

## **Chapter 5**

# **Comparison of Activity Coefficients Models for Atmospheric Aerosols Containing Mixtures of Electrolytes, Organics, and Water\***

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## 5.1 Abstract

Atmospheric aerosols generally comprise a mixture of electrolytes, organic compounds, and water. Determining the gas-particle distribution of volatile compounds, including water, requires equilibrium or mass transfer calculations, at the heart of which are models for the activity coefficients of the particle-phase components. We evaluate here the performance of four recent activity coefficient models developed for electrolyte/organic/water mixtures typical of atmospheric aerosols. Two of the models, the CSB model [J. Aerosol Sci. 32 (2001) 713-738] and the ADDEM model [Atmos. Chem. Phys. 5 (2005) 1223-1242] treat ion-water and organic-water interactions but do not include ion-organic interactions; these can be referred to as "decoupled" models. The other two models, Ming and Russell [AIChE J. 48 (2002), 1331-1348] and X-UNIFAC.3 [Atmos. Environ. 40 (2006) 6437-6452], include ion-organic interactions; these are referred to as "coupled" models. We address the question - Does the inclusion of a treatment of ion-organic interactions substantially improve the performance of the coupled models over that of the decoupled models? Performance is judged by the extent to which each model is able to reproduce experimental water activity data for mixtures of organic acids (malonic, succinic, glutaric, citric, maleic, and malic acids) and inorganic electrolytes (NaCl and  $(\text{NH}_4)_2\text{SO}_4$ ). It is found, based on the comparisons reported here, that the decoupled models perform as well as, and in some cases better than, the coupled models. Since such activity coefficient models are likely to continue to be developed in the future and because we consider here only a limited set of organic compounds, the current study should be viewed as an interim assessment. The scarcity of experimental

data for mixtures of atmospheric relevance remains a limitation for testing activity coefficient models.

## 5.2 Introduction

Atmospheric aerosols generally contain both inorganic components, such as sulfate, nitrate, and ammonium, and an organic fraction comprising a wide range of organic compounds of diverse physical and chemical properties. Water and volatile species are distributed between the gas and aerosol phases, governed by gas-particle (G/P) thermodynamic equilibrium. G/P partitioning of any individual organic compound to the aerosol phase is governed by its vapor pressure and its liquid-phase activity coefficient. An aerosol phase equilibrium calculation requires also activity coefficients. The phase equilibrium calculation determines whether the aerosol phase is a liquid, solid, or a mixture of solid and liquid phases; it also determines the quantities of the constituent species distributed among the various phases. Some organic/water mixtures exhibit phase separation which can be either initiated or modified by the presence of electrolytes (or indeed other organic compounds).

The fundamental difference from a theoretical point of view is between ions and uncharged molecules. The development of models reflects this: electrolyte models are based upon a single solvent, water, which is the medium in which the ions exist. In dilute solutions ion interactions with the solvent, with its particular dielectric constant and other properties, determine solvent and solute activity coefficients. Models for uncharged species, including water, start with the assumption of a liquid mixture in which no single component is the solvent. The challenge in modeling systems containing water, electrolytes, and organic compounds is twofold: (1) there is no satisfactory model for such mixtures; and (2) there are insufficient data to constrain a model, as compared, say, to models of electrolyte mixtures. The models that do exist work only over limited ranges

of composition and concentration. This is a difficulty in atmospheric applications in which a wide range in relative humidity (hence liquid-phase concentration) exists, and a model is desired that is at least as accurate as those for ions + water and organic + water.

Current atmospheric models that represent aerosols as consisting of mixtures of organic compounds, electrolytes, and water generally assume that two liquid phases exist, one of which is relatively polar (containing mostly water and electrolytes) and the other mostly organic (containing primarily non-electrolytes) (see, for example, Griffin et al., 2003; Pun et al., 2002). Existing activity coefficient methods are applied to the separate phases.

Considerable effort has been devoted to developing activity coefficient models for mixed inorganic-organic water systems (Clegg et al. 2001, 2003; Clegg and Seinfeld, 2004, 2006a, b; Erdakos et al., 2006; Ming and Russell, 2002; Raatikainen and Laaksonen, 2005; Topping et al., 2005b). As noted above, experimental data for mixed electrolyte-organic-water systems of atmospheric interest are generally lacking. The inorganic fraction in atmospheric aerosol usually comprises a relatively small number of key ions, such as ammonium, nitrate, sulfate; sodium and chloride ions may be present as well. The organic fraction, however, is composed of a large variety of organic compounds (Hemming and Seinfeld, 2001). For example, dicarboxylic acids are ubiquitous among atmospheric organic compounds (e.g. Kawamura et al., 1996; Kawamura and Sakaguchi, 1999). Limited experimental data exist for mixed dicarboxylic acids and electrolyte solutions (Choi and Chan, 2002b; Lightstone et al., 2000; Marcolli et al., 2004). Also as noted above, a generally accepted thermodynamic model for aqueous solutions containing both ions and organic solutes at high concentrations is

lacking. Certain models for calculating activity coefficients in mixed organic-electrolyte solutions use only binary solution data (e.g. Clegg et al., 2001; Topping et al., 2005). Predictions could theoretically be improved if ion-organic interactions are represented explicitly (e.g. Erdakos et al., 2006; Ming and Russell, 2002).

In the present study we select four recent thermodynamic models for organic/electrolyte/water systems and evaluate their performance against experimental water activity data for a variety of solutions. In two of the models contributions of ion-ion interactions (the electrolyte term) and organic-water interactions (the non-electrolyte term) are treated independently, and in two of the models ion-organic interactions are explicitly accounted for. The essential question we address is – For these current classes of models, does explicit inclusion of ion-organic interactions improve predictive performance versus that in models that do not include these interactions? To address this question we consider experimental water activity data for electrolyte solutions, organic acid solutions, and mixed organic acid-electrolyte solutions.

In Section 2 we briefly introduce the four activity coefficient models. Section 3 contains detailed comparisons of predictions and experimental data for a number of organic-electrolyte systems. We draw general conclusions from the comparison in Section 4. The Appendix contains a more complete exposition of the theoretical basis of the models considered.

### **5.3 Activity Coefficient Models**

The aerosol inorganic model (AIM) (Clegg et al., 1998a, b), based on the Pitzer-Simonson-Clegg (PSC) model, contains among the most comprehensive aerosol inorganic chemistry and thermodynamics; AIM thus serves as benchmark for inorganic

activity predictions (see Appendix 5.7.1). A general, and widely-used, predictive thermodynamic model for organic liquid mixtures is UNIFAC (Fredenslund et al., 1977). Based on a group contribution method, UNIFAC has been widely used for liquid mixtures of non-electrolytes, including organic compounds and water, and has proven useful for modeling the formation of organic particular matter (OPM) phases (Pankow et al., 2001; Seinfeld et al., 2001), and hygroscopic growth of OPM (Peng et al., 2001). Activity coefficient models for organic/inorganic/water mixtures use, in some measure, both of these models (Table 5.1).

**Table 5.1: Summary of four activity coefficient models for mixtures of inorganic salts, organic compounds, and water**

Reference	Type of method	Comments
CSB Model	Ion-water (AIM), organic water, and ion-organic (Pitzer molality-based model) interactions are treated separately	<ol style="list-style-type: none"> <li>1. Concentrations of organic species in a mixture should be low enough that water is considered as the solvent.</li> <li>2. Organic-water interactions for seven dicarboxylic acids can be treated using explicit correlations (Clegg and Seinfeld, 2006a), while UNIFAC can be used for other organics.</li> <li>3. The Pitzer ion-organic mixing terms can assume unreasonable values in concentrated solutions. Similar to the study by Clegg and Seinfeld (2006a), they are set to zero here.</li> <li>4. Organic solute ion dissociation can be included (Clegg and Seinfeld, 2006b)</li> </ol>
X-UNIFAC.3	Debye-Hückel theory (long-range), second virial coefficient expression (mid-range), and UNIFAC equation (short-range)	<ol style="list-style-type: none"> <li>1. Organic-ion interaction parameters are taken from Raatikainen and Laaksonen (2005).</li> </ol>
Ming and Russell model	Ion-water (AIM), organic-water/organic-ion (UNIFAC) interactions are treated separately	<ol style="list-style-type: none"> <li>1. Concentrations of organic species in a mixture should be low enough that water is considered the solvent.</li> <li>2. Organic-ion interaction parameters are re-fitted with experimental data (Raatikainen and Laaksonen, 2005).</li> <li>3. Normalization term for the inorganic-only mole fraction used in the inorganic-water contribution was dropped in the modified model.</li> </ol>
ADDEM	Ion-water (AIM), organic-water/organic-ion (UNIFAC) interactions are treated separately. Organic-ion interactions are not included.	<ol style="list-style-type: none"> <li>1. Water associated with each separate fraction is determined by ZSR relationship.</li> <li>2. Concentrations of organic species in a mixture should be low enough that water is considered the solvent.</li> <li>3. Organic-water interactions are treated using UNIFAC with updated parameters by Peng et al. (2001)</li> </ol>

### 5.3.1 CSB Model

The activity coefficient model proposed by Clegg et al. (2001) (hereafter termed the CSB model) treats organic-water and ion-water interactions separately. Additional terms, which are proportional to ion and organic compound molalities, can be included to describe organic-ion interactions; organic-water, ion-water and organic-ion interactions are combined within a self-consistent framework. In the CSB approach, the molal activity coefficient for each component  $j$  is given by,

$$\ln \gamma_j = \ln \gamma_j^{IW/Ow} + \ln \gamma_j^{IO} \quad (5.1)$$

where the  $\ln \gamma^{IW}$  term represents the ion-water contribution if component  $j$  is an ion, and  $\ln \gamma^{Ow}$  is the organic-water interaction if component  $j$  is an organic solute. The ion-water interaction for the electrolytes ( $\ln \gamma^{IW}$ ) is calculated using AIM, while the organic-water interaction of the organic solution ( $\ln \gamma^{Ow}$ ) is calculated employing UNIFAC.

Interactions between the electrolytes and organics ( $\ln \gamma^{IO}$ ) are accounted for by additional terms derived from the Pitzer molality-based model (see Appendix 5.7.2). Experimental data are required to determine the mixture parameters, which are unavailable for many systems. If the mixture parameters are available, the Pitzer equations are well validated for solutions at low to moderate concentrations. Predictions tend to degrade as solutions become more concentrated. The reason for this is that the expressions are formulated in terms of molality and can therefore attain extremely high values in systems containing little water. For the systems studied in this work, mixture parameters are not available and are set to zero, as in the study of Clegg and Seinfeld (2006a). Dissociation equilibria of the organics are not treated in the version of the CSB model used here, but the treatment of dissociation equilibria is explored in another study

by Clegg and Seinfeld (2006b).

### 5.3.2 X-UNIFAC.3

A recently developed activity coefficient model, termed X-UNIFAC.3, is based on an extension of the UNIFAC concept (Erdakos et al., 2006). For X-UNIFAC.3, energetic interactions in organic + inorganic + water solutions can be considered to involve long-, mid-, and short-range effects,

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{MR} + \ln \gamma_i^{SR} \quad (5.2)$$

The long-range (LR) effect, describing long-range electrostatic interactions of ions, is based on the Debye-Hückel theory. The short-range (SR) effect term is represented by the traditional UNIFAC equations, for which the UNIFAC terms are extended to include ions. The mid-range (MR) term is described by a second virial coefficient expression (Appendix A.4). The SR term accounts for the short-range contribution resulting from molecule/molecule, molecule/ion, and ion/ion interactions. The MR term accounts for ionic interactions (e.g. ion/ion and ion/molecule) that are not included in the long-range term. As compared to the CSB model, X-UNIFAC.3 is a more integrated model for which ion-organic interactions are represented in both the MR and SR terms.

Extended UNIFAC models can be problematic in modeling aqueous aerosols for which phase separation may occur, owing to errors introduced by the use of independent reference states between different components in the liquid phase. The X-UNIFAC.3 model (Erdakos et al., 2006) addresses this problem by adopting the reference state and concentration unit assignments of Wang et al. (2002). Each multiphase component has the same reference state in each solution phase.

### 5.3.3 Ming and Russell Model

In the thermodynamic model developed by Ming and Russell (2002), the activity coefficients are calculated as a sum of ion-water interactions and organic-water/organic-ion interactions, as shown in equation (5.1). Ion-water interactions ( $\ln \gamma^{IW}$ ) are calculated using AIM (Clegg et al., 1998a, b) and organic-water/organic-ion interactions ( $\ln \gamma^{OW/OI}$ ) are calculated with UNIFAC.

UNIFAC surface area and volume parameters for the ions are taken to be the same as those for water, and all ion-water and ion-ion interaction parameters are set equal to zero. As a result, in solely aqueous electrolyte solutions, the  $\ln \gamma^{OW/OI}$  contribution is zero, and the Ming and Russell model reduces to AIM. Organic-water parameters for the non-electrolytes are the same as those in the original UNIFAC (Hansen et al., 1991). Raatikainen and Laaksonen (2005) refitted the organic-ion parameters and organic group-group ( $\text{CH}_n$ ,  $\text{COOH}$ ,  $\text{OH}$ , and  $\text{H}_2\text{O}$ ) interaction parameters of the Ming and Russell model for binary aqueous solutions of dicarboxylic and hydroxy-carboxylic acids; in the present study we employ the Ming and Russell model with these updated parameters.

