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Analysis of Some Electrolyte Models including Their Ability to Predict the Activity Coefficients of Individual Ions

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Short Introduction

This Supporting Information consists of three parts: Experimental Data Collection (Section A); Modelling Parameters (Section B); Basic Thermodynamic Equations (Section C).

Section A. Experimental Data Collection

Table S1. Summary of experimental studies for activity coefficients of individual ions.

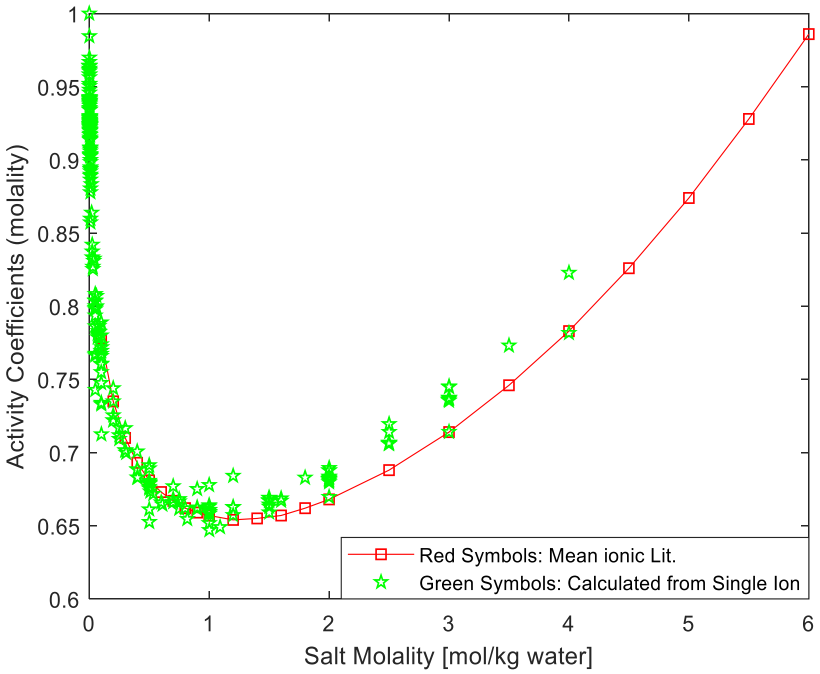
Salt	Cation	Anion	Molality	Ref
HCl	- [a]	X	0.003-2.0	[1]
	X	X	0.0005-0.506	[2]
NaCl	-	X	0.1-4.0	[3]
	X	X	0.001-3.0	[4]
	X	X	0.01632-1.091	[5]
	X	X	0.1-5.0	[6]
	X	X	0.003-4.0	[1]
	X	X	0.002-3.0	[7]
	X	X	0.0011-3.0004	[8]
	X	X	0.001-2.996	[9]
KCl	-	X	0.1-4.0	[3]
	X	X	0.001-3.0	[4]
	X	X	0.1-4.0	[6]
	X	X	0.003-4.0	[1]
	X	X	0.002-3.0	[7]
	X	X	0.002-3.0	[10]
	X	X	0.001-3.001	[9]
$CaCl_2$	-	X	0.1-4.0	[11]
	X	X	0.001-0.955	[4]

	-	X	0.01-3.0	[1]
$MgCl_2$	-	X	0.1-4.0	[11]
	-	X	0.01-3.0	[1]
LiCl	-	X	0.1-4.0	[3]
	-	X	0.01-3.0	[1]
CsCl	-	X	0.1-4.0	[3]
	-	X	0.003-3.0	[1]
$SrCl_2$	-	X	0.1-3.0	[11]
$BaCl_2$	-	X	0.1-2.0	[11]
	-	X	0.01-1.4	[1]
NH_4Cl	-	X	0.1-4.0	[3]
	-	X	0.002-3.0	[7]
Na_2SO_4	-	X	0.1-2.0	[12]
	X	-[b]	0.01-3.0	[1]
K_2SO_4	X	-	0.01-0.69	[1]
NaBr	-	X	0.1-4.0	[13]
	X	X	0.05532-1.2724	[5]
	X	X	0.1-5.0	[6]
	X	X	0.005-5.0	[1]
	X	X	0.002-3.0	[7]
KBr	-	X	0.1-4.0	[13]
	X	X	0.01-1.5	[1]

