Application of NLF-HB Theory to Electrolyte Systems with MSA Model

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Introduction

- Excess Gibbs energy model
  - Successful for describing the nonideality of electrolyte systems
  - Limitations
    - High pressure phase equilibria
    - Not possible to select a truly useful standard state for the supercritical components (Pausnitz et al., 1986)
    - Only applicable to liquid state => To use equation of state approach for vapor phase

- Eqaution of state approach to electrolyte system
  - Recently since about 1990 years ….
  - Jin and Donhue [1988], Furst and Renon [1993], Wu and Prausnitz [1998], and so on…

NLFHB with MSA

- The total change in the Helmholtz free energy for electrolyte solution

$$\left(\frac{A-A^0}{RT}\right)=\left(\frac{A-A^0}{RT}\right)_{SR}+\left(\frac{A-A^0}{RT}\right)_{HB}+\left(\frac{A-A^0}{RT}\right)_{LR}$$

- Short range contribution
  - Physical interaction for solvent-ion and ion-ion
- Hydrogen bonding contribution
  - Hydrogen bonding for water and alcohol
  - Solvation effect for solvent-cation
- Long range contribution
  - Mean spherical approximation by Harvey et al. [1988]

Short range contribution

- *Nonrandom Lattice Fluid Theory* by You et al. [1994 a, b]
- Physical interactions for solvent-solvent, solvent-ion, and ion-ion
- Parameters for NLF theory
  - Solvent
    - Fitting the energy and size parameters using density and vapor pressure.
  - Ionic species
    - Size parameters : Pauling(ionic) diameter
    - Energy parameters : Fitting by osmotic coefficient and density of solution

Hydrogen bonding contribution

- Expansion to associating system using Veytsman statistics [1990] by Yeom et al. [1999]

- A normalization of Veytsman statistics by Lee et al. [2001]

- Parameters
  - Hydrogen bonding for water-water
    - U = -15.5 kJ/mol and S=-16.6 J/mol·K
    - Two donors and two acceptors
  - Solvation effect for solvent-cation
    - Fitting the hydrogen bonding energy for each cation
    - Number of donors for cation : 1 charge => 6, 2 charges => 12

Long rang contribution

- Mean spherical approximation by Harvey et al. [1988]

$$\left(\frac{A\text{-}A^0}{RT}\right)_{LR} = -\frac{Ve^2}{4\pi\varepsilon_0 DRT}\left\{\Gamma\sum_{ions}\frac{\rho_{ion}z_{ion}^2}{1+\Gamma\sigma_{ion}} + \frac{\pi\Omega P_n^2}{2\Theta}\right\} + \frac{V\Gamma^3}{3\pi N}$$

$$\Theta = 1 - \frac{\pi}{6}\sum_{ions}\rho_{ion}\sigma_{ion}^3, \qquad \Omega = 1 + \frac{\pi}{2\Theta}\sum_{ions}\frac{\rho_{ion}\sigma_{ion}^3}{1+\Gamma\sigma_{ion}} \qquad P_n = \frac{1}{\Omega}\sum_{ions}\frac{\rho_{ion}\sigma_{ion}z_{ion}}{1+\Gamma\sigma_{ion}}$$

$$4\Gamma^2 = \frac{e^2}{\varepsilon_0 kTD}\sum_{ions}\frac{\rho_{ion}\left(z_{ion} - \pi\sigma_{ion}^2 P_n / 2\Theta\right)^2}{\left(1+\sigma_i\Gamma\right)^2}$$

- Size parameters σ
  - Anions : Pauling (ionic) diameter
  - Cations : Fitting by osmotic coefficient data

Estimation of pure parameters

- Method 1
  - Each ions are considered as independent species.

