Investigations of TII Suspensions

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Received July 20, 1972

Thallous iodide suspensions were obtained by direct mixing of TlNO₃ and NaI solutions. The amount of TII was kept constant in the systems, while the concentrations of NaI (in excess), laurylamine nitrate (LAN) or myristylamine nitrate (MAN) were varied. Tyndallometric values were recorded as the function of NaI, LAN, and MAN concentrations respectively, for suspensions aged for various times. Particle sizes of differently aged TII in suspensions containing NaI and Eu(NO₃)₃ in solution were determined. Tyndallometry and electronmicroscopy showed fast particle growth of TII in suspension. After about 10 minutes the TII particle grew up to 1.3 µ. The zero point of charge, determined by microelectrophoresis, was attained at 0.001—0.005 M NaI and 0.0001—0.0005 M LAN depending on the conditions under which the system had been prepared. The results of radiometrically recorded adsorption—desorption equilibria show a constant increase of the adsorption capacity as the electrolyte concentration increases.

INTRODUCTION

Freshly precipitated thallous iodide with TlNO₃ in excess or NaI present shows fast recrystallization₁,₂ of the formed primary sol particles. The heterogeneous exchange experiments² on Tl—I systems indicate that the chief recrystallization occurred within 30 minutes after the formation of TII sol. The concentration of the potential determining ions, the amount of the solid TII present in the suspension and the concentrations of the neutral electrolytes present influence the colloid behaviour of TII suspensions during the exchange experiments¹,₂. Similar dependences are known on typically colloidal AgI and AgBr systems³—⁵ which reach the equilibrium state only after a long time. Since the thallous iodide sols appear in the form of sediment after a very short time²,₈ it has been of interest to establish parameters of TII—I⁻ systems on which its colloidal state depends.

EXPERIMENTAL

Materials

All chemicals used were of p. a. (Darmstadt, Merck) or Analar quality (B. D. H.). Laurylamine nitrate (LAN) and myristylamine nitrate (MAN) were prepared from dialkylamines of puriss. quality (Fluka). The radionuclide of high specific radioactivity $^{132,134}$Eu was obtained from the Nuclear Institute at Vinca (Yugoslavia). Bidistilled water from an all-Duran distillation apparatus (Jena-er Glass, Schott und Gen., Mainz) was used. A solution of TlNO₃ was tested by the gravimetric chromate method. The solutions of La(NO₃)₃, Eu(NO₃)₃, LAN, and MAN were prepared by weighing. A solution of NaI was standardized by a standard AgNO₃ solution using an adsorption indicator, and a solution of AgNO₃ was also standardized with a dried sodium chloride using an adsorption indicator.
Electron microscopy

The systems $c_{\text{NaI}} = 0.001 \ M$, $c_{\text{Eu(NO}_3)_3} = 0.0001 \ N$, $c_{\text{TlI}} = 0.001 \ M/l$ were prepared by precipitation in statu nascendi. After given aging times $t_A = 35$ seconds, 1, 4, 9, and 17 minutes respectively, one part of the TlI sol was taken for electronmicrography. Movital films were used as support for the specimen under examination. Electron microscopy was carried out on a Trüb-Tauber Co. (Zürich) KM-4 electron microscope. Results are collected in Fig. 3.

Turbidity

The measurements of tyndallometric values, $T. V.$, were made by a Pulfrich photometer coupled with a turbidimetric extension (Carl Zeiss, Jena). Tyndallometric values were recorded as a function of the LAN at various amounts of AgI present in the suspension, and as a function of NaI concentration with or without LAN for variously aged TlI suspensions. The results are shown in Figs. 1, 4, and 7.

Microelectrophoresis

The particle charge and the electrophoretic mobility of the TII — LAN — NaI systems were determined by microelectrophoresis with a Smith-Lisse double cell on 1 minute aged in statu nascendi stable TII sols. The results are shown in Figs 6 and 8.

