



A Coupled Hydrophobic-Hydrophilic Model for Predicting Secondary Organic Aerosol Formation

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Abstract. The formation of secondary organic aerosol (SOA) results from the absorption of gas-phase organic oxidation products by airborne aerosol. Historically, modeling the formation of SOA has relied on relatively crude estimates of the capability of given parent hydrocarbons to form SOA. In more recent work, surrogate organic oxidation products have been separated into two groups, hydrophobic and hydrophilic, depending on whether the product is more likely to dissolve into an organic or an aqueous phase, respectively. The surrogates are then allowed to partition only via the dominant mechanism, governed by molecular properties of the surrogate molecules. The distinction between hydrophobic and hydrophilic is based on structural and physical characteristics of the compound. In general, secondary oxidation products, because of low vapor pressures and high polarities, express affinity for both the organic and aqueous aerosol phases. A fully coupled hydrophobic-hydrophilic organic gas-particle partitioning model is presented here. The model concurrently achieves mass conservation, equilibrium between the gas phase and the organic aerosol phase, equilibrium between the gas phase and the aqueous aerosol phase, and equilibrium between molecular and ionic forms of the partitioning species in the aqueous phase. Simulations have been performed using both a zero-dimensional model and the California Institute of Technology three-dimensional atmospheric chemical transport model. Simultaneous partitioning of species by both mechanisms typically leads to a shift in the distribution of products to the organic aerosol phase and an increase in the total amount of SOA predicted as compared to previous work in which partitioning is assumed to occur independently to organic and aqueous phases.

Key words: absorption, dissolution, equilibrium, model, organic aerosol.

1. Introduction

Organic species are ubiquitous constituents of atmospheric particulate matter (Murphy *et al.*, 1998; Seinfeld and Pandis, 1998). Organic aerosol (OA) is emitted directly from sources, such as combustion processes (Rogge *et al.*, 1993; Schauer *et al.*, 1999a, b, 2001), or formed in the atmosphere from the gas-phase oxidation

of volatile organic compounds (VOCs), products of which partition between the gas and aerosol phases (Pankow, 1994). Gas-particle partitioning is a result of decreased vapor pressure and/or increased water-solubility as compared with the precursor organic compound (Odum *et al.*, 1996, 1997; Saxena and Hildemann, 1996; Hoffmann *et al.*, 1997; Griffin *et al.*, 1999; Pankow *et al.*, 2001; Seinfeld *et al.*, 2001). Whereas it is now possible to predict with reasonable accuracy equilibrium atmospheric gas-particle partitioning of inorganic compounds, such as those involving sulfate, nitrate, ammonium, and chloride (Zhang *et al.*, 2000), only recently have theoretical approaches been advanced to do so for organic compounds (Strader *et al.*, 1999; Clegg *et al.*, 2001; Pankow *et al.*, 2001; Seinfeld *et al.*, 2001; Pun *et al.*, 2002).

The general gas-aerosol thermodynamic equilibrium problem is to predict the gas-particle equilibrium of a mixture of semi-volatile inorganic (including water) and organic compounds between the gas phase and a particle phase that may also consist of non-volatile inorganic and organic compounds. Atmospheric oxidation of VOCs leads to a variety of products containing an array of functional groups (Atkinson, 1997). Because the presence of such functional groups leads to molecules with low vapor pressures and high polarities, these species are often referred to as semi-volatile and are likely to partition to organic and aqueous condensed phases simultaneously. Models that represent the composition of aerosols compute the equilibrium phase distribution of such semi-volatile organic compounds. In the case of organics partitioning into an exclusively organic mixture (Pankow *et al.*, 2001) or organics and water into an organic-water mixture (Seinfeld *et al.*, 2001), predictions can be made that are in reasonable agreement with laboratory measurements. Applications to full inorganic electrolyte-organic-water mixtures are scarce (Clegg *et al.*, 2001).

The significant contribution of secondary organic aerosol (SOA) to atmospheric OA concentrations (Turpin and Huntzicker, 1995; Schauer *et al.*, 1996) has prompted the development of modules that represent organic gas-aerosol partitioning in atmospheric chemical transport models. The earliest approach depends on the ability to model the emission and dispersion of primary organic aerosol (POA). The difference between observed OA concentrations and predicted POA concentrations can be attributed to SOA (Schauer *et al.*, 1996; Strader *et al.*, 1999). Similarly, representative ratios of elemental carbon (EC) to OA (EC/OA) can be used to predict SOA concentrations for a region of interest (Turpin and Huntzicker, 1995; Strader *et al.*, 1999). EC/OA values are determined for both emissions sources and the ambient. Since EC is only primary in nature, any difference between these two ratios is attributed to ambient formation of SOA.

A fundamental approach to predict SOA formation is to model the gas-phase chemistry of the parent organic and apply saturation or equilibrium conditions to the semi-volatile products (Pandis *et al.*, 1992; Strader *et al.*, 1999; Andersson-Sköld and Simpson, 2001). This approach may be extended to include dynamic transfer between the gas phase and an aerosol aqueous phase (Jacobson, 1997;

Aumont *et al.*, 2000). Andersson-Sköld and Simpson (2001) have adapted the method of Kamens *et al.* (1999) for use in atmospheric models; this method expresses partitioning coefficients for secondary organic products as a balance between rates of evaporation and condensation.

In the partitioning model of Pun *et al.* (2002), it is assumed that the aerosol consists of two phases, an organic phase (with no associated water) and an aqueous phase. The assumption that the aerosol consists of these two phases is essentially a result of the fact that thermodynamic treatments of homogeneous organic-water-electrolyte solutions are not yet sufficiently well developed. Secondary organic molecules are categorized according to the dominant phase into which they partition, either organic or aqueous. Products classed as hydrophobic are allowed to partition only to the organic phase; conversely, hydrophilic species are allowed to partition only to the aqueous phase. This approach can be termed as the *decoupled module*. Partitioning of hydrophobic organic compounds is assumed to occur exclusively to an absorbing organic aerosol phase, governed by the model of Pankow (1994). Dissolution of hydrophilic species is governed by Henry's law and any subsequent dissociation(s) to the ionic form(s) in the aqueous phase; nonideality is treated through prediction of activity coefficients. Hydrophilic organic species may promote additional condensation of water, contributing to the overall liquid water content (LWC) of the aerosol and, as a result, alter the gas-particle distribution of soluble inorganic aerosol constituents. By not considering the interaction between the hydrophobic and hydrophilic portions of the aerosol, however, one is unable to resolve the effects that one portion may have on the other, such as the ability of hydrophobic organics to limit water uptake of hygroscopic aerosol components (Xiong *et al.*, 1998).