In the original Ming and Russell model, inorganic-only mole fractions are used to calculate the ion-water contributions, the ion-water activity coefficients ( $\ln \gamma^{IW}$ ) were then normalized to the solution mole fractions. In the original reference (Ming and Russell, 2002), there is a typographical error in the normalization term (Equations 20 and

21 in Ming and Russell, 2002); the corrected equations are  $\ln \gamma_i^{LR} = \ln \gamma_i^{LR*} / \left(1 - \sum_o x_o\right)$

and  $\ln \gamma_i^{SR} = \ln \gamma_i^{SR*} / \left(1 - \sum_o x_o\right)$ , where  $\ln \gamma_i^{LR}$  and  $\ln \gamma_i^{SR}$  are the electrolyte-water

contributions to  $\ln \gamma^{IW}$  for ions. Specific expression for  $\gamma_i^{LR}$  and  $\gamma_i^{SR}$  are given in Clegg et

al. (1992). With the correct normalization terms, the Ming and Russell model is self-consistent and reduces to UNIFAC in the absence of electrolytes.

Raatikainen and Laaksonen (2005) noticed the inconsistency owing to the typographical error and concluded that the normalization term should be ignored. As a result, in the version of the Ming and Russell model modified by Raatikainen and Laaksonen (2005), all mole fractions in  $\ln \gamma^{IW}$  are inorganic-only mole fractions. In the current work, the version of the Ming and Russell model as modified by Raatikainen and Laaksonen (2005) is used; the term “Ming and Russell model” refers to the modified version.

#### **5.3.4 Aerosol Diameter Dependent Equilibrium Model (ADDEM)**

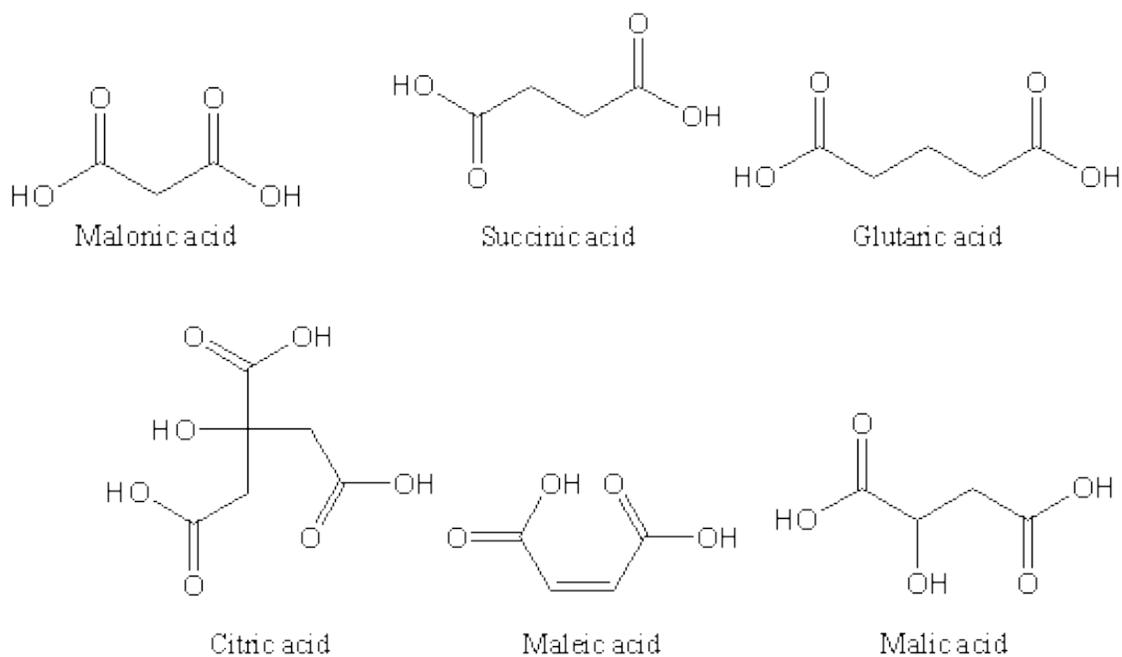
In the Aerosol Diameter Dependent Equilibrium Model (ADDEM) (Topping et al., 2005), two separate activity coefficient models are used additively for treating organic-electrolyte-water systems; thus, the inorganic and organic fractions are assumed to behave independently (see equation (5.1)). For the inorganic fraction ( $\ln \gamma_j^{IW}$ ), AIM (Clegg et al., 1998a, b) is employed to determine the solute activity. For the organic module ( $\ln \gamma_j^{OW}$ ), UNIFAC is used, with the revised interaction parameters (Peng et al., 2001). The interactions between the inorganic and organic components are neglected i.e. there is no  $\ln \gamma_j^{IO}$  term. In ADDEM the detailed activity models are used to calculate the water associated with both the inorganic and organic fractions. Water contents in the inorganic and organic fractions are coupled by using the Zdanovskii-Stokes-Robinson (ZSR) relationship (Stokes and Robinson, 1966), See, in addition, Chan et al. (2000), Choi and Chan (2002b), Ha et al. (2000) .

## 5.4 Comparison with experimental data

In this section the performance of the four thermodynamic models is examined by comparing calculated and measured water activities of various electrolyte and organic systems (Table 5.2). For water activity calculations in the present work, the total water content of the solution is prescribed from the experimental data. We focus on dicarboxylic and hydroxy-carboxylic acids because of their prevalence in the atmosphere and because they serve as surrogates for more complex aerosol organic compounds. Molecular structures for the organic species considered are shown in Figure 5.1. For all water activity calculations, the organic acids are treated as nondissociating solutes, and a single liquid phase is assumed with no solid phases present. All calculations are performed at atmospheric pressure (1 atm) and at 298 K; the 2 – 3 degree temperature range over that for the calculated water activities and those at which the measurements were carried out is considered negligible (Table 5.2).

Experimental data, see Table 5.2, include bulk solution and electrodynamic balance (edb) water activity measurements. These edb measurements provide supersaturated solution data for aqueous mixtures of dicarboxylic acids (Choi and Chan, 2002a; Peng et al., 2001) and aqueous solutions of dicarboxylic acids and single salts (Choi and Chan, 2002b). Water cycle (growth and evaporation) measurements are taken by varying the relative humidity (RH) in the edb chamber in discrete steps (Peng et al., 2001), or using a “scanning” edb technique (Choi and Chan, 2002b). Solute concentrations are determined indirectly from the balancing dc voltage, and they are standardised relative to the bulk solution water activity measurements. Clegg and Seinfeld (2006a) restandardised the data for some systems to obtain a closer match

between osmotic coefficients and bulk solution measurements. In this study the edb data, tabulated by Clegg and Seinfeld (2006a), for supersaturated aqueous solution droplets are used.



**Figure 5.1: Molecular structures of the organic species used in the present study**

**Table 5.2: Organics/water and electrolyte/organic/water systems studied in the present work.**

System	Experimental Temperature (K)	Reference <sup>a</sup>
<i>Organic acid + Water</i>		
Malonic acid	298	(Peng et al., 2001)
Succinic acid	298	(Peng et al., 2001)
Glutaric acid	298	(Peng et al., 2001)
Malic acid	298	(Peng et al., 2001)
Maleic acid	298	(Peng et al., 2001)
Citric acid	298	(Peng et al., 2001)
<i>Organic acid 1 + Organic acid 2 + Water</i>		
Malonic acid + Glutaric acid (1:1 mole ratio)	295 – 296	(Choi and Chan, 2002a)
Malic acid + Maleic acid (1:1 mole ratio)	295 – 295.7	(Choi and Chan, 2002a)
<i>Organic acid + Salt + Water</i>		
Malonic acid + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b)
Malonic acid + NaCl (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b)
Succinic acid + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b)
Succinic acid + NaCl (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b)
Glutaric acid + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b)
Glutaric acid + NaCl (1:1 mass ratio)	293 – 295	(Choi and Chan, 2002b)
Citric acid + NaCl (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b) <sup>b</sup>
Citric acid + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1:1 mole ratio)	293 – 295	(Choi and Chan, 2002b) <sup>b</sup>
<i>M5 (Malic + malonic + maleic + glutaric + methyl succinic) acids + salt + water</i>		
M5 acids + NaCl	298	(Marcolli et al., 2004)
M5 acids + (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	298	(Marcolli et al., 2004)

a. Most experimental data of the listed references have been tabulated by Clegg and Seinfeld (2006a, b) and are available at <http://www.aim.env.uea.ac.uk/aim/aim.htm>. The tabulated data are used in the present study.

b. Original experimental data for citric acid solutions by Peng et al. (2001) and Choi and Chan (2002a, b) are used. Data are available at <http://ihome.ust.hk/~keckchan/hygroscopic.html>.

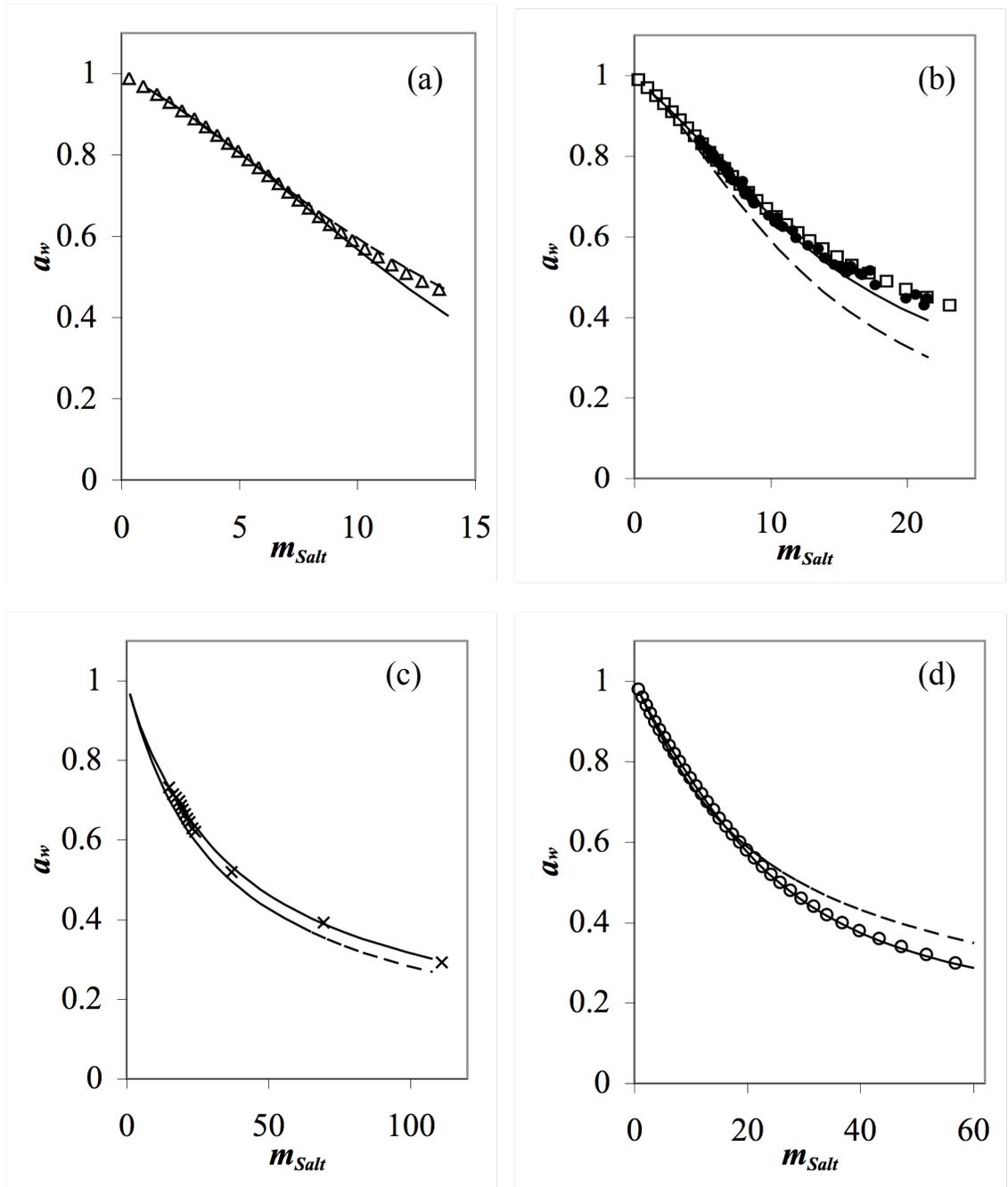
### 5.4.1 Aqueous electrolyte solutions

Predictions of X-UNIFAC.3 and AIM are compared for single aqueous electrolyte solutions of NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NaNO}_3$  (Figure 5.2). AIM is the inorganic thermodynamic model in three of the four models (CSB, Ming and Russell, and ADDEM models) for representing ion-water interactions. Clegg et al. (1998a) determined the model parameters in AIM using extensive experimental data for the system  $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$  at 298 K, and it is confirmed that the model can be used to predict the phase equilibria with satisfactory accuracy. In particular, single salt solution data are well represented by the model. (Differences between experimental data and the fitted values of AIM are shown in Figures 4, 5, 8 and 9 in Clegg et al. (1998a) for aqueous solutions of NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NaNO}_3$ ).

