Water-Soluble Organics in Atmospheric Particles: A Critical Review of the Literature and Application of Thermodynamics to Identify Candidate Compounds

PRADEEP SAXENA* and LYNN M. HILDEMANN
Environmental and Water Studies Program, Department of Civil Engineering, Stanford University, Stanford, CA 94305-4020, U.S.A.

Abstract. Although organic compounds typically constitute a substantial fraction of the fine particulate matter (PM) in the atmosphere, their molecular composition remains poorly characterized. This is largely because atmospheric particles contain a myriad of diverse organic compounds, not all of which extract in a single solvent or elute through a gas chromatograph; therefore, a substantial portion typically remains unanalyzed. Most often the chemical analysis is performed on a fraction that extracts in organic solvents such as benzene, ether or hexane; consequently, information on the molecular composition of the water-soluble fraction is particularly sparse and incomplete.

This paper investigates theoretically the characteristics of the water-soluble fraction by splicing together various strands of information from the literature. We identify specific compounds that are likely to contribute to the water-soluble fraction by juxtaposing observations regarding the extraction characteristics and the molecular composition of atmospheric particulate organics with compound-specific solubility and condensibility for a wide variety of organics. The results show that water-soluble organics, which constitute a substantial fraction of the total organic mass, include C2 to C7 multifunctional compounds (e.g., diacids, polyols, amino acids). The importance of diacids is already recognized; our results provide an impetus for new experiments to establish the atmospheric concentrations and sources of polyols, amino acids and other oxygenated multifunctional compounds.

Key words: organic particle composition, water-soluble organics, hygroscopic organics, Henry's law constants, organic solubility, polyols, multifunctional compounds.

1. Introduction and Purpose

Over the continents, organic compounds constitute a substantial portion of the fine (aerodynamic diameter $\leq$ 2.5 μm) particulate matter (PM) suspended in the lower troposphere. For instance, over the continental U.S., organics typically account for 20 to 50% of the total fine mass and are often the second largest component after sulfate or nitrate (Gray *et al.*, 1986; White, 1990; Sloane *et al.*, 1991; Sisler and Malm, 1994; Vasconcelos *et al.*, 1994; Meng *et al.*, 1995). However, in comparison to sulfate and nitrate, the composition of atmospheric particulate organics remains murky because organics are far more difficult to sample and ana-

---

* Now at Electric Power Research Institute, Palo Alto, California.

lyze (Cadle *et al.*, 1983; Turpin *et al.*, 1994, 1996; McMurry *et al.*, 1996), and the analytical techniques for measuring the molecular or functional group composition are resource-intensive. Yet molecular composition is important from the standpoint of understanding the sources of particulate organics; their impact on human health upon inhalation; wet scavenging of atmospheric particles; and the role of particulate organics in the formation of hazes and the modulation of earth's radiative balance.

The available evidence indicates that organic PM contains hundreds of compounds that cover a wide range of carbon numbers, functional groups, solubility in extraction media, and elution rates in gas chromatographs (GC) (e.g., Duce *et al.*, 1983; Finlayson-Pitts and Pitts, 1986; Graedel *et al.*, 1986; Helmig *et al.*, 1990). As a consequence, concentrations of only a minority of individual compounds (typically 10% or less of the total organic mass) have been quantified through chemical analysis of extracts using gas chromatography with mass spectrometry (GC/MS) (Finlayson-Pitts and Pitts, 1986; Rogge *et al.*, 1993a). Most often the chemical analysis is performed on a fraction that extracts in relatively nonpolar organic solvents such as benzene, ether, hexane or cyclohexane (Wauters *et al.*, 1979; Mazurek *et al.*, 1987) and hence information on the molecular composition of the more polar and potentially water-soluble organic PM is particularly sparse. Recent empirical studies find that some of the organic compounds in atmospheric particles absorb water (Novakov and Penner, 1993; Saxena *et al.*, 1995); thus, a need exists for better characterization of this presumably water-soluble fraction.

Experimental studies test, explicitly or implicitly, *a priori* hypotheses about the molecular composition: the compounds being sought govern the choice of the analytical method and signal processing procedures. Our paper represents a theoretical effort to create tenable hypotheses that can be tested by subsequent experiments. Specifically, our objective is to propose a list of compounds that are expected to contribute to the water-soluble fraction of atmospheric particulate organics. Most frequently, ambient particle samples have been analyzed for those compounds that are either known to be emitted directly into the atmosphere (Rogge *et al.*, 1991; 1993b–d) or that are expected to be formed in the atmosphere on the basis of theoretical and experimental studies (Grosjean, 1977, 1992a; Grosjean and Seinfeld, 1989; Palen *et al.*, 1992, 1993; Wang *et al.*, 1992). Our work utilizes information on solubility and condensibility to propose additional organic compounds meriting consideration in future experiments.

For brevity, hereafter the phrases water-soluble fraction and water-soluble organics will be used to refer to the organic components of atmospheric particulate samples.

2. Background and Theses

Most techniques for identifying or quantifying specific organic molecules in atmospheric PM samples require extraction of the sample in some liquid solvent. Alter-

native techniques such as Fourier Transform Infra-Red (FTIR) microscopy or spectroscopy (Allen *et al.*, 1994), laser microprobe mass spectrometry (LAMMS), and rapid single particle mass spectrometry (RSMS) are beginning to receive more use (Mansoori *et al.*, 1994; Carson *et al.*, 1995; Murphy and Thompson, 1995; Reents *et al.*, 1995); however, quantitative molecular level atmospheric concentrations (mass of organic compound/unit air volume) are not yet obtainable using any of these methods. A beneficial outcome of this historic dependence on wet extraction methods is that it offers insights into the extraction characteristics of particulate organic samples. In this section, we provide a brief literature review of these chemical analysis methods and data to (1) highlight the gaps in the observed composition of particulate water-soluble organics; and (2) formulate theses regarding the characteristics of the missing material.

Experimentation with various solvents began in the 1950s with the emphasis on extracting the potentially carcinogenic and relatively nonpolar polycyclic aromatic hydrocarbons or PAHs (e.g., Cholak *et al.*, 1955; Stanley *et al.*, 1967; Wauters *et al.*, 1979). The amount of organic carbon recovered was not commonly measured: instead the fraction of the PM sample that extracted in a solvent was assumed to be organic. Since polar solvents such as water extract inorganics as well as organics, nonpolar solvents such as cyclohexane and benzene (which are not expected to extract inorganics) were favored for extraction of organics (Stanley *et al.*, 1967; Grosjean, 1975; Wauters *et al.*, 1979). Nonetheless, even some of the earliest studies suggested that secondary organics may contain substantial quantities of both polar and nonpolar compounds. For instance, Renzetti and Doyle (1959) found that irradiating automobile exhaust produced PM containing on an average approximately 20% water-soluble organics and 50% ether-soluble organics.

Starting in the 1970s, investigators began measuring the amount of total noncarbonate (elemental and organic) carbon in particulate samples (Mueller *et al.*, 1972) and the amount of particulate organic carbon (OC) extracted in water or other solvents (Grosjean, 1975). Some investigators (e.g., Daisey *et al.*, 1982; Gundel and Novakov, 1984) attempted to characterize the concentrations of particulate organics in terms of broad polarity classes (e.g., nonpolar, moderately polar, polar), or origin (primary vs. secondary) defined operationally on the basis of the amount extracted in solvents of different polarity (e.g., cyclohexane, dichloromethane, acetone). Other studies quantified the fraction of the total particulate carbon in the sample that was extractable in water (Cadle and Groblicki, 1982; Mueller *et al.*, 1982). These investigators anticipated that water would extract different organic compounds from the sample than nonpolar solvents: the water-soluble fraction would consist of polar (secondary) organics, whereas the benzene- or cyclohexane-soluble fraction would contain nonpolar (primary) organics. Although these studies did not examine the molecular composition of the water-soluble fraction, they provide valuable quantitative information concerning the relative extractability of particulate organics in polar vs. nonpolar solvents; we will examine this information in detail in a later section.

Experimental determination of the molecular composition of the water-soluble fraction by GC/MS requires that polar solutes be derivatized (i.e., converted to nonpolar compounds) prior to GC injection; without derivatization, highly polar multifunctional compounds such as dicarboxylic acids and polyols would not elute through a GC column (e.g., Wauters *et al.*, 1979; Yokouchi and Ambe, 1986; Kawamura and Gagosian, 1988). Derivatization is aimed at a specific type of polar functional group. Published studies to determine the concentration of water-soluble organics have targeted dicarboxylic acids and to a lesser extent ketoacids and dicarbonyls (Grosjean *et al.*, 1978; Kawamura and Kaplan, 1987; Sempere and Kawamura, 1994). Consequently, most derivatization procedures for atmospheric samples have been aimed at converting organic acids to esters by reacting them with reagents such as butanol or diazomethane (e.g., Kawamura and Kaplan, 1987; Rogge *et al.*, 1993a). Thus, although dicarboxylic acids, ketoacids and dicarbonyls have been identified in the water-soluble organic fraction, other hitherto unidentified compounds may also contribute substantially to this fraction.

Based on the foregoing review, we will examine the following theses in this paper:

- Water-soluble compounds constitute a substantial fraction of particulate organics in the atmosphere.
- Available data characterize the molecular composition of only a fraction of the water-soluble organics.
- Additional candidate water-soluble organic compounds can be tentatively identified on the basis of their solubility and condensibility.

3. Approach

Our approach is based upon the premise that to partition into the particle phase and subsequently to extract in water, an organic compound must be soluble in water and condensible under atmospheric conditions. We examine this premise via the following steps:

1. *Extraction characteristics of atmospheric organic carbon (OC).* We first examine data on the fraction of OC extracted in water and other polar and nonpolar solvents. If polar vs. nonpolar solvents are likely to extract two distinct fractions of OC, then a) the amount of water-soluble organic carbon (WSOC) may be indicative of the relative contribution of polar compounds to OC; and b) published data on the solubility of specific compounds in water are an important resource for identifying compounds that may contribute to WSOC.

2. *Atmospheric occurrence and water solubility of organic compounds.* Here we compile a comprehensive list of candidate water-soluble organic compounds based upon information regarding their presence in the atmosphere and their solubility in

water. Since the objective of this paper is to identify compounds that may contribute to this frequently unanalyzed portion of particulate organics, we examine those water-soluble compounds that are known *or might be expected* to be present in the atmosphere.

3. *Molecular composition of the water-soluble fraction.* We then review the available measurements of the molecular composition of the WSOC to assess how much of the total WSOC can be explained by the compounds observed. The remaining fraction then consists of other compounds, which we endeavor to identify in the next step.

4. *Gas-particle distribution at atmospheric conditions.* Finally, gas-particle distribution factors are examined for the candidate compounds identified in Step 2 to determine which compounds are likely to contribute to the unanalyzed fraction of the water-soluble organic PM.

4. Findings

4.1. EXTRACTION CHARACTERISTICS OF ATMOSPHERIC ORGANIC CARBON

As shown in Table I, studies encompassing both urban and rural locations have reported that approximately one-fifth to two-thirds of the total particulate carbon in the atmosphere consists of WSOC. To assess whether polar vs. nonpolar solvents tend to extract distinct subsets of organic compounds from atmospheric samples, we examine two studies in which the extractability of PM samples in a wide variety of solvents was compared.

Grosjean (1975) and Cadle and Groblicki (1982) conducted parallel extractions, in which portions of the same PM sample were extracted in different solvents. The expectation was that polar solvents would extract secondary, polar organics, nonpolar solvents would extract primary, nonpolar organics, and mixed solvents would extract both polar and nonpolar organics. Grosjean (1975) also conducted sequential extractions wherein a sample was first extracted in benzene and then in water.

Cadle and Groblicki's (1982) results indicate that at least some WSOC was extracted by nonpolar solvents. Toluene extracted 69% of the OC present in Denver TSP samples, compared with a 40% recovery using water; thus, at least 9% of the OC extracted in both toluene and water. The earlier work of Cholak *et al.* (1955) and Grosjean and Friedlander (1974) corroborates this observed overlap: utilizing a 'cross-extraction' technique, these two groups found that a substantial fraction of the OC initially extracted in benzene subsequently extracted in water. At the same time, Cadle and Groblicki's (1982) observations also suggest that the affinity of various solvents for solutes exhibits some specificity, since mixtures of polar and nonpolar solvents extracted more OC ($\geq$ 75% of the total) than each type of solvent by itself.

Table I. Water-soluble fraction of atmospheric particulate organic matter[a]

Investigators	Location	Time period	No. of samples	WSOC/ TC (%)
Cadle & Groblicki (1982)	Denver, CO	1978	6[b]	27 ± 12
Mueller et al. (1982)	2 urban & 7 nonurban locations in northeastern U.S.	1977–78	18 per location[c]	20 to 60
Mueller et al. (1982)	2 locations in Los Angeles area	1977–78	48 per location[b]	30 to 67
Sempere & Kawamura (1994)	Tokyo	1992	4[b]	28 to 55

[a] WSOC, TC and OC, all expressed in terms of (noncarbonate) carbon mass, refer to water-soluble organic carbon, total carbon and total organic carbon, respectively. Due to the dynamic nature of extraction (e.g., sonication, Soxhlet), WSOC may include some 'water-washable' organics that are not soluble in water; this also applies to other solvents discussed in the text.
[b] TSP (total suspended particulate matter) samples.
[c] Fine particle samples (aerodynamic diameter ≤ 2.5 μm).

Using parallel extractions (TSP samples, Pasadena, CA, summer and fall of 1973), Grosjean (1975) found that water and other polar solvents (alcohols and acetone) extracted 0.60 to 2.3 times the OC recovered using benzene: on an average the polar solvents extracted 5 to 35% more OC than benzene. He too found that mixtures of polar and nonpolar solvents yielded higher OC extraction efficiencies than individual solvents. His sequential extractions showed unequivocally that substantial amounts of water-soluble organics could not be recovered using nonpolar solvents: 17 to 43% of the total organic carbon recovered in the two-step process extracted in water after not extracting in benzene (Grosjean, 1975; Grosjean and Friedlander, 1975).

In summary, polar and nonpolar solvents tend to extract distinct but intersecting subsets of organic compounds from atmospheric samples. Thus, as Grosjean (1975) has shown, traditional extraction techniques that utilize nonpolar solvents will not recover all of the water-soluble organics.

4.2. ATMOSPHERIC OCCURRENCE AND WATER SOLUBILITY OF ORGANIC COMPOUNDS

As mentioned before, hundreds of individual organic compounds have been identified in atmospheric particulate matter. Based upon their sources, these compounds can be broadly grouped into two classes: 1) primary compounds such as plant waxes and resin residues as well as long-chain hydrocarbons characteristic of petroleum residues that are emitted into the atmosphere in particulate form; and 2) smaller, secondary multifunctional oxygenated compounds formed by gas-to-particle conversion of anthropogenic and biogenic emissions (Went, 1960; Schuetzle, 1975; Cronn et al., 1977; Duce, 1978; Hahn, 1980; Simoneit and Mazurek, 1982; Finlayson-Pitts and Pitts, 1986). Laboratory and theoretical studies of organic particle formation from precursor gases indicate that secondary compounds include carboxylic acids, alcohols, carbonyls, nitrates and other single and multifunctional oxygenated compounds (Grosjean, 1977, 1992a; Franzblau et al., 1984; Palen et al., 1992, 1993; Wang et al., 1992). Some compounds such as dicarboxylic acids are believed to originate both from primary emissions (Kawamura and Kaplan, 1987) and secondary gas-to-particle conversion processes (Grosjean and Friedlander, 1980).

In this step we create a comprehensive initial list of candidate water-soluble organic compounds via concurrent surveys of: i) compound solubilities in water; and ii) the published literature regarding both primary and secondary organics that are known or expected to be present in the atmosphere. The solubilities of various organic compounds in polar and nonpolar solvents are also compared to assess to what extent water-soluble compounds may have been extracted and identified using nonpolar solvents.

To organize and review compound-specific information, we first divide the organics in atmospheric PM into two classes: water-insoluble and water-soluble (Tables II and III). A solubility of 1 g solute/100 g water is used here as a convenient threshold to define this distinction. Table II shows that except for aliphatic dicarboxylic acids, all major organic compounds identified by the most comprehensive GC/MS studies (such as those of Rogge et al., 1993a) are 1) water insoluble; and 2) either large ($\geq$C9), aromatic, or both.

To construct a list of candidate water-soluble compounds, we start with the knowledge that they are likely to be oxygenated compounds containing one or more of the following functional groups: COOH, COH, C=O, COC, CONO$_2$, CNO$_2$, and CNH$_2$ (Grosjean, 1977, 1992a; Grosjean and Friedlander, 1980; Gorzelska et al., 1992; Grosjean et al., 1994; Atkinson and Aschmann, 1995). We first consider oxygenated and amino compounds that have been measured in the emissions or in the atmosphere in either the gas or particle phase, using the compilation of Graedel et al. (1986) as a principal reference for atmospheric presence, particularly for the pre-1986 literature. We also summarize, where available, the range of reported atmospheric concentrations in both the particle and gas phases. By conducting a

Table II. Water-insoluble organic compounds in atmospheric particles

Compound class	Solubility[a] in water	Reference[c] for atmospheric presence
C10-C34 n-alkanes	<0.002	FP,HB,RM
C9-C30 n-alkanoic and n-alkenoic acids & their esters	≤0.026	HB,RM
C10-C35 n-alkanols	≤0.0037	SC,SS
C9, C14 aldehydes	<0.1	MH,RM
Dehydroabietic and other diterpenoid acids and retene	i[b]	RM
Phthalic and other aromatic polycarboxylic acids & their esters	≤0.7	HB,RM
Polycyclic aromatic hydrocarbons (PAH)	0.003	FP,HB,RM
Polycyclic aromatic ketones and quinones	N/A[b]	RM
Cholesterol and other steroids	0.26	RM
1,2-dimethoxy-4-nitro-benzene and other aromatic N-containing compounds	N/A[b]	RM
Lignans	0.03	MH
Cellulose	i[b]	PK

[a] Solubility in g of solute/100 g of water at temperature closest to 25 °C taken from values reported in 15 to 25 °C range. Data taken from Seidell (1941); Markley (1960); Perry and Chilton (1973); Shinoda (1978); Streitwieser and Heathcock (1985); and Morrison and Boyd (1992). Solubilities for some compound classes are illustrated by the value for a specific compound in that class (e.g., napthalene for PAH and anisic acid for lignans). Based upon available data for n-alkanes, n-alkanols and alkanoic acids, we assume that for a compound class, solubility in water decreases with increasing molecular weight.

[b] Either solubility data not readily available (N/A) or listed as 'insoluble' (i). Based upon their molecular size and functional group composition, these compounds can safely be assumed to be water insoluble. Nitrophenol, which is water soluble, is included in Table III.

[c] FP: Finlayson-Pitts and Pitts (1986); HB: Helmig, Bauer et al. (1990); MH: Mazurek, Hallock et al. (1993); PK: Puxbaum and Kunit (1994); RM: Rogge, Mazurek et al. (1993a); SC: Simoneit, Crisp et al. (1991); SS: Simoneit, Sheng et al. (1991).

systematic review of the solubilities of individual compounds with these functional groups, we find that only the smaller (C7 or less) oxygenated and amino compounds tend to be water soluble (Table III). To keep the list of water-soluble compounds as comprehensive as possible at this stage, we have included in Table III some oxygenated aliphatic compounds whose solubilities are not known (e.g., 1,2,3-butanetriol, which may be completely miscible with water like 1,2,4-butanetriol), or are slightly less than 1 g solute/100 g solvent (e.g., 1,2-ethane dinitrate).

