Scientific paper

Effects of Different Gas Phases and Gas Bubbles on the Nucleation Kinetics

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Abstract

In this study, the effects of different gas phases and gas bubbles on the Induction time were investigated. In the first step, the effects of different kinds of gases (N_2, Ar, dry air-N_2 and dry air-Ar) which are fed into solution-gas interphase and into the solution were determined. After determining the most effective gas upon the Induction time, the next step was to use this gas in the presence of the seed crystals, to specify variation in the Induction time. The experimental results show that gassing and the presence of seed crystal tend to shorten the Induction time as compared to the normal crystallization condition.

Keywords: Nucleation, Induction time, metastable zone width, gas phase

1. Introduction

Crystallization is a process applied in chemical industries in order to obtain materials dissolved in solutions in their solid and pure states. The process is done in three steps; namely formation of supersaturation, nucleation and crystal growth.[1]

Nucleation is the most important step in achieving crystals with required particle size distribution, purity and shape. The nucleation step is directly related to supersaturation ratio and hence to the width of the metastable zone. The metastable zone width and Induction time show variation depending on influences of a number of factors. There are several studies existing in the literature that estimate factors leading to the possible effects of the mentioned variation.[2–17]

Within the scope of this study, interaction of the liquid phase-gas phase interface has been dealt with, although it has not been considered in previous studies regardless of its crucial effects.

Magnitude in liquids is found based on the type of the fluid and the varying intermolecular attraction forces among the molecules.

The inner sections of the liquids (different liquid depths) are under the effects of equally applied intermolecular forces from neighbor molecules at all directions; (in other words, in globally symmetric way).

In this way, the forces affecting a molecule in liquid balance one another. Together with this, as the density on the vapor phase of a molecule (when the liquid-phase interface is taken into account) is lower than that on the liquid phase, the liquid is drawn inside more forcefully by the molecules under the surface.[18]

As for solutions, due to the fact that drawing in of the solvent molecules on the surface by the dissolved particles is hindered at a certain degree, the surface tension of the solutions is generally lower than that of a pure solvent. Substances that drop the surface tension of a solvent are termed as surface active, while those that do not alter it, are known as surface inactive.[18]

Besides, substances dissolved in terms of ionic salts, generally increase the surface tension of aqueous solutions with respect to pure water, but the increase is not at the extent of the drop imposed by the active substances.[16,18]

An over increase in the gas density over the liquid or addition of another insoluble liquid on it will cause the surface tension of the liquid to drop slightly as a result of the interactions between incoming molecules and those on the phase.[16,18]

Regardless of the fact that there are various studies on metastable zone width and Induction time that deal with reducing or modifying the surface tension by using different surface active materials,[6,12] there are so far, no studies conducted that have ever dealt with different gas phases on liquid in this respect.

Measurements of Induction time in determining nucleation characteristics of a supersaturated solution play an important role. Induction time is a characteristic property of a system and an important parameter in prediction of crystal sizes, shapes and particle distributions of a product formed as a result of crystal nucleation and growth in industrial crystallization processes.

Essentially, Induction time depends on factors such as temperature, nature of the solution, amount of cooling, presence of impurity and mechanical effects. Most of these factors are involved in nucleation in the solution. The studies conducted so far have been mostly concentrated on topics like experimental system designs and formation of empirical expressions that will present metastable zone and nucleation in pure states or in the presence of impurity,[7,19–25] prediction of possible effects of seed crystals and additives purposely made available in a crystallization state and investigation of uses of different devices used in predicting metastable zone widths.[26,27]

Apart from the study that investigates the effects of air on metastable zone width in a solution state, there is no other study in the literature that has ever investigated effects of the gas phase on the subject.[28]

Under the scope of our study, the gas phase on the solution where the liquid phase is in contact has been changed by replacing it with other gases of different nature (air, Nitrogen, Argon, air-Nitrogen, air-Argon). Then changes occurred in Induction time both in pure state and those caused by the presence of seed crystals (3, 5, 7 or 10) were measured. The measurements were respectively made in such a way that the effects of gas feedings on upper part of the solution and into the solution are studied separately.

2. Experimental

Effects of different gas phases on Induction time were studied through the experimental set given in Figure 1.

