

PREDICTION OF AEROSOL OPTICAL PROPERTIES IN CANBERRA ACT

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Summary

Prediction of aerosol particle optical properties, as a function of relative humidity, is an essential step in modelling the visual impact of aerosol from observed or modelled chemical composition. In this paper we discuss some results of thermodynamically modelling the optically-active component of the Canberra winter aerosol, using size dependent chemical data obtained during a field campaign in 1997. Results from this modelling are presented for the dry and hydrated aerosol. Refractive indices from this study are in good agreement with other studies which demonstrates a potential applicability of this approach to the refractive index estimation of aerosols.

Keywords: Tropospheric Aerosols, Refractive Index, Thermodynamic Model, SCAPE2

1. Introduction

Ambient aerosols are known to have significant effect on human health, air quality and visibility degradation. In the past, numerous studies investigated the role of aerosols on visibility degradation, and the focus in recent years has been to assess and estimate the role of individual chemical species in visibility degradation. The prediction of refractive index from size-resolved chemical data is an essential step towards the determination of scattering and absorption of light by fine particles (Tang *et al.*, 1981; Sloane, 1983, 1984). It has been demonstrated that the mean refractive index of any common ambient urban aerosol chemical composition can be accurately predicted by the Partial Molar Refraction approach (Stelton, 1990). The Partial Molar Refraction approach is a weighed summation of molar refraction of individual species present in a chemical system concerned.

While the composition of aerosol is temporally and spatially variable, it is generally believed that the major chemical constituents of aerosols are water, sulphates, ammonium, nitrates, chlorides, sodium, crustal elements, organic carbon (OC), elemental carbon (EC) or soot and various trace elements. It has been reported that carbonaceous aerosols typically consist of 25-50% of total fine aerosol mass and the rest is inorganic salts and trace elements (Gray *et al.*, 1986; Heintzenberg, 1989; Vasconcelos *et al.*, 1994).

Accurate prediction of water content and the state of individual species in aerosol is an essential step towards the accurate prediction of refractive index of ambient aerosol. Major gas-aerosol atmospheric aerosol models include EQUIL (Bassett & Seinfeld, 1983), KEQUIL (Bassett & Seinfeld, 1984), MARS (Saxena *et al.*, 1986), SEQUILIB (Pilinis & Seinfeld, 1987), AIM (Wexlar &

Seinfeld, 1991), SCAPE (Kim *et al.*, 1993a, 1993b; Kim *et al.*, 1995; Meng *et al.*, 1995) and SCAPE2 (Saxena *et al.*, personal communication). The differences between these models include the species treated, the thermodynamic approach employed and the computational approach used (Kim *et al.*, 1995). Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) and SCAPE2 are the most recent development in gas-aerosol equilibrium models. In addition to sulphate, nitrate and ammonium, SCAPE and SCAPE2 can treat species such as sodium, chloride, potassium, calcium, magnesium and carbonate. The inclusion of these crustal elements and carbonate is an improvement over other thermodynamic models as soil or mineral dust is rich in alkaline species and a considerable fraction of crustal elements exist as form of carbonate (Kim *et al.*, 1995; Meng *et al.*, 1995).

The objective of this study is to use thermodynamic modelling to calculate refractive indices by the Partial Molar Refraction approach. We present the results of applying the SCAPE2 model to size dependent aerosol chemical data obtained during a field campaign in Canberra, winter 1997. Estimated refractive indices will be presented.

2. Description of Physical Model

2.1. Estimation of Refractive Index

The molar refractivity of sample, R_m , is normally expressed as

$$R_m = V_m \left(\frac{n_r^2 - 1}{n_r^2 + 2} \right) \quad V_m = \sum \frac{x_i M_i}{\rho} \quad (1)$$

Where V_m is the molar volume in cm^3/mol , n_r is the refractive index, x_i is the molar fraction of species i , M_i is the molecular weight of species i in g/mol and ρ is the density of the phase concerned in g/cm^3 (Moelwyn-Hughes, 1961). The molar refraction of mixture can be estimated by summation of the partial molar refraction value, R_i

$$R_m = \sum x_i R_i \quad (2)$$

After calculating the molar refractivity by summing up the various contributions, we can estimate the refractive index of the sample by

$$n_r = \left(\frac{V_m + 2R_m}{V_m - R_m} \right)^{\frac{1}{2}} \quad (3)$$

For the ambient aerosol, the evaluation of refractive index for both electrolytes and ionic solids may be needed since inorganic salts can exist in both the solid and liquid phase depending on the relative humidity. It has been suggested that the partial molar refraction for the electrolytes can be considered equivalent to that of the ionic solid (Stelton, 1990).

