

Stability of Submicron Aqueous Solution Droplets in the Atmosphere

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1. Introduction

Submicron aqueous solution droplets constitute an important fraction of atmospheric condensation nuclei at high relative humidities. Their stability in the atmosphere under different conditions of relative humidity needs to be studied in connection with their role in the

formation of haze, smog and clouds. Experimental determination of particle size for submicron solution droplets is generally difficult, and it is necessary to estimate the stable size of the particles theoretically for different compositions. Kelvin's equation combined with Raoult's law as used by Mason (1959) and others

is applicable only to dilute solution droplets. In the atmosphere the solution concentrations of the droplets are highly variable and it is necessary to use methods based on the chemical activity of the solvent in which the concentration of the solution can be taken into account. For the solutes of interest and the range of solution concentrations in the atmospheric particulates, the solvent-solute interactions are too complex for a complete theoretical treatment. However, the empirical values of the chemical activity of the solvent for different compositions and concentrations of the solute provide a good tool for the estimation of the stable size of the particles.

In the atmosphere, submicron solution droplets can be formed by gas phase reactions taking place in the presence of water vapor and are likely to constitute a major fraction of the Aitken nuclei. The activation of these nuclei to cloud nuclei would also be governed by the chemical activity of the solvent. This study is particularly significant in the search for a source of cloud nuclei within the atmosphere. In the formation of solution droplets of the Aitken size range it is also important to consider the embryo formation mechanism. The embryos may be formed by chemical nucleation in which the effect of chemical interactions can give stable aggregates of the reaction products. In this note, starting with basic considerations in nucleation and Kelvin's equation, criteria for the stability of airborne solution particles are developed.

2. Chemical nucleation and embryo formation

The formation of acid nuclei from certain trace gases in the atmosphere provides a very good example of chemical nucleation in which the embryos can be formed by chemical interactions. The initial cluster, consisting of one solute molecule and a few molecules of water, may be formed by chemical or electrostatic interactions. The role of the solute molecules in stabilizing the embryo can be considered in terms of providing stronger binding for water molecules. The initially formed cluster of molecules constituting the embryo does not represent the liquid phase, because the surface layer is not fully developed and the concept of surface tension is not valid. However, due to chemical bond formation the molecules are held closer together in the cluster than in the gas phase and the free energy of the cluster is lowered. The embryos of the liquid phase are formed when the cluster growth is accompanied by dissipation of excess energy which may be taken by the evaporating water molecules or by the rotational or vibrational states. At equilibrium with the ambient vapor, the size of the embryo of the liquid phase is governed by the free energy balance of the system. Total free energy can be represented by the following equation for Gibb's free energy change of the embryo including the effect of the solute:

$$\Delta G = -\frac{4}{3}\pi r^3 \rho (RT/M) \ln S + 4\pi r^2 \sigma - E, \quad (1)$$

where r is the radius of the embryo, R the gas constant, ρ the density of the solution at absolute temperature T , M the molecular weight of the solvent, S the supersaturation ratio, σ the surface tension of the solution, and E the decrease in free energy due to the effect of the solute. In this equation, σ is considered to be independent of curvature because the surface tension change with curvature is not significant in the size range that can be treated thermodynamically.

The first two terms of the equation give the change in free energy due to volume and surface area change, respectively, and the third term gives the decrease in free energy of the embryo due to chemical interaction between the constituents of the embryo. Thus, from (1), the effect of chemical interactions is essentially to lower the free energy of the embryo and give rise to stable particles of smaller radii; if nucleation is purely physical, only the first two terms are necessary for finding the stable size of the embryo. The exact nature of the last term giving the effect of chemical interactions is considered below in connection with the formation and stability of the solution droplets.

3. Stability of solution particles

Stable embryos of solution droplets are formed if the conditions for their stability are satisfied, assuming some mechanism for the initial formation of embryos. For a specific case of formation of acid solution droplets from the gas phase, embryo formation by possible ionic reactions has been suggested by Vohra *et al.* (1970). More detailed discussion on the initial formation of embryos is beyond the scope of this note. The criteria for the stability of embryos and larger solution droplets are assumed to be the same. The stable size for the droplets of all sizes calculated on the basis of Raoult's law using the Van't Hoff factor, and on the basis of chemical activity of water, can thus be compared.

