

Fig. 1. Scheme of the idealized ion transport through an asymmetric membrane based on a neutral carrier S.

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Solid-Liquid (S-L) and Liquid (L-L) Phase Transfer of Salts *via* 'Encapsulated' Crown Ether Cation Complexes

D. N. REINHOUDT

Department of Organic Chemistry, Twente University of Technology, Enschede, The Netherlands

In recent years crown ethers have been successfully used for the transport of salts, both inorganic and organic, from an aqueous phase to organic solvents. Our work has extended the applicability of these crown ethers to the transport of salts from the solid state into solution both aqueous and non-aqueous. For this purpose a number of novel crown ethers have been synthesized that have in addition to a polar 'cavity' formed by donor atoms of the macrocyclic ring, (an) additional anionic functional group(s) covalently bound to the macroring.

The first part of the lecture will deal with the design of such macrocycles that can encapsulate a spherical cation in a flexible cavity or that can encapsulate *non*-spherical cations, *e.g.* uronium cations, in a relatively rigid cavity.

Together with the synthesis results of complexation studies using ¹H NMR spectroscopy will be discussed.

In the second part the use of crown ethers for the transport of sparingly soluble salts from the solid state into aqueous solutions will be dealt with. The emphasis will be placed on theoretical models that can be used to describe such phase transfer processes and to predict thermodynamic stability constants of complexes required for solubilisation.

The lecture will conclude with a comparison of these models with experimental results.

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Ion Transport and Complex Formation Properties of Artificial Membrane Carriers

E. GRELL

Max-Planck-Institut für Biophysik, Heinrich-Hoffmann-Str. 7, D-6000 Frankfurt am Main 71, F.R.G.

Many natural compounds of antibiotic nature such as valinomycin [1], streptogramins (group B) [2] and calcimycin [3] exhibit the general structural properties of macrocyclic or pseudo-macrocyclic compounds. Such compounds act as artificial membrane carriers and increase the cation permeability of phospholipid bilayer membranes and of certain biological membrane systems. The study of these membraneactive compounds acting as multidentate ligands for cations has substantially contributed to our present knowledge of the basis of transport mechanisms and cation specificity.

Spectroscopic methods have been applied to the investigation of the physicochemical properties of these macrocyclic compounds as far as structural aspects and cation selectivity in homogeneous solution and in the membrane-bound state are concerned [4]. Thermodynamic parameters of the complex formation equilibria (stability constants, equilibrium enthalpies, stoichiometric coefficients) have been obtained from spectrophotometric titrations. For the fast and precise determination of these parameters a computer-controlled high performance titrator has been developed [5]. In order to identify the relevant groups of the antibiotics which are involved in the direct coordination of the cations, a large number of suitable model compounds have been synthesized and investigated. The experimentally observed alkali and