In the present work, the first fully *coupled module* for the gas-particle partitioning of organic compounds, the Model to Predict the Multi-phase Partitioning of Organics (MPMPO), is presented. An important component of the MPMPO is a novel numerical algorithm that significantly decreases computation time in a three-dimensional atmospheric model. Results from zero-dimensional test calculations indicate that, in general, somewhat higher total SOA concentrations result when compounds are considered to partition simultaneously into both aqueous and organic phases as compared to the decoupled approach. In the following sections, the MPMPO is described and representative case studies are presented to investigate the response of SOA formation to variations in temperature, aerosol LWC, aerosol pH, and partitioning species and POA concentrations. The MPMPO is then implemented into the California Institute of Technology (CIT) three-dimensional atmospheric chemical transport model, and the predictions of the MPMPO and the decoupled model within the CIT model (Griffin *et al.*, 2002a) are then compared for a 1993 smog episode in the South Coast Air Basin of California (SoCAB).

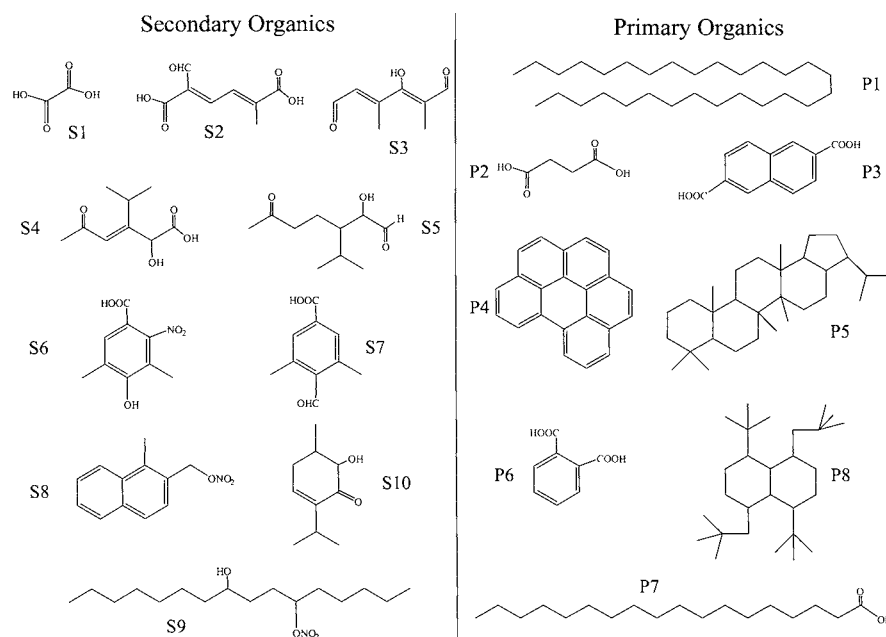


Figure 1. Molecular structures of the secondary (left panel) and primary (right panel) organic aerosol species used in the gas-particle partitioning module. Bonds between carbon atoms are shown with vertices representing carbon atoms; hydrogens bonded to carbon are not shown. Labels next to the molecules are used in the text when describing the appropriate molecule. A more detailed description of these species is presented in Griffin *et al.* (2002a, b) and Pun *et al.* (2002).

2. Model to Predict the Multi-Phase Partitioning of Organics (MPMPO)

The first step in the formation of SOA is the gas-phase oxidation of a parent VOC to produce total concentrations (c_i) of semi-volatile organic species with assumed molecular structure. For example, in previous work ten surrogate species were defined to represent secondary organic oxidation products occurring as a result of the oxidation of urban/regional mixtures of VOCs (Griffin *et al.*, 2002a, b; Pun *et al.*, 2002). Figure 1 presents these species, together with POA compounds used in a three-dimensional atmospheric modeling study of the SoCAB.

The MPMPO is described as follows. Let the organic aerosol-phase concentrations of each of the partitioning secondary organic species be denoted as O_i ($\mu\text{g m}^{-3}$ air), $i = 1, 2, \dots, n$, where n is the number of partitioning species, in this case, ten. Given an initial estimate of O_i , $i = 1, 2, \dots, n$, based, for example, on species vapor pressure, the equilibrium organic aerosol-phase partitioning coefficient, $K_{om,i}$ ($\text{m}^3 \text{air } \mu\text{g}^{-1}$), that describes the distribution of each product

between the gas phase and an absorbing organic aerosol phase can be calculated from (Pankow, 1994)

$$K_{om,i} = \frac{RT}{10^6 M_{om} \gamma_i p_{L,i}^o}, \quad (1)$$

where R is the ideal gas constant ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$), T is temperature (K), M_{om} is the average molecular weight (g mol^{-1}) of the absorbing organics (including both primary organic compounds and secondary products), $p_{L,i}^o$ is the pure component vapor pressure (atm) of species i , and γ_i is the activity coefficient of species i in the organic phase. The factor 10^6 converts g to μg .

The molecular identities of the condensing and primary non-volatile species must be known in order to calculate parameters in Equation (1). These include species-specific molecular weights and vapor pressures as a function of temperature. A number of semi-empirical techniques exist to estimate the vapor pressure of organic compounds. In the present work, the method of Myrdal and Yalkowsky (1997) is employed. The basic premise of this method is that the vapor pressure of an organic non-electrolyte can be found by integrating the total enthalpy of vaporization or sublimation over temperature through the Clausius–Clapeyron equation. The resulting temperature-dependent vapor pressure is a function of boiling and melting points, entropies of boiling and melting, and changes in compound heat capacity associated with phase changes. These variables are estimated from the characteristics of the molecule, including the length of the principal carbon chain, the number of torsional bonds (a measure of molecular flexibility), the likelihood of hydrogen bonding, and the structural symmetry.

In the present work, the UNIFAC method is employed to calculate activity coefficients (Fredenslund *et al.*, 1977; Smith and Van Ness, 1987; Saxena and Hildemann, 1996; Pankow *et al.*, 2001; Seinfeld *et al.*, 2001). The UNIFAC method assumes that a solution can be represented by a mixture of the structural units (subgroups) that comprise the molecules in the solution. Properties of the individual subgroups, as well as parameters describing the subgroup interactions, are used to calculate the activity coefficients, which are related to the excess Gibbs free energy of the solution.