In evaluating the chemical activity of the solvent, it is necessary to consider the variety of solvent-solute interactions. However, there is no complete theory to take into account the interactions involving the variety of solute ions and their effects on the free energy of the solvent molecules. Difficulties arise because of: 1) differences in the size of the ions and the formation of solvated ions, which determines short-range interactions between the ions and the solvent molecules; 2) long-range electrostatic forces between ions involving a variation of dielectric constant with concentration and effective dimensions of the ions; 3) ion association and formation of ion pairs which behave as separate physical entities reducing the effect of lowering of vapor pressure by the dissolved electrolytes; and 4) non-electrolyte effects, i.e., effects depending on the relative dimensions of the solvent and solute particles and the non-electrolytic interactions between them. Therefore, each solvent-solute system has to be considered separately. The combined effect of the above factors determines the

activity of the solvent for different compositions and concentrations. The solvent activity can be determined experimentally for the aqueous solutions of most solutes of interest in the study of atmospheric nuclei.

The stable sizes of solution droplets calculated on the basis of Raoult's law and on the basis of "solvent activity" can now be compared. The term E in Eq. (1) for the free energy change in the formation and stability of solution droplets can be written in terms of the activity of the solvent, which takes into account the parameters discussed above. By definition, the solvent activity a is similar to the supersaturation ratio S . Therefore, to include the solvent activity, Eq. (1) for the free energy change can be written as

$$\Delta G = -\frac{4}{3}\pi r^3 \rho (RT/M) \ln S + 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \rho (RT/M) \ln a, \quad (2)$$

where a is the activity of water in the solution of same molality as the droplets, and represents the vapor pressure reduction coefficient for solution droplets. In this equation the last term gives the value of E , i.e., the decrease in free energy due to the effect of the solute. At equilibrium

$$\partial \Delta G / \partial r = 0,$$

so that

$$\ln S = (2/RT)(M\sigma/\rho)(1/r) + \ln a. \quad (3)$$

The above equation can be used for calculating the stable size of solution droplets. The solvent activity can be found experimentally by vapor pressure measurements over solutions of different molality. It can also be derived from the osmotic pressure of the solution. The molal osmotic coefficient ϕ (a function of the osmotic pressure) can be related to the solvent activity by $\phi = [(1Q)/\nu(P)] \ln a$, where ν is the total number of moles of ions given by one mole of the electrolyte and Q/P is the ratio of the numbers of solvent and solute molecules.

Kelvin's equation modified on the basis of Raoult's law can also be written in the following form for comparison with the equation based on the activity of the solvent:

$$\ln S = (2/RT)(M\sigma/\rho)(1/r) + \ln f, \quad (4)$$

where $f = (1 + iP/Q)^{-\rho'/\rho}$, i is the Van't Hoff factor, and ρ'/ρ the ratio of the densities of the pure solvent and the solution.

Eqs. (3) and (4) for the equilibrium conditions of the solution droplets can be compared. The vapor pressure reduction factor in Eq. (3) is represented by the activity a of the solvent for a given solution. The same factor in Eq. (4) is represented by the term based on Raoult's law. It is immediately obvious that Eq. (3) is based on more realistic conditions, where the experimentally found values of the solvent activity can be used and the role of the chemical nature of the electrolyte can be

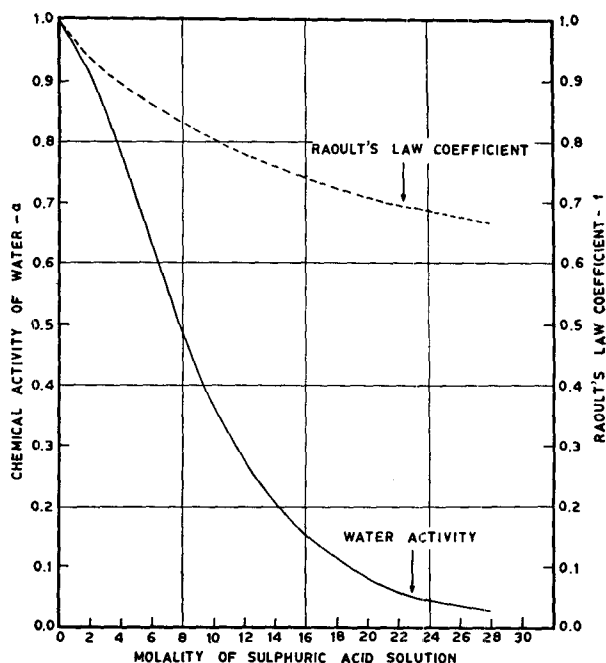


Fig. 1. Chemical activity a of water and Raoult's law coefficient f for different molalities of a sulphuric acid solution.

taken into account. In Eq. (4) based on Raoult's law, only the concentration and density of the solution can be considered. The Van't Hoff factor i is not quite adequate to account for the difference in the electrolyte.

