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# Deviations from ideality in solutions of dicarboxylic acid salts modeled within a BiMSA theory for flexible chains

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The binding mean spherical approximation (BiMSA) theory is used to describe the thermodynamic properties of dicarboxylic acid salts by adding a chain term in the free energy. The dianions in these solutions are modeled as flexible charged chains composed of two, three, or four spheres. Five aqueous solutions of such salts are studied in different concentration ranges: dipotassium oxalate, disodium malonate, disodium succinate, potassium tartrate and sodium tartrate. A description of the experimental deviations from ideality (osmotic and activity coefficients) for these salts is obtained. The model is compared with a previous one that does not include a chain contribution. It is found that the model with a chain contribution provides a more physically sound framework.

## I. INTRODUCTION

Electrostatic interactions have a major influence on the thermodynamic properties of electrolytes and polyelectrolytes. For simple electrolytes consisting of monatomic ions in aqueous solution the variation of the activity coefficients with the concentration are fairly well described at least up to 1 M. At high dilution, the theory of Debye and Hückel (DH) describes well the behavior of this thermodynamic quantity as a function of the charge and size of the ions, assumed these to be spherical<sup>1,2</sup>. In this model the solvent is seen as a continuum characterized only by its dielectric constant. For higher concentrations, the DH electrostatic model becomes insufficient. Two types of corrections must be made: (i) First, because ions have a finite size, an additional contribution from excluded volume effects must be added in the Helmholtz energy of the system. When the ions can be represented as charged hard spheres, a hard sphere contribution must be added to the various contributions thermodynamic quantities<sup>3-5</sup>. (ii) Moreover, the electrostatic contribution is poorly described by the DH expressions, so a more efficient theory must be used. To this end, the mean spherical approximation theory (MSA), which better accounts for finite size effects between charged species in concentrated solutions has been used<sup>6-9</sup>.

In contrast, analytic descriptions of the properties of polyelectrolyte solutions are much less advanced. Polyelectrolyte solutions are macromolecular systems made up of charged polymer chains dissolved in a solvent. They are at the crossroads of research in the fields of chemistry, physics and biology. Polyelectrolyte solutions exhibit peculiarities resulting from their high total charge and their complex geometry. In particular, when the distance between charges along a polyion is small, counterions seem to associate with the charged groups present on the polymer chain. This phenomenon of condensation of counterions tends to reduce the

effective charge and the mobility of the polyions<sup>10,11</sup>. Describing the transport and thermodynamic properties of these highly charged solutes is beyond the scope of this study.

However, low charged molecules exist in which the total charge is distributed along the chain, some of them, called bolaform ions, have two identical charges located symmetrically at the two ends of the molecule. When the charges are separated by a great number of atoms, the counterions seem to associate less with these charged molecules. This change in association, related to the distance between the charges, has similarities with the specific association called condensation of counterions in theories of polyelectrolyte solutions. In the past, the properties of these particular electrolytes have been considered within Mayer's theory or with extensions to DH where bolaform ions have been represented as ellipsoids or rods with a uniform surface charge distribution.<sup>12-15</sup> However, these linear molecules carry charges only on the two atoms at the ends. In such cases, a uniform charge distribution along the length of the molecule is unrealistic. Moreover, when association occurs on some of the charged groups it is necessary to represent these groups explicitly within the molecule. Furthermore, because of the charges carried by identical groups, association on one group can strongly influence association on another group when they are sufficiently close to each other. This type of interaction can lead to the condensation of counterions on polyelectrolytes. Then, in the case of small weakly-charged molecules, considering that the total charge is distributed over several atoms may allow us to describe such electrolytes more realistically. Ions with only two identical charged groups, separated by a few neutral atoms, are among the simplest examples of such a charge distribution. In this respect, salts of dicarboxylic acids seem to be systems with interesting chemical characteristics. The negative charges of these salts are located on the two carboxylic end groups separated by uncharged atoms. In this article, we have modeled the thermodynamic properties of oxalate, malonate, succinate and tartrate of alkali cations (sodium or potassium).

Then, to go further, such molecules can be modeled as a linear chain of hard spheres. It is advisable to use a suitable

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theoretical model to describe the excluded volume effects specific to this type of structure. New theoretical tools have been introduced in the literature to describe the thermodynamic and structural properties of molecules represented as assemblies of hard spheres bound together<sup>16,17</sup>. Thermodynamic perturbation theory (TPT) led to the statistical associative fluid theory (SAFT), which describes association of hard spheres that build chain molecules<sup>18–22</sup>.

In addition, interactions between chains were also addressed using integral equations. In order to allow a finite number of bonds between hard spheres, highly directional attractive potentials at short distances have been added. A bond between two particles is induced by these potentials only when they are properly oriented towards each other. As a result, pair distribution functions are split into several contributions depending on whether or not each of the particles is bonded to another. Therefore, new integral equations have been established to describe the interactions connecting all of these contributions<sup>16,23,24</sup>. As usual, these equations relate the various contributions of the total correlation functions to those of additional functions called direct correlation functions. In order to solve these integral equations, closure relations are required between the total and direct correlation functions. The closure relations used are very similar to those used with the standard integral equations. However, as the integral equations are not the same, the correlation functions are different. The Percus-Yevick relation has been used in the case of uncharged hard spheres chains. Thermodynamic properties of these constituents were derived from these correlation functions<sup>16,25–27</sup>.

For charged hard spheres, the binding mean spherical approximation (BiMSA), also called associative MSA or polymer MSA, closure relation has been introduced<sup>28–31</sup>. It assumes that the direct correlation function between two charged species  $i$  and  $j$  is equal to  $-V_{ij}(r)/k_B T$  for distances greater than the distance of least approach for hard spheres (with  $V_{ij}(r)$  the Coulomb potential,  $k_B$  the Boltzmann constant and  $T$  the temperature). Within the BiMSA, integral equations were solved for ion pairs in a continuum solvent<sup>28–30,32</sup>, and analytical expressions for the electrostatic contribution to the thermodynamic properties were obtained<sup>33,34</sup>. Subsequently, the BiMSA was solved for a general charged hard-sphere chain fluid<sup>31,35–38</sup> and the thermodynamic behavior has been obtained within this framework<sup>39–42</sup>.

In this work the BiMSA theory for some flexible linear chain molecules is used to describe the thermodynamic properties of aqueous solutions of dicarboxylate salts, such as potassium oxalate, sodium malonate, sodium succinate and potassium or sodium tartrate. These salts are of 2:1 type, with two identical cations,  $K^+$  or  $Na^+$ , for one molecular dianion of valency -2:  $C_2O_4^{2-}$ ,  $C_3H_2O_4^{2-}$ ,  $C_4H_4O_4^{2-}$  and  $C_4H_4O_6^{2-}$  (A graphical representation of these dianions can be seen in Fig. 1). The tartrate ion has a structure similar to that of the succinate one because it possesses the same number of carbon atoms. Like the succinate, it contains two carbon groups separating the carboxylic heads. However, in each of these two intermediate groups a hydrogen atom is replaced by an OH group.

This article is organized as follows. Section II provides the main theoretical ingredients of the BiMSA theory, including proposed expressions for the variation of cation size and permittivity with concentration, and association contributions (pair and trimers formation) to the thermodynamics of the system. It is also detailed how the dianion can be modeled as a chain consisting of two, three or four spheres. In section III, the main results are presented and discussed. Finally, in section IV some conclusions about this study are presented. The complete equations used in this work are given separately in the appendices.

## II. THEORY

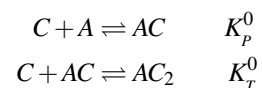
The model proposed in this research considers molecules made up of charged hard spheres (cation  $C$ ) and charged chains (dianion  $A$ ). The chains include two, three or four spheres that will be used to represent the oxalate, malonate and succinate molecules, respectively (see Fig. 2). Cations have a diameter  $\sigma_+$  and a positive valence  $z_+$ . The oxalate ion is represented by a chain built up of two spheres of diameter  $\sigma_-$  and valence  $z_-$  each; the malonate and the succinate ions are modeled as the previous chain to which one and two neutral spheres of diameter  $\sigma_m$ , respectively, are added between the two end spheres of diameter  $\sigma_-$ . The latter two negatively charged spheres represent the carboxylic groups. Subsequently they will be referred to as the charged heads of these anions. Cations and dianions interact through a Coulomb potential and they can form pairs (cation-dianion) and trimers (cation-dianion-cation). The solvent is regarded as a continuum with a relative permittivity  $\epsilon$ . Within the framework of this theory, the excess Helmholtz free energy,  $A$ , per volume unit is given by

$$\beta\Delta A = \beta\Delta A^{HS} + \beta\Delta A^{ch} + \beta\Delta A^{BiMSA} \quad (1)$$

where  $\Delta A^{HS}$  is the contribution from hard sphere exclusion,  $\Delta A^{ch}$  is the contribution from the chains and  $\Delta A^{BiMSA}$  is the BiMSA contribution that includes effects arising from electrostatic interactions  $\Delta A^{el}$  and those coming from association  $\Delta A^{MAL40}$  (in which  $MAL$  stands for mass action law)

$$\beta\Delta A^{BiMSA} = \beta\Delta A^{el} + \beta\Delta A^{MAL} \quad (2)$$

In what follows, a two component electrolyte is considered in which the anion ( $A$ ) can form either a pair ( $AC$ ) or a trimer ( $AC_2$ ) with the cations ( $C$ ). A pair is defined as a cation being in contact with one of the two charged heads of a dianion. A trimer is defined as two cations being in contact with each of the two charged heads of the same anion. Then the following two chemical equilibria occur between the ions  $C$  and  $A$



where  $K_p^0$  and  $K_t^0$  are the thermodynamic association constants for the formation of pairs and trimers. As usual, the mean activity coefficient of the salt (on molar scale),  $\ln \gamma_{\pm}$ , the osmotic

pressure  $P$  and the osmotic coefficient  $\phi$  can be deduced by differentiation of the excess Helmholtz free energy  $\Delta A$  with respect to the number densities of the constituents.

In addition, the degree of hydration of the cation and the solution permittivity are allowed to vary with the solute concentration.

This is done as follows. As in previous work<sup>43,44</sup>, a linear variation with respect to concentration for  $\sigma_+$  and  $1/\varepsilon$  is assumed as

$$\sigma_+ = \sigma_+^{(0)} + \sigma^{(1)} C, \quad \varepsilon^{-1} = \varepsilon_w^{-1} (1 + \alpha C) \quad (3)$$

where  $C$  is the solute concentration,  $\sigma_+^{(0)}$  is the size of cation at infinite dilution,  $\sigma^{(1)}$  is a parameter that accounts for the rate of variation of the cation size with concentration;  $\varepsilon_w$  is the dielectric constant of pure water, and  $\alpha$  is a parameter accounting for the variation of the relative permittivity with concentration<sup>43-45</sup>.

A linear dependency for  $1/\varepsilon$  was chosen because experimental data have been observed to approximately vary this way<sup>46</sup>. From the free energy, contributions to the activity and osmotic coefficients can be determined by differentiation with respect to the number densities, on the one hand by considering the parameters  $\sigma_+$  and  $\varepsilon$  as being constant, and on the other hand by taking into account the variations of these parameters with the densities. To distinguish the quantities determined by assuming the parameters  $\sigma_+$  and  $\varepsilon$  constant the subscript 0 is added to the symbol.

Additional contributions are denoted with the subscripts  $\sigma_+$  and  $\varepsilon$ . Then one has for the activity and osmotic coefficients,

$$\ln y = \ln y_0 + \ln y_{\sigma_+} + \ln y_{\varepsilon} \quad (4)$$

$$\phi = \phi_0 + \phi_{\sigma_+} + \phi_{\varepsilon} \quad (5)$$

Explicit expressions for these quantities will be provided below.

