Impact of Ion-pairs in SAFT-type models for aqueous and mixed-solvent salt solutions

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INTRODUCTION

Helmholtz free energy

Mole fraction based Mean ionic activity coefficient

$$RT \ln(\gamma_{\pm}) = \left(\frac{\partial(A^{res}(T,V))}{\partial n_{ion}} - \frac{\partial(A^{res,*}(T,V))}{\partial n_{ion}} \right) - RT ln \left(\frac{Z}{Z^*} \right)$$

Reference state

Van der Waals forces | Polar interaction | Solvation energy

ePPC-SAFT

$$A^{res} = A^{hc} + A^{disp} + A^{assoc} + A^{polar} + A^{elec} + A^{Born}$$

Repulsion | Chemical association | Long-range electrostatic interactions between ions(A^{MSA})

- Strong physical meaning
- Extension to complex systems
- Hight Temperature or pressure systems
- Prediction capability

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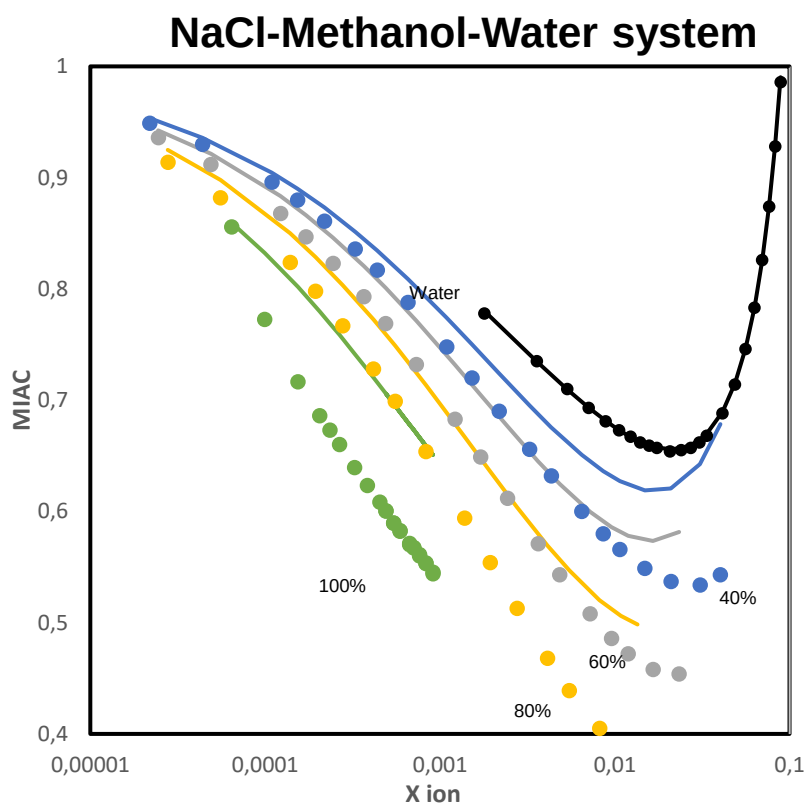
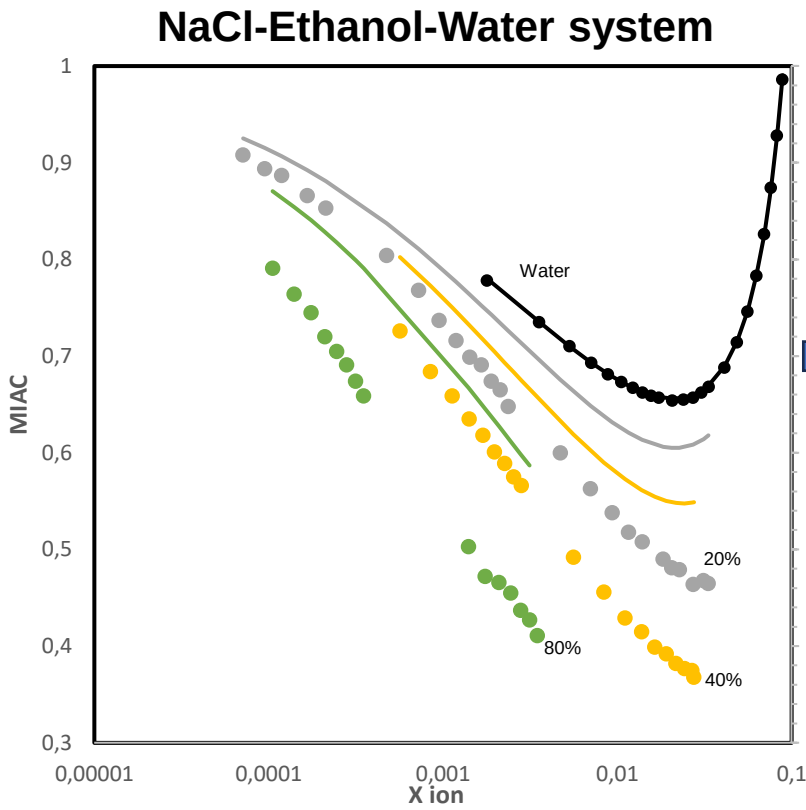
THESIS OBJECTIVE

