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Temperature Dependence of the Parameters in the Pitzer Equations

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ABSTRACT The effects of temperature on the virial coefficients in the Pitzer equations are not known in general, and this is because the vast majority of experiments performed to investigate the properties of the aqueous electrolytes were conducted only at a temperature of 25 °C. Consequently, most of the parameters in the Pitzer equations that are available in the literature were estimated at this temperature. Therefore, finding a way to estimate the virial coefficients at different temperatures is highly important. To achieve this, new equations that correlate the virial coefficients with the temperature and the properties of the ions, i.e. ionic radius and ionic charge are derived. As a result, these new derived equations were able to accurately predict the apparent relative molal enthalpies at 25 °C, as well as the activity and osmotic coefficients at temperatures up to 150 °C for electrolytes that are unlikely to form ion pairs. Moreover, comparison plots are presented to demonstrate the good agreement between the predictions of the correlating equations and the experimental data obtained from the literature.

KEYWORDS Pitzer model, temperature dependence, virial parameters, aqueous electrolytes.

INTRODUCTION

The Pitzer equations are semi-empirical equations developed in the 1970s by the chemist Kenneth S. Pitzer[1], and these equations have been extensively used in the literature to calculate the thermodynamic properties of the electrolytes, especially at high molalities. These equations evolved from the Debye-Hückel model as well as from other more realistic methods, e.g. the Guggenheim model, on basis of theoretical insights[1]. In addition, a key improvement of the Pitzer model is the recognition of the ionic strength dependence of short-range forces in binary interactions. Later, the Pitzer equations[1], which were originally conceived to describe the osmotic and activity coefficients of aqueous electrolytes, were further developed to also describe enthalpy and heat capacity[2]. The enthalpy version of the Pitzer equations, for instance, is important for the development of this study.

If on one hand the properties of the electrolytes in aqueous solutions have been extensively studied at a temperature 25 °C, on the other hand only a few studies have been performed to investigate these properties at different temperatures. For instance, investigations related to the influence of the temperature on the thermodynamic properties of the solution, such as heat capacity, enthalpy, osmotic and activity coefficients over a wide range of temperatures are practically limited to the studies performed by Holmes at al.[3-12], Silvester and Pitzer[2] and Wang et al.[13]. Therefore, the task of modeling the temperature dependence of the Pitzer equation parameters is highly challenging due to the lack of experimental data. At the same time, this lack of experimental data from the literature implies that the equations developed in this study can be very valuable, because they can be applied to a large set of electrolytes for which the information on the osmotic and activity coefficients is still unknown.

Likewise, the literature is very scarce in terms of modeling. The most important attempt of calculating the activity coefficients at different temperatures was performed by Criss and Millero[14]. In their investigation, both the apparent relative molal heat capacities and the apparent relative molal enthalpies at 25 °C were used to estimate the activity coefficients for 1-1 electrolytes in the temperature range 0 to 75 °C and at molalities between 0 and 2 mol.kg^{-1}. Although they obtained a good agreement between the predictions and the experimental data for the activity coefficients, there was no attempt to extend the validity of these equations to temperatures higher than 75 °C, and also to higher concentrations. Also, no examples were provided by Criss and Millero in their follow-up paper[15] to demonstrate that the model produced to calculate the osmotic and activity coefficients for 1-1 electrolytes[14] at non-ambient temperatures would also be applicable for higher valence electrolytes. In addition, no attempt has been made to correlate the activity coefficients with the properties of the ions, e.g. the ionic radius and the ionic charge.

In contrast to Criss and Millero[14], this study not only investigates the activity and osmotic coefficients over a wider range of temperatures, but also over a broader range of molalities. In addition, the activity and osmotic coefficients of higher valence electrolytes were included in the analysis. To achieve this, firstly the temperature derivatives of the virial parameters in the Pitzer equations are fitted to the experimental data of apparent relative molal enthalpy obtained from the literature at 25 °C. Secondly, these temperature derivatives are correlated with the properties of the solutions for electrolytes that are unlikely to form ion pairs. Thirdly, these correlations are used to predict the activity and osmotic coefficients at higher temperatures and concentrations. Finally, the predictions obtained through the correlating equations are compared with the experimental data for the osmotic and activity coefficients obtained from the literature.

GENERAL EQUATIONS

Extended Pitzer Equations

The Pitzer equation that correlates the temperature derivatives of the virial coefficients and the apparent relative molal enthalpy is given as follows:[2]

$$\Phi_L = v|z_M z_X|(A_H/3.6)\ln(1 + 1.2I^{1/2}) - 2v_M v_X RT^2(mB'_{MX} + m^2 C'_{MX}) \tag{1}$$

where

$$B'_{MX} = \left(\frac{\partial B_{MX}}{\partial T}\right)_{I,P} \tag{2}$$

$$B_{MX} = B^{(0)}_{MX} + \left(\frac{2B^{(1)}_{MX}}{\alpha^2 I}\right)\left[1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\right] \tag{3}$$

$$C'_{MX} = \frac{(v_M v_X)^{1/2}}{2}\left(\frac{\partial C^\varphi_{MX}}{\partial T}\right)_{I,P} \tag{4}$$

$$I = 0.5(m_M z_M^2 + m_X z_X^2) \tag{5}$$

$$v = v_M + v_X \tag{6}$$

$$A_H = 698 \text{ cal mol}^{-1} \text{ at } 25\,°C \tag{7}$$

METHOD OF FITTING AND DATA USED

The least mean squares was the fitting method chosen to estimate the parameters in the Pitzer equation for the apparent relative molal enthalpy[2]. This is achieved by minimizing the following objective function:

$$S(\Phi_L) = \sum_{i=1}^{n}\left(\Phi_{L_i}^{exp} - \Phi_{L_i}^{calc}\right)^2 \tag{8}$$

In terms of the data used, they were obtained from reliable sources from the literature, as follows. For all 1-1 electrolytes, it was adopted from the tabulations produced by Parker[16], which constitute a reviewed concise database, except for CsBr, CsCl, CsI, HBr, HI, NH$_4$Cl, RbBr, RbCl

and RbI for which the apparent relative molal enthalpy data were taken from more recent references[17–20], which are the same references that were used by Silvester and Pitzer[21]. For higher valence electrolytes, all the references adopted[22–28] coincide with the references used by Pitzer et al.[29] and Silvester and Pitzer[21], except for BaCl$_2$, CaCl$_2$ and SrCl$_2$, which were taken from the concise recommended values from Holmes et al.[30], as well as for MgCl$_2$, which was from the experimental data reported by Jahn and Wolf[31]. Also, two electrolytes that had not been included in the investigations performed by Pitzer et al.[29] and Silvester and Pitzer[21] were included in this study, namely Ba(ClO$_4$)$_2$[32] and Cr(ClO$_4$)$_3$[33]. Finally, it is important to mention that the electrolytes for which the information on the apparent relative molal enthalpy is available only at molalities up to 0.1 mol.kg^{-1} were not included in this study, e.g. BaBr$_2$, MgBr$_2$ and SrBr$_2$[21], and this is because the virial coefficients in the Pitzer equations are normally estimated by considering a broader range of concentrations that also include the molalities higher than 0.1 mol.kg^{-1}.

Correlations between the Temperature Derivatives and the Properties of the Ions

The ionic charge and the radius of the ions were correlated with the temperature derivatives in Table 1 using the equations as follows:

$$\left(\frac{\partial B_{MX}^{(0)}}{\partial T}\right) = \kappa_1 z_M^{\varepsilon_1} + \kappa_2\left(r_M^{\varepsilon_2} + r_X^{\varepsilon_3}\right)z_M^{\varepsilon_1} \tag{9}$$

$$\left(\frac{\partial B_{MX}^{(1)}}{\partial T}\right) = \kappa_3 z_M^{\varepsilon_4} + \kappa_4\left(r_M^{\varepsilon_5} + r_X^{\varepsilon_6}\right)z_M^{\varepsilon_4} \tag{10}$$

$$\left(\frac{\partial C_{MX}^{\varphi}}{\partial T}\right) = \kappa_5 z_M^{\varepsilon_7} + \kappa_6\left(r_M^{\varepsilon_8} + r_X^{\varepsilon_9}\right)z_M^{\varepsilon_7} \tag{11}$$

If the electrolyte is chaotrope, then r_M and r_X refer to the hydrated radius[34], otherwise r_M and r_X refer to the ionic radius[34]. The electrolytes were classified as either kosmotropes or chaotropes

using the criteria indicated by Marcus[35], which takes into account the influence of the solutes on the average number of hydrogen bonds in which a water molecule participates.

Integration of the Equations 9 to 11 with respect to the Temperature

The integration of the eqs 9 to 11 with respect to the temperature between T_R (25 °C) and T gives the values of the virial coefficients as follows:

$$B_{MX\,T}^{(0)} = B_{MX\,R}^{(0)} + \left[\kappa_1 z_M^{\varepsilon_1} + \kappa_2 (r_M^{\varepsilon_2} + r_X^{\varepsilon_3}) z_M^{\varepsilon_1}\right](T - T_R) \tag{12}$$

$$B_{MX\,T}^{(1)} = B_{MX\,R}^{(1)} + \left[\kappa_3 z_M^{\varepsilon_4} + \kappa_4 (r_M^{\varepsilon_5} + r_X^{\varepsilon_6}) z_M^{\varepsilon_4}\right](T - T_R) \tag{13}$$

$$C_{MX\,T}^{\varphi} = C_{MX\,R}^{\varphi} + \left[\kappa_5 z_M^{\varepsilon_7} + \kappa_6 (r_M^{\varepsilon_8} + r_X^{\varepsilon_9}) z_M^{\varepsilon_7}\right](T - T_R) \tag{14}$$

These equations are simpler than the equations that are normally used to describe the temperature dependence of the virial terms in the Pitzer equations, including those developed by Silvester and Pitzer[2] as well as those derived by Criss and Millero[14]. However, in the discussion section we demonstrate that these equations are accurate enough to describe the behavior of the electrolytes with low tendency to form ion pairs up to 150 °C.

RESULTS

Two cases have been analyzed in this study, as follows: (i) considers the temperature derivatives of the three virial parameters $B_{MX}^{(0)}$, $B_{MX}^{(1)}$ and C_{MX}^{φ}, and (ii) considers the temperature derivatives of only two virial parameters, namely $B_{MX}^{(0)}$ and $B_{MX}^{(1)}$, with the temperature derivative of the C_{MX}^{φ} term being set to zero. In particular, case (ii) is important because normally the C_{MX}^{φ} term is not required at molalities below 2 mol.kg^{-1}, and thus it can be disregarded[36].

Temperature Derivatives of the Virial Parameters in the Pitzer Equation

Tables 1 and 2 show the temperature derivatives of the virial parameters in the Pitzer equation for the apparent relative molal enthalpy[2] that were obtained by fitting eq 1 to the experimental data for the apparent relative molal enthalpy from the literature for cases (i) and (ii), respectively.

These tables include only the electrolytes that are unlikely to form ion pairs. They do not include the following electrolytes that are likely to form ion pairs: (i) 1-1 electrolytes: nitric and perchloric acids[37], as well as alkali metal hydroxides and fluorides. In particular, the alkali metal hydroxides and fluorides were excluded because the results obtained in a previous study[38], using the equations that correlate the virial coefficients with the properties of the ions, presented a poor agreement with the experimental data. Furthermore, it is possible to find in the literature experimental evidence that shows that these alkali metal hydroxides and fluorides tend to the ion pair formation. For instance, Manohar and Atkinson[39] investigated the association constants of the alkali metal fluorides using spectrophotometry and Moskovits and Michaelian[40] used Raman spectroscopy to investigate ion pair formation of aqueous alkali hydroxides, (ii) all 1-2 and 2-2 electrolytes [41,42], (iii) all 2-1 and 3-1 electrolytes nitrates[36,42].

Moreover, Tables 1 and 2 show the radius of the cation and the anion, and these data were taken from Marcus[34,43]. Also, Tables 1 and 2 include the maximum molalities to which the parameters in the Pitzer equation for the apparent relative molal enthalpy were fitted. Finally, the standard deviations of the fit are shown in Tables 1 and 2, and these standard deviations were calculated as follows:

$$\delta = \left[\frac{\sum_{i=1}^{n}\left(\Phi L_i^{exp} - \Phi L_i^{calc}\right)^2}{n}\right]^{1/2} \tag{15}$$

Table 1. Temperature derivatives of the virial parameters in the Pitzer equation for the apparent relative molal enthalpy at 25 °C for the three-parameter case, case (i).

