In discussing the threshold, we begin by noting that a calculation (Erickson, 1978) of the shape and volume of deposited droplets indicates that coalescence across the *solid* surface must have occurred at D-levels well below D_c in each case—e.g., see Figure 3a. Nonetheless, flux data suggest that fluid failed to enter or cover the pores until $D \gtrsim D_c$. Scanning electron micrographs (Erickson, 1978) also support this conclusion and, moreover, indicate that 5 μm pores were essentially completely full at $D \gtrsim D_c$. One is led, then, to envision cases for $D > D_c$ and $D < D_c$ as drawn schematically for small and large pores in Figure 4. These diagrams help to explain why the 0.8 μm pores would yield an abrupt drop in flux, while with $d = 10$ μm only a gradual flooding of the pores would occur as $D > D_c$. In the latter case, one expects that complete pore conclusion would occur only when $D >> D_c$, and that local occlusion could occur in random fashion so that repeatability would be poor; both these predictions are borne out by Figure 3b.

Despite the qualitative success of this picture, there is still no satisfactory explanation as to why the unexpected threshold at D_c should exist at all. It is, perhaps, worth noting that the product $d \times D_c$ is nearly constant; its value ranges only from 20 to 30×10^{-10} kg/m in Figures 2-3, while d varies 12-fold and D_c 9-fold. This observation has important implications, in general, for the filling of porous surfaces by aerosol liquid deposition. It means that small-pore surfaces (e.g., when plant stomates are small or nearly closed) will be difficult to occlude, and very high D will be necessary to achieve significant flux reduction. In practice, the use of spray droplets larger than d would occlude pores if a direct superposition occurs, but spreading into neighboring pores still might not result. This is probably the case for most agricultural film-forming *AT*'s in the past.

We suggest that further research with *AT* surface chemistry should be productive, inasmuch as D_c is surely sensitive to these properties. It is also likely, because of d-dependence, that successful products and delivery systems may have to be specifically matched to the stomata sizes of individual crops. Finally, as an immediate practical matter, it may be important that *VO* works well as an *AT* and is cheap enough (Erickson, 1978), and its films stable enough, so that it may be directly usable as an environmentally acceptable *AT* at the present time.

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NOTATION

AT	= antitranspirant
d	= diameter of pore in membrane; μm
D	= deposition density of AT on membrane surface (an average); kg/m^2
D_c	= critical, or threshold, value of D above which some reduction of transmission of vapor is noted; kg/m^2
VO	= vegetable oil

LITERATURE CITED

Anderson, J. E. and F. Kreith, *Plant and Soil*, **49**, 161 (1978).

Angus, D. E. and H. Bielorai, "Transpiration Reduction by Surface Films," *Aust. J. Agric. Research*, **16**, 107 (1965).

Davenport, D. C., P. E. Martin, and R. M. Hagan, "Aerial Spraying of Phreatophytes with Antitranspirant," *Water Resources Research*, **12**, 991 (1976).

Davenport, D. C., K. Uriu, and R. M. Hagan, "Effects of Film Antitranspirants on Growth," *J. Exp. Botany*, **25**, 410 (1974).

Erickson, C. M., "Development of an Antitranspirant," M. S. Thesis, University of California, Berkeley, CA (1978).

Fisher, M. A. W. and T. L. Lyon, "Antitranspirant Film Detection by Scanning Electron Microscopy of Cathodoluminescence," *HortScience*, **7**, 245 (1972).

Gale, J. and R. M. Hagan, "Plant Antitranspirants," *Ann. Rev. Plant. Physiol.*, **17**, 269 (1966).

Keller, K. H. and T. R. Stein, "A Two-Dimensional Analysis of Porous Membrane Transport," *Math. Biosci.*, **1**, 421 (1967).

Meyer, B. S., D. B. Anderson, and R. H. Bohning, *Introduction to Plant Physiology*, Van Nostrand, New York (1960).

Waggoner, P. E. and N. C. Turner, "Transpiration and Its Control by Stomata in a Pine Forest," *Conn. Agric. Exp. Sta. Bull.*, #726 (1971).

