

Development of CPA for Electrolyte Mixtures

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Introduction

- Electrolytes play a key role in many industrial processes. In many industries, the petroleum industry in particular, scaling of salts can be a problem, and also salt can have big effects on the equilibrium between two compounds, by salting out, salting in, or even by inducing an otherwise nonexistent liquid-liquid equilibrium phase split, thus being helpful in many separation processes.
- Our electrolyte CPA Equation of State have been developed through the past years, and was first presented by Maribo-Mogensen et. al [1] illustrating the possible applications of the model, and later extended to solid-liquid equilibria by Schlaikjer et al. [2].
- In the initial first work with this model the parameterizations have been done on a salt specific basis, thus each salt is parameterized individually yielding an issue with dealing with salt mixtures. In this work a ion specific parameterization is presented along with its performance for some key systems.

Parameter Estimation

We have parameterized the model for 10 cations and 7 anions to osmotic coefficient and mean ionic activity coefficient data up to an ionic strength of 6, in the temperature range: 273.15 K – 591 K [3].

The parameterization is conducted simultaneously for all the ions to the data of 55 salts that can be combined by the 17 ions. In table 1 below the deviations from the activity coefficient and osmotic coefficient data used in the estimation is shown. On average the relative deviation in activity coefficient is 5.9% and in osmotic coefficient 4.2%. Density is accurately correlated with the use of a Peneloux volume translation. For the majority of the salts the deviation and behavior are acceptable, but for a small number of the salts the performance is not satisfactory, as for instance Na_2SO_4 . A potential solution to these few problematic salts could be to introduce ion-ion interaction parameters, which can correct for most of the issues.

Table 1: Relative absolute deviation for activity coefficient and Osmotic coefficient data for all the salts in the estimation.

RAD (%) γ^\pm / Φ	H ⁺	Na ⁺	K ⁺	Li ⁺	Cs ⁺	Rb ⁺	Mg ⁺⁺	Ca ⁺⁺	Sr ⁺⁺	Ba ⁺⁺
OH ⁻	-	7.5 / 2.7	5.6 / 2.6	6.3 / 6.1	8.3 / 2.9	-	-	-	-	-
Cl ⁻	6.5 / 2.8	2.6 / 1.3	6.7 / 3.4	10.4 / 4.2	7.6 / 4.2	1.7 / 1.2	7.1 / 3.4	9.7 / 5.0	5.5 / 5.2	9.4 / 6.4
Br ⁻	4.2 / 12.5	5.5 / 2.4	4.3 / 0.8	8.2 / 5.6	5.4 / 1.7	4.1 / 1.2	6.9 / 1.8	14.1 / 3.0	3.7 / 2.6	5.1 / 5.7
I ⁻	8.2 / 9.9	5.3 / 4.4	0.6 / 0.5	-	4.0 / 1.4	6.6 / 1.8	1.9 / 1.7	6.8 / 4.8	4.0 / 2.6	5.5 / 3.6
F ⁻	-	5.0 / 4.4	4.0 / 7.1	-	6.4 / 2.6	3.9 / 2.0	-	-	-	-
NO ₃ ⁻	4.7 / 3.5	6.5 / 6.1	2.1 / 5.5	4.8 / 4.0	5.0 / 10.2	1.6 / 1.9	5.9 / 4.1	12.4 / 5.3	5.0 / 6.0	2.9 / 9.4
SO ₄ ²⁻	-	7.0 / 9.4	5.6 / 4.3	10.7 / 5.1	6.7 / 6.6	1.5 / 1.6	3.6 / 4.9	10.7 / 1.6	-	-

