily on the concentration of the constituent ion (I^-) which was kept constant and consequently the exchange rate was constant with the concentration of Co^{2+} and slow as compared with *in situ* precipitates.

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IZVOD

Heterogena zamjena na precipitatima. XI. Utjecaj koncentracije koagulacionog Co^{2+} iona na $AgI-I^-$ zamjenu

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Na temelju prethodnih istraživanja, koja su pokazala da koloidno-kemijske karakteristike sistema determiniraju brzinu procesa heterogene $AgI-I^-$ zamjene (koncentracija konstitucionog iona, starost AgI precipitata i valencija koagulacionog iona) istraživan je u opisanom radu utjecaj koncentracije koagulacionog Co^{2+} iona na tok ovog procesa.

Istraživanja su vršena na $AgI-I^-$ sistemima sa AgI partikulama formiranim *in statu nascendi* (*in situ*) i izoelektričnom koagulacijom (*isoel*). Tok procesa heterogene zamjene praćen je analizom migracije radionuklida ^{131}I . Koncentracija koagulacionog iona varirana je u granicama od $c_{Co(NO_3)_2} = 0,00010 M$ do $1,0 M$, uz konstantnu koncentraciju konstitucionog I^- iona od $pH 3$. Partikule AgI starene su u tim uvjetima, prije početka promatranja procesa zamjene, od 10 minuta do 30.000 minuta.

Rezultati pokazuju različitu ovisnost brzine zamjene o koncentraciji koagulacionog iona na različito pripremanim sistemima. Na *in statu nascendi* precipitatima brzina zamjene raste sa porastom koncentracije Co^{2+} do $0,10 M$ ($t_A = 100$ minuta) odnosno $0,010 M$ ($t_A = 30.000$ minuta), a zatim opada sa daljnjim porastom Co^{2+} do $0,010 M$ ($t_A = 100$ minuta) odnosno $0,0010 M$ ($t_A = 30.000$ minuta). Na sistemima sa sušenim izoelektričnim AgI utjecaj koncentracije Co^{2+} nije evidentan. U diskusiji se na temelju ovih rezultata analiziraju različiti tokovi procesa $AgI-I^-$ zamjene kao posljedica utjecaja koncentracije $Co(NO_3)_2$ na procese koagulacije i starenja AgI partikula.

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