A Statistical Associating Fluid Theory for Electrolyte Solutions

based on SAFT-VRE (Gil-Villegas et al. *Molecular Physics*, **2001**, 99, 531-546)

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Introduction

- Application of Electrolyte Equation of State (EoS)
  - high pressure phase equilibria, ionic surfactant systems, gas hydrate systems containing salts, and so on.

- Approach of SAFT-VR to electrolyte systems
  - SAFT-VR
    - A second-order high-temperature perturbation expansion of a variable-ranged potential (Square well potential).
    - Dispersion term : The mean-field level of van der Waals is used.
  - Contribution due to the ion-ion interaction
    - Primitive models : Debye-Hückel theory, Mean Spherical approximation (MSA)

Primitive Models for Electrolyte Solutions

- The solvent contribution is described by a constant dielectric constants.
- Interaction potential : $u_{ij}(r) = \phi_{ij}(r) + \psi_{ij}(r)$ (1)
  - Potential $\phi_{ij}(r)$
    - The repulsive interactions with a hard-sphere potential.
    - $\phi_{ij}^{HS}(r;\sigma) = \begin{cases} \infty, \text{if } r < \sigma \\ 0, \text{if } r > \sigma \end{cases}$ where, $\sigma = (\sigma_i + \sigma_j)/2$ (2)
  - Electrostatic potential : $\psi_{ij}(r) = q_i q_j / Dr + \psi_{ij}^{CS}(r)$ (3)
    - The first term : the Coulomb potential between two ions.
    - The second term : Oppositely charged co-ions surrounding each one of the interacting ions *i* and *j*, as well as the reaction-field potential.

Primitive Models(PM) for Electrolyte Solutions

- Expressions for $\psi_{ij}(r)$
  - An average electrostatic potential $\Psi(r)$ is considered as follows

$$\psi_{ij}(r) = q_j \Psi(r) \qquad (4)$$

  - Poisson-boltzmann equation

$$\nabla_j^2 \Psi(r) = -\frac{4\pi}{D} \sum_j q_j \rho_j \exp[-w_{ij}(r)/kT] \qquad (5)$$

  - Potential of mean force (PMF), $w_{ij}(r)$
    - It is possible to obtain $w_{ij}(r)$ by solving the Ornstein-Zernike (OZ) equation for the interionic pair potential.
    - At low density, the PMF reduces to the intermolecular pair potential.

$$w_{ij}(r) = u_{ij}(r) \qquad (6)$$

Debye-Hückel Theory (I)

- A low density fluid of ions of the same diameter

$$\nabla_j^2\Psi(r) = -\frac{4\pi}{D}\sum_j q_j\rho_j \exp[-u_{ij}(r)/kT] \qquad (7)$$

$$= \frac{4\pi}{DkT}\sum_j q_j\rho_j\phi_{ij}(r) + \kappa^2\Psi(r) \quad \text{where, } \kappa^2 = \frac{4\pi}{DkT}\sum_j q_j^2\rho^2$$

- Boundary condition
  - Continuity of $\Psi(r)$ and $D\nabla\Psi(r)$ at $r=\sigma$
  - $\Psi(r)$ vanishes at infinity
- Solution of average electronic potential

$$\Psi(r) = \frac{q_i}{Dr}\left[\frac{\exp[-\kappa(r-\sigma)]}{1+\kappa\sigma}\right] \qquad (8)$$

Debye-Hückel Theory (II)

- Radial distribution function

$$g_{ij}(r) = \exp[-\phi_{ij}(r)/kT - q_j\Psi/kT] \tag{9}$$

$$= g_{ij}^{HS}(r)\exp\left[-\frac{q_i q_j}{DrkT}\left[\frac{\exp[-\kappa(r-\sigma)]}{1+\kappa\sigma}\right]\right] = 1 - \frac{q_i q_j}{DrkT}\exp[-\kappa r]$$

- Internal energy

$$\frac{U^{ION}}{NkT} = \frac{2\pi}{\rho}\sum_i\sum_j \rho_i\rho_j\int r^2 u_{ij}(r) g_{ij}(r)\,dr \tag{10}$$

- Free energy

$$\frac{A^{ION}}{NkT} = -\frac{\kappa^3}{12\pi} \tag{11}$$

Debye-Hückel Theory (Summary)

- The low density of ions has been assumed.

$$w_{ij}(r) = u_{ij}(r)$$

- The size of the ions has been neglected.

