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An Evaluation of Four Electrolyte Models for the Prediction of Thermodynamic Properties of Aqueous Electrolyte Solutions

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Abstract

In this work, the performance of four electrolyte models for the prediction of the osmotic and activity coefficients of different aqueous salt solutions at a temperature of 298 K, at atmospheric pressure, and in a wide range of concentrations is evaluated. In two of these models, namely electrolyte non-random two-liquid (e-NRTL) and mean spherical approximation non-random two-liquid (MSA-NRTL), the association between ions of the opposite charges for simplification purposes is ignored, but in the other two ones, namely associative mean spherical approximation non-random two-liquid (AMSA-NRTL) and binding mean spherical approximation (BiMSA), association and solvation effects are considered. The predictions of these four models for the osmotic and activity coefficients of electrolyte solutions at a temperature of 298 K and at atmospheric pressure are compared with the experimental data reported in the literature. This comparison is performed for 28 different aqueous salt solutions, including thio-cyanates, perchlorates, nitrates, hydroxides, quaternary ammonium salts, and others. The results show that the performance of the models which consider association effects is better than the others, especially for higher salt concentrations. However, the best performance belongs to the BiMSA model, which has some parameters with physical meaning.

Keywords: Electrolyte Models, Osmotic Coefficient, Activity Coefficient, Thermodynamic Properties

1. Introduction

The reliable prediction of thermodynamic properties of electrolyte solutions is crucial in design and operation of oil and gas production and processing facilities. Vapor-liquid phase equilibria simulation is the most important process which needs reliable thermodynamic properties of aqueous electrolyte solutions. Formation water produced with oil and gas contains dissolved salts, which makes the vapor-liquid phase equilibria simulation for hydrocarbon systems in the presence of aqueous electrolyte solutions be a practical case. Therefore, it is needed to have accurate and reliable theoretical models for the predictions of thermodynamic properties of aqueous electrolyte solutions

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(Najibi et al., 2015). Different models have been developed and presented so far in the literature (Loehe and Donohue, 1997; Rafael et al., 1994), but semi-empirical and theoretical models developed based on mean spherical approximation theory have received more attention in recent years (Bernard and Blum, 1996; Chen et al., 1982; Papaiconomou et al., 2002; Simonin et al., 2006). The challenge facing these models is the validity of the results for a wide range of salt concentrations in the aqueous electrolyte solutions.

Four of the important models developed in this context are e-NRTL proposed by Chen et al. (1982); MSA-NRTL proposed by Papaiconomou et al. (2002); AMSA-NRTL proposed by Simonin et al. (2006); and BiMSA proposed by Bernard and Blum (1996). In the first two models, the main simplifying assumption is that no association of ions of opposite charges will take place in the aqueous electrolyte solution. In this work, these four models are used to predict the osmotic and activity coefficients of different aqueous electrolyte solutions, and the results are compared.

2. Electrolyte models

The e-NRTL and MSA-NRTL models are developed based on this assumption that the salt is completely dissolved in the liquid phase and dissociates into its forming ions, and no ion pairing takes place in the liquid phase. The dissociation reaction can be written as follows:

$$C_{\nu_C} A_{\nu_A} \rightarrow \nu_C C^{z_C^+} (\mathrm{aq}) + \nu_A C^{|z_A|^-} (\mathrm{aq}) \tag{1}$$

where, ν_i is the stoichiometric valence of the ions making the salt. The e-NRTL model provides an expression for the excess Gibbs molar energy of electrolyte systems, which is assumed to be the sum of two terms

$$G_{\text{e-NRTL}} = G_{\text{PDH}} + G_{\text{NRTL}} \tag{2}$$

where, the effect of long-range electrostatic interactions is described using the Pitzer-Debye-Hückel (PDH), and short-range interactions are described using the classic NRTL for all the species (ions and molecules) in the solution. Main assumption made in the classical e-NRTL is that the number of cations surrounding a central solvent molecule is the same as the number of anions surrounding it, i.e. local electro neutrality assumption. With this simplification, this model has three basic parameters which need to be adjusted using experimental data. These parameters are the non-randomness factor α_{CA} and the dimensionless energetic interaction parameters, i.e. $\tau_{CA,W}$ and $\tau_{W,CA}$. The non-randomness factor in this model is often set to a fixed value of 0.2 (Chen et al., 1982). In this model, it is assumed that $\tau_{CW} = \tau_{AW}$ (denoted by $\tau_{CA,W}$) and $\tau_{WC,AC} = \tau_{WA,CA}$ (denoted by $\tau_{W,CA}$). More details of the model are described elsewhere (Chen et al., 1982; Chen and Evans, 1986).

The MSA-NRTL model is a combination of the MSA model with the classic NRTL model (Papaiconomou et al., 2002). The latter is used to take into account the short-range interactions, but the former describes the long-range electrostatic interactions. The MSA model can yield analytic expressions in terms of parameters, such as ion size and permittivity, which have physical meaning. In the MSA-NRTL approach, the molal activity coefficient for each component is given by the following expression:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{MSA}} + \ln \gamma_i^{\mathrm{NRTL}} \tag{3}$$

where, $\ln \gamma_i^{MSA}$ represents the MSA contribution, which has one adjustable parameter, i.e. σ (mean ionic diameter), and $\ln \gamma_i^{NRTL}$ is the NRTL interaction contribution and contains four adjustable parameters, including $\tau_{C,W}$, $\tau_{A,W}$, and two concentration dependent parameters, i.e. $\tau^1_{WC,AC}$ and $\tau^2_{WC,AC}$ as follows:

$$\tau_{WC,AC} = \tau^1_{WC,AC} + \tau^2_{WC,AC} x_W \tag{4}$$

where, x_W is the mole fraction of water in solution. The non-randomness factor in this model is also set to 0.2. The details of the model equations are described elsewhere (Papaiconomou et al., 2002).

