

## Minisymposium: Artificial Ion Carrier Molecules and Transport Processes

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### 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]. Macrocyclic 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  $\text{Ca}^{2+}/\text{K}^{+}$  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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### H2

#### 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  $\text{Li}^{+}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , 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  $\text{Ca}^{2+}$ -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  $\text{Li}^{+}$  and  $\text{Cd}^{2+}$  [4, 5]. Trioctyltin chloride seems to facilitate the permeation of bicarbonate ions and has been introduced in liquid membrane electrodes selective for  $\text{HCO}_3^{-}$ .

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 electro-dialytically in different directions (see Fig. 1).

The model membrane shown in Fig. 1 transports the divalent ion  $\text{M}^{2+}$  preferentially in one direction and the monovalent ion  $\text{N}^{+}$  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.