If G_i denotes the gas-phase concentration of species i ($\mu\text{g m}^{-3} \text{ air}$) and M_o the total mass concentration ($\mu\text{g m}^{-3} \text{ air}$) of OA available to act as an organic medium into which the n species may partition, then (Pankow, 1994)

$$K_{om,i} = \frac{O_i}{M_o G_i}, \quad (2)$$

where M_o is the sum of all O_i and the mass concentrations of each POA species present. Once the set of $K_{om,i}$ values is calculated according to Equation (1), G_i for each species is computed from Equation (2).

If A_i represents the aqueous-phase concentration of species i ($\mu\text{g m}^{-3}$ air) and H_i the Henry's law coefficient of species i ($(\mu\text{g } \mu\text{g}^{-1} \text{H}_2\text{O})/(\mu\text{g m}^{-3} \text{air})$),

$$A_i = \frac{G_i(\text{LWC})H_i}{\gamma_{aq,i}}, \quad (3)$$

where LWC has units of $\mu\text{g H}_2\text{O m}^{-3}$ air, and $\gamma_{aq,i}$ is the activity coefficient of organic species i in the aqueous phase (normalized by that at infinite dilution) (Schwarzenbach *et al.*, 1993). Activity coefficients in the aqueous phase are again calculated using the UNIFAC method.

The aqueous-phase equilibrium solution is also subject to constraints imposed by dissociation of the dissolved organic species. Assume species J undergoes first and second dissociations with equilibrium constants K_1 and K_2 ($\text{mol kg}^{-1} \text{H}_2\text{O}$). If each dissociation removes a proton into solution, the dissociation equilibria is expressed as

$$\text{J} \leftrightarrow \text{J}^- + \text{H}^+ : K_1 = \frac{[\text{J}^-][\text{H}^+]\text{MW}_\text{J}}{[\text{J}](\text{MW}_\text{J} - \text{MW}_{\text{H}^+})} \quad (4)$$

$$\text{J}^- \leftrightarrow \text{J}^{2-} + \text{H}^+ : K_2 = \frac{[\text{J}^{2-}][\text{H}^+](\text{MW}_\text{J} - \text{MW}_{\text{H}^+})}{[\text{J}^-](\text{MW}_\text{J} - 2\text{MW}_{\text{H}^+})}, \quad (5)$$

where $[\]$ represents concentrations in $\mu\text{g m}^{-3}$ air, except for $[\text{H}^+]$. If the molecular and ionic species are to have units consistent with Equations (1)–(3) and the units of K_1 and K_2 given above, $[\text{H}^+]$ must be expressed in units of $\text{mol kg}^{-1} \text{H}_2\text{O}$. MW_J is the molecular weight of species J (g mol^{-1}) and MW_{H^+} is the molecular weight of the hydrogen ion (1 g mol^{-1}); these are needed to convert between mass and molar units of molecular and ionic solutes. If J represents one of the n partitioning species in the SOA module, the concentration of singly charged ion from species i , AM_i ($\mu\text{g m}^{-3}$ air), and the concentration of the doubly charged ion from species i , AD_i ($\mu\text{g m}^{-3}$ air), can be represented as

$$\text{AM}_i = \frac{K_{1i}A_i(\text{MW}_i - \text{MW}_{\text{H}^+})}{[\text{H}^+]\text{MW}_i} \quad (6)$$

$$\text{AD}_i = \frac{K_{2i}\text{AM}_i(\text{MW}_i - 2\text{MW}_{\text{H}^+})}{[\text{H}^+](\text{MW}_i - \text{MW}_{\text{H}^+})}. \quad (7)$$

Because of a general lack of experimental data on combinatory reactions between organic anions and inorganic electrolytes in the aqueous phase for the compounds of interest here, such reactions are neglected (Macedo *et al.*, 1990; Kikic *et al.*, 1991; Clegg *et al.*, 2001).

As shown, both the organic and aqueous phase equilibrium relations require activity coefficients, γ_i and $\gamma_{aq,i}$. An iterative solution to determine the organic- and aqueous-phase equilibrium concentrations is necessary because activity coefficients are themselves a function of composition. This solution must also satisfy

Table I. Baseline variables for the case studies of organic gas-particle partitioning

Variable ^a	Value	Variable ^a	Value ($\mu\text{g m}^{-3}$)
LWC	$5 \mu\text{g m}^{-3}$	S1	0.5
T	298K	S2	1.468
pH	4	S3	0.1
P1	$1.86 \mu\text{g m}^{-3}$	S4	0.6
P2	$1.86 \mu\text{g m}^{-3}$	S5	1.135
P3	$1.86 \mu\text{g m}^{-3}$	S6	1.205
P4	$1.86 \mu\text{g m}^{-3}$	S7	0.53
P5	$1.86 \mu\text{g m}^{-3}$	S8	0.2
P6	$1.86 \mu\text{g m}^{-3}$	S9	5.501
P7	$1.86 \mu\text{g m}^{-3}$	S10	0.1
P8	$1.86 \mu\text{g m}^{-3}$		

^a See Figure 1 for species identification.

mass conservation: the sum of the values for O_i , G_i , A_i , AM_i , and AD_i must equal c_i . Like the calculations of activity coefficients, an iterative procedure is required to satisfy mass conservation. This algorithm is described in the Appendix.

3. Case Studies of Organic Gas-Particle Partitioning

The goal of the remainder of this paper is to investigate how gas-particle partitioning depends on temperature, aerosol LWC (in effect, the relative humidity, RH), aqueous-phase pH (in effect, influence of inorganic electrolytes), total concentration of the partitioning species, and concentrations of POA. In addition, differences in predicted partitioning that result between the MPMPO presented here and the decoupled hydrophobic-hydrophilic model of Pun *et al.* (2002) in both a zero-dimensional model and a three-dimensional atmospheric model are assessed. Baseline variable values that reflect a potential urban situation on a relatively warm, dry day for use in the zero-dimensional model study are given in Table I. The ten surrogate oxidation products shown in Figure 1 are used to represent SOA species, and the eight surrogate primary organics shown in the same figure are used to represent POA species.