The AMSA-NRTL model (Simonin et al., 2006) is a modified version of MSA-NRTL, which includes ionic solvation and physical association for the ions present in the electrolyte solution. The inclusion of ion pairing causes a better prediction of the thermodynamic properties of aqueous electrolyte solutions. In this model, the hydration of ions is accounted by introducing a constant hydration number which is independent of salt concentration, as used in the classical model of Robinson and Stokes (Robinson and Stokes, 1959). Five adjustable parameters of this model are two dimensionless interaction energy parameters ($\tau_{CA,W}$, $\tau_{WC,AC}$); hydration number (h); equilibrium constant of ion-pair formation reaction (K); and mean ionic diameter (σ). These parameters are optimized by fitting the data to experimental data. To reduce the total number of model parameters as much as possible, it is assumed that:

$$\tau_{C,W} = \tau_{A,W} = \tau_{CA,W} \tag{5}$$

$$\tau_{P,W} = \tau_{W,P} = 0 \tag{6}$$

$$\tau_{C,P} = \tau_{C,W} , \tau_{A,P} = \tau_{A,W} \left(= \tau_{CA,W}\right) \tag{7}$$

$$h = h_A + h_C \tag{8}$$

where, subscript P represents the molecular species in solution. Hydration numbers for cations and anions are denoted as h_C and h_A respectively. The overall equation which describes this model is given by:

$$\ln\left(\gamma_\pm\right) = \ln\left(g_\pm\right) - \frac{h}{v}\ln\left(a_W\right) + \ln\left(y_1\right) + \frac{1}{v}\left(v_C \ln\left(1 - \frac{v_A}{v_C} x\right) + vA \ln\left(1 - \frac{v_A}{v_C} x\right)\right) \tag{9}$$

where, y_1 is defined as $y_1 = \left\{1 + mM_W\left[v - v_A x - h + v_A h\right]\right\}$, and the fraction of the bounded ion (x) is obtained by the following equation:

$$x - K \frac{mM_W\left(v_C - v_A x\right)\left(1 - x\right)}{1 + mM_W\left[v - v_A x - h + v_A h\right]} \frac{g_C g_A}{g_{ip} a_W^h} = 0 \tag{10}$$

where, g_i is fugacity coefficients of ionic species in the model level, and $v = v_C + v_A$ is the total stoichiometric number; m is molality of salt (mol.kg^{-1}), and M_W stands for the molecular weight of water (18.0153 g·mol^{-1}). The detail description of this model is presented by Simonin and his co-workers elsewhere (Simonin et al., 2006).

BiMSA model is developed based on the Wertheim formalism theory (Wertheim, 1988, 1987) and is proposed by Bernard and Blum (1996). The parameters in this model have some physical meaning from a microscopic point of view. The two important parameters are cation diameter (σ_C) and the relative permittivity of the solution (ε), which, in this work, are chosen as a function of salt concentration (C_S) as follows:

$$\sigma_C = \sigma_C^{(0)} + \sigma_C^{(1)} C_S \tag{11}$$

$$\varepsilon^{-1} = \varepsilon_W^{-1}(1 + \beta C_S) \tag{12}$$

where, $\sigma_C^{(0)}$ is the diameter of cation at an infinite dilution of salt, and $\sigma_C^{(1)}$ is the concentration dependent term of cation diameter; ε_W is the relative permittivity of the pure solvent and is calculated using relation proposed by Uematsu and Frank (1980); β accounts for the variation of the permittivity of solution against concentration. This model can predict the properties of very non-ideal salt solutions up to high concentrations, and its detail description is presented elsewhere (Bernard and Blum, 1996; Papaiconomou et al., 2012; Simonin et al., 1998).

3. Results and discussion

The experimental data for the osmotic and activity coefficients of 28 strong electrolyte aqueous solutions at a temperature of 298 K, at atmospheric pressure, and in a wide range of salt concentrations are gathered from literature. The model parameters are fitted to the gathered data using a reliable technique which works based on genetic algorithm (GA) optimization method. This technique allows finding the global optimum for all the parameters. In this method, the best parameters for the selected models are found by minimizing the summation of differences between the calculated and experimental values of the properties. For example, for the activity coefficients, the following objective function is minimized:

$$\mathrm{AARD}\gamma_{\pm} = (100/N)\sum_{j=1}^{N}\left|\gamma_{\pm,\mathrm{cal}}(j) - \gamma_{\pm,\exp}(j)\right| \Big/ \gamma_{\pm,\exp}(j) \tag{13}$$

All the minimizations are performed by using MATLAB software version R2011a. More details about genetic algorithm technique used herein can be found in the literature (Alvarez et al., 2008).

The performance of four electrolyte models selected in this study is investigated by comparing the calculated values with the data gathered from literature for the osmotic and activity coefficients of various aqueous salt solutions (Bonner, 1981a, 1982; Bonner, 1981b; Hamer and Wu, 1972; Kálmán and Schwabe, 1979; Lindenbaum and Boyd, 1964; Macaskill and Bates, 1986; Rard et al., 2003). All calculations are performed for single aqueous solution up to the highest concentration for which data are available at atmospheric pressure (0.1 MPa) and a temperature of 298 K. The fitted parameters and average absolute relative deviation percent (AARD (%)) of the osmotic and mean activity coefficients for the four electrolyte models selected in this work are shown in Tables 1 to 4. The results presented in these tables show that the values of $\tau_{CA,W}$ ($\tau_{C,W}$ and $\tau_{A,W}$ in MSA-NRTL model) for all the solutions are negative, which can be interpreted as the stronger the hydrated ion–solvent interaction than the solvent–solvent interaction which are basically identical to those given by Chen et al. (1982). Moreover, the values of $\tau_{WC,AC}$ are positive for all the solutions, which means that the hydrated cation/anion–solvent interaction is weaker than the hydrated cation–hydrated anion interaction, and for all the solutions, except for some cases in AMSA-NRTL model, $\left|\tau_{CA,W}\right|$ is much smaller than $\left|\tau_{WC,AC}\right|$, i.e. $\left|\tau_{CA,W}\right| \ll \left|\tau_{WC,AC}\right|$.

