

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

Mónika Valiskó¹, Douglas Henderson² and Dezső Boda^{1,3}

¹Institute of Chemistry, Department of Physical Chemistry, University of Pannonia, Veszprém, Hungary

²Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah, USA

³Institute of Advanced Studies Kőszeg (iASK), Kőszeg, Hungary



Introduction

It is a well-known experimental fact that the activity coefficient (γ) of electrolytes (the excess chemical potential, μ_i^{EX}) depends on the electrolyte concentration (c) non-monotonically; it decreases near infinite dilution according to the Debye-Hückel limiting law, goes through a minimum, and increases at high concentrations close to saturation. Experimental determination of the mean activity coefficient from experiments is obvious, but there has been a heated debate about the measurability of the activity of individual ions. From a theoretical point of view, the individual ionic activity coefficient is a well-defined quantity. We present our II+IW theory to understand the behaviour of this important function.

Ion-Ion + Ion-Water Theory (II+IW)

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

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

- The chemical potential of species i can be expressed as:

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

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

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

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

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

- 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 for solvation using the Born radii. The equivalent form of the equation with the hydration free energy (ΔG_i^S) contains only experimental parameters:

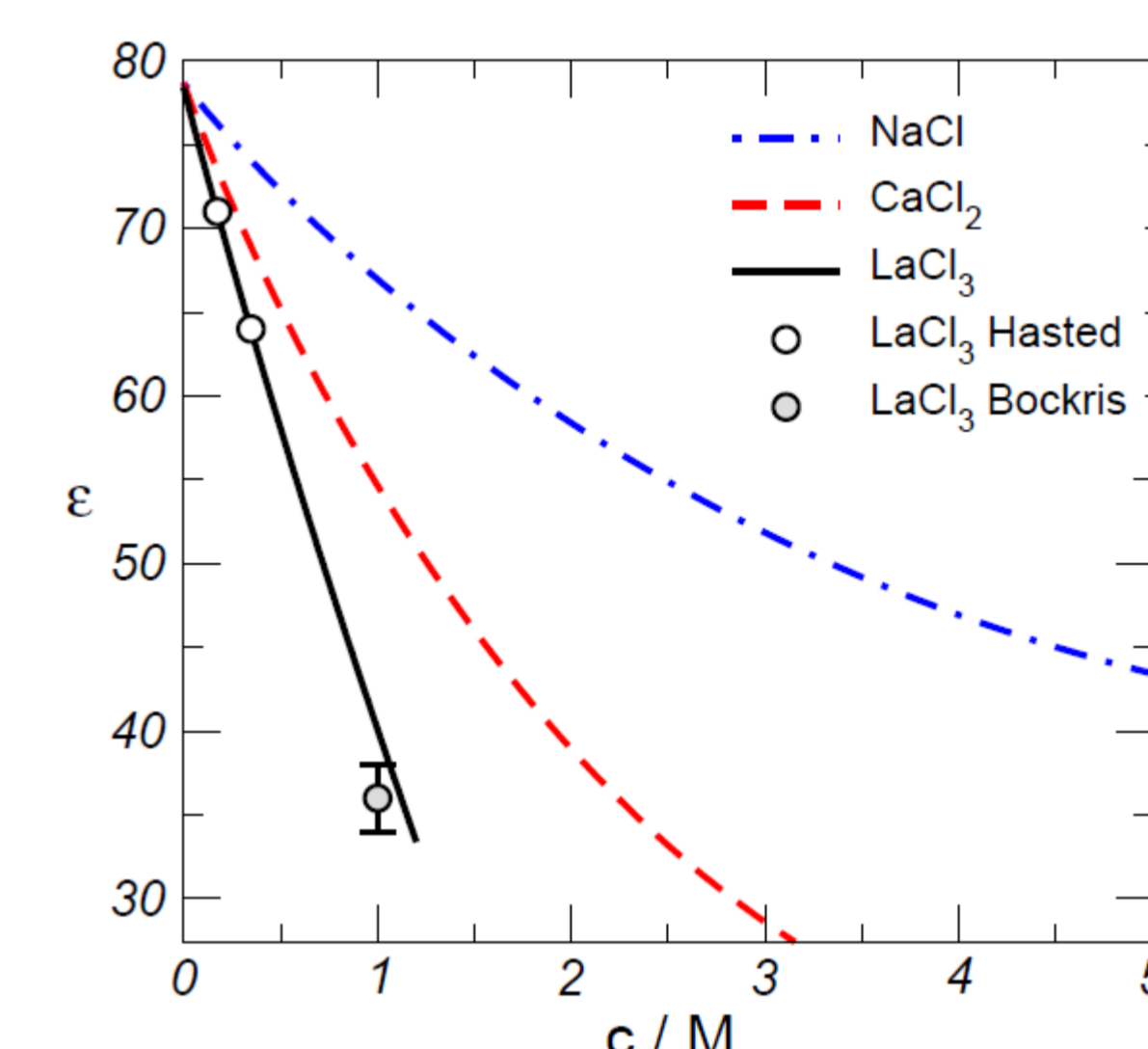
$$\mu_i^{IW}(c) = \Delta G_i^S \frac{\epsilon(c) - \epsilon_W}{\epsilon(c)(\epsilon_W - 1)}$$

