An Electrolyte NLF-HB Equation of State Applicable to Concentrated Electrolyte systems

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Introduction

- Electrolyte solutions
  - Wastewater treatment, extraction, distillation, seawater desalination, salt-added bioseperation…
  - Need for understanding of thermodynamics
  - For engineering purposes
    - Experimental work
    - A good model capable of describing the phase behavior

Introduction

- More difficult to model than most other solutions
  - Ions : Interaction both each other and with solvents
  - Charged particles
    - Low concentration : dominant electrostatic force
    - High concentration : Short-range forces become important.
  - The chemistry of solutions changes at different conditions such as temperature and density.

Introduction

- Excess Gibbs function
  - Debye-Hückel, Pitzer model, electrolyte NRTL …
  - Useful for non-idealities of electrolyte solutions
  - Not adequate to high pressure applications

- Equation of state approch
  - Applicable to wide range of pressure
  - Description of phase equilibria using unified model

Electrolyte NLF-HB Equation of State

- Development of an equation of state for electrolyte systems
  - Fully ionized electrolyte solutions
  - Electrostatic interactions => Mean spherical approximation(MSA) model
  - Association(or hydration) => Veytsman statistics

Electrolyte NLF-HB Equation of State

- Helmhlotz free energy

$$A = A_{athm} + A_{res} + A_{ass} + A_{lr}$$

  - Athermal contribution
    - Guggenheim-Huggins-Miller approximation
  - Residual contributions
    - Quasi-chemical approximation
  - Association contributions
    - Normalized Veytsmann statistics
  - Long-range contributions
    - Mean spherical approximation

Electrolyte NLF-HB Equation of State

- Helmhlotz free energy

$$\beta A_{athm} = -\ln N_r! + \sum \ln N_i! - \left(\frac{z}{2}\right)\left[N_q \ln N_q - N_{fq} - N_r \ln N_r + N_r\right]$$

$$\beta A_{res} = -\left(\frac{z\beta N_q}{2}\right)\left[\sum\sum \theta_i \theta_j \varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum \theta_i \theta_j \theta_k \theta_l \varepsilon_{ij}(\varepsilon_{ij} + \varepsilon_{kl} - \varepsilon_{ik} - \varepsilon_{jk})\right]$$

$$\beta A_{ass} = N^{HB} \ln N_r - \sum_i^m (N^i{}_d \ln N^i{}_d - N^i{}_d) + \sum_i^m (N_{i0} \ln N_{i0} - N_{i0})$$
$$+ \sum_i^m \sum_j^n (\beta N_{ij}{}^{HB} A_{ij}{}^{HB} + N_{ij}{}^{HB} \ln N_{ij}{}^{HB} - N_{ij}{}^{HB})$$
$$- \sum_i^n (N^i{}_a \ln N^i{}_a - N^i{}_a) + \sum_j^m (N_{j0} \ln N_{j0} - N_{j0})$$

$$\beta A_{lr} = \frac{\Gamma^3 V}{3\pi} - \frac{\alpha^2}{4\pi} \sum_{ions} \left(\frac{N_k z_k^2 \Gamma}{1 + \Gamma \sigma_k}\right)$$

Electrolyte NLF-HB Equation of State

- Chemical potential :

$$\mu_i/RT = \mu_i/N_a kT = \left(\frac{\partial \beta A^C}{\partial N_i}\right) + r_i \nu_H \beta P$$

$$\beta\mu_i = (r_i + l_i)\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - r_i \ln(1-\rho) + \ln\left(\frac{\theta_i}{q_i}\right)$$

$$+\left(\frac{z\beta}{2}\right) q_i \varepsilon_M \theta^2 \times \left[1 - \frac{r_i}{q_i} - \frac{2\sum \theta_k \varepsilon_{ik} + \beta \sum\sum\sum \theta_j \theta_k \theta_l \varepsilon_{ij} (\varepsilon_{ij} + 2\varepsilon_{kl} - 2\varepsilon_{jk} - \varepsilon_{ik})}{\varepsilon_M \theta^2}\right]$$

$$\beta\mu_{ass} = -\sum_i d_i^k \ln \frac{N_d^i}{N_{i0}} - \sum_j a_j^k \ln \frac{N_a^j}{N_{j0}}$$

$$\beta\mu_{i,lr} = -\frac{\alpha^2}{4\pi} \frac{z_i \Gamma}{(1 + \Gamma\sigma_i)} + \frac{\alpha^2}{4\pi D}\left(\frac{\partial D}{\partial N_i}\right)_{T,V,N_j} \sum_{ions}\left(\frac{z_k^2 \Gamma}{1 + \Gamma\sigma_k}\right)$$

