

# Binary homogeneous nucleation in water–succinic acid and water–glutaric acid systems

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Binary homogeneous nucleation of water–succinic acid and water–glutaric acid systems have been investigated. The numerical approach was based on the classical nucleation theory. Usually, nucleation is discussed in terms of kinetics, but the thermodynamics involved is undoubtedly equally important. In this paper we studied the above mentioned binary systems giving a quantitative insight into the nucleation process and a detailed consideration of the thermodynamics involved. Both diacids in study are in solid state at room temperature. They behave in environment according to their liquid state properties because of the absence of crystalline lattice energies, and therefore their subcooled liquid state thermodynamics have to be considered. The lack of consistent thermodynamic data for pure organic components and their aqueous solutions represent a high source of uncertainty. However, the present simulations indicate that in atmospheric conditions these binary systems will not form new particles. © 2004 American Institute of Physics.

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## I. INTRODUCTION

The study of homogeneous nucleation is important for a fundamental understanding of a wide range of phenomena that occur in the atmosphere. The classical theory of binary homogeneous nucleation was first treated in the 1930s by Flood,<sup>1</sup> but it was not until almost 20 years later that Reiss<sup>2</sup> published a complete treatment of binary nucleation. Doyle<sup>3</sup> was the first to publish predicted nucleation rates for the sulphuric acid/water system. Because a free sulphuric acid molecule tends to gather water molecules around it to form hydrates, Heist and Reiss<sup>4</sup> and Jaeger-Voirol *et al.*<sup>5</sup> improved the classical theory taking into account the effect of sulphuric acid hydration. Stabilizing the vapor hydrates reduce nucleation rates by a factor  $10^3$ – $10^8$ . Wilemski<sup>6</sup> presented a revised classical nucleation theory, and pointed out that the previous standard nucleation theory was thermodynamically inconsistent. The numerical method to search the critical cluster (the smallest thermodynamically stable cluster) was not correct, and it resulted in a erroneous cluster compositions and nucleation rates.<sup>7</sup>

Most of the studies of heteromolecular nucleation have focused on inorganic species. Only little information is currently available concerning the organics, mostly on water–alcohol systems.<sup>8–10</sup> As a result of numerous studies carried out in the last few years, it has become obvious that organic matter typically accounts for 10%–70% of the total fine par-

ticle mass,<sup>11,12</sup> especially over continental regions.<sup>13</sup> The variety of the organic compounds that can be found in both anthropogenic and natural aerosols cover a wide range of carbon number and functional groups, also exhibiting a range of chemical properties. A first classification of the organic compounds would involve their water solubility, since this property affects the water uptake and the homogeneity of the particle. Recent empirical studies show that water soluble organics constitute a substantial fraction of particulate organics.<sup>11,12,14,15</sup>

Carboxylic acids are late products of the photochemistry of hydrocarbons. They have low vapor pressures and therefore they are likely to partition into the particulate matter almost exclusively. The low molecular weight dicarboxylic acids (C2–C5) represent the major fraction of the organic particulate matter.<sup>16</sup> Oxalic acid is by far the most abundant dicarboxylic acid in ambient air,<sup>17</sup> but the thermodynamic data are scarce. Therefore our study focused on the two second most abundant species (succinic and glutaric acids) for which all the relevant thermophysical properties can be found in the literature.

Recently Gao *et al.*<sup>18</sup> have studied the nucleation of water–glutaric acid system by applying the classical binary nucleation theory, but without taking into consideration Zeldovich nonequilibrium factor. They concluded that glutaric acid–water homogeneous nucleation was too slow to account for the experimentally observed nucleation rates. We will show that a better parameterization for water and glutaric acid liquid phase activities will alter the final result significantly.

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In the present paper, using the classical theory of nucleation, we investigate the feasibility of the atmospherically relevant C4 (succinic acid) and C5 (glutaric acid) dicarboxylic acid binary nucleation together with water vapor. The importance of the thermodynamically consistent parameterizations for surface tension and chemical activities is emphasized.

## II. CLASSICAL THEORY OF NUCLEATION

Consider a liquidlike cluster containing  $n_1$  molecules of water and  $n_2$  molecules of organic acid. The formation energy of the cluster is assumed to be given by<sup>19</sup>

$$\Delta G = -kT \sum_{i=1}^2 n_i \ln \left( \frac{P_i}{P_{s,i}} \right) + 4\pi\sigma r^2, \quad (1)$$

where  $P_i$  is the ambient partial pressure of free molecules of species  $i$ ,  $P_{s,i}$  is the equilibrium vapor pressure of species  $i$  above a flat solution surface,  $r$  is the radius of the droplet, and  $\sigma$  is the surface tension of a flat liquid–vapor interface at the composition of the nucleus. The total numbers of molecules in the nucleus  $n_i$  are

$$n_i = n_{il} + n_{is}, \quad (2)$$

where  $n_{il}$  are the numbers of molecules in the uniform liquid phase encompassed by the surface of tension and  $n_{is}$  is the surface excess number of molecules arising from the difference between the density profiles of the uniform Gibbsian droplet model and the actual droplet. The composition of the critical cluster  $x^*$  is found by solving the following equation numerically

$$\ln \left( \frac{P_1}{P_{s,1}(x,T)} \right) v_2(x,T) = \ln \left( \frac{P_2}{P_{s,2}(x,T)} \right) v_1(x,T), \quad (3)$$

where  $v_i$  is the partial molar volume of species  $i$ .

As shown by Laaksonen *et al.*,<sup>19</sup> Eq. (3) is a very general thermodynamic relation which holds for incompressible liquids, and can be derived without any assumptions concerning the free energy of the droplet. Setting  $(\partial\Delta G/\partial n_i)_{n_j} = 0$  yields the Kelvin equation, from which the radius of the critical cluster is obtained:

$$r^* = \frac{2\sigma v_i}{kT \ln \left( \frac{P_i}{P_{s,i}} \right)} \quad (4)$$

and the formation energy is given by

$$\Delta G^* = \frac{4}{3}\pi r^{*2} \sigma. \quad (5)$$

Usually the kinetics of nucleation is thought to be of minor importance. Here the binary system is reduced to unary system so that the evaluation of the kinetic part of the nucleation rate is easier. The nucleation rate is<sup>20</sup>

$$I = R_{AV} F Z \exp \frac{-\Delta G^*}{kT}. \quad (6)$$

For nonassociated vapors, the average growth rate is

$$R_{AV} = \frac{R_{11} R_{22}}{R_{11} \sin^2 \chi + R_{22} \cos^2 \chi}, \quad (7)$$

where  $R_{11}$  and  $R_{22}$  are the rates at which water and organic acid molecules, respectively, collide with the critical cluster. The growth angle  $\chi$  in the  $(N_1, N_2)$  plane can be approximated by using  $\tan \chi = x/(1-x)$ . In the case of virtual monomers the molecular concentration in the gas phase will be

$$F = N_1 + N_2, \quad (8)$$

where  $N_1$  and  $N_2$  are the number concentration of water and succinic acid molecules in the vapor phase. In the approximation based on virtual monomer, the Zeldovich factor is given by<sup>21</sup>

$$Z = \sqrt{\frac{-1}{2\pi kT} \frac{\partial^2 \Delta G}{\partial n^2}} = \sqrt{\frac{\sigma}{kT} \frac{v}{2\pi r^{*2}}}, \quad (9)$$

where  $v$  is the volume of an average virtual monomer.

