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Original Scientific Paper

Precipitation of Strontium Sulphate in Aqueous and Mixed Media of Different Dielectric Constants*

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The influence of ethanol on the precipitation of strontium sulphate was investigated in aqueous solutions *in statu nascendi.* Sol formation and kinetics of precipitation were investigated by the tyndallometric technique, as well as by the electrophoresis method (determination of the charge sign by means of an ultramicroscope), and by measuring *p*H values. The results of investigations are given in from of general precipitation diagrams. Concentrational regions as well as concentration ratio of Na_2SO_4 to $Sr(NO_3)_2$ of precipitation/non precipitation limits show the limited area where the constant ionic product may be applied. Outside of this area there is presumably a formation of ionic associates. Lowering of the dielectric constant and increase of the ethanol content results in (1) decrease of solubility of solid phase and (2) change in kinetics of precipitation.

INTRODUCTION

The mechanism and kinetics of precipitation of slightly soluble salts can be considered as composed of several elementary processes: formation of complex species, embryonation, nucleation, direct growth resulting in formation of particles having their colloid individuality and, finally, secondary aggregation and/or crystal growth[1]. In this sense genotypical and phenotypical characteristics of strontium sulphate precipitation have been investigated both in aqueous solutions and in water-ethanol mixtures. Previous studies on the $SrSO_4$ precipitation have been mainly made in rather narrow concentration ranges[2-10] in the vicinity of the equivalence point. In the present paper the range of concentrations has been extended to determine the precipitation boundaries.

EXPERIMENTAL

All measurements were performed by the turbidimetric method using a Zeiss tyndallometer joined to a Pulfrich photometer. The method has been described earlier[11].

Chemicals used were of analytical reagent quality and were not purified further: strontium nitrate (Carlo Erba S.A., Milano), sodium sulphate (E. Merck, Darmstadt) and ethanol abs. (Kemika, Zagreb). Investigated precipitation systems were prepared by mixing equal volumes of solutions of the precipitating components. The concentrations given refer to the final mixtures. The glass test tubes with samples were

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kept in a constant temperature bath at 20.0±0.1° C. The pH values were measured with a glass electrode 24 hours afted mixing. The charge sign of the particles was determined in a microelectrophoresis apparatus similar to that described[12].

RESULTS

Information on the rate of precipitation of $SrSO_4$ can be obtained from time tyndallograms like the one shown in Fig. 1a. The arrows indicate that after that particular period most of the particles have sedimented leaving a clear supernatant liquid. A more informative picture can be obtained from concentration tyndallograms where the turbidity values for given times after mixing are plotted. A typical concentration tyndallogram is shown in Fig. 1b.

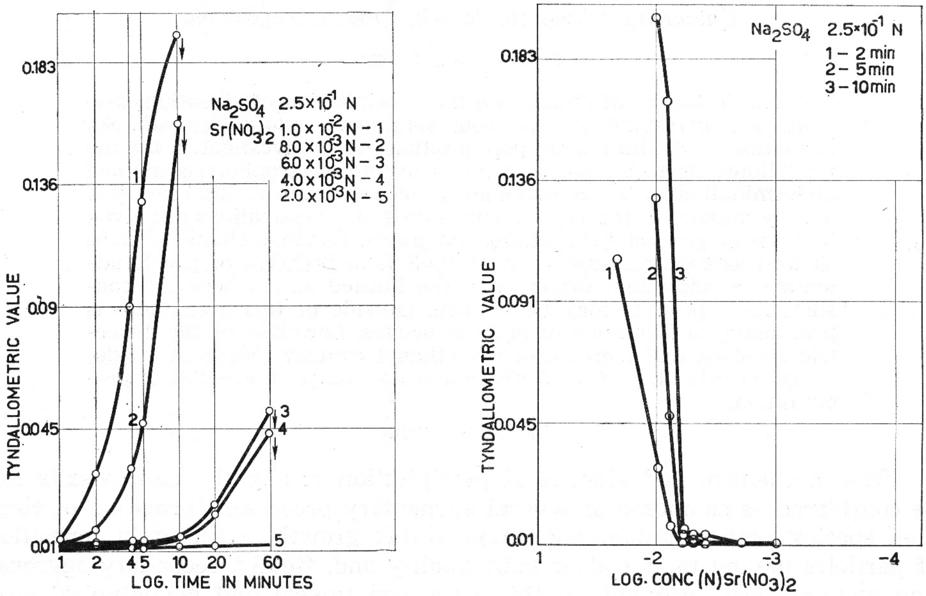

Fig. 1 ab. Time and concentration tyndallograms of the system $Sr(NO_3)_2 - Na_2SO_4$

From such data the boundaries of the general precipitation body (PB) could be determined graphically. In order to obtain a general picture of the influence of ethanol on the $SrSO_4$ precipitation a series of experiments was made in which the ethanol content was varied (20, 30, 40. vol. %) keeping the concentrations of Sr^{2+} and SO_4^{2-} constant. In Fig. 2 a-d the boundaries of PB's are shown for mixtures with varying ethanol content. There are two boundaries which can be distinguished from concentration tyndallograms. One of them is placed on the side of the optically clear solution. The other is characterized by a steep increase of turbidity. The systems precipitated in pure water or in solutions containing 30 and 40% ethanol show these double boundaries. In the system with 20% ethanol the boundaries are fused into one distinct boundary. It can be seen that the precipitation boundaries move towards lower concentrations as the macroscopic dielectric constant becomes lower. Also, the lowering of the dielectric constant influences the kinetics of precipitation as can be seen from Fig. 3.

