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

Characterization of Colloidal Gas Aphron Suspensions Generated from Plant-Based Natural Surfactant Solutions

R. R. Kommalapati[a]; D. Roy[b]; K. T. Valsaraj[c]; W. D. Constant[d]
[a] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISANA, USA [b] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING, POLYTECHNIC UNIVERSITY, BROOKLYN, NEW YORK, USA [c] DEPARTMENT OF CHEMICAL ENGINEERING, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, USA [d] DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING HAZARDOUS SUBSTANCE RESEARCH CENTER (S & SW), LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, USA

To cite this Article Kommalapati, R. R. , Roy, D. , Valsaraj, K. T. and Constant, W. D.(1996) 'Characterization of Colloidal Gas Aphron Suspensions Generated from Plant-Based Natural Surfactant Solutions', Separation Science and Technology, 31: 17, 2317 — 2333

To link to this Article: DOI: 10.1080/01496399608001050

URL: http://dx.doi.org/10.1080/01496399608001050

SEPARATION SCIENCE AND TECHNOLOGY, **31**(17), pp. 2317–2333, 1996

Characterization of Colloidal Gas Aphron Suspensions Generated from Plant-Based Natural Surfactant Solutions

R. R. KOMMALAPATI
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISANA 70803, USA

D. ROY
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING
POLYTECHNIC UNIVERSITY
BROOKLYN, NEW YORK 11201, USA

K. T. VALSARAJ*
DEPARTMENT OF CHEMICAL ENGINEERING
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA 70803, USA

W. D. CONSTANT
DEPARTMENT OF CIVIL AND ENVIRONMENTAL ENGINEERING

HAZARDOUS SUBSTANCE RESEARCH CENTER (S & SW)
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA 70803, USA

ABSTRACT

Colloidal gas aphron (CGA) suspensions generated using commercial surfactants are found to have great potential in the remediation of contaminated soils and waste streams. A plant-based natural surfactant solution prepared from the fruit pericarps of *Sapindus mukorossi* was used in this study to generate CGA suspensions. The CGA suspensions generated from this surfactant solution have size distributions similar to those of commercial surfactants. The stability of the CGA suspensions generated with natural surfactant solutions was observed to be

---

* To whom correspondence should be addressed.

higher than those generated using synthetic surfactants. However, the quality or the gas fraction of the suspensions is lower for a natural surfactant solution than that for commercial surfactants. The crude solution of natural surfactant prepared using simple water extraction contains saponins, the essential surface-active agent, and many other extraneous natural organic compounds. Yet, the CGA suspensions prepared from the crude solution seem to be comparable to those generated using synthetic surfactants in size distribution and stability.

INTRODUCTION

An innovative technology shown to have potential for in-situ soil flushing is the use of microbubbles or colloidal gas aphron (CGA) suspensions. Research on CGA generation and application has been extensive in recent years (1–4). A CGA dispersion typically contains about 65% gas and is classified as Kugelschaum foam. The CGA size is typically 25–300 μm. These microbubbles do not coalesce easily and are markedly different from conventional soap bubbles in their stability and flow properties. CGA suspensions have viscosities similar to water, which make them suitable for pumping without deterioration in quality. Two important considerations in the application of CGA suspensions are: 1) their colloidal size, resulting in a large surface area to volume ratio, and 2) the existence of a double film of surfactant encapsulating the gas that retards the coalescence of the bubbles. CGA suspensions are found to be very effective for separating hydrophobic organic compounds from aqueous waste streams (2, 5). Soil flushing of residual nonaqueous phase liquids and other hydrophobic organic compounds with CGA suspensions has been promising (1, 3, 4). CGA suspensions were also employed for transporting microorganisms into the porous media to enhance in-situ biodegradation of contaminated soils (6, 7).

CGA suspensions can also be generated from suitable natural surfactants. To date there has been no reported research on application of plant-based natural surfactants for hazardous waste remediation. However, surfactants derived from plants belonging to the genus *Sapindaceae* have been traditionally used as a soap substitute for fabric washing and bathing (8, 9). Fruit pericarps of *Sapindus mukorossi*, a widely grown plant in India and other tropical and subtropical regions of Asia, are used to prepare these natural surfactant solutions. These are locally known as Soapnut or Ritha in the Indian subcontinent. The recorded use of this natural surfactant as a washing soap does not cite any toxic effects on human skin or eyes (10). Saponins, which are complex glycosides, impart the surface-active properties of these natural surfactants. Several researchers tried to isolate and identify the saponins from the fruit pericarps of the plants of genus *Sapindus* (11–13). The saponin content was determined to be 10.1% of the weight of the pericarp and 6.1% based on the weight of the fruit (11). Extraction with water has been the most common method for preparing natural surfactant solutions from the fruit pericarps due to its simplicity and modest cost of operation. These natural surfactant solutions were shown to have great potential in the remediation of contaminated soils (14). The preparation and characterization and application of natural surfactant solutions are discussed elsewhere (14).