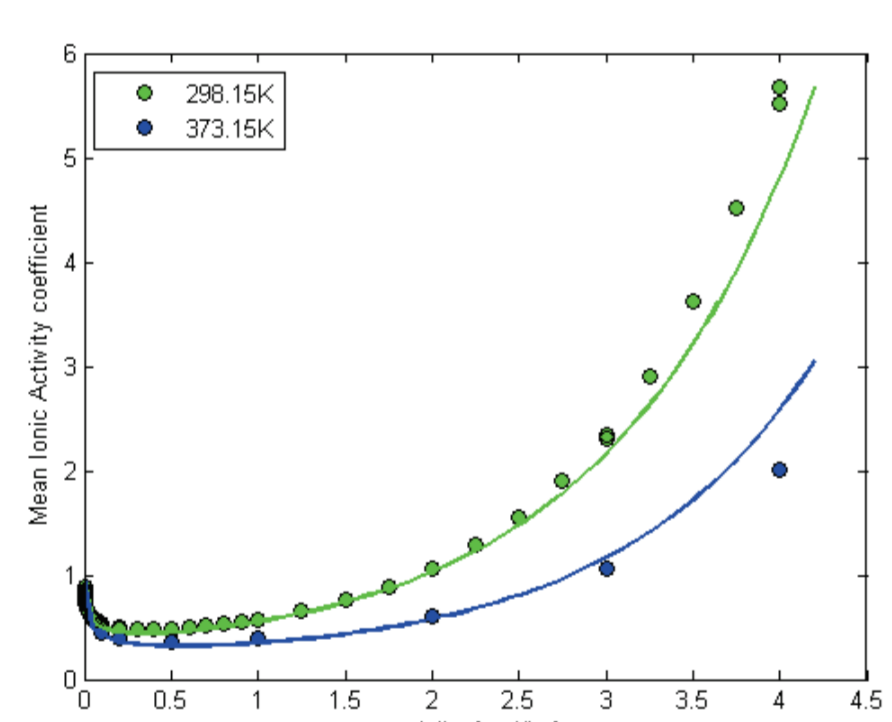


Figure 1: Mean Ionic Activity coefficient of a MgCl_2 solution in water, up to an ionic strength of 12.

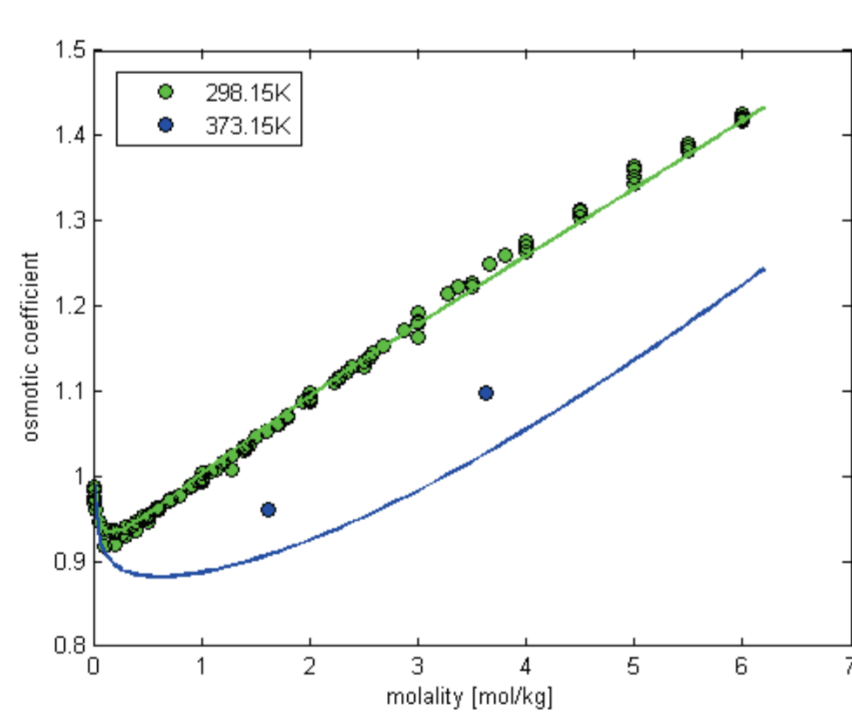


Figure 2: Osmotic Coefficient of a LiNO_3 solution in water.