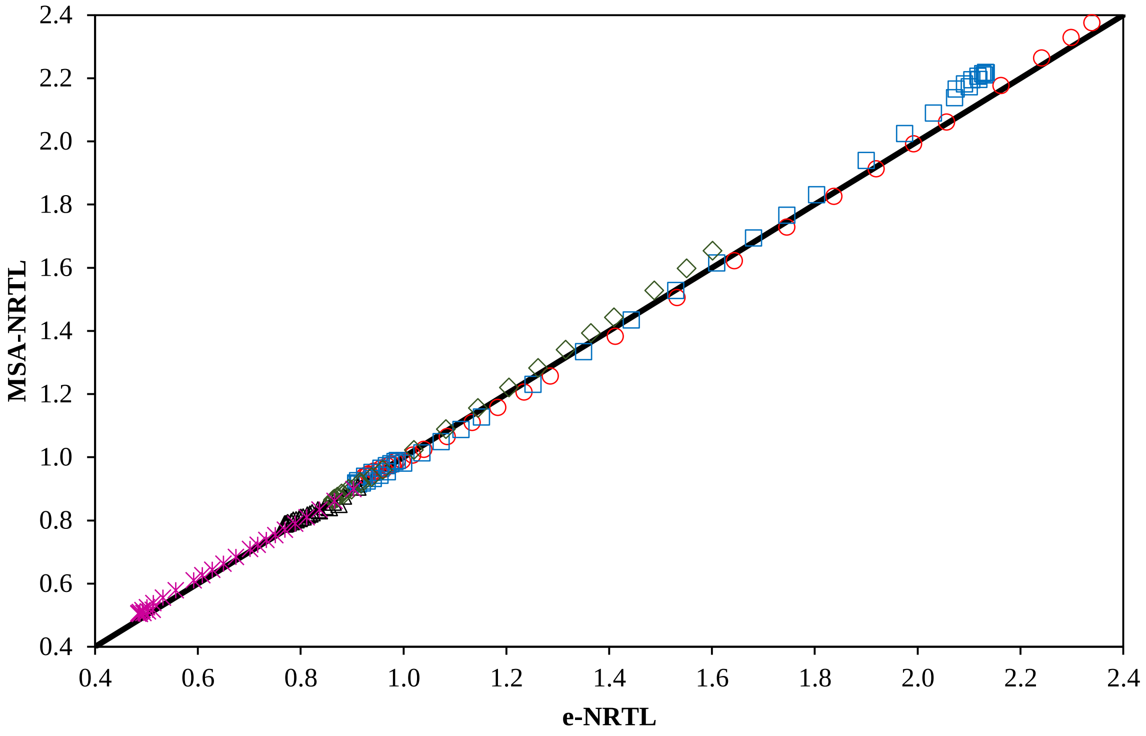

Figure 1

Osmotic coefficients calculated by e-NRTL versus those calculated by MSA-NRTL; the solid line is the 1:1 correspondence line; symbols are define as follows: (○) $HClO_4$; (□) KOH; (Δ) Me_4NBr; (◊) Et_4NBr; and (*) Bu_4NBr.

For the first two models (e-NRTL and MSA-NRTL), which do not consider ion pairing, the total AARD (%) of MSA-NRTL is slightly better than that of e-NRTL model. However, the MSA-NRTL model has five fitting parameters, while e-NRTL needs two parameters to be fitted. Therefore, it can be concluded that the predictive ability of the MSA-NRTL method is limited and has no special priority to the e-NRTL model. The performance of e-NRTL model for the prediction of osmotic coefficients of different single-salt aqueous solutions in the entire range of molality is compared with the MSA-NRTL model in Figure 1. As shown in this figure, the predictions of these two models for the osmotic coefficients of different single salt aqueous solutions are quite comparable.

Table 1

e-NRTL model parameters for a number of single electrolyte solutions and AARD (%) of its predictions for osmotic and activity coefficients at T=298.15 K and P=0.1 MPa.

Electrolyte	**max *m* (mol.kg^{-1})**	$\tau_{WC,AC}$	$\tau_{CA,W}$	**AARD$_{\Phi}$ (%)**[a]	**AARD$_{\gamma\pm}$ (%)**[b]
LiBr	17	11.016	-5.545	12.35	26.68
LiCl	20	11.113	-5.524	8.921	20.04
LiOH	4.0	8.962	-4.388	1.259	1.706
$LiNO_3$	20	9.705	-4.961	3.035	5.467
$LiCH_3SO_3$	5.5	8.565	-4.549	0.437	0.630
$HClO_4$	16	10.96	-5.546	10.33	21.98
HNO_3	28	9.320	-4.767	2.664	4.437
CsBr	5.0	8.468	-4.173	0.426	0.529
CsCl	9.0	8.454	-4.182	0.301	0.389
RbCl	7.8	8.247	-4.153	0.181	0.183
$RbNO_3$	4.5	7.684	-3.454	0.659	0.686
KCl	5.0	8.085	-4.118	0.875	0.340
KF	17.5	9.856	-4.917	4.823	8.115
KOH	20	10.69	-5.349	8.296	17.83
$NaClO_4$	6.0	7.977	-4.112	0.509	0.751
$NaCF_3SO_3$	5.4	6.498	-3.754	0.555	0.887
NaSCN	18	9.673	-4.902	3.209	5.531
Me_4NBr	5.5	9.017	-4.303	1.241	1.364
Me_4NCl	19	9.523	-4.670	2.575	3.591
Et_4NBr	12	9.947	-4.653	1.355	1.679
Et_4NCl	9.0	10.18	-4.993	2.121	3.813
Pr_4NBr	9.0	10.367	-4.856	2.604	3.013
Pr_4NCl	18	9.888	-4.992	3.610	6.271
Bu_4NBr	10	8.186	-3.617	3.487	3.285
NH_3MeCl	20	7.996	-4.059	0.978	1.511
NH_3MeNO_3	9.5	7.227	-3.530	0.332	0.324
$NH_2Me_2ClO_4$	7.5	7.683	-3.530	1.704	2.132
NH_4SCN	23.5	7.221	-3.712	0.900	2.113
Average				2.848	5.188

