Thermodynamic and statistical studies of supersaturated ternary solutions

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The influence of chromium ions Cr^{3+} on properties of supersaturated aqueous solution of ammonium sulfate $(NH_4)_2SO_4$ has been studied employing containerless electrodynamic levitation of single microdroplets of this solution with known concentration of Cr^{3+} ions. The water activity versus solute concentration was measured in three different sets of experiments corresponding to different initial concentrations of Cr^{3+} ions. Theoretical treatment of the experimental results obtained is developed employing the theory of supersaturated electrolyte solutions [Phys. Rev. E **52**, 1325 (1995)]. This treatment has allowed the following two conclusions. First, spinodal concentration is a decreasing function of Cr^{3+} concentration. Second, solute clusters formed in the presence of Cr^{3+} ions demonstrate complex behavior with respect to binding water molecules: (a) at low and moderate supersaturations, they bind more water molecules than clusters formed in the absence of an impurity; and (b) at high supersaturations, they bind less water molecules than clusters formed in the absence of an impurity. [S1063-651X(99)12509-1]

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I. INTRODUCTION

It is well known that small amounts of an impurity can profoundly effect nucleation and crystal growth phenomena. For example, it was found that Pb^{2+} ion acts as a nucleation agent in a NaCl solution [1], whereas Co^{2+} ion inhibits nucleation in KNO_3 solution [1]. The effect of K^+ and Fe^{3+} ions on nucleation of ammonium-aluminum sulfates was studied in Refs. [2,3]. The study of Cr^{3+} impurities in different supersaturated solutions has demonstrated that in their presence nucleation and crystal growth are suppressed [4–6]. All these studies have been performed in bulk solutions and, therefore, have only qualitative reproducibility. In addition, no mechanistic understanding of these effects can be drawn from the bulk experiments. In particular, it is not possible to distinguish whether the impurity affects the thermodynamics of the system in some way or alters the kinetics of the growth and nucleation processes. In order to obtain reproducible results related to the effect, which impurity might have, on nucleation and crystal growth, an accurate and sensitive experimental technique is required. This technique should be capable of, at least, producing stable supersaturated solutions (metastable states with a long lifetime). One of the best experimental techniques capable of achieving this is based on containerless levitation of solution microdroplets in a solvent atmosphere [7–21]. This technique has already been employed in the study of impact of Cr^{3+} ions on the properties of supersaturated state and nucleation of ammonium sulfate $[(NH_4)_2SO_4]$ in aqueous solution. In this study the dependence of water activity on $(NH_4)_2SO_4$ concentration was investigated at different Cr^{3+} concentrations. Preliminary results of this work was reported in Ref. [21].

In our study we employ the electrodynamic levitator trap (ELT) technique. This technique allows containerless con-

finement of microdroplets of supersaturated solutions. Three major advantages which make the ELT technique so attractive for the study of metastable state and nucleation are, (a) the absence of container walls which usually serve as a major source of heterogeneities triggering heterogeneous nucleation; (b) the levitation of ultrasmall volumes (picoliters) of the initially purified solutions; and (c) the suppression of convective flows. The first advantage is self-explanatory. The second advantage can be understood if one specifies the probability $P(x=K)$ to have exactly K impurities in volume V_0 (V_0 is the microdroplet volume), where x is the corresponding random variable describing number of impurities inside of the microdroplet. Assuming that the random variable x has the Poisson distribution, the probability $P(x=K)$ has the form

$$P(x=K) = \frac{\lambda^K}{K!} e^{-\lambda}, \quad \lambda = E(x) = V_0 \frac{N_{\text{tot}}}{V},$$

where $E(x)$ is the mathematical expectation of the event $x=K$, and N_{tot} is the total number of impurities in the initial solution volume V. Therefore, the probability to have K impurities inside of the microdroplet is the sharply decreasing function of the microdroplet volume V_0. The third advantage is again due to small solution volumes being levitated. There is simply not enough room for the convective flows to develop. In order to specify this statement, let us note that convectional flows are proportional to the microdroplet radius R_0 as $R_0^{3/2}$ or R_0^3. Therefore, even comparing with regular μl-size solution drops, the approximately 10^3 or 10^6 factor difference in sizes between the μl-size drops and pl-size levitated microdroplets would essentially reduce convectional effects to zero in these microdroplets.

