Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

A Study of the Size Distribution and Stability of Colloidal Gas Aphrons Using a Particle Size Analyzer

P. G. Chaphalkar[a]; K. T. Valsaraj[a]; D. Roy[a]
[a] DEPARTMENTS OF CIVIL AND CHEMICAL ENGINEERING, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA

To cite this Article Chaphalkar, P. G. , Valsaraj, K. T. and Roy, D.(1993) 'A Study of the Size Distribution and Stability of Colloidal Gas Aphrons Using a Particle Size Analyzer', Separation Science and Technology, 28: 6, 1287 — 1302
To link to this Article: DOI: 10.1080/01496399308018037
URL: http://dx.doi.org/10.1080/01496399308018037

SEPARATION SCIENCE AND TECHNOLOGY, 28(6), pp. 1287–1302, 1993

A Study of the Size Distribution and Stability of Colloidal Gas Aphrons Using a Particle Size Analyzer

P. G. CHAPHALKAR, K. T. VALSARAJ, and D. ROY*
DEPARTMENTS OF CIVIL AND CHEMICAL ENGINEERING
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA 70803

ABSTRACT

Application of colloidal gas aphrons (CGA) in decontaminating soils and aqueous solutions is one of the emerging innovative technologies. This paper addresses the size distribution and stability of CGAs as studied by using a particle size analyzer. Cationic, anionic, and nonionic surfactants were used to generate the CGAs. Size distribution spectrum and volume fraction of microbubbles in sample solutions were studied as functions of time. The effects of surfactant concentrations used to produce CGAs and the presence of an electrolyte, such as sodium chloride, on the characteristics of the suspension were also studied.

INTRODUCTION

The name "colloidal gas aphron" (CGA) was originally proposed by Sebba for microgas dispersions (1). Initially, Sebba generated CGA dispersions by using a Venturi flume (1). Later, he developed another efficient method to produce CGAs in large quantities (2). The most striking feature of a CGA suspension is its stability. CGAs are stable enough to be pumped from the point of generation to the point of application.

CGAs have been shown to be useful in a variety of environmental applications. They are more effective than conventional sparged air in the separation of organics from aqueous waste streams (3). CGAs have also been used in the microflotation of colloids and in the removal of heavy metal ions from wastewater using precipitate flotation (4–6). The ability of CGAs to adhere and be retained as small bubbles in various saturated and subsurface matrices has been demonstrated by Michelsen et al. (7).

*To whom correspondence should be addressed.

They observed 60% degradation of phenol after a combination of CGAs and *Pseudomonas putida* was injected into a contaminated sand matrix.

The fundamental properties of CGAs were studied and discussed by Sebba (8). He hypothesized that the encapsulating soap film has an inner as well as an outer surface and that these surfaces have surfactant monolayers adsorbed on them (Fig. 1). The encapsulation of a microbubble in a double layer of surfactant molecules, as observed with CGAs, retards its coalescence, thereby increasing its stability. "Stability" of a microbubble dispersion can be defined as the length in time over which the number of bubbles and their size distribution remain constant. CGA dispersions, if left undisturbed, will eventually cream and be converted to ordinary foam, leaving a clear aqueous layer below. In studies thus far, the stability of CGAs was measured by rapidly transferring about 200 mL of CGA suspension into a 250-mL cylinder. The volume of liquid drained was measured with respect to time and interpreted in terms of life or stability of CGAs (9). These observations, however, did not take into account the stability of a CGA dispersion when mixed in an aqueous system. In practice, CGAs

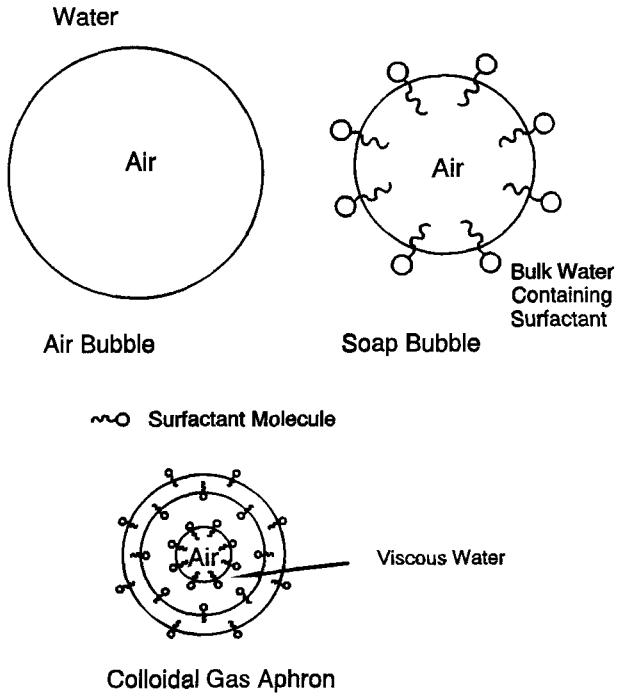

FIG. 1 Structure of an air bubble, a soap bubble, and CGA.

have to be pumped into a solution for the purpose of separation or flotation, and therefore a study of their stability is important under conditions when CGAs are pumped and mixed with an aqueous stream.