We have also included many compounds in Table III on the basis of their water solubility and constituent functional groups even though experimental evidence corroborating the presence of these specific compounds in the atmosphere is not available. For instance, we have included alcohols and several diols (aka glycols), triols and other polyols based on the following considerations:

Table III. Possible water-soluble organic compounds in atmospheric particles

Compound	Particle phase conc[a] (ng/m^3)	Gas phase conc[a] (ppb)	Solubility in water[a,b] (g solute per 100 g water)	Reference[c] for atmospheric presence
Monocarboxylic acids				
Formic acid	0 to 27% of total[d]	0.1 to 45	Infinity	G1,G2,HA,HG,JD, K1,KN,LK,SF,SS, TT,WP,WW
Acetic acid	0 to 41% of total[d]	< 0.2 to 21	Infinity	G1,H1,HA,HG,JD, K1,KN,LK,SF,SS, TT,WP,WW
Propanoic acid		0.02 to 0.66	Infinity	H1,KN,LK,S1
Butanoic acid		0.006 to 0.25	Infinity	H1,KN,S1
2-Methyl propanoic acid		0.003 to 0.031	20	H1,KN
Pentanoic acid		< 0.02	4.97	H1,S1
3-Methyl butanoic acid		< 0.05	4.2	H1,S1
2,2-Dimethyl 1-propanoic acid				KB
Hexanoic acid		< 0.02	0.97	S1
Dicarboxylic acids				
Oxalic acid	36 to 1680		12	K1,KI,KK,SK,YA
Malonic acid	6.4 to 453		161	K1,KI,KK,RM, SK,YA
Succinic acid	11 to 280		8.8	K1,KI,KK,LK,RM, SK,YA
Glutaric acid	3.2 to 110		116	KI,KK,LK,RM, SK,YA
Adipic acid	3 to 483		2.5	KI,KK,LK,RM,SK, YA
Maleic acid	0 to 204		80.4	KI,KK,SK
Carbonyls				
Glyoxal	38 to 46		$\geq 67^e$	BH,KK,SK
Formaldehyde		2 to 48	vs[e]	BH,G2,G4,KK,ZH
Hydroxyacetaldehyde			vs[e]	BH
Acetaldehyde		1 to 35	Infinity	G2,G3,G4,KK,ZH
Methyl glyoxal	24 to 67		$\geq 67^e$	BH,KK,SK
Acetone		< 1 to 94	Infinity	HM,KC,SH
2-Butanone		< 0.2 to 58	26	G4,KC
Propanal		0 to 14	16	G3,G4,KK,ZH
Butanal		0.08 to 7	7	G4,KK,ZH
Alcohols				
Methanol		6 to 47	Infinity	KC
Ethanol		< 1 to 38	Infinity	KC
1-Propanol			Infinity	GH
2-Propanol		< 1 to 20	Infinity	KC
2-Propen-1-ol			Infinity	GH
1-Butanol		< 0.2 to 5.4	7.2	KC
2-Butanol			12.5	GH
2-Methyl 1-propanol			10	GH

Table III. *(Continued)*

Compound	Particle phase conc[a] (ng/m^3)	Gas phase conc[a] (ppb)	Solubility in water[a,b] (g solute per 100 g water)	Reference[c] for atmospheric presence
2-Buten-1-ol			16.6	GH
1-Pentanol			2.2	GH
2-Methyl 2-propanol			Infinity	GH
2,2-Dimethyl 1-propanol			Infinity	
Benzyl alcohol			4.	GH
Phenol			9.3	GH
Polyols[f]				
1,2-Ethanediol			Infinity	GH
1,2-Propanediol			Infinity	GH
1,3-Propanediol				
1,2,3-Propanetriol			Infinity	GH
1,3-Butanediol			Infinity	
1,4-Butanediol			Infinity	
2,3-Butanediol			Infinity	
1,2,3-Butanetriol				
1,2,4-Butanetriol			Infinity	
1,2,3,4-Tetrahydroxy butane			63.7 to 880	
1,5-Pentanediol			Infinity	GH
2,3-Pentanediol				GH
2,4-Pentanediol			726	
1,2,3,4,5-Pentahydroxy pentane			151 to 211	WV
1,6-Hexanediol			vs	GH
2,5-Hexanediol			Infinity	
2-Methyl-1,3-pentanediol			11	
2-Methyl-2,4-pentanediol			Infinity	
1,2,6-Hexanetriol			Infinity	
1,2,3,4,5,6-Hexahydroxy hexane			3.2 to 449	WV
1,2,4,5-Tetrahydroxy cyclohexane				WV
Hexahydroxy cyclohexane				WV
1,7-Heptanediol				GH
2,4-Heptanediol			Infinity	
2,3-Diethyl-1,3-propanediol			33.3	
2-Ethyl-1,3-hexanediol			4.4	
1,2,3,4,5-Pentahydroxyheptane				WV
1,2,3,4,6-Pentahydroxyheptane				WV
1,2,3,5,7-Pentahydroxyheptane				WV
1,2,3,4,5,6-Hexahydroxyheptane				WV
Polyglycols[g]				
Diethylene glycol			Infinity	GH
Triethylene glycol			Infinity	GH
Keto-carboxylic acids				
Pyruvic acid	27 to 103		Infinity	GH,K1,LS,SK
Glyoxylic acid	26 to 238		Infinity	K1,LS,SK

Table III. *(Continued)*

Compound	Particle phase conc[a] (ng/m^3)	Gas phase conc[a] (ppb)	Solubility in water[a,b] (g solute per 100 g water)	Reference[c] for atmospheric presence
3-Oxopropanoic acid	17 to 28		Infinity[h]	LS,SK
4-Oxobutanoic acid	0.02 to 70		Infinity[h]	KG,LS,SK
5-Oxopentanoic acid	0.01 to 29			KG,LS,SK
Ethers				
Dimethyl ether			vs[i]	GH
Methyl tert-butyl ether		< 0.2 to 2.8		GH,KC
Ethyl methyl ether				GH
Diethyl ether			8	GH
Miscellaneous multifunctional compounds				
1-Malic acid	17 to 100		145	GH,KI,SK
Citric acid			162	GH
α-Keto glutaric acid			177	
Lactic acid			Infinity	GH,LW
Tartaric acid			140	
Glyceraldehyde			3	RD
Organic nitrates and nitro compounds				
Methyl nitrate			3.85	KS
Ethyl nitrate			1.3	KS
1-Propyl nitrate				KS
2-Propyl nitrate				KS
1-Butyl nitrate				KS
2-Butyl nitrate				KS
2-Methyl 1-propyl nitrate				KS
1-Pentyl nitrate				KS
2-Pentyl nitrate				KS
1,2-Ethane dinitrate			0.68	KS
2-Nitrooxy-ethanol				KS
2-Nitrooxy-1-propanol				KS
1-Nitrooxy-2-propanol				KS
1,2-Propane dinitrate				KS
Nitrooxy acetone				KS
p-Nitrophenol			1.7	GH
Amines and amino acids				
Methyl amine			vs	GG
Ethyl amine			Infinity	GG
Ethanol amine			Infinity	GG
Glutamic acid			1.5	GG
Asparagine			3.5	GG
Serine			5.	GG
Glutamine			4.5	GG
Glycine			25.	GG

Table III. *(Continued)*

Compound	Particle phase conc[a] (ng/m^3)	Gas phase conc[a] (ppb)	Solubility in water[a,b] (g solute per 100 g water)	Reference[c] for atmospheric presence
Arginine			15.	GG
Alanine			16.7	GG
Leucine			2.4	GG

[a] If available in the literature.

[b] 'Infinity' denotes complete miscibility with water; 'vs' denotes very soluble as reported in the literature. When quantitative values are available for compounds with finite solubility, we select the value at the temperature closest to 25 °C from the values for the range 14 to 30 °C (except for ethyl nitrate, which is for 55 °C) reported in the following sources: Seidell (1941); Curme and Johnston (1952); Mellan (1962); Stephen and Stephen (1963); Carlo (1971); Raridon and Kraus (1971); Perry and Chilton (1973); Shinoda (1978); Loudon (1984); Streitwieser and Heathcock (1985); Apelblat and Manzurola (1987); Budavari *et al.* (1989); Burrows (1992); Kames and Schurath (1992); Morrison and Boyd (1992); Cohen *et al.* (1993); Aldrich (1994). For some polyols, we show the solubility range over various stereoisomer forms as reported in Cohen *et al.* (1993).

[c] References for atmospheric presence: BH: Betterton and Hoffmann (1988); G1: Grosjean (1989); G2: Grosjean (1991); G3: Grosjean (1992b); G4: Grosjean (1982); GG: Gorzelska, Galloway *et al.* (1992); GH: Graedel, Hawkins and Claxton (1986); H1: Hoshika (1982); HA: Hartmann, Andreae and Helas (1989); HG: Harrington, Gertler *et al.* (1993); HM: Hoff, MacKay *et al.* (1993); JD: Johnson and Dawson (1993); K1: Khwaja (1995); KB: Khan, Brimblecombe and Clegg (1995); KC: Kelly, Callahan *et al.* (1993); KG: Kawamura and Gagosian (1987); KI: Kawamura and Ikushima (1993); KK: Kawamura and Kaplan (1987;1991); KN: Kawamura, Ng and Kaplan (1985); KS: Kames and Schurath (1992); LK: Lawrence and Koutrakis (1994; 1996a,b); LS: Le Lacheur, Sonnenberg *et al.* (1993); LW: Li and Winchester (1993); RD: Renzetti and Doyle (1959); RM: Rogge, Mazurek *et al.* (1993a); S1: Satsumabayashi *et al.* (1995); SF: Solomon, Fall *et al.* (1988); SH: Singh, O'Hara *et al.* (1994); SK: Sempere and Kawamura (1994); SS: Sanhueza, Santana and Hermoso (1992); TT: Tokos, Tanaka *et al.* (1992); WP: Winiwarter, Puxbaum *et al.* (1988); WV: Wauters, Vangaever *et al.* (1979); WW: Willey and Wilson (1993); YA: Yokouchi and Ambe (1986); ZH: Zhang, He and Lioy (1994).

[d] Filterpack measurements in reference G1 indicate that of the total (gas plus particle), this % was in the particle phase. Measurements in K1 show that less than 10% of the total was in the particle phase.

[e] Formaldehyde is a very soluble gas at room temperature and pressure, up to 55% in solution is reported (Budavari *et al.*, 1989); lower limits of solubilities of glyoxal and methylglyoxal are derived from the data in Betterton and Hoffmann (1988), Budavari *et al.* (1989) and Aldrich (1994). Hydroxyacetaldehyde is crystalline at room temperature (Sigma, 1995). Experiments of Betterton and Hoffmann (1988) indicate that hydroxyacetaldehyde has an unusually high affinity for water; therefore, we characterize it as 'very soluble' in water.

[f] Information in Hort (1972) indicates that (a) glycols with a secondary hydroxyl group are much more soluble in water than diprimary glycols; (b) chain branching increases solubility; (c) the solubility of glycols in lower alcohols parallels water solubility except that it falls off less rapidly as carbon number increases; (d) different classes of cycloaliphatic glycols exhibit similar solubility behavior (e.g., cyclohexanediols are all very soluble in water and in lower alcohols); (e) the solubility of aliphatic as well as cycloaliphatic diols in benzene, although as high as 45 g/100 g for diethylene glycols, is much lower than their solubility in water and lower alcohols.

[g] The IUPAC names for these compounds (oxydiethanols, oxybisethanol, etc.) are not commonly used; therefore, we have used common names.

[h] Although the solubility of these specific acids could not be found in the literature, based upon the solubility of 3-oxobutanoic acid (completely miscible with water) and its structural similarity to these two acids, we assume that these two acids are also completely miscible with water.

[i] At 18 °C, 100 g of water dissolves 3700 cm^3 of dimethyl ether (gas).

1. Some experimental evidence exists for the presence of alcohols in the atmosphere (Graedel *et al.*, 1986; Kelly *et al.*, 1993; Allen *et al.*, 1994).

2. Wauters *et al.* (1979) identified numerous C5-C7 polyols in the polar (methanol extract) fraction of atmospheric PM.

3. Smog chamber and theoretical studies indicate that oxidation of aliphatic volatile organic compounds (VOCs) by the hydroxyl radical can lead to the formation of alcohols (Grosjean, 1977, 1992a; Palen *et al.*, 1992, 1993).

4. Numerous alcohols, including polyols, are known to be emitted directly into the atmosphere (Graedel *et al.*, 1986; Konig *et al.*, 1995).

We have also included polyglycols (e.g., diethylene glycol) – despite a lack of evidence suggesting their occurrence or formation in the atmosphere – because they are known to be emitted directly into the atmosphere (Graedel *et al.*, 1986).

Table III includes numerous compounds that are completely miscible with water. Prominent among them are monocarboxylic acids and alcohols (complete miscibility up to C4 or C5); diols and triols (complete miscibility up to C7); and keto-carboxylic acids (complete miscibility up to C4). Other notable compounds are multifunctional acids (e.g., 1-malic acid, lactic acid) that can form more than a 50% (solute, by weight) solution with water.

Since atmospheric acids can be neutralized by alkaline substances in the atmosphere, water solubility of the neutralization products is also important. In general, the evidence is that the solubility of many acids increases due to neutralization by a strong alkaline ion (e.g., Na^+, K^+). For instance, dodecanoic (lauric) acid is insoluble in water (0.0055 g/100 g water); however, upon neutralization by an alkaline ion it becomes a 'water-soluble' surfactant, i.e., a soap (Myers, 1991). The available data also indicate that the solubility of salts formed from lower molecular weight dicarboxylic acids is larger than those of the parent acids. For instance, whereas the solubility of succinic acid is approximately 0.73 M (Seidell, 1941; Carlo, 1971), that of sodium hydrogen succinate is $\geq$ 5M (Robinson and Stokes, 1968). On the other hand, esterification generally reduces the solubility of carboxylic and dicarboxylic acids. For example, the solubility of methyl acetate and diethyl glutarate in water are 33 and 0.88 (g/100 g water), respectively (Seidell, 1941; Perry and Chilton, 1973). In fact, esterification is routinely used in laboratory analysis of atmospheric PM to derivatize water-soluble acids. In summary, reaction products of the acids listed in Table III may also be present in atmospheric particles, with neutralization by a strong alkaline ion leading, in general, to an increase in water solubility and esterification leading to a decrease in water solubility.

Next we examine how the solubility of various organic compounds in polar and nonpolar solvents may influence the extraction and subsequent identification of these compounds in atmospheric PM samples. Figures 1 and 2 compare the solubility of mono and dicarboxylic acids in water, methanol, benzene and cyclohexane; for this discussion, a solute is termed "soluble" in a solvent if the solubility $\geq$ 1 g/100 g.
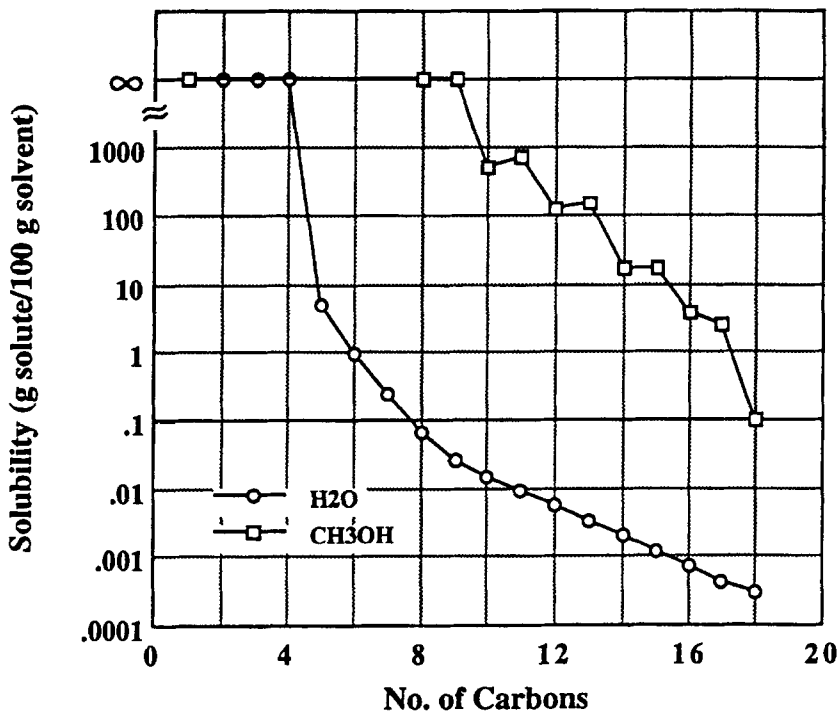
Figure 1a.

Figure 1 shows that only C1 through C6 monocarboxylic acids are soluble in water. In contrast, C1 through C17 monoacids are soluble in methanol (complete miscibility up to C9) and C1 through C18 monoacids are soluble in benzene and cyclohexane. Therefore, the *n*-alkanoic acids included in Table II have a much higher solubility in benzene and cyclohexane than in water.

The other compounds listed in Table II are generally either slightly soluble in both benzene and water (e.g., the solubility of phthalic acid in water, benzene and methanol is, respectively, 0.7, 0.0095 and 28 g/100 solvent) or are more soluble in benzene than in water (e.g., benzanthracene). Dicarboxylic acids exhibit a peculiar but well-known solubility behavior in which solubility alternates with the number of carbon atoms in the molecule. This behavior is called the odd-even effect; it is generally not perceptible beyond C10 (Pryde and Cowan, 1972; Burrows, 1992). Figure 2 shows that C2 through C6 dicarboxylic acids are soluble in water and methanol but not in benzene.

Together, Figures 1 and 2 show that (1) solutes with high solubility in polar solvents have low solubility in nonpolar solvents and vice versa; and (2) for a given compound class (e.g., *n*-alkanoic acids), an increase in the size of the solute molecule leads to a decrease in its solubility in a polar solvent but, up to a certain carbon number, an increase in its solubility in a nonpolar solvent.
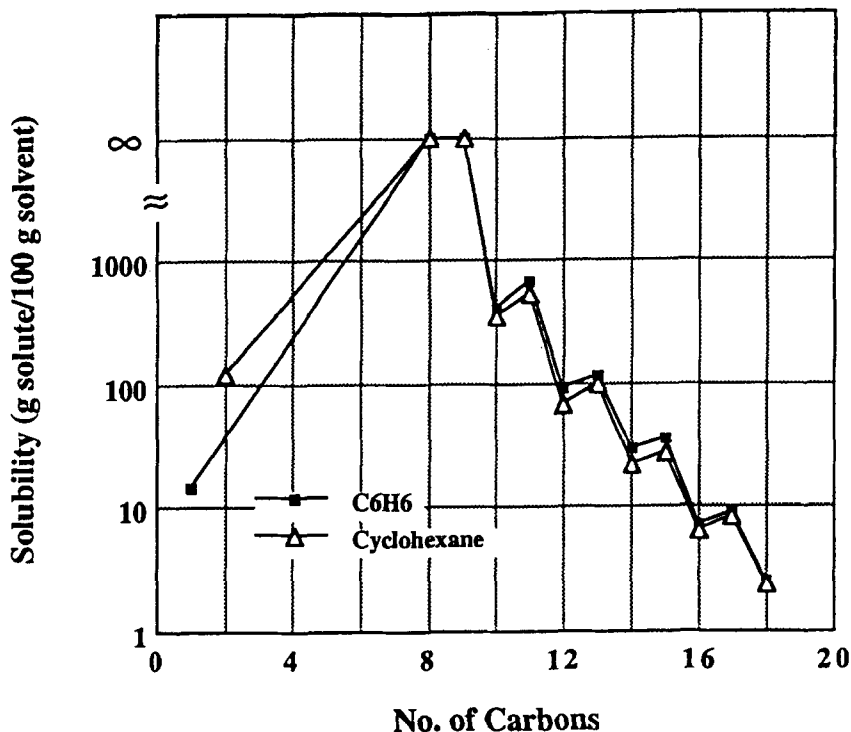
Figure 1b.

Figure 1. Solubility of *n*-alkanoic (monocarboxylic) acids in (a) water and methanol; and (b) cyclohexane and benzene. Data are shown by points; lines drawn are for distinguishing patterns for different solvents, not for extrapolating missing values. Infinite solubility means complete miscibility. Water solubility data taken from Markley (1960) and Streitwieser and Heathcock (1985); methanol from Markley (1960) and Dean (1992); cyclohexane from Seidell (1941) and Markley (1960); and benzene from Seidell (1941) and Markley (1960). $T = 20$ to $25\,^{\circ}C$, except for acetic acid in cyclohexane, which is at $4.2\,^{\circ}C$. Data in Markley (1960) show that the solubility of these acids in methanol, benzene and cyclohexane (but not water) increases dramatically with increasing temperature: for instance, at $30\,^{\circ}C$, complete miscibility is observed up to C11 for all three solvents. Since formic acid is completely miscible with ethanol, we have assumed that it is completely miscible with methanol as well.