No adjustable parameters are used

- Pauling radii for the hard sphere ions (R_i)
- Concentration dependent dielectric constant [4-9]: ($\epsilon_W = 78.5$)

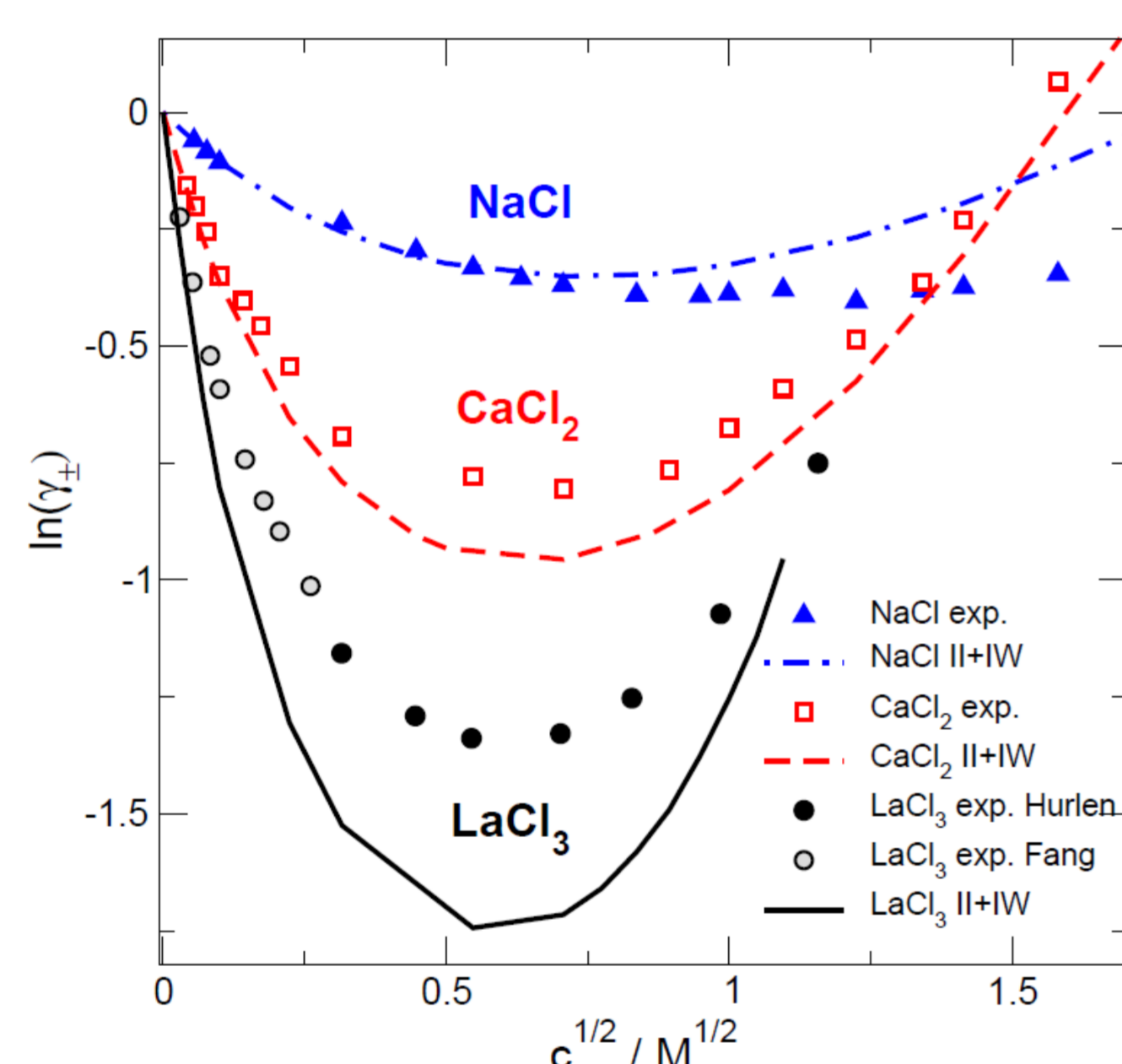
$$\epsilon(c) = \epsilon_W - \delta_s c + bc^{3/2}$$