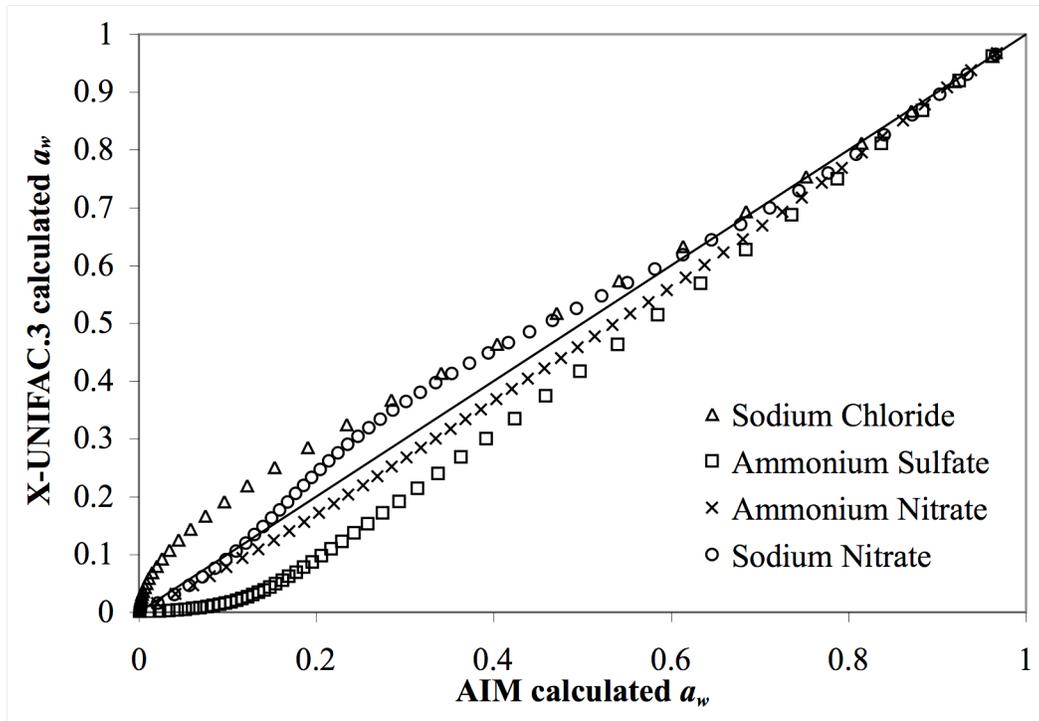
Literature data, as shown in Figures 5.2a, b, and d, are obtained from the fitted equations by Tang (1997). Tang and co-workers (Tang et al., 1986; Tang and Munkelwitz, 1994; Tang, 1997) reported water activities at 298 K for various single salt solutions, including NaCl,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{NaNO}_3$ , and they fitted the results with a polynomial expression in either molality or solute weight percent. The fitted equations are shown to reproduce the experimental data with excellent accuracy (for example, see Figures 3 and 8 in Tang and Munkelwitz, 1994). For  $\text{NH}_4\text{NO}_3$  aqueous solutions, experimental measurements from Lightstone et al. (2000) are shown for comparison (Figure 5.2c). Figure 5.2 shows water activities as a function of salt molality for NaCl,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NaNO}_3$  solutions over the concentration range valid for the fitted equations. For aqueous NaCl and  $\text{NaNO}_3$  solutions, predictions of both AIM and X-UNIFAC.3 are in excellent agreement with the literature data (Figures 5.2a and d). Both

AIM and X-UNIFAC.3 can represent the single  $\text{NH}_4\text{NO}_3$  system with reasonable accuracy (Figure 5.2c, see also Figure 1b in Lightstone et al., 2000); predictions of X-UNIFAC.3 deviate slightly more from the experimental data than those of AIM at low salt concentrations (up to about  $20 \text{ mol kg}^{-1}$ ). For aqueous  $(\text{NH}_4)_2\text{SO}_4$  solutions, predictions of AIM are in better agreement with the literature data than those of X-UNIFAC.3. Experimental measurements by Clegg et al. (1995) are also shown in Figure 5.2b for comparison. Predictions of AIM are in better agreement with the experimental data by Clegg et al. (1995), compared to the literature data from the fitted equations (Tang and Munkelwitz, 1994; Tang, 1997). As noted earlier, AIM is one of the models that can provide accurate predictions for systems containing  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  ions. In Figure 5.3 we benchmark the performance of X-UNIFAC.3 using AIM; comparison between predictions of AIM and those of X-UNIFAC.3 over the entire range of water activities for single-salt  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$  aqueous solutions are shown, with the solid line showing the 1:1 correspondence. Water activities predicted by X-UNIFAC.3 for  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{NaNO}_3$  aqueous solutions agree reasonably with those predicted by AIM at low to moderate electrolyte concentration (corresponding to the water activity range of  $\sim 0.6$  to  $\sim 1.0$ ). As expected, the deviation between AIM and X-UNIFAC.3 generally increases as the solution becomes more concentrated. To represent the thermodynamic properties of electrolyte solutions at high salt concentrations accurately, additional experimental data are required for model parameterization, and refinement of the model equations may be needed, as suggested by Clegg et al. (1998a). As with the Ming and Russell model, X-UNIFAC.3 is limited to single-salt solutions because interaction parameters for different mixtures of cations and

anions were not determined when the model was developed.



**Figure 5.2:** Comparison between the water activities ( $a_w$ ) calculated by AIM (solid lines) and X-UNIFAC.3 (dash lines) as a function of the salt molality for single-salt solutions of (a) NaCl; literature data obtained from the fitted equation of Tang (1997) (triangles) (b)  $(NH_4)_2SO_4$ ; literature data obtained from the fitted equation of Tang (1997) (squares) and Clegg et al. (1995) (dots) (c)  $NH_4NO_3$ ; experimental data obtained from Lightstone et al. (2000) (crosses) (d)  $NaNO_3$ ; literature data are obtained from the fitted equation of Tang (1997) (circles).



**Figure 5.3:** Water activities calculated by X-UNIFAC.3 versus those calculated by AIM. The solid line is the 1:1 correspondence line

#### 5.4.2 Aqueous Dicarboxylic Acids Solutions

In this section, predictions of the different organic modules are compared to experimental water activities. The UNIFAC model is employed to account for organic-water interactions in all four activity coefficient models, although different sets of UNIFAC interaction parameters ( $A_{no}$  and  $A_{on}$ ) may be used. Table 5.3 shows the different sets of UNIFAC parameters used in the electrolyte-organic-water activity coefficient models. The most widely used set of UNIFAC interaction parameters, derived from vapor-liquid equilibrium data, are given as a reference set and are referred to as UNIFAC-VL (Hansen et al., 1991) in Table 5.3. Optimized interaction parameters for

dicarboxylic acids and hydroxy-carboxylic acids by Raatikainen and Laaksonen (2005), denoted by UNIFAC-RL, are used in both X-UNIFAC.3 and the Ming and Russell model. Peng et al. (2001) modified the interaction parameters for functional group pairs COOH-H<sub>2</sub>O, OH-H<sub>2</sub>O, and OH-COOH by fitting the UNIFAC equations to electrodynamic balance data. These parameters, denoted UNIFAC-Peng, are used in the CSB and ADDEM models.

**Table 5.3: UNIFAC energy interaction parameters,  $A_{no}$  and  $A_{on}$ , between the main groups: UNIFAC-VL/UNIFAC-RL/UNIFAC-Peng**

Group	CH <sub>n</sub>	OH	H <sub>2</sub> O	COOH
CH <sub>n</sub>	×	986.5/19.236/ 986.5	1318/170.22/ 1318	663.5/2693.3/ 663.5
OH	156.4/143.48/ 156.4	×	353.5/-1.3932/ 265.97	199.0/238.13/ 224.4
H <sub>2</sub> O	300.0/2650.8/ 300.0	-229.1/-407.5/ -467.4	×	-14.09/271.04/ -69.29
COOH	315.3/-150.91/ 315.3	-151.0/-492.09/ -103.0	-66.17/-437.73/ -145.9	×

In the CSB model, explicit correlation equations (Clegg and Seinfeld, 2006a) are available for aqueous solutions of several dicarboxylic acids (oxalic, malonic, succinic, glutaric, malic, and maleic acid) at 298.15 K. Clegg and Seinfeld (2006a) correlated water and solute activities of aqueous dicarboxylic acid solutions to a set of equations derived from an explicit expression for the excess Gibbs energy function (Brewster and McGlashan, 1973; Marsh, 1978), and these correlations are used in place of UNIFAC-Peng for organic-water interactions for the selected organic acids.

Figure 5.4 shows the calculated water activities for single-solute (malonic, succinic, glutaric, malic, maleic, citric acid) aqueous solutions, and for the aqueous organic acids mixtures (malic + maleic acids and malonic + glutaric acids solutions) using the correlation equations, UNIFAC-RL and UNIFAC-Peng. Model predictions are plotted against the experimental data (Choi and Chan, 2002a; Peng et al., 2001), with the solid line showing the 1:1 correspondence. For the single-solute aqueous systems, the correlation equations are shown to reproduce the experimental data with good agreement (Figures 5.4a – c). Also, predictions of CSB (using the correlation equations) for aqueous malic + maleic acids and malonic + glutaric acids solutions (Figure 5.4d) are slightly more accurate than those of UNIFAC-RL and UNIFAC-Peng (see Table 5.4). This is not an unexpected result, as the equations are directly fitted to the experimental data. Since the UNIFAC-Peng interactions were developed specifically for dicarboxylic and hydroxy-carboxylic acid aqueous solutions, the predictions are in good agreement with the experimental data for both single dicarboxylic acid aqueous solutions and dicarboxylic acids + water mixtures (see Table 5.4). UNIFAC-RL parameters were developed by fitting to experimental data that include single salt + dicarboxylic acid

aqueous solutions. When UNIFAC-RL is applied to organic acid aqueous solutions only, water activity predictions deviate somewhat further from the experimental data, with a slightly larger standard deviation (0.0571) than UNIFAC-Peng.