In this study, CGA suspensions are generated using the plant-based natural surfactant solutions, and their size distribution and stability are determined. The results are compared to those generated with commercial surfactants. The effect of the presence of electrolyte on the CGA size distribution is also investigated.

MATERIALS AND METHODS

Sapindus mukorossi (Ritha)

Dry fruits of *Sapindus mukorossi* were procured from the city of Calcutta, India. The fruits are golden brown in color and globular in shape, with diameters ranging from 1 to 3 cm. Seeds were removed from the fruit, and the pericarps were dried in an oven at 50°C for about 2 days. The pericarps were ground and sieved through a US standard #20 sieve (840 μm). The dry powder was stored in amber glass bottles with air-tight screw caps to prevent photodegradation and contact with atmospheric moisture.

Preparation of Natural Surfactant Solutions

The dry natural surfactant powder was weighed and added to deionized water. Ten grams of the powder was added to 100 mL of water and the mixture was stirred for 3 hours at room temperature. The un-extracted residue was separated using a cloth, and the liquid was centrifuged at 10,000 rpm for 45 minutes at room temperature. The supernatant was filtered through a prefilter, followed by a 0.45-μm filter. Appropriate concentrations were then prepared from this stock solution.

Size Distribution of CGA Suspensions

A unit was developed in our laboratory for generating CGA suspensions from surfactant solutions (3–5). The size distribution of CGA suspensions was determined using a Microtrac model 9210 standard range particle size analyzer (Leeds and Northrup, North Wales, PA). The analyzer has a range from 0.69 to 704 μm. The sample was added manually to the reservoir, and the sample was mixed with the recirculating liquid so that a stream of well-dispersed particles passes continuously through the transparent sample cell for analysis. About 10 mL of sample was added to the reservoir, which holds about 300 mL of water. The analyzer was set to measure the particle size every 2 minutes.

Stability and Quality of CGA Suspensions

The stability was measured in terms of half-life, the time required for half of the liquid content to drain (1). This was measured by transferring about 250 mL of CGA suspension into a 250-mL graduated cylinder and monitoring the drainage with time. The quality of CGA suspensions defined as the gas fraction was calculated from the final liquid volume and the total volume.

RESULTS AND DISCUSSION

Typical size distribution of colloidal gas aphron suspensions is shown in Fig. 1 (a, b, and c) for three concentrations of the plant-based natural surfactant, 0.1, 0.5, and 1.0% (w/w) respectively. As can be seen from the figure, the size distribution follows a pattern with most of the CGA having sizes in the range of 30 to 100 μm. The CGA bubbles, during formation, are found to range from submicron to several hundred microns in size. However, with the passage of time the big bubbles disappear at the expense of small bubbles, and very small bubbles (<25 μm) tend to disappear due to interbubble gas diffusion (15). The size range of the CGA suspensions is defined using 10 and 90 percentile bubble size. The typical size range of CGA suspensions in this study is in the range of 30 to 300 μm. This range is similar to that observed by Chaphalkar (5) and much wider than that reported by Sebba (15) and Longe (1) for commercial surfactants. However, in these studies the size distribution was determined under static conditions using photomicrographic methods (1, 15). The present method uses a dynamic system where the bubbles are pumped into a mixing chamber and continuously recirculated through a viewing cell. Close examination of the figures indicate that the size distribution of CGA suspensions generated with 0.1% (Fig. a) has a much wider range than those generated with 0.5 and 1.0% natural surfactant (Figs. b and c). As will be discussed later, CGA suspensions generated with low concentrations of natural surfactant (0.1%) become increasingly unstable, promoting the formation of bigger size bubbles.

The variations of 10, 50, and 90 percentile sizes and mean volume diameter (mv) with time are shown in Fig. 2 (a and b) for CGA suspensions generated with 0.5 and 1.0% natural surfactant, respectively. Mean vol-

