Radiometric Analysis of Silver Iodide Sols
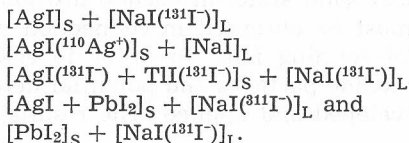
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With the ultimate goal to investigate (*a*) the formation of the solid phase by precipitation from electrolytic solutions, and (*b*) processes characteristic of the interaction between the solid phase and the electrolytic solution, the well-known radiometric methods of analyses have been applied, as well as new radiometric methods for the analysis of colloidal system developed. The methods applied are extremely sensitive, selective, and accurate. The new methods have been checked up by comparison of the obtained results with the standard classical methods, such as X-ray diffraction, turbidimetry, conductometry, differential thermic analysis, and also by published data. As models, the following systems were applied:

$$[AgI]_S + [NaI(^{131}I^-)]_L$$
$$[AgI(^{110}Ag^+)]_S + [NaI]_L$$
$$[AgI(^{131}I^-) + TlI(^{131}I^-)]_S + [NaI(^{131}I^-)]_L$$
$$[AgI + PbI_2]_S + [NaI(^{311}I^-)]_L \text{ and}$$
$$[PbI_2]_S + [NaI(^{131}I^-)]_L.$$

The abundance of interesting data on the formation of a colloidal system, transformation of substructures, and the interaction between the solid and liquid phase are contained in tables and figures. The results are viewed through the analysis of

   (*i*) heterogeneous exchange process on isoelectric AgI;

  (*ii*) precipitation of silver iodide at various temperatures;

 (*iii*) coagulation of electrolytes of various valencies;

(*iiii*) comparison on tyndallometric maxima and the sedimentation rates of sol particles;

   (*v*) comparison of sedimentation rates of variously aged particles;

  (*vi*) determination of ideal concentrations characteristic of coagulation, flocculation, and deflocculation by radiosedimentation analysis and by turbidimetry;

 (*vii*) comparison of sedimentation fraction with tyndallometric results for negative sols in the presence of anionic surfactant;

(*viii*) the interaction of precipitation components during the emergence of a polycomponent colloid system with the verification of the radiometric method by the application of classical methods;

(ix) the development of a quantitative radiometric analysis that enables one to follow the emergence of the solid phase sub-structures and the transformations;

(x) »nascent« structures from the ideal liquid to the ideal solid phase;

(xi) effects of amphoteric cationic species on the complex solubility of silver iodide, and

(xii) heterogeneous exchange processes in colloid systems prepared by the addition of different cationic precipitating components.

INTRODUCTION

The phenomenon of colloid stability of inorganic sols in aqueous media is scientifically interesting and very important from a practical point of view. There is a voluminous literature with various results related to the phenomenology of colloid systems. A well-known systematic approach is the Težak concept[1] described by Težak and co-workers in the last forty years. The main subject of the majority papers by Težak and co-workers seems to be the interrelations between various substructures of growing or nascent colloid species and surrounding media. In a series of papers it was shown that the chemical characteristics of solvents and dissolved substances are closely related to the colloid properties of the observed systems[1]. The role of silver halide complexes[2], hydrolytic species[3] and acidity of media[4], electrochemical properties[5,6], influences of polyelectrolytes[7], adsorption capacity[8], particle size and crystal modifications of silver iodide[9] are well-described subjects of Težak's school. The very good agreement of the results obtained by various techniques confirm the Težak concept[1], especially on the relation of interactions and the dependency of colloid particles versus chemical conditions at which sols form.

Strictly following the idea of spontaneous but step-by-step growing process from the ideal liquid state to the ideal solid state, in each transition or non-equilibrium state a colloid particle must be observed in connection with surrounding constitutive or potential-determining ions. In order to collect data on interactions between colloid silver iodide particles and potential-determining ions, radiometric techniques were developed and applied. The results obtained are given in the present paper.

EXPERIMENTAL

Analar grade B. D. H. chemicals Al-, Ag-, Co-, Mg-, Na-, Pb-, and Tl-nitrate, and KI and NaI, were used throughout the experiments. Sodium n-dodecyl sulfate NaDDSO$_4$ of a special purity grade was supplied by B. D. H. Solutions were prepared and standardized by the standard methods. n-Dodecylammonium nitrate DDANO$_3$ was prepared from the purity grade n-dodecylamine and p. a. nitric acid. The samples were recrystallized twice from 50% ethanol solution. The recrystallized DDANO$_3$ was dried in vacuo at 330 K. The water used was double distilled in an all-DURAN 50 apparatus. The prepared systems were kept at a constant temperature of 293.0 ± ± 0.2 K in HAAKE constant temperature circulators. Radioiodine $^{131}I^-$ was used as a carrier-free $^{131}I^-$ solution in NaI form. Radioactive $^{110}Ag^+$ was of high specific radioactivity. The radioactive samples were counted in a well type NaI—TlI scintillation counter with an EKCO Electronics scaler.

The following designations were used for the prepared systems:

(i) Silver iodide sols containing AgI 0.001 mol/dm^3 and NaI 0.001 mol/dm^3 were prepared by the standard procedure[10]. Sols aged for 600 s were labelled with $^{131}I^-$, and an aliquot of clear supernatant was used after t_A seconds to determine the radioactiviti A_t. The initial radioactivity A_o was determined on identical systems labelled in the same way and having the same composition as the experimental systems but

without AgI. Different equilibrium radioactivities $A_{(\infty)_i}$ were calculated by the equation after Zimen[11]

$$A_{(\infty)_i} = [A_o - (x/V) \sum_{1}^{i-1} A_{t_i}] [\alpha + 1 - (x/V)(i-1)]^{-1}$$

where A_o — is the radioactivity of the system at the beginning of the process (t_o);

x — the volume of the sample whose radioactivity A_t is being determined;

V — the total volume of the system;

A_t — the radioactivity of the system at time t_A;

α — the ratio of the amount of I⁻ in the liquid (n^L) phase and the amount of I⁻ in the present solid (n^S) phase: $\alpha = n^S/n^L$;

i — ordinal number of the sample.
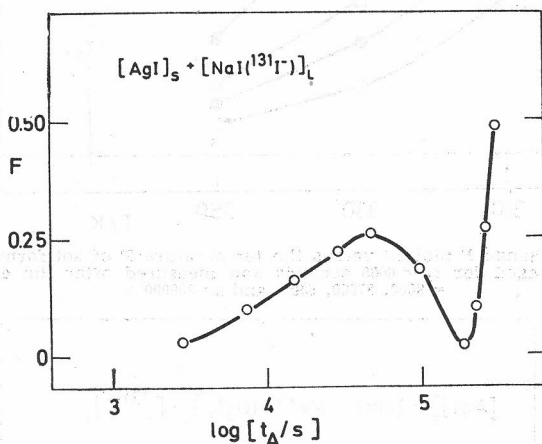
The results are presented in Figure 1.

Figure 1. System: $AgI_S + NaI(^{131}I^-)_L$. Fraction exchange F ploteed versus exchange time t_E (log scale, seconds).

(ii) The influence of precipitation temperature on a heterogeneous exchange process in $[AgI]_S + [I^-]_L$ systems was analysed on sols prepared by mixing 0.002 mol/dm³ AgNO₃ and 0.004 mol/dm³ NaI solutions at 310 K, 330 K, and 350 K. The process of heterogeneous exchange was determined in the same way as for the systems described in (i). The results are presented in Figure 2.

