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Pseudolattice Theory of electrolyte solutions: Consistency analysis of the Quasi-Random Lattice model at infinite dilution

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ABSTRACT

In recent years, the study of the electrolyte solutions has significantly drawn advantage from the Pseudolattice Theory, developed through various approaches and successfully applied to systems of technological and scientific interest such as ionic liquids and rare-earth fluids. However, promising potentialities from the applicative point of view are counterbalanced by a limited investigation about general consistency of pseudolattice models with fundamentals of Solution Theory. This article focuses on the Quasi-Random Lattice approach and discusses, in particular, the theoretical consistency at infinite dilution, since convergence to the Debye-Hückel Limiting Law is a notoriously difficult task for lattice models not developed within the Debye-Hückel-Poisson-Boltzmann frame. The discussion throws a new light on the pseudolattice treatment of electrolyte solutions, and definitely states in what sense an ionic lattice is included in the QRL model at strong, and even infinite, dilution. Present developments generalize previous QRL formalism and allow for advancing toward a unified pseudolattice approach.

1. Introduction

During the extensive study of the electrolytic solutions, researchers have often resorted to the idea of some lattice-like ordering of ions and molecules in the solution that would explain, in particular, the formation of local structures experimentally observed in medium-high concentrated solutions. Numerous theories have been therefore developed around a lattice concept, many of them with focus on the activity-coefficient modeling.

In most local-composition models, notably based on quasi-chemical and/or molecular thermodynamic approaches (Wilson Equation, UNIQUAC, UNIFAC, NRTL, plus numerous refinements and hybrid treatments, see, e.g., Ref. [1] for a detailed review), a lattice-like behavior is considered through the presence of non-randomness factors that account for the tendency of molecules to show some preference in choosing their immediate neighbors. Originally developed for non-electrolytes, local-composition models were proposed for electrolyte solutions by inclusion of a modified Debye-Hückel (DH) term to account for long-range ion-ion interactions. On the whole, these models deal with most thermodynamic functions and properties, and offer flexible sets of equations suitable for engineering applications under very general conditions in terms of chemical composition, pressure, and temperature ranges [1]. However, a relevant drawback is represented by the number and the variety of required adjustable parameters, often empirical or semi-empirical in character, which must account for incompleteness in the available information about size and shape of particles, ionic and molecular interactions, and thermodynamic excess functions. A corollary difficulty is that even parameters with a very similar definition from one model to another can yield very dissimilar results. One should also state that, despite their huge parameterization, sometimes these models present inaccurate [2], and are forced to undergo an almost continuous upgrading [2–4].

Some theories, adopting nearest-neighbor interaction principles, put a particular emphasis on the electrostatic character of ionic and dipolar interactions, and in this connection it is to quote the Lattice Restricted Primitive Model (LRPM) [5,6], developed with main application to critical phenomena and phase transitions (topics generally treated by the Lattice Density Functional Theory [7]). Grand canonical Monte-Carlo simulations and fine-lattice discretization methods have supported LRPM results [5], however direct applicability of LRPM is thus far quite limited and proved useful under very specific conditions (e.g., for modeling defects in ionic crystals). In consideration of the infinite-dilution analysis presented in this article, it is also outlined that the LRPM equation

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combines the linearized Poisson-Boltzmann (PB) equation with a lattice Laplacian represented by a sum of nearest-neighbor difference potentials [6]. However, since the LRPM equation is built on the DH equation, it does not allow for an independent derivation of the DH Limiting-Law (DHLL) based on a pseudolattice approach.

Pseudolattice approaches developed almost independently of the DH-PB theory first appeared in literature in the early twentieth century [8]. Most of them include the so called “cube-root law”, originally motivated by the incompatibility between the fine-grainedness of the ionic atmosphere, implied in the DH treatment, and the coarse-grainedness of actual solutions [9]. The law describes ion-ion long-range interactions as depending on the cubic root of the concentration, that is, on the mean distance between neighboring ions within an ionic crystal. The formal similarity with ionic crystals justifies the presence of the Madelung constant [10] in the electrostatic contribution to the mean activity coefficient $\gamma_{\pm}$(molal scale), the latter typically provided by an equation such as below.

$$\ln(\gamma_{\pm}) = Ac^{1/3} + Bc + Dc^2 - \ln\left(1 + \frac{(\nu_+ + \nu_-)mM_1}{1000}\right) \tag{1}$$

