Radiochemical Investigations of Ion Exchange on Silver Halide Crystals

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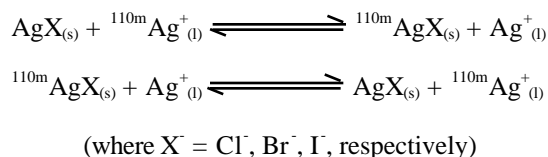## Abstract

We have made radiochemical investigations to the ion exchange in the systems $^{110m}AgCl_{(s)}$—$Ag^+_{(l)}$ and $^{110m}AgBr_{(s)}$—$Ag^+_{(l)}$ for the calculation of the activation energy for the self diffusion of the $^{110m}Ag^+$ ions inside the crystal. The mass transfer of the $^{110m}Ag^+$ ions from the crystal to the solution in the systems $^{110m}AgCl_{(s)}$—$Ag^+_{(l)}$ and $^{110m}AgBr_{(s)}$—$Ag^+_{(l)}$ is a very complex problem. A report is given of the diffusion of Ag^+ ions in AgCl and AgBr crystals. The kinetics of re-exchanges of the $^{110m}Ag^+$ ions from the crystals to the solution was measured. In the aqueous solution an excess of the inactive Ag^+ ions was present in the experiments. The evaluation of the kinetic curves showed three steps, which are in correlation to the dissolution of AgX, the self diffusion of the $^{110m}Ag^+$ ions in the AgX crystal and the recrystallization process. The activation energies were measured for all these three steps. The activation energy for the self diffusion of the $^{110m}Ag^+$ ions in AgCl and AgBr crystal lattice is of interest for the quantum theoretical calculation of the activation energy. The activation energies of the transport of the Ag^+ ions in AgCl and AgBr crystals are calculated in an earlier investigation with the help of a quantum theoretical equation involving the frequency of the optical phonons of the lattice, a mean coordination number for the diffusing ions and the vibrational quantum number. The comparison of the calculated activation energies with values available from the radiochemical measurements in the systems $AgCl_{(s)}$ — $^{110m}Ag^+_{(l)}$, $^{110m}AgCl_{(s)}$ — $Ag^+_{(l)}$, $AgBr_{(s)}$ — $^{110m}Ag^+_{(l)}$ and $^{110m}AgBr_{(s)}$ — $Ag^+_{(l)}$ shows a good agreement. The influence of photographically active substances (antifoggants) is discussed on the mass transfer rate during the Ostwald ripening of AgCl and AgBr.

Introduction

The aim of this work is to analyze the kinetics of the $^{110m}Ag^+$ mass transfer on silver halide crystals with the help of radiochemical measurements. From that the problem of the interstitial diffusion mechanism of the silver ions in the silver halide crystals is a focal point.

Experimental

The measurements were carried out as ion exchange measurements in the following systems:

$$AgX_{(s)} + {}^{110m}Ag^+_{(l)} \rightleftharpoons {}^{110m}AgX_{(s)} + Ag^+_{(l)}$$

$$^{110m}AgX_{(s)} + Ag^+_{(l)} \rightleftharpoons AgX_{(s)} + {}^{110m}Ag^+_{(l)}$$

(where $X^- = Cl^-$, Br^-, I^-, respectively)

This means that the $^{110m}Ag^+$ ions were a d d e d first of all which diffused into the silver halide crystals and after a certain reaction time, inactive Ag^+ ions were a d d e d to the AgX-dispersion. The inactive silver ions displaced the radioactive silver ions from the silver halide crystals and the increase of the radioactivity in the aqueous solution was determined. The change in the gradient of the radioactivity under various conditions of reversed exchange like temperature, reaction time, silver ion concentration of the solution and specific surface of the silver halide crystals had now become point of interest. The silver ion concentration of the solution has an influence on the Ag^+ mass transfer up to a pAg value of 2.1. The rate of the mass transfer increased with increasing the silver ion concentration of the solution. The rate of the mass transfer remained constant at concentrations with pAg value greater than 2.1. Therefore a height concentration of inactive silver ions was used for the measurements.