(iii) The influence of the valency of inorganic ions on the heterogeneous exchange process was determined for sols prepared in the presence of 0.10 mol/dm³ NaNO₃, 0.0020 mol/dm³ Co(NO₃)₂, and 0.000020 mol/dm³ Al(NO₃)₃ at pH = 2.7. The same procedure was applied to determine a fraction (F) of heterogeneous exchange[12]; the results obtained are presented in Figure 3.

(iv) The influence of valency of coagulating ions on the sedimentation rate was determinated as follows: (A) In the first step, tyndallometric values τ were recorded as a function of concentration of coagulating ions of various valency (NaNO₃ for x = 1; Co(NO₃)₂ for x = 2; Al(NO₃)₃ for x = 3 all at pH = 2.7) for silver iodide sols with AgI 0.001 mol/dm³ at NaI 0.001 mol/dm³. Tyndallometric values were determined for systems aged for 10 and 1500 minutes. The tyndallometric values thus obtained, were higher for aged systems and lower for fresh ones, as presented schematically in Figure 4. (B) Next, the rates of sedimentations were determined radiometrically for the same silver iodide sols prepared at coagulation concentrations C_c of mono-, two-, and three-valent coagulating ions. The radioanalytical procedure was the same as described previously[13]. The results are presented schematically in Figure 4.
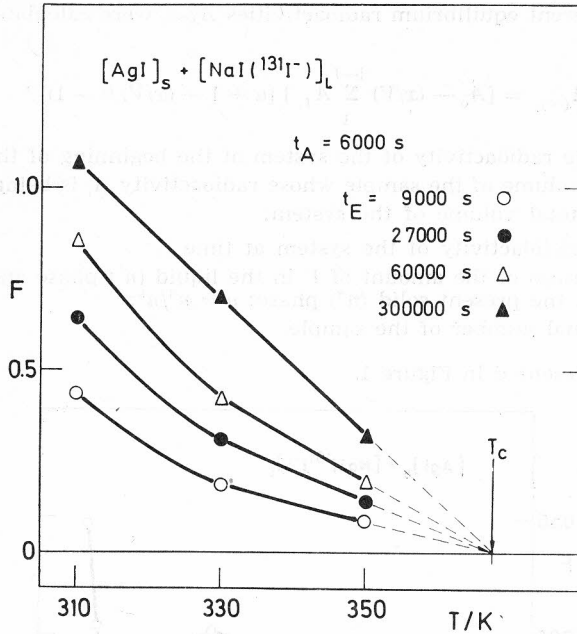
Figure 2. Fraction exchange F plotted versus the temperature T of sol formation (T Kelvins K) for silver iodide sols aged for $t_A = 6000$ seconds and measured after the exchange times $t_E = 9000$, 27000, 6000, and/or 300000 s.
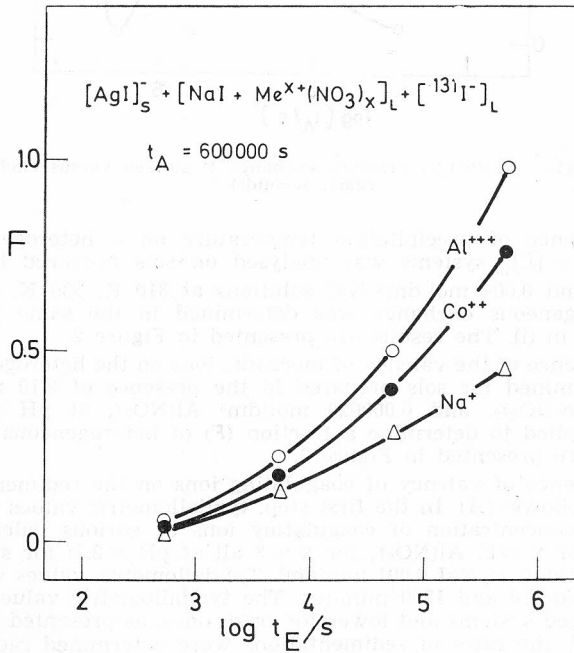

Figure 3. The influence of the valency of coagulating ions on the heterogeneous exchange process in the systems labelled by [131]I^-, aged for 600000 s prior to the initiation of the exchange process.
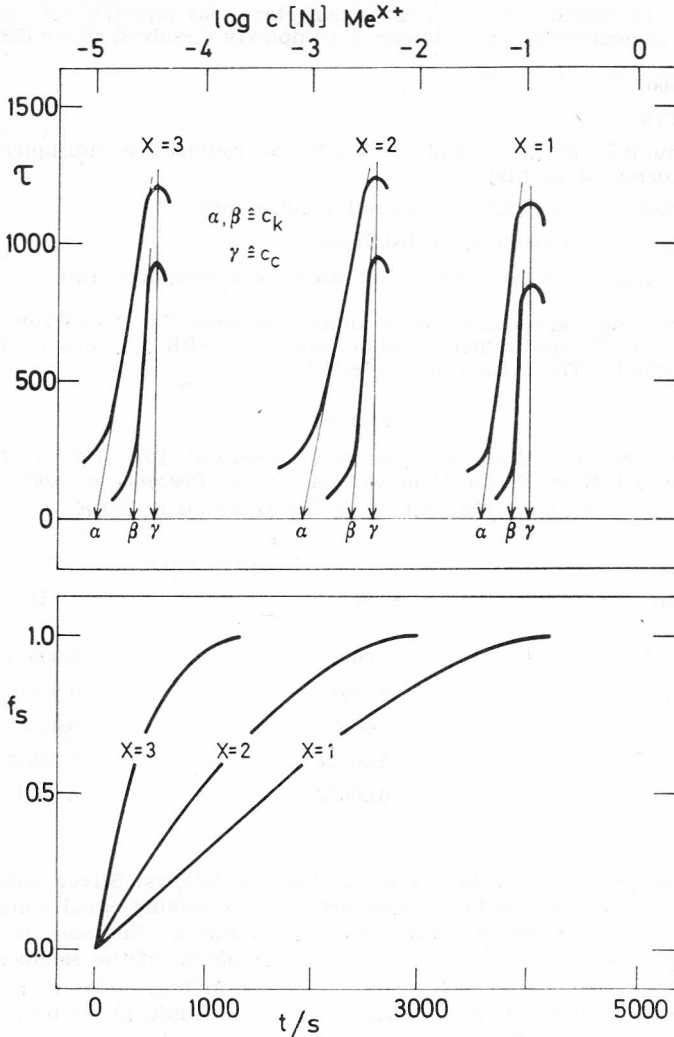
Figure 4. Upper: Tyndallometric value τ as a function of concentration and valency ($x = 1$, 2, 3) of coagulating metal ions Me^{x+} (log scale, normal concns.) in silver iodide sols aged from 600 to 60000 seconds. Alfa-values correspond to the results obtained for well aged sols and beta-values for the fresh ones. Gamma-values lie below the tyndall maxima for both fresh and well aged sols. Down: Fraction f_S of a silver iodide sol precipitated following the sol aging for t second s under the »critical coagulating concentrations« of sodium ($x = 1$), cobaltous ($x = 2$), and lanthanum ($x = 3$) nitrates.

