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TECHNICAL NOTE

Effect of Sonication on Crystal Properties

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ABSTRACT

Ultrasonic irradiation resulting in acoustic cavitation was employed during the partial crystallization of diphenyl oxide and dimethyl phenyl carbinol from their respective crude melts. The crystals obtained showed improved purity and better olefactory values for both compounds. This was confirmed by melting point measurements and image analysis of the crystals thus obtained. The beneficial effect of ultrasonic irradiation on the resultant properties is explained on the basis of the theory of acoustic cavitation.

INTRODUCTION

Partial crystallization is an important operation in the chemical industry as a method of purification and for providing product material of the desired size. The various methods used for crystallization include cooling, dilution with a nonsolvent, salting out, slow evaporation, from a solvent, and sublimation. Some of these methods require additional solvents and extra equipment, and they also pose the problem of recovery of the solvents used. Power ultrasound is known to be useful in a large number of applications in chemical, physical, and biological fields (1). Ultrasound in crystallization has been used to speed up the rate of nucleation of sucrose, D-fructose, and sorbitol (2), and also to induce nucleation in crystallization systems (3). This has been found to give crystals of uniform size and texture, useful in the food industry.

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Crystallization involves two steps: nucleation and crystal growth. In the nucleation period, microscopic crystals are formed which then grow to macroscopic size during the growth stage. The size of the individual crystals produced will depend on the total number of nuclei formed during the nucleation stage, the time, the degree of supersaturation, and the final temperature and pressure of the system. Efficient nucleation leads to a larger number of small crystals; poor nucleation gives rise to fewer and larger crystals.

In the present work, crystallization of diphenyl oxide (DPO) and dimethyl phenyl carbinol (DPC) (Herdillia Chemical Ltd, India) was carried out from a crude melt by using an ultrasonic horn (DAKSHIN, 22 kHz, 240 W electrical power). DPO and DPC are used as fragrance components for perfuming soaps, and thus the purity, and hence the olefactory value, is of prime importance.

EXPERIMENTAL

The experimental setup is shown in Fig. 1. In case of DPO, the crude liquid was placed in a beaker and kept in an ice bath. The temperature of the liquid was maintained at 13°C. The whole assembly was then mounted on a magnetic stirrer. Crystallization was carried out by gentle agitation for about 40–45 minutes in an ice bath. After this time, the melt turned turbid. This turbidity indicated the nucleation stage. Cooling was continued, and after a further 15 minutes a few crystals appeared. They

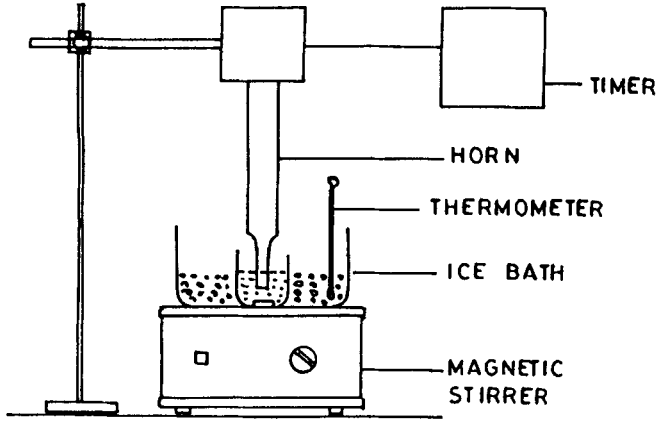

FIG. 1 Experimental setup.

were filtered and stored at a temperature below their melting point. The second set of experiments was identical except that when the solution turned turbid, the solution was irradiated with ultrasound for 45 seconds. This resulted in a substantial reduction in the turbidity with a simultaneous rise in the temperature to 15–16°C. On cooling, the liquid turbidity reappeared at a greater intensity. This was repeated 4 or 5 times, with the extent of turbidity increasing after every sonication step. Then the crystals were allowed to grow. The crystals were filtered and stored. In the third set of experiments, sonication was continued during the crystal growth stage. The crystals obtained were again filtered and stored. The crystals obtained under each of the crystallization procedures were tested for their melting point and were observed under a microscope.

