Contact Nucleation of Para-Dichlorobenzene

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Of major concern in a crystallization process is the control of the crystal size distribution leaving the crystallizer. Investigations by Mason and Strickland-Constable (1963), Melia and Moffitt (1964), Cayey and Estrin (1967), Lal et al. (1969), Johnson et al. (1970), Clontz and McCabe (1969), Denk and Botsaris (1972), Rousseau and McCabe (1973), and Bauer et al. (1974) indicate that contact nucleation is the most effective means of controlling the crystal size distribution. Contact nucleation is the formation of nuclei attributable to the contact of a seed crystal with another crystal, the vessel walls, or the agitator of a crystallizer.

The aforementioned investigators have shown that the phenomenon of contact nucleation applies (1) to aqueous solutions of virtually all inorganic salts, (2) in a single instance to an aqueous solution of an organic acid (citric acid), and (3) to an organic melt (benzophenone). It has yet to be shown whether or not organic crystals in a binary organic solution (with one of the components of the solution being the same component as the organic crystals) will exhibit contact nucleation. This note provides information on the contact nucleation of such an organic system.

EXPERIMENTAL

Well-formed, three-dimensional seed (or parent) crystals of para-dichlorobenzene were grown for this study. A para- and ortho-dichlorobenzene solution, slightly supersaturated at room temperature, was cooled to the point that a limited number of crystals were formed. These crystals were allowed to grow at a controlled supersaturation level until they were approximately 10 by 4 by 3 mm in size. On attaining this size, the crystals were retrieved from the solution and stored in distilled water until needed. Storage of the crystals in air resulted in an alteration of the shape of the crystals due to their strong tendency to sublime; the crystals were stored in water to minimize this problem.

For all further experimentation, solutions composed of 60% para-dichlorobenzene and 40% ortho-dichlorobenzene, by weight, were prepared and put into two separate bleakers. These bleakers were stoppered and placed in a water bath that had temperature control capabilities of ±0.01°C. By keeping the bleakers stoppered, evaporation losses were minimized, and a solution of virtually constant composition was maintained. Crystallization of para-dichlorobenzene on the interior walls of the bleakers (above the liquid level of the solution) was prevented by keeping the water in the water bath at a level just below the rim of the bleakers.

By slowly cooling the solutions in the water bath, a supersaturation of 0.6°C was reached. At this temperature spontaneous nucleation occurred. The solutions were reheated to melt the crystals and then recooled to a supersaturation of 0.5°C and left at this temperature for 12 hr. After this 12 hr period, no crystals were visible in the bleakers. By repeating this experiment several times, with a fresh solution each time, identical results were obtained. It was thus concluded that no spontaneous crystallization would occur in the solution provided the supersaturation level was less than 0.5°C.

It is known that inorganic salts in aqueous solutions exhibit a characteristic known as initial breeding. Initial breeding is the formation of crystal nuclei that occurs when an air dried crystal is placed in a supersaturated solution without physical contact of the crystal and any other solid object. The crystal nuclei are believed to form from crystal dust that falls from the dry crystal when it is immersed in the supersaturated solution. These secondary nuclei proceed to grow in the supersaturated solution.

The following procedure was used to determine if para-dichlorobenzene crystals exhibited initial breeding. A crystal was taken directly from the reagent container and glued to a glass rod. The crystal was then placed without contact into a 60% para-dichlorobenzene and 40% ortho-dichlorobenzene solution which was cooled to a supersaturation of 0.2°C. After 2 min the crystal was removed and the solution was restoppered and left at a constant supersaturation of 0.2°C for 2 hr. A large number of minute crystals were visible in the bottom of the bleaker after this 2 hr period. Results obtained from several trials indicate that para-dichlorobenzene crystals do exhibit initial breeding.

Since initial breeding does occur with para-dichlorobenzene, it is important that the seed crystals used in contact nucleation experiments be cured. Preceding the curing process, a seed crystal was removed from its storage under water, dried off, glued to a glass rod, and then allowed to set for 1 hr to insure bonding between the crystal and the glass rod. The seed crystal was then cured by placing it in an undersaturated solution of about 0.5°C until its edges become slightly rounded. This process usually took 15 s to 1 min.