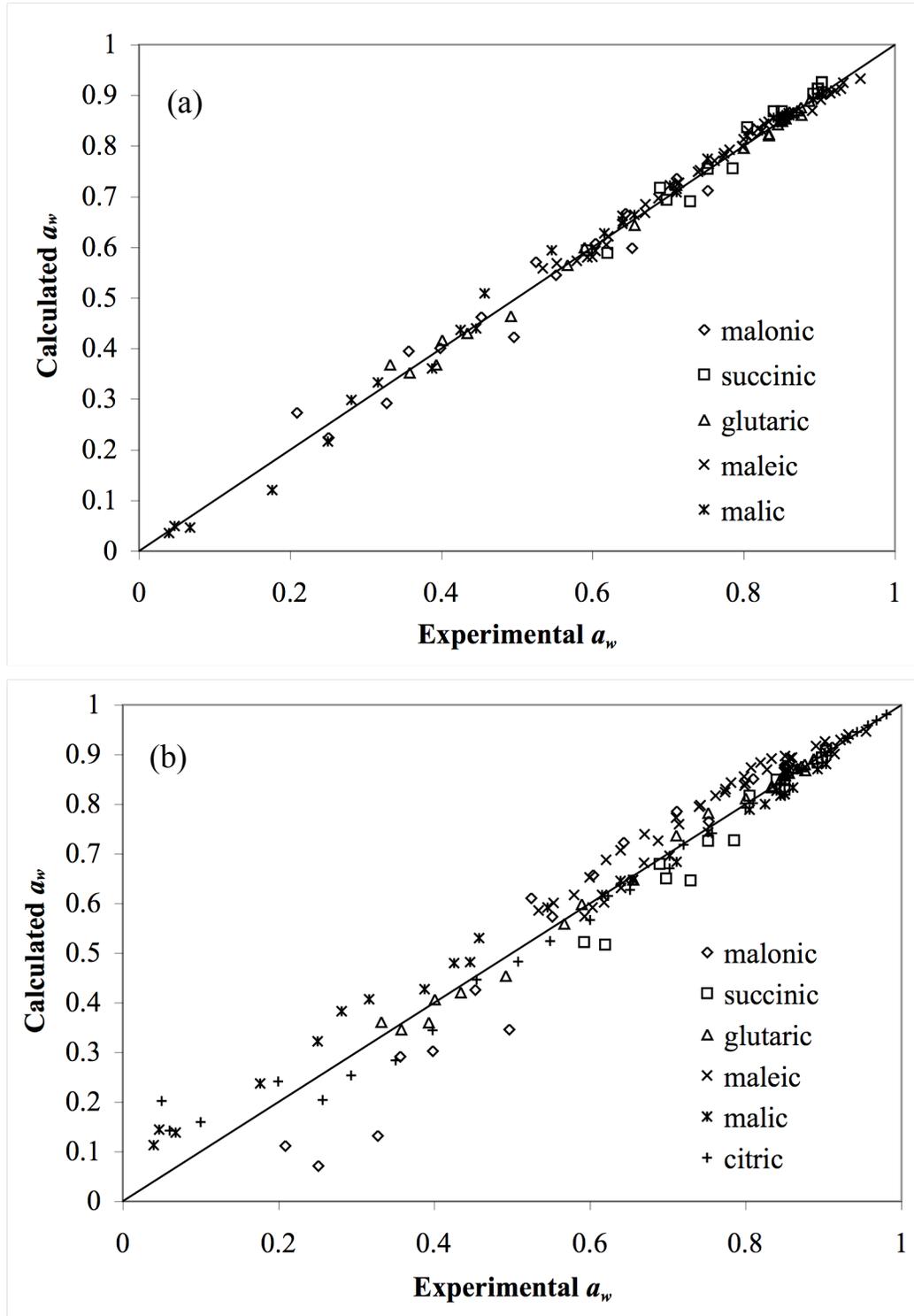
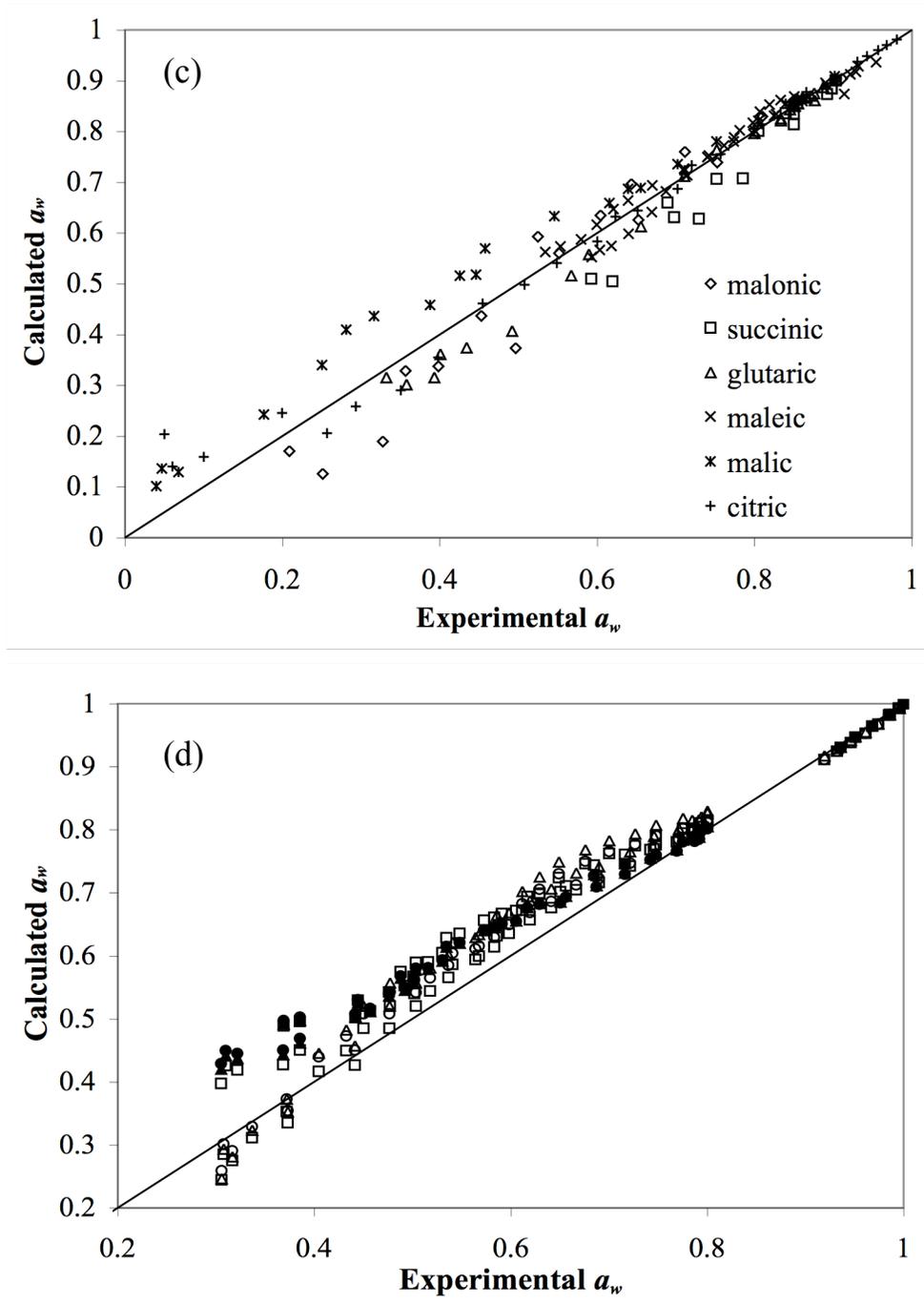


Figure 5.4



**Figure 5.4:** Water activities ( $a_w$ ) calculated for aqueous malonic, succinic, glutaric, maleic, malic, and citric solutions using the (a) Correlation equations, (b) UNIFAC-RL, and (c) UNIFAC-Peng. (d) For aqueous mixtures of malic + maleic acids (solid symbols) and malonic + glutaric acids (open symbols), water activities are calculated using CSB (squares), UNIFAC-RL (triangles), and UNIFAC-Peng (circles). All calculated water activities are plotted against the experimental water activities (Choi and Chan, 2002a; Peng et al., 2001). The solid line is the 1:1 correspondence line.

**Table 5.4: Standard deviations of difference between predictions and the experimental water activity data type,  $a_w(x, m)^a$  for the non-electrolyte modules used in the CSB model, ADDEM, X-UNIFAC, and the Ming and Russell model.**

Standard Deviation	N <sup>b</sup>	CSB (Correlation equations) <sup>d</sup>	UNIFAC-RL <sup>e</sup>	UNIFAC-Peng <sup>f</sup>
<i>Binary organic acid + water solutions</i>				
Malonic/succinic/glutaric acids	69	0.0222	0.0515	0.0455
Malic/maleic/citric acids	96 (67) <sup>c</sup>	0.0171	0.0455	0.0423
<i>Ternary organic acids + water solutions</i>				
Malic + Maleic/ malonic + glutaric solutions	49	0.0511	0.0580	0.0531
<i>Overall</i>	214 (185) <sup>c</sup>	0.0402	0.0571	0.0520

a. Tabulated Choi and Chan (2002b) data by Clegg and Seinfeld (2006a, b) at <http://www.aim.env.uea.ac.uk/aim/aim.htm> are used.

b. N = number of data points

c. Number in parenthesis indicates the number of data points used for the correlation equations, excluding data points for the citric acid solutions.

d. Correlation equations are used in the CSB model for selected organic acids.

e. UNIFAC-RL parameters are used in X-UNIFAC.3 and the Ming and Russell model

f. UNIFAC-Peng parameters are used in ADDEM as well as in the CSB model for organic compounds for which the Correlation equations are not available.

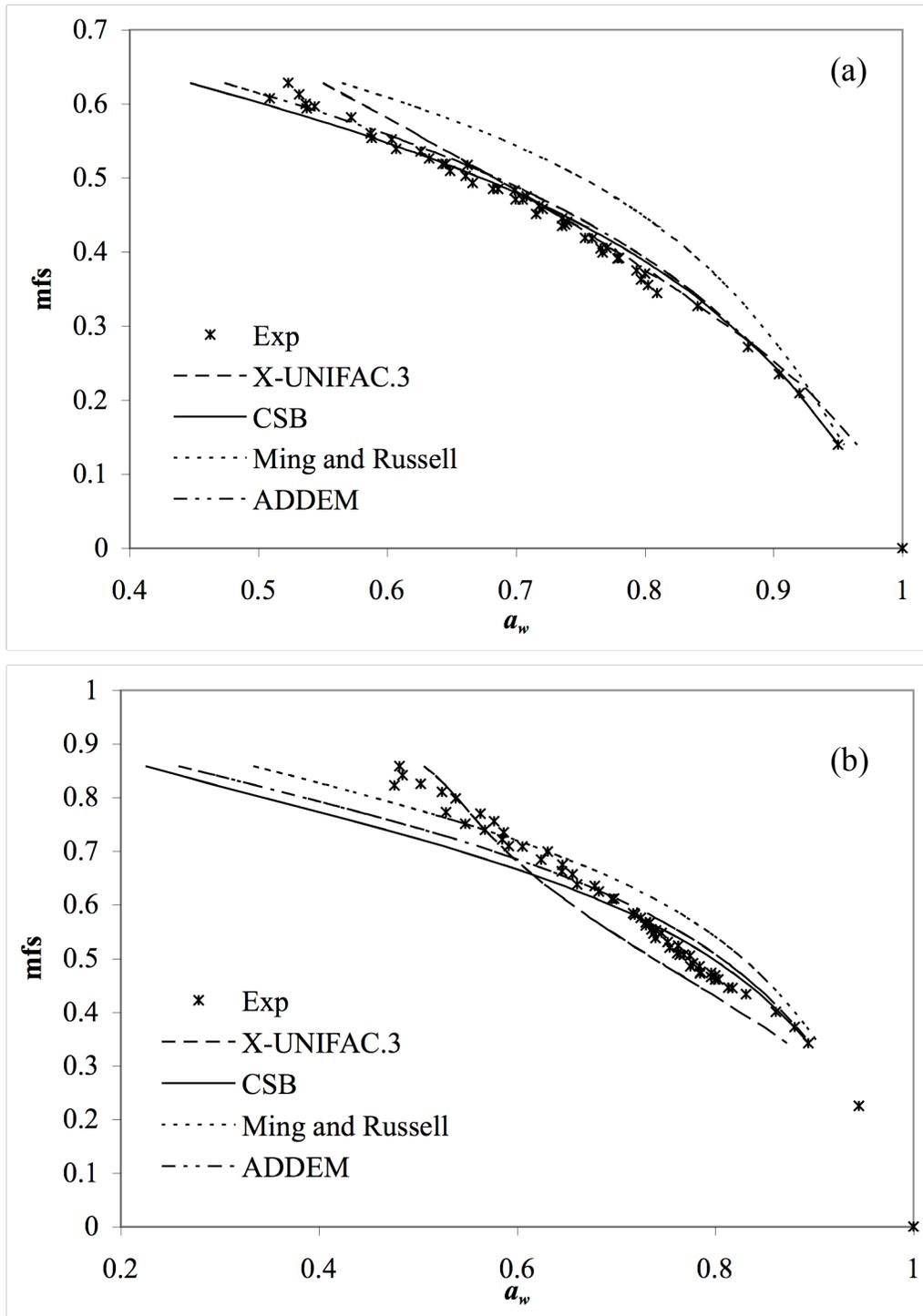
### 5.4.3 Aqueous Solutions of Dicarboxylic Acids and Single salt

In this section, predictions of the CSB model, X-UNIFAC.3, the Ming and Russell model, and ADDEM, are compared with data on mixtures of dicarboxylic acid and the salts, NaCl and  $(\text{NH}_4)_2\text{SO}_4$  (Choi and Chan, 2002b), and also mixtures of five acids (malic, malonic, maleic, glutaric, and methyl succinic) with salts, NaCl and  $(\text{NH}_4)_2\text{SO}_4$  (Marcolli et al., 2004). In theory, the CSB model (without mixture parameters) and ADDEM are similar, as each uses the same model for the electrolyte (AIM) and non-electrolyte (UNIFAC-Peng) terms. Both the CSB and ADDEM models do not represent ion-organic interaction and are referred to as “decoupled” models. Since ion-organic interactions are represented explicitly in X-UNIFAC.3 and Ming and Russell they are referred to as “coupled” models. Comparing predictions between the coupled and decoupled models, the significance of the ion-organic parameters may be assessed.

