CROATICA CHEMICA ACTA CCACAA **49** (1) 1—5 (1977)

YU ISSN 0011—1643
CCA-967 546.57:541.18
Original Scientific Paper

On the Aging and Colloid Properties of AgI Sols

R. Despotović and J. Kapetanović

Laboratory of Colloid Chemistry, Ruđer Bošković Institute, 41001 Zagreb,
P.O. Box 1016, Croatia, Yugoslavia

Received September 26, 1975

The literature data concerning the critical coagulation concentration, c_k, may differ by as much as a factor ten. The detailed analysis of the changes of various silver iodide sol properties shows the role of the aging process for characterization of the system. The analysis of the c_k changes and the sedimentation rates with time and electrophoretic mobility of sols containing sodium, cobalt or lanthanum shows, that the sols in presence of various counter ions have not strictly equal colloid properties, although the counter ions were present at critical coagulation concentrations.

INTRODUCTION

Težak and co-workers have made extensive studies of the coagulation-by-electrolytes processes of silver halide sols; in total their results confirm the linear Schulze Hardy rule that the critical coagulation concentration, c_k, for an ion of opposite charge to that of the sol decreases with the ionic charge[1]. The age of the specimen was pointed out to be an important criterion for the colloid systems; the results reported for variously prepared silver iodide sols show a marked dependence of c_k, the adsorption capacity, crystallite sizes, crystal modifications and the colloid stability on the age of sols[2]. The mixing method of the reaction components has also a marked influence on the colloid properties and the growth of AgI sol particles[2].

The age appears to be an important colloidal feature of AgI since its properties are changing considerably with time (t). Thus *e. g.*, $c_k = f(t)$. The function $f(t)$ depends on various conditions, such as concentration of other ions. In further qualitative considerations it will be simply called »time factor« (TF). In the series of silver iodide sols coagulated by uni-, bi-, tri- and tetravalent counter ions, present at c_k and in all cases for equally aged sols, the colloid properties are different for each sol, because of different crystal growth of sol particles in the presence of counter ions of various valencies[3].

The stable negative silver iodide sols in a wide concentration range of iodide ions are polydisperse and of polymorphous crystal shape, for the systems prepared in aqueous media[4]. A consequence of such origin of the silver iodide sols is a low number of coherent quantitative data and models about processes of the solid phase formation after the mixing of precipitation components. The detailed radiometric analysis of the negative silver iodide sols reveals a number of simultaneous processes in stable AgI sols; the embryos disappear, transforming into the solid phase, the silver iodide particles grow and the methoric mass disappears, turning into the solid phase[5]. All observed phenomena are strongly dependent on the age of system indicating the importance of TF for the characterization of the examined systems. Taking into consideration Težak's scheme[1] (according to which the properties of sols are closely connected with the initial conditions of the sol preparation), in the present paper the effects of the counter ions, present *in statu nascendi,* on the stability of sols are followed through the ageing process.

EXPERIMENTAL

Dried isoelectric silver iodide was obtained as follows; A 0.02 M $AgNO_3$ solution was added during 10 minutes to an agitated 0.02 M NaI solution until a paraffined Ag/AgI electrode indicated a pAg value of 6.2. The precipitate was aged for 1000 minutes in the supernatant liquid, filtered and washed until the washings showed a constant conductivity. The AgI precipitate was vaccum dried, crushed and passed through a silver sieve (30—60 mesh). The chemicals used were of high purity (Analar, B. D. H.). Water used to prepare the solutions was purified by two-stage distillation with an all-glass Duran 50 apparatus.

A standard complex solution of silver iodide in NaI solution was prepared as follows; 2.3480 g of dried AgI and 5.9956 g of NaI were placed into a 5 ml measuring flask, and dissolved in added water; the solution was 0.2 M AgI and 0.8 M NaI. The solution of $(AgI)_x (NaI)_y$ was prepared in a Haake ultrathermostat at 293 K.