- The structure of the fluid is governed by the electrostatic interactions.

- This approach is applicable up to 0.001 molal.

Augmented Debye-Hückel Theory (I)

- Electrostatic corrections
  - Consideration for the size of the ions

$$g_{ij}(r) = 1 - \frac{q_i q_j}{DrkT}\left[\frac{\exp[-\kappa(r-\sigma)]}{1+\kappa\sigma}\right] \tag{12}$$

$$\frac{A^{ION}}{NkT} = -\frac{1}{4\pi\sigma^3}\left[\ln(1+\kappa\sigma) - \kappa\sigma + \frac{\kappa^2\sigma^2}{2}\right] \tag{13}$$

  - Taking into account the quadratic term in $g_{ij}(r)$

$$g_{ij}(r) = 1 - \frac{1}{kT} q_j \Psi(r) + \frac{1}{2(kT)^2} q_j^2 \Psi^2(r) \tag{14}$$

$$\frac{A^{ION}}{NkT} = -\frac{\kappa^2}{24\pi\sigma^3}\left[\ln(1+\kappa\sigma) + \frac{1}{(1+\kappa\sigma)}\right] \tag{15}$$

Augmented Debye-Hückel Theory (II)

- Non-electrostatic corrections
  - For higher densities of ions, the non-ionic packing information must be considered.

$$\phi(r) = \phi^{HS}(r;\sigma) - \varepsilon\Phi(r;\sigma) \qquad (16)$$

  - The radial distribution function and the free energy can be calculated in the context of perturbation theory as follows.

$$g_{ij}^{M}(r) = g_{ij}^{HS}(r) + \frac{\varepsilon}{kT} g_1(r) + \ldots \qquad (17)$$

$$\frac{A^M}{NkT} = a^{HS} + \frac{1}{kT} a_1 + \frac{1}{(kT)^2} a_2 \ldots \qquad (18)$$

Mean Spherical Approximation (MSA)

- Ornstein-Zernike (OZ) equation
  - Linking the total correlation function $h(r) = g(r) - 1$ to the direct correlation function $c(r)$ according to

$$h(r_{12}) = c(r_{12}) + \rho \int dr_3 c(r_{13}) h(r_{32}) \qquad (19)$$

- MSA
  - The direct correlation function is given by the intermolecular pair potential outside the repulsive core of the molecule.
  - The radial distribution function is zero inside the core.

MSA-Restricted Primitive Model (MSA-RPM)

- Assumption
  - All the ions in the solution are of the same size.
  - The pair potential is given by equations (1) to (3) and $\psi_{ij}^{CS} = 0$.

- MSA expressions with RPM

$$h_{ij}(r) = -1 \quad \text{for } r < \sigma \qquad (20)$$

$$c_{ij}(r) = -\frac{q_i q_j}{DkTr} \quad \text{for } r > \sigma \qquad (21)$$

MSA-Restricted Primitive Model (MSA-RPM)

- The radial distribution function (Blum et al., 1970)

$$g_{ij}(\sigma) = g_{ij}^{HS}(\sigma) - \frac{q_i q_j}{DkTr}(1-\tau^2), \qquad (22)$$

$$\tau = \frac{x^2 + x - x(1+2x)^{1/2}}{x^2} \qquad (23)$$

Where, $x = \kappa\sigma$

- The electrostatic residual free energy

$$\frac{A^{ION}}{NkT} = -\frac{3x^2 + 6x + 2 - 2(1+2x)^{3/2}}{12\pi\rho\sigma^3} \qquad (24)$$

MSA-Primitive Model (MSA-PM)