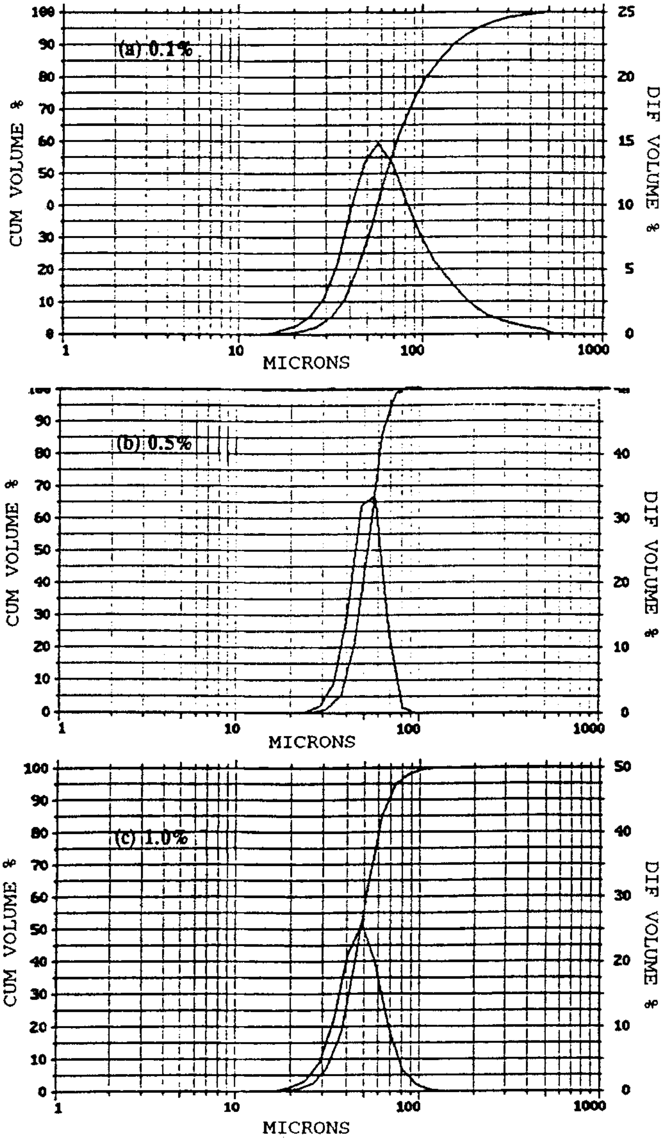

FIG. 1 Typical size distribution curves for CGA suspensions generated with (a) 0.1%, (b) 0.5%, and (c) 1.0% natural surfactant solutions.

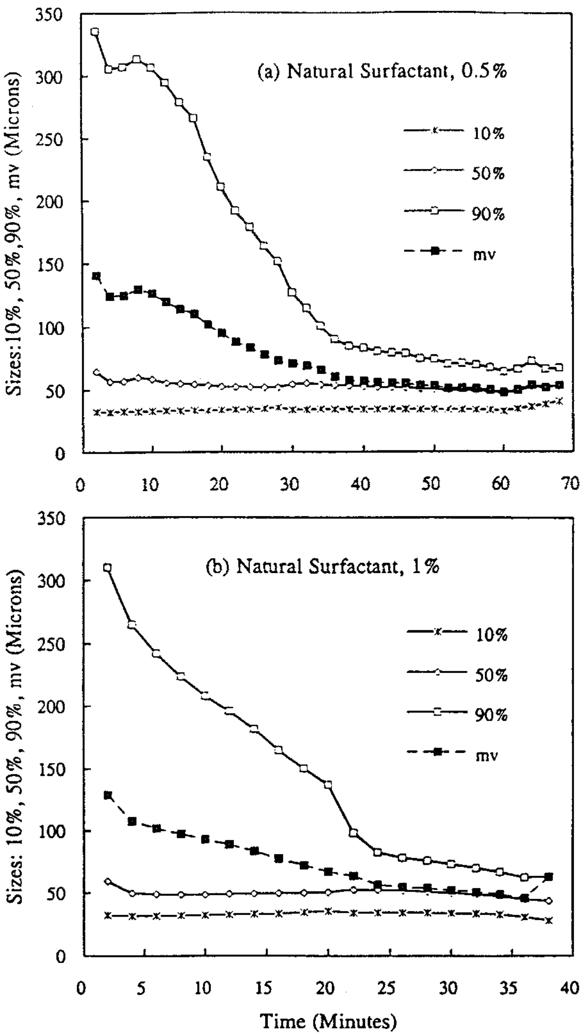

FIG. 2 Typical variation in size distribution with time for CGA suspensions generated with (a) 0.5% and (b) 1% natural surfactant solutions.

ume diameter, which is calculated based on the sample volume in the system, was used as a parameter by Chaphalkar (5) to represent the average size distribution of suspensions as this value remained stable over the period of measurement. However, the mv in this study seemed to decrease with time, and also a marked difference between the initial value and the value at the end of the run was noted (Fig. 2). However, as seen in Fig. 2, the 10 and 50 percentile sizes did not change significantly over the length of the run, indicating that the small bubbles remain stable. The 90 percentile size bubbles continually decreased in size until they stabilized at the end of the run, suggesting that the large bubbles underwent dynamic changes. This phenomenon directly influences the mv. These dynamic changes that occur over the entire range of the bubbles were not reported by earlier researchers, and hence it is necessary to discuss the variation of all the size fractions rather than just looking at the average size of the suspensions.

