

Application of the quasi-random lattice model to rare-earth halide solutions for the computation of their osmotic and mean activity coefficients

Elsa Moggia*

(Department of Naval, Electric, Electronic and Telecommunications Engineering, Faculty of Engineering, University of Genoa Via Opera Pia 11A, 16145 Genoa, Italy)

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Abstract: This work dealt with the computation of the mean activity coefficients of rare-earth halide aqueous solutions at 25°C, by means of the Quasi Random Lattice (QRL) model. The osmotic coefficients were then calculated consistently, through the integration of the Gibbs-Duhem equation. Using of QRL was mainly motivated by its dependence on one parameter, given in the form of an electrolyte-dependent concentration, which was also the highest concentration at which the model could be applied. For all the electrolyte solutions here considered, this parameter was experimentally known and ranged from 1.5 to 2.2 mol/kg, at 25 °C. Accordingly, rare-earth halide concentrations from strong dilution up to 2 mol/kg about could be considered without need for best-fit treatment in order to compute their osmotic and mean activity coefficients. The experimental knowledge about the parameter was an advantageous feature of QRL compared to existing literature models. Following a trend already observed with low charge electrolytes, a satisfactory agreement was obtained with the experimental values for all the investigated rare-earth chlorides and bromides. For the sake of compactness, in this work the considered rare-earth halides were all belonging to the $P6_3/m$ space group in their crystalline (anhydrous) form.

Keywords: mean activity coefficient; osmotic coefficient; pseudo lattice model; rare earth halide solution

This work deals with the application of the Quasi Random Lattice model (QRL)^[1-3] to aqueous electrolyte solutions, where solutes are rare-earth chlorides or bromides. QRL is a general approach to calculate the mean molal activity coefficient γ_{\pm} , at the experimental level of description^[4]. The model embodies one adjustable parameter, indicated with c_{lim} (molar scale, mol/L), defined as the (upper) concentration at which the electrolyte should exhibit $\gamma_{\pm}=1$, at the experimental temperature and pressure. In general, for a given electrolyte QRL considers concentrations up to c_{lim} . If saturation occurs at a lower concentration, then c_{lim} behaves as the adjustable parameter for the whole available concentration range.

The structure and thermodynamic properties of dense ionic solutions represent an extremely interesting up-to-date topic, currently under very active scrutiny due to the strong interest in highly concentrated solutions, ionic liquids and molten salts in different fields of science and technology. In particular, aqueous solutions of the electrolytes considered in the following are important in the field of rare earths^[5-7]. Despite their importance, however, there is some lack of knowledge about their thermodynamic properties, as outlined by recent works concerning solubility^[8-10] and transport properties^[11,12]. Moreover, their peculiarities do not allow for any foregone conclusion when applying a model, though general or successful with lower charge electrolytes^[13,14]. With 3:1 systems,

often models work less well, for example, results from the Primitive Model (PM) plus the Hypernetted Chain (HNC) are much less satisfactory for 3:1 electrolytes than for 2:1 electrolytes^[13]. Fortunately, the results obtained by the application of QRL to 3:1 electrolytes show the same quality and agreement with experimental data as previous results for symmetric and 2:1 electrolytes. This is an important achievement of this work, which consolidates the research interest in QRL.

From the experimental point of view, the work relies on published literatures^[13-17], where issues were discussed concerning, in particular, the (indirect) evaluation of the mean activity coefficient from isopiestic measurements of the osmotic coefficients^[13-15,18], since there is some lack of data for 3:1 solutions. The osmotic and activity coefficients reported in literatures by different authors are unfortunately affected by a larger spreading for 3:1 electrolytes than usually observed with 1:1 or 2:1 electrolytes. These experimental issues are not yet completely overcome, and for this reason some of the rare-earth halide solutions were not included in this work.

From the theoretical point of view, some formal and general refinements of QRL are proposed in the following. In particular, the main formula for calculating $\ln(\gamma_{\pm})$ is given in a closed form. Integral formulae were proposed^[1-3] involving elliptic functions, which provide a powerful tool, however more suitable for numerical pur-

* Corresponding author: Elsa Moggia (E-mail: elsa@biosafetyengineering.it; Tel.: + 39 3402536867)

poses. A further refinement concerns the analytical behaviour and the continuity requirement that must be satisfied by the statistical parameters defined in QRL, an important aspect that may cause theoretical issues with more accentuated effects on the modelling of high charge-asymmetry electrolytes.

