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On Some Properties of Silver Iodide*

R. Despotović, Z. Grabarić, and S. Popović

»Ruđer Bošković« Institute, Zagreb, Croatia, Yugoslavia

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In order to obtain the relation between several factors affecting the colloido-chemical properties of silver iodide in the heterogeneous exchange processes, the following measurements were carried out: determination of the adsorption capacity of silver iodide (radio-metry) tempered from 20 up to 400 °C, dry aged for 20 days to 5 years, pressed at 500 and 1500 kg cm⁻² (on dried isoelectric precipitate); determination of the relation between particle size (electron microscopy) and crystallite size (X-ray diffraction analysis), and of the adsorption capacity of AgI (formed by dilution of KI + AgI complex solution) in the presence of sodium laurylsulphate (SLS); determination of the surface area (BET) of the tempered isoelectric dried silver iodide; determination of particle size and determination of the volume fraction of cubic and hexagonal modifications of AgI in the tempered samples. In conclusion, the effect of the inner surface as a possible relevant factor for the elucidation of the influence of surface active substances on acceleration of the exchange rate is pointed out. Interactions with sodium laurylsulphate are also discussed.

INTRODUCTION

The process of heterogeneous exchange of precipitates is convenient for obtaining information on the equilibration of the precipitates or solids with the supernatant liquor or the surrounding solutions. These investigations revealed several phenomena which are closely related to the processes in the boundary region of the solid phase¹. In previous papers^{1,2} it has been shown that the heterogeneous AgI—I⁻ exchange is predominantly characterized by the recrystallization process while AgI—Ag⁺ exchange is determined by auto-diffusion of the Ag⁺ ion in the crystal lattice of the precipitates. It seems that the crystal modification and the surface area are important factors in the process of heterogeneous exchange. Silver iodide in a suspension is polymorphic and the fractions of cubic and hexagonal modifications of AgI and the adsorption capacity vary with experimental conditions²⁻⁵. In order to elucidate these interrelations, the role of the crystal modification and the role of the surface area in the exchange processes have been examined and the results obtained are described in the present paper.

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EXPERIMENTAL

Experiments were carried out by several different physical and chemical techniques.

(i) In order to obtain data on the influence of dry aging on the adsorption capacity, the isoelectric *in vacuo* dried silver iodide powder (prepared for the experiments as described before²), was left in the dark in a brown bottle with a glass stopper. Dried silver iodide was aged for 20 days and for five years. The samples of AgI were separately put into the same NaI solutions at $pI = 3$ containing $\text{Eu}(\text{NO}_3)_3$ from 1.67×10^{-6} to 3.33×10^{-4} M labelled with Eu-152, 154 at $pH = 2.8$ and at $20.0 \pm 0.2^\circ\text{C}$. After 1000 minutes adsorption-desorption equilibria were reached. The samples, decanted with care, washed, dried and weighed, were counted in a well type NaI(Tl) scintillator connected with an EKCO Electronic scaler.

(ii) The same dried isoelectric silver iodide powder was tempered for 2500 minutes at various temperatures from 20 to 400°C at normal atmosphere. After cooling, by using the same radioactive tracer techniques as before (i), adsorption capacities were determined at $20.0 \pm 0.2^\circ\text{C}$ in the systems with tempered AgI. By means of BET method the surface area of the investigated isoelectric dried silver iodide was determined (silver iodide was kept in vacuum for 2500 minutes at 20°C and at 400°C). The silver iodide prepared in the same thermal treatment was also used for X-ray diffraction analysis in order to obtain the volume fractions of cubic, C, and hexagonal, H, modifications of AgI, as well as the crystallite sizes, D, in the samples. To this end integrated intensities and diffraction broadening (corrected for the instrumental broadening) of several prominent reflections were measured.³ Diffraction patterns including hexagonal reflections (100) and (101) and overlapping cubic (111) and hexagonal (002) reflections were recorded (at 20°C) by a diffractometer with a scintillation counter and a single channel pulse height analyser. Melted AgI was also analysed and the results are collected in Table I.

