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Original Scientific Paper

Heterogeneous Exchange of Precipitates. XIII. Influence of *n*-Myristylamine and *n*-Dodecylamine on the Dried AgI — I⁻ Exchange*

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The influence of the surface active substances (SAS): *n*-myristylamine nitrate $[MAH]NO_3$ and *n*-dodecylamine nitrate $[DDAH]NO_3$ on the heterogeneous exchange $AgI—I^-$ process has been investigated with radioactive ^{131}I. Dried isoelectric AgI, which prior to the observation of the exchange process was in contact with the prepared mother liquor for $t_G = 10$ to 30,000 minutes, was used. The concentrations of $[MAH]NO_3$ and $[DDAH]NO_3$ were 1.0×10^{-5} *M* and 5.0×10^{-4} *M*, respectively, with $c_{NaI} = 1.0 \times 10^{-3}$ *M*, $c_{AgI} = 1.0 \times 10^{-3}$ *M*/l. The results show that $[MAH]NO_3$ and $[DDAH]NO_3$ influence the rate of the $AgI—I^-$ exchange process at concentrations for which the zeta potential is changed.[5] From the results of previous investigations it is suggested that the $AgI—I^-$ exchange is most probably determined by a recrystallization of the AgI particles. The results obtained indicate there a possibility of accelerating the radionuclide fixation by using the appropriate SAS concentration.

INTRODUCTION

In an earlier paper of this series[1] the influence of the surface active substances (SAS) *n*-decylamine and *K*-caprinate on the heterogeneous exchange of freshly prepared $AgI — Ag^+$ was studied and it was shown that the process is independent of the concentration of SAS and characterized by the autodiffusion of the Ag^+ ion in the crystal lattice of the precipitate. In this paper, analogous experiments are described for the $AgI — I^-$ exchange, with *n*-myristylamine $[MAH]\,NO_3$ and *n*-dodecylamine nitrate $[DDAH]\,NO_3$ are used as the surface active substances. The influence of high concentrations of Co^{2+} and Al^{3+} has already described[2,3] for the same exchange. We hope that these experiments will throw some light onto the role of the surface active substances in the surface processes, as revealed by the heterogeneous exchange phenomenon.

EXPERIMENTAL

Details of the experimental technique have been given earlier[3,4,6] and a preparation procedure for dried isoelectric AgI is given in refs. 3 and 4.

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The specific radioactivities A_t, of the I^- ion were measured at different times t_E after labelling from aliquot samples of clear supernatant solution. These were then used to calculate the fraction exchange F values. Initial radioactivity A_0 was determined on equally marked systems without AgI. The activity at equilibrium A_∞ for each sample was determined from the radioactivity A_t and A_0. The systems consisted of selected concentrations of AgI (1.0×10^{-3} *M*/l.) of a surface active substance (1.0×10^{-5} *M* to 5.0×10^{-4} *M*), and of NaI (1.0×10^{-3} *M*), in a given total volume (100 ml.). Before labelling, the contact time between AgI and the liquid was varied (described as the time t_G). Carrier free $Na^{131}I$ solution was used for labelling.

The *n*-dodecylamine and *n*-myristylamine solutions were obtained from the purity grade *n*-myristylamine, *n*-dodecylamine and nitric acid. The samples were twice recrystallized from 50% ethanol solution and neutralized to *p*H 3 with HNO_3. The concentrations were determined by weighing the substance, dried at 20° C in vacuum.