AAD%	MAX AAD%
6.67	32.10



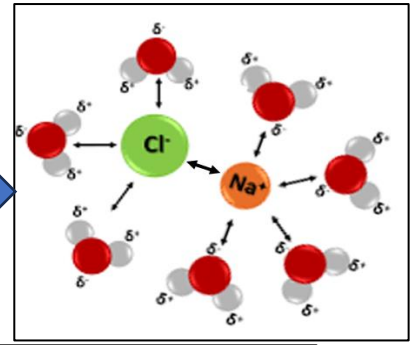


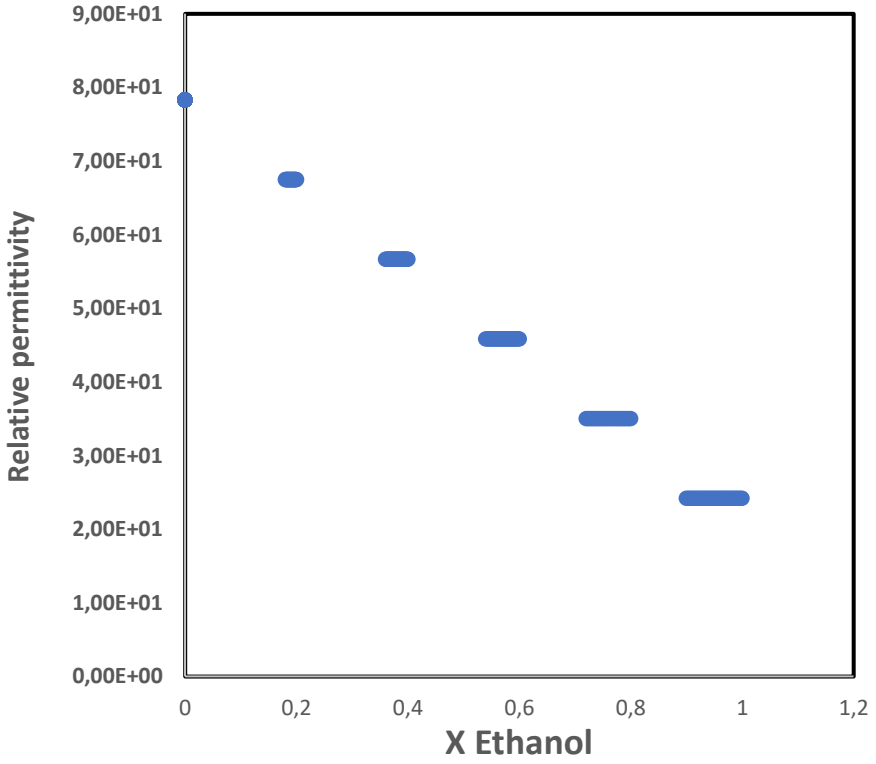
AAD%	MAX AAD%
16.31	56.17

Fig 1. MIAC versus ion mole fraction for NaCl in water-ethanol and water methanol systems using the ePPC-SAFT model (previous model)

METHODOLOGY OF ION-PARING (WHY ION PAIRING IS IMPORTANT)

Ion-pair: **Association of two unlike ions** (increase the non-ideality of the system)





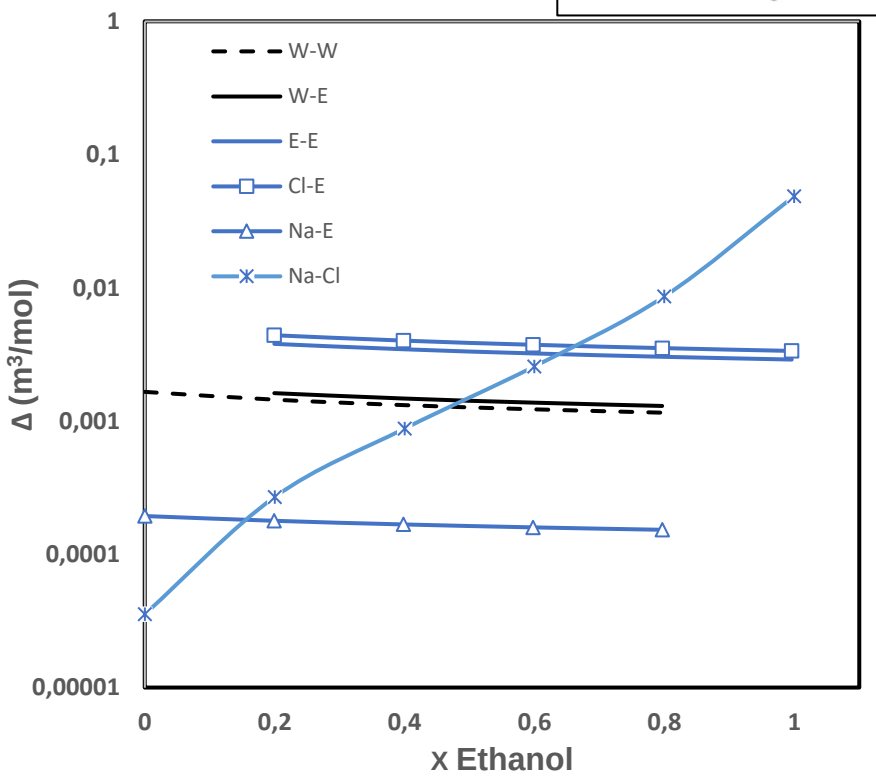
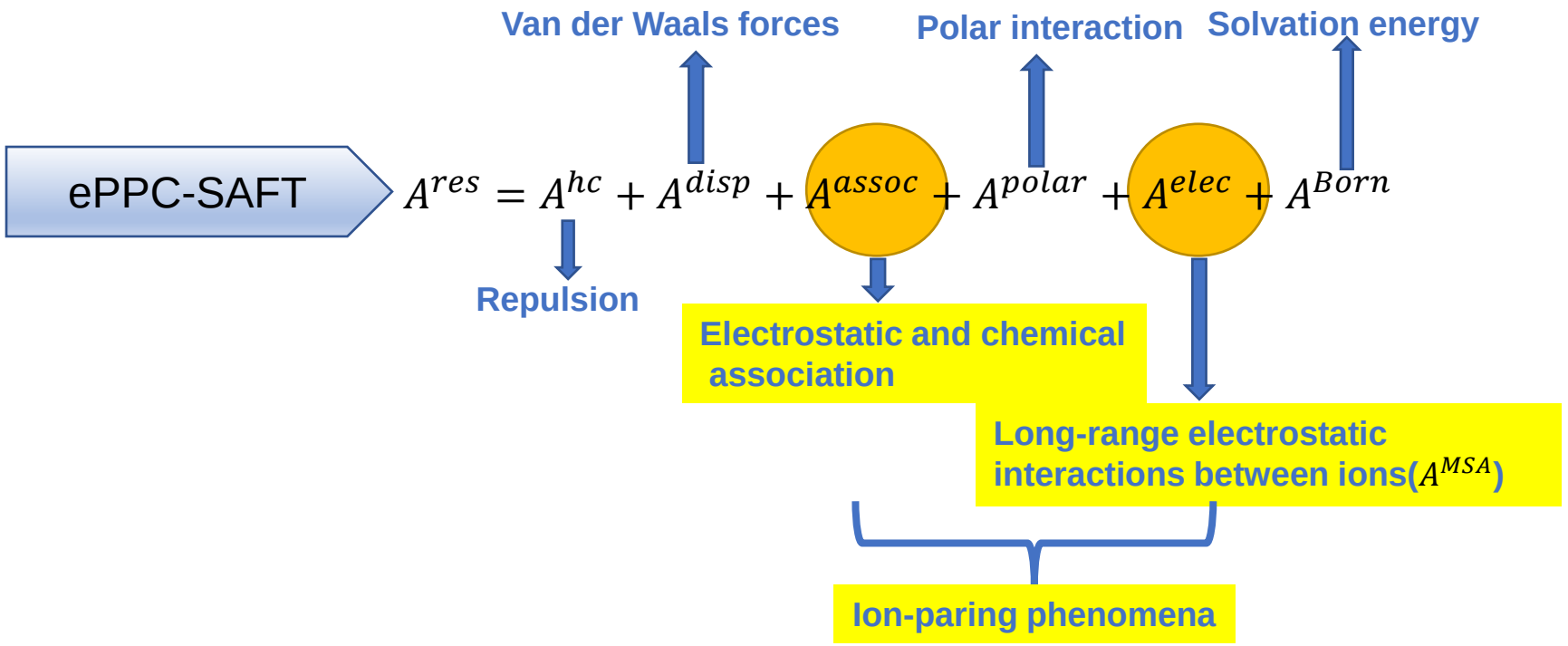


