Application to the Lithium ionic Electrolyte Systems with Excess Gibbs Energy Model including Solvation

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Scheme

- Introduction
- Theoretical Background
- Results
- Conclusion

Introduction

- **Aqueous Electrolyte Solution**
  - A wide variety of important chemical processes

    Wastewater treatment, extractive distillation, solution crystallization, desalination, gas scrubbing etc.
- **Previous Models**
  - G^E Model
    - Debye-Hückel (1923), Bromley (1973), Pitzer (1973)

      Meissner & Tester (1972), Chen et al. (1982)
  - Primitive Model
    - Wasman et al. (1972), Blum (1975), Harvey et al. (1989), Taghikhani et al. (2000)
  - Nonprimitive Model
    - Planche et al. (1981), Ball et al. (1985),

      Fürst et al. (1993), Zuo et al. (1998)
  - Acceptable accuracy up to I=6.0 or less

Hydration Theory

G^E model

- **Ghosh and Patwardhan (1990)**
  - Based on lithium chrolide as a reference electrolyte
  - Hydration energy, function of the total moles of water hydrated per kg of solution
  - Up to I=24 for 150 electrolyte solutions

- **Schoenert (1990, 1991,1993, 1994)**
  - Modified hydration model of Robinson and Stokes
  - Transfer of water to the hydration spheres of ions
  - Up to m=1 for HCl,LiCl,NaCl,KCl,CsCl,NH_4Cl,NaBr

Hydration Model

SAFT Approach

- Gil-Villegas et al. (2001)
  - Ionic contribution : MSA
  - Solvent-solvent, solvent-ion, ion-ion pairing
  - Applied to the NaCl solution up to 10 m
- Paricaud et al. (2001)
  - Applied to the NaOH solution up to 22 m

In present work

- Solvation contribution from the Veytsman statistics
  Explicitly added to Lee et al. model
- Application to LiCl, LiBr, LiI and $LiClO_4$ solutions

Excess Gibbs Function

- **Long-range + Physical + Solvation**

$$G^E = G^E_{DH} + G^E_A + G^E_R + G^E_{HB}$$

  - **In high pressure limit, holes are vanished**

$$A^E(T, P=\infty, x_i) = A^E(T, low\ \ P, x_i) = G^E(T, low\ \ P, x_i)$$

  - **Physical interaction : Athermal + Residual**

    From Lee et al. model (1996)

  - **Solvation interaction**

    From a normalized Veytsman statistics (Park et al.,2001)

Activity Coefficient

- **For solvent in symmetric convention**

$$\ln\gamma_j = \ln\gamma_{DH,j} + \ln\gamma_{A,j} + \ln\gamma_{R,j} + \ln\gamma_{HB,j}$$

- **For solute in asymmetric convention**

$$\ln\gamma_j^* = \ln\gamma_j - \lim_{x_i \to 0} \ln\gamma_j$$

$$\ln\gamma_{\pm i}^* = \ln\gamma_{DH,\pm i}^* + \ln\gamma_{A,\pm i}^* + \ln\gamma_{R,\pm i}^* + \ln\gamma_{HB,\pm i}^*$$

Solvation Contribution

- **For solvent,**

$$\ln\gamma_{HB,j} = -\sum_{k}^{m} d_j^k \ln\frac{N_{k0}^{j} N_{k0}^{0}}{N_{k0} N_{k0}^{j,0}} - \sum_{k}^{n} a_k^j \ln\frac{N_{0k}^{j} N_{0k}^{0}}{N_{0k} N_{0k}^{j,0}}$$

- **For solute,**

$$\ln\gamma^{*}_{HB,\pm i} = -\frac{\nu_{+i}}{\nu_{\pm i}}\sum_{k}^{m} d_i^k \ln\frac{N_{k0}^{0} N_{k0}^{\infty}}{N_{k0} N_{k0}^{0,\infty}} - \frac{\nu_{-i}}{\nu_{\pm i}}\sum_{k}^{n} a_i^k \ln\frac{N_{0k}^{0} N_{0k}^{\infty}}{N_{0k} N_{0k}^{0,\infty}}$$