To illustrate the point, we shall consider a typical case of the stability of sulphuric acid droplets in air for different concentrations of acid in the droplets. Fig. 1 is a plot of the vapor pressure reduction coefficients, defined by a in Eq. (3) and f in Eq. (4), vs the molality of the sulphuric acid solution. The values of a (the activity of water) used in this graph are based on experimentally determined values for different molalities of sulphuric acid solutions (Robinson and Stokes, 1959).

Fig. 1 shows that at any concentration the vapor pressure reduction is greater when estimated on the basis of solvent activity than that given by Raoult's law. The implications of this are that the equilibrium sizes of the droplets should be smaller than those estimated from Raoult's law. Fig. 2 shows the stable sizes of acid solution droplets calculated on the basis of Eqs. (3) and (4). It is interesting to note that for stability the required solute contents of stable droplets of any size are lower when estimated from the water activity data than those estimated by applying Raoult's law. At lower humidities, there is a significant difference in the stable particle size calculated by the two methods. For example, at 50% relative humidity, if water activity is used as the basis for calculating the stable size, stable particles of 50–100 Å radius require only half the quantity of solute calculated on the basis of Raoult's law.

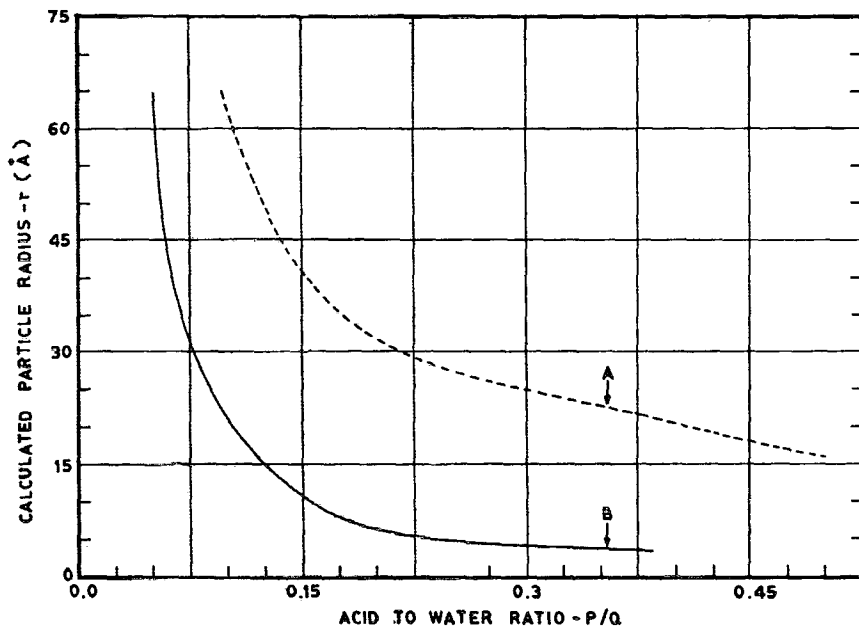


FIG. 2. Calculated sizes of particles at equilibrium for different ratios of sulphuric acid to water molecules from Raoult's law, A, and from water activity data, B.

4. Comparative study of the solutes of interest in atmospheric condensation nuclei

The solutes of interest as atmospheric condensation nuclei are sulphuric acid, hydrochloric acid and the salts ammonium sulphate and sodium chloride. Except for sodium chloride, the other solutes are

mainly formed by gas phase reactions and the nucleation of solution droplets is governed by chemical reactions in the atmosphere in the presence of water vapor.

After an embryo is formed, the stable size of the droplet would depend on the quantity of solute in the droplet and the chemical activity of water. Fig. 3 shows the