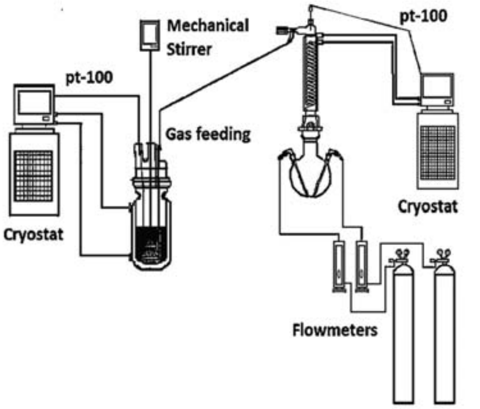

Figure 1. Schematic diagram of apparatus for measurement of nucleation rates

All the experiments were conducted by using the same stock solution. In this way, the differences that might likely emerge at saturated temperature were controlled. The solution prepared was filtered on a 0.45 micron porous filter, set at a saturated temperature of above 4-5 °C and kept in a sterilizer. Chemicals at analytical purity (K_2SO_4, KCl and $Na_2B_4O_7 \cdot 10H_2O$) and gases (dry air, Nitrogen, Argon) were used with de-ionized water in the experiments. In the first step of the experimental study, the gas phase (in normal conditions the air phase) in contact with the solution, was changed by using gases of different nature.

With this aim, mixtures of Nitrogen-Argon, dry air-Argon and dry air-Nitrogen were used. The experiments were conducted in a 0,5 liter jacketed reactor and the crystallization temperature was controlled with a remote controlled cryostat. After arranging the pressures of pure nitrogen, pure argon and mixtures of these gases with dry air by using a regulator, they were fed into the system by adjusting their flow rates using a rotameter. To prevent instant cooling likely to form on the solution surface, the gas fed into the system was warmed up. To accomplish this, a second cryostat was used to help keeping the gases feeding the reactor to the solution temperature. After the gas on the solution surface was full saturated the gas flow was interrupted and the gas entry/exit valves on the reactor's cover were closed and the experiments started. Solution was stirred with using mechanical stirrer and the experiments were carried out at a constant stirring rate of 300 rpm. The temperature inside the reactor was continuously controlled with a digital thermometer.

In the second step, the effects of feeding different gases into the solution were studied. The results of the first step were taken into account where the most effective gaseous state and the material with wide Induction time were used to carry on the experiments.

Gas entrance into the solution was made possible through the use of a 50 cm long glass tube having its bottom circular cross section covered with a 10 μm porous ceramic filter. The use of this unit has enabled gas bubbles to be fed into the system at a smaller size and over a wider area. Gas entrance into the system was made at certain periods and at specified time intervals. In the third step of the study, effects of the presence of seed crystal (3, 5, 7, 10 crystal) in the solution on Induction time were considered by taking into account both the normal conditions and the effective gas phase situation.

As it is known, the supersaturation value given to the system during measurements of Induction time is achieved with super cooling. For this reason, solutions prepared to be saturated at 40 °C, were cooled in order to achieve the required supersaturation level. Then, the first nuclei formation time in the solution was recorded and necessary calculations were made based on the classic nucleation theory.[1] According to the classic nucleation theory, free energy change necessary for a spherical cluster nuclei formation in a solution is expressed as shown in equation (1) below;

$$\Delta G = \Delta G_v + \Delta G_s = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (1)$$

Where, ΔG_v and ΔG_s are respectively, the necessary free energy change per unit volume and per unit area for the formation; r is the critical nuclei radius and γ is the surface tension for the nuclei-system interface. The two terms on the right hand side of the equation are in different signs and both depend on r.

For this reason, necessary free energy change $d(\Delta G)/dr = 0$ for nuclei formation passes through a maximum. Therefore, the critical nucleus radius, r^*, is defined as given below;

$$r^* = -\frac{2\gamma}{\Delta G_v} \qquad (2)$$

Where, ΔGv

$$\Delta G_v = -\frac{kT\ln(S)}{v} \qquad (3)$$

S is supersaturation ratio, given as $S=(C/C^*)$. C is the existing saturation value C^* refers to equilibrium saturation value, k Boltzmann constant and ν shows molar volume of the crystal.

