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Heterogeneous Exchange of Precipitates. XII. AgCl — Ag^+ and AgCl — Cl^- Exchange*

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The influence of aging of AgCl precipitate and the change of electrolyte concentrations of liquid phase upon the course of heterogeneous AgCl—Ag^+ and AgCl—Cl^- exchange has been investigated by means of radionuclides ^{110}Ag and ^{36}Cl.

In AgCl—Ag^+ systems it has been found that the rate of exchange decreases with the increase of Ag^+ concentration and by aging of AgCl (for 10 to 10,000 minutes) in the mother liquor.

The influence of $La(NO_3)_3$ concentration upon the course of exchange during the formation of AgCl was followed in AgCl—Cl^- systems. The results reveal that the exchange rate is also reduced by aging of AgCl precipitate. Also it was found that in the range of concentration: 1.0×10^{-4} to 1.0×10^{-2} N $La(NO_3)_3$ the rate of exchange increases with the $La(NO_3)_3$ concentration, and from 1.0×10^{-2} to 1.0 N is reduced.

The results reveal that the kinetics of the heterogeneous AgCl—Ag^+ and AgCl—Cl^- exchanges depend on age of the precipitate, concentrations of the constituent and the coagulating ions and that the change of the liquid phase on a formed system causes the change of its properties.

INTRODUCTION

Our earlier investigations of the influence of aging of AgCl precipitates in the mother liquor upon the rate of AgCl—Cl^- exchange process have shown that after sufficient aging time (critical time) the exchange proceeds at an almost unmeasurable slow rate similarly to observations on TlI—Tl^+ systems.[1,2] It was also shown that a larger quantity of NaCl added to the AgCl—Cl^- system in which AgCl has formed by isoelectric coagulation brings about faster rate of the exchange process.[1] Similar investigations with AgBr and AgI precipitates have indicated that the exchange rate also depends upon the concentration of the constituent ion in the liquid phase.[3,4]

According to some authors[5-7] the mechanism of the heterogeneous exchange of AgCl precipitate with Ag^+ in excess differs from that containing Cl^- ion in excess. With this in mind we undertook the experiments of AgCl—Ag^+ exchange to determine the dependence of the exchange characteristics upon the concentration of ions in excess. AgCl particles were formed by isoelectric coagulation and the process was followed on the systems with various additions of $AgNO_3$ solution.

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The influence of the concentration of coagulating ions[3,8,10,12] upon the exchange process established previously on the systems containing AgBr and AgI was also examined on AgCl—Cl^- systems. The exchange processes were followed up by means of radionuclides ^{110}Ag and ^{36}Cl.

The results have revealed that the course of exchange is modified in the presence of Ag ions added in excess to the liquid phase after the period of aging of the precipitate in isoelectric mother liquor. The influence on AgCl—Cl^- exchange of the coagulating electrolyte $La(NO_3)_3$ has been found to be different with the systems prepared *in statu nascendi* from those where concentrations of the liquid phase changed before the beginning of the exchange process.

EXPERIMENTAL

A. AgCl—Ag^+ exchange at *p*Ag 4.7 during aging changed to *p*Ag 0.55—2.6 during exchange: The AgCl sol was prepared by the addition of 10.00 ml. 0.00204 *N* active $AgNO_3$ to 10.00 ml. 0.00200 *N* NaCl, which was swirled by a magnetic stirrer in a beaker. The sol still stable was transferred in batches of 2.00 ml. and the samples were left for aging. At indicated times (aging times) 0.05—0.20 ml. of 0.1—5.0 *N* $AgNO_3$ was added to each 2 ml. sample. All other operations of sampling and counting the radioactivity were performed as described before.[1]

B. AgCl—Cl^- exchange at *p*Cl 3.0 during aging changed to *p*Cl 2.0 during exchange at various $La(NO_3)_3$ concentrations: The AgCl sol was prepared by the addition of 10.00 ml. 0.00200 *N* $AgNO_3$ to a mixture of 10.00 ml. 0.00400 *N* active NaCl and 1.00 ml. of $La(NO_3)_3$. All operations were performed as described above. The concentration of $La(NO_3)_3$ was 1.0×10^{-5} *N* — 3.0×10^{-3} during aging and 9.54×10^{-6} *N* — 2.87×10^{-3} *N* during exchange.