	$\frac{\partial B_{MX}^{(0)}}{\partial T}10^4$	$\frac{\partial B_{MX}^{(1)}}{\partial T}10^3$	$\frac{\partial C_{MX}^{\varphi}}{\partial T}10^4$	standard deviation (δ)	maximum molality (mol.kg^{-1})	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
				1-1 electrolytes					
CsBr	8.1095	2.6800	-	4.07	0.94	2.19, 2.31	c	c	19
CsCl	7.4629	1.9600	-1.0491	4.32	3.00	2.19, 2.24	c	c	16,20
CsI	9.9150	3.4200	-	1.10	0.72	2.19, 2.46	c	c	19
HBr	-2.1526	0.4827	-0.5388	2.61	6.00	0.3, 2.31	k	c	17
HCl	-3.5024	0.2889	-0.4713	1.77	4.50	0.3, 2.24	k	c	16
HI	0.2745	0.7560	-0.9632	1.15	3.00	0.3, 2.46	k	c	18
KBr	8.1489	1.2200	-0.8517	3.09	5.55	2.12, 2.31	c	c	16
KCl	6.8104	0.8941	-0.8338	1.11	5.00	2.12, 2.24	c	c	16
KI	9.5603	1.6000	-0.8623	4.36	7.00	2.12, 2.46	c	c	16
KSCN	10.5000	1.8600	-0.9674	7.95	7.00	2.12, 2.42	c	c	16
LiBr	-1.7403	0.9195	-0.2860	3.98	6.00	0.69, 2.31	k	c	16
LiCl	-1.7834	0.7848	-0.4326	2.17	6.00	0.69, 2.24	k	c	16
LiClO$_4$	0.7680	0.6067	-0.9464	1.20	3.50	0.69, 2.69	k	c	16
NaBr	7.8676	1.0100	-0.9741	2.70	7.00	2.18, 2.31	c	c	16
NaCl	7.5248	0.7709	-1.1318	3.01	6.00	2.18, 2.24	c	c	16
NaClO$_3$	11.0000	2.2200	-1.2914	4.86	6.00	2.18, 2.33	c	c	16
NaClO$_4$	12.6000	2.3000	-1.5263	6.08	6.00	2.18, 2.69	c	c	16
NaI	9.0878	0.9640	-1.0924	1.29	6.00	2.18, 2.46	c	c	16
RbBr	6.2918	2.2200	-	1.49	0.95	2.13, 2.31	c	c	19
RbCl	5.5763	1.4800	-	0.24	0.80	2.13, 2.24	c	c	19
RbI	8.5816	2.3900	-	0.39	0.71	2.13, 2.46	c	c	19
				2-1 electrolytes					
Ba(ClO$_4$)$_2$	17.8000	6.8400	-3.1921	6.34	2.68	1.36, 2.69	k	c	32
BaCl$_2$	4.6486	3.9700	-	8.50	1.00	1.36, 2.24	k	c	30

Table 1. Continued

	$\frac{\partial B_{MX}^{(0)}}{\partial T}10^4$	$\frac{\partial B_{MX}^{(1)}}{\partial T}10^3$	$\frac{\partial C_{MX}^{\varphi}}{\partial T}10^4$	standard deviation (δ)	maximum molality (mol.kg^{-1})	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
Ca(ClO$_4$)$_2$	7.1800	5.5100	-2.6402	14.64	4.63	1, 2.69	k	c	25
CaCl$_2$	1.3476	3.0900	-1.3762	11.74	4.00	1, 2.24	k	c	30
Co(ClO$_4$)$_2$	4.9958	5.5800	-3.4295	11.36	4.00	0.75, 2.69	k	c	26
Mg(ClO$_4$)$_2$	5.3685	4.5400	-3.6048	3.91	3.00	0.72, 2.69	k	c	27
MgCl$_2$	-3.5888	3.6400	-1.0651	26.04	5.70	0.72, 2.24	k	c	31
Mn(ClO$_4$)$_2$	3.9598	5.0400	-3.3534	5.68	3.70	0.83, 2.69	k	c	25
Ni(ClO$_4$)$_2$	5.9971	5.0600	-3.6067	15.09	4.00	0.69, 2.69	k	c	26
Sr(ClO$_4$)$_2$	11.4000	5.4900	-3.0617	6.18	3.00	1.13, 2.69	k	c	27
SrCl$_2$	5.0989	2.1800	-2.2236	10.70	4.00	1.13, 2.24	k	c	30
Zn(ClO$_4$)$_2$	5.6794	5.2200	-3.7395	14.14	4.12	0.75, 2.69	k	c	24
3-1 electrolytes									
Cr(ClO$_4$)$_3$	9.9101	18.4600	-4.9757	19.50	2.00	0.62, 2.69	k	c	33
Dy(ClO$_4$)$_3$	12.3000	15.5700	-6.5529	10.55	2.10	0.91, 2.69	k	c	23
DyCl$_3$	-2.6157	9.3700	-2.8488	27.67	3.63	0.91, 2.24	k	c	22
Er(ClO$_4$)$_3$	12.8000	15.5300	-6.6620	11.27	2.10	0.89, 2.69	k	c	23
ErCl$_3$	-2.4578	9.6900	-2.7512	22.43	3.78	0.89, 2.24	k	c	22
EuCl$_3$	-0.5535	8.9800	-2.9860	15.25	3.59	0.95, 2.24	k	c	22
Gd(ClO$_4$)$_3$	13.1000	15.2300	-6.2780	7.74	2.10	0.94, 2.69	k	c	23
GdCl$_3$	-1.6124	9.0600	-2.8839	15.98	3.59	0.94, 2.24	k	c	22
HoCl$_3$	-2.3094	9.5000	-2.9022	23.98	3.69	0.9, 2.24	k	c	22
La(ClO$_4$)$_3$	15.8000	14.9000	-7.0068	8.86	2.10	1.05, 2.69	k	c	23
LaCl$_3$	-0.2252	10.2300	-2.8655	34.21	3.90	1.05, 2.24	k	c	22
Lu(ClO$_4$)$_3$	13.2000	15.6600	-6.6954	10.68	2.10	0.86, 2.69	k	c	23
LuCl$_3$	-2.3574	9.9800	-2.5270	30.29	4.13	0.86, 2.24	k	c	22
Nd(ClO$_4$)$_3$	16.8000	15.5100	-6.9414	9.12	2.10	0.98, 2.69	k	c	23
NdCl$_3$	1.9337	9.3600	-3.2802	8.65	3.93	0.98, 2.24	k	c	22
Pr(ClO$_4$)$_3$	16.4000	15.6300	-6.9115	9.69	2.10	1, 2.69	k	c	23
PrCl$_3$	1.7724	9.3500	-3.3215	12.63	3.89	1, 2.24	k	c	22

Table 1. Continued

	$\frac{\partial B_{MX}^{(0)}}{\partial T}10^4$	$\frac{\partial B_{MX}^{(1)}}{\partial T}10^3$	$\frac{\partial C_{MX}^{\varphi}}{\partial T}10^4$	standard deviation (δ)	maximum molality (mol.kg^{-1})	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
Sm(ClO$_4$)$_3$	15.5000	15.5600	-6.4438	9.40	2.10	0.96, 2.69	k	c	23
SmCl$_3$	0.8108	9.0300	-3.1777	12.93	3.64	0.96, 2.24	k	c	22
TbCl$_3$	-2.4506	9.4000	-2.9216	18.81	3.57	0.92, 2.24	k	c	22
TmCl$_3$	-2.1937	9.6800	-2.7239	24.83	3.88	0.88, 2.24	k	c	22
YbCl$_3$	-2.3389	10.0200	-2.6074	26.80	4.00	0.87, 2.24	k	c	22

Table 2. Temperature derivatives of the virial parameters in the Pitzer equation for the apparent relative molal enthalpy at 25 °C for the two-parameter case, case (ii).

	$\dfrac{\partial B_{MX}^{(0)}}{\partial T}10^4$	$\dfrac{\partial B_{MX}^{(1)}}{\partial T}10^3$	$\dfrac{\partial C_{MX}^{\varphi}}{\partial T}10^4$	standard deviation (δ)	maximum molality (mol.kg^{-1})	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
				1-1 electrolytes					
CsBr	8.1095	2.6800	-	4.07	0.94	2.19, 2.31	c	c	19
CsCl	7.2001	1.9400	-	7.42	1.10	2.19, 2.24	c	c	16,20
CsI	9.9150	3.4200	-	1.10	0.72	2.19, 2.46	c	c	19
HBr	-2.6820	0.5497	-	2.80	2.00	0.3, 2.31	k	c	17
HCl	-4.2554	0.4517	-	2.67	2.00	0.3, 2.24	k	c	16
HI	-1.2084	1.0600	-	2.75	2.00	0.3, 2.46	k	c	18
KBr	7.0888	1.4000	-	2.93	2.00	2.12, 2.31	c	c	16
KCl	5.5660	1.1500	-	2.62	2.00	2.12, 2.24	c	c	16
KI	8.6342	1.7200	-	3.07	2.00	2.12, 2.46	c	c	16
KSCN	9.7339	1.8800	-	5.93	2.00	2.12, 2.42	c	c	16
LiBr	-2.4598	1.1100	-	3.80	2.00	0.69, 2.31	k	c	16
LiCl	-2.6506	0.9945	-	1.05	2.00	0.69, 2.24	k	c	16
LiClO$_4$	-0.6910	0.9115	-	2.56	2.00	0.69, 2.69	k	c	16
NaBr	6.5946	1.2300	-	2.41	2.00	2.18, 2.31	c	c	16
NaCl	5.9813	1.0600	-	4.94	2.00	2.18, 2.24	c	c	16
NaClO$_3$	9.4378	2.4800	-	4.65	2.00	2.18, 2.33	c	c	16
NaClO$_4$	10.8000	2.6000	-	8.35	2.00	2.18, 2.69	c	c	16
NaI	7.4507	1.5300	-	3.14	2.00	2.18, 2.46	c	c	16
RbBr	1.9493	0.6074	-	2.14	2.00	2.13, 2.31	c	c	19
RbCl	6.2918	2.2200	-	1.49	0.95	2.13, 2.24	c	c	19
RbI	5.5763	1.4800	-	0.24	0.80	2.13, 2.46	c	c	19
				2-1 electrolytes					
Ba(ClO$_4$)$_2$	8.5816	2.3900		0.39	0.71	1.36, 2.69	k	c	32

Table 2. Continued

	$\frac{\partial B_{MX}^{(0)}}{\partial T} 10^4$	$\frac{\partial B_{MX}^{(1)}}{\partial T} 10^3$	$\frac{\partial C_{MX}^{\varphi}}{\partial T} 10^4$	standard deviation (δ)	maximum molality (mol.kg⁻¹)	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
BaCl₂	10.7000	9.6400	-	57.69	2.68	1.36, 2.24	k	c	30
Ca(ClO₄)₂	4.6486	3.9700	-	8.50	1.00	1, 2.69	k	c	25
CaCl₂	6.0295	5.5100	-	1.61	0.74	1, 2.24	k	c	30
Co(ClO₄)₂	-1.3055	4.0900	-	26.08	2.00	0.75, 2.69	k	c	26
Mg(ClO₄)₂	2.1573	6.0800	-	4.16	1.00	0.72, 2.69	k	c	27
MgCl₂	1.5257	5.5500	-	5.04	1.00	0.72, 2.24	k	c	31
Mn(ClO₄)₂	-4.0373	3.4200	-	10.90	1.38	0.83, 2.69	k	c	25
Ni(ClO₄)₂	2.0721	5.3300	-	0.97	0.55	0.69, 2.69	k	c	26
Sr(ClO₄)₂	2.9793	5.5600	-	4.19	1.00	1.13, 2.69	k	c	27
SrCl₂	8.3455	6.2400	-	4.33	1.00	1.13, 2.24	k	c	30
Zn(ClO₄)₂	-2.4449	6.4000	-	111.91	4.00	0.75, 2.69	k	c	24
3-1 electrolytes									
Cr(ClO₄)₃	2.4800	5.8400	-	4.76	1.00	0.62, 2.69	k	c	33
Dy(ClO₄)₃	1.9229	22.2300	-	58.91	1.50	0.91, 2.69	k	c	23
DyCl₃	4.1202	18.9000	-	37.92	1.10	0.91, 2.24	k	c	22
Er(ClO₄)₃	-5.2373	9.9100	-	32.97	1.10	0.89, 2.69	k	c	23
ErCl₃	4.4530	18.9200	-	37.30	1.10	0.89, 2.24	k	c	22
EuCl₃	-5.1215	10.3200	-	27.03	1.10	0.95, 2.24	k	c	22
Gd(ClO₄)₃	-3.7989	10.0200	-	26.99	1.10	0.94, 2.69	k	c	23
GdCl₃	5.2190	18.4500	-	36.79	1.10	0.94, 2.24	k	c	22
HoCl₃	-4.6657	10.0000	-	28.08	1.10	0.9, 2.24	k	c	22
La(ClO₄)₃	-5.1911	10.2300	-	30.04	1.10	1.05, 2.69	k	c	23
LaCl₃	6.9001	18.5200	-	38.12	1.10	1.05, 2.24	k	c	22
Lu(ClO₄)₃	-2.6345	10.5300	-	34.48	1.10	0.86, 2.69	k	c	23
LuCl₃	4.8416	19.0600	-	38.54	1.10	0.86, 2.24	k	c	22
Nd(ClO₄)₃	-4.4425	10.1700	-	27.43	1.10	0.98, 2.69	k	c	23