Critical free energy change, ΔG^* is given by;

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \qquad (4)$$

Number of molecules in the critical nuclei, i^*, is expressed as;

$$i^* = \frac{4\pi(r^*)^3}{3v} \qquad (5)$$

The relationship between nucleation rate per unit time, per unit volume (defined as number of nucleus) and Induction time necessary for formation of the first visual nuclei formation within a solution is as given below;

$$J = \frac{1}{\tau} = A.exp(-\frac{\Delta G^*}{kT}) = A.exp(-\frac{16\pi\gamma^3}{kT\Delta G_v^2}) \qquad (6)$$

The expression for the surface tension (γ) over the crystal-solution interface can be obtained by linearizing Equation (6)

$$ln(\tau) = -ln(A) + \frac{16\pi\gamma^3 v^2}{3k^3T^3(lnS)^2} \qquad (7)$$

From slope and sliding values of the graphs of $1/(lnS)^2$ and $ln(\tau)$ the values of γ and A can be found.

3. Results and Discussion

In the experimental study, saturated solutions of K_2SO_4, $Na_2B_4O_7 \cdot 10H_2O$ and KCl at a temperature of 40 °C were used. Initially, the Induction times were measured both in normal air conditions and in the presence of different gas /gaseous mixtures. The results obtained are as shown in Figure 2.

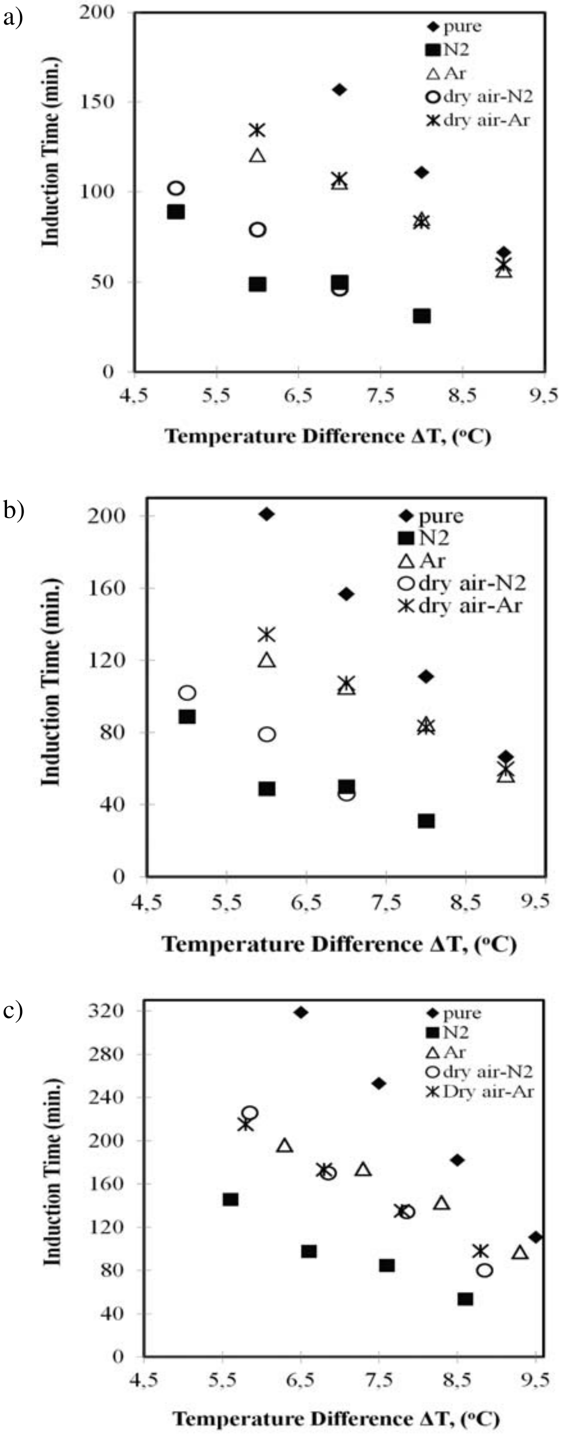

Figure 2. Induction time's Measurement Results for Saturated Solutions of a) KCl b) $Na_2B_4O_7$ c) K_2SO_4 at 40 °C under normal conditions and in the presence of gas/gaseous mixes

The Induction times recorded in the presence of different gas/gaseous mixes have shown remarkable decrease as compared to those found in pure medium.