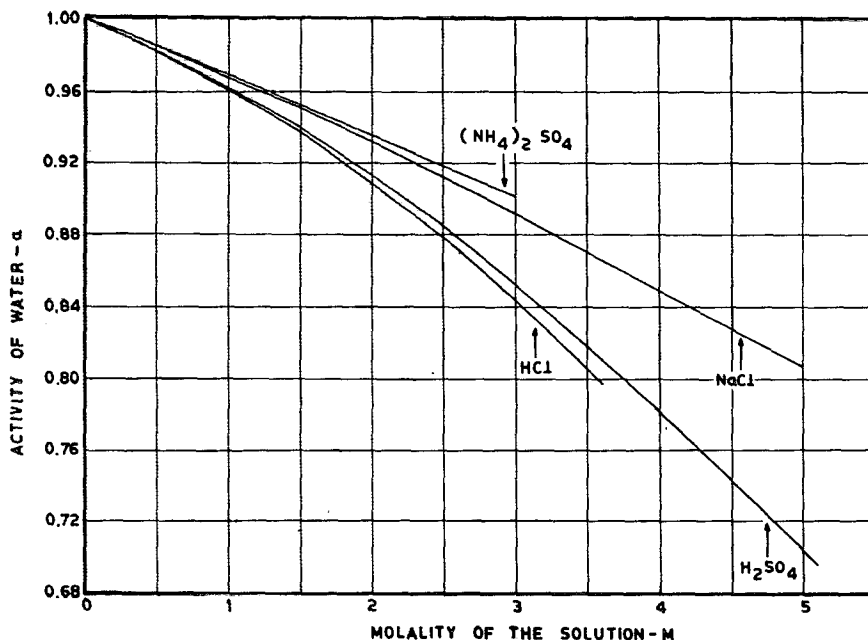


FIG. 3. Chemical activity of water in solutions of different molality for hydrochloric acid, sulphuric acid, sodium chloride and ammonium sulphate.

chemical activity of water for solutions of different molality, for the acids and salts of interest as atmospheric nuclei (*International Critical Tables*, 1928). It is seen that hydrochloric acid and sulphuric acid show lower water activity than the two salts ammonium sulphate and sodium chloride. This would mean that the acids would give smaller stable particle sizes than the salts in solutions of the same molality. At high molality the contrast between the acids and salts is even greater. However, for the same quantity of solute, acid solution droplets will grow to larger stable sizes than salt solution droplets. This is of considerable significance in determining the effect of relative humidity on the growth of nuclei of soluble substances.

5. Activation of atmospheric nuclei to cloud nuclei

It can be shown that activation of 50–500 Å size stable nuclei of certain soluble species to cloud nuclei can take place by an increase in relative humidity in the atmosphere leading to only moderate supersaturations. Stable embryos containing one or a few molecules of the solute may be readily formed at normal relative humidity by one of the processes of gas-to-particle conversion. Due to the very high number concentration of such embryos, especially in the lower atmosphere, the initial growth can take place due to rapid coagulation of the particles.

For any given relative humidity and amount and type of solute there will be a stable equilibrium particle size for which the vapor pressure over the particle equals the vapor pressure of water in the atmosphere (represented by the relative humidity). We again take the case of H_2SO_4 nuclei having an equilibrium size in the Aitken size range. Fig. 4 gives the stable equilibrium sizes of nuclei for different values of relative humidity and quantity of H_2SO_4 per particle. The figure shows that Aitken nuclei increase in size with an increase in relative humidity. For drier nuclei having larger amounts of acid, the growth is more rapid than for the nuclei containing smaller amounts of acid. The quantity of acid in the nuclei will be governed by the concentration of the parent gas SO_2 in the air and the efficiency of gas-to-particle conversion reactions. As both of these are quite variable in the atmosphere, the distribution of nuclei sizes in stable equilibrium shown in Fig. 4 seems to be quite reasonable. The graphs in Fig. 4 are based on Eq. (3), for $T=295\text{K}$, which takes into consideration both the physical and chemical bases of stable equilibrium particle size. Different solutes will give different stable equilibrium particle sizes, depending on the chemical activity of water and the solution particles of different molality.

For these nuclei to become active, leading to the formation of cloud nuclei, it is necessary to have water vapor supersaturation in the atmosphere. The supersaturation associated with the normal updrafts in the atmosphere is generally small and the maximum value

rarely exceeds 1%. An interesting feature of the soluble nuclei is that in addition to having a stable equilibrium size at and below 100% relative humidity, there is also an unstable equilibrium size at water vapor supersaturation. When the nuclei attain the unstable equilibrium size, they constitute active cloud nuclei capable of growing indefinitely. Fig. 5 shows the growth of the stable equilibrium nuclei of Fig. 4 as the relative humidity exceeds 100% over the range of 100 to 101%. It is thus shown that even very small Aitken nuclei consisting of soluble materials can grow to cloud nuclei size, with a part of the growth taking place up to 100% relative humidity, and a part after 100%. In both Figs. 4 and 5 the concept of water activity has been used and the results are somewhat different from the Kohler's curves (Fletcher, 1962) which are based on Raoult's law.