Based on the foregoing, employment of the ELT technique allows a unique opportunity in the study of properties of supersaturated solutions and nucleation phenomenon. This includes an opportunity to separate factors, affecting properties of supersaturated solutions, such as solution supersaturation and presence of impurities in the convection-free envi-
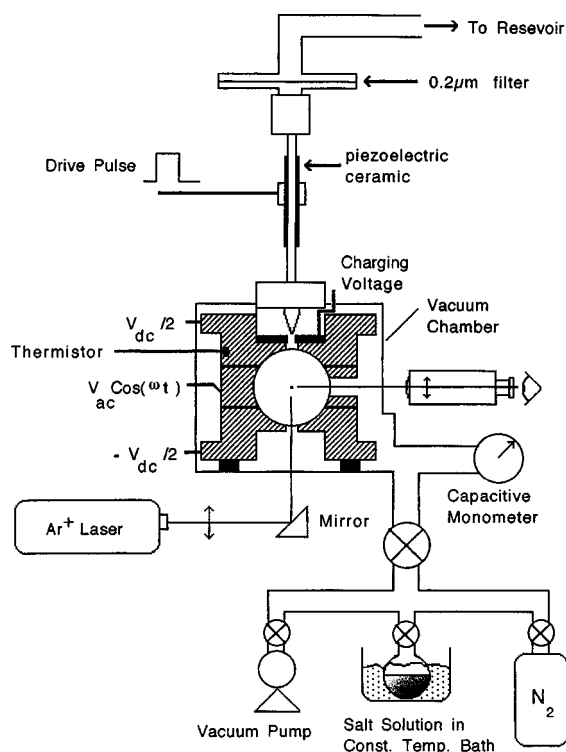
FIG. 1. Schematic drawing of the SVELT experimental apparatus, including a levitation chamber of adjustable humidity and temperature.

ronment. In addition to that, the ELT technique has allowed us to investigate the relative importance of these factors by controlling number of impurities in the microdroplets levitated. The study was conducted in a wide range of solution supersaturations, with the upper limit approaching the supersaturation of the spinodal at the given temperature and pressure. The unique capabilities of the ELT technique in the study of metastable state and nucleation were reported earlier in detail in Refs. [7–21]. In this paper we present results of an experimental and theoretical study describing the impact of small amounts of ionic impurities such as Cr^{3+} on properties of $(NH_4)_2SO_4$ aqueous supersaturated solution.

II. SPHERICAL VOID ELT TECHNIQUE APPLICATION TO THE STUDY OF TERNARY SUPERSATURATED SOLUTIONS

The spherical void ELT (SVELT) technique first described in Ref. [22] (see Fig. 1 for its schematic) was employed in order to determine the solute activity (chemical potential) as a function of supersaturation and impurity concentration. This technique allows the containerless suspension of the electrically charged microdroplets (5–20 μm in diameter) containing supersaturated solution in the solvent atmosphere. The advantages of this technique, described and discussed in Sec. I provide a unique opportunity to reach extremely high supersaturations. These supersaturations, which are usually 5–10 times greater than those obtainable in bulk solutions, allow very deep penetration into the metastable zone.

One of the objectives of the experimental study performed was to distinguish the relative role of impurity concentration

on the possibility of nucleation occurrence. For this purpose microdroplets containing supersaturated solutions with impurities of known character and concentration were levitated. Therefore, a heterogeneous solution of known mean solute n_{slt} and impurity n_{imp} concentrations was prepared and injected into the SVELT chamber in the form of microdroplets of radius 5 μm. For a stationary microdroplet, trapped in the SVELT null point, its weight mg is balanced by the opposing electrostatic force qU_{dc},

$$mg = C\frac{qU_{dc}}{z_0}, \qquad (1)$$

where q is the microdroplet electrical charge, U_{dc} is the dc voltage which retains the microdroplet at the SVELT geometric center, $2z_0$ is the distance between the SVELT spheroid electrodes, and C is the SVELT geometrical constant. Thus, by means of this equation and under the assumption that the microdroplet charge remains unaltered during an experiment, the relative change of the microdroplet mass can be easily determined by measuring the balancing dc voltage U_{dc} required to balance the weight mg of the charged solution microdroplet. The assumption of constant microdroplet charge q during the course of experiment can be easily verified in each experiment [23].

In the levitation experiments, the mass m of the solution microdroplet and the solvent vapor pressure in the SVELT chamber can be easily determined [see expression (1)] and directly measured, respectively. In all experiments performed for this work, we first evacuate the entire solvent from the SVELT chamber in order to determine the combined mass m_{com} of solute m_{slt} and impurity m_{imp} masses ($m_{com} = m_{slt} + m_{imp}$) by measuring the balancing dc voltage $(U_{dc})_{dry}$ for the anhydrous (dry) microdroplet and applying relationship (1). After carrying out this measurement, the solvent vapor is allowed back to the SVELT chamber until complete deliquescence of the dry microdroplet. In the following measurements the balancing dc voltage $(U_{dc})_{wet}$ and solvent vapor pressure are recorded continuously while gradually evacuating solvent vapor from the SVELT chamber by adjusting the needle valve. This procedure increases the relative solute and impurity concentrations n_{slt} and n_{imp}, leaving the ratio of their masses, $r = m_{imp}/m_{slt}$, constant. Therefore, a deeper penetration into the supersaturated (metastable) region at constant r takes place. Evacuation is continued at a slow rate until nucleation occurs. At the nucleation point, the balancing dc voltage U_{dc} drops precipitously. This drop is understandable from a thermodynamic point of view: after nucleation occurs the solute concentration in the microdroplet solution decreases dramatically, leading to a violation of thermodynamic equilibrium between the solution solvent inside the microdroplet and the solvent atmosphere surrounding this microdroplet. Establishment of this thermodynamic equilibrium initiates intensive evaporation of the solvent from the microdroplet solution, resulting in a dramatic decrease of the microdroplet mass. After nucleation occurs the solvent evacuation is continued, to ensure that there has bene no charge loss during the cycle.

Recording of the balancing dc voltage $(U_{dc})_{wet}$ together with the knowledge of $(U_{dc})_{dry}$ allows the expression of the normalized solute n_{slt} and impurity n_{imp} concentrations in the microdroplet solution as follows:

$$n_{slt} = \frac{m_{slt}}{m} = \frac{1}{1+r} \frac{(U_{dc})_{dry}}{(U_{dc})_{wet}},$$

$$n_{imp} = \frac{m_{imp}}{m} = \frac{r}{1+r} \frac{(U_{dc})_{dry}}{(U_{dc})_{wet}} \quad (2)$$

(in number density units),

where $(U_{dc})_{dry}$ and $(U_{dc})_{wet}$ are the balancing voltages for the dry and deliquescent (wet) microdroplets, respectively. Therefore, the following two, experimentally justified, assumptions can be made: (a) solute and impurities are nonvolatile, and (b) the solution microdroplet is in the partial thermodynamic equilibrium with the surrounding solvent atmosphere. These assumptions allow achievement of the desired concentrations n_{slt} and n_{imp} inside of the solution microdroplet by adjusting pressure of the solvent vapor in the SVELT chamber. Assumption (b) means that the chemical potentials $\mu_{slv}^L(T;n_{slt},r)$ and $\mu_{slv}^G(T;n_{slt},r)$ of solvent in the liquid (solution) and gaseous (vapor) phases are equal. Therefore, the activities

$$\lambda_{slv}^L(T;n_{slt},r) = \lambda_{slv}^L(T;0,0) \exp[\beta \mu_{slv}^L(T;n_{slt},r)],$$

$$\lambda_{slv}^G(T;n_{slt},r) = \lambda_{slv}^G(T;0,0) \exp[\beta \mu_{slv}^G(T;n_{slt},r)],$$

should also be equal. Assuming that solvent vapor can be considered as an ideal gas it is straightforward to demonstrate that [24]

$$\frac{\lambda_{slv}^L(T;n_{slt},r)}{\lambda_{slv}^L(T;0,0)} = \frac{\lambda_{slv}^G(T;n_{slt},r)}{\lambda_{slv}^G(T;0,0)} = \frac{P(T;n_{slt},r)}{P(T;0,0)} = \frac{P(T;n_{slt},r)}{P_{sat}(T)}$$

$$= R_H(T;n_{slt},r), \quad (3)$$

where $P(T;n_{slt},r)$ and $R_H(T;n_{slt},r)$ are the pressure and relative humidity, respectively, of the solvent vapor which is in partial thermodynamic equilibrium with the microdroplet solution. The pressure $P(T;0,0) = P_{sat}(T)$ is the pressure of solvent vapor which is in equilibrium with the pure liquid solvent [this pressure is the solvent vapor saturation pressure $P_{sat}(T)$ at the given temperature T]. The temperature dependent relative humidity $R_H(T)$ of the solvent atmosphere inside of the SVELT chamber was measured employing the VAISALA (Finland) polymer sensors utilizing the R_H-sensitive capacitance. The applicable temperature range of these sensors is very wide, from $-22\,°C$ up to $60\,°C$, their accuracy is at least 2%, and their resolution is 0.1%. The solution solvent activity can be assumed to be dependent on the microdroplet surface curvature and charge. However, these effects are known to be insignificant for the size of microdroplets used in our experiments [23].

The experimental procedure described above allows continuous recording of the chamber relative humidity $R_H(T;n_{slt},r)$ and the balancing dc voltage U_{dc}. In the result of evacuation of solvent atmosphere inside of the lavitator chamber, the balancing dc voltage U_{dc} decreases steadily, and the solution in the microdroplet becomes more and more supersaturated until eventually nucleation occurs. These measurements (recordings) were repeated several (at least four) times to ensure the reproducibility of experimental re-

sults for the given solution microdroplet. Therefore, by suspending the microdroplets of supersaturated solution with the known initial concentrations n_{slt} and n_{imp}, we studied properties of highly supersaturated solutions and the dependence of these properties on the depth of supersaturation and concentration of impurities.

III. THERMODYNAMICS OF TERNARY SUPERSATURATED SOLUTIONS WITH ELECTROLYTE SOLUTE AND IMPURITY

The metastable or supersaturated region is bounded on one side by the saturation (binodal) line and on the other side by the spinodal line, which mark the limits of the metastable zone. At concentrations above the spinodal, the solution is absolutely unstable and rapidly phase separates. In a metastable state the dissolved solute molecules can associate with each other into subcritical solute clusters. These clusters appear due to local fluctuations of the mean solute concentration n_{slt}. However, it is energetically favorable for the subcritical solute clusters to dissolve rather than to grow. Therefore, homogeneous nucleation occurs when clusters become large enough for their growth to be energetically favorable. In this way a one-phase metastable state of a homogeneous supersaturated solution with the mean solute concentration n_{slt} relaxes to a two-phase stable state by forming a heterogeneous saturated solution with the solute concentration $n_{slt,sat}$. The excess solute concentration $\Delta n_{slt} = n_{slt} - n_{slt,sat}$ goes into the creation of heterogeneities—the solid phase. In this two-phase solution the critical and supercritical solute clusters, and their aggregates are identified with the new solute-rich phase, whereas the solution itself is identified with the solute-poor phase. Such a relaxation process from a one-phase metastable state to a two-phase stable state is known as a nucleation process. The next stages of the metastable state relaxation are related to the growth of supercritical solute clusters, which is followed by their coalescence.