2.2. Thermodynamic Model

2.2.1. Estimation of Activity

For an ideal solution the chemical potential of a component can be expressed as a function of concentration.

$$\mu_i = \mu_i^0 + RT \ln \frac{m_i}{m^0} \quad (4)$$

where μ_i is the chemical potential or partial molar free energy of species i , μ_i^0 is the chemical potential at standard state, m_i is the molality of species i and m^0 is 1 mol/kg.

Such ideal behaviour assumes that there is no interaction between the individual components of the solution. For neutral species, such as dissolved gases or undissociated molecules of dilute solution, there is little interaction so ideal behaviour can be assumed. However, for electrolytes in multicomponent solutions such as ambient aerosol, the changes in the ionic component can interact at quite low concentration ($\sim 10^{-3}$ M) leading to non-ideal behaviour. For a non-ideal solution, chemical potential is related to the effective concentration known as activity, a_i , in solution rather than the stoichiometric amount of component.

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (5)$$

The concentration and activity are related by the activity coefficient, γ_i .

$$a_i = \gamma_i \frac{m_i}{m^0} = \gamma_i m_i \quad (6)$$

The chemical potential of non-ideal solution is then,

$$\mu_i = \mu_i^0 + RT \ln \gamma_i m_i \quad (7)$$

At equilibrium, the slope of reaction, Gibbs free energy of the system, ΔG , is zero (Atkins, 1992), so that the activities have their equilibrium values

$$\Delta G_r = \sum_i v_{ij} \mu_i = 0 \quad (8)$$

where v_i is the stoichiometric coefficient of i th species in the j th reaction, μ_i is the chemical potential of species i .

By substituting equation (5) into (8), we yield

$$\sum_i v_{ij} \mu_i^0 + RT \ln \prod_i a_i^{v_{ij}} = 0 \quad (9)$$

Therefore

$$\exp\left(-\frac{1}{RT}\right) \sum_i v_{ij} \mu_i^0 = \prod_i a_i^{v_{ij}} \equiv K_j \quad (10)$$

where v_i is the stoichiometric coefficient of i th species in the j th reaction, μ_i is the chemical potential of species i and K_j is the thermodynamic equilibrium constant of the j th reaction (Kim *et al.*, 1993a). By substituting a_i by equation (6), equation (10) becomes

$$K_j = \prod_i (\gamma_i m_i)^{v_{ij}} \quad (11)$$

By accurately predicting activity coefficients an equilibrium concentration can be calculated accurately at given K values (Kim *et al.*, 1993a).

There are several methods to estimate activity coefficients for aerosols. The most straightforward approach involves a mixing rule of some kind. This approach predicts the activity coefficient of solutes, and the solvent activity by averaging the value of the individual components at the total ionic strength of the mixture concerned. The Bromley (Bromley, 1973) and the K-M method (Kusik & Meissner, 1978) are widely used mixing rules in aerosol thermodynamic models.

The K-M method proposes that in any specific electrolytes identified by cation i and anion j

$$\ln \gamma_{ij}^{\frac{1}{Z_i Z_j}} = \frac{Z_i}{I_T (Z_i + Z_j)} (V_{i2} I_2 \ln \gamma_{i2}^{\frac{1}{Z_i^2}} + V_{i4} I_4 \ln \gamma_{i4}^{\frac{1}{Z_i^4}} + \mathbf{L}) + \frac{Z_j}{I_T (Z_i + Z_j)} (V_{j1} I_1 \ln \gamma_{j1}^{\frac{1}{Z_j^2}} + V_{j3} I_3 \ln \gamma_{j3}^{\frac{1}{Z_j^4}} + \mathbf{L}) \quad (12)$$

where γ and γ^0 is the mixed and pure solution mean ionic activity coefficient for the electrolyte indicated by the subscript respectively, Z is the absolute number of unit charges on the ion species indicated by the subscript, I is the ionic strength of species indicated by the subscript, I_T is the total ionic strength, V is the weighting factor $0.5(Z_i + Z_j)^2 / (Z_i Z_j)$ of the species indicated by the subscript (Kusik & Meissner, 1978).