		Solvent	Cation	Anion
NLF	Size	Fitting	Pauling Dia.	Pauling Dia.
	Energy	Fitting	Fitting	Fitting
HB	U and S	Literature value	Fitting	None
	Donor/Acceptor	Literature value	Fix	None
MSA	Size	None	Fitting	Pauling Dia.
No. of parameters		2	3	1

Estimation of pure parameters

- Method 2
  - Each salts are considered as independent species.
  - More accurate results, but maybe not applicable to mixed salt

		Solvent	Salt
NLF	Size	Fitting	Pauling dia. for each ions
	Energy	Fitting	Fitting of ε_{anion}(ε_{cation}= 0)
HB	U and S	Literature value	Fitting of hydration energy for cation
	Donor/Acceptor	Literature value	Fix
MSA	Size	None	Fitting of σ_{caton} (σ_{anion}= Pauling dia.)
No. of parameters		2	3

Physical interactions between molecules

- For solvent-ion and cation-anion,

$$\varepsilon_{ij} = \left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2}$$

- For cation-cation and anion-anion,

$$\varepsilon_{ij} = 0$$

- Summary

	Solvent	Cation	Anion
Solvent	O	O	O
Cation	O	X	O
Anion	O	O	X

- Requirement of clear explanation for ion-ion interactions

Thermodynamic variables

- Osmotic coefficient

$$\Phi = -\left[\left(\frac{\mu_w - \mu_w^0}{RT} \right) - \left(\frac{\mu_w - \mu_w^0}{RT} \right)^{ref} \right] \frac{x_s}{\sum_{ion} x_{ion}}$$

$$= -\frac{x_s}{\sum_{ion} x_{ion}} \ln[x_{solvent} \gamma_{solvent}]$$

where reference state is pure solvent at system temperature.

◆ Advantageous for emphasizing the departure from ideality in low concentration region of salt.

