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Estimation of the Pitzer parameters for 1-1, 2-1, 3-1, 4-1 and 2-2 single electrolytes at 25 °C

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ABSTRACT The Pitzer model is one of the most important thermodynamic models to predict the behavior of aqueous electrolyte solutions, especially at high ionic strengths. However, most of the parameters in the Pitzer equations have to be obtained experimentally and this represents an important drawback to this model. Therefore, in order to make the Pitzer equations less dependent on experimental data and more dependent on the properties of the solution, new equations that correlate the Pitzer equations with the properties of the solution have been successfully developed for 1-1, 2-1, 3-1, 4-1 and 2-2 electrolytes. In particular, these equations were developed for two cases: (i) considers the original Pitzer equations and (ii) considers some simplifications to the Pitzer equation (assuming C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 = 0$). In particular, for case (ii), the second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ of the Pitzer equations were re-estimated using published experimental data of the osmotic coefficient obtained from the literature. As a conclusion, both the simplified and the original Pitzer equations presented a very good match with this published experimental data for the osmotic coefficients. Additionally, the second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ for both cases were successfully correlated with the ionic radius and the ionic charge, and this is confirmed by the very high coefficients of

determination achieved (R^2>0.96). However, these new equations are valid only to cases in which no significant ion association occurs, which is also the basic premise of the original Pitzer model.

INTRODUCTION

The Pitzer model is a semi-empirical model that is very important for the understanding of the behavior of ions dissolved in water. This model was first described by the chemist Kenneth Pitzer and it characterizes interactions amongst the ions and the solvent through linear combinations of parameters involving a virial expansion of the excess Gibbs free energy[1]. Moreover, this model is very efficient at predicting the behavior of the electrolyte solutions ranging from infinitely diluted solutions to very concentrated ones, up to a molality of 6mol/kg [2]. On the other hand, the Pitzer model is largely empirical and the virial parameters representing short-range interactions cannot be directly correlated to the properties of the solution, and thus cannot be extrapolated for different cases. In fact, this is an important drawback of the Pitzer model since in many cases the experiments required to obtain the parameters in the Pitzer equations are very difficult to perform, e.g. experiments involving radioactive species[3]. Therefore, finding a way to correlate the virial terms in the Pitzer equation with the properties of the solution is highly important.

Some attempts at describing the dependence of the second virial coefficients on the properties of the solution, especially with regards to the ionic radii, can be found in the literature. Weian et al.[4] reformed the Pitzer osmotic equation in order to obtain relationships between the second virial parameters and the ionic radii, and the equations obtained could satisfactorily predict the parameters $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ in the Pitzer equations for some 1-1 electrolytes. However, the values of ionic radii used by Weian et al.[4] to calculate the second virial parameters were not the ones available in the literature, but rather values adjusted to fit the experimental data for the osmotic and activity coefficient. Consequently, this model cannot be easily extended to different electrolytes, since the values of the ionic radii found by Weian et al. [4] do not coincide with the tabulated values of ionic radii and hydrated radii available in the literature, e.g. Marcus[5].

Another attempt to correlate the virial coefficients in the Pitzer equation with the properties of the solution was made by Rosenberg et al.[3]. They estimated the second and third virial coefficients for $RaBr_2$, $RaCl_2$ and $RaSO_4$ as a function of the hydrated radii of the ions using a linear regression involving chlorides of magnesium, calcium, barium and strontium, which belong to the same group of the periodic table as the radium ion. Despite a very clear linear trend between the parameter $B_{MX}^{(0)}$ and the hydrated radii of the ions being achieved, the parameters $B_{MX}^{(1)}$ and C_{MX}^{ϕ} presented a poor linear correlation. However, this was considered a reasonable approach by Rosenberg et al.[3] due to the unavoidable lack of experimental data.

Finally, Zareen et al.[6] used the dielectric constants of the water at different temperatures as well as the ionic radii to estimate the activity coefficients of salt mixtures by a Monte Carlo Simulation procedure. The good agreement with experimental data achieved reinforces the strong connection between the ionic radii and the activity coefficients of the species for concentrated solutions, which indicates that the second virial parameters of the Pitzer equations may also have a strong connection with the ionic radii of the species.

In terms of the properties of the solution, it is important to note that diluted solutions (in this study, diluted solutions refers to the maximum ionic strength that can be covered by the Debye-Huckel model, i.e. approximately 0.01 molal) behave differently from concentrated solutions. While the diluted solutions can be well explained by the Debye-Huckel theory, which assumes that ions are geometrical points that have no volume of exclusion and these ions do not come into contact with each other[7], concentrated solutions require a more complex analysis, and this can be attributed to the fact that the point ion assumption is no longer valid. This is because ions can now come into contact with each other, and the cloud of orbiting electrons surrounding their nuclei creates a harsh repulsive core that does not allow overlapping[7]. On top of this, other properties of the solution become more and more relevant as the solution shifts from diluted to concentrated, such as the effect of the hydration by the shell of water molecules surrounding the ions, the ion pairing, the geometry of the ion that is not always spherical, the dispersion forces, the predominance of repulsive or attractive short-range forces, the structure maker

and structure breaker character of a particular ion, etc. Considering all of these important properties, the second virial coefficients can be interpreted as a result of the combination of all of these properties together, but the weighting of each property to the final numerical value of the virial coefficients may vary from case to case. Nevertheless, it is evident that the size of the ions may have a distinguishable importance, since all the relevant properties of the solution mentioned are to some degree linked to the dimension of the ion, e.g. hydration, ion pairing and dispersion forces.

Therefore, this study aims to find the correlations between the Pitzer equation parameters and the properties of the solution, as well as the understanding of the physical meaning of these interaction parameters. To achieve this, two cases are analyzed, in the first case considering the original Pitzer equation for the osmotic coefficient and in the second case by considering some simplifications to this equation. For the simplified case, the second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ were re-estimated using the available published data on the osmotic coefficient.

THERMODYNAMIC MODEL AND SIMPLIFICATIONS TO THE PITZER EQUATIONS

The Pitzer Model

The Pitzer model was developed in order to incorporate the effect of short-range forces between pairs of ions as well as the dependence of these forces on the ionic strength[1]. The Pitzer equation for the osmotic coefficient of single electrolytes can be expressed as follows[1]:

$$\varphi_{MX} - 1 = |z_M z_X| f^{\varphi} + 2m\left(\frac{\nu_M \nu_X}{\nu}\right) B_{MX}^{\varphi} + 2m^2\left[\frac{(\nu_M \nu_X)^{3/2}}{\nu}\right] C_{MX}^{\varphi} \quad (1)$$

where the terms f^{φ} and B_{MX}^{φ} are given as follows [8]:

$$f^{\varphi} = -A^{\varphi}\left[\frac{\sqrt{I}}{1+1.2\sqrt{I}}\right] \quad (2)$$

$$B_{MX}^{\varphi} = B_{MX}^{(0)} + B_{MX}^{(1)}\exp\left(-\alpha_1 I^{1/2}\right) + B_{MX}^{(2)}\exp\left(-\alpha_2 I^{1/2}\right) \quad (3)$$

$$I = 0.5(m_M z_M^2 + m_X z_X^2) \quad (4)$$

$$\nu = \nu_M + \nu_X \quad (5)$$

For all the electrolytes, except 2-2 electrolytes[9]:

$$\alpha_1 = 2 \text{ and } \alpha_2 = 0 \quad (6)$$

For the 2-2 electrolytes[8]:

$$\alpha_1 = 1.4 \text{ and } \alpha_2 = 12 \quad (7)$$

Simplifying the Pitzer Equation for the Osmotic Coefficient

The correlation of the Pitzer parameters with the properties of the solution is not a simple task, since this equation requires a large number of parameters ($B_{MX}^{(0)}$, $B_{MX}^{(1)}$, $B_{MX}^{(2)}$, C_{MX}^{φ}, α_1 and α_2) to be determined in order to accurately represent the behaviour of the various electrolytes in aqueous solutions. Thus, the elimination of the parameters that do not significantly impact on the precision of the Pitzer equation would be very convenient and useful, since this simplification would allow the estimation of the activity and osmotic coefficients in a much simpler way. In this context, there are three parameters that appear to be the most promising candidates to set to zero, namely the parameters $B_{MX}^{(2)}$, C_{MX}^{φ} and α_2, for the following reasons:

- The parameters $B_{MX}^{(2)}$ and α_2 are only required for 2-2 electrolytes, and they represent corrections for the anomalous behavior of these 2-2 electrolytes considering concentrations lesser than 0.1M[8]. Moreover, Pitzer[10] stated that the omission of $B_{MX}^{(2)}$ introduce systematic errors at high concentrations. Therefore, this approximation would be suitable only when intermediate molalities are the range of interest. This maximum molality to which this approximation is valid is evaluated in the discussion section.

- The effect of the third virial coefficient C_{MX}^{φ} is small and sometimes negligible according to Pitzer et al.[9], and for this reason eliminating this coefficient appears also to be a promising option to be analyzed.

For the condition C_{MX}^{φ}, $B_{MX}^{(2)}$ and α_2 all zero, eq 1 can be simplified as follows:

$$\varphi_{MX} - 1 = |z_M z_X| f^{\varphi} + 2m\left(\frac{\nu_M \nu_X}{\nu}\right)\left(B_{MX}^{(0)} + B_{MX}^{(1)} \exp\left(-\alpha_1 I^{1/2}\right)\right) \quad (8)$$

Re-estimating the Second Virial Coefficients in the Pitzer Equation for the Osmotic Coefficient

The re-estimation of the second virial coefficients of the Pitzer equations is important because it allows the estimation of the impact of eliminating the parameters $B_{MX}^{(2)}$, C_{MX}^{φ} and α_2 in the accuracy of the Pitzer model. In contrast to Pitzer et al.[9], who estimated the second virial coefficients based mainly on the experimental data of the osmotic and activity coefficients recommended by Robson and Stokes[11–15], which were obtained in the 1960s, this study also includes newer published data for the osmotic coefficients, e.g.[16,17,18,19,20,21,22,23] as well as data from some secondary sources, such as Goldberg et al.[24–27] and Hamer et al.[28]. These sources are secondary sources in the sense that their work includes tables of recommended values rather than experimental data. Particularly, these secondary sources were used because these authors performed a very rigorous selection of consistent experimental data for the osmotic coefficient from the literature, including several sources and different measurement methods, e.g. isopiestic, vapor pressure measurements, freezing point depression, etc. Then, the measurements that presented large uncertainties were eliminated, and hence only reliable values were used to generate the tables of recommended values for the osmotic coefficients.

The second virial coefficients were re-estimated by reforming eq 8 to the *Y=AX+B* format, as follows:

$$\frac{\varphi_{MX} - 1 - |z_M z_X| f^{\varphi}}{2m\left(\frac{\nu_M \nu_X}{\nu}\right)} = B_{MX}^{(0)} + B_{MX}^{(1)} \exp\left(-\alpha_1 I^{1/2}\right) \quad (9)$$

where:

$$Y = \frac{\varphi_{MX} - 1 - |z_M z_X| f^{\varphi}}{2m\left(\frac{\nu_M \nu_X}{\nu}\right)} \quad (10)$$

$$X = \exp\left(-\alpha_1 I^{1/2}\right) \quad (11)$$

$$A = B_{MX}^{(1)} \quad (12)$$

$$B = B_{MX}^{(0)} \quad (13)$$

Therefore, a plot of Y as a function of X can be used to obtain the second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$.

Correlation accuracy relative to the uncertainty of the data

The majority of the data for the osmotic coefficients used in this study were taken from Hamer et al.[28], Goldberg et al. [24–27], Robinson and Stokes[11–14] and Stokes[15]. While the data from Robinson and Stokes[11–14] and Stokes[15] was based only on the isopiestic method, Hamer et al.[28] and Goldberg et al. [24–27]also included other measurement methods to generate their tables of recommended values for the osmotic coefficients, e.g. vapor-pressure lowering, electromotive forces (emfs) of galvanic cells without liquid junctions, emfs of galvanic cells with transference, freezing point depression, etc.

In terms of these measurement methods, the isopiestic vapor pressure method is very accurate, being better than 1% at molalities above approximately 0.1 mol/kg, but this method is not very precise for more dilute solutions[29]. In this case, the freezing point depression is the most precise method, but this method has the disadvantage that additional calculations are required to convert the value found at lower temperatures to higher temperatures[30]. Regarding direct vapor pressure measurements, this method is less accurate than is the isopiestic method since these vapor pressure measurements are more sensitive to temperature variations than the isopiestic method[31]. Finally, Emf measurements can yield very

accurate results near room temperature for systems where reversible and reproducible electrodes have been developed[29].

In terms of reliability, the tables of activities and osmotic coefficients from Robinson and Stokes[11–14] and Stokes[15] are well-known and widely accepted and used in the chemical literature[32], and thus these tables represent a consistent source of information. Likewise, the tables of activities and osmotic coefficients generated by Hamer et al.[28], Goldberg et al. [24–27] are very reliable because as mentioned just above, these authors performed a very rigorous selection of consistent experimental data (including in several cases the data from Robinson and Stokes[11–14] and Stokes[15]), comprising several sources and different measurement methods, in order to finally come up with the best values for the osmotic coefficients.

Therefore, based on the high accuracy of the methods to estimate the osmotic coefficients as well as the high reliability of the sources of information used in this work, it appears that the impact of the uncertainty of the data in the correlation accuracy is low.