Results and Discussion

Figure 1 shows the kinetics of the $^{110m}Ag^+$ mass transfer in the systems $^{110m}AgCl_{(s)}$ − $Ag^+_{(l)}$ in dependence on labeling time of AgCl with $^{110m}Ag^+$ at 10 °C. It is shown the relative radioactivity of the $^{110m}Ag^+$ in the solution in dependence on time at different labeling times of the AgCl crystals. At short labeling times the rate of the reversed ion exchanges is greater than at long labeling times. The time for the labeling of the AgCl crystals with the $^{110m}Ag^+$ isotope has a great influence on the rate of the ion exchange. Therefore we have selected for the evaluating of the activation energies for the $^{110m}Ag^+$ diffusion in the AgX crystals a long labeling time. For the discussion of the experimental results a law shall be found. An equation for the crystallization was proposed in

the form

$$\ln (\alpha - \alpha_{min}) = k \cdot t \qquad (1)$$

where α is the actual degree of re-exchange of $^{110m}Ag^+$ and α_{min} is the lowest degree of re-exchange of $^{110m}Ag^+$. The re-exchange of the silver ions ($^{110m}Ag^+$) from the AgCl-crystals to the solution is a first order law.[1]

In Figure 2 is shown that $\ln(\alpha - \alpha_{min})$ corresponding equation[1] against time for the exchange in the system $^{110m}AgCl_{(s)}$ — $Ag^+_{(l)}$ gives straight lines only in different time periods. The explanation for this curve is the change of the mechanism in dependence of time. The first step represents the partial change of the solubility of AgCl crystals, that is the formation of complexes between the AgCl and the Ag^+ ions in accordance with the reaction $Ag^+ +$ AgCl $\rightleftharpoons$ Ag_2Cl^+. The influence of temperatures on the first step is very low. The second step in Figure 2 represents the diffusion of the silver ions in the AgCl crystal. In contract to the first step, the temperature has an influence at the second step. The 4th step represents the recrystallization of the silver halide crystals.

Figure 3 shows the Arrhenius curves for the second step of the diffusion of $^{110m}Ag^+$ ions in the AgCl crystals. The measured activation energies for this step is in the range of 16.2-16.4 kJ/mol. The addition of the diffusion- and the recrystallization process results in step three.

In Figure 4 the Arrhenius curve is seen for the second step of the $^{110m}Ag^+$ transfer from the $^{110m}AgBr$ crystals to the solution. The activation energy for the transport of the 110mAg+ ions in the AgBr crystals was calculated to 12.2 kJ/mol.
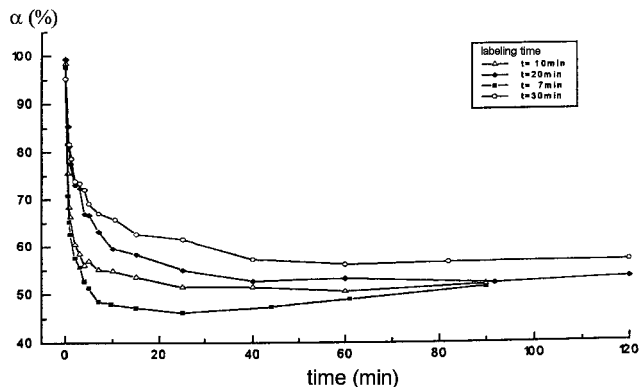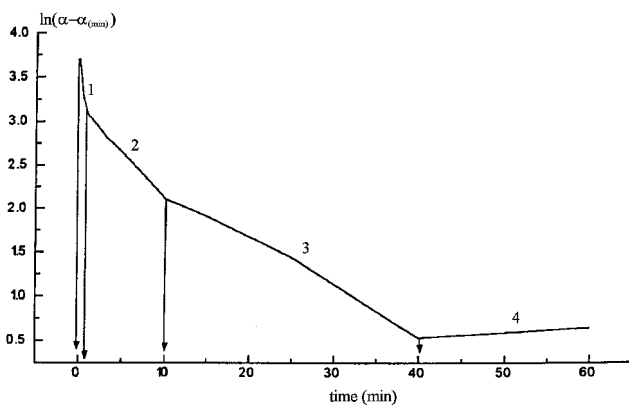

Figure 2. Degree of re-exchange $ln(\alpha - \alpha(min))$ in dependence on time for the system $^{110m}AgCl_{(s)}Ag^+_{(l)}$, (labeling: time 30 min. at 25°C; re-exchange: 0.5 g $^{110m}AgCl$, 100 mg Ag^+/100 ml solution)

