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Determination of membrane hydration numbers of alkali metal ions by insertion in a conducting polymer

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Abstract

In aqueous solutions, the alkali metals ions, Li^+, Na^+, K^+, Rb^+ and Cs^+ are known to be associated with a number of H_2O molecules. Traditionally, a distinction is made between a primary solvent shell, (or inner solvation shell), consisting of H_2O molecules directly coordinated to the metal ion, and a secondary (or outer) solvation shell, consisting of all other water molecules whose properties are still influenced significantly by the cation.

Knowing the hydration number is important when considering, for instance, the transport of Na^+ and K^+ in biological cell membranes, since their different behavior may depend on the details of ion hydration.

Although the solvation of alkali metal ions in aqueous solution has been discussed for many years, there is still no clear consensus. Part of the discrepancy is simply that different methods measure over different time scales, and therefore do not necessarily define the same hydration shell.

This work presents a systematic study of one special variant of the hydration numbers of the 5 alkali metal ions, using the electrochemical insertion of the ions in a conducting polymer (polypyrrole containing the large immobile anion DBS^-). The technique of Electrochemical Quartz Crystal Microbalance (EQCM) has been used to simultaneously determine the mass

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the total mass of metal ions and H_2O entering the film quite accurately. The charge inserted allows direct calculation of the number of M^+ ions entering the film, and therefore the inserted M^+ mass. The mass of the water molecules can then be calculated as a difference. The values determined this way may be called membrane hydration numbers.

The results yield the following membrane hydration numbers:

Li^+: 5.3–5.5; Na^+: 4.3–4.5; K^+: 2.0–2.2; Rb^+: 0.8–0.9; Cs^+: ~ 0. The most important result is the clear distinction between all the 5 cations, including a clear difference between Na^+ and K^+. The method is attractive because of the relative simplicity of interpretation—it may also be akin to transport in a cell membrane.

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Keywords

Hydration number; Cation solvation shell; Conducting polymer

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