Various techniques have been applied to determine the diameter of a microbubble in solution. Amiri and Woodburn (10) carried out an analysis of the rate of rise of CGA bubbles in a measuring cylinder and showed that it is equivalent to that of hindered rising of a 35-μm spherical bubble with a 0.75-μm outer shell. Photographic techniques have also been used for the determination of bubble sizes (11, 12). In these techniques the bubbles were observed in the plane of contact between them and the glass wall. Longe (9) studied bubble size distributions in CGA suspensions and factors affecting their distribution. He examined bubbles in a specially designed cell under a microscope. However, his observations did not incorporate changes in size distribution patterns with time. When introduced into an aqueous system, CGAs in the dispersion undergo variation in both size and number density with time because of coalescence and/or creaming. So far, these dynamic changes have not been addressed in the literature.

The shortcomings of the above methods can be overcome by using a particle size analyzer to examine the size and stability of CGAs. Particle size analyzers, when equipped with a flow-through cell, allow us to add CGA samples in a mixing chamber. The mixed solution is then circulated continuously through a "viewing" cell where a laser beam is utilized to monitor the bubbles in the system. The analyzer allows us to collect data periodically, enabling the determination of size distribution as a function of time. The samples can thus be mixed with water, and the dynamic nature of the bubble size distribution can be determined in an aqueous environment to simulate the use of CGAs in flotation columns.

This study presents the results of size distribution and stability analysis of CGAs generated from cationic, anionic, and nonionic surfactants in concentrations above, below, and near their critical micellar concentration (CMC) values. The effect of the ionic strength of the solution on the characteristics of CGA was also studied.

EXPERIMENTAL

Surfactants

CGAs were generated using Tergitol 15-S-12 (Union Carbide), sodium dodecylbenzene sulfonate (Sigma), and hexadecyltrimethylammonium bromide (Eastman Kodak). Tergitol is a nonionic surfactant that has an average chain length of 15 carbon atoms with a CMC value of 0.15 mM (MW = 738). Sodium dodecylbenzene sulfonate (DDBS) is a salt of dodecylbenzene sulfonic acid with a chain of 12 carbon atoms. It is an anionic

surfactant with a CMC value of 1.5 mM (MW = 348.5). Hexadecyltrimethylammonium bromide (HTAB) is a cationic surfactant with a chain of 16 carbon atoms and has a CMC value of 0.9 mM (MW = 364.6).

Production of CGAs

Based on methods suggested by Sebba (2), a unit was fabricated in our laboratory for the production of CGAs. A 0.5-hp motor was fitted on top of a 3-L cylindrical container (Fig. 2). A flat disk, 50 mm in diameter, was mounted at the end of a shaft. The level of the surfactant solution was initially adjusted to be approximately 15 mm above the disk which can rotate up to 8000 rpm. Two flat baffles were fixed to the lid of the container. The disk, when rotated at very high speeds, creates strong waves on the liquid surface. The waves strike the baffles, and upon reentering the so-

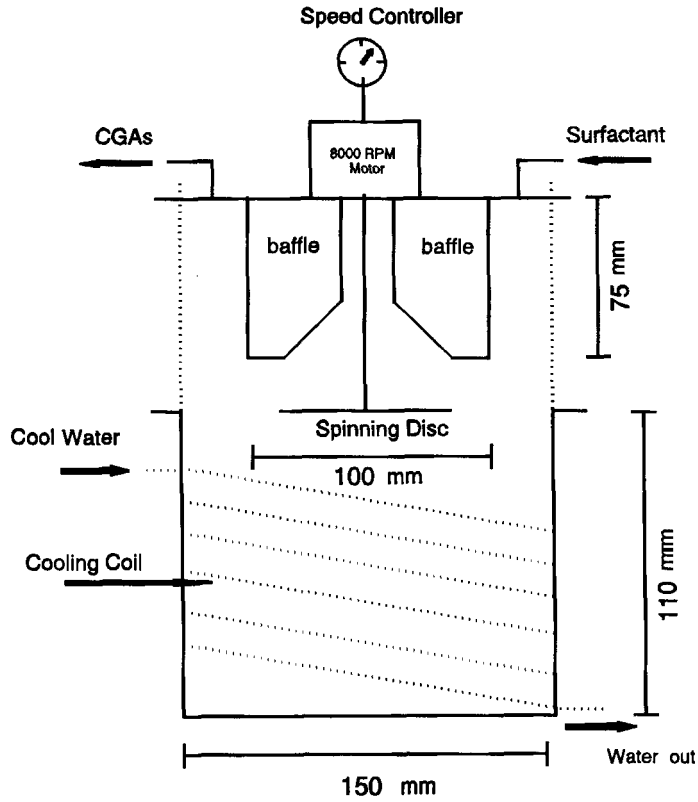

FIG. 2 Schematic drawing of CGA generator.

lution they entrain air in the form of a microbubble dispersion or colloidal gas aphrons (CGA).