Fig 2. Relative permittivity (left) and ion-ion association strength (right) of NaCl-water-ethanol system using the Bjerrum theory.

CONSTRUCTION OF ION-PAIRING MODEL



CONSTRUCTION OF ION-PAIRING MODEL(ELECTROSTATIC TERM A^{elec})

- Electrostatic models:
  - Different version of MSA theory:

a. SMSA model

$$A^{MSA} = -\frac{e^2 V}{4\pi\varepsilon_0\varepsilon}\left\{\frac{\Gamma}{V}\sum_{i=1}^{n_{ion}}\frac{n_i z_i^2}{1+\Gamma\sigma_i}\right\}+\frac{V\Gamma^3}{3\pi}kT$$

$$\Gamma^2 = \frac{\pi e^2}{4\pi\varepsilon_0\varepsilon k_b T}\sum_{i=1}^{n_{ion}}\frac{n_i}{V}\left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2 \rightarrow r^{\mathrm{MSA}} = \sigma_{\mathrm{MSA}}/\sigma_{\mathrm{HS}}$$

b. Simplified-Binding-MSA model

$$A^{SBIMSA} = -\frac{e^2 V}{4\pi\varepsilon_0\varepsilon}\left\{\frac{\Gamma}{V}\sum_{i=1}^{n_{ion}}\frac{n_i z_i^2}{1+\Gamma\sigma_i}\right\}+\frac{V\Gamma^3}{3\pi}k_b$$

$$\Gamma^2 = \frac{\pi e^2}{4\pi\varepsilon_0\varepsilon k_b T}\sum_{i=1}^{n_{ion}}\frac{n_i}{V}\left(\frac{Z_i}{1+\Gamma\sigma_i}\right)^2 + \frac{e^2 n_p}{4\pi\varepsilon_0\varepsilon k_b T\sigma_p}\left(\frac{Z_{cation}Z'_{anion}}{1+\Gamma\sigma_{cation}}+\frac{Z_{anion}Z'_{cation}}{1+\Gamma\sigma_{anion}}\right)^2 \rightarrow r^{\mathrm{MSA}} = \sigma_{\mathrm{MSA}}/\sigma_{\mathrm{HS}}$$