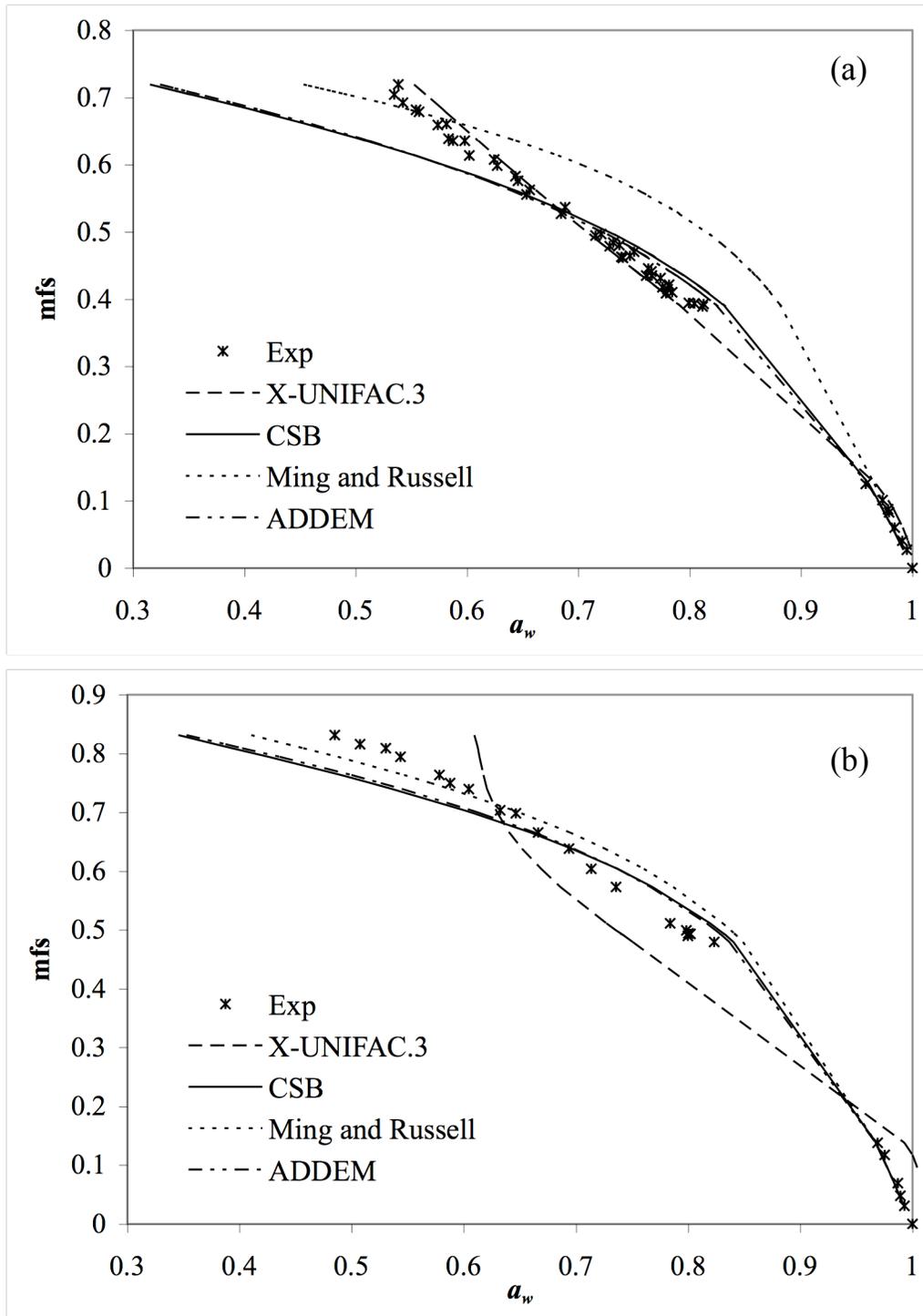
Figures 5.5 to 5.8 show the calculated water activities by all four models for malonic, succinic, glutaric, and citric acid aqueous solutions with either NaCl or  $(\text{NH}_4)_2\text{SO}_4$ , compared to experimental water activities (see Table 5.2). For the aqueous NaCl and  $(\text{NH}_4)_2\text{SO}_4$  solutions with citric acid, UNIFAC-Peng is used in CSB instead of the correlation equation for the organic-water interaction. The total mass fraction solute (mfs) is shown against the water activity ( $a_w$ ), where mfs = mass of solute on a dry basis/mass of solution. For the dicarboxylic acid (malonic, succinic, glutaric, or citric) + NaCl aqueous solutions, water activities predicted by the CSB model, ADDEM, and X-UNIFAC.3 are in good agreement with experimental data (Figures 5.5a, 5.6a, 5.7a, and 5.8a). Deviations between experimental data and water activities calculated by the Ming and Russell model are relatively large as compared to those of the other three models.

The Ming and Russell model consistently overestimates  $m_{fs}$  as a function of  $a_w$ . Predictions of X-UNIFAC.3 are closer to the experimental data than those of Ming and Russell, perhaps owing to the fact that X-UNIFAC.3 includes more ion-organic parameters. For mixtures of NaCl and dicarboxylic acids, the current models that account for ion-organic interaction parameters may not have any advantage over those that do not include ion-organic parameters.

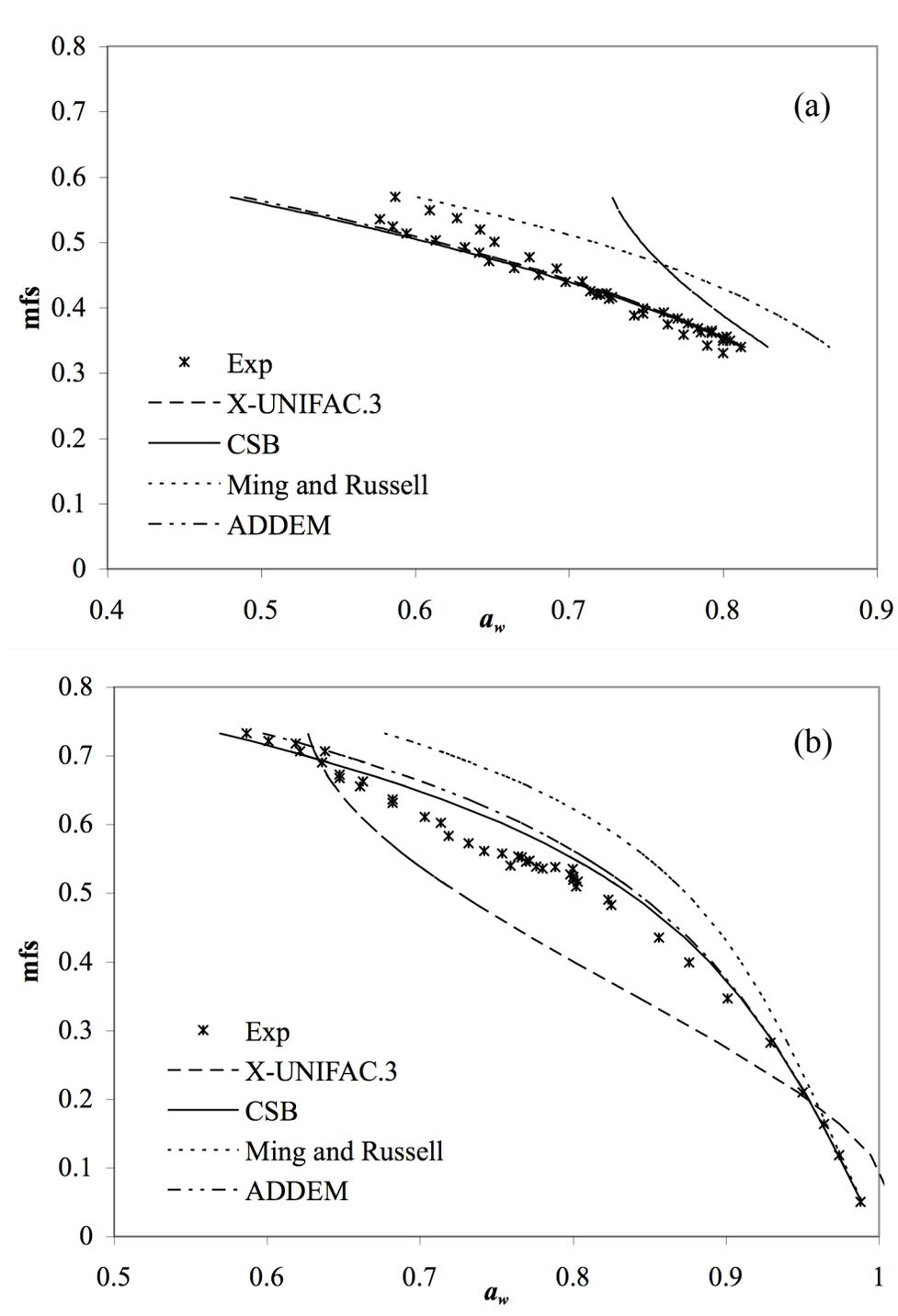
For the aqueous solutions of  $(\text{NH}_4)_2\text{SO}_4$  with malonic, succinic, and glutaric (Figure 5.5b, 5.6b, and 5.7b), predictions of the CSB and ADDEM models are comparable to the those of X-UNIFAC.3 and the Ming and Russell model. In the case of glutaric acid +  $(\text{NH}_4)_2\text{SO}_4$  aqueous solutions, the decoupled models (CSB and ADDEM) are more accurate than those of X-UNIFAC.3 and the Ming and Russell model.



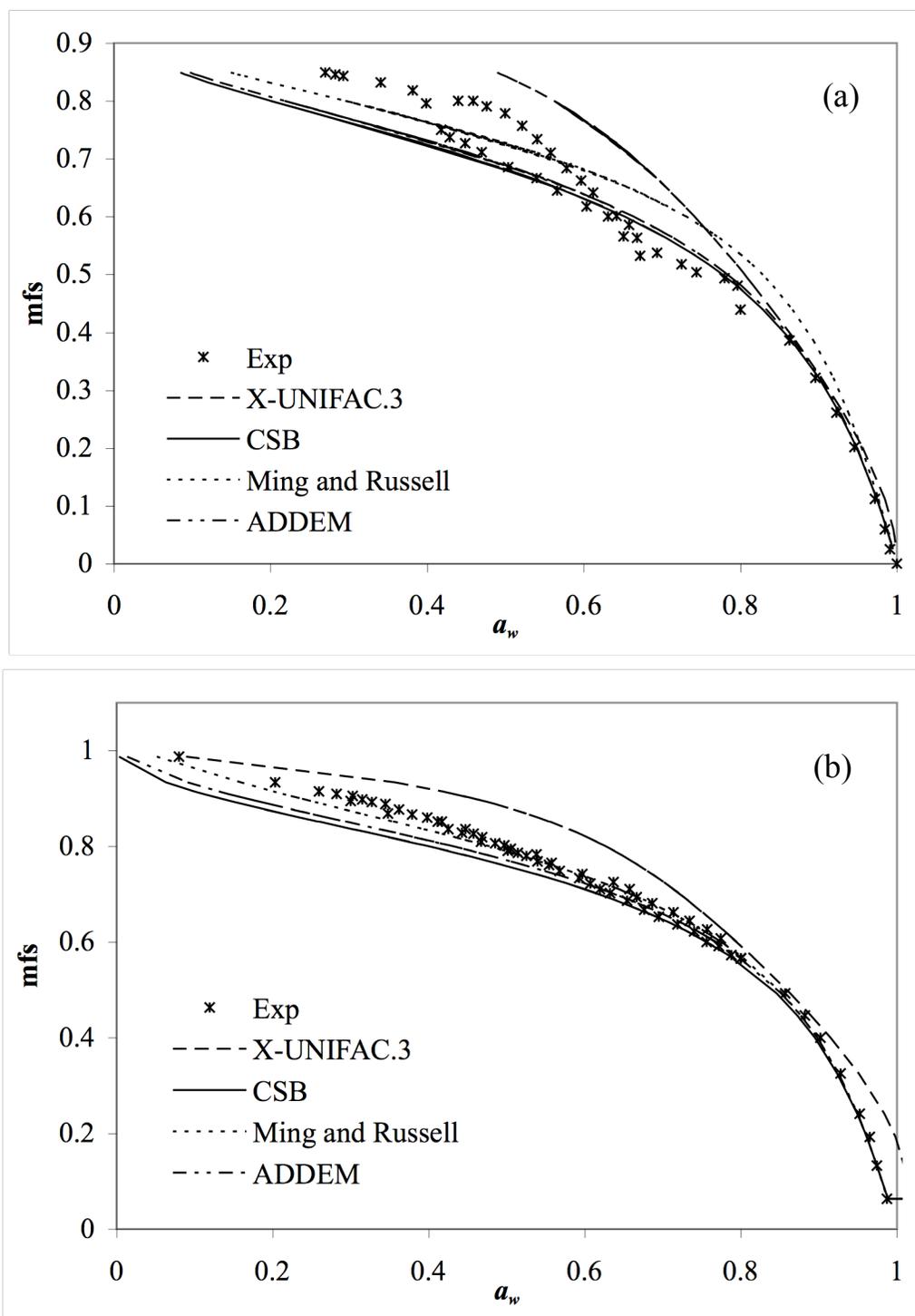
**Figure 5.5: Water activities ( $a_w$ ) calculated using X-UNIFAC, CSB model, Ming and Russell model, and ADDEM for aqueous solutions at mole ratio of acid : salt = 1:1 for malonic acid and (a) NaCl (b)  $(\text{NH}_4)_2\text{SO}_4$ . Experimental data are from original reference (Choi and Chan, 2002b)**



**Figure 5.6: Water activities ( $a_w$ ) calculated using X-UNIFAC, CSB model, Ming and Russell model, and ADDEM for aqueous solutions at mole ratio of acid : salt = 1:1 for succinic acid and (a) NaCl (b)  $(\text{NH}_4)_2\text{SO}_4$ . Experimental data (dots) are from original reference (Choi and Chan, 2002b)**

