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Size and/or charge asymmetry effects in coulombic fluids in the presence of external fields: an update

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Highlights:

- The role of size and/or charge asymmetry of coulombic fluids is discussed.
- The capacitive compactness is calculated in non-zero surface potentials at the point of zero charge.
- Aqueous multivalent macroions enhance the capacitance of supercapacitors.
- Aqueous macroions are a safer alternative to ionic liquids in supercapacitors.
- Ion correlations and excluded volume are crucial at strong electrostatic coupling.

Abstract: In a recent review, "Size and/or charge asymmetry effects in coulombic fluids in the presence of external fields: From simple electrolytes to molten salts", Guerrero-García, Biophysical Chemistry 282, 106747 (2022), one of the present authors analyzed some consequences of breaking the symmetry in the valence and/or ionic size of charged fluids, such as aqueous electrolytes, macroion solutions, or molten salts, when ion correlations and ionic excluded volume effects were taken into account. In this review article, we would like to discuss some additional effects of breaking the symmetry in the valence and/or size of charged particles of coulombic fluids (i) next to a rigid cylindrical charged polymer, and (ii) in the electrostatic properties of an electrical double layer planar supercapacitor. These effects were studied in approaches beyond the classical non-linear Poisson-Boltzmann theory of point ions, by using classical integral equations theory, the Modified Poisson-Boltzmann theory, and Monte Carlo simulations in implicit solvent. As a result, the relevance of the asymmetry in the valence and/or size of charged particles, at microscopic level, is illustrated here either in simple electrolytes or in aqueous colloidal suspensions of macroions, when both are under the influence of an external electric field.

Keywords: asymmetry; electrical double layer; charged fluids

1. Introduction

Aqueous electrolytes, ionic liquids, and plasmas are some examples of coulombic fluids. These charged fluids are ubiquitous in nature, and they are very relevant in a wide variety of technological applications, such as electronics, transport and/or energy storage [1–5], just to mention a few examples. In a recently published review [6], one of the present authors analyzed some consequences of breaking the symmetry in the valence and/or ionic size of charged fluids, when ion correlations and ionic excluded volume effects were theoretically included. In particular, the roles of ion correlations, excluded volume effects, ionic solvation energy and image charges, or polarization effects, were discussed in a wide variety of physicochemical systems, such as electrode/water and oil/water interfaces, as well as multivalent macroions dissolved in supporting aqueous electrolytes.

In these systems, charge inversion, charge reversal, and the inversion of the electric field were observed at high ionic strengths. Briefly, we remind the reader that the phenomenon of charge inversion is the local inversion of the roles of the ionic species constituting the electrical double layer, as counterions and coions, near an electrified colloidal surface or charged electrode [6,7]; the charge reversal is the local sign inversion of the net integrated charge of the diffuse ionic cloud neutralizing a charged colloid or an electrified electrode [6]; and the inversion of the mean electrostatic potential is defined as the appearance of an inverted sign of this quantity regarding the sign of the bare surface charge of the colloid or electrode that exerts an external electric field in a supporting coulombic fluid [6]. In addition, the like-charge attraction between macroions equally charged immersed in size- and/or charge-asymmetric aqueous electrolytes, in the absence of specific ionic adsorption, and the expansion and shrinkage of the electrical double layer in the presence of multivalent coions were also discussed in [6]. As a particular and useful application of the breaking of the symmetry in the solvation energy of simple electrolytes, it was possible to propose the construction of an experimental liquid-state diode, whose rectification mechanism was explained—from first principles—by using Monte Carlo simulations and the classical non-linear Poisson-Boltzmann theory of point ions.

In this mini-review, we would like to discuss some additional effects that appear when the symmetry in the valence and/or size of charged fluids is broken in two interesting scenarios: (i) next to a rigid cylindrical charged polymer, and (ii) in planar electrical double layer supercapacitors when the working electrolyte is an aqueous solution of multivalent macroions. In particular, in this last instance, we are interested in the corresponding microscopic and macroscopic electrical properties such as the mean electrostatic potential, the electric capacitance, and the differential capacitance. These theoretical descriptions have been performed beyond the classical non-linear Poisson-Boltzmann theory of point ions, via integral equations theory, the Modified Poisson-Boltzmann theory, and Monte Carlo simulations in implicit aqueous solvent. The advantage of these approaches is that they include, consistently, ion correlations and ionic excluded volume effects. Such calculations were reported in detail in a couple of papers published after the publication of the 2022 Biophysical Chemistry review mentioned above [6], and they illustrate the relevance of the asymmetry in the valence and/or size of charged particles, at microscopic level, in strongly correlated coulombic fluids when external electrostatic fields are applied.

