Short Communications

An Ion Exchange Study of Anionic Complexes in the Zinc Thiosulfate System

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The complex formation in the zinc thiosulfate system has been investigated by employing the anion exchange method elaborated by Fröneus.\(^1\) The distribution of zinc complexes between an anion exchanger saturated with thiosulfate ions and complex zinc thiosulfate solutions was studied at varying ligand concentration using a radioactive zinc isotope for analysis.

Earlier potentiometric measurements\(^2\) indicate that anionic zinc thiosulfate complexes are formed, and from the stability constants it may be estimated, that the distribution function \(\phi\) should have a maximum at a free thiosulfate ion concentration of about 50 mM. A pronounced maximum is indeed obtained at \([S_2O_3^{2-}] = 40\) mM and thereby the existence of anionic zinc thiosulfate complexes is verified.

Earlier potentiometric measurements\(^3\) on the thiosulfate systems of zinc(II) and cadmium(II) could be interpreted by assuming the formation of three mononuclear zinc complexes and four cadmium complexes and in addition one weak dinuclear complex, \(M_2A_4\), in each system. The zinc complexes were found to be comparatively weak and the cadmium complexes rather strong.

In investigations of weak complex systems the ionic medium must be changed substantially to permit a thorough study of presumptive anionic complexes. There is then always the risk that medium changes are falsely interpreted as a continued complex formation.

An interesting example of the difficulties in interpreting measurements on weak complex systems is provided by the investigations on the cadmium sulfate system performed by Leden\(^8\) and Fröneus.\(^4\) To describe potentiometric measurements with a cadmium amalgam electrode Leden had to assume that three mononuclear cadmium sulfate complexes exist.\(^8\) Investigations with the aid of a silver electrode indicated, however, that on the whole only one complex, \(\textit{viz.}\) \(\text{CdSO}_4\), was formed. Leden interpreted the difference between the results from these two methods as a change in activity factors depending on the exchange of perchlorate ions for sulfate ions. From anion exchange measurements Fröneus concluded that anionic cadmium sulfate complexes exist but that they are very weak.\(^4\)

Even if the existence of anionic zinc thiosulfate complexes appeared to be well established by the potentiometric measurements,\(^2\) it seemed important to confirm these results by an independent method since it is obvious that measurements with metal amalgam electrodes may be seriously misinterpreted because of systematic errors (cf. also Sandell\(^6\)). In this case the method of anion exchange is a natural choice.\(^1\)

It may be shown,\(^1\) that if anionic complexes are formed, the distribution function, \(\phi\), shows a maximum when plotted against the ligand concentration, [A]. This maximum of \(\phi\) occurs at the ligand concentration at which the concentration of the neutral complex is maximal. If no anionic complexes are formed the sorption is insignificant at all ligand concentrations and no maximum of \(\phi\) is obtained.

Experimental. Chemicals. The anion exchanger was Dowex 2 x 4 20-50 mesh. It was saturated with thiosulfate ions, washed with demineralized water and air-dried.

A radioactive \(^{65}\)Zn isotope (a \(\gamma\)-emitter with \(t_1/2 = 245\) days) was used for analysis. \(^{65}\)ZnCl\(_2\) (New England Nuclear, radiometric purity 99\%) was transferred to \(^{65}\)Zn(ClO\(_4\))\(_2\) by fum-
ing three times to dryness with concentrated perchloric acid. An inactive zinc perchlorate solution was prepared from zinc oxide (Merck p.a.) and perchloric acid (Baker p.a.). From this inactive zinc perchlorate solution and the active preparation a radioactive stock solution, 7.84 mM Zn(ClO₄)₂, was prepared. A sodium thiocyanate solution was prepared from Merck's p.a. preparation. It was standardized against KBrO₃ (Baker p.a.).

Measurements. A set of solutions was prepared by adding a volume v of 1.011 M Na₂S₂O₃ and 0.500 ml 7.84 mM radioactive Zn(ClO₄)₂ to a 50 ml volume flask and then distilled water to 50 ml. 25 ml of each solution were shaken with 1.000 g of the thiocyanate saturated and air-dried anion exchanger at 25.0°C for one day. Then the total zinc concentration in the solution, C_M, was analyzed by use of a Landis and Gytr scintillation γ-counter. The zinc concentration in the ion exchanger, C_MR, was calculated and finally \( \phi = C_{MR}/C_{M} \text{ (g/g)} \). The corresponding values of

\[ v, C_A, C_M, C_{MR}, \text{ and } \phi \] are collected in Table 1 and \( \phi \) is represented as a function of \( C_A \) in Fig. 1.

Discussion. A calculation based on the stability constants, obtained from potentiometric measurements, shows that a maximum of \( \phi \) can be expected to appear at about 50 mM thiocyanate ion concentration. (These constants refer to 3 M NaClO₄.) From Fig. 1 it is clear that \( \phi \) has a maximum at \( C_A = (40 \pm 15) \text{ mM} \). In view of the large difference in ionic medium the agreement is satisfactory. The measurements with the anion exchanger thus support the assumption of formation of anionic zinc thiocyanate complexes, based on the potentiometric measurements. Considering these results it does not seem to be necessary to investigate the cadmium thiocyanate system by anion exchanger measurements. The complex formation in this system is much stronger and the influence of medium changes on the results from the potentiometric measurements must be much less for cadmium than for zinc thiocyanate.

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