

An Insight into Colloidal Gas Aphron Drainage Using Electrical Conductivity Measurement

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ABSTRACT: In the present paper Electrical Conductivity (EC) of Colloidal Gas Aphron (CGA) suspensions was measured for anionic and cationic surfactants (Sodium Dodecyl Sulfate (SDS) and Tetradecyl Trimethyl Ammonium Bromide (TTAB)). Experiments were made for different concentrations of SDS (6, 8.1, 10 mM) and TTAB (2, 3.51, 5 mM). CGA drainage behavior was observed and measured using 1 liter measuring cylinder while recording EC. Studying the results, CGA drainage process was observed as four-phase mechanism, instead of three conventional phases. Regardless of surfactant concentration and type, the drainage process is divided in to absorption, macroscopic, bubble, and microscopic phases. Drainage rate did not change at the end of bubble phase, with the maximum value at the end of absorption phase. Results showed that electrical conductivity is a more sensitive property for studying CGA characterization.

KEY WORDS: Colloidal Gas Aphron (CGA), Electrical Conductivity (EC), Liquid drainage, Drainage mechanism, SDS, TTAB.

INTRODUCTION

Colloidal Gas Aphrons are microbubbles with colloidal properties which were first introduced by *Sebba* [1]. The spherical bubbles are typically 10-100 μm in diameter and consist of a gaseous inner core surrounded by a thin aqueous surfactant film composed of at least two surfactant layers and an outer electrical layer shown in Fig. 1.

CGAs are produced by intense stirring of a surfactant solution at the speed of (5000-10000 rpm). This, leads to entraining air and finally micro bubble formation. Generally production time is less than 5 minutes and can vary depending on surfactant concentration. When CGA produced, volume almost triples; and therefore 65-70 % volume fraction of suspension consists of air. This

property makes CGA the third lightest fluids after hydrogen and helium. CGAs separate easily from bulk liquid and transform into a clear solution at the bottom and foamy suspension at the top which is called CGA drainage. Due to CGA structure and size distribution, they exhibit high stability, and can be transferred by Peristaltic pump. Their high interfacial area makes them efficient in separation processes. Several applications have been proposed and studied for CGA summarizing as:

- 1- Firefighting [2]
- 2- Separation techniques in:
 - Biotechnology [2-4]
 - Waste treatment [5-7]
 - Heavy metal removal [8-10]

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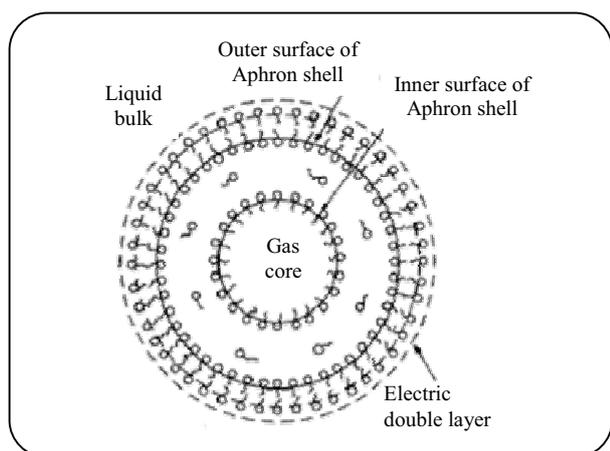


Fig. 1: Colloidal Gas Aphron structure [2].

- Protein recovery [11-13]
- Bioremediation [14, 15]
- 3- Flotation [2, 16-18]
- 4- Enhancement in mass transfer [19-21]
- 5- Well bore drilling fluid [22-27]

In contrast to vast number of researches devoting to CGA application, fewer attempts have been made to characterize CGA dispersion. To fill the gap, first Amiri and Woodburn [28] proposed a mathematical model for drainage rate using modified Kynch analysis. Save and Pangarkar [29], studied characteristics of CGA and presented a theoretical model by modifying Haas and Johnson model [30]. Jauregi *et al.*, [31] investigated the structural features of CGA, and predicted Aphron diameter.

Yan *et al.*, [32] suggested an empirical drainage model, with an eye on Save and Pangarkar results. They tested their model with Arrhenius equation. A first-order model for CGA drainage was proposed and correlated with experimental data by Bhatia *et al.* [33]. The purpose of this work is to provide more information on CGA drainage by studying electrical conductivity of CGA suspension for the first time.

