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On Silver Iodide Suspensions

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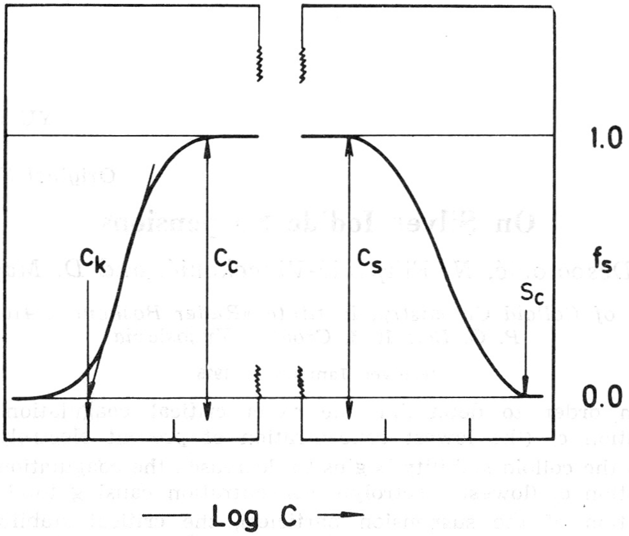
In order to determine the exact critical coagulation concentration c_k (the lowest concentration of present electrolyte at which the colloid stability begins to decrease), the coagulation concentration c_c (lowest electrolyte concentration causing total sedimentation of the suspension particles), the critical stabilization concentration c_s (lowest electrolyte concentration causing an increase of colloid stability or peptization) and the stabilization concentration s_c (lowest electrolyte concentration at which all the colloid particles are suspended) an experimental method was developed. As a model system silver iodide sols with magnesium nitrate and with *n*-laurylamine in the presence of sodium iodide were applied. By radiometric analysis of the distribution of constituent ions between the crystal lattice and the electrolyte, and by centrifugation of samples at various relative centrifugal forces it is possible to determine the real coagulation concentration c_c and the real stabilization concentration s_c exactly, as shown for the investigated systems.

INTRODUCTION

It is usual to determine the critical coagulation concentration, c_k, of an electrolyte for various sols by determination of the tyndallometric values, τ, as a function of the coagulation electrolyte concentration, c; the intersection of the tangent sloped on »τ *vs.* log c« curve with the X-axis (log c) corresponds to the c_k value (Scheme 1). If the coagulation electrolyte is present at the concentration c_k the particles of sol retain the sign of electric charge but the charge is reduced in magnitude and by aging it continualy decreases[1]. At the same conditions, particles of the suspension begin to agglomerate, and in a certain time interval one part of the agglomerated particles settles down. In all observed systems the aging of the system is one of the dominating parameters determining their stability. Because of this fact, it is of importance to determine the actual coagulation concentration, c_c, of a coagulation electrolyte at which the whole sol can be settled down in a short time interval. The lowest concentration of an electrolyte at which the sign of the charge of the colloid particles can be reversed is called the critical stabilization concentration c_s. The effect of overcharging at a certain c_s concentration in the suspension is dependent on the period of aging as was shown for the negative silver iodide suspensions in aqueous solution of a cationic *n*-laurylamine LAN[2]. At a certain stabilization concentration, s_c, all colloid particles are overcharged and stabilized



Scheme 1. The fraction f_s of sedimented sol plotted as a function of concentration c of coagulating or stabilizing electrolyte. The corresponding critical coagulation concentration, c_k; coagulation concentration, c_c; critical stabilization concentration, c_s and stabilization concentration, s_c are indicated by arrows. Schematicaly the shape of a »f_s *vs.* c« curve is similar to the shape of a »τ *vs.* c« curve.