- Experimental hydration free energy (ΔG_i^S)

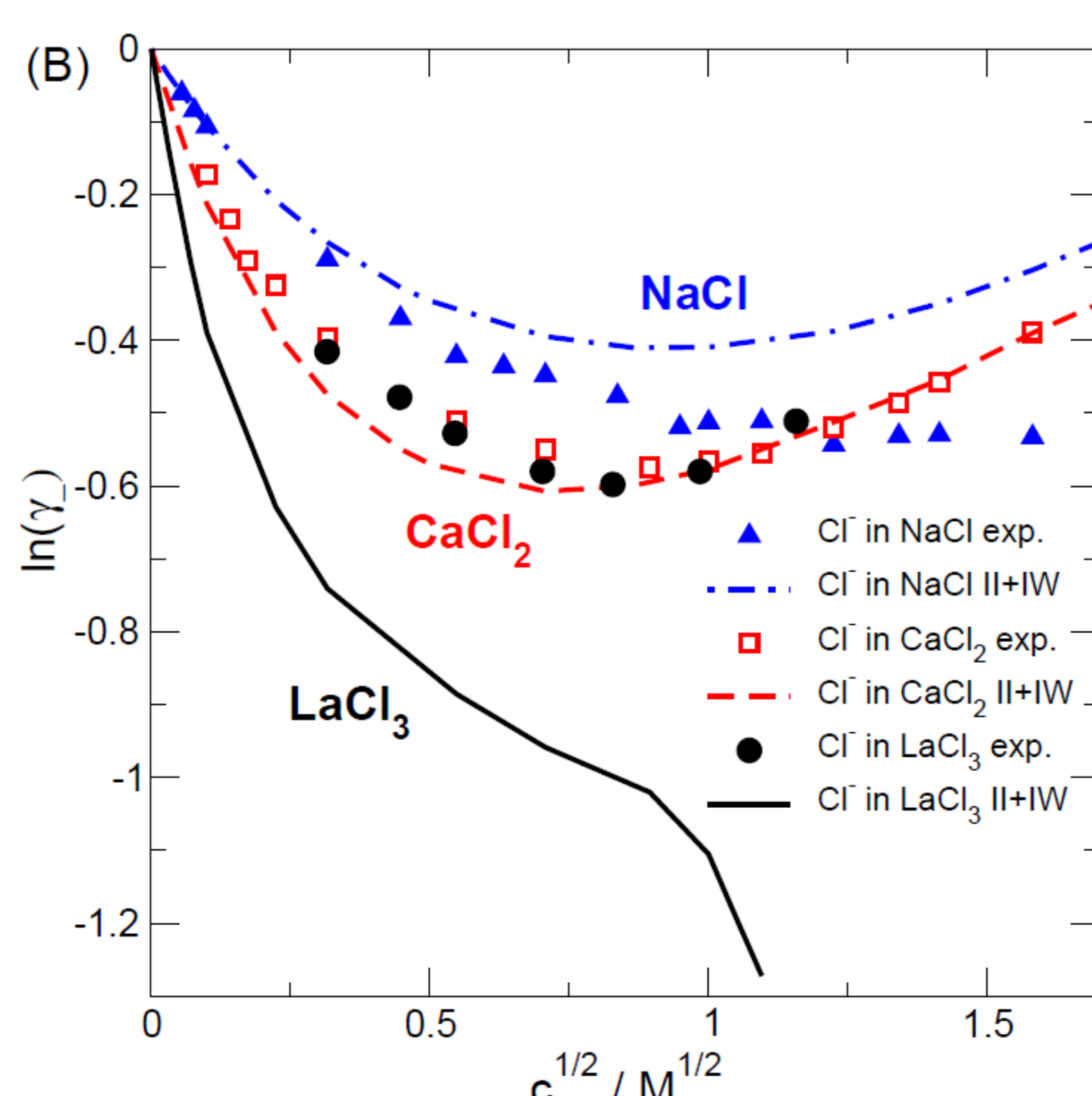