Ion-pairs

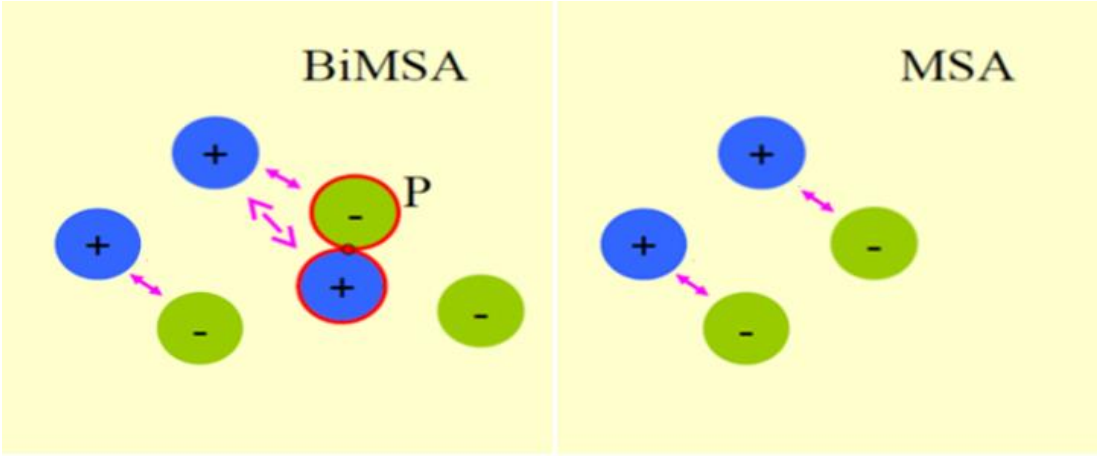


Fig 3. In the extended version of MSA theory (Binding-MSA), the effect of the formation of ion pairs and the long-range electrostatic interaction between ion pairs and free ions are added to the model.

CONSTRUCTION OF ION-PAIRING MODEL(ASSOCIATION TERM A^{assoc})

$$A^{assoc} = \sum_i n_i \sum_{A_i} \left[(lnX^{A_i}) + \frac{1}{2}(1 - X^{A_i}) \right]$$

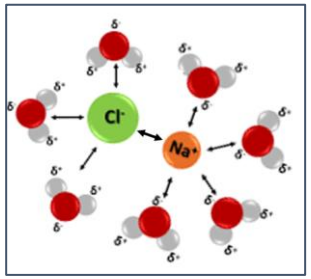
X^{A_i} =non-bonded fraction

$$X^{A_i} = \left[1 + N_{Av} \sum_{B_j} \left(\rho X^{B_j} \Delta^{A_i B_j} \right) \right]^{-1}$$

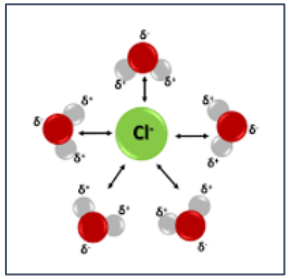
Delta= apparent association strength

Bjerrum | Wertheim

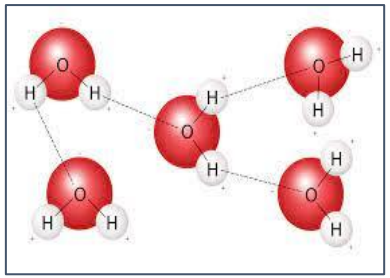
$$A^{\text{assoc}} = A^{\text{ion-ion}} + A^{\text{ion-solvent}} + A^{\text{solvent-solvent}}$$



Ion-ion



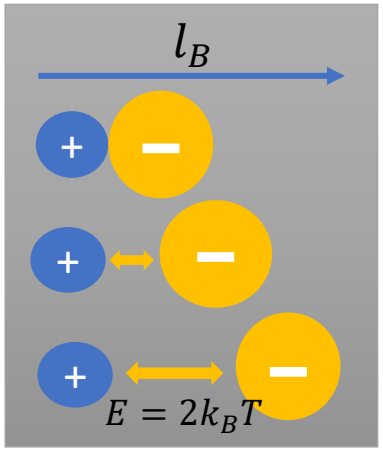
Ion-Solvent


Solvent-Solvent

Bjerrum theory:

$$\Delta^{A_i B_j} = 4\pi N_A \int_{\sigma_{ij}^{HS}}^{\lambda_{ij}^{BJ} \cdot l_B} exp\left(\frac{2l_B}{r_{ij}}\right) {r_{ij}}^2 dr_{ij}$$

$$l_B = \frac{b_{ij} |z_i z_j| e^2}{8\pi\varepsilon_o \varepsilon_r k_B T}, \quad (b_{ij} \text{ is an adjustable parameter})$$



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RESULTS AND DISCUSSION

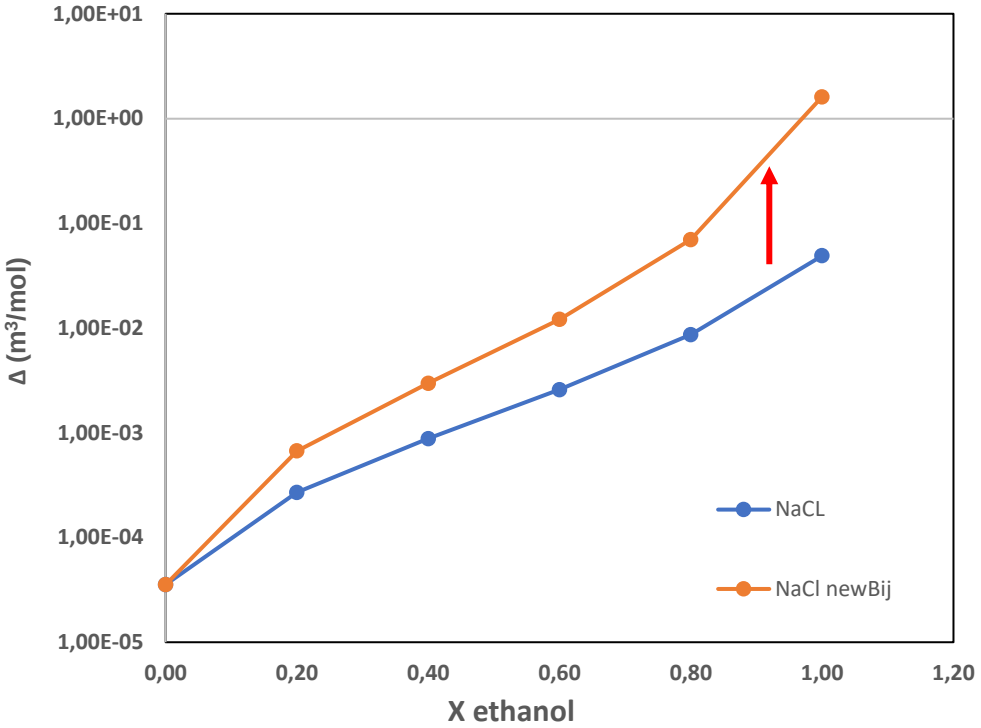
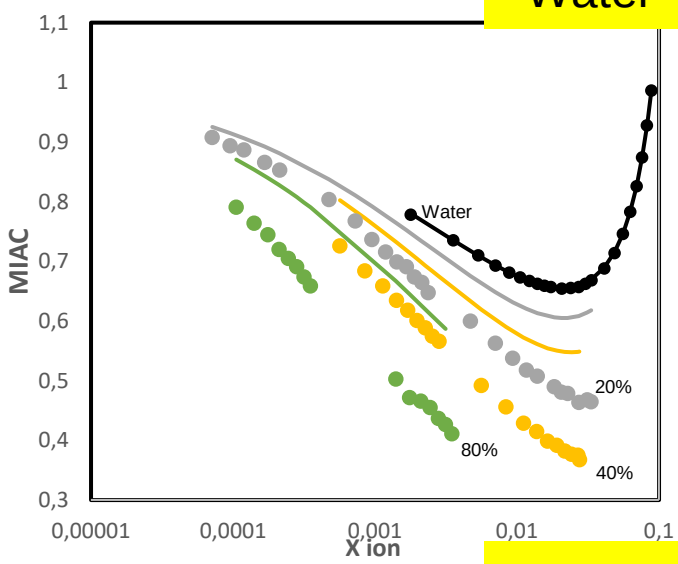