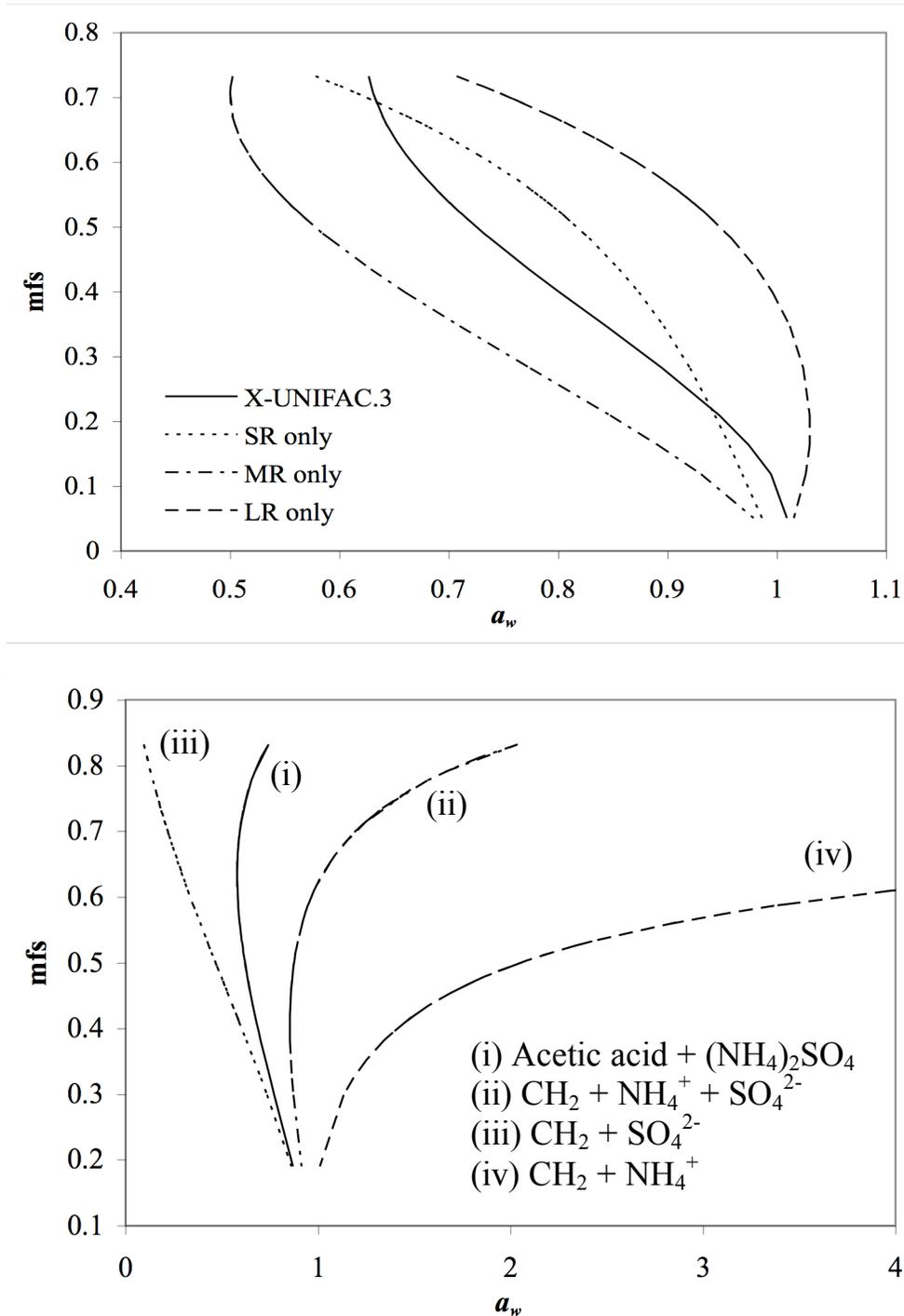


**Figure 5.7: Water activities ( $a_w$ ) calculated using X-UNIFAC, CSB model, Ming and Russell model, and ADDEM for aqueous solutions at mass ratio of acid : salt = 1: 1 for glutaric acid and (a) NaCl (b)  $(NH_4)_2SO_4$ . Experimental data are from original reference (Choi and Chan, 2002b).**



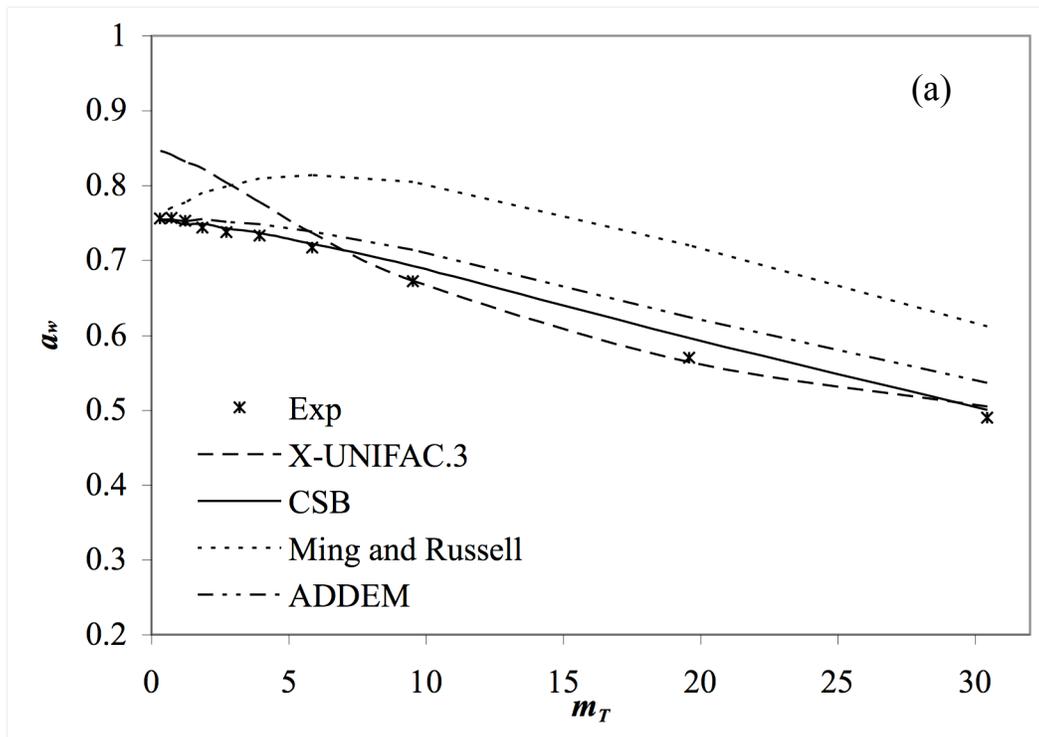
**Figure 5.8:** Water activities ( $a_w$ ) calculated using X-UNIFAC, CSB model, Ming and Russell model, and ADDEM for citric acid aqueous solutions of (a) NaCl and (b)  $(NH_4)_2SO_4$  at mole ratio of acid : salt = 1:1. Experimental data are the evaporation and bulk solutions measurements (Choi and Chan, 2002b)

The X-UNIFAC.3 predicted curves (Figures 5.5b, 5.6b, and 5.7b) for these single dicarboxylic acid (malonic, succinic, or glutaric) +  $(\text{NH}_4)_2\text{SO}_4$  solutions exhibit an unusual shape, as compared with the predicted curves by CSB and the experimental data. Since the unusual behavior does not appear for the pure organic and pure electrolyte mixture predictions (Figures 5.2 – 5.4), we hypothesize that the MR effect term in the model is responsible for this behavior. As shown in Figure 5.9a, the MR effect term is, indeed, the explanation for the shape for the X-UNIFAC.3 predictions for the  $(\text{NH}_4)_2\text{SO}_4$  solutions of dicarboxylic acids. Since the unsubstituted dicarboxylic acids contain only two functional groups,  $-\text{CH}_2-$  and  $-\text{COOH}$ , and the curving behavior is not observed for the dicarboxylic acid + NaCl solutions (Figures 5.5a, 5.6a, and 5.7a), the shape of the curve is likely a result of the  $\text{CH}_2/(\text{NH}_4)_2\text{SO}_4$  and  $\text{COOH}/(\text{NH}_4)_2\text{SO}_4$  interactions. Figure 5.9b shows the different ion-group interactions when setting the appropriate MR parameters to zero. The behavior of predictions for systems containing unsubstituted dicarboxylic acids and  $(\text{NH}_4)_2\text{SO}_4$  is a combined effect of the MR interaction of  $\text{CH}_2/\text{SO}_4^{2-}$  (curve iii in Figure 5.9b) and other MR interactions that may take the same form as  $\text{CH}_2/\text{NH}_4^+$  (curve iv in Figure 5.9b).

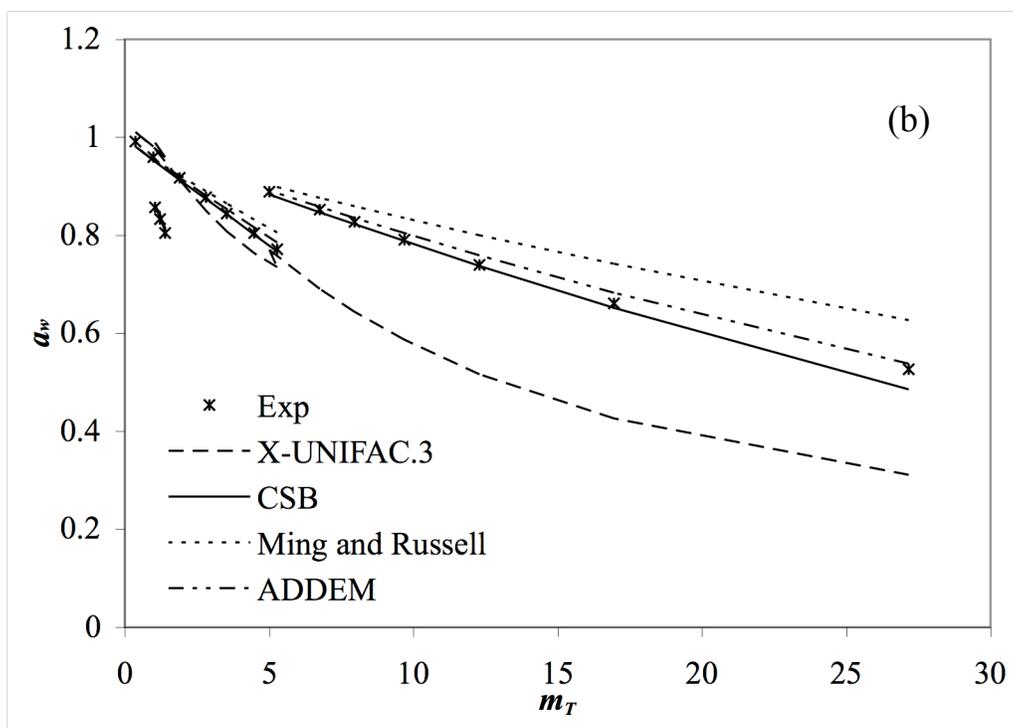


**Figure 5.9:** (a) Long-range, mid-range, and the short-range contributions are illustrated separately for the aqueous glutaric acid and  $(NH_4)_2SO_4$  solution. The overall results of X-UNIFAC.3 are also shown. (b) (i) Mid-range contribution of acetic acid and  $(NH_4)_2SO_4$  solution. (ii) The mid-range parameters for  $CH_2/NH_4^+$  and  $CH_2/SO_4^{2-}$ . (iii)  $CH_2/SO_4^{2-}$  mid-range contributions (iv)  $CH_2/NH_4^+$  mid-range contributions.

Experimental water activities for the saturated aqueous solutions containing each of the salts,  $(\text{NH}_4)_2\text{SO}_4$ , NaCl, and the five acids, malic, malonic, maleic, glutaric, methyl succinic (referred to as M5) (Marcolli et al., 2004), are shown with the calculated water activities by all four models in Figure 5.10. Water activities ( $a_w$ ) are plotted against the total acid molality ( $m_T$ ), where  $m_T = m_{\text{malic}} + m_{\text{malonic}} + m_{\text{maleic}} + m_{\text{glutaric}} + m_{\text{methylsuccinic}}$ . The measurements for mixtures containing  $(\text{NH}_4)_2\text{SO}_4$  include water activities of solutions both saturated and subsaturated with respect to the salts (Marcolli et al., 2004); the measured water activities do not follow a single curve (Figure 5.10b).



**Figure 5.10**



**Figure 5.10: Water activities ( $a_w$ ) calculated using X-UNIFAC, CSB model, Ming and Russell model, and ADDEM for aqueous solution of M5 (malic + malonic + maleic + glutaric + methyl succinic) acids and (a) NaCl (b)  $(\text{NH}_4)_2\text{SO}_4$ , plotted against the total acid molality ( $m_T$ ), where  $m_T = m_{\text{malic}} + m_{\text{malonic}} + m_{\text{maleic}} + m_{\text{glutaric}} + m_{\text{methylsuccinic}}$ . Experimental data are shown with the original reference (Marcolli et al., 2004).**

Calculated water activities by CSB and ADDEM agree well with measurements. Deviations between predictions of the Ming and Russell model and data are relatively large, as compared to those of the CSB model and ADDEM. The predictions by X-UNIFAC.3, however, for both mixtures are qualitatively incorrect.

The major difference between the decoupled models (CSB and ADDEM) and the coupled models (X-UNIFAC.3 and the Ming and Russell model) lies in the treatment of ion-organic interactions. Results of the comparisons presented here indicate that the accuracy of the predictions is not necessarily correlated to the extent of ion-organic

interaction represented in the models; overall, predictions of the decoupled models are comparable to those of the coupled models. Though X-UNIFAC.3 appears to produce the best predictions among the four models (Table 5.5) for binary aqueous mixtures of dicarboxylic acid and the salts, it may be unsuitable for aqueous mixtures of unsubstituted dicarboxylic acids and  $(\text{NH}_4)_2\text{SO}_4$  in its present form. Since the term that causes the atypical shape (Figures 5.5b, 5.6b, and 5.7b) involves  $\text{CH}_2$ , similar problems can occur for many organic compounds. Adjustment of the MR parameters for the  $\text{CH}_2/\text{SO}_4^{2-}$  interaction may be necessary.