[a] $\mathrm{AARD}_{\phi} = (100/N)\sum_{j=1}^{N}\left|\phi_{\mathrm{cal}}(j)-\phi_{\mathrm{exp}}(j)\right|/\phi_{\mathrm{exp}}(j)$, [b] $\mathrm{AARD}_{\gamma_{\pm}} = (100/N)\sum_{j=1}^{N}\left|\gamma_{\pm,\mathrm{cal}}(j)-\gamma_{\pm,\mathrm{exp}}(j)\right|/\gamma_{\pm,\mathrm{exp}}(j)$,

where, N is the number of experimental data points.

Table 2

MSA-NRTL model parameters for a number of single electrolyte solutions and AARD (%) of its predictions for osmotic and activity coefficients at T=298.15 K and P=0.1 MPa.

Electrolyte	**max m (mol.kg^{-1})**	$\tau^{1}_{WC,AC}$	$\tau^{2}_{WC,AC}$	$\tau_{C,W}$	$\tau_{A,W}$	**σ (Å)**	**AARD$_\Phi$ (%)**[a]	**AARD$_{\gamma\pm}$ (%)**[b]
LiBr	17	13.76	-2.383	14.12	-6.792	7.999	7.804	20.97
LiCl	20	11.186	0	-5.477	-5.465	10.00	8.196	18.16
LiOH	4.0	3.775	-0.086	-1.669	-3.162	1.147	0.071	0.051
$LiNO_3$	20	15.18	-4.791	-5.469	-5.057	4.45	0.939	38.03
$LiCH_3SO_3$	5.5	9.209	0	-4.254	-4.953	5.136	0.253	0.244
$HClO_4$	16	11.20	0	-5.526	-5.538	9.999	9.550	20.32
HNO_3	28	9.560	-0.039	-4.731	-4.729	9.999	1.757	2.495
CsBr	5.0	6.380	0	-4.952	-2.393	3.639	0.613	0.248
CsCl	9.0	9.304	-0.400	-4.386	-4.391	4.171	0.534	0.480
RbCl	7.8	8.200	0	-0.100	-4.973	4.031	0.252	0.315
$RbNO_3$	4.5	7.313	0	-1.685	-3.681	3.096	0.256	0.389
KCl	5.0	8.780	0	-3.195	-4.777	4.545	0.819	0.272
KF	17.5	10.19	-0.039	-4.935	-4.900	9.999	4.134	6.329
KOH	20	11.01	-0.003	-5.375	-5.364	9.999	7.704	16.10
$NaClO_4$	6.0	8.029	0	-4.478	-3.893	5.309	0.265	0.272
$NaCF_3SO_3$	5.4	8.048	0	-3.263	-4.626	5.688	0.348	0.147
NaSCN	18	9.850	0	-4.908	-4.823	9.999	2.427	3.537
Me_4NBr	5.5	5.490	0.576	-1.203	-3.377	2.408	0.604	0.776
Me_4NCl	19	9.604	0	-4.734	-4.598	5.543	2.505	3.264
Et_4NBr	12	5.874	0.520	-3.489	-2.729	3.027	1.551	1.612
Et_4NCl	9.0	10.346	-0.003	-4.992	-4.997	5.559	1.998	3.561
Pr_4NBr	9.0	4.361	0.132	-4.237	-0.613	4.000	1.789	2.081
Pr_4NCl	18	6.518	0	-6.139	-2.232	1.551	3.460	2.843
Bu_4NBr	10	5.109	0.347	-2.224	-2.224	3.241	3.155	3.155
NH_3MeCl	20	5.705	0	-4.961	-2.068	3.506	1.387	0.332
NH_3MeNO_3	9.5	5.829	0	-4.202	-2.235	4.158	1.294	0.343
$NH_2Me_2ClO_4$	7.5	7.200	0	-2.421	-3.598	2.817	0.664	2.512
NH_4SCN	23.5	6.178	0	-4.424	-2.486	7.117	0.701	0.904
Average							2.322	5.347

[a] $\mathrm{AARD}_{\phi} = (100/N)\sum_{j=1}^{N}\left|\phi_{\mathrm{cal}}(j)-\phi_{\exp}(j)\right|/\phi_{\exp}(j)$, [b] $\mathrm{AARD}_{\gamma_\pm} = (100/N)\Sigma_{j=1}^{N}\left|\gamma_{\pm,\mathrm{cal}}(j)-\gamma_{\pm,\exp}(j)\right|/\gamma_{\pm,\exp}(j)$,

where, N is the number of experimental data points.

Table 3

AMSA-NRTL model parameters for a number of single electrolyte solutions and AARD (%) of its predictions for osmotic and activity coefficients at T=298.15 K and P=0.1 MPa.