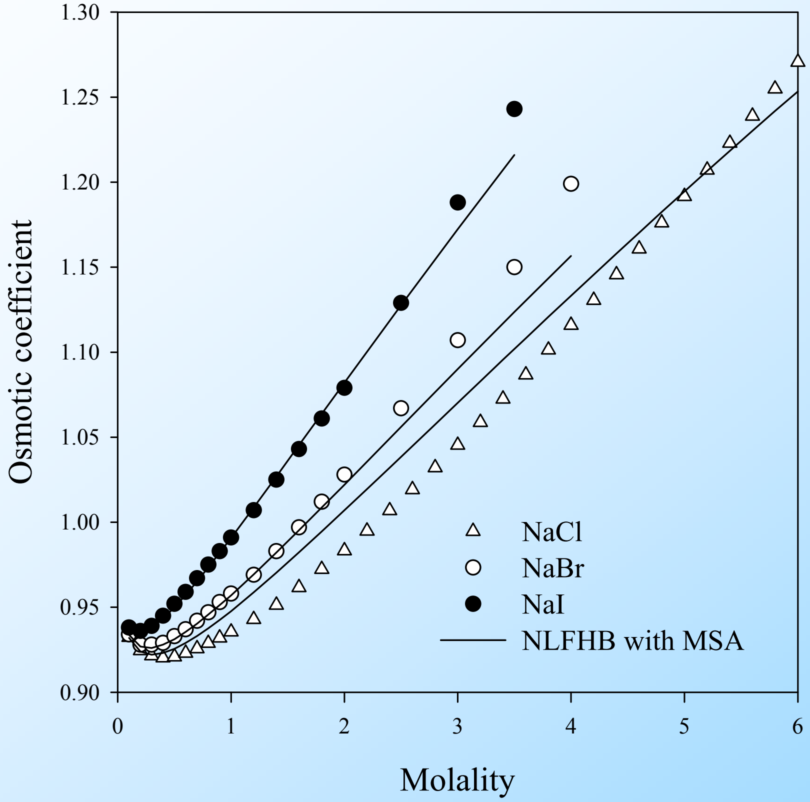
Result

- Dielectric constant : assume as independent of composition

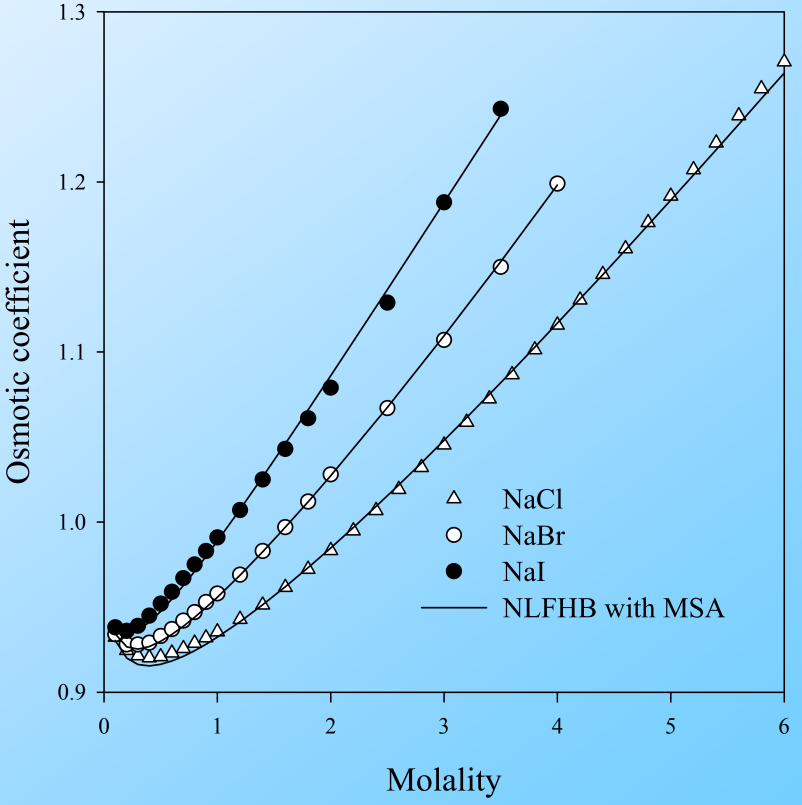
- Fitting procedure
    - Fix anion size parameter in MSA : use the Pauling diameter of anion
    - Fitting the HB parameter and ionic size parameter of cation using osmotic coefficient data
    - Calculated densities of solution are not affected strongly by fitting the parameters.

- % AADs in osmotic coefficients at 298.15 K

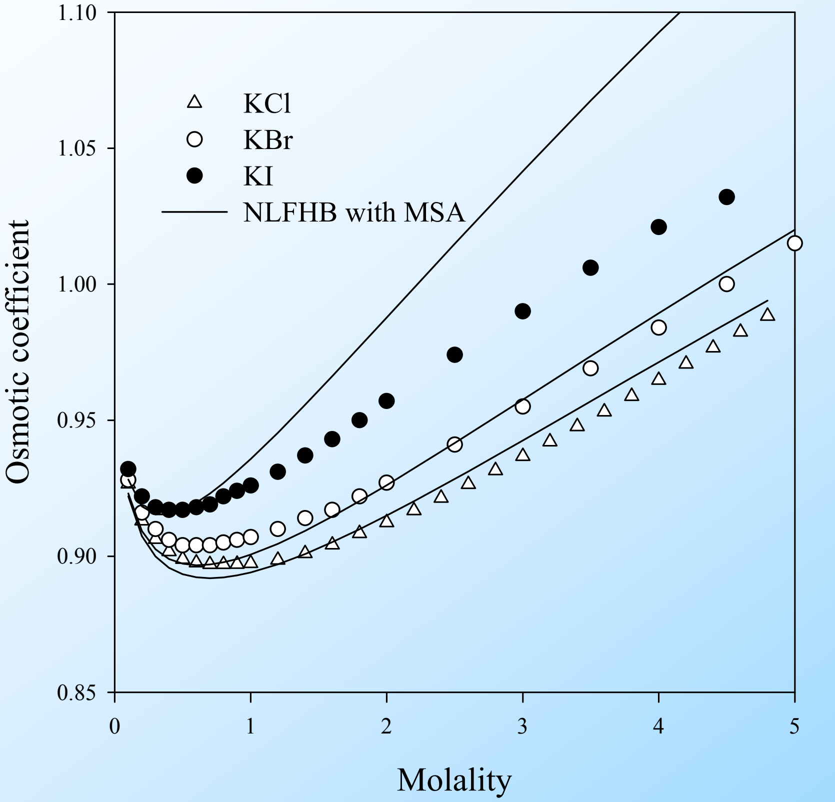
	Max. molality	Method 1	Method 2	Lee et al.
NaCl	6.0	1.31	0.27	1.46
NaBr	4.0	0.58	0.20	0.64
NaI	3.5	0.33	0.32	0.44
KCl	4.8	0.51	0.04	0.46
KBr	5.0	0.51	0.07	0.84
KI	4.5	2.35	0.07	2.59
LiCl	6.0	0.33	0.68	3.18
LiBr	6.0	2.48	1.05	4.51
LiI	3.0	1.29	0.97	1.74
$CaCl_2$	6.0	3.99	1.09	1.44
$CaBr_2$	6.0	5.19	1.23	1.97
CaI_2	6.0	1.57	0.65	3.26
Overall		1.70	0.53	1.88