RESULTS

Re-estimating the Second Virial Coefficients for the Simplified Pitzer Equation

Table 1 shows the re-estimated second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ based on the assumption that C_{MX}^{φ}, $B_{MX}^{(2)}$ and α_2 are zero, as well as the standard deviations associated with the estimation of these parameters, which were calculated as follows[33]:

$$\delta = \left[\frac{\sum_i^n \left(\varphi_i^{exp} - \varphi_i^{calc}\right)^2}{n}\right]^{1/2} \qquad (14)$$

Table 1 also shows the maximum molality to which the calculations for the simplified case presented are in very good agreement with the experimental data, with less than 3% difference between the calculated osmotic coefficient and the experimental osmotic coefficient in most cases. Furthermore, Table 1 shows the coefficients $B_{MX}^{(0)}$, $B_{MX}^{(1)}$, $B_{MX}^{(2)}$ and C_{MX}^{φ}, as well as the standard deviations and

maximum molalities related to the original Pitzer equation for the osmotic coefficient, and these values were obtained from the literature[8,9,10,16,23,10,34]. Finally, Table 1 includes the classification of each ion in terms of its effects on the structure of water, which can be either by increasing the stability of the water-water interactions (structure makers or kosmotropes) or by disrupting it (structure breakers or chaotropes). Ions that have strong interactions with water can increase its structuring and, thus, they are structure-makers or kosmotropes, whereas some ions that have weak interactions with water tend to decrease its structuring and, therefore, they are structure breakers or chaotropes[35]. Normally, chaotropes are large and of low charge and kosmotropes are small and highly charged[35]. The classification adopted in this study was based on the criteria established by Marcus[36], which is a function of the Gibbs free energy accounting for the effect of the solute on the number of hydrogen bonds in which a water molecule participates.

A comparison between the estimations considering the simplified and the complete Pitzer equation can be visualized in figure 1. This figure shows that on one hand the original Pitzer equation fits more accurately the experimental data than the simplified equation, but on the other hand it shows the simplified Pitzer equation can also provide a very satisfactory match with the experimental data of osmotic coefficient. Therefore, the simplifications to the Pitzer equation appear to be acceptable and only slightly less accurate than the original Pitzer equation.

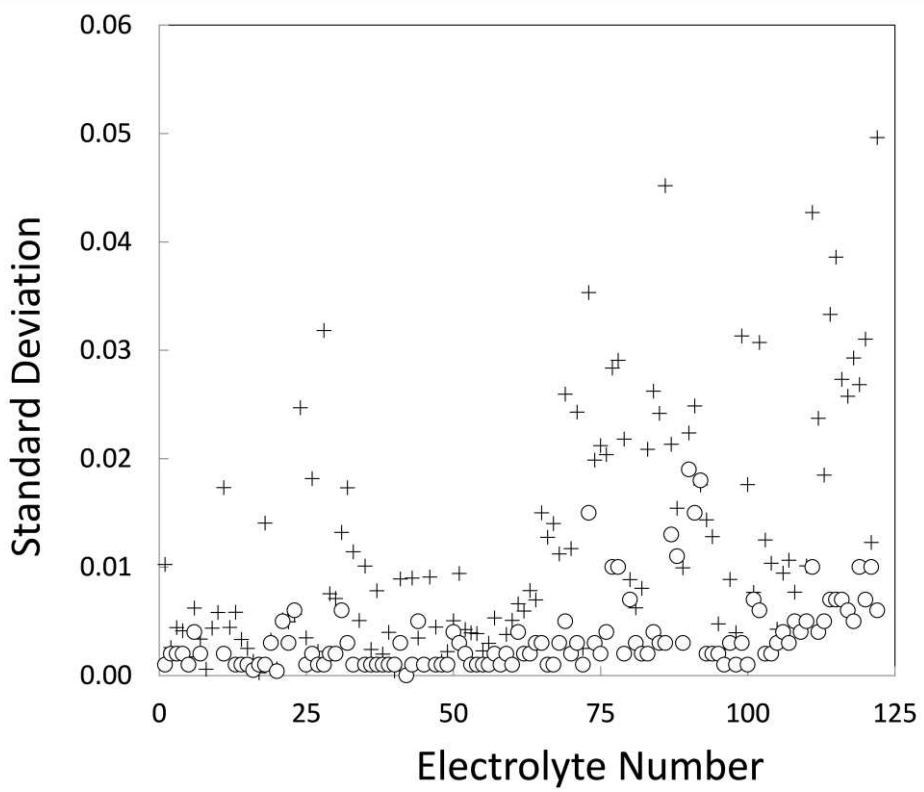

Figure 1. Standard deviation of different electrolytes calculated using the original Pitzer equation and the simplified Pitzer equation. The electrolyte number follows the order of the electrolyte appearance in Table 1 (○: original Pitzer equation, +: simplified Pitzer equation).

Table 1. Re-estimated second virial coefficients $B_{ca}^{(0)}$ and $B_{ca}^{(1)}$ for 1-1, 2-1, 3-1, 4-1, 1-2 and 2-2 electrolytes at 25 ^{o}C. The ionic radius of the ions (r_c and r_a) were taken from Marcus[5,37], except for the perchlorate ion, which was taken from Roobottom[38].

Electrolyte	Simplified Pitzer Equation , with C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 = 0$					Original Pitzer Equation, with C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 \neq 0$ (data from the literature)							r_M (Å)	r_X (Å)	Cation (kosm. or chao.)	Anion (kosm. or chao.)
	$B_{MX}^{(0)}$	$B_{MX}^{(1)}$	Standard Deviation (δ)	Reference of φ_{MX}^{exp}	Maximum molality (mol.kg^{-1})	$B_{MX}^{(0)}$	$B_{MX}^{(1)}$	$B_{MX}^{(2)}$	C_{MX}^{φ}	Standard Deviation (δ)	Reference	Maximum molality (mol.kg^{-1})				
1-1 electrolytes																
$AgNO_3$	-0.0576	-0.1489	0.010	28	5.00	-0.0856	0.0025	0.00	0.0059	0.001	9	6.00	1.15	1.79	c	c
CsBr	0.0276	0.0195	0.003	28	5.00	0.0279	0.0139	0.00	0.0000	0.002	9	5.00	1.7	1.96	c	c
CsCl	0.0307	0.0717	0.004	28	8.50	0.0300	0.0558	0.00	0.0004	0.002	9	5.00	1.7	1.81	c	c
CsF	0.1138	0.3346	0.004	28	3.50	0.1306	0.2570	0.00	-0.0043	0.002	9	3.50	1.7	1.33	c	k
CsI	0.0121	0.1124	0.002	28	3.00	0.0244	0.0262	0.00	-0.0037	0.001	9	3.00	1.7	2.2	c	c
$CsNO_2$	0.0203	0.1518	0.006	39	5.00	0.0427	0.0600	0.00	-0.0051	0.004	9	6.00	1.7	1.92	c	c
$CsNO_3$	-0.0741	-0.0794	0.003	28	1.50	-0.0758	-0.0669	0.00	0.0000	0.002	9	1.40	1.7	1.79	c	c
CsOH	0.1313	0.4219	0.001	28	1.20	0.1500	0.3000	0.00	0.0000	-	9	1.20	1.7	1.33	c	k
HBr	0.2180	0.2692	0.004	28	3.00	0.1960	0.3564	0.00	0.0083	-	9	3.00	0.3	1.96	k	c
HCl	0.1788	0.2936	0.006	28	8.00	0.1775	0.2945	0.00	0.0008	-	9	6.00	0.3	1.81	k	c
$HClO_4$	0.2133	0.0306	0.017	28	5.50	0.1747	0.2931	0.00	0.0082	0.002	9	5.50	0.3	2.25	k	c
HI	0.2373	0.4291	0.004	28	4.00	0.2362	0.3920	0.00	0.0011	-	9	3.00	0.3	2.2	k	c
HNO_3	0.0995	0.4008	0.006	28	3.50	0.1119	0.3206	0.00	0.0010	0.001	9	3.00	0.3	1.79	k	c
KBr	0.0485	0.2805	0.003	28	5.50	0.0569	0.2212	0.00	-0.0018	0.001	9	5.50	1.38	1.96	c	c
$KBrO_3$	-0.1221	0.2435	0.002	28	0.50	-0.1290	0.2565	0.00	0.0000	0.001	9	0.50	1.38	1.91	c	c
KCl	0.0451	0.2268	0.001	28	4.84	0.0484	0.2122	0.00	-0.0008	0.0005	9	4.80	1.38	1.81	c	c
$KClO_3$	-0.0946	0.2485	0.0003	28	0.70	-0.0960	0.2481	0.00	0.0000	0.001	9	0.70	1.38	2	c	c
KF	0.0842	0.2052	0.014	28	14.00	0.0809	0.2021	0.00	0.0009	0.001	9	2.00	1.38	1.33	c	k
KH_2PO_4	-0.0685	-0.1035	0.003	28	1.80	-0.0678	-0.1042	0.00	0.0000	0.003	9	1.80	1.38	2.38	c	c
$KHCO_3$	-0.0188	0.0730	0.001	16	1.00	-0.0220	0.0900	0.00	0.0000	-	16	1.00	1.38	1.85	c	c
KI	0.0573	0.3689	0.005	28	4.50	0.0746	0.2517	0.00	-0.0041	0.005	9	4.50	1.38	2.2	c	c
KNO_2	0.0087	0.0967	0.003	39	6.00	0.0151	0.0150	0.00	0.0007	0.003	9	5.00	1.38	1.92	c	c
KNO_3	-0.0592	-0.0451	0.006	28	3.50	-0.0816	0.0494	0.00	0.0066	0.006	9	3.50	1.38	1.79	c	c
KOH	0.1457	0.1971	0.025	28	14.00	0.1298	0.3200	0.00	0.0041	-	9	5.50	1.38	1.33	c	k
KSCN	0.0303	0.3086	0.003	28	5.00	0.0416	0.2302	0.00	-0.0025	0.001	9	5.00	1.38	2.13	c	c
LiBr	0.1998	0.2022	0.018	28	7.00	0.1748	0.2547	0.00	0.0053	0.002	9	2.50	0.69	1.96	k	c
$LiBrO_3$	0.0882	0.2541	0.002	20	5.00	0.0893	0.2157	0.00	0.0000	0.001	10	5.00	0.69	1.91	k	c

Table 1. continued

Electrolyte	Simplified Pitzer Equation , with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 = 0$					Original Pitzer Equation, with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 \neq 0$ (data from the literature)							r_M (Å)	r_X (Å)	Cation (kosm. or chao.)	Anion (kosm. or chao.)
	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	Standard Deviation (δ)	Reference of φ^{exp}_{MX}	Maximum molality (mol.kg^{-1})	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	$B^{(2)}_{MX}$	C^{φ}_{MX}	Standard Deviation (δ)	Reference	Maximum molality (mol.kg^{-1})				
LiCl	0.1667	0.2465	0.032	28	13.00	0.1494	0.3074	0.00	0.0036	0.001	9	6.00	0.69	1.81	k	c
$LiClO_3$	0.1526	0.3131	0.008	20	4.20	0.1705	0.2294	0.00	-0.00524	0.002	10	4.20	0.69	2	k	c
$LiClO_4$	0.1950	0.4307	0.007	28	4.50	0.1973	0.3996	0.00	0.0008	0.002	9	3.50	0.69	2.25	k	c
LiI	0.1990	0.4795	0.013	28	3.00	0.2104	0.3730	0.00	0.0000	0.006	9	1.40	0.69	2.2	k	c
$LiNO_2$	0.1075	0.3906	0.017	39	6.00	0.1336	0.3250	0.00	-0.0053	0.003	9	6.00	0.69	1.92	k	c
$LiNO_3$	0.1153	0.4488	0.011	28	5.50	0.1420	0.2780	0.00	-0.0055	0.001	9	6.00	0.69	1.79	k	c
LiOH	0.0457	-0.1257	0.005	28	3.00	0.0150	0.1400	0.00	0.0000	-	9	4.00	0.69	1.33	k	k
NaBr	0.1005	0.2720	0.010	28	9.00	0.0973	0.2791	0.00	0.0012	0.001	9	4.00	1.02	1.96	c	c
$NaBrO_3$	-0.0046	0.1201	0.006	28	2.50	-0.0205	0.1910	0.00	0.0059	0.001	9	2.50	1.02	1.91	c	c
NaCl	0.0798	0.2677	0.008	28	6.14	0.0765	0.2664	0.00	0.0013	0.001	9	6.00	1.02	1.81	c	c
$NaClO_3$	0.0257	0.2373	0.002	28	3.50	0.0249	0.2455	0.00	0.0004	0.001	9	3.50	1.02	2	c	c
$NaClO_4$	0.0505	0.2952	0.004	28	6.00	0.0554	0.2755	0.00	-0.0012	0.001	9	6.00	1.02	2.25	c	c
NaF	0.0197	0.2237	0.0004	28	0.983	0.0215	0.2107	0.00	0.0000	0.001	9	1.00	1.02	1.33	c	k
NaH_2PO_4	-0.0246	-0.1126	0.009	28	3.50	-0.0533	0.0396	0.00	0.0080	0.003	9	6.00	1.02	2.38	c	c
$NaHCO_3$	0.0290	0.0380	0.000	34	1.00	0.0277	0.0411	0.00	0.0000	-	34	1.00	1.02	1.85	c	c
NaI	0.1259	0.3038	0.009	28	11.00	0.1195	0.3439	0.00	0.0018	0.001	9	3.50	1.02	2.2	c	c
$NaNO_2$	0.0478	0.1776	0.003	39	3.00	0.0641	0.1015	0.00	-0.0049	0.005	9	5.00	1.02	1.92	c	c
$NaNO_3$	0.0036	0.1978	0.001	28	6.00	0.0068	0.1783	0.00	-0.0007	0.001	9	6.00	1.02	1.79	c	c
NaOH	0.1080	0.1927	0.009	28	6.00	0.0864	0.2530	0.00	0.0044	-	9	6.00	1.02	1.33	c	k
NaSCN	0.0952	0.3609	0.004	28	7.00	0.1005	0.3582	0.00	-0.00303	0.001	9	4.00	1.02	2.13	c	c
NH_4Br	0.0505	0.2350	0.001	21	2.50	0.0624	0.1947	0.00	-0.0044	0.001	9	2.50	1.48	1.96	c	c
NH_4Cl	0.0399	0.2661	0.002	28	4.00	0.0522	0.1918	0.00	-0.0030	0.001	9	6.00	1.48	1.81	c	c
NH_4ClO_4	-0.0064	-0.0648	0.005	40	2.10	-0.0103	-0.0194	0.00	0.0000	0.004	10	2.00	1.48	2.25	c	c
$NH_4H_2PO_4$	-0.0455	-0.5631	0.009	41	3.50	-0.0704	-0.4156	0.00	0.0067	0.003	10	3.50	1.48	2.38	c	c
NH_4I	0.0463	0.3583	0.004	22	4.00	0.0570	0.3157	0.00	-0.0031	0.002	10	7.50	1.48	2.2	c	c
NH_4NO_3	-0.0140	0.0895	0.004	28	11.00	-0.0154	0.1120	0.00	0.0000	0.001	10	6.00	1.48	1.79	c	c
NH_4SCN	0.0174	0.3320	0.004	23	5.00	0.0245	0.2615	0.00	-0.0013	0.001	23	8.00	1.48	2.13	c	c
RbBr	0.0331	0.2057	0.002	28	5.00	0.0396	0.1530	0.00	-0.0014	0.001	9	5.00	1.49	1.96	c	c
RbCl	0.0382	0.1827	0.003	28	6.00	0.0441	0.1483	0.00	-0.0010	0.001	9	5.00	1.49	1.81	c	c
RbF	0.0834	0.4198	0.005	28	2.50	0.1141	0.2842	0.00	-0.0105	0.002	9	3.50	1.49	1.33	c	k
RbI	0.0346	0.1786	0.002	28	5.00	0.0397	0.1330	0.00	-0.0011	0.001	9	5.00	1.49	2.2	c	c
$RbNO_2$	0.0054	0.0557	0.002	39	6.00	0.0269	-0.1553	0.00	-0.0037	0.002	9	5.00	1.49	1.92	c	c
$RbNO_3$	-0.0629	-0.0909	0.005	28	3.00	-0.0789	-0.0172	0.00	0.0053	0.001	9	4.50	1.49	1.79	c	c