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Table 2. Continued

	$\dfrac{\partial B_{MX}^{(0)}}{\partial T}10^4$	$\dfrac{\partial B_{MX}^{(1)}}{\partial T}10^3$	$\dfrac{\partial C_{MX}^{\varphi}}{\partial T}10^4$	standard deviation (δ)	maximum molality (mol.kg^{-1})	$r_M(\text{Å}), r_X(\text{Å})$	cation (kosm. or chao.)	anion (kosm. or chao.)	Ref.
NdCl$_3$	7.9619	19.1000	-	37.49	1.10	0.98, 2.24	k	c	22
Pr(ClO$_4$)$_3$	-1.8436	10.7000	-	26.07	1.10	1, 2.69	k	c	23
PrCl$_3$	7.6008	19.2200	-	36.38	1.10	1, 2.24	k	c	22
Sm(ClO$_4$)$_3$	-2.0276	10.6700	-	28.20	1.10	0.96, 2.69	k	c	23
SmCl$_3$	7.2794	18.9100	-	33.62	1.10	0.96, 2.24	k	c	22
TbCl$_3$	-2.9533	10.3900	-	21.81	1.10	0.92, 2.24	k	c	22
TmCl$_3$	-5.3550	10.2100	-	35.11	1.10	0.88, 2.24	k	c	22
YbCl$_3$	-4.7105	10.1900	-	28.41	1.10	0.87, 2.24	k	c	22

Value of the Fitting Parameters in eqs 9 to 11

The values of the constants κ_i as well as the power terms ε_i are shown in Table 3 and 4 for case (i) and case (ii), respectively. These parameters were obtained by minimization of the objective function represented by eq 8.

Table 3. Coefficients in eqs 9 to 11 for case (i).

κ_1	-1.40×10^{-3}	κ_3	2.72×10^{-4}	κ_5	1.38×10^{-4}
κ_2	3.34×10^{-4}	κ_4	4.62×10^{-6}	κ_6	-3.56×10^{-5}
ε_1	1.408	ε_4	2.664	ε_7	1.631
ε_2	1.556	ε_5	7.264	ε_8	0.909
ε_3	1.452	ε_6	4.868	ε_9	1.810

Table 4. Coefficients in eqs 9 to 11 for case (ii).

κ_1	-1.61×10^{-3}	κ_3	1.94×10^{-5}	κ_5	-
κ_2	3.73×10^{-4}	κ_4	2.76×10^{-5}	κ_6	-
ε_1	1.030	ε_4	2.712	ε_7	-
ε_2	1.485	ε_5	5.092	ε_8	-
ε_3	1.390	ε_6	3.561	ε_9	-

Figures 1 to 5 illustrate the very good agreement between the values in Tables 1 and 2 and the results calculated from eqs 9 to 11 using the values in Tables 3 and 4. In particular, Figures 1 to 3 refer to case (i), whereas Figures 4 and 5 refer to case (ii).
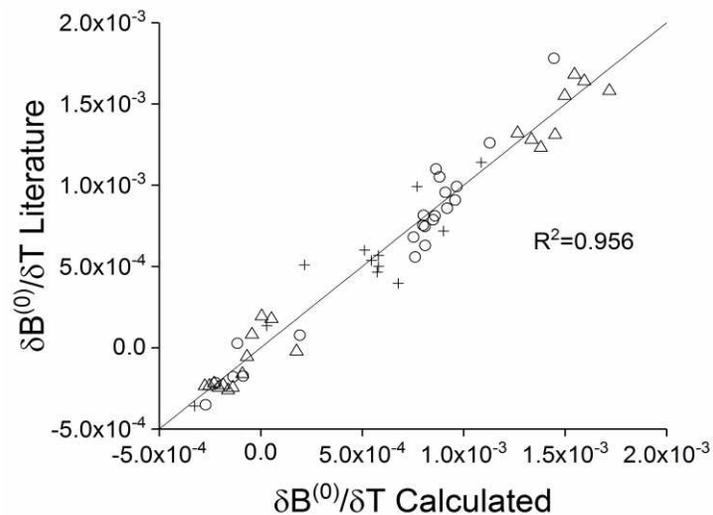
Figure 1. Parity plots comparing the values in Table 1 for $\left(\partial B_{MX}^{(0)}/\partial T\right)$ with those calculated through eq 10 for case (i) (dotted line: trendline, O: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).
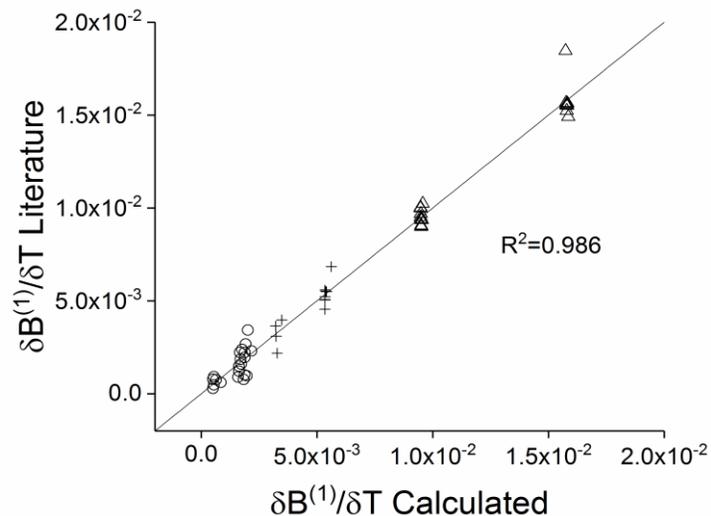
Figure 2. Parity plots comparing the values in Table 1 for $\left(\partial B_{MX}^{(1)} / \partial T \right)$ with those calculated through eq 11 for case (i) (dotted line: trendline, $\bigcirc$: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).
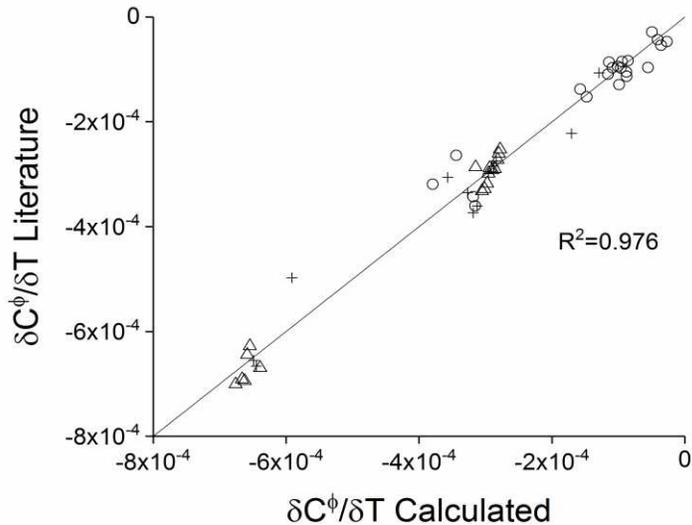
Figure 3. Parity plots comparing the values in Table 1 for $\left(\partial C_{MX}^{\varphi} / \partial T \right)$ with those calculated through eq 12 for case (i) (dotted line: trendline, $\bigcirc$: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).
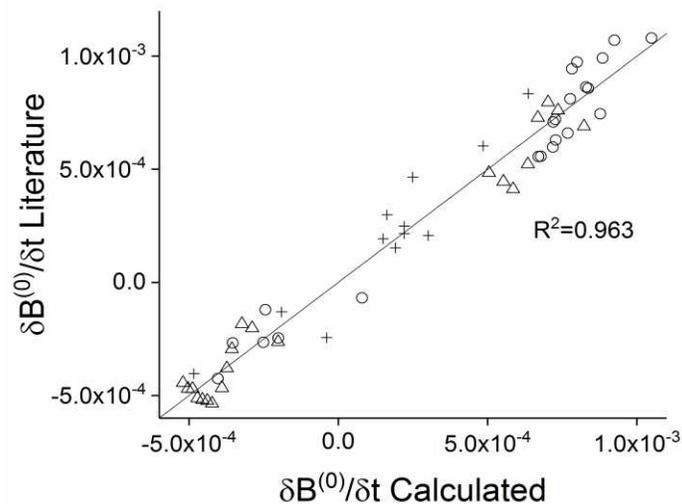
Figure 4. Parity plots comparing the values in Table 2 for $\left(\partial B_{MX}^{(0)}/\partial T\right)$ with those calculated through eq 10 for case (ii) (dotted line: trendline, $\bigcirc$: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).

Figure 5. Parity plots comparing the values in Table 2 for $\left(\partial B_{MX}^{(1)}/\partial T\right)$ with those calculated through eq 11 for case (ii) (dotted line: trendline, $\bigcirc$: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).

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DISCUSSION

Comparison Plots for the Apparent Relative Molal Enthalpy Using Data from Table 1 and 2 as well as the Parameters Calculated through Equations 9 to 11