## III. METHODS FOR CALCULATING THE CHEMICAL ACTIVITIES

Following the equation for vapor–liquid equilibrium, which states that the fugacities of the component in liquid and vapor phases are equal<sup>22</sup> and assuming the vapor phase is an ideal mixture of gases (the fugacity coefficient of all the components in the gas phase is unity), we obtain

$$y_i P = x_i \gamma_i f_i^0, \quad (10)$$

where  $y_i$  is mole fraction of the component in vapor phase,  $P$  is total pressure,  $x_i$  is mole fraction of the component in liquid phase,  $f_i^0$  = standard state fugacity of the component in liquid phase, and  $\gamma_i$  is the activity coefficient.

There are two possibilities for the standard state fugacity. The first choice is the pure liquid, more commonly known as Raoult's law. In this case the standard state fugacity equals the fugacity of pure liquid which, in equilibrium, equals the saturation vapor pressure of the component. The second choice is Henry's law standard state for which the activity coefficient at infinite dilution is unity. In this case

$$H = f_i^0, \quad (11)$$

where  $H$  is the Henry law's constant with units of pressure/mole fraction. Substituting  $f_i^0$  in Eq. (11):

$$H = \frac{P_i}{a_i} = \frac{y_i P}{x_i \gamma_i}, \quad (12)$$

where  $P_i$  is the ambient vapor pressure of the component and  $a_i$  is the activity of the component in liquid phase. If Henry law's constant has units of M/atm, Eq. (12) becomes

$$a_i' = P_i H. \quad (13)$$

As long as we account for the liquid phase nonideality, Eqs. (12) and (13) are valid for any concentrations. Equation (13) together with the well known definition of chemical activity based on Raoult's law

$$a_i = \frac{P_i}{P_{s,i}}, \quad (14)$$

where  $P_{s,i}$  is the saturation vapor pressure of the pure component, will be used in our calculations for chemical activities.

## A. van Laar equations

The calculation of binary vapor–liquid equilibrium using van Laar equations<sup>23</sup> requires the knowledge of the saturation vapor pressures  $P_{s,i}$  for both components and the availability of several experimental points. For each experimental point the activity coefficients  $\gamma_i$  can be calculated according to

$$\gamma_i = \frac{y_i P}{x_i P_{s,i}}, \quad (15)$$

with  $i = 1, 2$ .

Now, for the same experimental points, the molar excess Gibbs energy  $g^E$  can be calculated with

$$g^E = RT \sum_{i=1,2} x_i \ln \gamma_i, \quad (16)$$

where  $R$  is the molar gas constant and  $T$  is the temperature.

The van Laar excess Gibbs energy is defined as

$$g^E = \frac{ABx_1x_2}{x_1A + x_2B}, \quad (17)$$

where  $A$  and  $B$  are constants that have to be adjusted so that the deviation between the calculated  $g^E$  and the one found from the experimental data is minimal. Having  $A$  and  $B$  determined, the activity coefficients  $\gamma_i$  for the entire range of mole fractions can be calculated using

$$RT \ln \gamma_1 = A \left( 1 + \frac{Ax_1}{Bx_2} \right)^{-2}, \quad (18)$$

$$RT \ln \gamma_2 = B \left( 1 + \frac{Bx_2}{Ax_1} \right)^{-2}. \quad (19)$$

The steps presented above, although simple, represent a thermodynamically consistent procedure for calculating the activity coefficients as a function of composition. They are mathematically easy to handle and for moderately nonideal binary mixtures they give good results. Also, they can be used to interpolate and extrapolate the limited experimental data.

## B. UNIFAC

The group contribution method UNIFAC has been considered an useful tool for predicting thermodynamic properties, including activity coefficients in organic mixtures.<sup>24</sup> UNIFAC assumes that a physical property of the fluid is the sum of the contributions made by the functional groups of the molecule. UNIFAC has two terms: one combinatorial term that depends on the volume and surface area of each molecule and one residual term that is fit to the experimental data and is related to the energetic group interaction parameter among different functional groups. The activity coefficient  $\gamma_i$  is calculated as a sum of the combinatorial  $\gamma_i^c$  and residual  $\gamma_i^r$  terms

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r. \quad (20)$$

Unfortunately, the accuracy of the group contribution method remains controversial because of the interaction parameters. UNIFAC is not able to make a difference between isomers or

calculate proximity effects due to the internal geometry of the molecule. The recently revised interaction parameters in UNIFAC increased the reliability of the model and extended its range and applicability. Peng *et al.*<sup>25</sup> compared the UNIFAC predictions and the experimental data for water activity  $a_w$  of aqueous solutions of several organic compounds. They found that UNIFAC is able to predict  $a_w$  within 26% and 41% relative error for succinic acid and glutaric acid, respectively.

## C. Activities in this study

Davies and Thomas<sup>26</sup> did some isopiestic studies of aqueous dicarboxylic acid solutions, providing the vapor pressure lowering and the activities of solvent and solutes. It should be noted that the data from Davies and Thomas are normalized, so that the ratio  $a_i/m = 1$  when  $m = 1$  for glutaric acid and  $a_i/m = 1$  when  $m = 0.5$  for succinic acid, where  $a_i$  is the diacid activity and  $m$  is the diacid molality in aqueous solution. The constant of normalization can easily be found using the activities at the solubility limit  $a_{i,s}$  and the saturation vapor pressure of solid substances  $P_{s,s}$ . Denoting the normalization constant by  $c$ , Eq. (13) becomes

$$a_i' = P_i H c, \quad (21)$$

which, at the solubility limit where the saturated solution is in equilibrium with the solid phase and therefore  $P_i = P_{s,s}$ , becomes

$$a_{i,s}' = P_{s,s} H c. \quad (22)$$

Because the data given by Davies and Thomas are relatively closed to the solubility limit,  $a_{i,s}$  can be extrapolated within a good level of confidence. Having now the activities  $a_{i,s}$ , Henry's law constant, and the solid state saturation vapor pressure as described in Sec. IV A, the constant of normalization  $c$  can be calculated directly from Eq. (22).