(Scheme 1); as a sediment there is no measurable amount of the solid phase. Since both the values c_s and s_c are dependent on the age of sols, it is of practical and theoretical importance to determine both values quantitatively. For instance, the relation between the sedimentation-peptization, flocculation-deflocculation and overcharging-discharging always are characterized by the corresponding electrolyte concentration. For a detailed analysis of interrelations of such problems it is necessary to determine the c_k, c_c, c_s, and s_c values precisely. Using the centrifugation and radiometric techniques in combination, it is possible to determine the respective concentrations more exactly than by the usual tyndallometric method, which is important for all considerations based on quantitative data. The method and results obtained for the negative silver iodide suspensions in presence of magnesium nitrate and in presence of *n*-laurylamine nitrate are described in this paper.

EXPERIMENTAL

Materials

Pro analysi grade Merck (Darmstadt) chemicals $AgNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, analar grade BDH, NaI and puriss. Fluka *n*-laurylamine were used throughout the experiments, and solutions were standardized by standard methods. *n*-laurylamine nitrate LAN was prepared by dissolving *n*-laurylamine in nitric acid (*p. a.* Merck, Darmstadt).

Preparation of AgI Sols

The sols were prepared *in statu nascendi i. e.* by direct mixing of precipitation components. Silver iodide sols containing $Mg(NO_3)_2$ or LAN were prepared by adding 0.02 M or 0.002 M $AgNO_3$ to an equal volume of 0.04 M or 0.004 M NaI containing $Mg(NO_3)_2$ or LAN. The silver iodide sols were thermostated at 293 K in a Haake ultrathermostat.

Turbidity

10 cm^3 of thermostated silver iodide sols prepared *in statu nascendi* (0.01 M AgI 1, 0.01 M NaI) containing 0.0001 M to 0.02 M $Mg(NO_3)_2$ and aged for $t_A = 1$ min to 4500 minutes were used for turbidimetry. The measurements of tyndallometric values, τ, were made on a Pulfrich photometer combined with a turbidimetric extension (Carl Zeiss, Jena). 10 cm^3 of silver iodide sols (0.001 M AgI/l, 0.001 M NaI) containing 0.0000001 M to 0.01 M LAN and aged for $t_A = 100$ minutes were used for turbidimetry.

Microelectrophoresis

The particle charge and the electrophoretic mobility w of the systems prepared in the same way as for turbidity measurement were analysed by microelectrophoresis using the Smith-Lisse method on suspensions aged 1 minute to 30 000 minutes. The concentration of LAN was varied from 0.000001 M to 0.01 M LAN, and of $Mg(NO_3)_2$ from 0.001 M to 0.01 M.

Sedimentation

The course of sedimentation of silver iodide particles was analysed by means of a radiometric technique. The silver iodide sols were prepared in the standard way with labelled sodium iodide. Sodium iodide solutions containing LAN or $Mg(NO_3)_2$ were labelled with carrier free radioiodine ^{131}I before precipitation. 100 cm^3 of silver iodide suspensions divided into 5 equal samples and containing 0.000001 M to 0.001 M LAN were aged for $t_A = 10$ to 1500 minutes. After t_A minutes 0.20 cm^3 of clear supernatant above the precipitated AgI was pippeted off in order to determine the radioactivity A_t. 0.2 cm^3 of homogenized suspension was used for determining the A_o radioactivity. The fraction f_s of silver iodide which sedimented spontaneously can be derived as $f_s = (A_o - A_t)/(A_t)$. The fraction f_s is determined as a function of LAN concentration for suspensions aged 100 minutes and centrifuged for 5 minutes. Centrifugation was carried out with a SS-1 rotor (Sorvall RC2b type centrifuge) at 1000 to 17000 r. p. m. In the same way f_s was analysed as a function of magnesium nitrate concentration (0.001 M to 0.01 M Mg-nitrate) and as a function of aging ($t_A = 10$ to 1500 minutes).