The results obtained from all the three materials indicate similar variation. Variation of solution-gas phase interface properties has a catalyzing effect on nucleation.

The solid-liquid interface tension for homogeneous and heterogeneous nucleation were calculated by putting the data from the variation of supersaturation with induction time for K_2SO_4 solution into Equation 7.

For the situation where no gas feeding takes place onto the upper section of the solution, the solid-liquid interfacial tension were found to be 0,0021 j/m^2 for homogeneous and 0,0013 j/m^2 for heterogeneous nucleation. However; after feeding N_2 gas into the upper section of the solution, the solid-liquid interface, interfacial tension recorded the values of 0,0018 j/m^2 and 0,0013 j/m^2 for homogeneous and heterogeneous nucleation respectively. As it is known, the solid-liquid interface tension intensity is particularly effective on homogeneous nucleation. The calculated values are well compatible with this fact. The changes arising in the solid-liquid interfacial tension after N_2 feeding take the same structure even in situations where different types of gases are used.

The possible reasons that lead to this are:

- Changing of the properties on the liquid-gas interface as a result of the presence of gases of different nature
- Triggering of homogeneous nucleation on the liquid-gas interface and hence causing the surface nucleation to become more dominant.

Although no gas was fed into the solution, but only the upper section of the solution was fed with the gas and for which this event happened; it is a clear sign that if penetrating gas feeding is made into the solution, much lower Induction times will be recorded. Therefore, the next step in the study was to investigate K_2SO_4, on which the highest Induction time was recorded in the presence of N_2. The results obtained are as shown in Figure 3.

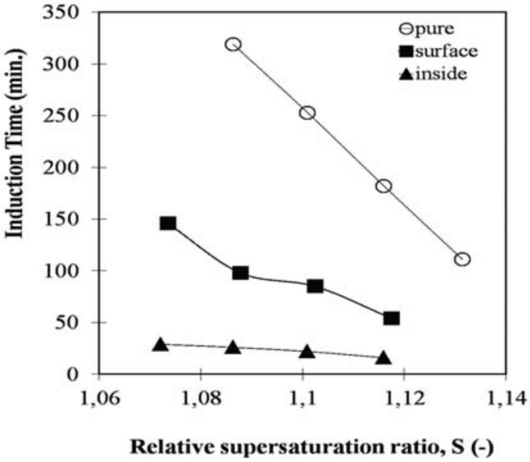

Figure 3. Variation of Induction time for a saturated solution of K_2SO_4 after feeding it with N_2

As seen in Figure 3, depending on the supersaturation level, the N_2 gas added into the solution has caused a decrease of the Induction time by 6 to 8 times as compared to the pure medium, whereas feeding of N_2 into the upper section of the solution has led to the Induction time decrease of 2 to 4 times the normal pure medium situation. This means that it becomes even harder to control the nucleation. The situation has, most probably happened as a result of the bubbles behaving themselves as centers of nucleation. The study conducted by Wohlgemuth et al,[28] where air was fed into the solution, shows parallelism to this situation as it gives similar results.

Ultimately; the rate of homogeneous nucleation within the solution is thought to be increased. Changes of interfacial tension occurred in the solid-liquid interface after the feeding of N_2 into the solution, were also calculated. For homogeneous nucleation, the value of 0,0016 j/m^2 was found whereas that of heterogeneous nucleation exhibited the value of 0,0008 j/m^2. The change in the interfacial tension within the solid-liquid interface is higher than the one obtained during the N_2 feeding onto the upper section of the solution.

An important result in our study is the fact that even the type of gas (not just any gas) fed into the solution inflicts some influence on the event. Another remarkable observation here is that the N_2 gas fed into the solution is relatively close to the Induction time results obtained. This creates the tendency that N_2 fed into the solution had imposed effects on nucleation without any dependency of the supersaturation levels.

