

SOLUBILITIES OF MIXED STRONG 1:1 ELECTROLYTES IN WATER AND WATER-METHANOL MIXTURES

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Abstract—A model [1] recently proposed for mixed electrolytes-mixed solvent systems was tested for activity coefficients of electrolytes, the transfer Gibbs free energy and the solubilities of electrolytes. The model is comprised of the Debye-Hückel term, the Born term and the NRTL term similar to Cruz and Renon's, but has several simplifying features. The model was found applicable to mixed electrolyte-aqueous systems without any interaction parameter between electrolytes. But since the available data are limited, the test for applicability to mixed solvent systems needs further studies.

INTRODUCTION

We have recently presented a method of calculating activity coefficients [1] and solubilities [2] of strong electrolytes in mixed electrolytes-mixed solvent systems up to about seven molal electrolyte concentration. The method is based on the model by Cruz and Renon [3], which is comprised of the Debye-Hückel term, Born term and NRTL term.

Three important simplifying features of this model are; (1) the solution volume in the Debye-Hückel term was replaced by the solvent volume, (2) the model for calculation of dielectric constant was modified, and (3) a systematic method for calculating binary parameters was suggested for mixed electrolytes-mixed solvents systems. Due to these features use of the model becomes relatively simple. The solution volume data are often not available. The dielectric constant data for such systems are rarely found in the literature and the measurement of dielectric constant for concentrated electrolyte solutions is known not very reliable [4]. We also developed a method for calculating the transfer Gibbs free energy which will be described later.

In this paper we apply the method to available literature data of activity coefficients and solubilities of mixed electrolytes in the pure and mixed solvents and discuss the applicability.

THEORETICAL BACKGROUND

We briefly summarize the working equations for the model given by Kim and Lee [1]. The total excess Gibbs free energy G^E which is suitable for calculation of activity coefficient of an electrolyte in the unsymmetric convention is defined as

$$G^E = G^E - RT \sum_j^I N_j \lim_{T \rightarrow 0} \left(\frac{\partial G^E}{\partial N_j} \right)_{T, P, N_{i \neq j}} \\ = G^E - \sum_j^I N_j (\mu_j^* - \mu_j) \quad (1)$$

where G^E is excess Gibbs free energy in the symmetric convention. Then

$$G^E = -(kTV/4000 \pi a^3) [\ln(1+aK) - aK + (aK)^2/2] \\ + (e^2 N_a/2)(1/D - 1/D^*) \sum_j^I (N_j z_j^2 / r_j) \\ + \sum_i^S N_i [(N_{Zi} + \sum_k^I N_k Z_{ik}) / (N_{Gi} + \sum_k^I N_k G_{ik})] \\ - \sum_i^I (N_i / N_{Gi}^2) (Z_{i1} N_{Gi} - G_{i1} N_{Zi}) \quad (2)$$

where

$$K = \left[\frac{8000 \pi e^2 N_a I}{D^* k T} \right]^{1/2} \quad (3)$$

$$I = \sum_j^I N_j z_j^2 / 2V \quad (4)$$

$$Z_{ik} = Z_{ki} + (v_i / v_k) Z_{ki} \quad (5)$$

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$$G_{+ki} = G_{ki} + (v_-/v_+)G_{ki} \quad (6)$$

$$N_{Zi} = \sum_{k \neq i} N_k Z_{ki} \quad (7)$$

and

$$N_{Gi} = \sum_{k \neq i} N_k G_{ki} + N_i \quad (8)$$

Superscripts for summation I, CI and S indicate that the summation is over all ions, all cations and all solvent components, respectively. Subscripts k and k' stand for cation and anion of an electrolyte. Also it is convenient to take total mass of solvents as 1 kilogram. Then N_i's for ions become molalities and V is the volume of 1 kg solvent. For 'a' we assume following mixing rule.

$$a = \sum_i^E N_i N_j a_{ij} / \left(\sum_i^E N_i \right)^2 \quad (9)$$

where the superscript E for summation indicates summation over all electrolytes, a_{ij} is the radius of an electrolyte i and a_{ij} is assumed as (a_{ii} + a_{jj})/2.

