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Some Properties of AgI Suspensions Formed by the Dilution Method

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The complex solution of AgI in concentrated KI was added to water or to diluted KI solution to give $pI = 2$ in the final system. Time tyndallograms (obtained by measuring turbidity as a function of time) of the AgI sols thus obtained were analysed. By a radiometric technique adsorption-desorption equilibria in the systems thus obtained were determined.

The results show that sols with a smaller degree of dispersion than sols *in statu nascendi* (by mixing precipitation components) formed under the same final chemical conditions ($pI = 2$) were obtained. The colloid particles grow faster and the process of the particles growth is the fastest after the mixing of the precipitation components. The measurement of the adsorption capacity (meq/gram) gave an equilibrium value which is one tenth of the capacity of sols obtained *in statu nascendi*. The mode of mixing reaction components also markedly influences the stability and the growth of AgI sol particles.

INTRODUCTION

AgI—I^- sols in aqueous media have a high colloidal stability. The sol particles are very small (10—500 mμ). These particles grow very slowly and parallelly decreases the colloid stability of systems[1-4]. During the aging process the ratio of cubic/hexagonal AgI changes in a stable sol. This change does not occur so fast in coagulated suspensions[2]. The adsorption capacity of silver iodide is dependent on the preparation conditions[5] and for coagulated systems *in statu nascendi* where various inorganic cations are present amounts to 3 milligram-equivalents of adsorbed cation per grammole of AgI[6]. X-ray diffraction analysis of the influence of the preparation conditions on the properties of silver iodide particles in the sol showed that by dilution of the complex, AgI dissolved, in concd. KI or NaI solutions, silver iodide particles of lower degree of dispersion were always obtained[2]. Exchange experiments also show[7] a marked dependence of the rate of the AgI—I^- process on preparation conditions. As the first step in the investigation of silver iodide sols prepared by the »dilution method« it was necessary to determine the colloid stability of systems thus prepared as well as the adsorption capacity of system. The results described in the present paper indicate several different characteristics as compared with systems prepared *in statu nascendi.*

EXPERIMENTAL

The chemicals used were of high purity (Analar, B. D. H.). Twice distilled water was used as a solvent. Dried silver iodide was obtained in the same manner as described before[5]. A standard complex solution of silver iodide in KI solution was prepared as follows: 5.87 g of dried AgI were placed into a 25.0 ml measuring flask. A fresh solution of 4.00 *M* KI was added and when the AgI was completely dissolved in the added KI solution, KI solution up to 25.0 ml was added into the flask. The solution was prepared in a Haake ultrathermostate. For tyndallometry, the systems were prepared by adding of (a) 20.0 μl complex solution into 8.0 ml of water (AgI_{DIL} — H_2O marked systems) or (b) into KI solution (AgI_{DIL} — KI marked systems). In all cases in the systems $pI = 2.0$ and $\alpha = 0.25$ ($\alpha = n^S/n^L$ where n^S is the total molar quantity of solid AgI in the suspension, n^L the total molar quantity of iodide ions in the liquid phase) were obtained. After adding complex solutions to the water or the KI solution, the systems were mixed by a magnetic stirrer (systems labelled MIX.) for 15, 30 and 45 seconds or by pouring from one tube into another 3, 7 and 15 times (systems labelled m). During aging all the systems were thermostated at 20.0 ± 0.2° C. Red and green filters were used for tyndallometric values (T. V.) against the aging of the suspension.

The adsorption experiments were carried out by means of a radioactive tracer technique in the same manner as described before[5,6]. However, samples of the solid phase were separated by using a high speed Sorvall centrifuge and not by decantation. The results are collected in Table I.

RESULTS AND DISCUSSION

Our principal aim is to point out *(i)* the influence of preparation conditions on colloid stability of AgI sols and *(ii)* to establish some differences between sols formed *in statu nascendi* and those formed by a »dilution method«. As a simple and sufficiently accurate method for determining colloid stability, tyndallometry is used. Since there was very good agreement between particle sizes determined by X-ray technique and by relative evaluation from tyndallometric data[2], we may draw conclusions about the crystal growth of silver iodide particles by measuring the change of T. V. during the aging of sols. The results presented in Figs. 1 and 2. show that tyndallometric maxima were reached in a shorter time in the systems mixed by pouring sol from one tube to another than when mixing was achieved by means of a magnetic stirrer. At the same time it is seen that the maxima are sharper in the systems mixed by a magnetic stirrer. The tyndallometric curves are also different in systems obtained by adding the complex solution into water as compared by adding into diluted KI solution. Taking into account the previously cited results[1-3] we can generally conclude that by the »dilution method«, because of fast increase of T. V. in these systems, crystal growth of silver iodide particles is markedly faster than in *in statu nascendi* systems. This conclusion is supported by adsorption results (Table I). In the

TABLE I

Adsorption of Eu^{3+} on AgI Sol Particles Formed by the Dilution Method

System: AgI_{DIL} — KI — $Eu(NO_3)_3$, $pH = 3$, $pI = 2$, $\alpha = 0.25$, $t_A = 10000$ minutes at $T = 20.0 \pm 0.2^0$ C. Adsorption capacity γ is expressed as milligramequivalent of adsorbed europium per gram mole AgI.