This type of model in which the solvent is modeled as a continuum falls within the framework of McMillan-Meyer (MM) solution theory. To describe the experimental data (which are at the Lewis-Randall (LR) level), it is necessary to perform a conversion of the corresponding theoretical quantities obtained at the MM level. To distinguish the experimental thermodynamic quantities (activity and osmotic coefficients) from those determined with this theoretical model, the superscripts *LR* and *MM* will be added to the experimental and theoretical quantities respectively. This conversion was done using the following expressions<sup>44,47</sup>

$$\phi^{LR} = \phi^{MM} (1 - C_i V_{\pm}), \quad (6)$$

$$\ln y_i^{LR} = \ln y_i^{MM} - C_i V_i \phi^{MM}, \quad (7)$$

and

$$y_i^{LR} = \gamma_i^{LR} V d_w, \quad (8)$$

TABLE I. Parameter values used in Eq. 10 for the salts considered in this work.

Salt	$d_1$ mol m <sup>-3</sup>	$d_2$ mol <sup>3/2</sup> kg <sup>-1/2</sup> m <sup>-3</sup>	$m_{max}$ mol kg <sup>-1</sup>	Reference
K <sub>2</sub> Oxalate	0.128977	-0.0208227	1.5	49
Na <sub>2</sub> Malonate	0.118184	-0.0210164	4.0	49
Na <sub>2</sub> Succinate	0.115644	-0.0207051	2.0	49
Na <sub>2</sub> Tartrate	0.142653	-0.0247199	1.3	50
K <sub>2</sub> Tartrate	0.160447	-0.0333483	5.7	51

where  $C_t$  is the total solute concentration ( $C_t = \nu C$ , with  $\nu$  the total stoichiometric number of the salt),  $V_{\pm}$  is the mean solute partial molar volume,  $V$  is the specific volume (volume of solution per kg of solvent),  $V_i$  is the partial molar volume of species  $i$ ,  $\gamma_i^{LR}$  is the LR activity coefficient of species  $i$ , and  $d_w$  is the density of pure water at 25°C. The concentration is calculated using the simple conversion for a given molality  $m$

$$C = \frac{m}{V} = \frac{m d(m)}{1 + mM}, \quad (9)$$

where  $d(m)$  is the solution density and  $M$  is the molar mass of the salt. The densities were parameterized using an expression similar to the one proposed elsewhere<sup>48</sup> in terms of molar salt concentration. Here, for convenience, the densities were expressed as a function of the salt molality as

$$d(m) = d_w + d_1 m + d_2 m^{3/2}, \quad (10)$$

where  $d_w$  is the density of pure water and  $d_1$  and  $d_2$  are reported in Table I.

In the following subsection, the various thermodynamic contributions (HS, chain, BiMSA) are described more precisely for the case of a model salt containing dumbbell-shaped oxalate ions at the MM level. The main differences of the model when the anion includes additional spheres (to represent the malonate, succinate and tartrate ions) are presented in the next subsection. Complementary formulas and contributions coming from the variation of  $\sigma_+$  and  $\varepsilon$  with concentration are presented in the appendices.

### A. Molecular dianion comprised of two bonded spheres

In this section, the model is detailed for the case of a salt comprised of two spherical cations and an anion composed of two spheres linked together, as shown in Fig. 2(a). This assembly of two spheres for the anion was used to represent the oxalate ion. The two negatively charged spheres which constitute the anion represent each of the carboxylic groups carried by the oxalate ion.

#### 1. Contributions from hard sphere exclusion and chain formation

To build this system, we can start with a collection of free spheres of diameter  $\sigma_+$  and  $\sigma_-$ , with number densities  $\rho_+$ , for

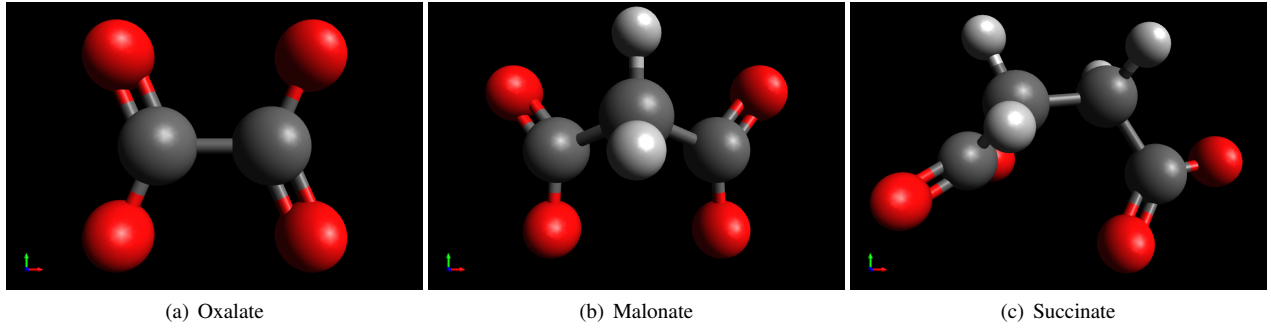
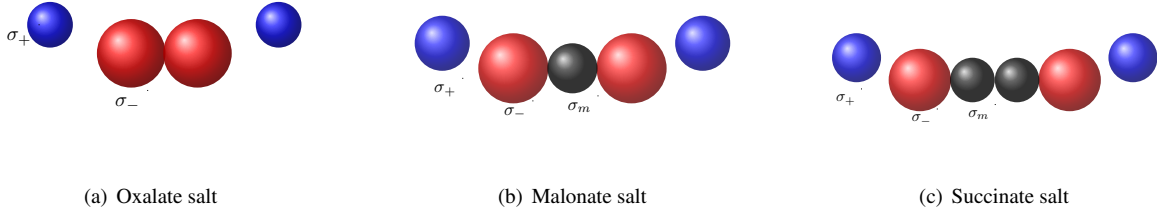


FIG. 1. Dicarboxylic molecules

FIG. 2. Representation of the molecules studied in this work. In the present model, the chains of malonate and succinate are not rigid (see text). The diameters of a counterion (blue sphere), end carboxylate group (red) and carbon group (black) are  $\sigma_+$ ,  $\sigma_-$ , and  $\sigma_m$ , respectively.

anion concentration (oxalate in Figure 2(a)) and  $\rho_+$  for cation one. The hard sphere part of the Helmholtz free energy for this system is<sup>5</sup>.

$$\frac{\pi}{6}\beta\Delta A^{HS} = \left[ \frac{\zeta_2^3}{\zeta_3^2} - \frac{\pi}{6}(\rho_+ + 2\rho_-) \right] \ln(1 - \zeta_3) + \frac{3\zeta_1\zeta_2}{1 - \zeta_3} + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2} \quad (11)$$

with

$$\zeta_k = \frac{\pi}{6}(\rho_+\sigma_+^k + 2\rho_-\sigma_-^k) \quad (12)$$

for  $k = 1, 2, 3$ . The contribution of hard spheres relates on the one hand to the spheres representing the cations and on the other hand to those which constitute the anions when they are linked together. A factor of 2 before  $\rho_-$  in equation (11) comes from the fact that oxalate ions contain two monomers.

To allow for the formation of ‘chains’ of two neutral hard spheres of diameter  $\sigma_-$ , it is necessary to add a contribution to the Helmholtz free energy related to these species. It is given by<sup>20</sup>

$$\beta\Delta A^{ch} = -\rho_- \ln g_{--}^{HS}(\sigma_-) \quad (13)$$

where  $g_{--}^{HS}(\sigma_-)$  is the contact value of the radial distribution function (RDF) expressed as<sup>4</sup>

$$g_{--}^{HS}(\sigma_-) = \frac{1}{1 - \zeta_3} + \frac{3\zeta_2}{2(1 - \zeta_3)^2} \sigma_- + \frac{\zeta_2^2}{2(1 - \zeta_3)^3} \sigma_-^2 \quad (14)$$

When the chain constituents are charged, the contact value of the RDF contains in addition an electrostatic contribution. This is defined using the exponential approximation in BiMSA theory as the product of a hard sphere term and an electrostatic interaction term<sup>33,40</sup>. The contribution to the formation of chains coming from the charges of the two spheres of diameter  $\sigma_-$  is included in  $\beta\Delta A^{el}$  presented below.

The system to be described requires that all spheres with diameter  $\sigma_-$  be involved in chains comprising two such spheres. If the spheres constituting the anions were not linked together then the ideal pressure would have been,  $\beta P^{ideal} = \rho_+ + 2\rho_-$ . However, because of the bond connecting them the ideal pressure reduces to:  $\beta P^{ideal} = \rho_+ + \rho_-$ . The total number density for this new system is  $\rho_t = \rho_+ + \rho_-$ . The total pressure is the sum of ideal and excess contributions.

If we neglect at this stage the electrostatic and associative contributions, it can be written as

$$\begin{aligned} \beta\Delta P &= (\rho_+ + \rho_-) + \beta\Delta P^{HS} + \beta\Delta P^{ch} \\ &= \rho_t \left[ 1 + \Delta\phi_0^{HS} + \Delta\phi_0^{ch} \right] \end{aligned} \quad (15)$$

where the HS pressure is

$$\beta\Delta P^{HS} = \frac{(\rho_+ + 2\rho_-)\zeta_3}{1 - \zeta_3} + \frac{18\zeta_1\zeta_2}{\pi(1 - \zeta_3)^2} + \frac{6(3 - \zeta_3)\zeta_2^3}{\pi(1 - \zeta_3)^3}; \quad (16)$$

and the chain contribution is given by

$$\beta\Delta P^{ch} = -\rho_- \left\{ \frac{\zeta_3}{1-\zeta_3} + \frac{1}{g_{--}^{HS}(\sigma_-)} \left[ \frac{3\zeta_2\sigma_-}{2(1-\zeta_3)^3} + \frac{\zeta_2^2\sigma_-^2}{(1-\zeta_3)^4} \right] \right\}. \quad (17)$$

Then one obtains

$$\Delta\phi_0^{HS} = \left( 1 + \frac{\rho_-}{\rho_t} \right) \frac{\zeta_3}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)^2} + \frac{(3-\zeta_3)\zeta_2^3}{\zeta_0(1-\zeta_3)^3} \quad (18)$$

in which  $\zeta_0 = \frac{\pi}{6}(\rho_+ + \rho_-)$  is different than the usual case where the negative spheres are not bonded. The chain contribution is

$$\Delta\phi_0^{ch} = \beta\Delta P^{ch}/\rho_t \quad (19)$$

where  $\beta\Delta P^{ch}$  is given by Eq. (17). By summing the two contributions, we observe that the term  $(\rho_-/\rho_t)\zeta_3/(1-\zeta_3)$ , added in  $\Delta\phi_0^{HS}$  is subtracted in  $\Delta\phi_0^{ch}$ . The activity coefficient for hard sphere can be written as

$$\Delta\ln y_0^{HS} = \frac{\beta\Delta A_0^{HS}}{\rho_t} + \Delta\phi_0^{HS} \quad (20)$$

where

$$\frac{\beta\Delta A_0^{HS}}{\rho_t} = \left( \frac{\zeta_2^3}{\zeta_0\zeta_3^2} - 1 - \frac{\rho_-}{\rho_t} \right) \ln(1-\zeta_3) + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_0\zeta_3(1-\zeta_3)^2} \quad (21)$$

In the same way, the chain contribution to the activity coefficient can be written as

$$\Delta\ln y_0^{ch} = -\frac{\rho_-}{\rho_t} \left[ \ln g_{--}^{HS}(\sigma_-) + \frac{\zeta_3}{1-\zeta_3} + \frac{1}{g_{--}^{HS}(\sigma_-)} \left( \frac{3\zeta_2\sigma_-}{2(1-\zeta_3)^3} + \frac{(\zeta_2\sigma_-)^2}{(1-\zeta_3)^4} \right) \right] \quad (22)$$

The purpose of this theoretical section is to illustrate chain formation in our model, so in order not to bore the reader with tedious equations, the contributions due to varying cation size and permittivity to the osmotic and activity coefficients are given in Appendix A.