Size Distribution of CGAs

Size distribution of CGAs was determined using a particle size analyzer (Microtrac 7995-10, Leeds and Northrup). The analyzer can "sense" objects such as droplets, soil particles, and bubbles. It utilizes a low angle, forward scattering laser beam projected through a viewing cell through which the sample is circulated. The amount and direction of light scattered by the particles is processed by an optical filter and directed to a photodetector. Electrical signals proportional to the transmitted light are processed by a microcomputer to form a multichannel histogram of particle size distribution in terms of the volume of particles in each of the channels. The output also provides volume mean diameter and standard deviation, percentile range of the diameter, and mean area of the particles. The analyzer covers a particle size range from 1.6 to 300 μm. A CGA suspension (50 mL) was added to the mixing chamber which held approximately 275 mL. The solution from the mixing chamber was circulated by a centrifugal pump through the viewing cell. The particle size analyzer was set to analyze the sample repetitively every 2 minutes.

RESULTS AND DISCUSSION

Structure of a CGA

Figure 1 illustrates the differences in the structures of an air bubble, a soap bubble, and a gas aphron. An air bubble in pure water can be treated as a cavity enclosed by water. When surfactant molecules are present in water, any cavity introduced in water creates a water–gas interface where surfactants are adsorbed. In the case of colloidal gas aphrons, the encapsulating soap film has an inner as well as an outer surface, and both these surfaces have surfactant monolayers adsorbed on them. These layers can be treated as expanded monolayers and consist largely of water, which has properties different from the bulk water because of enhanced hydrogen bonding. The sandwiched layer can therefore be treated as a different phase from the bulk water since surfactant molecules at this surface have hydrophilic ends pointing inward and hydrophobic ends pointing outward. Further, there is an interface between that phase and the water, with the hydrophobic ends facing the soapy shell.

The encapsulation of a colloidal gas aphron in a double layer of surfactant molecules retards its coalescence because when two aphrons collide, the momentum may not be enough to break the barrier of the six intervening surfactant-stabilized interfaces before the bubbles can coalesce.

Parameters of Particle Size Analysis

The volume of sample material in the circulating system that is used for an analysis is referred to as the "sample loading." The analyzer responds to this laoding and reports its measurement as a dimensionless number, V_s. A typical plot of V_s versus mass/volume of particles or bubbles in the system is linear up to a certain value of mass in the sampling system, which depends on sample characteristics. Further addition of sample to the circulating system beyond this value gives rise to a multiple scattering-attenuation effect, reducing the slope of the plot which then becomes nonlinear. In this study the addition of 50 mL of CGA suspension into the circulating system was found to fall within the optimum range of loading that was comparable in all cases of CGA used. The lower limit of sample loading is determined by the system noise and particle or bubble density needed to give statistically valid data. The least measurable V_s value that was reproducible was found to be approximately 0.002.

The quantity V_s was therefore used as a surrogate parameter, equivalent to the sample load in the circulating system, to determine the "stability" of the CGA suspension. In this study, "stability" of CGAs was determined as the time span for which V_s of the suspension remained measurable.

The parameter "mean diameter" (MD), which is calculated from the mean volume of the suspension, was used as a single parameter to identify the average size distribution of suspension. This was necessary because the size distribution of CGA at any given time varies over a wide range and it would be very difficult to extract useful information from the data collected. Figure 3 shows size distribution curves for DDBS near its CMC value at 2-minute intervals. It was also observed that the MD for the same surfactant remained more or less stable (Fig. 4), which further strengthens our argument that it can be used as a single parameter in characterizing the size distribution of a CGA suspension.

Microbubble Size Distribution

In an earlier work, Sebba (8) reported that the aphrons seem to be largely composed of bubbles between 10 and 30 μm in diameter. However Longe recently found (9) that the majority of bubbles diameters range approximately between 10 and 130 μm, with a mean value for all test conditions between 51 and 61 μm (Table 1). These studies were conducted at static conditions under a microscope where the CGAs were drawn into a viewing cell.