The data obtained were interpolated in a thermodynamically consistent way with respect to composition using van Laar equations<sup>23</sup> for the entire range of mole fractions as described in Sec. III A. In Figs. 1 and 2, the activity coefficient for water and both acids are shown as a function of liquid composition. Also the water activities measured by Peng *et al.*<sup>25</sup> are plotted. However, these data could not be used in the van Laar fitting, since this method required the knowledge of both water and organic acid activities. As shown in the figures, the measured water activities are in pretty good agreement with the fitted van Laar curves. The van Laar coefficients  $A$  and  $B$  for both glutaric and succinic acid aqueous solutions are listed in Table I.

## IV. THERMOPHYSICAL PROPERTIES OF WATER AND ORGANIC ACIDS

The largest problem for our calculations was the need of thermodynamic data which describes the interaction between water and organic vapor. In this study we present the organic acids for which the all of the thermophysical properties (surface tension, vapor pressure, chemical activity, Henry law's constant) of their aqueous solutions could be found in the literature. The water–organic compounds mixture densities

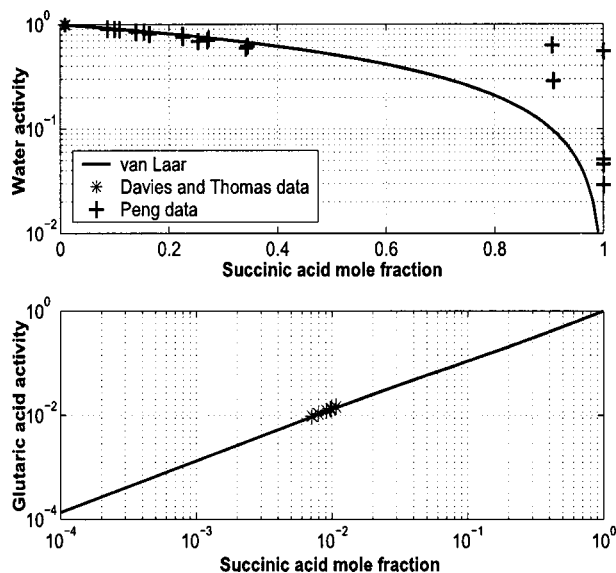


FIG. 1. The activities of water and succinic acid calculated with van Laar method: (star) experimental data from Davies and Thomas (1956) (Ref. 26); (plus) experimental data from Peng *et al.* (2001) (Ref. 25); (solid line) van Laar fitting. Temperature is 298 K.

have been calculated using pure compound densities and subsequently the ideal mixture theory, which assumes that the molecular volumes in the mixture equal those of the pure species. For comparison purposes only, the activities in aqueous solution have also been determined using the group contribution method UNIFAC.

### A. Vapor pressures of pure substances

The vapor pressure of water is obtained from Preining *et al.*<sup>27</sup> (see also Vehkamäki *et al.*<sup>28</sup>). The solid state vapor

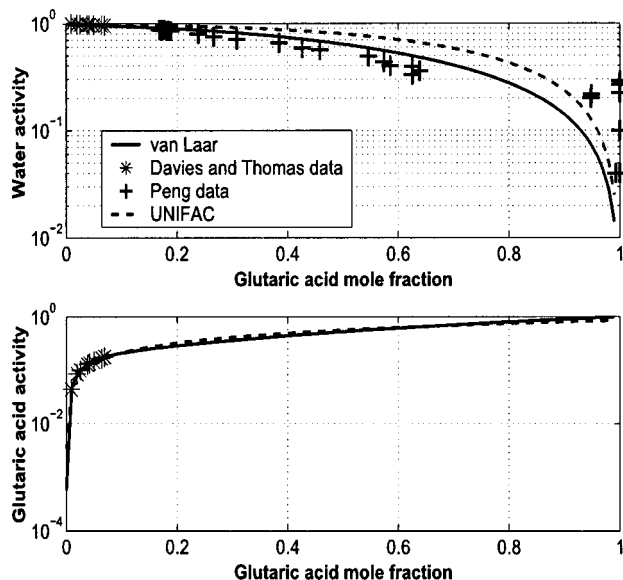


FIG. 2. The activities of water and glutaric acid calculated with van Laar method: (star) experimental data from Davies and Thomas (1956) (Ref. 26); (plus) experimental data from Peng *et al.* (2001) (Ref. 25); (solid line)—van Laar fitting; (dashed line) UNIFAC prediction. Temperature is 298 K.

pressures data for glutaric acid are given by Tao and McMurry<sup>29</sup> and confirmed by Bilde and Pandis<sup>30</sup> and by Bilde *et al.*<sup>31</sup> for succinic acid.

In this study we assume that the critical nuclei can be described as tiny liquid droplets regardless of the acid concentration. At the temperatures studied here, both of the acids are in the solid state. However, because of the liquid drop assumption, the saturation vapor pressures of the pure acids needed in the nucleation calculations cannot refer to the solid phase. Instead, we have to estimate the subcooled liquid vapor pressures for the acids. The subcooled vapor pressures could be calculated if acid activities defined by Eq. (14) were available simply by dividing the solid vapor pressure by the activity of the acid in the saturated solution. Unfortunately, only activities defined on the Henry's law basis are available, and the subcooled vapor pressure itself is needed for converting the activities given by Eq. (13) to Eq. (14). We therefore estimated the subcooled liquid state vapor pressures for succinic and glutaric acid by converting the solid state vapor pressures as described in Prausnitz *et al.*<sup>32</sup> using molar enthalpy of fusion ( $\Delta_{\text{fus}}h$ ) and melting points ( $T_m$ ) reported by the *Chemical Properties Handbook*<sup>33</sup> for glutaric acid and by the *CRC Handbook of Chemistry and Physics* (3rd electronic edition) for succinic acid.<sup>34</sup> The fugacity of the subcooled liquid ( $f^L$ ) at temperature  $T$  in terms of solid state fugacity ( $f^S$ ) and measurable thermodynamic properties  $\Delta_{\text{fus}}h$  and  $T_m$  is

$$\ln \frac{f^L}{f^S} = \frac{\Delta_{\text{fus}}h}{RT_m} \left( \frac{T_m}{T} - 1 \right), \quad (23)$$

where  $R$  is the molar gas constant. The values for melting temperatures and enthalpy of fusion are given in Table I.