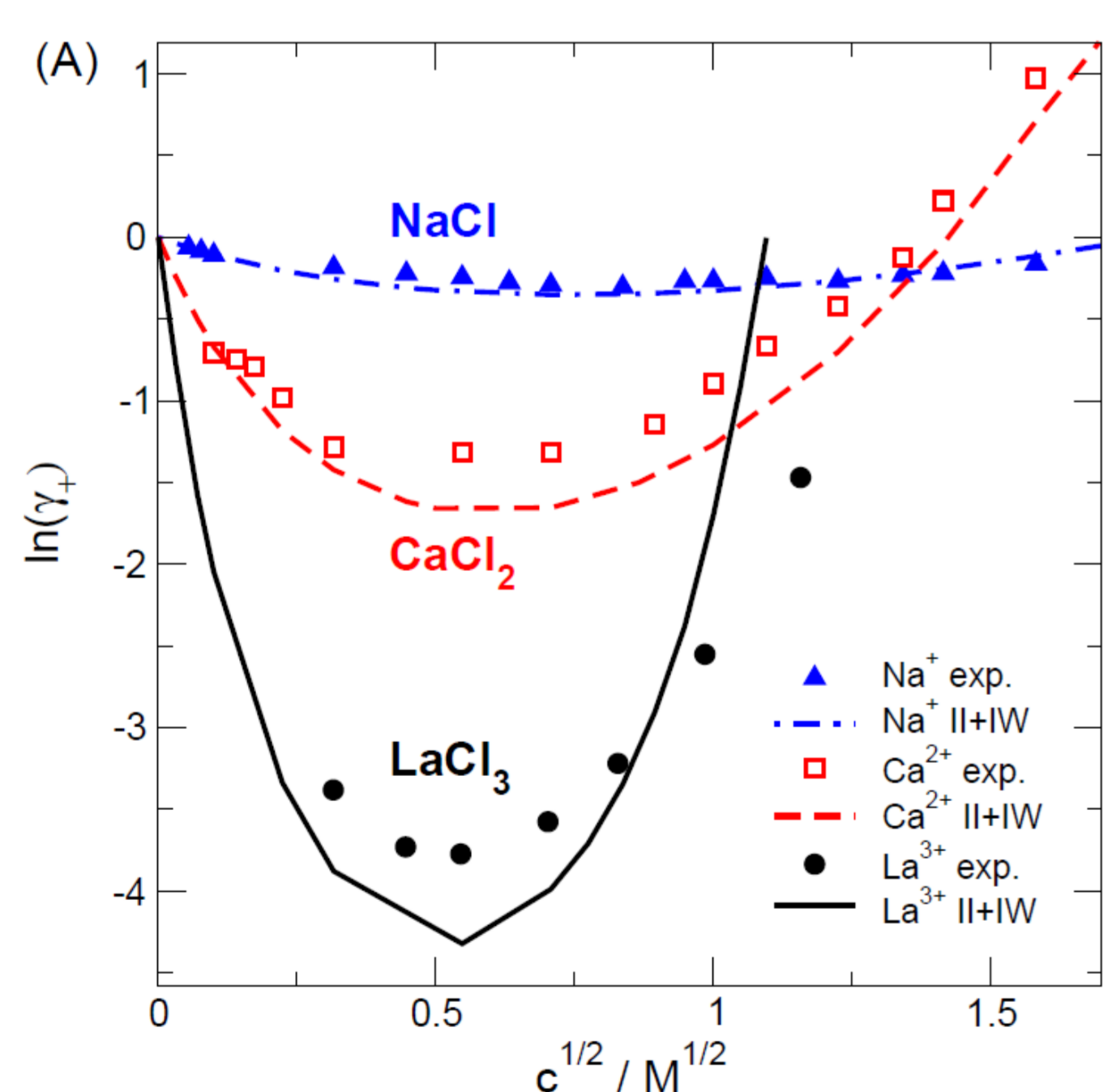


Concentration-dependent dielectric constant from measurements.