(C1–C6 monocarboxylic acids, which are soluble in both benzene and water, will be discussed later.) Therefore, the solubility data confirm the expectation that GC/MS analysis of nonpolar extracts will tend to identify only water-insoluble compounds and some water-soluble compounds that are extracted at trace levels and derivatized prior to GC injection. The finding that methanol dissolves large quantities of a broad range of organics (e.g., C1 to C17 *n*-alkanoic and phthalic acids) is consistent with the observation that on average methanol extracted more organics from TSP samples than any other polar or nonpolar solvent (Grosjean, 1975).
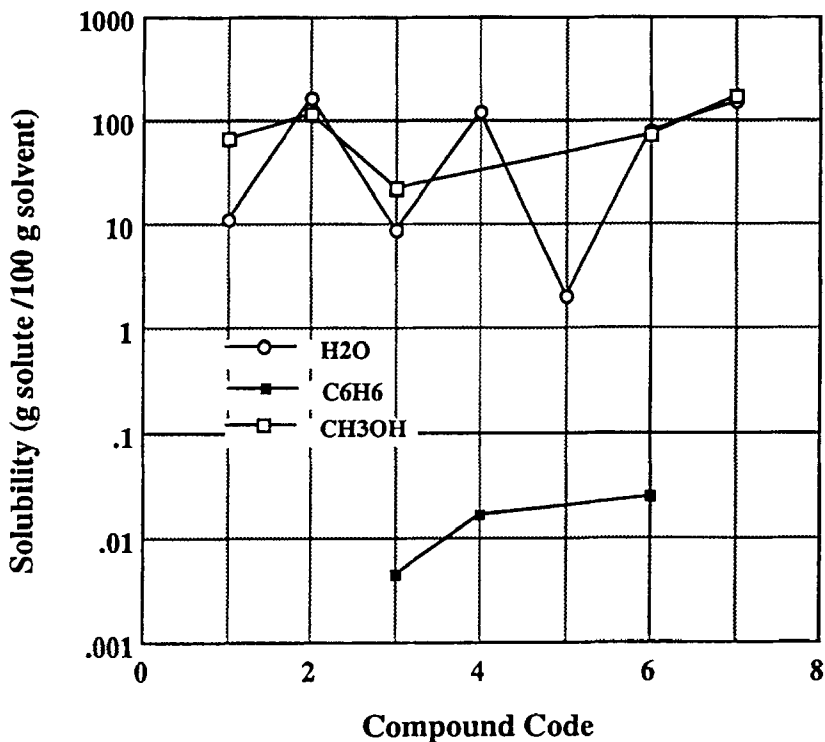
Figure 2. Solubility of dicarboxylic acids in water, methanol and benzene (*T*: 20 to 30 °C). Compound Code: 1: Oxalic, 2: malonic, 3: succinic, 4: glutaric; 5: adipic; 6: maleic; 7: 1-malic. Solubilities in water are taken from Table III. Solubilities in methanol and benzene are taken from Seidell (1941). Solubility of maleic acid in methanol is approximated with that in ethanol.

4.3. MOLECULAR COMPOSITION OF THE WATER-SOLUBLE FRACTION

The water-soluble compounds that have been most frequently identified in atmospheric PM are lower molecular weight (C2 to C6) dicarboxylic acids (e.g., Schuetzle *et al.*, 1975; Grosjean *et al.*, 1978; Kawamura and Kaplan, 1987; Rogge *et al.*, 1993a; Sempere and Kawamura, 1994). Sempere and Kawamura (1994) quantified the fraction of total particulate carbon in Tokyo that was water-soluble as well as the composition of a portion of the water-soluble fraction; therefore, their observations (summarized in Table IV) allow us to determine the extent to which the molecular composition of the water-soluble fraction is known. Dicarboxylic acids constitute the predominant compound class, with additional material identified as ketoacids and dicarbonyls. About 80 to 90% (range over four samples) of the total diacid, ketoacid and dicarbonyl mass consisted of compounds that are water-soluble according to our definition (Table III); the remaining compounds are slightly soluble in water (e.g., phthalic acid) or their solubility is not readily available (e.g., 6-oxohexanoic acid). However, altogether these three compound

Table IV. Composition of the water-soluble fraction[a]

Compound class	Mass conc[b]		Fractional conc[c]	
	$\mu g/m^3$	μg of C/m^3	% of WSOC	% of TC
Total WSOC	–	3 to 23	–	28 to 55
Total C2–C9 diacids	1.2 to 3.0[d]	0.4 to 1.0	4 to 14	1 to 5[d]
Total C2–C9 ketoacids	0.3 to 0.5	0.1 to 0.2	0.6 to 3	0.2 to 0.9
Total C2–C3 dicarbonyls	0.07 to 0.1	0.03 to 0.05	0.2 to 1.5	0.06 to 0.5
Total C2–C9 diacids & ketoacids & C2–C3 dicarbonyls	1.5 to 3.6	0.6 to 1.2	5 to 19	2 to 6
Total water soluble C2–C9 diacids & ketoacids & C2–C3 dicarbonyls[e]	1.2 to 3.2	0.4 to 1.0	4 to 15	1 to 5

[a] Summarized from Sempere and Kawamura (1994). Ranges over four TSP samples collected in Tokyo during February and July 1992.
[b] Mass concentrations of total WSOC are expressed as μg of carbon/m^3 of air; mass concentrations of total diacids, ketoacids and dicarbonyls represent a sum of the concentrations of specific compounds quantified and are expressed in μg of the compounds/m^3 of air as well as in μg of carbon/m^3.
[c] All fractional concentrations are derived on the basis of mass concentrations expressed as μg of carbon/m^3.
[d] These ranges are consistent with those reported for an earlier, longer-term (April 1988–February 1989; $n = 21$) study in Tokyo (Kawamura and Ikushima, 1993).
[e] Water-soluble compounds are defined on the basis of Table III as oxalic, malonic, maleic, succinic, malic, glutaric, adipic, pyruvic, glyoxylic, 3-oxopropanoic, 4-oxobutanoic and 5-oxopentanoic acids; glyoxal and methyl glyoxal.

classes accounted for only about 5 to 20% of the total water-soluble organic carbon in Tokyo.

Observations from various studies in the Los Angeles area also suggest that water-soluble dicarboxylic acids constitute only a small fraction of the total WSOC. The data of Rogge et al. (1993a) indicate that water-soluble dicarboxylic acids account for approximately 2 to 4% of the total organic mass. Rogge et al. (1993a) did not report the concentrations of oxalic acid; however, other available data show that oxalic acid accounts for roughly half of the total aliphatic dicarboxylic acid concentration in Los Angeles and Tokyo (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994). If we assume that oxalic acid concentrations in Rogge et al.'s samples were equal to the sum of the concentrations of all other aliphatic dicarboxylic acids, then water-soluble dicarboxylic acids accounted for 5 to 9% of the total organic mass. As an alternative approach, consider the measurements of Kawamura and Kaplan (1987) in Los Angeles (10 samples during June and October 1984), which indicate that the average total concentration of water-soluble dicarboxylic acids was approximately 1 $\mu g/m^3$. While Kawamura and Kaplan did not report the concentration of total organics, if we approximate

the total organic concentrations during their experiments by the annual average concentration of organics in Los Angeles during 1982 (7 μg/m^3 as reported by Rogge *et al.*, 1993a), then these dicarboxylic acids accounted for approximately 14% of the total organic mass. Therefore, the measurements of Rogge *et al.* (1993a) and Kawamura and Kaplan (1987) suggest that water-soluble dicarboxylic acids accounted for approximately 5 to 15% of the total organic mass. In contrast, the data of Mueller *et al.* (1982) indicate that 30 to 67% of the total carbon in Los Angeles area was water-soluble (the WSOC/OC ratio, which is not reported by Mueller *et al.*, would be even larger). Although samples were collected during different years (Mueller *et al.*: 1977–78; Rogge *et al.*: 1982; Kawamura and Kaplan: 1984), the nature of the PM is unlikely to have changed drastically between 1977 and 1984. Therefore, for Los Angeles as well as Tokyo, the observations appear to quantify the molecular composition of only a fraction of the WSOC.

Since dicarboxylic acids, ketoacids and dicarbonyls constitute only a portion of the WSOC, we test the following two hypotheses regarding the composition of the missing portion.

1. *The remaining portion of the WSOC consists solely of water-insoluble compounds (as defined in Table II).* Even water-insoluble compounds have a small but finite solubility in water; therefore, we expect that they would be present in water extracts, albeit in small concentrations. The results of Kawamura and Kaplan (1987) and Sempere and Kawamura (1994) confirm this: these studies detected slightly-soluble compounds such as phthalic and azelaic acids in the water-soluble fraction.

To examine the validity of this hypothesis we will use the binary solubility data (water and a single organic compound) shown in Figure 1. In reality, a multitude of slightly to highly soluble organics and inorganics would be present in the extract and the solubility of individual compounds in this multicomponent system would be different; in addition, the distinction between the solute and the solvent might blur and other phenomena such as cosolvence (e.g., a solute dissolving in a liquid phase containing two solvents) could come into play (Munz and Roberts, 1986). However, such complexities will be momentarily set aside for the following discussion.

The amount of a solute dissolving in water depends upon the amount of water used for extracting the sample. For instance, the standard amount of water used by Sempere and Kawamura (1994) in extracting WSOC would be sufficient to dissolve 58 μg of octadecanoic acid. Given the air volumes sampled, this mass of octadecanoic acid would correspond to an air concentration of 1 to 4 μg/m^3. Sempere and Kawamura (1994) did not report the concentrations of octadecanoic acid in their samples; typical urban concentrations of octadecanoic acid in Los Angeles are on the order of 50 ng/m^3 (Rogge *et al.*, 1993a). Therefore, it is possible in this case that all the octadecanoic acid measured in Sempere and Kawamura's (1994) samples did indeed extract in water and became included as WSOC.

Let us suppose all of the water-insoluble compounds listed in Table II fully dissolved in water and were measured as WSOC. This assumption would imply that the amount of solvent used was sufficiently large to allow most compounds to dissolve in it regardless of their solubility; while this scenario is inconsistent with the finding (Section 4.1) that different solvents extract different amounts of OC, it will serve as the extreme case for testing this first hypothesis.

According to the data of Rogge *et al.* (1993a), water-insoluble compounds account for approximately 8 to 9% of the total organic mass. Rogge *et al.* (1993a) did not report the concentrations of oxalic acid, ketoacids or dicarbonyls. Based on the observed relative abundance of these various compounds in Los Angeles and Tokyo (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993; Sempere and Kawamura, 1994), we assume that in Rogge *et al.*'s samples 1) oxalic acid concentrations were approximately equal to the sum of the concentrations of all other aliphatic dicarboxylic acids; and 2) aliphatic dicarboxylic acids accounted for approximately 80% of the total aliphatic diacids, ketoacids and dicarbonyl mass. Then by combining together the GC/MS results from these various urban studies (using water as well as other solvents for extraction) at best we can account for the molecular composition of 14 to 20% of the organic mass in Rogge *et al.*'s (1993a) samples. If we assume that the ratio of organic mass to organic carbon mass for water-soluble organics is equal to that for total organics, then the maximum values we derive for WSOC/OC and WSOC/TC are 0.20 and 0.12, respectively. Therefore, even our extreme assumptions are insufficient to explain the observed lower limit of WSOC/TC for the Los Angeles area (0.30, see Table I).

2. The remaining portion may contain substantial quantities of water-soluble compounds that were present in the particle samples but were not identified by the chemical analysis. In Rogge *et al.*'s (1993a) experiments, 40 to 55% (approximately half) of the organic mass either did not extract in the solvents (hexane followed by a mixture of benzene and isopropanol) or did not elute through the GC column; the nonextractable and nonelutable fractions are expected to contain high molecular weight (>C40) and/or highly polar compounds (Mazurek *et al.*, 1996). For instance, Puxbaum and Kunit (1994) estimate that cellulose and other biopolymers may account for 20% of the nonextractable plus nonelutable carbon in urban samples such as those analyzed by Rogge *et al.* (1993a).

As mentioned before, without derivatization, highly polar multifunctional compounds will not elute through a GC column. Since derivatization tends to target specific functional groups, it is not surprising that certain polar compounds would elude analysis. Polyols and amino acids are a case in point. Using specialized derivatization procedures, Wauters *et al.* (1979) determined that the majority of the polar compounds they identified in a TSP sample were polyols. The reagent used by Sempere and Kawamura (1994) and Kawamura and Kaplan (1987) (butanol) does not derivatize polyols. We are not clear whether the reagent used by Rogge *et al.* (1993a) (diazomethane) could derivatize highly polar polyols; however, even

if these polyols did convert to nonpolar forms and subsequently eluted from the GC, their peaks may have been unresolved, or their mass spectra unidentified (Cass, 1995). Using a derivation procedure targeted specifically at amino acids and amines, Gorzelska *et al.* (1992) were able to quantify the concentrations of many water-soluble compounds in precipitation samples; these compounds constitute another class that may contribute to particle samples but remains unanalyzed.

Smog chamber and chemical mechanism studies show that oxidation of VOCs can form highly polar multifunctional compounds. Nearly four decades ago, Renzetti and Doyle (1959) found that irradiation of auto exhaust produced highly oxygenated particulate organics: the infrared spectra indicated the presence of hydroxyl and carbonyl groups, and the material contained carbon, oxygen and hydrogen in the approximate proportion 3:3:5 (molar). They surmised that the compound could be glyceraldehyde ($CH_2(OH)CH(OH)CHO$). Laboratory studies (Milas *et al.*, 1937) have found that hydrogen peroxide reacts with double-bonded compounds in the presence of ultraviolet light to produce the corresponding glycol (e.g., ethanediol from ethylene). More recent smog chamber and mechanistic studies provide evidence for the formation of hydroxy- and dihydroxy carbonyls in the atmosphere (Atkinson, 1990; Atkinson and Aschmann, 1995; Klotz *et al.*, 1995; Wiesen *et al.*, 1995; Yu *et al.*, 1995).

In summary, this second hypothesis is more tenable because: 1) a substantial fraction of the particulate organic mass unidentified by GC/MS studies such as Rogge *et al.* (1993a) may be highly polar; 2) studies using specialized derivatization procedures have identified highly polar polyols in atmospheric particle samples; and 3) kinetic studies indicate that VOC oxidation leads to the formation of highly polar (e.g., polyhydroxy) organics. While we have focused upon particulate organic composition data for urban areas, other observations suggest that the second hypothesis is valid for nonurban areas as well. For instance, a comparison of OC/EC ratios and elutability of organics in GC columns for samples collected in the Los Angeles area vs. the Grand Canyon (nonurban) suggests that particulate organics in nonurban areas contain even a higher fraction of oxygenated, polar compounds than those in urban areas (Hildemann *et al.*, 1994; Mazurek *et al.*, 1996; Saxena *et al.*, 1995; Turpin *et al.*, 1996).

4.4. GAS-PARTICLE DISTRIBUTION OF WATER-SOLUBLE ORGANICS IN ATMOSPHERE

In this final step, we identify those water-soluble compounds listed in Table III that are likely to partition appreciably into the particle phase while eliminating those compounds that are too volatile to condense onto atmospheric fine particles. The remaining condensible compounds are candidates for contributing to the water-soluble fraction. To be as inclusive as possible, partitioning is assessed for conditions which, while realistic, favor condensation. Several physical and chemical processes such as adsorption and absorption redistribute trace substances between the gas and the condensed phases in the atmosphere (Finlayson-Pitts and Pitts,

1986; Seinfeld, 1986). We first briefly review the relevance of various processes to select a governing process for our assessment, as described next.

Homomolecular Nucleation. A component in the vapor phase can either condense onto existing particles or form new single-component particles. Nucleation takes place only if the vapor phase is supersaturated with respect to the component; therefore, to condense, the component must first accumulate in the gas phase. In many studies, this process is considered to be the predominant mechanism leading to the formation of secondary organic PM (Grosjean, 1977; Grosjean and Seinfeld, 1989; Pandis *et al.*, 1992, 1993).

However, homomolecular nucleation may not be the governing process for condensation of water-soluble compounds. For instance, consider glutaric acid, which is commonly measured in atmospheric particles (e.g., Rogge *et al.*, 1993a; Sempere and Kawamura, 1994). Using the vapor pressure data of Tao and McMurry (1989), we find that glutaric acid could condense via homomolecular nucleation only if its gas phase concentration exceeded approximately 10 ppb; such high concentrations appear improbable in the atmosphere. The vapor pressure is useful, nonetheless, as the upper limit of volatility.

Heteromolecular Nucleation. Water vapor and another solute can condense by heteromolecular nucleation to form binary aqueous droplets even if both components are undersaturated, as long as they are supersaturated with respect to an aqueous solution droplet. Most studies of heteromolecular nucleation have focused on inorganic compounds such as sulfuric acid (Roedel, 1979; Seinfeld, 1986); little information is currently available concerning the behavior of organics.

Condensation on Solid Surfaces (Adsorption). Gases can be adsorbed on particle surfaces and pores; the interfacial distribution is estimated by a temperature-dependent equilibrium constant and the relationship is referred to as an adsorption isotherm (Adamson, 1976; Hanel, 1976). Adsorption can occur at gas-phase adsorbate concentrations below the saturation level. Several investigators have applied adsorption theory to study the partitioning of relatively nonpolar compounds such as PAHs and pesticides to atmospheric aerosol and fog systems (e.g., Junge, 1977; Pankow, 1987; Storey and Pankow, 1992; Valsaraj *et al.*, 1993).

Condensation on Existing Droplets (Absorption). If aqueous aerosol particles, cloud or fog droplets are already present (e.g., sea-salt particles in marine environments; inorganic particles containing sulfate and nitrate in continental air masses), then a water-soluble organic compound would distribute between the vapor and liquid phases according to its air-water equilibrium constant and the relative volumes of the two phases. No threshold gas-phase concentration is needed: condensation on existing droplets would take place at all partial pressures.

Adsorption and absorption are often viewed as complementary processes (described by analogous and additive equilibrium relationships) whose relative importance depends upon factors such as compound solubility in water and relative humidity (Hanel, 1976; Thibodeaux *et al.*, 1991; Pankow *et al.*, 1993; Pankow, 1994a,b). For water-soluble compounds, the increasing availability of condensed water (e.g., droplet vs. dry particles) would render absorption the predominant process. Moreover, in comparison to absorption, adsorption remains poorly understood and the properties for specific adsorbate and adsorbent pairs are not generally known. Since the intent here is to examine conditions favoring condensation of water-soluble compounds, we assume that absorption on existing aqueous droplets is the governing mechanism.

4.4.1. *Estimation of Air-Water Equilibrium Constants*

In Appendix A, we derive an expression for estimating the fraction of the total (vapor plus aqueous) organic solute mass that is present in the aqueous phase using air-water and other equilibrium constants, and those extreme values of particle properties (liquid water content and pH) that favor condensation. Bounding calculations in this appendix indicate that compounds with an effective air-water equilibrium constant of $1E+6$ M-atm^{-1} or less would partition virtually completely ($\geq 99\%$) into the gas phase. Therefore, we will use this value as a cut-off: compounds with an effective air-water equilibrium constant (K_{AW} or K_{AW}^*) $\geq 1E+6$ M-atm^{-1} will be viewed as contributors to the water-soluble organic fraction.

For many compounds (e.g., monocarboxylic acids, alcohols), air-water equilibrium constants are available in the literature. However, for many other (especially multifunctional) compounds these constants are not available; for such cases we must estimate them using available data.

We use two alternative methods for estimating equilibrium constants. In the first method, vapor-liquid equilibrium observations available in the literature for binary aqueous organic solutions are utilized. A group contribution method that does not require compound-specific vapor-liquid equilibrium observations but uses information on a compound's functional group constitution is our second method. We test the reliability of each estimation method and quantify the error bars on our estimates by comparing them against observations for those compounds for which K_{AW} is reported in the literature.

