Available online at www.sciencedirect.com
ScienceDirect
Atmospheric Environment 40 (2006) 6422–6436
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

# Prediction of activity coefficients in liquid aerosol particles containing organic compounds, dissolved inorganic salts, and water—Part 2: Consideration of phase separation effects by an X-UNIFAC model

Elsa I. Chang, James F. Pankow*

*Department of Environmental and Biomolecular Systems, OGI School of Science & Engineering,*
*Oregon Health & Science University, 20000 NW Walker Rd. Beaverton, OR 97006-8921, USA*

Received 12 August 2005; accepted 5 April 2006

## Abstract

A thermodynamic model is presented for predicting the formation of particulate matter (PM) within an aerosol that contains organic compounds, inorganic salts, and water. Neutral components are allowed to partition from the gas phase to the PM, with the latter potentially composed of both a primarily aqueous ($\alpha$) liquid phase and a primarily organic ($\beta$) liquid phase. Partitioning is allowed to occur without any artificial restraints: when both $\alpha$ and $\beta$ PM phases are present, ionic constituents are allowed to partition to both. X-UNIFAC.2, an extended UNIFAC method based on Yan et al. (1999. Prediction of vapor–liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept. Fluid Phase Equilibria 162, 97–113), was developed for activity coefficient estimation. X-UNIFAC.2 utilizes the standard UNIFAC terms, a Debye–Hückel term, and a virial equation term that represents the middle-range (MR) contribution to activity coefficient effects. A large number (234) of MR parameters are already available from Yan et al. (1999). Six additional MR parameters were optimized here to enable X-UNIFAC.2 to account for interactions between the carboxylic acid group and $Na^+$, $Cl^-$, and $Ca^{2+}$. Predictions of PM formation were made for a hypothetical sabinene/$O_3$ system with varying amounts of NaCl in the PM. Predictions were also made for the chamber experiments with $\alpha$-pinene/$O_3$ (and $CaCl_2$ seed) carried out by Cocker et al. (2001. The effect of water on gas-particle partitioning of secondary organic aerosol. Part I. $\alpha$-pinene/ozone system. Atmospheric Environment 35, 6049–6072); good agreement between the predicted and chamber-measured PM mass concentrations was achieved.

*Keywords:* Activity coefficients; Particulate matter (PM); Organic; Inorganic; Inorganic salts; Phase separation

## 1. Introduction

### 1.1. General

Samples of atmospheric particulate matter (PM) typically contain a myriad of different organic compounds, significant amounts of different inorganic

---

*Corresponding author.
*E-mail address:* pankow@ese.ogi.edu (J.F. Pankow).

1352-2310/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2006.04.031

salts, and water (e.g., Saxena and Hildemann, 1996; Middlebrook et al., 1998). Under such circumstances, multiple liquid phases may be present in the PM, with the presence of more than one liquid phase affecting the properties of the PM. Proper modeling of atmospheric PM (including amount formed) requires an understanding of multiphasic PM. This requires prediction of chemical activity coefficients as a function of PM composition: a liquid phase will undergo phase separation when the chemical activities underlying enough material in the phase can be reduced by creation of a separate phase.

Most thermodynamic models for organic–electrolyte–water PM focus on predicting aerosol hygroscopic growth (e.g., Clegg et al., 2001; Ming and Russell, 2002; Marcolli et al., 2004; Chan and Chan, 2003; Chan et al., 2005). This type of model predicts only the gas-particle partitioning of water; the organic and inorganic components are locked in the PM. A few models seek to simulate the formation of organic particulate matter (OPM) containing organic compounds, electrolytes, and water (Pun et al., 2002; Griffin et al., 2003). Pun et al. (2002) assumed that OPM may be located in two phases, an organic phase that contains 100% of the "hydrophobic" organic compounds and no water, and an aqueous phase that contains 100% of the "hydrophilic" organic compounds and 100% of the inorganic salts. Griffin et al. (2003) modified the Pun et al. (2002) model to allow equilibration of all organic compounds between both phases, but did not allow similar equilibration of either the water or the salts. In a given circumstance, though the difference may be small, higher OPM levels will be predicted by the Griffin et al. (2003) model as compared to the Pun et al. (2002) model: the freedom to occupy both PM phases corresponds to a state with an overall lower free energy.

The models of Pun et al. (2002) and Griffin et al. (2003) provide useful approximations when modeling OPM formation. They also, however, place some artificial constraints on the overall gas/particle (G/P) partitioning equilibrium. In this work we develop and describe a model that: (1) allows the formation of PM composed of either one or two liquid phases ($\alpha$, primarily aqueous; and $\beta$, primarily organic); (2) considers the complete partitioning of all organic compounds and water among all phases; and (3) when the PM is predicted to be composed of both an $\alpha$ and $\beta$ phase, allows the salt ions to distribute between those phases.

### 1.2. Activity coefficient models for organic compound+salt+water mixtures

A thermodynamic model of a solution phase requires a means to predict activity coefficient ($\zeta$) values for each species of interest in the phase. In the atmosphere, the relative humidity (RH, %) varies widely, as do the levels and identities of the salts and organic compounds found in atmospheric PM. Liquid PM can range from being mainly aqueous to mainly organic. When not mainly aqueous, it may not be characterizable as having a primary solvent. $\zeta$ models for atmospheric PM must therefore be applicable over wide ranges in composition. And, since the compounds making up the majority of the organic portion of atmospheric PM are unknown and thus uncharacterized regarding their physical properties, a $\zeta$ model for atmospheric PM cannot presume knowledge of the physical properties of the organic constituents.

As a group contribution method (GCM), UNIFAC as developed by Fredenslund et al. (1975) carries considerable potential for modeling complex atmospheric PM because it assumes that $\zeta_i$ for each species $i$ can be expressed as a summation of interaction terms between the groups that constitute $i$ and all other groups in the solution. The interaction terms can be deduced by pooling the data from multiple simple experimental studies of phase equilibrium. Important types of phase-equilibrium experiments include vapor–liquid equilibrium (VLE) and liquid–liquid equilibrium (LLE) experiments. The advantage of the GCM approach is that it allows complex interactions between solution species to be broken down into interactions among group building blocks: knowledge of the interaction effects among a relatively small number of building blocks (which may include individual ions) allows prediction of interactions between the great variety of species that can be built from those groups.

Existing predictive $\zeta$ models for organic–salt–water mixtures are in many cases extensions of UNIFAC (e.g., Kikic and Fermeglia, 1991; Yan et al., 1999; Erdakos et al., 2006). The interaction parameters used in these UNIFAC extensions are obtained by fitting primarily to experimental phase equilibrium data obtained for solutions containing short-chain monofunctional compounds, and not the longer-chain and/or multifunctional species that can be found in atmospheric PM. Kikic and Fermeglia (1991) combine the basic UNIFAC term for short-range (SR) interactions with a