In order to illustrate the agreement between the apparent relative molal enthalpies calculated through eqs 9 to 11 using the Constants and Power Terms from Tables 3 and 4 and the experimental data, comparison plots are provided in Figures 6 to 13. In particular, Figures 6 to 9 refer to case (i), whereas Figures 10 to 13 refer to case (ii). Also, the curves obtained by using the values in Tables 1 and 2 are included to demonstrate the quality of the fit. As can be seen in these figures, in all cases the apparent relative molal enthalpies calculated through eqs 9 to 11 are in a good agreement with the experimental data obtained from the literature. Indeed, the percentage difference between the calculated values and the experimental ones did not exceed 20% in the vast majority of the electrolytes analyzed.
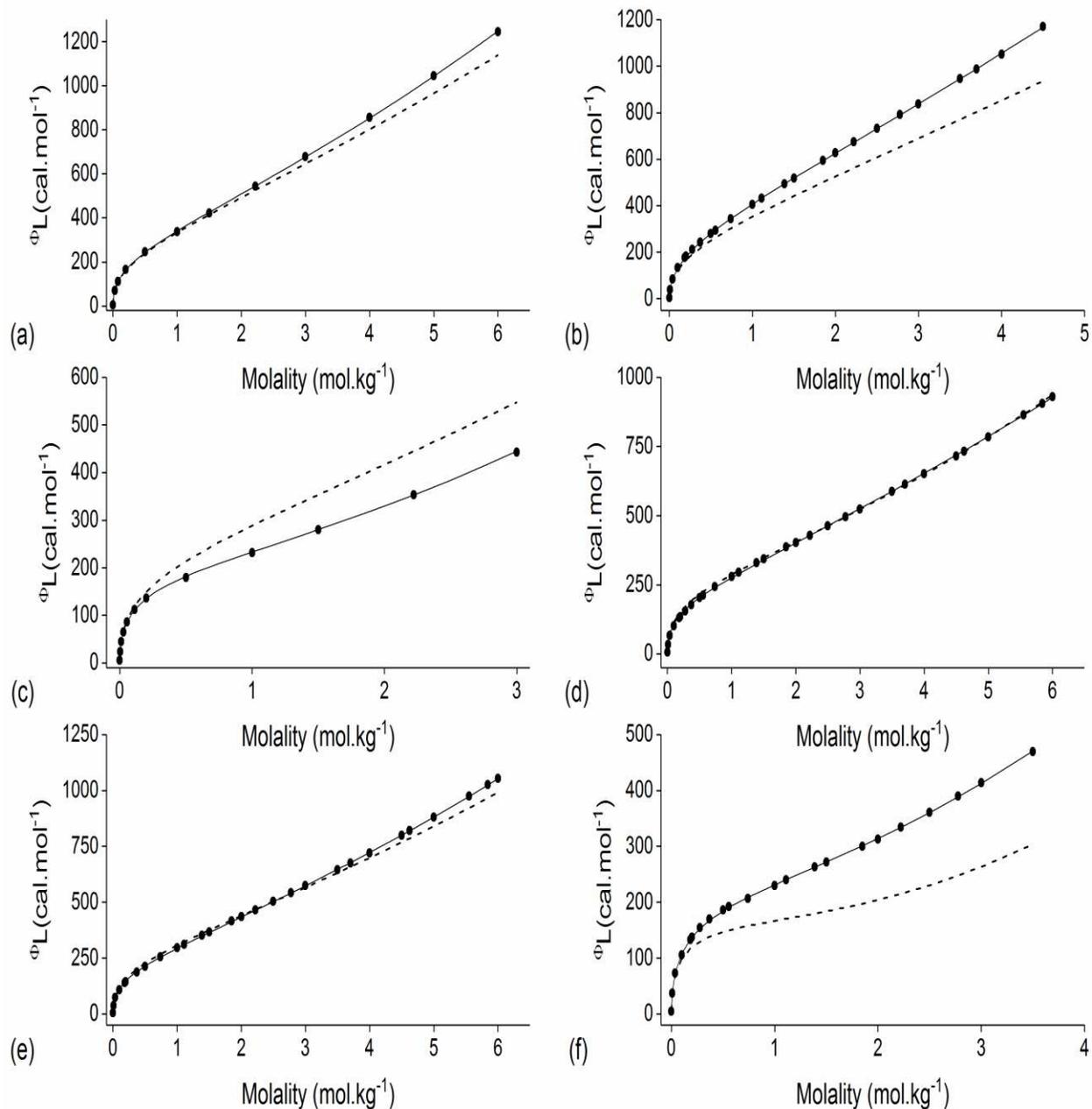
Figure 6. Comparison plots of 1-1 electrolytes considering kosmotrope/chaotrope combinations: (a) HBr, (b) HCl, (c) HI, (d) LiBr, (e) LiCl, (f) LiClO$_4$ for case (i) [●: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 1), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 1)].
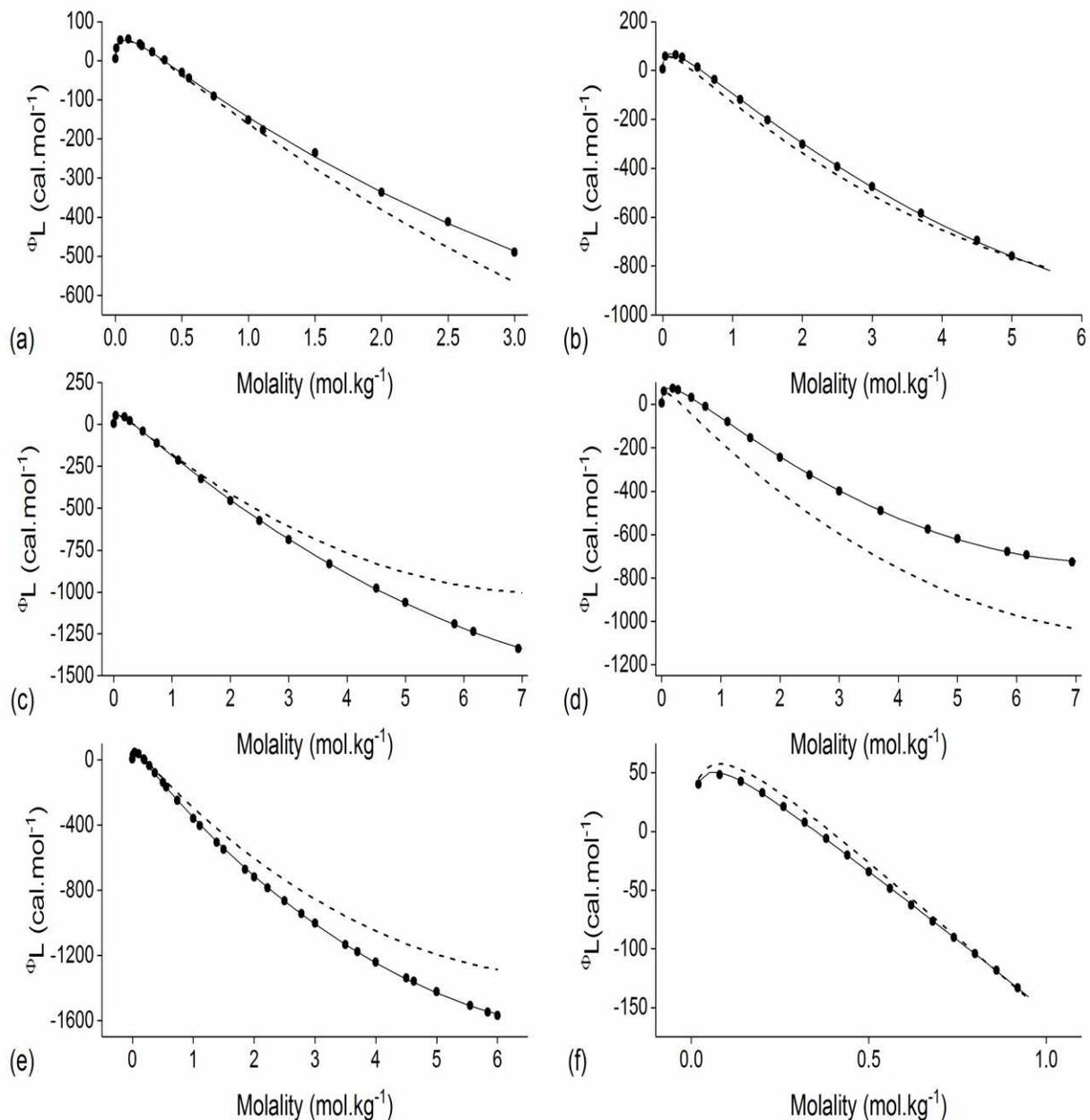
Figure 7. Comparison plots of 1-1 electrolytes considering chaotrope/chaotrope combinations: (a) CsCl, (b) KBr, (c) KI, (d) NaBr, (e) NaClO$_4$, (f) RbBr for case (i) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 1), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 1)].
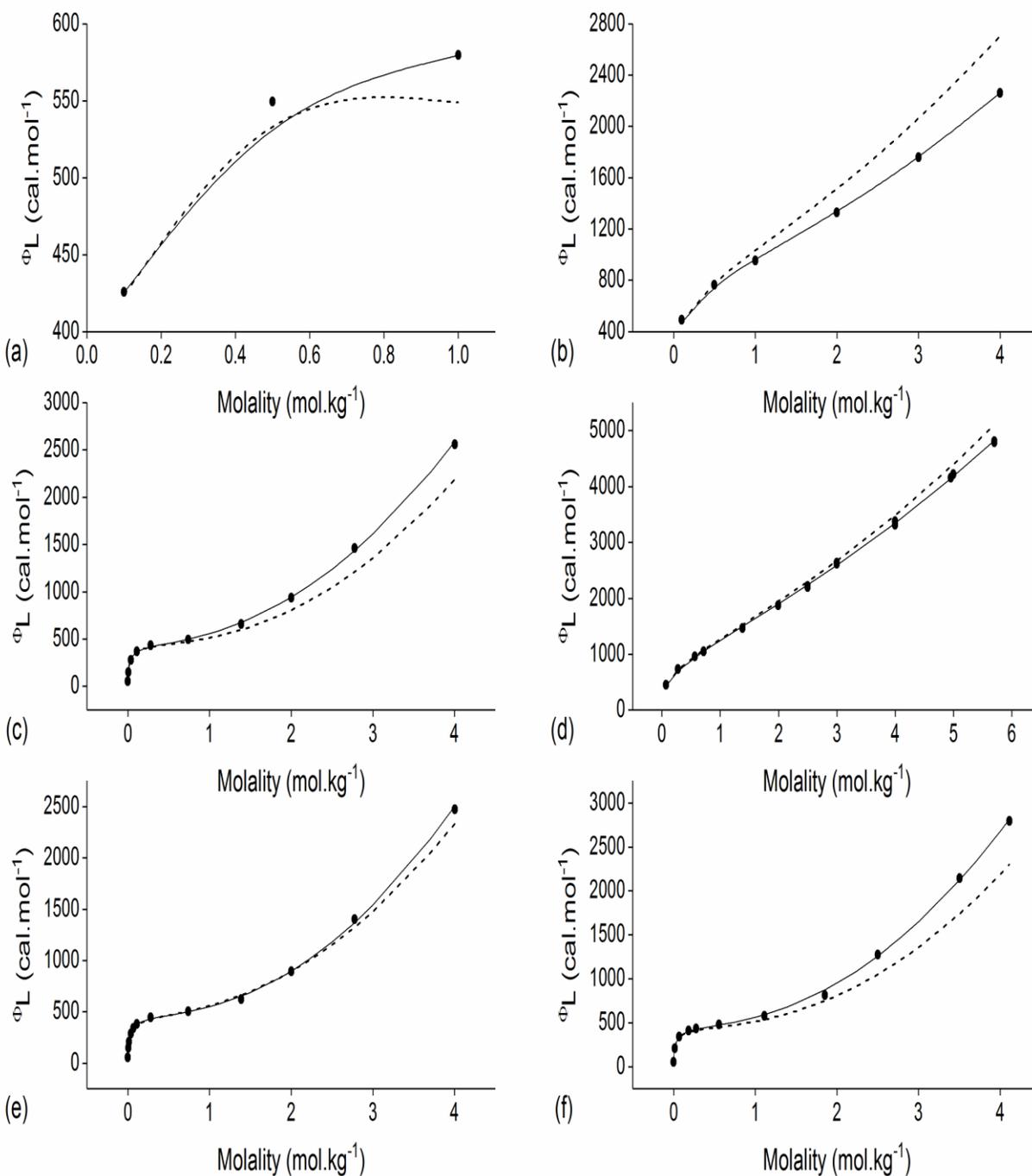
Figure 8. Comparison plots of 2-1 electrolytes: (a) $BaCl_2$, (b) $CaCl_2$, (c) $Co(ClO_4)_2$, (d) $MgCl_2$, (e) $Ni(ClO_4)_2$, (f) $Zn(ClO_4)_2$ for case (i) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 1), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 1)].
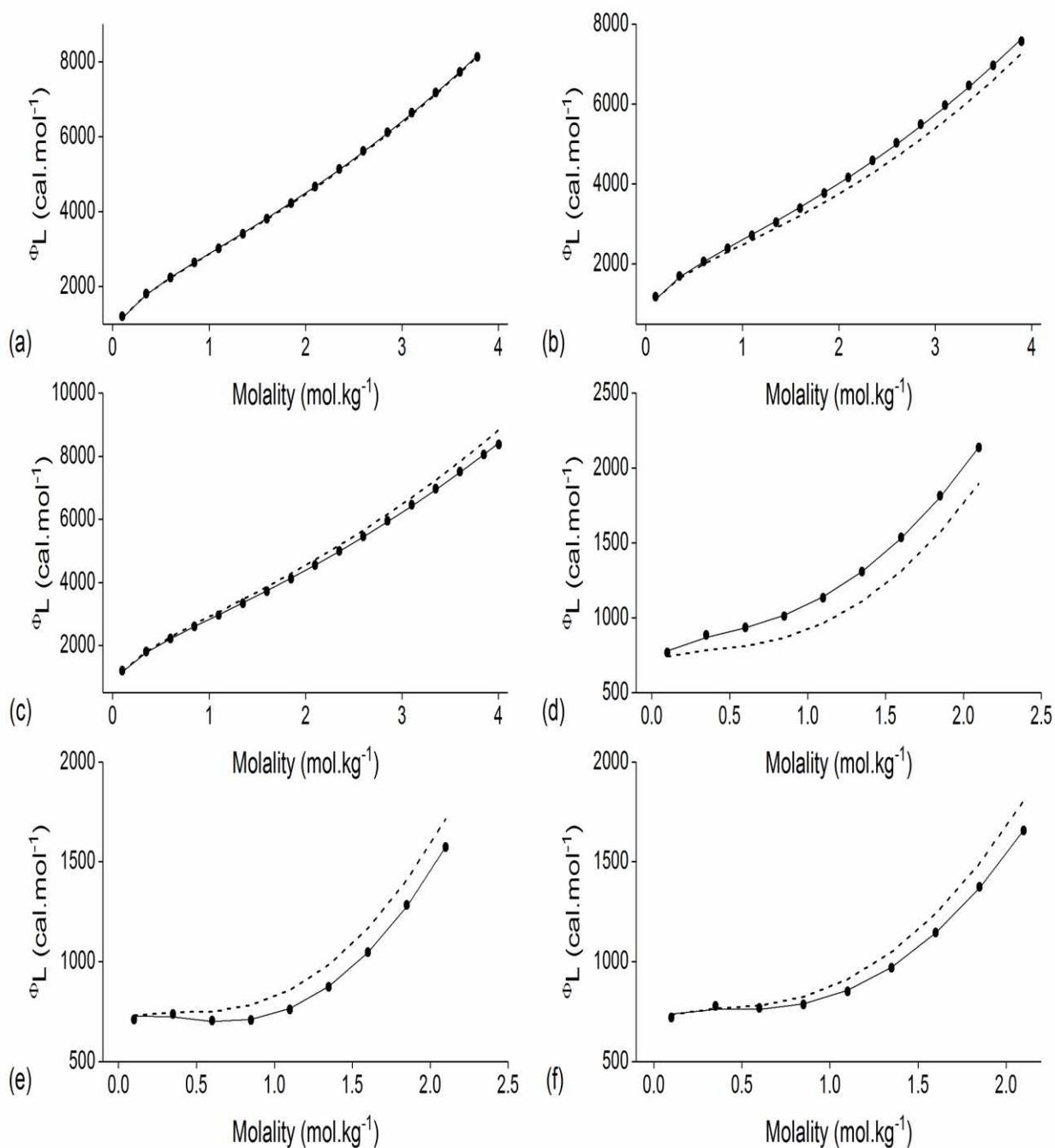
Figure 9. Comparison plots of 3-1 electrolytes: (a) $ErCl_3$, (b) $LaCl_3$, (c) $YbCl_3$, (d) $Gd(ClO_4)_3$, (e) $Nd(ClO_4)_3$, (f) $Sm(ClO_4)_3$ for case (i) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 1), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 1)].