D^e is the dielectric constant of solvent and D is that of solution, which may be calculated by the following equation.

$$D = D^e + (D^e - D^s) \left[\frac{1 - Y^*}{1 + Y^*/2} - \frac{(1 - Y'')}{2TV} \sum_i \frac{E_i N_i}{r_i} \right] \quad (10)$$

where

$$Y^* = (4000/3)\pi N_e \sum_i^I N_i r_i^3 / V \quad (11)$$

$$Y'' = (4000/3)\pi N_e \sum_i^I N_i r_i^3 / V \quad (12)$$

and D^e is the dielectric constant in vacuum.

Finally the activity coefficient of the salt MX in the presence of salt NY is given as follows.

$$\begin{aligned} \ln \gamma_{MX}^* &= -\frac{1}{8000 \pi a^3 N_e I} \left[\frac{(aK)^3}{2(1+aK)} + IV \bar{a}_{MX} \right. \\ &\quad \left. \left\{ \ln(1+aK) - \frac{aK}{2} - \frac{aK}{2(1+aK)} \right\} + IV \frac{\bar{a}_{MX}}{a} \right. \\ &\quad \left. \left\{ \frac{(aK)^3}{2(1+aK)} - 3\ln(1+aK) - \frac{3}{2}aK \right\} \right] + \frac{e^2}{4kT} \left(\frac{1}{r_M} + \frac{1}{r_X} \right) \\ &\quad \left\{ \frac{1}{D} - \frac{1}{D^e} - \frac{N_M}{D^2} \left(\frac{\partial D}{\partial N_M} + \frac{\partial D}{\partial N_X} \right) \right\} + \frac{1}{2RT} \sum_i^I \\ &\quad \left\{ N_i \frac{\sum_{k \neq i}^I N_k (G_{+ki} Z_{+i} - G_{-ki} Z_{-i}) + (Z_{+i} N_{Gi} - G_{+i} N_{Zi})}{(N_{Gi} + \sum_j^I N_j G_{+j})^2} \right. \\ &\quad \left. - \frac{Z_{+i} N_{Gi} - G_{+i} N_{Zi}}{N_{Gi}^2} \right\} - \ln \left\{ 1 + \frac{2(N_{MX} + N_{NY})}{(N_e + N_s)} \right\} \quad (13) \end{aligned}$$

where from the definition of V, $\bar{V}_{MX} = 0$ and from Eq.

$$(9) \bar{a}_{MX} = a_{MX}.$$

To apply the model we need one size parameter a for each electrolyte, three ion size parameters r₊, r₋, and r_i for the evaluation of solution dielectric constants, two NRTL parameters for each solution-electrolyte pair and three NRTL parameters for a solution-solution pair. We use Stokes radius for r₊ of cations and Pauling radius for that of anions. The saturated cavity radius r_i is related with the Hasted depression coefficient which is listed in a reference [3] as follows.

$$r_i = 3.089 \times 10^{-12} (|\delta_i| / D^e)^{1/3} \quad (14)$$

r_i is a fitting parameter which is assumed solvent independent and is zero for anions. We also need experimental data for volume V and dielectric constant D^e of pure or mixed solvents.

The solubility of an electrolyte is calculated by minimizing the total Gibbs free energy G which may be obtained using Eq. (1).

$$\begin{aligned} G &= \sum_j^I N_j \mu_j^* + G^e + \sum_j^I N_j (\mu_j^* - \mu_j) \\ &= \sum_j^I N_j \mu_j^* + \sum_j^I N_j \Delta \mu_j^* + RT \sum_j^I N_j \ln a_j, \end{aligned} \quad (15)$$

where $\Delta \mu_j^* = \mu_j^* - \mu_j^e$, and $a_{MX} = m_M m_X \gamma_M^* \gamma_X^* = m_M m_X \gamma_{MX}^2$, etc. For a mixed solvent of a fixed composition, the minimum Gibbs energy condition reduces to

$$\Delta \mu_j^* / RT = -\ln a_j \text{ for each electrolyte} \quad (16)$$

However, for an electrolyte species which exists less than its solubility, following total solubility condition has to be satisfied instead of Eq. (16).

$$\Delta \mu_j^* / RT > -\ln a_j \text{ for totally soluble electrolyte} \quad (17)$$

The calculation may be proceeded as follows for binary solute mixtures; (1) Assume a concentration of an electrolyte MX, (2) Calculate the solubility of NY by Eq. (16), (3) Check if Eq. (17) is satisfied for MX, (4) If satisfied then the calculated solubility in step(2) is correct and calculation is terminated, (5) If not satisfied then Eq. (16) is solved for both electrolytes and we have a point where both electrolytes and the mixed solvent is in equilibrium. This procedure is repeated for assumed concentration of NY to calculate the solubility of MX. The results of these calculation can be presented as a locus on a triangular diagram.

One of the remaining problem is if we can calculate $\Delta \mu_j^*$ of an electrolyte j in a mixed solvent once we know $\Delta \mu_{jW}^*$ in a reference solvent W.

$$\Delta\mu_j^o = \Delta\mu_{j,w}^o + \Delta\mu_{j,A}^o \quad (18)$$

where $\Delta\mu_{j,A}^o$ is called the transfer Gibbs free energy.

A relation was developed [1] for the calculation of the transfer Gibbs free energy and the result is given below for an electrolyte MX in the mixed solvent of W and A.

$$\begin{aligned} \Delta\mu_{j,MW}^o = & -\frac{e^2 N_o}{a} \left(\frac{1}{D_s} - \frac{1}{D_w} \right) - \frac{e^2 N_o}{4} \left[\frac{1}{D^s} \left(\frac{1}{r_M} + \frac{1}{r_X} \right) \right. \\ & \left. - \frac{1}{D^s} \left(\frac{1}{r_{M,w}} + \frac{1}{r_{X,w}} \right) \right] - \frac{1}{2} \left[(Z_{\pm MW} N_{GW} \right. \\ & \left. - G_{\pm MW} N_{ZW}) \frac{N_M}{N_{GW}^2} + (Z_{\pm MA} N_{GA} - G_{\pm MA} N_{ZA}) \right. \\ & \left. \frac{N_A}{N_{GA}^2} - Z_{\pm MW} \right] \end{aligned} \quad (19)$$

r_M, r_X are calculated once we know the solution dielectric constant using Eq. (14). Unfortunately we have no means to calculate D^s yet.

RESULTS AND DISCUSSION

For a single electrolyte-single solvent system a good fit of activity coefficients is possible with a number of different sets of pure and binary parameters [3]. An important problem in application is whether NRTL parameters determined for binary systems are valid for multicomponent systems. We found that a systematic approach is needed in determining these parameters [1]. With an appropriate set of parameters described in the previous section and listed in Tables 1

Table 1. Ionic properties

	H ⁺	Li ⁺	Na ⁺	K ⁺	Cl ⁻	Br ⁻
r [*] _w /10 ⁻¹⁰ m	0.263	2.40	1.84	1.30	1.81	1.95
r [*] _A /10 ⁻¹⁰ m	—	3.79	3.28	2.79	1.81	1.95
r [*] /10 ⁻¹⁰ m	2.26	3.05	2.66	2.54	0.0	0.0
δ/10 ⁻³ m ³ mol ⁻¹	-16.4	-9.8	-8.0	-6.6	-3.6	-4.1

The subscript w or A designates water or methanol, respectively.

Table 2. Binary parameters and $\Delta\mu_{j,w}^o$

	HCl	LiCl	NaCl	KCl	NaBr	KBr
a/10 ⁻¹⁰ m	6.1	5.6	4.80	4.10	5.1	4.6
Z _{j,w} /kJmol ⁻¹	82.946	99.37	120.0	83.57	83.985	98.074
G _{±w}	.0500	.2419	.2992	.4200	0.3512	0.4192
Z _{±A} /kJmol ⁻¹	—	130.0	160.7	128.0	—	—
G _{±A}	—	.8020	.3080	.4200	—	—
Δμ _{j,w} ^o /kJmol ⁻¹	-35.93	-40.23	-9.00	-5.16	-16.57	-6.57

The subscript w or A designates water or methanol, respectively. The NRTL parameter for solvents are Z_{WW}=0.5373 kJ/mol, Z_{AW}=-0.3040 kJ/mol, G_{WA}=0.8280 and G_{AA}=1.085.

and 2, experimental data of solvent volume [5] and dielectric constants [6] for water methanol system, and experimental $\Delta\mu^o$ of an electrolyte for a reference solvent which is also listed in Table 2, we should be able to calculate $\Delta\mu^o$ and γ^* of electrolyte j in mixed solvents. Then we can calculate solubilities.

Calculated values of $\Delta\mu^o$ agree with experimental values of Feakins and Voice [7] with an RMS deviation of 0.052 kcal/mol for NaCl and KCl and 0.134 kcal/mol for LiCl in water-methanol mixture. If we consider that the average difference in $\Delta\mu^o$ data by different investigators [7, 8] is about 0.2 kcal/mol for NaCl and KCl in water-methanol mixture, the agreement is probably within experimental errors.

Calculated values of γ^* were compared with experimental values as shown in Table 3. The agreement is generally good up to the total electrolyte concentration of 7 mol/kg solvent, beyond which calculated values tend to become larger than experimental data. This tendency may partly be due to the incomplete dissociation of electrolytes at high concentration, which is not included in the present model. Results of other investigators are summarized in Table 4. For single electrolyte-single solvent system results of Renon and Cruz [3] is approximately similar with ours over a wider concentration range, but their parameters are not applicable to mixed systems. Also they included the effect of incomplete dissociation in their model. For single electrolyte-mixed solvent system present results shows an improvement over those of Rastogi and Tassios [9]. For mixed electrolyte-single solute system, Pitzer and Kim's results [10] are better than ours. They have interaction parameters between electrolytes and their model parameters are not suitable for straightforward extension to mixed solvent systems.

Finally results of solubility calculation of mixed electrolytes in water and water methanol mixture are summarized in Table 5. No such calculations by other investigators are known to the authors. The calculation is limited to total electrolyte concentration of 7 mol/kg

Table 3. Comparison of calculated activity coefficients with experimental values at 25°C

System	Conc. range mol/kg solvent	No. of data point	RMS deviation*	Data ref.
HCl-H ₂ O	0.1-10.0	27	0.027	[11]
	0.1-7.0	24	0.024	[11]
LiCl-H ₂ O	0.1-10.0	27	0.034	[12]
	0.1-7.0	24	0.007	[12]
NaCl-H ₂ O	0.001-6.0	29	0.015	[13]
KCl-H ₂ O	0.001-4.5	26	0.007	[13]
NaBr-H ₂ O	0.1-4.0	19	0.035	[14]
KBr-H ₂ O	0.1-5.0	21	0.018	[14]
KCl-CH ₃ OH	0.0021-0.0707	10	0.076	[15]
HCl-LiCl-H ₂ O	HCl(0.01)			
	LiCl(0.01-4.0)	11	0.022	[4]
HCl-NaCl-H ₂ O	HCl(0.01)			
	NaCl(0.01-3.0)	9	0.013	[4]
HCl-KCl-H ₂ O	HCl(0.01)			
	KCl(0.01-3.5)	13	0.021	[4]
NaCl-KCl-H ₂ O	1.0-5.0 [#]	33	0.021	[15]
LiCl-CH ₃ OH-H ₂ O	CH ₃ OH(10-80) ["]			
	LiCl(0.04-0.2)	21	0.019**	[7]
NaCl-CH ₃ OH-H ₂ O	CH ₃ OH(25-90) ["]			
	NaCl(0.001-2.369)	34	0.034**	[16]
NaCl-CH ₃ OH-H ₂ O	CH ₃ OH(10-90) ["]			
	NaCl(0.04-0.2)	38	0.016**	[7]
KCl-CH ₃ OH-H ₂ O	CH ₃ OH(10-80) ["]			
	KCl(0.04-0.20)	28	0.003**	[7]
KCl-CH ₃ OH-H ₂ O	CH ₃ OH(10-90) ["]			
	KCl(0.016-3.875)	108	0.040**	[17]
NaCl-KCl-CH ₃ OH-H ₂ O	CH ₃ OH(10-40) ["]			
	0.51-1.00 [#]	27	0.012**	[18]

* $[\sum(\ln \gamma_{cal}/\gamma_{exp})^2/N]^{1/2}$

** average of RMS dev. for different solvent composition

[#] total molality of electrolytes["] weight percent in solvent

Table 4. Other investigators' results

Systems	Fitted properties	RMS deviation	Conc. range(total molality) [#]	Ref.
HCl-H ₂ O	φ	0.05	0.11-47.1	[3]
LiCl-H ₂ O	φ	0.01	0.10-20.0	[3]
NaCl-H ₂ O	φ	0.002	0.006-6.0	[3]
KCl-H ₂ O	φ	0.015	1.0-4.6	[3]
HCl-LiCl-H ₂ O	lnγ [*]	0.007	max. I=3.	[10]
HCl-NaCl-H ₂ O	lnγ [*]	0.002	max. I=5.	[10]
HCl-KCl-H ₂ O	lnγ [*]	0.010	max. I=3.5	[10]
LiCl-NaCl-H ₂ O	φ	0.001	max. I=6.0	[10]
LiCl-KCl-H ₂ O	φ	0.001	max. I=4.8	[10]
NaCl-KCl-H ₂ O	φ	0.001	max. I=4.8	[10]
NaBr-KBr-H ₂ O	φ	0.003	max. I=4.0	[10]
KCl-KBr-H ₂ O	φ	0.002	max. I=4.4	[10]
LiCl-CH ₃ OH-H ₂ O	lnγ [*]	0.077**	0.02-1.0	[9]
NaCl-CH ₃ OH-H ₂ O	lnγ [*]	0.061**	0.02-0.5	[9]

φ osmotic coefficient

** average relative error in lnγ^{*}.

Table 5. Comparison of calculated solubilities with experimental values at 25°C

System	No. of data points	Total electrolyte concentration	Average deviation*	Data ref.
NaCl-KCl-H ₂ O	6	6.09-7.31	3.0	a
NaCl-NaBr-H ₂ O	2	6.39-6.80	1.8	b
KCl-KBr-H ₂ O	19	4.91-6.20	7.4	c
NaBr-KBr-H ₂ O	3	5.93-6.96	8.9	d
LiCl-NaCl-H ₂ O	2	6.41-7.01	5.7	e
LiCl-KCl-H ₂ O	2	5.09-7.10	14.6	f
HCl-NaCl-H ₂ O	8	6.08-7.06	0.5	g
HCl-KCl-H ₂ O	9	4.89-7.16	16.0	h
NaCl-CH ₃ OH-H ₂ O	11	0.237-5.038	4.1	i
KCl-CH ₃ OH-H ₂ O	12	0.073-3.651	4.6	j
NaCl-KCl-CH ₃ OH-H ₂ O	14	1.70-5.07	4.0	k

* $\Sigma |Exp-Cald| /Exp \times 100/No. \text{ of Data}$

^aCor nec and Krombach, "Solubilities, Inorganic and Metal-Organic Compounds", Vol. II, pp. 147, 4ed., Washington D.C. (1965), ^bBergman and Vlassov, *ibid.*, pp. 836, 1949, ^cAmadori and Pampanini, *ibid.*, pp. 16, 1932, ^dBergman and Vlassov, *ibid.*, pp. 22, 1949, ^eSmith, Elgersma and Hardenberg, *ibid.*, pp. 396, 1924, ^fCampbell and Kartzmark, *ibid.*, pp. 140, 1956,

^gIngham, *ibid.*, pp. 147, 1928, ^hMalquori, *ibid.*, pp. 116, 1928, ⁱArmstrong and Eyre, *ibid.*, pp. 994, 1910, ^jAkerlof and Turck, *ibid.*, pp. 155, 1935, ^kHan, G. S., Jung, W. S. and Lee, C. S., *Hwangak Konghak*, **27**, 657 (1989)

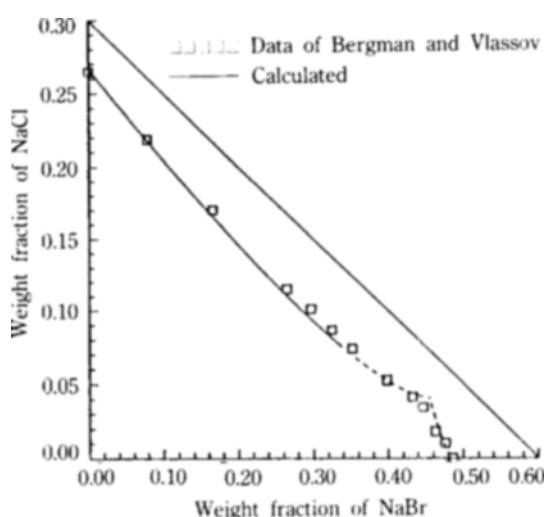


Fig. 1. Comparison of solubilities of electrolytes with calculated values for NaCl-NaBr-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

solvent. While the agreements of calculated results with experimental values are generally good and comparable with those of activity coefficients, in some cases the error exceeds 10%. Since no activity coefficient data are available for such systems, it is difficult to determine the source of errors. Typical results are also shown in Figs. 1-7.

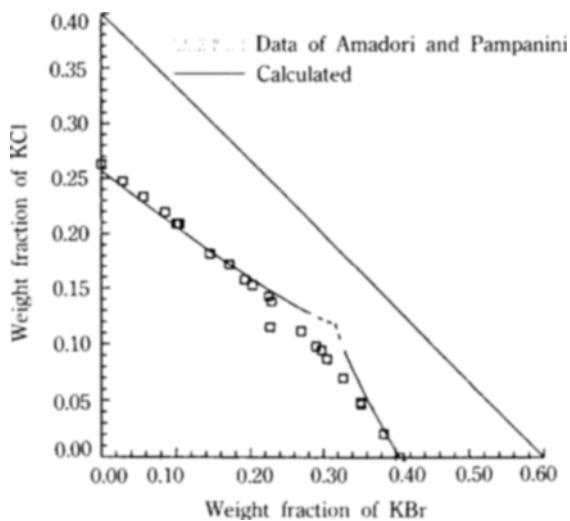


Fig. 2. Comparison of solubilities of electrolytes with calculated values for KCl-KBr-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

Experimental data for mixed electrolyte systems are available for aqueous systems and one water-methanol system and we cannot draw a firm conclusion on the applicability of the present model to mixed solvent systems. It is yet to be tested when the data becomes available. However present analysis indicates that the model is applicable to mixed electrolyte systems with-

