Polarographic Study of Tl\(^{+}\), Li\(^{+}\), Na\(^{+}\), K\(^{+}\), and Cs\(^{+}\) Complexes with Monensin Anion in Dipolar Aprotic Solvents

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Summary. The stability constants, \(K_s\), of monensin complexes with Li\(^{+}\), Na\(^{+}\), K\(^{+}\) and Cs\(^{+}\) ions were studied by a competitive polarographic method using the Tl\(^{+}\)/Tl(Hg) redox couple as a sensitive electrochemical probe. The \(K_s\) values are strongly influenced by the solvents (acetonitrile, propionitrile, acetone, N,N-dimethylformamide, N-methyl pyrrolidinone, N,N-dimethylacetamide, dimethylsulfoxide, N,N-diethylformamide and N,N-diethylacetamide were used in experiments) and vary inversely with the Gutmann donicity scale. Molecular mechanics computations revealed the probable structures of the complexes.

Keywords. Monensin complexes; Solvent effect; Molecular mechanics computation.

Introduction

It is well known that macrocyclic ligands are capable of forming stable complexes with many cations; most of the results can be found in valuable reviews [1, 2] given by Izatt et al. There are at least three factors that make a significant contribution to the binding of cations by these ligands: i) relative cation and ligand size, ii) the ligand topology and the number of the donor sites participating in the binding, and, especially iii) the solvent effect on the selectivity and stability constants of complexes. Of these factors, the third seems to be a somewhat neglected area of research. In Chapt. 7 of Ref. [2] ("Suggestion for Future Work") we can even read; "More data valid in a variety of solvents are needed in order to understand the effect of solvent parameters on thermodynamic and kinetic values".
We have recently been involved in the study of the complexation of thallium(I) [3] and alkali metal cations [4] by crown ethers in dipolar aprotic media. The stability constants of the resulting complexes were found to decrease with the Gutmann donicity [5] of the solvents. During the present work our attention has been focused on the complexes of monensin. The information for understanding their behaviour in solutions is rather sparse. The majority of earlier studies involved methanol as solvent and only in Ref. [6] some dipolar aprotic solvents (acetonitrile, propylene carbonate, N,N-dimethylformamide and dimethylsulfoxide) were included. The results of that work suggest strongly that it would be of interest to compare the stabilities of complexes in a series of aprotic solvents representing a wide variety of donicities.

In addition, the complexes of alkali metal cations with monensin are interesting from the biological and topological point of view. Monensin (hereafter abbreviated as MonH) is known to induce exchange of alkali metal and H⁺ ions across biological membranes [7]. X-ray analysis revealed macrocyclic structures of the ligand and its cation complexes; the Na⁺ [8] and Li⁺ [9] complexes with Mon⁻ involves coordination by six oxygen atoms.

In a previous communication [10] we have reported a study of the solvent dependence of the acid dissociation constant of MonH. In this paper we describe a polarographic study of Tl⁺, Li⁺, Na⁺, K⁺ and Cs⁺ complexes with Mon⁻ in acetonitrile, propionitrile, acetone, N,N-dimethylformamide, N-methyl pyrolidinone, N,N-dimethylacetamide, dimethylsulfoxide, N,N-diethylformamide and N,N-diethylacetamide. The possible structures of the complexes in methanol are discussed on the basis of molecular mechanics computations.

**Experimental**

Sodium monensin (Sigma) was purified and converted successively into the free acid and the tetrabutylammonium salt [11]. TiClO₄₂⁻, LiClO₄⁻, NaClO₄⁻, KClO₄⁻ and CsClO₄⁻ (high purity commercial reagents) were dried under vacuum at 120 °C. Tetrabutylammonium perchlorate, TBAP, was prepared by conversion of (n-C₄H₉)₄NI; it was recrystallized several times from water and dried in vacuo at 60 °C. All the solvents were dried as described in [12] and fractionally distilled at reduced pressure under an argon atmosphere immediately prior to use.

Polarographic and cyclic voltammetric curves were determined in a three electrode system, a Radelkis OH 105 apparatus being used. The working electrode was either a mercury drop electrode with a controlled drop time of 1.0 s or a hanging mercury drop electrode [13]. The auxiliary electrode was Pt-wire. The potentials were measured against an aqueous SCE, a two part salt bridge being used. One arm of this bridge contained solvent and electrolyte exactly as in the polarographic vessel. All