RESULTS

Tyndallometric values τ measured as a function of LAN and/or $Mg(NO_3)_2$ concentrations (Fig. 1) show the formation of twined maxima. The tyndallometric value τ of the silver iodide suspensions decreases with increasing $Mg(NO_3)_2$ concentration (0.0005 M to 0.0025 M Mg-nitrate). Between 0.0025 M and 0.004 M Mg-nitrate τ becomes very sharp, and after 0.005 M τ decreases (appereance of sediment) till 0.006 M Mg-nitrate. Between 0.006 M and 0.015 M lies a second maximum (0.01 M Mg-nitrate). For AgI + NaI + LAN systems the twinned maxima lie at 0.00006 M and 0.0002 M LAN. Sharp increases of τ take place at 0.00002 M to 0.00006 M LAN (negatively charged AgI particles) and at 0.0002 M to 0.0007 M LAN (positively overcharged particles).

The tyndallometric τ value measured as a function of the silver iodide suspension age depends on the Mg-nitrate concentration (Fig. 2). At higher Mg-nitrate concentration higher τ values are obtained (maxima for τ *vs.* log t_A at $t_A = 100$ minutes). After $t_A = 100$ minutes, in all cases τ sharply decreases with aging toward 1500 minutes.

Electrophoretic mobility w ($cm^2\,s^{-1}\,V^{-1}$) is measured as a function of the silver iodide suspension age in the systems with various Mg-nitrate concentrat-

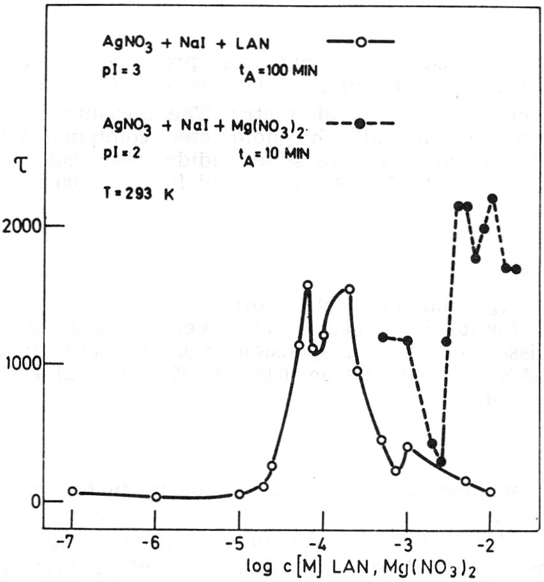


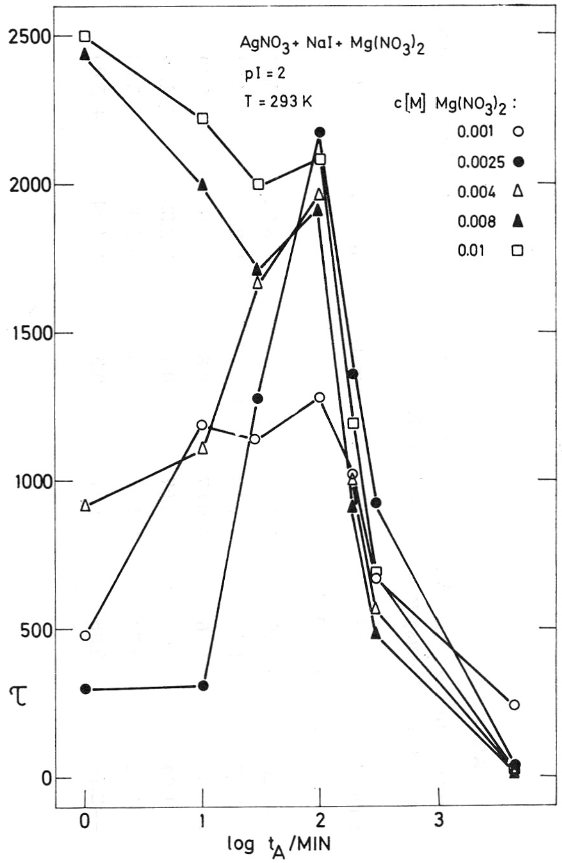
Fig. 1 — Systems: $AgNO_3 + NaI + LAN$ (full line) and $AgNO_3 + Mg(NO_3)_2 + NaI$ (broken line). Tyndallometric values τ measured as a function of the concentration of LAN and/or $Mg(NO_3)_2$ for suspensions aged at 293 K for $t_A = 10$ minutes or 100 minutes.