3.1. EFFECT OF TEMPERATURE ON PARTITIONING

Temperature affects gas-particle partitioning through $K_{om,i}$, which includes the effect of temperature on vapor pressure, as shown in Equation (1). Henry's law constants and aqueous-phase dissociation equilibrium constants also depend on temperature, although more weakly than vapor pressure. Figure 2 shows the tem-

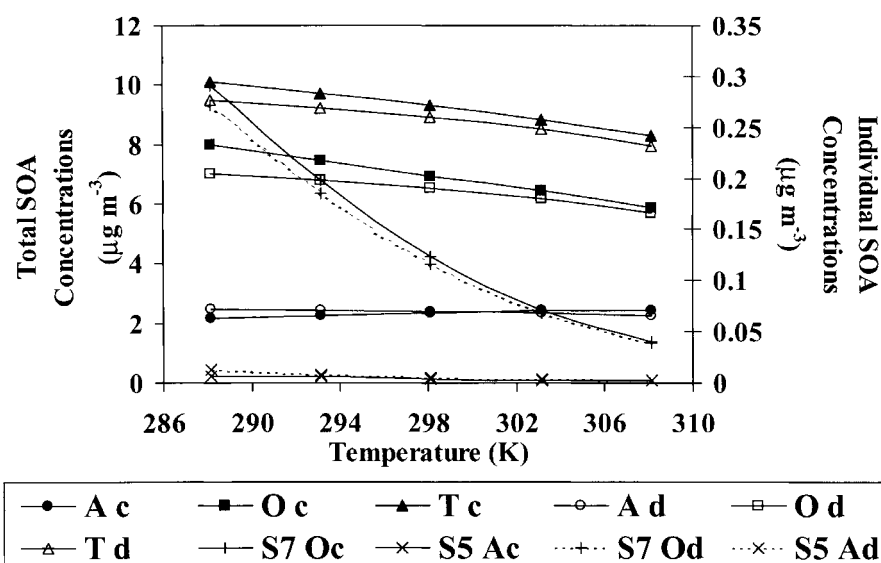


Figure 2. Particle-phase concentrations of total SOA (left axis) and two individual SOA constituents (S5 and S7) in individual phases (right axis) as a function of temperature with all other baseline variables held constant. T = total SOA (O + A), O = organic-phase SOA, A = aqueous-phase SOA, c = coupled module, d = decoupled module. T, O, and A concentrations represent the sum of all 10 partitioned species concentrations.

perature dependence of the total gas-particle partitioning, with all other baseline values (LWC, pH, etc.) held constant. Predictions show results similar to those of Sheehan and Bowman (2001). As expected, total aerosol-phase levels increase as temperature decreases, reflecting the strong influence of temperature on vapor pressure. Predictions of the MPMPO are compared to those of the decoupled model, with the MPMPO predicting a larger total aerosol-phase concentration than the decoupled model.

Figure 2 also shows the predicted phase distribution of condensable organics. While temperature has only a small effect on the aqueous-phase concentration of organics, the organic-phase concentration is highly sensitive to temperature. A greater preference for partitioning to the organic phase rather than the aqueous phase is exhibited with the fully coupled calculations than the decoupled calculations. This is intuitively reasonable since a greater number of species are allowed to partition to the organic phase in the coupled module and in general, compounds are more easily absorbed by species similar in nature to themselves. An interesting phenomenon of note is that the lines showing predicted total partitioning to the aqueous phase (Ac and Ad in Figure 2) cross as temperature varies. Because the Henry's Law's constants used in this model are not significantly affected by temperature, the aqueous partitioning in the decoupled model is essentially a flat line. However, the MPMPO predicts lower aqueous-phase SOA at lower temperatures because of the favorable partitioning to the organic phase at lower temperatures,

thereby decreasing the gas-phase concentration and subsequently that in the aqueous phase. As temperature increases, partitioning to the organic phase becomes less favorable, leading to an increase in the gas-phase concentration and a subsequent increase in the aqueous phase concentration because Henry's law must still be enforced.

Similar trends are observed in the partitioning trends of individual compounds (Figure 2). In the decoupled model, compound S5 is considered a hydrophilic compound and, therefore, is allowed to partition only to the aqueous phase. (See Figure 1 for species notation.) Conversely, S7 is considered a hydrophobic compound and is allowed to partition only to the organic phase. Figure 2 shows the organic-phase concentration of S7 and the aqueous-phase concentration of S5 for each module. The MPMPO generally predicts lower aqueous-phase concentrations and higher organic-phase concentrations relative to the decoupled module. The higher aqueous-phase concentrations predicted by the decoupled model result from not allowing relatively non-volatile (yet polar) compounds to partition to the organic aerosol phase. The hydrophobic compounds still partition primarily to the organic phase in the MPMPO. However, allowing the hydrophilic compounds to partition into the organic phase increases the organic phase concentrations and decreases the aqueous phase concentrations. Overall, the total amount of SOA predicted from individual species increases in the MPMPO since both mechanisms for partitioning are allowed.

3.2. EFFECT OF LWC ON PARTITIONING

Aerosol LWC is determined by the ambient RH, through the relationship between water activity, the product of water mole fraction and water activity coefficient, and RH (Seinfeld and Pandis, 1998). The effect of LWC on the distribution of organic aerosol constituents is evident in Equation (3).

As LWC increases, the capacity for the dissolution of organics increases: A_i increases as mass is drawn out of the gas phase, decreasing G_i , and causing a subsequent decrease in O_i in order to satisfy mass conservation and maintain gas-organic particle phase equilibrium. Therefore, in the MPMPO, the condensable organic species concentrations in both the organic aerosol phase and the aqueous aerosol phase are affected by the LWC (Figure 3). This phenomenon is not represented in the decoupled module, in which LWC does not affect the partitioning of hydrophobic organics to the organic aerosol phase. Thus, in Figure 3, the amount of SOA in the organic phase in a decoupled model (O_d) is independent of LWC. Total dissolved (in the aqueous phase) organics increase as LWC increases in both the MPMPO and the decoupled module, with the MPMPO showing a larger increase because a greater number of species are allowed to participate in the aqueous partitioning. These trends are most pronounced at smaller LWC values. Consistent with results shown in Figure 2, an overall increase in total condensed organic mass is observed in the MPMPO as compared to the decoupled module. Greater formation

