

Systematic evaluation of parameterization approaches for the ePPC-SAFT model for aqueous alkali halide solutions

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Contents

S1. Salt-specific parameters and regression boundaries	1
S2. Ion-specific parameters and regression boundaries	4
S3. Additional aqueous NaCl solution parameter sets discussed in Section 4.2	5
S4. Contributions of the salt-specific parameterization strategies	6

S1. Salt-specific parameters and regression boundaries

Tables S1 shows the ionic Pauling diameters and Born diameters. Table S2 shows the salt-specific parameter sets and regression boundaries for the aqueous alkali chloride solutions. The Pauling diameter are obtained from Ref [1].

Table S1. Ionic Pauling diameters and Born diameters.

	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Cl ⁻
σ_{Pauling}	1.90	2.66	2.96	3.38	3.62
σ_{Born}	3.23	3.90	4.17	4.48	4.51

Table S2. Salt-specific parameter sets and regression ranges for the aqueous alkali chloride solutions.

	Boundaries	Asso-1	Asso-2	Disp-1	Disp-2	Disp-3	Disp-4	Full-1	Full-2	Full-3	Full-4
NaCl											
r^{HS}	(0.5, 1.5)	0.93797	0.9432	0.79824	0.81010	0.89391	0.84955	1.0057	0.87103	0.95236	0.95479
r^{MSA}	(1, 2)	1.6532	1.4918	1.6827	1.6118	1.5782	1.6007	1.6639	1.5052	1.7643	1.7333
ε_{c}	(50, 1000)			372.97	615.18	998.78	934.45	883.51	84.157	348.93	648.83
ε_{a}	(50, 1000)			636.92	606.15	458.11	426.13	545.07	50.822	679.78	642.27
$k_{\text{c-a}}$	(-1, 1)			0.18847	0.054152	0.99844	0.99788				
$\varepsilon_{\text{c}}^{\text{AB}}$	(100, 5000)	1365.1	1655.2					1909.6	597.61	787.75	1073.9
$\varepsilon_{\text{a}}^{\text{AB}}$	(100, 5000)	1999.3	2461.8					4111.1	109.32	3134.0	2161.3
$\beta_{\text{c}}^{\text{AB}}$	(0.001, 0.3)	0.068387	0.030752					0.017451	0.12651	0.27136	0.088845
$\beta_{\text{a}}^{\text{AB}}$	(0.001, 0.3)	0.20385	0.15822					0.085959	0.22784	0.20751	0.22494
$w_{\text{c-a}}$	(-1, 1)	0.39136	0.23042					-0.03462	0.6875	0.30825	0.34287
KCl											
r^{HS}	(0.5, 1.5)	0.98266	0.95795	0.91936	0.92353			0.93837	0.97596	0.99569	0.98943
r^{MSA}	(1, 2)	1.3263	1.0966	1.3232	1.2709			1.4427	1.1306	1.4200	1.1069
ε_{c}	(50, 1000)			999.94	999.99			321.90	774.69	851.94	864.25
ε_{a}	(50, 1000)			999.98	999.99			376.38	130.16	4989.4	540.96
$k_{\text{c-a}}$	(-1, 1)			-0.30035	0.36228						
$\varepsilon_{\text{c}}^{\text{AB}}$	(100, 5000)	1090.8	1784.8					565.87	4885.2	819.02	1203.6
$\varepsilon_{\text{a}}^{\text{AB}}$	(100, 5000)	4900.0	3365.4					1071.4	774.69	641.47	4099.5
$\beta_{\text{c}}^{\text{AB}}$	(0.001, 0.3)	0.028834	0.001495					0.13315	0.060491	0.03841	0.007401
$\beta_{\text{a}}^{\text{AB}}$	(0.001, 0.3)	0.22725	0.019287					0.011558	0.14717	0.15829	0.22507
$w_{\text{c-a}}$	(-1, 1)	0.15762	0.11202					-0.30999	-0.09838	0.15818	0.092892