## 2. Contributions from electrostatic interactions and association

The electrostatic and associative contributions to the Helmholtz energy have been derived from previous studies on polyelectrolyte thermodynamics within the framework of BiMSA<sup>40,42</sup>. In these works, the polyion was represented as a sequence of  $n$  charged hard spheres. Within each polyion, association equilibria between two consecutive charged hard

spheres were considered. By taking the limit where the association constants tend to infinity, a chain of  $n$  charged hard spheres is formed. In order to adapt this polyion model to the molecules studied in this article we first considered symmetrical chains in which only the two hard spheres at the ends carry a charge. Lastly, between these charged spheres, neutral spheres all of the same size can be added, in order to describe dianions of greater length. In addition, an association between each of the charged ends and a counterion was considered. Then, to describe each of the systems considered we started from the expressions describing chains that can have  $n+2$  constituents (including two counterions possibly attached to each end). When the molecular dianion contains only two bonded spheres, one has  $n=2$ . The formulas presented are therefore special cases of the expressions established previously. Furthermore, for longer chains in particular, more details are given in Appendix B. Initially, the Helmholtz energy was determined by integrating the electrostatic internal energy  $\Delta E$  obtained in the BiMSA framework. Then  $\beta\Delta A^{el}$  has been separated into two parts, namely the average activity coefficient  $\ln y_{\pm}^{el}$  and the osmotic coefficient  $\Delta\phi^{el}$ , deduced by differentiation. Finally, the electrostatic contribution to the Helmholtz energy  $\beta\Delta A^{el}$  obtained from the BiMSA theory can be written in terms of these two thermodynamic quantities according to<sup>40</sup>

$$\beta\Delta A^{el} = \rho_t \ln y_{\pm}^{el} - \rho_t \Delta\phi^{el} \quad (23)$$

which greatly simplifies its expression. The electrostatic contribution to the activity coefficient,  $\ln y_{\pm}^{el}$ , has been split in a first contribution  $\Delta\ln y_0^{el}$ , obtained by assuming that  $\sigma_+$  and  $\epsilon$  are independent of densities, and other terms  $\Delta\ln y_{\sigma_+, \epsilon}^{el}$ , coming from the variation of these parameters with densities. It has been found

$$\Delta\ln y_0^{el} = \frac{\lambda}{\rho_t} \left[ \rho_{+z} M_+^0 + 2\rho_{-z} M_-^0 - \eta\rho_+ \sigma_+ \left( \mathcal{X}_+^0 + \frac{\eta}{3} \sigma_+^2 \right) - 2\eta\rho_- \sigma_- \left( \mathcal{X}_-^0 + \frac{\eta}{3} \sigma_-^2 \right) + \frac{\rho_-}{\sigma_-} \left( \mathcal{X}_-^0 \mathcal{X}_-^0 - z_-^2 \frac{\epsilon}{\epsilon_w} \right) \right] \quad (24)$$

where the Bjerrum length  $\lambda$  is given by

$$\lambda = \frac{\beta e^2}{4\pi\epsilon_0\epsilon} \quad (25)$$

and the following quantities are defined:

$$M_k^0 = -\frac{\Gamma z_k + \eta\sigma_k}{1 + \Gamma\sigma_k}, \quad (26)$$

$$\mathcal{X}_k^0 = \frac{z_k - \eta\sigma_k^2}{1 + \Gamma\sigma_k}.$$

The last term in Eq. (24) represents the charge contribution to chain formation within the dianion. The preceding terms are similar to those found in a dissociated electrolyte<sup>41,43,44</sup>. The

parameters  $\Gamma$  and  $\eta$  are given by the implicit equations

$$\begin{aligned} \frac{\Gamma^2}{\pi} = & \lambda \left[ \rho_+ (\mathcal{X}_+^0)^2 + 2\rho_- (\mathcal{X}_-^0)^2 + 2\rho_- \frac{(\mathcal{X}_-^0)^2}{1 + \Gamma\sigma_-} \right. \\ & + 2(\rho_p + 2\rho_T) \frac{\sigma_+^* + \sigma_-^*}{\sigma_+ + \sigma_-} \mathcal{X}_+^0 \mathcal{X}_-^0 \\ & + 2 \frac{(\rho_p + 2\rho_T)}{1 + \Gamma\sigma_-} \frac{\sigma_+^* + 2\sigma_-^*}{\sigma_+ + 2\sigma_-} \mathcal{X}_+^0 \mathcal{X}_-^0 \\ & \left. + 2 \frac{\rho_T}{(1 + \Gamma\sigma_-)^2} \frac{\sigma_+^* + \sigma_-^*}{\sigma_+ + \sigma_-} (\mathcal{X}_+^0)^2 \right], \end{aligned} \quad (27)$$

and

$$\begin{aligned} \eta = & \frac{\pi}{2\Delta} \left[ \rho_+ \sigma_+ \mathcal{X}_+^0 + 2\rho_- \sigma_- \mathcal{X}_-^0 + \rho_- \sigma_-^* \mathcal{X}_-^0 \right. \\ & + \frac{\rho_p + 2\rho_T}{\sigma_+ + \sigma_-} (\mathcal{X}_+^0 \sigma_-^{2*} + \mathcal{X}_-^0 \sigma_+^{2*}) \\ & + \frac{\rho_p + 2\rho_T}{(\sigma_+ + 2\sigma_-)(1 + \Gamma\sigma_-)} (\mathcal{X}_+^0 \sigma_-^{2*} + \mathcal{X}_-^0 \sigma_+^{2*}) \\ & \left. + \frac{\rho_T}{(\sigma_+ + \sigma_-)(1 + \Gamma\sigma_-)^2} \mathcal{X}_+^0 \sigma_+^{2*} \right]. \end{aligned} \quad (28)$$

where  $\Delta = 1 - \zeta_3$ , and the following notations have been used:

$$\begin{aligned} \sigma_k^* &= \frac{\sigma_k}{1 + \Gamma\sigma_k}, \\ \sigma_k^{2*} &= \frac{\sigma_k^2}{1 + \Gamma\sigma_k}. \end{aligned} \quad (29)$$

In the same way, the electrostatic contribution to the osmotic coefficient,  $\Delta\phi^{el}$  may be split in a first contribution,  $\Delta\phi_0^{el}$ , obtained by assuming that  $\sigma_+$  and  $\varepsilon$  are independent of densities, and a second one,  $\Delta\phi_{\sigma_+, \varepsilon}^{el}$ , coming from the variation of these parameters with densities. The thermodynamic relation<sup>9,45</sup>,  $\Delta\phi_0^{el} = \rho_t \frac{\partial}{\partial \rho_t} [\beta\Delta A^{el} / \rho_t]_{\Gamma, \sigma_+, \varepsilon}$ , was used to calculate the osmotic coefficient

$$\Delta\phi_0^{el} = -\frac{2\lambda}{\pi\rho_t} \eta^2 - \frac{\Gamma^3}{3\pi\rho_t}. \quad (30)$$

Furthermore, association equilibria between the cations and the negative spheres were taken into account. Chemical equilibria relating the concentrations of pairs  $\rho_p$  and trimers  $\rho_T$  to the fraction  $\alpha_+$  of free cations (C) and to the fraction  $\alpha_-$  of free anions (A) can be expressed as follows<sup>40</sup>

$$K_p = \frac{\rho_p}{\rho_+ \alpha_+ \rho_- \alpha_-} = K_p^0 G_p, \quad (31a)$$

$$K_T = \frac{\rho_T}{\rho_+ \alpha_+ \rho_p} = K_T^0 G_T, \quad (31b)$$

with the fractions of unbound ions

$$\alpha_+ = 1 - \frac{\rho_p}{\rho_+} - 2 \frac{\rho_T}{\rho_+}, \quad (32a)$$

$$\alpha_- = 1 - \frac{\rho_p}{\rho_-} - \frac{\rho_T}{\rho_-}. \quad (32b)$$

The terms  $G_p$  and  $G_T$  express the departures of the apparent constants  $K_p$  and  $K_T$  from the corresponding thermodynamic association constants  $K_p^0$  and  $K_T^0$ . They are given by the following exponential approximations<sup>33,40,52</sup>

$$\begin{aligned} G_p = & g_{+-}^{HS}(\sigma_{+-}) \exp \left\{ -\lambda \left[ 2 \frac{(\mathcal{X}_+^0 \mathcal{X}_-^0 - z_+ z_- b_0)}{\sigma_+ + \sigma_-} \right. \right. \\ & \left. \left. + \frac{2}{\sigma_+ + 2\sigma_-} \left( \frac{\mathcal{X}_+^0 \mathcal{X}_-^0}{1 + \Gamma\sigma_-} - z_+ z_- b_1 \right) \right] \right\}, \end{aligned} \quad (33)$$

and

$$G_T = G_p \exp \left[ -\frac{\lambda}{(\sigma_+ + \sigma_-)} \left( \frac{\mathcal{X}_+^0 \mathcal{X}_+^0}{1 + \Gamma\sigma_-} - z_+^2 b_0 \right) \right] \quad (34)$$

where

$$\begin{aligned} b_0 &= \frac{(\sigma_+ + \sigma_-)}{(\sigma_+^{(0)} + \sigma_-)} \frac{\varepsilon}{\varepsilon_w}, \\ b_1 &= \frac{(\sigma_+ + 2\sigma_-)}{(\sigma_+^{(0)} + 2\sigma_-)} \frac{\varepsilon}{\varepsilon_w}. \end{aligned} \quad (35)$$

In Eq. (33), the two terms in the exponential are contributions from the charges of the anion and the cation. The first contribution comes from the contact electrostatic interaction energy, at the distance  $(\sigma_+ + \sigma_-)/2$ , between two ions bound together. The second one represents the interaction energy between the bound cation and the other charged end of the dianion. In Eq. (34), the term in the exponential represents the interaction energy between the two cations and the chain. The contribution from association to the Helmholtz energy is<sup>40</sup>

$$\beta\Delta A^{MAL} = \rho_+ \ln \alpha_- + \rho_- \ln \alpha_+ + \rho_p + 2\rho_T. \quad (36)$$

Then the association contribution to the activity coefficient, deduced from the free energy  $\Delta A^{MAL}$ , is

$$\begin{aligned} \Delta \ln y_0^{MAL} = & \frac{1}{\rho_t} \left[ \rho_+ \ln \alpha_+ + \rho_- \ln \alpha_- \right. \\ & \left. - (\rho_p + 2\rho_T) \sum_{k=+,-} \rho_k \frac{\partial \ln g_{+-}^{HS}(\sigma_{+-})}{\partial \rho_k} \right] \end{aligned} \quad (37)$$

and that of the osmotic coefficient is

$$\Delta\phi_0^{MAL} = -\frac{\rho_p + 2\rho_T}{\rho_t} \left[ 1 + \sum_{k=+,-} \rho_k \frac{\partial \ln g_{+-}^{HS}(\sigma_{+-})}{\partial \rho_k} \right], \quad (38)$$

where the contact value of the radial distribution function used to evaluate  $\Delta \ln y_0^{MAL}$  and  $\Delta\phi_0^{MAL}$  is expressed as<sup>4</sup>

$$g_{+-}^{HS}(\sigma_{+-}) = \frac{1}{1 - \zeta_3} + \frac{3\zeta_2}{(1 - \zeta_3)^2} \sigma_p + \frac{2\zeta_2^2}{(1 - \zeta_3)^3} \sigma_p^2, \quad (39)$$

with

$$\sigma_p = \frac{\sigma_+ \sigma_-}{\sigma_+ + \sigma_-}. \quad (40)$$

which allows one to determine the derivatives of  $g_{+-}^{HS}(\sigma_{+-})$  with respect to the  $\rho_k$ 's appearing in the formula for  $\Delta \ln y_0^{MAL}$  and  $\Delta \phi_0^{MAL}$ . This leads to

$$\sum_{k=+,-} \rho_k \frac{\partial \ln g_{+-}^{HS}(\sigma_{+-})}{\partial \rho_k} = \frac{\zeta_3}{1-\zeta_3} + \frac{1}{g_{+-}^{HS}(\sigma_{+-})} \left[ \frac{3\zeta_2\sigma_p}{(1-\zeta_3)^3} + \frac{4\zeta_2^2\sigma_p^2}{(1-\zeta_3)^4} \right] \quad (41)$$

The main starting equations for molecular dianions composed of three or four spheres are presented in the next subsection.

