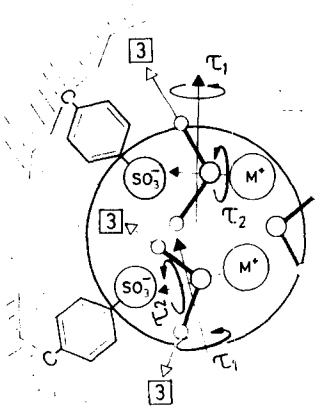
MOLECULAR MOTIONS OF SORBED WATER IN CROSS-LINKED POLYELECTROLYTES

M.Busch and E.v.Goldammer

Institut für Biophysik,Ruhr-Universität, D-4630 Bochum 1,FRG

The behavior of ions closely associated with water molecules is of interest in understanding the physical properties in the region of primary hydration around ions in solution. Short-range interactions are also of importance in regard to the behavior of ions in membranes and living cells.



In dealing with sorption on ion-exchange resins, the amount of sorbed water can be defined as n moles per equivalent of exchange group. Thermodynamic data, such as the partial molal entropy or enthalpy of sorption can be determined experimentally, as described elsewhere (1). Table 1 gives some of the experimental data. Both, $\Delta\bar{S}$ and $\Delta\bar{H}$ have a minimum for all alkaline cations at a water concentration of $n \approx 0.8$, i.e., there are 0.8 water molecules per $-SO_3$ group. The first sorbed water molecule is characterized by an anisotropic rotation, as it is visualized in the figure. The two different correlation times τ_1 and τ_2 can be extracted from 1-H NMR relaxation time measurements at varying frequencies. Their values are listed in Tab.1.
For deuteron, the pertinent relaxation interaction is along the O-D bond (axis 3 - in the figure), which is described by the correlation time τ_3. This time constant can be calculated from the values τ_1 and τ_2. The result is also given in Tab.1. These correlation times are in good agreement -within experimental error- with corresponding data extracted from 2-H NMR relaxation time measurements taken at 13.82 MHz and 27.64 MHz (2).

TABLE 1. Minimum values of the partial molal Entropy and Enthalpy of Sorption with some Correlation Times of Sorbed Water - as indicated in the Figure.

	$\Delta\bar{S}$	$\Delta\bar{H}$	τ_1*)	τ_2*)	τ_3*)
	$kJ \cdot mol^{-1}K^{-1}$	$kJ \cdot mol^{-1}$	ns	ps	ns
Li	-0.14	-48	40	32	0.27
Na	-0.16	-55	45	29	0.27
K	-0.18	-60	100	32	0.46
Cs	-0.27	-86	200	32	0.77

*) values for n = 0.8 at 299K

1) E.v.Goldammer, A.Müller & B.E.Conway, (1974), Ber.Bunsenges.phys.Chem.78, 35.
2) M.Busch & E.v.Goldammer, (1980), Bull.Magnet.Res.2, 333.