Electrolyte NLF-HB Equation of State

- Pressure

Athermal and residual contributions

$$\frac{PV_H}{RT} = \frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho) + \frac{\rho}{r_M} - \frac{z\beta}{2}\varepsilon_M\theta^2 - \nu_{HB}\rho$$

Association contribution

$$\varepsilon_M = \frac{1}{\theta^2}\left[\sum\sum\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\sum\sum\sum\sum\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right]$$

$$\beta P_{lr} = -\frac{\Gamma^3}{3\pi} - \frac{\alpha^2}{4\pi D}\left(\frac{\partial D}{\partial V}\right)_{T,N}\sum_{ions}\left(\frac{N_k z_k^2\Gamma}{1+\Gamma\sigma_k}\right)$$

Electrolyte NLF-HB Equation of State

- Parameters for solvent
  - energy and size parameters

$$\varepsilon_{ii} / k = \varepsilon_a + \varepsilon_b (T - T_0) + \varepsilon_c [T \ln(T_0 / T) + (T - T_0)]$$

$$r_i = r_a + r_b (T - T_0) + r_c [T \ln(T_0 / T) + (T - T_0)]$$

  - Hydrogen bonding energy and number of donor and acceptor

  - Obtained by fitting saturated vapor pressure and density

Electrolyte NLF-HB Equation of State

- Three parameters for salts
  - Interaction energy and segment number
    - Mean values of cation and anion

$$\varepsilon_{salt} = \varepsilon_{cation} = \varepsilon_{anion} \quad \text{and} \quad r_{salt} = r_{cation} = r_{anion}$$

    - Size in MSA term

$$\sigma_i^3 = 6 f_c V_H r_i / \pi$$

  - Hydration energy and donor number for cations
    - Fixed to 7 for donor number
  - Obtained by fitting mean activity coefficients and osmotic coefficients

Thermodynamic properties

- Mean ionic chemical potential and mole fractions

$$\mu_{\pm i}(\nu_{+i}+\nu_{-i}) = \mu_{+i}\nu_{+i} + \mu_{-i}\nu_{-i} \qquad x_{\pm i}^{(\nu_{+i}+\nu_{-i})} = x_{+i}^{\nu_{+i}} x_{-i}^{\nu_{-i}}$$

- Molal mean activity coefficient and osmotic coefficient

$$\ln \gamma_{\pm i}^{m*} = \ln \gamma_{\pm i}^{l*} - \ln\left(1 + \sum_{k=1}^{salt} \nu_{\pm k} x_k \Big/ \sum_{j=1}^{solvent} x_j\right)$$

where $\gamma_{\pm i}^{l*} = \exp[(\mu_{\pm i}^{l} - \mu_{\pm i}^{l\infty})/RT] / x_{\pm i}^{l} \times x_{\pm i}^{\infty}$