### B. Molecular dianion composed of three or four spheres

Here, the molecular dianion is modeled as a chain made up of two negative spheres at the ends and one or two neutral spheres in between as sketched in Figs. 2(b) and 2(c). The number of neutral spheres is denoted by  $n$ . As previously, it is allowed that the dianion can form pairs and trimers with the cations. The HS contribution to the Helmholtz energy is<sup>5</sup>

$$\frac{\pi}{6} \beta \Delta A^{HS} = \left[ \frac{\zeta_2^3}{\zeta_3^2} - \frac{\pi}{6} (\rho_+ + 2\rho_- + n\rho_-) \right] \ln(1-\zeta_3) + \frac{3\zeta_1\zeta_2}{1-\zeta_3} + \frac{\zeta_2^3}{\zeta_3(1-\zeta_3)^2} \quad (42)$$

where

$$\zeta_k = \frac{\pi}{6} (\rho_+ \sigma_+^k + 2\rho_- \sigma_-^k + n\rho_- \sigma_m^k) \quad (43)$$

for  $k = 1, 2, 3$  and  $\zeta_0 = \frac{\pi}{6} (\rho_+ + \rho_-)$  as previously. The expression for the osmotic contribution  $\Delta \phi_0^{HS}$  is

$$\Delta \phi_0^{HS} = \left[ 1 + (n+1) \frac{\rho_-}{\rho_t} \right] \frac{\zeta_3}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)^2} + \frac{(3-\zeta_3)\zeta_2^3}{\zeta_0(1-\zeta_3)^3} \quad (44)$$

The activity coefficient for hard spheres can be written as<sup>40</sup>

$$\Delta \ln y_0^{HS} = \frac{\beta \Delta A_0^{HS}}{\rho_t} + \beta \Delta \phi_0^{HS} \quad (45)$$

where

$$\frac{\beta \Delta A_0^{HS}}{\rho_t} = \left( \frac{\zeta_2^3}{\zeta_0 \zeta_3^2} - 1 - (n+1) \frac{\rho_-}{\rho_t} \right) \ln(1-\zeta_3) + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)} + \frac{\zeta_2^3}{\zeta_0 \zeta_3(1-\zeta_3)^2} \quad (46)$$

The contribution from chain formation is different here because the charged heads are no longer directly linked to each

other, they are bonded to intermediate neutral spheres. Consequently, the corresponding free energy  $\beta \Delta A^{ch}$  no longer depends on  $g_{--}^{HS}(\sigma_-)$  but rather on  $g_{-m}^{HS}(\sigma_{-m})$  and  $g_{mm}^{HS}(\sigma_m)$ <sup>20</sup>

$$\beta \Delta A^{ch} = -2\rho_- \ln g_{-m}^{HS}(\sigma_{-m}) - (n-1)\rho_- \ln g_{mm}^{HS}(\sigma_m) \quad (47)$$

where  $g_{-m}^{HS}(\sigma_{-m})$  and  $g_{mm}^{HS}(\sigma_m)$  are the contact values of the RDF between negative and neutral spheres, and between two neutral spheres, respectively. The expression given in Ref. 4 is used here. The resulting expressions for  $\Delta \phi_0^{ch}$  and  $\Delta \ln y_0^{ch}$  are given in Appendix B.

The electrostatic contribution to the osmotic coefficient  $\Delta \phi_0^{el}$  is given by

$$\Delta \phi_0^{el} = -\frac{2\lambda}{\pi\rho_t} \eta^2 - \frac{\Gamma^3}{3\pi\rho_t} \quad (48)$$

which is formally similar to Eq. (30), but with different  $\Gamma$  and  $\eta$  because now neutral spheres are present in the chain. The electrostatic contributions to the activity coefficient  $\Delta \ln y_0^{el}$  also contain similar additional contributions. The explicit formulas for  $\Gamma$ ,  $\eta$  and  $\Delta \ln y_0^{el}$  are given in Appendix B.

In the same way the associative contributions  $\Delta \ln y_0^{MAL}$  and  $\Delta \phi_0^{MAL}$  are given by expressions formally similar to (37) and (38), respectively. However, the fractions of unbound cations  $\alpha_+$  and anions  $\alpha_-$ , as well as the concentrations  $\rho_p$  and  $\rho_t$ , are different. In order to determine these quantities, the relationships for the chemical equilibria (31) and mass conservation (32) must be solved. However, the terms  $G_p$  and  $G_t$  are again different. The equations allowing one to evaluate  $G_p$  and  $G_t$  are provided in Appendix B.

## III. RESULTS AND DISCUSSION

### A. Results from the present model

The theoretical predictions obtained from the above theoretical development were compared with experimental data for activity and osmotic coefficients for disodium succinate<sup>53</sup> ( $C_4H_4Na_2O_4$ ), disodium malonate<sup>54</sup> ( $C_3H_2Na_2O_4$ ) and dipotassium oxalate solutions<sup>55</sup> ( $C_2K_2O_4$ ). For this latter salt, only values for the activity coefficient are reported. However, by using a procedure described by Hamer and Wu<sup>56</sup>, osmotic coefficient values could be computed from the activity coefficient data. They are presented in Table II. Additionally, two more salts, potassium tartrate ( $K_2C_4H_4O_6$ ) and sodium tartrate ( $Na_2C_4H_4O_6$ ), were considered although their chain is not flexible. The tartrate-related dianion ( $C_4H_4O_6^{2-}$ ) was modeled as a succinate-like chain, with two spheres at the ends representing the  $CO_2$  group and two intermediate spheres for the  $CH_2O$  group.

The comparison between theoretical and experimental data was performed using a least squares fit implemented in a FORTRAN routine of the Marquardt type with the following four free parameters:  $\sigma^{(1)}$ ,  $\alpha$ ,  $K_p^0$ , and  $K_t^0$ . The cation diameter at infinite dilution was taken from previous works where



TABLE II. Osmotic coefficient for dipotassium oxalate calculated using the procedure proposed by Hamer and Wu<sup>56</sup>.

m	$\phi$
mol kg <sup>-1</sup>	
0.0005864	0.9696
0.003	0.9373
0.006994	0.9119
0.05098	0.8301
0.09136	0.8029
0.188	0.7691
0.402	0.7360
0.8074	0.7349

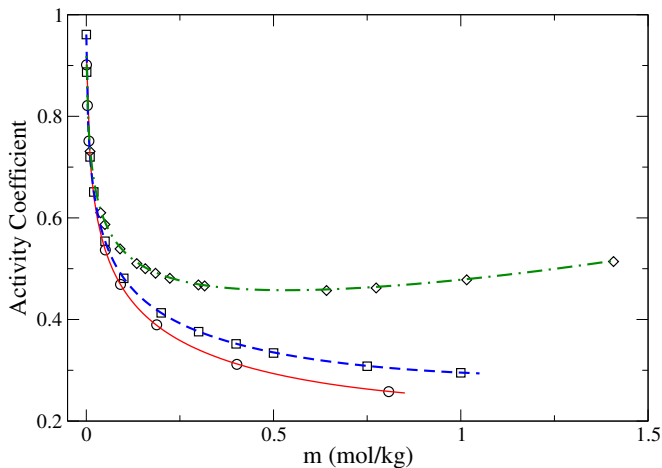


FIG. 3. Activity coefficient of dipotassium oxalate ( $\circ$ ), disodium malonate ( $\square$ ) and disodium succinate ( $\diamond$ ). Symbols: experimental data; Lines: results from BiMSA theory for each salt.

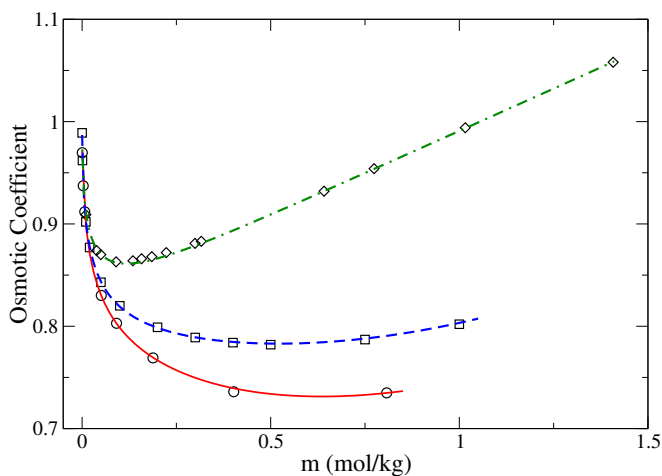


FIG. 4. Osmotic coefficient for dipotassium oxalate ( $\circ$ ), disodium malonate ( $\square$ ) and disodium succinate ( $\diamond$ ). Symbols: experimental data; Lines: results from BiMSA theory for each salt.

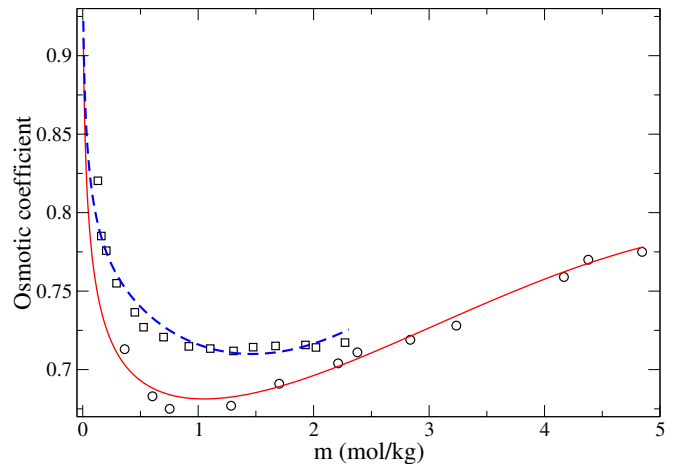


FIG. 5. Osmotic coefficient for disodium tartrate ( $\square$ ) and dipotassium tartrate ( $\circ$ ). Symbols: experimental data; Lines: results from BiMSA theory for each salt.

the MSA theory was used<sup>43,44</sup>, namely  $\sigma_+^{(0)} = 3.45 \text{ \AA}$  for the potassium cation and  $\sigma_+^{(0)} = 3.87 \text{ \AA}$  for the sodium. The diameters of the spheres that form the chain were calculated using the known geometry of the molecules, which suggested the values:  $\sigma_- = 4.5 \text{ \AA}$  and  $\sigma_m = 1.6 \text{ \AA}$ <sup>57</sup>.

In Figure 3, experimental data and theoretical results for the activity coefficients of the salts considered in this work are presented. As can be seen, our model is able to reproduce the experimental data on the whole concentration range with a good accuracy, and with plausible values for the parameters (see Table III). The osmotic coefficients are displayed in Figures 4 and 5. As expected in view of the very good agreement obtained for the activity coefficients, those for the osmotic coefficients are also well described within the BiMSA framework.

