

CCA-219

541.18:532.7:546.57-38-128

Heterogeneous Exchange of Precipitates. IV. Influence of *n*-decylamine, K-caprinate, Al^{3+} and Co^{2+} on the AgI-Ag^+ Exchange*

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Received September 26, 1961

0.0025 *M* *n*-decylamine nitrate, 0.001 *M* K-caprinate, 1 *N* Al^{3+} - or Co^{2+} -nitrates do not measurably influence the process of heterogeneous AgI-Ag^+ exchange.

In the discussion the conclusion was reached that the double layer has to be considered as a structure in which the individuality of particles is maintained.

On the positive AgI the Ag may be present either as Ag atom in electrochemical equilibrium, as hydrated Ag^+ -ion, as associated ion pair Ag^+ -ion — counter ion or as Ag^+ -ion in the crystal lattice.

In the preceding paper of this series¹ the problem of the basic process causing the AgI-Ag^+ exchange was discussed. The presented results showed that this exchange is of a character different from the exchange of many other precipitates and of the silver halide-halide ion exchange. By aging, in this latter case, the precipitates in contact with the halide solution lose the property of exchange, while in the case of silver halides in contact with a Ag^+ -ion solution a complete exchange was always observed. The conclusion was made that the halide ion exchange is a process caused by recrystallization while the Ag^+ -ion exchange is always effectuated by selfdiffusion of the Ag ion through the solid.

If the transfer of the halide ions across the surface is prevented, or if the transfer of the Ag^+ ions is directed or effectuated by the properties of the electrical double layer, then factors supposed to influence this layer should affect also the silver halide- Ag^+ exchange.

In the above mentioned paper¹ it was shown that the silver iodide- Ag^+ exchange can be prevented neither by the aging of the precipitate, nor by different $p\text{Ag}$ values during the aging.

In the present paper it will be shown that the Ag^+ -ion exchange is not influenced significantly either by the presence of high concentrations of bi- and trivalent cations or by surface active agents in the concentrations in which they otherwise cause the reversal of the electrokinetic potential².

EXPERIMENTAL

The general experimental technique remained essentially the same as described in the previous paper.¹ 0.01 *N* NaI solution was added from a pipet into an agitated solution of AgNO_3 containing the added substances in the predetermined concen-

* Contribution number 96 from the Laboratory of Physical Chemistry.

trations. Exceptionally, K-caprinate was added to the NaI solution. The precipitating systems containing *n*-decylamine were adjusted to $\text{pH } 4.6 \pm 0.3$ by the addition of HNO_3 to the AgNO_3 solution.

To determine the A_t values the precipitating systems were labelled by the addition of $100 \mu\text{l}$ 0.04 N solution in AgNO_3 containing Ag^{110} at given aging times, or before the precipitation when determining the A_∞ value. The A_0 value was obtained from a system to which an equal volume of bidistilled water was added instead of NaI solution.

The A_t , A_0 and A_∞ were determined by counting 2.00 ml samples of clear supernatant solutions of the above systems in a well type NaI scintillation counter (Type EKCO Electronics).

Pure grade chemicals and redistilled water, from a two stage glass still, were used for the preparation of the systems.

RESULTS

Results are represented by Fig. 1 in which the exchange fraction is plotted against the logarithm of exchange time.

