

CHROM. 10,908

Note

Flocculation of colloidal As_2S_3 by a series of tervalent cobalt(III) complexes and their thin-layer chromatography on silica gel

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(Received January 23rd, 1978)

Flocculation of a hydrophobic colloid on the addition of electrolytes occurs as a result of neutralization of the electrical charge of the colloid particles by the adsorption of oppositely charged ions. In this phenomenon, there is a linear relationship rule between the charge number of the counter ion to be adsorbed and the logarithm of the minimal concentration of it that will cause flocculation. This empirical rule was also verified^{1,2} with complex salts, and the application of flocculation in the determination of the charge number of complex ions was suggested.

We previously investigated the relationship between hydration and association of ions by studying the electrophoretic and chromatographic behaviour of a series of inert cobalt(III) complexes.³⁻⁶ The results indicated that strongly hydrated complexes associate more with strongly hydrated anions and weakly hydrated complexes associate more with weakly hydrated anions. Our results were supported by the chromatographic examination on alumina by Lederer and Battilotti⁷, and their results on silica gel agreed closely with our investigations.

Thus, it was recognized that association of ions is dependent not only on the ionic charge but also on the state of hydration of ions. As the flocculation of a hydrophobic colloid is caused by the association of counter ions with the colloidal particles, it is reasonable to presume that factors which govern flocculation are not only the ionic charge but also the state of hydration of the counter ions to be adsorbed. In other words, the difference in the state of hydration of ions should be reflected by differences in flocculation values. Therefore, if we determine the flocculation values of a series of ions which have the same charge but are in different states of hydration, a wide range of values will be obtained.

In this study, we prepared a series of hexamine-type cobalt(III) complexes and determined their flocculation values for colloidal As_2S_3 , and these values were compared with the R_F values in thin-layer chromatography on silica gel.

EXPERIMENTAL

Preparation of the hexamine-type cobalt(III) complexes (abbreviations in parentheses)

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Conventional methods were used for the preparation of $[\text{Co}(\text{NH}_3)_6](\text{NO}_3)_3$ (a_6), $[\text{Co}(\text{en}_3)](\text{NO}_3)_3$ (en_3) and $[\text{Co}(\text{phen})_3](\text{NO}_3)_3$ (phen_3). $[\text{Co}(\text{NH}_3)_4\text{en}](\text{NO}_3)_3$ ($a_4\text{en}$) was prepared according to our previously reported method⁸. The other complexes, $[\text{Co}(\text{NH}_3)_2\text{en}_2](\text{NO}_3)_3$ ($a_2\text{en}_2$), $[\text{Co}(\text{NH}_3)_4\text{phen}](\text{NO}_3)_3$ ($a_4\text{phen}$), $[\text{Co}(\text{en})_2\text{phen}](\text{NO}_3)_3$ (en_2phen), $[\text{Co}(\text{NH}_3)_2\text{phen}_2](\text{NO}_3)_3$ ($a_2\text{phen}_2$) and $[\text{Co}(\text{en})\text{phen}_2](\text{NO}_3)_3$ (en phen_2) were prepared by using dimethyl sulphoxide and dimethylformamide as solvents. The details of the preparation will be reported elsewhere.

Preparation of As_2S_3 sol

Three grams of As_2S_3 were dissolved in 300 ml of boiling water. The solution was allowed to stand for 12 h at room temperature, then filtered through a membrane filter (Toyo Roshi, Tokyo, Japan). To 30 ml of this solution were added successively 30 ml of distilled water, 30 ml of hydrogen sulphide solution prepared by 30-fold dilution of a saturated solution and 210 ml of hydrogen sulphide solution prepared by 10-fold dilution of a saturated solution. The final concentration of the sol was about 0.1%.

Determination of flocculation values

Incremental amounts from 1 to 10 ml of a solution of a complex were pipetted into ten glass-stoppered test-tubes and the contents of each test-tube were made up to 10 ml with distilled water. To each of these solutions were added 10 ml of the As_2S_3 sol. The series of mixed solutions thus obtained was allowed to stand for 20 min. Some of them showed definite flocculation and others no sign of flocculation. The flocculation value was determined by finding the test-tube whose contents were slightly more turbid than a reference sol prepared by the two-fold dilution of the original sol and by regarding the concentration of the complex ion in the next test-tube as the critical concentration of the counter ion.

Thin-layer chromatography

Silica gel H (E. Merck, Darmstadt, G.F.R.) was used as an adsorbent without further purification. Each complex was dissolved in water to a concentration of 0.02 M, and 2.5 μl of the solution was spotted on the plate. Development was carried out at room temperature with 0.2 M sodium chloride. The developed spot was detected by spraying the with sodium sulphide solution.

RESULTS AND DISCUSSION

In Fig. 1, the complexes are arranged on the abscissa in decreasing order of the number of N-H bonds from left to right, and the corresponding flocculation values of the colloidal As_2S_3 with these complex ions are plotted on the ordinate together with the R_F values obtained in thin-layer chromatography on silica gel. It can be seen that the flocculation value and the R_F value are highest for $[\text{CO}(\text{NH}_3)_6]^{3+}$, with the largest number of N-H bonds, smallest for $[\text{Co}(\text{phen})_3]^{3+}$, which has no N-H bonds, and show a stepwise decrease for the intermediate complexes. The number of N-H bonds within the complex corresponds to the possibility of the complex forming hydrogen bonds with water molecules and can be regarded as a measure of the degree of hydration of the complex ion. Hence it can be concluded that the

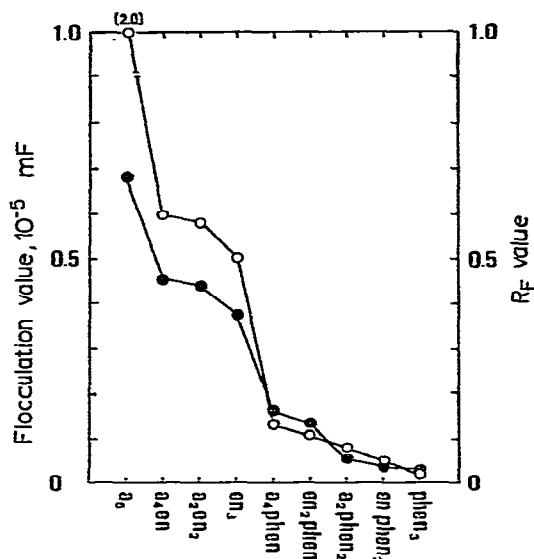
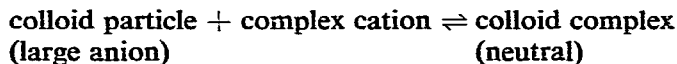


Fig. 1. Flocculation values in As_2S_3 sol (O—O) and R_F values on silica gel in 0.2 M NaCl solution (●—●).

flocculation value of colloidal As_2S_3 and the R_F value on silica gel decrease with a decrease in the degree of hydration of the complex ion.

A smaller flocculation value means that the charge on a colloid particle is more effectively neutralized by complex ions and that adsorption on to the surface of the colloid takes place more easily. In other words, the following association takes place at lower concentrations of the complex ion:



If it is taken into consideration that colloidal As_2S_3 is hydrophobic, this trend in flocculation values means that the less hydrophilic the complex ion, the more easily the adsorption on to a colloid particle takes place. This agrees with the conclusion drawn in a previous study³⁻⁶ of association between the complex cation and ordinary small anions. The same trend in R_F values means that silica gel is also hydrophobic like colloidal As_2S_3 and that the R_F value is determined by the strength of adsorption of the complex ion on silica gel.

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