In order to see with more clarity the different contributions in the model, two salts were selected. The different terms in the osmotic coefficient for potassium oxalate (shorter chain) and sodium succinate (longer chain) are plotted in Figures 6 and 7, respectively. For both salts, the larger contributions are those from the HS and electrostatic interactions. It can be seen that the chain term is more relevant for sodium succinate (longer chain) and high concentrations. On the other hand, the association term clearly depends on the salt being analyzed; it is significant for potassium oxalate and negligible for sodium succinate.

An interesting outcome of the model is that it allows one to assess the speciation in the solution. In Figures 8 and 9, the fractions of pairs and trimers are shown as a function of concentration for the five salts considered in this work. In particular, the fraction of complex formed in the case of disodium succinate is practically zero on the whole concentration range. For the other four salts, pairs and/or trimers are formed in appreciable amounts.

In Table III a summary of the adjusted parameter values for each salt is presented. As can be seen from the  $\sigma^{(1)}$  values displayed in the table, the variation of the cation size is more

TABLE III. Fitted parameter values obtained using the model presented in this work. For all salts, the values  $\sigma_- = 4.5 \text{ \AA}$  and  $\sigma_m = 1.6 \text{ \AA}$  were used.

Salt	$\sigma^{(1)} \times 10^2$	$\alpha \times 10$	$\alpha \times 10^a$	$K_p^0$	$K_r^0$	$m_{max}$	AARD% <sup>b</sup>	
	$\text{\AA mol}^{-1} \text{ L}$	$\text{mol}^{-1} \text{ L}$	$\text{mol}^{-1} \text{ L}$	$\text{mol}^{-1} \text{ L}$	$\text{mol}^{-1} \text{ L}$	$\text{mol kg}^{-1}$	$\phi$	$\gamma$
K <sub>2</sub> Oxalate	-2.063	1.140	-	3.028	2.297	0.80	0.09	0.30
Na <sub>2</sub> Malonate	-9.137	1.972	2.014	2.755	1.014	1.00	0.07	0.10
Na <sub>2</sub> Succinate	-19.80	2.359	2.667	$1 \times 10^{-6}$	$1 \times 10^{-10}$	1.40	0.32	0.35
K <sub>2</sub> Tartrate	-19.037	1.992	-	11.091	$1 \times 10^{-3}$	4.84	0.61	-
Na <sub>2</sub> Tartrate	-19.892	2.976	-	4.722	$1 \times 10^{-5}$	2.72	0.75	-

<sup>a</sup> These  $\alpha$ 's values were obtained by fitting the experimental data of the permittivity using the relation for the permittivity in Eq. 3.

<sup>b</sup> AARD% for a quantity X (=  $\phi$  or  $\gamma$ ) is the average absolute relative deviation for the calculated value of X against the experimental:  $\text{AARD}(\%) = (100/N) \sum_{i=1}^N |X_i^{cal}(C) - X_i^{exp}(C)| / X_i^{exp}(C)$ , with N the number of (C) points.

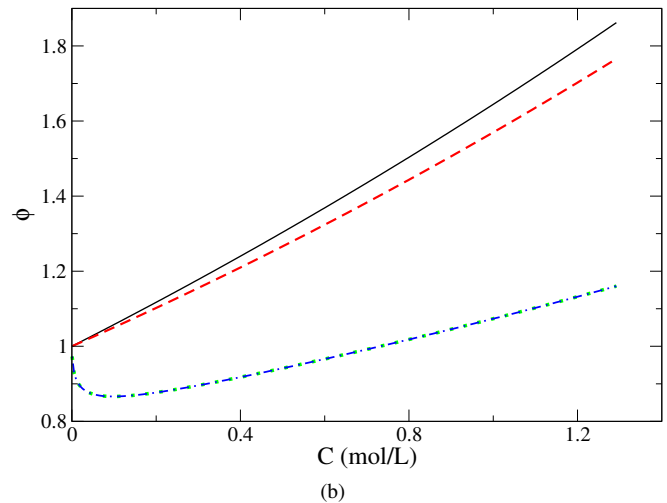
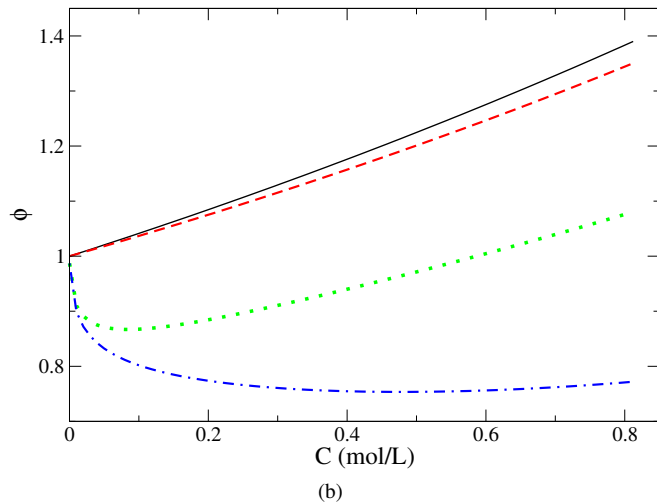
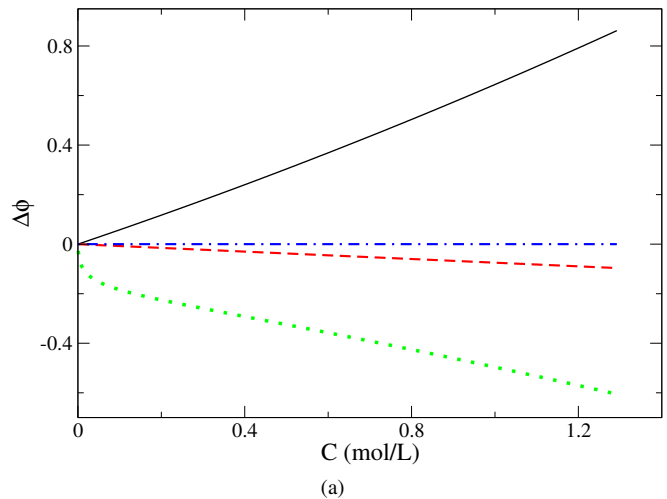
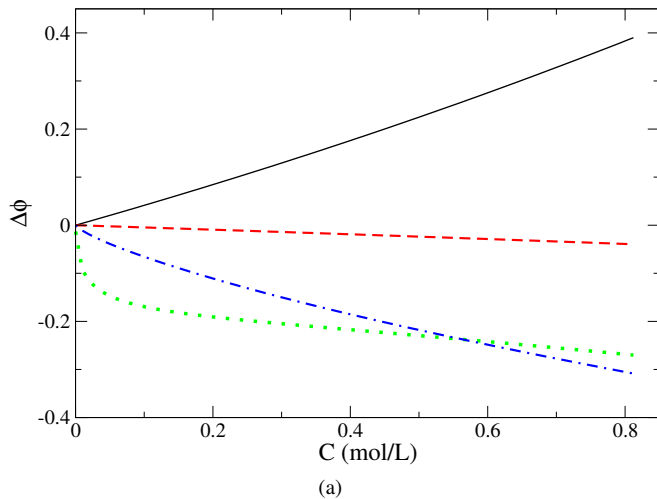


FIG. 6. a) Contributions to the osmotic coefficient for potassium oxalate: HS (black solid line); chain (red dashed line); electrostatic (green dotted line) and association (blue dotdash line). b) Cumulative contributions to total osmotic coefficient. HS alone (black solid line); HS + chain (red dashed line); HS + chain + electrostatic (green dotted line); HS + chain + electrostatic + association (blue dotdash line).

FIG. 7. Same as Figure 6 for the case of disodium succinate.

pronounced for succinate and tartrate, less for malonate, and still less for oxalate. This behavior is quite satisfactory because it is in keeping with the size of these molecules. More precisely, a bigger molecule must yield a larger cation diameter variation because the amount of available water is lower for a given salt concentration, which must result in a lower

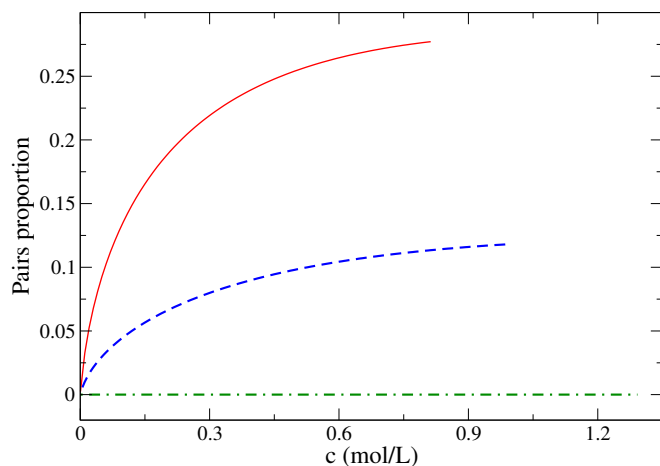


FIG. 8. Fraction of pairs as a function of concentration. From top to bottom: Solutions of dipotassium oxalate, disodium malonate and disodium succinate.

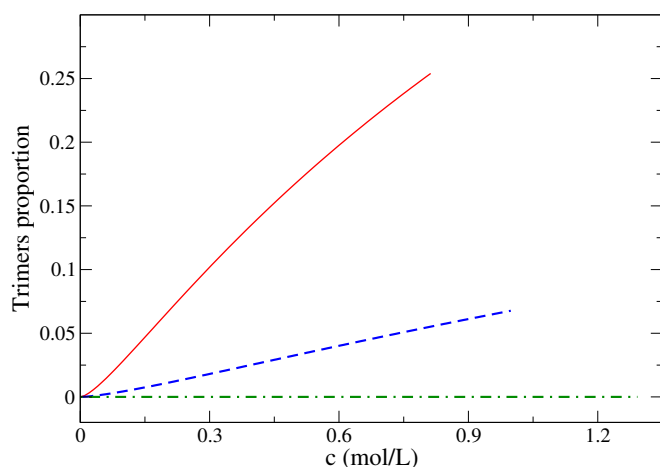


FIG. 9. Fraction of trimers as a function of concentration. From top to bottom: Solutions of dipotassium oxalate, disodium malonate and disodium succinate.

hydration of the cation. Concerning the  $\alpha$  values, the value of the permittivity for a given concentration decreases in the order:  $\epsilon(\text{oxalate}) > \epsilon(\text{malonate}) > \epsilon(\text{succinate}) > \epsilon(\text{sodium tartrate})$ . Moreover, it is seen in Table III that the association constants,  $K_p^0$  and  $K_t^0$ , decrease from oxalate, to malonate, and to succinate. For tartrates, apparently, only pair association constants are relevant.