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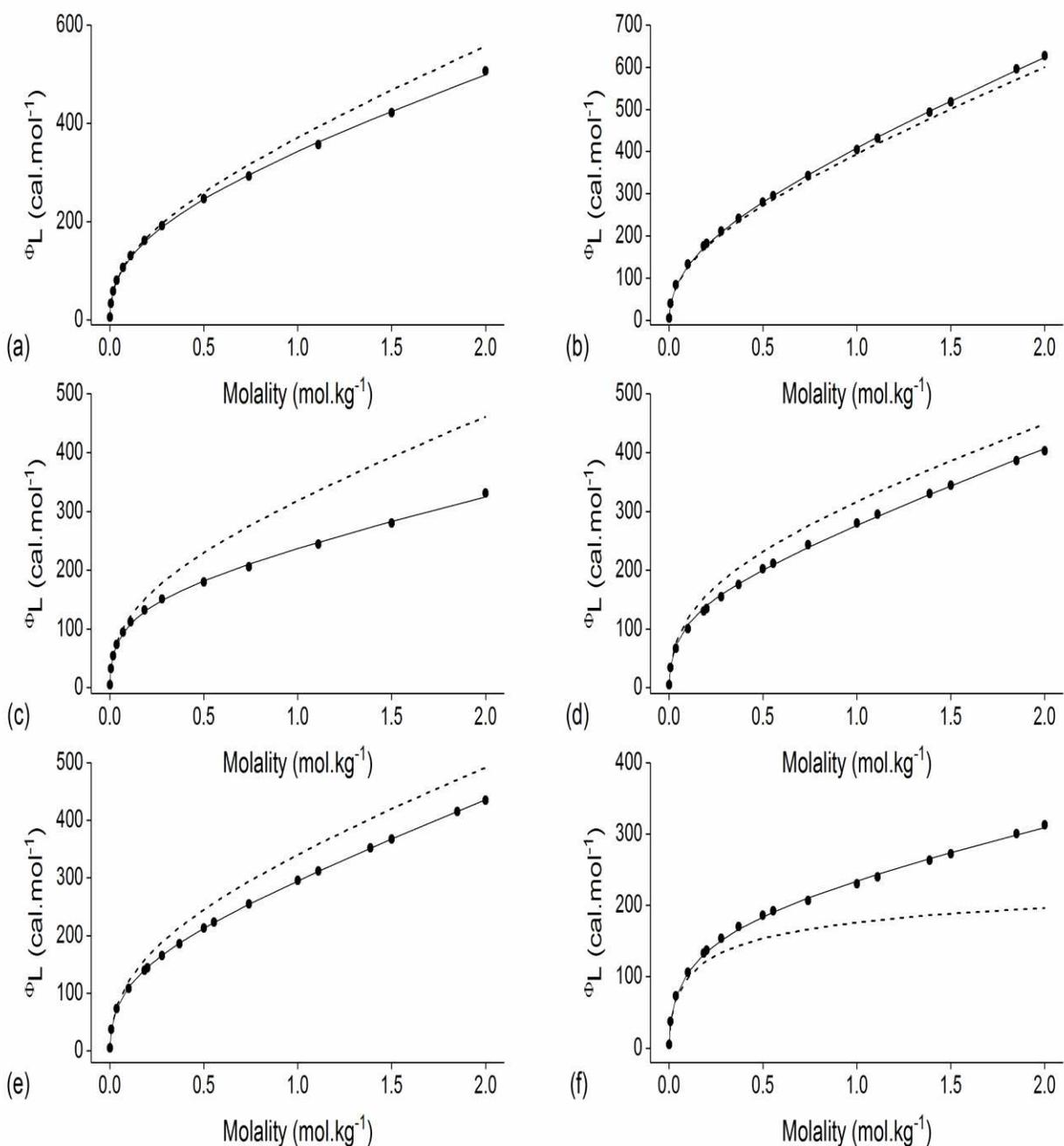
Figure 10. Comparison plots of 1-1 electrolytes considering kosmotrope/chaotrope combinations: (a) HBr, (b) HCl, (c) HI, (d) LiBr, (e) LiCl, (f) LiClO$_4$ for case (ii) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 2), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 2)].
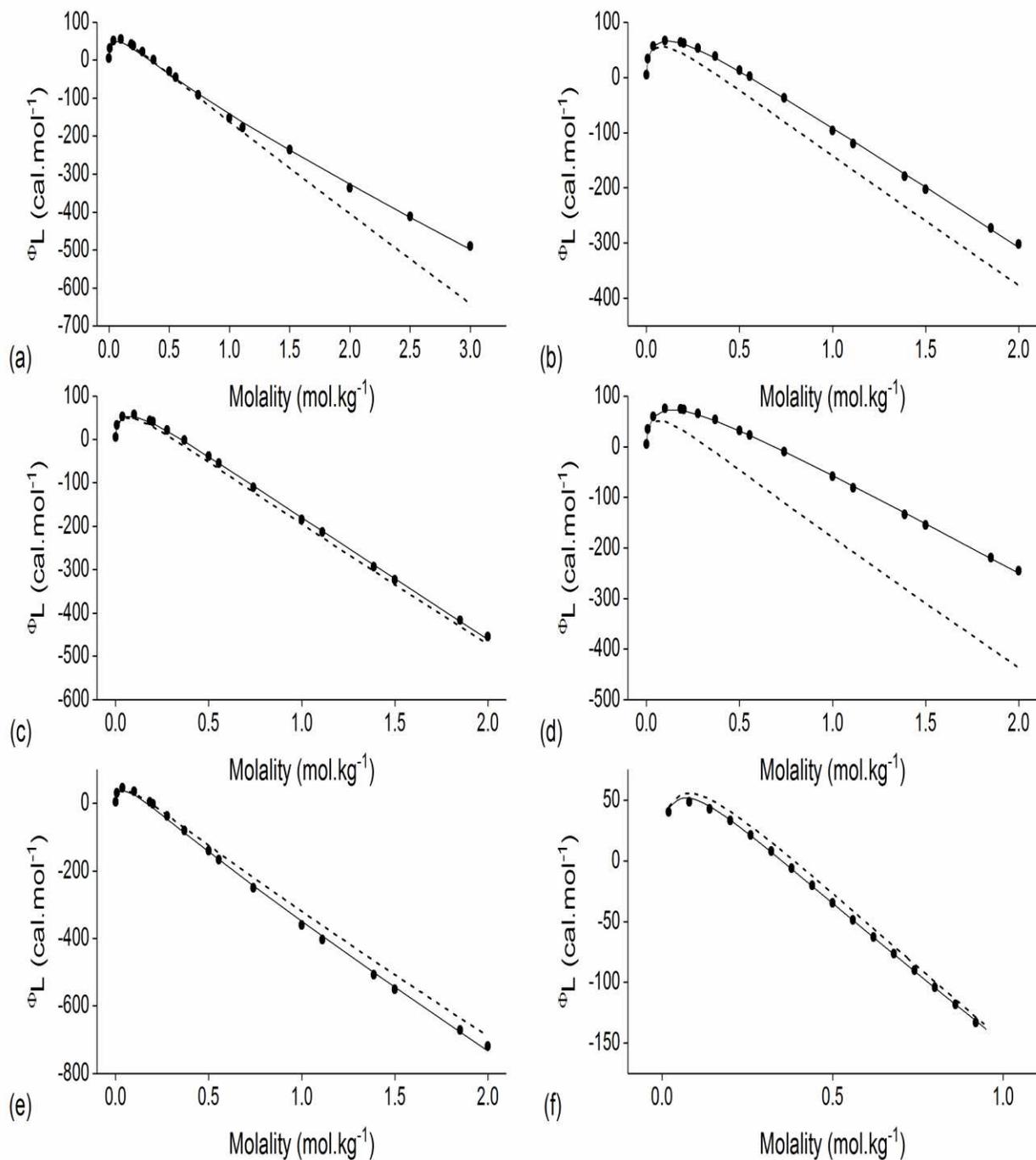
Figure 11. Comparison plots of 1-1 electrolytes considering chaotrope/chaotrope combinations: (a) CsCl, (b) KBr, (c) KI, (d) NaBr, (e) NaClO$_4$, (f) RbBr for case (ii) [●: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 1), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 1)].
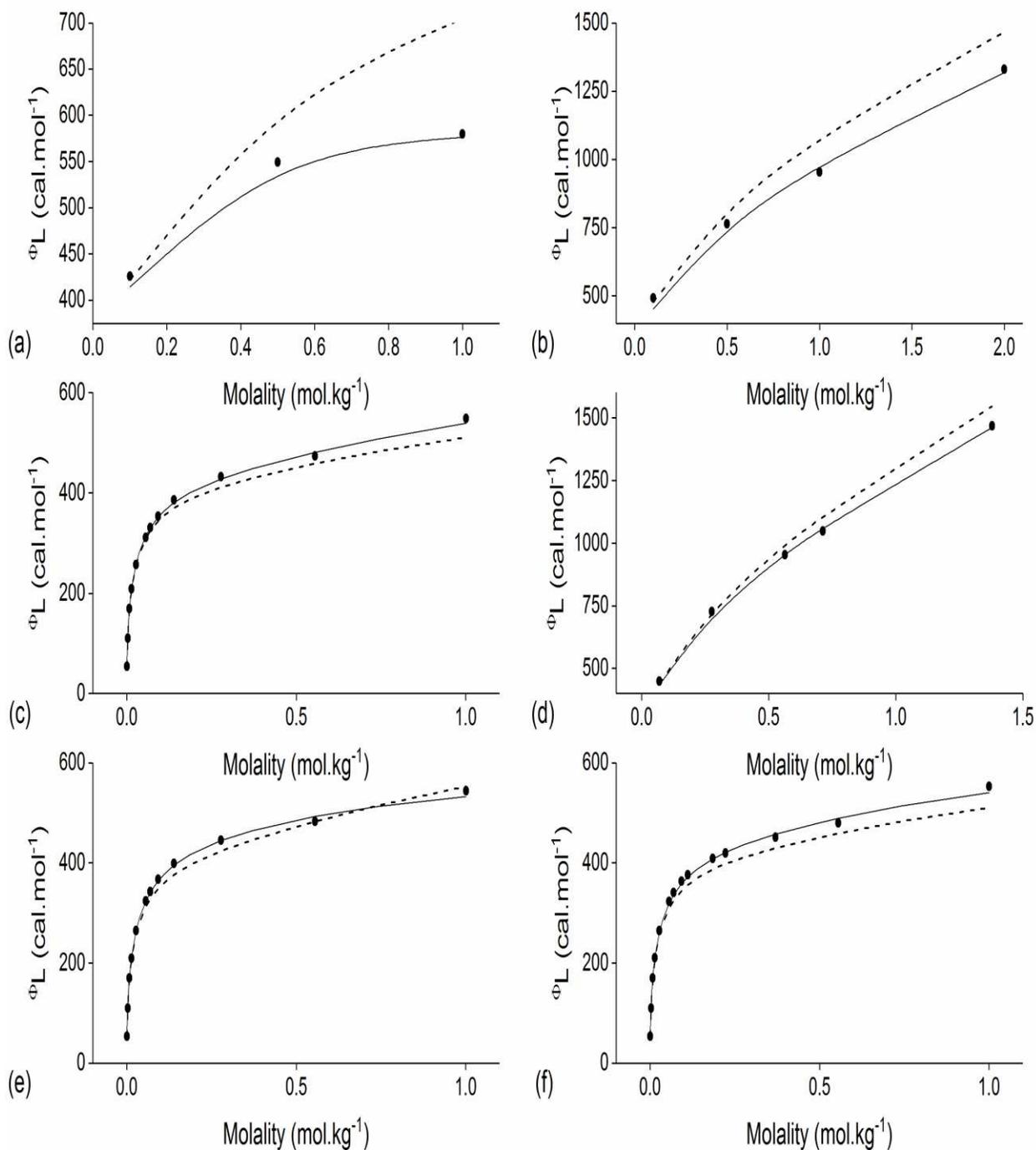
Figure 12. Comparison plots of 2-1 electrolytes: (a) $BaCl_2$, (b) $CaCl_2$, (c) $Co(ClO_4)_2$, (d) $MgCl_2$, (e) $Ni(ClO_4)_2$, (f) $Zn(ClO_4)_2$ for case (ii) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 2), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 2)].
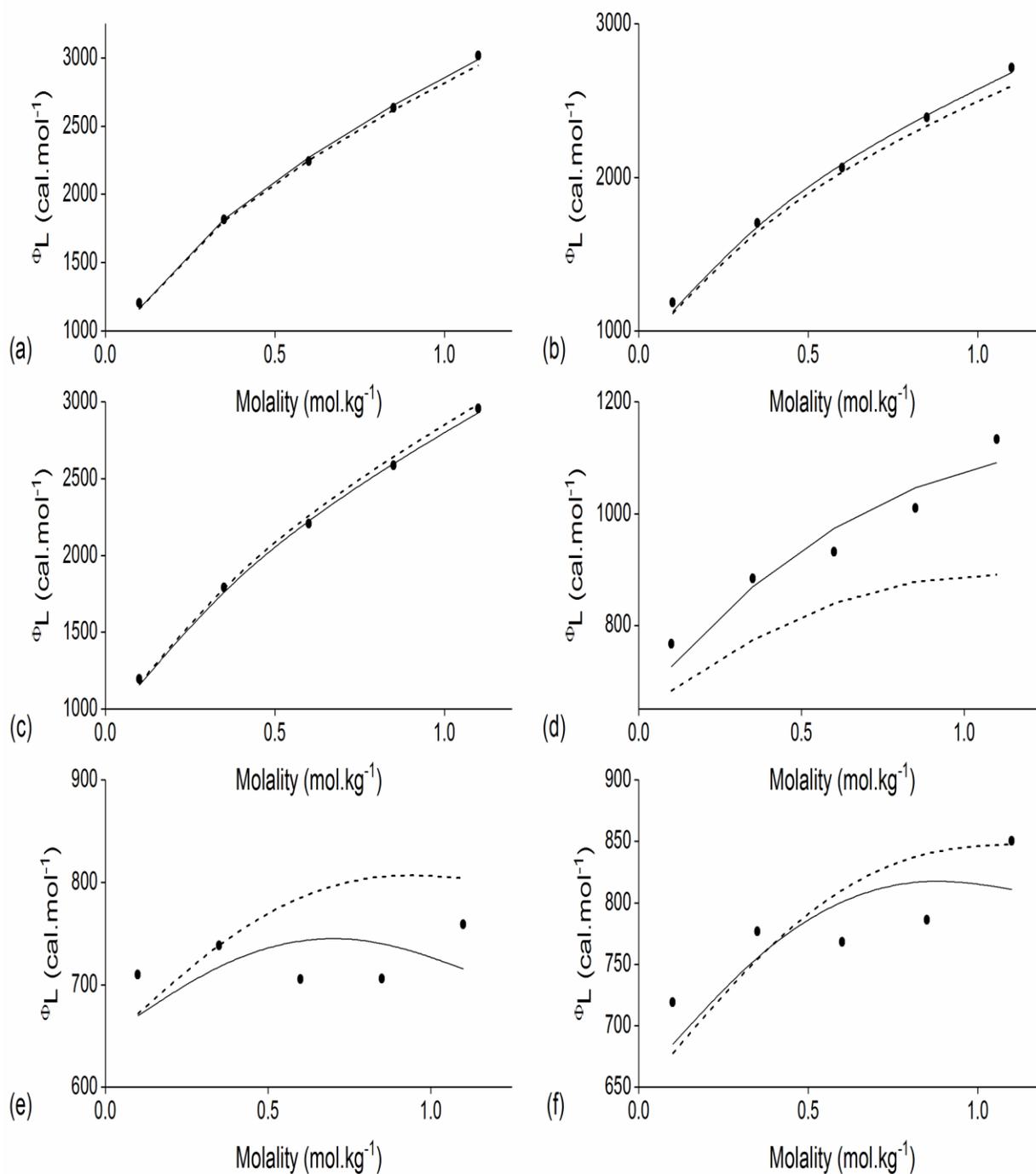
Figure 13. Comparison plots of 3-1 electrolytes: (a) $ErCl_3$, (b) $LaCl_3$, (c) $YbCl_3$, (d) $Gd(ClO_4)_3$, (e) $Nd(ClO_4)_3$, (f) $Sm(ClO_4)_3$ for case (ii) [•: Experimental data for the apparent relative molal enthalpy from the literature (see references in Table 2), dashed line: calculated through eqs 9 to 11, solid line: calculated through the parameters in Table 2)].