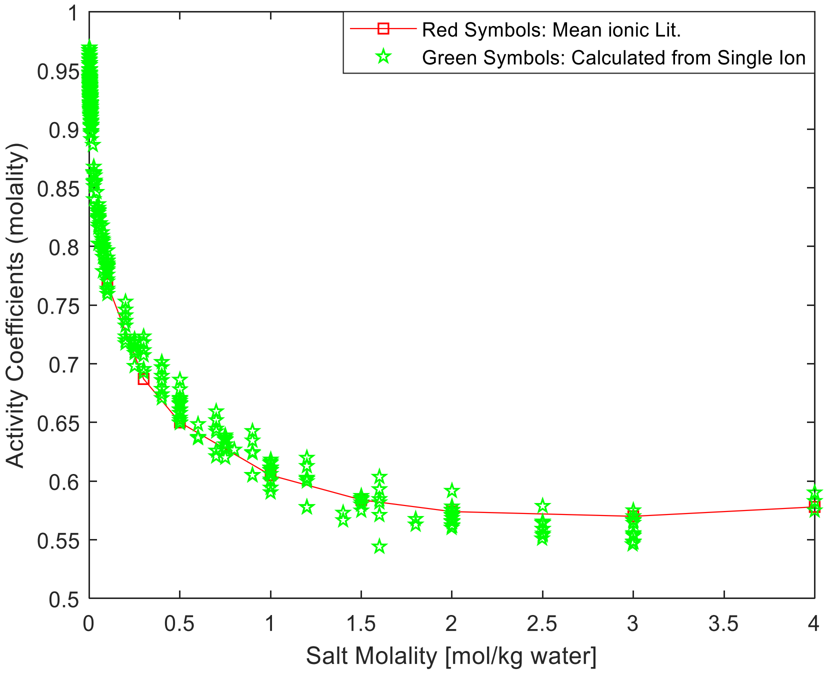
LiBr	-	X	0.1-4.0	[13]
	-	X	0.01-3.0	[1]
CsBr	-	X	0.1-4.0	[13]
$CaBr_2$	-	X	0.01-3.0	[1]
$MgBr_2$	-	X	0.01-3.0	[1]
$BaBr_2$	-	X	0.01-2.3	[1]
NaF	X	X	0.0214-0.9834	[5]
	X	X	0.01-1.0	[1]
KF	X	X	0.01-3.0	[1]
NaOH	X	-	0.002-2.0	[1]
KOH	X	-	0.002-1.9	[1]
$NaNO_3$	X	X	0.004-3.5	[1]
KNO_3	-	X	0.002-3.5	[1]
$LaCl_3$	X	X	0.1-1.4	[14]

a. only activity coefficients of anion are measured;

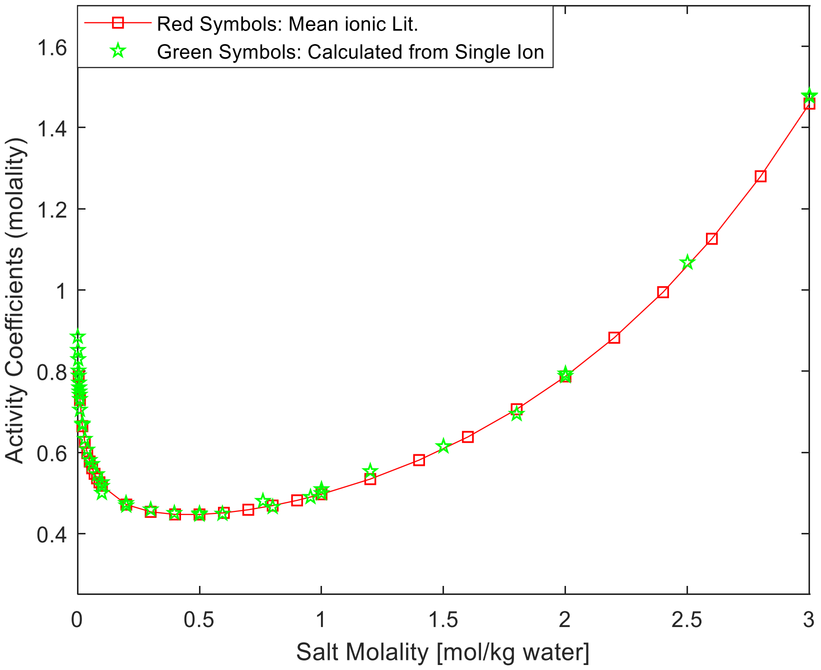
b. only activity coefficients of cation are measured.