RESULTS

The results are illustrated in the diagrams (Figs. 1—8) where the fraction exchange is plotted versus exchange time (t_E) or contact time (t_G). In Figs. 1—4, the exchange time t_E is variable, a particular contact time t_G is selected, and the fraction exchange is plotted for several concentrations of the SAS. In Figs. 5—8 the contact time t_G is variable, a particular concentration of the SAS

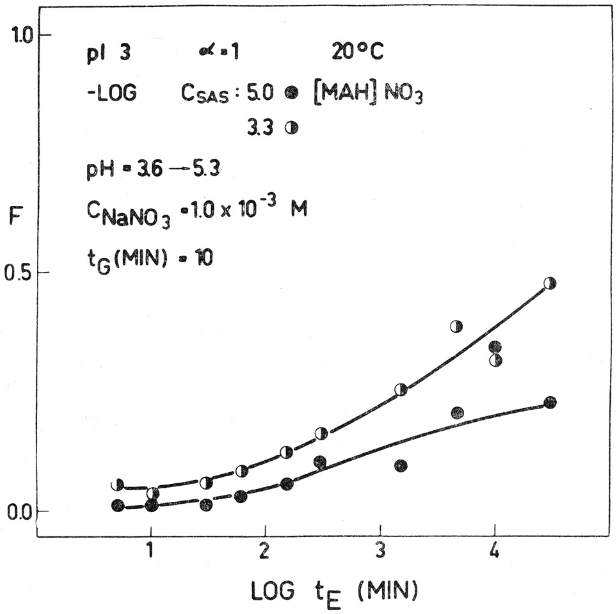

Fig. 1. Fraction exchange (F) plotted against the logarithm exchange time in minutes [LOG t_E, (min.)]. System: dried isoelectric AgI—I^- (^{131}I). The dried AgI precipitate was in contact with the prepared mother liquor for $t_G = 10$ minutes prior to the exchange process, $C_{NaI} = 0.0010$ *M* ($= n^L$), $c_{AgI} = 0.0010$ *M*/l ($= n^S$), $\alpha = n^S/n^L = 1.0$, concentrations of surface active substance (C_{SAS}) *n*-myristylamine nitrate ($[MAH]NO_3$) $C_{SAS} = 0.000010$ *M* (*pH* 5.3) and $C_{SAS} = 0.00050$ *M* (*p*H 3.6), $c_{NaNO_3} =$ $= 0.0010$ *M*.

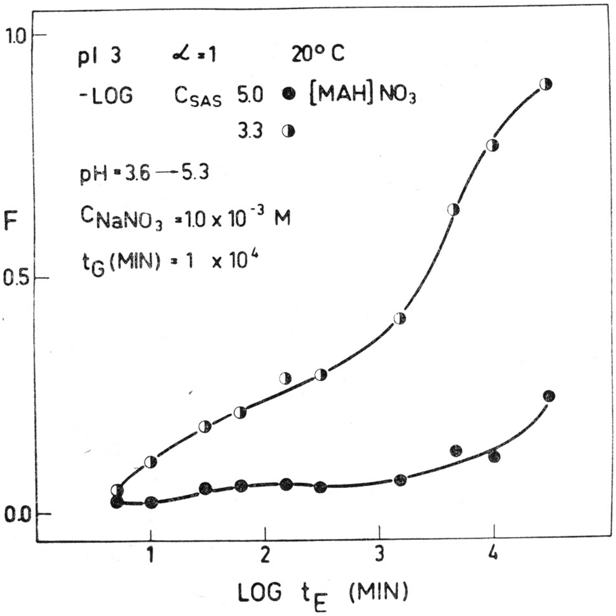

Fig. 2. Fraction exchange (F) plotted against the logarithm of exchange time in minutes [LOG t_E (min.)]. System: dried isoelectric AgI—I⁻ (^{131}I), the parameters the same as in Fig. 1. except t_G = 1000 minutes.