Method 1 (Vapor-Liquid Equilibrium Data). When vapor-liquid equilibrium constants are not reported in the literature for aqueous-organic systems, they can be derived from vapor-liquid equilibrium observations, which are typically in the form of gas-phase composition as a function of the liquid-phase composition (often referred to as $y-x$ or $x-y$ data). For a two component, two-phase system there are two degrees of freedom. The data are obtained either in isothermal experiments (constant temperature, varying pressure; for each pressure there is one unique set

of x and y values) or isobaric experiments (constant pressure, varying temperature; for each temperature, there is one unique set of x and y values).

We use vapor-liquid equilibrium data in the DECHEMA Chemistry Data Series compilation (Gmehling and co-author(s), 1977, 1981, 1988). The DECHEMA data are in the form of $y(x)$: therefore, either K_{AW} must be based upon the data at the lowest concentration of the solute, or it must be derived by fitting to the data a thermodynamic model (i.e., a functional form) which is then evaluated at a solute concentration of zero. These procedures are described in Appendix B.

The reader should note that all K_{AW} values, whether in the literature or whether deduced here, are estimates. When experiments are conducted specifically for deducing K_{AW} at a given temperature and pressure, the temperature and pressure conditions are chosen accordingly and the experiments are conducted at very low liquid-phase concentrations of the solute (so that activity coefficients can be assumed to be 1.0). Moreover, in such experiments, an inert third component (e.g., nitrogen gas) is used in the gas phase. The presence of the third component increases the degrees of freedom by one and thus enables the experimentalist to select any combination of temperature and pressure and to conduct the experiment at solute vapor phase concentrations that can be several orders of magnitude smaller than those in the two-component system. The vapor-liquid equilibria data we use here are for two component systems and often at temperatures and pressures different from the conditions of interest; therefore, adjustments are necessary to interpolate or extrapolate to $T = 25\,^{\circ}\mathrm{C}$ and $P = 1$ atmosphere. While these adjustments are derived from established thermodynamic relationships, they nonetheless involve assumptions and approximations.

Method 2 (Group Contribution). An alternative to x–y data are group contribution estimation (GCE) methods, wherein physical properties of organic compounds are estimated from the properties of the atoms and functional groups constituting the molecule. The underlying postulate is that the free energy of transferring an organic compound from the gas to the aqueous phase is approximately an additive function of the functional groups constituting the compound (Hine and Mooker-jee, 1975). Group contribution methods are particularly useful for compounds for which neither K_{AW} nor x–y data are readily available in the literature. Several group contribution methods are available for estimating K_{AW} of organic compounds for $T = 25\,^{\circ}\mathrm{C}$ (Hine and Mookerjee, 1975; Meylan and Howard, 1991; Suzuki *et al.*, 1992). Unfortunately, these methods do not adequately treat the interactions between polar functional groups in a multifunctional compound. Despite this limitation, the group contribution approach is the only choice available to us for multifunctional compounds such as polyols and dicarboxylic acids for which vapor-liquid equilibrium data are not readily available. We use an interactive software package called Data Evaluation System for Organic Compounds, or DESOC (Drefahl and Reinhard, 1995), which employs Suzuki *et al.*'s (1992) method to estimate K_{AW}.
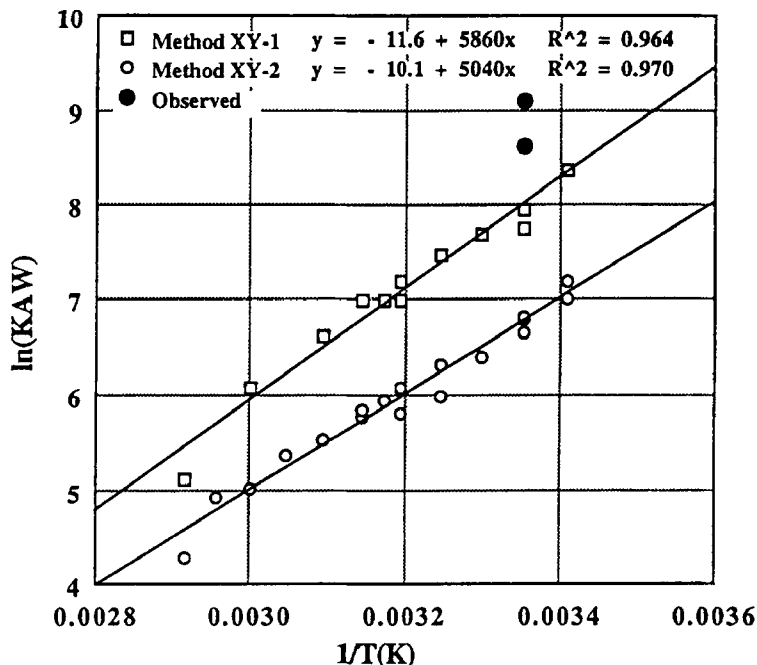
Figure 3a.

Reliability of Estimates. Table V compares K_{AW} values estimated using x–y data and DESOC with experimental values from the recent literature. We first discuss monofunctional compounds, for which a relatively large corpus of experimental values is available for a broad range of temperatures. Figure 3 shows this comparison as a function of temperature for acetic acid, ethanol, and acetaldehyde to illustrate the range of method performance from worst to best; results for other compounds fall within this range. For monofunctional compounds, the following judgments can be made based on Table V and Figure 3:

- The dependence of the estimated K_{AW} on temperature is consistent with thermodynamic theory (Equation (B.15) in Appendix B). Although this finding does not validate our estimation approach, it does serve as one test. Moreover, for acetaldehyde, the temperature-K_{AW} relationship estimated here is consistent with the relationships reported in the literature.

- In general, estimates from Method *XY*–1 are larger than those from Method *XY*–2 and GCE (see Appendix B for a description of *XY*–1 and *XY*–2).

- With the exception of acetic acid, propanoic acid and formaldehyde, recently reported observations at 25 °C are approximately within the range of values estimated using Methods *XY*–1, *XY*–2 and GCE. For formic acid and 2-methyl propanoic acid, the observations themselves cover a broad range and at least one of the observations falls within the estimated range.
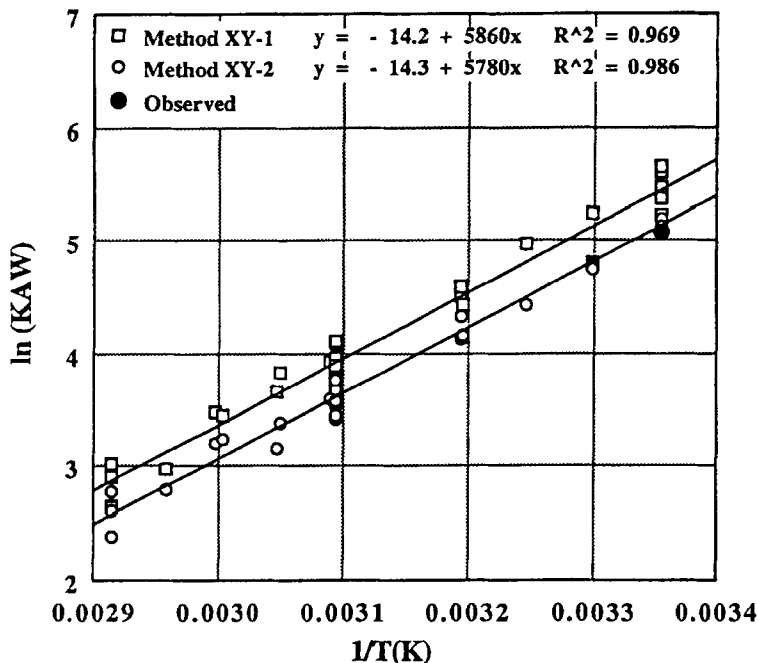
Figure 3b.

• For acetic acid, propanoic acid and formaldehyde, recently reported observations at 25 °C are outside the range we have estimated. The maximum deviation between an estimate and a measured value is approximately a factor of 10. One possible explanation for the large deviations between our estimates and literature values for monocarboxylic acids is the nonideal behavior of these compounds in the vapor phase: monocarboxylic acids associate in the vapor phase forming dimers and tetramers (Sebastiani and Lacquaniti, 1967; Gmehling and Onken, 1977). For instance, at 25 °C, only about one-fifth of the vapor pressure of acetic acid is due to the monomer. These nonidealities are only partially accounted for in our estimates. The literature values, on the other hand, are typically derived for very low vapor-phase concentrations of the solute ~1–100 ppm); at these concentrations, 90 to $\geq$ 99.9% of the partial pressure of acetic acid is due to the monomer. Nonetheless, to put these deviations in perspective, experimental values (as reported by different investigators) for formic acid, acetic acid, 2-methyl propanoic acid and formaldehyde differ among themselves by approximately a factor of 2 to 5, as shown in Table V (also see Betterton and Hoffmann, 1988; Servant *et al.*, 1991; Khan *et al.*, 1995). In fact, polymerization could explain the large differences (up to a factor of 3.6) among the K_{AW} values of monocarboxylic acids reported by Servant *et al.* (1991) for various solute concentrations.
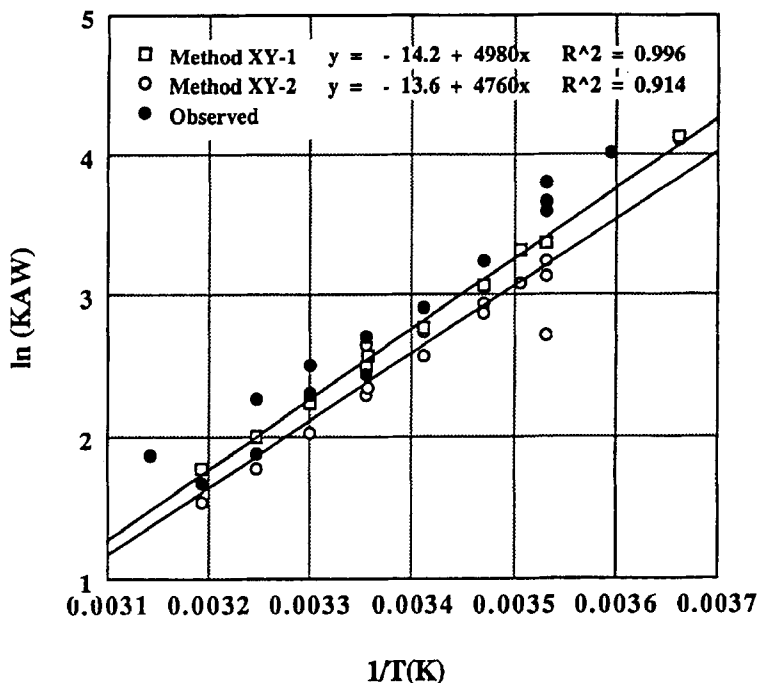
Figure 3c.

Figure 3. Air-water equilibrium constants as a function of temperature estimated in this work using x–y observations in the DECHEMA compilation (Gmehling and co-author(s), 1977, 1981, 1988) as compared with values reported in literature. (a) Acetic acid; observed values from Keene and Galloway (1986), Servant *et al.* (1991) and Khan *et al.* (1995). (b) Ethanol: observed value from Hine and Mookerjee (1975). (c) Acetaldehyde; observed values from Betterton and Hoffmann (1988), Zhou and Mopper (1990) and Benkelberg *et al.* (1995).

To our knowledge, only limited observations are available to test the reliability of our estimates of K_{AW} for dicarboxylic acids, polyols, amino acids, and other multifunctional compounds. As Table V shows, for ethanediol, propanediol and ethanol amine, the accuracy of our estimates is similar to those for monofunctional compounds. Suleiman and Eckert (1994) recently reported infinite-dilution activity coefficients ($T = 24$ to $26\,^\circ$C) for several diols (1,2-ethane-, 1,2-propane-, 1,3-propane-, 1,3-butane-, 1,4-butane- and 2,3-butane-). We estimate K_{AW} values using infinite-dilution activity coefficients reported by Suleiman and Eckert (1994) along with vapor pressure reported in Yaws (1994): these values are either within the range we derive by using XY methods in conjunction with DECHEMA data (extrapolated from higher temperature) and the GCE method or are within a factor of 10 of the GCE estimate (when no data are available in DECHEMA). For oxalic acid, we compare our estimates to the results of an alternative approach. Using vapor-solid and ionic equilibria data, Clegg *et al.* (1996) have recently estimated K_{AW} for

oxalic acid to be 7E8; the value we derive using the group contribution method is 5E8. These two estimates are within 40% of each other.

Based upon the above tests we conclude that in broad terms our estimates of K_{AW} are accurate to within a factor of 10.

4.4.2. Air-Water Equilibrium Constants and their Application

In Table VI we summarize the K_{AW} values for all candidate compounds initially classified as water-soluble (Table III). Wherever available, we use observed values. When using estimates or observations with relatively large uncertainties as reported by experimentalists (e.g., 1,3-propanediol), we decrease our previously-discussed cut-off value of K_{AW} or $K^*_{AW} = 1E+6$ M-atm^{-1} by a factor of 10 as a safety margin against errors in estimation methods or the measurement uncertainty that may under-represent the condensibility. The safety margin is also applied to ethanediol since observations for this difunctional compound are limited and, on the basis of the differences in values reported in two studies (Table V), in our judgment, potentially imprecise. For completeness, Table VI also includes information on compound vapor pressures where available. The distribution between air and aqueous phases can be viewed as a competition between a compound's affinity for water (i.e., solubility) and its volatility (vapor pressure). For compounds with similar solubility, vapor pressure is indicative of a tendency to partition into the gas phase (e.g., propanol vs. propanetriol). Likewise, for compounds with similar vapor pressure, solubility is indicative of a tendency to partition into the aqueous phase (e.g., hexanoic acid vs. propanediol).

Specific compounds included in Table VI are intended to be representative of various compound classes. Numerous other, particularly multifunctional, compounds such as hydroxyacids, ketoacids, and hydroxy- and dihydroxy carbonyls merit consideration as well (e.g., Kawamura and Gagosian, 1987, 1988, 1990; Atkinson and Aschmann, 1995; Klotz et al., 1995; Wiesen et al., 1995; Yu et al., 1995). For instance, particulate phase concentrations have been reported for 5-hydroxy pentanoic and 6-hydroxy hexanoic acids in Los Angeles (Cronn et al., 1977) and 3-methyl 3-hydroxy 1-butanoic acid was detected in Tsukuba, Japan (Yokouchi and Ambe, 1986).

The following compound classes emerge as likely to contribute to the water soluble fraction:

- Dicarboxylic acids (C2 to C6)
- Dicarbonyls (glyoxal)
- Ketoacids (C2 to C5)
- Multifunctional compounds (e.g., 1-malic acid) containing acidic, basic and carbonyl functional groups (C3 to C6)
- Polyols (C2 to C7)
- Hydroxyamines, amino acids (C2 to C6) and nitrophenol

Table V. Comparison of estimated and measured (literature) K_{AW} in M/atm at T = 25 °C

Compound	Measured value (ref)[a]	Estimate from x-y data[b]		Estimate from GCE[b]
		Method XY-1	Method XY-2	
Hydrogen peroxide	7.1E4 (MD); 1.E5 (LK)	–	7.3E4	–
Formic acid	5530 (KB); 13,400 (SK)	5800	1400	–
Acetic acid	5500 (KB); 9300 (SK)	3000	900	1400
Propanoic acid	5710 (KB); 6200 (SK)	1900	920	1100
2-Methyl propanoic acid	1130 (KB); 5700 (SK)	1100[c]	–	780
Formaldehyde[d]	2970 (BH1); 3400 (ZM)	6800	–	–
Acetaldehyde[d]	11.4 (BH1); 13.4 (BH2); 14.9 (ZM)	12	11	6.5
Acetone[d]	27 (HM1,BH2); 33 (B1); 34.6 (ZM)	31	27	9.1
2-Butanone[d]	7.7 (AH); 19.8 (ZM)	26	17	7.1
Butanal[d]	8.7 (HM2[e], ZM))	15	11	3.7
Methanol	215 (HM2[e])	240	190	200
Ethanol	159 (HM2[e])	230	170	140
1-Propanol	149 (HM2[e])	210	120	110
2-Propanol	124 (HM2[e])	110	93	93
1-Butanol	118 (HM2[e])	140	83	82
2-Butanol	98 (HM2[e])	150	69	73
2-Methyl 2-propanol	84 (HM2[e])	100	61	59
2-Propen-1-ol	200 (HM2[e])	640	130	430
Diethyl ether	0.78 (HM2[e]); 1.15 (NO)	0.82	0.88	0.70
Methyl amine	140 (BC)			180
1,2-Ethanediol	4.0E5 (BC)	2.9E5	6.9E5	9.2E6
1,3-Propanediol	9.1E5[f] (BC)			7.0E6
Ethanol amine	6.0E6 (BC)			8.4E6

[a] References: AH: Ashworth, Howe *et al.* (1988); B1: Betterton (1991); BC: Bone, Cullis and Wolfenden (1983)–values at 20 °C; BH1: Betterton and Hoffmann (1988); BH2: Benkelberg, Hamm and Warneck (1995); HM1: Hoff, Mackay *et al.* (1993); HM2: Hine and Mookerjee (1975); KB: Khan, Brimblecombe and Clegg (1995); LK: Lind and Kok (1994); MD: Martin and Damschen (1981); NO: Nielsen, Olsen and Frendenslund (1994); SK: Servant, Kouadio *et al.* (1991) – values shown here are for the lowest liquid phase concentration reported and temperatures between 23 and 24 °C; ZM: Zhou and Mopper (1990).

[b] For estimates, we report two significant figures only. Method XY–1 utilizes vapor-liquid equilibria data for the lowest reported liquid-phase solute concentration, while Method XY–2 uses the activity coefficient at infinite dilution derived by fitting an excess Gibbs free energy model to the vapor-liquid equilibria data; see Appendix B for further details.

[c] Extrapolated from value at $T = 20$ °C using $\Delta H° = 50$ kJ/mole (Khan *et al.*, 1995).

Table V. *(Continued)*

---

[d] Effective air-water equilibrium constant K_{AW}^* (see Equation (A.6) in Appendix A).

[e] These are taken from the compilation of Hine and Mookerjee (1975), whose source for 1-propanol, 2-propanol, 1-butanol, 2-butanol and 2-methyl 2-propanol is the original work of Butler *et al.* (1935). Hine and Mookerjee compilation also contains K_{AW} values for 1,2-ethanediol and 1,2,3-propanetriol (aka glycerol) that are taken from a companion paper by Butler and Ramchandani (1935). However, Butler and Ramchandani (1935) data for these two less volatile substances (1,2-ethanediol and glycerol) appear to be unreliable: for instance, the partial pressure over a dilute solution of glycerol exceeds the vapor pressure of glycerol as reported by Tang and Munkelwitz (1991) and Yaws (1994); on the basis of their own measurements of 1,2-ethanediol partial pressure over dilute aqueous solution, Bone *et al.* (1983) also concluded that Butler and Ramchandani's (1935) measurements are anomalously high, perhaps due to the low sensitivity of the measurement method used. Therefore, we do not use the Butler and Ramchandani (1935) data for 1,2-ethanediol and glycerol.

[f] The uncertainty reported in the measured value is relatively high: K_{AW} ranges from 5.5E5 to 2.7E6.

5. Discussion

We first examine the plausibility of above results, and then discuss their significance.

Our finding that C1-C6 monocarboxylic acids, alcohols, carbonyls and ethers are too volatile to be distributed in fine particles is largely consistent with the available experimental evidence, wherein these compounds most commonly are observed in the gas phase (Graedel *et al.*, 1986; Grosjean, 1989, 1991, 1992b; Kelly *et al.*, 1993; Lawrence and Koutrakis, 1994; Koutrakis, 1995). Using measurements of vapor-aqueous equilibrium constants and the method described in Appendix A, Khan *et al.* (1995) also concluded that for aerosols (rather than clouds and fogs), C1 to C6 monocarboxylic acids would be completely partitioned into the gas phase. Our finding that dicarboxylic acids, ketoacids and multifunctional compounds such as 1-malic acid are sufficiently soluble and condensible to be present in the water-soluble fraction is also consistent with observations: these compounds have been measured in the water-soluble fraction (e.g., Sempere and Kawamura, 1994).

