

Activity coefficients of individual ions: Comparison of experiment and II+IW theory

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Introduction

The central question of numerous theoretical and experimental studies is that how does the chemical potential (μ_i) or its multiplicative counterpart, the activity coefficient (γ_i) depend on the concentration (c) of the electrolyte. The measurability of the activity of individual ions is an open question: some authors suggested that it is possible to determine it using ion-selective electrodes and to perform reproducible experiments; others denied it. Whether it is just a practical problem or whether it undermines the whole concept of the individual excess chemical potential is still the subject of heated debates. From a theoretical point of view, the individual ionic activity coefficient is a thermodynamically well-defined quantity that can be computed straightforwardly in computer simulations and theories.

II+IW Theory

- The activity coefficient describes deviation from ideality through the excess chemical potential:

$$\mu_i^{\text{EX}} = kT \ln \gamma_i$$

- where the excess chemical potential of species i is defined through:

$$\mu_i = \mu_i^0 + kT \ln c_i + \mu_i^{\text{EX}}$$

- Our approach:** the excess chemical potential is split into two terms corresponding to ion-ion (II) and ion-water (IW) interactions [1-2]:

$$\mu_i^{\text{EX}} = \mu_i^{\text{II}} + \mu_i^{\text{IW}}$$

- II term:** determined from the adaptive grand canonical Monte Carlo (A-GCMC) simulation method [3] using the primitive model (PM) of electrolytes:

$$u_{ij}^{\text{PM}}(r) = \begin{cases} \infty & \text{for } r < R_i + R_j \\ \frac{z_i z_j e^2}{4\pi\epsilon_0\epsilon(c)r} & \text{for } r \geq R_i + R_j, \end{cases}$$

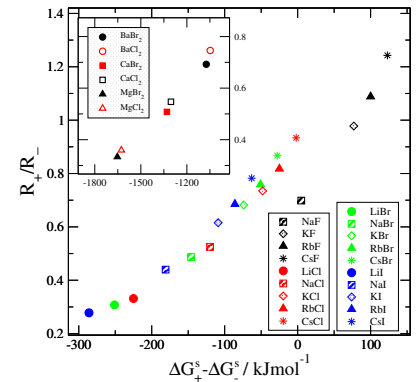
- IW term:** contains the interaction of an ion with the surrounding water represented as a continuum dielectrics. It is estimated from the treatment of Born [4] for solvation using the Born radii. The equivalent form of the equation with the hydration free energy (ΔG_i^{S}) contains only experimental parameters ($\epsilon_w = 78.5$):

$$\mu_i^{\text{IW}}(c) = \Delta G_i^{\text{S}} \frac{\epsilon(c) - \epsilon_w}{\epsilon(c)(\epsilon_w - 1)}$$

No adjustable parameters are used

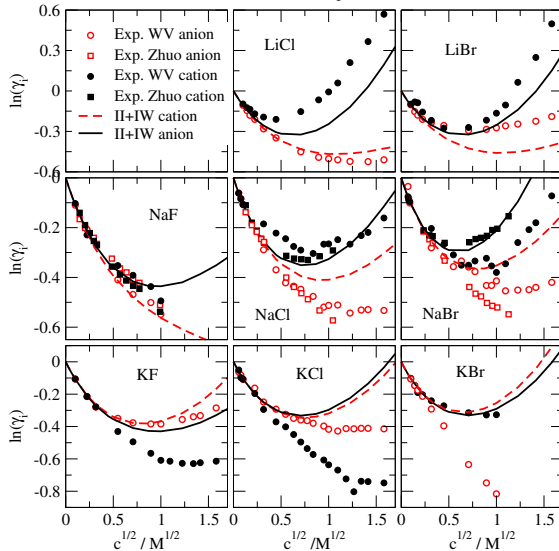
- Pauling radii [5] for the hard sphere ions: R_i
- Concentration dependent dielectric constant** [6-8]:

$$\epsilon(c) = \epsilon_w - \delta_S c + b_S c^{3/2}$$
- Experimental hydration free energy [9]: ΔG_i^{S}
- The difference $\mu_+^{\text{EX}} - \mu_-^{\text{EX}}$ depends on R_+/R_- (influencing the II term) and $\Delta G_+^{\text{S}} - \Delta G_-^{\text{S}}$ (influencing the IW term)
- These factors correlate with each other:

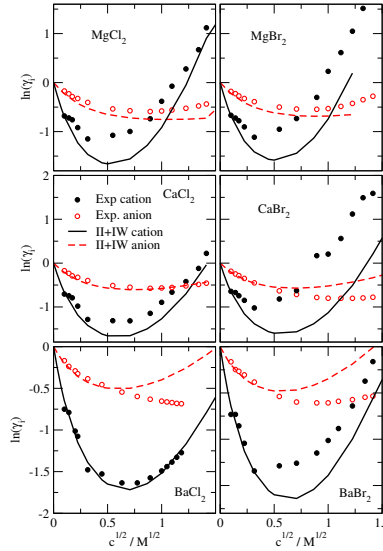


Results

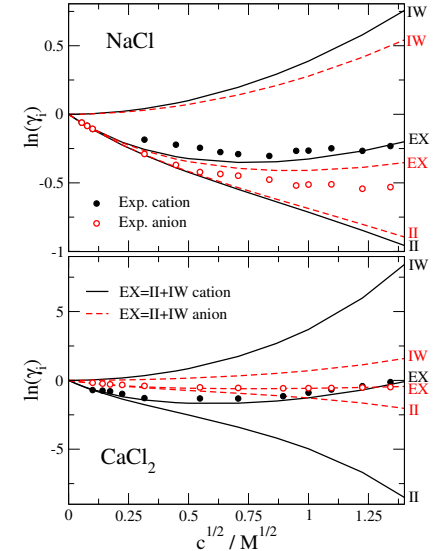
Individual activity coefficients for 1:1 electrolytes ...



and for 2:1 electrolytes



II and IW terms for NaCl and CaCl2



Experimental data are from Wilczek-Vera et al. [10] (WV) and from Zhuo et al. [11] (Zhuo).

Discussion

- The agreement with experiments is qualitative for LiX and NaX electrolytes, while it is unsatisfactory for KX electrolytes.
- In the case of K^+ , additional features should be included in the model.
- The agreement is surprisingly good for 2:1 electrolytes.
- This is especially rewarding regarding that the range of variation of $\ln \gamma_i$ is 2-3 kT .
- The behavior of $\mu_i^{\text{EX}}(c) = kT \ln \gamma_i$ is the result of the balance of the II and IW terms.
- The order of magnitude of these terms at $c = 2$ M is about
 - $\pm 0.5kT$ for 1:1 systems,
 - $\pm 2kT$ for anions in 2:1 systems, while
 - $\pm 8kT$ for cations in 2:1 systems
- The good behavior of the sum of the large positive IW and large negative II term is remarkable.
- Our results support the experimental data.
- The concept of "solvated ionic radius" is not needed to produce these results.**
- Solvation, instead, should be taken into account explicitly with the IW term.**

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