- N_{ij}^{HB} **: the number of proton donor-acceptor pair for hydrogen bonding**

$$N_{ij}^{HB} N_r = \left(N_d^i - \sum_{j=1}^{n} N_{ij}\right)\left(N_a^j - \sum_{i=1}^{m} N_{ij}\right)\exp\left(-\beta A_{ij}^{HB}\right)$$

- N_{ij}^{0} **with** $A_{ij}^{HB} = 0$

Parameters

- For physical interaction
  - ▶ Size parameter of each ion and water, r_i
  - ▶ Energy parameters

    Cation-water & anion-water, $\tau_{13}, \tau_{23}, \tau_{31}, \tau_{32}$
- For solvation
  - ▶ Solvation number
    - ❑ Cation : donor number, d
    - ❑ Anion : acceptor number, a
    - ❑ Water : donor & acceptor number (d=2, a=1)
  - ▶ Solvation energy
    - ❑ Cation-water & anion-water, A_{13}^{HB}, A_{32}^{HB}

Parameter Determinations

- **Size parameter**
  - Cation : from crystalline ionic volume
  - Water : from Lee et al. model (2.5)
- **Solvation number**
  - From coordination numbers in hydration shells of ions

    (Krestov et al., 1994)
- **Solvation energy of water : from Luck(1980)**
- **Data for solute activity coefficients**
  - Size parameter of each anion
  - Energy parameters for physical interaction
  - Solvatoin energy parameters of cation- & anion-water

Results

Table 1. Parameters for Lithium ionic Electrolyte Systems

	r_i	τ_{13} (or τ_{23})	d_{ii} (or a_{ii})	A_{13} (or A_{32}) x 10^{-3} /J mol^{-1}
Li^+	0.1229	0.156	6	-15.61
Cl^-	0.615	0.143	5	-4.75
Br^-	1.145	1.167	8	-4.70
I^-	1.756	1.350	8	-4.45
ClO_4^-	1.845	1.052	8	-3.85