In the third step of the study, where N_2 gas was fed into saturated solution of K_2SO_4 at 40 °C, the effects of seed crystal presence was investigated. From the initial observations, it was found that nucleation can hardly be controlled with the increasing number of seed crystals in the solution and that instantaneous nucleation is inevitable. For this reason, the maximum number of seed crystals added into the solution was limited to 10. In addition, the increasing supersaturation value and the result of catalytic effects of the seed crystal have led to the impossibility of measuring the Induction time. For this reason, the presence of seed crystal could be studied for the low supersaturation value. Figure 4 shows the effects of seed crystal on Induction time in pure medium, where no gas feeding was made. The increase in the number of seed crystals abruptly decreases the Induction time. The results obtained indicate that, there is a decrease of 5 to 8 times as compared to the normal (pure) medium. therefore, measurements of the Induction time was made for the N_2 gas feedings that will be made into the solution and on its upper section by taking into account this lowest cooling value of 1 °C that occurs in pure medium. It was not possible to measure the Induction time for higher super cooling conditions.

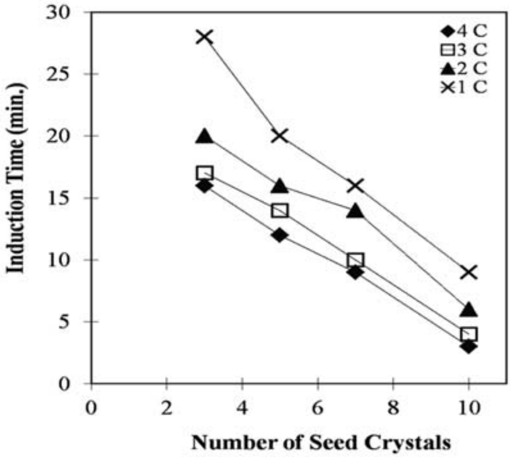

Figure 4. Effects of presence of different numbers of seed crystals on Induction time for different super cooling levels in a saturated solution of K_2SO_4 at 40 °C

Figure 5 shows how the presence of different numbers of seed crystals affects the Induction time for situations where N_2 gas is fed into the solution and on the upper layer of the solution.

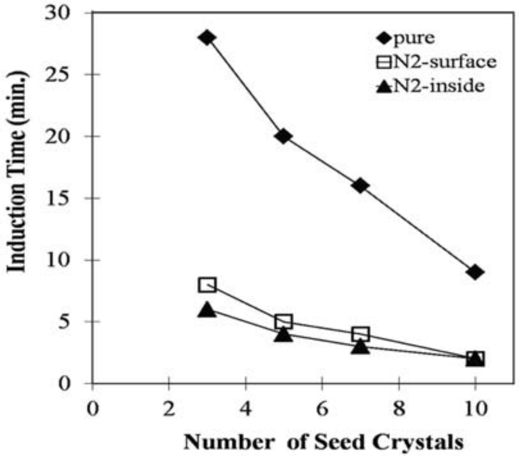

Figure 5. Variation of Induction time in the presence of seed crystal for a saturated solution of K_2SO_4 at 40 °C super cooled at 1 °C under the situation where N_2 gas was fed into the solution

With three seed crystals in a solution super-cooled at 1 °C, where no gas feeding was made, the Induction time specified at 25 to 30 minutes dropped to 10 minutes as the number of seed crystals increased.

As for situations where N_2 gas was fed into the top layer of the solution and inside the solution, the Induction times obtained are less than 10 minutes even with the presence of three seed crystals. With the increase of the seed crystals, the Induction time had shown a further drop to 2 minutes. The injection of N_2 gas into the solution or solution's upper layer has shown that this can almost exhibit catalytic effects on nucleation.

After different gas feedings, it was investigated what types of variations the kinetic parameters had exhibited (as given in Figure 6). The nucleation rate in the presence of N_2 gas exceeds that of nucleation under normal conditions by approximately 7 to 8 times; when compared with the situation where the feeding is made onto the upper section of the solution, the nucleation rate increases twice