(*v*) The solubility of silver iodide in Al-nitrate solutions was determined by a radioactive tracer technique[14] at (293.0 ± 0.1) K. Radioactive silver iodide $Ag(^{110}Ag)I$ was prepared in the same way as the dried isoelectric silver iodie[10,14] except that prior to the precipitation the silver nitrate solution was lebeled by the addition of $Ag(^{110}Ag)NO_3$ solution of a high specific radioactivity. The dried redioactive $Ag(^{110}Ag)I$ of specific γ radioactivity was placed into $KI + Al(NO_3)_3$ solutions of various concentrations and stirred at a constant temperature of (293.0 ± 0.1) K for 70 hours.

After 70 hours of equilibration, a clear supernatant was pipetted out for the determination of β radioactivity. The number of complexly dissolved silver iodide was

$$n = 1000 \; \beta \, g \, (M \cdot x \cdot I^0)^{-1}$$

where $\gamma = I^0/N$

N = number of gram mol $(N = g/M)$ of radioactive substances giving I^0 corrected counts;

M — molecular weight of radioactive substances;

g — grams of radioactive substances;

x — volume of clear supernatant used for radiometry (ml).

The applied method enables one to determine from the radioactivities β and I^0 for selected x ml of equilibrated solution saturated with g grams of substance of molecular weight M. The results are collected in Table I.

TABLE I

Complexes Solubility (n = Number of Moles of Dissolved AgI) of Silver Iodide in KI Solutions of m_o KI Molar Initial Concentration in the Presence of 0.005 mol/dm³ (A) and 0.5 mol/dm³ (B) Al-nitrate Solutions at 293 K

m_o KI	n/mol dm⁻³	
mol/dm³	A	B
0.005	0.00010	0.00015
0.01	0.00012	0.00018
0.05	0.00022	0.00033
0.1	0.00034	0.00052
0.5	0.00032	0.00043

(vi) The sedimantation rate vas determined as follows: Silver iodide sols AgI 0.001 mol/dm³ in NaI 0.001 mol/dm³ were prepared by mixing equal volumes of 0.002 mol/dm³ AgNO₃ and 0.004 mol/dm³ NaI(^{131}I) solutions. The sols thus prepared were left aging for t_A seconds prior to the determination of the sedimentation rate. The same aliquots of sols were transferred into centrifuge tubes at predetermined t_A intervals. Silver iodide sol was separated from the liquid phase by centrifugation at 20000 G for t_R seconds. The radioactivity A of the liquid phase was determined by a standard method[13]. The equilibrium radioactivity A_∞ was determined in the same way but for systems with 0.001 mol/dm³ La-nitrate as a coagulating electrolyte. An aliquot of clear supernatant following centrifugation contained no silver iodide. In order to determine the standard initial radioactivity A_0, the volume of 0.001 mol/dm³ NaI corresponding to the volume of systems with silver iodide was labelled with NaI(^{131}I). The same volume of aliquot of labelled clear solution was used to determine the value of A_0. The sedimentation rate as a function of centrifuging time was presented as a change of radioactivity in the liquid phase from A_0 to A_∞ (Figure 5).

(vii) The coagulating concentration C_c, critical coagulating concentration C_k, stabilizing concentration S_c, and critical stabilizing concentration C_s were determined for silver iodide sols in the presence of various concentrations of n-dodecylammonium nitrate DDANO₃. Sols were prepared by mixing an equal volume of 0.002 mol/dm³ AgNO₃ solution with a mixture of 0.004 mol/dm³ NaI(^{131}I) containing various con-
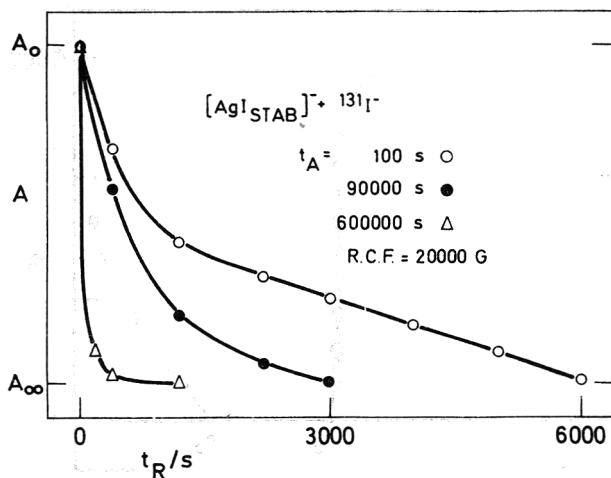
Figure 5. The sedimentation rate of silver iodide sols, obtained by measuring the radioactivity of a clear supernatant A for variously aged sols (t_A seconds). Centrifugation was carried out at constant relative centrifugal forces (R.C.F. = 20000 G) for the time t_R (in second). Recorded results lie between the initial radioactivity A_0 and the equilibrium radioactivity $A\infty$.

centrations of DDANO$_3$. The sols thus prepared were left aging for $t_A = 6000$ s before centrifugation. The centrifugation was performed at various relative centrifugal forces corresponding to an acceleration from 0 to 15000 G. The values obtained for C_c, C_k, S_c, and C_s for sols centrifuged at various G are presented in Figure 6.

(viii) The analysis of the interaction between negative silver iodide sols and sodium n-dodecyl sulfate NaDDSO$_4$ was based on tyndallometric measurements and radiometric determination of sol particle sedimentation. Systems for analysis were prepared as follows:

A solution of 0.002 mol/dm^3 AgNO$_3$ mixed with various concentrations of NaDDSO$_4$ was aged for $t_D = 600$ s prior to mixing with 0.004 mol/dm^3 NaI solution. The sols thus prepared were left aging for $t_A = 72000$ s before tyndallometry and radionalysis. Tyndallometric values were obtained by means of a Pulfrich photometer with a turbidimetric extension. Precipitation with sodium iodide, labelled with radioactive ^{131}I, made possible the separation of a fraction of sedimentation f_S using a Sorvall RC2B superspeed centrifuge at 30000 G. The procedure was the same as described previously[15]. The results are presented in Figure 7.