Table 1. continued

Electrolyte	Simplified Pitzer Equation , with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 = 0$					Original Pitzer Equation, with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 \neq 0$ (data from the literature)							r_M (Å)	r_X (Å)	Cation (kosm. or chao.)	Anion (kosm. or chao.)
	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	Standard Deviation (δ)	Reference of φ^{exp}_{MX}	Maximum molality (mol.kg^{-1})	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	$B^{(2)}_{MX}$	C^{φ}_{MX}	Standard Deviation (δ)	Reference	Maximum molality (mol.kg^{-1})				
1-2 electrolytes																
$(NH_4)_2SO_4$	0.0349	0.6801	0.007	17	5.00	0.0409	0.6585	0.00	-0.0012	0.004	9	5.50	1.48	2.4	c	c
K_2SO_4	0.0481	0.8619	0.006	17	0.80	0.0500	0.7793	0.00	0.0000	0.002	9	0.70	1.38	2.4	c	c
Li_2SO_4	0.1231	1.4417	0.008	17	3.00	0.1363	1.2705	0.00	-0.0040	0.002	9	3.00	0.69	2.4	k	c
Na_2SO_4	0.0366	0.9084	0.007	17	3.00	0.0196	1.1130	0.00	0.0050	0.003	9	4.00	1.02	2.4	c	c
2-1 electrolytes																
$Ba(ClO_4)_2$	0.2960	1.8167	0.015	12	1.60	0.3614	1.5758	0.00	-0.0313	0.003	9	2.00	1.36	2.25	k	c
$BaBr_2$	0.2716	2.0187	0.013	26	2.30	0.3146	1.5698	0.00	-0.0160	0.001	9	2.00	1.36	1.96	k	c
$BaCl_2$	0.2246	1.7213	0.014	26	1.79	0.2628	1.4963	0.00	-0.0194	0.001	9	1.79	1.36	1.81	k	c
BaI_2	0.3861	1.9611	0.011	26	2.00	0.4219	1.6868	0.00	-0.0174	0.003	9	1.80	1.36	2.2	k	c
$Ca(ClO_4)_2$	0.4273	1.9530	0.029	12	5.00	0.4511	1.7565	0.00	-0.0050	0.005	9	2.00	1	2.25	k	c
$CaBr_2$	0.3795	1.7029	0.012	26	3.25	0.3816	1.6133	0.00	-0.0026	0.002	9	2.00	1	1.96	k	c
$CaCl_2$	0.3118	1.7044	0.024	26	6.00	0.3159	1.6140	0.00	-0.0003	0.003	9	2.50	1	1.81	k	c
CaI_2	0.4357	1.8225	0.002	26	1.90	0.4379	1.8068	0.00	-0.0008	0.001	9	2.00	1	2.2	k	c
$Co(ClO_4)_2$	0.5493	1.6522	0.035	27	3.50	0.5303	1.9643	0.00	0.0076	0.015	this study	3.50	0.75	2.25	k	c
$Co(NO_3)_2$	0.2815	1.7480	0.020	27	3.25	0.3119	1.6905	0.00	-0.0076	0.003	9	5.50	0.75	1.79	k	c
$CoBr_2$	0.3986	1.9156	0.021	27	3.75	0.4270	1.6598	0.00	-0.0007	0.002	9	2.00	0.75	1.96	k	c
$CoCl_2$	0.3113	1.7699	0.020	27	3.00	0.3643	1.4753	0.00	-0.0152	0.004	9	3.00	0.75	1.81	k	c
CoI_2	0.5108	1.7666	0.028	27	4.25	0.5213	1.6725	0.00	-0.0047	0.010	9	2.00	0.75	2.2	k	c
$Cu(ClO_4)_2$	0.5138	1.8475	0.029	24	3.50	0.5076	1.8749	0.00	0.0044	0.010	this study	3.50	0.73	2.25	k	c
$Cu(NO_3)_2$	0.2477	1.8031	0.022	24	3.50	0.3168	1.4303	0.00	-0.0219	0.002	9	2.00	0.73	1.79	k	c
$CuBr_2$	0.3408	1.9977	0.009	24	1.25	0.3616	1.8575	0.00	-0.00902	0.007	this study	1.25	0.73	1.96	k	c
$CuCl_2$	0.2513	1.5432	0.006	24	1.00	0.3080	1.3763	0.00	-0.0404	0.003	9	2.00	0.73	1.81	k	c
$FeCl_2$	0.3155	1.7278	0.008	27	2.00	0.3359	1.5323	0.00	-0.0086	0.002	9	2.00	0.78	1.81	k	c
$Mg(ClO_4)_2$	0.5230	1.9144	0.021	15	3.00	0.4961	2.0085	0.00	0.0096	0.002	9	2.00	0.72	2.25	k	c
$MgBr_2$	0.4470	1.6462	0.026	26	5.50	0.4327	1.7528	0.00	0.0031	0.004	9	5.00	0.72	1.96	k	c
$MgCl_2$	0.3765	1.5968	0.024	26	4.50	0.3524	1.6815	0.00	0.0052	0.003	9	4.50	0.72	1.81	k	c
MgI_2	0.5267	1.4252	0.045	26	5.00	0.4902	1.8041	0.00	0.0079	0.003	9	5.00	0.72	2.2	k	c
$Mn(ClO_4)_2$	0.5518	1.7120	0.021	24	3.50	0.5316	2.1996	0.00	0.0061	0.013	this study	3.50	0.83	2.25	k	c
$MnBr_2$	0.3747	2.0363	0.015	24	2.50	0.3971	1.7686	0.00	-0.0070	0.011	this study	2.50	0.83	1.96	k	c
$MnCl_2$	0.2919	1.6033	0.010	24	1.50	0.3272	1.5503	0.00	-0.0205	0.003	9	2.50	0.83	1.81	k	c
$Ni(ClO_4)_2$	0.5453	1.7027	0.022	27	2.75	0.5273	1.9156	0.00	0.0089	0.019	this study	3.50	0.69	2.25	k	c
$Ni(NO_3)_2$	0.2970	2.1632	0.025	42	4.00	0.3037	2.1307	0.00	-0.0032	0.015	this study	5.00	0.69	1.79	k	c
$NiBr_2$	0.4181	1.7725	0.018	27	4.25	0.4181	1.7725	0.00	0.0000	0.018	this study	4.25	0.69	1.96	k	c

Table 1. continued

Electrolyte	Simplified Pitzer Equation , with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 = 0$					Original Pitzer Equation, with $C^{\varphi}_{MX}, B^{(2)}_{MX}$ and $\alpha_2 \neq 0$ (data from the literature)							r_M (Å)	r_X (Å)	Cation (kosm. or chao.)	Anion (kosm. or chao.)
	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	Standard Deviation (δ)	Reference of φ^{exp}_{MX}	Maximum molality (mol.kg^{-1})	$B^{(0)}_{MX}$	$B^{(1)}_{MX}$	$B^{(2)}_{MX}$	C^{φ}_{MX}	Standard Deviation (δ)	Reference	Maximum molality (mol.kg^{-1})				
$NiCl_2$	0.3306	1.6622	0.014	27	3.25	0.3479	1.5810	0.00	-0.0037	0.002	9	2.50	0.69	1.81	k	c
$Sr(ClO_4)_2$	0.3879	1.8158	0.013	12	2.50	0.4269	1.5668	0.00	-0.0131	0.002	9	2.50	1.13	2.25	k	c
$Sr(NO_3)_2$	0.0992	1.6050	0.005	15	1.00	0.1346	1.3800	0.00	-0.0199	0.002	9	2.00	1.13	1.79	k	c
$SrBr_2$	0.3321	1.7626	0.002	26	2.00	0.3311	1.7115	0.00	0.0012	0.001	9	2.00	1.13	1.96	k	c
$SrCl_2$	0.2823	1.5771	0.009	19	3.80	0.2858	1.6673	0.00	-0.0013	0.003	9	4.00	1.13	1.81	k	c
SrI_2	0.4043	1.9170	0.004	26	2.00	0.4013	1.8600	0.00	0.0027	0.001	9	2.00	1.13	2.2	k	c
$Zn(ClO_4)_2$	0.5444	1.6016	0.031	25	3.25	0.5060	1.7970	0.00	0.0113	0.003	9	2.00	0.75	2.25	k	c
$Zn(NO_3)_2$	0.2990	1.9419	0.018	25	3.00	0.3481	1.6913	0.00	-0.0157	0.001	9	2.00	0.75	1.79	k	c
$ZnBr_2$	0.3378	2.0164	0.008	25	0.80	0.4660	1.6343	0.00	-0.1079	0.007	9	1.60	0.75	1.96	k	c
$ZnCl_2$	0.0959	2.2348	0.031	25	13.00	0.2602	1.6425	0.00	-0.0880	0.006	9	1.20	0.75	1.81	k	c
ZnI_2	0.4536	2.1785	0.013	25	1.00	0.4821	1.9455	0.00	-0.0143	0.002	9	0.80	0.75	2.2	k	c
2-2 electrolytes																
$CdSO_4$	0.2358	2.3479	0.010	13	3.50	0.2053	2.6170	-48.07	0.0114	0.002	8	3.50	0.95	2.4	k	c
$CuSO_4$	0.2347	2.4875	0.004	17	1.40	0.2358	2.4850	-47.35	-0.0012	0.003	8	1.40	0.73	2.4	k	c
$MgSO_4$	0.2842	2.8749	0.009	17	2.50	0.2210	3.3430	-37.23	0.0250	0.004	8	3.00	0.72	2.4	k	c
$MnSO_4$	0.2414	2.6899	0.011	17	2.50	0.2010	2.9800	0.00	0.0182	0.003	8	4.00	0.83	2.4	k	c
$NiSO_4$	0.2268	2.6082	0.008	17	1.60	0.1702	2.9070	-40.06	0.0366	0.005	8	2.50	0.69	2.4	k	c
$ZnSO_4$	0.2565	2.4986	0.005	17	2.00	0.1949	2.8830	-32.81	0.0290	0.004	8	3.50	0.75	2.4	k	c
3-1 electrolytes																
$AlCl_3$	0.7047	5.7690	0.010	13	1.80	0.6993	5.8447	0.00	0.0027	0.005	9	1.60	0.53	1.81	k	c
$CeCl_3$	0.5562	5.5669	0.043	13	1.80	0.6125	5.4847	0.00	-0.0311	0.010	9	1.80	1.01	1.81	k	c
$Cr(NO_3)_3$	0.6136	5.6223	0.024	13	1.20	0.7040	5.1847	0.00	-0.0590	0.004	9	1.40	0.62	1.79	k	c
$CrCl_3$	0.6661	5.7568	0.018	13	1.20	0.7364	5.2553	0.00	-0.0451	0.005	9	1.20	0.62	1.81	k	c
$EuCl_3$	0.5742	5.7733	0.033	13	1.80	0.6247	5.5900	0.00	-0.0264	0.007	9	1.80	0.95	1.81	k	c
$LaCl_3$	0.5495	5.7110	0.039	13	1.80	0.6105	5.4873	0.00	-0.0320	0.007	9	1.80	1.05	1.81	k	c
$NdCl_3$	0.5592	5.5343	0.027	13	1.60	0.6117	5.4027	0.00	-0.0284	0.007	9	2.00	0.98	1.81	k	c
$PrCl_3$	0.5497	5.6079	0.026	13	1.60	0.6020	5.4540	0.00	-0.0280	0.006	9	2.00	1	1.81	k	c
$ScCl_3$	0.6426	5.5572	0.029	13	1.60	0.7000	5.3187	0.00	-0.0323	0.005	9	1.80	0.75	1.81	k	c
$SmCl_3$	0.5697	5.6701	0.027	13	1.60	0.6220	5.5153	0.00	-0.0280	0.010	9	1.80	0.96	1.81	k	c
YCl_3	0.5989	5.5042	0.031	13	1.80	0.6399	5.4440	0.00	-0.0226	0.007	9	1.80	0.9	1.81	k	c
4-1 electrolytes																
Th(NO3)4	0.8148	12.0772	0.012	11	0.40	0.9663	11.3875	0.00	-0.1846	0.010	9	1.00	0.94	1.81	k	c
ThCl4	0.9008	14.7995	0.050	13	1.00	1.0138	13.3313	0.00	-0.1034	0.006	9	1.00	0.94	1.79	k	c

The trends between the second Virial coefficients in the Pitzer equations and the properties of the solution

On considering the simplifications applied to the Pitzer equation for the osmotic coefficient, only two parameters need to be correlated with the properties of the solution, namely $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$. However, before starting these correlations, it is important to identify which electrolytes are likely to form ion pairs or complexes. This is because the second virial coefficients were estimated assuming that ions are completely dissociated (or slightly associated) in the aqueous media and this assumption is not valid for some of the electrolytes listed in Table 1.

