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Effect of Impurities on Nucleation with Applications to Sodium Chloride

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ABSTRACT

Previous measurements of concentration gradients formed in long columns of supersaturated solutions of glycine and potassium sulfate indicate that small amounts of impurities can affect the magnitude of the gradient (Ginde and Myerson, 1991b). The gradient is enhanced if the impurity is a nucleating agent and decreases if the additive is a nucleation inhibitor. This might indicate that the impurity affects the degree of cluster formation. The metastable zone width measurements of these supersaturated solutions confirmed the results of the concentration gradient column experiments. In this work, the concentration gradients were measured for pure supersaturated sodium chloride solutions and in the presence of small amounts of additives such as lead sulfate and chromium chloride. The cluster sizes are estimated both in the presence and absence of impurities and compared with the changes noted in the metastable zone widths.

INTRODUCTION

Bulk or solution crystallization is an important separation and purification process in the chemical industry. The shape and size of the crystals influence several unit operations, such as filtration and drying, in the manufacture of chemicals. It is generally agreed that the crystallization from the solution is a two step process nucleation or the 'birth' of a crystal followed by crystal growth. Both processes can occur simultaneously and are influenced by a host of factors such as the supersaturation of the solution, thermal history or solution 'age' and the presence of impurities. A recent review of nucleation and crystal growth may be found in the *Handbook of Industrial Crystallization* (1992).

A supersaturated solution is required for crystallization to occur. Supersaturation can be achieved in several ways — for example by cooling a solution or by changing the pH of the solution. A supersaturated solution, although in thermal equilibrium, is not at thermodynamic equilibrium. Concentration fluctuations in the solution can cause the solute molecules to come together as clusters. On a microscopic level a dynamic situation exists. Clusters, in the form of dimers, trimers, tetramers etc. are continuously formed and destroyed. At all times, the supersaturated solution is a mixture of monomers, dimers, tetramers etc. Eventually, a critical cluster size is reached and a crystal is born.

Experimental evidence for the presence of clusters falls into three categories. Mullin and Leci (1969) observed that concentration gradients developed in long columns of supersaturated citric acid solutions whereas the concentration was uniform in under-saturated solutions. This was attributed to the formation of clusters which migrated towards the bottom of the column under a gravitational field. Similar observations were reported by several other investigators (Larson and Garside, 1986; Lo, 1989). Recently, Ginde and Myerson (1992) have analyzed the column data using the concept of number average cluster size. They concluded that the number average cluster size was of the order of 2–100 molecules and was a function of the solution 'age', temperature, supersaturation and thermal history.

Qualitative changes in the light transmission through supersaturated solutions also indicate the presence of an ordering phenomena. Khamskii (1969) observed that light transmission through supersaturated solutions increased continuously prior to crystallization. Hussmann et al. (1984) and McMahon et al. (1984) investigated the structure of

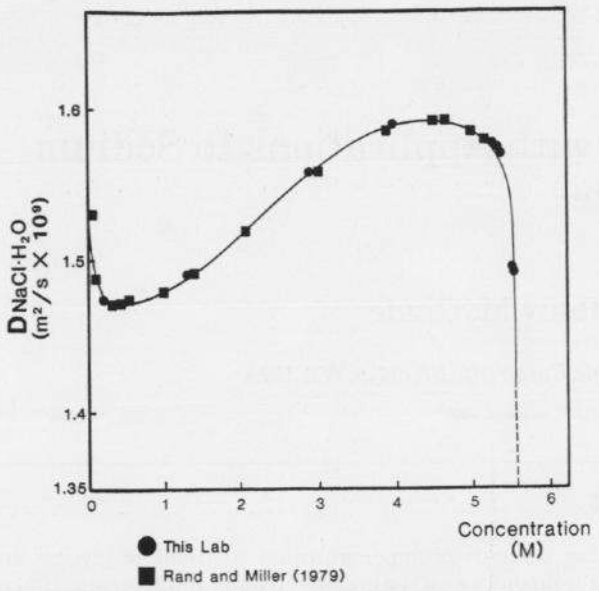

Fig. 1. Diffusion coefficient as a function of concentration for sodium chloride–water system at 25°C.

supersaturated solutions of sodium nitrate using Raman spectroscopy. Reproducible spectral shifts were observed due to various types of ionic and molecular aggregation.

