

DETECTION OF AN ANIONIC SULPHATOBERYLLIUM COMPLEX, USING A MODIFIED ELECTRODIALYTIC TRACER TECHNIQUE*

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While investigating the solvent extraction of beryllium from aqueous solutions at low pH we have obtained evidence of the existence of an anionic sulphato complex. Sidgwick (1950) suggests that the bis(sulphato)beryllium complex $\text{Be}(\text{SO}_4)_2^-$ may be present in the solid double sulphates formed between Be and several other metals, but says it does not appear to exist in solution to any great extent. Such a complex being rather weak in the acid region, a definite proof of its presence is not readily obtainable. No evidence of its existence in solution appears to have been reported. The high dissociation of sulphuric acid does not favour potentiometric work, especially when investigating a system of at least two complexes.

We have therefore resorted to a radioactive tracer method employing electrodialysis. Electrolytic transport measurements have been used by other workers in conjunction with radioactive tracers to show the presence of complex anions (McLane, Dixon, and Hindman 1949; Yakovlev and Kosyakov 1955). However, a small increase of activity arising from electromigration in the direction of the anode can be rendered inconclusive by diffusion. Isolation of the space around the anode by means of an ion selective membrane overcomes this objection, but the penetration of the anionic membranes by the labelled anionic species is slow. If the stability of such an anionic species is very low, then the current will cause a substantial proportion of the cationic species of the metal to migrate to the cathode, thus disturbing the equilibrium responsible for the formation of the complex anion. This makes the detection of the anionic species more difficult and also makes a negative result less conclusive.

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To overcome these difficulties we have made use of two anion-selective membranes to separate the solution under investigation from both electrode compartments. Our apparatus consisted of three adjoining coaxial cylindrical chambers of about 2 in. diameter, made of Perspex. These were separated by Permaplex A20 membranes (Permutit Co.), and at the outer ends two platinum foil electrodes of about 2 in. diameter were mounted on the end-plates which completed the apparatus.

In a typical experiment the membranes were converted to their sulphate form and the apparatus was filled with a 1M sodium sulphate solution which had been previously adjusted to pH 2 by the addition of 2N sulphuric acid. A steady e.m.f. of 6 V was then applied and a beryllium sulphate solution labelled with ^7Be tracer was added to the middle compartment so that its ^9Be content was 10^{-8}M with approximately 10^6 disintegrations per minute per ml. For the first half-hour, no significant γ -activity was detected in either electrode compartment. Within 3 hr about 5% of the original Be content of the centre compartment had been transferred to the anode chamber, while only about 0.005% had been transported to the cathode compartment. The current was initially 350 mA, but decreased to 280 mA owing to polarization. The pH was then checked again and was 11.3, 2.3, and 1.3 in the cathode, middle, and anode compartments respectively. The current efficiency for the transport of the complex anion would be expected to be low because of the presence of the more mobile HSO_4^- and SO_4^{2-} ions.

After a similar experiment using 1M lithium chloride and the chloride form of the anion-selective membranes, the anode compartment contained slightly less than 1%, and the cathode compartment approximately 0.02% of the beryllium initially introduced into the centre compartment. The cationic transport had increased somewhat, but was still about two orders of magnitude lower than the anionic. In 1M sodium perchlorate no anionic transport of ^7Be could be detected and the cathode chamber showed about 10% of the γ -activity after 8 hr.

In each experiment the seals were checked for seepage by removing the electrolyte from both electrode chambers, washing, refilling, and electrolysis in the reverse direction. The results were reproducible, but not sufficiently accurate for quantitative interpretation. We hope to improve the method sufficiently to overcome this defect, mainly by keeping constant ligand and hydrogen ion concentrations and by a better sampling technique.

References

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