$c_N \times 10^5$ $Eu(NO_3)_3$:	1	2	3	5	7	30	70	100
$\gamma \times 100$:	13	14	20	26	26	29	27	24

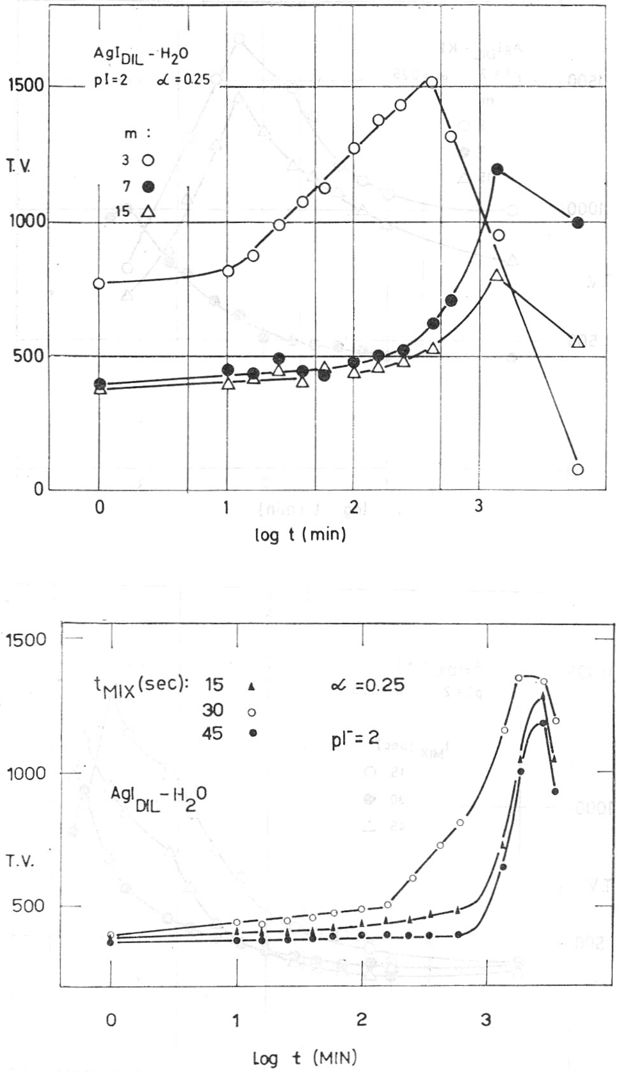

Fig. 1. The silver iodide sols were prepared by the addition of a complex (AgI in concd. KI) into water. For both diagrams (1. a, b) tyndallometric values T. V., are plotted against the age of the systems (log scale, time t in minutes). Fig. 1. a. The sol obtained was poured from one tube into another m = 3, 7 or 15 times; Fig. 1. b. Obtained sol was stirred by a magnetic stirrer for t_{MIX} = 15, 30 and 45 seconds.

in statu nascendi AgI—I^- systems the adsorption capacity[6] is up to 3 milligram equivalent of adsorbed inorganic cations per gram mole AgI, while in the sols obtained by the »dilution method« it is about one tenth of the capacity. If the outer crystal surface is responsible for the adsorption capacity, our adsorption results indicate directly the smaller degree of dispersion or faster crystal growth in the observed time interval. In this way tyndallometric data are supported by adsorption measurements, and we may conclude that in sols formed by the »dilution method« crystal growth is faster as compared