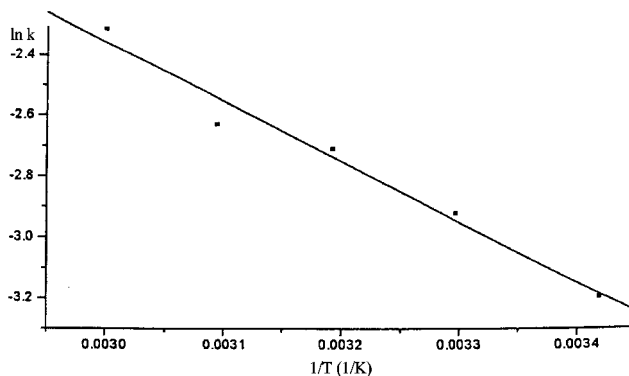*Figure 3. Arrhenius curve for the self diffusion of $^{110m}Ag^+$ in the system $^{110m}AgCl_{(s)}$-$Ag^+_{(l)}$, (re-exchange: 0.5 g $^{110m}AgCl$, 100 mg Ag^+/100 ml solution), $E_A = 16.7$ kJ/mol*

Figure 1. Kinetics of the $^{110m}Ag^+$ mass transfer in the system $^{110m}AgCl_{(s)}$—$Ag^+_{(l)}$ in dependence on the labeling time of AgCl with $^{110m}Ag^+$ (re-exchange: 0.5 g $^{110m}AgCl$, temperature 10°C, 100 mg Ag^+/100 ml solution)
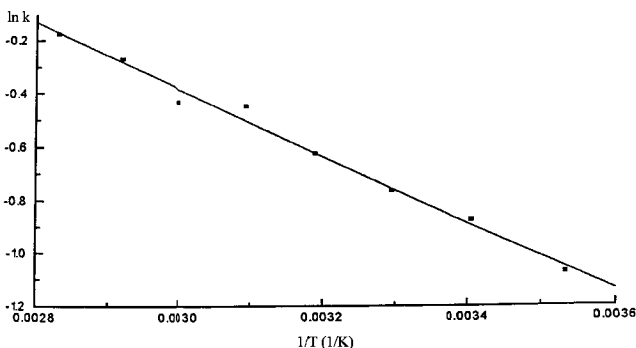

Figure 4. Arrhenius curve for the second step of the $^{110m}Ag^+$ transfer from the $^{110m}AgBr$ crystals to the solution, (re-exchange: 0.5 g $^{110m}AgBr$, 100 mg Ag^+/100 ml solution), $E_A = 12.2$ kJ/mol.

We have found that there is a causal connection between the activation energy for the self diffusion of the Ag^+ ions in the AgCl and AgBr crystals respectively and the frequency of the collective excitation states of the crystal in an earlier work.[2] Recent radiochemical investigations of the ion transport process in crystalline solids showed that a direct proportionality exists between the activation energy for the self diffusion of the Ag^+ ions in silver halide crystals on the one hand and the frequency of the optical phonons of these crystals on the other hand, with Planck's constant as the factor of proportionality. An equation for calculating the activation energy from the frequency of the optical phonons has been found:

$$E_A = 6 N_A \bar{h} \, \omega_{LO} \qquad (2)$$

where

E_A - activation energy for the mass transfer process
N_A - Avogadro's constant
ω_{LO} - frequency of optical phonons
$\bar{h}$ - Planck's constant

According to our investigations, the activation energies for ion transport in crystalline solids can be determined in a first order approximation from the frequency of the first excited vibrational state $\Delta\omega$, the vibrational quantum number n_q and the short range order for the respective diffusing ion (which corresponds to the mean coordination number α).

Also the following equation has been found earlier[3,4]:

$$E_A = \alpha N_A \bar{h} \, \frac{\Delta\omega}{2} \left(2 n_q + 1 \right) \qquad (3)$$

where

E_A - activation energy for the diffusion of the Ag^+ ions in the AgCl and AgBr crystals respectively in $J \cdot mol^{-1}$
α - mean coordination number of the Ag^+ ions
$\Delta\omega$ - energy for the first excited vibrational state in the AgCl and AgBr crystals respectively
n_q - vibrational quantum number

The activation energies E_A calculated according to equation (3) for the ion transport in the AgCl and AgBr crystals are given in Tables 1 and 2. From these considerations it is evident that the activation energy for the self diffusion of the Ag^+ ions increases with rising coordination number α. An increase in the E_A values for the ion transport is also found when the vibrational quantum number of the crystal lattices increases.