(ix) In polycomponent systems, the formation of intermolecular species and interactions were analysed for AgI + TlI systems in NaI solution. Mixed systems containing various molar ratios of silver f_{Ag} and thallous f_{Tl} iodide were used for radiometric analysis. The systems were prepared by the precipitation of AgNO$_3$ + TlNO$_3$ solutions with NaI(^{131}I) solution. The sols prepared »in statu nascendi« were taken for turbidity measurements. In order to obtain the phase diagram, differential thermal analysis was performed. The heating rate was 5 K/min. The structural properties of the silver--thallous iodide systems were determined by the X-ray diffraction technique. A narrow range of Bragg angles from $2\Theta = 20^0$ to $2\Theta = 50^0$ was selected. A high-frequency Cambridge conductivity bridge was used to determine the conductivity of the silver--thallous iodide systems. The measured conductivities were expressed as conductivities of the equilibrated and saturated liquors obtained after washing the silver-thallous iodide precipitates. The ratio of iodide ions in the solid phase and in the liquid phase is expressed as $\alpha_\Sigma = n^S/n^L$, where n^S is the amount of I$^-$ in the solid phase and n^L in the liquid phase. The results are collected in Figure 8.
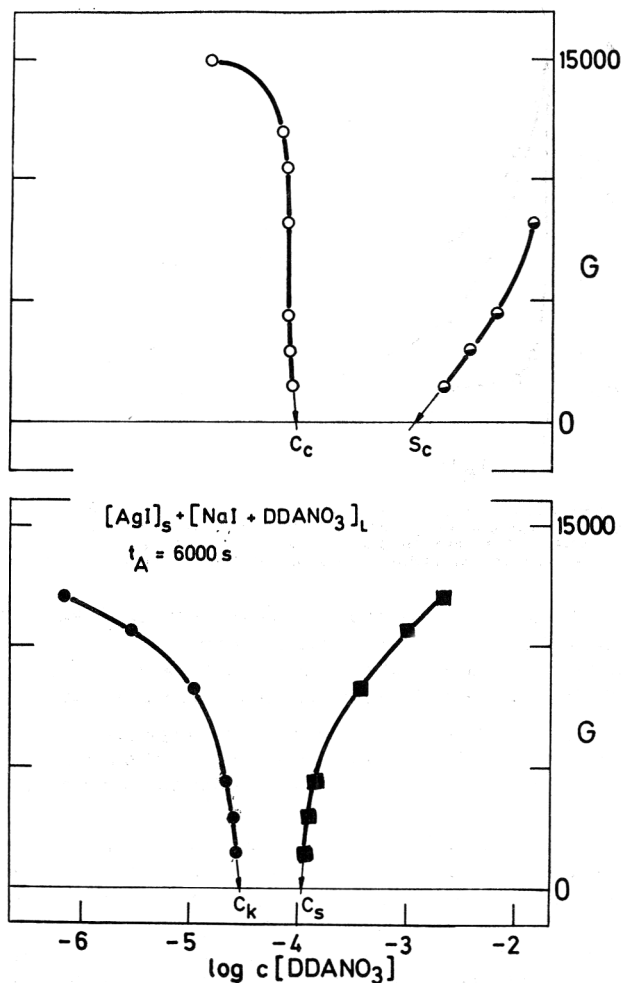
Figure 6. For silver iodide sols containing various concentration (log scale, normal concns.) of DDANO₃ and centrifuged at various relative centrifugal forces (corrsponding to acceleration G) four »G, vs. log c« curves are obtained. The four arrows at $G = 0$ indicate the four ideal characteristic concentrations C_c (open circles; coagulation concentration), S_c (semiopen circles; stabilization concentration), C_k (full circles; critical coagulation concentration), and C_s (critical stabilization concentrations; squares).

(x) The heterogeneous exchange between mixed silver-lead iodide and iodide ions in the liquid phase was examined as follows: Solutions containing cationic components (Ag, Ag + Pb, Pb) were added into KI solution. After $t_A = 600$ s, the systems were labelled with carrier free $^{131}I^-$ in NaI form. After a chosen time interval t_E the clear supernatant was taken off for measurements of the A_t radioactivity. The initial radioactivity A_o and the equilibrium radioactivity A_∞ were determined in the usual way. The results are expressed (Table II) in terms of the fraction exchange,

$$F = (A_o - A_t)/(A_o - A_\infty) \qquad \text{(eq 1)}$$

$$F_\Sigma = f_{Ag}F_{Ag} + f_{Pb}F_{Pb} \qquad \text{(eq 2)}$$

TABLE II

Fraction Exchange F (eq 1) and F_Σ (eq 2) for $[AgI]_S + [NaI(^{131}I^-)]_L$; $[AgI + PbI_2]_S +$
$+ [NaI(^{131}I^-)]_L$ and $[PbI_2]_S + [NaI(^{131}I^-)]_L$ Systems Measured for the Time $t_E (= 6000\ A$
and 90000 B Seconds) of Exchange, and for Various Molar Fractions F of Silver f_{Ag}
and Lead f_{Pb}

f_{Ag}	f_{Pb}	F	F_Σ	F	F_Σ
			A		B
1.00	0.00	0.52	—	0.90	—
0.95	0.05	0.80	0.51	1.02	0.89
0.00	1.00	0.40	—	0.65	—

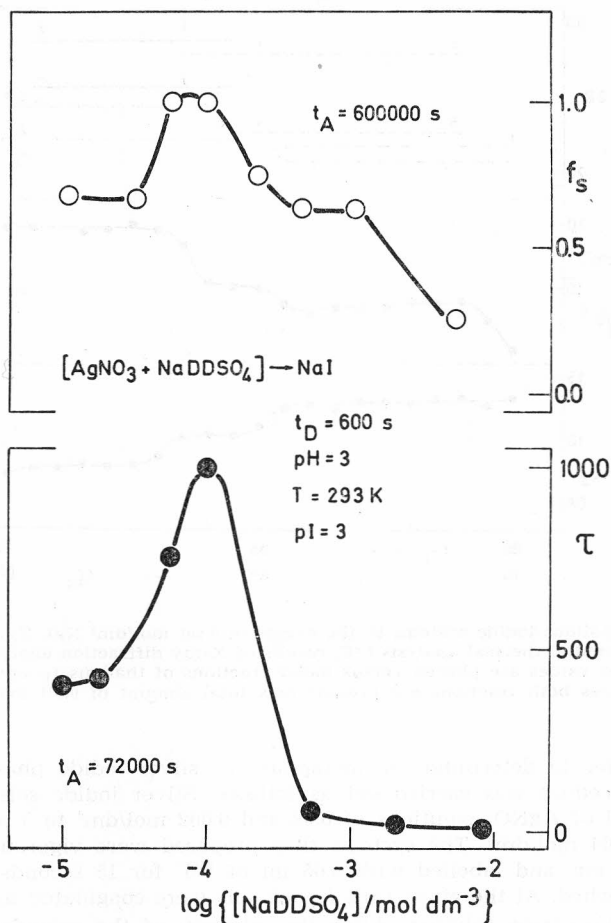Figure 7. Silver iodide sols were aged at 293 K for $t_A = 600000$ second in the presence of 0.001 M NaI at pH = 3. The AgNO₃ + NaDDSO₄ mixture was aged for $t_D = 600$ s prior to the initiation of sol formation. Tyndallometric value τ and fraction f_S of precipitated silver iodide are expressed as functions of NaDDSO₄ concentrations.
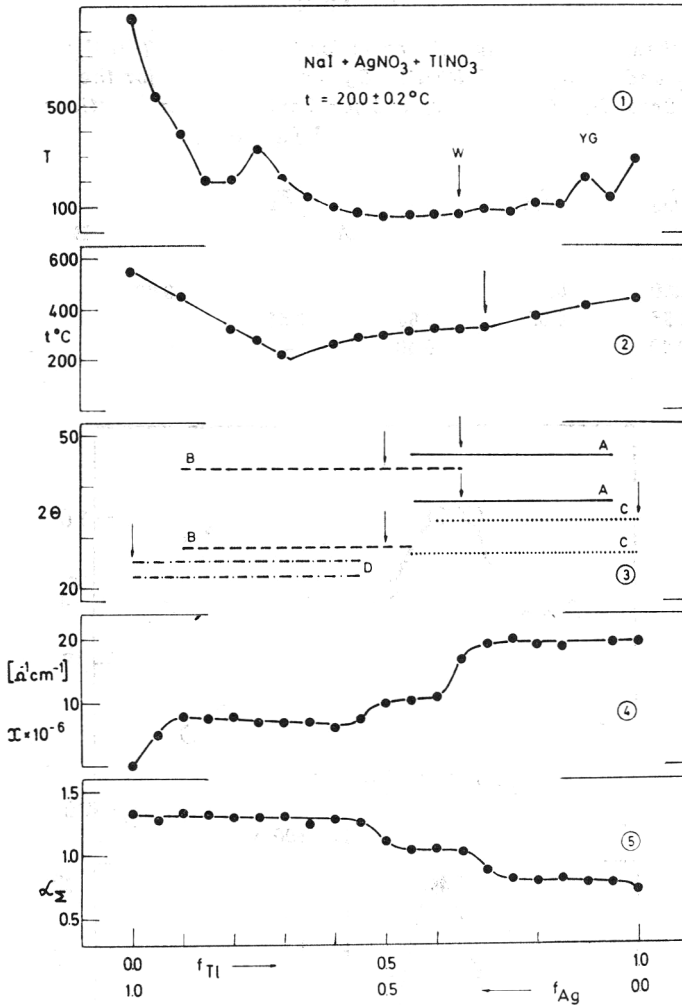
Figure 8. Silver-thallous iodide systems in the excess of 0.001 mol/dm³ NaI. Tyndallometric value τ, results of differential thermal analysis t °C, results of X-ray diffraction analysis 2 Θ, conductivity $κ × 10^{-6}$, and $α_Σ$ values are plotted versus molar fractions of thallous f_{Tl} and silver f_{Ag}, in the prepared mixtures both fractions are present in a total amount of 0.001 mol/dm³ of metals.