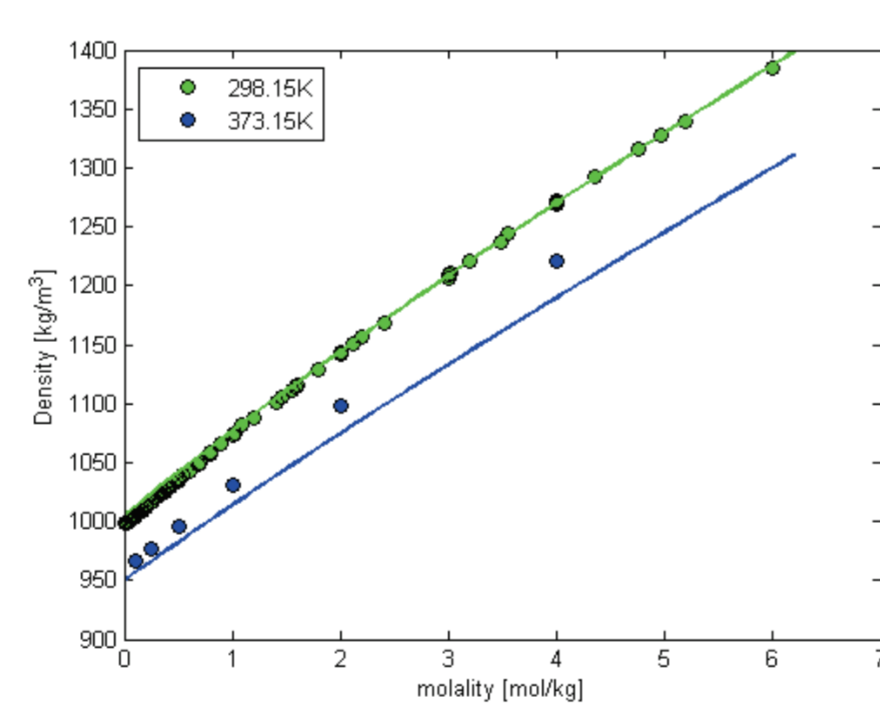


Figure 3: Density of a NaBr solution in water.