	Boundaries	Asso-1	Asso-2	Disp-1	Disp-2	Disp-3	Disp-4	Full-1	Full-2	Full-3	Full-4
RbCl											
r^{HS}	(0.5, 1.5)	0.98088	0.95763	0.87228	0.86747			0.92842	0.87392	1.0036	0.95582
r^{MSA}	(1, 2)	1.1552	1.1094	1.0051	1.0000			1.2890	1.8268	1.1692	1.0457
ε_c	(50, 1000)			195.82	878.11			295.74	911.28	887.20	146.21
ε_a	(50, 1000)			705.9	315.89			282.51	682.76	531.52	924.35
k_{c-a}	(-1, 1)			-0.56431	-0.37422						
$\varepsilon_c^{\text{AB}}$	(100, 5000)	1111.2	968.41					548.90	1237.6	2173.5	592.75
$\varepsilon_a^{\text{AB}}$	(100, 5000)	1298.5	1297.9					718.95	2399.6	1450.2	1020.9
β_c^{AB}	(0.001, 0.3)	0.22181	0.065462					0.10024	0.21254	0.066126	0.14558
β_a^{AB}	(0.001, 0.3)	0.022611	0.037939					0.031577	0.18086	0.069339	0.062192
w_{c-a}	(-1, 1)	0.68491	0.79562					-0.41528	-0.093280	0.15344	0.23956
CsCl											
r^{HS}	(0.5, 1.5)	0.96122	0.95905	0.89131	0.93815			0.97261	0.97129	1.0008	0.99292
r^{MSA}	(1, 2)	1.0000	1.0000	1.0000	1.0000			1.0000	1.0122	1.2130	1.0525
ε_c	(50, 1000)			668.75	999.92			478.04	310.41	861.81	953.09
ε_a	(50, 1000)			661.99	999.90			121.42	98.901	709.29	706.44
k_{c-a}	(-1, 1)			-0.48002	-0.46974						
$\varepsilon_c^{\text{AB}}$	(100, 5000)	310.10	1309.0					534.70	1252.8	896.94	959.67
$\varepsilon_a^{\text{AB}}$	(100, 5000)	3098.2	1114.2					1442.2	860.13	3526.7	798.86
β_c^{AB}	(0.001, 0.3)	0.080994	0.013196					0.11266	0.22713	0.06874	0.067508
β_a^{AB}	(0.001, 0.3)	0.00269	0.18117					0.049454	0.10294	0.042319	0.10233
w_{c-a}	(-1, 1)	0.75083	0.77701					-0.27435	-0.24659	0.15547	0.38783

S2. Ion-specific parameters and regression boundaries

Table S3 shows the ion-specific parameter sets and regression boundaries for the aqueous alkali chloride solutions.

Table S3. Ion-specific parameter sets and regression boundaries for the aqueous alkali chloride solutions.

