Minisymposium: Artificial Ion Carrier Molecules and Transport Processes

Convener: JEAN-MARIE LEHN; Paris and Strasbourg, France

H1

Artificial Transport Processes and Design of Synthetic Carrier Molecules

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The design of synthetic carrier molecules and of transport processes represents a major area of research into the functional features of supramolecular systems, in addition to molecular recognition and catalysis.

The investigation of artificial transport systems presents two main goals: (a) to set up transport processes which follow diverse mechanisms; (b) to design carrier compounds which mediate the selective transport of substrates.

Our work in this field has been concerned with a wide range of topics; the results obtained are reviewed and discussed [1, 2]. Macrobicyclic ligands forming cryptate complexes function either as selective receptors or carriers for alkali cations [3]; or toxic metal cations [4]; transport rates depend on carrier structure and on external factors like the counteranion. Dianionic macrocyclic carriers perform selective Ca^{2+}/K^+ transport which may be regulated by the pH [5]. Selective transport of primary ammonium cations, in particular of biogenic amines, may be achieved in artificial or natural systems [6, 7]. Cationic carriers transport anionic substrates and permit for instance the selective transfer and removal of phosphate in emulsion systems [8]. Electron transport, mediated by redox carriers, may be driven by light [9], or coupled to anion antiport, or coupled to cation symport in a two-carrier process displaying substrate selection and regulation [10]. Various extensions suggested by the analysis of these results are considered; in particular the prospects offered by cocarriers and artificial channels [11–13] are explored.

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Ion Transport in Artificial Membranes Induced by Neutral Ionophores

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Electrodialytic transport of ions has been studied on solvent polymeric membranes that contained neutral carriers selective for Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, Cd^{2+}, Pb^{2+}, organic cations, and anions, respectively [1, 2]. The measured transport numbers attest a high selectivity in ion permeation. Specific ion transport has been realized under zero-current conditions. A selective Ca^{2+}-pump, driven by a transmembrane pH gradient, was designed by adding proton carriers to a calcium-carrier membrane [3]. Similar systems were realized for pumping Li^+ and Cd^{2+} [4, 5]. Trioctyltin chloride seems to facilitate the permeation of bicarbonate ions and has been introduced in liquid membrane electrodes selective for HCO_3^-.

Using one given ionophore, the transport selectivity may depend on different parameters, such as the polarity of the membrane medium (plasticizer, polymeric matrix), the concentration of carriers, and the ionic composition of the solutions contacting the membrane [1, 6]. Asymmetric membranes have therefore been realized in order to exhibit different transport selectivities when ions M and N are pumped electrodialytically in different directions (see Fig. 1).

The model membrane shown in Fig. 1 transports the divalent ion M^{2+} preferentially in one direction and the monovalent ion N^+ in the opposite direction. This phenomenon is a consequence of the different environment of the carrier in the two membrane sections. Processes of the type shown in Fig. 1 may be used for ion separations.

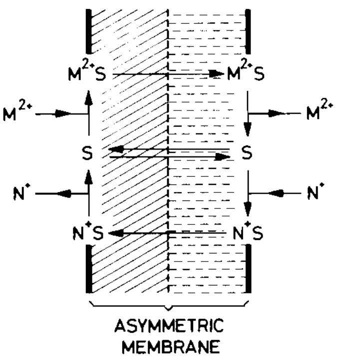

Fig. 1. Scheme of the idealized ion transport through an asymmetric membrane based on a neutral carrier S.

Acknowledgement. This work was partly supported by the Swiss National Science Foundation.

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H3

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

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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

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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 membrane-active 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