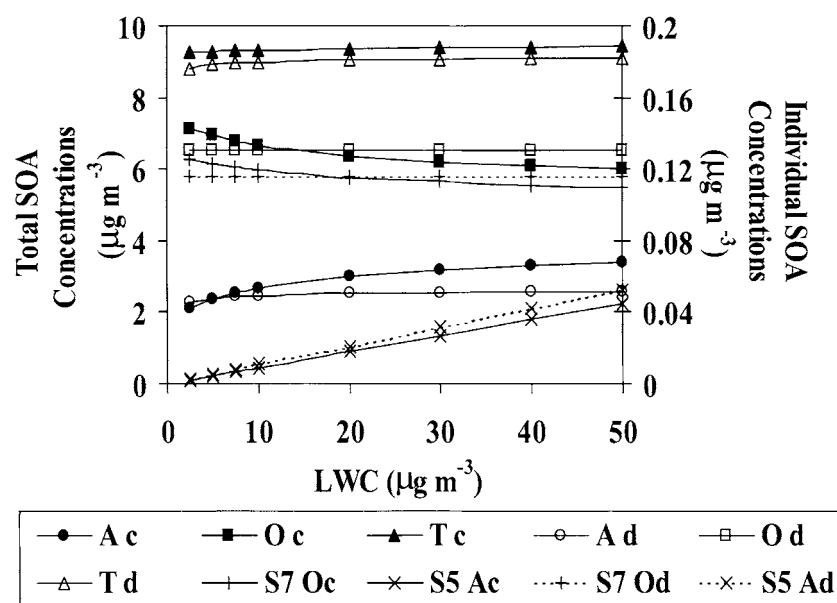


Figure 3. Particle-phase concentrations of total SOA (left axis) and two individual SOA constituents (S5 and S7) in individual phases (right axis) as a function of aerosol LWC with all other baseline variables held constant. T = total SOA (O + A), O = organic-phase SOA, A = aqueous-phase SOA, c = coupled module, d = decoupled module. T, O, and A concentrations represent the sum of all 10 partitioned species concentrations.

of SOA in the condensed organic phase compared to the aqueous phase is also observed in this case. Interestingly, the total amount of condensed organic material (sum of organic and aqueous phase aerosol material, solid triangles) is essentially independent of aerosol LWC. This is consistent with recent ambient observations in Pittsburgh, PA that show no strong correlation between total aerosol organic content and RH (S. N. Pandis, personal communication). An additional interesting phenomenon shown in Figure 3 is that the lines showing predictions of organic-phase SOA cross as LWC is varied. As stated above, the organic-phase SOA in the decoupled module is independent of LWC. In the MPMPO, partitioning to the organic phase is favored at low values of LWC, leading to O_c being greater than O_d . As LWC is increased, the capacity of organics to partition via aqueous dissolution increases, leading to a decrease in the corresponding gas-phase concentration and a subsequent decrease in O_c .

In the partitioning of individual compounds, it is seen that the effect of LWC depends on the compound and phase of interest (Figure 3). Species with large affinity for the aqueous phase (S5) show an almost linear increase in aqueous phase SOA partitioning as LWC increases in both the MPMPO and the decoupled module. However, there is a stronger dependence in the decoupled module in which no hydrophilic mass is allowed to partition to the organic phase. Conversely, those

species that partition primarily to the organic condensed phase (S7) experience the greatest effect of LWC at lower values of this variable in the MPMPO only.

3.3. EFFECT OF pH ON PARTITIONING

Aerosol aqueous-phase $[H^+]$ ($pH = -\log_{10}([H^+])$) is determined primarily by the amount of soluble inorganic electrolytes present. pH influences the quantity of organic species dissolving in the aqueous phase for dissociating organics through the equilibrium relations shown in Equations (6) and (7). Thus, pH determines the dominant form of an individual organic species (molecular or ionic) in the aqueous aerosol phase. An increase in pH results in an increase in the aqueous-phase concentration of dissociating organics, a phenomenon more pronounced in the MPMPO since a greater number of species are affected. Figure 4 shows the SOA concentrations of the aqueous and organic phases in the MPMPO and the decoupled module, as well as the total SOA concentrations. An example of individual product behavior, S7 in the organic aerosol phase, as a function of pH in the MPMPO is also exhibited in Figure 4. As in the case of increasing LWC, a decrease in the organic aerosol phase concentrations occurs at higher pH. For example, compound S7, which is described as hydrophobic in the decoupled model, shows this behavior. As pH increases, the organic-phase concentrations of species that dissociate must decrease due to the constraint of maintaining equilibrium among multiple phases. In the decoupled module, the concentration of S7 in the organic aerosol phase is independent of pH, as shown. Aqueous-phase dissolved organic concentrations are greatest at the highest values of LWC and pH. Conversely, at the lowest LWC and pH values, organic-phase concentrations are highest. However, total condensed organic concentrations are relatively independent of aerosol pH, and, as shown previously, are higher in the MPMPO.

3.4. EFFECT OF CONCENTRATION LEVELS ON GAS-PARTICLE PARTITIONING

As total available concentrations of partitioning species increase, both aqueous and organic phase concentrations increase since more material is available to partition. In addition, the presence of POA affects partitioning into the organic phase directly through the magnitude and chemical nature of M_o . (See Equations (1) and (2).) As the amount of POA is increased, organic partitioning species slightly decrease in concentration in the aqueous phase (Figure 5), an effect opposite to that when LWC is increased. When the amount of POA is increased, the concentration in the organic phase, O_i , increases, and A_i must accordingly decrease. This compensatory effect is not represented by the decoupled model as the aqueous phase is unaffected by the presence of primary organic material. Figure 5 exhibits behavior of SOA formation in an organic phase that is consistent with laboratory chamber data in which SOA formation is almost linear with respect to M_o at small values of M_o and approaches a constant value as M_o increases to greater and greater values