The results for the permittivity in Table III deserve a special mention. In the present BiMSA model, variation of permittivity with concentration is considered through relation in Eq. 3. By fitting the activity and osmotic coefficients, an optimum value for  $\alpha$  is obtained. Besides, experimental data for the permittivity as a function of concentration are available for disodium malonate and succinate salt solutions<sup>58</sup>. A fit of these data using Eq. 3 gives the values presented in Table III. Surprisingly enough, a very good agreement is observed between the two sets of values. The results for the relative permittivity are shown in Figure 10, together with the result from

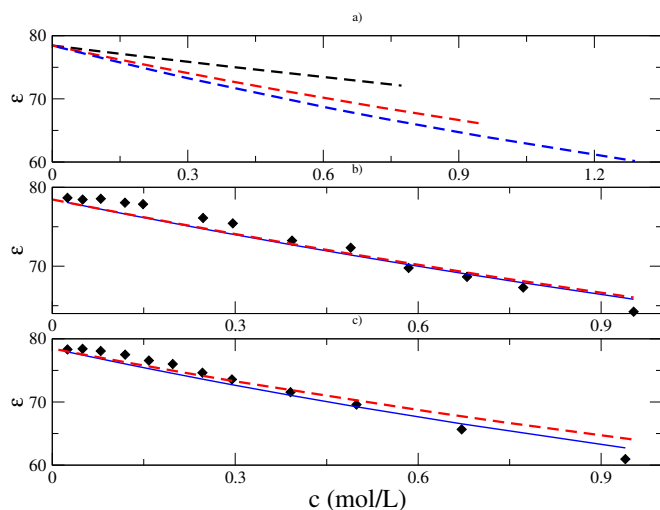


FIG. 10. Relative solution permittivity: (a) from top to bottom: dipotassium oxalate, disodium malonate and disodium succinate, (b) disodium malonate, and (c) disodium succinate. Symbols (diamonds): experimental data<sup>58</sup>; Solid line: fit of experimental data; Dashed line: BiMSA theory prediction.

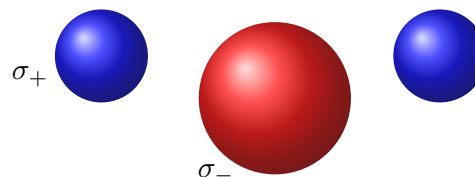


FIG. 11. Sketch of the type of molecule described within the previous BiMSA model. The diameters of the counterion (in blue) and the dianion (in red) are  $\sigma_+$  and  $\sigma_-$ , respectively.

BiMSA theory for dipotassium oxalate (for which no experimental data are available).

## B. Comparison with a previous model

In a previous work<sup>52</sup>, we addressed the problem of the formation of pairs and trimers of a trivalent cation like  $\text{Eu}^{3+}$  with an anion like  $\text{Cl}^-$  within the BiMSA framework. By interchanging cations and anions, this model can be applied in the present context by reducing the anionic chains into equivalent spheres (see Fig. 11). The equations describing the thermodynamic properties in this model are detailed in Appendix C.

It is then worth comparing results from the latter rough approximation of chains by spheres with those from the present more involved theory in order to assess the relevance of the latter. To carry out this comparison, two cases were considered. In the first case the parameters  $\sigma_-$  (dianion's diameter),

$\sigma^{(1)}$ ,  $\alpha$ ,  $K_p$  and  $K_T$  were left free in the fits; in the second, the  $\alpha$  parameter was fixed taking into account the values obtained for the chain model except for sodium malonate and sodium succinate, where the  $\alpha$  value was determined by fitting experimental data for the solution permittivity. The latter methodology was employed because it is observed that the use of the chain model gives values for the permittivity that are in agreement with experiment in the case of solutions of sodium malonate and succinate.

Table IV shows the parameter values obtained in the first case described above. It can be seen that  $\sigma_-$  increases in the following order of the dianions:  $\sigma_-(\text{oxalate}) < \sigma_-(\text{malonate}) < \sigma_-(\text{succinate})$ . However, the value of this parameter for tartrate is lower than for oxalate which does not make physical sense since the size of the tartrate and/or succinate must be larger than that of the oxalate. On the other hand, the value of  $\alpha$  obtained for succinate differs appreciably from that obtained using the chain model or that fitted directly from the experimental data. It should be noted that for all salts the trimer constant obtained is zero. Finally, for all salts, it is possible to reproduce the experimental data very well (AARD less than 1%).

For the second case, the parameter values obtained are presented in Table V. The value of  $\sigma_-$  is now reduced for oxalate, malonate and succinate as compared to the first case. However, the trend of increasing values is maintained. In the case of the two tartrates, a  $\sigma_-$  value closer to that of succinate is obtained which makes more physical sense. It is important to note that for the latter salts the deviations from the experimental data are larger (3.3% for potassium tartrate and 2.2% for sodium tartrate).

#### IV. CONCLUSION

In this work a thermodynamic model that takes into account electrostatic, association and chain contributions to the free energy of charged solutions, is proposed. This model was successfully applied to describe the osmotic and activity coefficients for solutions of some carboxylic salts at high concentrations (up to almost 5 M). A good agreement with the experimental values of the osmotic and activity coefficients could be obtained by regressing a few parameters having a direct physical meaning.

For comparison, a previous model with no chain contribution was also studied. Good fits of the experimental values for the osmotic and activity coefficients could also be obtained, but the values regressed for the adjustable parameters of the model are not as satisfactory as those found using the chain model. In particular, a remarkable result is the prediction for the variation of the permittivity with concentration. The chain model predicts very well this variation, while the model with no chain term does not. In general, the fitted parameters obtained from the chain model have more physically satisfying values than those obtained from the 'single sphere' model (no chain) for this kind of charged solutions.

#### ACKNOWLEDGMENTS

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#### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available within the article.

#### Appendix A: Contributions due to variation of cation size and permittivity for a dianion comprised of two spheres

The contribution to the HS osmotic coefficient arising from the variation of cation size is given by

$$\Delta\phi_{\sigma_+}^{HS} = \frac{\rho_+}{\rho_t} [f_1 + 2\sigma_+ f_2 + 3\sigma_+^2 f_3] D(\sigma_+) \quad (\text{A1})$$

where D is the operator,  $D = \sum_k \rho_k \frac{\partial}{\partial \rho_k}$ . Specifically,  $D(\sigma_+) = \sigma_+ - \sigma^{(0)}$ .

$$\begin{aligned} f_1 &= \frac{3\zeta_2}{1 - \zeta_3} \\ f_2 &= \frac{3\zeta_1}{1 - \zeta_3} + \frac{3\zeta_2^2}{\zeta_3(1 - \zeta_3)^2} + \frac{3\zeta_2^2 \ln(1 - \zeta_3)}{\zeta_3^2} \\ f_3 &= \frac{\zeta_0 - \zeta_2^3/\zeta_3^2}{1 - \zeta_3} + \frac{3\zeta_1\zeta_2 - \zeta_2^3/\zeta_3^2}{(1 - \zeta_3)^2} + \frac{2\zeta_2^3}{\zeta_3(1 - \zeta_3)^3} \\ &\quad - 2 \left( \frac{\zeta_2}{\zeta_3} \right)^3 \ln(1 - \zeta_3) \end{aligned} \quad (\text{A2})$$

and the chain contribution is

$$\begin{aligned} \Delta\phi_{\sigma_+}^{ch} &= -\frac{D(\sigma_+)}{\rho_t} \left( \frac{\rho_-}{g_{--}^{HS}(\sigma_-)} \right) \left[ \frac{\pi\rho_+\sigma_+}{2} \left( \frac{\sigma_-}{(1 - \zeta_3)^2} \right. \right. \\ &\quad \left. \left. + \frac{2\zeta_2\sigma_-^2}{3(1 - \zeta_3)^3} \right) + \frac{\pi\rho_+\sigma_+^2}{2} \left( \frac{g_{--}^{HS}(\sigma_-)}{1 - \zeta_3} + \frac{1}{(1 - \zeta_3)^2} \right. \right. \\ &\quad \left. \left. + \frac{3\zeta_2\sigma_-}{(1 - \zeta_3)^3} + \frac{3(\zeta_2\sigma_-)^2}{2(1 - \zeta_3)^4} \right) \right]. \end{aligned} \quad (\text{A3})$$

It is found that

$$\Delta \ln \gamma_{\sigma_+}^{HS+ch} = \beta \Delta\phi_{\sigma_+}^{HS+ch} \quad (\text{A4})$$

where

$$\beta \Delta\phi_{\sigma_+}^{HS+ch} = \beta \Delta\phi_{\sigma_+}^{HS} + \beta \Delta\phi_{\sigma_+}^{ch} \quad (\text{A5})$$

The contributions to the BiMSA part of the osmotic coefficient coming from the variation of permittivity and cation size are respectively given by

$$\Delta\phi_{\epsilon}^{BiMSA} = \frac{1}{\rho_t} \left[ \frac{\partial \beta \Delta A^{BiMSA}}{\partial \epsilon^{-1}} \right] \epsilon D(\epsilon^{-1}) = \frac{\beta \Delta E}{\rho_t} \epsilon D(\epsilon^{-1}) \quad (\text{A6})$$

TABLE IV. Fitted parameter values obtained using the model in which the dianion is regarded as a single sphere.

Salt	$\sigma_-$	$\sigma^{(1)} \times 10^2$	$\alpha \times 10$	$K_p^0$	$K_T^0$	$m_{max}$	AARD% <sup>a</sup>	
	Å	Å mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol kg <sup>-1</sup>	$\phi$	y
K <sub>2</sub> Oxalate	7.115	-1.72	2.61	4.746	0.0	0.80	0.02	0.24
Na <sub>2</sub> Malonate	7.517	-43.81	2.32	4.505	0.0	1.00	0.09	0.12
Na <sub>2</sub> Succinate	8.174	-90.59	1.10	2.553	0.0	1.40	0.20	0.24
K <sub>2</sub> Tartrate	6.582	-32.68	1.41	12.89	0.0	4.84	0.61	-
Na <sub>2</sub> Tartrate	6.144	-20.75	1.63	3.768	0.0	2.72	0.73	-

<sup>a</sup> AARD% is calculated in the same way as the values reported in Table III.

TABLE V. Fitted parameter values obtained using the model in which the dianion is regarded as a single sphere with  $\alpha$  fixed.

Salt	$\sigma_-$	$\sigma^{(1)} \times 10^2$	$\alpha \times 10$	$K_p^0$	$K_T^0$	$m_{max}$	AARD% <sup>a</sup>	
	Å	Å mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol <sup>-1</sup> L	mol kg <sup>-1</sup>	$\phi$	y
K <sub>2</sub> Oxalate	6.775	-8.08	1.140	4.256	1.489	0.80	0.04	0.24
Na <sub>2</sub> Malonate	6.980	-26.52	2.014	3.626	0.0519	1.00	0.10	0.13
Na <sub>2</sub> Succinate	7.247	-28.40	2.667	0.005	0.00	1.40	0.78	1.40
K <sub>2</sub> Tartrate	7.077	-41.28	1.992	8.597	0.00	4.84	3.31	-
Na <sub>2</sub> Tartrate	7.294	-33.66	2.976	3.476	0.00	2.72	2.18	-

<sup>a</sup> AARD% is calculated in the same way as the values reported in Table III.

and

$$\Delta\phi_{\sigma_+}^{BiMSA} = \frac{1}{\rho_t} \left[ \frac{\partial \beta \Delta A^{BiMSA}}{\partial \sigma_+} \right] D(\sigma_+), \quad (A7)$$

the latter quantity was computed numerically because the derivative w.r.t.  $\sigma_+$  cannot be obtained explicitly. Additionally, we have that  $\varepsilon D(\varepsilon^{-1}) = 1 - \varepsilon/\varepsilon_W$ .

For the activity coefficient, we have that  $\Delta \ln y_{\sigma_+, \varepsilon}^{BiMSA} = \Delta\phi_{\varepsilon}^{BiMSA} + \Delta\phi_{\sigma_+}^{BiMSA}$ .