EXPERIMENTS

Chemicals and testing method

Sodium Dodecyl Sulfate (SDS), an anionic surfactant, and Tetradecyl Trimethyl Ammonium bromide (TTAB), a cationic surfactant, (Loughborough, England), were tested for different concentrations. The CGA suspensions were generated according to method proposed by Sebba

[3]. SDS and TTAB suspension samples were prepared for concentrations of 6, 8.1 (CMC), 10 mM and 2, 3.51 (CMC), 5 mM respectively. A shaft driven by Yamaha electrical motor (Japan), stirred the suspension in a three-liter beaker at the speed of 7000 rpm for 5 minutes.

After production the suspension was transferred to a one-liter measuring cylinder in order to study CGA drainage rate by measuring EC. EC was measured using pH/EC Meter C732 (Belgium). In order to comprehend the exact effect of EC variation of CGA suspension, EC of blank solution (distilled water) was measured. Tests were repeated at least two times for each concentration to minimize experiment errors.

RESULTS AND DISCUSSION

Drainage results

Figs. 2 and 3 show variation of interface height of SDS and TTAB clear solution during drainage process. The figures show that drainage mechanism have the same trend independent of concentrations and surfactant types. But, Interface height of clear liquid (H_d) and drainage time (t_d) is affected by surfactant type and concentration. Higher concentrations result in decreasing H_d . This is due to smaller aphron bubbles in CGA suspension produced by higher surfactant concentrations. Experimental results show, drainage time extended for higher concentrations up to CMC; because of saturated absorption capacity on CGA surface. Adding more surfactant decreases t_d slightly.

Comparing TTAB and SDS drainage curves reveal that, more H_d and t_d is observed for TTAB. This can be related to their molecular structure as shown in Figs. 4a and 4b. Longer alkyl group of TTAB lowers CMC [34] and increase H_d . Increasing in hydrophobic chain length, results in more intercohesive forces that make CGA dispersion more stable and consequently increase t_d [35]. These comparisons are presented in Figs. 5 and 6.

Electrical conductivity results

In Fig. 7 electrical conductivity of CGA suspension for TTAB is shown at CMC. The alteration of electrical conductivity shows that drainage can be divided in to four phases which are specified in Fig. 7. The first stage is Absorption phase in which EC decreases for short minutes (disengagement time) and no drainage happens. There fore EC of CGA suspension is recorded.

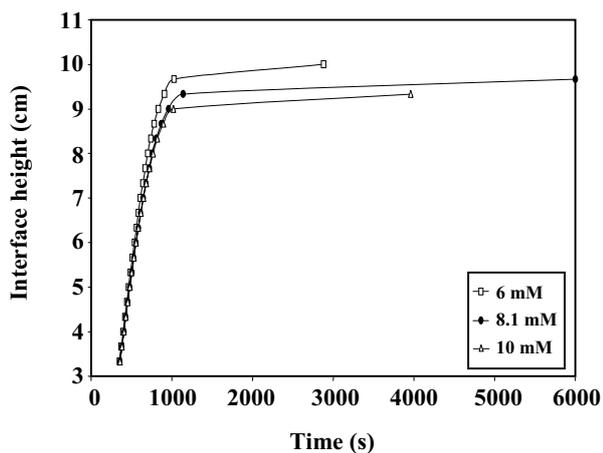


Fig. 2: Variation of Interface height in SDS clear solution during drainage process.

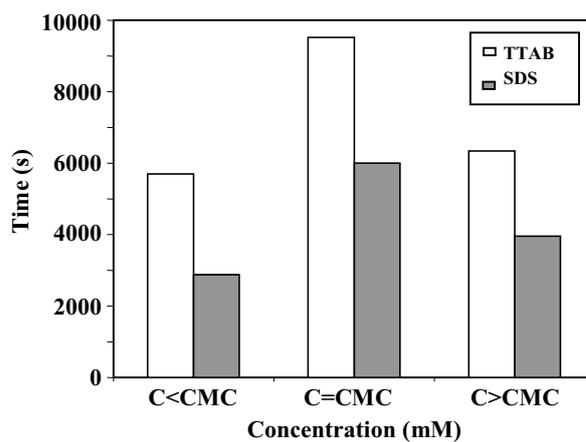


Fig. 5: Comparison of drainage time completion between SDS and TTAB.

