

## The influence of electric field on the nucleation of NaCl crystals

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Received 30 January 2002, accepted 18 April 2002

**Abstract** : A theory for the influence of an external electric field on the thermodynamics and kinetics of crystal nucleation is developed by employing the classical nucleation theory. A numerical analysis is performed with NaCl – water system at 300 K as the model. The theoretical predictions are compared with the results of an experiment done with the model system. It has been shown that an electric field of strength greater than  $10^6$  V/m would considerably enhance nucleation rate of NaCl crystals in aqueous medium.

**Keywords** Crystal growth, nucleation, electric field, sodium chloride

**PACS Nos.** 82.60.Nh, 83.60.Np, 81.10.Dn

### 1. Introduction

The formation of a new phase, either amorphous or crystalline, in a homogeneous, supersaturated liquid or vapor phase is considered as the result of thermodynamic fluctuations taking place in the system [1]. The creation of the free surface of the new phase is energetically unfavorable and the cluster formed does not transform into a macroscopic crystal, unless it reaches a critical size [2]. For a crystal, nucleating in a solution, the free energy of formation, critical size of the cluster and the concentration of the critical nuclei are usually governed by the degree of supersaturation. The condition for homogeneous, primary nucleation is established ordinarily by changing the temperature of the experimental system in the appropriate direction or by allowing the solvent to evaporate under a slow and controlled manner. It is well indicated in the crystal growth literature that a change in the physical ambience of the system like the presence of electric, magnetic and ultrasonic fields would influence the process of nucleation [3-5]. Macromolecular crystal growers have started exploiting this fact in many useful directions, though without much quantitative knowledge regarding the extent of the dependence [6-13]. It is very surprising that till date, no work has been reported which could unambiguously prescribe the strength of the electric field required to get a particular rate of nucleation or crystal growth.

This paper discusses the problem of crystal nucleation in the presence of an externally applied electric field. The major aim of the work is to determine, both theoretically and experimentally, the optimum strength of the field, which could affect the process of crystal nucleation.

### 2. Theory

The free energy change accompanying the formation of a new phase in the form of a cluster in a supersaturated liquid phase, kept at constant temperature and pressure in the presence of an externally applied electric field is written as [14]

$$\Delta G = \Delta G_{(S)} + \Delta G_{(\Omega)} + \Delta G_{(E)} \quad (1)$$

The first term is always positive and corresponds to the energy required for the creation of the cluster surface out of  $g$  molecules, which roamed the initial phase before the thermodynamic fluctuation leading to the formation of the cluster, took place. The middle term on the right hand side of the equation is referred to as the volume energy change which is negative for the initial concentration  $C$  of the solute in the mother phase, is greater than the critical concentration  $C^*$ . The third term is included to account for the change in electrostatic energy when the  $g$  molecules transform from the initial phase to the new phase in the presence of the applied electric field. The expansions of

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the first and second terms, which are very fundamental to the nucleation theory [15-19], results in the eq.

$$\Delta G = 4\pi r^2 \sigma - gkT \ln(\gamma C / \gamma^* C^*) + \Delta G_{(E)}, \quad (2)$$

where the cluster of the newly formed phase is considered as a sphere of radius  $r$  in the mother phase having initial activity coefficient  $\gamma$  and equilibrium activity coefficient  $\gamma^*$ . The solid-liquid interfacial tension  $\sigma$  is a function of the size of the cluster [20], but would be taken constant in the present work in order to avoid irrelevant mathematical complexities. There are different theoretical methods to determine the electrical contribution to the free energy of formation of a cluster, all of which taking into account, the values of the dielectric permittivities  $\epsilon_a$  and  $\epsilon_c$  of the amorphous phase and the crystalline phase respectively [14, 21-23]. There is a controversy between the results obtained by Kascheive [21,22] and Isard [23] for the case of  $\epsilon_c > \epsilon_a$ . However, Isard does not contradict Kascheive for the case  $\epsilon_c < \epsilon_a$ , and the results of other authors are also in harmony [24,25]. Kascheive obtained the expression for  $\Delta G_{(E)}$  by integrating the field energy in a sphere of radius  $R$ , before and after the introduction of the nucleus of radius  $r$  at the centre. Confining the discussion to the case  $\epsilon_c < \epsilon_a$  and substituting for  $\Delta G_{(E)}$  as obtained by Kascheive, eq.(2) is modified into:

$$\Delta G = 4\pi r^2 \sigma - gkT \ln(\gamma C / \gamma^* C^*) - g\epsilon_a f_{(\lambda)} \omega E^2 / 2, \quad (3)$$

where  $\omega$  is the volume of a kinetic element and  $f_{(\lambda)} = (1 - \lambda) / (2 + \lambda)$ , with

$$\lambda = \epsilon_c / \epsilon_a.$$

Expanding  $f_{(\lambda)}$  and neglecting the small variation in the activity coefficient, we write

$$\Delta G = 4\pi r^2 \sigma - gkT \ln \beta - g\omega \epsilon_0 K_a (K_a - K_c) \times E^2 / 2(2K_a + K_c), \quad (4)$$

where  $\beta = C / C^*$  and the  $K$ 's represent the respective dielectric constants. Defining a constant  $\Psi$ , by the eq.