C. AgCl — Cl^- exchange at constant *p*Cl value with $La(NO_3)_3$ concentration varied during the exchange: The samples of AgCl sol were prepared by the addition of 1.00 ml. 0.1000 *N* $AgNO_3$ to a mixture of 2.00 ml. 0.1000 *N* NaCl 2.00 ml. bidistilled water and 5.00 ml. of $La(NO_3)_3$ at concentrations from 2.0×10^{-4} to 2.0 *N* which was swirled by a magnetic stirrer. After $AgNO_3$ was added the swirling was continued for 5 minutes. After the indicated aging times t_A the samples were stirred during the labelling with 50 µl $Na^{36}Cl$ solution. In this way the initial volume of the sample was changed by 0.5% and the initial concentration of the Cl^- ions in the liquid phase increased by 1%. The final concentration of Cl^- ions was thus 1.0×10^{-2} *N*, of AgCl 1.0×10^{-2} *M*/l and of $La(NO_3)_3$ varied from 1.0×10^{-4} *N* to 1.0 *N*. At given times (exchange times) 100 µl of clear supernatant was taken for counting with a GM counter, *i. e.* for A_t determination. The A_t activity of the samples containing the stable sol was determined after centrifuging 200 µl of the sol which made possible the separation of clear supernatant liquor.

RESULTS

When the exchange process occurs at constituent ion concentration other than it was during the aging of AgCl precipitate, the results are presented as »the fraction of recrystallized AgCl moles«.[2]

$$F_r = \left(1 + \frac{n^S + n^L + n^L_0}{n^L + n^L_0} \cdot \frac{A_\infty - A_t}{A_t - A_0} \right)^{-1}$$

Here n^S are the moles of AgCl per milliliter of solution, n^L_0 moles of excess Ag^+ or Cl^- ions before the addition of the increased excess of Ag^+ or Cl^- ions, n^L the added moles per milliliter of Ag^+ or Cl^- ions. The average radioactivity of clear supernatants counted after centrifuging a few aged precipitates from a set of the samples was taken as A_0 activity. The radioactivity at equilibrium A_∞ was calculated from the expression[2]

$$A_\infty = A\,(n^L + n^L_0)\;/\;(n^S + n^L_0 + n^L)$$

where A represents the total activity of the sample. The value F_r is obtained by the assumption that the precipitate recrystallizes *via* solution phase and that at any time of the experiment the specific activity of the newly formed (recrystallized) precipitate is equal to the specific activity of the solution at the same time[2].

The systems containing positive AgCl particles were tested for the influence of aging of AgCl particles on the course of heterogeneous AgCl — Ag^+ exchange (Figs. 1 and 2). The dependence of the exchange process upon the change of concentration of $AgNO_3$ in the mother liquor was observed simultaneously. The plots demonstrate that the exchange rate decreases with the increase of aging time of AgCl particles in the mother liquor (Figs. 1 and 2). A certain slow down of the exchange process was observed when the fraction of recrystallized moles was $F_r = 0.7$. This value F_r was reached faster if the precipitate was aged for a shorter period of time.

By decreasing the pAg value in the mother liquor from 4.7 to 2.6, 1.6, 0.9, and 0.55 respectively, the exchange rate decreases equally for all precipitates regardless of their respective aging times (Fig. 1). This regularity demonstrated for the systems with exchange time $t_E = 60$ min was noticed in all the examined