For tyndallometry the systems were prepared by adding 50 μl of complex $(AgI)_x (NaI)_y$ solution into 40 ml of $NaNO_3$, $Co(NO_3)_2$ and $La(NO_3)_3$ solution. In all cases in the systems $pI = 2$, $\alpha = 0.25$ ($\alpha = n^S/n^L$ is the ratio of the amount of I^- in the solid phase, n^S, to that in the liquid phase, n^L). After adding the complex solution, the systems were mixed by a magnetic stirrer for 3 minutes. After aging for t_A minutes at 293 ± 0.2 K, the tyndallometric values τ of sols were measured. The average of ten measurements on the samples prepared in the same way was taken as the result (Figure 1).

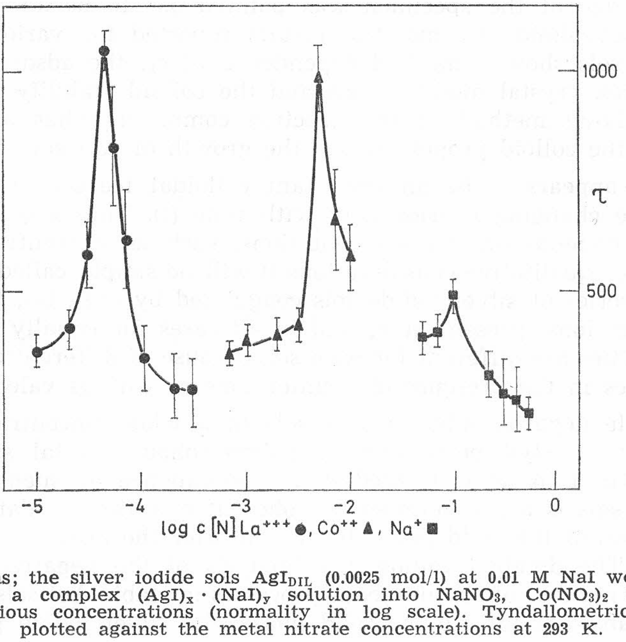

Figure 1. Systems; the silver iodide sols AgI_{DIL} (0.0025 mol/l) at 0.01 M NaI were prepared by the addition of a complex $(AgI)_x \cdot (NaI)_y$ solution into $NaNO_3$, $Co(NO_3)_2$ and/or $La(NO_3)_3$ solutions of various concentrations (normality in log scale). Tyndallometric values, τ, are plotted against the metal nitrate concentrations at 293 K.

For the sedimentation experiments the systems were prepared in the same manner as for tyndallometry using the $(AgI)_x(NaI)_y$ complex solution labelled by $^{131}I^-$. The systems were 0.1 M $NaNO_3$, 0.008 M $Co(NO_3)_2$ and 0.000126 M $La(NO_3)_3$ at 293 ± 0.1 K. After selected times of ageing $t_A = 10, 20, 30, 40, 50, 60, 70, 80, 90,$ and 100 minutes, the samples, free of flocs, were pipetted off and the radioactivity A_t determined in an EKCO NaI(Tl) well type scintillation counter. The radioactivity A was determined in an equal volume of fresh homogenized suspension. The equilibrium radioactivity of the liquid phase is $A_0 = A/(1 + \alpha)$, and the fraction of sedimentation is $f^0/_0 = 100\ (A - A_t)/(A - A_0)$. The results are represented as $f^0/_0$ *versus* the age of sols (Figure 2).

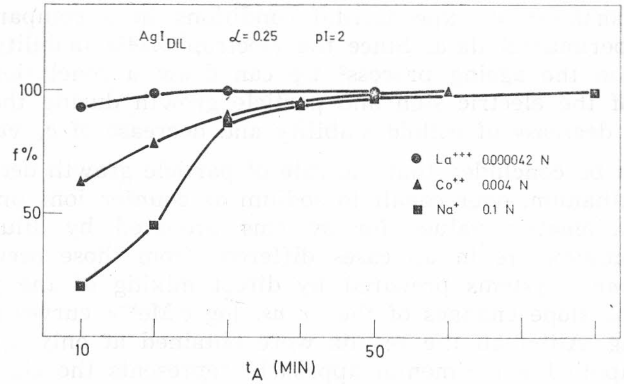

Figure 2. Systems; the silver iodide sols AgI_{DIL} (0.0025 mol/l) at 0.01 M NaI prepared by addition of a complex $(AgI)_x \cdot (NaI)_y$ solution into 0.1 N $NaNO_3$, 0.004 N $Co(NO_3)_2$ and/or 0.000042 N $La(NO_3)_3$ solution at 293 K. The fraction $f^0/_0$ of sedimented silver iodide is presented as a function of the aging time (t_A in minutes).