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Secondary Nucleation of Citric Acid due to Fluid Forces in a Couette Flow Crystallizer

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INTRODUCTION

Because of its importance in suspension crystallization processes, much recent effort has been directed toward investigating the phenomenon of secondary nucleation. Recent developments based on the results of single crystal experiments have revealed that secondary nucleation by collision breeding is the dominant nucleation mechanism (Botsaris and Denk, 1972; Strickland-Constable et al., 1969, 1972; McCabe and Coworkers, 1971, 1972; Larson and Bauer, 1974). The methods of the population balance, as formulated by Randolph and Larson

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(1962, 1971), have been widely used to determine nucleation characteristics in a stirred tank configuration. Ottens et al. (1972) and Evans et al. (1974) have successfully combined the results of these independent approaches to describe nucleation kinetics due to collision breeding in suspension crystallizers.

To determine to what extent fluid mechanical shear forces induce secondary nucleation has led to experiments described by Sung, Estrin and Youngquist (1973, 1974). These have demonstrated that fluid shear forces can induce secondary nucleation in a magnesium sulfate-water solution and that classical nucleation theory may be used to treat the experimental data. Evans, Margolis and Sarofim (1974) have studied the nucleation of ice in a brine solution by using a mixed suspension crystallizer and have estimated that as much as 25% of the nucleation may be caused by fluid shear. The secondary nucleation produced by fluid forces using a jet of brine solution upon a polycrystalline mass of ice has also been carried out by Estrin, Wang and Youngquist (1975), and a similar technique has been demonstrated for the potassium alum-water system by Jagannathan et al. (1980). In the study of fluid shear induced nucleation using a single crystal technique, it was found necessary to provide a region of undercooling greater than that contiguous to the parent crystal, to effect development of the nuclei.

The object of this work is to study the phenomenon of fluid shear induced secondary nucleation in a citric acid-water system using a Couette flow crystallizer. The fluid shear forces were generated by rotating the inner cylinder of the Couette flow apparatus. The number of nuclei produced due to fluid shear was observed primarily as a function of solution subcooling at the citric acid seed.

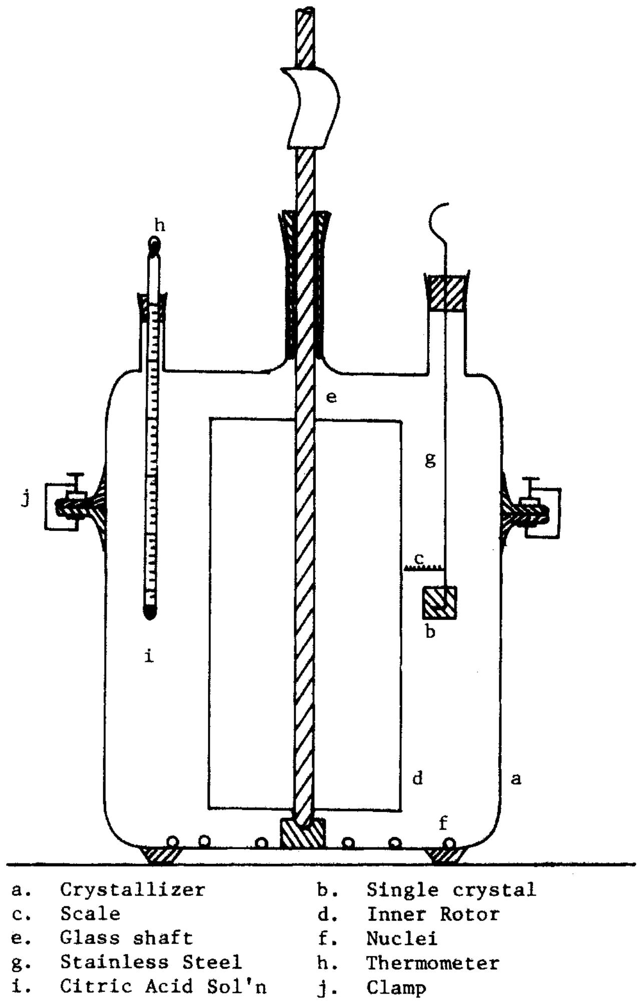

Figure 1. Schematic diagram of couette flow crystallizer.

