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## Water activity in supersaturated aqueous solutions of organic solutes

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### Abstract

Measurements of water activity in supersaturated aqueous organic solutions of glycine, alanine, succinic acid and itaconic acid were made far into the metastable zone by levitating micron-sized droplets electrostatically in a spherical void electrodynamic levitator trap (SVELT) with a water vapor reservoir. The concentration dependent behavior of the activity was examined in relationship to the molecular interactions for solutions.

### 1. Introduction

A knowledge of activity behavior in supersaturated solutions is required for an understanding of phenomena which occur in crystallization processes. For these reasons, the properties of supersaturated solutions are of great interest. A number of empirical and semi-empirical methods have been proposed to estimate the water activity of supersaturated solutions [1–3]. At high supersaturations the validity of these approximations is in doubt. Until recently thermodynamic data available in supersaturated solutions were scarce. This is because solute crystallization induced by heterogeneous nucleation on container surfaces or on minute particles in conventional bulk samples takes place even at low supersaturations. This makes precise measurements of thermodynamic

properties impossible in highly supersaturated solutions.

Recently, there has been a growing interest in electrodynamic balance techniques since they are capable of providing thermodynamic data of supersaturated solutions far into the metastable region. Basically the present experiments are an improved version of the traditional Millikan oil drop experiment previously developed to determine the charge of an electron and Avogadro's number. In this technique, a single charged solution droplet, which is trapped by the fields created by the electrodes of the apparatus, can be continuously weighed. Through this technique, a containerless supersaturated solution may be investigated. The levitation of a small droplet in an electric field allows a very large supersaturation to be achieved before crystallization since the risk of heterogeneous nucleation is greatly reduced. In addition, the small solution particle responds rapidly to the ambient vapor pressure allowing

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control of concentration. This technique, therefore, provides an effective means for experimental measurements of thermodynamic properties in the supersaturated region. Tang et al. [4] obtained water activity data for aqueous solutions of NaCl and KCl at 25°C over the entire metastable range approaching the spinodal concentration and evaluated various approaches for predicting the properties of supersaturated solutions. Cohen et al. [5,6] investigated the activity behavior of several aqueous electrolytes and mixed salt solutions in a continuous humid flowing system. Also the electrodynamic balance technique has been used to study the thermodynamics of aqueous solutions of ammonium sulfate [7], lithium iodide [8] and lithium chloride [9].

In the present work, measurements of the water activity were made for supersaturated solutions of glycine, alanine, succinic acid and itaconic acid over most of the metastable region at 25°C using a spherical void electrodynamic levitator trap (SVELT) with a controlled water vapor reservoir environment.

## 2. Experimental apparatus and procedures

The principal parts of the apparatus to be used in this work are an electrodynamic levitator enclosed in a vacuum chamber, a particle generator, the vacuum system and the optics including a detection system. A diagram of the experimental apparatus is shown in Fig. 1.

Water from a constant temperature bath is circulated through a copper tube on the outwall of the supporter of the levitator to control the temperature. The temperature of the levitator itself could be maintained within  $\pm 0.1^\circ\text{C}$  and measured with a thermistor (10 k $\Omega$  at 25°C). A MKS capacitance manometer is used to measure the pressure of the vacuum chamber. The whole assembly is connected to the temperature-controlled water reservoir which serves as the source of water vapor for the suspended droplet and a vacuum pump. This is composed of a precision valve in order to control the relative humidity in the chamber.

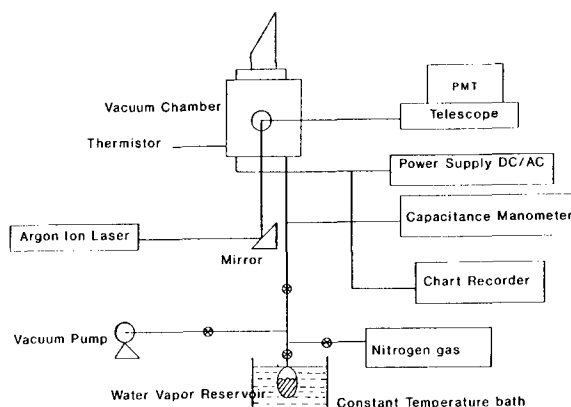


Fig. 1. Schematic apparatus.