Comparison Plots Involving the Activity and Osmotic Coefficients Calculated through Equations 12 to 14 and the Experimental Data obtained from the Literature

As mentioned before in the results section, eqs 12 to 14 are simpler than the equations that are normally used in the literature to describe the temperature dependence of the virial coefficients in the Pitzer equations, including those developed by Silvester and Pitzer[2] as well as those derived by Criss and Millero[14]. However, Figures 14 to 18 related to case (i) as well as Figures 19 to 23 related to case (ii) show that these equations do a very good job at predicting the activity and osmotic coefficient up to 150 °C, although these simpler equations may not be applicable for electrolytes with a high tendency to form ion pairs at non-ambient temperatures, such as electrolytes formed by chaotrope/chaotrope combinations. For example, the temperature dependence of the osmotic coefficients for KCl solutions investigated by Holmes et al.[3] is very irregular, with the curve at 298.15 K being located between the curve at 382 K and the curve at 413 K. On the other hand, in this same study[3] it is easy to note that the osmotic coefficients for $CaCl_2$ and $MgCl_2$ change linearly with the temperature, and this reinforces the assumption that the electrolytes with lower tendency to form ion pairs tend to have a more linear variation of their properties with the temperature.
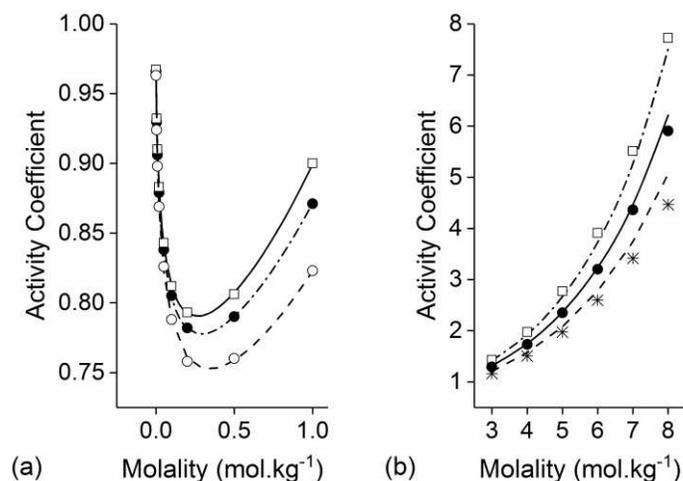
Figure 14. Comparison plots of 1-1 electrolytes: (a) HBr, (b) HCl [Symbols: experimental activity coefficients obtained from the literature[44–46] for case (i) (□: 0 °C, •: 25 °C, ∗: 50 °C, ○: 60 °C); Lines: calculated activity coefficients using eqs 12 to 14 (dash dotted line: 0 °C, solid line[36]: 25 °C, dashed line: 50 °C, dotted line: 60 °C)].
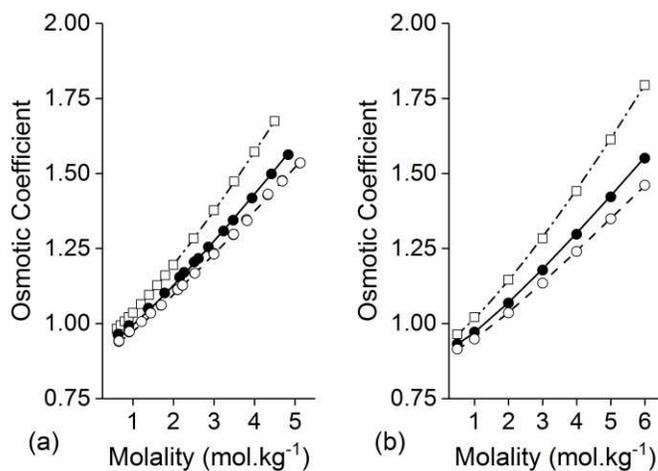
Figure 15. Comparison plots of 1-1 electrolytes: (a) LiBr, (b) LiCl [Symbols: experimental osmotic coefficients obtained from the literature[9,11,46] for case (i) (□: 25 °C, •: 109.81 °C, ○: 140.21 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line: 25 °C, solid line[36]: 109.8 °C, dashed line: 140.2 °C)].
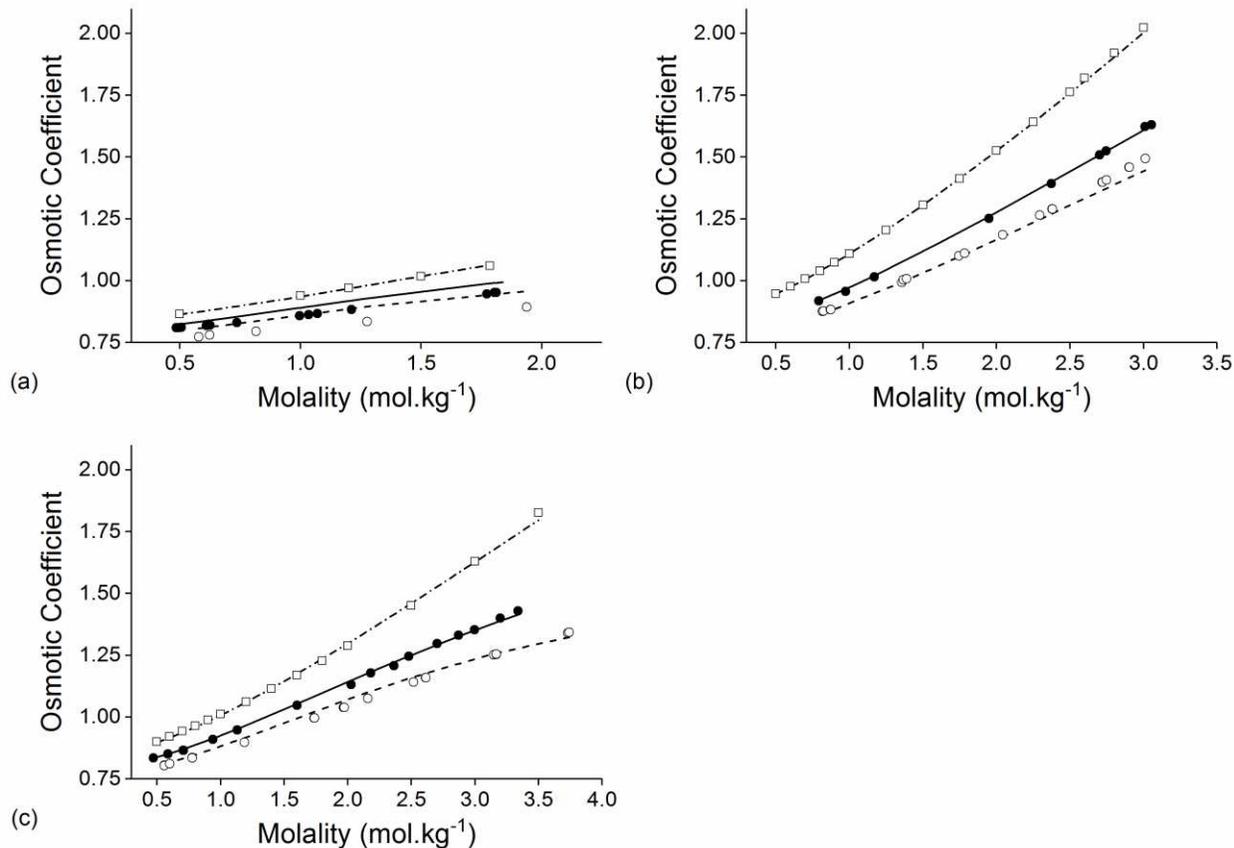
Figure 16. Comparison plots of 2-1 electrolytes for case (i): (a) $BaCl_2$, (b) $MgCl_2$, (c) $SrCl_2$ [Symbols: experimental osmotic coefficients obtained from the literature[3,5,47] (□: 25 °C, ●: 109.8 °C, ○: 140.2 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[36]: 25 °C, solid line: 109.8 °C, dashed line: 140.2 °C)].