EXPERIMENTAL APPARATUS AND PROCEDURE

The nucleation experiments were carried out in a Couette flow crystallizer which consisted of an outer stationary cylinder made of Pyrex glass, and an inner rotating cylinder, made of acryl. The schematic diagram of the experimental apparatus is shown in Figure 1. It is through the rotation of the inner cylinder (6 cm OD, 10 cm height) that fluid mechanical shear forces were produced and a well-mixed solution of uniform temperature maintained within the crystallizer. There were three ports on the top of the outer cylinder (12 cm ID, 16 cm height): one for the introduction of the seed, and the other two for insertion of a Beckman thermometer and the rotor shaft. The citric acid seed was about one cubic centimeter in size and was grown on a small L-shaped stainless steel holder, similar to the method of Sung, Estrin and Youngquist (1973). The crystallizer was immersed in a Plexiglass rectangular tank whose water contents were maintained at constant temperature.

In preparation for a run, citric acid solution of desired concentration was prepared by dissolving citric acid crystals of high purity in distilled water. The saturation temperature was determined by observing the surface of seed crystal in the solution through a microscope; at the saturation point, a crystal neither grows nor dissolves in the solution and this point is readily determined to within 0.1°C. To start an experiment, the solution in the crystallizer was heated to about 5°C above the saturation point for one night to ensure that all solid citric acid crystals were dissolved. Then both the crystallizer and the water bath were maintained at a temperature which was 2°C above the saturation point. A seed crystal was pretreated by immersing it in distilled water for about 2 minutes and then introduced carefully into the crystallizer for 1/2 hour. Then the desired operating temperature was obtained by adjusting the temperature of water bath for about 1 hour when thermal equilibrium was obtained. The agitator was operated at a known RPM, between 480 and 1660 RPM, for 30 seconds. In this range, the Taylor number criterion for Couette flow (Taylor, 1935) revealed that the flow was turbulent. After this cooling water was circulated through the bath to lower the temperature of the crystallizer contents until it was 15°C below that of the saturation temperature. The number of nuclei generated and their quality were observed over a period of about 30-90 minutes. The agitation speed, and the distance between the seed crystal and the stirrer, as observed microscopically, were recorded.

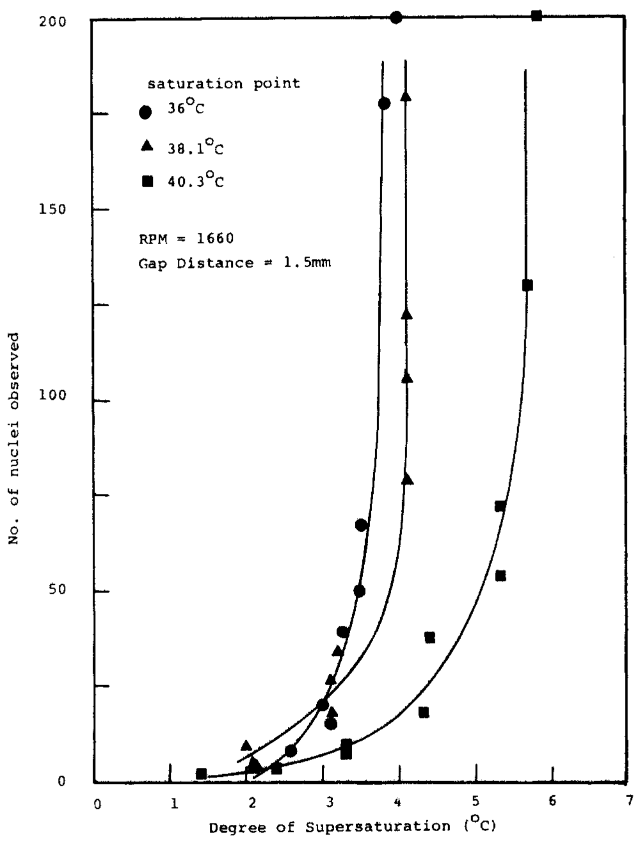

Figure 2. Relation of no. of nuclei with saturation point of citric acid.