The results of the present study, along with the results of Longe (9), are presented in Table 1 for comparison. It was found that in our system, wherein a CGA suspension was pumped into a mixing chamber and cir-

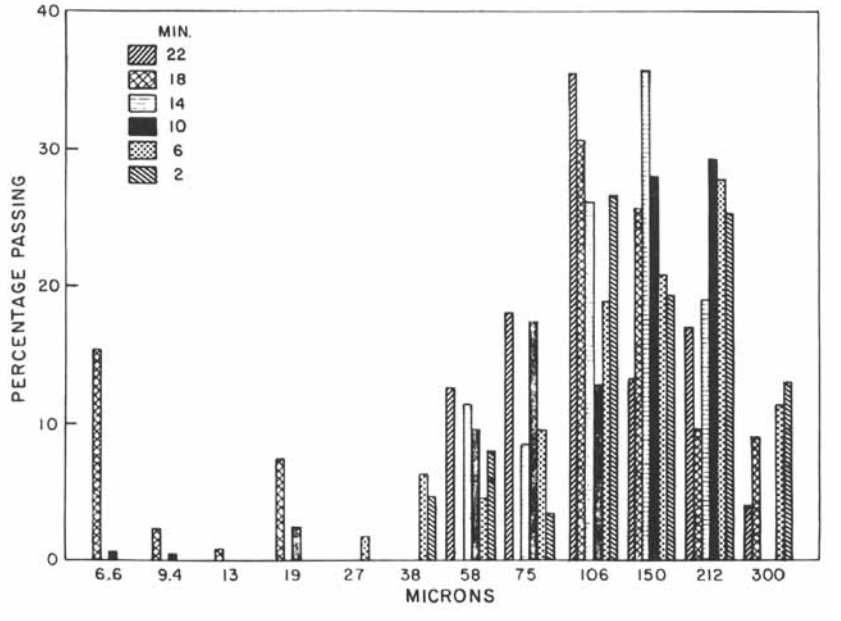

FIG. 3 Size distribution of CGAs at different times for DDBS (500 mg/L).

culated through a viewing cell, the range of microbubble size distribution was much wider than previously reported. A majority of the bubbles were found to have diameters between 30 and 300 μm, rarely falling below 30 μm. The mean diameter was found to e characteristic of the surfactant, as the following discussion will demonstrate. The standard deviation of bubble diameter varied between 50 and 77 μm for ionic surfactants and between 29 and 35 μm for the nonionic surfactant. When introduced into an aqueous system, CGAs in the dispersion undergo variation in size and number with time because of coalescence and/or creaming, and these effects are reflected in our study, which shows larger bubble sizes with a wider distribution than reported earlier. It should be noted that particle size analysis is a direct measurement of the bubble sizes at that particular time, and therefore it is a reliable measure of the size ranges.

Effects of Surfactant Type

Figure 4 shows the V_s and mean diameter of CGA suspension plotted versus time for all three surfactants at their CMC values. It reveals that the variation in the range of mean diameter of the CGAs was specific to the surfactant. Mean diameter of CGAs generated with sodium *dodecyl-*

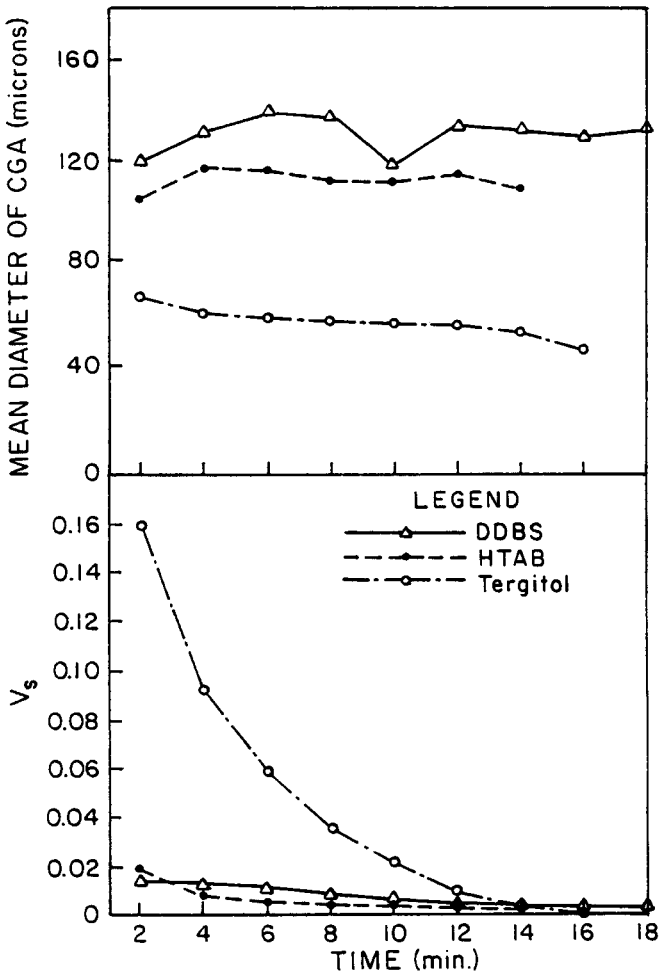

FIG. 4 Changes in CGA characteristics due to different surfactants (concentration near CMC).

benzene sulfonate (DDBS) ranged between 118 and 138 μm, while for hexadecyltrimethylammonium bromide (HTAB) the range was between 104 and 117 μm. For Tergitol, the mean diameter ranged from 46 to 66 μm.