Our experiments are performed in a spherical void electrodynamic levitator trap (SVELT) which is developed by the Microparticle Photophysics Laboratory at Polytechnic University. The design and theoretical details are described elsewhere [10,11]. Charged particles may be trapped in this device without the aid of a constant component to the electric field. With moderate AC voltage, the particle oscillates vertically along the axis of the trap below the geometric center of the device. Introducing a DC potential allows the particle to be brought to the trap center, where the AC field is zero and the particle comes to rest.

For a stationary particle in the null point, the weight of the particle suspended,  $mg$ , is balanced against opposing forces:

$$mg = CqV_{\text{DC}}/Z_0, \quad (1)$$

where  $q$  is the charge of the particle,  $Z_0$  is the characteristic length of the cell and  $C$  is a geometric constant. From Eq. (1), the relative mass changes of solution droplet to dry particle can be easily determined by measuring the DC balancing voltage required to balance a charged, suspended particle against the gravity force, provided that the particle charge remains unaltered during an experiment. The assumption of constant particle charge can be easily verifiable in each experiment.

For a nonvolatile solute, if the balancing DC voltage of a particle which is anhydrous in its dry

state,  $V_{DC}^{wet}$ , is measured, the molality can be calculated from

$$m = \left( \frac{V_{DC}^{wet}}{V_{DC}^{dry}} - 1 \right)^{-1} \frac{1000}{MW}, \quad (2)$$

where MW is the molecular weight of the solute. By adjusting the humidity of the chamber, the relative weight of the suspended particle, and thus the desired concentration of the solution, can be achieved.

In reality, the activity is dependent on curvature and surface charge of the droplet. However, these effects are known to be insignificant for the size of the droplets being suspended [12]. These effects, therefore, may be negligible and the activity can be written as:

$$a_w = P_w/P_w^{sat} = RH, \quad (3)$$

where RH is the relative humidity of the vapor phase.

Therefore, the solution concentration and the corresponding water activity at any point can be easily determined from the measurements of the DC balancing voltage of a droplet and the vapor pressure of the chamber. Once a particle is caught and centered at the null point, the chamber can be evacuated. After the DC voltage of the dry particle is recorded, water vapor above the vapor reservoir is allowed to bleed back slowly into the chamber until the solid particle is transformed into a solution droplet. A second evacuation is then commenced at a slower rate by adjusting the needle valve. This procedure increases the concentration into the supersaturated region. Evacuation is continued at a slower rate until the crystallization point. At that pressure the balancing voltage drops precipitously. After crystallization, the evacuation is continued to ensure that there has been no charge loss during the cycle. During the run, the DC balancing voltage is continuously tuned in order to retain the particle at the center of the electrodynamic trap, and the DC balancing voltage and pressure in the chamber are recorded.

As a result of water vapor evaporation, the DC balancing voltage decreases steadily and the solution droplet becomes supersaturated and eventu-

ally crystallizes. This measurement is repeated several times to ensure reproducibility for a given particle.

### 3. Results and discussion

Water activities of supersaturated aqueous solutions of glycine, alanine, succinic acid and itaconic acid were measured at 25°C. The range of concentrations measured for glycine were 3.33–45.03 molal (saturation = 3.33 molal), alanine 2.38–19.63 molal (saturation = 1.87 molal [13]), succinic acid 1.73–25.71 molal (saturation = 0.65 molal [14]) and itaconic acid 2.15–60.32 molal (saturation = 0.73 molal [15]). The water activity results are shown in Figs. 2–5 and show the deep penetration into the metastable region achieved. Water activity data in the supersaturated region were curve fit and are shown by the solid lines in Figs. 2–5. Equations for the fit data appear in Table 1 along with the standard deviation which was better than 2.5% in all cases. Data were taken at relative humidities below 0.92 because of instabilities of the droplets at higher humidities.