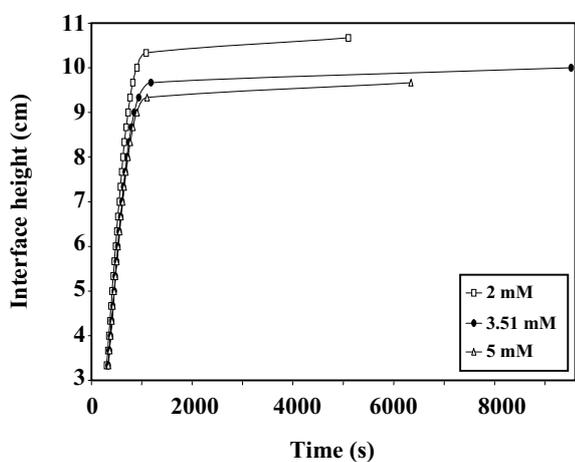


Fig. 3: Variation of Interface height in TTAB clear solution during drainage process.

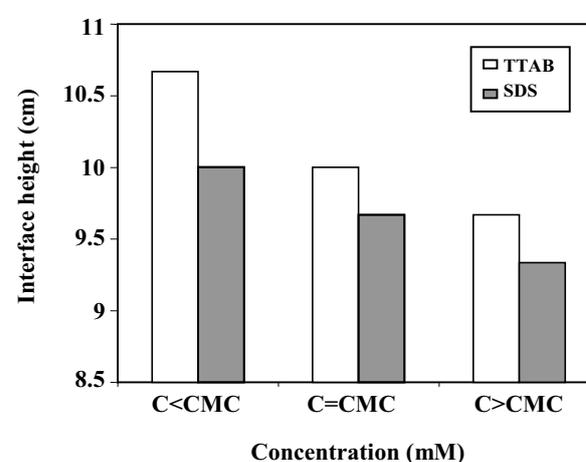


Fig. 6: Interface height comparison between SDS and TTAB.

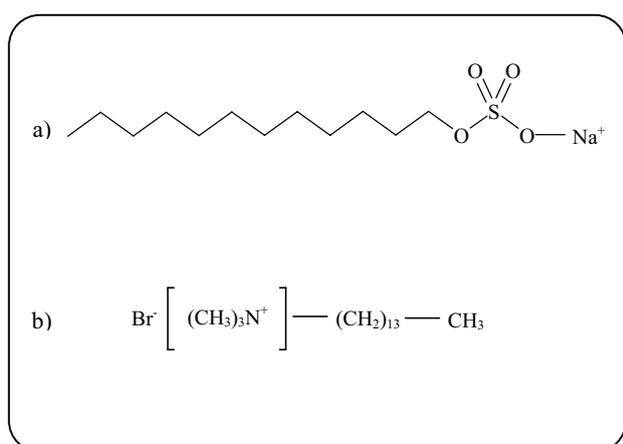


Fig. 4: a) SDS molecular structure, b) TTAB molecular structure.

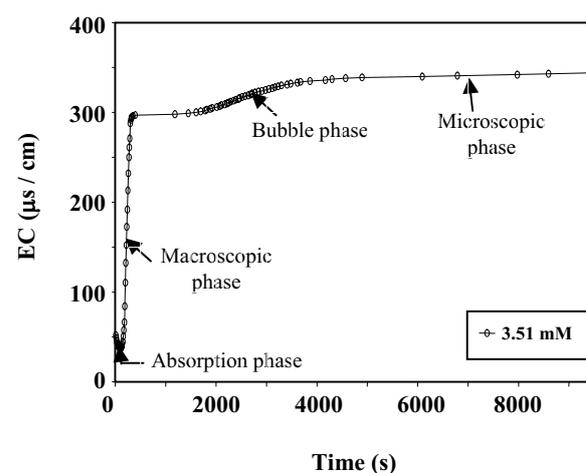


Fig. 7: Four phases of drainage process, TTAB at CMC.

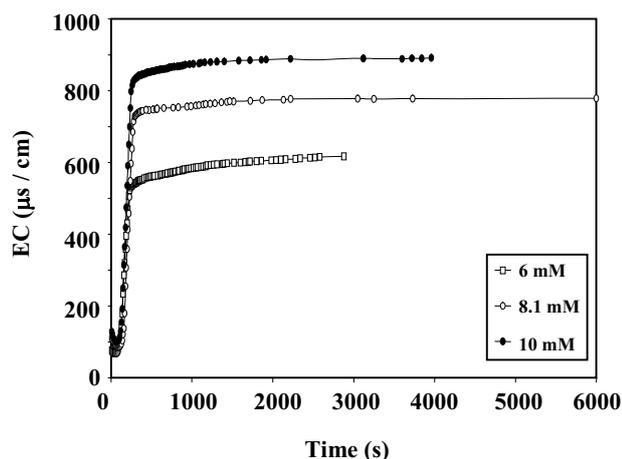


Fig. 8: SDS Electrical Conductivity curve for CGA suspension four phases.