The advantage of a mixing rule is that it is relatively simple. The alternative approach widely used in aerosol modelling is to use an ion interaction model to estimate activity coefficients, such as the Pitzer method (Pitzer & Simonson, 1986). The Pitzer method is potentially more accurate due to its rigorous thermodynamic treatment. The Pitzer method is derived from the definition of excess Gibbs free energy. In general, the ion interaction model takes the form

$$\ln \gamma_i = \ln \gamma_{DH} + \sum_j B_{ij} X_j + \sum_j \sum_k C_{ijk} X_j X_k + \mathbf{L} \quad (13)$$

where γ_i is the activity coefficient of species i , γ_{DH} is the activity coefficient given by Debye-Hückel equation (Limiting Law), X_j and X_k are the molar concentrations of given species j and k which interact with i and B_{ij} and C_{ijk} are the interaction or virial coefficients obtained by fitting data (Stumm & Morgan, 1981). The limitation of the Pitzer method is that it cannot deal with ionic strengths of greater than 30 which limits its application to ambient aerosols at low humidity.

In SCAPE and SCAPE2, the Bromley, K-M and Pitzer methods can be switched by option.

3. Sampling and Analysis

3.1. Sample Collection

Samples were collected at the Environment ACT Air Quality Monitoring site at Monash in the Tuggeranong Valley on 4 May, 16 May and 3 June 1997 for 24 hours duration (from midnight to midnight for 4 and 16 May, and from 3 June 10:22 AM to 4 June 10:22 AM for 3 June). The samples were collected by a 12 stage MOUDI (Micro-Orifice Uniform Deposit Impactor), operated at the design flow rate of 30 l/min (Marple *et al.*, 1991). Polycarbonate Poretics filters, 47 mm in diameter with 0.4 μm pore size, were used on the first 11 stages (Inlet to stage 10) and a teflon-backed Fluoropore filter 37 mm in diameter with 1 μm pore size was used on the back-up stage.

3.2. Sample Analysis

Mass and the determination of EC, Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , NO_3^- , SO_4^{2-} , Br^- , NO_2^- , PO_4^{3-} , F, acetate, formate, oxalate and methanesulfonic acid (MSA) from the MOUDI filters were performed at CSIRO Atmospheric Research. Gravimetric mass was determined using a Mettler MT2 microbalance at a relative humidity of less than 20%. Elemental carbon (EC) concentration was determined by light absorption at the wavelength of 565 nm using the integrated plate method (Lin *et al.*, 1973). The instrumentation was calibrated for the elemental carbon by using an aerosol made of pyrolysed acetylene, which produced a specific mass absorption of 10.4 m^2/g (Gras 1996). The concentrations of soluble species were measured by Dionex DX500 suppressed ion chromatography

equipped with Dionex columns, (AS11 column and ARS1 suppressor for anions and CS12 column and CRS1 suppressor for cations).

Chemical mass concentration data derived from the MOUDI stages were inverted using an efficient, non-linear iterative inversion procedure (Twomey & Zabalsky, 1981; Winklmayr *et al.*, 1990) to yield a smooth size distribution.

3.2. Data Analysis

The SCAPE2 model with the KM method for the determination of thermodynamic equilibrium was chosen over the Pitzer method in order to deal with low humidity and high ionic strength. The inverted size resolved chemical mass concentration data were amalgamated from 72 size bins to 12 size bins by taking geometric means. Input species for SCAPE2 are Na^+ , SO_4^{2-} , NH_4^+ , NO_3^- , Cl^- , K^+ , Ca^{2+} , Mg^{2+} , and CO_3^{2-} . The concentration of H_2CO_3 was derived from an annual average CO_2 of 356.2 ppm at Cape Grim in 1994 (Steele *et al.*, 1996). Relative humidities of 20% for the dry

Table 1. Density and Refractive Index Values for Output Species

Species	Density (g/cc)	Refractive Index	Ref.
$(\text{NH}_4)_2\text{SO}_4$	1.77	1.52	1
$(\text{NH}_4)_2\text{H}(\text{SO}_4)_2$	2.30	1.53-0.005i	3
H_2CO_3	2.30	1.53-0.005i	3
H_2SO_4	1.84	1.42	2
$\text{Ca}(\text{HCO}_3)_2$	2.30	1.53-0.005i	3
$\text{Ca}(\text{NO}_3)_2$	2.23	1.50	2
CaCl_2	2.15	1.40	2
CaCO_3	2.83	1.66	1
CaSO_4	2.96	1.58	1
HCl	1.19	1.53-0.005i	3
HNO_3	1.67	1.47	2
K_2CO_3	2.20	1.53-0.005i	3
K_2SO_4	2.66	1.49	2
KCl	1.99	1.49	1
KHCO_3	2.17	1.53-0.005i	3
KHSO_4	2.32	1.49	2
KNO_3	2.11	1.51	2
$\text{Mg}(\text{HCO}_3)_2$	2.30	1.53-0.005i	3
$\text{Mg}(\text{NO}_3)_2$	2.30	1.51	2, 3
MgCl_2	2.33	1.51	2
MgCO_3	3.05	1.74	1
MgSO_4	2.66	1.46	1
Na_2CO_3	2.54	1.51	1
Na_2SO_4	2.70	1.48	1
NaCl	2.17	1.54	2
NaHCO_3	2.20	1.53-0.005i	3
NaHSO_4	1.78	1.53-0.005i	3
NaNO_3	2.26	1.59	2
$(\text{NH}_4)_2\text{CO}_3$	2.30	1.53-0.005i	3
NH_4Cl	1.52	1.64	2
NH_4HCO_3	1.59	1.53-0.005i	3
NH_4HSO_4	1.78	1.53-0.005i	3
NH_4NO_3	1.72	1.55	2
Water	1.00	1.33	1
Organic Species	1.40	1.55	3
Elemental Carbon	2.25	1.96-0.66i	4