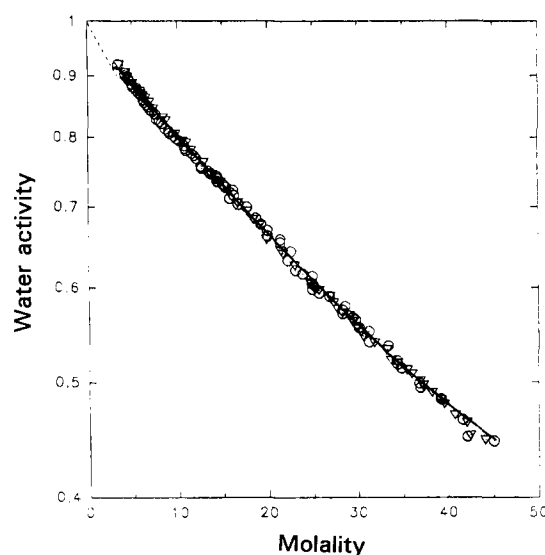


Fig. 2. Water activity versus concentration for the glycine–water system at 25°C. Solid line represents fitted data in the supersaturated region, dashed line represents undersaturated data from Ellerton et al. [17].

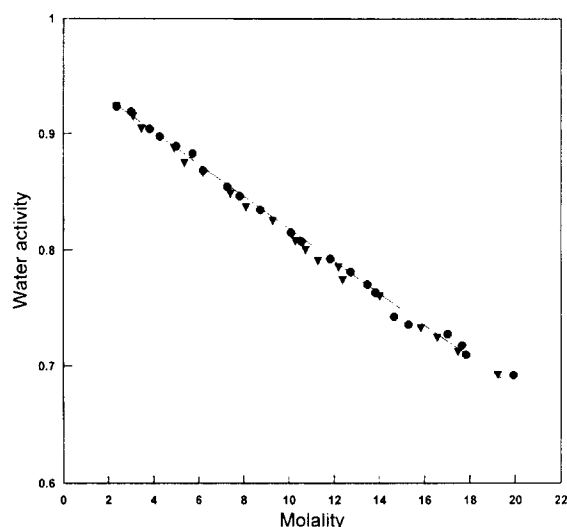


Fig. 3. Water activity versus concentration for the alanine-water system at 25°C. Solid line represents fitted data.

The solution concentrations are calculated from the DC balancing voltage of the suspended solution particle. This calculation is based on the DC balancing voltage of the solid particle at the initial and final states being the same, and the charge on the particle during an experiment being constant. This has been verified in a number of studies [4,7,8,16]. In the experiments employing succinic and itaconic acid, however, the dry balancing DC voltage at the final dry state was found to decrease about 30% and 10%, respectively. The amount of solute mass evaporated during an experiment is very small (on the order of  $10^{-9}$  g) and has a negligible effect on the vapor pressure of the chamber. It was necessary to account for this solute evaporation in the determination of concentration. The volatilization rate of the solute is typically lower at lower

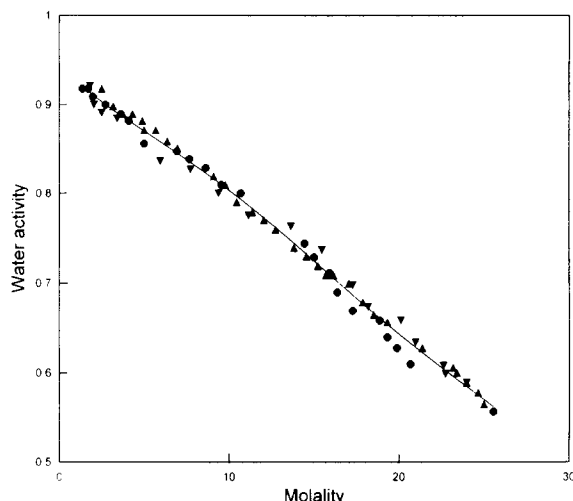


Fig. 4. Water activity versus concentration for the succinic acid-water system at 25°C. Solid line represents fitted data.