Results

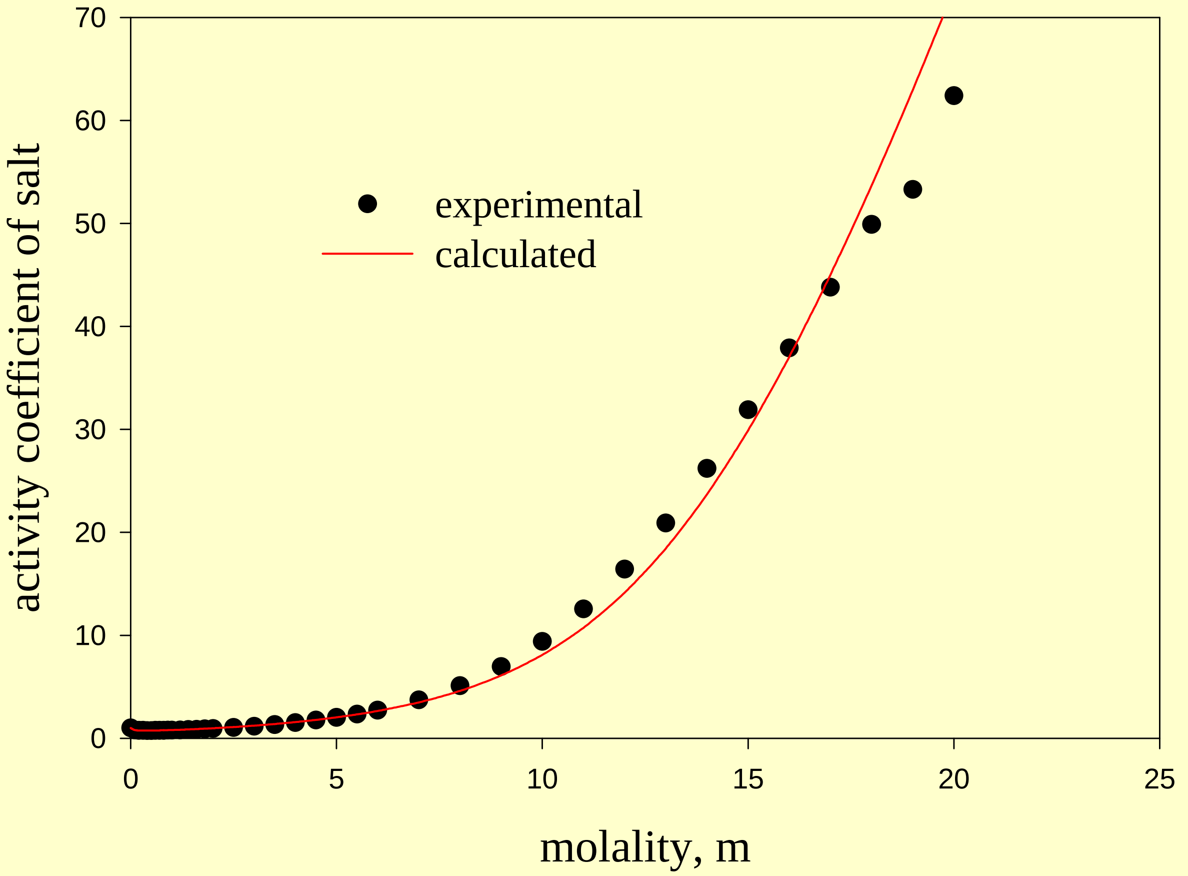

Fig.1 The activity coefficient of LiCl.