Myerson and co-workers measured the transport properties of supersaturated solutions to investigate the formation of clusters. They employed interferometric techniques to show that diffusivity declined rapidly with increasing concentration in supersaturated solutions of glycine (Chang and Myerson, 1984, 1986), urea (Sorell and Myerson, 1982), potassium chloride and sodium chloride (Chang and Myerson, 1985). The diffusion coefficients in sodium chloride solutions are shown in Fig. 1. In addition, they (Lo, 1989) were also able to demonstrate that diffusivity was a function of the solution 'age' declining with increasing 'age'. This was attributed to the evolution of molecular clusters with time. Concomitantly, they (Myerson et al., 1990; Ginde and Myerson, 1991a) were also able to detect a more rapid increase in the viscosity of the supersaturated solution than in under-saturated solutions. Using the theory of Binder and Mirold (1977), Lo and Myerson (1990) were able to show from diffusivity and viscosity data that glycine existed mostly as a dimer in supersaturated solutions. This was corroborated by the analysis of the concentration gradient column data for glycine by Ginde and Myerson (1992) mentioned previously. The cluster size estimation for sodium chloride data using the diffusivity data is shown in Table 1. From the data we see that sodium chloride exists mainly as a monomer in solution.

It is well known that a small amount of impurity can profoundly affect the nucleation rate; however, it is impossible to predict the effect *a priori*. The presence of additives can either enhance or inhibit the solubility of a substance. Enhanced solubilities would lead to lower supersaturations and lower growth rates. If it is postulated that the impurity adsorbs on the crystal surface, two opposing effects come into play — the presence of an additive would lower the surface tension and lead to higher growth rates, however, the impurity adsorption blocks potential growth sites and lowers nucleation rates. Thus, the effect of impurities is complex and unpredictable.

Several experimental investigations have been undertaken to clarify the situation. For example, it was shown that Pb^{2+} acts as a nucleation agent in a NaCl system whereas Co^{2+} inhibits nucleation in a KNO_3 solution (Cooke, 1966). Although it is difficult to generalize, certain trends can be observed from the experimental evidence. The inhibiting effect appears to increase with increasing charge of the cation e.g. $Cr^{3+} > Fe^{3+} > Ni^{2+} > Na^{+}$. The inhibiting effect also appears to decline above a certain critical impurity concentration.

TABLE 1

Cluster size estimation from diffusion measurements

Material	Solution		Supersat. S	Diff. coeff. at saturation $D_s \times 10^5$ cm^2/s	Diff. coeff. of solution $D \times 10^5$ cm^2/s	Av. no of molecules in cluster $n = (D_s/D)^{1.5}$
	Time (h)	Temp (°C)				
Glycine (Lo and Myerson, 1990)	24	25	1.14	0.71	0.46	1.92
Urea (Sorell and Myerson, 1982)	18	25	1.10	0.75	0.15	11.2
Potassium chloride (Chang and Myerson, 1986)	20	25	1.04	2.20	1.92	1.23
Sodium Chloride (Chang and Myerson, 1984)	24	25	1.03	1.57	1.48	1.10

TABLE 2
Physical properties of the starting materials

Material	Formula and mol. wt.	Additive concn. (ppm)	Solution properties			Specific volume (cc/g)
			Temp (°C)	Solub. (g/100 g)	Density (g/cc)	
Sodium chloride	NaCl 58.44		30	36.16	1.196687	0.4619
			50	36.56		
Lead sulfate	$PbSO_4$ 303.28	50	30	36.0	1.196720	0.1613
		100	30	35.9	1.197125	
		200	30	35.63	1.195901	
Chromic nitrate	$CrN_3O_9 \cdot 9H_2O$ 400.15	50	30	34.59	1.196244	
		100	30	35.9	1.196620	
		200	30	36.32	1.196688	

In our previous investigations (Ginde and Myerson, 1992) we examined the concentration gradients in long columns of supersaturated solutions of glycine (in presence of small amounts of valine) and potassium sulfate (in presence of small amounts of cobalt acetate). The presence of valine increased the density gradients in the supersaturated glycine column whereas cobalt acetate suppressed the gradients in supersaturated potassium sulfate solutions. If we assume that the cluster size is proportional to the density gradient, we can conclude that valine was a nucleating agent for the glycine–water system whereas cobalt acetate inhibited the nucleation of potassium sulfate. The metastable zone width (MZW) decreased for the glycine–valine system and increased for the potassium sulfate–cobalt acetate system which further confirmed the role of valine as a nucleating agent and cobalt acetate as a nucleation inhibitor for the glycine–water and potassium sulfate–water systems respectively.