Application Examples

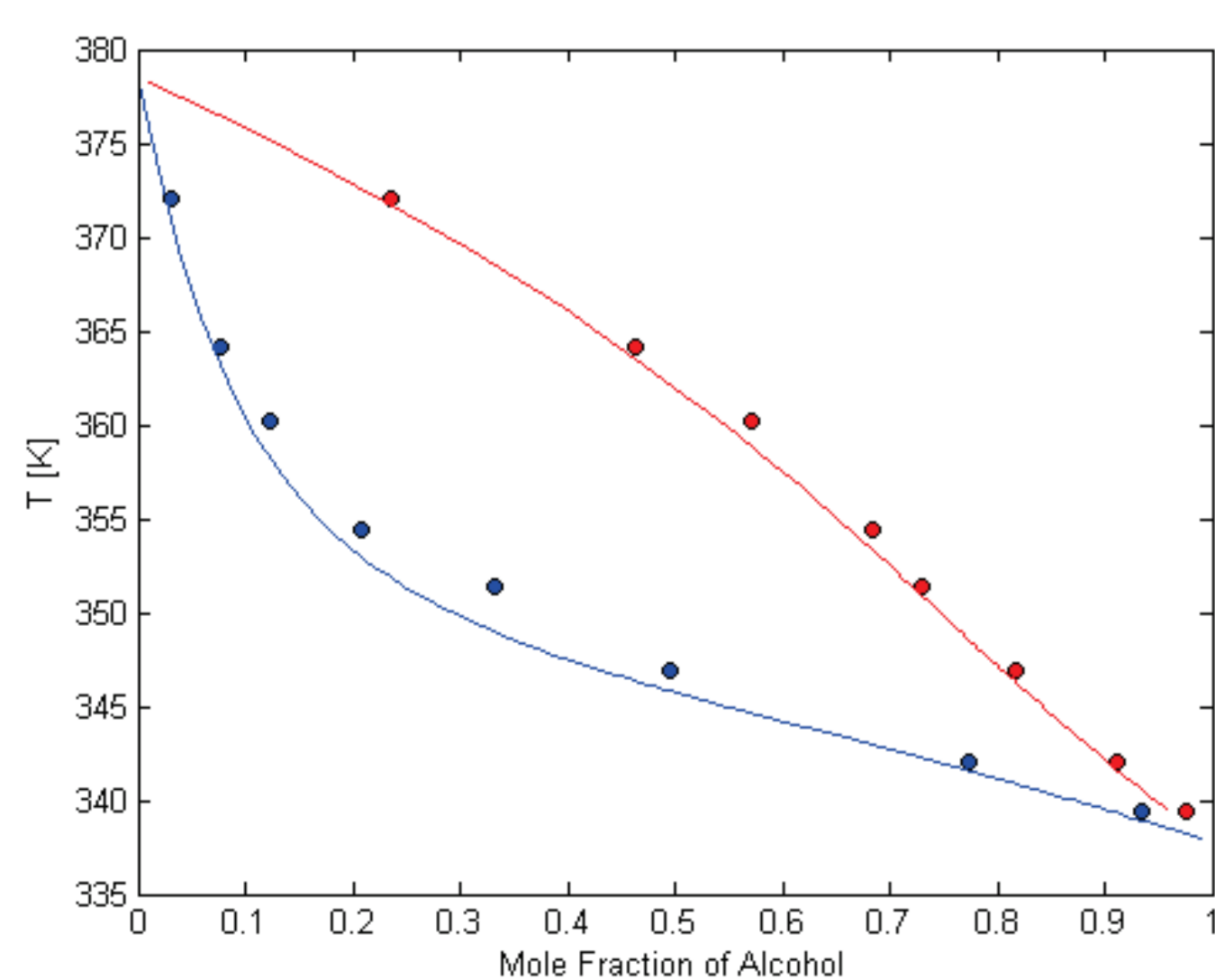


Figure 5: VLE of Water-Methanol-LiCl (4 molal)