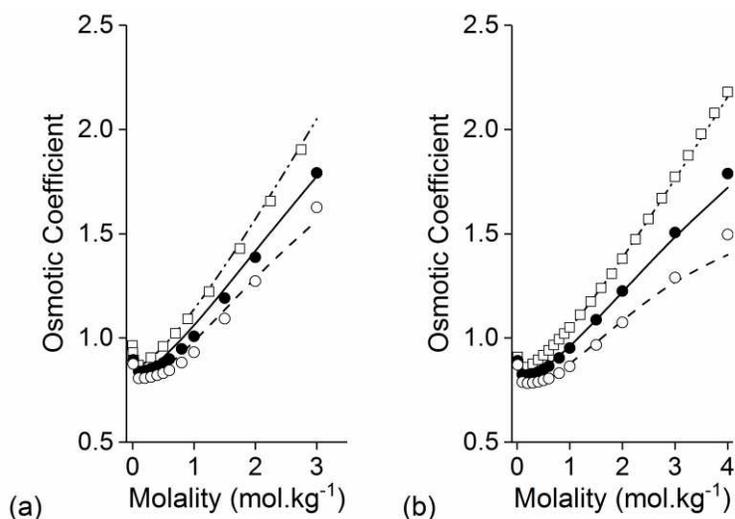
Figure 17. Comparison plots of 2-1 electrolytes for case (i): (a) CaBr$_2$, (b) CaCl$_2$ [Symbols: experimental osmotic coefficients obtained from the literature[47–49] (□: 25 °C, •: 100 °C, ○: 150 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[36]: 25 °C, solid line: 100 °C, dashed line: 150 °C)].
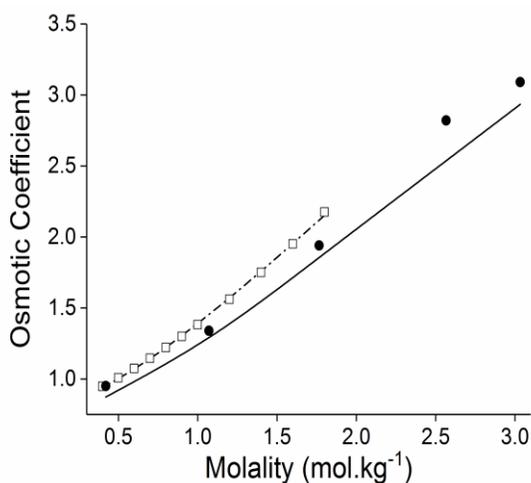
Figure 18. Comparison plots of 3-1 electrolytes[50,51] for case (i): AlCl$_3$ [Symbols: experimental osmotic coefficients obtained from the literature (□: 25 °C, •: 70.4 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[36]: 25 °C, solid line: 70.4 °C)].
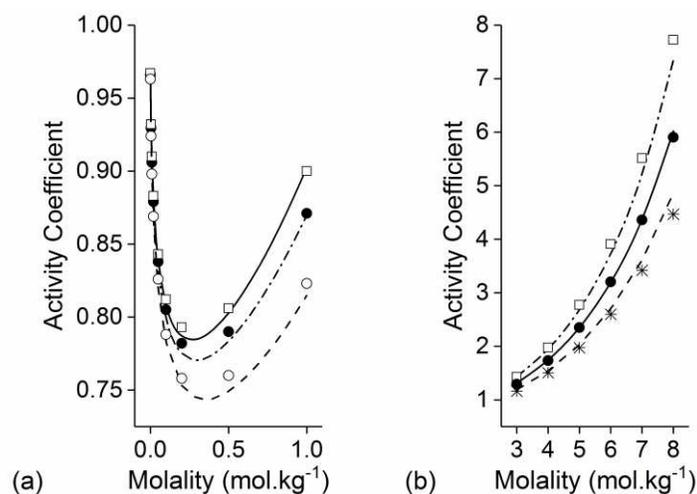
Figure 19. Comparison plots of 1-1 electrolytes: (a) HBr, (b) HCl [Symbols: experimental activity coefficients obtained from the literature[44–46] for case (ii) (□: 0 °C, •: 25 °C, ∗: 50 °C, ○: 60 °C); Lines: calculated activity coefficients using eqs 12 to 14 (dash dotted line: 0 °C, solid line[38]: 25 °C, dashed line: 50 °C, dotted line: 60 °C)].
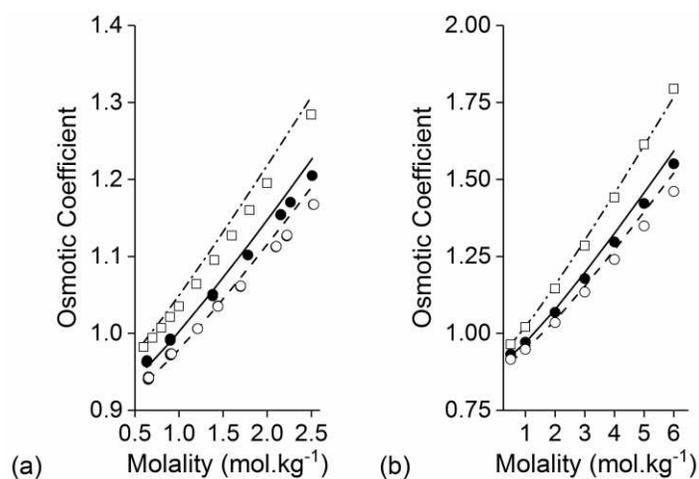
Figure 20. Comparison plots of 1-1 electrolytes: (a) LiBr, (b) LiCl [Symbols: experimental osmotic coefficients obtained from the literature[9,11,46] for case (ii) (□: 25 °C, •: 109.81 °C, ○: 140.21 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line: 25 °C, solid line[38]: 109.8 °C, dashed line: 140.2 °C)].
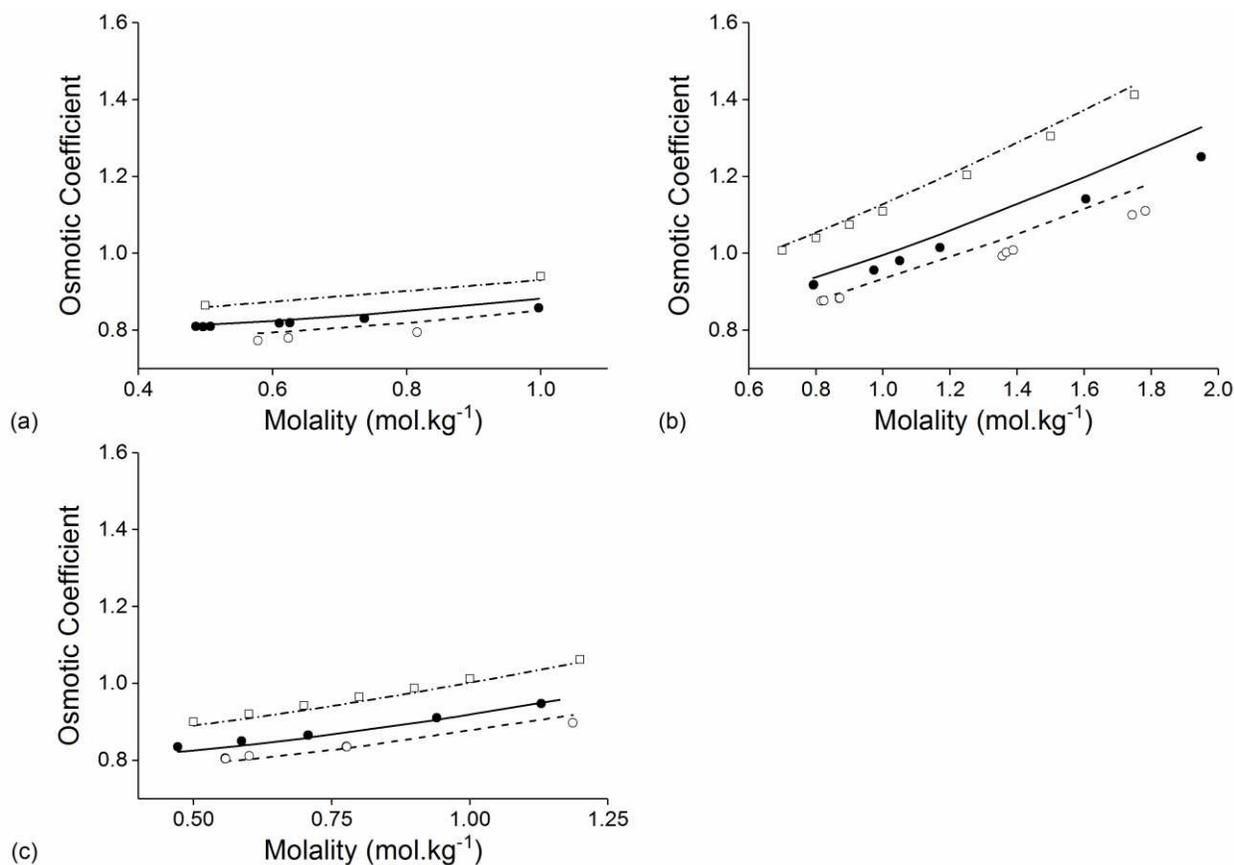
Figure 21. Comparison plots of 2-1 electrolytes for case (ii): (a) $BaCl_2$, (b) $MgCl_2$, (c) $SrCl_2$ [Symbols: experimental osmotic coefficients obtained from the literature[3,5,47] ($\square$: 25 °C, $\bullet$: 109.8 °C, $\circ$: 140.2 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[38]: 25 °C, solid line: 109.8 °C, dashed line: 140.2 °C)].
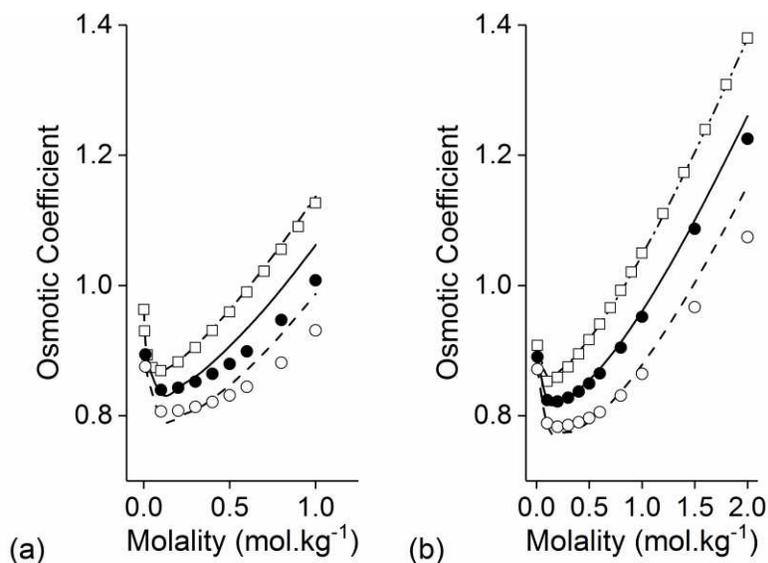
Figure 22. Comparison plots of 2-1 electrolytes for case (ii): (a) CaBr$_2$, (b) CaCl$_2$ [Symbols: experimental osmotic coefficients obtained from the literature[47–49] (□: 25 °C, •: 100 °C, ○: 150 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[38]: 25 °C, solid line: 100 °C, dashed line: 150 °C)].
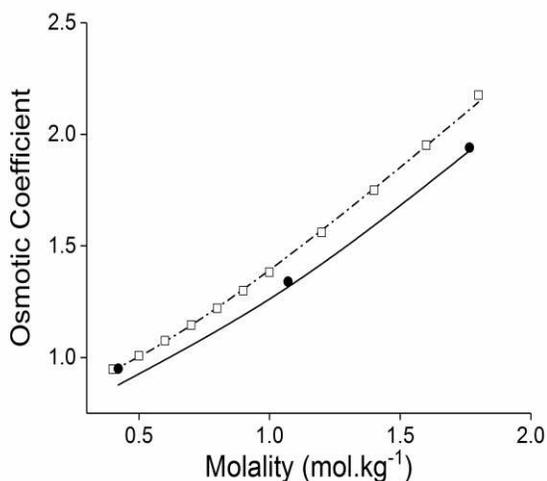
Figure 23. Comparison plots of 3-1 electrolytes[50,51] for case (ii): AlCl$_3$ [Symbols: experimental osmotic coefficients obtained from the literature (□: 25 °C, •: 70.4 °C); Lines: calculated osmotic coefficients using eqs 12 to 14 (dash dotted line[38]: 25 °C, solid line: 70.4 °C)].