Electrolyte	**max m (mol.kg^{-1})**	$\tau_{WC,AC}$	$\tau_{CA,W}$	**σ (Å)**	h	κ **(L.mol^{-1})**	**AARD$_{\Phi}$ (%)**[a]	**AARD$_{\gamma\pm}$ (%)**[b]
LiBr	17	0.001	-1.595	3.310	3.012	0	1.363	3.743
LiCl	20	0.601	-1.469	3.886	2.987	0	1.201	2.799
LiOH	4.0	3.144	-1.960	1.491	2.000	0.071	0.347	0.206
$LiNO_3$	20	0.558	-1.332	4.723	1.875	0.0002	0.348	0.165
$LiCH_3SO_3$	5.5	3.129	-1.777	5.163	4.398	0.013	0.217	0.275
$HClO_4$	16	0.382	-1.567	3.810	3.468	0	1.224	2.708
HNO_3	28	3.391	-1.715	5.772	5.160	0.028	0.390	0.570
CsBr	5.0	5.506	-2.666	3.902	2.670	0.208	0.098	0.105
CsCl	9.0	0.214	-0.274	2.831	2.124	0	1.581	0.691
RbCl	7.8	0.527	-0.013	3.705	3.207	0.072	0.149	0.133
$RbNO_3$	4.5	4.659	-1.793	3.942	1.882	0.279	0.192	0.137
KCl	5.0	0.527	-0.010	4.106	2.981	0.021	0.771	0.194
KF	17.5	0.257	-0.715	3.802	2.660	0.001	0.361	0.501
KOH	20	0.169	-1.463	3.248	2.489	0	0.525	1.216
$NaClO_4$	6.0	0.669	-0.010	4.712	3.301	0.019	0.277	0.138
$NaCF_3SO_3$	5.4	0.118	-0.820	6.693	3.266	0.040	0.299	0.403
NaSCN	18	0.541	-0.728	5.391	3.011	0.002	0.439	0.503
Me_4NBr	5.5	5.455	-2.331	4.973	7.857	1.000	0.565	0.750
Me_4NCl	19	0.875	-0.806	2.016	2.570	0.004	2.634	1.150
Et_4NBr	12	6.184	-2.797	2.481	2.611	0.068	1.782	1.555
Et_4NCl	9.0	0.198	-0.010	1.774	4.991	0.007	2.652	0.941
Pr_4NBr	9.0	7.017	-2.978	4.700	11.34	1.224	1.355	1.235
Pr_4NCl	18	2.583	-1.999	1.043	3.163	0.002	3.582	3.598
Bu_4NBr	10	5.610	-2.040	8.00	2.160	2.710	3.540	1.170
NH_3MeCl	20	0.803	-0.541	3.309	2.901	0.089	0.340	0.238
NH_3MeNO_3	9.5	1.043	-0.010	4.611	1.369	0.316	0.293	0.244
$NH_2Me_2ClO_4$	7.5	4.085	-1.603	4.771	1.129	0.752	0.347	0.359
NH_4SCN	23.5	0.510	-0.010	6.186	2.453	0.169	0.976	0.653
Average							0.997	0.942

[a] $\mathrm{AARD}_{\phi} = (100/N)\sum_{j=1}^{N}\left|\phi_{\mathrm{cal}}(j)-\phi_{\mathrm{exp}}(j)\right|/\phi_{\mathrm{exp}}(j)$, [b] $\mathrm{AARD}_{\gamma_\pm} = (100/N)\sum_{j=1}^{N}\left|\gamma_{\pm,\mathrm{cal}}(j)-\gamma_{\pm,\mathrm{exp}}(j)\right|/\gamma_{\pm,\mathrm{exp}}(j)$,

where, N is the number of experimental data points.

Table 4

BiMSA model parameters for a number of single electrolyte solutions and AARD (%) of its predictions for osmotic and activity coefficients at T=298.15 K and P=0.1 MPa.

Electrolyte	**Max m (mol.kg^{-1})**	$\sigma_C^{(0)}$ **(Å)**	$\sigma_C^{(1)}$ **(Å.L.mol^{-1})**	β **(L.mol^{-1})**	K **(L.mol^{-1})**	**AARD$_{\Phi}$ (%)^{a}**	**AARD$_{\gamma\pm}$ (%)^{b}**
LiBr	17	4.900	-0.066	0.0001	0.240	0.739	2.301
LiCl	20	4.900	-0.069	0.0001	0.145	1.435	3.306
LiOH	4.0	4.900	-0.104	0.048	1.266	0.236	0.117
$LiNO_3$	20	4.900	-0.074	0.061	0.025	0.504	0.947
$LiCH_3SO_3$	5.5	4.900	-0.266	0.127	0.531	0.574	0.138
$HClO_4$	16	5.100	-0.103	0.060	0.347	0.754	2.407
HNO_3	28	5.100	-0.076	0.110	0.065	1.488	2.652
CsBr	5.0	5.100	-0.032	0.054	0.667	0.336	0.295
CsCl	9.0	3.842	-0.058	0.092	0.852	0.935	0.421
RbCl	7.8	3.561	-0.025	0.036	0.252	0.176	0.182
$RbNO_3$	4.5	3.561	-0.0003	0.112	0.910	0.375	0.352
KCl	5.0	4.700	-0.064	0.102	0.428	0.737	0.097
KF	17.5	4.700	-0.042	0.033	0.237	0.701	1.202
KOH	20	4.700	-0.040	0.003	0.000	0.375	0.740
$NaClO_4$	6.0	3.550	-0.078	0.102	0.217	0.165	0.123
$NaCF_3SO_3$	5.4	3.550	-0.391	0.093	0.196	0.359	0.407
NaSCN	18	5.382	-0.142	0.179	0.439	0.831	1.293
Me_4NBr	5.5	5.470	-0.061	0.150	1.531	0.807	0.877
Me_4NCl	19	5.470	-0.022	0.075	1.124	0.622	0.921
Et_4NBr	12	6.725	-0.050	0.413	2.000	0.778	0.865
Et_4NCl	9.0	6.725	-0.013	0.246	1.193	0.670	1.231
Pr_4NBr	9.0	8.610	-0.328	0.814	3.350	0.960	0.394
Pr_4NCl	18	8.610	-0.286	0.472	2.331	1.187	1.919
Bu_4NBr	10	8.292	-0.364	0.677	2.722	4.163	2.429
NH_3MeCl	20	4.530	-0.084	0.039	0.594	0.825	0.261
NH_3MeNO_3	9.5	3.903	-0.030	0.069	0.326	0.422	0.410
$NH_2Me_2ClO_4$	7.5	3.611	-0.052	0.102	1.072	0.348	0.446
NH_4SCN	23.5	3.455	-0.083	0.092	0.061	1.234	1.722
Average						0.812	1.016