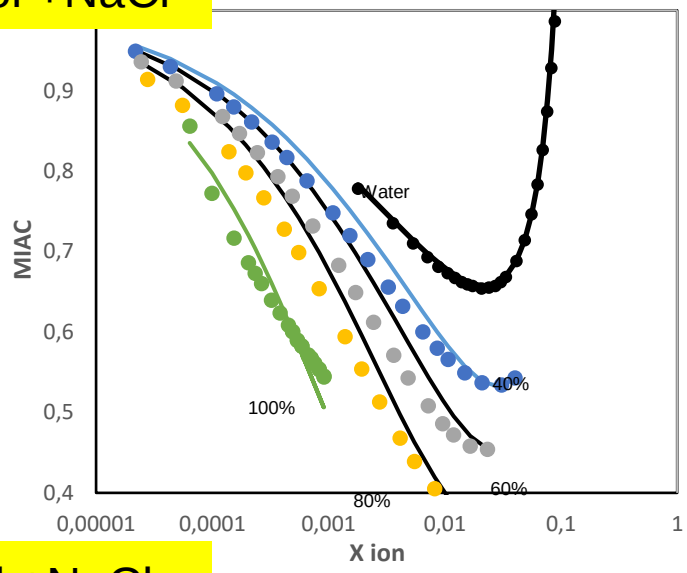
Fig 4. Obtained ion-ion association strength using a new bij for the NaCl-water-Ethanol system

NEW RESULTS FOR MIXED SOLVENT SYSTEMS USING NEW BIJ)

Water +Methanol +NaCl

AAD%	MAX AAD%
6.58	31.88

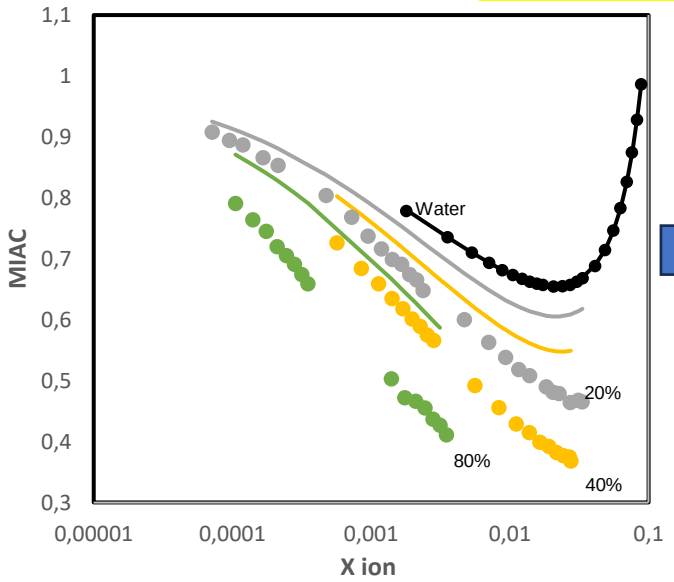


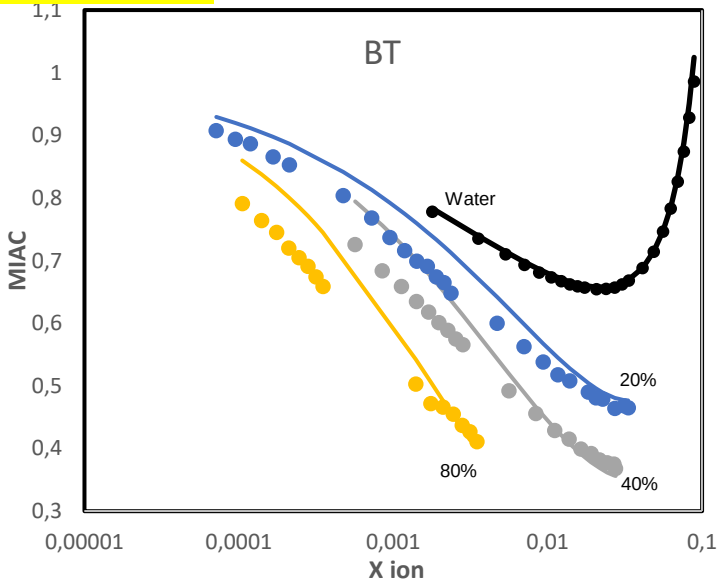


AAD%	MAX AAD%
3.36	9.99

Water +Ethanol +NaCl

AAD%	MAX AAD%
16.31	56.17





AAD%	MAX AAD%
5.5	23.61

CONCLUSION

- Bjerrum and BIMSA model successfully applied with in the ePPC-SAFT framework.
- New model can predict and correlate with the experimental data of mixed-solvent systems including alcohols