Another important parameter in the characterization of CGAs is the dimension-less parameter, D_v, which represents the volume of sample material in the circulating system. This is also referred as sample loading. About 10 mL of the sample was added to the mixing chamber containing 300 mL water to give a satisfactory range of loading for all the concentrations used. The sample load in the system, as indicated by the parameter D_v, starts with a high value of about 1.0–3.0 depending on the concentration of natural surfactant, and it exponentially decreases with time. The size distribution was measured until D_v reached a value of about 0.005, at which point the bubbles generally become unstable and larger (400–700 μm). When the sample loading parameter D_v reached a value of 0.01 or less, it was noted that the size distribution of CGA suspensions changed to a bimodal distribution. This bimodal distribution has one mode in the usual size range (40–60 μm) and the other at a larger size range (around 200 μm). A typical size distribution of the suspensions following a bimodal distribution is shown in Fig. 3. This type of bimodal distribution observed for CGA suspensions generated with plant-based surfactant solutions was not reported in earlier studies with commercial surfactants (1, 5, 15). As can be seen from the figure, the distributions are identical for all the 0.5, 1.0, and 1.5% concentrations of natural surfactant. About 60% of the bubbles have diameters less than 100 μm.

Effect of Concentration on the CGA Size Distribution

Figure 4 (a and b) shows the effect of surfactant concentrations on the 10 and 50 percentile sizes, respectively. As can be seen from the figure, the 10 percentile size decreased with an increase in the natural surfactant concentration but only marginally. As the surfactant concentration increased from 0.1 to 1.5%, the 10 percentile size decreased from 35.5 to 31.5 μm. A Tukey multiple comparison test with a 95% confidence level was performed to establish the statistical difference in bubble sizes generated from different surfactant concentration levels (16). An increase in

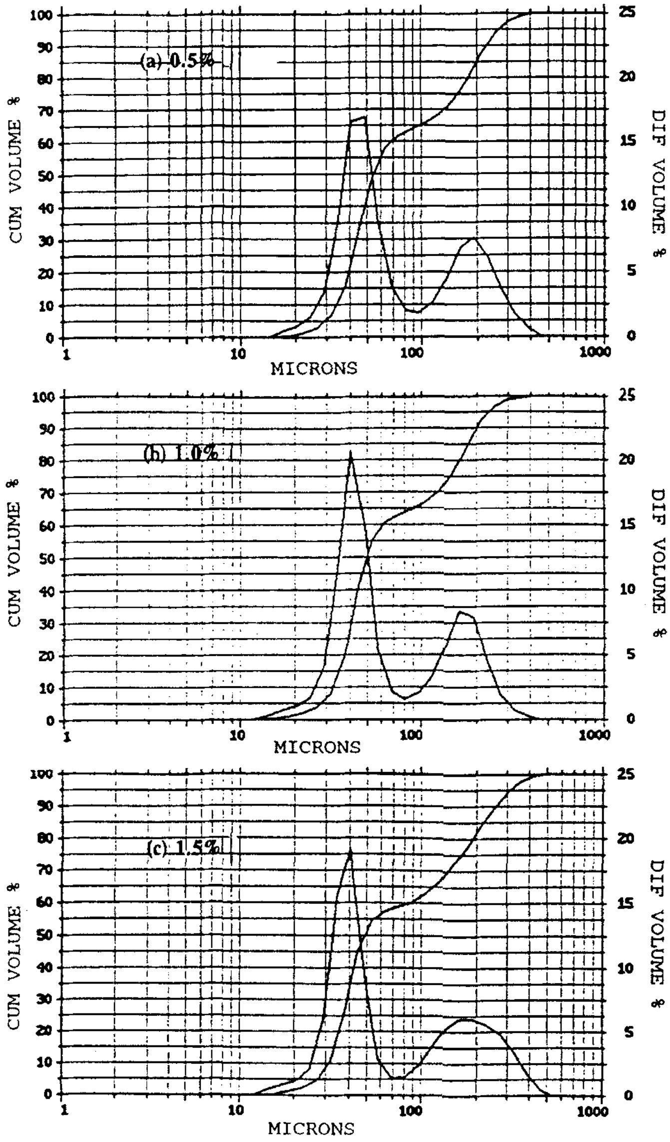

FIG. 3 Bimodal size distribution curves for CGA suspensions generated with (a) 0.5%, (b) 1.0%, and (c) 1.5% natural surfactant solutions.

