

Effect of Electrochemical Reduction on the Stability of Complexes of Alkali Metal Ions with Crown Ether Derivatives

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The ability of synthetic ionophores such as macrocyclic polyethers to bind, recognise and transport cations through membranes is an interesting subject with important applications in several areas.[1] These properties result from specific characteristics of those host molecules such as binding strength and selectivity towards specific guest cations. The presence on the host molecules of electroactive groups capable of being electrochemically reduced can lead to an enhancement of the cation binding properties and larger selectivity.[2,3]

In this communication we present a study of the factors that can influence the complexation strength between alkali metal ions and electrochemically reduced molecules. These ligand molecules are macrocyclic polyether systems of the crown ether type with six and seven oxygen atoms in the macroring and in which has been incorporated an anthraquinone unit. This study was realised in acetonitrile medium using cyclic voltammetry and potentiometry as analytical techniques.

When the ligand molecules are electrochemically reduced on the presence of alkali cations, the observed changes in the redox potentials to more positive values indicate a more strong binding of the metal cations to the corresponding radical anions and dianions, comparatively to the interaction of the neutral form of the ligands. These results indicate a coupling between complexation of the cation by the crown ether and the redox process.

The redox potential shifts together with the stability constants of the neutral ligands[4] have been used to determine the conditional formation constants of the alkali metal ions with the reduced ligands in the radical anion and dianion forms. The magnitude of the potential shifts and the binding constants was larger for the smaller and harder Li^+ cation, which evidences the strongest affinity to the reduced ligands, and was smaller for the larger and less hard Rb^+ and Cs^+ cations. It was found that the binding of alkali cations with the reduced ligands, radical anion and dianion forms, decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+, \text{Cs}^+$ and is consistent with the decrease of the ionic potential of the complexed cation. Electrochemical results indicated a degree of selectivity for the Li^+ over the other alkali cations.

The size and number of oxygen atoms and the electronic structure of the macrocyclic cavity of the ligand appear to be less relevant on the complexation process of the reduced ligands in contrast to the behaviour of the complexation of the ligands in the neutral state where such factors play a dominant role.

The results also indicate that the electrochemically reduced redox group that originates the radical anion is the carbonyl oxygen atom that is inside the macrocyclic cavity. An additional charge-charge electrostatic interaction between ligand and cation and the appropriate sterical position of that reduced group with respect to the cation binding centre contribute to a very strong binding with the alkali cations. The dianion originated from the reduced carbonyl group not located in the macrocyclic cavity is too distant to interact strongly with a cavity-bound cation and thus induces a smaller increase on the complexation strength, although it is also appreciable.

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2. J.M. Caridade Costa, B. Jeyashri and D. Bethell, *J. Electroanal. Chem.*, **351**, 259 (1993).
3. J.M. Caridade Costa and D. Bethell, *J. Coord. Chem.*, **46**, 551 (1999).
4. J.M. Caridade Costa and P.M.S. Rodrigues, submitted to publication.

References: