Model for Mixed-Electrolyte, Aqueous Mixed-Solvent Systems (Ind. Eng. Chem. Res. 1996)

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Thermodynamics & Properties LAB

Introduction

- Debye- Hückel
  - for dilute electrolyte solution
- Pitzer (1973)
  - Single salt aqueous system
- Bromley (1973)
  - 2 ionic constants for each ion
  - 1salt parameter, extend to mixed- electrolyte

Introduction

- Meissner (1972)
  - 1 salt parameter, extended to mixed-electrolyte
  - extrapolated to high concentration

- Chen, Evans (1986)
  - NRTL term + D-H term ; nonidealities
  - 2 parameters

Introduction

- Gibbs function
  - D-H term + short range interaction term
  - NRTL : Cruz and Renon (1978)
    Chen et al (1982), Mock et al (1986)
  - UNIFAC : Kikic et al (1991)
    Achard et al (1994)
  - UNIQUAC : Polka et al (1994), Li et al(1994)
    Macedo et al (1990), Sandler (1986)

Introduction

- Different models for solute and solvent

- In this work,
  - unified model for mixed solute and mixed solvent system
  - : short range : electrostatic interaction ,
                    non-electrostatic interaction

Excess Gibbs Function Model

- D-H term

$$G_{DH}^{E*} = -\frac{RTV}{4\pi a^3 N_a}\left[\ln(1 + aK) - aK + \frac{(aK)^2}{2}\right]$$

  - by De M.Cardoso and O’Connell (1987)

$$\ln\gamma_{DH,j} = \frac{\overline{V_j}}{4\pi a^3 N_a}\left[\ln(1+aK) - \frac{aK}{2} - \frac{aK}{2(1+aK)}\right]$$

For Solvent

$$\ln\gamma^{*}_{DH,\pm i} = -\frac{|z_{+i}z_{-i}|}{16\pi a^3 N_a I}\frac{(aK)^3}{(1+aK)}$$

For Solute

Excess Gibbs Function Model

- Short-range interaction term
  - segment number , surface area parameter, nonelectrostatic interaction energy parameter
  - from Helmholtz function

    new lattice-hole theroy (Yoo et al 1995)
  - $A \cong G^E$ (Wong and Sandler, 1992)

Excess Gibbs Function Model

$$G^E = G_A^E + G_R^E$$

- atermal contribution in symmetric convention

$$\beta G^E = \sum N_i \ln \frac{\theta_i}{x_i} + \left(1 - \frac{z}{2}\right) \sum N_i q_i \ln \frac{q_M r_i}{r_M q_i}$$

- residual contribution of UNIQUAC

$$\beta G^E = -\frac{zN_q}{2} \sum \theta_i \ln\left(\sum \theta_j \tau_{ji} \right)$$

Excess Gibbs Function Model

- Solvent Activity coefficients

$$\ln \gamma_{A,j} = \ln \frac{\theta_j}{x_j} + r_j \left(1 - \frac{z}{2}\right) \ln \frac{q_M r_j}{r_M q_j}$$

$$\ln \gamma_{R,j} = \frac{z q_j}{2} \left\{ 1 - \ln\left(\sum \theta_k \tau_{kj}\right) - \sum_k \frac{\theta_k \tau_{jk}}{\sum_l \theta_l \tau_{lk}} \right\}$$

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

Excess Gibbs Function Model

- osmotic coefficient : $\phi = -n_{sol} \ln x_i \gamma_i / \sum_{k}^{salt} \nu_{\pm k} n_k$

- solute activity coefficient

$$\ln \gamma^*_{A,\pm i} = \sum \frac{\nu_i}{\nu_\pm} \ln \frac{\theta_i x_i^\infty}{\theta_i^\infty x_i} + \left(1 - \frac{z}{2}\right)\left(\sum \frac{r_i \nu_i}{\nu_{\pm i}}\right) \ln \frac{q_M r_M^\infty}{q_M^\infty r_M}$$

$$\ln \gamma^*_{R,\pm i} = \frac{z}{2} \sum \frac{\nu_i q_i}{\nu_{\pm i}} \left\{ \ln \frac{\sum \theta_j \tau_{ji}}{\sum \theta_j^\infty \tau_{ji}} + \sum \frac{\theta_j \tau_{ij}}{\sum_l \theta_k \tau_{kj}} - \sum \frac{\theta_j^\infty \tau_{ij}}{\sum_l \theta_k^\infty \tau_{kj}} \right\}$$

Excess Gibbs Function Model

- Interaction between ions $\varepsilon_{ij} = \varepsilon_{ij}^{(e)} + \varepsilon_{ij}^{(n)}$
- interaction with uncharged species $\varepsilon_{ij} = \varepsilon_{ij}^{(n)}$
  - nonelectrostatic interaction

$$\varepsilon_{ij}^{(n)} = (\varepsilon_{ii}^{(n)} \varepsilon_{jj}^{(n)})^{1/2} (1 - k_{ij})$$

➢Parameters : molecular (r_i, ε_{ii}),
ions ($r_i, \varepsilon_{ii}, r_{s,+i}, r_{s,-i}$), k_{ij}
by Robinson and Stokes 1955 data

parameters

Single Electrolyte Aqueous Systems

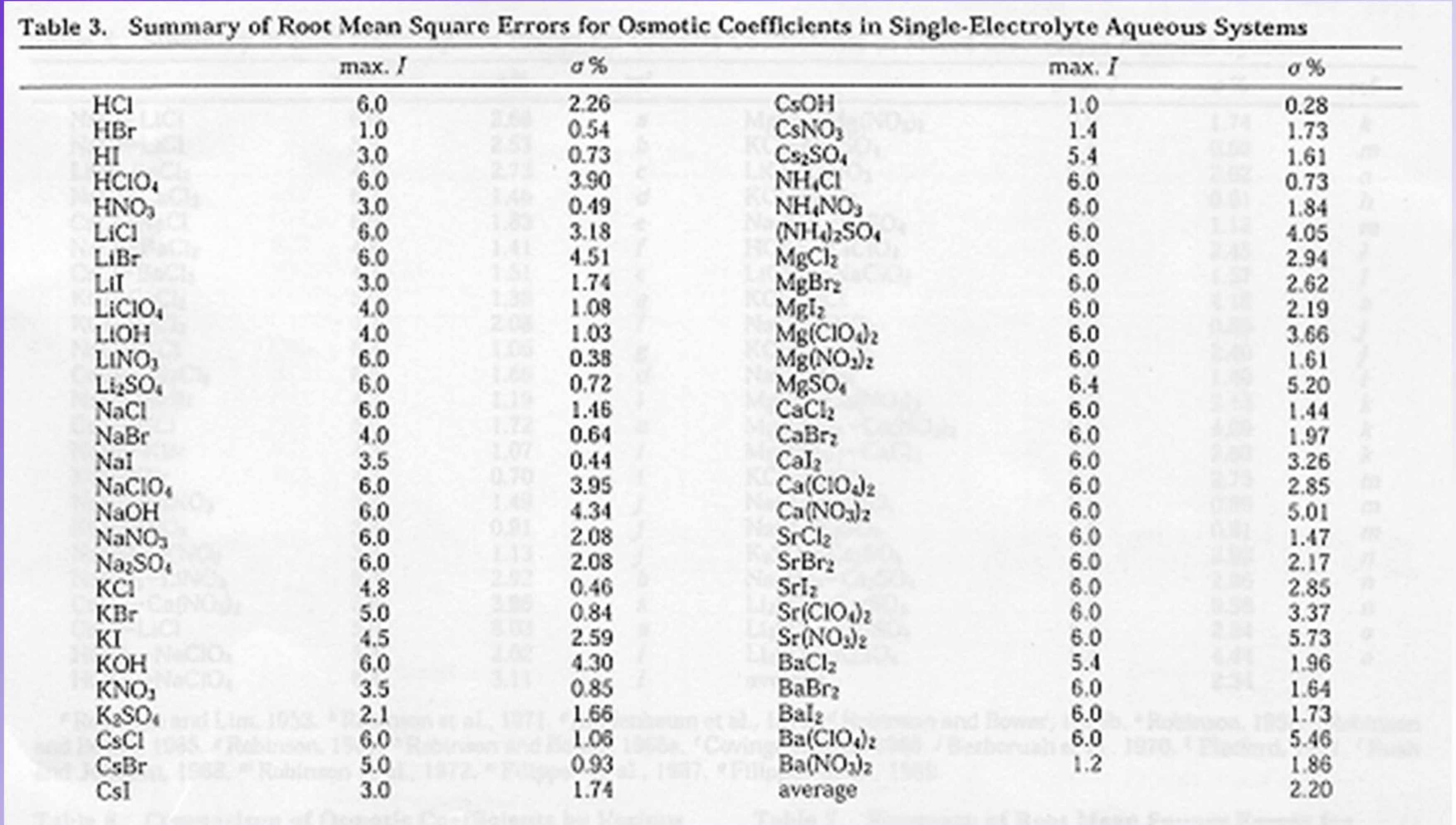

Table 3. Summary of Root Mean Square Errors for Osmotic Coefficients in Single-Electrolyte Aqueous Systems

	max. I	σ %		max. I	σ %
HCl	6.0	2.26	CsOH	1.0	0.28
HBr	1.0	0.54	$CsNO_3$	1.4	1.73
HI	3.0	0.73	Cs_2SO_4	5.4	1.61
$HClO_4$	6.0	3.90	NH_4Cl	6.0	0.73
HNO_3	3.0	0.49	NH_4NO_3	6.0	1.84
LiCl	6.0	3.18	$(NH_4)_2SO_4$	6.0	4.05
LiBr	6.0	4.51	$MgCl_2$	6.0	2.94
LiI	3.0	1.74	$MgBr_2$	6.0	2.62
$LiClO_4$	4.0	1.08	MgI_2	6.0	2.19
LiOH	4.0	1.03	$Mg(ClO_4)_2$	6.0	3.66
$LiNO_3$	6.0	0.38	$Mg(NO_3)_2$	6.0	1.61
Li_2SO_4	6.0	0.72	$MgSO_4$	6.4	5.20
NaCl	6.0	1.46	$CaCl_2$	6.0	1.44
NaBr	4.0	0.64	$CaBr_2$	6.0	1.97
NaI	3.5	0.44	CaI_2	6.0	3.26
$NaClO_4$	6.0	3.95	$Ca(ClO_4)_2$	6.0	2.85
NaOH	6.0	4.34	$Ca(NO_3)_2$	6.0	5.01
$NaNO_3$	6.0	2.08	$SrCl_2$	6.0	1.47
Na_2SO_4	6.0	2.08	$SrBr_2$	6.0	2.17
KCl	4.8	0.46	SrI_2	6.0	2.85
KBr	5.0	0.84	$Sr(ClO_4)_2$	6.0	3.37
KI	4.5	2.59	$Sr(NO_3)_2$	6.0	5.73
KOH	6.0	4.30	$BaCl_2$	5.4	1.96
KNO_3	3.5	0.85	$BaBr_2$	6.0	1.64
K_2SO_4	2.1	1.66	BaI_2	6.0	1.73
CsCl	6.0	1.06	$Ba(ClO_4)_2$	6.0	5.46
CsBr	5.0	0.93	$Ba(NO_3)_2$	1.2	1.86
CsI	3.0	1.74	average		2.20

Mixed Elecrolyte Aqueous System

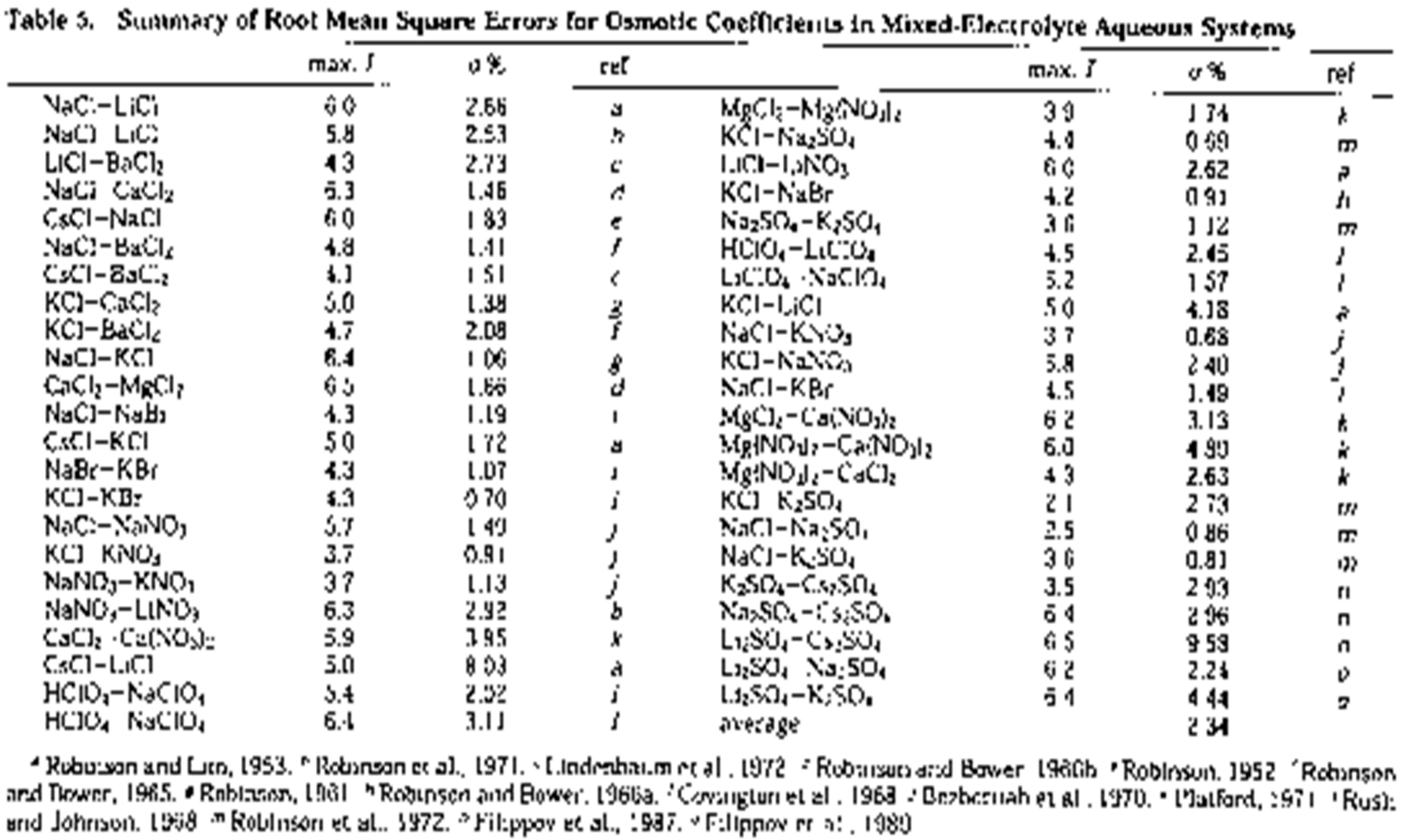

Table 5. Summary of Root Mean Square Errors for Osmotic Coefficients in Mixed-Electrolyte Aqueous Systems

	max. I	σ %	ref		max. I	σ %	ref
NaCl–LiCl	6.0	2.66	*a*	$MgCl_2$–$Mg(NO_3)_2$	3.9	1.74	*k*
NaCl–LiCl	5.8	2.53	*b*	KCl–Na_2SO_4	4.4	0.69	*m*
LiCl–$BaCl_2$	4.3	2.73	*c*	LiCl–$LiNO_3$	6.0	2.62	*a*
NaCl–$CaCl_2$	6.3	1.46	*d*	KCl–NaBr	4.2	0.91	*h*
CsCl–NaCl	6.0	1.83	*e*	Na_2SO_4–K_2SO_4	3.6	1.12	*m*
NaCl–$BaCl_2$	4.8	1.41	*f*	$HClO_4$–$LiClO_4$	4.5	2.45	*l*
CsCl–$BaCl_2$	4.1	1.51	*c*	$LiClO_4$–$NaClO_4$	5.2	1.57	*l*
KCl–$CaCl_2$	5.0	1.38	*g*	KCl–LiCl	5.0	4.18	*a*
KCl–$BaCl_2$	4.7	2.08	*f*	NaCl–KNO_3	3.7	0.68	*j*
NaCl–KCl	6.4	1.06	*g*	KCl–$NaNO_3$	5.8	2.40	*j*
$CaCl_2$–$MgCl_2$	6.5	1.66	*d*	NaCl–KBr	4.5	1.49	*i*
NaCl–NaBr	4.3	1.19	*i*	$MgCl_2$–$Ca(NO_3)_2$	6.2	3.13	*k*
CsCl–KCl	5.0	1.72	*a*	$Mg(NO_3)_2$–$Ca(NO_3)_2$	6.0	4.90	*k*
NaBr–KBr	4.3	1.07	*i*	$Mg(NO_3)_2$–$CaCl_2$	4.3	2.63	*k*
KCl–KBr	4.3	0.70	*i*	KCl–K_2SO_4	2.1	2.73	*m*
NaCl–$NaNO_3$	5.7	1.49	*j*	NaCl–Na_2SO_4	2.5	0.86	*m*
KCl–KNO_3	3.7	0.91	*j*	NaCl–K_2SO_4	3.6	0.81	*m*
$NaNO_3$–KNO_3	3.7	1.13	*j*	K_2SO_4–Cs_2SO_4	3.5	2.93	*n*
$NaNO_3$–$LiNO_3$	6.3	2.92	*b*	Na_2SO_4–Cs_2SO_4	6.4	2.96	*n*
$CaCl_2$–$Ca(NO_3)_2$	5.9	3.95	*k*	Li_2SO_4–Cs_2SO_4	6.5	9.59	*n*
CsCl–LiCl	5.0	8.03	*a*	Li_2SO_4–Na_2SO_4	6.2	2.24	*o*
$HClO_4$–$NaClO_4$	5.4	2.52	*i*	Li_2SO_4–K_2SO_4	5.4	4.44	*o*
$HClO_4$–$NaClO_4$	6.4	3.11	*l*	average		2.34	

[a] Robinson and Lim, 1953. [b] Robinson et al., 1971. [c] Lindenbaum et al., 1972. [d] Robinson and Bower, 1966b. [e] Robinson, 1952. [f] Robinson and Bower, 1965. [g] Robinson, 1961. [h] Robinson and Bower, 1966a. [i] Covington et al., 1968. [j] Bezboruah et al., 1970. [k] Platford, 1971. [l] Rush and Johnson, 1968. [m] Robinson et al., 1972. [n] Filippov et al., 1987. [o] Filippov et al., 1989.

Mixed Electrolyte Aqueous System

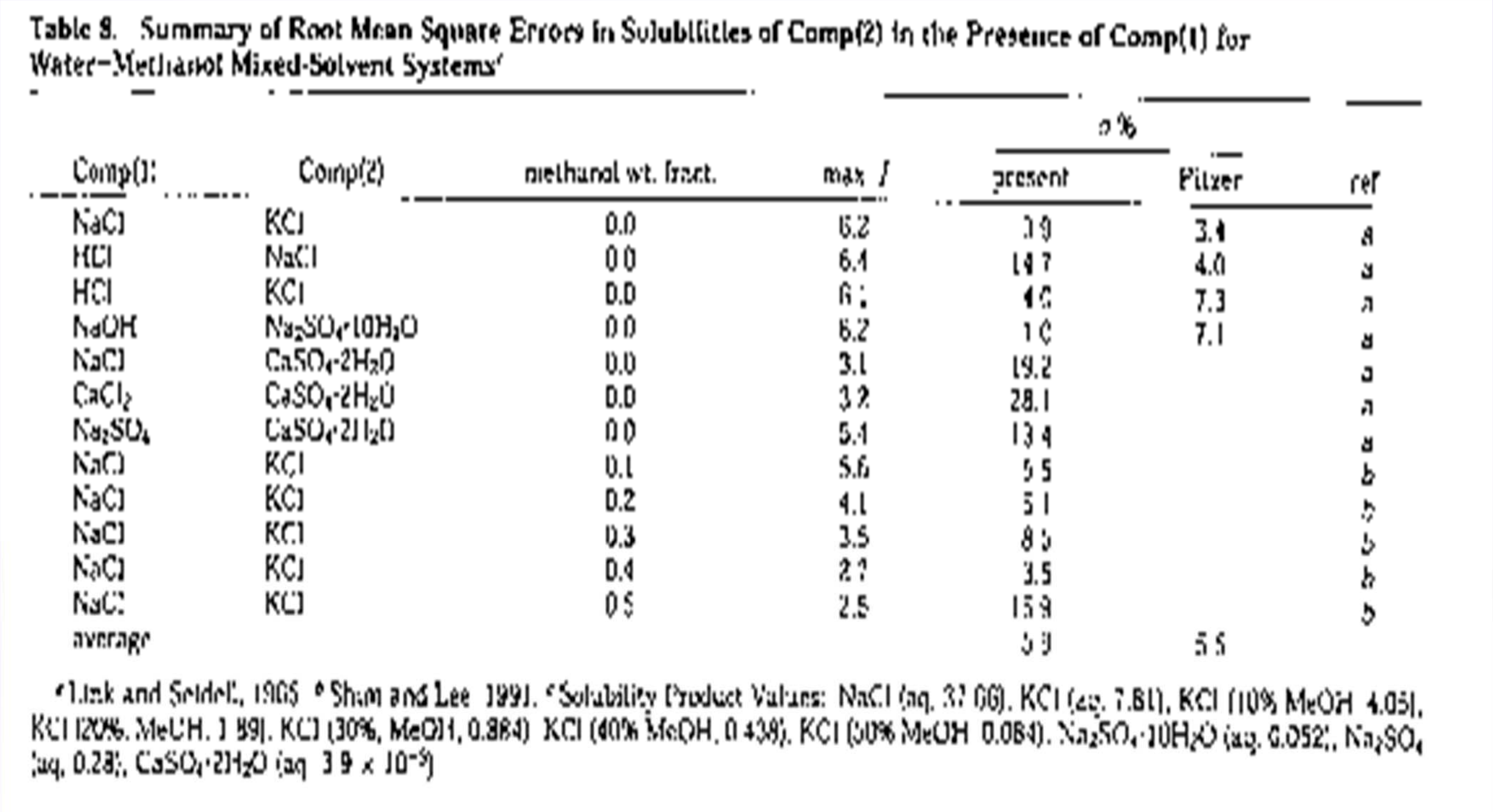

Table 8. Summary of Root Mean Square Errors in Solubilities of Comp(2) in the Presence of Comp(1) for Water–Methanol Mixed-Solvent Systems[c]

Comp(1)	Comp(2)	methanol wt. fract.	max *I*	σ% present	σ% Pitzer	ref
NaCl	KCl	0.0	6.2	3.9	3.4	a
HCl	NaCl	0.0	6.4	14.7	4.0	a
HCl	KCl	0.0	6.1	4.6	7.3	a
NaOH	$Na_2SO_4 \cdot 10H_2O$	0.0	6.2	1.0	7.1	a
NaCl	$CaSO_4 \cdot 2H_2O$	0.0	3.1	19.2		a
$CaCl_2$	$CaSO_4 \cdot 2H_2O$	0.0	3.2	28.1		a
Na_2SO_4	$CaSO_4 \cdot 2H_2O$	0.0	5.4	13.4		a
NaCl	KCl	0.1	5.6	5.5		b
NaCl	KCl	0.2	4.1	5.1		b
NaCl	KCl	0.3	3.5	8.5		b
NaCl	KCl	0.4	2.7	3.5		b
NaCl	KCl	0.5	2.5	15.9		b
average				5.9	5.5	

[a] Link and Seidell, 1965. [b] Sham and Lee 1991. [c] Solubility Product Values: NaCl (aq, 37.06), KCl (aq, 7.81), KCl (10% MeOH, 4.05), KCl (20% MeOH, 1.89), KCl (30%, MeOH, 0.884), KCl (40% MeOH, 0.438), KCl (50% MeOH, 0.084), $Na_2SO_4 \cdot 10H_2O$ (aq, 0.052), Na_2SO_4 (aq, 0.28), $CaSO_4 \cdot 2H_2O$ (aq, 3.9×10^{-5})