Activity Coefficients (molality)
Salt Molality [mol/kg water]
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0
1
2
3
4
5
6
Red Symbols: Mean ionic Lit.
Green Symbols: Calculated from Single Ion

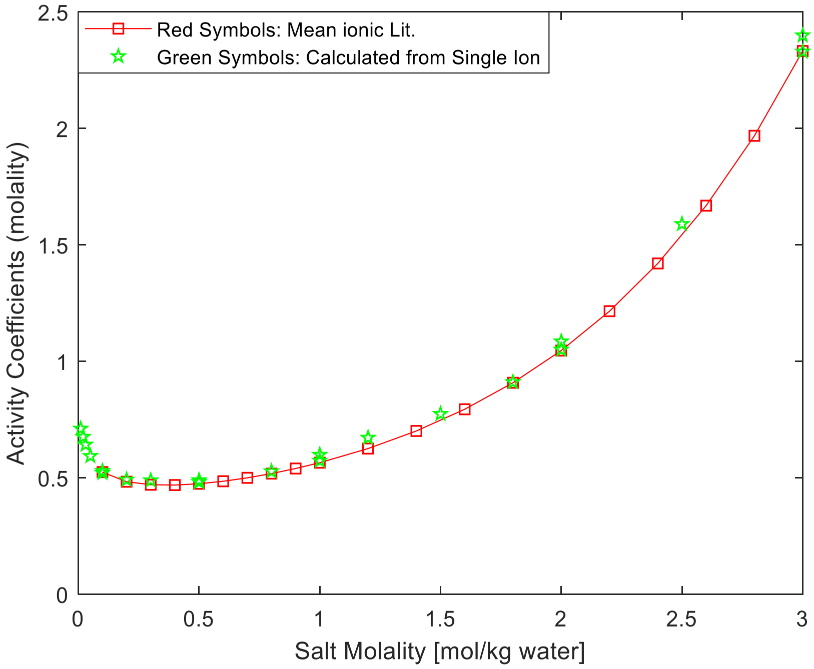
(a) NaCl


Activity Coefficients (molality)
Salt Molality [mol/kg water]
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0
0.5
1
1.5
2
2.5
3
3.5
4
Red Symbols: Mean ionic Lit.
Green Symbols: Calculated from Single Ion

