

XVIII

**INTERNATIONAL
SYMPOSIUM ON
MACROCYCLIC
CHEMISTRY**



BOOK OF ABSTRACTS

**JUNE 27 -
JULY 2
1993**

**UNIVERSITY OF TWENTE
ENSCHEDA
THE NETHERLANDS**

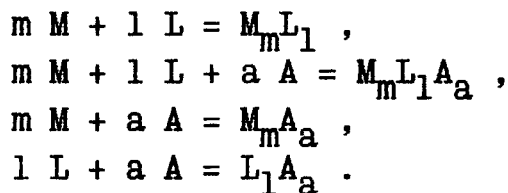
THE THERMODYNAMICS OF CATION-MACROCYCLE-ANION-SOLVENT INTERACTIONS

V.P. Solov'ev, O.A. Raevsky, N.N. Strakhova

Laboratory of Computer-Aided Molecular Design
Institute of Physiologically Active Compounds of Russian Academy
of Sciences, 142432 Chernogolovka, Moscow region, RUSSIA

The thermodynamic study of the complexation of unsubstituted, benzo, 4'-R-benzo and dibenzo crown ethers containing 12-24 ring atoms with alkali and alkaline earth salts was carried out in acetonitrile, ethanol and water at 298 K by using a calorimetric, IR spectrophotometric and NMR technique.

The original universal computer package of programs by using general nonlinear least squares curve fitting procedures is applied for estimations the stoichiometry each complexes and number of complexes in solution, the stability constants, the reaction enthalpies and entropies from any combination experimental data [1]. In the system **M-L-X-S**, where **M**, **L**, **A** and **S** are the metal cation, the ligand, the anion and the solvent, several equilibriums were taken into account :



The influence of the substituents and the macrocyclic size on the stoichiometry and number of complexes in solution and also the essential effect of anion of the salt on the thermodynamic values are discussed.

The general approach to estimate selectivity of the complexation in cases, when there are the complexes of various stoichiometry and various metals and ligands in solution, is suggested:

$$\text{Sel}(M_k) = \frac{\sum_{i=1}^n \nu_{ik} \cdot C_i}{\sum_{k=1}^m \sum_{i=1}^n \nu_{ik} \cdot C_i} = \frac{\sum_{i=1}^n \nu_{ik} \cdot \exp(\ln\beta_i + \sum_{j=1}^b \nu_{ij} \cdot \ln C_j)}{\sum_{k=1}^m \sum_{i=1}^n \nu_{ik} \cdot \exp(\ln\beta_i + \sum_{j=1}^b \nu_{ij} \cdot \ln C_j)} ,$$

where $\text{Sel}(M_k)$ - the selectivity to metal M_k , when in solution there are one ligand and m metals; C_i - the concentration of the metal complex i ; ν_{ik} , ν_{ij} - stoichiometric coef.; β_i - complex stability constant ; C_j - the concentration of reagent j .

[1]. Solov'ev V.P., Vnuk E.A., Strakhova N.N., Raevsky O.A. "Thermodynamic of complexation of the macrocyclic polyethers with salts of alkali and alkaline-earth metals". VINITI, Moscow, 1991, 373PP.