- Anions and cations are not restricted to be of the same size.
- The structural and thermodynamic properties are written as functions of a characteristic inverse length, *Γ*.

$$\Gamma = \left(\frac{\pi}{DkT} \sum_{i=1}^{n} \rho_i Q_i^2 \right)^{1/2} \qquad (25)$$

$$Q_i = \frac{q_i - (\pi / 2\Delta)\sigma_{ii}^2 P_n}{1+\Gamma\sigma_{ii}}, \qquad P_n = \frac{1}{\Omega} \sum_{i=1}^{n} \frac{\rho_i \sigma_{ii} q_i}{1+\Gamma\sigma_{ii}}$$

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_{i=1}^{n} \frac{\sigma_{ii}^3}{1+\Gamma\sigma_{ii}}, \qquad \Delta = 1 - \frac{\pi}{6} \sum_{i=1}^{n} \rho_i \sigma_{ii}^3$$

MSA-Primitive Model (MSA-PM)

- The radial distribution function (Blum et al., 1975)

$$\sigma_{ij} g_{ij}(\sigma) = \frac{\sigma_{ij}}{1-\varsigma_3} + \frac{3\varsigma_2 \sigma_{ii}\sigma_{jj}}{2(1-\varsigma_3)^2} - \frac{Q_i Q_j}{DkT} \qquad (26)$$

- The residual free energy

$$\frac{A^{ION}}{NkT} = -\frac{1}{\rho DkT}\left[\Gamma \sum_{i=1}^{n} \frac{\rho_i q_i^2}{1+\Gamma\sigma_{ii}} + \frac{\pi}{2\Delta}\Omega P_n^2\right] + \frac{\Gamma^3}{3\rho\pi} \qquad (27)$$

Where $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ and $\varsigma_l = \sum_{i=1}^{n} \rho_i \sigma_{ii}^l$.

SAFT-VRE Approach

- SAFT-VRE

$$\frac{A}{NkT} = \frac{A^{IDEAL}}{NkT} + \frac{A^{M}}{NkT} + \frac{A^{CHAIN}}{NkT} + \frac{A^{ASSOC}}{NkT} + \frac{A^{ION}}{NkT} \qquad (28)$$

- Ideal free energy of the mixture

$$\frac{A^{IDEAL}}{NkT} = \sum_{i=1}^{n} x_i \ln \rho_i \Lambda_i^3 - 1 \qquad (29)$$

where, Λ_i is the thermal de Broglie wavelength of species i.

SAFT-VRE Approach

- The monomer-monomer interaction

$$\frac{A^M}{NkT} = a^M = a^{HS} + \frac{1}{kT} a_1 + \frac{1}{(kT)^2} a_2 \qquad (30)$$

  - a^{HS} is the hard-sphere free energy of the mixture
  - a_1 and a_2 are the first two terms of the perturbation expansion associated with the attractive energy.

$$a_1 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_1^{ij} = -\rho \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \alpha_{ij}^{VDW} g_{ij}^{HS}[\sigma_{ij};\varsigma_3^{eff}] \qquad (31)$$

$$\alpha_{ij}^{VDW} = 2\pi\varepsilon_{ij}\sigma_{ij}^3(\lambda_{ij}^3 - 1)/3 \qquad (32)$$

$$a_2 = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_2^{ij} = \frac{\rho}{2}\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j K^{HS} \varepsilon_{ij} \frac{\partial a_1^{ij}}{\partial \rho} \qquad (33)$$

SAFT-VRE Approach

- Association term
  - Water-water (hydrogen bonding), ion-water (solvation), ion-ion (ion-pairing) interactions.
  - $$\frac{A^{ASSOC}}{NkT} = \sum_{i=1}^{n} x_i \left[\sum_{a=1}^{S_i} \left(\ln X_{a,i} - \frac{X_{a,i}}{2} \right) + \frac{s_i}{2} \right] \qquad (34)$$
  - The effect of the association interactions depends on the range of densities, temperatures, and the nature of the solvent.
  - Solvation : the formation of hydration shells in aqueous solutions
  - Ion-pairing is not important in aqueous solutions of strong electrolytes at ambient temperature.