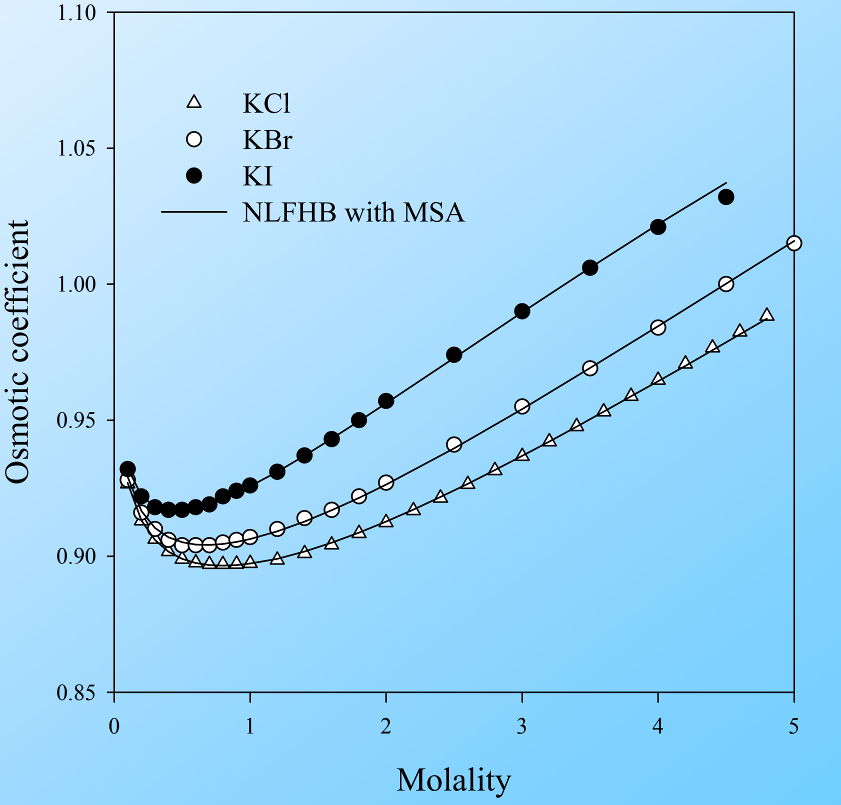
Osmotic coefficient of Sodium halide at 298.15 K (Method 1)