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CONSTRUCTION OF ION-PAIRING MODEL(A^{assoc} =ASSOCIATION TERM)

- **Apparent delta or Apparent association strength** of ion pairs ($A^{\mathrm{ion-ion}}$):

$$X^{A_i} = \left[1 + N_{Av} \sum_{B_j} \left(\rho X^{B_j} \Delta^{A_i B_j}\right)\right]^{-1}$$

→ **Delta= Apparent association strength (**quasi-chemical association constant**)**

- **Apparent delta of ion pairs:**

$$\Delta^{A_i B_j} = \frac{[A_i B_j]}{[A_i][B_j]}$$

$[A_i B_j]$ → Concentration of associated sites

$[A_i][B_j]$ → concentration of free sites of ions i and j

$$\Delta^{A_i B_j} = \frac{(1-\alpha)}{\alpha^2 c^0} = \frac{\rho_{AB}}{\rho_A^+ \rho_B^-}$$

- **True delta of ion pairs (True association constant)** from mass action low:

$$K_{ip} = \frac{a_{AB}}{a_B a_B} = \frac{\rho_{AB}\gamma_{AB}\rho^0}{\rho_A^+\gamma_A^+ * \rho_B^-\gamma_B^-} = \frac{\rho_{AB}\rho^0}{\rho_A^+ * \rho_B^-}\frac{\gamma_{AB}}{\gamma_A^+ * \gamma_B^-} \Rightarrow \Delta^{A_i B_j} = \frac{K_{ip}}{\rho^0}\frac{\gamma_A^+ * \gamma_B^-}{\gamma_{AB}}$$

- **How to use True delta in equation of state approach**

$$\Delta^{A_i B_j} = \frac{K_{ip}}{\rho^0} * \frac{\gamma_A^+ * \gamma_B^-}{\gamma_{AB}} \approx K(T) * \beta$$

β → Ratio of activity coefficients

$$\Delta^{A_i B_j} = \Delta^0 * \beta$$

Association constant of ions at infinite dilution

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CONSTRUCTION OF ION-PAIRING MODEL(MODEL COMBINATION)

Table 1.summary of model combinations.

Contributions:					
hs	PC-SAFT				
disp	PC-SAFT				
Born	Born				
MSA	sBiMSA (slide 9)				
Assoc (ion-solvent and solvent-solvent)	Wertheim				
Assoc (ion-ion)	Wertheim	Bjerrum (gel=1)		Bjerrum * gel	
RSP	Schreckenberg	Schreckenberg	Zuo & Fürst and Maryott & Smith	Schreckenberg	Zuo & Fürst and Maryott & Smith
Model names:	WS	BS	BT	BgS	BgT

Zuo & Fürst and Maryott & Smith models= RSP is only Temperature function ⇒ $\mathrm{D}_s = d_1 + \frac{d_2}{T} + d_3 T + d_4 T^2 + d_5 T^3$

Schreckenberg model= RSP is volume and composition function ⇒ $\varepsilon_r = 1 + \frac{n_{\mathrm{solv}}}{V} d_v \left(\frac{d_T}{T} - 1 \right)$

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RESULTS AND DISCUSSION (IMPACT OF RSP ON DELTA0)

Comparison of **BS (Bjerrum+Schreckenberg)** and **BT (Bjerrum+ Zuo & Fürst)** models