The percentage differences between all the experimental values and all the calculated values shown in figures 14 to 23 at all the temperatures analyzed can be visualized in figures 24 and 25 for case (i) and case (ii), respectively. As can be seen, the accuracy of the estimations was within 5% in most cases, and this confirms that eqs 12 to 14 are very efficient at predicting the values of the osmotic and activity coefficients at temperatures up to 150 °C.
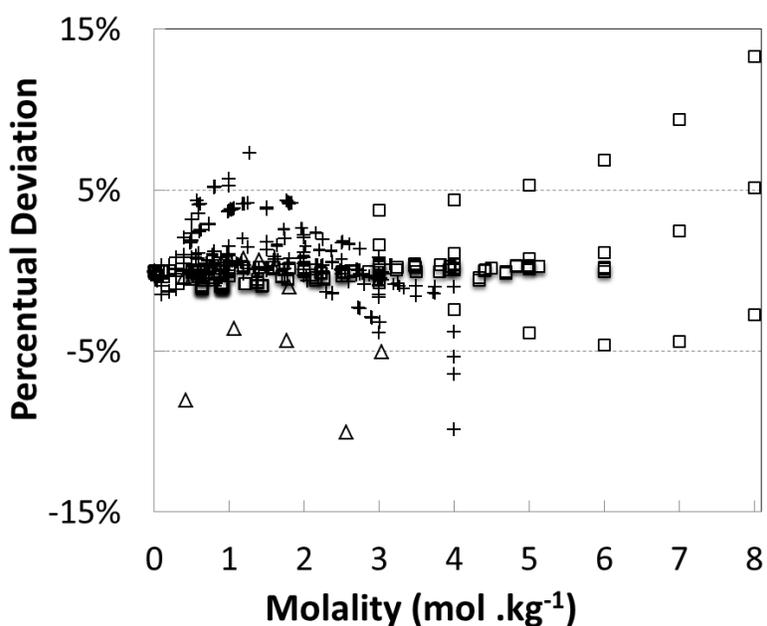
Figure 24. Percentage difference between all the experimental and the calculated values from figures 14 to 18 at all the temperatures analyzed for case (i) ($\square$: 1-1 electrolytes, $+$: 2-1 electrolytes, $\triangle$: 3-1 electrolytes).
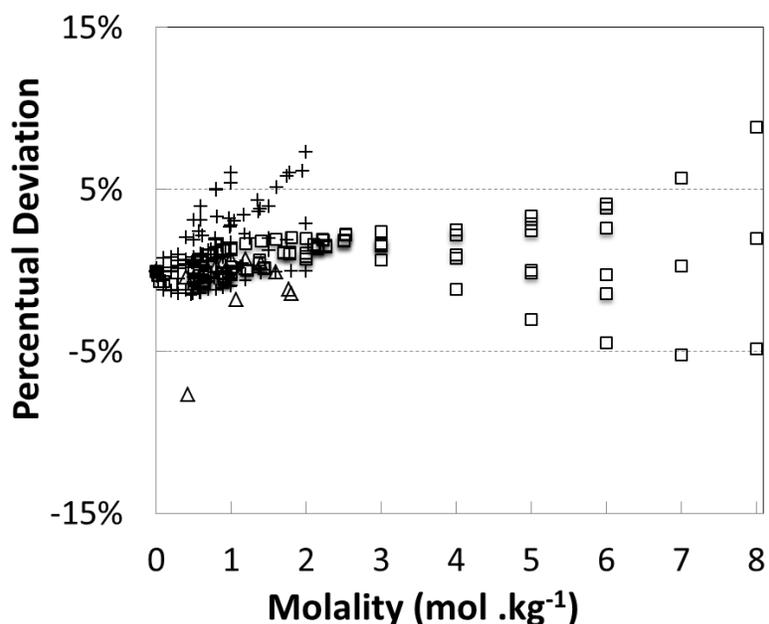
Figure 25. Percentage difference between all the experimental and the calculated values from figures 19 to 23 at all the temperatures analyzed for case (ii) (□: 1-1 electrolytes, +: 2-1 electrolytes, △: 3-1 electrolytes).

Pressure Effects

The effect of pressure on the activity coefficients has not been investigated in this study because the relevant data is very scarce in the literature. All the activity and osmotic coefficients used in this study were taken at pressures equal to or lower than the saturation pressure.

Predicting the Properties of the Electrolytes that were not Included in Tables 1 and 2

Both CaBr$_2$ in figures 17 and 22 and AlCl$_3$ in figures 18 and 23 are examples of electrolytes that were not included in Tables 1 and 2 due to the lack of data for the apparent relative molal enthalpy at 25 °C, but could be accurately described by the eqs 12 to 14. This demonstrates that

eqs 12 to 14 are very reliable and efficient to estimate the values of the virial coefficients at different temperatures for electrolytes with lower tendency to form ion pairs.

Predicting the Properties of the Chaotrope/Chaotrope Combinations

In contrast to kosmotrope/chaotrope combinations, electrolytes containing chaotrope/chaotrope combinations could not be accurately predicted using eqs 12 to 14 at non-ambient temperatures. In this case, more complex equations are required, probably involving the second derivative of the virial parameters in the Pitzer equations, in a similar manner to Criss and Millero[14], which predict the osmotic and activity coefficients of aqueous solutions containing NaCl using both the first and the second derivative of the virial parameters in the Pitzer equations.

Comparison between Calculated and Literature Values for HCl Considering Case (i) and Case (ii)

As illustrated in Figures 14b and 19b, the agreement between the calculated and the literature values for HCl is very good. However, it is important to note that the experimental data on the activity coefficients for HCl[45] are very accurate, since these data were obtained from cell potential difference, and thus it is clear that the full precision of these data cannot be obtained from the models developed in this study, which are based on correlations obtained from calorimetric data. In this context, Tables 5 and 6 are included in order to allow a more detailed comparison between the experimental data on the activity coefficients[45] and the calculated ones. As can be seen in these tables, these percentage errors can be as large as 13% at high molalities, but they are relatively small at molalities less than 5 mol.kg^{-1}. This illustrates the good consistency of the models developed in this study.

Table 5. Comparison between calculated and literature data for HCl at 50 °C for case (i).

molality (mol.kg^{-1})	Calculated Activity Coefficients	Literature Activity Coefficients[45]	Percentage deviation
3	1.205	1.161	3.8%
4	1.571	1.505	4.4%
5	2.077	1.973	5.3%
6	2.776	2.598	6.9%
7	3.737	3.416	9.4%
8	5.061	4.467	13.3%

Table 6. Comparison between calculated and literature data for HCl at 50 °C for case (ii).

molality (mol.kg^{-1})	Calculated Activity Coefficients	Literature Activity Coefficients[45]	Percentage deviation
3	1.189	1.161	2.4%
4	1.542	1.505	2.5%
5	2.029	1.973	2.9%
6	2.697	2.598	3.8%
7	3.611	3.416	5.7%
8	4.862	4.467	8.8%

CONCLUSIONS

The temperature derivatives of the virial parameters in the Pitzer equations were fitted to the experimental data of the apparent relative molal enthalpy obtained from the literature at 25 °C, and then these temperature derivatives were correlated with the properties of the solutions for electrolytes that are unlikely to form ion pairs. In particular, these correlations obtained were very strong, and this is confirmed by the high coefficients of determination achieved, with $R^2 \geq 0.95$ in all cases. Then, these correlating equations were used to predict both the apparent relative molal enthalpies at 25 °C and the activity and osmotic coefficients up to 150 °C, considering only the electrolytes with a lower tendency to form ion pairs. Finally, comparison

plots were provided to show the remarkable agreement between the predictions obtained through the correlating equations and the experimental data obtained from the literature.

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ABBREVIATIONS

Latin Symbols

A_H, Debye Huckel coefficient for enthalpy

B'_{MX}, temperature derivative of the second virial coefficient

$B^{(0)}_{MX}$, $B^{(1)}_{MX}$, second virial coefficients representing short-range binary interactions

$B^{(0)}_{MX\,R}$, $B^{(1)}_{MX\,R}$, second virial coefficients representing short-range binary interactions at a temperature T_R

$B^{(0)}_{MX\,T}$, $B^{(1)}_{MX\,T}$, second virial Coefficients representing short-range binary interactions at a temperature T

C'_{MX}, temperature derivative of the third virial coefficient

C^{φ}_{MX}, third virial coefficient representing short-range interaction of triplets

$C^{\varphi}_{MX\,R}$, third virial coefficient representing short-range interaction of triplets at a temperature T_R

$C^{\varphi}_{MX\,T}$, third virial coefficient representing short-range interaction of triplets at a temperature T

I, ionic strength

m, molality

n, number of experimental data points

r_M, ionic radii for kosmotrope cations / hydrated radii for chaotrope cations

r_X, ionic radii for kosmotrope anions / hydrated radii for chaotrope anions

$S(\Phi_L)$, objective function

T, temperature

T_R, temperature of reference (25 °C)

z_M, charge of the cation

z_X, charge of the anion

Greek Symbols

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

δ, standard deviation of the fit

ε_i, power terms of the equations that correlate the apparent relative molal enthalpy with the ionic properties of the solution

κ_i, constants of the equations that correlate the apparent relative molal enthalpy with the ionic

ν, number of cationic and anionic species

ν_M, number of cationic species

ν_X, number of anionic species

Φ_L, apparent relative molal enthalpy

Subscripts

M, cation

X, anion

Superscripts

calc, calculated

exp, experimental

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