ion (Table I.). The obtained results show a decrease of w_- values with increasing concentration of Mg-nitrate present in the systems, and an insignificant influence of the suspension aging for the time interval of 10 to 1500 minutes (Fig. 3). The average w value determined for the AgI suspensions which were stirred before microelectrophoretic measurements is in all cases higher than the values for the suspensions which were not stirred before microelectrophoretic measurements is in all cases higher, than the values for the suspensions which were not stirred before the measurements (Table I). The electrophoretic mobility of silver iodide suspensions with LAN was measured as a function of aging (Table II). The results obtained show a marked

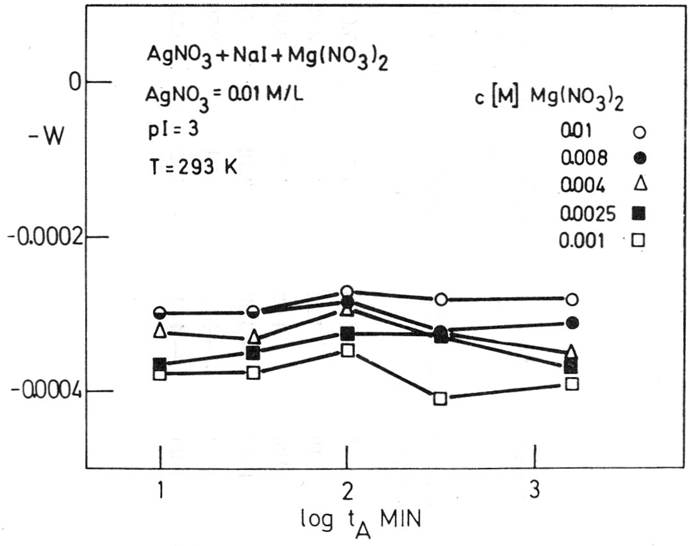
TABLE I

System: $AgNO_3 + Mg(NO_3)_2 + NaI$. *Electrophoretic mobility* w_- *of the silver iodide sols determined as a function of age of the systems containing* $Mg(NO_3)_2$ *at various concentrations. Sols were aged for* $t_A = 10$ *to* 1500 *minutes at* 293 K *in the presence of* 0.001 M NaI.

c(M) $Mg(NO_3)_2$:	0.001	0.0025	0.004	0.008	0.01
t_A/min:				$[w_-/cm^2\ V^{-1}\ c^{-1}] \times 10^4$	
10	3.7	3.7	3.2	3.0	3.0
30	3.7	3.5	3.3	3.0	3.0
100	3.5	2.9	2.9	2.8	2.9
300	4.1	3.3	3.3	3.3	2.8
1500	3.9	3.5	3.5	3.1	2.8



tem: $AgNO_3 + Mg(NO_3)_2 + NaI$. Tyndallometric value τ measured as a fuction of age at various Mg-nitrate concentrations in the system.



ystem: $AgNO_3 + Mg(NO_3)_2 + NaI$. Electrophoretic mobility w_- determined as a ge of the systems containing Mg-nitrate at various concentrations. Sols were aged r $t_A = 10$ to 1500 minutes at 293 K in the presence of 0.01 M NaI (pI = 3).