Model parameter study for a model solution of NaCl

- Effect of the dielectric constant
  - Determining the nature of the solvent
  - The higher the dielectric constant the better the ionic solvent
  - Using DH and MSA-RPM theories

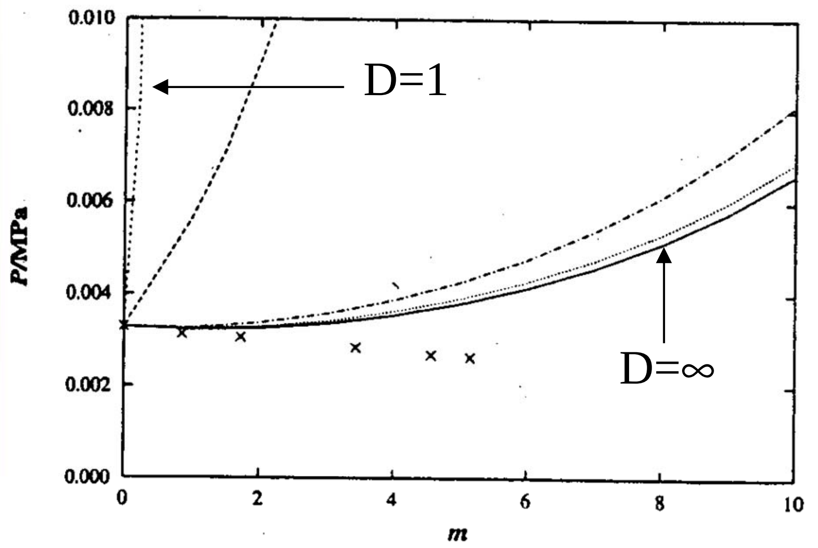
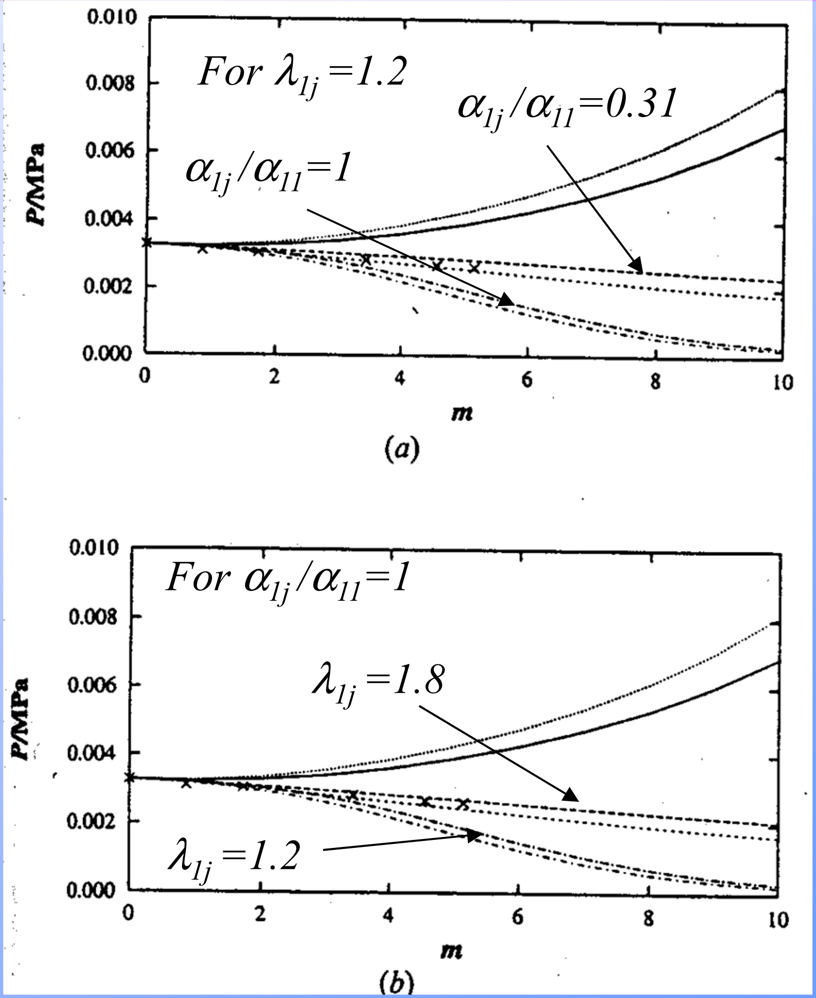