Let us consider a ternary solution consisting of a solute of concentration n_{slt}, an impurity of concentration $n_{imp} = rn_{slt}$, and a solvent of concentration $n_{slv} = 1 - n_{slt} - n_{imp} = 1 - (1+r)n_{slt}$. This specific arrangement for the concentrations n_{slt}, n_{imp}, and n_{slv} is characteristic of our experiment, and means that there is only one independent concentration variable: solute concentration n_{slt}. Under this condition the Gibbs-Duhem equation for such a ternary solution at a given constant temperature T and pressure P has the form [24]

$$N \frac{d\mu_{slv}}{dn} + n \frac{d\mu_{slt}}{dn} + r \frac{(M_W)_{slt}}{(M_W)_{imp}} n \frac{d\mu_{imp}}{dn} = 0, \quad (4)$$

where N and n are the solvent and solute concentrations in molal units, respectively; μ_{slv}, μ_{slt}, and μ_{imp} are the chemical potentials of solvent, solute, and impurity, respectively; and $(M_W)_{slt}$ and $(M_W)_{imp}$ are the molecular weights of the solute and impurity, respectively.

Let us now take into account that solute ammonium sulfate $(NH_4)_2SO_4$, and impurity chromium sulfate $(Cr)_2(SO_4)_3$

are electrolytes. In our previous research papers [19,20] we demonstrated that for strong electrolytes there exist the following expressions for the derivatives of their chemical potentials with respect to concentration n:

$$\frac{d\mu_{\text{slt}}}{dn} = \frac{k_b T}{n} + \frac{1}{2} c_{\text{slt},1}(T;r) n^{-1/2} + c_{\text{slt},2}(T;r), \quad (5a)$$

$$\frac{d\mu_{\text{imp}}}{dn} = \frac{k_B T}{n} + \frac{1}{2} c_{\text{imp},1}(T;r) \left[r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} \right]^{1/2} n^{-1/2}$$
$$+ c_{\text{imp},2}(T;r) \left[r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} \right], \quad (5b)$$

where coefficients $c_{\text{slt},1}(T;r)$, $c_{\text{slt},2}(T;r)$ and $c_{\text{imp},1}(T;r)$, $c_{\text{imp},2}(T;r)$ have to be determined by comparing solvent activity, expressed through these coefficients, with experimental data. Substitution of expressions (5a) and (5b) into the Gibbs-Duhem equation (4) yields the simple differential equation for the solvent chemical potential. Solution of this equation is straightforward:

$$\mu_{\text{slv}}(T;n,r) = -\frac{n}{N} \left[1 + r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} \right] k_B T - \frac{n^{3/2}}{3N} c_{\text{slv},1}(T;r)$$
$$- \frac{n^2}{2N} c_{\text{slv},2}(T;r), \quad (6)$$

where

$$c_{\text{slv},1}(T;r) = c_{\text{slt},1}(T;r) + \left[r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} \right]^{3/2} c_{\text{imp},1}(T;r),$$

$$c_{\text{slv},2}(T;r) = c_{\text{slt},2}(T;r) + \left[r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} \right]^2 c_{\text{imp},2}(T,r).$$

Analytical expression for the coefficient $c_{\text{slt},1}(T;0)$ found in Refs. [19,20] is in correspondence with the result presented in Ref. [25]. Therefore, an expression for the relative solvent vapor humidity $R_H(T;n,r)$, a.k.a. solvent activity, acquires the form

$$R_H(T;n,r) = e^{-[(M_W)_{\text{slv}}/1000]Nn\Phi_{\text{slv}}(T,n,r)}, \quad (7)$$

$$\Phi_{\text{slv}}(T;n,r) = 1 + r \frac{(M_W)_{\text{slt}}}{(M_W)_{\text{imp}}} + n^{1/2} p_1(T;r) + n p_2(T;r),$$

where

$$p_1(T;r) = \frac{c_{\text{slv},1}(T;r)}{3 k_B T}, \quad p_2(T;r) = \frac{c_{\text{slv}}(T;r)}{2 k_B T}.$$

In this expression $(M_W)_{\text{slv}} = 18$ is the molecular weight of solvent (water). The functional parameters $p_1(T;r)$ and $p_2(T;r)$ of expression (7) are strongly dependent on the solute-impurity concentration ratio r. They can be identified by direct comparison with experimental data, since the relative humidity $R_H(T;n_{\text{slt}}r)$ as the function of solute concentration n has been measured in our experiments for different r.