It is believed that in this phase, bulk ions absorb to the surface of CGAs and reduce EC. The Macroscopic drainage phase started with an increase in EC of CGA clear solution. It continued sharply, and finished in less than 4 minutes. At this phase, bulk liquid started flowing down because of gravity force. EC and drainage rate reached their maximum value and CGAs maintained their spherical shapes which is consistent with Amiri observations [36].

In the third phase, spherical CGAs enlargement became observable and increasing trend for both EC and drainage rate hindered. In this phase, namely Bubble phase, drainage took less than 15 minutes to complete. Smaller bubbles merged in to larger bubbles under influence of Laplas pressure and enlarged larger bubbles.

The last phase (Microscopic phase), bubbles change morphology to polyhedral foam. It is extremely sluggish to complete (about 1-3 hours), because of lamella and plateau border drainage. Therefore EC and drainage rate variations were negligible. An interesting point about Microscopic phase is EC fluctuations at the end of the phase which is devoted to surfactant molecules migration to the gas-liquid surface. This reduces EC while polyhedral foam collapsing increased EC as a result of releasing the surfactant molecules which were entrapped in CGA shell.

Figs. 8 and 9 revealed the variation of electrical conductivity in clear solution for different concentrations and surfactants. As is illustrated by the figures, the drainage mechanism is independent of surfactant type and

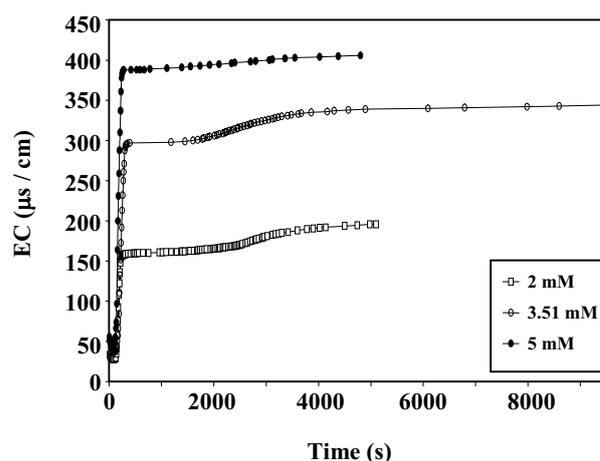


Fig. 9: TTAB Electrical Conductivity curve for CGA suspension four phases.

concentration. They also showed that the most stable CGA suspension is produced at CMC concentration.

Drainage (t_d) and phase completion time, for SDS and TTAB are reflected in Figs. 10 and 11. It is recognized that comparing different concentrations, at CMC, all stages lengthened more to finish; which reflects the most stable CGA structure at CMC. In the case of TTAB, completion time for each phase is longer than SDS.

EC of blank solution for all samples were 5 ± 1 ($\mu\text{s}/\text{cm}$) before adding surfactant. Although adding surfactant to the blank solution raised EC, but in the case of CGA clear solution, the increasing in EC is extremely sharp for the same surfactant concentrations. Furthermore CGA clear solution shows greater EC amount than blank solution at the same time intervals. This fact depicts that diffusion of surfactant in to clear solution is completely different when drainage is involved.

The advantage of using electrical conductivity property, rather than conventional volume method, is in choosing a more sensitive parameter when studying CGA suspension stability. It also gives better insight in distinguishing different drainage stages and transforming moment in CGA morphology.

Since drainage rate diminishes as it progresses, it can be concluded that at microscopic phase, the drainage rate reaches zero. Therefore when considering drainage rate, dominant stages are macroscopic and bubble. As is reflected in Fig. 12, a second order correlated curve fits the drainage cure well. Therefore it can be concluded that CGA drainage process is a constant acceleration mechanism due to aphyron enlargement while rising to

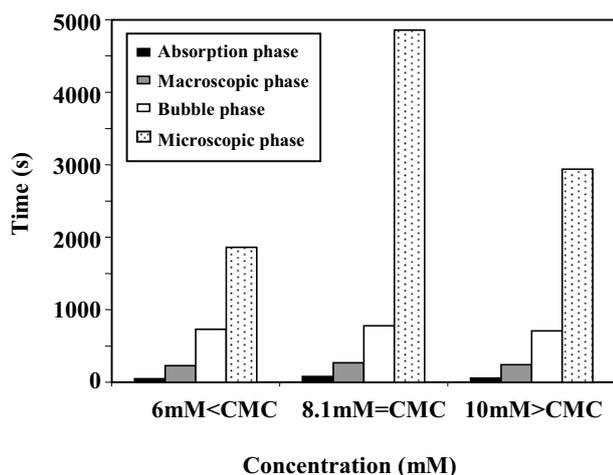


Fig. 10: Phase completion time for SDS.