concentration. A solution droplet at low concentration requires a longer equilibrium time than a solution droplet at higher concentration. The amount of solute mass evaporated during each equilibrium state in an experiment is, therefore, roughly the same. We, therefore, can assume that the mass of the solute in solution decreases linearly between the initial dry mass and final dry mass measured with decreasing vapor pressure of the chamber. The difference in water activities obtained under this assumption for several measurements of the same and different particles were at the worst case 0.02 for both systems. Therefore the uncertainty in determining the concentration incurred by this assumption is small (1–2% at saturation, 2–4% at the crystallization point).

The water activity is generally a monotonic function of the concentration. The actual data

Table 1

Coefficients of  $a_w$  from the polynomial fit at 25°C:  $a_w = c_0 + c_1m + c_2m^2 + c_3m^3 + c_4m^4 + c_5m^5$

| System        | $c_0$ | $c_1$  | $c_2$                  | $c_3$                  | $c_4$                 | $c_5$                   | Standard deviation |
|---------------|-------|--------|------------------------|------------------------|-----------------------|-------------------------|--------------------|
| Glycine       | 1.014 | −0.033 | 0.169                  | −6.864                 | 1.395                 | −1.062                  | 0.49%              |
| Alanine       | 0.958 | −0.014 | $5.003 \times 10^{-6}$ | 0                      | 0                     | 0                       | 1.7%               |
| Succinic acid | 0.946 | −0.020 | $1.65 \times 10^{-3}$  | $−1.59 \times 10^{-4}$ | $6.06 \times 10^{-6}$ | $−8.055 \times 10^{-8}$ | 1.2%               |
| Itaconic acid | 0.927 | −0.016 | $4.96 \times 10^{-4}$  | $−2.57 \times 10^{-5}$ | $5.33 \times 10^{-7}$ | $−3.59 \times 10^{-9}$  | 2.5%               |

Range of molalities: glycine 3.44–45.03, alanine 2.38–19.63, succinic acid 1.73–25.71, itaconic acid 2.15–60.32.

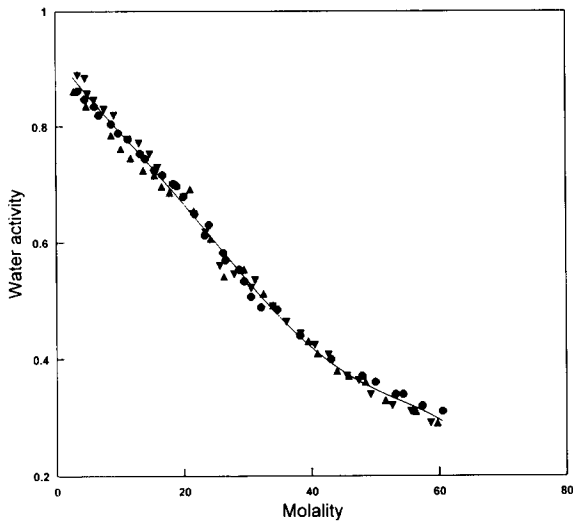


Fig. 5. Water activity versus concentration for the itaconic acid–water system at 25°C. Solid line represents fitted data.

measured lie on a smooth continuous plot in the supersaturated region. The dashed lines shown in Fig. 3 indicate data for undersaturated glycine solution from the literature [17]. The difference in the water activity at the saturation point was at most 0.02 (less than 3%). For the succinic acid solution, the value of water activity at saturation estimated from the literature at 25°C is 0.97 [18]. The difference in the water activity data at that concentration is at most 0.004. There is no literature data available for the other systems in the undersaturated region. We were not able to measure water activities in the undersaturated region because of droplet instabilities at the high humidities required. Such measurements, however, should be possible with appropriate system modifications.