Mixed Electrolyte Aqueous System

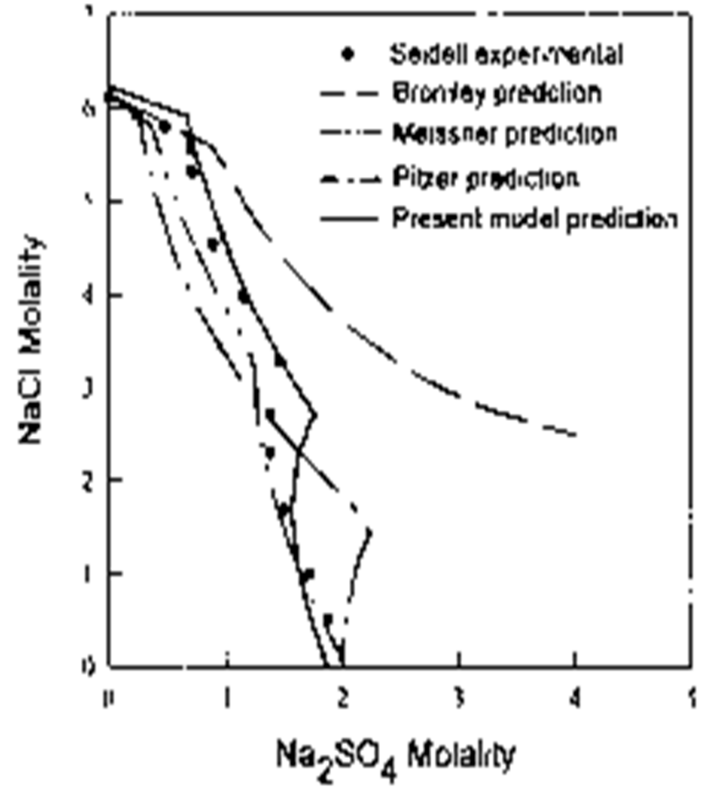

Figure 1. Comparison of solubilities for NaCl, Na_2SO_4, and $Na_2SO_4 \cdot 10H_2O$ in the H_2O–Na_2SO_4–NaCl system by various methods at 25 °C.

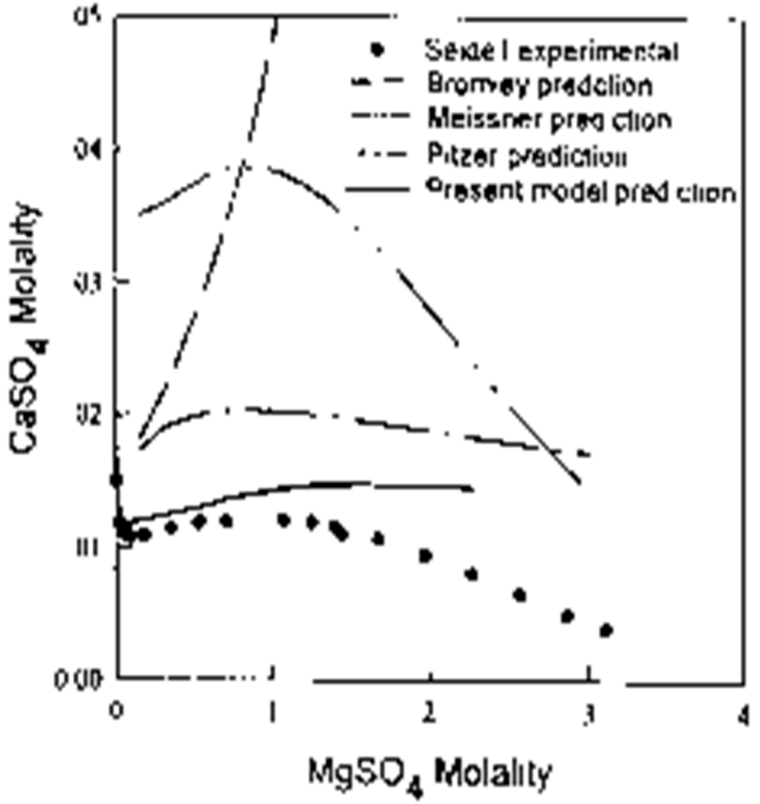

Figure 2. Comparison of solubilities for $CaSO_4 \cdot 2H_2O$ in the H_2O–$MgSO_4$–$CaSO_4$ system by various methods at 25 °C.

Conclusion

- A unified excess Gibbs function moldel for mixed-electrolyte mixed-solvent system
- Short range interaction term : new lattice-hole Helmholtz free energy
- 2 parameters for solvent, 3 parameters for each ionic species