The particle charge and electrophoretic mobility w of 10 and 60 minutes aged AgI were determined on an ultramicroscope with a double capillary in a Smith-Lisse type electrophoretic cell. The average of seven measurements on samples was taken as the result (Figure 3).

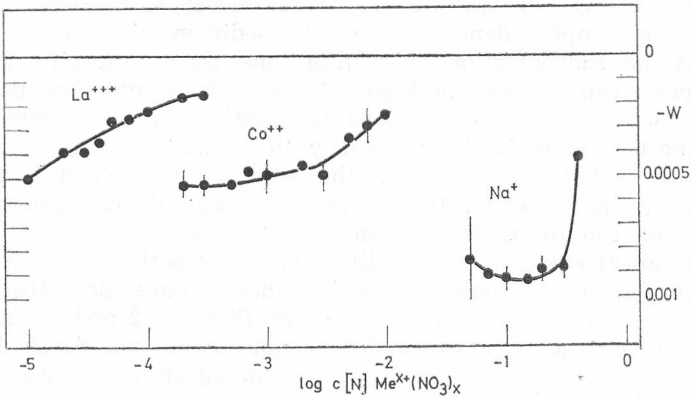

Figure 3. Systems; the silver iodide sols AgI_{DIL} (0.0025 mol/l) at 0.01 M NaI prepared by addition of a complex $(AgI)_x \cdot (NaI)_y$ solution into $NaNO_3$, $Co(NO_3)_2$ and/or $La(NO_3)_3$ solutions of various concentrations. Electrophoretic mobility w ($cm^2\ s^{-1}\ v^{-1}$) plotted against the metal nitrate $Me^{x+}(NO_3)_x$ concentrations (normality N in logarithmic scale).

RESULTS AND DISCUSSION

Typical curves »τ *vs.* log *c*« of the counter ion show sharp maxima (Figure 1). The usual method of the determination of critical coagulation concentrations, c_k, using the extrapolation to zero turbidity renders variable results. Because of that the values at the maximum turbidity τ (the »Tyndall maxima«) are chosen as c_k values. Absolute τ values determined according to Težak's extrapolation method decrease with ageing of sols in all cases. The observed phenomena are in good agreement with X-ray data on the crystal growth in silver iodide suspensions[4]. The adsorption capacity of the sol particles decreases markedly with ageing, yet differently at different conditions[2], indicating the importance of experimental conditions in a comparative consideration of experimental data. Since the electrophoretic mobility data show a dependence on the ageing process[2] we can draw a conclusion about the parallel drop of the electric sign and particle growth during the aging; the results are the decrease of colloid stability and decrease of c_k values.

Thus it can be concluded that the rate of particle growth decreases when going from lanthanum, over cobalt to sodium as counter ions present in the systems. Tyndallometric values for systems prepared by dilution of the $(AgI)_x(NaI)_y$ complex are in all cases different from those occuring in the *'in statu nascendi'* systems prepared by direct mixing of the precipitating components. The slope changes of the »τ *vs.* log c Me^{x+}« curves are a consequence of aging. Although the results were obtained at only approximately equal c_k, the applied experimental approach, represents the closest approximation to the 'equivalent' colloid conditions. The results represented in Figure 2 show the fastest sedimentation of sols in the presence of lanthanum at c_k, and the slowest sedimentation for systems with sodium counter ions present at c_k.