We were able to achieve very high supersaturations in these experiments. A comparison of the crystallization concentrations observed in this work and maximum attainable supersaturation obtained from the measurements of the effective metastable zone width for glycine [19] and itaconic acid [15] solutions is given in Table 2. From the data, it is clear that the maximum attainable supersaturation obtained from measurements using conventional bulk cooling methods are much

Table 2

Comparison of the values of supersaturation

| System        | This work<br>(at 25°C)<br>$S$ | Metastable zone width |                  |      |
|---------------|-------------------------------|-----------------------|------------------|------|
|               |                               | $T_{eq}$              | $\Delta T_{max}$ | $S$  |
| Glycine       | 13.52                         | 50.0 <sup>a</sup>     | 15.10            | 1.27 |
| Itaconic acid | 82.63                         | 34.4 <sup>b</sup>     | 11.20            | 1.66 |

$S$ : supersaturation ( $m/m^*$ ),  $T_{eq}$ : saturation temperature (°C),  $\Delta T_{max}$ : maximum supercooling temperature (°C).

<sup>a</sup> From Ref. [19].

<sup>b</sup> From Ref. [15].

lower. This is likely due to dust, dirt and container walls in a bulk solution.

The solute activity behavior in solutions can be understood by looking at molecular interactions of the solute molecules (association) and interactions of the solute and the solvent (mainly due to the hydrogen bonding to water molecules). The effect of solvation (hydration) tends to decrease activity while association tends to counteract this effect. Solute activity ratios ( $a/a^*$  where  $a^*$  is the activity at saturation and  $a$  is the activity at the concentration of interest) up to the crystallization concentration were calculated employing the Gibbs–Duhem relationship and are plotted as a function of molal concentration in Fig. 6.

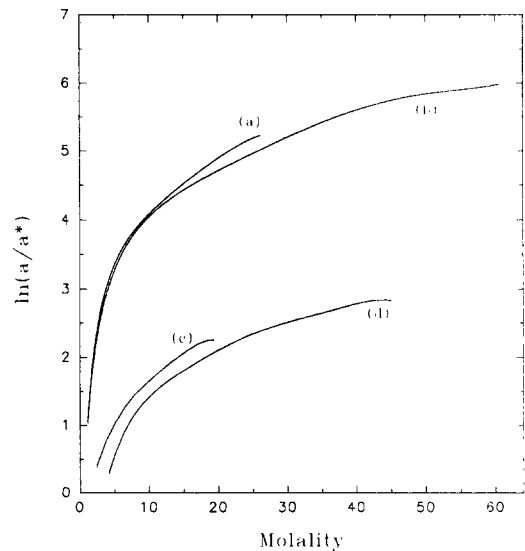


Fig. 6. Saturation ratio of solute activity. Curve a: succinic acid; curve b: itaconic acid; curve c: glycine; curve d: alanine.

The thermodynamic limit of the metastable region is the spinodal, in which  $\partial\mu_1/\partial x_1 = \partial \ln a_1/\partial x_1 = 0$ . As can be seen from Fig. 6, the slopes of the data are declining throughout the metastable region and begin to approach zero at the crystallization point. This indicates that the crystallization concentrations observed in these experiments are near the spinodal. The degree of curvature indicates the deviation from an ideal solution since for an ideal solution, activity versus molal concentration is linear. The solute activity exhibits appreciable deviation from ideality in the supersaturated region. At higher supersaturations, association effects will generally dominate over hydration effects due to the lower mobility of the hydrogen ions in the water. This restriction fits quite well with the concept of substantial semi-ordered solute clusters, which are thought to exist in supersaturated solutions [20–22]. To clarify the molecular state for the solute in solution, the values of supersaturation based on activity are plotted against the fractional supersaturation based on molal concentration in Figs. 7 and 8. Fractional supersaturation can be expressed as:

$$\vartheta = (a - a^*)/a^* = S - 1, \quad (4)$$

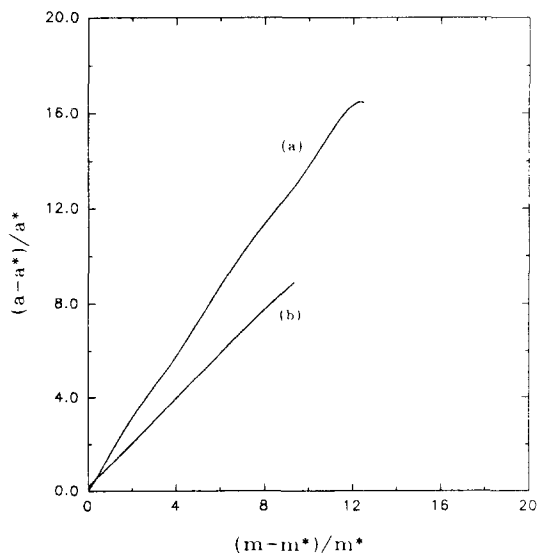


Fig. 7. Concentration dependence of supersaturation based on activity. (a): glycine; (b): alanine.

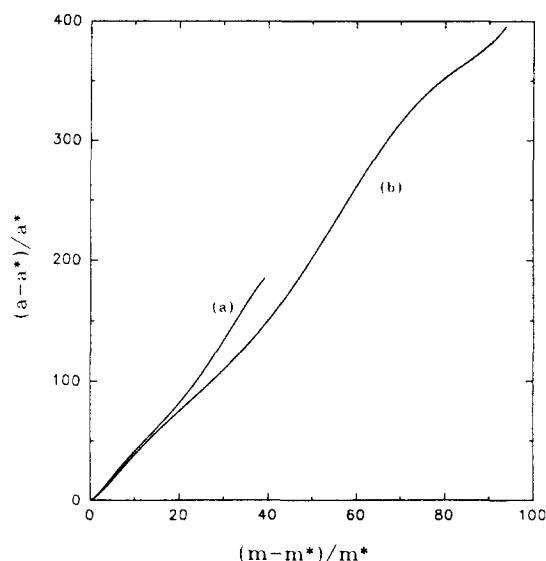


Fig. 8. Concentration dependence of supersaturation based on activity. (a): succinic acid; (b): itaconic acid.

in which  $a$  and  $a^*$  are the solute activity in supersaturated and saturated state at a given temperature, respectively. Supersaturation is often expressed in terms of concentration instead of activity, because the activity in the supersaturated region is usually not known. The slope corresponds to the activity coefficient at a given concentration. In case of ideal solution, the slope should be unity. It was found that supersaturation based on activity has roughly a linear relation with molal concentration scale. Therefore, a simplified linear equation may be used to estimate the solute activity of a supersaturated solution as an approximation. Solute activity coefficients in glycine and alanine solutions are smaller than succinic and itaconic acid solutions. This can be explained based on electrostatic interactions. There are strong hydrogen-bondings between carboxyl groups and water. The solute molecules of succinic and itaconic acid with two carboxyl groups in solutions will have a greater tendency to bind to the water molecules. This hydration effect makes solute activities higher than in glycine and alanine solutions. In addition, amino acids in solution at neutral pH are predominantly zwitterions rather than un-ionized molecules. In

the zwitterions of an amino acid, the amino group is protonated ( $-\text{NH}_3^+$ ) and the carboxyl group is dissociated ( $-\text{COO}^-$ ). In amino acid solutions, the association effects prevail due to the zwitterions, because the ionic bonding energy of solute to solute is much larger than the hydrogen bonding energy of solute to water solvent. Glycine and succinic acid solutions have slightly larger values in slopes than alanine and itaconic acid solutions. This would explain the tendency to interact between solute molecules and water molecules. The above results demonstrate that the association–solvation treatment in the study of solution thermodynamics is a useful tool to analyze the activity behavior even at high supersaturations.

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