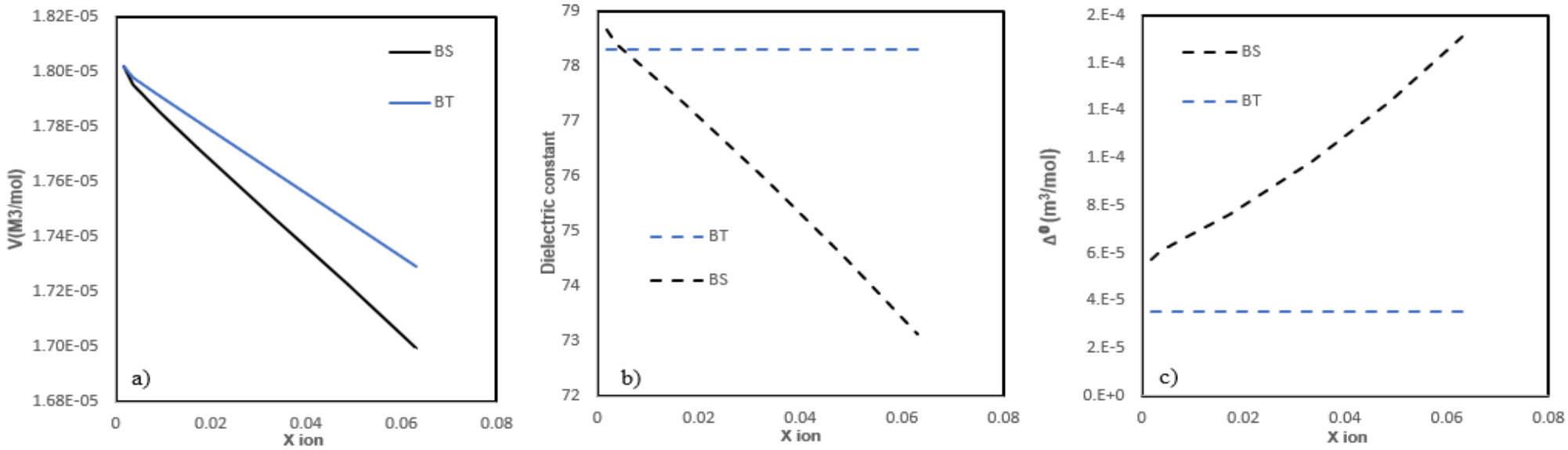

Figure 4. 6a shows the molar volume trend in equation of state framework using BS and BT models. In EoS framework volume (molar volume) has always negative slope using any type models. 6b and 6c compare Δ^0 and dielectric constant of sodium chloride salt in water using the BT and BS models at 298 K.

- **As a result, RSP should be independent from volume and salt concentration in order to have flat delta0).**

RESULTS AND DISCUSSION (IMPACT OF GEL ON DELTA0 AND DELTA)

Comparison of **BgT (Bjerrum*gel (Schreckenberg))** and **BgS (Bjerrum*gel (Zuo & Fürst))** models

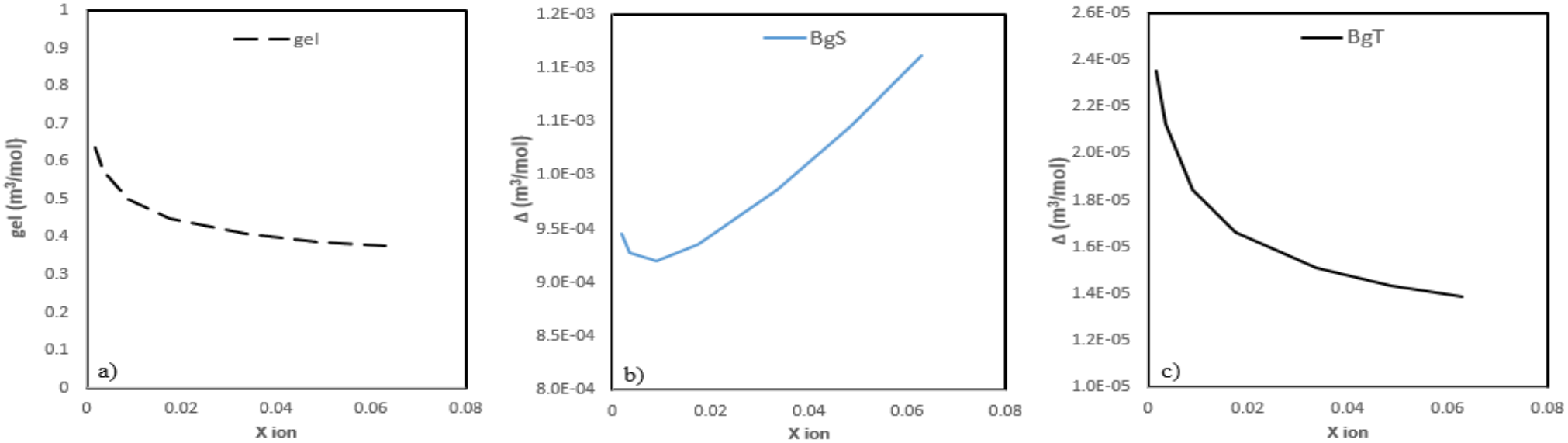

Figure 5. 7a shows gel shape using BgT model for sodium chloride salts in water at 298 K. 7b and 7c presents the Obtained association constant of ions for sodium chloride salts in water at 298 K using the BgS and BgT models respectively.

- **As a result, RSP should be independent from volume and salt concentration in order to have an appropriate shape for delta).**

RESULTS AND DISCUSSION (MODELS COMPARISON)

Table 3.summary of model combinations.

Contributions:					
Assoc (ion-ion)	Wertheim	Bjerrum (gel=1)		Bjerrum * gel	
RSP	Schreckenberg	Schreckenberg	Zuo & Fürst and Maryott & Smith	Schreckenberg	Zuo & Fürst and Maryott & Smith
Model names:	WS	BS	BT	BgS	BgT

- Wertheim delta is not a good solution for the calculation of ion-ion association for aqueous and mixed solvent systems specially when the concentration of ion-pairs is significant (high temperature or alcohol concentration).
- RSP should be independent from volume and salt concentration to have **flat delta0**.
- RSP should be independent from volume and salt concentration to have **an appropriate shape for delta**(downward slope).

RESULTS AND DISCUSSION (COMPARISON OF BJERRUM AND WERTHEIM FOR THE CALCULATION OF DELTA0)

Comparison of **WS (Wertheim+Schreckenberg)** and **BS (Bjerrum+ Schreckenberg)** models