According to Marcus et al.[43], the difference between ion pairs and complexes is that the ion pairs are held by long-range, non-directional electrostatic forces, whereas the complexes are formed by short-range, spatially directed covalent interactions. On the other hand, Marcus et al.[43] state that this difference is largely semantic because there is no method for determining the origins of the attractive forces that hold the species together and thus complexes and ion pairs should be seen as essentially indistinguishable. Therefore, no effort will be employed in order to rigorously group species in ion pairs or complexes.

The following electrolytes from Table 1 were identified in the literature as electrolytes that could form ion pairs or complexes [44,45]:

- 1-1 electrolytes: According to Collins[44], combinations of kosmotrope cations with kosmotrope anions as well as chaotrope cations with chaotrope anions tend to lead to the formation of ion pairs, because the association in this case is energetically favorable. Therefore, only combinations of chaotrope-kosmotrope and kosmotrope-chaotrope will be considered for the 1-1 electrolytes, with the exception of NaF, which forms ion pairs[45].
- All the 1-2 electrolytes listed in Table 1[45].
- The following 2-1 electrolytes[45]: $Co(NO_3)_2$, $Cu(NO_3)_2$, $CoCl_2$, $CuBr_2$, $CuCl_2$, $MnCl_2$, $Ni(NO_3)_2$, $NiBr_2$, $NiCl_2$, $Sr(NO_3)_2$, $Zn(NO_3)_2$ $ZnBr_2$, $ZnCl_2$, ZnI_2.

- All the 2-2 electrolytes listed in Table I tend to form complexes[45,8]. However, Pitzer et al.[8] stated that these 2-2 electrolytes could be well represented without the assumption of association equilibrium, and for this reason these electrolytes will be retained in the analysis.
- 3-1 electrolytes: it was not identified any electrolyte forming ion pairs/complexes.
- 4-1 electrolytes: $Th(NO_3)_4$[46].

After eliminating the electrolytes that are more likely to form ion pairs or complexes, now the attention can be focused on the trends between the second virial coefficients and the properties of the solution. The properties of the solution investigated were: z_M, z_X, r_M, r_X, r_{hM} and r_{hX}. Several trials were performed to fit the second virial coefficients of the Pitzer equation with these properties and finally it was found that both $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ have strong correlations with z_M, z_X and $|r_M\text{-}r_X|$, as illustrated in figures 2, 3, 4 and 5. Figures 2 and 3 contain the relationships for $B_{MX}^{(0)}$ considering the simplified Pitzer equation (C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 = 0$) and the original Pitzer equation (C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 \neq 0$) respectively, whereas figures 4 and 5 contain the relationships for $B_{MX}^{(1)}$ considering these two same cases, respectively. As it can be seen in figures 2 and 3, a very good correlation among the $B_{MX}^{(0)}$, the ionic charge and the ionic radius was found, and this is reflected in the high coefficients of determination achieved (R^2=0.96 for the simplified Pitzer equation, R^2=0.97 for the original Pitzer equation). Likewise, in figures 4 and 5, it is possible to observe that the parameter $B_{MX}^{(1)}$ also has a very strong correlation (R^2=0.99 for both the simplified and the original Pitzer equation) with the ionic charge and the ionic radius, but with a quadratic correlation rather than a linear one. Furthermore, it can be observed that there are no significant differences between the curves considering the simplified and the original Pitzer equation and this means that the elimination of the parameters $B_{MX}^{(2)}$, C_{MX}^{φ}, α_2 did not cause significant changes in the values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$.

To summarize, the second virial coefficient $B_{MX}^{(0)}$ for the simplified Pitzer equation and for the original Pitzer equation can be respectively expressed as follows:

$$B_{MX}^{(0)} = 0.04432\, z_M^{1.62} z_X^{-1.35} |r_M - 1.5 r_X|^{1.2} + 0.05758 \qquad (15)$$

$$B_{MX}^{(0)} = 0.04850\, z_M^{1.62} z_X^{-1.35} |r_M - 1.5 r_X|^{1.2} + 0.03898 \quad (16)$$

Also, the second virial coefficient $B_{MX}^{(1)}$ for the simplified Pitzer equation and for the complete Pitzer equation can be respectively expressed as follows:

$$B_{MX}^{(1)} = 0.01001 z_X^{-0.4} \left(z_M^2 z_X^{0.6} (1 + |r_M - 1.2 r_X|^{0.2}) \right)^2 + 0.12017 z_M^2 z_X^{0.2} (1 + |r_M - 1.2 r_X|^{0.2}) + 0.05226 z_X^{-0.4} \quad (17)$$

$$B_{MX}^{(1)} = 0.00738 z_X^{-0.4} \left(z_M^2 z_X^{0.6} (1 + |r_M - 1.2 r_X|^{0.2}) \right)^2 + 0.16800 z_M^2 z_X^{0.2} (1 + |r_M - 1.2 r_X|^{0.2}) - 0.09320 z_X^{-0.4} \quad (18)$$

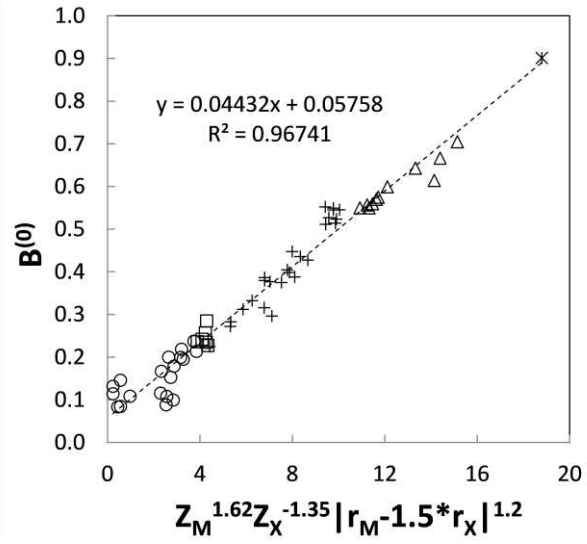

Figure 2. Relationship between the second virial coefficient $B_{MX}^{(0)}$, the ionic charge and the absolute difference between the ionic radius of the cation and the anion for the simplified Pitzer equation, i.e. $C_{MX}^{\varphi}, B_{MX}^{(2)}$ and $\alpha_2 = 0$ (○: 1-1 electrolytes, +: 2-1 electrolytes, □: 2-2 electrolytes, △: 3-1 electrolytes, ∗: 4-1 electrolytes, dashed line: linear regression).

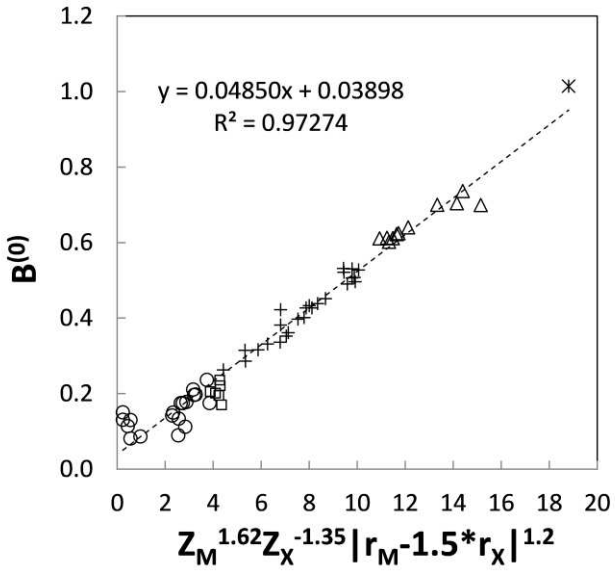

Figure 3. Relationship between the second virial coefficient $B_{MX}^{(0)}$, the ionic charge and the absolute difference between the ionic radius of the cation and the anion for the original Pitzer equation, i.e. $C_{MX}^{\varphi}, B_{MX}^{(2)}$ and $\alpha_2 \neq 0$ (○: 1-1 electrolytes, +: 2-1 electrolytes, □: 2-2 electrolytes, △: 3-1 electrolytes, ∗: 4-1 electrolytes, dashed line: linear regression).

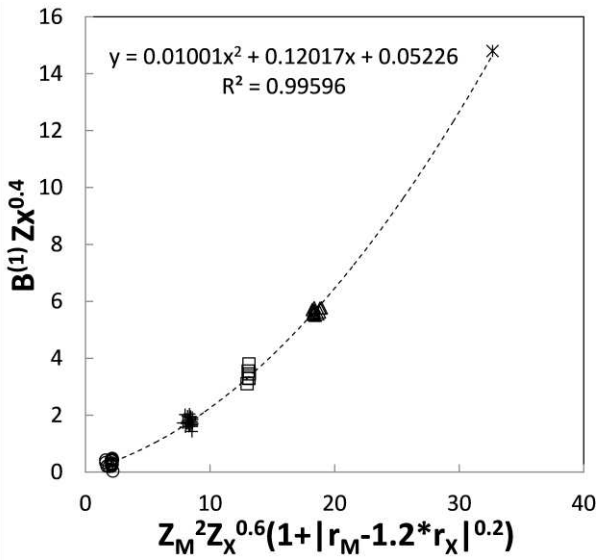

Figure 4. Relationship between the second virial coefficient $B_{MX}^{(1)}$, ionic charge and the absolute difference between the ionic radius of the cation and the anion for the simplified Pitzer equation, i.e. $C_{MX}^{\varphi}, B_{MX}^{(2)}$ and $\alpha_2 = 0$ (○: 1-1 electrolytes, +: 2-1 electrolytes, □: 2-2 electrolytes, △: 3-1 electrolytes, ∗: 4-1 electrolytes, dashed line: polynomial regression).

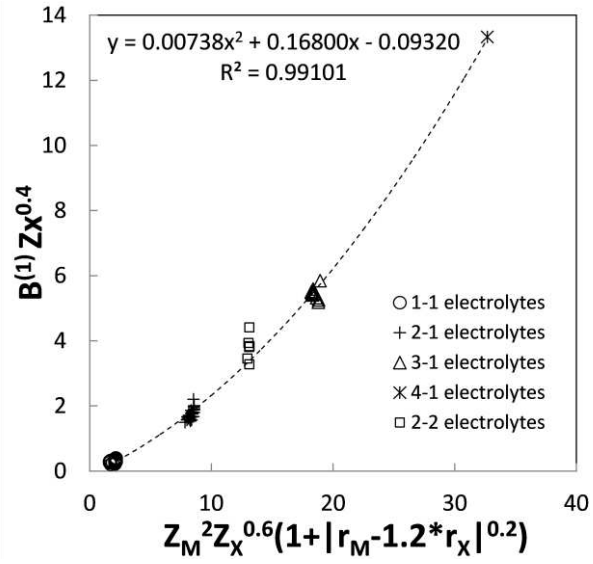

Figure 5. Relationship between the second virial coefficient $B_{MX}^{(1)}$, ionic charge and the absolute difference between the ionic radius of the cation and the anion for the original Pitzer equation, i.e. C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 \neq 0$ (○: 1-1 electrolytes, +: 2-1 electrolytes, □: 2-2 electrolytes, △: 3-1 electrolytes, ∗: 4-1 electrolytes, dashed line: polynomial regression).

DISCUSSION

As mentioned before in the introduction section, the Pitzer equation coefficients can be interpreted as being the combination of several properties of the solution with different weighting factors. As shown before in the results section, the Pitzer equation can be satisfactorily simplified to an equation containing only the two second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$, and these coefficients were shown to be strongly dependent on the ionic radii of the species as well as the ionic charge, see figures 2, 3, 4 and 5. In addition to this, some other important aspects related to the properties of the aqueous solution are discussed below.

Comparison plots involving the original Pitzer model, the simplified Pitzer model, the correlation equations and the experimental data

1-1 electrolytes

The comparison plots related to the 1-1 electrolytes can be visualized in figures 6 and 7. As it can be seen in these figures, all electrolytes analyzed can be well described by both the simplified Pitzer model

and the original Pitzer model, but the original Pitzer model is slightly more accurate in general. Likewise, the correlating equations (eqs 15 and 17) predict very well the behavior of the chlorides, bromides, iodides and perchlorates, but these equations generally fail to predict the properties of bromates, nitrates, nitrites, hydroxides and fluorides, and this is probably due to the high tendency of these ions to form ion pairs or complexes.

1-2 electrolytes

The comparison plots related to the 1-2 electrolytes can be visualized in figure 8. Since these electrolytes form ion pairs[45], hence only the simplified Pitzer equation and the original Pitzer equation were included in comparison with the experimental data. This figure shows that all electrolytes analyzed can be well described by both the simplified Pitzer model and the original Pitzer model, but the original Pitzer model is slightly more precise in general.

2-1 electrolytes

The comparison plots related to the 2-1 electrolytes can be visualized in figure 9. Since the nitrates, nitrites, bromates were excluded from the analysis due to the formation of ion pairs (please refer to the results section to more details), then only chlorides, bromides, iodides and perchlorates were used to estimate the correlating equations (eqs 15 and 17). As stated previously in the analysis of 1-1 electrolytes, the chlorides, bromides, iodides and perchlorates can be well predicted not only by the simplified Pitzer equation and the original Pitzer equation, but also by the correlating equations (eqs 15 and 17). It is possible to confirm this good agreement between the three equations and the experimental data in figure 9.

