The solubility and behaviour of dicarboxylic acids in the atmosphere / Mohd Zul Helmi Rozaini.

THE SOLUBILITY AND BEHAVIOUR OF DICARBOXYLIC ACIDS IN THE ATMOSPHERE

MOHD ZUL HELMI ROZAINI

A thesis submitted for the Degree of
Doctor of Philosophy
in the
School of Environmental Sciences
University of East Anglia
Norwich, England

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ABSTRACT

The dicarboxylic acids (DCA's) are an important group of highly soluble organic aerosol components. The solubility of low molecular weight DCA's in water and electrolyte solutions was measured in the laboratory to understand the behaviour of DCA's in the atmosphere. The Pitzer model allowed the calculation of water activity and deliquescence properties from the solubility measurements. In general, DCA's with an even number of carbon atoms have much lower solubitily. Aqueous electrolytes generally lead to *salting-out*, with the exception of nitrates which lead to *salting-in* with odd carbon number. The observations of solubility may be reflected in the distribution of DCA's in aerosols. Smaller DCA's predominate in urban aerosols, but superimposed on this decrease with molecular weight is an odd-even effect, where DCA's with even carbon number (i.e. oxalic and succinic acid) are typically more concentrated in both urban and nonurban aerosols. This pattern is consistent with the *carbon preference index* (CPI) for acids and could reflect a primary biological source, but solubility driven transformations within the atmosphere seem a potentially more likely cause of this pattern. Acids in the atmosphere can react with calcium carbonate in aerosols, but only the smaller acids lead to dicaboxylates. The larger ones, here notably glutaric acid, seem to block some of the calcium carbonate lattice sites and provoke the transformation of calcium carbonate into the metastable vaterite polymorph. There is some evidence of vaterite in organic-rich urban atmospheres. Although vaterites have also been detected on urban cements and mortars, they have not been described within crusts on building stones. Typically the high concentrations of calcium dicarboxylates in crusts, largely as oxalate are considered to arise from biological transformations rather than atmospheric deposition. However, the experimental work here would suggest any higher DCA's formed in the crust might favour the presence of vaterite.

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