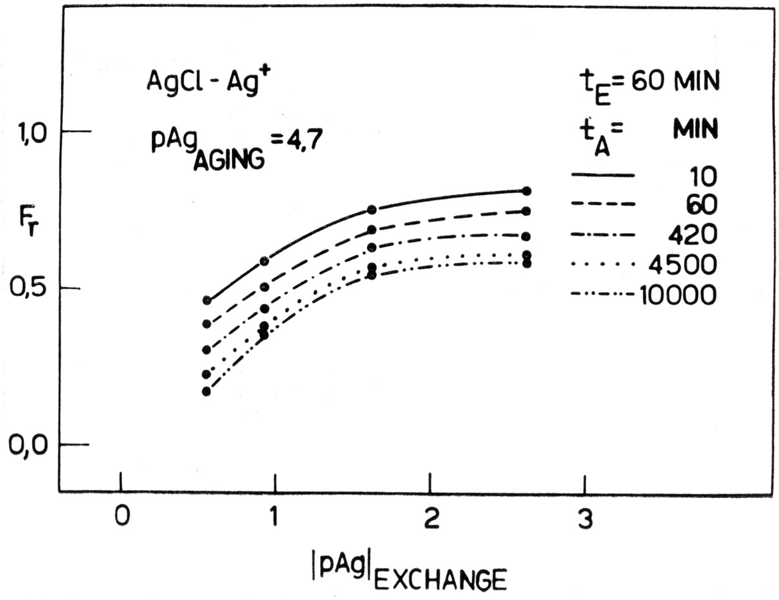

Fig 1. Fraction of recrystallized moles F_r against the negative logarithm of the concentration of the Ag^+ ions (*p*Ag). Exchange time $t_E = 60$ minutes. Aging time $t_A = 10$, 60, 420, 4,500, 10,000 minutes.

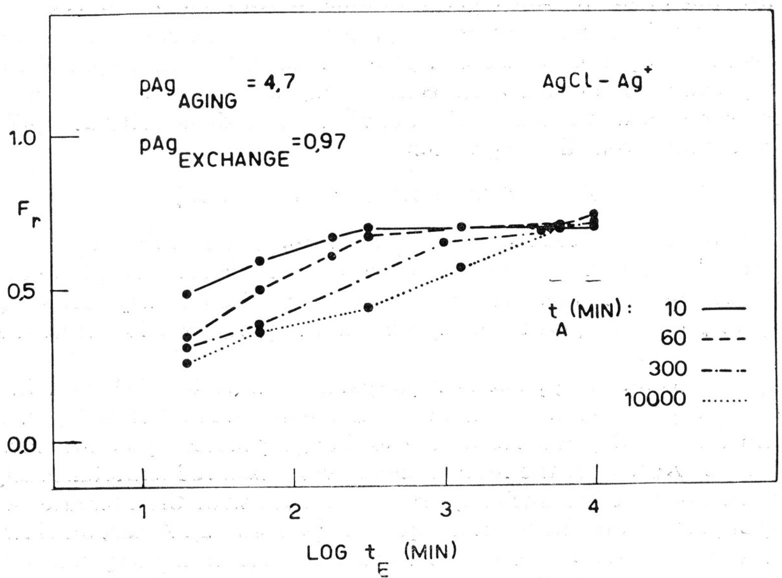

Fig. 2. Fraction of recrystallized moles F_r against the logarithm of exchange time (log t_E minutes). Aging time t_A = 10, 60, 300, 10,000 minutes.

range of exchange times (not shown here) from $t_E = 20$ to 10,000 minutes. It can be seen (Fig. 1) that the lowering of the exchange rate is more pronounced when the final *p*Ag value is smaller, or the change of silver nitrate concentration greater in relation to the initial concentration in the mother liquor.

