



## Osmotic coefficients

Nielsen, Ole Faurkov; Bilde, Merete; Kjærgaard, Henrik Grum

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# OSMOTIC COEFFICIENTS

O. F. Nielsen<sup>1</sup>, M. Bilde<sup>2</sup>, H.G. Kjaergaard<sup>1</sup>

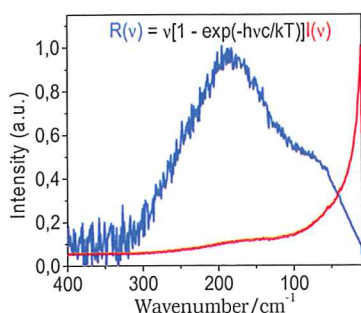
<sup>1</sup>Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

<sup>2</sup>Department of Chemistry, University of Aarhus, Langelandsgade 140, Aarhus, Denmark

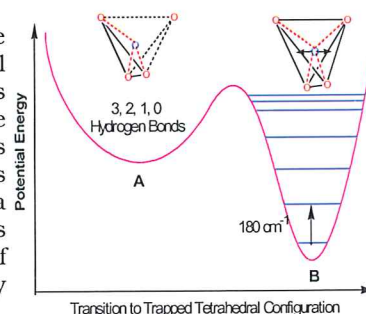
## Introduction

To preserve the overall shape of living cells the osmolarity/osmolality plays an important role. The osmolarity of the extracellular fluid is due to small inorganic ions from dissociated strong electrolytes. In a paper by Niels Bjerrum at the 16<sup>th</sup> Scandinavian Scientist Meeting in 1916, he concluded that the van't Hoff factor had erroneously been considered as a measure of the degree of dissociation of strong electrolytes.<sup>1</sup> Bjerrum proposed that strong electrolytes were completely dissociated and he introduced an osmotic coefficient to account for the measured osmotic pressure.<sup>1</sup> The molal osmotic coefficient,  $\phi$ , was expressed by Robinson and Stokes in terms of water activity (the vapour pressure of water over an aqueous solution relative to that of pure water).<sup>2</sup> We proposed the osmotic coefficient to be a product of two factors,  $\phi = \phi^d \phi^w$ .<sup>3</sup> The term  $\phi^d$  depends on the degree of dissociation of the dissolved strong electrolyte and  $\phi^w$  (obtained from Raman spectra) depends on changes in hydrogen bonded water clusters with solute concentration.

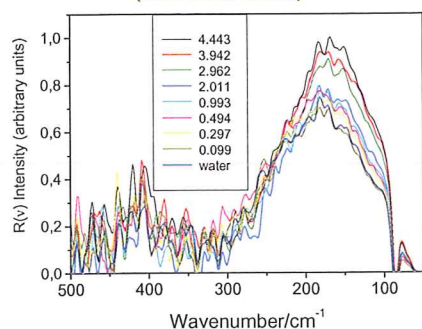
## Low Wavenumber Raman Spectroscopy



The Raman spectrum,  $I(\nu)$  is dominated by the very intense Rayleigh line extending to several hundred wavenumbers in water and aqueous solutions. This problem is overcome by use of the  $R(\nu)$ -representation.<sup>4</sup> A water band at  $180 \text{ cm}^{-1}$  is observed. The intensity of this band is proportional to the amount of water trapped in a tetrahedral configuration. In pure liquid water it is 43%. In the electrolyte solutions the amount of trapped water,  $\phi^w$ , is estimated from the intensity of the  $180 \text{ cm}^{-1}$  band.

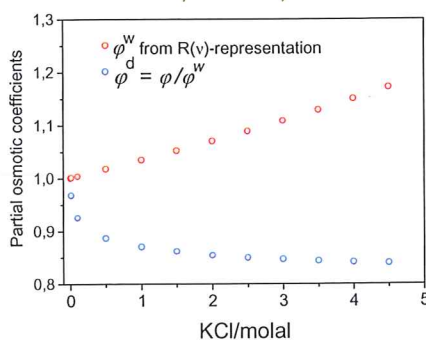


### R(ν)-representation (KCl molalities)

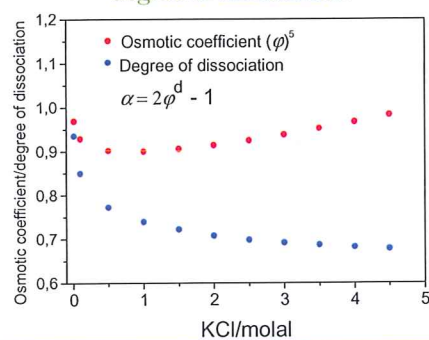


### KCl

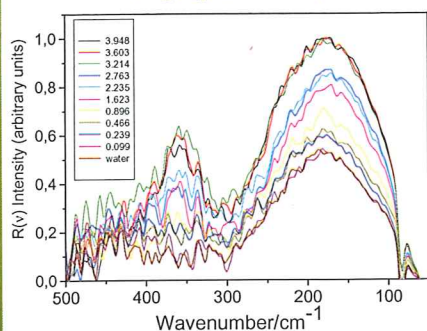
#### $\phi^w$ and $\phi^d$



### Osmotic coefficient and degree of dissociation

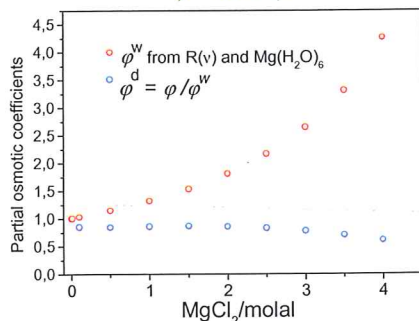


### R(ν)-representation (MgCl<sub>2</sub> molalities)

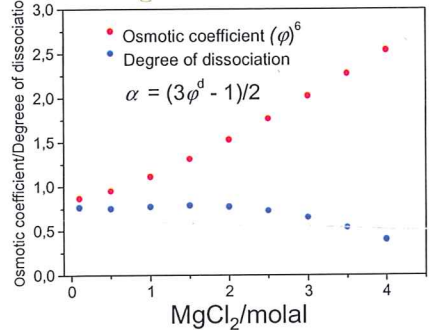


### MgCl<sub>2</sub>

#### $\phi^w$ and $\phi^d$



### Osmotic coefficient and degree of dissociation



## Conclusion

Strong electrolytes are not completely dissociated in aqueous solutions. The conventional molal osmotic coefficient,  $\phi$ , can be expressed by a product of two terms, one,  $\phi^w$ , taking into account water trapped in water clusters and water strongly bound to ions, like  $\text{Mg}(\text{H}_2\text{O})_6$ , and the other,  $\phi^d$ , describing the degree of dissociation of the electrolyte.

References: (1) N. Bjerrum, *Fysisk Tidsskrift* **15**, 58 (1917); (2) R.A. Robinson, R.H. Stokes, *Electrolyte Solutions* Butterworths, London, Sec Ed. 1959; (3) M. Frosch, M. Bilde, O.F. Nielsen, *J. Phys. Chem. A* **114**, 11933 (2010); (4) O.F. Nielsen, *Chem. Phys. Lett.* **60**, 515 (1979); (5) W.J. Hamer, Y-C Wu, *J. Phys. Chem. Ref. Data* **1**, 1047 (1972); (6) R.H. Stokes, *Trans. Faraday Soc.* **341**, 642 (1945)