**Table 5.5: Standard deviations of difference between predictions and data for the CSB model, ADDEM, X-UNIFAC.3 and the Ming and Russell model using the experimental water activity data type,  $a_w(x, m)^a$ .**

Standard Deviation	N <sup>b</sup>	CSB	ADDEM	X-UNIFAC.3	Ming and Russell
<i>Aqueous malonic/succin/glutaric/citric acid + NaCl solutions</i>					
NaCl mixtures	183	0.070	0.065	0.077	0.080
Supersaturated solutions ( $m_{\text{NaCl}} > 6.146 \text{ mol kg}^{-1}$ )	85	0.101	0.094	0.101	0.087
Subsaturated solutions ( $m_{\text{NaCl}} < 6.146 \text{ mol kg}^{-1}$ )	98	0.020	0.021	0.049	0.073
<i>Aqueous malonic/succin/glutaric/citric acid + <math>(\text{NH}_4)_2\text{SO}_4</math> solutions</i>					
$(\text{NH}_4)_2\text{SO}_4$ mixtures	188	1.216	1.511	0.428	0.856
Supersaturated solutions ( $m_{(\text{NH}_4)_2\text{SO}_4} > 5.779 \text{ mol kg}^{-1}$ )	96	0.648	1.446	0.317	0.688
Subsaturated solutions ( $m_{(\text{NH}_4)_2\text{SO}_4} < 5.779 \text{ mol kg}^{-1}$ )	92	1.613	1.583	0.521	1.006
<i>Overall</i>					
All NaCl and $(\text{NH}_4)_2\text{SO}_4$ solutions	371	0.866	1.075	0.309	0.611
All supersaturated solutions	181	0.476	1.053	0.240	0.503
All subsaturated solutions	190	1.119	1.098	0.363	0.700

a. Tabulated Choi and Chan (2002b) data by Clegg and Seinfeld (2006a, b) at <http://www.aim.env.uea.ac.uk/aim/aim.htm> are used.

b. N = number of data points.

It is expected that ion-organic interactions are of most importance in solutions with high solute concentrations, for which inclusion of ion-organic parameters would be beneficial. Standard deviations of the difference between predictions and data for all supersaturated solutions (Table 5.5) are 0.240 (X-UNIFAC.3), 0.503 (the Ming and Russell model), as compared to 0.476 (CSB) and 1.053 (ADDEM); the results seem to indicate that concentrated electrolyte solutions may be better represented by models with ion-organic parameters, as expected. However, even with such additional interactions the models may still show only relatively small improvements as they neglect ion pairing and other effects that are likely to occur in systems containing very little water. Additional comparisons seem warranted.

## 5.5 Discussion and Conclusions

In theory, X-UNIFAC.3 and the Ming and Russell model provide a more complete treatment by including ion-organic interactions for mixed organic-electrolyte solutions. The present results indicate that, for the four models evaluated, the ion-organic terms do not necessarily lead to improved model predictions. Fitting ion-organic interaction parameters to data, in addition, can be challenging. It is difficult to determine mixture parameters to represent the thermodynamic properties of aqueous electrolyte-organic systems to high concentrations. For instance, the mixture terms based on the Pitzer molality-based equations, which can be included in the CSB model, are suitable for low to moderate concentrations only (up to about 6 mol kg<sup>-1</sup>). In X-UNIFAC.3, mid-range (MR) parameters can lead to the atypical shape in the predictions (Figures 5.5b, 5.6b, and 5.7b). The MR term is calculated as sums of terms that are proportional to parameters determined by fits to data, ion/solvent group concentrations, and ionic

strength (see Appendix 5.7.3), and these terms have large numerical values in concentrated solutions. Consequently, a slight change in the MR parameters or salt concentrations can lead to a significant change in the predicted activity coefficient, which can be difficult for parameter optimization over a wide range of systems. For coupled models, the major limitation remains the scarcity of experimental data from which ion-organic parameters can be determined.

For the CSB and ADDEM models, calculations of the electrolyte term (AIM) and the non-electrolyte term (UNIFAC) are independent. As a result, the CSB and ADDEM models have the advantage in the flexibility of the choice of activity coefficient model. If needed, different combinations of activity coefficient models can be used for specific organic mixtures or concentration ranges. For instance, both the correlation equations and UNIFAC can be used in the CSB model.

An alternate modeling approach has also been proposed by Clegg et al. (2003) for predicting water and solute activities in aqueous atmospheric aerosols containing both dissolved electrolyte and organic compounds; the model is based upon an extended Zdanovskii-Stokes-Robinson (ZSR) scheme (hereafter referred to as the extended ZSR model). Though the extended ZSR model is not included in the present work, a comprehensive comparison of the extended ZSR model and the CSB model with literature data is performed in a previous study by Clegg and Seinfeld (2006a), and the results are summarized here. Similar to the CSB model, mixture parameters in the extended ZSR model can be set to zero so that the predicted properties (e.g. water activities) of the mixture are based only on the pure solution properties of the components. Predicted water activities of the extended ZSR model are compared to

literature data (Choi and Chan, 2002b) for mixtures of succinic, malonic, glutaric acids and the salts, NaCl and  $(\text{NH}_4)_2\text{SO}_4$ . In the absence of mixture parameters, predictions of the extended ZSR model are in very good agreement with the measurements (see Figures 15, 16, 20, 24, 26, 29 in Clegg and Seinfeld, 2006a). For the aqueous mixtures of dicarboxylic acids (M5) and the salts, NaCl and  $(\text{NH}_4)_2\text{SO}_4$ , calculated water activities of the extended ZSR model agree very well (see Figures 35 and 36 in Clegg and Seinfeld, 2006a) with the experimental data (Marcolli et al., 2004). The extended ZSR model (without mixture parameters) is found to yield more accurate predictions than the CSB model for aqueous mixtures containing dicarboxylic acids only. For aqueous mixtures of acids and salts, predictions of the extended ZSR model and the CSB model are comparable in accuracy, though the extended ZSR model performs slightly better than the CSB model. However, as noted by Clegg and Seinfeld (2006a), the extended ZSR model requires the pure solution properties at the water activity of the mixture, and this information is not likely to be available for many other systems.

Even in the absence of mixture parameters, the CSB, ADDEM, and the extended ZSR models produce predictions that are in excellent agreement with experimental data for most systems for low to moderately concentrated solutions. On the other hand, despite the difficulties in determining the ion-organic mixture parameters, it should be remembered that the ion-organic interaction parameters can improve model performance (Clegg et al., 2001; Clegg and Seinfeld, 2006a), and they are probably important in representing solutions with high solute concentrations. When experimental data become available, further development in the application of the ion-organic parameters should be considered.

In atmospheric aerosol modeling, the chemical composition and physical properties of the organic fraction are largely unknown. Therefore, the additive approaches of the decoupled models (CSB, ADDEM, and the extended ZSR) are more feasible than the coupled models. We conclude that, at present, decoupled approaches, such as those in CSB, ADDEM and the extended ZSR models, are generally to be preferred.

## **5.6 Acknowledgment**

This work was supported by the Electric Power Research Institute. The authors would like to thank Professor Lynn M. Russell, Dr. David Topping for helpful discussion about this work.

## 5.7 Appendix

### 5.7.1 Aerosol Inorganic Model (AIM)

The Aerosol Inorganic Model (AIM) is a thermodynamic model developed based on the Pitzer, Simonson, Clegg (PSC) mole fraction-based model for inorganic systems  $\text{H}^+$ -  $\text{NH}_4^+$ -  $\text{SO}_4^{2-}$  -  $\text{NO}_3^-$  -  $\text{H}_2\text{O}$  and  $\text{H}^+$ -  $\text{NH}_4^+$ -  $\text{SO}_4^{2-}$  -  $\text{NO}_3^-$  -  $\text{Cl}^-$  -  $\text{Br}^-$  -  $\text{H}_2\text{O}$  for tropospheric and stratospheric conditions, and  $\text{H}^+$ -  $\text{NH}_4^+$ -  $\text{Na}^+$  -  $\text{SO}_4^{2-}$  -  $\text{NO}_3^-$  -  $\text{Cl}^-$  -  $\text{H}_2\text{O}$  at 298.15K (Clegg et al., 1998a, b). AIM is based upon extensive thermodynamic data for binary (single electrolyte plus water) and ternary (two electrolyte plus water) systems and has been thoroughly tested for the systems it treats.

The equations for the excess Gibbs energy and solvent and solute activity coefficients for mixtures are expressed on a mole fraction basis and comprise a Debye-Hückel term extended to include the effects of unsymmetrical mixing, and a Margules expansion carried out to the four suffix level. The model is developed for salt solutions containing an indefinite number of ions of arbitrary charge over the entire concentration range. An infinitely dilute reference state with respect to the solvent, water, is used for the solute species. That is, the activity coefficients of the solute,  $\gamma_i^* \rightarrow 1$  as  $x_i \rightarrow 0$  in the pure solvent. For the activity coefficient of the solvent,  $\gamma_l \rightarrow 1$  as  $x_l \rightarrow 1$  (Clegg et al., 1992).

Mole fractions are calculated on the basis of complete dissociation of all salts, therefore, the mole fraction ( $x_j$ ) of species  $j$  is given as  $x_j = n_j / \sum_i n_i$  where  $n_i$  is the number of moles of all species  $i$  present, with cations and anions included separately. The excess Gibbs energy per mole of particle ( $g^E$ ) is defined as  $g^E = G^E / \sum_i n_i$ . Activity

coefficients ( $\gamma_i$ ) are related to the excess Gibbs energy by  $g^E = RT \sum_i x_i \ln \gamma_i$ . The excess Gibbs energy per mole ( $g^E$ ) is assumed to consist of short-range force ( $g^S$ ) and long-range Debye-Hückel ( $g^{DH}$ ) components:

$$g^E = g^S + g^{DH} \quad (5.3)$$

For unsymmetrical mixing of ions of the same sign, a higher order electrostatic contribution to the Debye-Hückel expression is included, which is a function only of the nature of the solvent, ionic strength, and charge. It is also unrelated to short-range forces and should be seen simply as a modification to the Debye-Hückel term. As a result, the total long-range force contribution to the excess Gibbs energy,  $g^{DHT}$ , is

$$g^{DHT} = g^{DH} + g^{HOE} \quad (5.4)$$

where  $g^{HOE}$  is the higher order electrostatic contribution, and  $g^{DHT}$  replaces  $g^{DH}$  in equation A1. Activity coefficient model equations derived from the excess Gibbs energy involve a large number of parameters. Given the complexity of the equations and the definitions of the parameters, the formulae are not repeated here, and the reader is referred to Clegg et al. (1992) for a complete description.

### 5.7.2 CSB Model

The aerosol inorganic model (AIM) is extended to include organic species in the CSB model. The approach is based upon the use of existing models of ion/water and organic/water mixtures, and the effect of the ion/organic interactions within the mixtures is expressed with thermodynamically consistent terms (Clegg et al., 2001). In the CSB approach, the molal activity coefficient for each component  $j$  is given by:

$$\ln \gamma_j = \ln \gamma_j^{IOW} + \ln \gamma_j^{IO} \quad (5.5)$$

where the  $\ln \gamma_j^{IW}$  term represent the ion-water contribution if component  $j$  is an ion, and

$\ln \gamma^{ow}$  is the organic-water interaction term for component  $j$  being an organic solute. The ion-water interaction for the electrolytes,  $\ln \gamma^{iw}$ , can be calculated using an existing model such as AIM (Clegg et al., 1998a, b), and UNIFAC can be used for the organic-water interaction of the organic solutes,  $\ln \gamma^{ow}$ .

The water activity is defined in terms of the osmotic coefficients of the solution,  $\phi$ :

$$\phi - 1 = (\phi' - 1) \left( \frac{\sum_i m_i}{\sum_j m_j} \right) + (\phi'' - 1) \left( \frac{\sum_n m_n}{\sum_j m_j} \right) + (\phi''' - 1) \quad (5.6)$$

where  $\phi'$  is the osmotic coefficient contribution from the ionic component of the solution,  $\phi''$  is the contribution from organic solutes, and  $\phi'''$  is the contribution from ion-organic interactions;  $m_i$  denotes the molality of ions  $i$ ;  $m_n$  is the molality of uncharged solute  $n$ ;  $m_j$  represents the molality of solute species  $j$  (either ion or molecule). If one of the osmotic coefficients is not calculated, it is assumed to have a value of unity so that its contribution to the overall  $(\phi - 1)$  is zero.

It should be noted that most activity coefficient models are based on the mole-fraction scale, therefore, two adjustment terms in the pseudo-mole fractions of water are needed to convert the mole fraction activity coefficients to molal activity coefficients. Moreover, in models for calculating the organic/water interactions such as UNIFAC, the reference state is the pure liquid for each component. Conversion to the same infinite dilution state as the ions is also needed.

The ion-organic interaction ( $\ln \gamma^{io}$ ) is derived from a Pitzer molality-based model:

$$\frac{G^{ex}}{w_w RT} = 2 \sum_n \sum_i m_n m_i \lambda_{ni} + \sum_n \sum_c \sum_a m_n m_a m_c \xi_{nca} \quad (5.7a)$$

$$\ln \gamma_i^{IO} = 2 \sum_n m_n \lambda_{ni} + \sum_n \sum_k m_n m_k \xi_{nik} \quad (5.7b)$$

$$\ln \gamma_n^{IO} = 2 \sum_n m_i \lambda_{ni} + \sum_c \sum_a m_c m_a \xi_{nca} \quad (5.7c)$$

$$\phi''' - 1 = \left( 2 / \sum_j m_j \right) \left[ \sum_n \sum_i m_n m_i \lambda_{ni} + \sum_n \sum_c \sum_a m_n m_c m_a \xi_{nca} \right] \quad (5.7d)$$

In equation (5.7), species  $i$  is an ion;  $n$  is an uncharged organic molecule;  $c$  is a cation;  $a$  is an anion, and  $k$  can be either an ion or organic molecule. The term  $w_w$  is the number of kg of water, and  $m$  denotes the molality for each component. The parameters in the expressions ( $\lambda_{ni}$  and  $\xi_{nca}$ ) are determined from experimental data (Clegg et al., 2001). In the study of Clegg and Seinfeld (2006a), the ion-organic parameters are set to zero. In the absence of ion-organic interaction, the relationship for the water activity of a mixture is:

$$a_w = \prod_j a_{w(j)} \quad (5.8)$$

where  $a_{w(i)}$  is the water activity of a pure aqueous solutions of  $j$  at the same molality as in the mixture. This relationship is in fact equivalent to osmotic coefficient equation (5.6).