Nonetheless, some discrepancies exist between theoretical assessments (e.g., our work, Khan *et al.*, 1995) and observations. For example, Grosjean (1982, 1989) reported that although formic and acetic acids and C1-C4 carbonyls in the Los Angeles area were distributed predominantly in the gas phase, they also were found in the particle phase in measurable concentrations; Khwaja (1995) too observed particle-phase formic and acetic acids in samples collected in Schenectady, New York. Although the reason for such discrepancies between observations and theoretical calculations is not known, possible hypotheses are: 1) sampling biases that lead to misclassification of gaseous material as particulate; or 2) modification of air-water distribution of these compounds as a result of aqueous phase reactions and/or the presence of an organic film (Grosjean, 1982; Saxena *et al.*, 1995). In addition, for some compounds our estimates of K_{AW} may be unrealistically low: for instance, given the range of particle water contents and pHs reported for the Los Angeles area (Meng *et al.*, 1995), our K_{AW} estimate for oxalic acid

Table VI. Water-soluble organic compounds likely to partition onto atmospheric particles (T = 25 °C)

Compound	Vapor pressure[a] (mm Hg)	K^b_{AW} (M/atm)	Source for K^c_{AW}	In water soluble fraction?
Monocarboxylic acids				
Formic acid	4.26E1	5.53E3	KB	No
Acetic acid	1.57E1	5.50E3	ibid	No
Propanoic acid	3.70E0	5.71E3	ibid	No
Butanoic acid	9.46E-1	4.73E3	ibid	No
2-Methyl propanoic acid	1.82E0	1.13E3	ibid	No
Pentanoic acid	2.44E-1	2.30E3	ibid	No
3-Methyl butanoic acid	4.39E-1	1.20E3	ibid	No
2,2-Dimethyl propanoic acid	–	3.53E2	ibid	No
Hexanoic acid	4.35E-2	1.34E3	ibid	No
Dicarboxylic acids				
Oxalic acid	8.26E-5	5E8	GCE	Yes
Malonic acid	–	4E8	GCE	Yes
Succinic acid	7.9E-6 (6.76, 188)	3E8	GCE	Yes
Glutaric acid	7.78E-6	2E8	GCE	Yes
Adipic acid	1.11E-7	2E8	GCE	Yes
Maleic acid	3.6E-5 (7.0E-1,130)	1E9	GCE	Yes
Carbonyls				
Glyoxal	–	$\geq$ 1.4E0 ($\geq$ 3.00E5)	BH1	Yes
Formaldehyde	3.89E3	2,5E0 (2.97E3 to 3.4E3)	BH1,ZM	No
Hydroxyacetaldehyde	–	4.1E3 (4.14E4)	BH1	No
Acetaldehyde	8.99E2	4.8E0 (1.14E1 to 1.49E1)	BH1,ZM	No
Methyl glyoxal	–	1.4E0 (3.71E3)	BH1	No
Acetone	2.30E2	(2.7E1 to 3.5E1)	HM1,BH2, B1,ZM	No
2-Butanone	9.55E1	(7.7E0 to 1.98E1)	AH,ZM	No
Propanal	3.17E2	(1.22E1 to 1.35E1)	HM2,ZM	No
Butanal	1.11E2	(8.7E0)	ibid	No
Alcohols				
Methanol	1.26E2	2.15E2	HM2	No
Ethanol	5.92E1	1.60E2	ibid	No
1-Propanol	2.07E1	1.50E2	ibid	No
2-Propanol	4.56E1	1.24E2	ibid	No
2-Propen-1-ol	2.61E1	2.00E2	ibid	No
1-Butanol	7.05E0	1.18E2	ibid	No
2-Butanol	1.83E1	9.8E1	ibid	No

Table VI. *(Continued)*

Compound	Vapor pressure[a] (mm Hg)	K_{AW}^b (M/atm)	Source for K_{AW}^c	In water soluble fraction?
2-Methyl 1-propanol	1.04E1	8.4E1	HM2	No
2-Buten-1-ol	–	3.0E2	GCE	No
1-Pentanol	2.47E0	8.0E1	HM2	No
2-Methyl 2-propanol	4.19E1	8.4E1	ibid	No
2,2 Dimethyl 1-propanol	9.6E0 (5.7E1,54)	5E1	GCE	No
Benzyl alcohol	8.09E-2	9E3	GCE	No
Phenol	5.3E-1 (1.6,41)	2.52E3	HM2	No
Polyols				
1,2-Ethanediol	9.18E-2	4.0E5	BC	Yes
1,2-Propanediol	1.29E-1	1E5 to 6E6	XY,GCE	Yes
1,3-Propanediol	4.41E-2	9.1E5	BC	Yes
1,2,3-Propanetriol	1.06E-4 to 1.69E-4	6E8 to 4E11	XY,GCE	Yes
1,3-Butanediol	2.01E-2	5E6	GCE	Yes
1,4-Butanediol	1.04E-2	1E5 to 5E6	XY,GCE	Yes
2,3-Butanediol	1.82E-1	4E4 to 4E6	XY,GCE	Yes
1,2,3-Butanetriol	–	3E11	GCE	Yes
1,2,4-Butanetriol	–	3E11	GCE	Yes
1,2,3,4-Tetrahydroxy butane	–	2E16	GCE	Yes
1,5-Pentanediol	3.90E-3	4E6	GCE	Yes
2,3-Pentanediol	–	3E6	GCE	Yes
2,4-Pentanediol	–	3E6	GCE	Yes
1,2,3,4,5-Pentahydroxy pentane	–	9E20	GCE	Yes
1,6-Hexanediol	9.9E-4 (6.7E-3,42)	3E6	GCE	Yes
2,5-Hexanediol	–	2E6	GCE	Yes
2-Methyl-1,3-pentanediol	–	3E6	GCE	Yes
2-Methyl-2,4-pentanediol	–	2E6	GCE	Yes
1,2,6-Hexanetriol		2E11	GCE	Yes
1,2,3,4,5,6-Hexahydroxy hexane	–	4E25	GCE	Yes
1,2,4,5-Tetrahydroxy cyclohexane	–	4E16	GCE	Yes
Hexahydroxy cyclohexane	–	1E26	GCE	Yes
1,7-Heptanediol	–	2E6	GCE	Yes
2,4-Heptanediol	–	2E6	GCE	Yes
2,3-Diethyl-1,3-propanediol	–	2E6	GCE	Yes
2-Ethyl-1,3-hexanediol	–	2E6	GCE	Yes
1,2,3,4,5-Pentahydroxyheptane	–	5E20	GCE	Yes
1,2,3,4,6-Pentahydroxyheptane	–	4E20	GCE	Yes
1,2,3,5,7-Pentahydroxyheptane	–	5E20	GCE	Yes
1,2,3,4,5,6-Hexahydroxyheptane	–	3E25	GCE	Yes

Table VI. *(Continued)*

Compound	Vapor pressure[a] (mm Hg)	K^b_{AW} (M/atm)	Source for K^c_{AW}	In water soluble fraction?
Polyglycols				
Diethylene glycol	5.68E-3	2E9	GCE	Yes
Triethylene glycol	–	9E11	GCE	Yes
Keto-carboxylic acids				
Pyruvic acid	1.27E0	3.11E5 (3.3E8)	KB	Yes
Glyoxylic acid	–	9E3 (9E6)	GCE	Yes
3-Oxopropanoic acid	–	7E3 (7E6)	GCE	Yes
4-Oxobutanoic acid	–	5E3 (5E6)	GCE	Yes
5-Oxopentanoic acid	–	4E3 (4E6)	GCE	Yes
Ethers				
Dimethyl ether	4.43E3	1.0E0	HM2	No
Methyl tert-butyl ether	2.50E2	1.7E0	ibid	No
Ethyl methyl ether	1.51E3	9E-1	GCE	No
Diethyl ether	5.36E2	7.8E-1 to 1.15E0	HM2,NO	No
Miscellaneous multifunctional compounds				
1-Malic acid	3.3E-8 (2.09E-2, 130)	2E13	GCE	Yes
Citric acid	1.7E-11 (2.55E-3, 153)	3E18	GCE	Yes
α-Keto glutaric acid	–	1E9	GCE	Yes
Lactic acid	8.13E-2	7E7	GCE	Yes
Tartaric acid	2.4E-12 (1.07E-1,206)	1E18	GCE	Yes
Glyceraldehyde	–	2E10	GCE	Yes
Organic nitrates and nitro compounds				
Methyl nitrate	1.23E2	2.00E0	KS	No
Ethyl nitrate	5.5E1	1.59E0	KS	No
1-Propyl nitrate	5.5E1	1.10E0	KS	No
2-Propyl nitrate	3.0E1	7.90E-1	KS	No
1-Butyl nitrate	9.0E0	1.01E0	KS	No
2-Butyl nitrate	1.2E1	6.5E-1	KS	No
2-Methyl 1-propyl nitrate	1.2E1	7.1E-1	KS	No
1-Pentyl nitrate	2.0E0	1.2E0	KS	No
2-Pentyl nitrate	3.0E0	3.7E-1	KS	No
1,2-Ethane dinitrate	4.0E-2	4.80E-2	KS	No
2-Nitrooxy-ethanol	1.5E-1	3.99E4	KS	No
2-Nitrooxy-1-propanol	2.0E-1	7.30E3	KS	No
1-Nitrooxy-2-propanol	2.0E-1	6.70E3	KS	No
1,2-Propane dinitrate	7.0E-2	1.75E2	KS	No
Nitrooxy acetone	–	1.01E3	KS	No
p-Nitrophenol	–	2.4E6	HM2	Yes

Table VI. *(Continued)*

Compound	Vapor pressure[a] (mm Hg)	K_{AW}^{b} (M/atm)	Source for K_{AW}^{c}	In water soluble fraction?
Amines & amino acids				
Methyl amine	2.65E3	1.40E2	BC	No
Ethyl amine	1.05E3	9.8E1	HM2	No
Ethanol amine	3.69E-1	6.0E6	BC	Yes
Glutamic acid	4.9E-9 (1.4,224)	1E13	GCE	Yes
Asparagine	–	1E13	GCE	Yes
Serine	–	4E12	GCE	Yes
Glutamine	–	1E13	GCE	Yes
Glycine	–	9E7	GCE	Yes
Arginine	–	1E17	GCE	Yes
Alanine	–	6E7	GCE	Yes
Leucine	–	2E7	GCE	Yes

[a] All vapor pressures (P^{sat}) are taken from Yaws (1994) except the following: oxalic acid (de Kruif *et al.*, 1975); glutaric and adipic acids (Tao and McMurry, 1989); all organic nitrates (Kames and Schurath, 1992). For nitrates, P^{sat} is at 20 °C; for all other compounds P^{sat} is at 25 °C. For glycerol, we show the range as defined by the data reported by Tang and Munkelwitz (1991) (the lower value) and Yaws (1994) (the higher value). For some relatively less volatile compounds, we have extrapolated the vapor pressure at 25 °C from observations at higher temperature according to the temperature-vapor pressure functional relationship prescribed in the reference. Extrapolation could entail substantial error: for oxalic acid, extrapolation of more recent data (de Wit *et al.*, 1983) for $T \geq 38$ °C to $T = 25$ °C using the Antoine equation yields a value of 1.4E-4. Therefore, for these compounds we also list in parentheses the lowest temperature (T_{min} in degrees celsius) at which vapor pressure is reported and the vapor pressure at T_{min} in the form (P^{sat} at T_{min}, T_{min}).

[b] For 1,2-ethanediol, 1,3-propanediol, 1-pentyl nitrate, 2-nitroxy-ethanol, 2-nitroxy-1-propanol, 1-nitroxy-2-propanol, 1,2-propane dinitrate, nitroxy acetone, methyl amine and ethanol amine, K_{AW} is at 20 °C; for all other compounds K_{AW} is at 25 °C. Estimates are shown with one significant figure. We report K_{AW}^{*} (shown in parentheses) only for those compounds for which K_{AW} is smaller than our cut-off value but K_D or K_A is sufficiently large to make the effective air-water equilibrium constant (K_{AW}^{*}) larger than the cut-off value. For carbonyls (which associate) we show K_{AW}^{*} as reported in the literature and K_{AW} if available. For monocarboxylic acids, dicarboxylic acids, multifunctional compounds and amino acids, we derived K_{AW}^{*} at pH = 5.5 using the first dissociation constants reported in the following sources: Robinson and Stokes (1968); Serjeant and Dempsey (1979); Popovych and Tomkins (1981); Trivedi and Culbertson (1982); Streitwieser and Heathcock (1985); Weast (1986); and Morrison and Boyd (1992). For monocarboxylic acid, K_{AW}^{*} ranges between 6.3E3 and 3.2E5 M-atm^{-1}; for dicarboxylic acids between 3E9 and 9E12; for miscellaneous multifunctional compounds between 3E9 to 7E20; and for amino acids between 4E10 and 7E20. For pyruvic acid, we use the K_D value reported by Fischer and Warneck (1991). For glyoxylic, 3-oxopropanoic, 4-oxobutanoic and 5-oxopentanoic acids, either K_D is not available or the value reported in Serjeant and Dempsey (1979) for either the compound of interest or nearest isomer (e.g., 4-oxopentanoic acid) is uncertain: for these acids, we use K_D of pyruvic acid. This assumption tends to maximize the estimated K_{AW}^{*} and thus prevents elimination of these compounds due to uncertainties in the reported K_D.

[c] AH: Ashworth, Howe *et al.* (1988); B1: Betterton (1991); BC: Bone, Cullis and Wolfenden (1983); BH1: Betterton and Hoffmann (1988); BH2: Benkelberg, Hamm and Warneck (1995); GCE: estimated from group contribution method; HM1: Hoff, MacKay *et al.* (1993); HM2: Hine and Mookerjee (1975); KB: Khan, Brimblecombe and Clegg (1995); KS: Kames and Schurath (1992); NO: Nielsen, Olsen and Frendenslund (1994); XY: estimated from x–y data; ZM: Zhou and Mopper (1990).

would imply that in some instances a substantial fraction of oxalic acid may be present in the gas phase. To our knowledge, oxalic acid has not been observed in the gas phase in measurable quantities: Lefer *et al.* (1994) detected vapor-phase oxalic acid in biomass burning plumes, but the concentrations in the background air were below the detection limit (~ 10 ppt).

In summary, although some discrepancies do exist between our findings (Table VI) and published observations, our results are broadly consistent with: a) observed gas-particle distribution of monocarboxylic acids, carbonyls, alcohols, and ethers; and b) the observed presence of ketoacids, dicarboxylic acids, and multifunctional compounds such as 1-malic acid in the particle phase.

Many contemporary studies have already established that dicarboxylic acids, and to a lesser extent ketoacids and dicarbonyls, are important constituents of atmospheric organic PM. The finding here that polyols, amino acids and other multifunctional compounds (e.g., hydroxy acids and hydroxy carbonyls) may also be important offers a tentative explanation for the gap in the observed composition of particulate organics, and creates motivation for confirmation via further theoretical and experimental studies. As mentioned before, some albeit limited and qualitative experimental evidence supports our deductions (Wauters *et al.*, 1979; Gorzelska *et al.*, 1992). In addition, FTIR analysis of inhalable particle samples collected in Elizabeth, New Jersey shows a relatively high OH-to-carbon ratio (Gundel *et al.*, 1993, 1995). Our results offer a molecular-level explanation for these observations; however, further experimentation is needed to determine the atmospheric concentrations of polyols, amino acids and other multifunctional compounds.

Some, albeit insubstantial, information is available regarding primary sources of polyols and amino acids. While some polyols stem directly from industrial activities (Graedel *et al.*, 1986), Wauters *et al.* (1979) and Gorzelska *et al.* (1992) have speculated that microbiological processes in the atmosphere, direct emissions from plants, and degradation of organic litter may also contribute polyols as well as amino acids. Sub- and supermicron bioaerosols (e.g., fungi, bacteria, pollen, plant debris) containing amino acids and other organic compounds can be transported hundreds of kilometers and have been hypothesized to play an important role in cloud physics (Matthias-Maser and Jaenicke, 1994; Muilenberg, 1995). Researchers have found, using plant wax tracers, that both urban and nonurban locations have an appreciable fraction of plant detritus in the airborne PM (Simoneit, 1986; Mazurek *et al.*, 1991; Hildemann *et al.*, 1996). Although some components of plant detritis and other bioaerosols are water insoluble (e.g., waxes, cellulose and other biopolymers), these findings broadly support the view that bioaerosols may be a potential source for water-soluble compounds as well. In fact, Gorzelska *et al.* (1992) have argued that water-soluble amino acids may be released by plants during the flower development stage, and Duce *et al.* (1983) have estimated that fungal spores may contribute 1 to 2 μg/m^3 of particulate carbon to aerosols over land surfaces. However, due to extreme paucity of data on this topic, such notions are proposed by their authors

as hypotheses or crude estimates to illustrate the possible importance of vegetative and microbiological sources in explaining observations.

Secondary sources of polyols and other multifunctional compounds may be photo-oxidation of anthropogenic and biogenic VOC emissions in the atmosphere. As mentioned before, some theoretical and experimental evidence indicates that polyhydroxy alkanes, and hydroxy- and polyhydroxy carbonyls (e.g., glyceralde-hyde, the simplest carbohydrate) may be formed by photo-oxidation of alkanes, alkenes, carbonyls and aromatics emanating from anthropogenic sources (Milas *et al.*, 1937; Renzetti and Doyle, 1959; Hort, 1972; Atkinson, 1990; Atkinson and Aschmann, 1995; Klotz *et al.*, 1995; Wiesen *et al.*, 1995; Yu *et al.*, 1995). Oxi-dation of biogenic isoprene yields multifunctional compounds such as hydroxy acetone (Yu *et al.*, 1995). Moreover, plants and other natural sources directly emit oxygenates. For instance, the recent measurements of Konig *et al.* (1995) indicate that agricultural and natural plant species in mid-Europe emit, relative to reactive hydrocarbons such as isoprene and terpene, substantial quantities of unsaturated and saturated oxygenates (e.g., 3-methyl-3-buten-1-ol and 1-butanol). Guenther *et al.* (1995) estimate that these two oxygenate classes account for approximately 22.5% each of the total nonmethane VOC global emission flux attributable to nat-ural sources. The photo-oxidation of unsaturated oxygenates is expected to yield bifunctional compounds such as hydroxy carbonyls (Grosjean *et al.*, 1993).

Taken together with these published findings, our study provides an impetus for new observational and mechanistic studies to investigate the sources of polyols, amino acids and other water-soluble organics in the atmosphere, and to assess the relative importance of primary emissions vs. secondary gas-to-particle conversion processes.

Water solubility of organic compounds is relevant to the water-absorbing char-acteristics of atmospheric particles. Water-insoluble compounds may form micelles or surface films that prevent the condensation or evaporation of water from particles (Warner and Warne, 1970; Husar and Shu, 1975; Gill *et al.*, 1983; Hameri *et al.*, 1992; Andrews and Larson, 1993; Saxena *et al.*, 1995). On the other hand, accord-ing to phase equilibrium theory, water-soluble compounds in atmospheric particles will absorb water to remain in equilibrium with water vapor. The expectation is that compounds with finite solubility (e.g., 1-malic acid) will exhibit deliquescence (water absorption above a certain relative humidity, RH) whereas completely mis-cible compounds (e.g., 1,3-butanediol) will be hygroscopic (water absorption at all RH values $> 0\%$) (Saxena *et al.*, 1995). For instance, oxalic, glyoxylic and citric acids; ethanediol, propanediol, propanetriol, butanediols and diethylene glycol are known to be either hygroscopic or deliquescent (Budavari *et al.*, 1989). Therefore, our results indicate that in addition to sulfate and nitrate, dicarboxylic acids, poly-ols, amino acids and other multifunctional compounds in atmospheric PM may also absorb water.