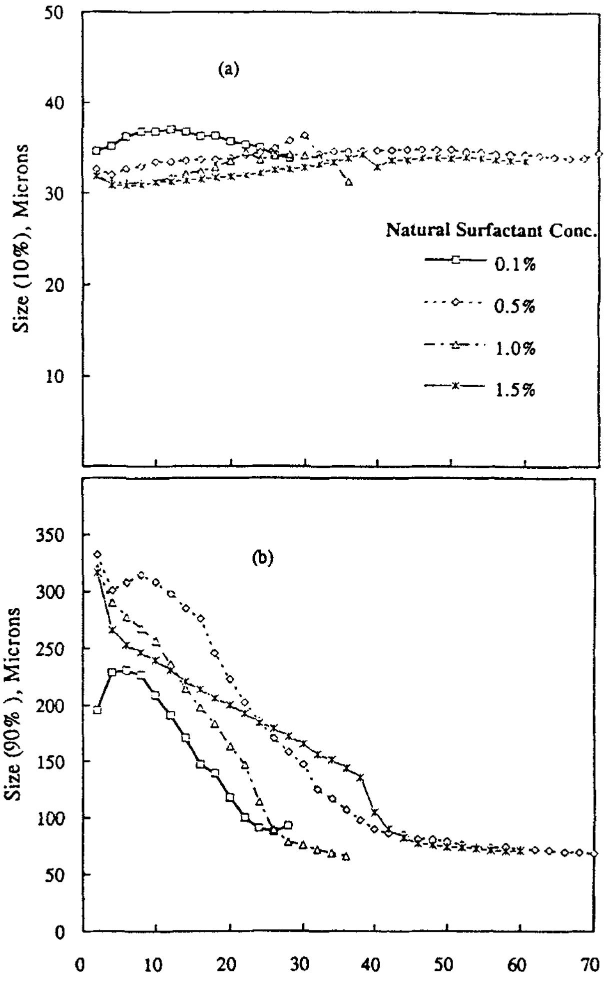

FIG. 4 Effect of natural surfactant concentration on the (a) 10 percentile and (b) 50 percentile size of CGA suspensions.

surfactant concentration up to 1.0% resulted in a significant decrease in 50 percentile bubble size. At surfactant concentrations beyond 1.0%, the 50 percentile bubble size did not significantly decrease. The CGA suspensions with a 0.1% natural surfactant concentration have the lowest 90 percentile size whereas a 0.5% surfactant concentration produced the highest 90 percentile size. The primary reason for these observations is micelle formation at the CMC, which is around 0.1% for a natural surfactant (14). The bubbles have been reported to be unstable at concentrations below the CMC due to the nonavailability of surfactant molecules to stabilize the enormous interfacial area of the microbubbles (1). The significant differences in size distribution for higher surfactant concentrations are due to the crowding of surfactant molecules on the bubble surface which in turn reduces the interfacial tension between the bubble and bulk water. This reduced interfacial tension reduces the bubble size. As the concentration of a natural surfactant increased beyond 1.5%, the CGA suspensions became very thick, which prevents air from entraining into the solution. This results in a low gas fraction (poor quality) of the CGA suspensions. However, the suspensions are very stable as indicated by the longer liquid drainage time.

The variation of sample loading parameter (D_v) with time for different concentrations of a natural surfactant is plotted in Fig. 5. As the concentration of a natural surfactant increased from 0.1 to 1%, the D_v value increased significantly. However, the change was marginal when the concentration increased from 1 to 1.5% natural surfactant. The bubbles

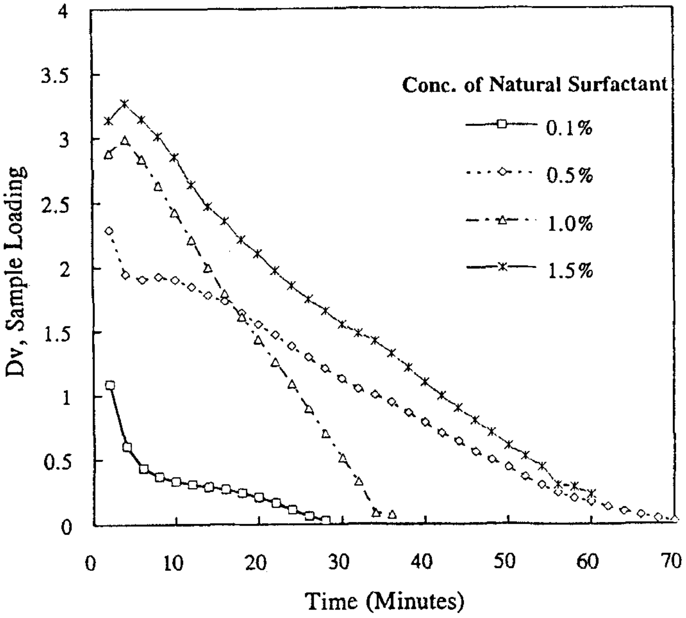

FIG. 5 Effect of natural surfactant concentration on sample loading parameter (D_v).

generated with 0.5% natural surfactant were more stable and persisted for a longer time than the bubbles generated with a low concentration (0.1%) or higher concentrations (1 and 1.5%). The D_v values decreased approximately exponentially with time for all the natural surfactant concentrations. For CGA suspensions made with natural surfactant concentrations higher than 1.5%, the D_v value was very high (about 4), and it took considerable time for the D_v value to reach 0.005 when the run was stopped. This indicates that the bubbles are stable; however, the quality (air content) of suspensions, as mentioned earlier, was very low.