$$\Psi = \omega \epsilon_0 K_a (K_a - K_c) / 2kT(2K_a + K_c), \quad (5)$$

eq.(4) reduces to  $\Delta G = 4\pi r^2 \sigma - gkT(\ln \beta + \Psi E^2)$ . (6)

It is to be noted that in the region of interest of this discussion,  $\epsilon_c < \epsilon_a$ , the value of  $\Psi$  is always positive. Making use of the eq.

$$4\pi r^3 / 3 = g\omega,$$

one can write the above equation as

$$\Delta G = 4\pi r^2 \sigma - 4\pi r^3 kT (\ln \beta + \Psi E^2) / 3\omega. \quad (7)$$

The radius  $r^*$  of the critical nucleus determined by minimizing  $\Delta G$  with respect to  $r$  is given as

$$r^* = 2\sigma\omega / kT(\ln \beta + \Psi E^2). \quad (8)$$

The corresponding eq. in the absence of the electric field, does not contain the second term in the denominator. Hence, the influence of the field is to decrease the critical size of the nucleus for the case  $\epsilon_c < \epsilon_a$ .

Substituting for  $r^*$  in eq. (7), one obtains the value of the critical free energy in the form given below :

$$\Delta G^* = 16\pi\sigma^3\omega^2 / 3 [kT (\ln \beta + \Psi E^2)]^2 \quad (9)$$

The contribution of the field is evident from the second term in the denominator and this makes the value of the critical free energy less.

The concentration of the critical nuclei developed in the mother phase could be determined by using the Maxwell-Boltzman distribution function [26] as

$$N^* = N_1 \exp(-\Delta G^* / kT), \quad (10)$$

where  $N_1$  is the concentration of monomers. Substituting for  $\Delta G^*$  from eq. (9) in eq. (10), we have

$$N^* = N_1 \exp\left[-\frac{16\pi\sigma^3\omega^2}{3k^3T^3}(\ln \beta + \Psi E^2)^2\right] \quad (11)$$

The corresponding equation for the concentration of the critical nuclei obtained in the absence of the field could be read as

$$N_0^* = N_1 \exp\left[-\frac{16\pi\sigma^3\omega^2}{3k^3T^3}(\ln \beta)^2\right] \quad (12)$$

### 3. Numerical analysis

It is quite evident from eq.(11) that the influence of electric field on nucleation, would be determined by the magnitude of  $\Psi E^2$  compared to  $\ln \beta$ . Selecting NaCl-water system at 300 K as a model for a numerical analysis, we found that  $\Psi = +1.864843253 \times 10^{-18}$  S I units. The values adopted for the calculation are:  $K_c = 5.62$ ,  $K_a = 80$ [27] and  $\omega = 4.854 \times 10^{-29} \text{m}^3$ [28].

Dividing eq. (11) by eq.(12) and discarding the higher powers of  $\Psi E^2$  on the assumption that  $\Psi E^2 \ll \ln \beta$  for all values of interest of  $\beta$ , one finds the ratio of the concentrations of the critical nuclei, with and without the field as

$$N^* / N_0^* = \exp\left[\xi \Psi E^2 / \ln \beta (\ln \beta + \Psi E^2)^2\right], \quad (13)$$

where  $\xi = 32\pi\sigma^3\omega^2 / 3k^3T^3$ .

Neglecting  $\Psi E^2$  compared to  $\ln \beta$ , this equation takes the form

$$N^*/N_0^* = \exp\left[\frac{\xi \Psi E^2}{(\ln \beta)^3}\right]. \quad (14)$$

At 300 K, substituting  $\sigma = 0.07 \text{ J/m}^2$  [27], we find that  $\xi = 1.1121334216 \times 10^3 \text{ S I units}$ . The percentage variations in nucleation rate, calculated for the model system as a function of the applied field, are given in Table 1.