### B. Surface tension

Surface tension of succinic and glutaric acid aqueous solutions have been measured in the laboratory at the Institute of Atmospheric Sciences and Climate, Bologna, Italy using a SINTECH Profile Analysis Tensiometer for various concentrations up to the limit of solubility. The surface tensions relative to pure water  $-\Delta\sigma/\sigma$  are in agreement with the data published by Shulmann *et al.*<sup>35</sup> The surface tensions of the mixtures decreased with increasing acid concentrations, displaying a nonlinear trend. Because of the lack of experimental data concerning the surface tension of pure organic compounds, they have been estimated using the Macleod–Sugden method.<sup>23</sup> At a temperature of 298 K, succinic acid and glutaric acid are solid substances. The estimated surface tensions should be understood to refer to their subcooled liquid states. Fitting the Szyskowski–Langmuir equation<sup>23,36</sup>

$$\sigma = \sigma_w - aT \log_{10}(1 + bx) \quad (24)$$

to the experimental data [where  $\sigma_w$  is the pure water surface tension,  $T$  is temperature (K),  $x$  is the organic acid mole fraction, and  $a$  and  $b$  parameters that have to be determined], yielded a curve as shown in Fig. 3. It should be mentioned here that although the mixtures exhibit in practice a solubility limit (at 64 g/100 g water as reported by Dean<sup>37</sup> or 116 g/100 g water according to Saxena *et al.*<sup>24</sup> for glutaric acid and at

TABLE I. Thermophysical properties of organic acids:  $M$ =molecular weight (g/mol),  $\rho$ =the density (kg/m<sup>3</sup>),  $p_s$ =the equilibrium vapor pressure for solid state (Pa),  $\sigma$ =surface tension (N/m),  $A, B$ =van Laar coefficients for water and organic acid activities,  $H$ =Henry's law constant (M/atm),  $T_m$ =melting temperature (K),  $\Delta_{fus}h$ =enthalpy of fusion (kJ/mol),  $x$ =solute mole fraction, and  $T$ =temperature (K).

Organic acid	Thermophysical properties
Succinic acid HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	$M = 118.09$ $\rho^a = 3200 - 5.8T$ $p_s = \exp\left(19.8 - \frac{7196.8}{T}\right)^c$ $\sigma^b = 10^{-3}(72 - 0.0127T \log(1 + 175.28x))$ $A = 107, B = 763$ $H = 3E8$ $T_m = 461.05$ $\Delta_{fus}h = 32.4$
Glutaric acid HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH	$M = 132.11$ $\rho^a = 1847 - 1.45T$ $p_s = \exp\left(14.95 - \frac{5347}{T}\right)^d$ $p_s = \exp\left(8.467 - \frac{3501}{T}\right)^c$ $\sigma^b = 10^{-3}(72 - 0.0222T \log(1 + 189.61x))$ $A = 886.1, B = 4292$ $H = 2E8$ $T_m = 370.65$ $\Delta_{fus}h = 20.676$

<sup>a</sup>Pure component.

<sup>b</sup>Aqueous solution.

<sup>c</sup>Reference 31.

<sup>d</sup>Reference 29.

<sup>e</sup>Reference 30.

8.8 g/100 g water for succinic acid),<sup>25</sup> the measurements of Peng *et al.*<sup>25</sup> have shown that micron sized solution droplets of both glutaric and succinic acid can be made strongly supersaturated before crystallization takes place. We therefore treat the systems as completely soluble and neglect the crystallization for simplification of the problem. The question of solubility will be addressed in the future.

### C. Density

The water density is given by Kell<sup>38</sup> for temperatures exceeding 0 °C and by Pruppacher and Klett<sup>39</sup> for temperatures between -50 and 0 °C. The densities of the aqueous solutions of glutaric and succinic acids have been calculated using pure compound densities and the ideal mixture theory. The pure subcooled acid densities have been estimated as a function of temperature using the Yen-Woods method.<sup>40</sup> The calculated values agreed well with the existing experimental values (usually only available for 298 K) found in the literature (see e.g., Table I in Peng *et al.*<sup>25</sup>). The density of aqueous solutions of succinic and glutaric acids have been measured for various concentrations by weighing known volumes of solutions, of known concentrations and compared to the theoretical estimation mentioned above. The result is depicted in Fig. 4.

All the thermodynamic properties and the parameterizations for succinic acid and glutaric acid are collected in Table I.

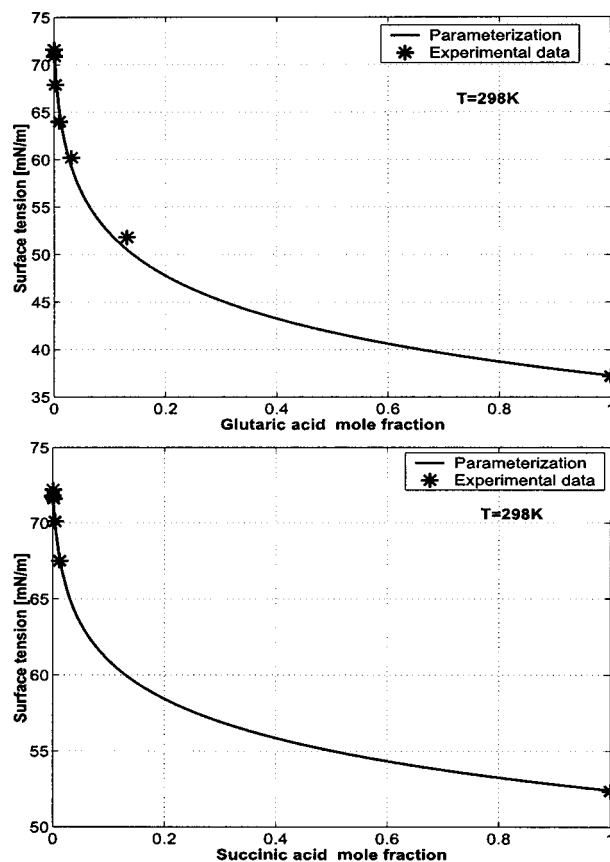


FIG. 3. Surface tension (mN/m) for glutaric acid (top) and succinic acid (bottom) aqueous solutions as a function of glutaric and respectively succinic acid mole fractions: (stars) experimental points; (solid line) parameterizations. The point for pure glutaric and succinic acids (mole fraction 1) have been calculated using the Macleod-Sugden method. Temperature is 298 K.

## V. RESULTS

### A. Succinic acid

The binary homogeneous nucleation of water-succinic acid (SA) vapor system has been calculated for two different temperatures (273 and 298 K). The ambient relative humidity has been chosen as 50% or 80%. The model output (Fig. 5) shows the particle nucleation rate as a function of succinic acid concentration in the gas phase (molecules/cm<sup>3</sup>). According to the numerical calculations, the SA-H<sub>2</sub>O system will reach a relevant nucleation rate (for example 1 particle/cm<sup>3</sup>s) when the succinic acid gas phase concentration is more than 10<sup>15</sup> molecules/cm<sup>3</sup>. The highest reported atmospheric concentrations of succinic acid<sup>41,42</sup> are 10<sup>8</sup>-10<sup>9</sup> molecules/cm<sup>3</sup>, 6-7 orders of magnitude smaller than our calculated critical concentration, showing an extremely low probability of occurrence of nucleation in water-succinic acid mixture.

