

Short Communications

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

HANS PERSSON

Division of Physical Chemistry, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund 7, Sweden

The complex formation in the zinc thiosulfate system has been investigated by employing the anion exchange method elaborated by Fronæus.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 measurements² indicate that anionic zinc thiosulfate complexes are formed, and from the stability constants it may be estimated, that the distribution function ϕ should have a maximum at a free thiosulfate ion concentration of about 50 mM. A pronounced maximum is indeed obtained at $[S_2O_3^{2-}] \approx 40$ mM and thereby the existence of anionic zinc thiosulfate complexes is verified.

Earlier potentiometric measurements² 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 Leden³ and Fronæus.⁴ To describe potentiometric measurements with a cadmium amalgam electrode Leden had to assume that three mononuclear cadmium sulfate complexes exist.³ Investigations with the aid of a silver electrode indicated, however, that on the whole only one complex, *viz.* $CdSO_4$, 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 Fronæus 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 Sandell⁵). 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, ϕ , shows a maximum when plotted against the ligand concentration, $[A]$. This maximum of ϕ 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 ϕ is obtained.

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

A radioactive ⁶⁵Zn isotope (a γ -emitter with $t_{1/2} = 245$ days) was used for analysis. ⁶⁵ZnCl₂ (New England Nuclear, radiometric purity 99 %) was transferred to ⁶⁵Zn(ClO₄)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 $\text{Zn}(\text{ClO}_4)_2$, was prepared. A sodium thiosulfate solution was prepared from Merck's *p.a.* preparation. It was standardized against KBrO_3 (Baker *p.a.*).

Measurements. A set of solutions was prepared by adding a volume v of 1.011 M $\text{Na}_2\text{S}_2\text{O}_3$ and 0.500 ml 7.84 mM radioactive $\text{Zn}(\text{ClO}_4)_2$ 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 thiosulfate saturated and air-dried anion exchanger at 25.0°C for one day. Then the total zinc concentration in the solution, C_M , was analysed by use of a Landis and Gyr scintillation γ -counter. The zinc concentration in the ion exchanger, C_{MR} , was calculated and finally $\phi = C_{MR}/C_M$ (l/g). The corresponding values of

Table 1. Corresponding values of the added volume, v , the total thiosulfate concentration, C_A , the total zinc concentration in the solution, C_M , the total metal concentration in the ion exchanger, C_{MR} , and the distribution function, ϕ . (v in ml, C_A and C_M in M, C_{MR} in mol/g and ϕ in l/g.)

v	$C_A \times 10^3$	$C_M \times 10^6$	$C_{MR} \times 10^6$	ϕ
0.100	2.02	33.6	1.121	0.0334
0.200	4.04	15.23	1.578	0.103
0.400	8.08	7.35	1.776	0.242
0.500	10.10	6.17	1.806	0.293
0.600	12.13	5.71	1.817	0.318
0.700	14.15	4.99	1.835	0.368
0.800	16.17	5.02	1.835	0.366
0.900	18.19	4.73	1.842	0.390
1.200	24.25	4.34	1.852	0.427
1.400	28.29	4.25	1.854	0.437
1.600	32.3	4.27	1.853	0.434
1.800	36.4	4.27	1.853	0.434
2.000	40.4	4.41	1.850	0.420
3.000	60.6	4.34	1.851	0.426
4.00	80.8	5.13	1.832	0.357
5.00	101.0	5.36	1.826	0.341
6.00	121.3	6.47	1.798	0.278
8.00	161.8	7.67	1.768	0.231
10.00	202.1	8.87	1.738	0.196
12.00	242.5	9.83	1.714	0.174
15.00	303	12.17	1.656	0.136
20.00	404	16.43	1.549	0.094
30.00	606	24.73	1.342	0.054

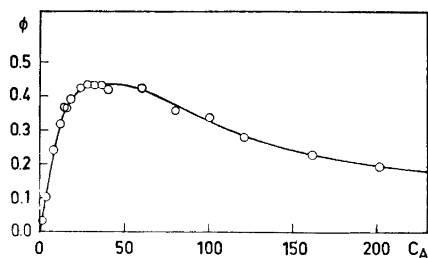


Fig. 1. The distribution ϕ as a function of the thiosulfate concentration, C_A . (ϕ in l/g and C_A in mM.)

v , C_A , C_M , C_{MR} , and ϕ are collected in Table 1 and ϕ is represented as a function of C_A in Fig. 1.

Discussion. A calculation based on the stability constants, obtained from potentiometric measurements,² shows that a maximum of ϕ can be expected to appear at about 50 mM thiosulfate ion concentration. (These constants refer to 3 M NaClO_4 .) From Fig. 1 it is clear that ϕ has a maximum at $C_A = (40 \pm 15)$ 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 thiosulfate complexes, based on the potentiometric measurements² must be much less for cadmium than for zinc thiosulfate.

Acknowledgements. I want to express my gratitude to Professors Sture Fronæus and Ido Leden for valuable discussions and to Fil.mag. Ingegerd Lind for valuable assistance with the measurements.

1. Fronæus, S. *Svensk Kem. Tidskr.* **65** (1953) 1.
2. Persson, H. *Acta Chem. Scand.* **24** (1970) 3739.
3. Leden, I. *Acta Chem. Scand.* **6** (1952) 971.
4. Fronæus, S. *Acta Chem. Scand.* **8** (1954) 1174.
5. Sandell, A. *Acta Chem. Scand.* **25** (1971) 1795.

Received August 4, 1972.