(xi) In order to determine the metaphase — silver iodide phase rate. the experimental procedure was carried out as follows: Silver iodide sols were prepared by adding 5 ml of AgNO₃ solutions of 0.02 and 0.002 mol/dm³ to 5 ml NaI solutions of 0.04 and 0.004 mol/dm³. The systems thus prepared were vigorously stirred with a magnetic stirrer, and labelled with 0.05 ml of ¹³¹I⁻ for 15 seconds before a given time t_A was reached. At the given time t_A, the sols were coagulated by adding 0.05 ml of saturated Mg-nitrate solution. After the addition of the coagulating electrolyte, the systems were stirred for a given exchange time t_E. In order to interrupt the exchange process and separate the phases, a part of the system was centrifuged after a given time t_E was reached. The clear supernatant was used to determine the radio-

activity A^L of the liquid phase. The experimental determination of the total radio-activity A_o and a_S was described earlier[23].

RESULTS AND DISCUSSION

Applied radioactivity in colloid chemistry for the last 20 years has produced numerous new results. In an attempt to explain direct interaction processes between colloid particles and surrounding solutions, i. e. heterogeneous reactions between the solid and the liquid phase, the radioactive tracer technique was applied. As a model, the Ostwald ripening process[17] was proposed.

The results of the heterogeneous exchange process in the $[AgI]_S$ + + $[NaI(^{131}I)]_L$ system (Figure 1) indicate the occurrence of a typical Ostwald process, confirming the X-ray analysis data[18] obtained previously. The heterogeneous exchange process is important for elucidation of the equilibration in the silver iodide sol. As it was shown[21], the high exchange rate observed in a short time interval is, as a rule, caused by recrystallization, whereas the low exchange rate after prolonged exchange time may be caused by several processes including repeated surface recrystallizations and autodiffusion into solid[20,21].

The fraction exchange F against the exchange temperature indicates a critical temperature T_c, as a condition at which no exchange processes between the solid and the liquid phase occur (Figure 2). The surprising results could be explained by the strong interaction between the water dipole and the interface structure, which is responsible for the solid-liquid interactions[1,9,10,19,21,22]. The fraction exchange F vs. the exchange time is higher for systems containing coagulating ions of higher valency than for lower-valency coagulants of the same concentration (Figure 3). The influence of the chemical nature and Coulombic interactions at the solid/liquid interface is probably caused by the various rates of the primary particle formation, because in the presence of various cations the crystal growth and the crystallographic modification of the solid phase are different[9]. In order to obtain the »pure« effect of valency, the characteristic concentrations at which mono-, di-, and three-valent cations in the negative silver iodide sols attain the »same« coagulating effect are found. Tyndallometric data (Figure 4) indicate a strong dependence of critical coagulating concentrations on the sol age for the same coagulating ion. For these reasons, lower and maximum tyndall values are given schematically. For variously aged sols in the presence of one of the coagulating ions, the tyndall maxima in all cases appear at the same concentration. Thus the maxima are used as a characteristic concentration for the sol coagulation. Radiometric analysis of the relationship between the sedimentation fraction f_S and the sol age t shows that f_S at coagulating concentrations increases with increasing valency of coagulating ions, wich confirms the Težak concept that the chemical characteristics of liquid media influence the colloid properties of a solid/liquid system. The spontaneous decrease of colloid stability caused by sol aging indicates a very high stability of fresh stable silver iodide sols (Figure 5) and also supports the idea of equilibration processes in the crystal space[19] closely related with a surrounding liquid phase[1]. Many interesting results on colloid interactions[25,26] were obtained in systems with organic molecules or ions. These

indicate several characteristic surfactant groups with distinguished colloid characteristics[27]. On the basis of various measurements[15,29], it is necessary to distinguish the coagulation by inorganic ions from formally the same effect called flocculation produced by organic ions. These phenomena will be discussed separately owing to the different mechanisms and chemical compositions of the respective solid phases. Aged silver iodide sols, prepared in the presence of DDANO$_3$[29], exhibit a very interesting »tyndall value vs. DDANO$_3$ concen. vs. time« diagram.

By aging, two tyndall maxima appear, but by prolonged aging two well maxima emerge. Radiosedimentation analysis on 600 s aged sols carried out with various DDANO$_3$ concentrations present in the systems after centrifugation and at equilibrium relative centrifugal force[29], gives (Figure 6) four separate curves of four characteristic concentrations C_c, S_c, C_k, and C_s: extrapolation to zero acceleration gives the »characteristic« ideal concentrations at which flocculation can be induced (C_k) or reached completely in a short time (C_c), and the concentration of the surfactant at which stabilization can be induced (C_s) or reached completely in a short time (S_c). The relationship with the time needed for the flocculation or stabilization is very important from the practical point of view since the flocculation or stabilization can be reached by spontaneous processes through a long period of time. In this light, the critical coagulation and critical flocculation concentration in relation to the coagulation and flocculation concentration must be considered as a function of time.

Very interesting results were obtained in the systems »negative silver iodide sol + anionic surfactant«[18,29,30]. A minute analysis of such systems shows that in all cases the present surfactant has a very strong influence on the change of surface tension at solution/air interfaces. Following this fact, a series of surface tension measurements were carried out, and analysis of mixed systems[31] indicates that the mutual interaction between surfactant associates and silver iodide particles is responsible for the observed colloid phenomena[15,29]. Palisade adsorption[32] in surfactant solutions[31] and the existence of associates with distinguished colloid properties indicate that also colloid interactions must be observed in the »negative inorganic particles + cationic surfactant« systems. The results (Figure 7) obtained for the »negative silver iodide sol + NaDDSO$_4$« systems support the idea of colloid interactions in the »negative-negative« systems. Tyndallometric measurements give a typical tyndall maximum, and radiometric analysis of sol sedimentation reached a maximum f_S value at the same surfactant concentration as the tyndall maximum. The results are very interesting, because the high Ostwald ripening process attained in the surfactant solution[18] can be explained by the formation of the surfactant matrix in the volume of all systems in which colloid inorganic particles cannot be agglomerated. For these reasons the progress of crystal growth is higher compared with systems without surfactant. In this way, an inorganic sol in the presence of surfactants is a polycomponent system, because the excluded or sedimented agglomerates are composed of the inorganic solid phase surrounded with excluded surfactant associates[29,33]. The appearance of a polycomponent colloid system is scientifically interesting, and in order to perform minute analyses of

such systems, the radiometric technique was developed and verified on a silver-thallous iodide system[34].