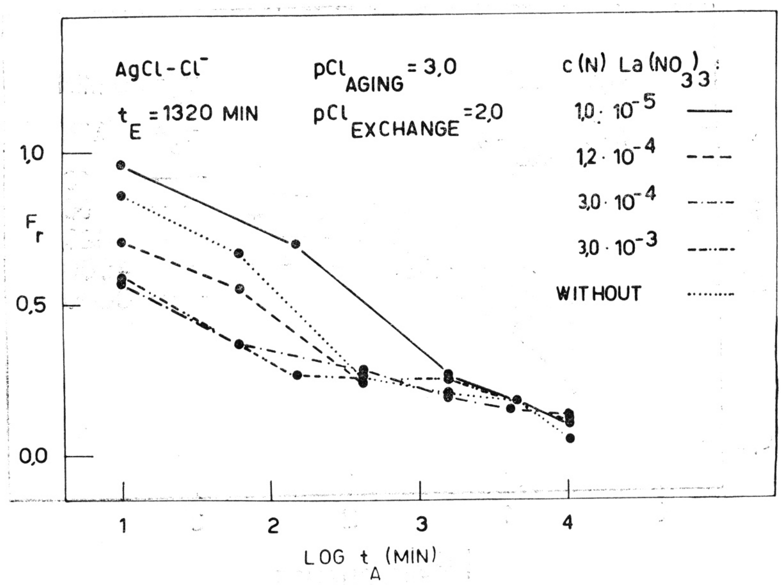

Fig. 3. Fraction of recrystallized moles F_r against logarithm of aging time (log t_A minutes). Exchange time $t_E = 1320$ minutes. Concentration (normal, *N*) of coagulating electrolyte $La(NO_3)_3$ c(*N*) = 1.0×10^{-5}, 1.2×10^{-4}, 3.0×10^{-4}, 3.0×10^{-3}, 0 *N* (without La-nitrate).

Fig. 3 represents the influence of the $La(NO_3)_3$ concentration upon the course of $AgCl - Cl^-$ exchange after 1,320 minutes of exchange for AgCl particles aged for periods of 10 to 10,000 minutes. The system with pCl 3.0 during

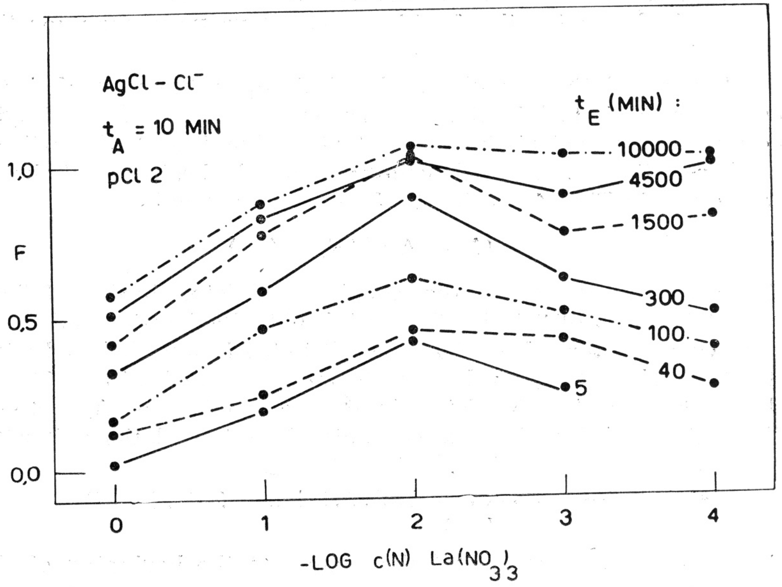

Fig. 4. Fraction exchange F against the negative logarithm of the normal concentration of the La-nitrate. Aging time $t_A = 10$ minutes, exchange time $t_E = 5$, 10, 100, 300 1,500, 4,500, 10,000 minutes. $p\mathrm{Cl}_{\mathrm{AGING}} = p\mathrm{Cl}_{\mathrm{EXCHANGE}} = 2.0$.