The sedimentation rate for the sols with cobalt present at c_k lies inbetween the values obtained for the systems with lanthanum and sodium, respectively. 20 minutes after the start of sol formation at 0.000042 N $La(NO_3)_3$ the fraction of sedimentation reaches $f\% = 100$; with 0.004 N $Co(NO_3)_2$ or 0.1 N $NaNO_3$ 50 to 55 minutes are needed for $f\% = 100$. All counter ions are present at c_k; the different $f\%$ values indicate the direct effect of counter ionic charge illustrating the complex dependence of the sedimentation rates on both the valence and the concentration of counter ions. Such a specific influence of cationic species can be seen in Figure 3, too. The electrophoretic mobilities at various counter ion concentrations for lanthanum differ markedly with respect to the w_- values for the systems with sodium, showing a similar curve to those when cobalt is present in the systems. The effect is probably a consequence of the total electrolyte concentration of the system. Low w_- values for sols containing lanthanum in comparison to systems with other ions indicate lower electrostatic stability. The result is the faster sedimentation of sol in the presence of counter ions of higher valence. Both the differences and similarities among the shapes of curves (Figures 2 and 3) indicate that the electrostatic charge of the sol particles is not the only parameter determining the sol stability. In this way, the data considered show complex interfering effects in the systems which appear to be only approximately at 'equal' conditions and the properties of which are dependent on the aging process pointing out the role of TF in a broad sense.

REFERENCES

1. B. Težak, *Faraday Soc. Discuss.* **18** (1954) 196; *Discuss. Faraday Soc.* **42** (1966) 175; B. Težak, E. Matijević, K. Schulz, M. Mirnik, J. Herak, V. B. Vouk, M. Slunjski, S. Babić, J. Kratohvil, and T. Palmar, *J. Phys. Chem.* **57** (1953) 301; B. Težak, E. Matijević, K. F. Schulz, J. Kratohvil, M. Mirnik, and V. B. Vouk, *Faraday Soc. Discuss.* **18** (1954) 63; B. Težak, E. Matijević, K. Schulz, J. Kratohvil, R. Wolf, and B. Černicki, *J. Colloid Sci.* Suppl. 1 (1954) 118; E. Matijević, K. F. Schulz, and B. Težak, *Croat. Chem. Acta* **28** (1956) 81.
2. R. Despotović, M. Herak, M. Mirnik, and Z. Selir, *Tenside* **7** (1970) 245; R. Despotović and V. Karaivanova, *Croat. Chem. Acta* **44** (1972) 215; R. Despotović, Z. Grabarić, and S. Popović, *Croat. Chem. Acta* **45** (1973) 441; R. Despotović, V. Horvat, S. Popović, and Z. Selir, *J. Colloid Interface Sci.*, **49** (1974) 147.
3. M. Mirnik, P. Strohal, M. Wrischer, and B. Težak, *Kolloid Z.* **160** (1958) 146.
4. R. Despotović, Z. Despotović, M. Jajetić, M. Mirnik, S. Popović, and Ž. Telišman, *Croat. Chem. Acta* **42** (1970) 445.
5. R. Despotović, in A. L. Smith (Ed.), »*Particle Growth in Suspensions*«, Pergamon Press, London 1973, p. 121.

SAŽETAK

O starenju i koloidnim svojstvima sola AgI

R. Despotović i J. Kapetanović

Kritične karakteristične veličine nekog koloidnog sistema u objavljenim podacima mogu se razlikovati i za red veličine. Detaljna analiza promjene različitih svojstava solova srebrnog jodida tokom procesa starenja pokazuje ulogu 'vremenskog faktora' u karakterizaciji sistema. Praćenje promjene kritične koagulacijske koncentracije i brzine sedimentacije tokom vremena te elektroforetske gibljivosti u solovima s natrijem, kobaltom i lantanom, pokazuje da strogo uzevši, solovi s različitim koagulacijskim ionima, iako su pojedinačno prisutni u kritičnoj koagulacijskoj koncentraciji, nemaju jednaka koloidna svojstva.

INSTITUT »RUĐER BOŠKOVIĆ«
410001 ZAGREB

Prispjelo 26. rujna 1975.