Integration of Eq. (5b) gives the following simple expression for the solute activity $A(T;n,r)$:

$$A(T;n,r) = e^{[(M_W)_{\text{slt}}/1000]n\Phi_{\text{slt}}(T,n,r)}, \quad (8)$$

$$\Phi_{\text{slt}}(T;n,r) = \ln(n) + 3n^{1/2} p_1(T;r) + 2n p_2(T;r).$$

In deriving this expression we have taken into account that $r(M_W)_{\text{slt}}/(M_W)_{\text{imp}} \ll 1$. This has always been the case in our experimental study. Therefore, knowledge of the functional parameters $p_1(T;r)$ and $p_2(T;r)$ allows a determination of the solute activity $A(T;n,r)$. In our previous study of supersaturated electrolyte solutions [19,20] we assumed the following simplified, but physically reasonable, description of ions dissolved in the solvent of fixed dielectric constant ϵ.

(a) Ions can be treated as rigid unpolarized spheres submerged into a continuous medium (solvent).

(b) Ions do not move entirely randomly, since there exist Coulomb forces between them. As a result of this, each ion creates around itself a non-uniformly charged ''ion cloud'' which on average is spherically symmetrical.

(c) Nonpolar quantum bonds between ions as well as the ion-solvent interaction are neglected.

(d) Two ions of opposite electric charge have a tendency to form an electrically neutral Bjerrum pair at the distance $r < r_{\text{ass}}(T)$ (see Refs. [19,20,26]). If the ions are of like sign the probability of their association is very small.

Among results obtained in Refs. [19,20] for the special case of binary supersaturated electrolyte solutions we utilize and generalize the following two for the case of ternary electrolyte solutions.

(a) Inside the region of solute concentrations where the electrolyte solution is supersaturated (metastable), there is a particular solute association concentration $n_{\text{ass}}(T;r)$ when the supersaturated electrolyte solution experiences a dramatic decrease to zero of its electrical conductivity. In other words, at this solute concentration the solution becomes nonconductive since all ions are associated into electrically neutral Bjerrum pairs, and their associations (clusters). Further penetration into metastable zone leads back to the appearance of free ions and, thus, to nonzero conductivity. The analytical expression obtained in Refs. [19,20] for the concentration $n_{\text{ass}}(T;r)$ has the form

$$n_{\text{ass}}(T;r) = \left[\frac{3 p_1(T;r)}{5 p_2(T;r)} \right]^2. \quad (9)$$

(b) The analytical expression for spinodal concentration $n_{\text{spin}}(T;r)$ in terms of the experimentally determinable functional parameters $p_1(T;r)$ and $p_2(T;r)$ has the form

$$n_{\text{spin}}(T;r) = \frac{9}{32} \left[\frac{p_1(T;r)}{p_2(T;r)} \right]^2 + \frac{1}{2 p_2(T;r)} + \frac{3}{4} \frac{p_1(T;r)}{r|p_1(T;r)|}$$
$$\times \left(\frac{9}{64} \left[\frac{p_1(T;r)}{p_2(T;r)} \right]^2 + \frac{1}{2 p_2(T;r)} \right)^{1/2}. \quad (10)$$