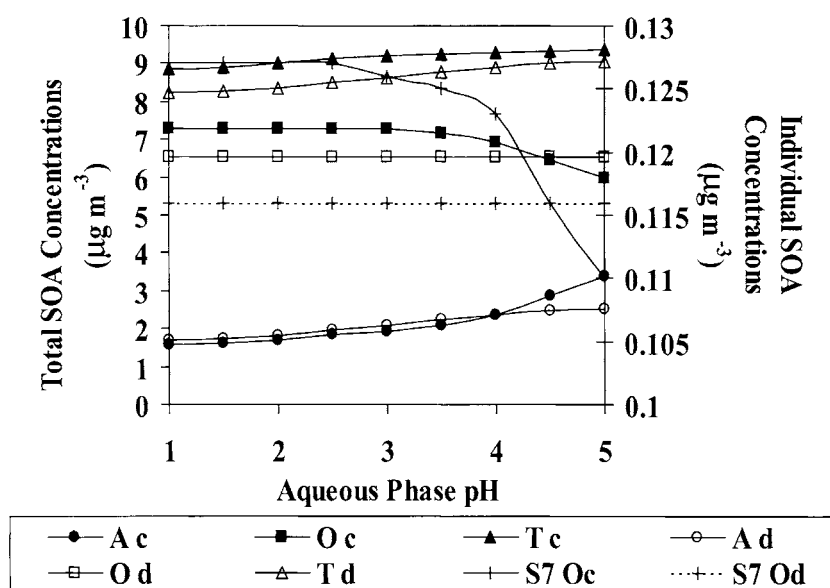


Figure 4. Particle-phase concentrations of total SOA (left axis) and organic particle-phase concentration of species S7 in the coupled module (right axis) as a function of aqueous phase pH with all other baseline variables held constant. T = total SOA (O + A), O = organic-phase SOA, A = aqueous-phase SOA, c = coupled module, d = decoupled module. S7 is considered hydrophobic in the decoupled module and is unaffected by pH in that case. T, O, and A concentrations represent the sum of all 10 partitioned species concentrations.

(Odum *et al.*, 1996, 1997; Hoffmann *et al.*, 1997; Griffin *et al.*, 1999; Cocker *et al.*, 2001). Figure 5 also shows an increase in total aerosol organics as POA increases, with the MPMPO again showing a slight increase in total SOA when compared to the decoupled module. It should be noted that in the cases of varying total POA concentrations discussed here, the chemical nature of the POA remains unchanged because the concentration of each individual POA species is multiplied or divided by the same factor.

To verify that the MPMPO predictions adhere to the fact that polar compounds are more likely to be absorbed by a polar POA mixture than a non-polar one, concentrations of individual POA species were also varied. Figure 6 shows how the chemical nature of POA influences partitioning in the MPMPO by varying the concentration of only one POA species. In part A, the concentration of primary organic P5 is varied by two orders of magnitude. (See Figure 1 for species notation.) The largest predicted organic-phase concentration occurs in the case in which the concentration of P5 is decreased by an order of magnitude; increase of the concentration of species P5 by a factor of 10 leads to the lowest organic-phase concentration. Correspondingly, the opposite trend is observed in the aqueous-phase concentrations of SOA. Compound P5 contains no functional groups, indicating that this lack of functional groups leads to an increase in the activity coefficients

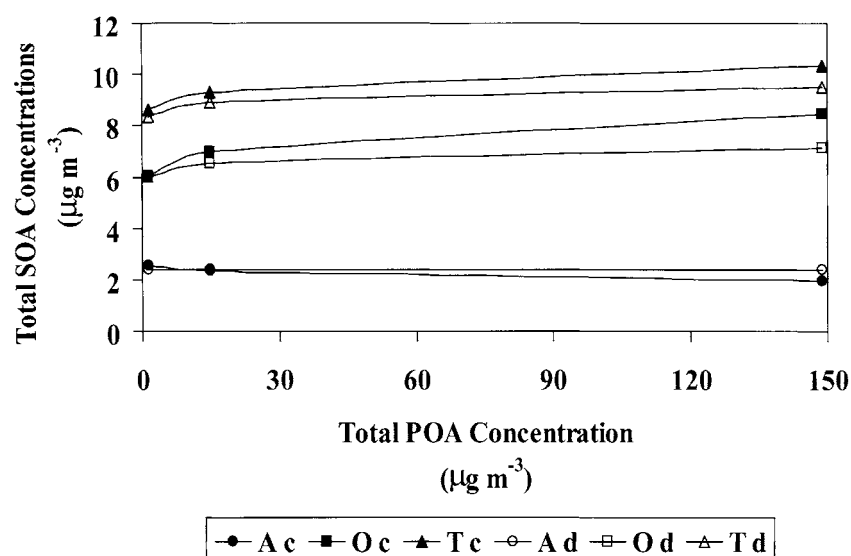


Figure 5. Particle-phase concentrations of SOA as a function of total POA concentration with all other baseline variables held constant. T = total SOA (O + A), O = organic-phase SOA, A = aqueous-phase SOA, c = coupled module, d = decoupled module. T, O, and A concentrations represent the sum of all 10 partitioned species concentrations.

in the condensed organic phase of the secondary partitioning species that contain functional groups. Part B shows similar calculations for compound P3. In this case, the lowest condensed organic-phase concentrations are predicted to occur when the concentration of P3 is decreased. Since species P3 is an oxygenated compound, its presence decreases the activity coefficients of oxygenated condensed species in the organic aerosol phase. The predicted behavior of species S7 in the organic aerosol phase is identical to that of the total SOA predictions.

3.5. CASE STUDIES SUMMARY

It has been shown that dividing gas-phase organic oxidation products into two groups (hydrophobic and hydrophilic) typically underpredicts SOA concentrations by preventing simultaneous SOA formation via absorption and dissolution. In considering the more than 50 individual test scenarios described in Sections 3.1–3.5, it is found that the decoupled module consistently underpredicts total SOA concentrations by approximately 7.6% relative to the MPMPO ($R^2 = 0.999$). In addition, the MPMPO accounts for phenomena such as the effect of POA on aqueous-phase partitioning of organic oxidation products and the effect of pH on organic-phase partitioning of species that dissociate within the aqueous phase.