[a] $\mathrm{AARD}_{\phi} = (100/N)\sum_{j=1}^{N}\left|\phi_{\mathrm{cal}}(j)-\phi_{\mathrm{exp}}(j)\right|/\phi_{\mathrm{exp}}(j)$, [b] $\mathrm{AARD}_{\gamma_{\pm}} = (100/N)\Sigma_{j=1}^{N}\left|\gamma_{\pm,\mathrm{cal}}(j)-\gamma_{\pm,\mathrm{exp}}(j)\right|/\gamma_{\pm,\mathrm{exp}}(j)$,

where, N is the number of experimental data points.

The results shown in Tables 1 to 4 reveal that the consideration of ion pairing increases the accuracy of the model, especially at higher concentrations of salt. The accuracy of the four models for the prediction of mean activity coefficients of KOH and Me_4NCl single salt aqueous solutions are compared versus experimental data in Figures 2 and 3 respectively. As shown in these figures, the accuracy of e-NRTL and MSA-NRTL models considerably decreases at higher concentrations of salt solutions.

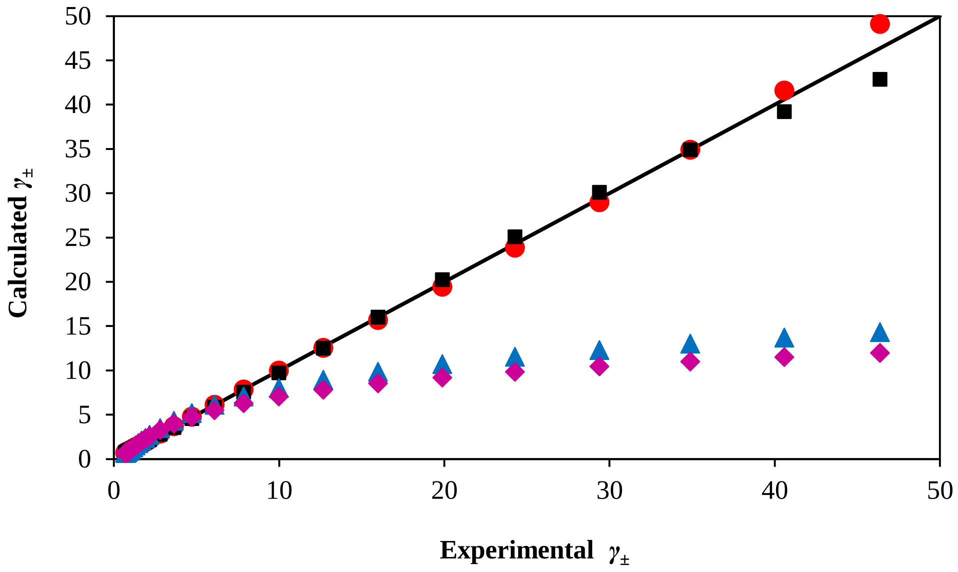

Figure 2

Mean activity coefficients (γ±) calculated for aqueous KOH solution using the (♦) e-NRTL, (▲) MSA-NRTL, (■) AMSA-NRTL, and (●) BiMSA models; the experimental values are from Hamer and Wu, (1972) and Lindenbaum and Boyd (1964).

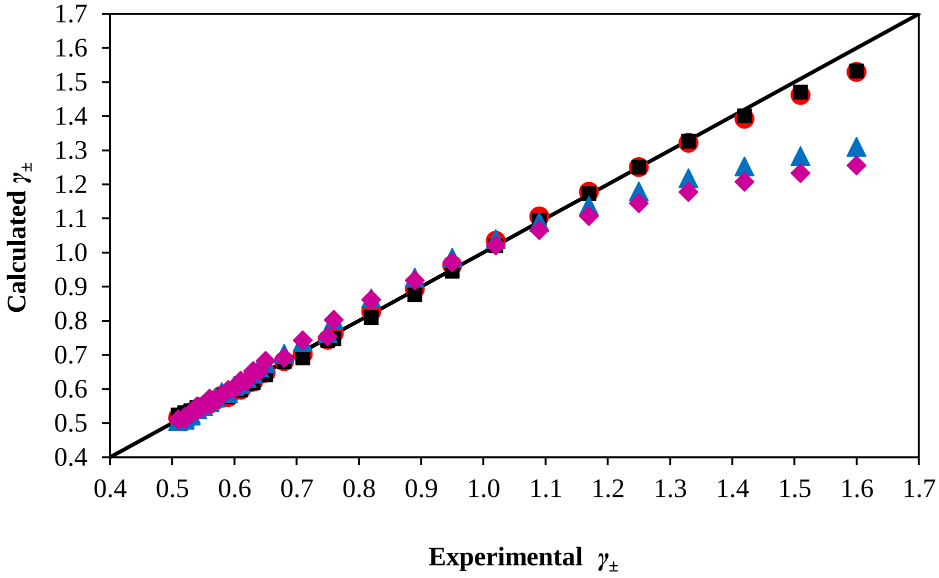

Figure 3

Mean activity coefficients (γ±) calculated for aqueous Me_4NCl solution using the (♦) e-NRTL, (▲) MSA-NRTL, (■) AMSA-NRTL, and (●) BiMSA models; the experimental values are from Hamer and Wu (1972) and Lindenbaum and Boyd (1964).