1. CRC handbook of chemistry, 78th ed., 1997-1998, Editor Lide.

2. International Critical Tables of Numerical Data; Physics Chemistry and Technology, Volume 1, 1926, Editor Washburn.

3. Larson *et al.*, 1988

4. Bergstrom, 1973

Table 2. Aerosol Geometric Mean Diameter and Estimated Refractive Index

Geometric mean diameter (μm)	Refractive Index					
	4/5/97 20%	4/5/97 80%	16/5/97 20%	16/5/97 80%	6/3/97 20%	3/6/97 80%
0.0149	1.64-0.09i	1.54-0.06i	1.64-0.09i	1.57-0.06i	1.62-0.10i	1.59-0.05i
0.0294	1.62-0.07i	1.49-0.01i	1.62-0.07i	1.53-0.03i	1.57-0.04i	1.54-0.02i
0.0581	1.63-0.08i	1.50-0.03i	1.63-0.08i	1.59-0.06i	1.66-0.16i	1.57-0.05i
0.115	1.68-0.13i	1.58-0.08i	1.68-0.13i	1.62-0.10i	1.66-0.15i	1.62-0.09i
0.227	1.64-0.09i	1.59-0.09i	1.64-0.09i	1.59-0.08i	1.58-0.05i	1.58-0.03i
0.449	1.57-0.03i	1.53-0.05i	1.57-0.03i	1.51-0.02i	1.55-0.02i	1.55-0.01i
0.886	1.57-0.02i	1.52-0.04i	1.57-0.02i	1.49-0.01i	1.55-0.01i	1.55-0.01i
1.752	1.57-0.03i	1.48-0.03i	1.57-0.03i	1.52-0.02i	1.55-0.02i	1.55-0.01i
3.462	1.57-0.02i	1.45-0.01i	1.57-0.02i	1.54-0.02i	1.57-0.05i	1.56-0.03i
6.841	1.56-0.02i	1.45-0.01i	1.56-0.02i	1.53-0.01i	1.59-0.08i	1.57-0.03i
13.520	1.57-0.03i	1.47-0.02i	1.57-0.03i	1.54-0.01i	1.59-0.08i	1.56-0.03i
26.718	1.61-0.07i	1.52-0.04i	1.61-0.07i	1.57-0.02i	1.54-0.04i	1.58-0.05i

Table 3. Comparison of Mean Refractive Index from Other Studies

Location	Refractive Index	Ref.
Calgary, Canada	1.53 \pm 005	Matai & Harrison, 1980
Los Angeles Basin, CA	1.50	Ensor <i>et al.</i> , 1972
Los Angeles Basin, CA	1.43 \pm 0.02 min	Stelton, 1990
	1.47 \pm 0.03 max	
Tyson, MO	1.55 \pm 003	Bhardwaja <i>et al.</i> , 1974

aerosols and 80% for the ambient aerosols were assumed, and temperature was assumed to be 298K. The thermodynamic equilibrium calculation was performed on each size bin for both dry and ambient aerosols. The SCAPE2 outputs the concentration of species in both liquid phase and solid phase. In this work, however, we concentrate on the refractive index and density calculation. The output species from SCAPE2 are $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, H_2CO_3 , H_2SO_4 , $\text{Ca}(\text{HCO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, CaCl_2 , CaCO_3 , CaSO_4 , HCl , HNO_3 , K_2CO_3 , K_2SO_4 , KCl , KHCO_3 , KHSO_4 , KNO_3 , $\text{Mg}(\text{HCO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, MgCl_2 , MgCO_3 , MgSO_4 , Na_2CO_3 , Na_2SO_4 , NaCl , NaHCO_3 , NaHSO_4 , NaNO_3 , $(\text{NH}_4)_2\text{CO}_3$, NH_4Cl , NH_4HCO_3 , NH_4HSO_4 , NH_4NO_3 , and water.