The effect of temperature in the nucleation rate is small as demonstrated in Fig. 5. A temperature increase of 25 °C corresponds to an increase in nucleation rate of about 2 orders of magnitude in the case of high nucleation rates while for nucleation rates smaller than 10<sup>7</sup> molecules/cm<sup>3</sup>s the same temperature increase leads to a decrease in nucleation

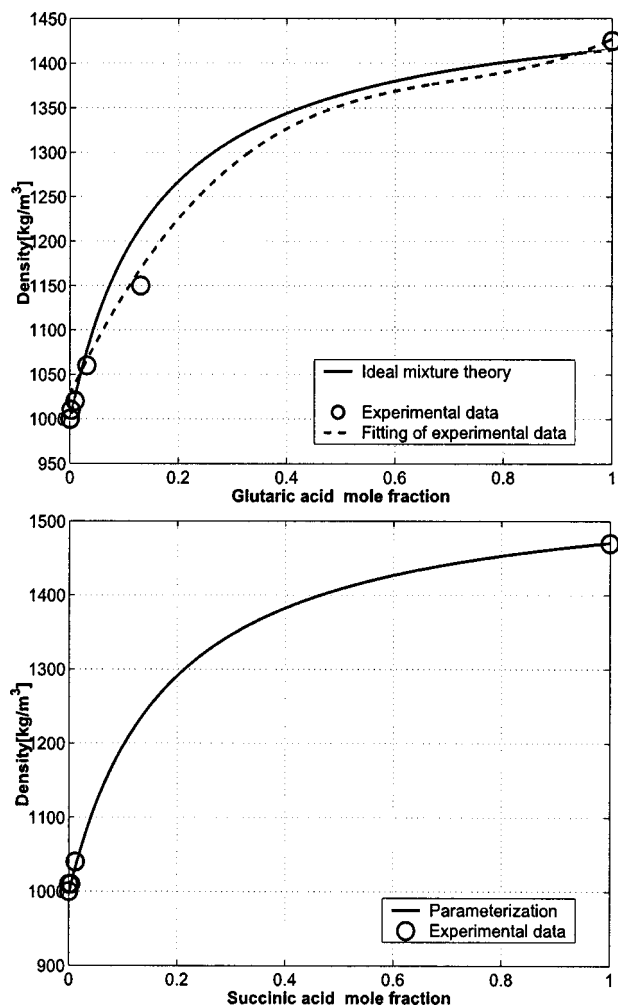


FIG. 4. Density ( $\text{kg/m}^3$ ) for glutaric acid (top) and succinic acid (bottom) aqueous solutions as a function of glutaric and succinic acid mole fractions, respectively: (○) experimental points; (solid line) ideal mixture theory estimation; (dashed line) fitting of experimental points. Temperature is 298 K.

rate. Relative humidity also has a negligible effect on the calculated nucleation rates.

More detailed results of the calculations are presented in Table II only for  $T=273$  and relative humidity (RH) = 50% and  $T=298$  K and RH = 80%. The diameter of the critical cluster is about 9–10 Å. The mole fraction of succinic acid in the critical cluster varies between 0.6 and 0.8 and the Gibbs free energy between 20 and  $50kT$ . The nucleation onset activities at 298 K are given in Fig. 6, together with the onset activities for nucleation rate of  $10^6/\text{cm}^3 \text{ s}$ .

The activities for water and succinic acid in the liquid phase have also been estimated using the UNIFAC group contribution method. According to the model output, for the SA–water system to achieve the critical (onset) nucleation rate of  $1 \text{ cm}^{-3} \text{ s}^{-1}$  at  $T=298$  K and relative humidities below 100%, the succinic acid gas phase activities are very close to those obtained using the van Laar activities, and not shown in the figure for clarity. No nucleation can occur in such a system under atmospheric conditions.

The effect of density variation on the nucleation rate was also studied by changing its functional form. A fourth degree polynomial for density replaced the equation presented in

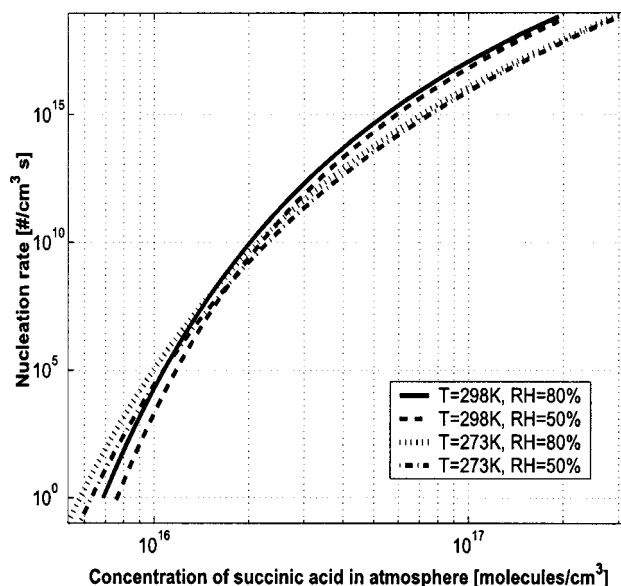


FIG. 5. Binary homogeneous nucleation of succinic acid–water vapors for two temperatures (273 and 298 K) and two relative humidities (50% and 80%). Activities in liquid phase are based on experimental data and the parametrization is done using van Laar equations.

Table I. The functional form can be chosen arbitrarily as long as it follows well the shape of the initial function describing the thermodynamic property and also fits the experimental data. Figure 7 presents the original density of succinic acid aqueous solution and its different functional form (fourth degree polynomial).

Because of the very big uncertainty in the surface tension outside the range of the experimental data (remember that the surface tension for pure succinic acid was calculated and not measured), a sensitivity analysis has been carried out by estimating the pure succinic acid surface tension with the Sasri and Rao method.<sup>23</sup> The new estimated value was 43.05 mN/m, about 9.5 units lower than the one calculated with Macleod–Sugden method. The results of the sensitivity analysis for the nucleation rate in the water–succinic acid system as a function of succinic acid concentration in gas phase for a temperature of 273 K and relative humidity of 80% are depicted in Fig. 8. Changing the functional form for density does not have any significant effect on the nucleation rate leading to a change in nucleation rate of only 2 orders of magnitude. The sensitivity analysis for surface tension changes the nucleation rate result with 2–5 orders of magnitude showing that this parameter does not have a significant impact on the model output.

## B. Glutaric acid

To the authors' knowledge, there is only one study of binary nucleation involving water–glutaric acid (GA) system.<sup>18</sup> They applied the classical theory of nucleation but neglected the Zeldovich nonequilibrium factor (see Fig. 9).

We followed a similar approach, but estimated also the effect of Zeldovich factor. We used the same input data (temperature  $T=299.84$  K and relative humidity RH = 65.7%) as Gao *et al.*,<sup>18</sup> but a more rigorous thermodynamic approach, as described in Section III B.