The seed crystal, which was still attached to the glass rod, was removed from the undersaturated solution. It was immediately placed without contact into one of the two fleakers containing the supersaturated solution. The crystal was allowed to remain in the 0.2°C supersaturated solution for 2 min. It was then removed, the bleaker was resealed, and the solution remained at virtually the same supersaturation level (0.2°C) for 2 hr. This allowed any nuclei formed to grow to a discernable size.

The same seed crystal was then placed in the undersaturated solution and cured in the same method previously described. The crystal, still attached to the glass rod, was then placed in the solution contained in the second fleaker and contacted by one of three methods: (1) gently sliding along the bottom of the vessel, (2) tapping softly against the bottom of the vessel, or (3) carefully rubbing a glass rod along the side of the crystal. The solution was left at the same supersaturation of 0.2°C for 2 hr so any nuclei formed could grow to an observable size.

After 2 hr the number of nuclei in the solution where contact of the seed crystal took place and in the solution where the seed crystal was immersed without contact were counted.

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RESULTS AND DISCUSSION

Solubility data for the chlorobenzene isomers were obtained from the Dow Chemical Company via a private communication. At a solution concentration of 60% para- and 40% orth-dichlorobenzene, by weight, a slight variation was noted between the solubility data provided by Dow and the solubility data observed by the authors of this paper. The solubility data obtained by the authors were about 0.8°C higher than the data provided by Dow for the aforementioned concentration. This discrepancy was carefully investigated using a calibrated thermometer with an accuracy of ±0.05°C. This observation was important, since a supersaturation level of 0.6°C was the largest supersaturation level the solution would support before spontaneous, homogeneous nucleation would occur.

Although the organic solution, in the absence of any seed crystals, could be supercooled 0.6°C before any homogeneous nucleation would occur, crystallization occurred at lower levels of supersaturation if a crystal were present but uncontacted in the solution.

Using the experimental procedure previously described, a crystal attached to a stirring rod could be placed without contact into a solution supersaturated from about 0.3° to 0.6°C with the result that many nuclei would be formed; however, if the same procedure is repeated at a lower supersaturation level (less than about 0.3°C), no nuclei are formed. What was observed to happen was that at the higher supersaturation level (0.3° to 0.6°C), the crystal growth rate was quite great with dendritic growth occurring. Being mechanically weak, these dendrites, owing to their mass, broke away from the parent crystals and fell to the bottom of the vessel giving birth to a host of progeny. This phenomenon was described as needle breeding by Mason and Strickland-Constable (1963). At supersaturation levels less than about 0.3°C, the growth rate was reduced and dendritic growth didn't occur, so no nucleation of the noncontacted crystal occurred.

Experiments performed at a supersaturation level of about 0.2°C with no crystal contact resulted in no nuclei being formed. If at this same supersaturation level the seed was slid along or tapped softly against the bottom of the vessel or carefully rubbed with another glass rod, formation of new crystals always resulted. Qualitatively, it was observed that the greater the force of contact between the crystal and the solid object it was being contacted with, the larger the number of crystals formed. Generally, the number of crystals produced by the gentle contacting procedures were in the range of two to six.

It can therefore be concluded that para-dichlorobenzene crystals in solutions of para- and ortho-dichlorobenzene do exhibit the phenomena of initial breeding, needle breeding, and contact nucleation similarly to aqueous solutions of inorganic salts, aqueous solutions of citric acid, and benzophenone from its melt.

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The Effect of Single Stationary Objects Placed in the Fluid Stream on Mass Transfer Rates to the Tube Walls

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Mass transfer rates to tube walls or to single spheres, cylinders, and other objects suspended in the flowing stream have been studied extensively. However, the effect of objects placed in tubes on mass transfer to the walls, to our knowledge, has not been investigated. The interaction of the wake formed by the body with the boundary layer at the tube wall affects the local mass transfer rates and deserves further attention. This phenomenon of wake—boundary layer interaction is interesting from the fundamental point of view. At the same time, its better understanding may lead to improved performance (design) of related process equipment.

The objective of this work was to investigate the effect of stationary geometrical objects placed into a fluid stream on the mass transfer rates to the wall of a cylinder through which the fluid is flowing. The presence of a single stationary body in the fluid is reflected on mass transfer due to the reduction of the free cross section, that is, increase of the flow velocity around the body, and due to the wake formed beyond the body. Both effects should increase the mass transfer rate. By applying the adsorption method to the study of mass transfer in such cases, one could expect to obtain not only discrete, local values of mass transfer, but also a complete image of this complex diffusion field.

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