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EDITORIAL

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Theoretical chemistry of metal and single ions in solutions

If a Maxwell daemon were to travel from the outer space towards the center of the planet Earth, enroute, it would pass from a low density matter state to a more dense gas-phase state when entering into the earth's atmosphere. Once at the Earth's surface, the daemon would discover a combination of big extensions of water forming oceans, seas, lakes and rivers, mixed up with solid surfaces constituting the continents and islands, in such a way that liquid and solid states of matter would coexist. In going ahead towards the center of the Earth, the daemon would find that the solid material which dominates the Earth's crust is replaced by a dense liquid phase composed of heavy elements. As far as the daemon observed, Life is only found on the Earth's surface, that is, Life is strongly associated with the inter-phase between gas and solid states enclosing the Earth's surface. Ambient pressure and temperature at the Earth's surface are adequately wide spread to allow for the liquid state for water, enabling the matter transport and the formation of solutions by dissolving minerals and organic materials. Then, once the Maxwell daemon realize's how easily water combines with many chemical compounds present on the Earth's surface, it would recognize that Life must be intimately joined to liquid water and aqueous solutions.

A significant number of the species dissolved in water are electrolytes, that is, substances having the ability to decompose in charged fragments in such a way that the capacity of water to stabilize ions is revealed. As a consequence, electrolyte solutions are ubiquitous in nature and, by extension, in technical systems designed by man since antiquity. This has compelled scientists from many fields to study electrolytes in solution.

From the end of the nineteenth century, when the electrolyte concept was clearly established, progress in the comprehension of its theoretical basis has been made in the disciplines of Physics, Chemistry, Biology and Engineering. A grasp of the present knowledge on electrolyte solutions and the estimation of their physico–chemical properties can be achieved by reading a set of excellent books and reviews [1–6]. In one of the more recent compilations, Barthel et al. [1] point out that experimental information and technical developments have built a complete body of knowledge which allows wide and complete empirical answers to practical questions. Nevertheless, the same authors note that the development of a complete theory based on all types of interaction energy effects in electrolyte solutions meets physico–mathematical difficulties which are not yet overcome. In fact, we are in front of a condensed media formed by particles affected due to significant mobility with long distance interactions due to the presence of charged particles and lacking long-range order. The intrinsic complex nature of electrolyte solutions requires that the theoretical methods combine quantum and statistical mechanics ingredients in their developments [7,8].

Pioneer works from Born [9], Debye and Hückel [10] and Onsager [11] at the beginning of the previous century yielded reliable equations based on long- and short-range forces between solute and solvent. Their generality and simplicity are really fruitful in the characterization of the phenomenological behavior of simple electrolyte solutions. Their models did not include quantum considerations, but they supplied a simple and elegant model for ionic solutions allowing useful applications in many of the fields where ionic solutions are involved. Although phenomenological factors are contained in these models to fit experimental results, the success of these rather crude theories are based on the fact that they retain some of the main features of the ion solvation [12–15].

This special issue, devoted to the theoretical chemistry study of metal and single ions in solution, aims to show a representative number of works, where the molecular basis of the solution are dealt either with quantum mechanics or statistical mechanics or a combination of both methodologies. This issue does not intend to cover all the research activities currently under development in this field. But it tries to show pieces of work belonging to groups which have long been establishing well-defined lines of research in Ion Solution

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Chemistry from different viewpoints. Topics included in the issue enclose the detailed examination of the quantum basis of intermolecular interactions [16–18], the methodological developments of a new formalism to deal with chemical species in solution [19] new strategies to obtain effective intermolecular potentials [20,21], the analysis of the structure and dynamics of metal ions in water at ambient [22] or supercritical conditions [23], the combination of statistical results with quantum mechanics theory to obtain spectrocopical properties sampled appropriately, such as isotropic hyperfine coupling constants [24] or EXAFS spectra [25], and the examination of the basic chemical processes of metal ion in solutions, such as hydrolysis [26] or electron transfer reaction [27].

A wide range of ions and chemical species are included in the studies collected in the issue. Bock et al. [17] examined a series of metal cations (e.g. Li^+, Be^{2+}, Al^{3+}, Ti^{4+}) surrounded by two hydration shells. Vallet et al. [18] review the chemistry in solution of actinides, particularly actinyls complexes, such as UO_2^{2+} and NpO_2^{2+} . Singh et al. [16] analyze the interaction of several single ions (H^+, H_3O^+, NH_4^+ , Na^+, X^-, OH^-), acids (HF, HCl), bases (NaOH, CsOH) and salts (NaF, NaCl) with water clusters. Glezakou et al. [25] simulate the EXAFS spectra of K^+ in aqueous solutions for different concentrations of KCl. Egorov et al. [22] detail the structure and dynamics of the Ni^{2+} hydration. Rustad and Casey [26] describe the pH dependence of hydrolysis of a model trivalent metal ion, a representative case being Fe^{3+}. Yazyev and Helm [24], deal with the evaluation of the hyperfine coupling constants for the first and second sphere oxygen in a Cr^{3+} aqueous solution. Rode et al. [19] test their new QM/MM–MD procedure on the Mn^{2+}, Cu^{2+} and Al^{3+} hydration. Guárdia et al. [23] give structural and dynamical results on NaCl aqueous solutions of different concentrations at ambient and supercritical conditions. San-Román et el. [20] present a new intermolecular potential for Li^+ in water and determine structural and thermodynamical properties of the corresponding aqueous solution. Blumberger and Sprik [27] compare quantum and classical approaches to redox reaction of the pair Ru^{2+}/Ru^{3+} in water on the basis of Marcus theory. Finally, Torrico et al. [21] present a new intermolecular potential to describe the Pt^{2+} aqua ion in water, and compare its structural and dynamical properties with those of the Pd^{2+}.

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