TABLE 1. EXPERIMENTAL DATA

Run No.	Sat'd Temp. (°C)	Run Temp. (°C)	Subcooling, ΔT (°C)	Gap distance (mm)	RPM	No. of nuclei observed	Remark
1	38.1	23.1	15	—	1660	0	(Blank Test overnight)
2	38.1	23.1	15	1	1660	0	(dummy, overnight)
3	38.1	36.1	2	1.5	1660	9	
4	38.1	36	2.1	1.5	1660	3	
5	38.1	34	4.1	1.5	1660	105	
6	38.1	35	3.1	1.5	1660	18	
7	38.1	36	2.1	1.5	1660	4	
8	38.1	36	2.1	1.5	1660	4	
9	38.1	36	2.1	—	1660	0	Blank Test
10	38.1	35.1	3	1.5		4	Slower RPM
11	38.1	34.9	3.2	1.5	1660	34	
12	38.1	34.9	3.2	1.5	1660	0	Kept at 34.9°C for 1 Hr
12a	└→					6	Cooled to 23°C
13	38.1	35.1	3	1.5	1660	0	Kept at 35.1°C for 1 Hr
13a	└→					15	Cooled to 23°C
14	38.1	36.8	1.3	1.5	1660	0	
15	38.1	34	4.1	1.5	1660	79	
16	38.1	34	4.1	3	1660	39	
17	38.1	34	4.1	0.7	1660	105	
18	38.1	34	4.1	3	1660	29	
19	38.1	34	4.1	0.5	1660	172	
20	38.1	34	4.1	0.5	1660	122	
21	38.1	36	2.1	0.5	1660	19	
22	38.1	35	3.1	0.5	1660	68	
23	38.1	35	3.1	1.5	480	4	
24	38.1	35	3.1	1.5	1160	15	
25	38.1	35	3.1	1.5	2100	27	
26	38.1	35	3.1	1.5	600	11	
27	38.1	35	3.1	1.5	810	20	
28	38.1	35	3.1	1.5	980	23	
29	38.1	35	3.1	1.5	1160	26	
30	38.1	35	3.1	1.5	1160	22	
31	38.1	35	3.1	1.5	1660	25	
32	38.1	35	3.1	1.5	1800	28	
33	38.1	35	3.1	1.5	2100	28	
34	38.1	36	2.1	0.5	1660	7	
35	40.3	35	5.3	1.5	1660	72	
36	40.3	35	5.3	1.5	1660	54	
37	40.3	34	6.3	1.5	1660	over 400	
38	40.3	37	3.3	1.5	1660	9	
39	40.3	37.9	2.4	1.5	1660	3	
40	40.3	38.9	1.4	1.5	1660	2	
41	40.3	35.9	4.4	1.5	1660	38	
42	40.3	36	4.3	1.5	1660	18	
43	40.3	37	3.3	1.5	1660	7	
44	40.3	37	3.3	1.5	1660	8	(Rotating for 1 min.)
45	40.3	34.6	5.7	1.5	1660	130	
46	36	33	3	1.5	1660	20	
47	36	32.2	3.8	1.5	1660	177	
48	36	34	2	1.5	1660	0	
49	36	32	4	1.5	1660	over 200	
50	36	32.5	3.5	1.5	1660	67	
51	36	32.75	3.25	1.5	1660	39	
52	36	32.5	3.5	1.5	1660	50	
53	36	33.4	2.6	1.5	1660	8	

RESULTS AND DISCUSSION

The results of the present experiments show that fluid shear can induce secondary nuclei of citric acid from aqueous solution. As shown in Table 1, Runs 1 through 34 were carried out at a saturation temperature of 38.1°C, Runs 35 to 45 at a saturation temperature of 40.3°C, and Runs 46 to 53 at a saturation temperature of 36°C. The number of nuclei generated within the crystallizer strongly depended on the subcooling of solution, the saturation temperature, and the agitation speed. The results are plotted in Figure 2 and indicate the strong relationship between the number of nuclei observed and the subcooling of the citric acid. This finding is consistent with the results of Sung, Estrin and Youngquist for the $MgSO_4 \cdot 7H_2O$-water system.