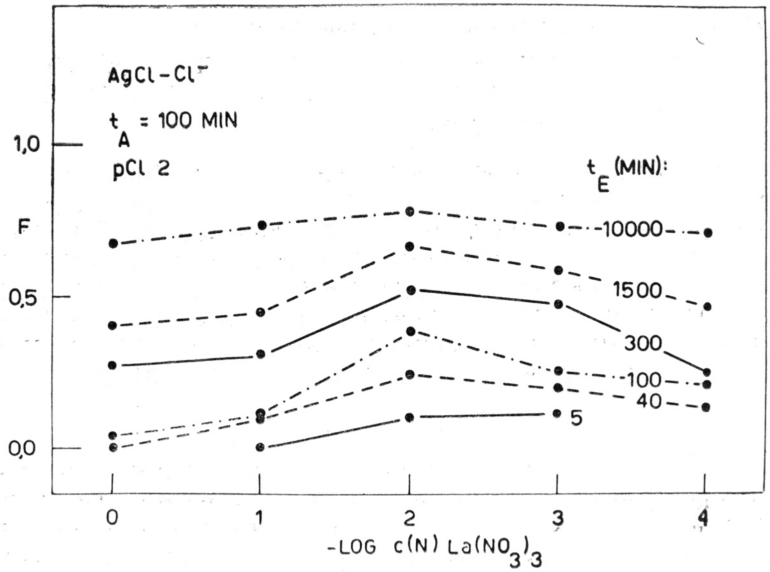

Fig. 5. Fraction F against the negative logarithm of the normal concentration of the La-nitrate. Exchange time $t_g = 5$, 40, 100, 300, 1,500, 10,000 minutes. $p\mathrm{Cl}_{\mathrm{AGING}} = p\mathrm{Cl}_{\mathrm{EXCHANGE}} = 2.0$.

the aging changed to *p*Cl 2.0 during the exchange. The plots indicate that the exchange rate of the freshly prepared AgCl particles is strongly affected by the presence of $La(NO_3)_3$, the influence of which is lost with the precipitates aged for longer periods of time. The curves also demonstrate the effect that the exchange rate is faster for the freshly prepared particles than for the aged ones.

The influence of the coagulating ion La^{3+} upon the rate of AgCl — Cl^- exchange was also studied in the systems where the processes of aging and exchange were performed at the constant *p*Cl value. The AgCl particles were aged for different times in the mother liquor before the beginning of observation. Results are given in Figs. 4 and 5. The fraction exchange is

$$F = (A_0 - A_t) / (A_0 - A_\infty)$$

The initial radioactivity A_0 of the samples was determined as follows: the mixtures of 2.00 ml. 0.1000 *N* NaCl, 3.00 ml. bidistilled water and 5.00 ml. of $La(NO_3)_3$ at concentrations from 2.0×10^{-4} *N* to 2.0 *N* were labelled with 50 µl $Na^{36}Cl$ solution. The average value of 5 samples counted with a GM counter at equal conditions as for A_t determinations was taken as A_0 activity. The radioactivity at equilibrium A_∞ was calculated from the relations after Zimens[9]:

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

where A_0 — is the radioactivity of the system at the beginning of the process (t_0)

x — the volume of the sample whose radioactivity (A_t) is being determined

V — total volume of the system

A_t — the radioactivity of the system at time t

α — the ratio of the amount of Cl^- in the liquid (n^L) phase and the amount of Cl^- in the present solid (n^S) phase (AgCl), $\alpha = n^S/n^L$

i — ordinal number of the sample.

The values of fraction exchange for equal exchange times t_E depend on the $La(NO_3)_3$ concentration. The final values of fraction exchange are higher with the systems aged for 10 minutes than for those aged for 100 minutes prior to the beginning of exchange. The rate of exchange of AgCl particles increases with the increase of $La(NO_3)_3$ concentration from 1.0×10^{-4} *N* to 1.0×10^{-2} *N* (Figs. 4 and 5). Further additions, however, of $La(NO_3)_3$ decrease the exchange rate as the concentration of coagulating ion increases from 1×10^{-2} *N* to 1.0 *N*. In this way a certain maximum is formed at 1×10^{-2} *N* $La(NO_3)_3$.

DISCUSSION

The present results of AgCl — Ag^+ exchange show that the rate of exchange falls with the aging of the precipitate. These experimental data indicate the considerable difference existing in the influence of aging upon the exchange of silver in the previously investigated silver iodide[10] and silver chloride. This difference could be interpreted by the higher diffusion coefficient of Ag^+ in silver iodide than in silver chloride.

Furthermore, the results reveal that the AgCl — Ag^+ exchange is reduced when the concentration of $AgNO_3$ in the mother liquor increases in the course of the exchange process (Fig. 1). By the addition of $AgNO_3$ the concentration of the constituent Ag^+ and the coagulating NO_3^- ions increase simultaneously. It is generally assumed that the formation of the precipitate and the aging at a given pAg result in the structures and the dispersity equilibrium which are characteristic of such conditions. As a consequence of the constituent ion in excess, the aged AgCl precipitate dissolves partly owing to the change in solubility of the precipitate, and as a consequence the new conditions of equilibrium between the precipitate and the liquid phase are established. On the other hand the coagulating NO_3^- ions at an increased concentration are even more likely to reduce the exchange process by changing the dispersity equilibrium and the colloido-chemical features of the system.