To test the efficiency of the quantum theoretical relationship stated above we compared the activation energies measured for the mass transfer process and the activation energies available from the literature for the transport processes of Ag^+ ions in the silver halide crystals with the activation energies calculated in accordance with equation.[3] An earlier work summarizes the activation energies for the transport of the Ag^+ ions in the AgCl and AgBr crystals de-

termined by very differing physical measuring methods, such as measurements of the dielectric loss, electric conductivity measurements, radiochemical measurements of the mass transfer and measurements of the Dember effect. It can be seen that there is a fairly good agreement between the calculated and the experimentally determined activation energies.[2,3]

Table 1: Calculated activation parameters for the Ag^+ transport processes in AgCl in dependence on coordination number and vibrational quantum number ($\omega_{LO} = 3.4 \cdot 10^{13} \, s^{-1}$)

E_A (kJ mol^{-1})						
α	$n_q = 1$	$n_q = 2$	$n_q = 3$	$n_q = 4$	$n_q = 5$	$n_q = 6$
1	3.2	5.4	7.6	9.7	11.9	14.0
2	6.5	10.8	15.1	19.4	23.8	28.1
3	9.7	16.2	22.7	29.2	35.6	42.1
4	11.6	21.6	30.2	38.9	47.5	56.2
5	16.2	27.0	37.8	48.6	59.4	70.2
6	19.4	32.4	45.4	58.3	71.3	84.2

Table 2: Calculated activation energies for the transport of the Ag^+- ions in the AgBr crystal in dependence on coordination number and vibrational quantum number ($\omega_{LO} = 2.525 \cdot 10^{13} \, s^{-1}$)

E_A (kJ mol^{-1})						
α	$n_q = 1$	$n_q = 2$	$n_q = 3$	$n_q = 4$	$n_q = 5$	$n_q = 6$
1	2.4	4.0	5.6	7.2	8.8	10.4
2	4.8	8.0	11.2	14.4	17.6	20.9
3	7.2	12.0	16.8	21.6	26.5	31.3
4	9.6	16.0	22.5	28.9	35.3	41.5
5	12.0	20.1	28.1	36.1	44.1	52.1
6	14.4	24.1	33.7	43.3	52.9	62.6

Radiochemical investigations in the systems $AgCl_{(s)}$—$^{110m}Ag^+_{(l)}$ and $AgBr_{(s)}$—$^{110m}Ag^+_{(l)}$

Radiochemical measurements carried out in the systems $AgCl_{(s)}$—$^{110m}Ag^+_{(l)}$ and $AgBr_{(s)}$—$^{110m}Ag^+_{(l)}$ showed activation energies in the same region of those measured for the diffusion of Ag^+ ions through the interstitial sites in silver halide crystals. From this it can conclude that in the above systems the transition of $^{110m}Ag^+$ ions through the K-centers of the crystal surface and hence the diffusion of the Ag^+ ions in the silver halide lattice is also rate determining. The activation energy for the system $AgCl_{(s)}$—$^{110m}Ag^+_{(l)}$ is at 12.9 kJ/mol and for $AgBr_{(s)}$—$^{110m}Ag^+_{(l)}$ at 9.5 kJ/mol. This shows that the coordination number of the diffusing Ag^+ ion is 4 (Tables 1 and 2). In this case the diffusion of the Ag^+ ions takes place preferable through the interstitial places in the crystals. With $\alpha = 4$ the mean coordination number of the interstitial ions in the AgCl and AgBr lattice, respectively, and $n_q = 1$ according to equation (3) results in activation energies at 12.9 kJ/mol for the system $AgCl_{(s)}$—$^{110m}Ag^+_{(l)}$ and at 9.6 kJ/mol for the system $AgBr_{(s)}$—$^{110m}Ag^+_{(l)}$.

In the case of the diffusion of the Ag^+ ions we have measured the activation energies in the systems $AgCl_{(s)}$ — $^{110m}Ag^+_{(l)}$ and $AgBr_{(s)}$ — $^{110m}Ag^+_{(l)}$ in the presence of a high concentration of Ag^+ ions in the solution. In this experimental construction the diffusion of the Ag^+ ions into the crystal is the rate determining step. The measured activation energies are in relation to the diffusion of the Ag^+ inside the AgCl and AgBr crystals respectively.
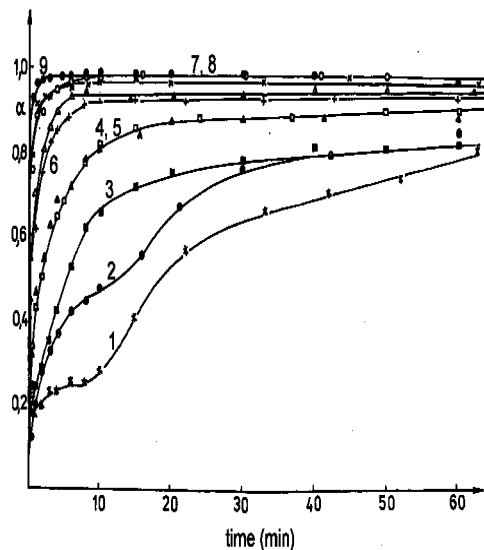