$$\phi = -x_S \ln x_S \gamma_S \Big/ RT \sum\nolimits_{ions} x_k$$

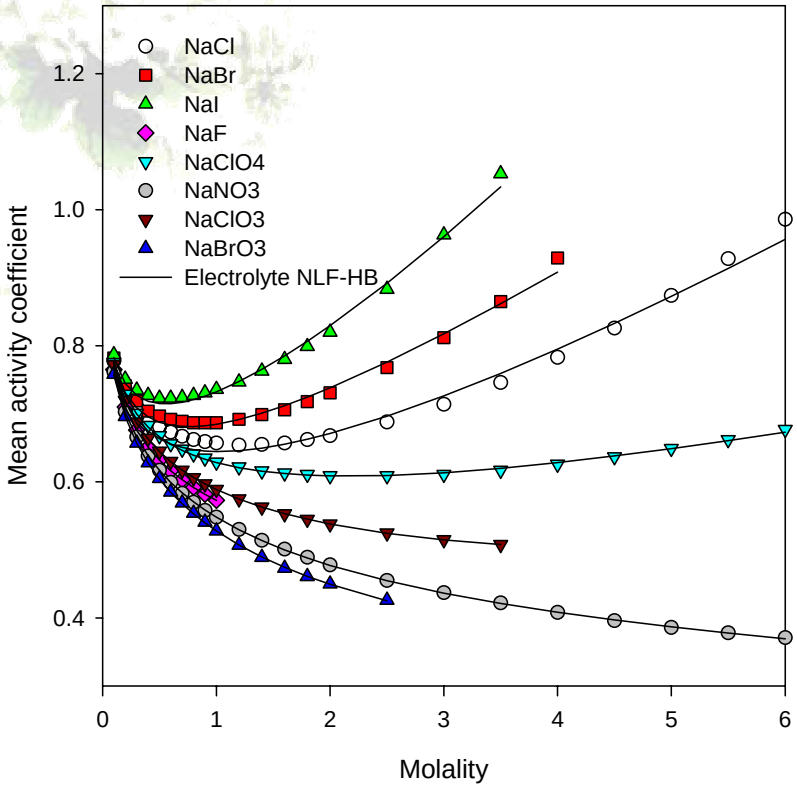
Parameters for salts

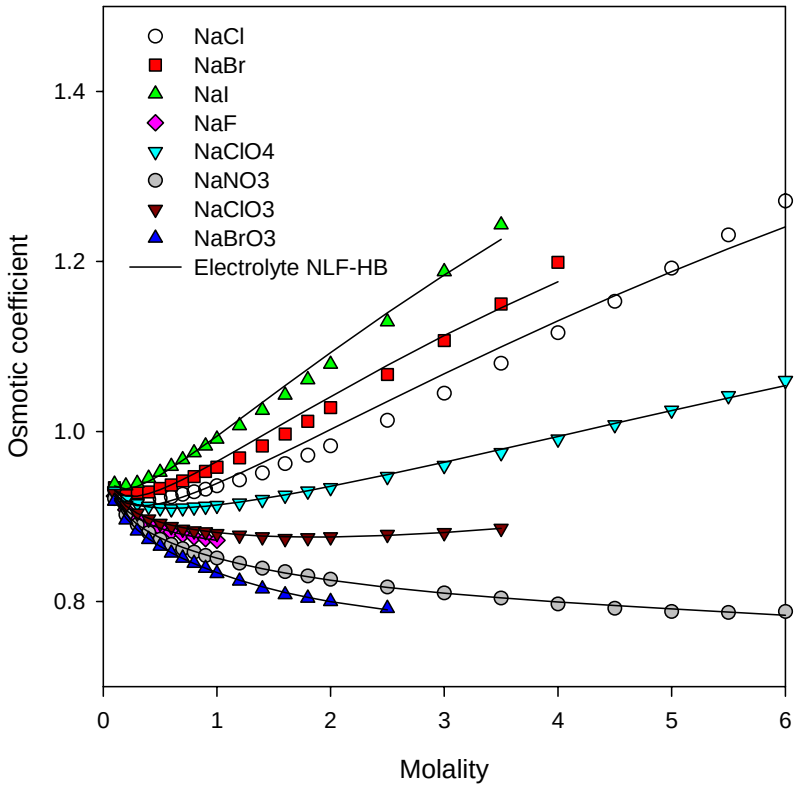
Salt	ε_{ii}	r_i	Hydration energy	Salt	ε_{ii}	r_i	Hydration energy
HCl	160.625	1.13	1887	NaI	90.828	2.05	1650
HBr	90.711	3.67	1890	$NaClO_4$	66.075	3.22	1770
HI	120.453	2.65	1900	$NaNO_3$	47.111	2.29	1620
$HClO_4$	175.063	1.00	2270	NaOH	53.504	2.05	2100
HNO_3	74.686	4.23	2180	$NaClO_3$	62.809	3.36	1746
LiCl	117.406	1.05	1955	NaAc	79.484	3.70	1895
LiBr	129.781	1.16	2170	NaTol	69.260	4.64	1658
LiI	89.563	3.65	2290	NaF	52.414	2.49	1690
$LiClO_4$	87.395	3.60	2380	$NaBrO_3$	39.049	2.25	1715
$LiNO_3$	79.959	3.52	1800	Na formate	72.371	3.66	1760
LiOH	66.219	0.84	1260	Na propionate	85.461	3.70	1860
LiAc	71.973	2.87	1798	Na H molanate	47.152	2.18	1650
LiTol	70.379	4.68	1905	Na H succinate	46.344	2.20	1768
NaCl	247.250	1.26	1130	NaCNS	76.408	4.35	1905
NaBr	186.688	1.62	1160	NaH_2PO_4	7.232	1.55	1875