Table 1. Calculated values of the percentage increase in the nucleation rate of NaCl as a function of the strength of electric field, for supersaturation ratios 1.01 to 1.1

E (V/m)	Percentage increase in nucleation rate for different supersaturation values					
	1.01	1.02	1.04	1.06	1.08	1.1
0	0	0	0	0	0	0
$10^2$	0	0	0	0	0	0
$10^3$	0.00210	0.00009	0.00001	0	0	0
$10^4$	0.21073	0.00916	0.00118	0.00036	0.00016	0.00008
$10^5$	23.4316	0.92027	0.11798	0.03596	0.01560	0.00822
$10^6$	$1.3 \times 10^{11}$	149.942	12.5142	3.66110	1.57223	0.82539
$10^6$	$\infty$	$\infty$	$1.3 \times 10^7$	3544.01	373.882	127.504

A perusal of the tables leads to the conclusion that in the range of supersaturation ratio 1.01 to 1.04, electric fields stronger than  $10^4 \text{ V/m}$  alone would influence the nucleation rate (Figure 1) and for higher supersaturations, the effect would be appreciable for field values greater than  $10^5 \text{ V/m}$  (Figure 2). Though, the influence is enormous for fields stronger than  $10^6 \text{ V/m}$ , it is not advisable to work in this region of field, since it may cause the dielectric breakdown of air and other media involved in the experiment. In short, one may expect moderate control over the nucleation and crystal growth rate, for the range of supersaturation ratio 1 to 1.1, working with fields of strength  $10^4$  to  $10^6 \text{ V/m}$ .

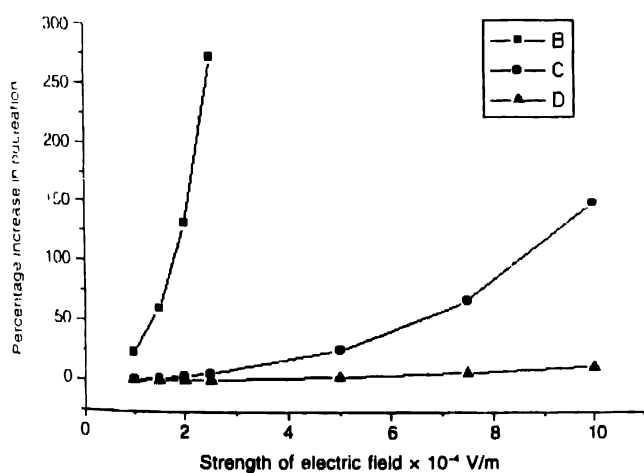


Figure 1. Percentage increase in nucleation rate as a function of the applied electric field, for different supersaturation ratios (B = 1.01, C = 1.02, D = 1.04)

#### 4. Experiment

An experiment has been conducted to study the dependence of electric field on the nucleation rate in the model NaCl-water system. Crystal nucleation was studied in sitting drops [3],

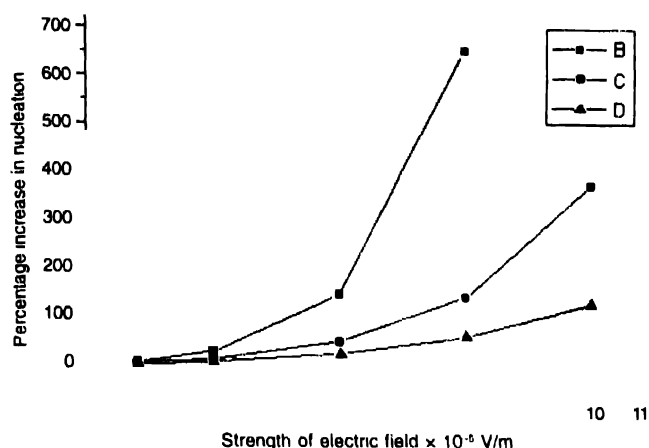


Figure 2. Percentage variation in nucleation rate as a function of the applied electric field, for different supersaturation ratios (B = 1.06, C = 1.08, D = 1.10)

placed on small, extremely clean glass slides in the presence of electric fields of strength up to  $10^6 \text{ V/m}$ . Aqueous solution of AR grade NaCl, which would be supersaturated to a ratio 1.06 at 300 K, was prepared in double distilled water and it was then micro-filtered. Drops of exactly equal volume ( $100 \mu\text{l}$ ) were formed on small glass slides using micropipettes. Meticulous care was taken to minimize heterogeneous nucleation on impurity agents. This included, selection of scratch-free slides, repeated cleaning of the slides in alkali, acid, running water and circulating distilled water for hours and vacuum drying. The slides with the drops on them were placed between the electrodes kept in airtight, cylindrical glass vessels just large enough to accommodate the electrodes (Figure 3). The glass vessels were kept in a thermally insulated chamber and the temperature was lowered gradually to 300 K. Electric fields of different strengths were applied by connecting the electrodes to constant high voltage d.c. sources. The drops were kept undisturbed for 12 hours. Then they were taken out and the drops were examined using a high-resolution optical microscope. The number of crystals formed, crystal shapes, and all other relevant parameters have been investigated. Each experiment was performed at least five to six times to rule out any erroneous conclusion, which may arise due to minute