Figure 5. Relative $^{110m}Ag^+$ activity α of the AgBr crystals in dependence of time for different concentrations of the anti-foggant 1-Phenyl-5-mercaptotetrazole (PMT); T = 25 °C; 1: 0.6 mg PMT; 2: 0.7 mg; 3: 0.5 mg; 4: 0.4 mg; 5: 0.2 mg; 6: 0.175 mg; 7: 0.15 mg; 8: 0.1 mg; 9: curve without antifoggant PMT

Radiochemical Investigations in the System $^{110m}AgCl_{(s)}$— $Ag^+_{(l)}$ and $^{110m}AgBr_{(s)}$—$Ag^+_{(l)}$

The measured activation energy of the silver ions in the silver chloride crystals is at 16.4 kJ • mol^{-1}, whereas in the silver bromide at 12.1 kJ • mol^{-1}. The activation energies for the displacement (diffusion) of the interstitial silver ions were compared with the values calculated on a quantum mechanical basis. There resulted a good correspondence of the measured with the calculated values. These experimental values compared with the values calculated on a quantum mechanical basis (Equation 3) resulted in a middle coordination number of 5 for the migrating Ag^+ ions. This on the other hand describes a jump mechanism, where by the diffusing ions occupy alternately the interstitial positions (coordination number 4) and lattice positions (coordination number 6). So in the investigated range of temperature (10-80 °C) the movement of the silver ions through the silver halide crystal is based on the jump mechanism.

Influence of Antifoggants

The presence of impurities ($RhCl_3$ • 3 H_2O, Na_3IrCl_6 • 2 H_2O, H_2PtCl_6 • x H_2O (Pt = 40 %) and $K_4[Fe(CN)_6]$ respectively) in a AgCl- or AgBr-system can have a profound effect on the Ostwald ripening of a crystal. Some photo-

graphically active substances can exert an influence at very low concentrations, less than one part per million, whereas others need to be present in fairly large amounts before having any effect.[5] In the case of the antifoggant 1-Phenyl-5-mercaptotetrazole (PMT) a decrease of the velocity of the mass transfer was found, if using $^{110m}Ag^+$ ions in a high specific activity, if the concentration of this antifoggant increased (Figure 5). Characteristic points were found by evaluating the kinetic curves at 0.05 mg PMT/0.5 g AgBr (= 1.054 • 10^{-4} mol PMT/mol AgBr), 0.1 mg PMT/0.5 mg AgBr (= 2.11 • 10^{-4} mol PMT/mol AgBr) and 0.2 mg PMT/ 0.5 g (= 4.22 • 10^{-4} mol PMT/mol AgBr) (Figure 6). These points are in agreement with results that were found in the system AgBr-antifoggant-PMT-^{82}Br.[6] The activation energies for the kinetics of the $^{110m}Ag^+$ mass transfer change also only a little with increasing the concen-trations of photographically active substances at higher Ag^+ concentrations.
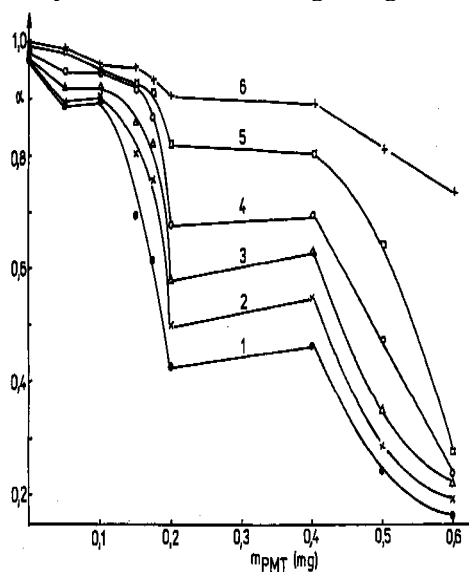

Figure 6. Relative $^{110m}Ag^+$ activity α of the AgBr crystals in dependence on concentration of 1-Phenyl-5-mercapto-tetra-zole (PMT) for a different time of adsorption; curve 1: 1 min; 2: 2; 3: 3; 4: 5; 5: 10; 6: 50; T = 25 °C

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