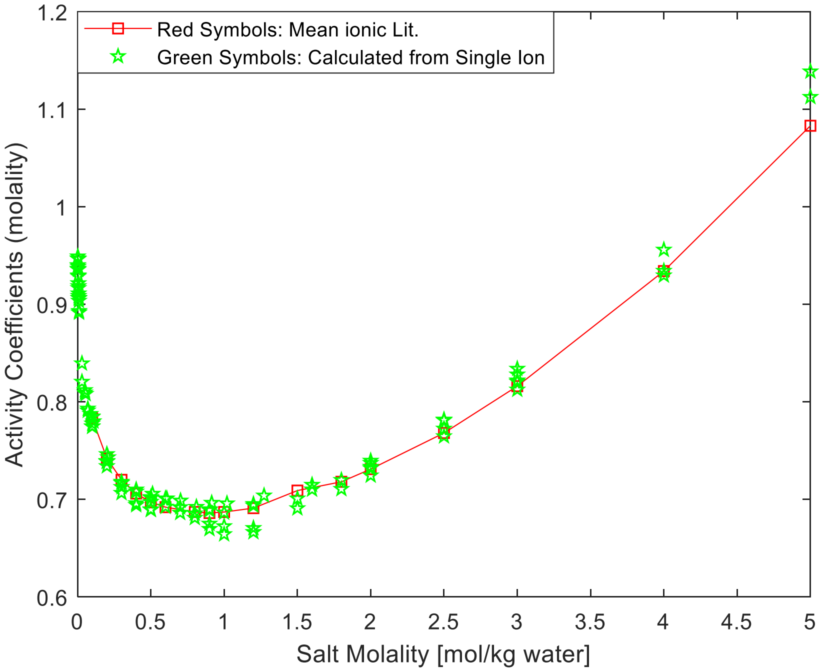
(b) KCl



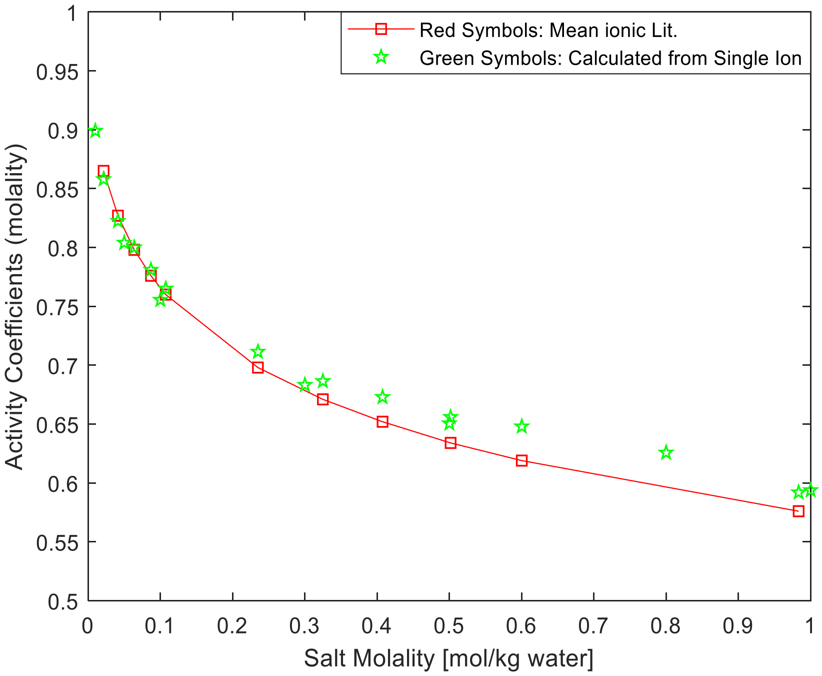
(c) CaCl2



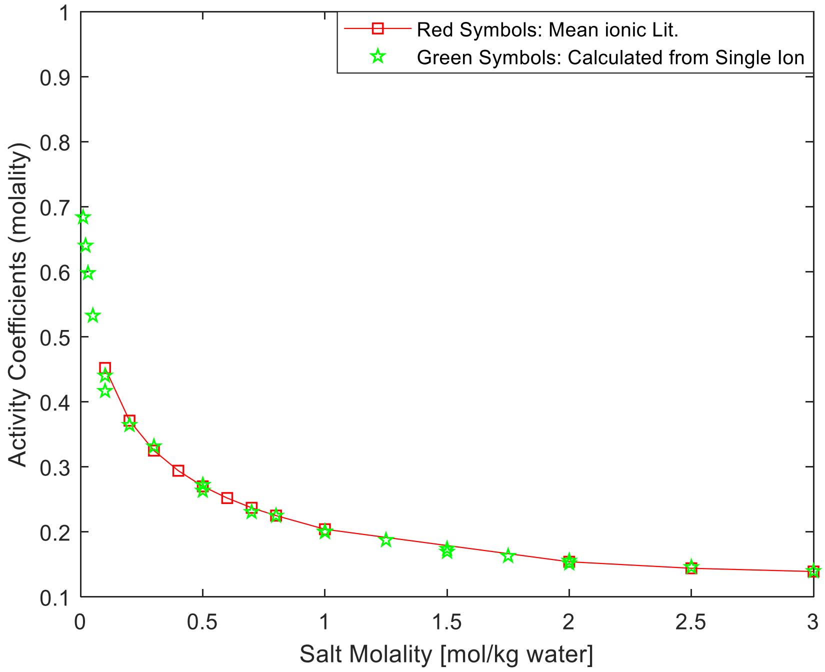
(d) $MgCl_2$


1.2
1.1
1
0.9
0.8
0.7
0.6
Activity Coefficients (molality)
0
0.5
1
1.5
2
2.5
3
3.5
4
4.5
5
Salt Molality [mol/kg water]
Red Symbols: Mean ionic Lit.