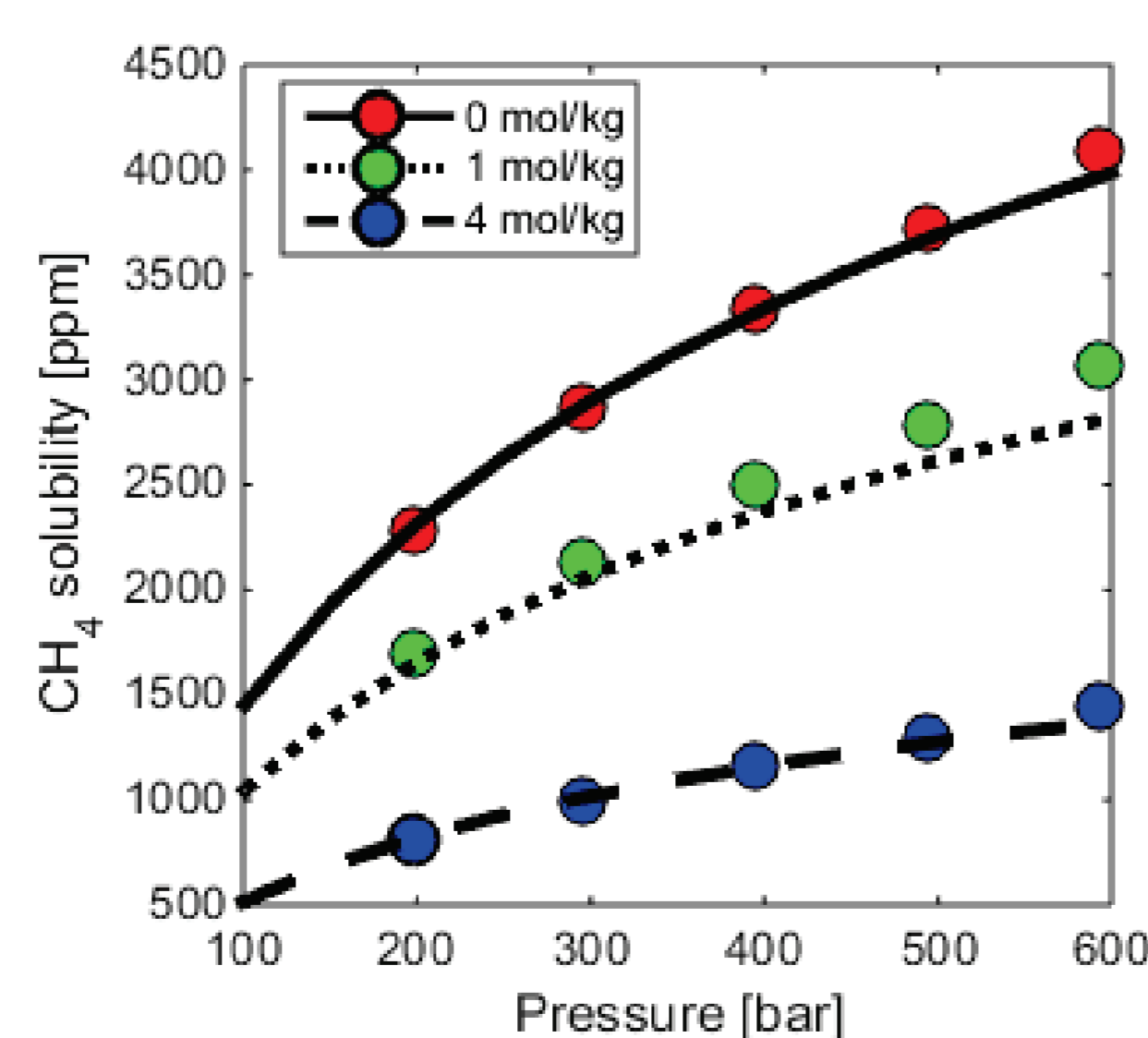


Figure 6: Methane solubility in Water-NaCl at 324K

The Electrolyte CPA Equation of State

The Electrolyte CPA Equation of State as proposed by Maribo-Mogensen et al. [1] is a direct extension to the CPA Equation of State. The model takes the long range electrostatic interactions into account through the Debye-Hückel Theory and accounts for ion solvation through the Born term.

The model is built as a ion specific framework, where instead of using the traditional van der Waals one fluid mixing rule, the Huron-Vidal/NRTL mixing rule is applied for the interaction between solvent and ions. The mixing rule is simplified by setting the non-randomness parameter to zero by default, yielding:

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,\infty}}{\ln 2}, \quad \frac{g^{E,\infty}}{RT} = \frac{1}{b} \sum_j x_j b_j \frac{\Delta U_{ji}}{RT}$$

For the binary energy parameter in the Huron-Vidal/NRTL mixing rule, a temperature dependence is found to be needed:

$$\frac{\Delta U_{ij}}{R} = \frac{\Delta U_{ij}^{ref}}{R} + \alpha_i \left[\left(1 - \frac{T}{T_\alpha} \right)^2 - \left(1 - \frac{T_{ref}}{T_\alpha} \right)^2 \right]$$

Here there are 3 adjustable parameters: ΔU_{ij}^{ref} , α_i , T_α , where the reference energy parameter is the energy parameter at the reference temperature (298.15 K). In total the model utilizes 2 pure compound adjustable parameters along with the three interaction parameters from the above temperature dependence for each ion, while the dielectric constant is adopted from a model by Maribo-Mogensen et al. [4], and the Born radius is adjusted to match the hydration enthalpy.

Electrolyte CPA

CPA

Electrostatics

SRK

Association
From SAFT

Debye-
Hückel
Term

Born Term
(Solvation)

$$\frac{A_{eCPA}^r}{RT} = \frac{A_{SRK}^r}{RT} + \frac{A_{Association}^r}{RT} + \frac{A_{Debye-Hückel}^r}{RT} + \frac{A_{Born}^r}{RT}$$

Mixed Salt Osmotic coefficients

System	RAD(%)
$\text{MgCl}_2 - \text{KNO}_3$	1.59
$\text{Na}_2\text{SO}_4 - \text{MgCl}_2$	2.41
$\text{NaCl} - \text{MgSO}_4$	3.66
$\text{KCl} - \text{NaCl}$	3.81
$\text{NaCl} - \text{NaSO}_4$	1.18
$\text{CaCl}_2 - \text{NaCl}$	2.72
$\text{NaCl} - \text{KCl} - \text{MgCl}_2$	3.73