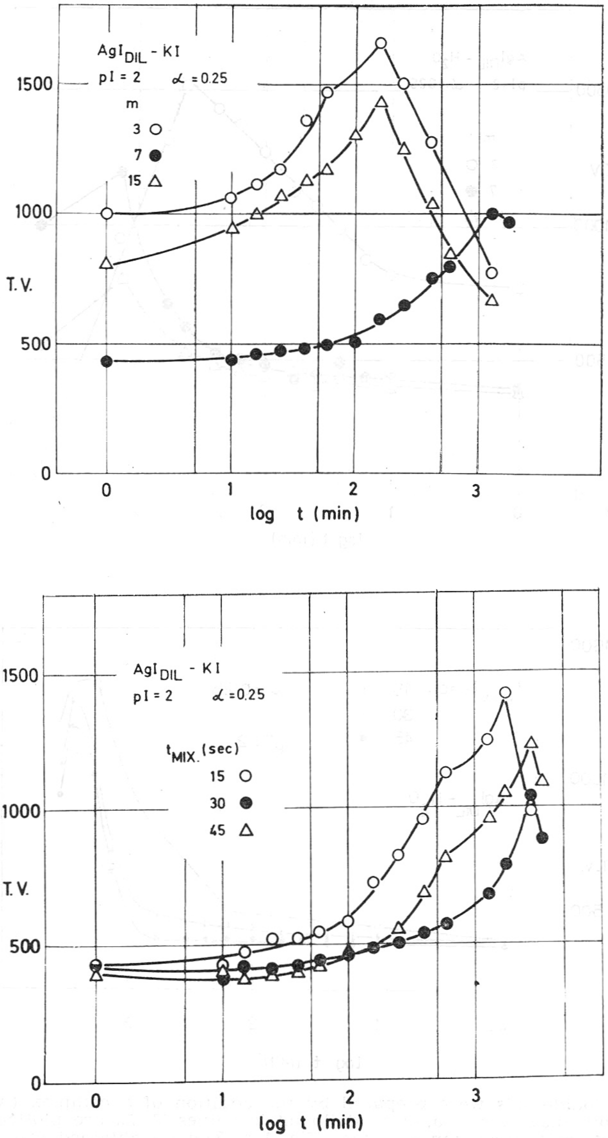

Fig. 2. The silver iodide sols were prepared by the addition of a complex solution (AgI in concd. KI) into dil. KI solution. For both diagrams (2. a, b.) tyndallometric values T. V., are plotted against the age of the systems (log scale, time t in minutes). Fig. 2. a. The sols obtained were poured from one tube into another m = 3, 7 or 15 times; Fig. 2. b. Sols obtained were stirred by a magnetic stirrer for t_{MIX} = 15, 30 and 45 seconds.

with systems formed *in statu nascendi.* Crystal growth is accelerated by agitation of systems, *i. e.* by pouring or stirring. In the systems formed by pouring sol from one tube to another 3 times (Fig. 1. a.) a faster increase of T. V. is obtained, because it represents the turbidity of the whole sol. In the case of sols poured 7 and 15 times, the crystal growth is so fast that in these systems a sediment appears after halft an hour and the T. V. corresponds to only one part of total solid phase present. The descending part of the curve after the maximum is steeper for the sols poured 3 times, because the decrease of turbidity is the result of sedimentation of a bigger quantity of solid phase than in the other two cases (sols poured 7 and 15 times) for which we obtained minor slopes of the curves after the maximum. In this case the fastest crystal growth takes place at the beginning of the aging process. This is in very good agreement with heterogeneous exchange experiments[7]. For the above reasons in all other cases (Figs. 1. b. and 2. a, b.) the course of »T. V. — log t« curves is not monotonic. Comparing Figs. 1. a. with 2. a. and 1. b. with 2. b. we can see curves with different slopes for AgI_{DIL}-H_2O compared with AgI_{DIL}-KI systems. The results on 1. a.—1. b. and 2. a. indicate that the mode of sol preparation (which will be at last at the »same« chemical and physical conditions as concentration of potential determining ion, quantity of solid phase and the age of system) is one of very important factor determining the properties of an AgI sol. All these results show that the systems obtained by the »dilution method« are different from those formed *in statu nascendi* (i) preparation conditions influence the sol characteristics and mode of mixing is an important factor because the fastest crystal growth in such systems takes place after the mixing of precipitation components and (ii) by the »dilution method« the sols obtained grow faster than the *in statu nascendi* ones, forming after a short time of precipitation so big particles that their adsorption capacity is one tenth of the capacity of sols obtained *in statu nascendi.*

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IZVOD

Neka svojstva AgJ solova pripremljenih metodom razrjeđivanja

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Kompleksna otopina AgJ u KJ (5,87 g AgJ kompleksno je otopljeno u 4,00 *M* KJ do ukupnog volumena od 25.0 ml) dodavana je u vodu ili razrijeđenu otopinu KJ tako da je u sistemu postignuto *pJ* = 2. Analiziran je vremenski tyndallogram dobivenih AgJ solova. Radiometrijskom tehnikom određivana je adsorpciono-desorpciona ravnoteža u takvim sistemima.

Rezultati pokazuju da su dobiveni solovi s mnogo manjim disperzitetom, nego solovi formirani *in statu nascendi* uz iste uvjete ($pJ = 2$), da mnogo brže rastu koloidne čestice, da je stabilnost solova znatno manja i da je proces rasta partikula najbrži odmah nakon miješanja taložnih komponenata. Mjerenja adsopcionog kapaciteta daju kao ravnotežnu vrijednost oko 10 puta manji kapacitet na ovim sistemima u odnosu na kapacitet *in statu nascendi* solova. Način miješanja reakcionih komponenata također znatno utječe na stabilitet i rast čestica AgJ sola.

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