Whether a compound is completely miscible with water, or has a finite solu-bility, or is surface active depends upon its molecular size and structure: namely

the number of carbon atoms, the type and position of functional groups, and their spatial orientation. For instance, consider polyols, which have particularly high affinity for water, with some compounds up to C7 being completely miscible. Whereas 2,5-hexanediol is completely miscible, 1,2-hexanediol is surface active and 1,2,3-hexanetriol forms hydrophobic aggregates (Curme and Johnston, 1952; Coudert *et al.*, 1993, 1994). For tetra-hydroxy butanes, pentahydroxy pentanes and hexahydroxy hexanes, the solubility and the quantity of water absorbed (per gram of solute at a given RH) differ for different stereoisomers (Cohen *et al.*, 1993). Therefore, characterizing and estimating the interactions of water with atmospheric aerosols, which may contain a broad range of hydrophilic and hydrophobic inorganic and organic compounds within single particles, are problems ripe for investigation. To this end, there is a need for i) methods to estimate the activity coefficients of mixtures of electrolytes and organics (Fredenslund and Sorensen, 1994); and ii) concurrent data on composition and water absorption behavior of atmospheric particles. As a step in this direction, we will present in a forthcoming paper a model for estimating the water absorption behavior of atmospheric dicarboxylic acids, polyols and other multifunctional organic compounds.

6. Summary and Conclusions

The molecular composition of fine particulate organics remains poorly characterized because these particles contain hundreds of organic compounds that cover a wide range of carbon numbers, functional groups and solubility in extraction media. Such diversity is a challenge to chemical analysis methods; even in the most diligent experiments, typically only about 10% of the organic mass has been attributed to specific compounds. The composition of highly polar, water-soluble organic carbon (WSOC) is especially obscure because the analytical methods commonly used are not aimed at fully characterizing this fraction.

Because experimental studies test, explicitly or implicitly, *a priori* hypotheses about the molecular composition, the creation of new hypotheses is itself an important endeavor. Historically, progress has been made through a leapfrogging of theoretical and experimental studies. Within this context, our paper represents an endeavor to characterize more fully the water-soluble organics in the atmosphere by juxtaposing atmospheric observations with the thermodynamic properties of individual compounds.

To be as comprehensive as possible, we have examined the solubility and condensibility in aqueous-organic systems for a broad range of (over one hundred) compounds. Where necessary, compound properties are estimated and error bounds in the estimation method are factored into our assessment. The findings are:

- In prior experimental studies conducted in urban and nonurban locations in the continental U.S. and Japan, a substantial fraction (one-fifth to two-thirds) of the total particulate carbon (organic plus elemental) has been found to be WSOC. The observed differences in the extractability of carbon in atmospheric

particle samples by polar vs. nonpolar solvents stem from differences in the solubility of the material extracted. Relatively polar organic compounds tend to extract in water; many of these compounds are suspected to be at least partly secondary in origin.

- Observations regarding the molecular composition of the water-soluble organic fraction are limited. In one study that reported the total concentration and composition of WSOC, only approximately 5 to 20% of the total water-soluble organic carbon mass was resolved into specific compounds. By and large, the emphasis in most contemporary experiments has been on measuring dicarboxylic acids and ketoacids.

- A review of thermodynamic properties shows that in addition to dicarboxylic and ketoacids, polyols, amino acids and other multifunctional compounds that contain acidic, basic and carbonyl functional groups may be present in the water-soluble organic fraction of atmospheric fine particles. Hydrocarbons substituted with two or more of these functional groups tend to be water-soluble as well as condensible. For instance, polyols can be completely miscible with water up to C7, and have low volatility. On the other hand, lower molecular weight (C1–C6) water-soluble compounds with a single polar functional group (e.g., monocarboxylic acids, carbonyls and alcohols) are too volatile to condense on fine particles, while higher molecular weight singly-substituted compounds are too nonpolar to be water-soluble.

Specific compounds are examined here as representative of various compound classes; our list of candidate water-soluble organic compounds is not intended to be exhaustive. Nonetheless, besides underscoring the need for a more complete understanding of the molecular composition of water-soluble organics in atmospheric particles, our work singles out specific compounds (e.g., polyols, amino acids, polyhydroxy carbonyls) whose presence and formation in the atmosphere merits further investigation via both observational and mechanistic studies.

Appendices

A. Estimation of the Limiting Value of the Air-Water Equilibrium Constant

Here we estimate the value of the air-water equilibrium constant required for at least 1% of the solute mass to be present in the particle phase. We are interested in atmospheric suspensions containing particles (e.g., $d_p \leq 10 \ \mu m$) rather than cloud and fog droplets.

Consider the following generic interfacial, dissociation and association equilibria reactions for a solute A:

$$A(g) \rightleftharpoons A(aq), \tag{A.1}$$

$$A(aq) \rightleftharpoons H^+ + B^-, \tag{A.2}$$

$$A(aq) + H_2O \rightleftharpoons A \cdot H_2O(aq). \tag{A.3}$$

For many compounds only Reaction 1 is relevant; Reactions 1 *and* 2 are relevant for some compounds (e.g., carboxylic acids) and Reactions 1 *and* 3 for others (e.g., carbonyls). These reactions can be represented by the following mathematical relationships:

$$K_{AW} = \frac{[A(aq)]\gamma_A}{p_A},$$

$$K_D = \frac{[H^+][B^-]\gamma_{H^+}\gamma_{B^-}}{[A(aq)]\gamma_A},$$

$$K_A = \frac{[A \cdot H_2O]\gamma_{A \cdot H_2O}}{[A(aq)]\gamma_A},$$

where K_{AW}, K_D and K_A are equilibrium constants.

Conditions in which the liquid water content of particles is high tend to maximize the fraction of substance A (total over various forms: $A(aq)$, B^-, and $A \cdot H_2O$) in the liquid phase. For such conditions, the solution would be dilute and we assume that

$$\gamma_{H^+} \cong \gamma_{B^-} \cong \gamma_A \cong \gamma_{A \cdot H_2O} \cong 1.0.$$

Then the fraction of the total mass of A present in the liquid phase is given by

$$f_{aq} = \frac{K_{AW}[1 + K_A + K_D/[H^+]]LWC}{K_{AW}[1 + K_A + K_D/[H^+]]LWC + 1/RT}, \tag{A.4}$$

where LWC is the liquid water content of the particles (mass per unit air volume); R is the universal gas constant and T is the absolute temperature. The above equation can be rewritten as

$$f_{aq} = \frac{K_{AW}^* LWC}{K_{AW}^* LWC + 1/RT}, \tag{A.5}$$

where K_{AW}^* is the effective air-water equilibrium constant. For compounds that associate:

$$K_{AW}^* = K_{AW}[1 + K_A], \tag{A.6}$$

while for acidic compounds, K_{AW}^* is a function of pH as follows:

$$K_{AW}^* = K_{AW}[1 + K_D/[H^+]]. \tag{A.7}$$

On the basis of experimental data and theoretical estimates (Seinfeld, 1986; Zhang *et al.*, 1993; Meng *et al.*, 1995; Saxena *et al.*, 1995), we use a value of 400 $\mu g/m^3$ as the upper limit for the LWC of air containing suspended particulate matter (rather

than fog or clouds). Then for $f_{aq} \geq 0.01$ (i.e., for at least 1% of the solute to be partitioned in the particle phase) at $T = 25\,°C$, we find from Equation (A.5):

$$K_{AW}^* \geq 1 \times 10^6 \, M/atm \, .$$

Equation (A.7) shows that less acidic conditions favor the condensation of compounds that dissociate. To relate K_{AW} and K_{AW}^*, we will use 5.5 as the upper limit of pH (Seinfeld, 1986; Khan *et al.*, 1995; Meng *et al.*, 1995).

B. Estimation of the Air-Water Equilibrium Constant from Vapor-Liquid Equilibrium Composition Data

The basic equation for vapor-liquid equilibrium is (Smith and Van Ness, 1975; Abbott and Prausnitz, 1994):

$$\hat{f}_i^v = \hat{f}_i^l \, , \tag{B.1}$$

where $\hat{f}_i^v$ and $\hat{f}_i^l$ are the fugacities of component i in the vapor and the liquid phases, respectively.

To describe nonidealities, as is customary, we use fugacity coefficients for the vapor phase and activity coefficients for the liquid phase:

$$\hat{f}_i^v = y_i \hat{\Phi}_i^v P \, , \qquad \hat{f}_i^l = x_i \gamma_i f_i^0 \, , \qquad y_i \hat{\Phi}_i^v P = x_i \gamma_i f_i^0 \, , \tag{B.2}$$

where

$\quad y_i$ = mole fraction of i in the vapor phase,

$\quad \hat{\Phi}_i^v$ = fugacity coefficient of i in the vapor phase,

$\quad P$ = total system pressure,

$\quad x_i$ = mole fraction of i in the liquid phase,

$\quad \gamma_i$ = activity coefficient of i in the liquid phase,

$\quad f_i^0$ = fugacity of i in the liquid phase at some standard state.

The value of the activity coefficient is defined with reference to the standard state chosen.

If we assume that the vapor phase is an ideal gas (a plausible assumption for atmospheric pressure and temperature), then $\hat{\Phi}_i^v = 1$ and Equation (B.2) simplifies to:

$$y_i P = x_i \gamma_i f_i^0 \, . \tag{B.3}$$

Classical thermodynamics indicates that $\lim \gamma_i \rightarrow 1$ as $x_i \rightarrow 1$ (i.e., the real behavior approaches ideal behavior as the component approaches purity). However, classical thermodynamics does not provide any information about $\lim \gamma_i$ as $x_i \rightarrow 0$

(Abbott and Prausnitz, 1994). This quantity is called the activity coefficient at infinite dilution and is defined as follows:

$$\lim \gamma_i = \gamma_i^{\infty} \quad \text{as } x_i \to 0. \tag{B.4}$$

Returning to Equation (B.3), one common choice for the standard state is pure liquid i (real or hypothetical) at the system temperature (T) and pressure (P). This standard state is called Raoult's law (RL) or the Lewis–Randall standard state. Then

$$f_i^0(\text{RL}) = f_i \,, \tag{B.5}$$

where f_i is the fugacity of pure liquid i. If we assume that the vapor phase is an ideal gas and the fugacity of pure liquid i is insensitive to pressure then for pure liquid i in equilibrium with its vapor:

$$f_i = f_i^v = P_i^{\text{sat}} \,,$$

where P_i^{sat} is the vapor pressure of i. Substituting the above definition of the standard state into Equation (B.3), we obtain:

$$y_i P = x_i \gamma_i(\text{RL}) P_i^{\text{sat}} \,, \tag{B.6}$$

where $\gamma_i(\text{RL})$ is the activity coefficient based upon RL standard state. Equation (B.6) further simplifies into the familiar Raoult's law if one assumes that the liquid phase is an ideal solution ($\gamma_i(\text{RL}) = 1$).

The second common choice of the standard state is known as the Henry's law (HL) standard state. Here Henry's constant is defined as:

$$H_{ij} = \lim(\hat{f}_i^l / x_i) \quad \text{as } x_i \to 0 \,. \tag{B.7}$$

The constant H_{ij} is a function of T and P and is specific to the components i (solute) and j (solvent). The Henry's law standard state corresponds to a choice of the scale for activity coefficients such that

$$\lim \gamma_i(HL) = 1 \quad \text{as } x_i \to 0. \tag{B.8}$$

This indicates that the activity coefficient at infinite dilution (based upon HL standard state) is unity. Equations (B.3), (B.7) and (B.8) can be combined to obtain:

$$H_{ij} = f_i^0(\text{HL}) \,, \tag{B.9}$$

which upon substitution in Equation (B.3) gives

$$H_{ij} = \frac{y_i P}{x_i \gamma_i} = \frac{y_i P}{\hat{a}_i} \,, \tag{B.10}$$

where $\hat{a}_i$ is the activity of i in the liquid phase. H_{ij} has units of pressure/mole fraction in the liquid phase. It represents the ratio of the concentration in the vapor

phase to the liquid phase activity. If the liquid phase is assumed to be ideal (e.g., very dilute solution), the activity coefficient becomes unity and Equation (B.10) simplifies to the familiar Henry's law:

$$H_{ij} = \frac{y_i P}{x_i} \, . \tag{B.11}$$

However, Equation (B.10) is valid for any concentration as long as we account for liquid phase nonideality by using the solute activity coefficient.

The activity coefficients based upon the two standard states are interconvertible as follows:

$$\frac{\gamma_i(\text{RL})}{\gamma_i(\text{HL})} = \frac{H_{ij}}{f_i} \, .$$

Comparing Equation (B.3) in terms of both standard states for $x_i \rightarrow 0$ and assuming that the vapor phase is an ideal gas:

$$H_{ij} = f_i \gamma_i^{\infty}(\text{RL}) = P_i^{\text{sat}} \gamma_i^{\infty}(\text{RL}) \, . \tag{B.12}$$

The above equation relates Henry's constant to the vapor pressure of the solute and its infinite dilution activity coefficients based upon RL standard state. Note that when the standard state is RL, γ_i^{∞} has a finite value. We choose an asymmetric convention wherein for the solvent (water) the standard state is RL and for the solute it is HL.

Equations (B.11) and (B.12) provide us two techniques for deriving values of H_{ij} from x–y data. The first technique (hereafter referred to as Method XY–1) is applicable when x–y data are available at relatively low liquid phase concentrations (x_i) where the solution can be assumed to be ideal: then H_{ij} can be estimated from Equation (B.11). This is the most common method for experimentally determining H_{ij} (e.g., Khan *et al.*, 1995). In the second technique (hereafter referred to as Method XY–2), x–y data are used to estimate the liquid phase activity coefficients (using Equation (B.6)). These activity coefficients are fitted to one or more physical models for relating activity coefficients and excess Gibbs free energy to liquid phase composition; the models are extrapolated to $x_i = 0$ to estimate the activity coefficient at infinite dilution; and finally, Equation (B.12) is used to estimate H_{ij}.

Method XY–1 is the most straightforward way to estimate H_{ij} solely from observations without the use of a model to relate the excess Gibbs free energy or the activity coefficients to observations: what one needs are observations $y(x)$ at liquid phase concentrations x_i that are low enough to yield a linear relationship between y and x. H_{ij} is then obtained from the slope of the x–y diagram. However, x–y data often are not available for low x values; in these instances, Method XY–2 provides a tenable means for combining data and activity coefficient models to estimate H_{ij}.

H_{ij} is a function of temperature and pressure. The temperature dependence is generally strong (Reid *et al.*, 1977), and is given by the following equation (Smith and Van Ness, 1975):

$$\frac{d(\ln H_{ij})}{dT} = \frac{\Delta H^0}{RT^2} ,$$ (B.13)

where ΔH^0 is the standard enthalpy change of the reaction involving transfer of solute i from the liquid to the vapor phase and R is the universal gas constant. If ΔH^0 can be assumed to be constant for the temperature range of interest, then

$$\ln \frac{H_{ij}(T_2)}{H_{ij}(T_1)} = -\frac{\Delta H^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$ (B.14)

or

$$\ln H_{ij} = A - \frac{B}{T} ,$$ (B.15)

where A and B are constants.

H_{ij} also depends upon pressure and the relationship is given by (Abbott and Prausnitz, 1994):

$$\frac{H_{ij}(P_2)}{H_{ij}(P_1)} = \exp \int_{P_1}^{P_2} \frac{\overline{v_i^\infty}}{RT} dP ,$$ (B.16)

where $\overline{v_i^\infty}$ is the partial molar volume of the solute at infinite dilution. If $\overline{v_i^\infty}$ can be assumed to be independent of pressure over the range considered, then the above equation simplifies to (Reid *et al.*, 1977):

$$\frac{H_{ij}(P_2)}{H_{ij}(P_1)} = \exp \left(\frac{\overline{v_i^\infty}(P_2 - P_1)}{RT} \right) .$$ (B.17)

Lastly, K_{AW}, which is used in Appendix A and the text, and H_{ij} are representations of the same quantity on two different concentration scales: they are interconvertible for aqueous solutions as follows:

$$K_{AW} = \frac{55.55 g_i(\mathrm{HL})}{(1 - x_i) H_{ij} \gamma_i(\mathrm{HL})} ,$$ (B.18)

where $g_i(\mathrm{HL})$ and $\gamma_i(\mathrm{HL})$ are the solute activity coefficients on molal and mole fraction scales, respectively (both based on HL standard state). The above equation must be valid for $x_i \rightarrow 0$. Therefore,

$$K_{AW} = \frac{55.55}{H_{ij}} .$$ (B.19)

A common approximation for estimating K_{AW} is to set it equal to the ratio of the solute solubility and vapor pressure (e.g., Lyman *et al.*, 1990; Brimblecombe *et*

al., 1992; Aneja, 1993). The underlying assumption is that the saturated solution is ideal (i.e., $\gamma_i = 1$ in Equation (B.10)): this assumption, and thus the approximation, is more likely to hold for compounds with relatively low solubility than for compounds with high solubility. For instance, the value of γ_i for saturated solutions of 1-malic and succinic acids are 2.0 and $\sim$ 1.0, respectively (Carlo, 1971). Moreover, this approximation cannot be used for compounds that are completely miscible with water (i.e., solubility = ∞).

We use x–y data in DECHEMA data bank (Gmehling and co-author(s), 1977, 1981, 1988). These three volumes represent an attempt to assemble into a single compilation all binary and multicomponent vapor-liquid equilibrium data reported in the literature for aqueous organic systems. Most data are for binary aqueous systems consisting of water and an organic solute. The binary observations consist of the vapor-phase composition reported as a function of the liquid-phase composition either at a fixed temperature or at a fixed pressure. Often more than one set of observations is available for a given system and temperature. Gmehling *et al.* performed thermodynamic consistency tests on observations reported in the literature and provide information concerning the quality of various data sets to the reader. In addition, the observations are fitted to a number of activity coefficient models and the parameters and the goodness of fit are given. Also reported are solute and solvent (water) activity coefficients at infinite dilution as estimated from the activity coefficient models.

We estimate K_{AW} by applying Methods XY–1 and XY–2 to data reported in DECHEMA as follows:

- Whenever available, we use isothermal data. Isobaric data are used only when isothermal data are not available.

- We estimate K_{AW} using all observation sets available for temperatures between 0 and 70 °C; when sufficient observations are not available for deriving the relationship between temperature and K_{AW} for this temperature range (e.g., for less volatile compounds such as diols), we use data for higher temperatures (up to 135 °C) as well. The relationship between ln K_{AW} and $1/T$ is used to gauge the quality of the estimate (according to Equation (B.15), the relationship should be linear). Moreover, in instances where x–y data are not available for $T = 25$ °C, K_{AW} for this temperature is estimated by interpolation or extrapolation of values for other temperatures using Equation (B.15).

- The DECHEMA compilation contains solute vapor pressure (P_i^{sat}) at several temperatures (as reported by various investigators) as well as the parameters for the Antoine equation, which relates vapor pressure to temperature. In most cases, the P_i^{sat} values reported by various investigators and derived from the Antoine equation are consistent (generally within 5%) with one another as well as with the values reported in other compilations, such as Perry and Chilton (1973) and Yaws (1994). We use the P_i^{sat} value reported by the original investigator with the following exceptions. For some compounds

with low volatility (1,2-propanediol, 1,2,3-propanetriol and 1,4-butanediol), DECHEMA volumes do not contain vapor pressure data at the temperature of interest. For 1,2-propanediol and 1,4-butanediol we use the P_i^{sat} values reported in Yaws (1994). For 1,2,3-propanetriol at $T = 25\,°C$, according to Yaws (1994), $P_i^{sat} = 0.000169$ mm of Hg, whereas according to Tang and Munkelwitz (1991) $P_i^{sat} = 0.000106$ mm of Hg; we estimate a range of K_{AW} using these two values.

- Each data set reported in DECHEMA covers a broad range of x_i values between 0 and 1; however often only one observation is available for dilute solution. We estimate K_{AW} via Method XY–1 by using the x–y observation pair for the lowest x_i value. Method XY–1 is not used for data sets in which the lowest x_i value is greater than 0.1.

- Data reported in the DECHEMA volume are for two component systems (two degrees of freedom). Therefore, for an isothermal data set, the system pressure is not fixed (it is a function of x_i). Often the pressure is different from 1 atmosphere. Using Equation (B.17), we found that for the pressure ranges and the solutes considered, the dependence of K_{AW} on pressure is insignificant (less than 1%). Therefore, the K_{AW} values we estimate from observations at pressures other than 1 atmosphere are assumed to be valid for $P = 1$ atmosphere as well.

Acknowledgements

References

Abbott, M. M. and Prausnitz, J. M., 1994, Modeling the excess Gibbs energy, in S. I. Sandler (ed.), *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York, pp. 1–86.

Adamson, A. W., 1976, *Physical Chemistry of Surfaces*, John Wiley and Sons, New York.