Green Symbols: Calculated from Single Ion

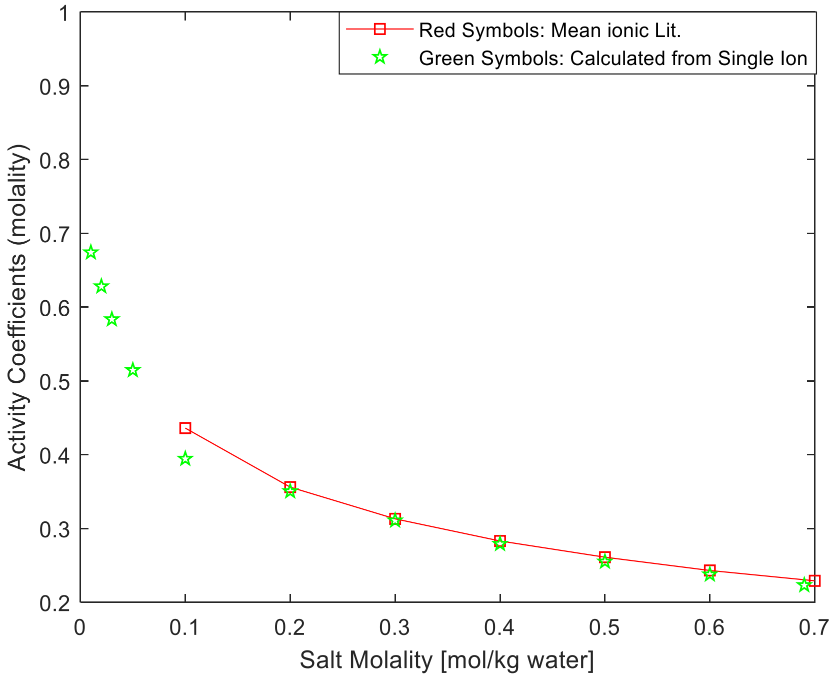
(e) NaBr


1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
Activity Coefficients (molality)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Salt Molality [mol/kg water]
Red Symbols: Mean ionic Lit.
Green Symbols: Calculated from Single Ion