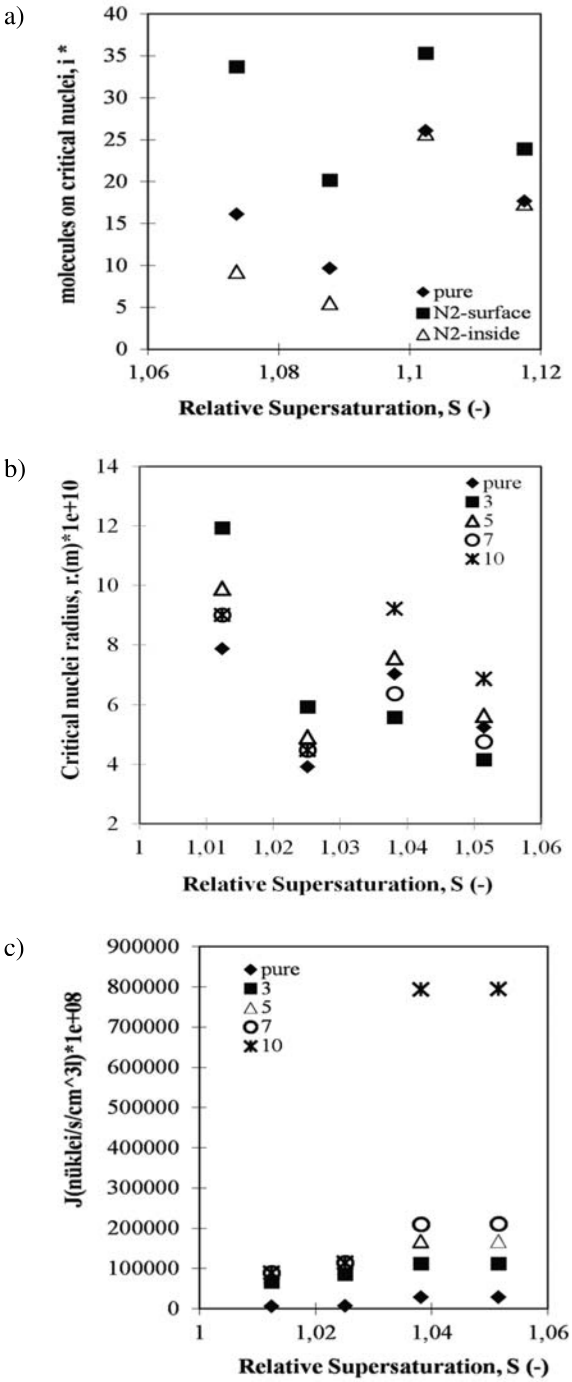

Figure 6. Variation of nucleation constants (I*, r, J) with supersaturation for situations where N_2 gas has been fed into pure medium, solution/gas interface and into solution

as much. This situation will complicate the nucleation control. This phenomenon can be evaluated as a result of the bubbles within the solution to act as nucleation centers and to speed up stirring of the solution.

The relatively lower effects resulted from feeding the N_2 gas onto the upper section of the solution can be considered as due to limited molecular interactions on the liquid-gas inter-phase rather than solution stirring. Together with this, the nucleation rates in both cases are still higher than those under normal conditions. N_2 gas feeding onto the liquid-gas interface has led to the increase in the number of molecules in the critical nuclei. The lowest number of molecules in the critical nuclei appears when N_2 gas is fed into the solution. This leads to a reduced diameter of the critical nucleus. The results obtained seem to support this phenomenon. This is so because the smallest size of the critical nucleus occurs when the N_2 is fed into the solution. The presence of seed crystal in crystallization medium has the effects of speeding up the nucleation rate. Figure 7 shows variation of different numbers of seed crystals with the nucleation rates for experiments carried out in the presence of seed crystals.