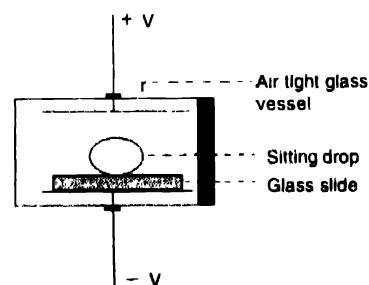


Figure 3. Experimental set-up for the sitting drop in electric field

factors like nonuniform evaporation from the drops and heterogeneous nucleation on impurity sites. The data thus obtained are presented in Table 2. The microphotographs (Figure 4) illustrate the effect of electric field on the nucleation process of NaCl.

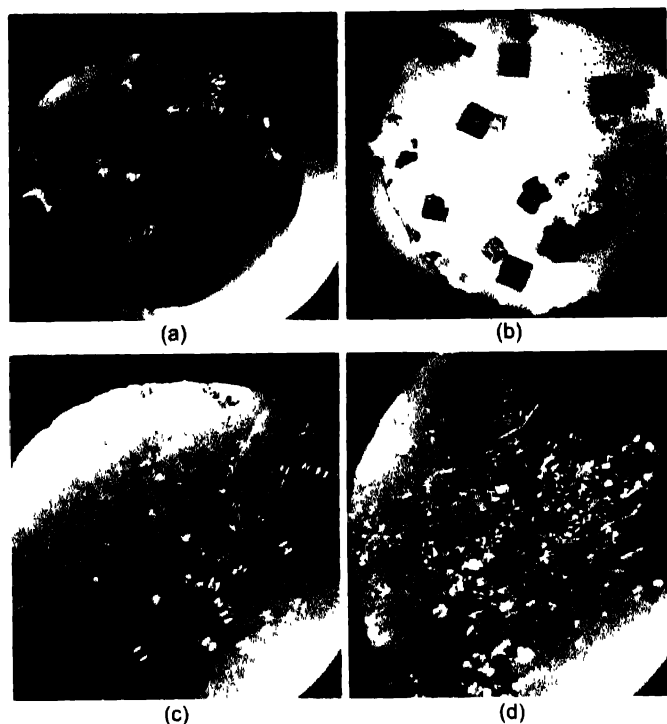


Figure 4. Crystal nuclei formed in sitting drops under external electric fields of strength (a) 0, (b)  $10^5$ , (c)  $2.5 \times 10^6$ , (d)  $5 \times 10^6$  V/m

## 5. Results and discussion

An analysis of Table 2 and the microphotographs leads to the following conclusions. For the supersaturation ratio 1.06 of NaCl in water, electric fields of strength upto  $10^4$  V/m have no influence on the number of nucleation sites formed within 12 hours. The nature of nucleation for fields between  $10^4$  to  $10^5$  V/m was ambiguous and hence not included in the table. The impact

Table 2. The number of NaCl crystals formed in the sitting drops placed under different electrostatic conditions for  $\beta = 1.06$

$E$ (V/m)	Number of crystals formed within 12 hours
0	5-10
10	5-10
$10^2$	5-10
$10^3$	5-10
$10^4$	5-10
$10^5$	20-30
$2.5 \times 10^5$	50-75
$5.0 \times 10^5$	100-150
$7.5 \times 10^5$	200-300

becomes evident for a field of strength  $10^5$  V/m, at which the average number of sites formed changes from 7.5 to 25. This corresponds to 233 % increase in nucleation rate, whereas the percentage increase indicated by the numerical analysis is only 3.66% (Table 1). A similar difference between the theoretical prediction and experimental observation could be seen for every higher value of field. However, it is hoped that there is no point in projecting this difference as a demerit of the theory, when one considers the inherent limitations of the classical nucleation theory, which is mainly due to the uncertainty in the value of interfacial tension [28]. The theoretical prediction that electric fields of strength greater than  $10^5$  V/m would influence the nucleation process for supersaturations greater than 1.04, is in full harmony with the experimental observation.

## 6. Conclusion

It has become evident that externally applied electric field can influence the nucleation of crystals in aqueous medium. The theoretical work, numerical analysis and experiment on NaCl-water system indicate that the effect is appreciable for fields of strength greater than  $10^5$  V/m, especially at lower supersaturation ratios. This quantitative knowledge may be utilized for obtaining better rates of nucleation and crystal growth in any system, provided that the dielectric constant of the crystal is less than that of the saturated solution.

## Acknowledgments

One of the authors, K V Saban is grateful to the University Grants Commission, Government of India for the award of a fellowship under the FIP- IX plan.

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