An illustrative example is a simple system in which a binary system is formed according to the scheme

$$f_A AX + f_B BX = ABX_2 \text{ for } f_A = f_B$$
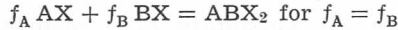
where f_A and f_B are molar fractions of the A^+ and B^+ cations. If n^L (moles of X^- anion in the liquid phase) is not an entirely non-measurable value, the α ratio ($\alpha = n^S/n^L$, where n^S represents the total amount of X^- anion in the solid phases) will be denoted by α_Σ, and in the systems with radioactive X^- for the α_Σ versus f_A, f_B at $f_A = f_B$ a characteristic maximum will be formed (Scheme 1).
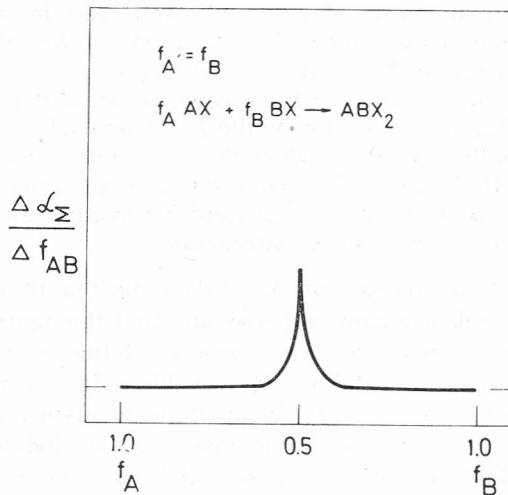
Scheme 1. Differential radiometric analysis of AX + BX mixtures. The change of the radio-nuclide distribution ratio α_Σ is presented as a "$\Delta\alpha_\Sigma/\Delta f_{A,B}$ vs. f_A, f_B" function, where f_A and f_B are molar fractions and Δf_{AB} is the constant differences of molar fractions for $|f_A - f_B|$ in the systems with an excess of X^- ions in the liquid phase.

Radiometric analysis of such systems enables one to perform in easy determination of data on intermolecular interactions for polycomponent systems. Analysis of silver-thallous mixtures shows (Figure 8) several inflections for the vs. f_A, f_B function, indicating the formation of a silver-thallous iodide poly-component system. In order to verify the obtained results, several parallel tests were performed. Turbidity values show the appearance of several particles: a white (Figure 8, w-arrow) and greenyellowish (YG maximum); at approximately the same molar fractions the differential thermal analysis data, indicate a significant change in enthalpy (arrow in Figure 8.2); X-ray diffraction analysis at several prominent diffraction angles indicates the formation of two pure AX and BX or AgI and TlI substances: and one corresponding to A_2BX_3 or Ag_2TlI_3; conductivity measurements (Figure 8.4) confirm X-ray diffraction data and at the same time also confirm radiometric analysis data (Figure 8.5). The obtained data show that the radiometric method enables one to perform an accurate and simple analysis of the mixed sols prepared by precipitation in aqueous media.

The radiometric determination of AgI solubility in the presence of Al-nitrate (Table I) disclosed the effect of increased silver iodide solubility as a function of potassium iodide and Al-nitrate concentration. If the hydrolytic species of Al-nitrate are responsible for the observed effect of lower solubility, the results can be explained by a direct KI influence on the hydrolysis of Al-nitrate.

In order to explore the possibility of a quantitative interpretation of heterogeneous equilibrium processes in mixed sols, a model of silver-lead iodide system containing an excess of potassium iodide in the liquid phase was prepared. The results of the heterogeneous exchange process for the (silver-lead iodide)$_S$ + (iodide)$_L$ systems show (Table II) a nonlienar change of the exchange fraction value, with a maximum at 5⁰/₀ lead in the silver-lead iodide mixture. Fraction exchange values calculated for F [eq 1] and for F_Σ [eq 2] indicate that an interaction occur between silver iodide and lead iodide during the sol formation via precipitation, since the observed values of F are different from those for F_Σ. Time analysis gives a high value for a higher t_E which is in agreement with the single value for both pure lead iodides. Differential thermal analysis showed a change in enthalpy, while X-ray analysis showed a measurable shift of the peak, both analyses support the radiometric results[35]. Therefore, it may be concluded that radiometric analysis of mixed sols, prepared by precipitation in statu nascendi, gives sufficiently sensitive and also sufficiently accurate data on the intermolecular interaction.

Radiosedimentation analysis of AgI sols indicated that primary and secondary particles of sols are monodisperse, and that the aggregation of primary particles to secondary ones is a kinetic process of the second order[1,36]. It was also observed that negative, stable silver iodide sols consist of two types of silver iodide: a solid, crystallographically defined silver iodide and a metaphasic, crystallographically amorphous modification. Iodide ions and silver ions within the metaphase still remain solvated and very mobile. The dynamic equilibrium of iodide ions between the metaphase and the liquid phase in the presence of coagulation electrolyte is reached quickly compared with the system with no electrolyte. Such a metaphasic structure corresponds in many elements to the second subsystem or embryo in Težak's general scheme of precipitation. Hence, embryos will be called primary particles consisting of the metaphase only. On the basis of experimental results we propose a model of transformation of the metaphase into the crystallographically defined solid phase. In such a model, primary particles or embryos aggregate to the secondary ones by a second-order kinetic process[23,36] It is also assumed that in each collision of two embryos, only part of the metaphase transforms into the solid phase[23,36]. The proposed model is represented in scheme 2, where t_A is the aging time and k_1 is a constant of the second-order kinetic process. The value $t_{p.eq}$ is the time of pseudo-equilibrium passed for the faster process of sol aging, and n is the number of particles, n_1 is the number of primary particles and n_2 is the number of secondary particles. The abbreviations p. p. and s. p. refer to primary and secondary particles, respectively. Such a process can be expressed mathematically by the relation[23,36]