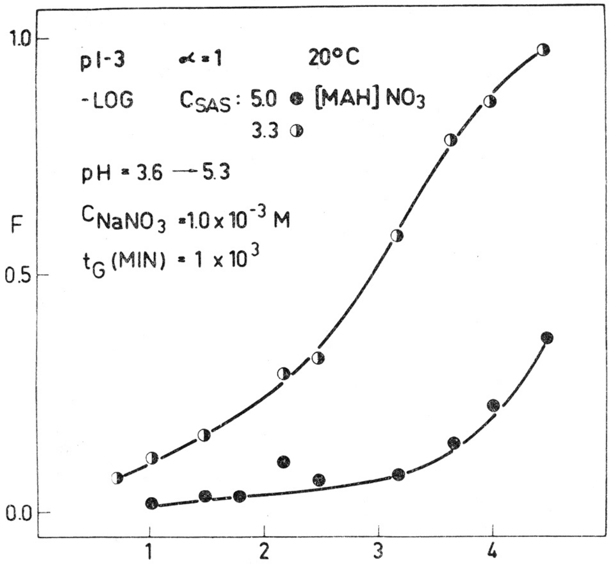

Fig. 3. Fraction exchange (F) plotted against the logarithm of exchange time in minutes (LOG t_E. (min.)]. System: dried isoelectric AgI—I⁻ (^{131}I), the parameters the same as in Fig. 1. except t_G = 10,000 minutes.

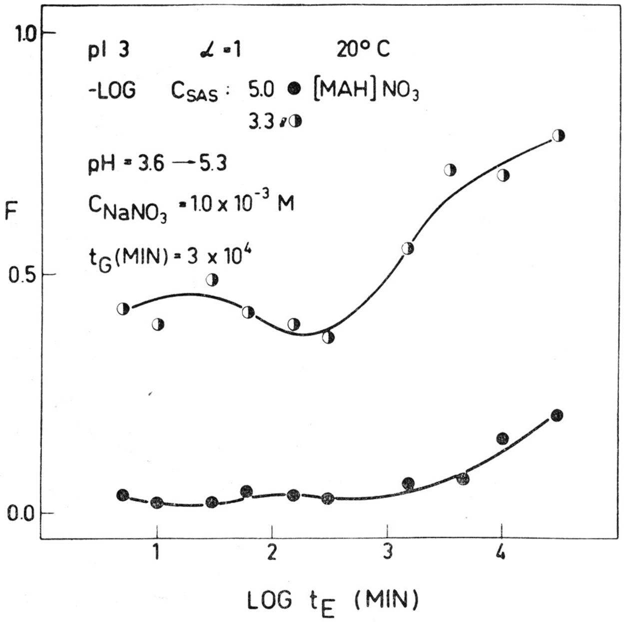

Fig. 4. Fraction exchange (F) plotted against the logarithm of exchange time in minutes [LOG t_E (min.)]. System: Dried isoelectric AgI—I⁻ (^{131}I), the parameters the same as in Fig. 1. except t_G = 30,000 minutes.

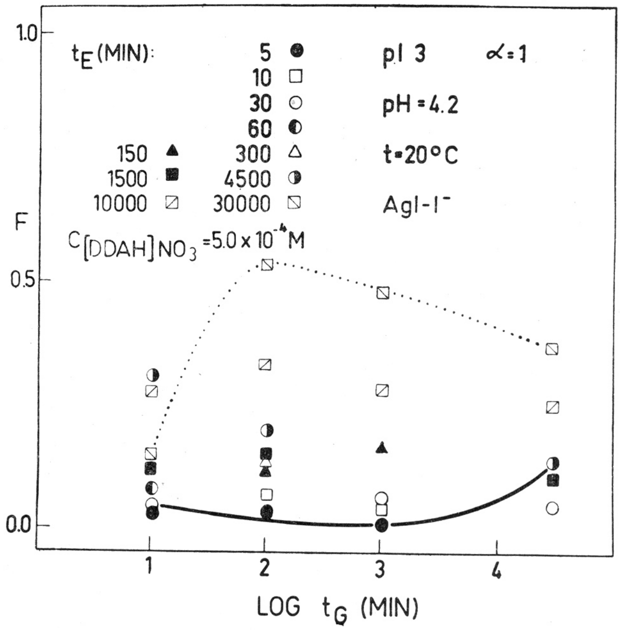

Fig. 5. Fraction exchange (F) plotted against the logarithm of aging time (minutes) [LOG t_G (min.)]. Exchange time in minutes t_E = 5, 10, 30, 60, 150, 300, 1500, 4500, 10,000, and 30,000 minutes, concentration of surface active substance *n*-myristylamine nitrate $C_{[MAH]NO_3} = 0.000010$ *M*, $c_{NaNO_3} = 0.0010$ M, $c_{NaI} = 0.0010$ M ($= n^L$), $c_{AgI} = 0.0010$ M/l. ($= n^S$), $\alpha = n^S/n^L = 1.0$, pH = 3.6 → 5.3. System: dried isoelectric AgI—I⁻ (^{131}I).

