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THERMODYNAMICS IN NON AQUEOUS SOLVENTS. SILVER (I) AND URANIUM (VI) COMPLEXES WITH AMINES IN DIMETHYL SULOFOXIDE.

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In recent years a wide number of papers has been reported concerning the thermodynamics of uranyl (VI) complex formation in aqueous solution (1). From the investigations quoted in the literature, the uranyl (VI) ion displays a tipically " hard " behaviour (2) with a strong preference for oxygen donor ligands. A number of equilibrium studies, however, cannot be carried out, in aqueous solution, on account of the hydrolytic reactions of the uranyl (VI) ion occurring already in moderately acidic solutions. This is the case with ligands coordinating through nitrogen, such as amines. These ligands are, in fact, protonated in the pH region where the protolytic equilibria of the uranium (VI) ion are negligible. In order to get some information on the complexing ability of uranium (VI) with such ligands a solvent is therefore to be chosen where the hydrolysis of the uranyl (VI) ion cannot occur and the ligands are not protonated.
For this purpose dimethyl sulfoxide, DMSO, seems to be a very suitable solvent. In the present investigation we report the thermodynamic functions for the complex formation in DMSO between the uranyl (VI) ion and a number of ligands, all coordinating via nitrogen, ranging from simple mono-amines to poly-amines. The investigation has been carried out at 25° C and in a medium of an ionic strength 0.1 M with ET_4NClO_4.
The stability constants of the uranium (VI) complexes have been obtained by potentiometric measurement using the method of competitive complex formation. In the present study silver (I) was the auxiliary central group. The method of

course requires the preliminary determination of the stability constants of the silver (I) complexes with the same ligands.

The enthalpy changes for the uranium (VI) complexes as well as for the silver (I) ones have been obtained by direct calorimetric measurements.

Both the silver (I) and uranyl (VI) complexes are heavily enthalpy stabilized whereas the entropy contribution counteracts the complex formation, generally quite strongly. The lower stability of uranyl (VI) complexes as compared with the analogous silver (I) systems are likely mainly due to the stronger solvation of UO_2^{2+} ion in DMSO, which is also confirmed by less favourable enthalpy contributions and more favourable entropy changes to the complex formation.

REFERENCES

1) L.G. Sillen and A.E. Martell, "Stability Constants", Spec.Publ.No.17, the Chemical Society, London 1964; idem, supplementum,No.25,1971; D.D.Perrin,"Stability Constants, Organic Ligands", Pergamon, Oxford, 1979.

2) R.G. Pearson, J...Amer. Chem. Soc. 85 (1963) 3533.