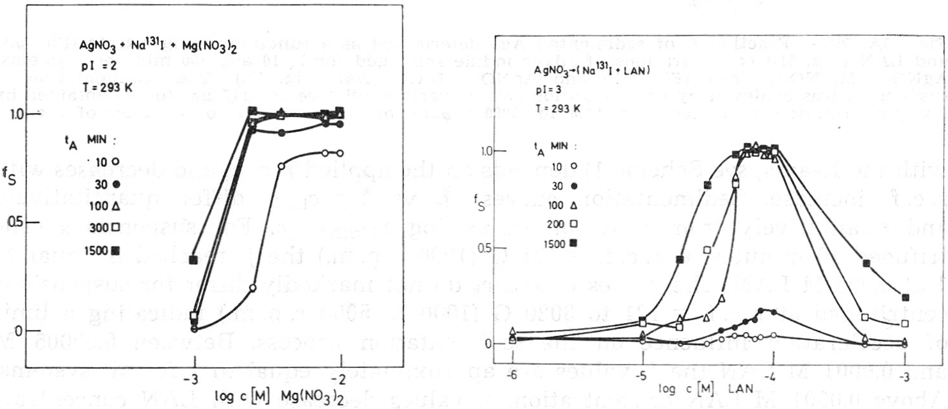
TABLE II.

System: AgI 0.001 mol/dm^3, 0.001 M NaI, c_{LAN} = 0.0000001 M to 0.01 M. *Electrophoretic mobilities* w (cm^2 s^{-1} V^{-1}) *are determined for* t_A *minutes aged suspensions at* 293 K.

c_{LAN}/M	0.0000001	0.000001	0.00001	0.00003	0.00006	0.00007	0.0001	0.0003	0.01
t_A/min					w (cm^2 s^{-1} V^{-1})				
1	— 5.25	--4.71	— 5.07	— 3.26	— 1.46	+ 1.09	+ 1.45	+ 3.62	+ 4.71
10	— 4.22	— 4.09	— 3.83	— 2.70	— 1.46	+ 0.88	+ 1.28	+ 2.67	+ 4.04
100	—4.52	— 4.29	— 3.67	— 2.63	— 1.46	+ 0.67	+ 0.88	+ 2.98	+ 5.49
1500	— 3.08	— 3.18	— 3.18	— 1.99	— 1.29	+ 0.57	+ 0.78	+ 2.33	+ 4.06
10000	— 4.13	— 4.94	— 3.50	— 1.82	— 0.73	+ 1.26	+ 1.58	+ 2.07	+ 5.53
30000	— 4.01	— 6.32	— 3.30	— 2.77	— 0.98	— 1.77	+ 0.99	+ 1.74	+ 5.09

influence of the LAN concentration. For $t_A = 1500$ min at constant LAN concentrations negative electrophoretic mobilities increase, and positive mobilities decrease within the same time interval. In systems aged for $t_A = 100$ minutes (the same system as for the τ determination) the zero point of the electrophoretic mobility w_o lies between 0.00006 M and 0.00007 M LAN. If the electrophoretic mobility is not measured on a stirred sample, *i. e.* if the »optically clear« supernatant is pippetted off, both electrophoretic mobilities, negative and positive, increase with aging (not shown) with the time interval from 10 to 1500 minutes.

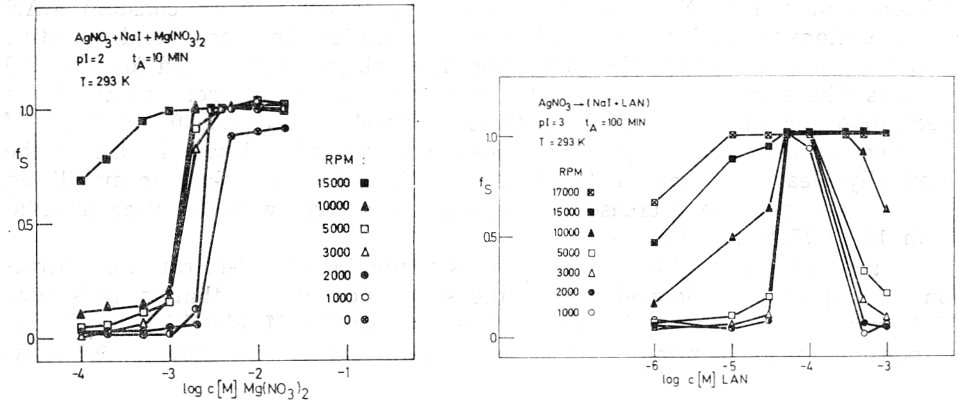
Fraction sedimentation f_s measured as a function of Mg-nitrate concentration (Fig. 4) shows a dependence on the suspension age, so that for sols aged 1500 minutes f_s reaches the value $f_s = 1$ at 0.0025 M $Mg(NO_3)_2$ while for suspensions aged 10 minutes at 0.01 M Mg-nitrate, f_s is as low as 0.8 only.