It was noted that V_s, the surrogate parameter for the volume occupied by the bubbles in the circulating system, and its decay with time also remained specific to the surfactant. At time $t = 2$ minutes, CGAs generated

TABLE 1
Comparison of CGA Size Distributions[a]

Solution	Size distribution (9)				Particle size analyzer results[b]			
	Minimum	Mean	Maximum	Standard deviation	10%	50%	90%	Standard deviation
DDBS, 200 mg/L	13	61	129	29	50	123	244	66
DDBS, 500 mg/L	14	61	120	25	54	124	194	64
DDBS, 500 mg/L, + NaCl, 200 mg/L	12	57	107	24	44	98	187	73
DDBS, 750 mg/L			NA		46	112	198	77
DDBS, 1000 mg/L	15	53	104	22			NA	
Tergitol, 50 mg/L			NA		31	58	106	29
Tergitol, 100 mg/L			NA		32	57	128	34
Tergitol, 100 mg/L, + NaCl, 200 mg/L			NA		32	58	123	32
Tergitol, 500 mg/L			NA		35	64	126	33
Tergitol, 1000 mg/L	14	51	98	21	34	63	112	30
HTAB, 200 mg/L			NA		52	152	258	70
HTAB, 328 mg/L			NA		46	105	186	65
HTAB, 328 mg/L, + NaCl, 200 mg/L			NA		42	83	171	50
HTAB, 500 mg/L			NA		50	112	200	63

[a]All sizes are in microns.
[b]The percentile distribution reported is at $t = 2$ minutes.

with Tergitol had the largest V_s value while HTAB and DDBS had V_s values that were comparable. Interestingly, the "stability," defined as the time span for which V_s of the suspension remained measurable, was found to be unaffected by the initial value of V_s and remained nearly similar. In short, it appeared that CGAs generated from all three surfactants had comparatively similar degrees of stability but Tergitol CGAs had a larger air content than the other two surfactants at $t = 2$ minutes. Since there are no net charges on CGAs generated from nonionic surfactants, collective surface repulsive forces on the bubble are probably smaller, which may

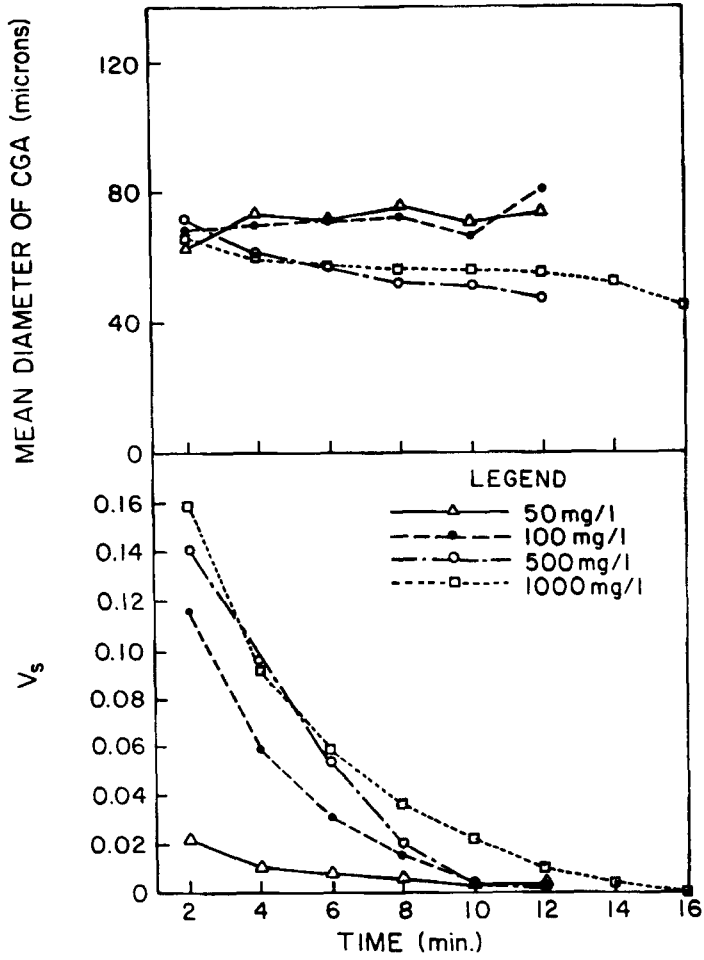

FIG. 5 Effects of surfactant concentration on the characteristics of CGA (surfactant Tergitol).