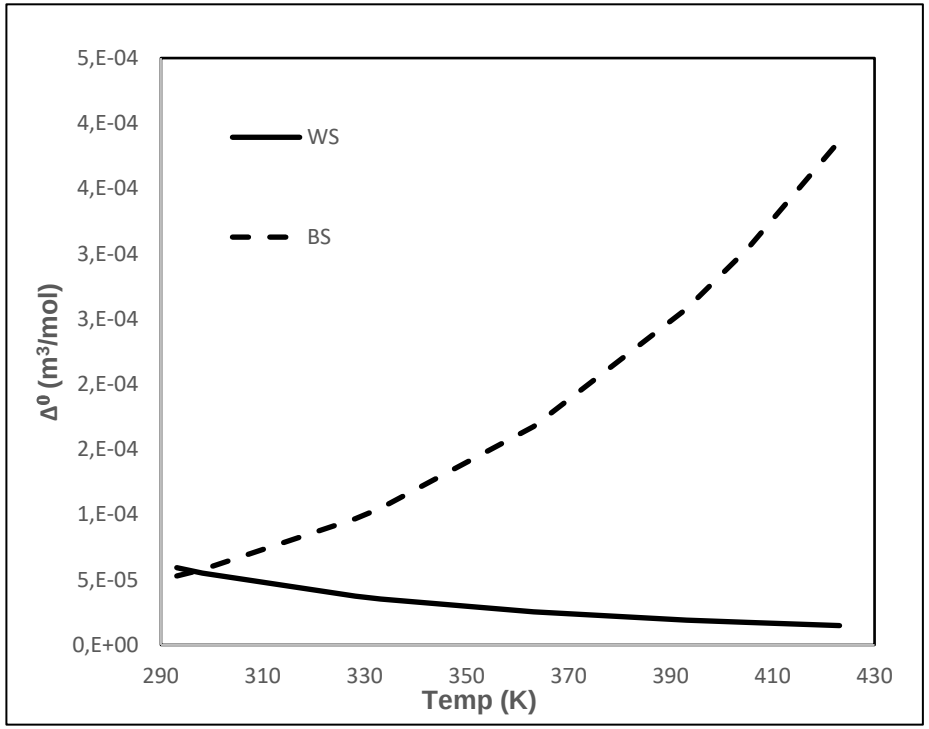

Fig 2. Comparison of delta0 for sodium chloride salts in water using the WS and BS models in the temperature range of 298 to 420 k.

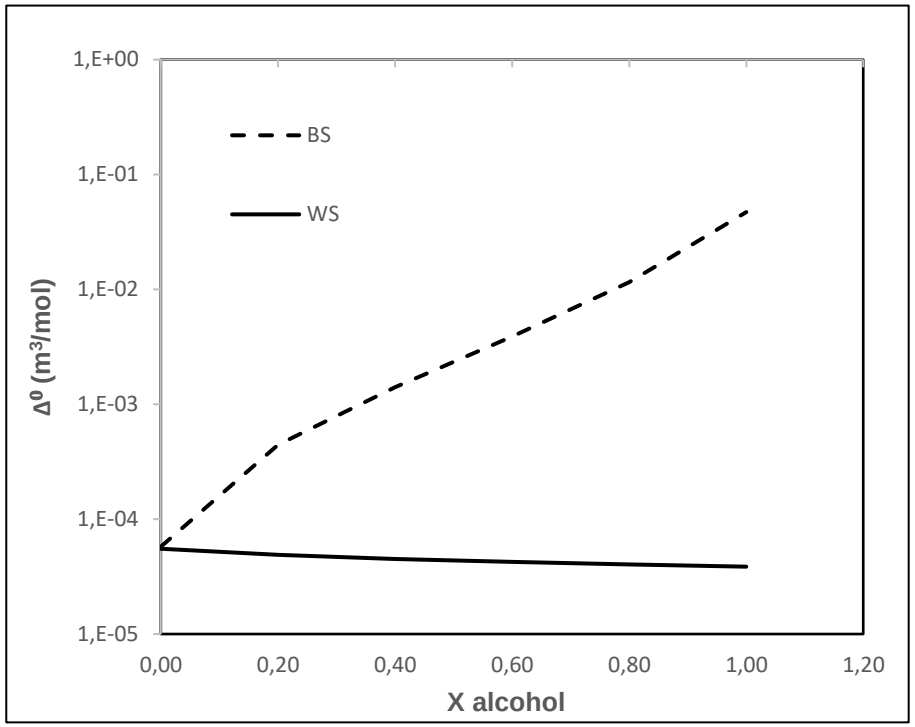

Fig 3. Comparison of delta0 for sodium chloride salt in water-ethanol mixture using the WS and BS models at 298K.

- **As a result, Wertheim association theory is not a good solution for the calculation of ion-ion association for aqueous and mixed solvent systems specially when the concentration of ion-pairs is significant (high temperature or alcohol concentration).**

CONSTRUCTION OF ION-PAIRING MODEL(ASSOCIATION TERM)

- Association models for calculation of Delta (apparent association strength of ion pair):
  - Wertheim association: **chemical association model** mostly used for hydrogen bonding or ion-solvent interaction

$$\Delta^{A_iB_j} = d_{ij}^3 g_{IJ}^{HS} k^{A_iB_j} \left[exp\left(\frac{\varepsilon^{A_iB_j}}{kT}\right) - 1 \right] \Rightarrow \Delta^{A_iB_j} = \Delta^0 * g_{ij}^{hs}$$

Ratio of activity coefficients at infinite dilution is one

  - Bjerrum model: **Electrostatic association model** for calculation of **delta at infinite dilution (Δ^0)**

$$\Delta^0 = 4\,\pi N_A \int_{\sigma_{ij}^{HS}}^{\lambda_{ij}^{BJ} \cdot l_B} exp\left(\frac{2l_B}{r_{ij}}\right) r_{ij}^2 dr_{ij} \Rightarrow \Delta^{A_iB_j} = \Delta^0 * 1$$

$$l_B = \frac{b_{ij} |z_i z_j| e^2}{8\,\pi \varepsilon_o \varepsilon_r k_B T}$$

  - BIMSA **correction factor** (gel): **Electrostatic correction factor($\beta = gel$)**

$$\Delta^{A_iB_j} = \Delta^0 * gel$$

Δ^0: Obtain from Bjerrum or Wertheim delta zero (Δ^0)

gel: Predictive term

OUTLINE

- introduction
- Thesis Objective
- Methodology of ion-paring
- Construction of ion-pairing model
- Results and discussion
- Conclusions