Figs. 4A, 4B — Fraction f_s of sedimented AgI determined as a function of Mg-nitrate (Fig. 4A) and LAN (Fig. 4B) concentration of silver iodide sols aged for t_A from 10 to 1500 minutes. Systems: $AgNO_3 + Mg(NO_3)_2 + NaI$ (Fig. 4A) and $AgNO_3 + LAN + NaI$ (Fig. 4B). The sedimentation is a spontaneous process.

The sedimentation fraction f_s measured as a function of LAN concentration depends on the age of the silver iodide suspension (Fig. 4). The »f_s *vs.* log c_{LAN}« slopes between 0.000001 M and 0.0001 M LAN correspond to the negatively charged silver iodide particles, and between 0.0001 M and 0.001 M LAN to the positively overcharged silver iodide particles. The maxima at $f_s = 1$ correspond to the completely sedimented silver iodide.

The sedimentation fraction f_s of silver iodide suspensions measured as a function of LAN or $Mg(NO_3)_2$ concentrations depends on the applied centrifugal forces and on both LAN and/or Mg-nitrate concentrations (Fig. 5). Silver iodide particles in suspensions aged for 10 minutes before radiometric analysis (0 r. p. m.) cannot be completely separated even at 0.02 M Mg-nitrate. Suspensions centrifuged for 10 minutes at 1000 r. p. m. (*ca* 121 G = relative centrifugal force r. c. f.) settle down completely ($f_s = 1$) only at 0.003 M Mg-nitrate. At 15000 r. p. m. (r. c. f. ca 27000 G) silver iodide particles are completely sedimented ($f_s = 1$) at 0.001 M $Mg(NO_3)_2$. The lowest minimal concentrations c_c at which the suspensions are completely settled down ($f_s = 1$) decrease with r. c. f. increase. Critical coagulation concentration c_k at which sedimentation begins (obtained as intersection of the tangent on the steep part of the curve



Figs. 5A, 5B — Fraction f_s of sedimented AgI determined as a function of Mg-nitrate (Fig. 5A) and LAN (Fig. 5B) concentrations of silver iodide sols aged for t_A 10 and 100 minutes. Systems; $AgNO_3 + Mg(NO_3)_2 + NaI$ (Fig. 5A) and $AgNO_3 + LAN + NaI$ (Fig. 5B). The sedimentation of suspension was achieved by centrifugation sols at various relative centrifugal forces obtained by various rotation velocities from 1000 to 17000 r. p. m. or from G = 121 to G = 27000 of r. c. f.

with the X-axis; see Scheme 1) depends on the applied r. c. f., and decreases with r. c. f. increase. Sedimentation curves »f_s vs. log c_{LAN}« differ quantitatively and qualitatively from those of »f_s *vs.* log $c_{Mg(NO_3)_2}$«. For suspensions centrifuged 10 minutes at r. c. f. = 121 G (1000 r. p. m.) the f_s reached is equal to 1 at 0.005 M LAN. The values c_c and c_k do not markedly differ for suspensions centrifuged at r. c. f. = 121 to 3020 G (1000 to 5000 r. p. m.) indicating a limit of acceleration influence on the sedimentation process. Between 0.00005 M and 0.0001 M LAN the f_s values are approximately equal to 1 for all systems. Above 0.0001 M LAN concentration, f_s values decrease with LAN concentration. When higher r. c. f. are applied, the sedimentation fraction increases.