In order to demonstrate the capability of AMSA-NRTL model to predict the thermodynamic properties of electrolyte solutions, salting out effect of Bu_4NBr in a CO_2+water system is considered in this work. As discussed by Lin et al. (2008), the solubility of carbon dioxide in the presence of Bu_4NBr drops. This salting out effect is shown in Figure 4. The interaction parameters between CO_2 and water for these predictions are taken from Hou et al. (2013). The solubility data of carbon dioxide in pure water is predicted by Peng-Robinson equation of state (Melhem et al., 1989), and for the solution with a mass fraction of 0.09 Bu_4NB, solubility is predicted using AMSA-NRTL model. It is observed that the model results are in satisfactory agreement with the experimental data.

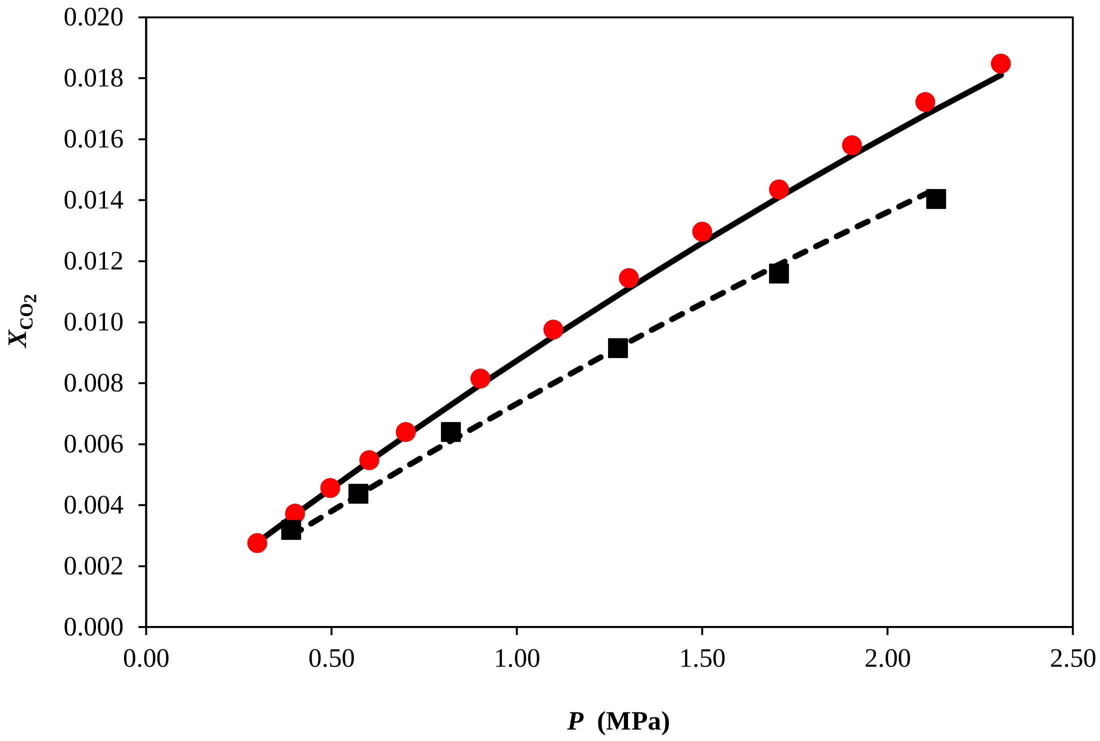

Figure 4

Carbon dioxide solubility versus pressure at a temperature of 283.15 K; symbols represent experimental data from literature: (●), pure water (Houghton et al., 1957); (■), 0.09 mass fraction Bu_4NBr (Lin et al., 2008); solid line (──) shows PR-EOS prediction for pure water, and dash line (----) denotes AMSA-NRTL model predictions for the electrolyte solution.

BiMSA is a model based on the Wertheim formalism theory (Wertheim, 1988, 1987) with considering ion pairing of unlike hydrated ions and chemical association. The capability of this model to predict the osmotic and activity coefficients of different aqueous salt solutions is reported in Table 4, and it is plotted in Figure 5 for some cases. Four adjustable parameters of this model, including $\sigma_C^{(0)}$, $\sigma_C^{(1)}$, β, and K are fitted using activity coefficients data found in literature for these solutions. The values obtained for these parameters in this work are very close to the values reported in the literature (Marcus, 2008; Wright, 2007). The positive value found for β is in accordance with the observation that solution permittivity decreases by increasing salt concentration. The results show that, among the four investigated models in this study, the BiMSA model can predict the osmotic and activity coefficients of different aqueous salt solutions better than the others.