An important feature of Figs. 4 and 5 is that after the droplet has grown to a critical size, further growth does not require an increase in relative humidity because larger droplets have a lower vapor pressure at the droplet surface. The vapor pressure over the droplet surface at critical size corresponds closely to the saturation vapor pressure over a plain surface. Whereas chemical effects of the solute promote growth with an increase in relative humidity, the physical process of growth predominates after the critical size is reached and growth can continue in spite of a decrease in the solute-to-solvent ratio. However, at any given maximum supersaturation only the fraction of the droplets growing to the critical size will be activated, and those below the critical size tend to form stable haze particles—continuously evaporating or growing as the water vapor decreases or increases. Aitken nuclei can be continuously formed in the atmosphere by gas phase reactions and

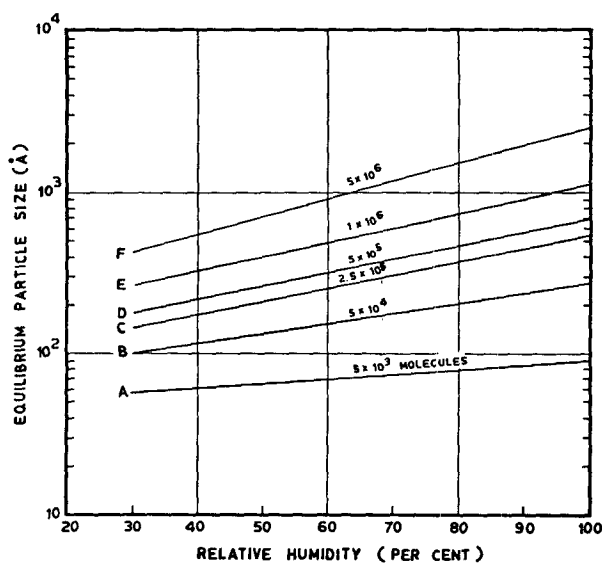


FIG. 4. Stable equilibrium sizes of nuclei for different values of relative humidity and concentration of sulphuric acid (number of molecules) per particle.

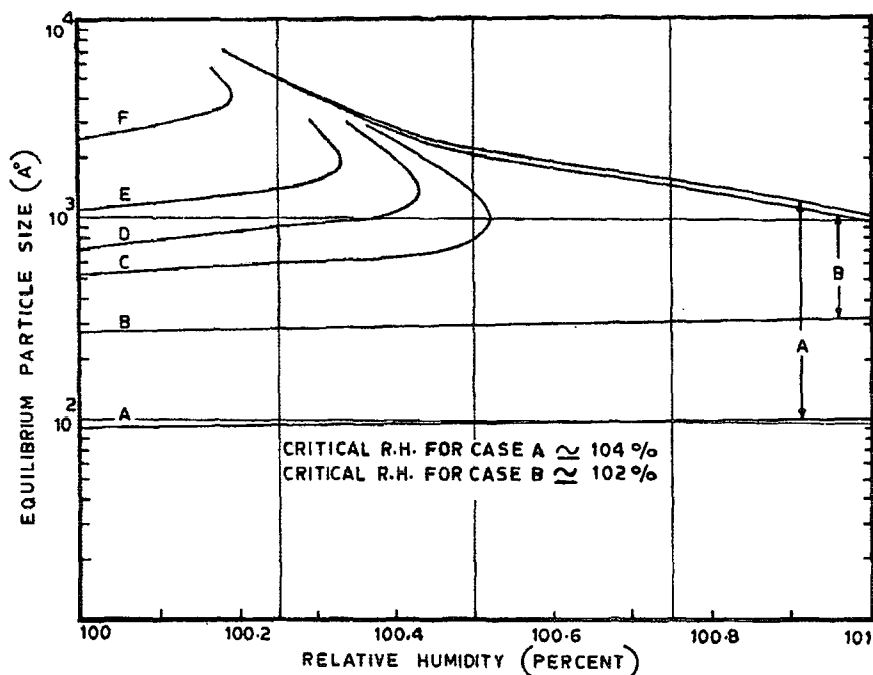


FIG. 5. Variation in particle size with supersaturation for cases A, B, C, D, E and F of Fig. 4.

the large soluble species among them may account for a continuous source of cloud nuclei.

The fact that increasing relative humidity will cause nuclei produced by gas phase reactions to reach sizes at which they can be activated with supersaturations likely in the atmosphere suggests a possible mechanism of formation of cloud nuclei in the atmosphere. Further theoretical and experimental studies on chemical nucleation, embryo formation, and physical and chemical effects of solutes in solution droplets are necessary for a better understanding of the mechanisms.

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