To verify that the secondary nucleation of citric acid from supersaturated solution was not caused by macro-dendrites, an experiment was carried out in which the surface of a growing seed crystal was carefully observed through a microscope. It was found that no evidence of dendritic growth existed on the surface of the parent crystal even when the temperature of the solution was 15°C below saturation.

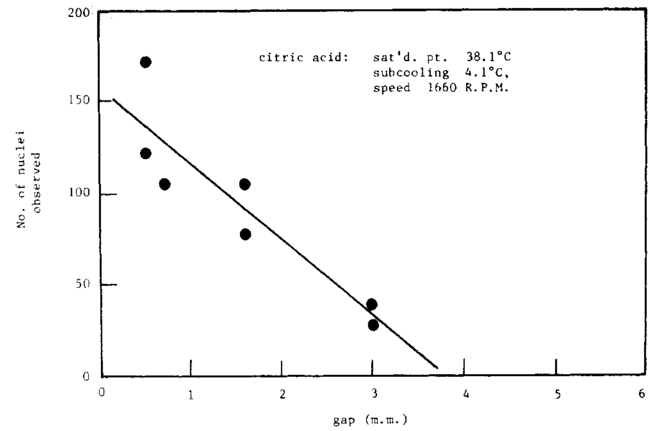

Figure 3. Relation of no. nuclei with gap distance.

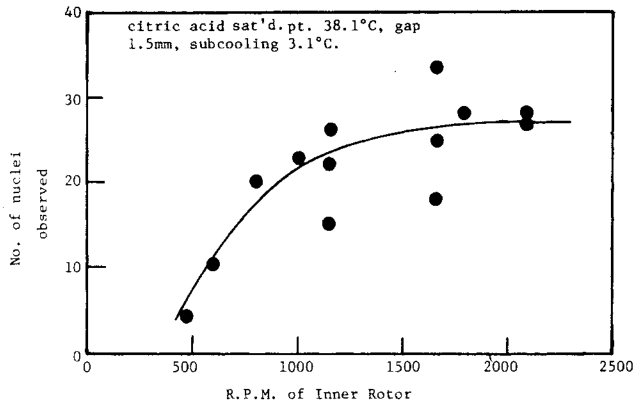

Figure 4. Relation of no. of nuclei with R.P.M. of inner rotor.

The purpose of the present study was to investigate the occurrence of secondary nuclei of citric acid subject to shear forces in a supersaturated solution. Therefore, a major requirement was the elimination of initial breeding and it was found that the pretreatment procedure was adequate. Experiments were carried out in the absence of the seed crystal and no nucleation occurred even when the crystallizer development was extended to an overnight period. These results show that homogeneous and heterogeneous nucleation do not occur and the new particles observed originate due to the seed crystal. Another requirement was the demonstration that the shear field is necessary. A cured crystal was located in the unagitated, supersaturated solution for a period of over five hours. No nucleation occurred even though the undercooling was 8° to 10°C. Above about 10°C the crystal grew more unevenly and was certainly polycrystalline; below this level, though, no major difference in growth behavior was observed.

The effect of fluid mechanical shear intensity between the seed crystal and the stirrer upon the generation of nuclei is shown in Figures 3 and 4. In Figure 3, it is seen that the number of nuclei generated is greater when the distance is smaller. This is readily explained by the fact that fluid shear is greater at the smaller separation distances. The number of nuclei generated within the crystallizer as a function of agitation speed is shown in Figure 4 and the trend is clear that increased speed increases the number of product nuclei—again confirming the influence of fluid shear. However, Figure 4 does suggest that the number of nuclei generated becomes independent of rotational velocity as it increases above about 2000. This is in accordance with the results of Sikdar and Randolph (1976) who found that the rate of citric acid nucleation was independent of RPM in a continuous stirred tank operation.

From the results indicated by Runs 12-13 in Table 1, it is shown that no nuclei are generated when the original 3°C undercooling was retained after the period of agitation for as long as one hour, that is, no subsequent increased subcooling is provided. Six nuclei were then obtained in Run 12a, and fifteen nuclei in Run 13a, after the solution temperature was eventually decreased to 23°C, an undercooling of 15°C. This demonstrates that a relatively severe undercooling is required to effect the survival of the species initially generated by the shear field at the seed. This "survival" characteristic is also in agreement with the observations of Sung et al. (1974) and Jagannathan et al. (1980). In addition, there are several runs (Runs 6, 7, 18, 26 and 31) which are carried out for 3-4 hours before termination of the each run. No difference in counting the number of nuclei generated within the crystallizer around 90 minutes or waiting several hours after agitating the stirrer.