In the case of DPC, seeding was done to facilitate crystallization because it was not possible to crystallize the crude material even at −1°C. Seeding was done while maintaining the melt temperature at 20°C. At the onset of crystallization, sonication was begun. The crystals obtained were filtered by decanting the mother liquor. The melting points of the crystals at various times of sonication were compared with those of crystals obtained in the absence of ultrasound.

RESULTS AND DISCUSSION

Table 1 shows the observations made during measurement of the DPO melting point. The melting point of the crystals obtained by sonication is higher and nearer to the reported melting point of pure DPO (26.8–28°C)

TABLE 1
Diphenyl Oxide: melting point (4) = 26.8–28°C

Crystal sample	Observed melting point (°C)	Comments
Without sonication	24–28	About 55% crystals melt before 27°C. Balance 45% melt between 27 and 28°C
Sonication during nucleation stage	25–28.5	About 35% crystals melt between 25 and 27°C. About 65% crystals melt between 27 and 28.5°C
Sonication during nucleation and crystal growth	25–28.5	About 15% crystals melt between 25 and 27°C. About 85% crystals melt between 27 and 28.5°C

(4). The crystals obtained during both stages of sonication (nucleation and growth) showed considerable improvement in purity (as assessed by the melting point increase). The preliminary olefactory analysis also indicated the improved fragrance value for the same crystals, although subjective nature of this conclusion needs to be considered in detail. Table 2 shows similar results for DPC. The trends reported earlier are also confirmed for this chemical.

Microscopic observations of crystals collected by various crystallization techniques indicated that the crystals obtained in the absence of ultrasound consisted of tiny lumps which agglomerated in a highly random arrangement. The proportion of needle-shaped crystals (the shape reported for pure DPO) was almost negligible, whereas the crystals were thin, long, and needle shaped in the presence of ultrasound (at nucleation only). The agglomerates consisted of thin, long needles arranged in a definite, ordered pattern. The proportion of randomly arranged lumps was very small. When ultrasound was applied in both the nucleation and crystal growth stage, the crystals were of the same shape as above (at the nucleation stage) but of much smaller size (40 to 60% smaller). The agglomerates were not needle shaped but were square or rectangle shaped. The tiny, needle-shaped microcrystals came together in a definite and ordered pattern.

A possible explanation for the observed phenomena is as follows. Sonication is known to induce acoustic cavitation in the liquid. These cavities or vapor bubble during collapse (during the compression part of the acoustic cycle), and develop very high temperatures and pressures. The duration of these hot-spot is a few nanoseconds. These hot-spots have low

TABLE 2
Dimethyl Phenyl Carbinol: Melting Point (5) = 35–37°C

Crystal sample	Melting point (°C)	Comments
Without sonication	21–26	50% melt between 21–24°C. Balance melt between 24 and 26°C
15 seconds sonication	23–32	50% melt between 23 and 25°C. Balance melt between 25 and 32°C
2 minutes sonication	24–33	50% melt between 24 and 26.5°C. Balance melt between 26.5 and 33°C
5 minutes sonication	29–34.5	50% melt between 29 and 31°C. Balance melt between 31 and 34.5°C

melting point impurities, probably due to their short duration. Continued sonication will reduce the concentration of low melting point impurities in the grown crystal, thus improving the crystal purity. Quantitative work is underway to optimize the sonication conditions (intensity and duration) to obtain optimum purity of a crystallized chemical, and the effect of the sonication field on the overall solid crystal field.

CONCLUSIONS

Ultrasound during crystallization was found to be beneficial for improving the quality and purity of DPO and DPC. The crystals obtained upon sonication have a higher melting point compared to those in the absence of sonication, indicating higher purity. The results from image analysis confirmed the favorable effect of ultrasonic irradiation on crystallization.

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