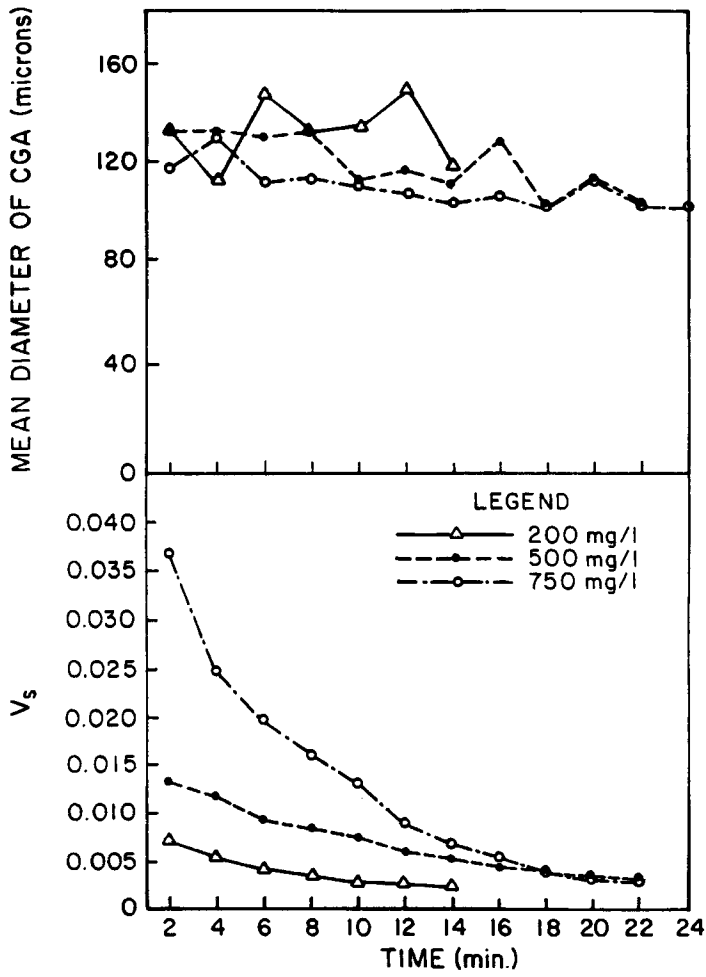

FIG. 6 Effects of surfactant concentration on the characteristics of CGA (surfactant DDBS).

allow bubbles to get closer, thus increasing the entrapped air volume. The data reflect that the bubbles generated from a nonionic surfactant will be compressed, and consequently they will be of smaller diameter compared to bubbles generated from ionic surfactants.

Effects of Surfactant Concentration

The concentration of surfactant in solutions used to generate CGAs was thought to be likely to influence the characteristics of microbubble dis-

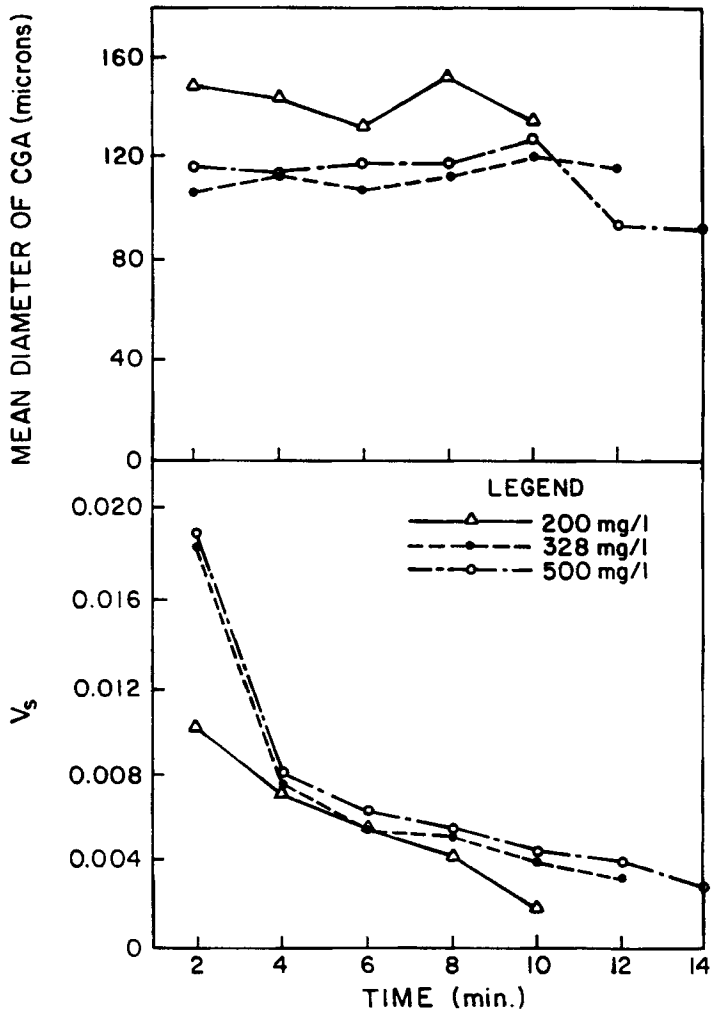

FIG. 7 Effects of surfactant concentration on the characteristics of CGA (surfactant HTAB).