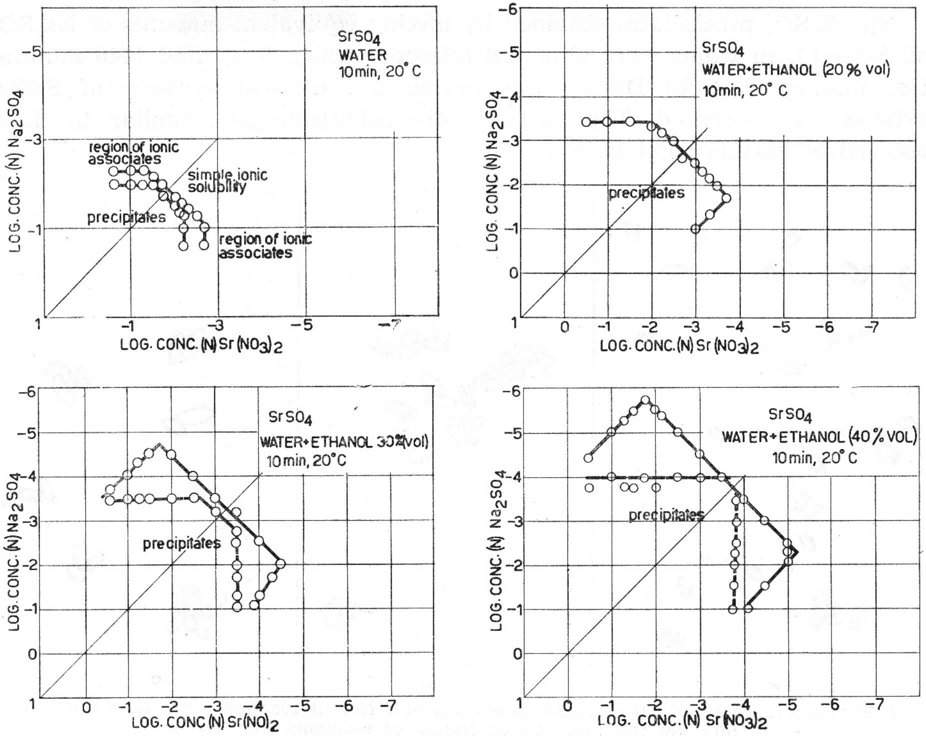

Fig. 2a—d. Effect of media (water-ethanol) on PB of $SrSO_4$ (at 20° C, 10 min.) (a) water, (b) 20% ethanol in water (c) 30% ethanol in water (d) 40% ethanol in water

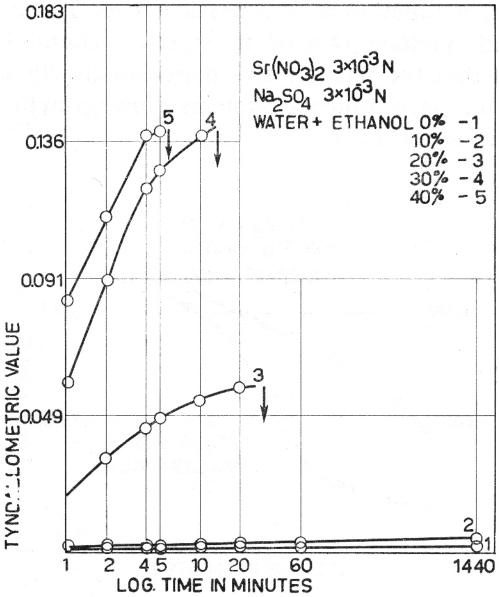

Fig. 3. Time tyndallogram of $SrSO_4$ precipitation systems in water-ethanol solution with their different ratios

The $SrSO_4$ precipitates obtained by mixing equivalent amounts of Na_2SO_4 and $Sr(NO_3)_2$ in water were observed microscopically, 5, 60 and 1440 minutes after mixing (Fig. 4.) During this period a continuous growth of $SrSO_4$ particles was observed. The particles are spindle-shaped, similar to those observed of barium sulphate[13,14].