### Appendix B: Molecular dianion made up of three or four spheres

The equations in this case are as follows. In order to evaluate the chain terms  $\Delta \ln y_0^{ch}$  and  $\Delta\phi_0^{ch}$  we used

$$g_{-m}^{HS}(\sigma_{-m}) = \frac{1}{1 - \zeta_3} + \frac{3\zeta_2}{(1 - \zeta_3)^2} \sigma_{am} + \frac{2\zeta_2^2}{(1 - \zeta_3)^3} \sigma_{am}^2 \quad (B1)$$

where we used the notation

$$\sigma_{am} = \frac{\sigma_- \sigma_m}{\sigma_- + \sigma_m} \quad (B2)$$

to distinguish  $\sigma_{am}$  from  $\sigma_{-m}$ , and

$$g_{mm}^{HS}(\sigma_m) = \frac{1}{1 - \zeta_3} + \frac{3\zeta_2}{2(1 - \zeta_3)^2} \sigma_m + \frac{\zeta_2^2}{2(1 - \zeta_3)^3} \sigma_m^2. \quad (B3)$$

The chain contribution to the osmotic coefficient is given by

$$\begin{aligned} \Delta\phi_0^{ch} = & -\frac{\rho_-}{\rho_t} \left[ (n+1) \frac{\zeta_3}{1 - \zeta_3} \right. \\ & + \frac{2}{g_{-m}^{HS}(\sigma_{-m})} \left( \frac{3\zeta_2 \sigma_{am}}{(1 - \zeta_3)^3} + \frac{4(\zeta_2 \sigma_{am})^2}{(1 - \zeta_3)^4} \right) \\ & \left. + \frac{(n-1)}{g_{mm}^{HS}(\sigma_m)} \left( \frac{3\zeta_2 \sigma_m}{2(1 - \zeta_3)^3} + \frac{(\zeta_2 \sigma_m)^2}{(1 - \zeta_3)^4} \right) \right] \quad (B4) \end{aligned}$$

and the chain part of the activity coefficient can be written as

$$\begin{aligned} \Delta \ln y_0^{ch} = & -\frac{\rho_-}{\rho_t} \left[ 2 \ln g_{-m}^{HS}(\sigma_{-m}) + (n-1) \ln g_{mm}^{HS}(\sigma_m) \right. \\ & + (n+1) \frac{\zeta_3}{1 - \zeta_3} \\ & + \frac{2}{g_{-m}^{HS}(\sigma_{-m})} \left( \frac{3\zeta_2 \sigma_{am}}{(1 - \zeta_3)^3} + \frac{4(\zeta_2 \sigma_{am})^2}{(1 - \zeta_3)^4} \right) \\ & \left. + \frac{(n-1)}{g_{mm}^{HS}(\sigma_m)} \left( \frac{3\zeta_2 \sigma_m}{2(1 - \zeta_3)^3} + \frac{(\zeta_2 \sigma_m)^2}{(1 - \zeta_3)^4} \right) \right]. \quad (B5) \end{aligned}$$

The osmotic contribution  $\Delta\phi_{\sigma_+}^{HS}$  is the same as in the previous case, and the contribution for the variation of cation size

$\Delta y_{\sigma_+}^{ch} = \Delta \phi_{\sigma_+}^{ch}$  is given by

$$\begin{aligned} \Delta \phi_{\sigma_+}^{ch} = & -\frac{2\pi\rho_-\rho_+}{g_{-m}^{HS}(\sigma_-)} \left[ \frac{\sigma_+}{3} \left( \frac{3\sigma_{am}}{(1-\zeta_3)^2} + \frac{4\zeta_2\sigma_{am}^2}{(1-\zeta_3)^3} \right) \right. \\ & + \frac{\sigma_+^2}{2} \left( -\frac{g_{-m}^{HS}(\sigma_-)}{1-\zeta_3} + \frac{1}{(1-\zeta_3)^2} \right. \\ & \left. \left. + \frac{6\zeta_2\sigma_{am}}{(1-\zeta_3)^3} + \frac{6(\zeta_2\sigma_{am})^2}{(1-\zeta_3)^4} \right) \right] \frac{D(\sigma_+)}{\rho_t} \\ & - \frac{(n-1)\pi\rho_-\rho_+}{g_{mm}^{HS}(\sigma_m)} \left[ \frac{\sigma_+}{3} \left( \frac{3\sigma_m}{2(1-\zeta_3)^2} + \frac{\zeta_2\sigma_m^2}{(1-\zeta_3)^3} \right) \right. \\ & + \frac{\sigma_+^2}{2} \left( -\frac{g_{mm}^{HS}(\sigma_m)}{1-\zeta_3} + \frac{1}{1-\zeta_3} + \frac{3\zeta_2\sigma_m}{(1-\zeta_3)^3} \right. \\ & \left. \left. + \frac{3(\zeta_2\sigma_m)^2}{2(1-\zeta_3)^4} \right) \right] \frac{D(\sigma_+)}{\rho_t}. \end{aligned} \quad (B6)$$

The BiMSA expressions used here have been obtained from a previous work on polyelectrolytes<sup>40</sup>. Previously, it was observed that the electrostatic Helmholtz free energy obtained in the framework of the BiMSA theory, can be split into two parts, namely an excess term related to the interaction between the ions and a term coming from the interaction energy between the charged subunits within each of the chains. At infinite dilution, this term provides an electrostatic contribution to the standard chemical potential of the polyions. Now in this study, only the excess free energy has been considered. Then, the electrostatic contribution to the Helmholtz energy for these systems is given by<sup>40</sup>

$$\begin{aligned} \beta \Delta A^{el} = & \beta \Delta E + \frac{[\Gamma]^3}{3\pi} - \sum_{\kappa=P,T} \rho_\kappa \left[ \frac{\beta \partial \Delta E}{\partial \rho_\kappa} \right]_\Gamma, \\ & - \lambda_0 \frac{2\rho_-}{2\sigma_- + n\sigma_m} z_-^2 \end{aligned} \quad (B7)$$

The last term in Eq. (B7) is the contribution which has been subtracted in order to consider only the excess free energy. Then as usual, the expressions for  $\ln y_{\pm}^{el}$  and  $\Delta \phi^{el}$  were determined by differentiation. It was found that  $\Delta \phi^{el}$  is given by Eq. (48). Then using Eqs. (23) and (B7),  $\Delta \ln y_0^{el}$  can be deduced, which gave

$$\begin{aligned} \Delta \ln y_0^{el} = & \beta \Delta E - \frac{2\lambda}{\pi} \eta^2 - \sum_{\kappa=P,T} \rho_\kappa \left[ \frac{\beta \partial \Delta E}{\partial \rho_\kappa} \right]_\Gamma, \\ & - \lambda_0 \frac{2\rho_-}{2\sigma_- + n\sigma_m} z_-^2 \end{aligned} \quad (B8)$$

A significant cancellation was noted between some parts of  $\Delta E$  and of its derivatives in particular, which simplifies the final result (given below). Subsequently, at this stage in order to evaluate  $\Delta A^{el}$ , it is not necessary to give the explicit expressions of  $\Delta E$  and its derivatives relative to the concentrations  $\rho_p$  and  $\rho_t$  of pairs and trimers. It seems simpler to represent  $\beta \Delta A^{el}$  as in Eq. (23) from the coefficients  $\ln y_{\pm}^{el}$  and  $\Delta \phi^{el}$ .

The electrostatic contribution to the activity coefficient is

given by

$$\begin{aligned} \Delta \ln y_0^{el} = & \frac{\lambda}{\rho_t} \left[ \rho_+ z_+ M_+^0 + 2\rho_- z_- M_-^0 \right. \\ & - \eta \left( \rho_+ \sigma_+ \left( \mathcal{X}_+^0 + \frac{\eta}{3} \sigma_+^2 \right) + 2\rho_- \sigma_- \left( \mathcal{X}_-^0 + \frac{\eta}{3} \sigma_-^2 \right) \right. \\ & \left. + n\rho_- \sigma_m \left( \mathcal{X}_m^0 + \frac{\eta}{3} \sigma_m^2 \right) \right) \\ & + 2\frac{\rho_-}{\sigma_m} \sum_{k=1}^n \frac{(n-k)(\mathcal{X}_m^0)^2}{(k+1)(1+\Gamma\sigma_m)^{k-1}} \\ & + 4\rho_- \sum_{k=1}^n \frac{\mathcal{X}_-^0 \mathcal{X}_m^0}{(\sigma_- + k\sigma_m)(1+\Gamma\sigma_m)^{k-1}} \\ & \left. + \frac{2\rho_-}{2\sigma_- + n\sigma_m} \left( \frac{(\mathcal{X}_-^0)^2}{(1+\Gamma\sigma_m)^n} - z_-^2 \frac{\epsilon}{\epsilon_w} \right) \right] \end{aligned} \quad (B9)$$

where

$$\mathcal{X}_m^0 = \frac{-\eta\sigma_m^2}{1+\Gamma\sigma_m}.$$

The last three terms in Eq. (B9) represent the contributions due to interactions within the chains. The preceding terms are similar to those for dissociated electrolytes. To evaluate the above quantities, the parameters  $\Gamma$  and  $\eta$  are expressed as<sup>40</sup>

$$\begin{aligned} \frac{\Gamma^2}{\pi} = & \lambda \left[ \rho_+ (\mathcal{X}_+^0)^2 + 2\rho_- (\mathcal{X}_-^0)^2 + n\rho_- (\mathcal{X}_m^0)^2 \right. \\ & + 2\rho_- \sum_{k=1}^n (n-k) \frac{\sigma_m^*}{\sigma_m} \frac{(\mathcal{X}_m^0)^2}{(1+\Gamma\sigma_m)^{k-1}} \\ & + 4\rho_- \sum_{k=1}^n \frac{\sigma_-^* + k\sigma_m^*}{\sigma_- + k\sigma_m} \frac{\mathcal{X}_-^0 \mathcal{X}_m^0}{(1+\Gamma\sigma_m)^{k-1}} \\ & + \frac{2\rho_-}{(1+\Gamma\sigma_m)^n} \frac{2\sigma_-^* + n\sigma_m^*}{2\sigma_- + n\sigma_m} (\mathcal{X}_-^0)^2 \\ & + 2(\rho_p + 2\rho_t) \left( \frac{\sigma_+^* + \sigma_-^*}{\sigma_+ + \sigma_-} \mathcal{X}_+^0 \mathcal{X}_-^0 \right. \\ & + \frac{\sigma_+^* + 2\sigma_-^* + n\sigma_m^*}{\sigma_+ + 2\sigma_- + n\sigma_m} \frac{\mathcal{X}_+^0 \mathcal{X}_-^0}{(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^n} \\ & \left. + \sum_{k=1}^n \frac{\sigma_+^* + \sigma_-^* + k\sigma_m^*}{\sigma_+ + \sigma_- + k\sigma_m} \frac{\mathcal{X}_+^0 \mathcal{X}_m^0}{(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^{k-1}} \right) \\ & \left. + 2\rho_t \frac{2\sigma_+^* + 2\sigma_-^* + n\sigma_m^*}{2\sigma_+ + 2\sigma_- + n\sigma_m} \frac{(\mathcal{X}_+^0)^2}{(1+\Gamma\sigma_-)^2(1+\Gamma\sigma_m)^n} \right] \end{aligned} \quad (B10)$$

$$\begin{aligned}
\eta = & \frac{\pi}{2\Delta} \left[ \rho_+ \sigma_+ \mathcal{X}_+^0 + 2\rho_- \sigma_- \mathcal{X}_-^0 + n\rho_- \sigma_m \mathcal{X}_m^0 \right. \\
& + 2\frac{\rho_-}{\sigma_m} \sum_{k=1}^n \frac{(n-k)\mathcal{X}_m^0 \sigma_m^{2*}}{(k+1)(1+\Gamma\sigma_m)^{k-1}} \\
& + \frac{2\rho_-}{2\sigma_- + n\sigma_m} \frac{\sigma_-^{2*} \mathcal{X}_-^0}{(1+\Gamma\sigma_m)^n} \\
& + 2\rho_- \sum_{k=1}^n \frac{\mathcal{X}_m^0 \sigma_-^{2*} + \mathcal{X}_-^0 \sigma_m^{2*}}{(\sigma_- + k\sigma_m)(1+\Gamma\sigma_m)^{k-1}} \\
& + (\rho_p + 2\rho_T) \left( \frac{\mathcal{X}_+^0 \sigma_-^{2*} + \mathcal{X}_-^0 \sigma_+^{2*}}{\sigma_+ + \sigma_-} \right. \\
& + \frac{\mathcal{X}_+^0 \sigma_-^{2*} + \mathcal{X}_-^0 \sigma_+^{2*}}{(\sigma_+ + 2\sigma_- + n\sigma_m)(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^n} \\
& + \left. \sum_{k=1}^n \frac{\mathcal{X}_+^0 \sigma_m^{2*} + \mathcal{X}_m^0 \sigma_+^{2*}}{(\sigma_+ + \sigma_- + k\sigma_m)(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^{k-1}} \right) \\
& \left. + \frac{2\rho_T}{2\sigma_+ + 2\sigma_- + n\sigma_m} \frac{\mathcal{X}_+^0 \sigma_+^{2*}}{(1+\Gamma\sigma_-)^2(1+\Gamma\sigma_m)^n} \right] \quad (\text{B11})
\end{aligned}$$