DISCUSSION

In the series of tyndallometric measurements carried out in order to establish the c_k values, the obtained »τ *vs.* log $c_{\text{coagulating electrolyte}}$« curves show the appearance of several maxima and minima[3]. Based on the tyndallometric data, for such a type of curve the determinations of critical coagulation and stabilization concentrations are problematic and doubtful. As was already shown[4] the distribution of constituent components (cationic and anionic) between the crystal lattice and the liquid phase can be determined with sufficient accuracy on the basis of the analysis of the radionuclide distribution in the »solid/liquid« phases. The change of colloid stability toward sedimentation of colloid particles (or to peptization) corresponds to a change of distribution of the constituent ions between the separated solid and the homogeneous liquid phase. Because of these facts, the changes of colloid stability at the critical concentrations must be detectable by means of the radiometric technique with adequate preciseness. The τ values plotted against the concentrations of LAN and/or Mg-nitrate show (Fig. 1) double Tyndall maxima. For the AgI + NaI + + LAN systems it was shown that the double maxima are a consequence of the aging processes[3]. In the systems with an inorganic coagulating electrolyte the results show (Fig. 2) the appearance of a broadened Tyndall maximum indicating the dependence of the c_k value on the suspension age. Because of this fact, variously aged systems were investigated.

The electrophoretic mobility is dependent on the valency and concentration of the coagulating ions. The zero point of electrophoretic mobility w_o is not achieved in all cases at the c_k concentrations[5]. The results collectted in Fig. 3 show no significant influence of age (up to 1500 minutes of aging) on w_{-} values, and a pronounced dependence on the coagulating electrolyte concentration. It is of importance that at 0.01 M $Mg(NO_3)_2$ the electrophoretic mobility is of negative sign, although all the particles settled down spontaneously (Fig. 4.A). Variously aged negative silver iodide suspensions at various Mg-nitrate concentrations reach different fractions of sedimentation f_s. Marked differences of »f_s *vs.* log c_{Mg}« slopes between 10 and 30 to 1500 minutes aged suspensions indicate a fast agglomeration process after 30 minutes of aging. Between 90 to 100 per cent of present silver iodide aged for 30 minutes is sedimented spontaneously at 0.0025 M Mg-nitrate. The suspension aged for 1500 minutes at the same concentration of coagulating electrolyte is completely settled down, $f_s = 1$. For this system 0.0025 M Mg-nitrate is the coagulating concentration c_c, while c_k is approximately 0.00057 M $Mg(NO_3)_2$. The difference between c_c and c_k values is larger for the system aged for 10 minutes only indicating the doubtful or relative meaning of the c_k value. Detailed electrophoretic examinations of these systems show a complex dependence of the w value on the coagulating electrolyte concentrations and on the age of samples, because for the »clear« fraction of suspension and the samples taken from a stirred suspension the directions of the electrophoretic mobility changes are opposite. Such behaviour of suspension properties indicate different agglomeration, ripening and nucleation processes, rates, and equilibria[6] at different conditions — age and concentration of the components.

In the silver iodide suspensions with added LAN the colloid stability depends on the LAN concentration variously for differently aged samples (Fig. 4.B). The effects are qualitatively similar to those observed in systems with $Mg(NO_3)_2$, but the c_k and c_c values differ. Since LAN causes the change of sign of particle charge (Table I.), at greater LAN concentrations the fraction f_s decreases. The decreases of f_s values are dependent on the LAN concentration in a different way for variously aged samples. The largest differences of stability changes toward to the agglomeration and the peptization or stabilization take place between 30 and 100 minutes of aging, indicating the largest changes of colloid properties within these time intervals.