	Boundaries	Asso-I-15	Asso-I-12	Disp-I-15	Disp-I-12	Full-I-15	Full-I-12	Full-I-20
r^{HS}	(0.8, 1.2)	0.99263	0.98602	0.89622	0.91281	0.93791	0.92718	0.99482
$r^{\text{MSA}}_{\text{Na}^+}$	(1, 2)	1.7507	2.0000	1.9995	1.9229	2.0000	1.5270	1.7008
$r^{\text{MSA}}_{\text{K}^+}$	(1, 2)	1.2151	1.6892	1.8534	1.6374	1.6203	1.0468	1.1963
$r^{\text{MSA}}_{\text{Rb}^+}$	(1, 2)	1.0000	1.3049	1.0000	1.0000	1.0000	1.4325	1.0777
$r^{\text{MSA}}_{\text{Cs}^+}$	(1, 2)	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
$r^{\text{MSA}}_{\text{Cl}^-}$	(1, 2)	1.3907	1.1859	1.0000	1.0000	1.0000	1.0000	1.4133
w_{NaCl}	(-1, 1)	0.30434	0.27668	-	-	0.61814	0.039203	0.39464
w_{KCl}	(-1, 1)	0.41073	0.27668	-	-	0.070352	0.039203	0.44717
w_{RbCl}	(-1, 1)	0.25334	0.27668	-	-	0.16303	0.039203	0.56454
w_{CsCl}	(-1, 1)	0.32633	0.27668	-	-	-	0.039203	0.24685
						0.047884		
$\varepsilon_{\text{Na}^+}^{\text{AB}}$	(100, 5000)	2112.4	2142.6	-	-	1047.1	3962.9	1267.3
$\varepsilon_{\text{K}^+}^{\text{AB}}$	(100, 5000)	1066.0	1034.6	-	-	618.29	1668.2	777.33
$\varepsilon_{\text{Rb}^+}^{\text{AB}}$	(100, 5000)	2028.6	1669.3	-	-	647.20	505.57	407.09
$\varepsilon_{\text{Cs}^+}^{\text{AB}}$	(100, 5000)	1672.5	1858.7	-	-	498.33	588.24	1686.9
$\varepsilon_{\text{Cl}^-}^{\text{AB}}$	(100, 5000)	2355.3	2650.1	-	-	711.52	833.11	1600.2
k_{NaCl}	(-1, 1)	-	-	-0.14635	-0.36970	0	0	0
k_{KCl}	(-1, 1)	-	-	-0.52355	-0.36970	0	0	0
k_{RbCl}	(-1, 1)	-	-	-0.47962	-0.36970	0	0	0
k_{CsCl}	(-1, 1)	-	-	-0.44331	-0.36970	0	0	0
$\varepsilon_{\text{Na}^+}$	(50, 1000)	-	-	693.51	449.01	201.75	201.75	165.68
ε_{K^+}	(50, 1000)	-	-	484.54	754.59	201.75	201.75	590.59
$\varepsilon_{\text{Rb}^+}$	(50, 1000)	-	-	389.14	643.75	201.75	201.75	790.50
$\varepsilon_{\text{Cs}^+}$	(50, 1000)	-	-	705.63	1000.0	201.75	201.75	933.53
$\varepsilon_{\text{Cl}^-}$	(50, 1000)	-	-	894.79	1000.0	201.75	201.75	721.91

S3. Additional aqueous NaCl solution parameter sets discussed in Section 4.2

As discussed in Section 4.2, when regressed to the evenly distributed pseudo-experimental MIAC dataset (from Ref [302] in the main text) for the aqueous NaCl solution, the obtained parameter set captures the MIAC maximum as temperature increases. Table S4 shows the parameter set, hereby noted as Asso-MIAC. Table S5 shows the deviations of this parameter set and the parameter set from Ref [40] in the main text, hereby noted as Asso-R40, from the databases that are compared with the parameterization strategies in this work (Table 1 in the main text). Representing the correct temperature-dependence trend, in terms of the average and maximum deviations, the parameter sets are slight more accurate than the salt- and ion-specific association parameter sets in this work, but are much less accurate for density.

Table S4. Parameters of Asso-MIAC for the aqueous NaCl solution.

Asso-MIAC	
r^{HS}	1.0976
r^{MSA}	1.4091
$\varepsilon_c^{\text{AB}}$	1863.5
$\varepsilon_a^{\text{AB}}$	3625.3
β_c^{AB}	0.0010027
β_a^{AB}	0.0013152
w_{c-a}	0.45277

Table S5. Percentage average absolute deviations (AADs) and percentage maximum absolute deviations (MADs) of Asso-MIAC and Asso-JSRP from datasets that are compared with the parameterization strategies in this work for the aqueous NaCl solution.

	MIAC		VLE		Density	
	AAD (%)	MAD (%)	AAD (%)	MAD (%)	AAD (%)	MAD (%)
Asso-MIAC	0.37	3.2	1.2	2.3	2.1	10
Asso-R40	0.91	3.6	1.3	3.0	2.1	10

S4. Contributions of the salt-specific parameterization strategies

Figure S1 shows the contributions to $\ln \gamma_{\pm}$ of the terms in the ion-specific strategies, Assoc-1, Disp-1, and Full-3, at 298.15 K and 0.1 MPa.