persions. To study this effect, CGAs were genrated using three types of surfactants at concentrations below, near, and above CMC levels. The results are presented in Figs. 5–7. In general, it was found that an increase in the concentration of the surfactant increased V_s and increased the stability of the suspension. The increase in V_s, was found to be specific to each surfactant. However, an increase in initial V_s did not increase the stability of CGA proportionately. Since decay of the bubbles in the cir-

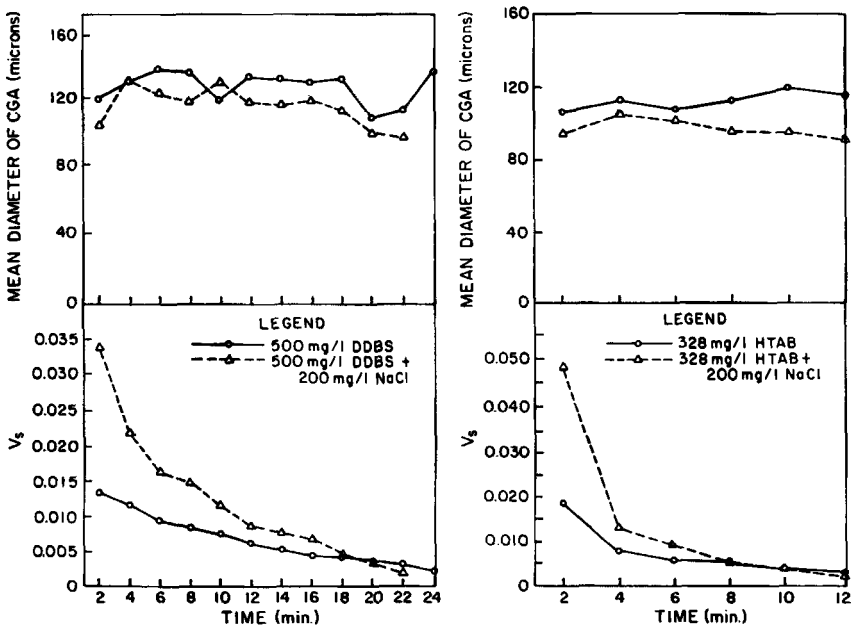

FIG. 8 Effects of NaCl on the characteristics of CGA (ionic surfactants).

culating system was approximately exponential, the bubbles remained in suspension only a few minutes longer.

Longe (9) reported that increasing the concentration of DDBS beyond CMC only slightly influenced CGA characteristics. However, in this study, increasing the concentration of DDBS from 500 to 750 mg/L was found to increase V_s almost threefold. Interestingly, in the case of HTAB the increase in concentration beyond CMC did not influence V_s (Fig. 7). Similar results were seen in the case of Tergitol (Fig. 6) where an increase in V_s was found to be only marginal for an increase in concentration from 100 to 500 mg/L; furthermore, the initial V_s was found to be nearly equal for concentrations 500 and 1000 mg/L. In practice, the parameter V_s can therefore be utilized to determine the optimum concentration of surfactants that would yield maximum air entrapment for the application of CGAs.

The increase in concentration, however, tended to reduce the mean diameter of the suspension of all three surfactants (Figs. 5–7). This observation follows the logic that an increase in the numbers of surfactant molecules beyond a certain value tends to crowd them on the microbubble surfaces, thereby reducing the interfacial tension between the bubble and