TABLE I

The Proportions of Cubic (C) and Hexagonal (H) Phases and the Crystallite Sizes (D) in AgI Samples:

Sample	Thermal treatment	C(%)	H(%)	$D_{H(100)}/\mu\text{m}$	$D_{C(111)}/\mu\text{m}$	$D_{H(101)}/\mu\text{m}$
1	dried <i>in vacuo</i> $t = 20^\circ\text{C}$	57	43	0.9	0.9	0.2
2	$t = 120^\circ\text{C}$	50	50	1.3	1.3	0.35
3	$t = 170^\circ\text{C}$	44	56	1.4	1.5	0.60
4	$t = 400^\circ\text{C}$	15	85	1.5	1.5	1.4
5	melted ground	49	51	1.4	1.5	0.20
6	melted	40	60	1.4	1.5	0.02

(iii) X-ray diffraction technique was used to determine crystallite sizes, D of silver iodide sols prepared »*in statu nascendi*« with 1.0×10^{-5} M and/or 1.0×10^{-2} M sodium laurylsulphate, SLS. Particle sizes R in these systems, were determined by electronmicroscopy and their adsorption capacity was measured in the same manner as above. The results obtained are tabulated in Table II. The influence of pressure on the adsorption capacity of AgI was measured on silver iodides pressed for 1 minute under 500 and 1500 kg/cm^2 , respectively. Adsorption capacity was determined on plates and crushed plates by the standard radioactive tracer technique.

TABLE II

Relation between Particle Sizes (D), Crystallite Sizes (R) and Adsorption Capacity of AgI in the Presence of Sodium Laurylsulphate SLS, at $20.0 \pm 0.2^\circ\text{C}$, $p\text{I} = 2$ and 0.01 M AgI

CSLS	γ	$D/\mu\text{m}$	$R/\mu\text{m}$	
	mmol ($1/3 \text{ Eu}^{3+}$) /mol (AgI)			
$1.0 \times 10^{-5} \text{ M}$	0.20 ± 0.02	0.17	0.02—0.8	(mainly 0.4—0.8)
$1.0 \times 10^{-2} \text{ M}$	0.80 ± 0.05	0.04	0.07—1.3	(mainly > 1.0)

RESULTS AND DISCUSSION

Aging and Adsorption Capacity

Dried isoelectric silver iodide precipitates obtained by »fast« precipitation² dry aged for 5 years show an about 50% smaller adsorption capacity ($\gamma = 0.17 \pm 0.02$ mmol of $1/3 \text{ Eu}^{3+}$ per mole of AgI) than the precipitates aged for 20 days only [$\gamma = 0.33 \pm 0.03$ mmol ($1/3 \text{ Eu}^{3+}$)/mol (AgI)]. This aging effect may be explained as follows. During fast precipitation the particles of silver iodide acquire larger adsorption capacity than those in slowly formed suspensions of AgI^2 . This difference of the adsorption capacity could be caused by different dispersity in suspension and by the formation of a bigger number of disorders in the solid AgI, which was precipitated faster^{2,5,7-11}. Tamman ripening, *i. e.* cold synering on 5 year aged samples takes place in the aging of dried AgI. Therefore both the outer and the inner surface of AgI decrease by aging. With the decrease of the outer crystal surface the crystal disorders disappear too, *i. e.* the capacity of the Grimley-Mott double electrical double-layer also decreases. For this reason the adsorption capacity γ diminished too.