TABLE II. Results of the simulation of the binary homogeneous nucleation in water–succinic acid system.  $T$  represents temperature in Kelvin, RH is the relative humidity,  $a_2$  is the activity of succinic acid in gas phase,  $x$  is the composition of the critical cluster (in mole fraction of succinic acid),  $n_1$  and  $n_2$  are the number of molecules of water and acid in the cluster,  $r$  is the radius of the critical cluster ( $\text{\AA}$ ),  $\Delta G$  is the Gibbs free energy required to form the critical cluster, and  $J$  is the nucleation rate ( $\text{No./cm}^3 \text{ s}$ ).

$T$ and RH	$a_2$	$x$	$n_1$	$n_2$	$r$ ( $\text{\AA}$ )	$\Delta G/kT$	$J$ ( $\text{No./cm}^3 \text{ s}$ )
$T=298 \text{ K}$	20.90	0.66	14.41	28.14	9.96	54.51	0.462
RH= 80%	22.99	0.67	12.86	26.20	9.71	51.76	7.88
...	25.28	0.68	11.49	24.43	9.47	49.20	1.11E+2
...	27.81	0.68	10.28	22.86	9.24	46.82	1.32E+3
...	30.59	0.69	9.21	21.31	9.02	44.59	1.34E+4
...	33.65	0.70	8.26	19.94	8.82	42.51	1.18E+5
...	40.72	0.72	6.69	17.53	8.42	38.75	6.17E+6
...	44.80	0.73	6.03	16.46	8.24	37.04	3.74E+7
...	49.28	0.73	5.45	15.47	8.06	35.44	2.04E+8
...	54.20	0.74	4.93	14.56	7.89	33.93	1.01E+9
...	65.59	0.76	4.06	12.93	7.57	31.19	1.92E+10
...	79.36	0.77	3.37	11.53	7.27	28.75	2.68E+11
...	96.03	0.78	2.81	10.31	7.00	26.58	2.88E+12
...	116.20	0.79	2.33	9.26	6.74	24.65	2.46E+13
...	140.60	0.80	1.99	8.34	6.50	22.91	1.72E+14
...	170.13	0.81	1.69	7.53	6.28	21.34	1.02E+15
$T=273 \text{ K}$	49.28	0.83	4.65	24.20	9.23	51.82	0.86
RH= 50%	54.20	0.841	4.23	22.66	9.03	49.54	9.38
...	59.63	0.846	3.86	21.25	8.84	47.41	8.78E+1
...	65.59	0.848	3.53	19.95	8.65	45.41	7.20E+2
...	72.15	0.854	3.24	18.76	8.47	43.54	5.24E+3
...	79.36	0.856	2.97	17.65	8.30	41.77	3.41E+4
...	87.30	0.858	2.73	16.63	8.13	40.11	2.00E+5
...	96.03	0.861	2.51	15.69	7.97	38.54	1.07E+6
...	116.2	0.867	2.13	14.00	7.67	35.67	2.37E+7
...	140.61	0.873	1.82	12.53	7.39	33.10	3.88E+8
...	154.66	0.875	1.69	11.89	7.26	31.92	1.42E+9
...	187.14	0.880	1.45	10.72	7.01	29.73	1.60E+10
...	226.44	0.884	1.26	9.69	6.77	27.76	1.47E+11
...	301.39	0.891	1.02	8.37	6.44	25.15	2.93E+12
...	364.69	0.895	1.00	7.63	6.24	23.60	1.78E+13

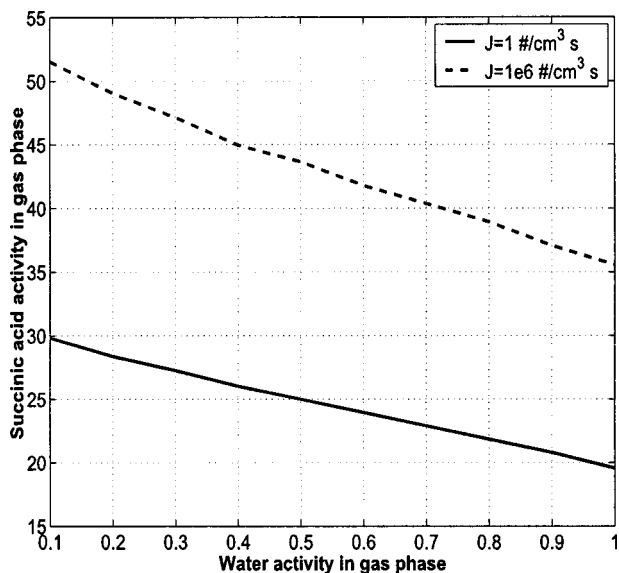


FIG. 6. The onset activities at nucleation rate of  $1/\text{cm}^3 \text{ s}$  (solid line) and  $10^6/\text{cm}^3 \text{ s}$  (dashed line) on water succinic acid system. Temperature is 298 K.

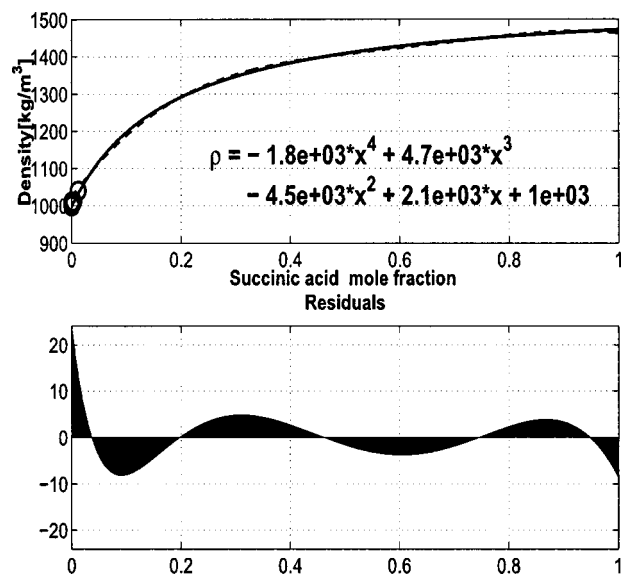


FIG. 7. Succinic acid aqueous solution density as a function of acid mole fraction and its fourth degree polynomial used for sensitivity analysis.

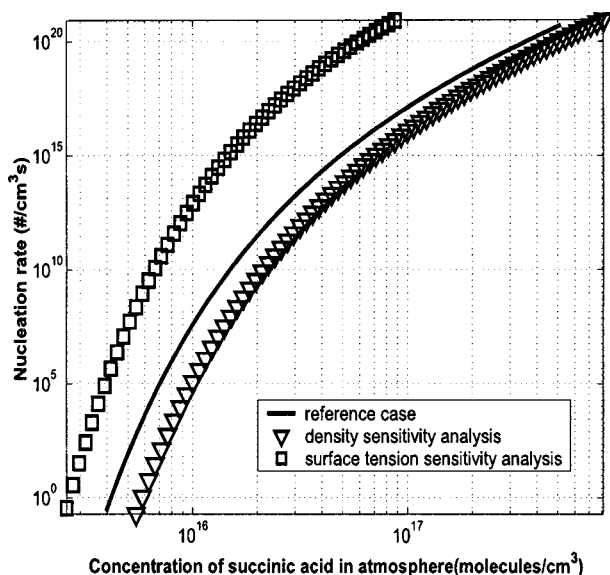


FIG. 8. Sensitivity analysis of binary nucleation for water–succinic acid vapors at temperature of 273 K and RH=80% as a function of succinic acid concentration in gas phase (molecules/cm<sup>3</sup>): (solid line) reference case (thermophysical properties listed in Table I); (triangles) density sensitivity analysis (squares) surface tension sensitivity analysis.