Organic mass is calculated from a gravimetric mass analysis, elemental carbon concentration analysis and inorganic concentration analysis. It is assumed that organic mass concentration is:

$$[\text{Organic Mass}] = [\text{Gravimetric Mass}] - [\text{Inorganic Mass}] - [\text{Elemental Carbon}] \quad (14)$$

The densities and refractive indices of chemical species concerned in this study are shown in Table 1. The molecular weight and density of organic species are assumed to be 84.0 g/mol and 1.40 g/cm³ respectively (Stelton, 1990; Larson *et al.*, 1988). The density and refractive index of some species not found in the literature are assumed to have a density and refractive index of 2.30 g/cm³ and 1.53-0.005i respectively (Larson *et al.*, 1988). A partial molar refraction and partial molar volume of species are calculated from the concentrations of the output species of SCAPE2 and Table 1 for each size bin. Successful summation of partial molar refraction, R_i , of individual species yields the molar refraction of a mixture, and hence the refractive index

Table 4. The Density of Aerosol and Geometric Mean Diameter

Geometric diameter (μm)	4/5/97 20%	4/5/97 80%	16/5/97 20%	16/5/97 80%	6/3/97 20%	3/6/97 80%
0.0149	1.64	1.85	1.67	1.82	1.62	1.82
0.0294	1.75	2.18	1.66	1.98	1.52	1.93
0.0581	2.27	1.90	1.66	1.80	1.79	2.12
0.115	2.26	1.69	1.78	1.82	1.71	1.75
0.227	1.63	1.62	1.69	1.66	1.53	1.54
0.449	1.57	1.50	1.57	1.47	1.46	1.46
0.886	1.57	1.52	1.54	1.44	1.44	1.44
1.752	1.95	1.92	1.53	1.50	1.48	1.58
3.462	2.11	1.98	1.58	1.82	1.60	1.94
6.841	2.12	2.00	1.62	1.93	1.76	2.18
13.520	2.11	2.00	1.67	2.04	1.74	2.14
26.718	1.59	1.86	1.70	1.97	2.23	2.16

for each size bin can be estimated. The results are shown in Table 2.

4. Discussion

The applicability of this approach was tested for the Canberra winter-time aerosol data. Several issues need to be addressed in order to apply this method for refractive index prediction. First, the estimation of density and refractive index for organic species and elemental carbon varies greatly in the literature (Horvath, 1993). The evaluation of these data is required since the mass concentration fraction of elemental carbon and organic species is much larger than that of inorganic species. Second, trace metals from soils and rocks such as silicates, alumina and lead oxides are not included in the refractive index estimation which brings an uncertainty to the estimation. Third, refractive index and density of some species are assumed. While these species are only a small fraction of aerosol in this study (usually less than 5% of the total molar concentration) this problem needs to be addressed in future work.

The results from the model predictions show that the smaller aerosol tends to have higher refractive indices, with a maximum refractive index observed in particles 0.1 μm in diameter (Table 2). Table 3 contains the refractive indices calculated in previous studies, that used the partial refraction approach (Stelton, 1990) and light scattering (Matai & Harrison, 1980; Ensor *et al.*, 1972; Bhardwaja *et al.*, 1974). The refractive indices from the present study are in reasonable agreement with both scattering and the partial molar refraction approach

data. A more rigorous assessment of the refractive indices calculated in the present modelling study, will involve comparison with aerosol scattering coefficients, for dry and hydrated aerosol, measured using nephelometers and calculated from the particle size distribution during the field campaign. This assessment is currently in progress.

The density of aerosol for each size bin is shown in Table 4. A minimum value of 1.44 g/cm³ and a maximum value of 2.27 g/cm³ are estimated. A bimodal distribution is observed for the density which may correspond to the size distribution of chemical species.

5. Conclusion

This study demonstrates the use of a thermodynamic model (SCAPE2) as pre-treatment for the estimation of mean aerosol refractive index. The use of this thermodynamic equilibrium model is potentially useful for the accurate prediction of refractive index of ambient aerosol. Good agreement is demonstrated with the refractive indices from other studies which indicates a potential capability of this approach. Future work includes checking the applicability of this approach using aerosol scattering coefficient data derived from nephelometer measurements for dry and hydrated aerosol which were acquired at same time as the chemical composition data.

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