Figure 2. Experimental vapour pressures of aqueous NaCl at 298.15 K (symbols) compared with the SAFT-VRE predictions using ion–ion interactions incorporated at the RPM level in the DH and MSA theories. Different values of the dielectric constant are examined. The dashed curves correspond to the calculations with $D = 1$ (short dash for DH and long dash for MSA), the dashed-dotted (DH) and dotted (MSA) curves correspond to the calculations with $D = 74.373$ (the experimental dielectric constant of water at 298.15 K). The continuous curve corresponds to the calculations when $D = \infty$ (see text for details of the molecular parameters).

- Solvent-ion attractive interactions : dispersive type
  - Interactions through the repulsive and Coulombic potentials only.

$$\alpha_{ij}^{VDW} = 2\pi\varepsilon_{ij}\sigma_{ij}^{3}(\lambda_{ij}^{3} - 1)/3$$

  - The vapor pressure is under-predicted as the solvent-ion interaction is strong.
  - For greater λ, a less deep well and higher vapor pressure.

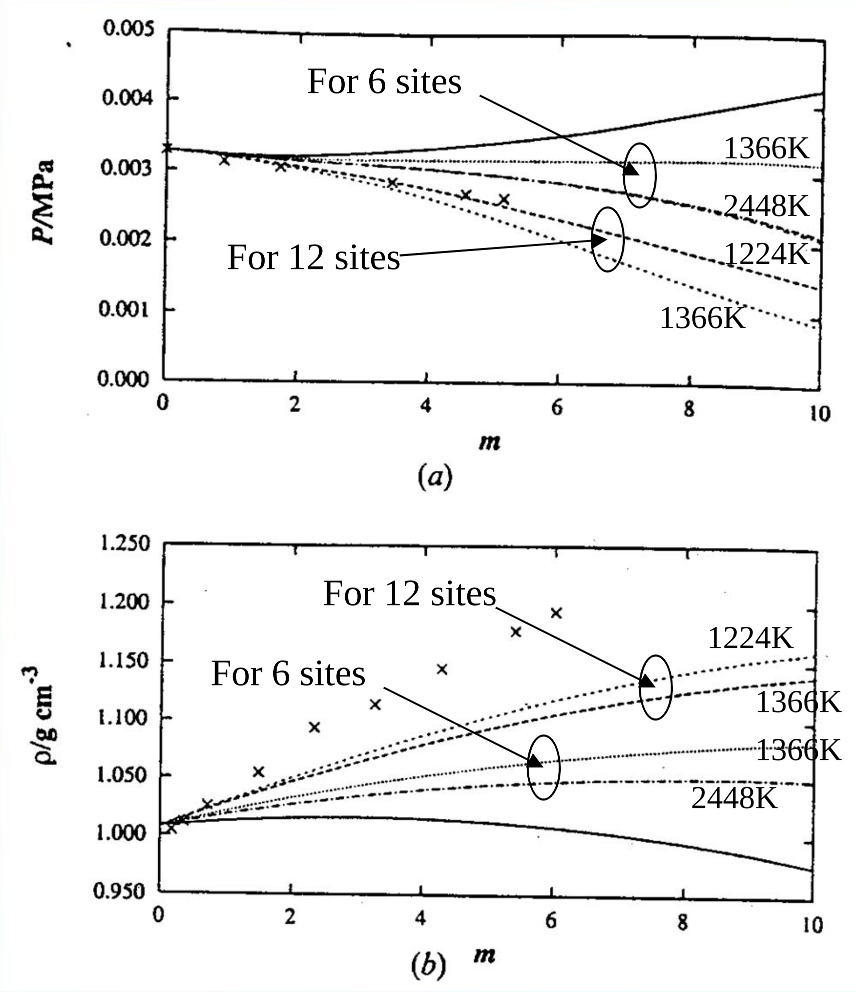


- Solvent-ion attractive interactions : associative type
  - To describe the solvent-ion interactions (solvation shell)
  - Adjustable parameter
    - Water-ion interations :