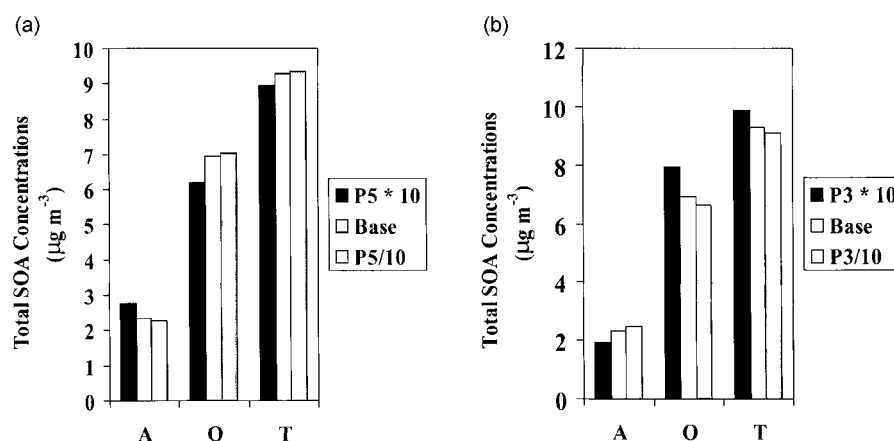


Figure 6. Particle-phase concentrations of SOA as a function of individual POA concentrations with all other baseline variables held constant in the coupled module. T = total SOA (O + A), O = organic-phase SOA, A = aqueous-phase SOA. (a) Variation of P5. (b) Variation of P3. T, O, and A concentrations represent the sum of all 10 partitioned species concentrations.

4. Implementation with Inorganic Aerosol Modules

The initialization of a typical aerosol equilibrium calculation in a chemical transport model requires meteorological information, such as temperature and RH, gas-phase concentrations of inorganic semi-volatile species, such as nitric acid, and particle-phase concentrations of non-volatile species. An inorganic equilibrium module such as SCAPE2 (Meng *et al.*, 1995) is used to determine LWC and aerosol pH based on these inputs. The MPMPO then determines the distribution of the organics between the gas phase and the two condensed phases (aqueous and organic); at this point the gas-phase concentrations of SOA constituents and the concentrations of POA species are also required. Next, water taken up due to the presence of the aqueous phase organics is estimated through the Zdanovskii–Stokes–Robinson method, as described by Meng *et al.* (1998) and Pun *et al.* (2002); SCAPE2 is called again to determine if the additional water and presence of organic anions affect the distribution of inorganic aerosol constituents. In this way, LWC is used as an iterative variable between the inorganic and organic aerosol thermodynamic modules.

5. Implementation into Three-Dimensional Atmospheric Chemical Transport Models

The organic partitioning module is linked to a gas-phase chemical mechanism that predicts the concentrations of semi- or non-volatile organic oxidation products. In the current application to the SoCAB, the Caltech Atmospheric Chemistry Mechanism (CACM) predicts spatially and temporally resolved concentrations of 42 species that are considered capable of forming SOA because of their solubilities or

low vapor pressures (Griffin *et al.*, 2002b). These secondary products are further lumped into one of the ten groups shown in Figure 1 (Pun *et al.*, 2002). After equilibrium calculations are performed, the gas-phase concentrations of the ten surrogate species are redistributed to the 42 CACM species so that they can participate in gas-phase chemistry, as described by Griffin *et al.* (2002a). When the partitioning model is employed in an atmospheric application, composition and concentration of the eight POA species are determined from POA emission inventories.

The MPMPO and the decoupled SOA module have been applied within the CIT model to simulate the air pollution episode of 8 September 1993 in the SoCAB (Griffin *et al.*, 2002a). Figure 7 shows the total (aqueous- plus organic-phase) four-hour average SOA concentrations simulated for four locations between 1200 and 1600 PST using both module applications. This figure shows the same general trends that are observed when investigating preliminary case studies using the zero-dimensional model. The MPMPO consistently predicts larger total SOA concentrations. Total SOA concentrations as a function of time in Central Los Angeles and Claremont are compared for the MPMPO and the decoupled module in Figure 8. The distinction between the two is most pronounced in the mid- to late afternoon, when concentrations of secondary organic species are expected to be greatest. Unfortunately, observations of secondary organic aerosol concentrations are unavailable for these dates and locations due to logistical and technical limitations. Total organic aerosol concentrations (SOA plus POA) predicted by the CIT model using MPMPO and the decoupled model are only slightly different because POA composition and concentration do not vary between the two applications; total organic aerosol concentrations match reasonably well observations of total organic aerosol, as exhibited in Griffin *et al.* (2002a). The MPMPO improves our ability to capture phenomenon potentially occurring in the aerosol phase.

6. Discussion

Secondary oxidation products of atmospheric VOCs often exhibit a variety of functional groups. Because such groups often lead to low vapor pressures and high polarities, such species are likely to partition simultaneously to organic and aqueous condensed phases. The coupled SOA prediction module described here theoretically predicts the phase distribution of secondary organic oxidation products by ensuring mass conservation and equilibrium among the various phases. Compared to previous predictions in which only the more dominant partitioning mechanism is allowed to occur for an individual product, the work presented here shows that higher concentrations of total SOA are predicted when allowing for both mechanisms to occur simultaneously. In addition, this work corroborates the hypothesis that partitioning to an absorptive organic phase (termed the hydrophobic mechanism in the decoupled module) is the dominant mechanism for atmospheric SOA formation (Pankow, 1994; Liang *et al.*, 1997; Mader and Pankow, 1999).

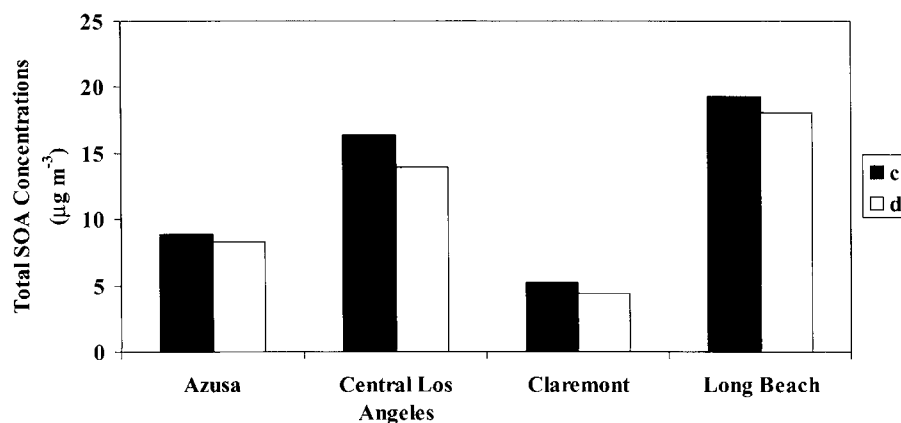


Figure 7. A comparison of the predicted total (organic- plus aqueous-phase) four-hour average concentration of SOA simulated by the three-dimensional California Institute of Technology atmospheric model between 1200 and 1600 PST on 8 September 1993 when the coupled (c) and decoupled (d) modules are implemented. Four locations are shown: Azusa; Central Los Angeles; Claremont; and Long Beach.