The present study was undertaken to investigate the role of lead and chromium salts on the nucleation and crystallization behavior of sodium chloride. We measured the concentration gradients and the metastable zone widths both in presence and absence of the impurities. In presence of the additive, an increase in the concentration gradient and a decrease in MZW compared to the pure system would indicate that the additive acts as a nucleating agent. The opposite effect would lead to the conclusion that the additive is a nucleation inhibitor.

EXPERIMENTAL

The solubilities of the sodium chloride–water system were measured in the presence and absence of impurities using the standard gravimetric technique. The data compared well with that reported in literature (Chianese et al., 1986). All chemicals were obtained commercially and were at least 99.5% pure. The solutions were made in deionized water at 52°C. The physical properties of the starting materials are shown in Table 2.

Concentration gradient column experiments

The solutions were charged into a jacketed column maintained at 45 ± 0.1°C by a circulating water bath. The solutions were cooled uniformly at 10°C/h to 25°C. Samples were withdrawn carefully at regular intervals from the three ports 25 cm apart. The density of the solutions was measured at 30°C by a Mettler–Paar density meter. The density measurements were accurate to 1×10^{-5} g/cm^3. A schematic of the experimental apparatus is shown in Fig. 2.

Metastable zone width measurement

When a saturated solution at a given temperature is cooled uniformly, the solution can be cooled

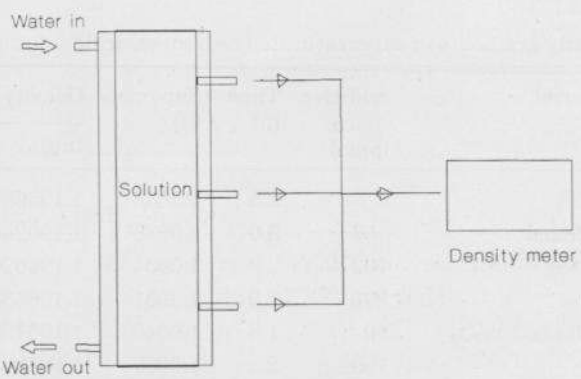

Fig. 2. Schematic of the concentration gradient measurement apparatus.

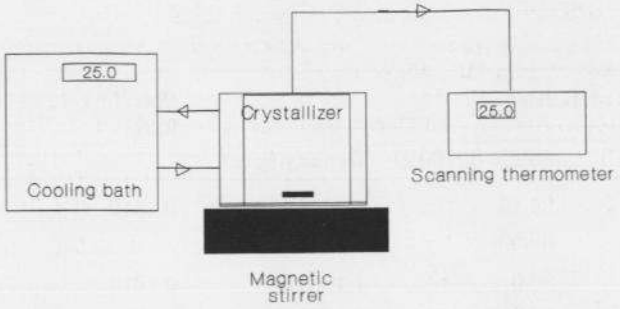

Fig. 3. Schematic of the apparatus used for the measurement of the metastable zone width.

several degrees below the saturation temperature before crystallization takes place. This region, between the saturation temperature and the temperature at which the first crystals appear is called the effective metastable zone and the difference in the two temperatures is the effective metastable zone width.

The effective metastable zone was measured in the laboratory using a batch crystallizer and an experimental apparatus shown in Fig. 3. Approximately 200 ml of solution saturated at 50°C was placed in a crystallizer and allowed to equilibrate thermally. The solution is stirred at a constant rate (approximately 100 rpm) and cooled slowly until a number of small crystals are formed. The temperature of the solution is then raised at a very slow rate till the last crystal disappears. This temperature is denoted as the saturation temperature, T_s. The solution is then heated to a temperature one degree above T_s and maintained for 30 min. The solution is now cooled at a constant rate and the temperature at which the first crystal appears is noted (T_1). The difference between this temperature and the saturation temperature is denoted as T_{1max} for the cooling rate r_1. The experiment was performed for the NaCl–water system (pure as well as in the presence of additives) at cooling rates of 20, 30 and 40°C/h. Each run was repeated eight times to obtain statistically significant results. All temperatures were controlled to ± 0.1°C.

RESULTS AND DISCUSSION

Concentration gradient column experiments

The concentration gradients observed in supersaturated columns of sodium chloride both in the presence and absence of additives are shown in Table 3. The presence of gradients is attributed to cluster formation in supersaturated solutions and we assume that the change in the density gradient is directly proportional to the degree of cluster formation. From the data it is clear that the gradients in the columns in presence of Pb and Cr impurities have increased compared to the gradients for the pure NaCl solution. Hence, we can say that the presence of these additives enhances cluster formation. Thus, these additives act as nucleating agents or enhancers for the NaCl–water system. Further proof of this beneficial effect could be obtained by observing the lowering of the metastable zone width in presence of these additives.