2. Valence asymmetric electrolytes, symmetric in size, next to a rigid cylindrical polyelectrolyte

The attraction between like-charged macroions, in the absence of specific adsorption, is a topic that has generated a lot of interest in the physical chemistry community since last century. In particular, in a theoretical and simulation paper published by some of the authors of this review, it was shown, from first principles, that the ionic size asymmetry was able to promote like-charge attraction between equally charged macroions, via an ion bridging mechanism promoted by the presence of small counterions [6]. Contrastingly, in the presence of big counterions, an enhanced repulsion between equally charged macroions was predicted. This last observation was confirmed experimentally in a system constituted by macroions, which could extend their solubility in aqueous media in the presence of big counterions [6].

On the other hand, in a subsequent paper, it was shown that polarization effects in the electrical double layer around a spherical macroion were able to promote the appearance of an effective ionic size asymmetry in equally sized electrolytes, which were asymmetric in valence [6]. This breaking of the symmetry in the valence of aqueous *z:1* electrolytes plus image charges or polarization effects (since the dielectric permittivity of the spherical macroion and that of the solvent were different) induced the appearance of surface charge amplification. This phenomenon can be defined as the observation of a local net charge around a colloid or electrode, whose numerical value is larger than the original bare charge of the colloid or the electrode, whereas the sign remains unchanged [6]. From this perspective, the ionic size asymmetry was able to yield not only like-charge attraction between equally charged macroions and surface charge amplification, but also the appearance of a non-zero electrostatic potential on the colloidal surface of a neutral or uncharged colloid, which is the so-called potential of zero charge. This behaviour was reported and studied in detail by Valleau and Torrie in planar geometry in 1982, by using the non-linear Poisson-Boltzmann theory of point ions [8]. In such a scenario, a non-zero potential of zero charge was observed in *z:z* electrolytes symmetric in valence by considering different closest approach ionic distances to the neutral colloidal surface. This ionic size asymmetry allowed the smallest ionic species to be present at closer distances to the neutral colloidal surface than the largest one. As a result, asymmetric charge density profiles yielded by the diffuse cloud of ions are expected next to a neutral (or uncharged) colloidal surface. The physical reality of this phenomenon was confirmed by simulations and theoretical calculations, beyond the non-linear Poisson-Boltzmann theory of point ions, in subsequent works [6]. One interesting question, which naturally arises from the previous observations, is the following: is it possible to observe a non-zero surface electrostatic potential around a symmetric neutral or uncharged colloid (at the point of zero charge) in the presence of electrolytes symmetric in size, but asymmetric in valence, in the absence of specific ionic adsorption? In order to solve this question, the electrical double layer of size symmetric aqueous electrolytes, asymmetric in valence, was studied next to a rigid cylindrical polyelectrolyte in implicit solvent [9]. In such a study, the non-linear Poisson-Boltzmann theory, Monte Carlo simulations, integral equations and the Modified Poisson-Boltzmann theory were used to elucidate the above question. Notice that all the previous approaches include ion correlations and excluded volume effects, except the non-linear Poisson-Boltzmann theory of point ions, which is a mean-field description. One of the main results of this work was to show that the valence asymmetry of equally sized ions was able to promote the appearance of a non-zero surface electrostatic potential at the point of zero charge. This means that either the charge asymmetry or the ionic size asymmetry alone is able to yield the same effect, that is, the appearance of non-zero

electrostatic potential around neutral colloids or electrodes. Interestingly, the Modified Poisson-Boltzmann theory displayed a good agreement regarding the Monte Carlo simulations near the point of zero charge, whereas the non-linear Poisson-Boltzmann theory of point ions and the integral equations theory, using the Hypernetted chain/Mean spherical approximation, erroneously predicted a zero surface electrostatic potential at the point of zero charge, even in the presence of valence asymmetric 2:1 and 3:1 electrolytes [9]. In addition, in that work it was proposed, for the first time, a recipe to calculate the capacitive compactness in the presence of a non-zero surface electrostatic potential at the point of zero charge, that is, in the presence of an uncharged colloid or electrode. In these conditions, the original definition of the capacitive compactness would have predicted numerical divergences when the surface charge density of a colloid, or an electrified electrode, goes to zero. We remind the reader that the capacitive compactness of the electrical double layer is a generalization of the Debye length. Moreover, the definition of capacitive compactness is based on the theoretical construction of an effective capacitor associated with the diffuse electrical double layer surrounding an electrified colloid or electrode. In addition, the capacitive compactness allows us to characterize the spatial extension of the electrical double layer as a function of the colloidal charge, including also many physical chemistry characteristics of coulombic fluids such as ion correlations, excluded volume effects, image charge or polarization effects, charge regulation, *etc*.