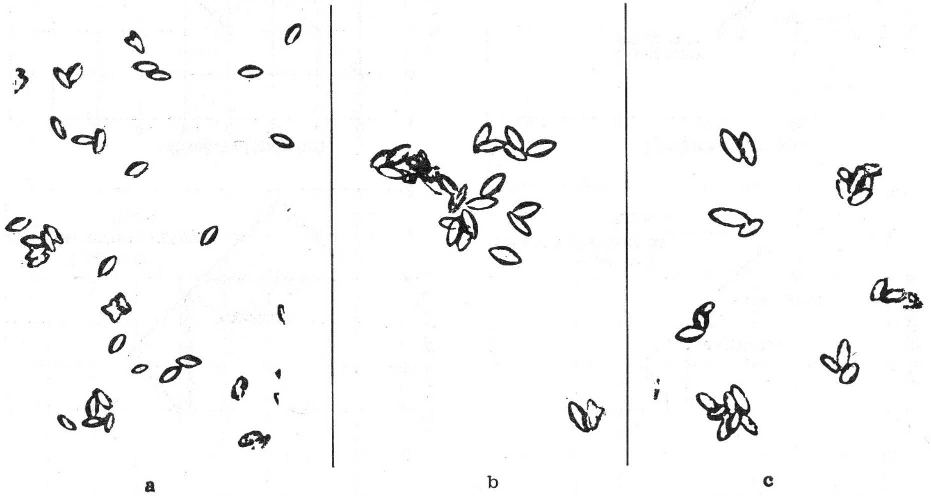

Fig. 4. Photomicrographs of $SrSO_4$ particles formed at different reaction times (a) 5 min; (b) 60 min; (c) 1440 min. (concentration of reactants 5.10^{-2} *N*)

Deželić *et al.*[15] have shown that the reciprocal of the dispersion quotient Q' should be a simple function of the particle size. Therefore, from the time dispersoidogram and tyndallogram of the systems containing ethanol (Fig. 5) it can be concluded that the particle size increases slowly with time. It should be mentioned that in pure aqueous systems slow growth of $SrSO_4$ particles could be observed in every case.

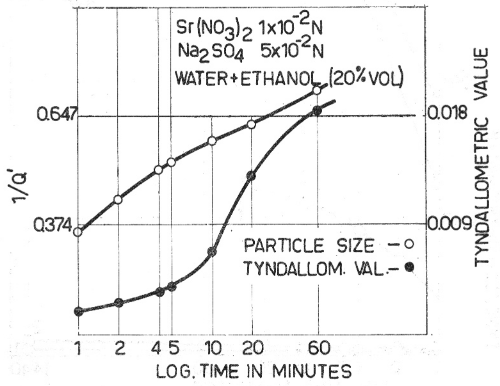

Fig. 5. Plot of reciprocal relative dispersion quotient Q' of strontium sulfate particles in dependence of time.

DISCUSSION

The influence of various precipitation mechanisms on the form of the general PB has been discussed by one of us[1]. According to the postulates made in this paper the following conclusions can be drawn on the basis of the data at hand:

Symmetrical ion pair formation is represented by the line normal to the equivalence line (see *e. g.* Fig. 2.). This part of the boundary is determined by the ionic product. The ionic product, as calculated from our data obtained with aqueus solutions was 7.53×10^{-4} (mole^2/l^2), which is not in accordance with literature values[16,17] ranging from 3.3×10^{-7} to 5.2×10^{-7} (mole^2/l^2). This discrepancy can be explained by the formation of supersaturated solutions in our precipitation experiments.

The existence of boundaries parallel to the coordinate axes may be caused by the formation, of ion associates, whereas the concentration changes may also cause changes of ionic state.

The lowering of the dielectric constant may affect several factors influencing the precipitation process. It was observed that the increase of ethanol content results in a decrease of solubility of the solid phase. Since the intensity of the scattered light depends on the number as well as on the size of the colloidal particles, the observed decrease of tyndallometric values in the systems containing ethanol (as compared with the aqueous systems) may be explained by the fact that the change of the dielectric constant changes the number and size of the particles by affecting the solubility. These changes are probably connected with the mechanism of nucleation as well as with the distribution of stabilizing ions.

The presence of ethanol drastically alters the kinetics of precipitation so that the precipitation can be observed much earlier in ethanolic solutions than in aqueous ones (Fig. 3.). This fact is also in accordance with the above statement.

For all systems the *p*H-values were nearly constant (6.6—7.4).

The charge of the particles was observed in a ultramicroscope-electrophoretic cell, and was positive or negative according strontium or sulphate ion was in excess in the precipitating medium.

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IZVOD

Precipitacija $SrSO_4$ u vodenim i miješanim otapalima različitih dielektričnih konstanti

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Ispitivan je utjecaj etanola na precipitaciju $SrSO_4$ u vodenim otopinama *in statu nascendi*. Stvaranje sola i kinetika precipitacije praćena je tindalometrijskom tehnikom i određivanjem naboja elektroforetski na ultramikroskopu. Rezultati ispitivanja dati su na precipitacionom diagramu. O koncentracionim odnosima komponenata $Sr(NO_3)_2$ i Na_2SO_4 ovisi stvaranje asocijata ili izlučivanje uzduž granice, gdje vrijedi produkt topljivosti. Smanjenjem dielektričke konstante s povećanjem koncentracije etanola (20, 30, 40% vol) dovodi do (1) smanjenja topljivosti čvrste faze, te (2) promjene u kinetici precipitacije.

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