is selected, and the results are given for several exchange times t_E. A logarithmic time scale is used for convenience, since the time intervals of the experiments are large. There is no other significance in such a presentation. In all cases the concentration of I^- ion was 1.0×10^{-3} *M* and the same amount of AgI was present giving the optimum ratio of the exchanging ion in the solid and liquid phase $\alpha = n^S/n^L = 1$. The *p*H was between 3.6 and 5.9 depending on the SAS concentration. Higher concentrations of SAS are limited due to their very low solubilities at the moderate *p*H values ($\sim$ 3.6). In all experiments the solutions were 1.0×10^{-3} *M* in $NaNO_3$. The plots of fraction exchange against logarithm exchange time for lower concentrations (10^{-5}*M*) of $[MAH]^+$ show that for all contact times up to 3×10^4 minutes (Figs. 1—4) the exchange remains low (less than 0.3 of fraction exchange) and that it becomes lower when the contact time is longer (Fig. 4). The 1.0×10^{-5} *M* concentration of $[MAH]^+$ is lower than the zero point concentration of the electrokinetic mobility (see ref. 5; Fig. 2) which is 1.5×10^{-5} *M*.

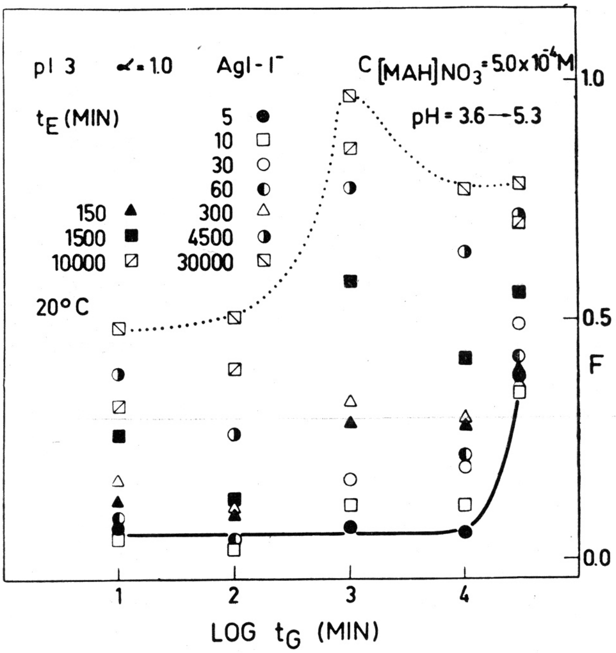

Fig. 6. Fraction exchange (F) plotted against the logarithm of aging time (minutes) [LOG t_G (min.)]. System: dried isoelectric Ag—I^- (^{131}I), the parameters the same as in Fig. 5. except $C_{[MAH]NO_3} = 0.00050$ *M*.

At higher concentrations of $[MAH]^+$ (5.0×10^{-4} *M*), after times of contact of 10^3 to 10^4 minutes, the fraction exchange increases gradually to unity after 3×10^4 minutes of exchange. The fraction exchange of the precipitate in contact with the liquid for 3×10^4 minutes was high, already about 0.4 after only 5 minutes of exchange, and possibly remains always less than one, irrespective of the extention of the exchange time. This higher concentration of $[MAH]^+$ was higher than the zero point concentration of the electrophoretic mobility.