Crystallite Sizes, Cubic/Hexagonal Ratios, Surface Areas and Adsorption Capacities of Tempered Samples

When the aging process is accelerated by heating of the silver iodide crystals, the adsorption capacity decreases with heating. For this reason the isoelectric silver iodide was tempered up to 400°C and X-ray diffraction, BET and adsorption determinations were carried out. It can be seen from Table I that the proportion of cubic phase, C, in the tempered sample is somewhat smaller than in the untreated sample 1. All crystallite sizes shown in Table I increase with temperature. $D_{\text{H}(100)}$ is always very similar to $D_{\text{C}(111)}$. For the sample 1 the c axis of the hexagonal crystallites is much shorter than the a axis, but for the sample 4 these two dimensions are even smaller. The growth rate of $D_{\text{H}(101)}$ is larger than the growth rate of $D_{\text{H}(101)}$. This difference between the a and c dimensions of hexagonal crystallites is still larger in the samples 5 and 6. This has caused some difficulties in measuring the half maximum breadths of sharp C(111) lines, as they are superimposed on very broad H(002) lines. By tempering, the part of hexagonal AgI increased up to 80%, and we may conclude that the crystallites of the silver iodide grew by tempering. At these conditions the mass of one crystallite increased by

a factor of about 11 and its surface by a factor of about 6. This increase was, of course, attended with an adequate decrease of dispersity. Meanwhile, BET analysis shows ($P_{20\text{ }^{\circ}\text{C}} = 0.60 \pm 0.15 \text{ m}^2/\text{g AgI}$ and $P_{400\text{ }^{\circ}\text{C}} = 0.02 \pm 0.01 \text{ m}^2/\text{g AgI}$) that the total surface of the system decreased by tempering much more, which undoubtedly indicates that by tempering the cubic-hexagonal mixtures of AgI, cubic and hexagonal small crystallites grow into bigger hexagonal crystallites with a very small total surface. At the same time this indicates that the dependence of the adsorption capacity on tempering is the combined effect of the change of at least two variables [$\gamma_{20\text{ }^{\circ}\text{C}} = 0.17 \pm 0.03$, $\gamma_{120\text{ }^{\circ}\text{C}} = 0.16 \pm 0.01$, $\gamma_{170\text{ }^{\circ}\text{C}} = 0.12 \pm 0.01$ and $\gamma_{400\text{ }^{\circ}\text{C}} = 0.05 \pm 0.01 \text{ mmol } (1/3 \text{ Eu}^{3+})/\text{mol (AgI)}$]: the change of the C/H ratio and the change of the total surface of the solid phase. In this way the adsorption appears to be dependent only on crystallite size and crystallographic modification.

Crystallite Sizes and Adsorption Capacities for Variously Pressed Samples and in Presence of SLS

The role of the intrinsic area of crystallites in the exchange processes can be elucidated by examination of the role of the inner area in the adsorption phenomena. To this end the experiments were carried out on pressed AgI (small intrinsic area) and on the systems with sodium n-dodecyl sulphate (high dispersity). It is known¹⁴ that by pressing, the isoelectric cubic-hexagonal mixture can be entirely transformed into the cubic modification, which was achieved. At a lower pressure of the silver iodide, the plate has the structure of the pressed powder and at a higher pressure it looks like yellow transparent glass. In both cases cubic AgI with very small adsorption capacity was obtained. In the case of the yellow transparent glass plate the capacity was even smaller [at 500 kg cm^{-2} $\gamma = 0.08 \pm 0.01$, at 1500 kg cm^{-2} $\gamma = 0.006 \pm 0.003 \text{ mmol } (1/3 \text{ Eu}^{3+})/\text{mol (AgI)}$]. By crushing the pressed silver iodide plates the adsorption capacity markedly increased [at 500 kg cm^{-2} $\gamma = 0.10 \pm 0.01$, at 1500 kg cm^{-2} $\gamma = 0.03 \pm 0.01 \text{ mmol } (1/3 \text{ Eu}^{3+})/\text{mol (AgI)}$]. We cannot determine crystallite sizes by X-ray technique because of the effects of preferred orientation and therefore we can only suppose that γ is lower on the glassy plate because of the lower surfaces accessible to the electrolyte solution. From the results tabulated in Table II we can see that the intrinsic surface can also assume a determining role. In the presence of the surface active substances such as sodium laurylsulphate, SLS, by dilution of a AgI + KI complex solution, the silver iodide particles were formed with higher γ for larger particles, because they were composed of many small crystallites. It seems that the inner surface of the silver iodide particles is accessible for communication with the electrolyte, *i. e.* it is open for adsorption-desorption processes and for heterogeneous exchange processes too. The silver and iodide ions in the suspension in heterogeneous exchange processes are in this case in direct connection with the outer and inner surface of silver iodide particles, which is of great importance in the explanation of the influence of surface active substances on heterogeneous exchange rate in AgI—I⁻ and AgI—Ag⁺ systems^{1,2,5,6}. The results of Table II can be understood also in terms of adsorption of europium Eu³⁺ to AgI containing a high surface concentration of anionic SLS. This consideration is particularly important for the highest SLS concentrations where in addition to adsorption, the interaction of the