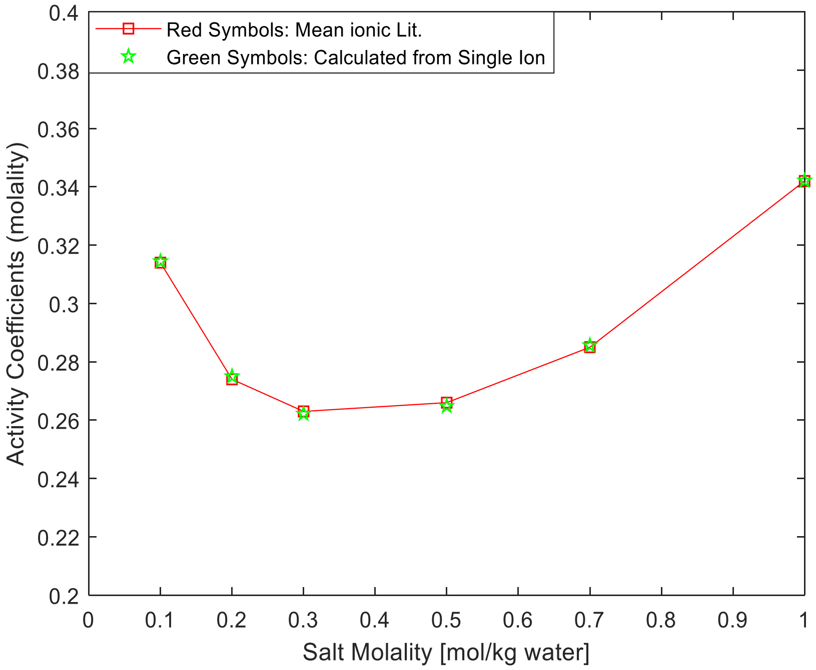
(f) NaF



(g) Na_2SO_4

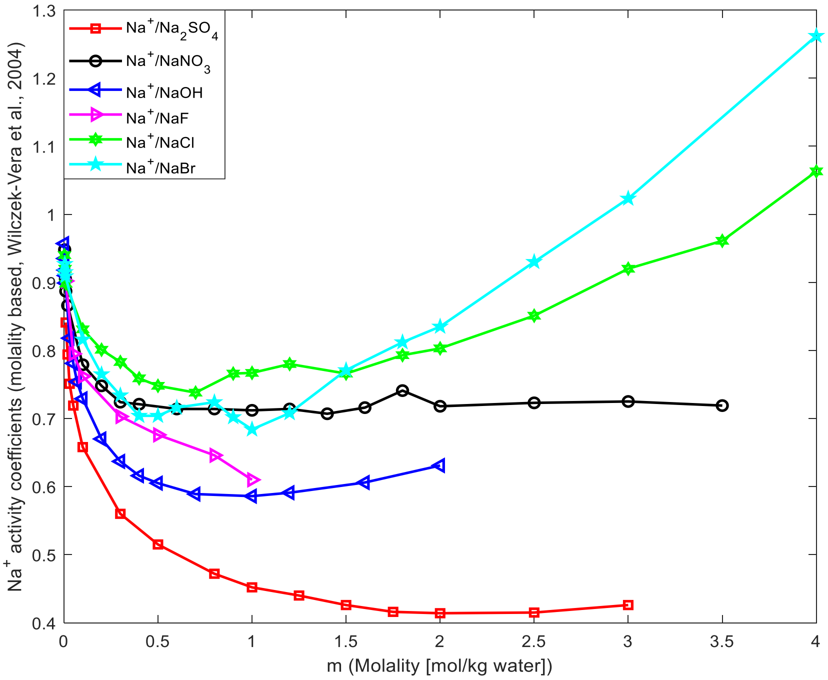


(h) K_2SO_4

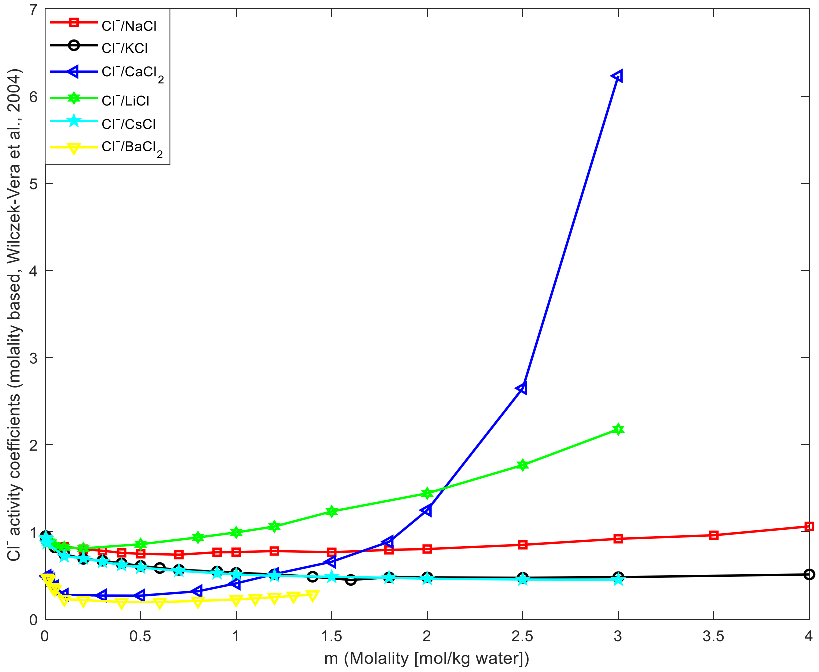


(i) $LaCl_3$

Figure S1. Comparison of mean ionic activity coefficients between calculated values from activity coefficients of individual ions and direct experimental values.



(a) Na^+



(b) Cl$^-$

Figure S2. Activity coefficients of individual ions in different aqueous electrolyte solutions.

Section B. Modelling Parameters

Table S2. Ion properties and parameters.

Ion	r_p [a] [Å][15]	r_{Born} [b] [Å][16-17]	e-CPA parameters		
			d [c] [Å][18]	r_{Born} [b] [Å][19]	b [d] [19]
Na^+	0.95	1.62	2.36	1.665	16.49
K^+	1.33	1.95	2.78	2.065	27.62
Ca^{2+}	0.99	1.71	2.42	1.759	17.91
Mg^{2+}	0.65	1.42	2.09	1.443	11.51
La^{3+}	1.05	1.96	-	-	-
F^-	1.36	1.60	2.63	1.411	22.94
Cl^-	1.81	2.26	3.19	1.828	40.83
Br^-	1.95	2.47	3.37	2.059	48.40
SO_4^{2-}	-	-	3.82	2.415	70.03
NO_3^-	-	-	3.58	2.04	39.80

a. Pauling radius; b. Born radius; c. hard-sphere diameter; d. CPA co-volume parameter.

Table S3. Modelling performance of mean ionic activity coefficients and osmotic coefficients for water-ions (metal halide salts) binary systems[19].

Salt	$\Delta U_{ij}^{ref}/R$[K]	$T_{\Delta U_{ij}}$[K]	$\omega_{\Delta U_{ij}}$[K]	T [K]	m_{max} [a] [mol/kg]	RAD [%] [c]	
						$\gamma_{\pm}^{m}$	Φ
NaCl	-223.5	340	1573	273.15-473.15[b]	7.973	2.3	1.6
KCl	-130.0	340	1361	273.15-373.15[b]	6.0	0.86	0.65