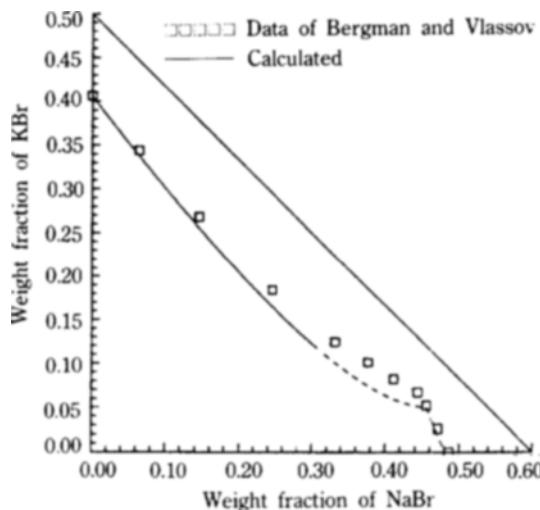


Fig. 3. Comparison of solubilities of electrolytes with calculated values for NaBr-KBr-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

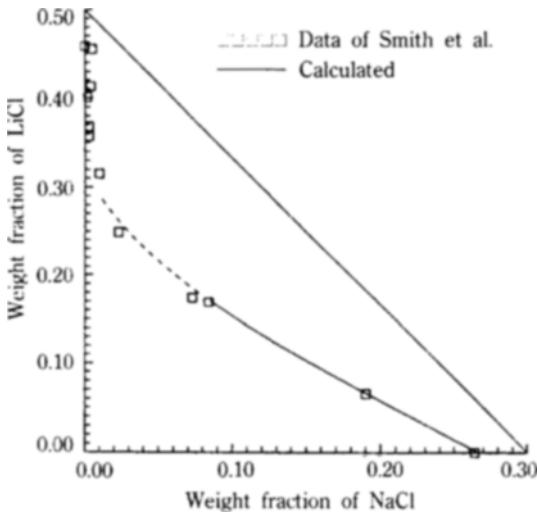


Fig. 4. Comparison of solubilities of electrolytes with calculated values for LiCl-NaCl-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

out any interaction parameter between electrolytes.

CONCLUSION

Based on the comparison of calculated results with

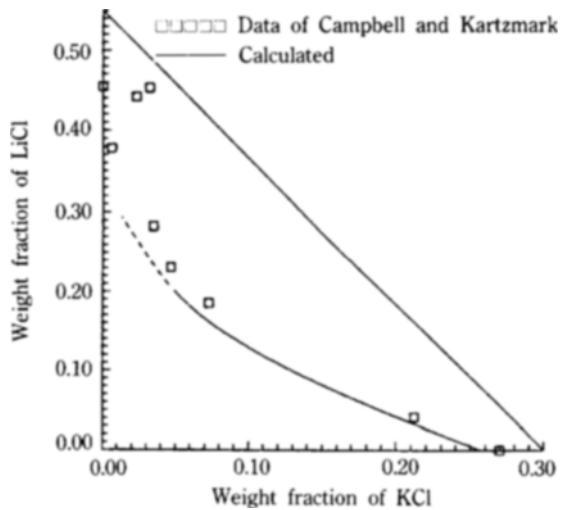


Fig. 5. Comparison of solubilities of electrolytes with calculated values for LiCl-KCl-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

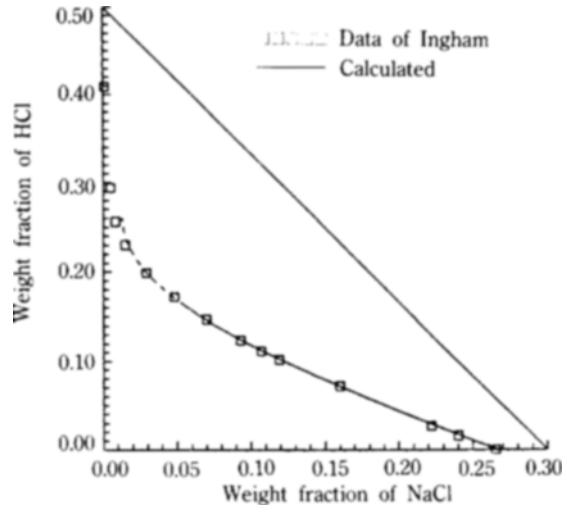


Fig. 6. Comparison of solubilities of electrolytes with calculated values for HCl-NaCl-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

available experimental data, the model described for mixed electrolytes-mixed solvent systems is tested for activity coefficients of electrolytes, the transfer Gibbs free energy and the solubilities of electrolytes. The model is found applicable to mixed electrolyte-single