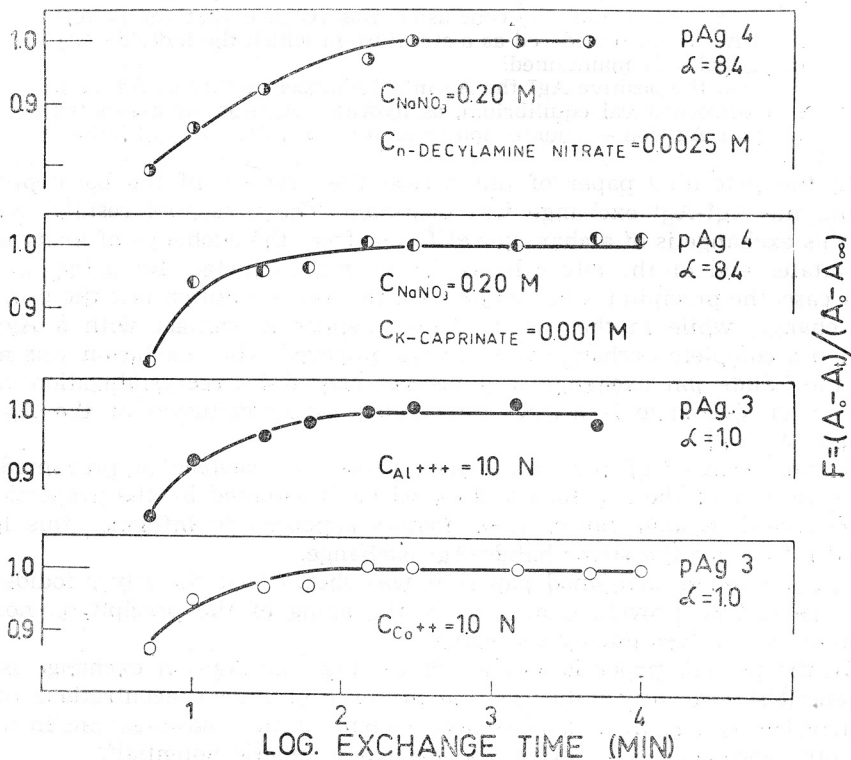


Fig. 1. Fraction exchange against logarithm of exchange time in the presence of:
 (1) 0.0025 M *n*-decylamine nitrate
 (2) 0.001 M K-caprinate, (3) 1 N $\text{Al}(\text{NO}_3)_3$ and (4) 1 N $\text{Co}(\text{NO}_3)_2$.
 0.001 M AgI, $\text{pAg } 4$ resp. 3.

The exchange was completed in all cases *i. e.* the exchange fraction became $F = 1$ after about 100 minutes irrespectively of whether 0.0025 M

n-decylamine nitrate, 0.0001 M K- caprinate, 1 N Al³⁺ or Co²⁺ were present in the systems. The exchange fraction was calculated by the formula

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

The value α of Fig. 1. is defined as $\alpha = n^s/n^l \cdot n^s$ is the quantity of Ag⁺ ions in the solid and n^l in the liquid phase. A_0 is the activity of the liquid phase at the beginning of the process, A_∞ the activity when the state of homogeneous distribution of the activity between the solid and liquid phase is established, and A_t the activity of the liquid phase in time t after the beginning of exchange.

DISCUSSION

If the electrical double layer were responsible for the transfer of the constituent ions from the liquid to the solid phase, counter and neben ions and adsorbable surface active substances should influence the exchange caused by selfdiffusion in the solid. The results of the preceding paper and of this paper indicate, however, that none of the above substances influences the exchange to a measurable extent.

If the electrical double layer were responsible for the transfer of the constituent ions (electrochemical adsorption³) is proportional to the logarithm activity of these ions, while the adsorbed quantity of these ions which is capable to associate with the coagulating counter ions is constant and independent of their activity in the solution⁴. Therefore it must be concluded that the modes of transfer of the potential determining ions (Ag⁺) across the surface are independent processes which do not interfere and can be achieved by: a) heterogeneous exchange, b) electrochemical adsorption and c) by the adsorption responsible for stabilization and coagulation. They can proceed independently of each other, with energy changes which are different for each process. Therefore the energy change defined by the electrochemical (surface, Nernst) potential cannot be connected either with the coagulation process or with the process causing the heterogeneous exchange. This suggests however that the double layer cannot be considered a structure with only one energy function for the Ag ions, but a structure where the individuality, *i. e.* the atomistic structure of the matter, is maintained as it is maintained in the solution. Thermodynamic laws for ions and molecules in the solution and on the surface, namely in the double layer, are the same. The atom in the surface can be present in different molecules causing thus different energetic states. For the positive AgI we may suppose that the silver may be present either as Ag atoms in electrochemical equilibrium with Ag⁺ ions in the solution, or as hydrated adsorbed Ag⁺ ions⁵ on stable particles and as associated ion pairs: »Adsorbed Ag⁺—counter ions« on coagulated particles, or as Ag atoms in the crystal lattice. Each of these particles has to be treated as an independent species with its independent thermodynamic potential.

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IZVOD

Heterogena izmjena taloga. IV. Utjecaj *n*-decilamina, K-kaprinata, Al^{3+} i Co^{2+} na $AgJ - Ag^+$ izmjenu.

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Primjenom radionuklida Ag^{110} konstatirano je, da 0,0025 *M* *n*-decilamin nitrat, 0,001 *M* K-kaprinat, 1,0 *N* Al^{3+} — ili Co^{2+} — nitrati ne pokazuju mjerljive utjecaje na proces heterogene $AgJ - Ag^+$ izmjene.

U diskusiji se zaključuje, da se dvostruki sloj može smatrati kao struktura, u kojoj se zadržavaju individualna svojstva adsorbiranih iona.

Na pozitivnom srebrnom jodidu Ag je predstavljen ili kao Ag atom u elektrokemijskoj ravnoteži, ili kao hidratizirani ion, ili kao asocirani ionski par »Ag ion — protuion« ili kao ion u kristalnoj rešetci.

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Primljeno 26. rujna 1961.