Results

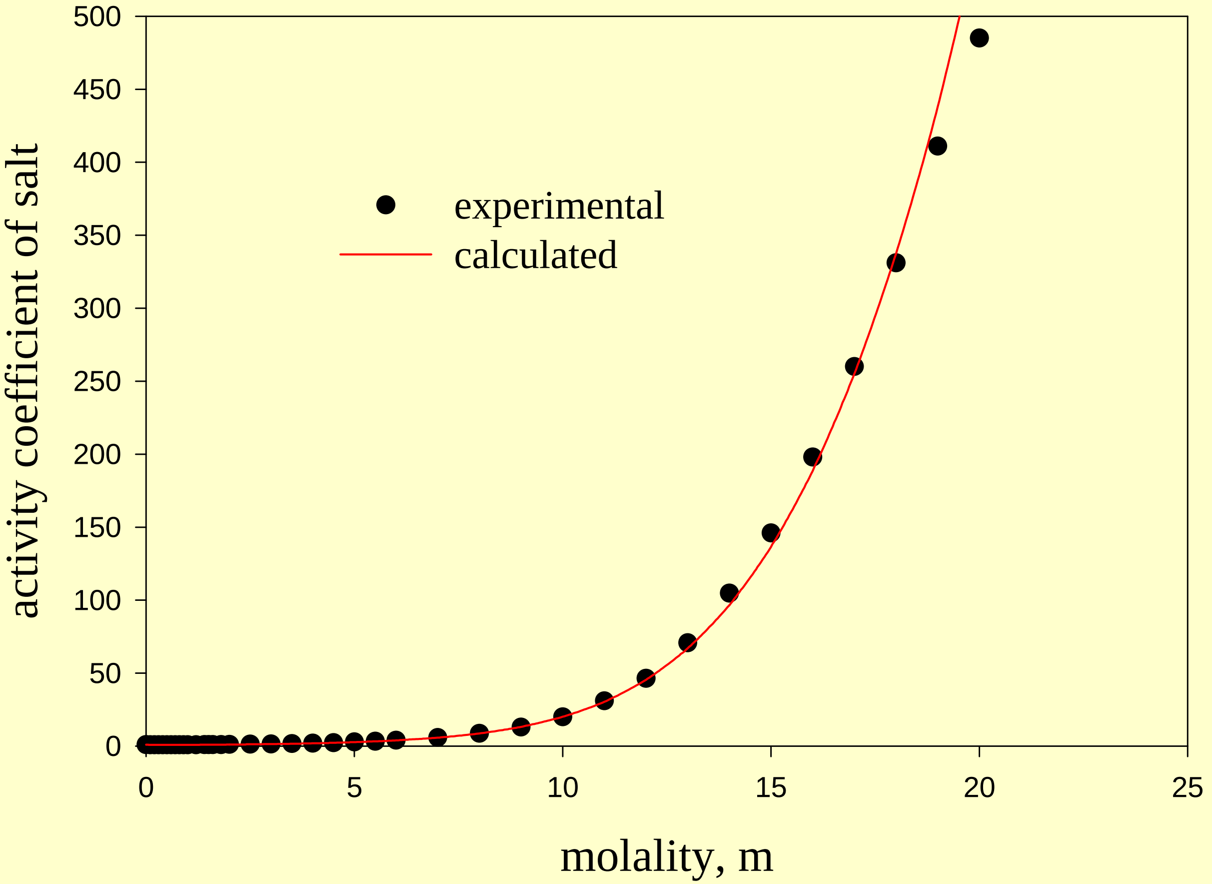

Fig.2 The activity coefficient of LiBr.

Results

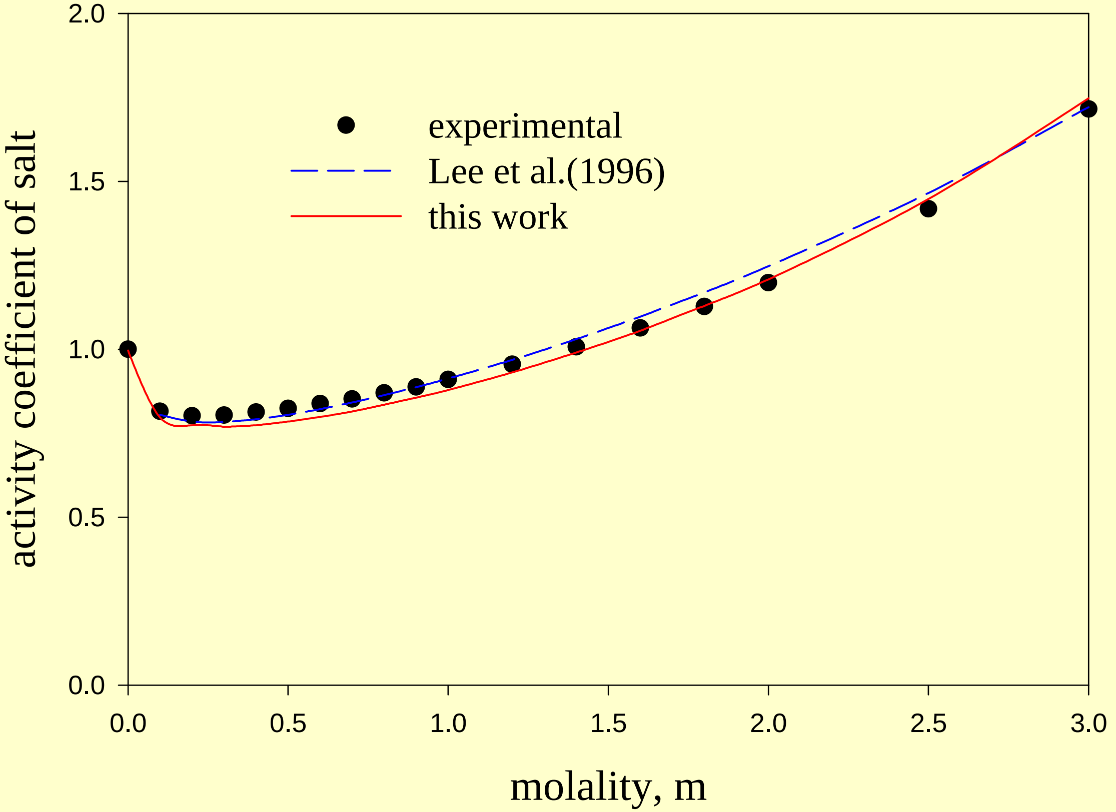

Fig.3 The activity coefficient of LiI.