Effect of Electrolytes

The effect of electrolytes on the size distribution of colloidal gas aphron suspensions was studied by adding 200 and 400 mg/L of sodium chloride to natural surfactant solutions before generating the CGA suspensions. Figure 6 (a and b) shows the effect of salt on 10 and 90 percentile sizes, respectively. It is evident from the figures that the presence of electrolyte did not affect the size of the bubbles significantly. A Tukey multiple comparison test performed with a 95% confidence level indicated no significant difference over the entire duration of the run. Lower amounts of salt (200 mg/L) used by the earlier researchers showed a decrease in the bubble size for commercial ionic surfactants. The decrease in bubble size was attributed to the adsorption of one of the ions of the salt at the interface of the bubble along with the surfactant, and that results in an increase of the effective surfactant concentration (1). However, for nonionic surfactants the electrolyte does not seem to affect the size distribution of the bubbles as the surface of the bubbles are neutral. The invariability of the different sizes due to the addition of the salt indicate that the natural surfactant solutions of *Sapindus* are likely to be nonionic in nature. We also noted that the D_v value did not change significantly at either salt concentration. However, the difference between the D_v value of the CGA suspensions generated with 200 and 400 mg/L salt appears to be significant. The D_v of CGA suspensions with 400 mg/L salt was lower than that for suspensions with 200 mg/L salt at the beginning of the run. However, the rate of change of the D_v value was lower for CGA suspensions generated with 400 mg/L. This indicates that bubbles generated with a higher concentration of salt are more stable.

Comparison with CGAs Generated from Commercial Surfactants

The size distribution of CGA suspensions generated with natural surfactant solutions were compared with that of CGAs generated from commer-

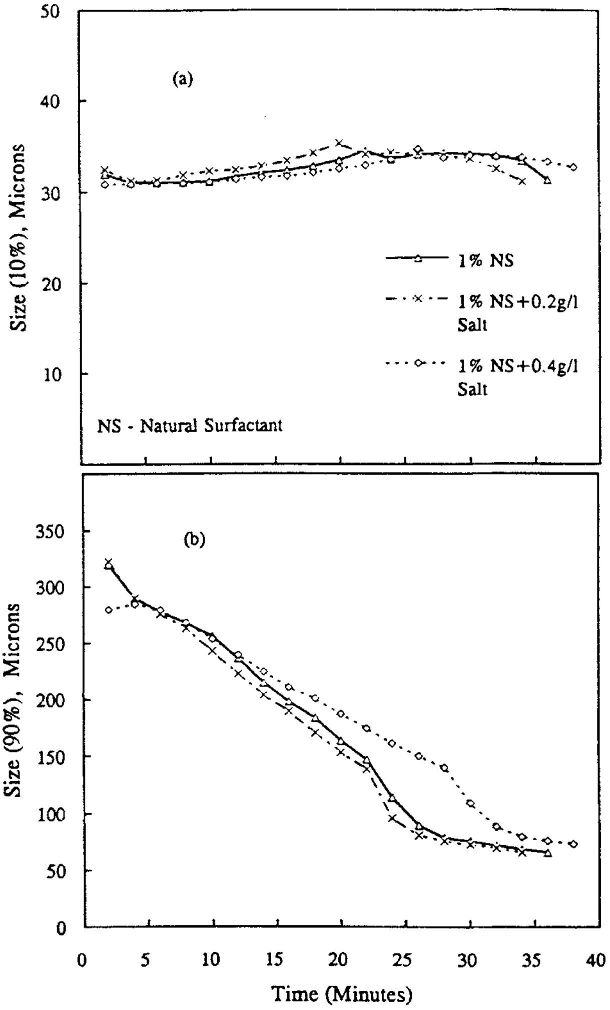

FIG. 6 Effect of the presence of salt on the (a) 10 percentile and (b) 90 percentile size of CGA suspensions generated with 1% natural surfactant solutions.

cial surfactants. The results of this study are presented in Table 1 along with those of Chaphalkar (5) for commercial surfactants, sodium dodecylbenzene sulfonate (NaDBS), Tergitol, and hexadecyltrimethylammonium bromide (HTAB). As can be seen from the table, the lower sizes (10 and 50 percentile sizes) of CGAs generated with a natural surfactant corre-

TABLE 1
Comparison of the Size Distribution of CGAs Generated with Natural Surfactant and Commercial Surfactants Used by Chaphalkar (5)[a]

	Size distribution of CGAs (microns)		
Surfactant	10%	50%	90%
Natural surfactant concentration:			
0.1%	34	55	202
0.5%	33	65	305
1.0%	32	60	290
1.0% + 200 mg/L salt	32	62	290
1.0% + 400 mg/L salt	31	48	279
1.5%	31	52	295
DDBS concentration, anionic:			
200 mg/L	50	123	244
500 mg/L	54	124	194
500 mg/L + 200 mg/L salt	44	98	187
750 mg/L	46	112	198
Tergitol concentration, nonionic:			
50 mg/L	31	58	106
100 mg/L	32	57	128
100 mg/L + 200 mg/L salt	32	58	123
1000 mg/L	34	63	112
HTAB concentration, cationic:			
200 mg/L	52	152	258
328 mg/L	46	105	186
328 mg/L + 200 mg/L salt	42	83	171
500 mg/L	50	112	200

[a] The percentile distribution reported is at 2 minutes.

spond very well with the CGAs produced with the nonionic surfactant Tergitol. The ionic surfactants have sizes at least 15 and 60 μm larger for the 10 and 50 percentile sizes, respectively. The 90 percentile size of CGA suspensions in this study is significantly higher than that of both ionic and nonionic synthetic surfactants.