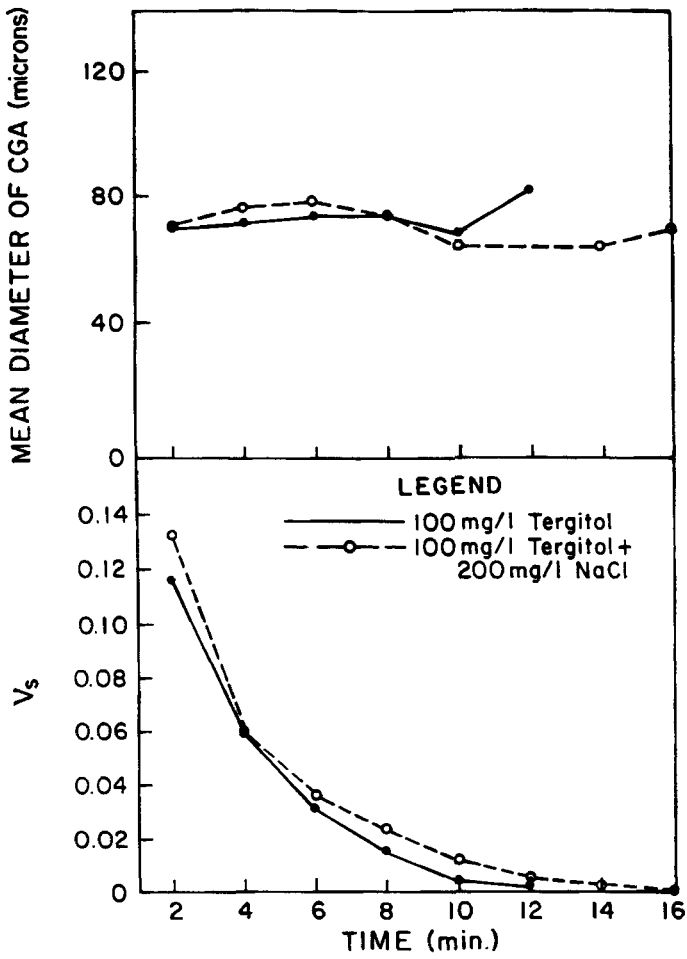

FIG. 9 Effects of NaCl on the characteristics of CGA (nonionic surfactant Tergitol).

the bulk water. Reduction in the interfacial tension would therefore reduce the bubble size.

Effects of Ionic Concentration

Figure 8 shows the effect of the addition of 200 mg/L NaCl on CGAs generated from ionic surfactants with concentrations near their CMC. For ionic surfactants (DDBS and HTAB), the presence of salt increased their V_s in the system and reduced the mean diameter of the suspension. These results are a direct consequence of the ionic nature of the encapsulating

film. The presence of ions in a CGA solution generated from an ionic surfactant would compress the film surrounding the bubble, shrinking its diameter. The increase in V_s can also be attributed to this factor (Fig. 8). In contrast, the properties of CGA made from the nonionic surfactant (Tergitol) were not affected by the ionic strength of the solution (Fig. 9).

CONCLUSIONS

The usefulness of a particle size analyzer is demonstrated in analyzing the size distribution and stability of CGAs. Microscopic analysis of the suspension, as carried out by earlier researchers, assessed the properties of CGAs at the time of generation, but particle size analysis carried out in a continuous flow cell gives a clue about the stability and size distribution under realistic conditions in real time. When introduced into an aqueous system, CGAs in a dispersion undergo variation in sizes and numbers with time due to coalescence and/or creaming. These dynamic changes can be addressed by using particle size analysis such as the one utilized in this study.

The parameters mean diameter (MD) and V_s, which is equivalent to the bubble volume fraction in the circulating system, were used to characterize CGAs produced under different conditions. The results were considerably different from those reported earlier. CGA size was found to have a wide range of values. MD of the suspension was found to be characteristic of the surfactant. In general, it was found that an increase in the concentration of surfactant increased both V_s and the stability of the suspension but reduced the mean diameter of CGAs. The increase in V_s was also found to be specific to the surfactant. The effect ions in the solution used for the generation of CGAs revealed the ionic nature of the encapsulating film around the bubbles. The presence of an electrolyte was found to affect only the characteristics of CGAs produced from the ionic surfactants, whereas no effect was observed on CGAs generated from a nonionic surfactant.

ACKNOWLEDGMENTS

Drs. Roy and Valsaraj thank the Louisiana Education Quality Support Fund for financial support [Grant LEQSF (1989–1992)-RD-B-07].

REFERENCES

1. F. Sebba, *J. Colloid Interface Sci.*, *35*, 643–646 (1971).
2. F. Sebba, *Chem. Ind.*, p. 91 (1985).

3. M. Caballero, R. Cela, and A. A. Perez-Bustamente, *Sep. Sci. Technol.*, *24*, 629–640 (1989).
4. O. J. Gregory, S. M. Barnett, and F. J. DeLuise, *Ibid.*, *15*, 1499–1512 (1980).
5. S. Ciriello, S. M. Barnett, and F. J. Deluise, *Ibid.*, *17*, 521–534 (1982).
6. F. Sebba and S. M. Barnett, "Separations Using Colloidal Gas Aphrons," *Proceedings of the Second World Congress of Chemical Engineering*, *IV*, 27 (1981).
7. D. L. Michelsen, D. A. Wallis, and F. Sebba, *Environ. Prog.*, *3*, 103–107 (1984).
8. F. Seba, *Investigations of the Contaminant Capture in CGA (MGD) Foams*, Report to U.S. Department of the Interior, Office of Water Resources and Technology, OWRT/RU-82/10, 1982.
9. T. A. Longe, Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 1989.
10. M. C. Amiri and E. T. Woodburn, *Trans. Inst. Chem. Eng.*, *68*, 154–160 (1990).
11. H. C. Cheng and R. Lemlich, *Ind. Eng. Chem., Fundam.*, *22*, 105–109 (1983).
12. A. J. De Vries, in *Adsorptive Bubble Separation Techniques* (R. Lemlich, Ed.), Academic Press, New York, 1972, pp. 7–31.

Received by editor May 11, 1992