Gao *et al.*<sup>18</sup> considered also Davies and Thomas<sup>26</sup> activity data without accounting for the normalization and supplied parameterizations for both water and GA activities as:

$$a_1 = -0.0097m + 0.994, \quad (25)$$

$$a_2' = 0.8107 \ln(m) + 1.0419, \quad (26)$$

where  $a_1$  is the solvent (water) activity and  $a_2'$  is the GA activity in terms of molality.

The activities calculated with Eqs. (25) and (26) exhibit unusual, thermodynamically inconsistent behavior with negative values for glutaric acid activities in dilute solutions and for water activities in concentrated solutions. These ac-

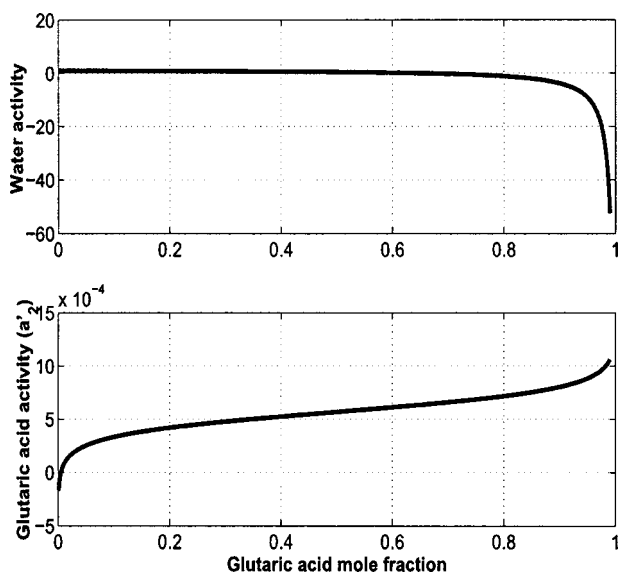


FIG. 9. The activities of water and glutaric acid in conformity with Eqs. (25) and (26). Both figures show thermodynamically inconsistent behavior.

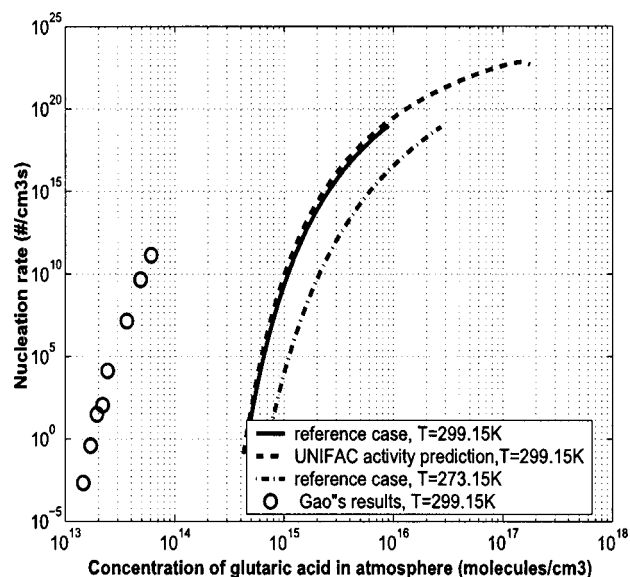


FIG. 10. The nucleation rate of water–glutaric acid system as a function of glutaric acid concentration in gas phase: (solid line) reference case at 298 K (thermophysical properties listed in Table I); (dash-dotted line) reference case at 273 K; (dashed line) UNIFAC activity prediction; (circles) Gao's results (Ref. 18). RH=65.7%.

tivities lead to high errors in the model output, as shown in Fig. 10. The reference case in Fig. 10 represents our model calculations using van Laar method for activities.

As an alternative approach, the activities were also calculated with UNIFAC. The activities predicted by UNIFAC are presented in Fig. 2. The UNIFAC activities appear to be reasonable for both water and glutaric acid. Peng *et al.*<sup>25</sup> reported that UNIFAC can predict water activity within 41% error for glutaric acid aqueous solution.

Figure 10 shows nucleation rates calculated using the above mentioned activity models, all other parameters being kept the same. The temperature and relative humidity have been taken from Gao *et al.*<sup>18</sup> When applying Gao's activity parameterizations, the only extra factor in our model was the Zeldovich factor, which does not create significant difference in the model output. The difference between calculations with Gao<sup>18</sup> and van Laar activities is significant (about 25 orders of magnitude difference in nucleation rate for the same GA concentration in the gas phase). The nucleation rates calculated using UNIFAC predictions is slightly discernible from the reference case.

A temperature variation of 25 °C corresponds to a shift in calculated nucleation rate of about 2–5 orders of magnitude, a variation that can be considered small (also Fig. 10).

To examine the sensitivity of nucleation rate to surface tension and density (Fig. 11), we repeated the analysis in a similar way as described in the previous subsection. The density function has been replaced by a third degree polynomial, which differs from the original one in its form but not in the quantitative details. The resulting nucleation rate presented an extremely limited sensitivity to this variation. The surface tension value for pure glutaric acid has been estimated using the Sasri and Rao method, leading to a new parameterization of the system's surface tension. In this case the difference



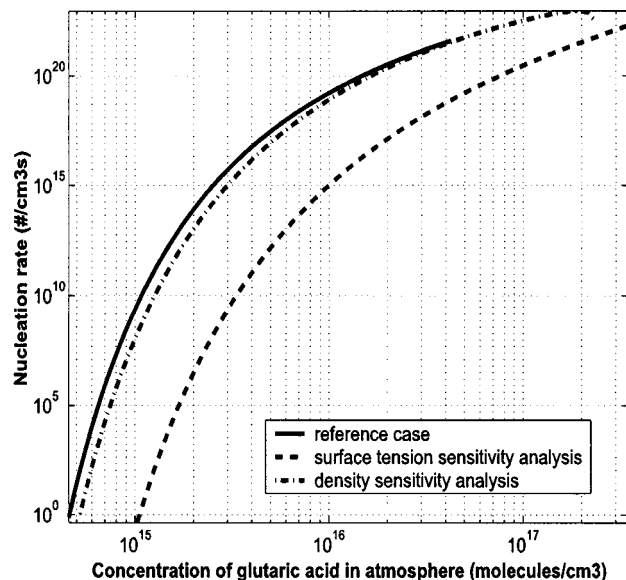


FIG. 11. Sensitivity analysis of binary nucleation for water–glutaric acid vapors as a function of glutaric acid concentration in gas phase (molecules/cm<sup>3</sup>): (solid line) reference case (thermophysical properties listed in Table I); (dash-dotted line) density sensitivity analysis; (dashed line) surface tension sensitivity analysis. Temperature is 299.84 K and RH = 65.7%.

relative to the reference case is higher than for succinic acid, between 2 and 7 orders of magnitude.