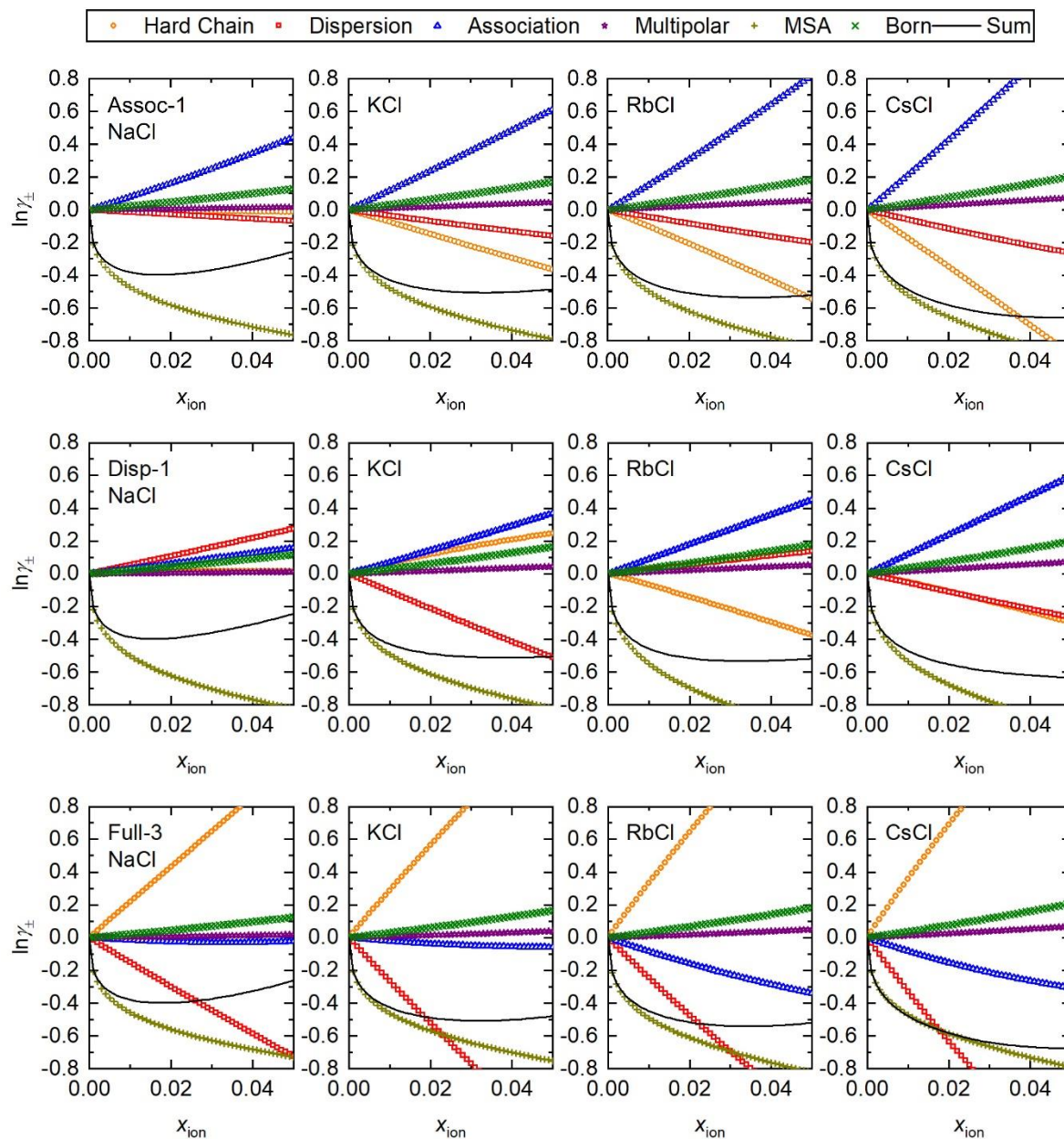


Figure S1. Contributions to $\ln \gamma_{\pm}$ of the terms in the ion-specific strategies, Assoc-1, Disp-1, and Full-3, at 298.15 K and 0.1 MPa.

Reference:

- [1] L. Pauling, The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry, Cornell University Press, Ithaca, NY, 1939.