$CaCl_2$	-380.8	340	2778	298.15 [b]	3.0	5.3	3.3
$MgCl_2$	-459.6	340	2439	298.15 [b]	3.0	5.9	4.0
Na_2SO_4	123.8	300	1163	298.15-323.15[b]	3.7	2.0	1.3
NaBr	-280.3	350	1322	246-523	6.0	7.6	2.4
NaF	-167.0	320	-2183	269-308	1.0	2.2	1.0
K_2SO_4	77.38	300	891.5	271-498	2.0	2.9	1.4

In Table S3, ΔU_{ij}^{ref} *is binary interaction parameter between cation/anion and solvent (or gas) at the reference temperature,* $\omega_{\Delta U_{ij}}$ *is an adjustable parameter for the linear dependency in interaction energy calculation,* $T_{\Delta U_{ij}}$ *is a parameter of the temperature dependency,* $\gamma_{\pm}^{m}$ *is the mean ionic activity coefficients,* Φ *is osmotic coefficients; a. In Maribo-Mogensen et al.'s work*[19]*, the regression molality limits are: 6, 6, 3, 2 mol/kg water for NaCl, KCl,* $CaCl_2$*,* $MgCl_2$*,* Na_2SO_4 *respectively; b. NaCl data source:* [3, 20-31]*, KCl data source:* [32-35]*,* $CaCl_2$ *data source:* [36-37]*,* $MgCl_2$ *data source:* [37-38]*,* Na_2SO_4 *data source:* [39-42]*; c. The results are typically listed as the relative average deviation (RAD):*

$$RAD\% = \frac{1}{Np}\sum_{i}^{Np}\left|\frac{y_i^{cal}-y_i^{exp}}{y_i^{exp}}\right| \times 100\% \qquad \text{(S1)}$$

Here, Np is the number of data points, y_i^{cal} represents the calculated results of any property, e.g. activity coefficient, and y_i^{exp} represents the experimental data of the given property.