Because the ideal mixture theory departure from the experimental points is significant (Fig. 4), a new density curve has been fitted to the data and used in the nucleation rate calculation (the dashed line in Fig. 4). The resulting curve (not shown in the figure for clarity) overlaps the sensitivity analysis for the density curve obtained before.

The composition and the size of the critical cluster together with the Gibbs free energy and nucleation rate are shown in Table III for  $T=299.15$  K and RH=65%. The radius of the critical cluster is about 11 Å, and the required

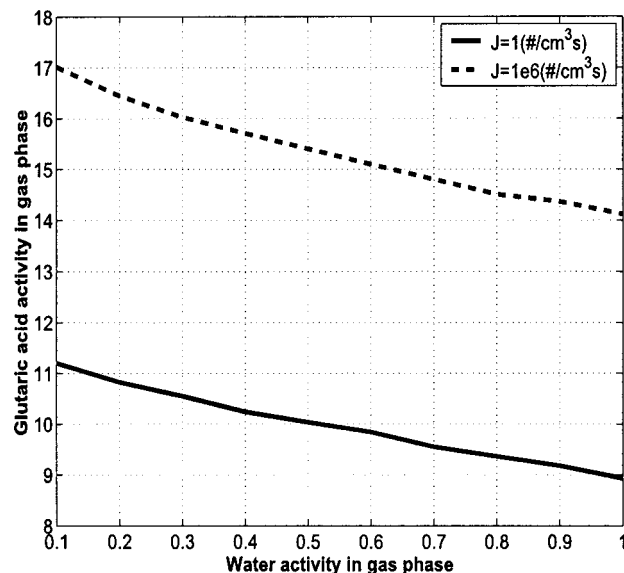


FIG. 12. The onset activities at nucleation rate of 1/cm<sup>3</sup> s (solid line) and 10<sup>6</sup>/cm<sup>3</sup> s (dashed line) on water succinic acid system. Temperature is 299.84 K.

energy for the formation of critical cluster in the case of critical nucleation rate is close to  $50kT$ . The acid mole fraction  $x$  in the critical cluster is around 0.7.

The glutaric acid activity in gas phase necessary for an onset nucleation rate of 1 particle/cm<sup>3</sup> s varies between 9 and 11 for a range of relative humidities between 10% and 100% at 298 K, while for an onset nucleation rate of 10<sup>6</sup> particles/cm<sup>3</sup> s the glutaric acid activity is somewhere between 13 and 15 for the same temperature (Fig. 12). These values are smaller than the ones obtained for succinic acid, but however high compared to probable atmospheric conditions.

## VI. CONCLUSIONS

Motivated by the new experimental information on aerosol composition, we have investigated the formation of new

TABLE III. Results of the simulation of the binary homogeneous nucleation in water–glutaric acid system.  $a_2$  is the activity of glutaric acid in gas phase,  $x$  is the composition of the critical cluster (in mole fraction of glutaric acid),  $r$  is the radius of the critical cluster (Å),  $\Delta G$  is the Gibbs free energy required to form the critical cluster, and  $J$  is the nucleation rate (No./cm<sup>3</sup> s).  $T=299.84$  K, RH=65.7%.

$a_2$	$x$	$n_1$	$n_2$	$r$ (Å)	$\Delta G/kT$	$J$ (No./cm <sup>3</sup> s)
9.35	0.697	16.55	37.89	11.47	52.80	0.22
10.28	0.705	14.57	34.18	11.08	49.18	9.25
11.31	0.706	12.88	30.94	10.71	45.91	2.71E+2
12.44	0.710	11.41	28.08	10.37	42.95	5.86E+3
13.68	0.715	10.15	25.56	10.04	40.25	9.69E+4
15.05	0.720	9.05	23.33	9.73	37.79	1.26E+5
16.56	0.725	8.09	21.35	9.45	35.55	1.33E+6
18.22	0.729	7.25	19.58	9.17	33.49	1.16E+7
20.04	0.734	6.51	18.00	8.91	31.60	8.59E+8
22.04	0.738	5.86	16.58	8.67	29.85	5.46E+9
24.25	0.743	5.29	15.30	8.44	28.25	3.03E+10
26.67	0.747	4.78	14.15	8.22	26.77	1.48E+11
32.27	0.755	3.93	12.17	7.81	24.12	2.60E+12
39.05	0.763	3.25	10.54	7.44	21.84	3.17E+13
47.25	0.771	2.71	9.18	7.10	19.85	2.86E+14
62.90	0.782	2.09	7.54	6.64	17.33	4.90E+015

particles from systems involving water and two-organic compounds (succinic and glutaric acid). Both acids are expected to have high nucleation potential considering their low vapor pressures and low volatilities. Although the potential of aerosol formation from organics has been predicted and discussed in the literature, the magnitude of their contribution is not known and has not been characterized.

The results presented here represent the first essential steps toward a better understanding of aerosol formation from organic acids. According to our results, binary homogeneous nucleation of water and organic acids takes place only for very high concentrations of organics in gas phase, but not at atmospheric conditions in which the concentrations of the acids are about 7 orders of magnitude smaller than the ones required in our model. Unfortunately, no experiments are so far available in the literature to provide comparison to the results presented here.

The importance of reliable thermodynamical data is also emphasized. In order to reduce the uncertainty in nucleation rate calculations, more experimental data concerning the thermodynamical properties of pure organics and their aqueous solutions are needed.

Furthermore, several other data regarding the ambient air concentration of the acids, the formation pathway, and the reaction rates are also required. Any attempt at reproducing the aerosol formation process requires at least a good knowledge of the atmospheric composition. The nucleation process is sensitive to the molecular concentration of the condensable species and any fluctuation in atmosphere determines where and if the nucleation takes place.

According to our calculations the binary systems water–glutaric acid and water–succinic acid will not form new particles at atmospheric conditions. On the other hand, their presence in particulate matter shows that at least they are implicated in the aerosol growth processes. Furthermore, the involvement of ammonia in the nucleation process may decrease the required gas phase concentrations of the acids considerably, as is the case also with the sulfuric acid–water system.<sup>43,44</sup>

## ACKNOWLEDGMENTS

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