3. Multivalent macroions boost the capacitance and the differential capacitance of planar electrical double layer supercapacitors

In recent years, electrical double layer supercapacitors have been used to enhance the storage of electrical energy in a wide variety of technological applications [1–5], as mentioned above. From a naive point of view, enhancing the electrostatic coupling of coulombic fluids can be a natural way to improve the capacitance of these kinds of devices. For this reason, the use of ionic liquids has been proposed, in the past, to improve the storage of electrical energy and the capacitance of electrical double layer supercapacitors regarding aqueous electrolytes. In aqueous electrolytes, the dielectric constant at room temperature does not vary significantly. Thus, one possible alternative to boost the electrostatic coupling is by considering multivalent electrolytes. In nature, however, aqueous electrolytes cannot achieve large valences, being trivalent or tetravalent ions the maximum limit typically observed. In contrast, even in monovalent ionic liquids, the absence of a solvent is able to decrease significantly the dielectric permittivity, which allows us to increase notably the electrostatic coupling of these charged fluids. Despite this very convenient feature, ionic liquids are usually easily flammable and can be carcinogenic. Thus, in a very recent study [10] it has been proposed to use aqueous multivalent macroions, as a green alternative to ionic liquids, in order to boost or enhance the electric capacitance and the differential capacitance of planar electrical double layer supercapacitors. One of the main advantages of this proposal is that the macroions can be chemically functionalized, which allows us to increase their valence (or surface charge density) significantly in comparison to natural trivalent or tetravalent electrolytes in aqueous media [10]. This procedure is safer and environmentally friendly regarding ionic liquids, as working electrolytes, in electrical double layer supercapacitors. Such a hypothesis was numerically tested by using Monte Carlo simulations, integral equations theory and the non-linear Poisson-Boltzmann theory of point ions, in the modelling of a planar supercapacitor containing multivalent macroions in implicit aqueous solvent. Simulations and integral equations theory using the

Hypernetted chain/Mean spherical approximation predicted an enhancement of the electric capacitance and the differential capacitance of the electrical double layer supercapacitors that used the above prescription. Moreover, both approaches displayed good agreement with each other regarding microscopic electrostatic properties such as the ionic profiles and the mean electrostatic potential. Charge inversion, charge reversal, and an inversion of the mean electrostatic potential appeared and increased as a function of the ionic strength. Moreover, the presence of concentrated solutions of aqueous macroions produced a curvature inversion of the corresponding differential capacitance near the point of zero charge. This phenomenon has been reported experimentally in systems composed of charged electrodes, which were neutralized by monovalent ionic liquids [11]. Thus, the electrostatic coupling in coulombic fluids can be fine-tuned in aqueous solutions of macroions by increasing the colloidal size and/or the bare charge of the dissolved macroions, via experimental chemical techniques.

4. Conclusions

The symmetry is usually associated with beauty in mathematics, and in science in general. However, interesting phenomena may arise if the symmetry, at molecular level, is broken. In this mini-review, we have discussed some interesting phenomena appearing when the valence or size symmetry is broken in charged fluids, which were not covered in [6]. The first one is the appearance of a non-zero mean surface electrostatic potential at the point of zero charge in the absence of specific ionic adsorption, which was driven by the ion correlations associated with multivalent electrolytes. The second one is the boost of the electric capacitance and the differential capacitance of electrical double layer supercapacitors, by considering multivalent macroions dissolved in aqueous solvents. In this last practical application, it was shown that the electrostatic coupling associated with the coulombic fluid can be significantly increased by increasing the valence of macroions (via chemical functionalization, for instance), surpassing the limit imposed by nature to trivalent and tetravalent aqueous electrolytes. Moreover, aqueous solutions of macroions are safer and more environmentally friendly than solvent-free ionic liquids (as working electrolytes) in supercapacitors, considering that ionic liquids are typically highly flammable and can be carcinogenic for human beings. An increasing interest on developing more efficient electrical double layer supercapacitors [12–15] highlights the relevance of using multivalent macroions in aqueous solutions.

Finally, and from a theoretical point of view, we expect that the breaking of symmetry in the ionic size or valence of charged fluids could have other interesting consequences in recently reported phenomena such as the underscreening [16]; particularly in the presence of mixtures of macroions, as well as in the associated electrophoretic mobility. Work along this direction is currently in progress, and it will be published elsewhere.

Declaration of generative AI and AI-assisted technologies

The authors did not use generative AI or AI-assisted technologies in the writing of this manuscript. During the preparation of this manuscript, the authors used generative AI tools only to improve language and readability. The authors take full responsibility for the content of the manuscript.

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Authors' contribution

Conceptualization, G.I.G.-G; methodology, J.J.E.-E.; software, J.J.E.-E.; validation, E.G.-T. and J.J.E.-E.; formal analysis, E.G.-T. and J.J.E.-E.; investigation, G.I.G.-G, E.G.-T., and J.J.E.-E.; resources, C.G.G.-P., D.S.-B. and F.J.-M.; data curation, J.J.E.-E.; writing—original draft preparation, G.I.G.-G.; writing—review and editing, C.G.G.-P., D.S.-B. and F.J.-M.; visualization, J.J.E.-E.; supervision, E.G.-T.; project administration, G.I.G.-G; funding acquisition, G.I.G.-G. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

Guillermo Iván Guerrero-García holds the position of Associate Editor for *Asymmetry* and has not peer reviewed or made any editorial decisions for this paper.

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