$$f_m = (1 - f_m^n)/(C_o k_\pi t_A + 1) + f_m^n \qquad \text{(eq 3)}$$
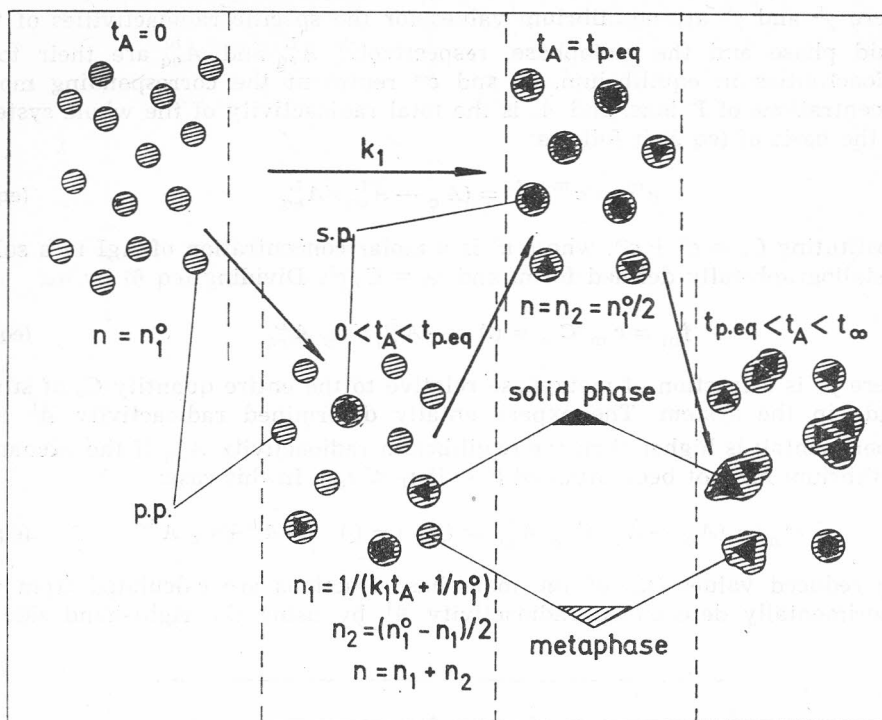
Scheme 2. Schematic representation of the methaphase transformation during the aggregation of primary particles (embryos) to secondary ones (nucleus) from $t_A = 0$ to $t_A = t_{p.eq}$. n_1 is the number of primary particles (p. p.), n_2 is the number of secondary particles (s. p.), and n_1^0 is the number of primary particles at $t_A = 0$. After $t_{p.eq}$, the other mechanisms are dominant.

where f_m represents a fraction of metaphase at time t_A, f_m^n is a fraction of metaphase that remain unchanged in the secondary particle after the collision of two primary particles, C_o is a molar concentration of AgI, and $k_\pi = k_1 k_2$, where $k_2 = C_o/n_1^0$, and n_1^0, is the number of primary particles at $t_A = 0$. In order to verify the proposed mechanism, a radiometric method for determining the metaphase fraction was employed. The method is based on the fact that in the absence of a potential barrier around particles (i. e. during coagulation), the dynamic equilibrium of I^- ions between the metaphase and the liquid phase is attained more rapidly than the equilibrium between the metaphase and the solid phase or between solid phase and the liquid phase[23]. If the sol is labelled by $^{131}I^-$ just (15 seconds) before the initiation of coagulation, the equilibrium of the radioactive ions between the metaphase and the liquid phase is defined as:

$$\gamma^L = \gamma^S = A_{eq}^L/c^L = A_{eq}^m/c^m \qquad \text{(eq 4)}$$

Since for equilibrium conditions $A_{eq}^m = A_o - A_{eq}^L$, equation (4) can be written as

$$\gamma^L = \gamma^S = A_{eq}^L/c^L = (A_o - A_{eq}^L)/c^m \qquad \text{(eq 5)}$$

where γ^L and γ^S are equilibrium values for the specific radioactivities of the liquid phase and the metaphase, respectively; A_{eq}^L and A_{eq}^m are their total radioactivities in equilibrium, c^L and c^m represent the corresponding molar concentrations of I^- ions, and A_o is the total radioactivity of the whole system. On the basis of (eq 5) it follows:

$$a^m = c^m/c^L = (A_o - A_{eq}^L)/A_{eq}^L \qquad (eq\ 6)$$

Substituting $C_o = c^S + c^m$, where c^S is a molar concentration of AgI in a solid, crystallographically defined form, and $a_S = C_o/c^L$. Dividing (eq 6) by a_S:

$$f_m = c_m/C_o = (A_o - A_{eq}^L)/a_S A_{eq}^L \qquad (eq\ 7)$$

where f_m is a fraction of metaphase relative to the entire quantity C_o of silver iodide in the system. The experimentally determined radioactivity A^L (see Experimental) is higher than the equilibrium radioactivity A_{eq}^L if the exchange equilibrium has not been attained (i. e. if $t_E < t_{eq}$). In this case:

$$f_m = (A_o - A_{eq}^L)/a_S A_{eq}^L > (f_m) = (A_o - A^L)/a_S A^L \qquad (eq\ 8)$$

The reduced values (f_m) of the metaphase fractions are calculated from the experimentally determined radioactivity A^L by using the right-hand side of
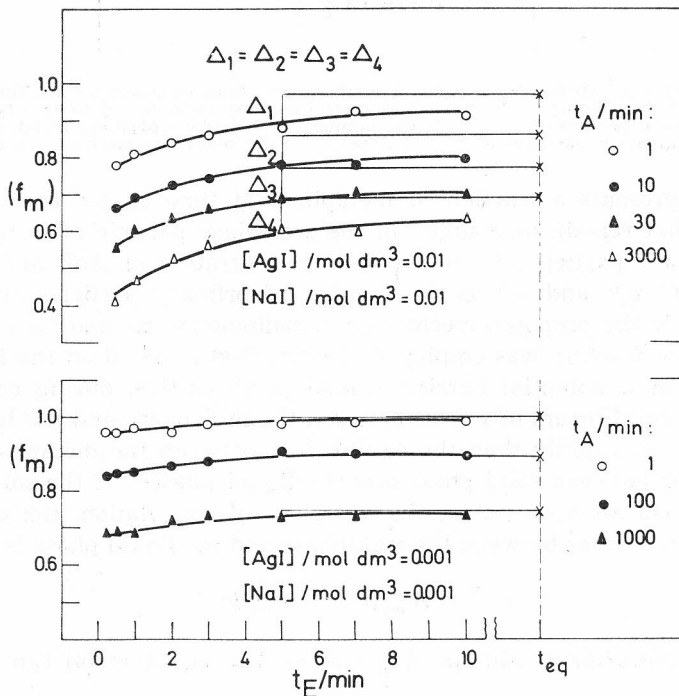

Figure 9. The reduced fractions of metaphase (f_m) measured for differently aged 0.01 and 0.001 mol/dm³ AgI sols, plotted against the exchange time t_E. The value t_{eq} corresponds to the equilibrium exchange time for which $(f_m) = f_m$.

(eq 8). For differently aged 0.01 and 0.001 mol dm^{-3} AgI sols, (f_m) is represented as a function of exchange time in Figure 9. In principle, the equilibrium radio-activity A_{eq}^L and thus the real f_m values (denoted by crosslets in Figure 9.) for each system may be reached if the time of exchange is rather long (if $t_E \gg t_{eq}$). Moreover, for sols of lower AgI concentration (0.001 mol dm^{-3}) the equilibrium is reached within the time of experiment, as shown in Figure 9. For practical purpose, the equilibrium values are not necessary since the differences Δf_m (Δ in Figure 9) between the real f_m values (crosslents) and the reduced (f_m) values are constant, if for a given C_o, t_E is also a constant (see Figure 9). In this case, for a given C_o one can write