It is found that, with the same degree of subcooling, the time for appearance of the nuclei at a lower temperature was greater than that at a higher temperature. For example, the time needed for observing the appearance of secondary nuclei in Run 38 was about 1/2 of the time needed in Run 51. However, it appears that the number of nuclei surviving or generated are fewer at the higher temperature. If one anticipates that the number generated should be at least the same at the higher temperature, it appears that the kinetics of survival dominate the number actually observed when comparing results of experiment, carried out at different temperature levels.

LITERATURE CITED

Bauer, L. G., M. A. Larson and V. J. Dallons, "Contact Nucleation of $MgSo_4 \cdot 7H_2O$ in a Continuous MSMPR Crystallizer", *Chem. Eng. Sci.*, **29**, 1253 (1974).

Botsaris, G. D. and E. G. Denk, "Crystallization, I & E C Annual Reviews", 337 (1972).

Clontz, N. A. and W. L. McCabe, "Contact Nucleation of Magnesium Sulfate Heptahydrate", CEP Symp. Series, Vol. 67, No. 110, 6 (1971).

Denk, E. G. and G. D. Botsaris, "Mechanism of Contact Nucleation", *J. of Crystal Growth*, **15**, 57 (1972).

Estrin, J., M. L. Wang and G. R. Youngquist, "Secondary Nucleation Due to Fluid Forces Upon a Polycrystalline Mass of Ice", *AIChE J.*, **21**, 392 (1975).

Evans, T. W., G. Margolis and A. F. Sarofim, "Mechanisms of Secondary Nucleation in Agitated Crystallizers", *AIChE J.*, **20**, 950 (1974).

Jagannathan, R., C. Y. Sung, G. R. Youngquist and J. Estrin, "Fluid Shear Secondary Nucleation of Magnesium Sulfate and Potassium Aluminum Sulfate", AIChE Symposium Series, Vol. 76, No. 193, 90 (1980).

Johnson, R. F., R. W. Rousseau and W. L. McCabe, "Factors Affecting Contact Nucleation", AIChE Symp. Series, Vol. 68, No. 121, 31 (1972).

Lal, D. F., R. E. A. Mason and R. F. Strickland-Constable, "Collision Breeding of Crystal Nuclei", *J. of Crystal Growth*, **5**, 1 (1969).

Ottens, E. P. K., A. H. Janse and E. J. DeJong, "Secondary Nucleation in a Stirred Vessel Cooling Crystallizer", *J. Crystal Growth*, **13/14**, 500 (1972).

Randolph A. D., and M. A. Larson, "Transient and Steady State Size Distributions in Continuous Mixed Suspension Crystallizers", *AIChE J.*, **8**, 639 (1962).

Randolph A. D., and M. A. Larson, "Theory of Particulate Processes", Academic Press, NY (1971).

Sikdar, S. K. and A. R. Randolph, "Secondary Nucleation of Two Fast Growth Systems in a Mixed Suspension Crystallizer: Magnesium Sulfate and Citric Acid Water Systems", *AIChE J.*, **22**, 110 (1976).

Strickland-Constable, R. F., "The Breeding of Crystal Nuclei—A Review of this Subject", AIChE Symp. Series, Vol. 68, No. 121, 1 (1972).

Sung, C. Y., J. Estrin and G. R. Youngquist, "Secondary Nucleation of Magnesium Sulfate by Fluid Shear", *AIChE J.*, **19**, 957 (1973).

Sung, C. Y., G. R. Youngquist and J. Estrin, "Secondary Nucleation by Fluid Shear", Paper presented at Joint AIChE/GVC Meeting, Munich (1974).

Taylor, G. I., "Distribution of Velocity and Temperature Between Concentric Rotating Cylinders", *Proc. Roy. Soc., A.*, **151**, No. 874, 494 (1935).

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