Parameters for salts

Salt	ε_{ii}	r_i	Hydration energy	Salt	ε_{ii}	r_i	Hydration energy
KCl	55.695	1.47	1500	RbCl	41.967	1.76	1680
KBr	59.129	1.78	1560	RbBr	41.967	1.76	1680
KI	70.719	2.32	1570	RbI	49.962	2.48	1792
KNO_3	9.852	1.71	1750	$RbNO_3$	0.777	1.32	1720
KOH	74.984	2.12	2070	RbAc	82.186	3.60	1950
$KClO_3$	50.609	3.01	1440	CsCl	36.219	1.92	1755
KAc	82.133	3.59	1900	CsBr	36.406	2.20	1900
KTol	74.413	7.32	1796	CsI	42.031	2.65	2000
KF	57.582	2.50	1971	$CsNO_3$	0.122	1.32	1780
$KBrO_3$	45.688	3.44	1750	CsOH	86.211	2.84	1760
KH malonate	39.477	2.18	1665	CsAc	82.672	3.95	1966
KH succinate	41.873	2.28	1801	NH4Cl	57.910	2.32	1642
KH adipate	61.344	3.38	1965	$NH4NO_3$	58.484	3.72	1712
KCNS	60.342	2.60	1636	$AgNO_3$	0.0256	1.20	1663
KH_2PO_4	5.178	1.81	2848	TlAc	7.350	0.94	1503