Stability of CGA Suspensions

Stability of a CGA suspension is defined as its ability to resist change in bubble size, liquid content, or degree of dispersion. Due to the constitution of the two phases of CGA suspensions, the bubble cannot retain its integrity without some external hydrodynamic force such as mixing or agitation. If agitation is discontinued, the bubbles tend to rise to the top and cream as a result of a density difference between the gas and liquid phases. The stability of CGA suspensions was determined using the simple method of gravity drainage under static conditions. Stability was expressed in terms of half-life, the time needed for 50% of the liquid content to drain. The total liquid volume used in this method was also used for calculating the quality (gas fraction) of the suspensions.

Typical drainage curves for the CGA suspensions are shown in Fig. 7. The figure shows the cumulative liquid volume with time for 0.5% natural surfactant concentration. Rate of drainage was fast in the beginning but slowed with time. Smaller bubbles appeared at the CGA/liquid interface while the size increased toward the top. Half-life was calculated from these drainage curves. The half-lives of CGA suspensions generated with different concentrations of plant-based surfactant are presented in Fig. 8 (a). The half-lives for CGA suspensions generated with sodium dodecyl sulfate (SDS) are also presented. The figure shows that the stability of the suspensions increases with natural surfactant concentration. However, the CGA suspensions generated using 0.5% concentration have the

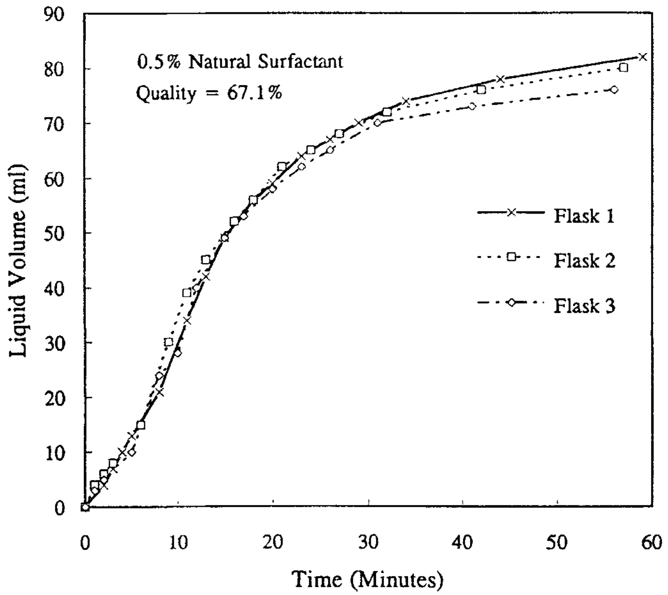

FIG. 7 Typical curves for drainage of liquid from CGA suspensions.

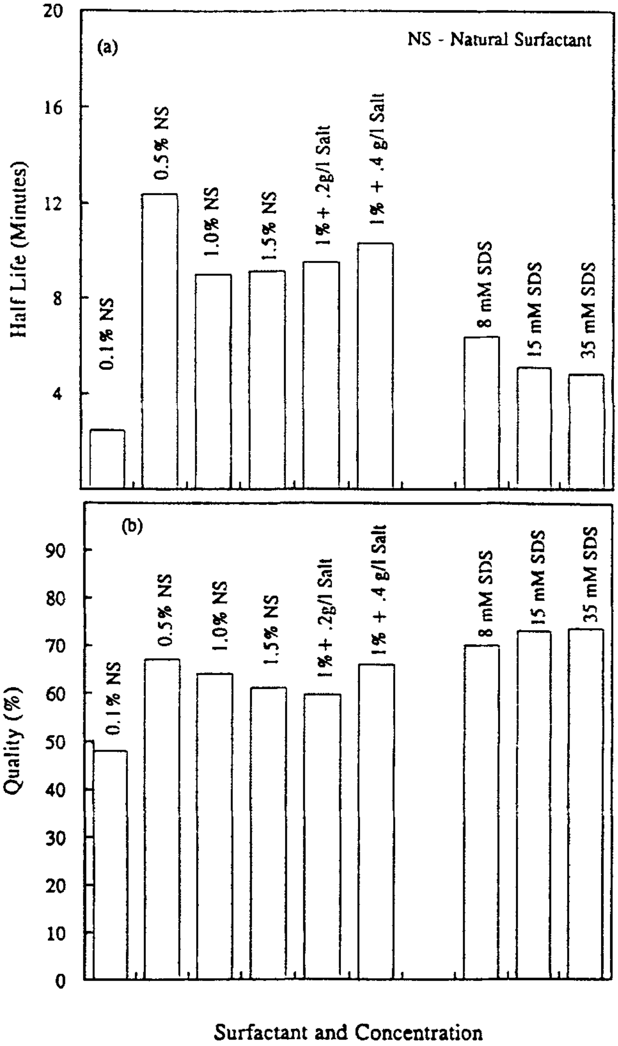

FIG. 8 Comparison of (a) the stability and (b) CGA suspensions generated with several concentrations of natural surfactant and SDS.