Aldrich, 1994, *Catalog Handbook of Fine Chemicals*. Aldrich Chemical Company, Milwaukee, WI.

Allen, D. T., Palen, E. J., Haimov, M. I., Hering, S. V., and Young, J. R., 1994, Fourier transform infrared spectroscopy of aerosol collected in a low pressure impactor (LPI/FTIR): method development and field calibration, *Aerosol Sci. Technol.* 21, 325–342.

Andrews, E. and Larson, S. M., 1993, Effect of surfactant layers on the size changes of aerosol particles as a function of relative humidity, *Environ. Sci. Technol.* 27, 857–865.

Aneja, V. P., 1993, Organic compounds in cloud water and their deposition at a remote continental site, *J. Air Waste Manage. Assoc.* **43**, 1239–1244.

Apelblat, A. and Manzurola, E., 1987, Solubility of oxalic, malonic, succinic, adipic, maleic, malic, citric, and tartaric acids in water from 278.15 to 338.15 K, *J. Chem. Thermodyn.* **19**, 317–320.

Ashworth, R. A., Howe, G. B., Mullins, M. E., and Rogers, T. N., 1988, Air-water partitioning coefficients of organics in dilute aqueous solutions, *J. Hazard. Mater.* **18**, 25–36.

Atkinson, R., 1990, Gas-phase tropospheric chemistry of organic compounds: a review, *Atmos. Environ.* **24A**, 1–41.

Atkinson, R. and Aschmann, S. M., 1995, Alkoxy radical isomerization products from the gas-phase OH radical-initiated reactions of 2,4-dimethyl-2-pentanol and 3,5-dimethyl-3-hexanol, *Environ. Sci. Technol.* **29**, 528–536.

Benkelberg, H.-J., Hamm, S., and Warneck, P., 1995, Henry's law coefficient for aqueous solutions of acetone, acetaldehyde and acetonitrile, and equilibrium constants for the addition compounds of acetone and acetaldehyde with bisulfite, *J. Atmos. Chem.* **20**, 17–34.

Betterton, E. A., 1991, The partitioning of ketones between the gas and aqueous phases, *Atmos. Environ.* **25A**, 1473–1477.

Betterton, E. A. and Hoffmann, M. R., 1988, Henry's law constants of some environmentally important aldehydes, *Environ. Sci. Technol.* **22**, 1415–1418.

Bone, R., Cullis, P., and Wolfenden, R., 1983, Solvent effects on equilibria of addition of nucleophiles to acetaldehyde and the hydrophilic character of diols, *J. Am. Chem. Soc.* **105**, 1339–1343.

Brimblecombe, P., Clegg, S. L., and Khan, I., 1992, Thermodynamic properties of carboxylic acids relevant to their solubility in aqueous solutions, *J. Aerosol Sci.* **23**, S901–S904.

Budavari, S., O'Neil, M. J., Smith, A., and Heckelman, P. E., 1989, *The Merck Index–An Encyclopedia of Chemicals, Drugs, and Biologicals*, Merck & Co., Rahway, NJ.

Burrows, H. D., 1992, Studying odd-even effects and solubility behavior using α, ω-dicarboxylic acids, *J. Chem. Educ.* **69**, 69–73.

Butler, J. A. V. and Ramchandani, C. N., 1935, The solubility of non-electrolytes. Part II. The influence of the polar group on the free energy of hydration of aliphatic compounds, *J. Chem. Soc.* **280**, 952–955.

Butler, J. A. V., Ramchandani, C. N., and Thomson, D. W., 1935, The solubility of non-electrolytes. Part I. The free energy of hydration of some aliphatic alcohols, *J. Chem. Soc.* **280**, 280–285.

Cadle, S. H., Groblicki, P. J., and Mulawa, P. A., 1983, Problems in the sampling and analysis of carbon particulate, *Atmos. Environ.* **17**, 593–600.

Cadle, S. H. and Groblicki, P. J., 1982, An evaluation of methods for the determination of organic and elemental carbon in particulate samples, in G. T. Wolff and R. L. Klimisch (eds.), *Particulate Carbon–Atmospheric Life Cycle*, Plenum Press, New York, pp. 89–109.

Carlo, M. J., 1971, Thermodynamic quantities of some biochemically important organic acids in aqueous buffered solutions at 25 °C. Ph.D. thesis, Department of Chemistry, Texas A&M University, College Station, TX.

Carson, P. G., Neubauer, K. R., Johnston, M. V., and Wexler, A. S., 1995, On-line chemical analysis of aerosols by rapid single-particle mass spectrometry, *J. Aerosol Sci.* **26**, 535–545.

Cass, G. R., 1995, Private communication concerning observations discussed in Rogge *et al.* (1993a).

Cholak, J., Schafer, L. J., Yaeger, D. W., and Kehoe, R. A., 1955, The nature of the suspended matter, in N. A. Renzetti (ed.), *An Aerometric Survey of the Los Angeles Basin August-November 1954*, Air Pollution Foundation, Los Angeles, CA, pp. 201–225.

Clegg, S. L., Brimblecombe, P., and Khan, I., 1996, The Henry's law constant of oxalic acid and its partitioning into the atmospheric aerosol, *Idojaras* (in press).

Cohen, S., Marcus, Y., Migron, Y., Dikstein, S., and Shafran, A., 1993, Water sorption, binding and solubility of polyols, *J. Chem. Soc. Faraday Trans.* **89**, 3271–3275.

Coudert, R., Paris, J., and Cao, A., 1994, Hydrophobic or micellar behavior of 2-butyl and 2-pentyl-2-(hydroxymethyl)-1,3-propaneDiol in water. Volumes and osmotic coefficients, *J. Colloid Interface Sci.* **163**, 94–99.

Coudert, R., Hajji, S. M., and Cao, A., 1993, Thermodynamics of micellar systems: volumes, osmotic coefficients, and aggregation numbers of a homologous series of 1,2,3-alkane triols in water, *J. Colloid Interface Sci.* **155**, 173–182.

Cronn, D. R., Charlson, R. J., Knights, R. L., Crittenden, A. L., and Appel, B. R., 1977, A survey of the molecular nature of primary and secondary components of particles in urban air by high-resolution mass spectrometry, *Atmos. Environ.* **11**, 929–937.

Curme, Jr., G. O. and Johnston, F., 1952, *Glycols*, Reinhold Publ. Corp., New York.

Daisey, J. M., Hershman, R. J., and Kneip, T. J., 1982, Ambient levels of particulate organic matter in New York City in winter and summer, *Atmos. Environ.* **16**, 2161–2168.

Dean, J. A., 1992, *Lange's Handbook of Chemistry*, 14th edn, McGraw-Hill, New York.

de Kruif, C. G., van Ginkel, C. H. D., and Voogd, J., 1975, Torsion-effusion vapour-pressure measurements of organic compounds, *Conf. Inter. Thermo. Chim.* August 26–30, Montpellier, France, pp. 11–18.

de Wit, H. G. M., Bouwstra, J. A., Blok, J. G., and de Kruif, C. G., 1983, Vapor pressures and lattice energies of oxalic acid, mesotartaric acid, phloroglucinol, myoinositol, and their hydrates, *J. Chem. Phys.* **78**, 1470–1475.

Drefahl, A. and Reinhard, M., 1995, Handbook for estimating physico-chemical properties of organic compounds and the companion software package DESOC (Data Evaluation System for Organic Compounds), Stanford University Bookstore, Stanford, CA.

Duce, R. A., 1978, Speculations on the budget of particulate and vapor phase non-methane organic carbon in the global troposphere, *Pure Applied Geophys.* **116**, 244–273.

Duce, R. A., Mohnen, V. A., Zimmerman, P. R., Grosjean, D., Cautreels, W., Chatfield, R., Jaenicke, R., Ogren, J. A., Pellizzari, E. D., and Wallace, G. T., 1983, Organic material in the global troposphere, *Rev. Geophys. Space Phys.* **21**, 921–952.

Finlayson-Pitts, B. J. and Pitts, Jr., J. N., 1986, *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, John Wiley and Sons, New York.

Fischer, M. and Warneck, P., 1991, The dissociation constant of pyruvic acid: determination by spectrophotometric measurements, *Bunsenges. Phys. Chem.* **95**, 523–527.

Franzblau, E., Burton, C. S., and Hidy, G. M., 1984, Aerosol particle formation from ozone-terminal olefin reactions, *Aerosol Sci. Technol.* **3**, 167–176.

Fredenslund, A. and Sorensen, J. M., 1994, Group contribution estimation methods, in S. I. Sandler (ed.), *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York, pp. 287–361.

Gill, P. S., Graedel, T. E., and Weschler, C. J., 1983, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes, *Rev. Geophys. Space Phys.* **22**, 903–920.

Gmehling, J., Onken, U., and Rarey-Nies, J. R., 1988, *Vapor-liquid Equilibrium Data Collection. Aqueous Systems (Supplement 2). DECHEMA Chemistry Data Series, Vol. 1, Part 1b*, DECHEMA (Deutsche Gesellschaft fur Chemisches Apparatewesen, Chemische Technik und Biotechnologie e. V.), Frankfurt, Germany.

Gmehling, J., Onken, U., and Arlt, W., 1981, *Vapor-liquid Equilibrium Data Collection. Aqueous-Organic Systems (Supplement 1). DECHEMA Chemistry Data Series, Vol. 1, Part 1a*, DECHEMA (Deutsche Gesellschaft fur Chemisches Apparatewesen), Frankfurt, Germany.

Gmehling, J. and Onken, U., 1977, *Vapor-liquid Equilibrium Data Collection. Aqueous-Organic Systems. DECHEMA Chemistry Data Series, Vol. 1, Part 1*, DECHEMA (Deutsche Gesellschaft fur Chemisches Apparatewesen), Frankfurt, Germany.

Gorzelska, K., Galloway, J. N., Watterson, K., and Keene, W. C., 1992, Water-soluble primary amine compounds in rural continental precipitation, *Atmos. Environ.* **26A**, 1005–1018.

Graedel, T. E., Hawkins, D. T. and Claxton, L. D., 1986, *Atmospheric Chemical Compounds–Sources, Occurrence, and Bioassay*, Academic Press, Orlando, FL.

Gray, H. A., Cass, G. R., Huntzicker, J. J., Heyerdahl, E. K., and Rau, J. A., 1986, Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, *Environ. Sci. Technol.* **20**, 580–589.

Grosjean, D., 1992a, In situ organic aerosol formation during a smog episode: estimated production and chemical functionality, *Atmos. Environ.* **26A**, 953–963.

Grosjean, D., 1992b, Atmospheric concentrations and temporal variations of C_1-C_3 carbonyl compounds at two rural sites in central Ontario, *Atmos. Environ.* **26A**, 349–351.

Grosjean, D., 1991, Ambient levels of formaldehyde, acetaldehyde, and formic acid in southern California: results of a one-year base-line study, *Environ. Sci. Technol.* **25**, 710–715.

Grosjean, D., 1989, Organic acids in southern California air: ambient concentrations, mobile source emissions, in situ formation and removal processes, *Environ. Sci. Technol.* **23**, 1506–1514.

Grosjean, D., 1982, Formaldehyde and other carbonyls in Los Angeles ambient air, *Environ. Sci. Technol.* **16**, 254–262.

Grosjean, D., 1977, Aerosols, in *Ozone and Other Photochemical Oxidants*, National Academy of Sciences, Washington, DC, pp. 45–125.

Grosjean, D., 1975, Solvent extraction and organic carbon determination in atmospheric particulate matter: the organic extraction-organic carbon analyzer (OE-OCA) technique, *Anal. Chem.* **47**, 797–805.

Grosjean, D., Grosjean, E., and William, II, E. L., 1994, Atmospheric chemistry of olefins: a product study of the ozone-alkene reaction with cyclohexane added to scavenge OH, *Environ. Sci. Technol.* **28**, 186–196.

Grosjean, D., Grosjean, E., and William, II, E. L., 1993, Atmospheric chemistry of unsaturated alcohols, *Environ. Sci. Technol.* **27**, 2478–2485.

Grosjean, D. and Seinfeld, J. H., 1989, Parameterization of the formation potential of secondary organic aerosols, *Atmos. Environ.* **23**, 1733–1747.

Grosjean, D. and Friedlander, S. K., 1980, Formation of organic aerosols from cyclic olefins and diolefins, in G. M. Hidy, P. K. Mueller, D. Grosjean, B. R. Appel, and J. J. Wesolowski (eds.), *The Character and Origins of Smog Aerosols–A Digest of Results from California Aerosol Characterization Experiment (ACHEX)*, John Wiley & Sons, New York, pp. 435–473.

Grosjean, D., Cauwenberghe, K. V., Schmid, J. P., Kelly, P. E., and Pitts, Jr., J. N., 1978, Identification of C_3-C_{10} aliphatic dicarboxylic acids in airborne particulate matter, *Environ. Sci. Technol.* **12**, 313–317.

Grosjean, D. and Friedlander, S. K., 1975, Gas-particle distribution factors for organic and other pollutants in the Los Angeles atmosphere, *J. Air Pollut. Control Assoc.* **25**, 1038–1044.

Grosjean, D. and Friedlander, S. K., 1974, Gas-particle distribution factors for organic pollutants in the Los Angeles atmosphere. Presented at the 67th Annual Meeting of the Air Pollution Control Association, June 9–13, Denver, CO.

Guenther, A., Hewitt, C. N., Erickson, D. *et al.*, 1995, A global model of natural volatile organic compound emissions, *J Geophys. Res.* **100**, 8873–8892.

Gundel, L. A., de Martins, B. S., and Daisey, J., 1995, Polar organic material in ambient particles. Presented at the Air and Waste Management Association's International Conference entitled Particulate Matter: Health and Regulatory Issues, April 4–6, Pittsburgh, PA.

Gundel, L. A., Daisey, J. M., de Carvalho, L. R. F., Kado, N. Y., and Schuetzle, D., 1993, Polar organic matter in airborne particles: chemical characterization and mutagenic activity, *Environ. Sci. Technol.* **27**, 2112–2119.

Gundel, L. A. and Novakov, T., 1984, Characterization of particles from several sources and three urban areas by solvent extraction, *Atmos. Environ.* **18**, 273–276.

Hahn, J., 1980, Organic constituents of natural aerosols, *Ann. N. Y. Acad. Sci.* **338**, 359–376.

Hameri, K., Rood, M. J., and Hansson, H.-C., 1992, Hygroscopic properties of a NaCl aerosol coated with organic compounds, *J. Aerosol Sci.* **23**, Sppl. 1, S437–S440.

Hanel, G., 1976, The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air, *Adv. Geophys.* **19**, 73–188.

Harrington, R. F., Gertler, A. W., Grosjean, D., and Amar, P., 1993, Formic acid and acetic acid in the Western Sierra Nevada, California, *Atmos. Environ.* **27A**, 1843–1849.

Hartmann, W. R., Andreae, M. O., and Helas, G., 1989, Measurements of organic acids over central Germany, *Atmos. Environ.* **23**, 1531–1533.

Helmig, D., Bauer, A., Muller, J., and Klein, W., 1990, Analysis of particulate organics in a forest atmosphere by thermodesorption GC/MS, *Atmos. Environ.* **24A**, 179–184.

Hildemann, L. M., Rogge, W. F., Cass, G. R., Mazurek, M. A., and Simoneit, B. R. T., 1996, Contribution of primary aerosol emissions from vegetation-derived sources to fine particle concentrations in Los Angeles, *J. Geophys. Res.* (in press).

Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1994, Seasonal trends in Los Angeles ambient organic aerosol observed by high-resolution gas chromatography, *Aerosol Sci. Technol.* **20**, 303–317.

Hine, J. and Mookerjee, P. K., 1975, The intrinsic hydrophilic character of organic compounds. Correlations in terms of structural contributions, *J. Org. Chem.* **40**, 292–298.

Hoff, J. T., Mackay, D., Gillham, R., and Shiu, W. Y., 1993, Partitioning of organic chemicals at the air-water interface in environmental systems, *Environ. Sci. Technol.* **27**, 2174–2180.

Hort, E. V., 1972, Glycols and bischloroformates, in J. K. Stille and T. W. Campbell (eds.), *Condensation Monomers*, Wiley-Interscience, New York, pp. 261–310.

Hoshika, Y., 1982, Gas chromatographic determination of lower fatty acids in air at part-per-trillion levels, *Anal. Chem.* **54**, 2433–2437.

Husar, R. B. and Shu, W. R., 1975, Thermal analyses of the Los Angeles smog aerosol, *J. Appl. Meteorol.* **14**, 1558–1565.

Johnson, B. J. and Dawson, G. A., 1993, A preliminary study of the carbon-isotopic content of ambient formic acid and two selected sources: automobile exhaust and formicine ants, *J. Atmos. Chem.* **17**, 123–140.

Junge, C. E., 1977, Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants, in I. H. Suffet (ed.), *Fate of Pollutants in the Air and Water Environments*, John Wiley and Sons, New York, pp. 7–25.

Kames, J. and Schurath, U., 1992, Alkyl nitrates and bifunctional nitrates of atmospheric interest: Henry's law constants and their temperature dependencies, *J. Atmos. Chem.* **15**, 79–95.

Kawamura, K. and Ikushima, K., 1993, Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, *Environ. Sci. Technol.* **27**, 2227–2235.

Kawamura, K. and Kaplan, I. R., 1991, Organic compounds in rain water, in L. D. Hansen and D. J. Eatough (eds.), *Organic Chemistry of the Atmosphere*, CRC Press, Boca Raton, FL, pp. 233–284.

Kawamura, K. and Gagosian, R. B., 1990, Mid-chain ketocarboxylic acids in the remote marine atmosphere: distribution patterns and possible formation mechanisms, *J. Atmos. Chem.* **11**, 107–122.

Kawamura, K. and Gagosian, R. B., 1988, Identification of isomeric hydroxy fatty acids in aerosol samples by capillary gas chromatography-mass spectrometry, *J. Chromatogr.* **438**, 309–317.

Kawamura, K. and Gagosian, R. B., 1987, Implications of ω-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids, *Nature* **325**, 330–332.

Kawamura, K. and Kaplan, I. R., 1987, Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.* **21**, 105–110.

Kawamura, K., Ng, L.-L., and Kaplan, I. R., 1985, Determination of organic acids (C_1-C_{10}) in the atmosphere, motor exhausts, and engine oils, *Environ. Sci. Technol.* **19**, 1082–1086.

Keene, W. C. and Galloway, J. N., 1986, Considerations regarding sources for formic and acetic acids in the troposphere, *J. Geophys. Res.* **91**, 14466–14474.

Kelly, T. J., Callahan, P. J., Pleil, J., and Evans, G. F., 1993, Method development and field measurements of polar volatile organic compounds in ambient air, *Environ. Sci. Technol.* **27**, 1146–1153.

Khan, I., Brimblecombe, P., and Clegg, S. L., 1995, Solubilities of pyruvic acid and the lower (C_1–C_6) carboxylic acids. Experimental determination of equilibrium vapour pressures above pure aqueous and salt solutions, *J. Atmos. Chem.* **22**, 285–302.

Khwaja, H. A., 1995, Atmospheric concentrations of carboxylic acids and related compounds at a semiurban site, *Atmos. Environ.* **29**, 127–139.

Klotz, B. G., Bierbach, A., Barnes, I., and Becker, K. H., 1995, Kinetic and mechanistic study of the atmospheric chemistry of muconaldehydes, *Environ. Sci. Technol.* **29**, 2322–2332.

Konig, G., Brunda, M., Puxbaum, H., Hewitt, C. N., Duckham, S. C., and Rudolph, J., 1995, Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species, *Atmos. Environ.* **29**, 861–874.

Koutrakis, P., 1995, Private communication concerning gas-particle distribution of C1-C8 organic acids in the observations discussed in Lawrence, J. E. and Koutrakis, P., 1996a&b.

Lawrence, J. E. and Koutrakis, P., 1996a, Measurement and speciation of gas and particulate phase organic acidity in an urban environment. 1. Analytical, *J. Geophys. Res.* (in press).

Lawrence, J. E. and Koutrakis, P., 1996b, Measurement and speciation of gas and particulate phase organic acidity in an urban environment. 2. Speciation, *J. Geophys. Res.* (in press).

