

**Physical Chemists**  
are  
**Frustrated**  
by  
**Real Solutions**

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**“ .... it is almost never valid  
to use Debye-Hückel theory ...**

it is important to take proper account of

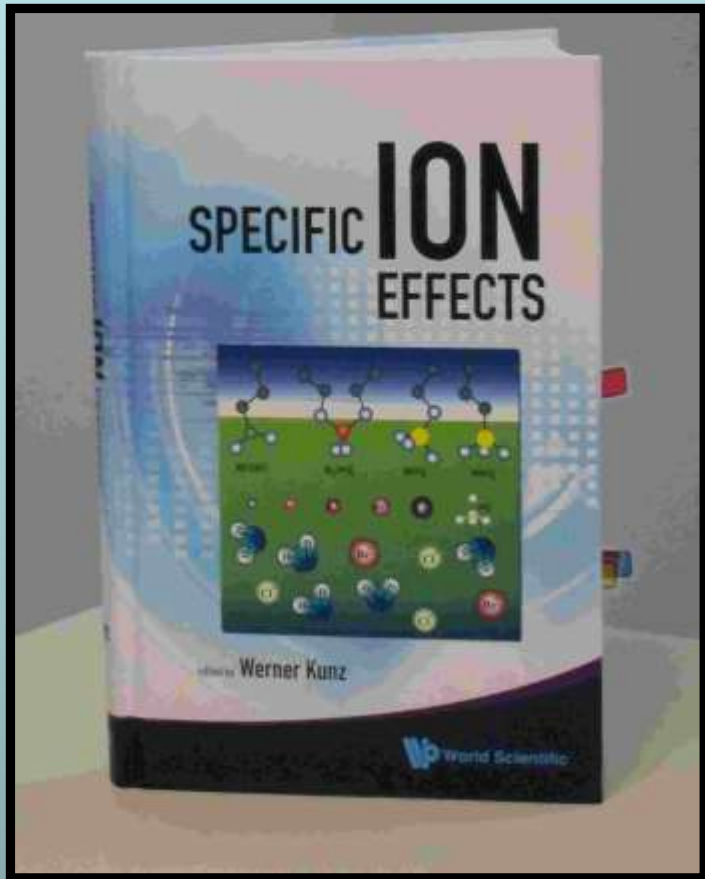
**ion size**

Stell, G. and C.G. Joslin *Biophys J*, 1986. **50(5): p. 855-859.**

The classical text of Robinson and Stokes  
(*not otherwise noted for its emotional content*)  
gives a glimpse of these feelings when it says

**“In regard to concentrated solutions,  
many workers adopt a counsel of  
despair, confining their interest to  
concentrations below about 0.02 M, ... ”**

p. 302 *Electrolyte Solutions* (1959) Butterworths ,  
also Dover (2002), emphasis added



Kunz, W. "Specific Ion Effects"  
World Scientific Singapore, 2009; p 11.

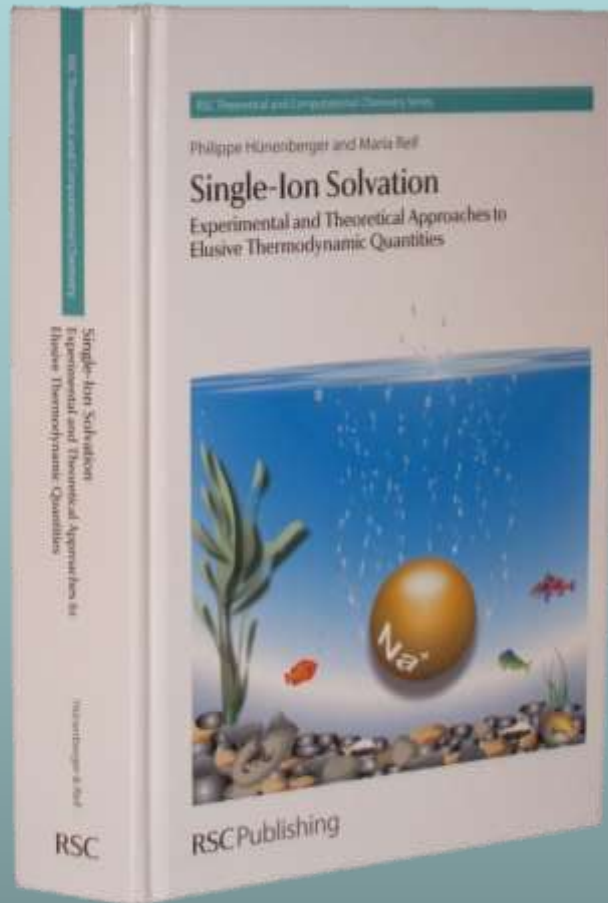


Werner Kunz

“It is still a fact that over the last decades,  
**it was easier to fly to the  
moon**  
than to describe the  
**free energy**  
**of even the simplest salt  
solutions**

*beyond a concentration of 0.1M or so.”*

# Electrolytes are Complex Fluids



After 690 pages and 2604 references, properties of

**SINGLE** Ions  
are  
**Elusive**\*

because

**Every Ion**  
**Interacts**  
with  
**Everything**

Hünenberger & Reif (2011)  
"Single-Ion Solvation  
... Approaches to **Elusive**\* Thermodynamic Quantities"

\*'elusive' is in the authors' choice in the title  
but **emphasis** is added

# **Electrolytes are Complex Fluids**

Treating a  
**Complex Fluid**  
as if it were a  
**Simple Fluid**  
will produce  
**Elusive Results**

# Ions

in a solution are a

## Highly Compressible Plasma

although the

**Solution is Incompressible**

Free energy of an ionic solution is mostly determined by the

**Number density of the ions.**

**Density varies from  $10^{-11}$  to  $10^1$ M**

in typical biological system of proteins, nucleic acids, and channels.

Learned from Doug Henderson, J.-P. Hansen, Stuart Rice, among others...Thanks!