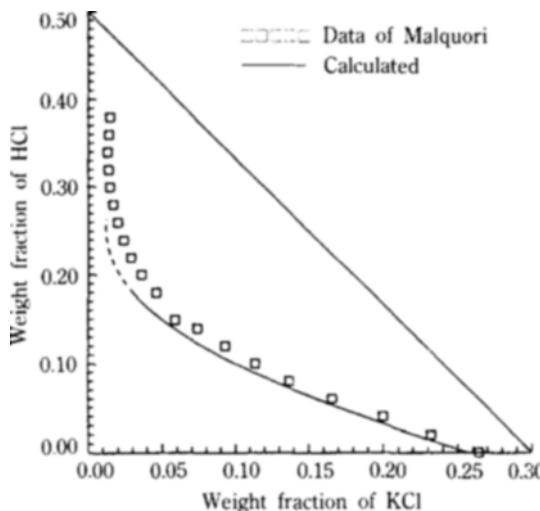


Fig. 7. Comparison of solubilities of electrolytes with calculated values for HCl-KCl-Water system at 298.15 K (Dashed line indicates the calculated results for total electrolytes concentration between 7-10 mol/kg solvent).

solvent systems without any interaction parameter between electrolytes. But with the limited data available, the applicability to mixed solvent systems is not conclusive and need further tests.

NOMENCLATURE

a : distance of closest approach between opposite charged ion [m]
 D : dielectric constant of electrolyte solution [$J^{-1} C^2 m^{-1}$]
 D^* : dielectric constant in vacuum [$1.113 \times 10^{-10} J^{-1} C^2 m^{-1}$]
 D^e : dielectric constant of solvent [$J^{-1} C^2 m^{-1}$]
 e : charge of an electron [$1.602 \times 10^{-19} C$]
 G^E : excess Gibbs energy of solution [$J mol^{-1}$]
 G : a NRTL parameter [-]
 I : ionic strength [$mol dm^{-3}$]
 k : Boltzmann constant [$1.381 \times 10^{-23} J^\circ K^{-1}$]
 K : reciprocal of Debye length [m^{-1}]
 N_j : no. of moles component j per kg solvent [mol/kg solvent]
 N_A : Avogadro's no. [$6.022 \times 10^{23} mol^{-1}$]
 $N_{i,j}$: defined by Eq. (8) [mol]
 $N_{j,i}$: defined by Eq. (7) [mol]
 r : saturated cavity radius [m]
 r^* : Stokes radius for cation and Pauling radius for anion [m]
 r'' : parameter in Eq. (12) [m]

R : gas constant [$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]
 T : absolute temperature [K]
 V : volume per kg solvent [dm^3]
 Y, Y'' : volume fraction defined Eq. (11) and Eq. (12)
 $[-]$
 Z : a NRTL parameter [$J mol^{-1}$]
 δ : Hasted depression [$m^3 mol^{-1}$]
 μ : chemical potential [$J mol^{-1}$]
 γ_{+MX} : mean ionic activity coefficient of the electrolyte MX
 v_{-v} : stoichiometric no. of ion [-]

Superscripts

$*$: infinite dilution reference state
 o : pure reference state
 E : excess properties

Subscripts

k : cation of electrolytes
 MX : an electrolyte
 i : chemical species
 ki : interaction of solvent k and i
 $\pm ki$: interaction between an electrolyte whose cation is k and solvent i

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