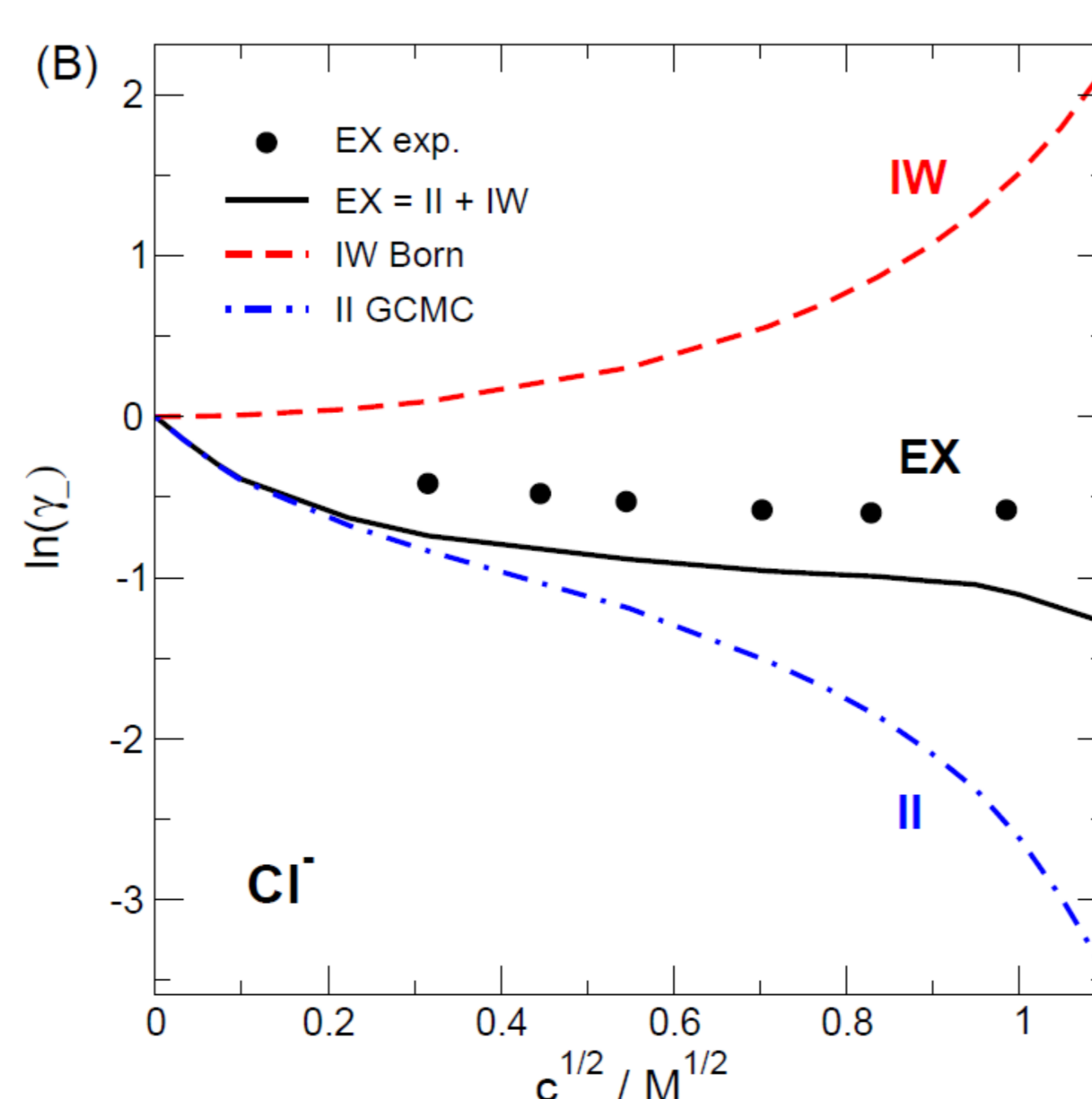
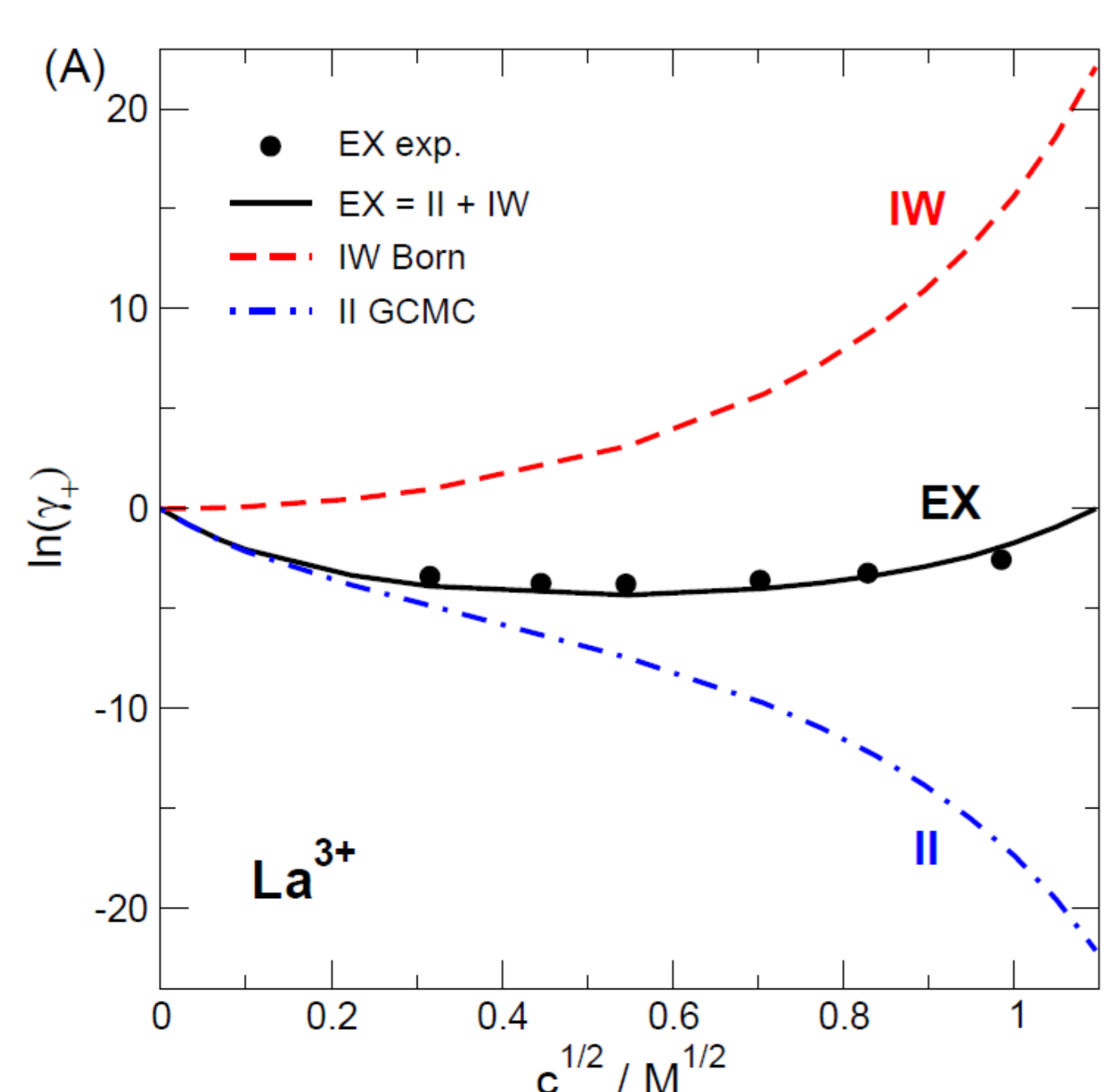
Results



Mean activity coefficients ($\gamma_{\pm} = \gamma_+^{v_+/v} \gamma_-^{v_-/v}$, where v_+ and v_- are the stoichiometric coefficients) for NaCl, CaCl₂ and LaCl₃ as obtained from experiments and the II+IW theory [10-12].



Individual activity coefficients of (A) the cations and (B) the anions in NaCl, CaCl₂, and LaCl₃ as obtained from experiments and the II+IW theory.



The II and IW components of the individual activity coefficients of (A) La³⁺ and (B) Cl⁻ in LaCl₃ as obtained from the II+IW theory.

Summary

- The non-monotonic behavior is the result of the balance of the II and IW terms.
- The agreement with experiments is qualitative, but we emphasize that our model does not contain any adjustable parameters.
- The La³⁺ II term goes down to $-20kT$ and the IW term goes up to $20kT$ at concentrations close to saturation. Nevertheless, their sum is close to experiment (with $0.5kT$ accuracy).
- Our theoretical results for the individual activities support experimental efforts.

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