PO D 1

Molecular ionics of anion receptor molecules: A microcalorimetric study

D. Grell [a)], E. Grell [b)], P. Bugnon [c)], B. Dietrich [a)] G. Quinkert [d)] and J.-M. Lehn [a)]

[a)] Institut Le Bel, Université Louis Pasteur, F-67000 Strasbourg
[b)] Max-Planck-Institut für Biophysik, D-60596 Frankfurt
[c)] Institut de Chimie Analytique, Université de Lausanne, CH-1015 Lausanne
[d)] Institut fur Organische Chemie, Johann-Wolfgang-von Goethe-Universität, D-60439 Frankfurt

Up to now, many synthetic molecules have been shown to form stable and sometimes selective anion complexes, mostly due to electrostatic interactions and hydrogen bond formation. However, no high affinity binding could so far be achieved in aqueous solution of neutral pH. Therefore, a pyrrole containing macrobicyclic receptor molecule of the polyammonium type, exhibiting C_3 symmetry, has been synthesized. Molecular modeling studies, based on the crystal structure of the perchlorate complex of the furan containing analogue, support the assumption that the pyrrole containing ligand can form a central cavity suitable to coordinate tetrahedral oxoanions. Shape and size of the cavity appear to be controlled by conformational properties of the ligand.

Qualitative phosphate and sulfate binding studies have been carried out with the pyrrole containing ligand on the basis of ^{31}P- and ^{3}H- NMR spectroscopy. Quantitative binding studies by titration microcalorimetry have been performed at pH 6.1 and 7.0 with phosphate, sulfate, bicarbonate, perchlorate and chloride. The ligand is anion selective, forms 1:1 complexes and exhibits affinities for sulfate and phosphate nearly up to 10^7, for bicarbonate around 10^3 and for chloride $<10^2$ M^{-1}. The interaction is dominated by a large enthalpic contribution, up to -53 kJ mol^{-1}, and an entropic contribution as high as -45 J K^{-1} mol^{-1}. The observed affinities are interpreted and discussed on the basis of the electrostatic interaction model introduced by Fuoss (J, Am. Chem. Soc. *80,* 5059 (1958). The unfavorable entropy contribution is attributed to anion deprotonation, specific binding of water molecules and conformational rearrangements occurring as a consequence of complex formation. Titration microcalorimetry proves to represent an extremely suitable method for the quantitative investigation of synthetic anion receptor molecules.