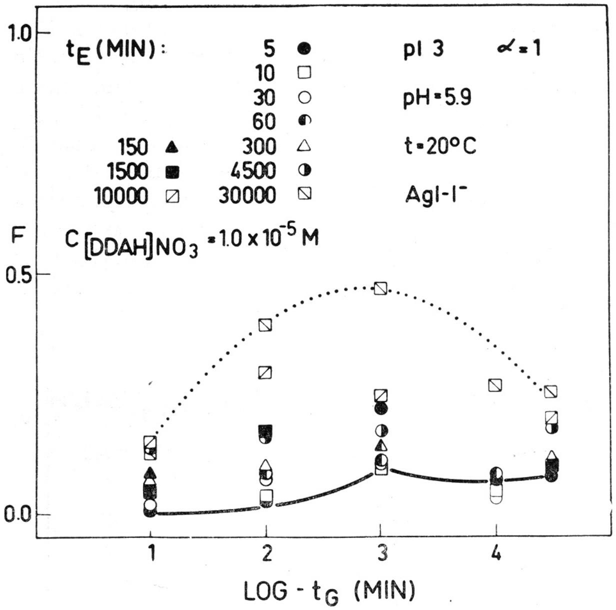

Fig. 7. Fraction exchange (F) plotted against the logarithm of aging time (minutes) (LOG t_G (min)]. Exchange time t_E = 5, 10, 30, 60, 150, 300, 1500, 4500, 10,000 and 30,000 minutes, concentration of surface active substances *n*-dodecylamine nitrate $c_{[DDAH]NO_3}$ = 0.000010 *M*, c_{NaNO_3} = 0.0010 *M*, C_{NaI} = = 0,0010 *M* (= n^L), c_{AgI} = 0.0010 *M*/l. (= n^S), $\alpha = n^S/n^L = 1.0$, *p*H = 5.9. System: dried isoelectric AgI—I⁻ (^{131}I).

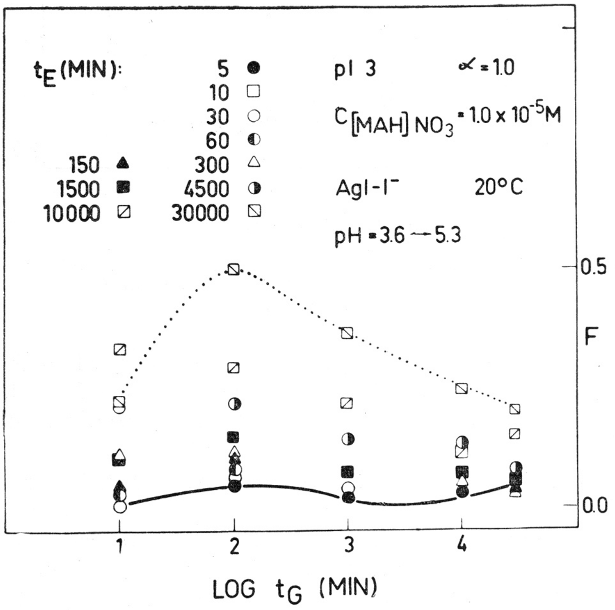

Fig. 8. Fraction exchange (F) plotted against the logarithm of aging time (minutes) [LOG t_G (min.)]. System: dried isoelectric Ag—I⁻ (^{131}I), the parameters the same as in Fig. 7 except *p*H = 4.2, $c_{[DDAH]NO_3}$ = 0.00050 *M*.

The plots of fraction exchange against logarithm contact time t_G display a maximum at longer times of exchange (Figs. 5 and 6 for $[MAH]^+$, Figs. 7 and 8 for $[DDAH]^+$). With short contact times (up to 1000 minutes) the exchange time at which the fraction exchange becomes unity would perhaps be too long and therefore was not observed. At medium contact times, from 10^3 minutes to 3×10^4 minutes of exchange are necessary for the fraction exchange to become unity. With longer contact times, most probably the fraction exchange remain always less than one.

The plots obtained for $[DDAH]^+$ (Figs. 7 and 8) are analogous to those for $[MAH]^+$, showing quantitative differences only. Thus for example at a higher concentration of $[DDAH]^+$ certainly the complete exchange could be observed as with $[MAH]^+$. At higher concentration (5.0×10^{-4} *M*), $[DDAH]^+$, as compared with $[MAH]^+$, has a smaller effect and causes a lower rate of exchange.