It is rather difficult to compare the present results of the two sets of experiments (Figs. 3—5) performed to determine the influence of the concentration of coagulating La^{3+} ions upon the AgCl — Cl^- process. In the first series (Fig. 3) pCl was changed prior to observation, whereas in the second (Figs. 4 and 5) pCl was kept constant during the aging and the exchange. In both cases the influence of $La(NO_3)_3$ concentration was more pronounced on freshly prepared precipitates than on the aged ones, *i. e.* on the precipitates with which the dispersity equilibrium was better established[11]. It may be of interest to point out the maxima of the curves F against log c (N) $La(NO_3)_3$. The maxima occur at 10^{-2} *N*. These results are in a suprising agreement with those obtained previously[8,12] from experiments of the influence of coagulating UO_2^{2+} and Co^{2+} ions on the rate of AgI — I^- exchange, where similar peaks could be noticed. The indicated conditions, in our opinion, provide such dispersity equilibrium and such colloido-chemical features as will allow the fastest rate of exchange.

Results, of our investigations therefore, reveal that the kinetics of the heterogeneous AgCl — Ag^+ and AgCl — Cl^- exchanges are completely dependent on the physico-chemical characteristics (age of the precipitate, concentrations of the constituent and the coagulating ions) of the system under observation and that the change of the liquid phase on a formed system cause the change of its properties.

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IZVOD

Heterogena zamjena na precipitatima. XII. Sistemi $AgCl—Ag^+$ i $AgCl—Cl^-$

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Ispitivan je utjecaj starenja AgCl precipitata i promjene elektrolitnog sastava tekuće faze na tok heterogene $AgCl—Ag^+$ i $AgCl—Cl^-$ zamjene. Proces zamjene je praćen primjenom radionuklida ^{110}Ag i ^{36}Cl.

U $AgCl—Ag^+$ sistemima, precipitati AgCl formirani su i stareni uz pAg 4,7. Prije početka procesa zamjene, koncentracija konstitucionog Ag^+ iona promijenjena je na $pAg = 2{,}6$, 1,6, 0,97 odnosno 0,55. Konstatirano je da brzina zamjene opada s povećanjem koncentracije Ag^+ u otopini i starenjem (10 do 10.000 minuta) AgCl u osnovnoj matičnici.

U $AgCl—Cl^-$ sistemima, precipitati AgCl su formirani i stareni uz pCl 3.0, Koncentracija Cl^- iona je prije početka procesa zamjene promijenjena na pCl 2,0. Koncentracija koagulacionog elektrolita $La(NO_3)_3$ se kretala od $1{,}0 \times 10^{-5}$ do $3{,}0 \cdot 10^{-3}$ *N*. Rezultati pokazuju, da brzina $AgCl—Cl^-$ zamjene pada sa porastom koncentracije $La(NO_3)_3$ i starenjem AgCl precipitata u osnovnoj matičnici. Utjecaj koncentracije ($1{,}0 \times 10^{-4}$ do 1,0 *N*) $La(NO_3)_3$ na tok zamjene promatran je i u $AgCl—Cl^-$ sistemima, u kojima je AgCl formiran i staren uz isti pCl kod kojeg je promatran i proces zamjene (pCl 2,0). Rezultati pokazuju, da brzina zamjene također opada starenjem AgCl precipitata i povećanjem koncentracije $La(NO_3)_3$ od $1{,}0 \times 10^{-2}$ do 1,0 *N*. Međutim, u intervalu od $1{,}0 \times 10^{-4}$ do $1{,}0 \times 10^{-2}$ *N* $La(NO_3)_3$, brzina procesa zamjene raste s porastom koncentracije $La(NO_3)_3$.

Dobiveni rezultati pokazuju, da je kinetika heterogene $AgCl—Ag^+$ i $AgCl—Cl^-$ zamjene direktno ovisna o fizičko kemijskim karakteristikama (starost i tretman precipitata, koncentracija konstitucionog Ag^+ i Cl^- i koagulacionog iona) promatranog sistema i da se promjenom sastava tekuće faze, na jednom formiranom sistemu, njegova svojstva mijenjaju.

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