Adsorption

The experimental technique remained essentially the same as described before. The sols were prepared by mixing the precipitation components (TlNO₃ and NaI) with added electrolytes (LAN, MAN, Eu(NO₃)₃, La(NO₃)₃) in predetermined concentrations. The component in excess [NaI, LAN, MAN, ¹⁵²,¹⁵⁴Eu³⁺ of high specific radioactivity, La (NO₃)₃, Eu(NO₃)₃] was stirred by a magnetic stirrer and the second precipitating component (TlNO₃ solution) was added continuously from the pipette. The systems were allowed to stand for one day, then they were separated by decantation, filtered through weighed filter papers, washed with a solution of the same pH as the original supernatant liquid and dried at 60°C. The weighed precipitate
was transferred to counting tubes and the radioactivities were determined in a well type NaI(TlI) scintillation counter with an EKCO Electronic scaler. The results are shown in Fig. 2 and 5.

Fig. 2. The adsorption capacity, \( \gamma \) (millilval adsorbed Eu\(^{3+}\)/grammole TII) of TII plotted against La(NO\(_3\))\(_3\) concentration at various Eu(NO\(_3\))\(_3\) concentrations.

Fig. 3. Electronmicrographs of TII particles prepared at 0.0001 \( N \) Eu(NO\(_3\))\(_3\) and 0.001 \( M \) NaI, and aged for 35 sec (A), 60 sec (B), 4 min (C), 9 min (D), and 17 min (E).
Fig. 4. Tyndallometric values, T.V., plotted against the NaI concentration. T.V. were recorded at various LAN concentrations and 1, 10, and 100 minutes after the preparation of TlI suspensions.

Fig. 5. The adsorption capacity, $\gamma$, (millilval adsorbed Eu$^{3+}$/grammole TII) of TlI plotted against LAN and MAN concentrations.
TII SUSPENSIONS

RESULTS

The results of the turbidity measurements show that T. V. is dependent on the aging of the thallous iodide suspension (Figs. 1 and 4): T. V. increases with the aging of sols. The T. V. depends on the concentration of NaI present in excess: at $5 \times 10^{-4}$ M NaI, the T. V. was highest and by increasing the concentration of NaI, the T. V. decreases to a minimum at about $0.01$ M NaI in excess. At NaI in excess over $0.1$ M, the T. V. increases. The T. V. of thallous

![Graph 1](image1)

**Fig. 6.** The electrophoretic mobility, $w_\pm$, of TII particles plotted against NaI concentration at various LAN concentrations.

![Graph 2](image2)

**Fig. 7.** Tyndallometric values, T. V., plotted against the LAN concentration at various NaI concentrations ($-\log C_I = pI$).
iodide sols containing LAN shows minimum dependence on the concentration of NaI present in excess: at smaller NaI concentrations the T. V.'s are higher (Fig. 7), dispersion of the results is largest and the minimum T. V. is reached at 0.001 M LAN. By increasing the NaI concentration, the T. V. decreases reaching its minimum at 0.01 M LAN. In all cases the particles of thallous iodide change their electrical sign between 0.0001 and 0.001 M LAN (Fig. 8). Microelectrophoresis shows the change of the electrical sign of the thallous iodide particles in suspensions for various LAN concentrations between 0.001 M and 0.01 M NaI (Fig. 6). The electronmicroscopy shows (Fig. 3) a fast increase of the particles in thallous iodide suspensions during the aging time. The obtained adsorption capacity values are dependent on the concentration of La(NO₃)₃ and Eu(NO₃)₃ respectively, and depend on the concentration of LAN and MAN. At the same molar concentration of surfactants the adsorption capacity is higher with MAN present in the system. In the systems with and without surfactants the adsorption capacity values are rather low, only ranging up to 0.05 millivals Eu³⁺ per gram mole TlI, (Figs. 2 and 5).