DISCUSSION

The aging of fresh *in statu nascendi* AgI preparations with an excess of I^- ions in the mother liquor causes a gradual decrease in exchange rate. It is estimated that after about 10^5 minutes the exchange rate becomes zero. The zero exchange indicates the state of equilibrium between the mother liquor and the precipitate.[2] The present results, which were obtained using dried isoelectric preparations of AgI, show that the exchange rate is highest when a sufficiently high concentration of SAS is present and, if prior to the beginning of the observation of the exchange, the contact between the solution and AgI is between 10^3 to 10^4 minutes. Still longer times cause an initially very fast exchange and it could be expected that with times of the order of 10^6—10^7 minutes the precipitates would not cause any more exchange and that they would be transformed normally into a state of equilibrium. These results confirm our hypothesis of the *in statu nascendi* technique, *i. e.* the shortest possible times are taken for the equilibrium between the precipitate and the mother liquor to be reached. The processes which follow the preparation of the precipitating system are then the processes of the establishment of equilibrium.That the concentrations of SAS which otherwise cause the reversal of charge are necessary to cause an appreciable exchange is also characteristic.

It is possible that during the observed times of contact up to and greater than 10^4 minutes the precipitate is partially trasformed into a form in which it does not exchange, while the remainder, which has not yet transformed in its final equilibrium form, exchanges very rapidly (Fig. 4).

From the present results we conclude that the process causing the exchange is a process of recrystallization *via* the solution phase, namely that the original precipitate particles redissolve and particles of the new form are recrystallized from the solution. Due to their low mobility, the autodiffusion of the I^- ions in the AgI can play only a subordinate role, *i. e.* only if the particles are very small.

The observation that SAS, in very low absolute concentrations, render the AgI precipitates into a form with a relatively high rate of exchange could be profitably used in the practical application of heterogeneous exchange for analytical separations or for the fixation and concentration of radionuclides.

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IZVOD

Heterogena zamjena na precipitatima. XIII. Utjecaj *n*-miristilamin nitrata i *n*-dodecilamin nitrata na $AgI—I^-$ zamjenu

R. Despotović i M. Mirnik

Istraživan je utjecaj površinski aktivnih supstanca (SAS) *n*-mirislilamin nitrata $[MAH]NO_3$ i *n*-dodecilamin nitrata $[DDAH]NO_3$ na tok procesa heterogene $Ag—I^-$ zamjene.

Tok procesa zamjene je praćen pomoću radionuklida ^{131}I. Upotrebljen je sušeni izoelektrični AgI, koji je prije promatranja procesa zamjene bio različito vrijeme (t_G = 10 do 30,000 minuta) u kontaktu sa pripređenom matičnicom. Matičnica sadrži: $[MAH]NO_3$ ili $[DDAH]NO_3$ $c_{SAS} = 1,0 \times 10^{-5}$ i $5,0 \times 10^{-4}$ *M*, $c_{NaI} = 1,0 \times 10^{-3}$ *M*, $c_{AgI} = 1,0 \times 10^{-3}$ *M*/l.

Rezultati pokazuju, da primjenjene SAS u koncentracijama, kod kojih se mijenja zeta potencijal (na istim sistemima) utječu i na brzinu procesa $AgI—I^-$ zamjene. Na temelju rezultata prethodnih istraživanja $AgI—Ag^+$ zamjene, čiji je tok neovisan o koncentraciji SAS i odvija se putem autodifuzije Ag^+ iona u kristalnoj rešetci precipitata, zaključuje se, da je za mehanizam $AgI—I^-$ zamjene najvjerojatnije odgovoran proces rekristalizacije partikula AgI. Dobiveni rezultati direktno ukazuju na mogućnost ubrzanja fiksacije radionuklida primjenom odgovarajuće koncentracije SAS.

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