It is understandable that these generalizations are correct when the concentration of one electrolyte (impurity) is orders of magnitude less than the concentration of another electrolyte (solute), i.e., the ratio of impurity to solute concentrations $r \ll 1$. This condition explicitly implies that direct interaction between two electrolytes, solute and impurity, might be neglected. The dependence on the solvent and sol-
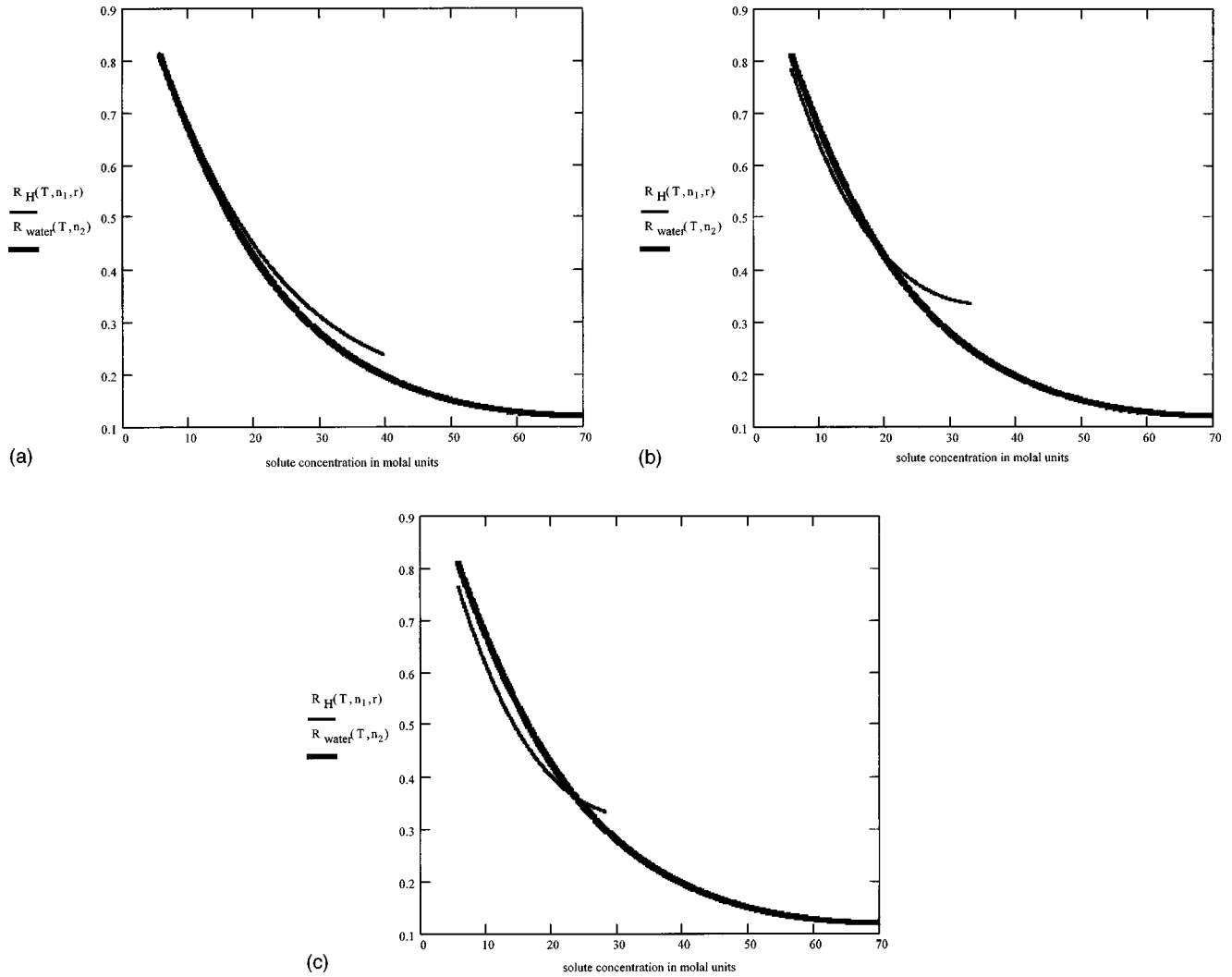
FIG. 2. (a) Water activity $R_H(T;n,r)=[R_H]_{ave}(T;n,r)$ obtained using parameters $p_{1,ave}(T;r_1)$ and $p_{2,ave}(T;r_1)$ vs $(NH_4)_2SO_4$ concentration (in molal units) in the case of an initial Cr^{3+} concentration equal to 0.01 ppm (thin solid line). The thick solid line represents water activity $R_{water}(T,n)=R_H(T;n,0)$ in the absence of an impurity. (b) Water activity $R_H(T;n,r)=[R_H]_{ave}(T;n,r)$ obtained using parameters $p_{1,ave}(T;r_2)$ and $p_{2,ave}(T;r_2)$ vs $(NH_4)_2SO_4$ concentration (in molal units) in the case of an initial Cr^{3+} concentration equal to 0.05 ppm (thin solid line). The thick solid line represents water activity $R_{water}(T,n)=R_H(T;n,0)$ in the absence of an impurity. (c) Water activity $R_H(T;n,r)=[R_H]_{ave}(T;n,r)$ obtained using parameters $p_{1,ave}(T;r_3)$ and $p_{2,ave}(T;r_3)$ vs $(NH_4)_2SO_4$ concentration (in molal units) in the case of an initial Cr^{3+} concentration equal to 0.10 ppm (thin solid line). The thick solid line represents water activity $R_{water}(T,n)=R_H(T;n,0)$ in the absence of an impurity.

ute chemical potentials on impurity comes through the dependence of functional parameters $p_1(T;r)$ and $p_2(T;r)$ on the ratio r. The complicated nature of this dependence is not addressed in our present research, and will be investigated later.

IV. TREATMENT OF EXPERIMENTAL DATA OBTAINED FOR THE SUPERSATURATED TERNARY ELECTROLYTE SOLUTIONS

In this paper we present three different sets of experimental data obtained for the water activity of a supersaturated ternary electrolyte solution of ammonium sulfate $(NH_4)_2SO_4$ as a solute dissolved in water in the presence of a chromium sulfate $(Cr)_2(SO_4)_3$ impurity. The experimental technique used in this study was the SVELT-based apparatus (see Sec. II). Each set of data, containing at least four experimental

trials, corresponds to different initial concentrations $n_{0,imp}$ of chromium sulfate $(Cr)_2(SO_4)_3$ impurity: $n_{0,imp,1}=0.01$ ppm, $n_{0,imp,2}=0.05$ ppm, and $n_{0,imp,3}=0.1$ ppm. All experiments were run with microdroplets of diameter 5 μm at 25 °C controlled with accuracy 10^{-4} μm and ± 0.1 °C, respectively. The ammonium sulfate saturation concentration n_{sat} in the absence of an impurity at 25 °C is 5.78 m

Results for the solvent vapor activity $R_H(T;n,r_i)$ at different initial concentrations of chromium sulfate $n_{0,imp,i}$ ($i=1, 2,$ and 3) are presented in Fig. 2. In this figure the solid thin lines represent our experimental data for $R_H(T;n,r_i)$ in ternary solutions averaged over four trials for each initial impurity concentration $n_{0,imp,i}$. Therefore, each solid thin line is given in terms of expression (7) with functional parameters $p_1(T;r_i)$ and $p_2(T;r_i)$ replaced by their averages $p_{1,ave}(T;r_i)$ and $p_{2,ave}(T;r_i)$ over four experimental trials run for each r_i ($i=1, 2,$ and 3):

TABLE I. Each number is determined on the basis of four experimental trials run under the same conditions. Percentage figures in parentheses, below actual numbers, give standard deviations in the determination of these numbers.