2-2 electrolytes

The comparison plots related to the 2-2 electrolytes can be visualized in figure 10. This figure shows that the original Pitzer model predicts well the behavior of the electrolytes over the entire range of concentration, in contrast to the simplified Pitzer model and the correlating equations (eqs 15 and 17), which are able to predict the behavior of the electrolytes only up to a molality of 2 mol/kg. In fact, the superiority of the original Pitzer model is not unexpected, because this model contains more parameters

than the other two models to account for different interactions, e.g. ion-pairing. Moreover, the fact that the simplified equation was not able to explain molalities above 2 mol/kg can be attributed to the omission of the term $B_{MX}^{(2)}$, which according to Pitzer[10] introduces a systematic error in the calculated values at high concentrations.

It is also possible to see in figure 10 that in some cases the correlating equations (eqs 15 and 17) did not produce results as accurate as the simplified Pitzer model and the original Pitzer model, e.g. $MgSO_4$ and $NiSO_4$, but the error did not exceed 10% in any molality analyzed. Nevertheless, in most cases the correlating equations (eqs 15 and 17) agreed well with the experimental data.

3-1 electrolytes

The comparison plots related to the 3-1 electrolytes can be visualized in figure 11. This figure shows that the original Pitzer model is slightly more accurate than the simplified Pitzer model and the correlating equations (eqs 15 and 17). Moreover, this figure shows systematic errors at molalities above 1 mol/kg for both the simplified Pitzer equation and the correlating equations (eqs 15 and 17), and these errors can be attributed to the omission of the term C_{MX}^{φ} in these equations, which accounts for interactions between triplets of ions. Nevertheless, the only case that the correlating equations (eqs 15 and 17) were not able to fit the experimental data within a 6% precision was relative to the $Cr(NO_3)_3$, and this is expected since nitrates normally tend towards the ion-pair formation.

4-1 electrolytes

The comparison plot related to the 4-1 electrolytes can be visualized in figure 12. This figure shows that neither the original Pitzer model nor the simplified Pitzer model and the correlating equations (eqs 15 and 17) fit very well the experimental data. In fact, more 4-1 electrolytes would need to be investigated in order to come to any conclusion regarding the accuracy of the models analyzed. However, information about 4-1 electrolytes is limited in the literature.

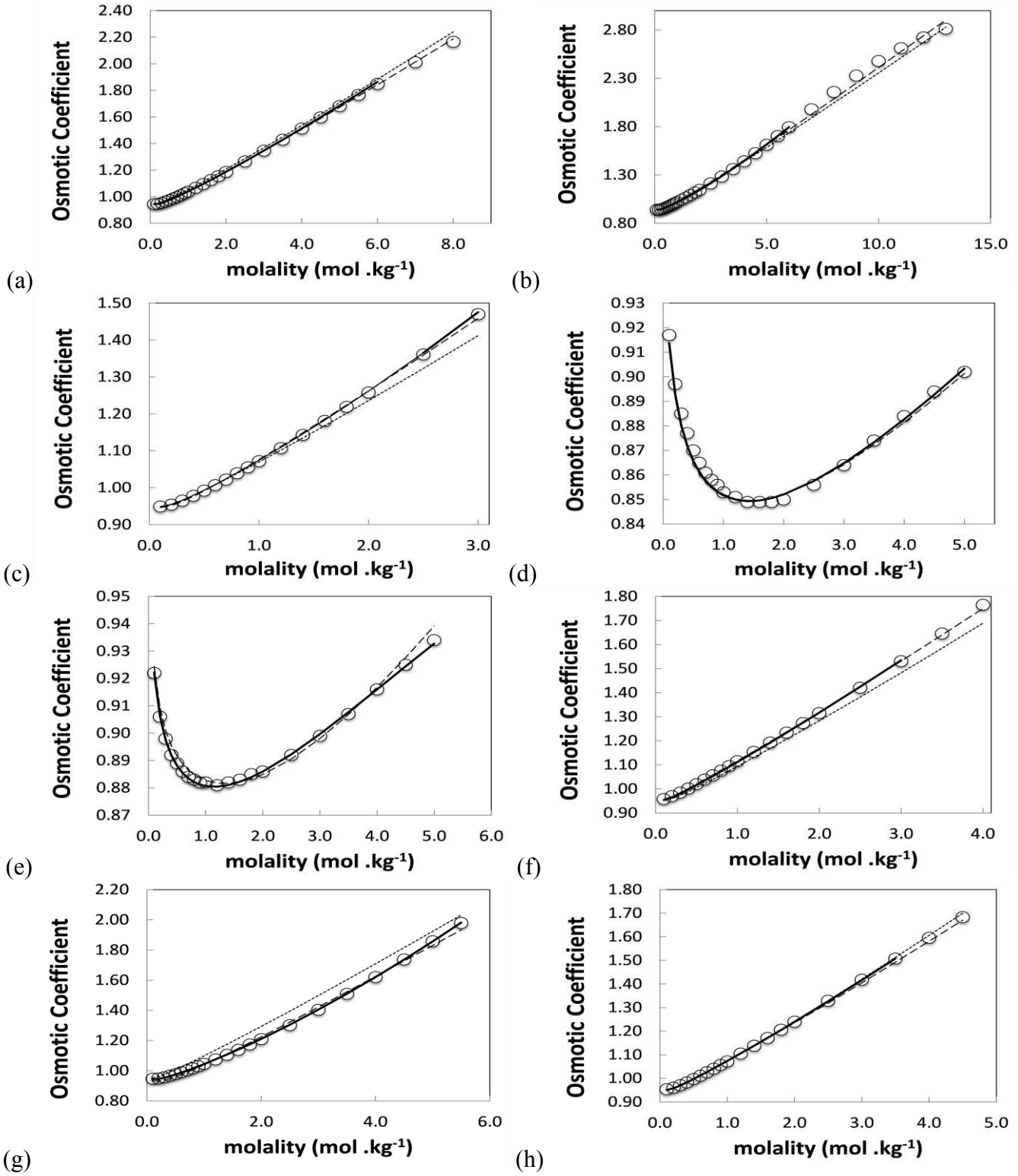

Figure 6. Comparison plots of 1-1 electrolytes involving chlorides, bromides, iodides and perchlorates: (a) HCl, (b) LiCl, (c) HBr, (d) CsBr, (e) RbBr, (f) HI, (g) $HClO_4$, (h) $LiClO_4$ (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

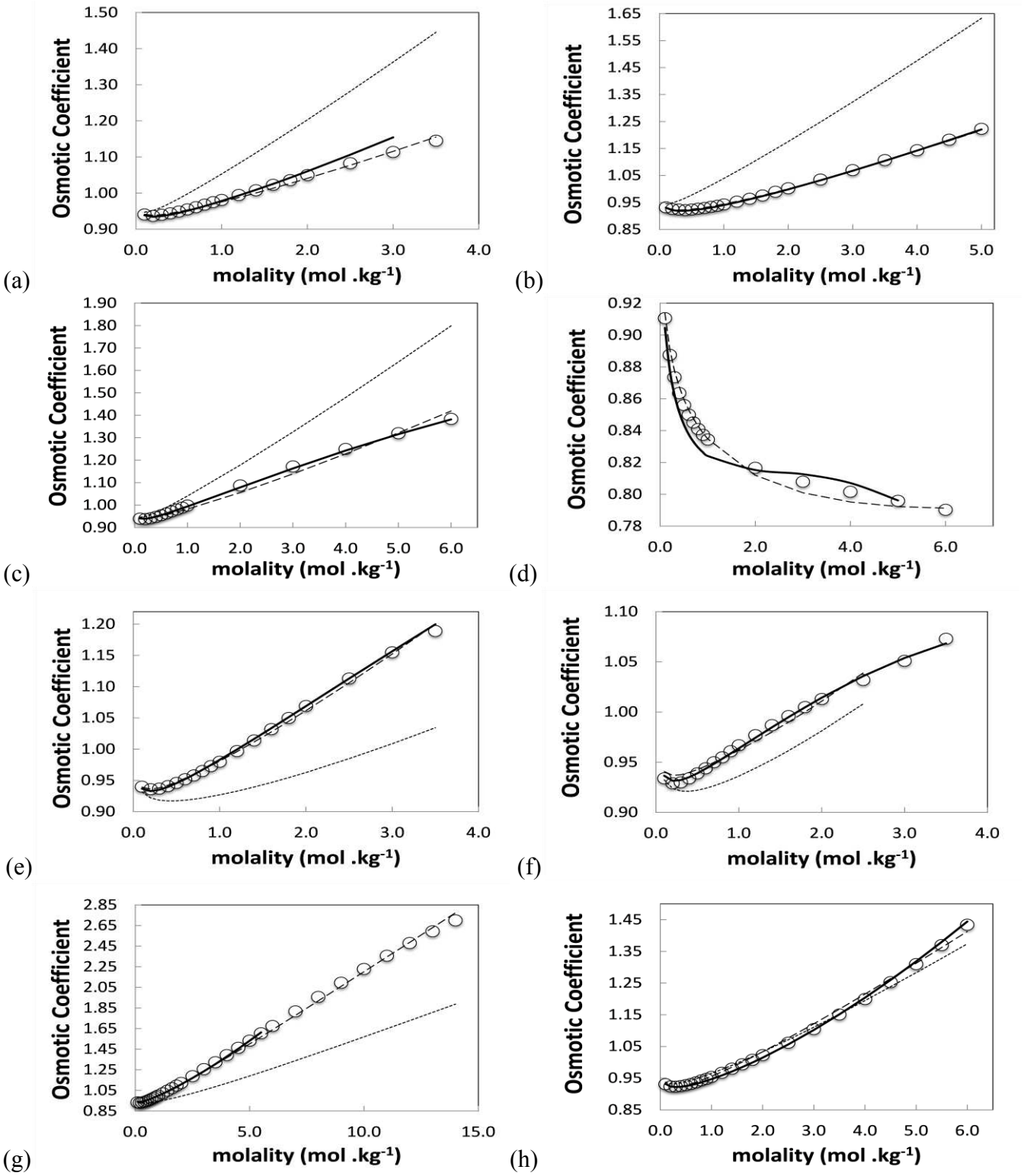

Figure 7. Comparison plots of 1-1 electrolytes involving nitrates, nitrites, bromates, hydroxides and fluorides: (a) HNO_3, (b) $LiBrO_3$, (c) $LiNO_2$, (d) $RbNO_2$, (e) CsF, (f) RbF, (g) KOH, (h) NaOH (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

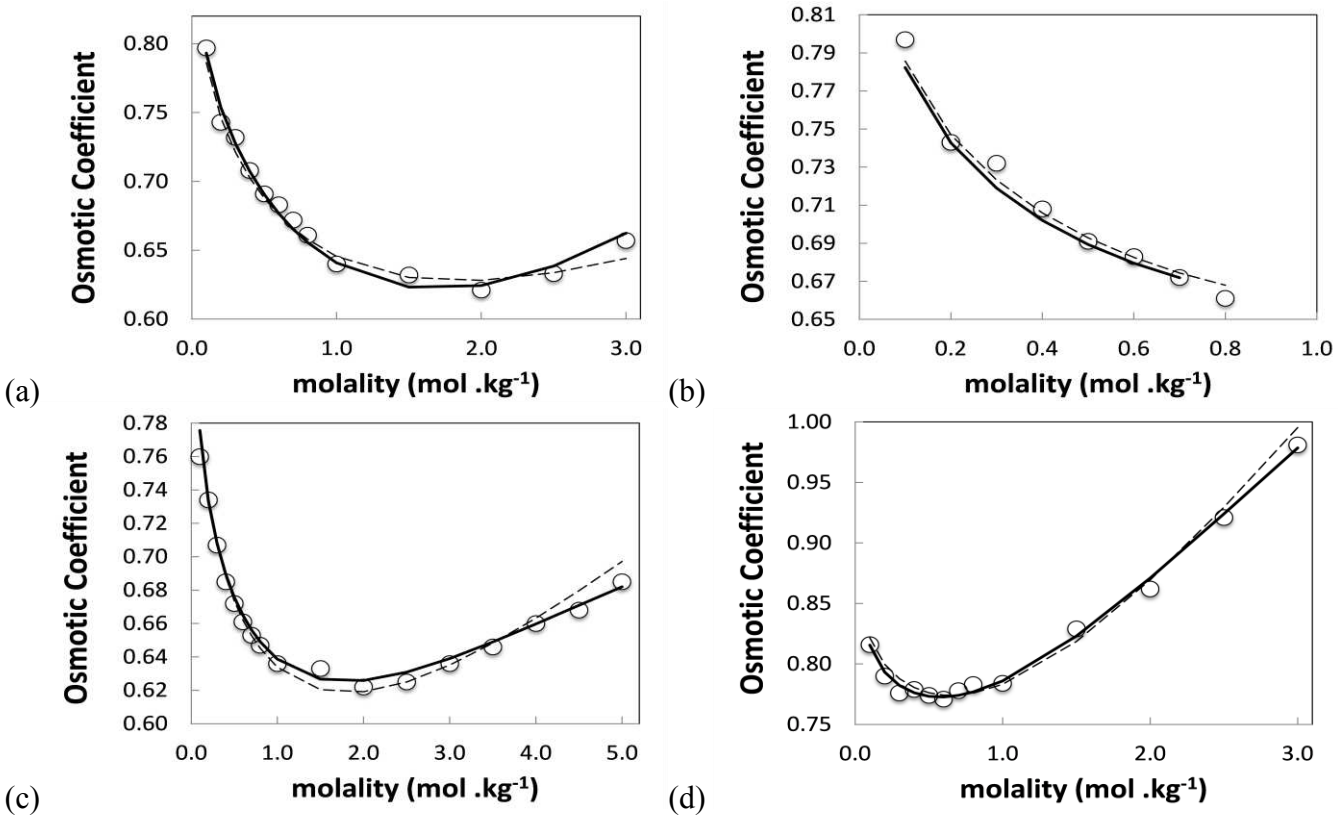

Figure 8. Comparison plots comprising the following 1-2 electrolytes: (a) Na_2SO_4, (b) K_2SO_4, (c) $(NH_4)_2SO_4$, (d) Li_2SO_4 (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model).