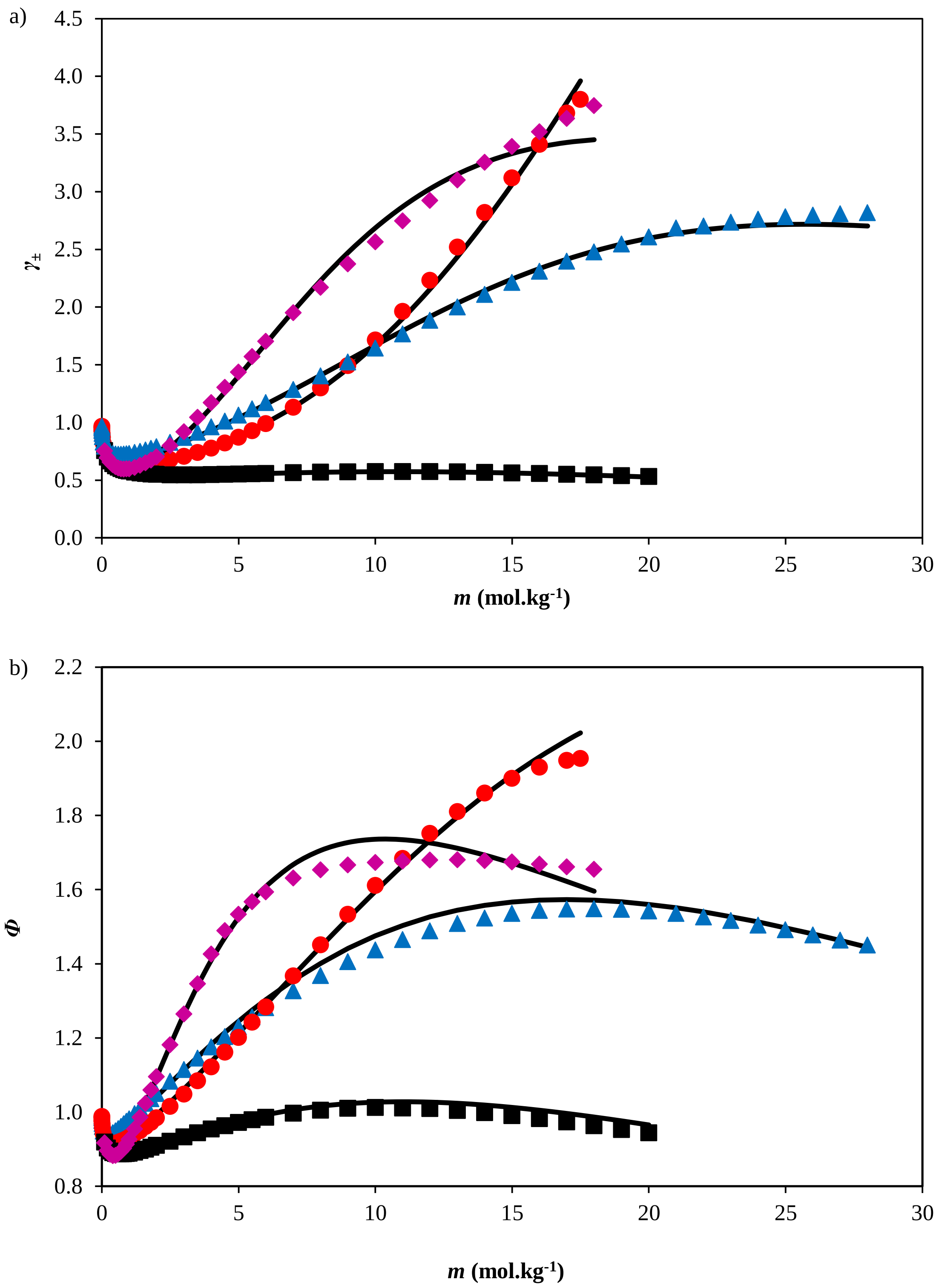

Figure 5

Predictions of the BiMSA model for (a) mean activity coefficient and (b) osmotic coefficient at a temperature of 298.15 K as a function of concentration; symbols represent experimental data: (●), KF(Hamer and Wu, 1972); (■), NH_3MeCl (Macaskill and Bates, 1986); (♦), Pr_4NBr (Lindenbaum and Boyd, 1964); (▲), HNO_3 (Hamer and Wu, 1972); solid line (—), model prediction.

4. Conclusions

Electrolyte models are widely used for modelling or predicting the thermodynamic behavior of chemical mixtures. In this work, the ability of four electrolyte models, including e-NRTL, MSA-NRTL, AMSA-NRTL, and BiMSA to predict the properties of different aqueous electrolyte solutions in a wide range of concentrations is comprehensively evaluated. Literature data for osmotic and activity coefficients of different solutions are used for these evaluations. The results indicate that models which do not consider association between ions present in the solution have relatively large errors, especially at higher concentrations of dissolved salt. The results also denote that both AMSA-NRTL and BiMSA models can accurately predict the experimental data of osmotic and activity coefficients of different electrolyte solutions. However, the BiMSA model, in comparison to the AMSA-NRTL model, requires lower number of adjustable parameters, and its parameters have physical meaning. Therefore, it can be concluded that among the four electrolyte models investigated for the prediction of 28 systems in this work, the BiMSA model presents the best performance. The average values of AARD (%) of the BiMSA model in the prediction of osmotic and activity coefficients of different systems investigated in this work are 0.856 and 1.016 respectively. For a further progress, it is recommended that the MSA terms be modified to the unrestricted primitive model, which leads to a more precise description of salt effects at low concentrations. Finally, the introduction of a hard sphere term could take the missing effect into account.

Nomenclature

A : Anion
C : Cation
K : Equilibrium constant
K_B : Boltzmann constant
N : Number of data
P : Ion-pair assuming as neutral species
P : Pressure
S : Salt
T : Temperature
x : Unbound ion fraction

Greek Letter

α : Non-randomness factor
β : Concentration dependent parameter of permittivity
ε : Relative permittivity
ϕ : Osmotic coefficient
$\gamma_{\pm}$: Mean ionic activity coefficient in the molality scale
σ : Ionic diameter
τ : Dimensionless interaction energy parameter
v : Stoichiometric number

Subscript and Superscript

A : Anion
aq : Aqueous phase
C : Cation
i : Component *i*

P	: Molecular species
W	: Water
Z	: Ion charge

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