Results

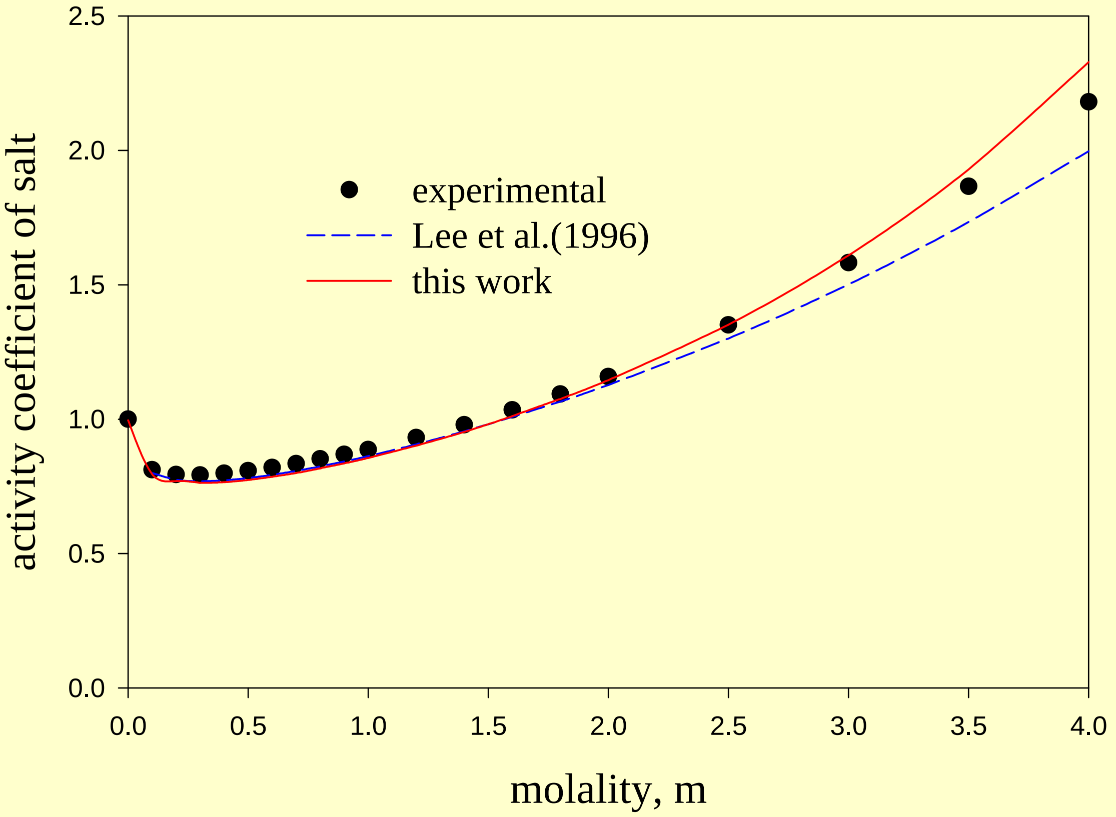

Fig.4 The activity coefficient of $LiClO_4$.

Conclusions

- **Lee et al. model was extended to the high concentrated electrolyte solutions, explicitly including solvation from a normalized Veytsman statistics.**
- **The fitted results give a good agreement with experimental activity coefficients of LiCl, LiBr, LiI and $LiClO_4$ up to 20 molal concentrations.**