europium with LS has to be considered. According to the Herz's¹⁵ and Padday's¹⁶ concept of the adsorption on selected sites and similarly to Mirnik's concept of adsorption at discrete charged sites¹⁷, constitutive I^- ions from the solution can be exchanged with the same constitutive ions from free crystal surfaces.

CONCLUSION

Conditions of precipitation and of aging (drying, tempering, pressing) as factors affecting crystallite or particle size, cubic/hexagonal ratio, surface area and adsorption capacity were investigated. Analysis of results shows mutual dependences of physicochemical properties of silver iodide on the conditions of precipitation and aging. The results show that the surface of AgI decreases by aging dry and in the supernatant. It is supposed that crystal disorders disappear causing a decrease of the adsorption capacity γ . X-ray diffraction analysis, BET and adsorption determination of the thermally treated isoelectric silver iodide indicate dependence of the adsorption capacity on crystallite sizes and on the crystallographic modification. Analysis of pressed AgI and the analysis in presence of SLS formed AgI show, in connection with other results, that in heterogeneous exchange processes the silver and iodide ions in the suspensions are in direct connection with outer and inner surface of silver iodide particles. This is of great importance in the explanation of the heterogeneous exchange rate in $AgI-I^-$ and $AgI-Ag^+$ systems, particularly in the systems containing surfactants. According to Težak's concept the results obtained show that the processes (adsorption equilibria and heterogeneous exchange) in the methoric layer are the direct resultant of the equilibria of the processes in the solid and liquid phase.

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IZVOD

O nekim svojstvima srebrnog jodida

R. Despotović, Z. Grabarić i S. Popović

S ciljem utvrđivanja karakteristika koje utječu na koloidno kemijska svojstva srebrnog jodida u procesima heterogene zamjene provedena su slijedeća mjerenja: određivanje adsorpcionog kapaciteta srebrnog jodida grijanog od 20 do 400 °C (radio-metrija i termički tretman), starenog kroz 20 dana do 5 godina i prešanog na 500 i 1500 kg/cm² (sve na sušenom izoelektričnom precipitatu); određivanje omjera veličina čestica (elektronska mikroskopija), veličine kristalita (rendgenska difrakcija) i adsorpcionog kapaciteta srebrnog jodida u prisustvu natrijevog laurilsulfata; određivanje vanjske površine (BET) termički tretiranog izoelektričnog srebrnog jodida; određivanje volumne frakcije kubičnog i heksagonalnog srebrnog jodida kao i veličine kristalita u termički tretiranom srebrnom jodidu (rendgenska difrakcija). U diskusiji rezultata pokazuje se interferencija kemijskih i karakteristika čvrstog stanja kao faktora koji utječu na koloidno kemijska svojstva srebrnog jodida. Pokazan je i utjecaj unutrašnje površine kao mogućeg relevantnog faktora u objašnjenju utjecaja površinski aktivnih supstanci na brzinu procesa heterogene zamjene. Interakcije sa SLS su također diskutirane.

INSTITUT »RUĐER BOŠKOVIĆ«
41000 ZAGREB

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