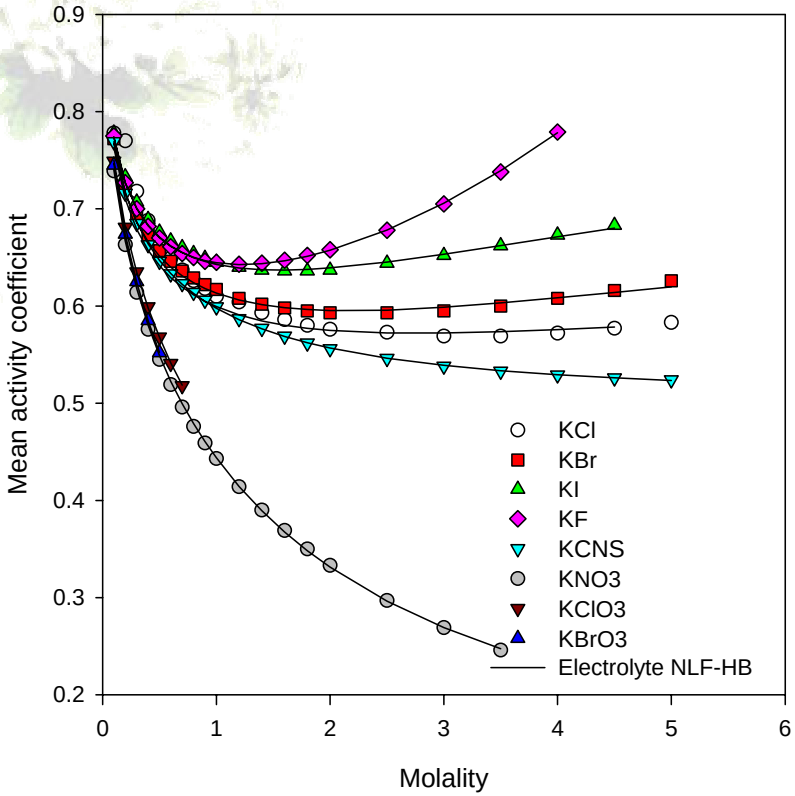
Results

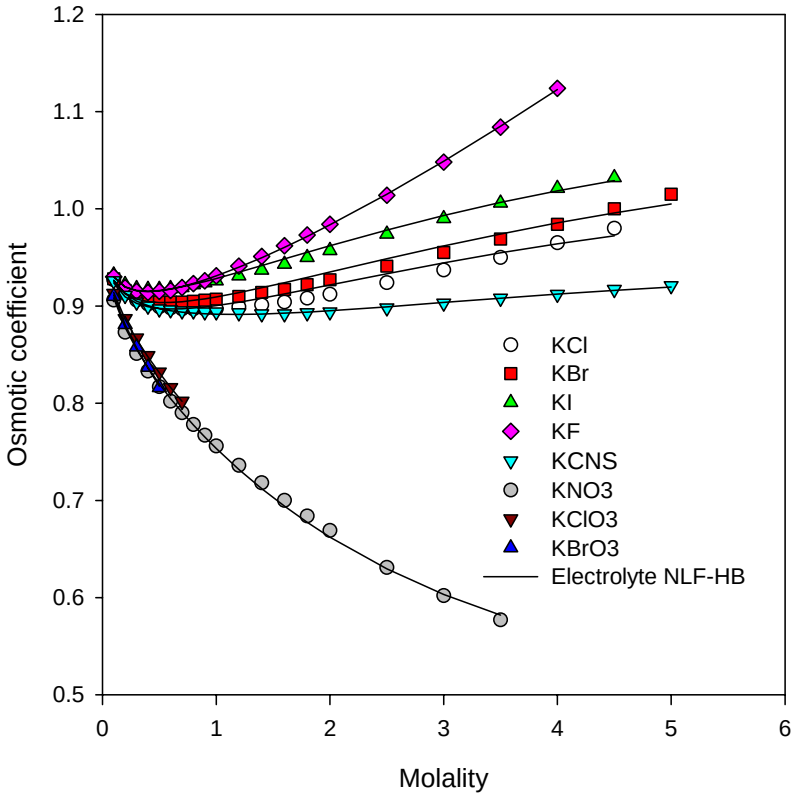




Comparison of experimental mean activity coefficient and osmotic coefficient and calculated results

Results





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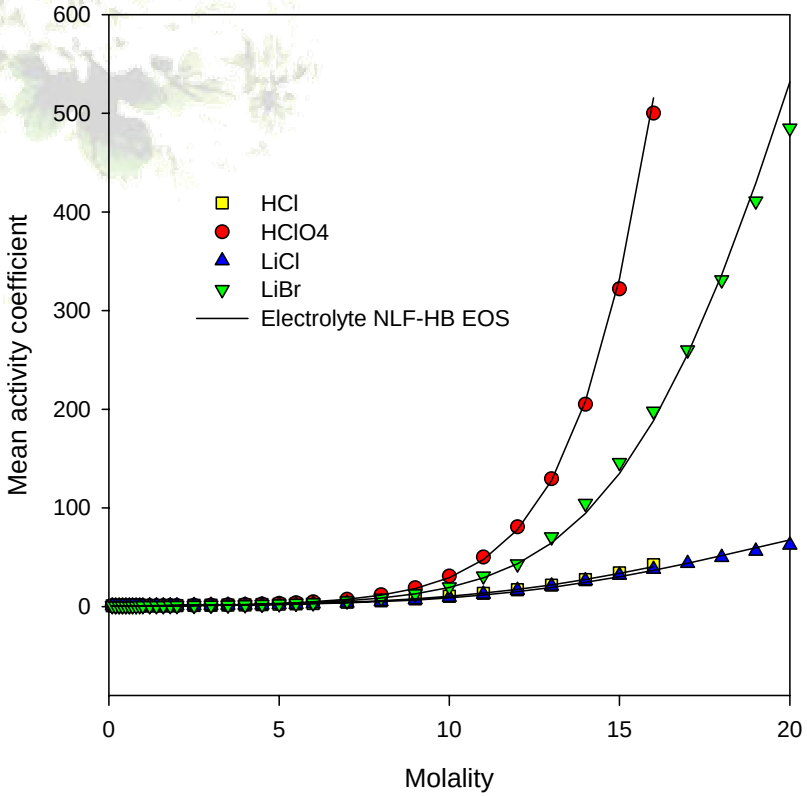