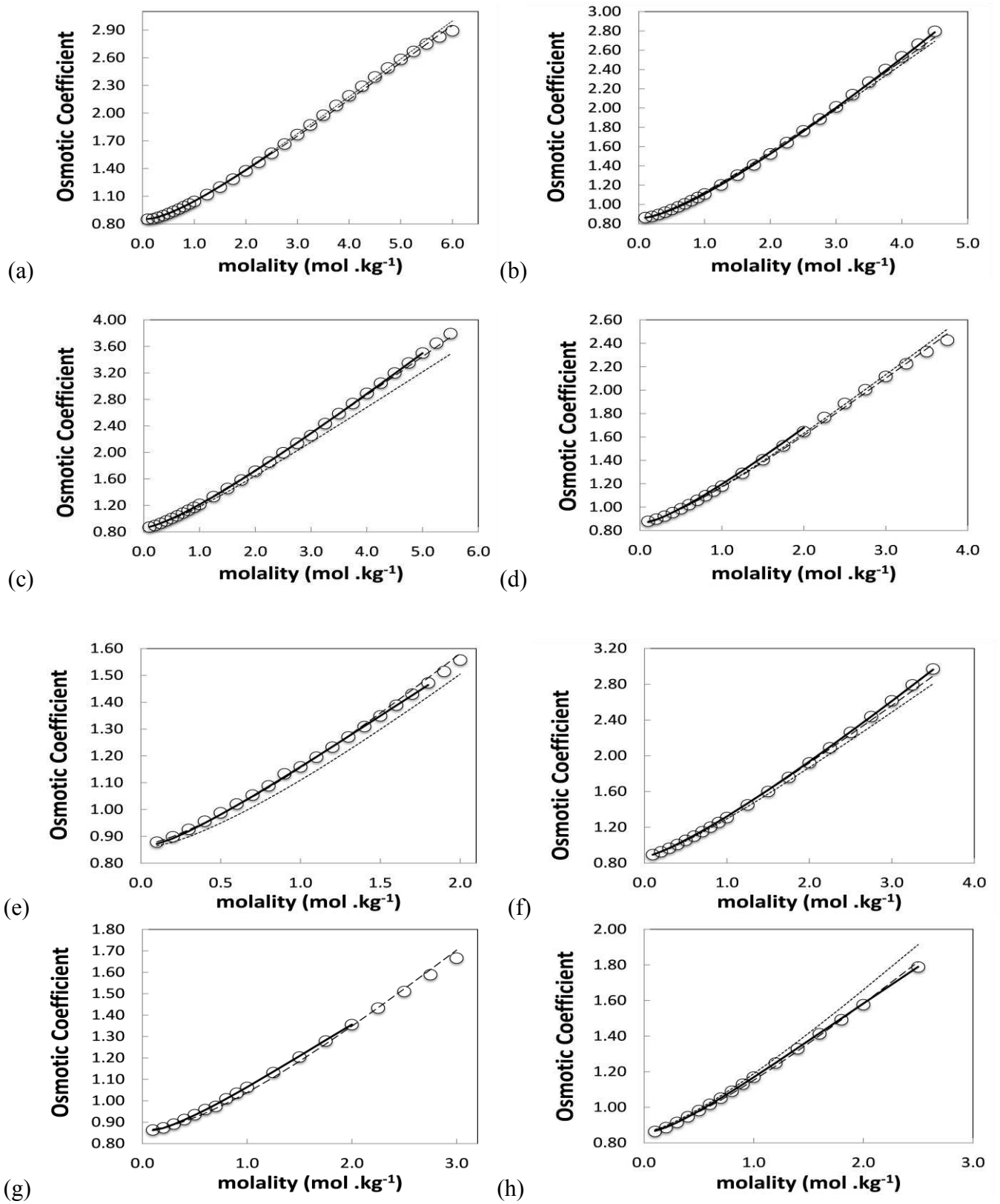

Figure 9. Comparison plots involving the following 2-1 electrolytes: (a) $CaCl_2$, (b) $MgCl_2$, (c) $MgBr_2$, (d) $CoBr_2$, (e) BaI_2, (f) $Cu(ClO_4)_2$, (g) $Zn(NO_3)_2$, (h) $Sr(ClO_4)_2$ (○: Experimental data for the osmotic coefficient from the literature(see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

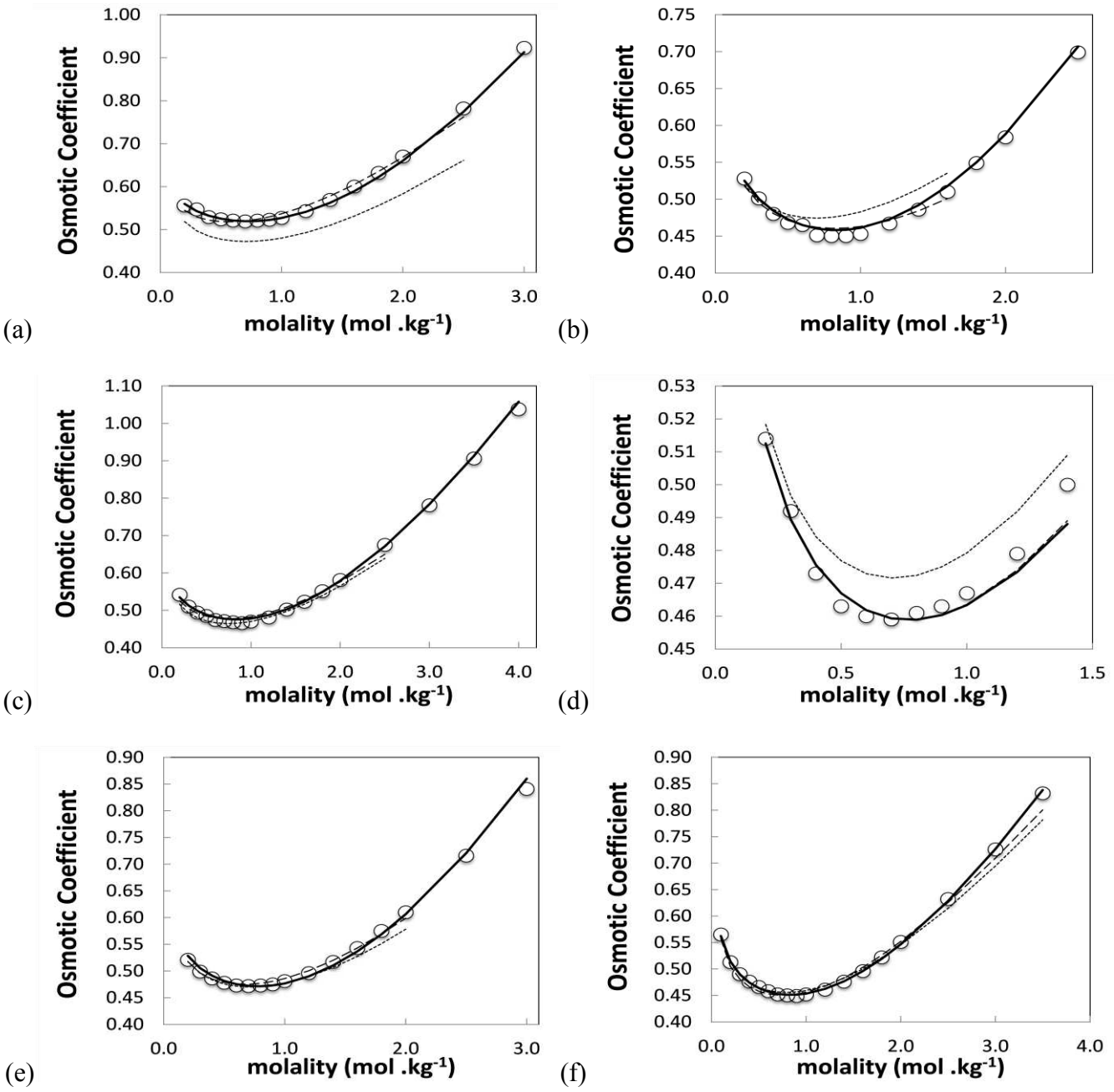

Figure 10. Comparison plots involving the following 2-2 electrolytes: (a) $MgSO_4$, (b) $NiSO_4$, (c) $MnSO_4$, (d) $CuSO_4$, (e) $ZnSO_4$, (f) $CdSO_4$ (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

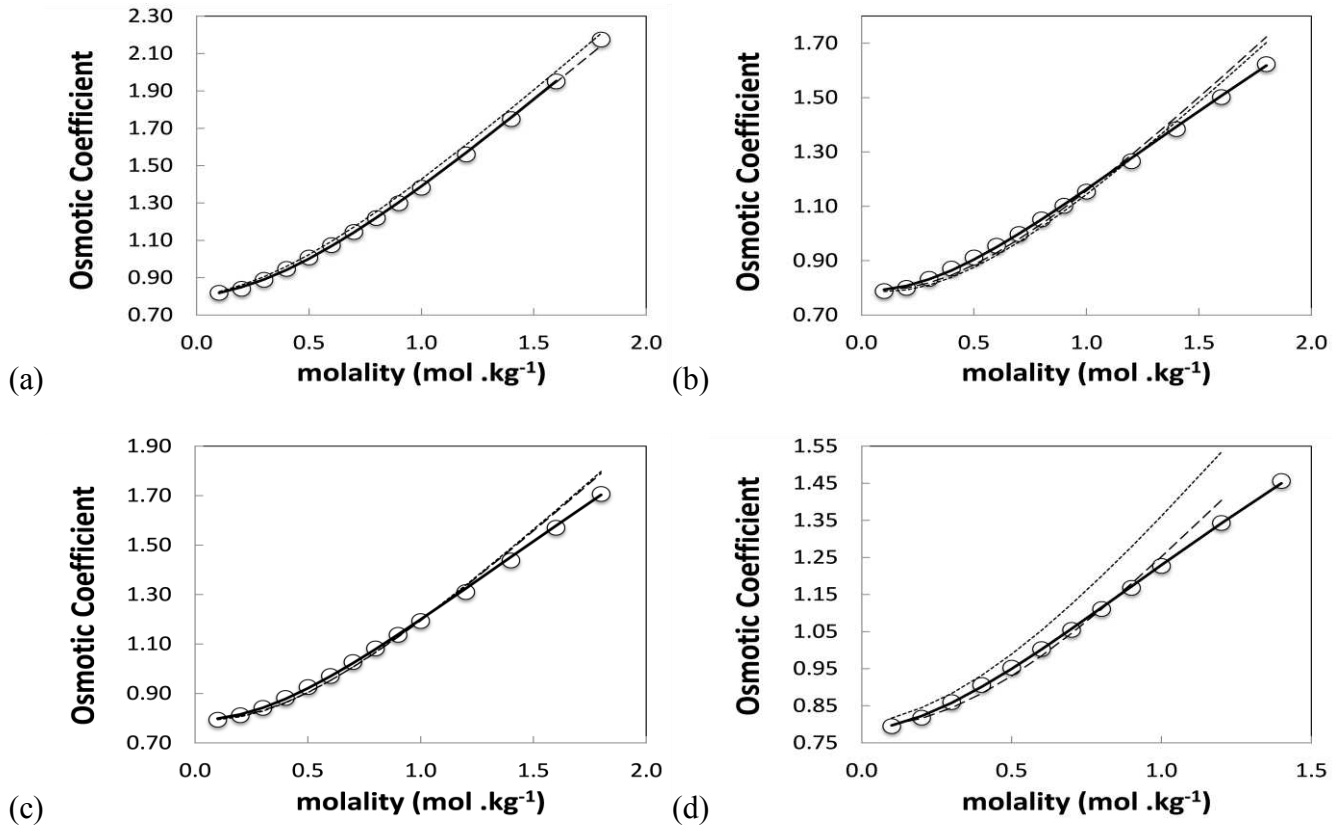

Figure 11. Comparison plots involving the following 3-1 electrolytes: (a) $AlCl_3$, (b) $LaCl_3$, (c) $EuCl_3$, (d) $Cr(NO_3)_3$ (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

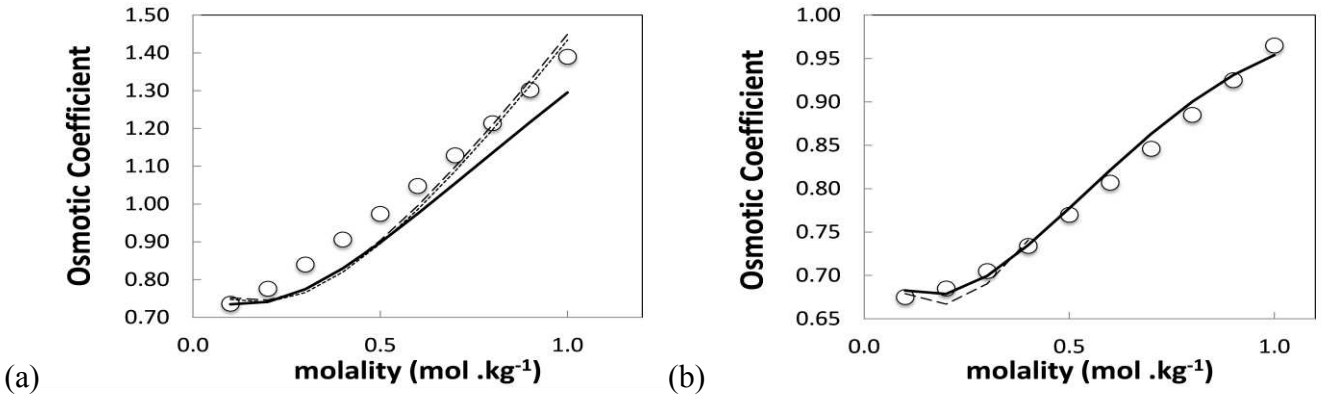

Figure 12. Comparison plots involving the following 4-1 electrolytes: (a) $ThCl_4$, (b) $Th(NO_3)_4$ (○: Experimental data for the osmotic coefficient from the literature (see references in Table 1), solid lines: original Pitzer model, dashed lines: simplified Pitzer model, dotted lines: correlating equations (eqs 15 and 17)).