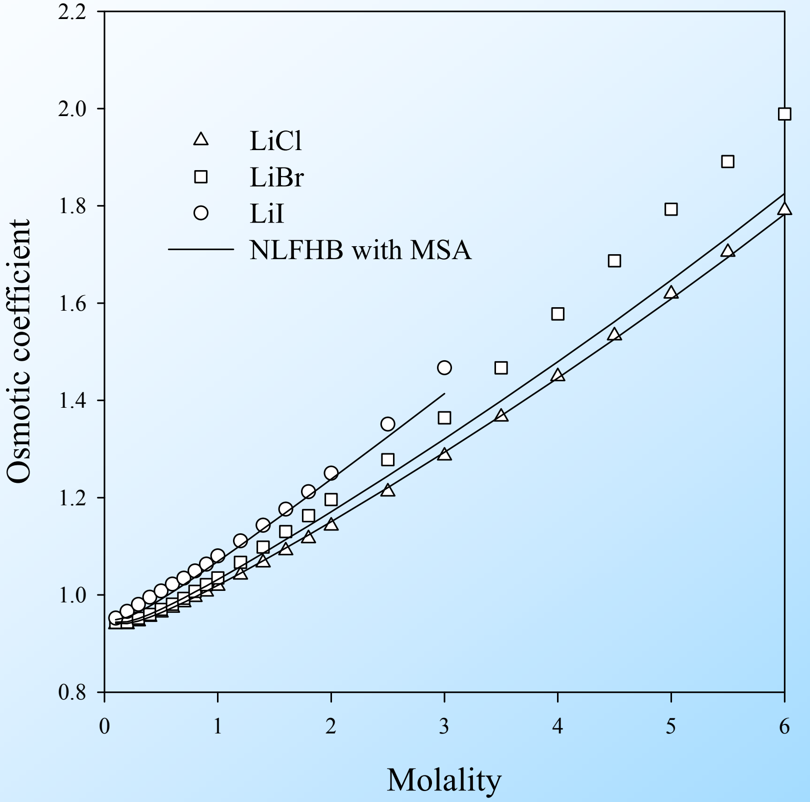
Osmotic coefficient of Sodium halide at 298.15 K (Method 2)



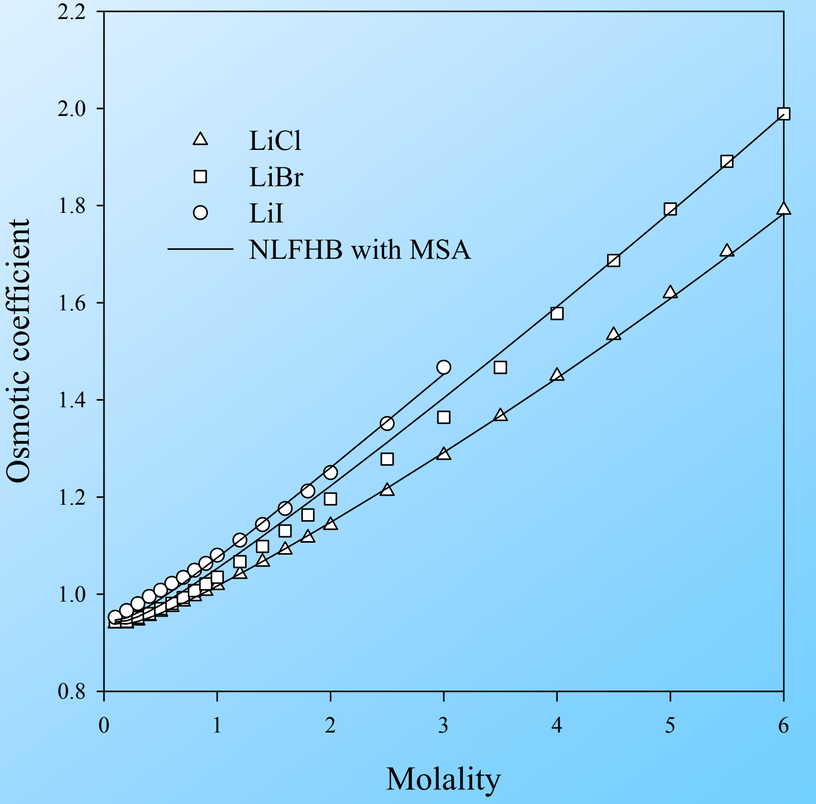
Osmotic coefficient of Potassium halide at 298.15 K
(Method 1)