The radiometric data obtained are collected in Fig. 4. They show that for the system aged for an adequate time the c_k and c_c values differ, and that the differences between the c values do not permit them to be taken as identical or substituted one for the other. The same conclusion can be drawn for the critical stabilization, c_s, and the stabilization concentrations, s_c, obtained by a spontaneous sedimentation for the systems with LAN. If the suspension particles are separated from the liquid phase within a short time (using for instance a centrifuge) at any of the c_k, c_c, c_s or s_c concentrations of Mg-nitrate or LAN the differences between the c_k and c_c values are small. The extrapolation of the tangent on the »f_s *vs.* log c« curve to the concentration axis (Scheme 1) indicates at the same time the c_k and c_c values which may be coincident with or significantly different from each other (Fig. 5). The results obtained show that at a certain relative centrifugal force, r. c. f., the acceleration, G, does not influence the separation efficiency since the f_s value remains constant ($f_s = 1$). The differences between the c_s and s_c values are larger in comparison to the c_k and c_c values, although the family of »f_s *vs.* log c« curves obtained for samples centrifuged at up to 5000 r. p. m., follows a very similar course indicating the same c_s value. The obtained s_c values cover a broader concentration range for a chosen and equal r. p. m. value than the c_k values. By extrapolation of the »G *vs.* log c_{CAN}« (Scheme 1) curve to G = 0 the real stabilization s_c concentrations have been determined (Fig. 6). Of course, by extrapolation to $f_s = 1$ the c_c or c_s values can be obtained (Scheme 1).

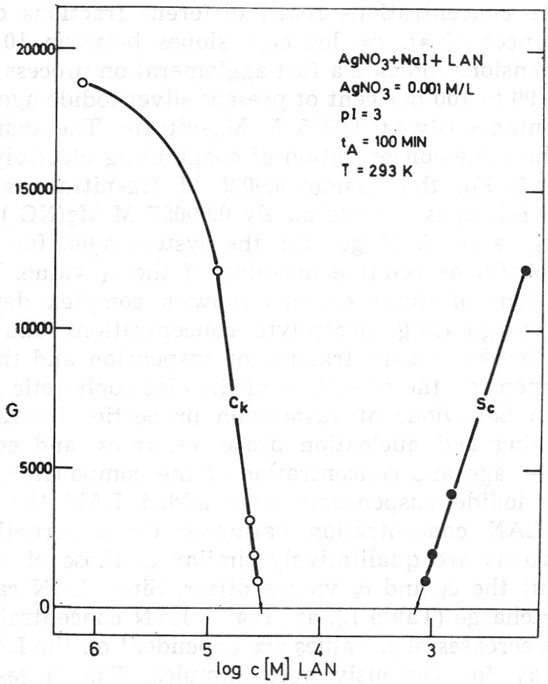


Fig. 6 — System; $AgNO_3$ + LAN + NaI. The relative centrifugal forces (shown as acceleration G) at which the c_k and s_c values were obtained are plotted as a function of LAN concentration (in log scale).

Finally we can conclude that by using a combination of centrifugation at various r. c. f. and radiometric analysis it is possible to determine the c_k, c_c, c_s, and s_c values with sufficient accuracy and much better than by tyndallometry, the values being independent of the aging processes.

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SAŽETAK

O suspenzijama srebrnog jodida

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U cilju određivanja točne vrijednosti kritične koagulacione koncentracije c_k (najniža koncentracija prisutnog elektrolita s kojom počinje opadati koloidna stabilnostnost), koagulacione koncentracije c_c (najmanja koncentracija koagulacionog elektrolita koja izazivlje potpuno taloženje čestica suspenzije), kritične stabilizacione koncentracije c_s najmanja koncentracija elektrolita koja izazivlje porast koloidne stabilnosti ili peptizacije) i stabilizacione koncentracije s_c (najniža koncentracija uz koju su sve koloidne čestice suspendirane) razvijena je mjerna metoda. Kao modelni sistemi primjenjeni su solovi srebrnog jodida sa magnezijevim nitratom, odnosno sa n-laurilaminom uz natrijev jodid. Pomoću radiometrijske analize raspodjele konstitucionog iona kristalne rešetke i koagulacionog elektrolita, centrifugiranjem uzoraka uz različite relativne centrifugalne sile moguće je točno odrediti stvarne koagulacione c_c i stabilizacione s_c koncentracije, kao što je to pokazano na ispitivanim sistemima.

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