Case study to demonstrate the predictability of the correlating equations (eqs 15 and 17)

In order to demonstrate the good predictability of the correlating equations (eqs 15 and 17), a case study involving rare-earth perchlorates was analyzed. The experimental data for the osmotic coefficients related to these rare-earth perchlorates were taken from Libus et al.[47]. Moreover, the ionic radii used were taken from Marcus[5], except for the perchlorate ion, which was taken from Roobottom[38].

The predicted values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ calculated by the correlating equations (eqs 15 and 17) are shown in Table 2. Also, the comparison between the osmotic coefficients calculated by the correlating equations (eqs 15 and 17) and the experimental osmotic coefficients related to these rare-earth perchlorates can be visualized in figure 13. Particularly, this figure shows a remarkable agreement between the predicted values and the experimental ones, and this confirms the good reliability of these equations to estimate the values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$.

Table 2. Estimated values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ using the correlating equations (eqs 15 and 17).

Electrolyte	$B_{MX}^{(0)}$	$B_{MX}^{(1)}$	Standard Deviation (δ)	Maximum molality ($mol.kg^{-1}$)	r_M (Å)	r_X (Å)
La(ClO4)3	0.7808	5.9231	0.105	4.50	1.05	2.25
Pr(ClO4)3	0.7995	5.9529	0.124	4.50	1	2.25
Nd(ClO4)3	0.8070	5.9647	0.124	4.50	0.98	2.25
Sm(ClO4)3	0.8145	5.9763	0.077	4.50	0.96	2.25
Gd(ClO4)3	0.8220	5.9879	0.093	4.50	0.94	2.25
Dy(ClO4)3	0.8333	6.0050	0.077	4.50	0.91	2.25
Ho(ClO4)3	0.8371	6.0107	0.066	4.50	0.9	2.25
Er(ClO4)3	0.8409	6.0163	0.063	4.50	0.89	2.25
Tm(ClO4)3	0.8447	6.0219	0.065	4.50	0.88	2.25
Yb(ClO4)3	0.8485	6.0275	0.065	4.50	0.87	2.25
Lu(ClO4)3	0.8522	6.0331	0.033	4.00	0.86	2.25

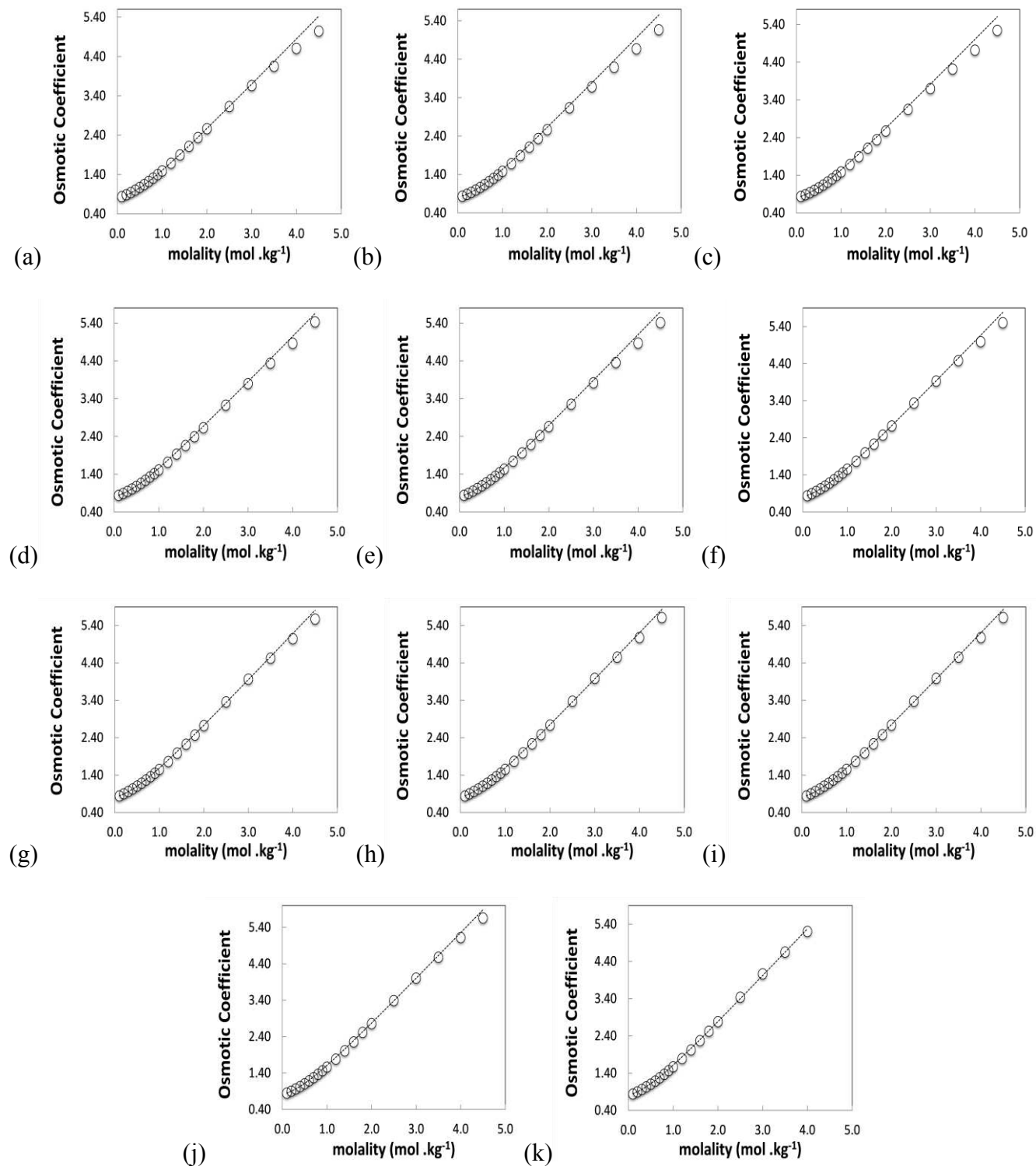

Figure 13. Comparison plots showing the predictability of the correlation equations (eqs 15 and 17) applied to rare-earth perchlorates: (a) $La(ClO_4)_3$, (b) $Pr(ClO_4)_3$, (c) $Nd(ClO_4)_3$, (d) $Sm(ClO_4)_3$, (e) $Gd(ClO_4)_3$, (f) $Dy(ClO_4)_3$, (g) $Ho(ClO_4)_3$, (h) $Er(ClO_4)_3$, (i) $Tm(ClO_4)_3$, (j) $Yb(ClO_4)_3$, (k) $Lu(ClO_4)_3$ (○: Experimental data of osmotic coefficients from the literature (see references in Table 1), dotted lines: correlating equations (eqs 15 and 17)).

Simplified Pitzer equation versus original Pitzer equation

It has been shown that the effects of the coefficients C^{φ}_{MX}, $B^{(2)}_{MX}$ and α_2 are small and it is in general a good approximation to estimate the activity and osmotic coefficients without these parameters.

In terms of $B^{(2)}_{MX}$ and α_2, the elimination of these parameters cause systematic errors at molalities higher than 2 mol/kg, and hence this approximation should not be performed if the molality of interest exceeds this value. In the case of C^{φ}_{MX}, this coefficient accounts for the short-range interaction of triplets of ions and the small influence of this parameter in the estimations of the osmotic coefficients suggests that these triplets of ions are not very abundant in the aqueous solution at moderate concentrations up to 6 M. However, especially at higher values of ionic strength, the presence of the C^{φ}_{MX} in the Pitzer equation improves the accuracy of the results and this is because the ions become closer to each other and then the probability of interactions of triplets of ions increases. Therefore, if this parameter is available then there is no reason to disregard it, but if this value is not available, the analysis performed suggests that it is a good approximation to estimate the activity and osmotic coefficients without this coefficient.

Repulsive and attractive forces

According to Pitzer et al.[9], the value of the second virial coefficient can be either positive or negative depending on the net predominance of the repulsive or attractive short-range forces. In other words, low values of $B^{(0)}_{MX}$ and $B^{(1)}_{MX}$ indicates an important contribution of the short-range attractive forces to the net short-range forces, whereas high values of these coefficients indicate an important influence of short-range repulsive forces. In this context, it is interesting to observe in figures 2, 3, 4 and 5 that the values of $B^{(0)}_{MX}$ and $B^{(1)}_{MX}$ increase as the absolute difference between the ionic radii of the cation and the anion increases, and this suggests that combinations of ions with different sizes lead to a net predominance of short-range repulsive forces. This is in agreement with Pitzer et al.[9], who stated that "we expect a larger repulsive effect for like-charged ions when there is a difference in size". Likewise, the values of the

second virial coefficients increase with the as the ionic charge of the cation increases, and this also indicates the predominance of repulsive forces. In contrast, the second virial coefficients decrease as the ionic charge of the anions increases and this indicates that the anions tend to contribute to the attenuation of the short-range repulsive forces. This is in agreement with the fact that all of the 1-2 and 2-2 electrolytes investigated in this study are forming to some extent ion pairs or complexes, which is associated to the attractive short-range forces.

Ion pairing and complex formation

The Pitzer equations were not originally created to deal with ion pairing or complex formation phenomena, except for 2-2 electrolytes where corrections for ion pairings were provided[8,9]. With the increased use of Raman spectroscopy and other investigation methods, it has been found that many of the electrolytes considered by Pitzer in his analysis as completely dissociated can actually form ion pairs/complexes in a significant scale, and thus these electrolytes require different theoretical treatments. Nevertheless, it is interesting to see how these excluded electrolytes behave in comparison with the electrolytes with smaller probability of forming ion pairs/complexes, and for this reason these two groups were plotted together in figures 14 and 15, which refer to the simplified Pitzer equation and the original Pitzer equation, respectively. In particular, it can be seen in both figures 14 and 15 that the values of $B_{MX}^{(0)}$ are lower for electrolytes that form ion pairs/complexes than for those that do not, and as mentioned before in the discussions of repulsive and attractive forces, these low values of $B_{MX}^{(0)}$ indicate an important contribution of the short-range attractive forces to the net short-range forces. Likewise $B_{MX}^{(0)}$, electrolytes forming ion pairs/complexes tend to have lower values of $B_{MX}^{(1)}$, but this behaviour changes for the 2-1 electrolytes for the simplified Pitzer equation case, see figure 14. However, since the original Pitzer equation did not present this unexpected behavior in a significant proportion then this increase of $B_{MX}^{(1)}$ for 2-1 electrolytes can be at least partially attributed to the absence of the factor C_{MX}^{φ}. Also, this increase of $B_{MX}^{(1)}$ for the 2-1 electrolytes can be explained by the presence of 2-2 electrolytes that are formed by speciation, e.g. the electrolyte $ZnCl_2$ forms the

species $ZnCl_4^{2-}$ [45], that in association with Zn^{2+} add interactions of the type 2-2 to the aqueous system, and as shown in figure 4 these 2-2 electrolytes have higher values of $B_{MX}^{(1)}$.

To summarize, the knowledge of the values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ and the comparison with the curve containing electrolytes that are unlikely to form ion pairs/complexes can give a good indication about the possible formation of ion pairs/complexes as well as formation of species of higher valence.

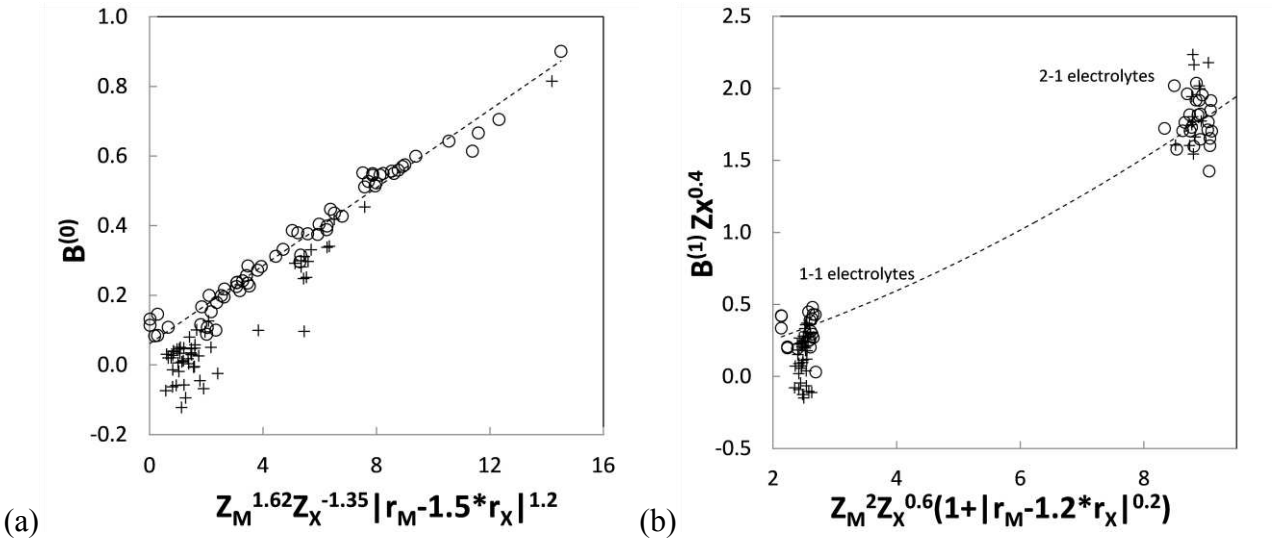

Figure 14. The coefficients (a) $B_{MX}^{(0)}$, and (b) $B_{MX}^{(1)}$ with and without ion pairing/complex formation for the simplified Pitzer equation, i.e. C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 = 0$ (+: ion pairing/complex formation, ○: highly dissociated electrolytes, dashed lines from (a) and (b): regression considering only highly dissociated electrolytes).