Dealing with 3:1 electrolytes, some computational cost is due to their Madelung constants, which enter into QRL for describing some aspects of the pseudo-lattice approach, and which are scarcely reported in literature in comparison with lower-charge systems.

As previously said, the QRL results for rare-earth halides are confirming the satisfactory trend already observed with other electrolytes. This may be motivated by the fact that the model is corroborated by experimental information available about the parameter, indeed c_{lim} is known for various electrolytes, and in particular for the rare-earth halide solutions here considered, whose c_{lim} values range from 1.5 to 2 mol/L (at 25 °C); that is, concentrations up to 40%–50% of the saturation values^[15,17] can be used without need for best-fit treatment. The availability of experimental information about the parameter in a relevant number of cases is an advantageous feature of QRL compared to existing one-parameter theories, mainly based on PM^[4]. In reason of their simplifying assumptions, one-parameter theories are not fully exhaustive, however they offer a compromise solution to the difficult problem of preserving the thermodynamic consistency of results while limiting the number of fitting (arbitrary) parameters to use. Indeed, some theoretical inconsistency is compensated by the adoption of one parameter, typically in the form of a suitable ion-size diameter. Unfortunately, even small changes in the adjustable diameter can significantly affect the fitting quality, with more evidence dealing with 3:1 electrolytes. High-quality results are obtainable by most theories when dilute solutions are concerned^[4], but there is no simple rule for extending their use to higher concentrations, where a best-fit value from a model is usually too inaccurate for another one even when the models are so intimately related such as DH (Debye-Hückel) and DHX (Exponential Debye-Hückel Theory)^[19]. This problem is generally afforded by adding more parameters^[20–25], often with extended Pitzer equations^[20,21,23]. However, parameters are usually to interpret numerically more than physically. And the advantages are not obvious by using theories that adopt effective dielectric constants, because of their experimental inaccessibility or disagreement with measured values, which is often the case with 3:1 electrolytes^[22].

1 QRL model

QRL^[1–3] is based on the concept of “effective carriers” of charge. Carriers are suitable groupings of solute ions

and solvent molecules, assembled by means of their short-range interactions, each grouping having a fixed overall charge whereas its size depends on concentration (at given pressure and temperature). A carrier is delimited by free solvent, in some analogy with a solvated ion whose spherical shape (in the PM frame) is delimited by the surrounding continuous medium. Within a carrier, cluster-like behaviour and ion association cannot be distinguished from each other, still in analogy with PM since such a distinction is not available from the sole concept of ion-size diameter.

However, the simplifying modellization of a carrier, introduced at mesoscopic level, allows for considering explicitly only carrier-carrier interactions. The overall charge of a carrier is that nominal of one solute ion, and N co-solvent molecules in a volume V correspond to v_+N carriers with charge Q_+ , and v_-N carriers with charge Q_- (the overall electro-neutrality holds true). The carrier population is described in a fixed space-frame where the solution volume is conceptually divided into $(v_+ + v_-)N$ cells, that is, each cell has volume \tilde{R}^3 , where \tilde{R} is the mean inter-ionic distance.

$$\tilde{R} = \frac{1}{\sqrt[3]{(v_+ + v_-)\rho}} \quad \rho = N/V \quad (1)$$

It must be outlined that, as well as the DH Theory, QRL assumes full dissociation of ions at strong dilution, so the model starts from considering N solute molecules fully dissociate (and a carrier can be depicted as a solvated ion, in a highly dilute solution). Full dissociation at strong dilution is verified by most electrolytes but few exceptions (for example some metal sulphates) that may show a significant ion association in such a concentration range. These situations are still tractable with QRL by means of the additional use of association constants at strong dilution and according to the procedure discussed in^[2]. However, these cases are not considered further in this work since, for the rare earth halides investigated, there is no experimental evidence of important ion association in highly dilute solutions^[13,14].

It is to remind that, when speaking about a carrier, some local formation (solute+solvent) is considered, which is moving within the solution. So, the average behaviour of all carriers interesting a given cell is evaluated, such a behaviour being mathematically described by a charge density that accounts for both the physical extent of carriers and for their movements inside the solution. An “effective carrier” is what is described by such a charge density, so the “size” of an effective carrier is to intend as a statistical property, which is measured from a reference space point, and not from a reference ion position as usually done with PM theories^[4]. Let R_A be the reference space point individuating the cell A. Along each principal axis of the space frame, the size of the effective carrier A is estimated by means of the (linear)

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