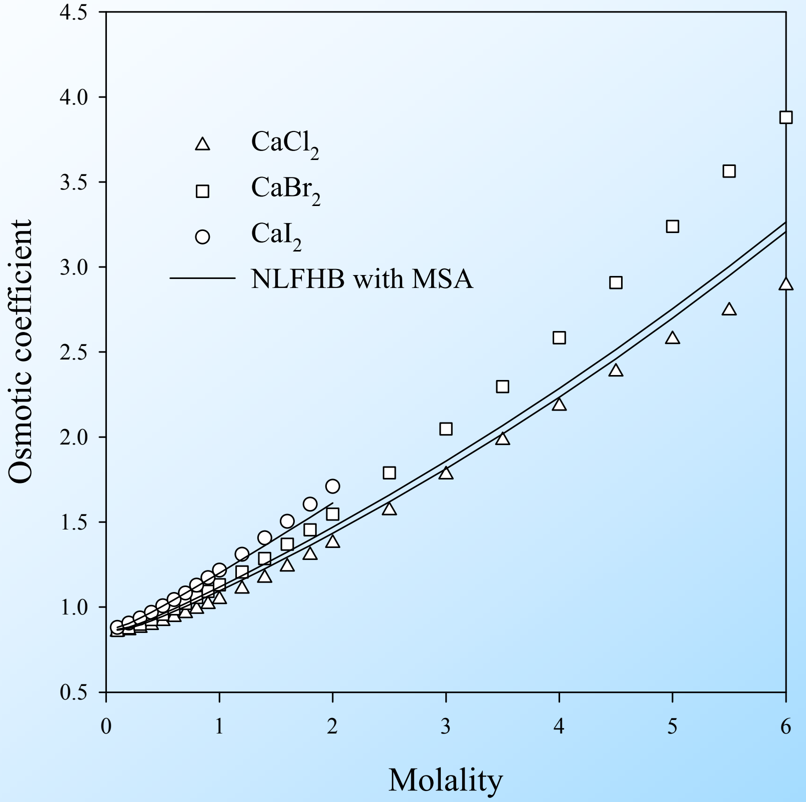
Osmotic coefficient of Potassium halide at 298.15 K
(Method 2)



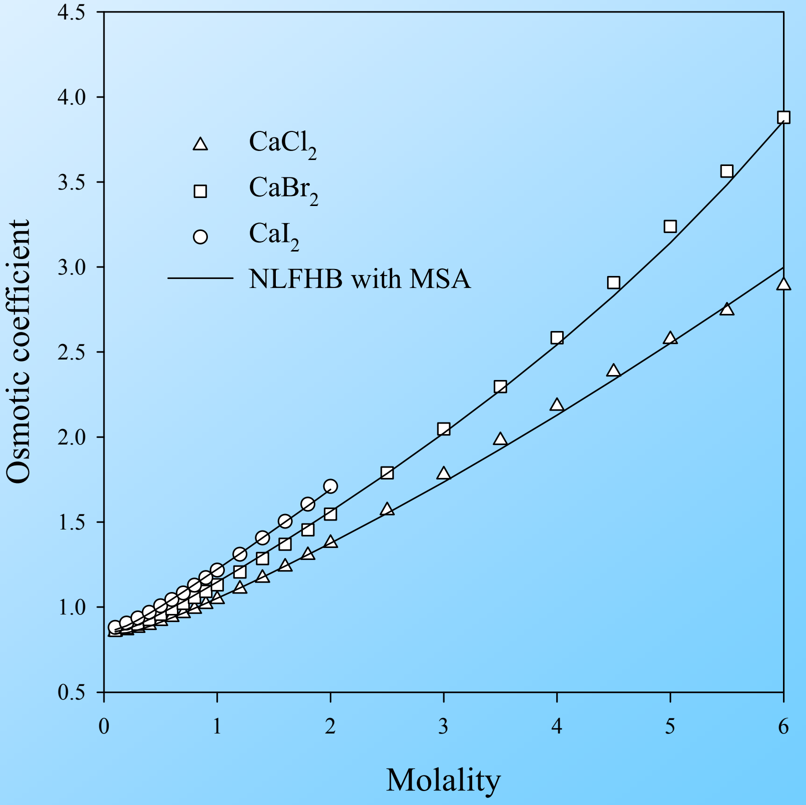
Osmotic coefficient of Lithium halide at 298.15 K
(Method 1)



Osmotic coefficient of Lithium halide at 298.15 K
(Method 2)



Osmotic coefficient of Calcium halide at 298.15 K
(Method 1)



Osmotic coefficient of Calcium halide at 298.15 K
(Method 2)

Conclusion

- In the present model a short-range interaction term derived from a NLFHB theory was superposed on the mean spherical approximation term.

- The model can be used with three parameters for cation and one parameter for anion to predict properties of electrolyte system.

- Binary interaction parameters were not used.