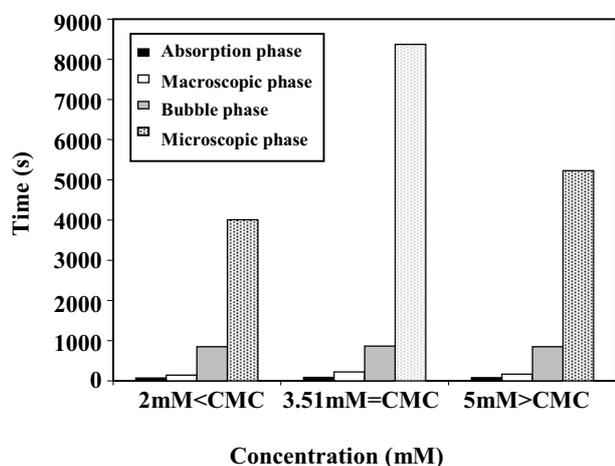


Fig. 11: Phase completion time for TTAB.

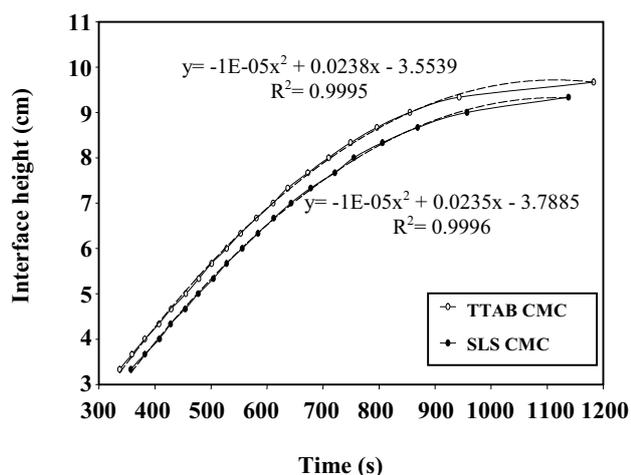


Fig. 12: Interface height correlation for SDS and TTAB at CMC.

the interface. Consequently applying Stoke's law for predicting CGA drainage velocity is inappropriate; as gravity and capillary forces are both interacting on drainage velocity as external forces. By differentiation of the obtained correlations by time, maximum velocity of interface movement can be calculated.

Table 1 shows maximum drainage rates for various surfactants and concentrations. Maximum drainage rate occurs at the end of first phase (end of disengagement time) and is approximately 1.5 cm/min.

CONCLUSIONS

Drainage mechanism of CGA suspension was conventionally assumed to be a two phase phenomenon, but in this work a four-phase mechanism is introduced to clarify CGA drainage process, and following results were obtained:

1- Electrical conductivity property of CGA suspension is a sensitive parameter and good indicator in understanding drainage mechanism completely. This property helps in distinguishing drainage phases and ranges.

2- Absorption, Macroscopic drainage, Bubble drainage and polyhedral foam drainage (Microscopic), are four phases of CGA drainage.

3- There is no absolute drainage in the first phase, but drainage rate reaches its maximum value in the second phase. This can be investigated by sharp increase of EC. In the third phase, Bubbles are big enough to be seen and the rate of increasing EC slows down as well as drainage rate. The Microscopic phase is the last and a very slow stage in the whole process. The last phase is the only stage in which Surfactant migration to the surface is sensible.

4- The entire CGA drainage occurs in the Macroscopic and Bubble drainage phases that are generally 18 minutes long. In these phases more than 90 % volume of bulk liquid drains with second order relation with time.

5- During disengagement time, free ions of suspension, absorb to the surface of CGAs.

6- To produce the most stable CGAs suspensions, the production should be done at CMC.

7- Maximum drainage rate is less at CMC due to CGA suspension high stability.

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Table 1: Maximum drainage rates for various surfactants and concentrations.

		Concentration (mM)		
		C<CMC	CMC	C>CMC
Maximum velocity of interface movement (drainage) (cm/min)	SDS	1.488	1.380	1.314
	TTAB	1.47	1.320	1.335

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