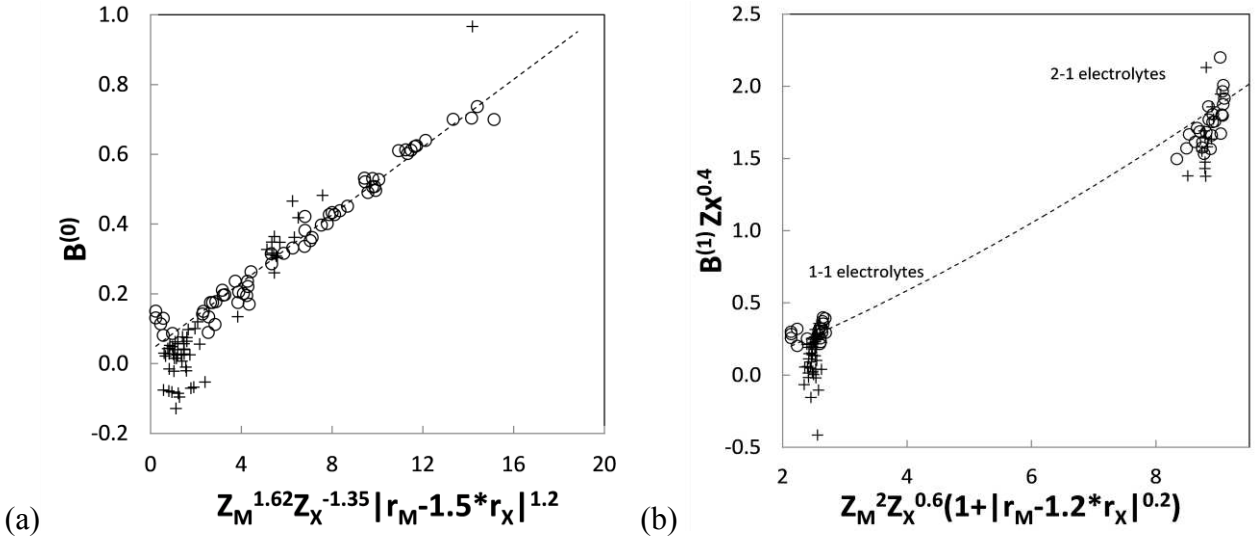

Figure 15. The coefficients (a) $B_{MX}^{(0)}$, and (b) $B_{MX}^{(1)}$ with and without ion pairing/complex formation for the original Pitzer equation, i.e. C_{MX}^{φ}, $B_{MX}^{(2)}$ and $\alpha_2 \neq 0$ (+: ion pairing/complex formation, ○: highly dissociated electrolytes, dashed lines from (a) and (b): regression considering only highly dissociated electrolytes).

Structure breaking and structure making ions

As mentioned before in the results section, according to the Collins[44], ions with similar affinities with the water molecules tend to form stable ion pairs[48]. In particular, this rule was very important to systematically eliminate the 1-1 electrolytes that are more likely to form ion pairs. In fact, the low values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ presented by all of the 1-1 electrolytes with similar affinities with the water molecules provides very strong evidence of the formation of ions pairs, and this is because as mentioned before in the discussions of repulsive and attractive forces, these low values indicate important contributions of the short-range attractive forces to the net short-range forces. Furthermore, Pitzer[9] also observed that ions with similar affinities with the water molecules tend to have lower values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$. Finally, it is possible to find in the literature experimental and theoretical evidence of the formation of ion pairs for ions with similar affinities with water. For example, Moskovits et al.[49] investigated the ion pair formation in alkali hydroxides using Raman Spectroscopy. Likewise, Gujt et al.[50] studied ion pairing associated to

alkali metal halides using the electrical conductivity and the Monte Carlo computer simulation methods. In the same way, Chen et al.[51] investigated ion pairing and cluster formation in strong 1-1 electrolytes by making direct comparison of the results from detailed molecular dynamics simulations to experimentally observed properties of these 1-1 electrolytes.

Geometry of the ions

Most of the cations analyzed in this study are fairly spherical, and thus no conclusion can be made regarding the influence of the geometry of the cations on the values of the second virial coefficients based on the data analyzed. In fact, most of the cations with complex geometries were not investigated in this study due to the lack of data in the literature, especially with regards to the thermochemical/ionic radii as well as the ion pair formation.

Regarding the anions, some of them have complex geometries, including the anions NO_2, SCN and NO_3 that are not exactly spherical. Considering these three anions, the first two, NO_2 and SCN, did not present any unexpected behavior, and this is in contrast to the nitrate ion that formed ion pairs/complexes in most of the cases analyzed. However, it is not possible to conclude that the geometry of the anion was the reason for this anomalous behavior of the nitrate ion, because the other two non-spherical ions NO_2 and SCN behaved normally.

Consequently, based on the set of data analyzed it is not possible to come to any conclusion about the influence of the geometry of the cations and anions on the values of the second virial coefficients.

Hydrated radius of the ions

As mentioned before in the results section, several trials were performed to fit the second virial coefficients with the hydrated radii, but they all failed. On the other hand, it was found that there is a very good correlation between the second virial coefficients and the ionic radii (R^2>0.96),

and this reinforces that the second virial coefficients are more strongly connected to the ionic radii than the hydrated radii.

Dispersion forces

Despite the fact that dispersion forces may have an influence on the values of the second virial coefficients, a more sophisticated analysis is required in order to account for these effects, but this is not within the scope of this study.

Effects of temperature on Virial coefficients

The effects of temperature on the virial coefficients are not known in general, but these effects are very important because many industrial processes deal with temperatures different from 25 ^{o}C. However these effects are beyond the scope of the present study but could be the subject of future research work.

CONCLUSIONS

Simplifications to the Pitzer equation

Some simplifications to the Pitzer equation have been suggested and analyzed, and these include the elimination of the terms C_{MX}^{φ}, $B_{MX}^{(2)}$ and α_2 in the Pitzer equation. Both the simplified and the original Pitzer equation can estimate the activity and osmotic coefficients with very high degree accuracy, but the original Pitzer equation is slightly more precise.

Estimation of the second Virial Parameters to the simplified Pitzer equation

The second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ were re-estimated for 122 inorganic electrolytes using published experimental data for the osmotic coefficients, see Table 1. This re-estimation was performed only for the simplified Pitzer equation, and this was because most of the coefficients of the original Pitzer equation can be found in the literature. Nevertheless, it was

found that in most cases, the elimination of the factors C_{MX}^{φ}, $B_{MX}^{(2)}$ and α_2 did not cause significant changes to the values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$.

Correlation between the second Virial coefficients, ionic radii and ionic charge

The second virial coefficients $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ were correlated with the properties of the solution, more particularly with the ionic charge and the ionic radii. This correlation found was very strong and this is confirmed by the high values of the coefficients of determination (R^2>0.96). However, this correlation was only possible to be achieved after eliminating from the analysis the electrolytes that have high probability of forming ion pairs/complexes. In fact, the Pitzer equations were not originally created to account for ion pairs/complexes, and thus it is justifiable to eliminate these factors in order to understand the meaning of the second virial coefficients as well as how the formation of ion pairs/complexes influences the values of the second virial coefficients.

The following relationships for $B_{MX}^{(0)}$ were achieved for the simplified and for the original Pitzer equation, respectively:

$$B_{MX}^{(0)} = 0.04432\ z_M^{1.62} z_X^{-1.35} |r_M - 1.5 r_X|^{1.2} + 0.05758 \qquad (R^2=0.96)$$

$$B_{MX}^{(0)} = 0.04850\ z_M^{1.62} z_X^{-1.35} |r_M - 1.5 r_X|^{1.2} + 0.03898 \qquad (R^2=0.97)$$

Also, the following relationships for $B_{MX}^{(1)}$ were achieved for the simplified and for the original Pitzer equation, respectively:

$$B_{MX}^{(1)} = 0.01001 z_X^{-0.4} \left(z_M^2 z_X^{0.6} (1 + |r_M - 1.2 r_X|^{0.2}) \right)^2 + 0.12017 z_M^2 z_X^{0.2} (1 + |r_M - 1.2 r_X|^{0.2}) + 0.05226 z_X^{-0.4} \quad (R^2=0.99)$$

$$B_{MX}^{(1)} = 0.00738 z_X^{-0.4} \left(z_M^2 z_X^{0.6} (1 + |r_M - 1.2 r_X|^{0.2}) \right)^2 + 0.16800 z_M^2 z_X^{0.2} (1 + |r_M - 1.2 r_X|^{0.2}) - 0.09320 z_X^{-0.4} \quad (R^2=0.99)$$

Comparison plots involving the original Pitzer model, the simplified Pitzer model, the correlation equations and the experimental data

Comparison plots were generated in order to illustrate the agreement between the experimental data for the osmotic coefficients and the three models analyzed, i.e. the original Pitzer model, the simplified Pitzer model and the correlating equations (eqs 15 and 17). In summary, the three models agree well with the experimental data for the osmotic coefficients, being the original Pitzer model slightly more accurate, and this is because this model contains more parameters to account for the various types of ion interactions in the aqueous solutions. However, the correlating equations (eqs 15 and 17) failed to predict the behavior of bromates, nitrites, nitrates, hydroxides and fluorides, and this indicates that these anions are likely to form ion pairs.

Case study to demonstrate the predictability of the correlating equations (eqs 15 and 17)

A case study involving rare-earth perchlorates was analyzed in order to demonstrate the predictability of the correlating equations (eqs 15 and 17). As a conclusion, the predictions agreed remarkably well with the experimental data for the osmotic coefficients, and this reinforces the reliability of these equations to estimate the properties of single electrolytes in aqueous solutions.

Correlation between the second Virial coefficients and the properties of the solution

The second virial coefficients were discussed in terms of the properties of the solution, as follows:

- Attractive and repulsive forces: Low values of the second virial coefficients represent a significant contribution of the short-range attractive forces, whereas high values represent a significant contribution of the short-range repulsive forces. Also, short-range repulsive forces are enhanced as the ionic charge of the cation increases. In contrast, the short-range repulsive forces are attenuated as the ionic charge of the anion increases, and good evidence of this is the formation of ion pairs/complexes for all of the 1-2 and 2-2 electrolytes analyzed, since the formation of ion pairs are related to short-range attractive forces.
- Ion pairing/complex formation: The electrolytes analyzed that are more likely to form ion pairs/complexes presented in general lower values of $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$ than electrolytes that are unlikely to form ion pairs, and these low values indicate important contributions of the attractive short-range forces to the net short-range forces.
- Structure breakers and structure makers: It has been shown that ions with similar affinity with water tend to form stable ion pairs.
- Geometry: Since most of the ions analyzed are almost spherical, it was not possible to precisely identify the influence of the geometry of the ions on the values of the second virial coefficients.
- Hydrated radius: No strong correlation between the second virial coefficients and the hydrated radius was achieved.
- Dispersion forces: The effect of the dispersion forces on the values of the second virial coefficients could not be identified based on the data analyzed, and a more sophisticated analysis would need to be performed in order to account for these effects.

- Temperature: The effects of temperature on the virial coefficients are not known in general, but they are very important in numerous practical situations. However, these effects are beyond the scope of the present study but could be the subject of future research work.

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ABBREVIATIONS

Latin Symbols

A^{φ}, Debye Huckel coefficient for the osmotic coefficient

B_{MX}^{φ}, second virial Coefficient for the osmotic coefficient

$B_{MX}^{(0)}$, $B_{MX}^{(1)}$, $B_{MX}^{(2)}$, second virial Coefficients representing short-range binary interactions

c, chaotrope

C_{MX}^{φ}, third virial Coefficient representing short-range interaction of triplets of ions

f^{φ}, function of the ionic strength representing long range forces

k, kosmotrope

m, molality

n, number of experimental data points

I, ionic strength

r_{hM}, hydrated radii of the cation

r_{hX}, hydrated radii of the anion

r_{M}, ionic radii of the cation

r_{X}, ionic radii of the anion

z_{M}, charge of the cation

z_{X}, charge of the anion

Greek Symbols

α_1, constant of the Pitzer equation related to B^{φ}_{MX}

α_2, constant of the Pitzer equation related to B^{φ}_{MX}

δ, standard deviation

φ_{MX}, osmotic coefficient of the electrolyte

ν, number of cationic and anionic species

ν_{M}, number of cationic species

ν_{X}, number of anionic species

Subscripts

h, hydrated

M, cation

X, anion

Superscripts

calc, calculated

exp, experimental

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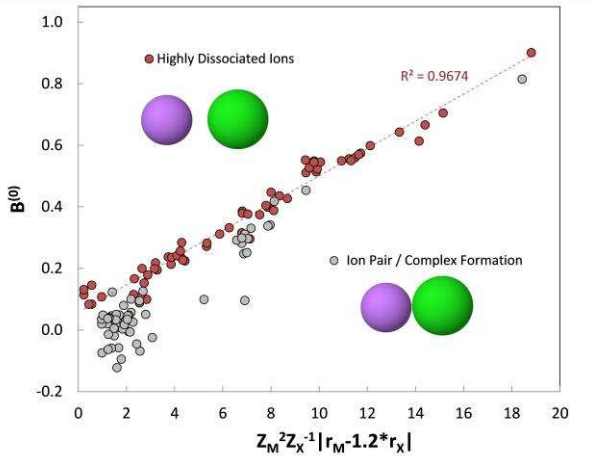
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