To solve the equations describing the equilibrium and take into account the presence of  $n$  spheres  $m$  between the charged heads of the dianion,  $G_p$  and  $G_T$  must be modified as follows

$$\begin{aligned}
G_p = & g_{+-}^{HS}(\sigma_{+-}) \exp \left\{ -2\lambda \left[ \frac{(\mathcal{X}_+^0 \mathcal{X}_-^0 - z_+ z_- c_0)}{\sigma_+ + \sigma_-} \right. \right. \\
& + \frac{1}{(\sigma_+ + 2\sigma_- + n\sigma_m)} \left( \frac{\mathcal{X}_+^0 \mathcal{X}_-^0}{(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^n} - z_+ z_- c_1 \right) \\
& \left. + \sum_{k=1}^n \frac{\mathcal{X}_+^0 \mathcal{X}_m^0}{(\sigma_+ + \sigma_- + k\sigma_m)(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^{k-1}} \right] \left. \right\} \quad (\text{B12})
\end{aligned}$$

and

$$\begin{aligned}
G_T = & G_p \exp \left[ -\frac{2\lambda}{(2\sigma_+ + 2\sigma_- + n\sigma_m)} \times \right. \\
& \left. \left( \frac{\mathcal{X}_+^0 \mathcal{X}_+^0}{(1+\Gamma\sigma_-)^2(1+\Gamma\sigma_m)^n} - z_+ z_+ c_2 \right) \right] \quad (\text{B13})
\end{aligned}$$

where

$$\begin{aligned}
c_0 = & \frac{(\sigma_+ + \sigma_-)\epsilon}{(\sigma_+^{(0)} + \sigma_-)\epsilon_w} \\
c_1 = & \frac{(\sigma_+ + 2\sigma_- + n\sigma_m)\epsilon}{(\sigma_+^{(0)} + 2\sigma_- + n\sigma_m)\epsilon_w} \\
c_2 = & \frac{(2\sigma_+ + 2\sigma_- + n\sigma_m)\epsilon}{(2\sigma_+^{(0)} + 2\sigma_- + n\sigma_m)\epsilon_w}. \quad (\text{B14})
\end{aligned}$$

The contribution  $\Delta\phi_e^{BiMSA}$  is calculated using Eq. (A6) but

with the internal energy given by

$$\begin{aligned}
\beta\Delta E = & \lambda \left[ \rho_+ z_+ M_+^0 + 2\rho_- z_- M_-^0 \right. \\
& + \frac{2\rho_-}{2\sigma_- + n\sigma_m} \left( \frac{z_-^* \mathcal{X}_-^0}{(1+\Gamma\sigma_m)^n} \right) \\
& + \sum_{k=1}^n \frac{2\rho_-}{\sigma_- + k\sigma_m} \left( \frac{z_-^* \mathcal{X}_m^0}{(1+\Gamma\sigma_m)^{k-1}} \right) \\
& + \frac{(\rho_p + 2\rho_T)}{(\sigma_+ + \sigma_-)} (z_+^* \mathcal{X}_-^0 + z_-^* \mathcal{X}_+^0) \\
& + \frac{(\rho_p + 2\rho_T)}{(\sigma_+ + 2\sigma_- + n\sigma_m)(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^n} \\
& + \sum_{k=1}^n \frac{\rho_p + 2\rho_T}{\sigma_+ + \sigma_- + k\sigma_m} \left( \frac{z_+^* \mathcal{X}_m^0}{(1+\Gamma\sigma_-)(1+\Gamma\sigma_m)^{k-1}} \right) \\
& \left. + \frac{2\rho_T}{(2\sigma_+ + 2\sigma_- + n\sigma_m)(1+\Gamma\sigma_-)^2(1+\Gamma\sigma_m)^n} \right]. \quad (\text{B15})
\end{aligned}$$

Finally,  $\Delta\phi_{\sigma_+}^{BiMSA}$  is also computed numerically as in the previous case.

### Appendix C: Molecular dianion made up of a single sphere

The equations presented below are related to a model that describes salts with a dianion made up of a single sphere with diameter  $\sigma_-$  and valence  $z_-$  and two cations with diameter  $\sigma_+$  and valence  $z_+$  (see Fig. 11) with the possibility of forming pairs and trimers. In addition, the cation size and permittivity are allowed to vary with concentration. Using the equations reported in a previous work<sup>52</sup>, the osmotic and activity coefficients can be assessed. Note that to preserve electroneutrality,  $z_-$  must be equal to the valence of the full dianion. That is, the valence  $z_-$  used in this model is twice the valence  $z_-$  used in dianion models containing multiple subunits, in order to conserve its total charge.

The Helmholtz free energy will be given by

$$\beta\Delta A = \beta\Delta A^{HS} + \beta\Delta A^{BiMSA} \quad (\text{C1})$$

where the hard sphere contribution is

$$\begin{aligned}
\frac{\pi}{6}\beta\Delta A^{HS} = & \left[ \frac{\zeta_2^3}{\zeta_3^2} - \zeta_0 \right] \ln(1 - \zeta_3) + \frac{3\zeta_1 \zeta_2}{1 - \zeta_3} \\
& + \frac{\zeta_2^3}{\zeta_3(1 - \zeta_3)^2}. \quad (\text{C2})
\end{aligned}$$

Clearly, the chain contribution for the Helmholtz free energy ( $\beta\Delta A^{ch}$ ) is not needed for this model.

When the dianion is represented as a single sphere,  $\zeta_k$  is given by

$$\zeta_k = \frac{\pi}{6} (\rho_+ \sigma_+^k + \rho_- \sigma_-^k). \quad (\text{C3})$$

The HS part of the osmotic coefficient is

$$\beta\Delta\phi_0^{HS} = \frac{\zeta_3}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\zeta_3)^2} + \frac{(3-\zeta_3)\zeta_2^2}{\zeta_0(1-\zeta_3)^3} \quad (C4)$$

and  $\Delta\ln y_0^{HS}$  can be deduced from

$$\Delta\ln y_0^{HS} = \frac{\beta\Delta A^{HS}}{\rho_t} + \Delta\phi_0^{HS} \quad (C5)$$

The contribution of BiMSA can be divided into two parts as in Eq. (2), where the association parts have the same forms as given in Eqs. (36), (37) and (38). The electrostatic part for the Helmholtz energy  $\beta\Delta A^{el}$  can be split into two parts according to Eq. (23). The mean activity coefficient contribution  $\Delta\ln y_0^{el}$  is now given by

$$\Delta\ln y_0^{el} = \frac{\lambda}{\rho_t} \left[ \rho_{+z_+} M_+^0 + \rho_{-z_-} M_-^0 - \eta \rho_+ \sigma_+ \left( \mathcal{X}_+^0 + \frac{\eta}{3} \sigma_+^2 \right) - \eta \rho_- \sigma_- \left( \mathcal{X}_-^0 + \frac{\eta}{3} \sigma_-^2 \right) \right] \quad (C6)$$

The osmotic part  $\Delta\phi_0^{el}$  can be determined by using eq. (30) but with different  $\Gamma$  and  $\eta$  parameters. For this model, the quantities  $\Gamma$  and  $\eta$  are given by

$$\frac{\Gamma^2}{\pi\lambda} = \sum_{k=+,-} \rho_k (\mathcal{X}_k^0)^2 + 2(\rho_p + 2\rho_T) \frac{\sigma_+^* + \sigma_-^*}{\sigma_+ + \sigma_-} \mathcal{X}_+^0 \mathcal{X}_-^0 + 2 \frac{\rho_T}{(1+\Gamma\sigma_-)} \frac{2\sigma_+^* + \sigma_-^*}{2\sigma_+ + \sigma_-} (\mathcal{X}_+^0)^2 \quad (C7)$$

and

$$\eta = \frac{\pi}{2\Delta\Omega} \left[ \sum_{k=+,-} \rho_k \sigma_k z_k^* + \frac{\rho_p + 2\rho_T}{\sigma_+ + \sigma_-} (z_+^* \sigma_-^{2*} + z_-^* \sigma_+^{2*}) + \frac{2\rho_T}{(2\sigma_+ + \sigma_-)(1+\Gamma\sigma_-)} z_+^* \sigma_+^{2*} \right] \quad (C8)$$

with  $z_k^* = \frac{z_k}{1+\Gamma\sigma_k}$ ,  $\Delta = 1 - \zeta_3$  and

$$\Omega = 1 + \frac{\pi}{2\Delta} \left[ \sum_{k=+,-} \rho_k \frac{\sigma_k^3}{1+\Gamma\sigma_k} + 2 \frac{\rho_p + 2\rho_T}{\sigma_+ + \sigma_-} \sigma_+^{2*} \sigma_-^{2*} + 2 \frac{\rho_T}{(2\sigma_+ + \sigma_-)} \frac{(\sigma_+^{2*})^2}{1+\Gamma\sigma_-} \right]. \quad (C9)$$

The contribution  $\Delta\phi_e^{BiMSA}$  is calculated using Eq. (A6) but with the electrostatic contribution to internal energy given by

$$\beta\Delta E = \lambda \left[ \sum_{k=+,-} \rho_k z_k M_k^0 + \frac{(\rho_p + 2\rho_T) (z_+^* \mathcal{X}_-^0 + z_-^* \mathcal{X}_+^0)}{(\sigma_+ + \sigma_-)} + \frac{2\rho_T (z_+^* \mathcal{X}_+^0)}{(2\sigma_+ + \sigma_-)(1+\Gamma\sigma_-)} \right] \quad (C10)$$

As in the previous cases,  $\Delta\phi_{\sigma_+}^{BiMSA}$  is computed numerically. The terms  $G_p$  and  $G_T$  related to the equilibria (31) also need to be modified, the expressions for this system are given by

$$G_p = g_{+-}^{HS}(\sigma_{+-}) \exp \left\{ -2\lambda \frac{(\mathcal{X}_+^0 \mathcal{X}_-^0)}{\sigma_+ \sigma_-} + 2\lambda_0 \frac{z_+ z_-}{\sigma_+^{(0)} + \sigma_-} \right\}, \quad (C11)$$

and

$$G_T = G_p \exp \left[ -2\lambda \frac{\mathcal{X}_+^0 \mathcal{X}_-^0}{(2\sigma_+ + \sigma_-)(1+\Gamma\sigma_-)} + 2\lambda_0 \frac{z_+^2}{2\sigma_+^{(0)} + \sigma_-} \right] \quad (C12)$$

where  $g_{+-}^{HS}(\sigma_{+-})$  is the same as in Eq. (39) but with  $\zeta_k$  defined by Eq. (C3).

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