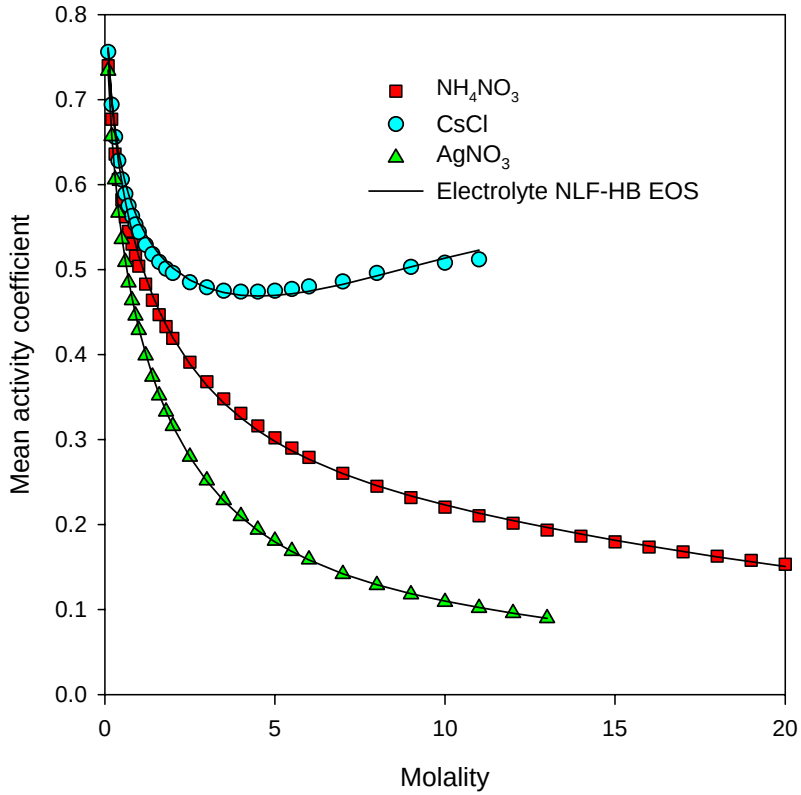

Comparison of experimental mean activity coefficients and calculated results for concentrated electrolyte solutions

Comparison of Models

- Electrolyte NRTL model(based on G^E model)
  - Chen et al. (1999)
  - Two adjustable parameters and hydration number

- Myers and Sandler (2002)
  - Equation of state approach
  - Three adjustable parameters for each salts
  - The Born contribution for hydration process and MSA model for electrostatic interaction

Results

	Electrolyte NLF-HB				NRTL	Sandler		Electrolyte NLF-HB				NRTL	Sandler
	$\gamma_{\pm}$	ϕ	ρ	Max. molal	$\gamma_{\pm}$	$\gamma_{\pm}$		$\gamma_{\pm}$	ϕ	ρ	Max. molal	$\gamma_{\pm}$	$\gamma_{\pm}$
HCl	2.03	0.89	0.98	16.0	0.53	0.63	NaI	0.84	0.58	0.59	3.5	0.57	0.19
HBr	0.12	0.79	3.68	1.0	0.75	0.09	$NaClO_4$	0.21	0.15	3.54	6.0	0.46	0.07
HI	1.33	0.89	2.20	3.0	0.62	2.61	$NaNO_3$	0.13	0.15	3.29	6.0	0.12	0.11
$HClO_4$	2.94	1.28	10.70	16.0	1.19	0.20	NaOH	1.55	0.97	19.32	20.0	0.63	0.67
HNO_3	0.09	0.13	6.64	3.0	0.80	0.06	$NaClO_3$	0.08	0.11	4.38	3.5	0.30	0.09
LiCl	3.56	1.53	0.18	20.0	0.88	0.25	NaAc	0.13	0.12		3.5	0.79	0.61
LiBr	3.24	1.26	1.83	20.0	0.95	0.37	NaTol	0.49	0.55		4.0	0.99	0.44
LiI	1.35	0.97	4.55	3.0	1.78	1.29	NaF	0.03	0.02	4.13	1.0	0.02	0.02
$LiClO_4$	0.88	0.57	4.14	4.0	1.32	4.26	$NaBrO_3$	0.12	0.12	0.82	2.5	0.10	0.08
$LiNO_3$	0.29	0.16	7.24	13.0	0.35	1.55	Na formate	0.17	0.25		3.5	0.71	0.31
LiOH	0.46	0.47	4.19	4.0	3.00	1.01	Na propionate	0.15	0.13		3.0	1.01	0.76
LiAc	0.19	0.13		4.0	0.22	0.30	Na H molanate	0.20	0.16		5.0	0.36	0.26
LiTol	0.59	0.61		4.5	0.97	0.58	Na H succinate	0.16	0.15		5.0	0.35	0.20
NaCl	1.63	1.20	0.99	6.0	0.44	0.08	NaCNS	0.27	0.14	7.09	4.0	1.22	0.36
NaBr	0.93	0.70	1.04	4.0	0.36	0.09	NaH_2PO_4	0.32	0.40	1.20	6.0	0.27	0.30