In Eq. (1), c is the molar concentration (mol/dm^3); the last term of Eq. (1) accounts for conversion from rational to molal scale; m is the molal concentration (mol/kg), M_1 the molecular weight of solvent, ν_+ and ν_- the stoichiometric numbers. In the long-range electrostatic term $Ac^{1/3}$, A is proportional to the Madelung constant of a suitable ionic crystal. The term Bc arises from the modeling of ion-solvent interactions that, in general, reflect into changes in the dielectric permittivity of the solvent from bulk to local values around an ion. These concepts are also present in local composition models [1] and Specific Ion Theory [8]. Theoretical expressions for B were proposed based on hydration salting-out effects [11], local ion-dielectric gradient interactions [12], and dispersion energy [13]. In Eq. (1), the Dc^2 term first appeared in Ref. [14] and was derived from the ion-ion short-range interaction potential, which includes both the hard-core and attractive tail (Van der Waals) parts. However, thus far the parameters B and D (that depend on pressure and temperature) have been used as adjustable parameters and their values only obtained by fitting Eq. (1) to experimental activity coefficients. Although quasi-ionic lattice structures are presently observed in non-dilute solutions by means of various experimental techniques (X Ray Diffraction, Raman Spectroscopy and Neutron Scattering [15]) and are supported by conductivity studies [16–18], pseudolattice approaches (Eq. (1)) have been subject to controversial attention over the last few decades. Competitive potentialities of Eq. (1) pertaining to highly concentrated solutions and ionic liquids [19], while using a limited number of adjustable parameters, are counterbalanced by the dependence on the cube-root law that causes problems in using the equation with dilute solutions (the electrostatic $Ac^{1/3}$ contribution becomes predominant and suggests unrealistic, crystal-like distribution functions). The main drawback of the cube-root law is the evident inconsistency with DHLL that predicts a square-root dependence on concentration. Many efforts were spent in the past [8] in order to circumvent this problem and to establish which starting concentration should be used such that the cubic-root law is indeed preferable. Glueckauf [20] proposed an extended version of the DH equation that approximated a cube-root law at intermediate concentrations, Pitzer [21] tested the equation by Glueckauf [20] versus the Virial Coefficient expansion, whereas Frank and Thompson [9], and Rasaiah [22] explored concentration ranges where a cubic-root law would collapse approximately into a square-root law. However, no theory was derived and only empirical rules, electrolyte-specific, were suggested.

The appealing potentialities of models depending on a limited number of adjustable parameters are notably appreciable in the Quasi-Random Lattice (QRL) model [23] developed independently of Eq. (1). In QRL the parameterization is generally given by one electrolyte-specific concentration parameter (at given temperature and pressure), which also sets the upper limit of applicability (in terms of concentration range) for the model. An undoubted advantage is that the concentration parameter is experimentally known [23–26] in a relevant number of cases including several saturated and supersaturated solutions of both symmetric and asymmetric electrolytes, for which no fitting procedure is needed for obtaining mean-activity and osmotic coefficients. In addition, previous comparison [23–26] made over common aqueous 1:1, 1:2 and 1:3 electrolytes with most familiar one-parameter theories developed within the PM frame (notably DH extended equations, MSA and HNC) has shown that QRL usually performs better in terms of agreement with experimental mean-activity and osmotic coefficients, and this is remarkable noting that, in PM developments, the agreement is often conditioned by use of ionic diameters adjusted through data regression techniques (in this connection, a further comparison will be proposed with a recent DH extended theory [27]). However, thus far the theoretical agreement of the QRL model with fundamentals of Solution Theory has been little investigated and needs to be analyzed in detail. To the aim, the present article discusses, in particular, the thermodynamic consistency of QRL at the infinite dilution. It will be shown that QRL represents an independent pseudolattice approach from which DHLL can formally be obtained (the existence of a relationship between QRL and DHLL was only qualitatively intuited in previous work [25]). The QRL-to-DHLL derivation will allow for advancing toward a unified pseudolattice approach, applicable from the infinite dilution, and able to enlarge scientific consensus and research efforts in regard to pseudolattice models that are already under active consideration [18,19,26,28].

In the QRL model an ionic lattice represents the reference electrostatic configuration which is, however, continually disordered by thermal forces and molecular collisions occurring in the solution. Lattice sites are conveniently used as points from which observing and evaluating (in a statistical sense) the dynamic behavior of carriers of charge, that are solute ions at strong dilution, groupings of solute ions and solvent molecules at higher concentrations. At each lattice point (and related cell volume) one can then associate an effective carrier, representing the average behavior of all carriers pertaining to the cell, and described by an effective (average) density of charge. The standard deviation (from the lattice point) associated with the effective density represents the “extent” of the effective carrier, and arises from combining effects due to size and stochastic movement of carriers. Standard deviations are generally large at strong dilution, causing the mean interaction energy (which yields the mean activity coefficient) to deviate significantly from the Madelung energy of the reference ionic-lattice.

The convenience in considering an “ordered” ionic lattice as the reference electrostatic configuration persists until the number of ions becomes too small even at microscopic scale, and charges orderly disposed according to their signs no longer represent the preferential configuration from the electrostatic point of view. Therefore, the key step in going from QRL to DHLL is to relax the reference configuration by replacing the ordered lattice with an almost randomized lattice, characterized by the minimum correlation in terms of site occupancy, i.e., correlation concerns only neighboring sites, while the average interaction involves the minimum number of ions, that is, two ions of opposite sign.

A milestone in the study of electrolyte solutions from the statistical-mechanical point of view is represented by the