	Initial Cr^{3+} concentration (ppm)	$P_{1,ave}(T,r)$	$P_{2,ave}(T,r)$	Discrepancy between theory and experiment averaged over four runs (%)	$n_{ass.ave}(T;r)$ (molal units)	$n_{spin}(T;r)$ (molal units)
Set 1	0.01	0.556 (3.4%)	−0.063 (8.8%)	2.5	28.50 (10.9%)	59.49 (1.4%)
Set 2	0.05	0.860 (4.6%)	−0.125 (12.2%)	2.9	17.83 (13.8%)	34.51 (4.0%)
Set 3	0.1	1.011 (6.8%)	−0.149 (13.8%)	3.4	16.62 (23.5%)	32.31 (12.6%)

$$p_{n,ave}(T;r_i) = \sum_{j=1}^{4} [p_n(T;r_i)]_j, \quad n=1 \text{ and } 2,$$

where parameters $[p_1(T;r_i)]_j$ and $[p_2(T;r_i)]_j$ $(j=1,...,4)$ are determined by applying regression analysis to experimental data for each j-trail run at the given initial impurity concentration $n_{0,imp,i}$ and temperature T. Despite the fact that expression (7) with functional parameters $[p_1(T;r_i)]_j$ and $[p_2(T;r_i)]_j$ was capable of describing experimental data in each j run $(j=1,...,4)$ at each given initial impurity concentration $n_{0,imp,i}$ with an accuracy not less than 95%, the mean functional parameters $p_{1,ave}(T;r_i)$ and $p_{2,ave}(T;r_i)$ are not that exact. Numbers for these parameters, given in Table I, have a standard deviation up to 13.8%, and the accuracy of determination of these parameters is a decreasing function of initial impurity concentration. Such inaccuracy is likely due to imperfections in the control of initial impurity concentrations $n_{0,imp,1}$, and temperature T, which deteriorates with impurity concentration. Comparison of the averaged activities $R_H(T;n,r_i)$ for each $i=1$, 2, and 3 with the case of no impurities present, i.e., $r=0$, is given in the same Fig. 2 (plot and data for the case $r=0$ were borrowed from our previous papers [19,20], and are given by solid thick lines).

It should be noted that water activity $R_H(T;n,r_i)$ in the presence of impurities is always slightly below water activity $R_H(T;n,0)$ in their absence when solute (i.e., ammonium sulfate) supersaturations are low. Somewhere at moderately high solute supersaturations $n^*(r_i)$, water activity lines $R_H(T;n,r_i)$ cross $R_H(T;n,0)$ from below. This observation is very important since it indicates that spinodal concentrations of solute should be lowered when impurities are present. The fact that at low supersaturations $R_H(T;n,r_i) \leq R_H(T;n,0)$ can be easily understood if one takes into account that impurity ions bind some water molecules, which inevitably leads to the decrease of water activity. This additional binding of water molecules due to impurity leads to an increase of the relative solute supersaturation with respect to water, which for any $r_i>0$ $(i=1$, 2, and 3) explains the following facts observed in our experiments: (a) $n_{ass,ave}(T;r_i)<n_{ass,ave}(T;0)$, and (b) $n_{spin}(T;r_i)<n_{spin}(T;0)$. Therefore, at relatively low solute concentration, i.e. at $n \leq n_{ass,ave}(T;r_i)$, the formation of electrically neutral Bjerrum's pairs between $[(NH_4)_2]^{2+}$ and $[SO_4]^{2-}$
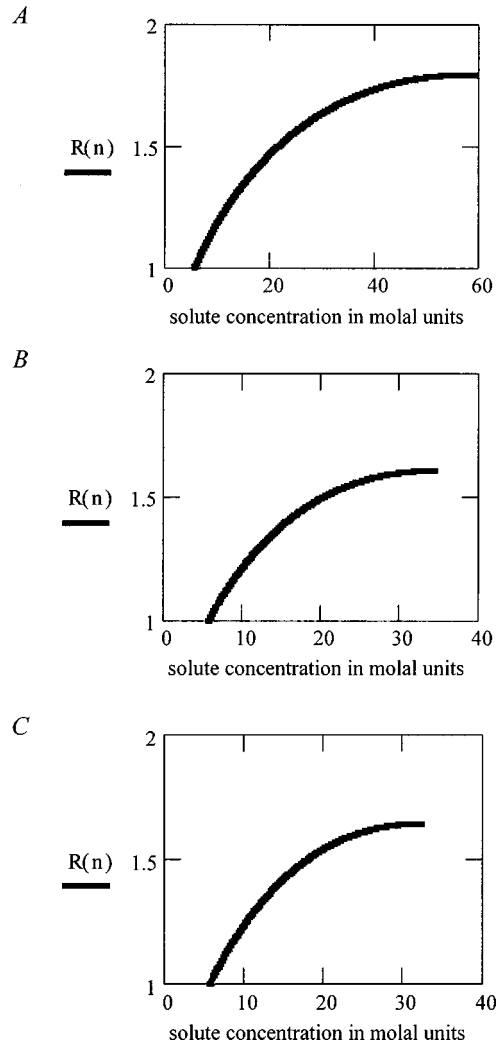
FIG. 3. Ratio $R(T;n,r_i)$ of solute activity $A(T;n,r_i)$ at different initial impurity concentrations r_i to its value $A(T;n_{sat},r_i)$ at saturation at the given temperature and pressure, where $i=1$, 2, and 3 and $n_{sat}=5.78$ m. Plotting A corresponds to $n_{0,imp}=0.01$ ppm, plotting B corresponds to $n_{0,imp}=0.05$ ppm, and plotting C corresponds to $n_{0,imp}=0.10$ ppm.