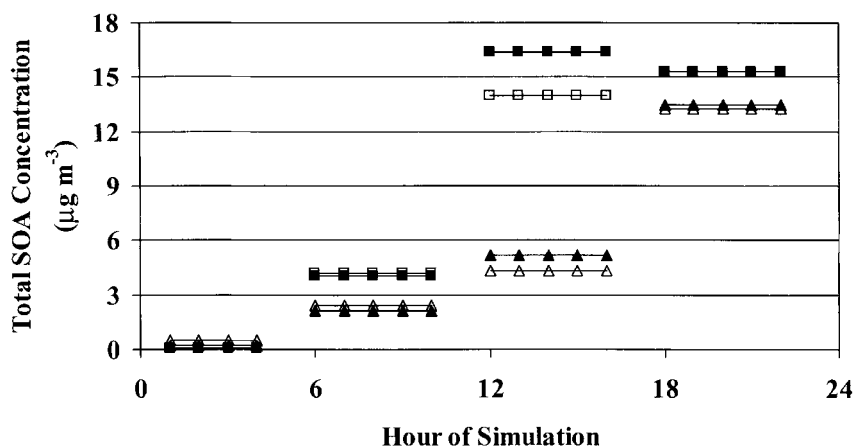


Figure 8. Four-hour average total (organic- plus aqueous-phase) SOA predictions as a function of time on 8 September 1993 in Central Los Angeles (squares) and Claremont (triangles) when the coupled (filled) and decoupled (open) modules are implemented into the three-dimensional California Institute of Technology atmospheric model.

The MPMPO improves the capability to simulate atmospheric PM by accounting for multiple mechanisms leading to SOA. Increasing POA leads to decreased aqueous-phase partitioning of secondary oxidation products; this phenomenon is not observed in a decoupled module. In addition, the effect of pH on the organic phase (hydrophobic) partitioning is not observable in a decoupled module. Like its predecessor (Pun *et al.*, 2002), the module described here still ignores explicit interactions between inorganic and organic ions in the aqueous phase. Such treatment awaits future developments in the thermodynamic theory of organic-

water-electrolyte systems. However, given the uncertainties and errors in chemical parameters, meteorological inputs, and observed data for this type of modeling, the performance of the MPMPO is extremely good given our current understanding of SOA formation.

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Appendix: Numerical Algorithm

The Newton–Raphson scheme to solve non-linear equations failed to provide convergent solutions for the majority of cases studied in this research. The successful method used to solve the equilibrium equations is based on a homotopy morphing (Baues, 1989) in conjunction with the Newton–Raphson scheme. A homotopy morphing uses the solution of a simple system to converge incrementally into the solution of a complex system. The method presented here can be employed in other atmospheric chemical equilibrium problems when traditional algorithms fail.

The equilibrium equations, (1) to (7), represent the concentrations of the secondary organic-phase aerosol and the secondary aqueous-phase organic aerosol that minimize the Gibbs free energy. The Gibbs free energy depends parametrically on the set $\sigma = \{T, \mathbf{c}, \mathbf{p}, \text{LWC}, [\text{H}^+]\}$, where $\mathbf{c}$ and $\mathbf{p}$ are the vectors of total concentrations of SOA species and POA species, respectively. T , LWC and $[\text{H}^+]$ are the temperature, liquid water content, and proton concentration respectively. Let $\mathbf{x}$ be the equilibrium concentration vector, then the equilibrium conditions form a constrained system of nonlinear equations

$$\mathbf{S}(\mathbf{x}^*; \sigma) = \mathbf{0}. \quad (\text{A1})$$

Namely, the system, $\mathbf{S}$, reaches equilibrium when $\mathbf{x} = \mathbf{x}^*$. The equilibrium concentration vector, $\mathbf{x}^*$, also depends on σ . In order to solve for $\mathbf{x}^*$, an initial guess of $\mathbf{x} = \mathbf{0}$ starts the iterations of the Newton–Raphson scheme

$$\mathbf{x}^{n+1} = \mathbf{x}^n - \mathbf{J}^{-1} \mathbf{S}(\mathbf{x}^n; \sigma). \quad (\text{A2})$$

The Jacobian, $\mathbf{J}$, is computed by a central difference. Although a forward or backward difference is more efficient, first-order approximations do not provide the necessary accuracy.

A homotopy morphing is applied for cases when the Newton–Raphson scheme fails to converge. In this paper the following homotopy is applied,

$$\mathbf{H}(\lambda) = \mathbf{S}(\mathbf{x}; \boldsymbol{\sigma}_{ideal} + 4^{1-\lambda}(\boldsymbol{\sigma}_{actual} - \boldsymbol{\sigma}_{ideal})), \quad (\text{A3})$$

where $\boldsymbol{\sigma}_{ideal} = \{\mathbf{T}_{ideal}, \mathbf{c}^{ideal}, \mathbf{p}^{ideal}, \text{LWC}_{ideal}, [\text{H}^+]_{ideal}\}$. $\boldsymbol{\sigma}_{actual}$ are the conditions where the equilibrium solution is desired (i.e., the conditions of the complex problem). $\boldsymbol{\sigma}_{ideal}$ are the conditions where the solution to the equilibrium problem is known. In this work, the ideal case, $\boldsymbol{\sigma}_{ideal}$, is set to the convergent case obtained from the previous time step. λ is the morphing variable that connects the simple problem to the complex problem. When $\lambda = 1$, the solution to $\mathbf{H}(\lambda) = 0$ is also the solution to Equation (A1). When $\lambda \gg 1$, the solution to $\mathbf{H}(\lambda) = 0$ is simple to attain since $\mathbf{H}(\lambda) \approx \mathbf{S}^*(\mathbf{x}, \boldsymbol{\sigma}_{ideal})$. The morphing starts with $\lambda = 1$ and increases until a convergent case is found. Once a convergent case is found, λ is then permitted to decrease back to one. For example, suppose a solution is found with $\lambda = 10$. That solution is then be used as an initial guess to the system when $\lambda = 9.9$. The solution for $\lambda = 9.9$ is then used for the initial guess for $\lambda = 9.8$ and so on. The simulations performed by this research have found that the convergence of Equation (A1) is essentially guaranteed with the aid of the homotopies.

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