The water and solute activities in pure aqueous solutions of the dicarboxylic acids are represented by the set of equations:

$$g^e / RT = x_s (1 - x_s) (c_1 + \sum_{i=2,m} c_i (1 - x_s)^{i-1}) \quad (5.9a)$$

$$\begin{aligned} d(g^e / RT) / d(x_s) = & (1 - 2x_s) (c_1 + \sum_{i=2,m} c_i (1 - x_s)^{i-1}) + \\ & x_s (1 - x_s) (-2c_2 - \sum_{i=3,m} 2(i-1)c_i (1 - 2x_s)^{i-2}) \end{aligned} \quad (5.9b)$$

For the activity coefficients of the solute,

$$\ln \gamma_s = g^e / RT + (1 - x_s) d(g^e / RT) / d(x_s) \quad (5.9c)$$

For the activity coefficients of the solvent,

$$\ln \gamma_w = g^e / RT + x_s d(g^e / RT) / d(x_s) \quad (5.9d)$$

where  $x_s$  is the stoichiometric mole fraction of the acid solute, and  $c_i$  are the fitted parameters. The reference state of  $\gamma_s$  is the hypothetical pure liquid, and  $\gamma_s$  is converted to a value based on a reference state of infinite dilution in water ( $\gamma_s^*$ ) by dividing by the value of  $\gamma_s$  calculated for  $x_s = 0$ . Available water activity and osmotic coefficient data for aqueous solutions of seven dicarboxylic acids at 298.15 K are fitted to equation (5.9).

### 5.7.3 UNIFAC

UNIFAC is the most widely used activity coefficient model for organic mixtures and aqueous organic solutions. Model equations are described by Fredenslund et al. (1977), and the most widely used solvent parameters are usually derived from vapor-liquid equilibrium (Fredenslund and Sorensen, 1994; Hansen et al., 1991). When additional functional groups for ions (Kikic et al., 1991) and organics (Balslev and Abildskow, 2002; Wittig et al., 2003) are introduced to the model, new parameters are needed and some adjustments are made for the reference states (Yan et al., 1999).

The UNIFAC activity coefficient expression consists of a combinatorial term and a residual term:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (5.10)$$

where the combinatorial term  $\ln \gamma_i^C$ :

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \left( \sum_k x_k l_k \right) \quad (5.11)$$

The value of  $z$  is set to 10,  $x_i$  is the mole fraction of component  $i$ , and the term  $l_i$  is calculated by the equation:  $l_i = (z/2)(r_i - q_i) - (r_i - 1)$ .  $\theta_i$  is the area fraction, defined as

$\theta_i = q_i x_i / \sum_k q_k x_k$ , and  $\Phi_i$  is the volume fraction, for which  $\Phi_i = r_i x_i / \sum_k r_k x_k$ . Parameters  $q_i$  and  $r_i$  represent the surface area and volume of component  $i$ . They are calculated by the surface area parameter ( $Q_o$ ) and volume parameter ( $R_o$ ) of the individual groups  $o$  in component  $i$ .  $q_i = \sum_o v_o^i Q_o$  and  $r_i = \sum_o v_o^i R_o$ . The residual term of the UNIFAC equation is:

$$\ln \gamma_i^R = \sum_o v_o^i [\ln Z_o - \ln Z_o^i] \quad (5.12)$$

where  $Z_o$  is the residual activity coefficient of the functional group  $o$ , and  $Z_o^i$  is the residual activity coefficient of group  $o$  in the reference solution of component  $i$ . Both parameters can be expressed by:

$$\ln Z_o = Q_o \left[ 1 - \ln \left( \sum_n \Theta_n \Psi_{no} \right) - \sum_n \left( \frac{\Theta_n \Psi_{on}}{\sum_p \Theta_p \Psi_{pn}} \right) \right] \quad (5.13)$$

where the summations cover all groups,  $n$ ,  $o$ , and  $p$ . The area fraction of group  $n$  is  $\Theta_n = Q_n x_n / \sum_o Q_o x_o$ . The interaction term,  $\Psi_{on}$ , is expressed as  $\exp(A_{on}/T)$ , where  $A_{on}$  is a group-group interaction parameter. For each pair of functional group  $o$  and  $n$ , there are two group-group interaction parameters,  $A_{on}$  and  $A_{no}$ , where  $A_{on} \neq A_{no}$ .

### 5.7.4 X-UNIFAC.3

In X-UNIFAC.3, appropriate reference states are selected for all solution components so that the reference state of any component in one phase of a multi-phase liquid solution is the same as that in any other phase in the same system. For solvent compounds, the symmetric activity coefficient convention is used, i.e. the pure liquid standard state is the reference state. On the mole fraction scale, the activity coefficient,  $\gamma_l \rightarrow 1$ , as the mole fraction,  $x_l \rightarrow 1$ . For ions, instead of the typical infinite dilution

reference state, pure fused salt is chosen as the reference state, i.e.  $\gamma_j \rightarrow 1$  as  $x_j \rightarrow \nu_j/\nu$ , where  $\nu_j$  is the number of cations or anions,  $j$ , of the salt with  $\nu$  is the sum of the cations and anions. Reference state corrections are included in the activity coefficient expressions by placing constraints on the optimization of interaction parameters (Wang et al., 2002).

The expression for the excess Gibbs energy can be represented by three terms:

$$\frac{G^{ex}}{RT} = \frac{G_{LR}^{ex}}{RT} + \frac{G_{MR}^{ex}}{RT} + \frac{G_{SR}^{ex}}{RT} \quad (5.14)$$

Similarly, the activity coefficient is given by:

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{MR} + \ln \gamma_i^{SR} \quad (5.15)$$

The long-range (LR) electrostatic interaction is represented by a Debye–Hückel long-range effect equation based on the pure fused salt reference state:

$$\begin{aligned} \ln \gamma_i^{LR} = & -A_x \left[ \frac{2z_i^2}{\rho} \ln \frac{1 + \rho I_x^{1/2}}{1 + \rho (I_x^*)^{1/2}} + \frac{I_x^{1/2} (z_i^2 - 2I_x)}{1 + \rho I_x^{1/2}} \right] \\ & - \frac{4A_x I_x}{\rho} \left[ \ln \frac{1 + \rho I_x^{1/2}}{1 + \rho (I_x^*)^{1/2}} \left( \sum_l n_l \right) \left( \frac{1}{2d_s} \frac{\partial d_s}{\partial n_l} - \frac{3}{2\varepsilon_s} \frac{\partial \varepsilon_s}{\partial n_l} \right) \right] \end{aligned} \quad (5.16a)$$

where  $n_i$  is the number of moles of component  $i$  (organics, water, or ion),  $I_x$  is the mole fraction-based ionic strength defined as  $I_x = \frac{1}{2} \sum_i x_i z_i^2$ , where  $z_i$  is the charge number of

the ion (e.g. 1 for  $\text{Na}^+$  and -1 for  $\text{Cl}^-$ ).  $I_x^*$  denotes the ionic strength for the pure fused salt.

The Debye-Hückel parameter is

$$A_x = \frac{1}{3} (2\pi N_A d_s)^{1/2} \left( \frac{e^2}{4\pi \varepsilon_0 \varepsilon_s k_B T} \right)^{3/2} \quad (5.16b)$$

where  $N_A$  is the Avogadro number;  $e$  is the electron charge;  $\varepsilon_0$  is the permittivity of free space;  $k_B$  is the Boltzmann constant, and  $T$  is temperature (K). The empirical parameter ( $\rho$ ) is set to be 17 in X-UNIFAC.3. The molar density of the salt-free solvent mixture ( $d_s$ )

is calculated by the mixing rule:  $d_s = \sum_l v_l d_l$ , where  $v_l$  is the salt-free volume fraction of solvent compound  $l$ .  $v_l$  is defined as  $v_l = x'_l V_l / \sum_i x'_i V_i$ , where  $x'_i$  is the salt-free mole fraction of solvent  $i$ , and  $V_i$  is the molar volume of solvent  $i$ . The dielectric constant of the salt-free solvent mixture ( $\epsilon_s$ ) is obtained from a mixing rule similar to that applied for calculating solvent mixture densities. That is,  $\epsilon_s = \sum_l v_l \epsilon_l$ . For unsymmetrical salts (e.g.  $(\text{NH}_4)_2\text{SO}_4$ ), an additional correction term is subtracted from the expression for ions:

$$\ln \gamma_i^{LR*} = -A_x \left[ \ln \frac{(I_x^*)^{1/2} (z_i^2 - 2I_x^*)}{1 + \rho(I_x^*)^{1/2}} \right] \quad (5.16c)$$

The LR equation does not contain any fitting parameter. Unknown dielectric constants of organic compounds are set equal to the value for water.

The mid-range (MR) interaction is accounted by a second virial coefficient-type term, for solvent groups,

$$\begin{aligned} \ln \gamma_k^{MR} = & - \sum_m \sum_j x_m x_j B_{mj}(I_x) - \sum_c \sum_a x_c x_a B_{ca}(I_x) \\ & + \sum_j B_{jk} + \left( \sum_o n_o \right) \left[ \sum_m \sum_j x_m x_j \frac{\partial B_{mj}(I_x)}{\partial n_k} + \sum_c \sum_a x_c x_a \frac{\partial B_{ca}(I_x)}{\partial n_k} \right] \end{aligned} \quad (5.17a)$$

For ions,

$$\begin{aligned} \ln \gamma_{ion}^{MR} = & - \sum_m \sum_j x_m x_j B_{mj}(I_x) - \sum_c \sum_a x_c x_a B_{ca}(I_x) + \sum_j B_{jion} + \sum_m B_{mion} \\ & + \left( \sum_o n_o \right) \left[ \sum_m \sum_j x_m x_j \frac{\partial B_{mj}(I_x)}{\partial n_{ion}} + \sum_c \sum_a x_c x_a \frac{\partial B_{ca}(I_x)}{\partial n_{ion}} \right] - \ln \zeta_{ion}^{MR*} \end{aligned} \quad (5.17b)$$

where the indices  $m$ ,  $o$ ,  $j$ ,  $c$ , and  $a$  refer to solvent groups, all groups, ions, cations, and anions. Binary interaction coefficients are defined as:

$$B_{mj}(I_x) = b_{mj} + c_{mj} \exp(-1.2I_x^{1/2} + 0.13I_x) \quad (5.17c)$$

$$B_{ca}(I_x) = b_{ca} + c_{ca} \exp(-I_x^{1/2} + 0.13I_x) \quad (5.17d)$$

The interaction coefficients are symmetric, i.e.  $B_{no}(I_x) = B_{on}(I_x)$  and  $B_{nn}(I_x) = B_{oo}(I_x) = 0$ , for any group pair. Ionic strength,  $I_x$ , is calculated using group mole fractions instead of the component mole fractions. Two adjustable parameters,  $b_{no}$  and  $c_{no}$ , are introduced and they are determined using experimental data.

The MR contribution to the activity coefficient of a solvent component  $i$  is given by,

$$\ln \gamma_i^{MR} = \sum_o v_o^i \ln \gamma_o^{MR} \quad (5.18)$$

where  $v_o^i$  is the number of group  $o$  in component  $i$ .

The parameters were optimized using data sets for relevant aqueous inorganic salts solutions and aqueous solutions containing organic compounds and inorganic salts of atmospheric interest, including several dicarboxylic and hydroxy-carboxylic acids,  $\text{NH}_4\text{NO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$ . The resultant parameter set represents group-group interactions for 12 different groups, including chemical groups  $\text{CH}_3-$ ,  $-\text{CH}_2-$ ,  $>\text{CH}-$ ,  $>\text{C}<$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  (Erdakos et al., 2006).

The short-range (SR) energetic contribution is calculated by the traditional UNIFAC equations that are extended to include ions. In order to set the reference state for the ions, a correction term is needed for the combinatorial term. It is obtained by subtracting the reference state value,  $\ln \gamma_i^{C*}$ , from the value calculated for the actual solution in equation (5.11). In X-UNIFAC.3, most solvent group parameters are taken from Fredenslund and Sorensen (1994). The SR parameters for  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  are obtained from Kikic et al. (1991). The parameters for  $\text{NH}_4^+$  are set equal to those of  $\text{Na}^+$ , and the parameters for  $\text{SO}_4^{2-}$  are set equal to those of  $\text{NO}_3^-$ . The group-group interaction

parameters for dicarboxylic acid and hydroxy-carboxylic acid solutions are set equal to the UNIFAC parameters optimized by Raatikainen and Laaksonen (2005).

Given that the interaction parameters are available for all relevant pairs, X-UNIFAC.3 can be used, in principle, to estimate activity coefficients in a liquid mixture containing organic compounds, inorganic salts, and water.

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