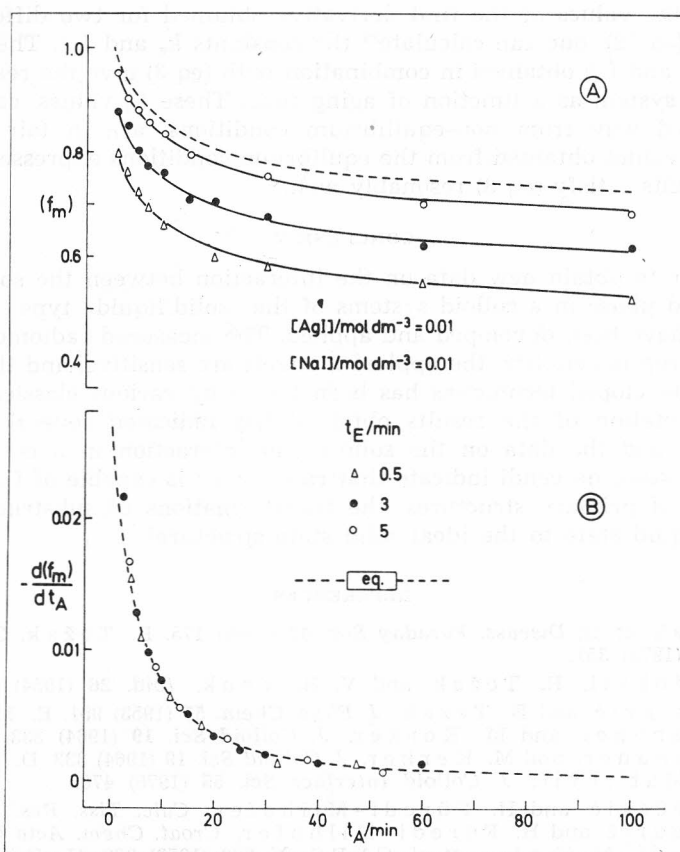$$f_m = (f_m) + \Delta f_m (t_E) \tag{eq 9}$$

Figure 10. The reduced fractions of metaphase (f_m) measured for $t_E = 0.5$, 3, and 5 minutes (A) in 0.01 mol/dm^3 AgI sol, and the corresponding first derivative $- \mathrm{d}\,(f_m)/\mathrm{d}t_A$ plotted against the aging time t_A (B).

where $\Delta f_m (t_E)$ is a function of exchange time only. It is apparent that in such a case the following relation is valid:

$$[\mathrm{d}\,(f_m)/\mathrm{d}t_A]\,t_{E_1} = [\mathrm{d}\,(f_m)/\mathrm{d}t_A]\,t_{E_2} = [\mathrm{d}\,(f_m)/\mathrm{d}t_A]\,t_{eq} = \mathrm{d}f_m/\mathrm{d}t_A \tag{eq 10}$$

The experimental evaluation of (eq 10) is represented in Figure 10. The (f_m) values determined for $t_E = 0.5$, 3 and 5 minutes in 0.01 molar AgI sol are plotted against the aging time t_A (Figure 10A). The function represented by the broken line is calculated from the equilibrium conditions given by (eq 6). This function satisfies equation (3) for $k_\pi = 8.76$ and $f_m^n = 0.7$ and thus represents the real values of f_m as a function of t_A. Figure 10B shows the first derivatives $d(f_m)/dt_A$ of the (f_m) vs. t_A. It is shown that $d(f_m)/dt_A$ is not dependent on t_E, which is a direct experimental proof for the validity of eqs 9 and 10. Then, combining eqs 3 and 7:

$$(f_m) = (1 - f_m^n)/(C_o k_\pi t_A + 1) + f_m^n - \Delta f_m(t_E) \qquad (eq~11)$$

and

$$d(f_m)/dt_A = df_m/dt_A = - C_o k_\pi (1 - f_m^n)/(C_o k_\pi t_A + 1)^2 \qquad (eq~12)$$

Combining the values of the first derivative obtained for two different aging times with (eq 12), one can calculate[23] the constants k_π and f_m^n. The calculated values of k_π and f_m^n obtained in combination with (eq 3) give the real f_m values for a given system as a function of aging time. These f_m values, calculated in the described way from non-equilibrium conditions, are in fair agreement with the f_m values obtained from the equilibrium conditions expressed by (eq 6), and the results satisfy (eq 3) resonably well.

CONCLUSION

In order to obtain new data on the interaction between the solid and the nascent solid phase in a colloid systems of the »solid/liquid« type, radiometric techniques have been developed and applied. The measured radiometric results are of high reproducibility, the applied methods are sensitive, and the application of the developed techniques has been tested by various classical methods. The interpretation of the results obtained has indicated several interesting phenomena, and the data on the solid/liquid interaction in a colloid system prepared in statu nascendi indicate that radiometry is capable of following the appearance of primary structures, the transformations of substructures from the ideal liquid state to the ideal solid state structure[1].

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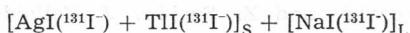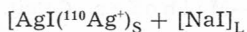36. B. Subotić, *Ph. D. Thesis,* University of Zagreb (1976).

SAŽETAK

Radiometrijska analiza solova srebro-jodida

R. Despotović

u suradnji s D. Čavčić, M. Čebulc, Lj. A. Despotović, Z. Despotović, N.Filipović-Vinceković, Z. Grabarić, J. Kapetanović. D. Mayer-Žitnik, S. Popović, L. Prodanović, Z. Selir, B. Subotić, V. Štengl i B. Tomaš

S ciljem da se prouče (a) procesi nastajanja čvrste faze taloženjem iz elektrolitnih otopina i (b) procesi koji su karakteristični za međudjelovanje između čvrste faze i elektrolitne otopine primijenjene su poznate radiometrijske metode i razvijene su nove radiometrijske metode analize koloidnog sistema. Primijenjene metode vrlo su osjetljive, selektivne i precizne. Nove su metode provjeravane uspoređivanjem sa standardnim metodama: rentgenskom difrakcijom, turbidimetrijom, konduktometrijom, diferencijalnom termičkom analizom i objavljenim podacima. Kao modeli primjenjivani su sistemi

$$[AgI]_S + [NaI(^{131}I^-)]_L$$

$$[AgI(^{110}Ag^+)]_S + [NaI]_L$$

$$[AgI(^{131}I^-) + TlI(^{131}I^-)]_S + [NaI(^{131}I^-)]_L$$

$$[AgI + PbI_2]_S + [NaI(^{131}I^-)]_L \quad i$$

$$[PbI_2]_S + [NaI(^{131}I^-)]_L.$$

Rezultati pokazani na slikama i tablicama sadržavaju niz zanimljivih podataka o nastajanju koloidnog sistema, pretvorbama substruktura i međudjelovanju između čvrste i tekuće faze, a promatrani su kroz analizu

(i) procesa heterogene zamjene na izoelektričkom AgI;

(ii) procesa heterogene zamjene na srebro-jodidu taloženjem pri različitim temperaturama;

(iii) uz koagulacijske elektrolite različitih valencija;

(iiii) uspoređivanjem tindalometrijskih maksimuma i brzine sedimentacije čestica sola;

(v) uspoređivanjem brzine sedimentacije različito starenih čestica;

(vi) utvrđivanjem idealnih karakterističnih koagulacijskih, flokulacijskih i deflokulacijskih koncentracija radiosedimentacijskom analizom i tindalometrijom;

(vii) uspoređivanjem frakcije sedimentacije i tindalometrijskih podataka za negativne solove u prisutnosti anionskog tenzida;

(viii) analizom međudjelovanja precipitacijskih komponenata u toku nastajanja višekomponentnog koloidnog sistema uz provjeravanje radiometrijske metode klasičnim metodama;

(ix) razvojem kvantitativne radiometrijske analize nastajanja substruktura čvrste faze i pretvorbi;

(x) nascentnih substruktura od idealne tekuće do idealne čvrste faze;

(xi) analizom utjecaja amfoternih kationskih vrsta na kompleksnu topljivost srebrnog-jodida i

(xii) analizom procesa heterogene zamjene u koloidnom sistemu priređenom miješanjem različitih kationskih taložnih komponenata.