The concept of number average cluster size can be used to analyze the column data to get an idea of the effectiveness of the additive (Ginde and Myerson, 1992). Since, at any given time, the supersaturated solution is a mixture of monomers, dimers, trimers, tetramers etc., one has to define the characteristic cluster in terms of the number average cluster size, n,

$$n = \frac{M_n}{M_0} = \frac{1}{M_0}\frac{\sum M_x N_x}{\sum N_x} \quad (1)$$

TABLE 3

Density gradients in supersaturated sodium chloride solutions

Material	Additive concn. (ppm)	Time (h)	Supersat. (S)	Density of the supersaturated solution (g/cc)			Density gradient × 10^5 (g/cc)	Number avg. cluster size (n)
				Initial	Top	Bottom		
NaCl		2.5	1.0035	1.196687	1.196469	1.196911	44.2	4.6
NaCl and $CrN_3O_9{\cdot}9H_2O$	50	3.0	1.0036	1.196244	1.195758	1.196739	98.1	9.0
	100	2.8	1.0034	1.196620	1.195991	1.197242	125.1	11.2
	200	2.0	1.0031	1.196688	1.195880	1.197487	160.7	14.0
NaCl and $PbSO_4$	50	1.8	1.0040	1.196720	1.196347	1.197082	73.5	7.0
	100	2.5	1.0037	1.197125	1.196494	1.197769	127.5	11.2
	200	3.0	1.0030	1.195901	1.195353	1.196457	110.4	9.8

Temperature: 25°C. Column height: 50 cm.

where M_n and M_0 are the number average molecular weight and molecular weight of the solute, respectively; M_x and N_x are molecular weight and number of clusters of size x.

The concentration gradient data would give us a measure of the weight average molecular weight of the cluster, M_w,

$$M_w = \frac{RT}{(1-\varrho v)hg}\left[\frac{C_B - C_T}{C_o}\right] \quad (2)$$

where h is the height of the column and v is specific volume of the solute. The two molecular weights defined in equations (1) and (2) are related through p, the extent of the reaction. Thus,

$$M_w = M_0 \frac{(1+p)}{(1-p)} \quad (3)$$

$$M_w = M_n (1+p) \quad (4)$$

Thus, the number of molecules in a cluster can be determined as a number average cluster size from equations (1)–(4).

The last column in Table 3 shows the number average cluster size obtained from the concentration gradient data using equations (1)–(4). From the data, it is clear that pure sodium chloride exists as a tetramer at the given supersaturation and 'age'. This compares well with the diffusion data which shows that a sodium chloride cluster exists mainly as a monomer (Table 1). Both chromium nitrate and lead sulfate cause an increase in the concentration gradient and hence, in the cluster size. Under almost identical conditions, the cluster size has doubled or tripled in the presence of additives. Thus, both additives act as nucleating agent or enhancer for the sodium chloride–water system.

Metastable zone width measurements

The metastable zone widths (MZW) for pure sodium chloride solutions as well as in the presence of additives is shown in Table 4. For the pure solutions, the MZW compares well to the value of 3.5°C reported (Chianese, 1986) for a pure saturated NaCl solution at 60°C, stirred at 300 rpm and cooled at a rate of 30°C/h. The concentration gradient data has shown that both additives act as nucleating agents and should decrease the MZW of the system. The decrease in MZW has been observed for the glycine–water system where valine acts as a nucleation enhancer. The values of the MZW in presence of additives do not change much from those observed for the pure solution. This is probably due to the slow increase in solubility of sodium chloride with increasing temperature. More precise experiments to determine the MZW are under way.

TABLE 4

Metastable zone-width measurements in supersaturated sodium chloride solutions

Material	Additive concn. (ppm)	Cooling rate (°C/h)	Metastable zone width (°C)
NaCl		10	3.6 ± 0.3
		30	3.7 ± 0.4
NaCl and $CrN_3O_9 \cdot 9H_2O$	50	20	3.7 ± 0.3
	100	20	3.7 ± 0.4
NaCl and $PbSO_4$	50	10	3.8 ± 0.3

Saturation temperature: 52°C.

CONCLUSIONS

The effect of the additives on the nucleation of sodium chloride has been investigated by measuring the concentration gradients in long columns and the metastable zone width (MZW) for different cooling rates. The presence of additives (lead sulfate and chromic nitrate) caused an increase in the concentration gradient. This would indicate that both additives were nucleation enhancers. Under identical conditions, it was shown that additives doubled the cluster size compared to the pure solution. The MZW were almost the same both in presence and absence of additives.

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