Results

	Electrolyte NLF-HB				NRTL	Sandler		Electrolyte NLF-HB				NRTL	Sandler
	$\gamma_{\pm}$	ϕ	ρ	Max. molal	$\gamma_{\pm}$	$\gamma_{\pm}$		$\gamma_{\pm}$	ϕ	ρ	Max. molal	$\gamma_{\pm}$	$\gamma_{\pm}$
KCl	0.71	0.56	0.20	4.8	0.23	0.08	RbCl	0.07	0.07	0.33	5.0	0.15	0.07
KBr	0.58	0.41	0.30	5.0		0.09	RbBr	0.12	0.09	0.33	5.0	0.16	0.07
KI	0.44	0.27	0.25	4.5	0.38	0.20	RbI	0.52	0.37	0.50	5.0	0.18	0.12
KNO_3	0.44	0.49	0.95	3.5	0.58	0.13	$RbNO_3$	0.59	0.59	2.99	4.5	0.85	0.19
KOH	1.12	0.47	12.35	16.0	0.48	0.60	RbAc	0.18	0.14		3.5	0.70	0.83
$KClO_3$	0.09	0.08	0.41	0.7	0.24	0.08	CsCl	1.39	1.01	1.48	11.0	0.52	0.28
KAc	0.19	0.13		3.5	0.66	0.61	CsBr	1.05	0.82	0.95	5.0	0.52	0.31
KTol	0.44	0.55		3.5	2.47	0.35	CsI	0.84	0.75	0.90	3.0	0.52	0.17
KF	0.08	0.09	6.90	4.0	0.36	0.08	$CsNO_3$	0.50	0.50	1.55	1.4	0.24	0.15
$KBrO_3$	0.08	0.11	0.61	0.5	0.14	0.08	CsOH	0.13	0.19	2.09	1.0		0.46
KH malonate	0.47	0.49		5.0	0.36	0.52	CsAc	0.20	0.18		3.5	0.79	0.65
KH succinate	0.19	0.17		4.5	0.21	0.22	NH_4Cl	0.09	0.09	1.90	6.0	0.06	0.29
KH adipate	0.10	0.06		1.0	0.12	0.09	NH_4NO_3	1.62	1.56	10.32	20.0	0.93	0.16
KCNS	0.12	0.12	0.08	5.0	0.13	0.13	$AgNO_3$	0.41	0.57	0.94	13.0	0.77	0.20
KH_2PO_4	0.61	0.43	0.78	1.8	0.22	0.08	TlAc	0.20	0.25		6.0	0.92	0.23

Results : Summary

	Electrolyte NLF			NRTL	Sandler
Property	$\gamma_{\pm}$	ϕ	ρ	$\gamma_{\pm}$	$\gamma_{\pm}$
AAD(%)	0.63(0.40 [a])	0.45(0.35 [a])	3.18(2.19[a])	0.61 [a]	0.41 [a]

a : calculated up to 6 molal

Conclusion

- Development of electrolyte NLF-HB equation of state
  - Electrostatic interactions by mean spherical approximation
  - Hydration(association) contribution by Veytsmann statistics

- Mean activity coefficients, osmotic coefficients, and densities were calculated for 60 electrolyte solutions