**DISCUSSION**

The thallous iodide suspensions formed in statu nascendi (by direct mixing of the precipitating components) show characteristic colloid instability. A high increase of the T. V. (Fig. 1) in the small time interval of 10 minutes is caused by the crystal growth of TlI particles as presented on electronmicrographs (Fig. 3). In 17 minutes the TlI particle changes its size from 0.27 µ to 1.3 µ. The slopes of the T. V.-log c NaI between 0.01 and 0.005 M NaI correspond to a maximum at limits of ionic solubility of TlI, while the slopes between 0.1 and 1.0 M NaI correspond to a maximum in the region of the complex solubility of TlI in NaI solution. Aged TlI particles obtained by spontaneous fast recrystallization have low adsorption capacity (Fig. 2), up to 0.05 millivals Eu³⁺ per grammole TlI. Such a low adsorption capacity is probably the consequence of a small dispersion of TlI suspension. It is of interest to note that the adsorption capacity shows a constant increase with the increase of Eu(NO₃)₃ concentration. This effect is probably caused by various nucleation
rates obtained at different Eu(NO₃)₃ concentrations at the beginning of the precipitation process. At a higher initial Eu(NO₃)₃ concentration the nucleation process is faster, and the formed TlI nuclei induce the growth of TlI with higher dispersity. In the case of lower Eu(NO₃)₃ concentration at the beginning of the mixing of the precipitation components the dispersity of thallous iodide is smaller. Slow chemical interactions, which cause the chemical transformation of the system, and which occur between the components present in the suspension are not precluded because it is known that for example the adsorption capacity of montmorillonite also increases with the increase of FeCl₃ concentrations.

In the presence of surfactants the thallous iodide suspensions show similar behaviour to silver halide suspensions. Tyndallograms (Fig. 4) of the thallous iodide suspensions containing, LAN, are similar to those without LAN. The T. V. increases faster at a lower LAN concentration indicating its influence on the coagulation of TlI particles. The T. V. measured as a function of the NaI concentration is similar in the systems with and without LAN, which indicates the dominant role of the constitutive ion.

The electrophoretic mobilities w± are dependent on the NaI concentration too, at all LAN concentrations in the systems (Fig. 6). At a low NaI concentration the influence of LAN on the electrophoretic mobility of TlI particles is markedly higher than at a high NaI concentration. It is probably caused by a rough dispersion of TlI at higher NaI concentrations (Fig. 7). It means that LAN can cause a strong change of electrophoretic mobilities on small TlI particles only. By alternate change in NaI and LAN concentrations (Figs. 6—8) the critical zero point of charge obtained lies between 0.001—0.005 M NaI and 0.0001—0.0005 M LAN. In this concentration interval the adsorption does not reach the adsorption equilibrium (Fig. 5). According to Traube’s rule with mristylamine nitrate the adsorption-desorption reaction occurs at a smaller MAN concentration in comparison with LAN. The maxima obtained in both cases (Figs. 2 and 5), similarly to the systems without surfactants, are probably caused by the processes of the formation of primary TlI particles and/or by chemical interactions between the components of the system. All mentioned results indicate that the thallous iodide suspensions are interesting colloid systems and it is hoped that the investigations described here have thrown some light onto several relevant colloido-chemical characteristics of TlI suspensions.

REFERENCES

IZVOD

Istraživanja suspenzija talijevog jodida

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Suspenzije talijevog jodida TlI priređivane su direktnim miješanjem otopina TiNO₃ i NaI. Uz istu količinu TlI u sistemima su mijenjane koncentracije NaI u suvišku, laurilamin nitrata (LAN) ili mristilamin nitrata (MAN). Tyndallometrijske vrijednosti mjerene su kao funkcija koncentracije NaI, LAN i MAN na supenzijama starenim različito vremena. Pomoću elektronskog mikroskopa određivane su veličine čestica TlI u različito starenim suspenzijama koje su sadržavale NaI i Eu(NO₃)₃ u tekućoj fazi. Rezultati tyndallometrije i elektronske mikroskopije pokazuju vrlo brzi rast čestica TlI u istraživanim suspenzijama: nakon cca 10 minuta čestice TlI narastu do 1,3 μ. Nul-točka naboja, određivana mikroelektroforezom, leži između 0,001—0,005 M NaI i 0,0001—0,0005 M LAN i ovisi o uvjetima formiranja suspenzije. Rezultati radiometrijskog određivanja adsorpciono-desorpcione ravnoteže pokazuju stalan porast adsorpcionog kapaciteta TlI s porastom koncentracije prisutnih elektrolita.