ions is more intense in the presence of an impurity than in its absence. It is also reasonable to conclude that the overall number of active (free) water molecules is a decreasing function of the number of Bjerrum's pairs. The decrease of the solute spinodal concentration $n_{spin}(T;r)$ with the increase of the impurity concentration suggests enhanced nucleation in the presence of a Cr^{3+} ion impurity. This conclusion contradicts results of previous observations [4–6] performed with bulk solutions at low supersaturations.

Further analysis of Fig. 2 demonstrates that in the region of solute concentrations $n > n_{ass,ave}(T;r_i)$ the number of active water molecules is an increasing function of impurity concentration. This can be explained only if one assumes that in this region of solute concentrations the impurity promotes the formation of ''water-depleted'' solute clusters leading to more active water molecules present in the solution.

In Table I the average spinodal concentrations $n_{spin,ave}(T;r_i)$ and the average association concentrations $n_{ass,ave}(T;r_i)$, obtained by utilizing parameters $p_{1,ave}(T;r_i)$ and $p_{2,ave}(T;r_i)$, are given for different initial impurity concentrations. In all cases studied it has been observed that there exists the approximate equality $n_{ass,ave}(T;r_i) \approx n^*(r_i)$. This means that $[(NH_4)_2]^{2+}$ ions are associated 100% into the electrically neutral Bjerrum pairs, and their associations at the unique solute concentration where water activity is insensitive to the presence of impurity, i.e. $R_H[T;n_{ass,ave}(T;r_i),r_i] = R_H[T;n_{ass,ave}(T;r_i),0]$ for $i = 1$, 2, and 3.

It has to be emphasized that these and all other results and conclusions in this paper are subject to experimental error. For example, results obtained for the average spinodal $n_{spin,ave}(T;r_i)$ and association $n_{ass,ave}(T;r_i)$ concentrations have a noticeable standard deviation (up to almost 24%). This is due to the fact that these concentrations are not directly measurable quantities, but are obtained by means of Eqs. (9) and (10) which are nonlinear with respect to the measurable parameters $p_{1,ave}(T;r_i)$ and $p_{2,ave}(T;r_i)$. The initial errors in determination of parameters $p_{1,ave}(T;r_i)$ and $p_{2,ave}(T;r_i)$ are likely to be enhanced by the nonlinearities in the dependencies of $n_{spin,ave}(T;r_i)$ and $n_{ass,ave}(T;r_i)$ on these parameters.

In Fig. 3 we present results of our calculations for the solute activity $A(T;n,r_i)$ at different initial impurity concentrations r_i ($i = 1$, 2, and 3) normalized by solute activity at saturation at the given temperature and pressure. First its grows with solute supersaturation, and then approaches an almost horizontal plato at supersaturations close to spinodal. Such a behavior suggests that at very high supersaturations there exists almost a constant ratio between numbers of unbounded electrically neutral Bjerrum's pairs and unbounded solute ions in the solution. This suggestion also implies that, bounded into solute clusters, Bjerrum's pairs do not contribute to the overall solute activity.

V. CONCLUSIONS

The results presented above raise more questions than they provide answers. Explanations which we have given for the data collected up to the present are hypotheseis rather than final answers. What is important from a practical point of view is that we have so far found no explanation for the observation that Cr^{3+} ions serve as inhibitors of nucleation. This observation was established in bulk experiments at low solute supersaturations. In that work, however, no attention was paid to the effect of the Cr^{3+} ions on thermodynamic properties of the solution (activity of solvent, solute, etc.). Our conclusion about the effect of Cr^{3+} ion impurity on nucleation in a supersaturated aqueous ammonium sulfate $(NH_4)_2SO_4$ solution is actually opposite: Cr^{3+} ions might serve as promoters of nucleation. In our current and forthcoming research we are planning to collect more accurate data which will allow us to address all the questionable issues discussed in this paper.

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