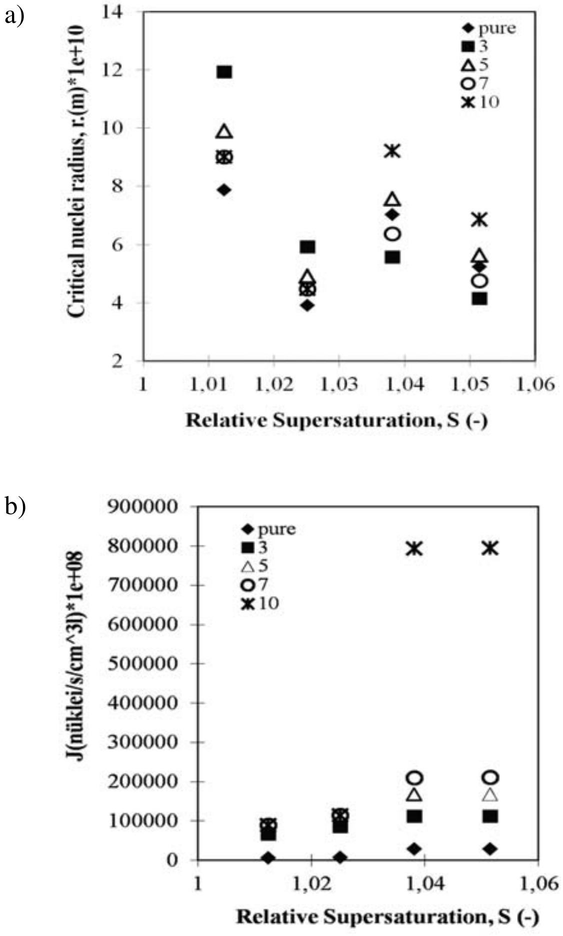

Figure 7. Different numbers of seed crystals taking place in a saturated solution of K_2SO_4 at 40 °C showing variation of a) nucleation rate b) diameter of the critical nucleus

Nucleation rate tends to increase based on the increasing supersaturation level and the number of seed crystals within the solution medium. After exceeding a certain level of supersaturation and the number of seed crystals exceeding 7, the nucleation rate exhibits an increase of almost 4 times. In cases where the number of seed crystals is higher in a solution, it is common to see that the critical nucleus diameter for nucleation formation is higher too. This gives a notion that a portion of supersaturation has been moved off over the seed crystals.

4. Conclusions

In this study, investigation has been made on effects of changing the gas phases over which the liquid makes contact by using gases of different nature and feeding of gases into solution over nucleation behavior.

It was found that when pure N_2, pure Ar, dry air-N_2 and dry air-Ar mixtures are fed into top layers of solutions and into the solution, the Induction times decrease with respect to normal conditions (air medium). The most remarkable decrease was observed when (nitrogen) N_2 gas was used. The effect prevails also when different solutions (KCl, $Na_2B_4O_7$, and K_2SO_4) are used.

The drop in Induction time becomes more vivid when different gases are fed into the solutions. This can be thought of being caused by the fact that the gas bubbles act as centers of nucleation and due to formation of stirring effects within the solution.

Apart from supersaturation, it was not possible to follow up nucleation behavior when the N_2 gas was fed either onto the top section of the solution or directly into the solution in the presence of seed crystals.

The results suggest that such outcome may be caused by combined effects of the seed crystals' catalytic influence, changing of liquid gas phase properties on the interface, behaving of the gas bubbles as nucleation centers and feeding of gases into the solution. Beside other factors known to affect nucleation, it is necessary that likely effects of different gases be taken into account too.

SYMBOLS

ΔG:	Necessary free energy change for formation of spherical nuclei
ΔG_v:	Free energy change per unit volume
ΔG_s:	Free energy change per unit area
ΔG^*:	Critical free energy change
γ:	Surface tension for nuclei-solution system
r^*:	Critical nuclei radius
S:	Supersaturation ratio (C/C^*)
C, C^*:	Existing and equilibrium saturation value
K:	Boltzmann constant
ν :	Crystal molar volume
i^*:	number of molecules on the critical nuclei

J : Number of nuclei per unit time, per unit volume
τ : Time required for the formation of the first visual nuclei in a solution
G : Total linear growth rate
m_1, m_2: Initial and final masses of the seed crystal
L_1: Initial size of the seed crystal

5. Acknowledgements

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6. References

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Povzetek

Proučevali smo efekt različnih plinskih faz in plinskih mehurčkov na indukcijski čas. Najprej smo v na medfazno področje raztopina-plin ter v raztopino uvajali različne pline (N_2, Ar, suh zrak-N_2 in suh zrak-Ar). Po določitvi najbolj učinkovitega plina po indukcijskem času smo ta plin uporabili v prisotnosti kristalnih kali, da bi določili spreminjanje indukcijskega časa. Rezultati kažejo, da prisotnost plinov in kristalnih kali zmanjša indukcijski čas v primerjavi s časom pri običajnih pogojih kristalizacije.