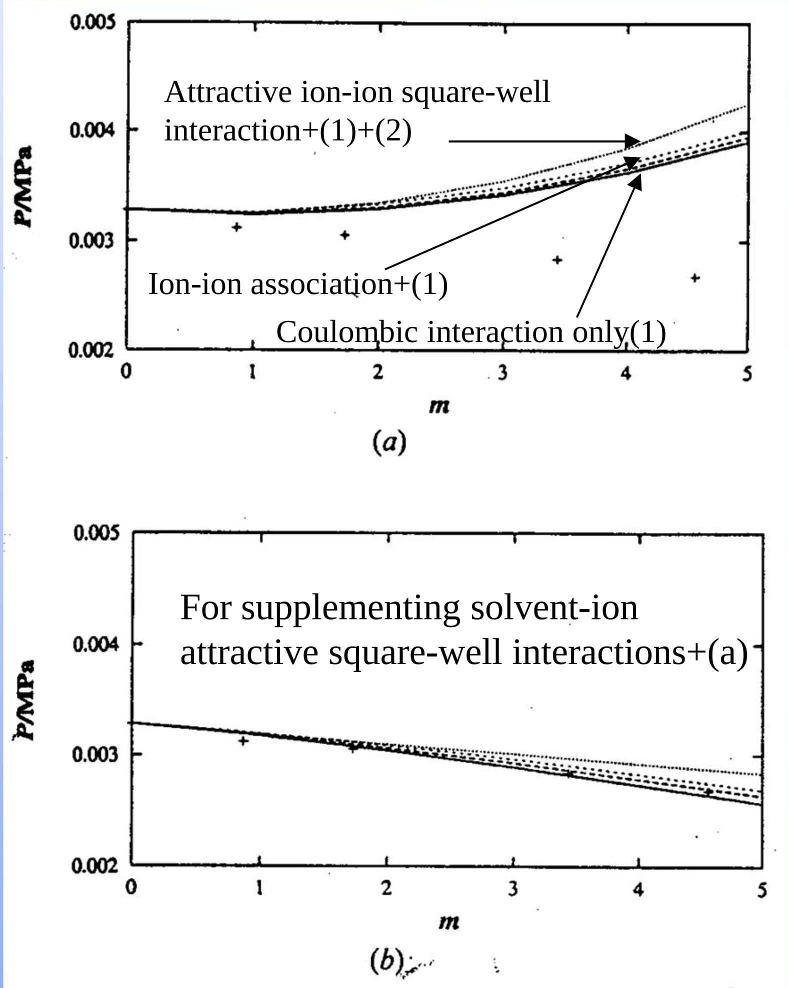
      $$\varepsilon_{1j}^{HB} / k[K]$$

    - The number of attractive site :

      $$S_i$$



- Ion pairing
  - ◆ ion-ion interactions
    - Strong electrolytes are fully dissociated.
    - The ion pairing occur around the critical region.
  - ◆ Three models
    - Coulombic interaction
    - Anion-cation attractive square-well interaction
    - Association via short-ranged attractive sites



Attractive ion-ion square-well interaction+(1)+(2)

Ion-ion association+(1)

Coulombic interaction only(1)

For supplementing solvent-ion attractive square-well interactions+(a)

Conclusion

- Several levels of approximation have been considered for primitive model theories.
- The solvent-ion interaction is modeled via an attractive potential of variable-range.
- Associative sites of ion-water interactions have been considered.
- SAFT-Electrolyte EoS is applicable to phase equilibria containing strong electrolyte.