highest stability. These results are also supported by the particles size analysis data presented earlier. The time required for the value of D_V to go down to near zero can be used to represent the stability of the CGA suspensions. This method seem to be more appropriate since it is used under dynamic conditions with an aqueous phase (5). As can be seen from Fig. 5, CGA suspensions generated with 0.5% natural surfactant have the highest stability. The stability of CGA suspensions generated with SDS solutions seems to be lower than that for CGAs generated with natural surfactant. The presence of salt seem to increase the half-life of CGA suspensions.

The quality of CGA suspensions defined as the gas fraction is shown in Fig. 8 (b) for natural surfactant and SDS solutions. The quality of CGA suspensions increased as the surfactant concentration increased from 0.1 to 0.5%, but as the concentration increased beyond 0.5% the quality of the suspensions decreased. The quality of suspensions was reduced drastically when the surfactant concentration was increased beyond 1.5%. Suspensions with quality lower than 50% are not desirable. CGA suspensions generated with SDS solutions under the same conditions have a significantly higher quality, and the quality is more or less constant. The lower quality in the case of natural surfactant solutions is attributed to the presence of extraneous natural organic compounds.

CONCLUSIONS

- Natural surfactant solutions obtained from fruit pericarps of *Sapindus mukorossi* can be used to generate CGA suspensions like any other commercial surfactant.
- CGA suspensions generated from natural surfactant solutions have 10 and 50 percentile sizes similar to those of commercial nonionic surfactants, and the 90 percentile size is higher than that of both ionic and nonionic surfactants.
- The stability of CGA suspensions generated with natural surfactant solutions is remarkably higher than those generated with commercial surfactants.
- The quality of CGA suspensions generated with natural surfactant solutions is lower than those generated from commercial surfactant.
- The increased stability and the lower quality of CGA suspensions generated with natural surfactant solutions are attributed to the constituent extraneous natural organic compounds.

ACKNOWLEDGMENT

This research was funded by the US District Court, Middle District of Louisiana, through the Louisiana State University Hazardous Waste Research Center.

REFERENCES

1. T. A. Longe, "Colloidal Gas Aphrons: Generation, Flow Characterization and Application in Soil and Groundwater Decontamination," Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA, 1989.
2. D. Roy, K. T. Valsaraj, and S. Kottai, *Sep. Sci. Technol.*, *27*(5), 573–588 (1992).
3. D. Roy, K. T. Valsaraj, and A. Tamayo, *Ibid.*, *27*(12), 1555–1568 (1992).
4. R. R. Kommalapati, "Soil Flushing of Non Aqueous Phase Liquids Using Conventional Surfactant Solutions and Colloidal Gas Aphron Suspensions," M.S. Thesis, Louisiana State University, Baton Rouge, LA, 1994.
5. P. G. Chaphalkar, "Characterization and Application of Colloidal Gas Aphrons for Ground Water Remediation," Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 1994.
6. D. L. Michelsen, D. A. Wallis, and F. Sebba, *Environ. Prog. 3*, 103–110 (1984).
7. D. Roy, W. A. Jackson, and P. G. Chaphalkar, *Transport of Bacteria through a Soil Matrix Using Colloidal Gas Aphron Suspensions*, In Preparation.
8. N. L. Bor, *Manual of Indian Forest Botany*, Oxford University Press, Calcutta, India, 1953.
9. J. C. T. Uphof, *Dictionary of Economic Plants*, Cramer, New York, NY, 1968.
10. M. Windholz (Ed.), *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, Merck & Co., Rathway, NJ, 1983.
11. J. Gedeon, *J. Sci. Ind. Res.*, *13B*, 427–428 (1954).
12. L. R. Row and C. Rukmini, *Indian J. Chem.*, *4*, 36–38 (1966).
13. L. R. Row and C. Rukmini, *Ibid.*, *4*, 149–150 (1966).
14. R. R. Kommalapati, "Remediation of Contaminated Soils Using a Plant Based Surfactant," Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 1995.
15. F. Sebba, *Investigation of the Modes of Contaminant Capture in CGA (MGD) Foams*, Report OWRT/RU-82/10 to US Department of the Interior, Office of Water Research and Technology, 1982.
16. J. W. Tukey, *The Problem of Multiple Comparisons* (mimeographed), Princeton, NJ, 1953.

Received by editor November 13, 1995