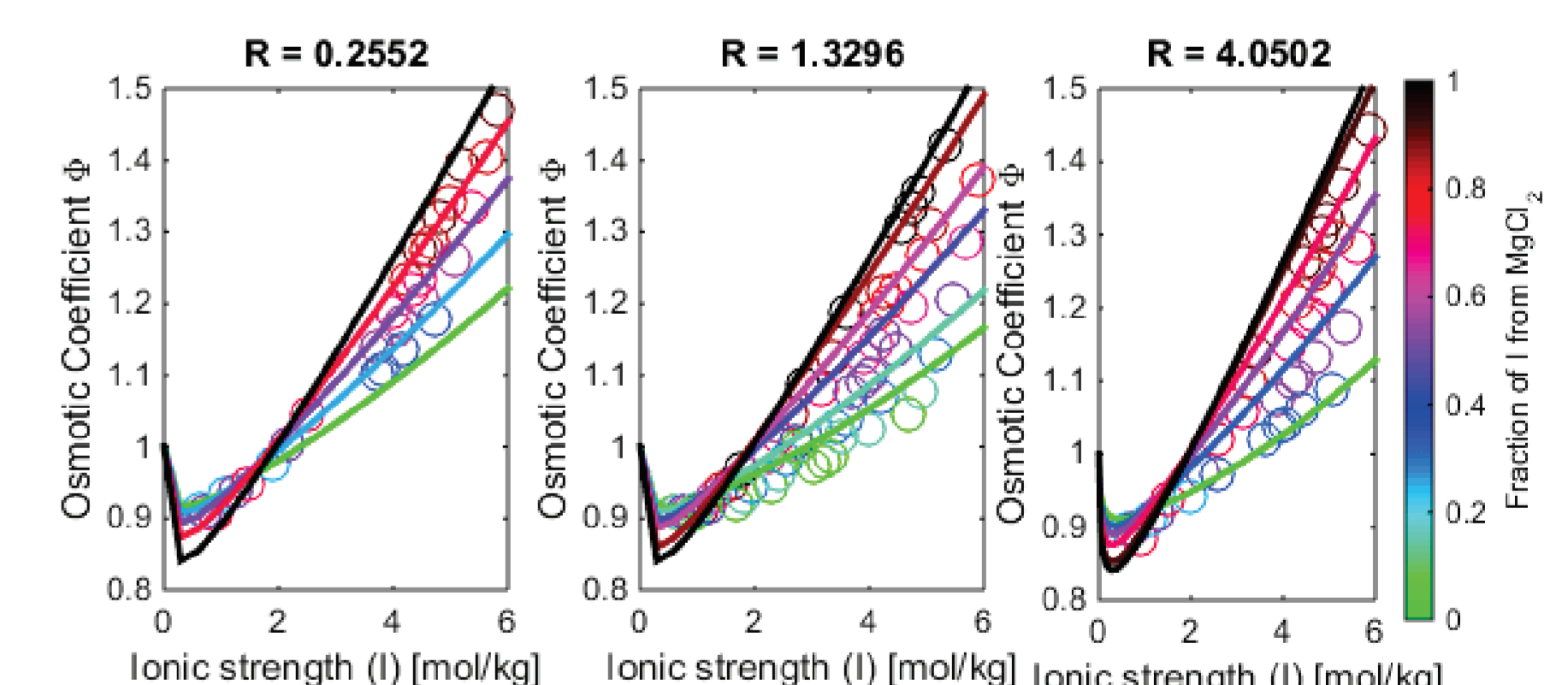


Figure 4: Osmotic coefficients of a $\text{NaCl} + \text{KCl} + \text{Na}_2\text{SO}_4$ solution in water at 298.15K. $R = m_{\text{NaCl}}/m_{\text{KCl}}$

Conclusions

- A parameter set with ion-specific parameters have been developed and show acceptable deviations from osmotic and activity coefficient data on average.
- For a few problematic salts ion-ion interaction parameters is needed to yield acceptable deviations.
- The parameters have successfully been applied to mixed salt systems for predicting the osmotic coefficient, as well as mixed solvent systems, also with very promising results.

References

- Maribo-Mogensen, B., Thomsen, K., Kontogeorgis, G. M. (2015). An electrolyte CPA Equation of state for mixed solvent Electrolytes. *AIChE Journal*, 61(9), 2933-2950
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