Table S4. Parameters for correlation of liquid densities of aqueous electrolyte solutions, equation 19 (from literature[43]).

Salt	$A \times 10^{-2}$	$-B \times 10$	$C \times 10^3$	$-D$	$E \times 10^2$	$-F \times 10^4$
NaCl	0.4485	0.9634	0.6136	2.712	1.009	0
KCl	0.4971	0.7150	0.6506	2.376	0	0
NaBr	0.8362	1.872	1.353	2.847	4.791	3.413
NaF	0.4940	2.985	3.365	4.752	16.22	18.72
$CaCl_2$	1.012	61.56	1.028	9.749	96.94	3.165
$MgCl_2$	0.8099	1.887	2.3156	6.029	7.449	8.305
Na_2SO_4	1.412	4.535	3.766	17.51	21.11	17.73
K_2SO_4	1.619	7.181	5.994	34.81	77.97	61.85
$LaCl_3$	2.319	0.8064	1.110	13.20	0	0

Table S5. Parameters for correlation of static permittivity of solvent for aqueous electrolyte solutions(from literature[17, 44-45]).

Salt	δ_s [mol^{-1}]	b_s [mol$^{-3/2}$]	c_{max} [a]
NaCl	16.2	3.1	4.0[44]
KCl	14.7	3.0	4.0[44]
NaBr	20.0	5.0	4.0[17]
NaF	15.45	3.76	4.0[17]
Na_2SO_4	30.1	9.6	1.2[45]
K_2SO_4 [a]	21.3	5.77	1.0 [b]
$LaCl_3$	46.48	8.21	1.0[16]

a. the maximum concentration (mol/L) of application of Eq. (5.17); b. fitted in this work, K_2SO_4[46].

Section C. Basic Thermodynamic Equations

A salt dissociates into νC cations C, and νA anions A with ionic charges Z_C and Z_A. The Greek letter ν is the sum of the stoichiometric coefficients:

$$\nu = \nu C + \nu A \tag{S2}$$

The molality m_i of an ion i is the number of moles n_i, of the ion per kg water in the liquid phase.

The mole fraction of water x_w is:

$$x_w = \frac{nw}{nw + \sum nion_k} = \frac{1000/M_w}{1000/M_w + \sum m_k} \tag{S3}$$

Where, nw is the mole numbers of solvent (water), $nion_k$ is the mole numbers of ion k, M_w is the molecular weight of the solvent (water in this work), and m_k is the molality of ion k and the sum is over all ions present.

The molality (based) activity coefficient is defined:

$$ln\gamma_i^m = \ln(x_w\gamma_i^*) = \ln\gamma_i^* - \ln[1 + 0.001M_w \sum m_k] \tag{S4}$$

γ_i^* is the rational, unsymmetrical activity coefficient of component i (solvent, cation, anion).

The mean molal activity coefficient is defined:

$$\gamma_\pm^m = ((\gamma_C^m)^{\mathrm{\nu C}}(\gamma_A^m)^{\mathrm{\nu A}})^{1/\nu} \tag{S5}$$

Chemical potentials were derived from the energy function by molar differentiation at constant temperature and volume[47]:

$$\mu_i{}^{EX} = \left[\frac{\partial A^{EX}}{\partial n_i}\right]_{T,V,n_j} \tag{S6}$$

The excess chemical potential for component *i* is:

$$\mu_i{}^{EX} = RT\ln\gamma_i^* \tag{S7}$$

Here, γ_i^* is the activity coefficient (rational) of ion i.

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