Lawrence, J. E. and Koutrakis, P., 1994, Measurement of atmospheric formic and acetic acids: methods evaluation and results from field study, *Environ. Sci. Technol.* **28**, 957–964.

Le Lacheur, R. M., Sonnenberg, L. B., Singer, P. C., Christman, R. F., and Charles, M. J., 1993, Identification of carbonyl compounds in environmental samples, *Environ. Sci. Technol.* **27**, 2745–2753.

Lefer, B. L., Talbot, R. W., Harriss, R. C. *et al.*, 1994, Enhancement of acidic gases in biomass burning impacted air masses over Canada, *J. Geophys. Res.* **99**, 1721–1737.

Li, S.-M. and Winchester, J. W., 1993, Water soluble organic constituents in Arctic aerosols and snow pack, *Geophys. Res. Lett.* **20**, 45–48.

Lind, J. A. and Kok, G. L., 1994, Correction to 'Henry's law determinations for aqueous solutions of hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid' by John A. Lind and Gregory L. Kok, *J. Geophys. Res.* **99**, 21119.

Loudon, G. M., 1984, *Organic Chemistry*, Addison-Wesley, Reading, MA.

Lyman, W. J., Reehl, W. F., and Rosenblatt, D. H., 1990, *Handbook of Chemical Property Estimation Methods*, American Chemical Society, Washington, DC.

Mansoori, B. A., Johnston, M. V., and Wexler, A. S., 1994, Quantitation of ionic species in single microdroplets by on-line laser desorption/ionization, *Anal. Chem.* **66**, 3681–3687.

Markley, K. S., 1960, *Fatty Acids: Their Chemistry, Properties, Production, and Uses. Part I*, Interscience, New York.

Martin, L. R. and Damschen, D. E., 1981, Aqueous oxidation of sulfur dioxide by hydrogen peroxide at low pH, *Atmos. Environ.* **15**, 1615–1621.

Matthias-Maser, S. and Jaenicke, R., 1994, Examination of atmospheric bioaerosol particles with radii > 0.2 μm, *J. Aerosol Sci.* **25**, 1605–1613.

Mazurek, M., Mason-Jones, M. C., Mason-Jones, H. D., Salmon, L. G., Cass, G. R., Hallock, K. A., and Leach, M., 1996, Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: 1. Properties observed by high resolution gas chromatography. Submitted to *J. Geophys. Res.*

Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1991, Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States, *Environ. Sci. Technol.* **25**, 684–694.

Mazurek, M. A., Hallock, K., Molkenbur, C., Cass, G. R., Jones, M., Mason, H., and Winner, D., 1993, Organic compounds emitted in smoke aerosol from combustion of green vegetation and seasoned firewood at Grand Canyon National Park. Presented at the annual meeting of the American Association for Aerosol Research, October 11–15, Oakbrook, IL. Document No. BNL-48753, Brookhaven National Laboratory, Upton, NY.

Mazurek, M. A., Simoneit, B. R. T., Cass, G. R., and Gray, H. A., 1987, Quantitative high-resolution gas chromatography/mass spectrometry analyses of carbonaceous fine aerosol particles, *Intern. J. Environ. Anal. Chem.* **29**, 119–139.

McMurry, P. H., Zhang, X., and Lee, C.-T., 1996, Issues in aerosol measurement for optical assessments, *J. Geophys. Res.* (in press).

Meng, Z., Seinfeld, J. H., Saxena, P., and Kim, Y. P., 1995, Contribution of water to particulate mass in the South Coast Air Basin, *Aerosol Sci. Technol.* **22**, 111–123.

Mellan, I., 1962, *Polyhydric Alcohols*, Spartan Books, Washington, DC.

Meylan, W. M. and Howard, P. H., 1991, Bond contribution method for estimating Henry's law constants, *Environ. Toxicol. Chem.* **10**, 1283–1294.

Milas, N. A., Kurz, P. F., and Anslow, Jr., W. P., 1937, The photochemical addition of hydrogen peroxide to the double bond, *J. Amer. Chem. Soc.* **59**, 543–544.

Morrison, R. T. and Boyd, R. N., 1992, *Organic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ.

Mueller, P. K., Fung, K. K., Heisler, S. L., Grosjean, D., and Hidy, G. M., 1982, Atmospheric particulate carbon observations in urban and rural areas of the United States, in G. T. Wolff and R. L. Klimisch (eds.), *Particulate Carbon–Atmospheric Life Cycle*, Plenum Press, New York, pp. 343–370.

Mueller, P. K., Mosley, R. W., and Pierce, L. B., 1972, Chemical composition of Pasadena aerosol by particle size and time of day. IV. Carbonate and noncarbonate carbon content, *J. Colloid Interface Sci.* **39**, 235–239.

Muilenberg, M. L., 1995, The outdoor aerosol, in H. A. Burge (ed.), *Bioaerosols*, Lewis Publishers, Boca Raton, FL, pp. 163–204.

Munz, C. and Roberts, P. V., 1986, The effects of solute concentration and cosolvents on the aqueous activity coefficients of halogenated hydrocarbons, *Environ. Sci. Technol.* **20**, 830–836.

Murphy, D. M. and Thompson, D. S., 1995, Laser ionization mass spectroscopy of single aerosol particles, *Aerosol Sci. Technol.* **22**, 237–249.

Myers, D., 1991, *Surfaces, Interfaces, and Colloids. Principles and Applications*, VCH Publ., New York.

Nielsen, F., Olsen, E., and Fredenslund, A., 1994, Henry's law constants and infinite dilution activity coefficients for volatile organic compounds in water by a validated batch air stripping method, *Environ. Sci. Technol.* **28**, 2133–2138.

Novakov, T. and Penner, J. E., 1993, Large contribution of organic aerosols to cloud-condensation-nuclei concentrations, *Nature* **365**, 823–826.

Palen, E. J., Allen, D. T., Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C., 1993, Fourier transform infrared analysis of aerosol formed in the photooxidation of 1-octene, *Atmos. Environ.* **27A**, 1471–1477.

Palen, E. J., Allen, D. T., Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C., 1992, Fourier transform infrared analysis of aerosol formed in the photo-oxidation of isoprene and β-pinene, *Atmos. Environ.* **26A**, 1239–1251.

Pandis, S. N., Wexler, A. S., and Seinfeld, J. H., 1993, Secondary organic aerosol formation and transport–II. Predicting the ambient secondary organic aerosol size distribution, *Atmos. Environ.* **27A**, 2403–2416.

Pandis, S. N., Harley, R. A., Cass, G. R., and Seinfeld, J. H., 1992, Secondary organic aerosol formation and transport, *Atmos. Environ.* **26A**, 2269–2282.

Pankow, J. F., 1994a, An absorption model of the gas/aerosol partitioning of organic compounds in the atmosphere, *Atmos. Environ.* **28**, 185–188.

Pankow, J. F., 1994b, An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol, *Atmos. Environ.* **28**, 189–193.

Pankow, J. F., 1987, Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere, *Atmos. Environ.* **21**, 2275–2283.

Pankow, J. F., Storey, J. M. E., and Yamasaki, H., 1993, Effects of relative humidity on gas/particle partitioning of semivolatile organic compounds to urban particulate matter, *Environ. Sci. Technol.* **27**, 2220–2226.

Perry, R. H. and Chilton, C. H., 1973, *Chemical Engineers' Handbook*, McGraw-Hill, New York.

Popovych, O. and Tomkins, R. P. T., 1981, *Nonaqueous Solution Chemistry*, John Wiley & Sons, New York.

Pryde, E. H. and Cowan, J. C., 1972, Aliphatic dibasic acids, in J. K. Stille and T. W. Campbell (eds.), *Condensation Monomers*, Wiley-Interscience, New York, pp. 1–153.

Puxbaum, H. and Kunit, M., 1994, Determination of the cellulose content of atmospheric aerosols. Presented at the Fifth International Conference on Carbonaceous Particles in the Atmosphere, 23–26 August, Berkeley, CA.

Raridon, R. J. and Kraus, K. A., 1971, Properties of mixtures. Activity coefficients of sodium chloride at saturation in aqueous solutions of some oxy-oxa compounds at 25 °C, *J. Chem. Eng. Data* **16**, 241–243.

Reents, Jr., W. D., Downey, S. W., Emerson, A. B., Mujsce, A. M., Muller, A. J., Siconolfi, D. J., Sinclair, J. D., and Swanson, A. G., 1995, Single particle characterization by time-of-flight mass spectrometry, *Aerosol Sci. Technol.* **23**, 263–270.

Reid, R. C., Prausnitz, J. M., and Sherwood, T. K., 1977, *The Properties of Gases and Liquids*, McGraw-Hill, New York.

Renzetti, N. A. and Doyle, G. J., 1959, The chemical nature of the particulate in irradiated automobile exhaust, *J. Air Pollut. Control Assoc.* **8**, 293–296.

Robinson, R. A. and Stokes, R. H., 1968, *Electrolyte Solutions*, Butterworths, London, UK.

Roedel, W., 1979, Meaurement of sulfuric acid saturation vapor pressure; implications for aerosol formation by heteromolecular nucleation, *J. Aerosol Sci.* **10**, 375–386.

Rogge, W. F., Mazurek, M. A., Hildemann, L. M., Cass, G. R., and Simoneit, B. R. T., 1993a, Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation, *Atmos. Environ.* **27A**, 1309–1330.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1993b, Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.* **27**, 636–651.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1993c, Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks, *Environ. Sci. Technol.* **27**, 1892–1904.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1993d, Sources of fine organic aerosol. 4. Particulate abrasive products from leaf surfaces of urban plants, *Environ. Sci. Technol.* **27**, 2700–2711.

Rogge, W. F., Hildemann, L. M., Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T., 1991, Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.* **25**, 1112–1125.

Sanhueza, E., Santana, M., and Hermoso, M., 1992, Gas- and aqueous-phase formic and acetic acids at a tropical cloud forest site, *Atmos. Environ,* **26A**, 1421–1426.

Satsumabayashi, H., Kurita, H., Chang, Y.-S., Carmichael, G. R., and Ueda, H., 1995, Photochemical formations of lower aldehydes and lower fatty acids under long-range transport conditions in central Japan, *Atmos. Environ.* **29**, 255–266.

Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H., 1995, Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.* **100**, 18755–18770.

Schuetzle, D., 1975, Analysis of complex mixtures by computer controlled high resolution mass spectrometry. I-Application to atmospheric aerosol composition, *Biomed. Mass Spectr.* **2**, 288–298.

Schuetzle, D., Cronn, D., Crittenden, A. L., and Charlson, R. J., 1975, Molecular composition of secondary aerosol and its possible origin, *Environ. Sci. Technol.* **9**, 838–845.

Sebastiani, E. and Lacquaniti, L., 1967, Acetic acid-water system thermodynamical correlation of vapor-liquid equilibrium data, *Chem. Eng. Sci.* **22**, 1155–1162.

Seidell, A., 1941, *Solubilities of Organic Compounds*, D. Van Nostrand, New York.

Seinfeld, J. H., 1986, *Atmospheric Chemistry and Physics of Air Pollution*, John Wiley & Sons, New York.

Sempere, R. and Kawamura, K., 1994, Comparative distributions of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban atmosphere, *Atmos. Environ.* **28**, 449–459.

Serjeant, E. P. and Dempsey, B., 1979, *Ionisation Constants of Organic Acids in Aqueous Solution*, International Union of Pure and Applied Chemistry (IUPAC) Chemical Data Series No. 23, Pergamon Press, New York.

Servant, J., Kouadio, G., Bernard, C., and Delmas, R., 1991, Carboxylic monoacids in the air of Mayombe Forest (Congo): Role of the forest as a source or sink, *J. Atmos. Chem.* **12**, 367–380.

Shinoda, K., 1978, *Principles of Solution and Solubility*, Marcel Dekker, New York.

Sigma, 1995, *Biochemicals, Organic Compounds and Diagnostic Reagents for Research*, Sigma Chemical Company, St. Louis, MO.

Simoneit, B. R. T., 1986, Characterization of organic constituents in aerosols in relation to their origin and transport: A review, *Int. J. Environ. Anal. Chem.* **23**, 207–237.

Simoneit, B. R. T., Crisp, P. T., Mazurek, M. A., and Standley, L. J., 1991, Composition of extractable organic matter of aerosols from the Blue Mountains and southeast coast of Australia, *Environ. Int.* **17**, 405–419.

Simoneit, B. R. T., Sheng, G., Chen, X., Fu, J., Zhang, J., and Xu, Y., 1991, Molecular marker study of extractable organic matter in aerosols from urban areas of China, *Atmos. Environ.* **25A**, 2111–2129.

Simoneit, B. R. T. and Mazurek, M. A., 1982, Organic matter of the troposphere–II. Natural background of biogenic lipid matter in aerosols over the rural western United States, *Atmos. Environ.* **16**, 2139–2159.

Singh, H. B., O'Hara, D., Herlth, D., Sachse, W., Blake, D. R., Bradshaw, J. D., Kanakidou, M., and Crutzen, P. J., 1994, Acetone in the atmosphere: distribution, sources and sinks, *J. Geophys. Res.* **99**, 1805–1819.

Sisler, J. F. and Malm, W. C., 1994, The relative importance of soluble aerosols to spatial and seasonal trends of impaired visibility in the United States, *Atmos. Environ.* **28**, 851–862.

Sloane, C. S., Watson, J., Chow, J., Pritchett, L., and Richards, L. W., 1991, Size-segregated fine particle measurements by chemical species and their impact on visibility impairment in Denver, *Atmos. Environ.* **25A**, 1013–1024.

Smith, J. M. and Van Ness, H. C., 1975, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill, New York.

Solomon, P. A., Fall, T., Salmon, L., Lin, P., Vasquez, F., and Cass. G. R., 1988, Acquisition of acid vapor and aerosol concentration data for use in dry deposition studies in the South Coast Air Basin. Vol. 1. Environmental Quality Laboratory, California Institute of Technology, Pasadena, CA.

Stanley, T. W., Meeker, J. E., and Morgan, M. J., 1967, Extraction of organics from airborne particles–effects of various solvents and conditions on the recovery of benzo(a)pyrene, benz(c)acridine, and 7H-benz(de)anthracen-7-one, *Environ. Sci. Technol.* **1**, 927–931.

Stephen, H. and Stephen, T., 1963, *Solubilities of Inorganic and Organic Compounds. Volume 1*, Pergamon Press, London, UK.

Storey, J. M. E. and Pankow, J. F., 1992, Gas-particle partitioning of semi-volatile organic compounds to model atmospheric particulate materials-I. Sorption to graphite, sodium chloride, alumina, and silica particles under low humidity conditions, *Atmos. Environ.* **26A**, 435–443.

Streitwieser, Jr., A. and Heathcock, C. H., 1985, *Introduction to Organic Chemistry*, Macmillan, New York.

Suleiman, D. and Eckert, C. A., 1994, Limiting activity coefficients of diols in water by a dew point technique, *J. Chem. Eng. Data* **39**, 692–696.

Suzuki, T., Ohtaguchi, K., and Koide, K., 1992, Application of principal components analysis to calculate Henry's constant from molecular structure, *Computers Chem.* **16**, 41–52.

Tang, I. N. and Munkelwitz, H. R., 1991, Determination of vapor pressure from droplet evaporation kinetics, *J. Colloid Interface Sci.* **141**, 109–118.

Tao, Y. and McMurry, P. H., 1989, Vapor pressures and surface free energies of C14-C18 monocarboxylic acids and C5 and C6 dicarboxylic acids, *Environ. Sci. Technol.* **23**, 1519–1523.

Thibodeaux, L. J., Nadler, K. C., Valsaraj, K. T., and Reible, D. D., 1991, The effect of moisture on volatile organic chemical gas-to-particle partitioning with atmospheric aerosols–competitive adsorption theory predictions, *Atmos. Environ.* **25A**, 1649–1656.

Tokos, J. J. S., Tanaka, S., Morikami, T., Shigetani, H., and Hashimoto, Y., 1992, Gaseous formic and acetic acids in the atmosphere of Yokohama, Japan, *J. Atmos. Chem.* **14**, 85–94.

Trivedi, B. C. and Culbertson, B. M., 1982, *Maleic Anhydride*, Plenum Press, New York.

Turpin, B. J., Saxena, P., Allen, G., McMurry, P. H., Koutrakis, P., and Hildemann, L. M., 1996, Characterization of the southwestern desert aerosol, Meadview, AZ, *J. Air Waste Manage Assoc.* (in press).

Turpin, B. J., Huntzicker, J. J., and Hering, S. V., 1994, Investigation of organic aerosol sampling artifacts in the Los Angeles Basin, *Atmos. Environ.* **28**, 3061–3071.

Valsaraj, K. T., Thoma, G. J., Reible, D. D., and Thibodeaux, L. J., 1993, On the enrichment of hydrophobic organic compounds in fog droplets, *Atmos. Environ.* **27A**, 203–210.

Vasconcelos, L. A. P., Macias, E. S., and White, W. H., 1994, Aerosol composition as a function of haze and humidity levels in the southwestern U. S., *Atmos. Environ.* **28**, 3679–3691.

Wang, S.-C., Paulson, S. E., Grosjean, D., Flagan, R. C., and Seinfeld, J. H., 1992, Aerosol formation and growth in atmospheric organic/NO_x systems–I. Outdoor smog chamber studies of C_7- and C_8-hydrocarbons, *Atmos. Environ.* **26A**, 403–420.

Warner, J. and Warne, W. G., 1970, The effect of surface films in retarding the growth by condensation of cloud nuclei and their use in fog suppression, *J. Appl. Meteorol.* **9**, 639–650.

Wauters, E., Vangaever, E., Sandra, P., and Verzele, M., 1979, Polar organic fraction of air particulate matter, *J. Chromatogr.* **170**, 125–131.

Weast, R. C., 1986, *Handbook of Chemistry and Physics*, 67th edn, CRC Press, Boca Raton, FL.

Went, F. W., 1960, Organic matter in the atmosphere, and its possible relation to petroleum formation, *Proc. Natl. Acad. Sci. U.S.A.* **46**, 212–221.

White, W. H., 1990, Contributions to light extinction, in *Visibility: Existing and Historical Conditions: Causes and Effects. Acidic Deposition: State of Science Report 24*, National Acid Precipitation Assessment Program, Washington, DC.

Wiesen, E., Barnes, I., and Becker, K. H., 1995, Study of the OH-initiated degradation of the aromatic photooxidation product 3,4-dihydroxy-3-hexene-2,5-dione, *Environ. Sci. Technol.* **29**, 1380–1386.

Willey, J. D. and Wilson, C. A., 1993, Formic and acetic acids in atmospheric condensate in Wilmington, North Carolina, *J. Atmos. Chem.* **16**, 123–133.

Winiwarter, W., Puxbaum, H., Fuzzi, S., Facchini, M. C., Orsi, G., Beltz, N., Enderle, K., and Jaeschke, W., 1988, Organic acid gas and liquid-phase measurements in Po Valley fall-winter conditions in the presence of fog, *Tellus* **40B**, 348–357.

Yaws, C. L., 1994, *Handbook of Vapor Pressure, Volumes 1 & 2*, Gulf Publ. Co., Houston, TX.

Yokouchi, Y. and Ambe, Y., 1986, Characterization of polar organics in airborne particulate matter, *Atmos. Environ.* **20**, 1727–1734.

Yu, J., Jefferies, H. E., and Le Lacheur, R. M., 1995, Identifying airborne carbonyl compounds in isoprene atmospheric photooxidation products by their PFBHA oximes using gas chromatography/ion trap mass spectrometry, *Environ. Sci. Technol.* **29**, 1923–1932.

Zhang, J., He, Q., and Lioy, P. J., 1994, Characteristics of aldehydes: Concentrations, sources, and exposures for indoor and outdoor residential microenvironments, *Environ. Sci. Technol.* **28**, 146–152.

Zhang, X. Q., McMurry, P. H., Hering, S. V., and Casuccio, G. S., 1993, Mixing characteristics and water content of submicron aerosols measured in Los Angeles and at the Grand Canyon, *Atmos. Environ.* **27A**, 1593–1607.

Zhou, X. and Mopper, K., 1990, Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange, *Environ. Sci. Technol.* **24**, 1864–1869.