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

Electrical Aspects of Foam Flotation: The Streaming Potential

Ann N. Clarke[a]; David J. Wilson[a]
[a] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Clarke, Ann N. and Wilson, David J.(1975) 'Electrical Aspects of Foam Flotation: The Streaming Potential', Separation Science and Technology, 10: 4, 371 — 380

To link to this Article: DOI: 10.1080/00372367508058026

URL: http://dx.doi.org/10.1080/00372367508058026

SEPARATION SCIENCE, 10(4), pp. 371-380, 1975

Electrical Aspects of Foam Flotation: The Streaming Potential

ANN N. CLARKE and DAVID J. WILSON

DEPARTMENT OF CHEMISTRY
VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

Abstract

Experimental verification of the existence of a streaming potential phenomenon in draining ionic surfactant foams is reported. The streaming potential is directly proportional to column length, inversely proportional to solution conductivity, and independent of gas flow rate over the ranges of parameters studied. The streaming potential is of opposite sign for sodium lauryl sulfate (anionic) and hexadecyltrimethylammonium bromide (cationic).

INTRODUCTION

The ready adaptability of foam separations to the removal of trace metals and other toxic contaminants from aqueous systems has led to an extensive literature, reviewed by Lemlich (*1*, *2*), Somasundaran (*3*), and others. It has been noted by a number of workers that some types of foam separations are markedly affected by the ionic strength of the solution being treated (*4–7*); this led us to propose a theory based upon the Gouy-Chapman model of the electric double layer (*8*) to account for the effect of ionic strength on the efficiencies of precipitate flotation and adsorbing colloid flotation (*9*). We note that Jorné and E. Rubin had previously used this model in studying the effects of ionic charge and size on foam fractionation selectivity (*10*).

In our earlier work (*9*) we noted that the Gouy-Chapman model leads one to anticipate the existence of a streaming potential phenomenon in draining foams, and gave the following approximate equation for the streaming potential of a draining single film in a vertical orientation:

$$V_s = \frac{D\rho g b\zeta}{4\pi\eta c(\lambda_0{}^+ + \lambda_0{}^-)} \tag{1}$$

Here V_s = streaming potential
D = dielectric constant
g = gravitational acceleration
b = length of film
ζ = zeta potential of surface
η = viscosity of liquid
ρ = density of liquid
c = concentration of 1–1 electrolyte
$\lambda_0{}^+$ = cationic equivalent conductance
$\lambda_0{}^-$ = anionic equivalent conductance

Obviously Eq. (1) cannot be applied as it stands to the exact calculation of the streaming potential of a draining foam. Still, it should predict the functional dependence of the streaming potential on the variables in the system. We note that the streaming potential is predicted to be proportional to the length of the foam column along which the potential is developed, that it is proportional to and has the same sign as the zeta potential of the film surface, and that it is inversely proportional to the conductivity of the solution. No dependence on gas flow rate is predicted.

We report here an experimental study of the streaming potential in water–detergent foams (hexadecyltrimethylammonium bromide, HTA; and sodium lauryl sulfate, NLS) in which sodium nitrate is used to adjust the ionic strength.

EXPERIMENTAL

The experiments were carried out using a column 90 cm in length with an inside diameter of 3.5 cm. Along one side of the column were placed five equally spaced ports, approximately 15 cm apart. These side arms held the measuring electrodes. Opposite the lowest port was a single side arm to accommodate a microcombination pH electrode. The rubber stopper plug in the bottom of the column held the gas inlet tubing to the sparger and a septum and a stopcock for small and large sampling capabilities, respectively (see Fig. 1).

House air was used. Its flow was regulated by a pressure regulator fol-

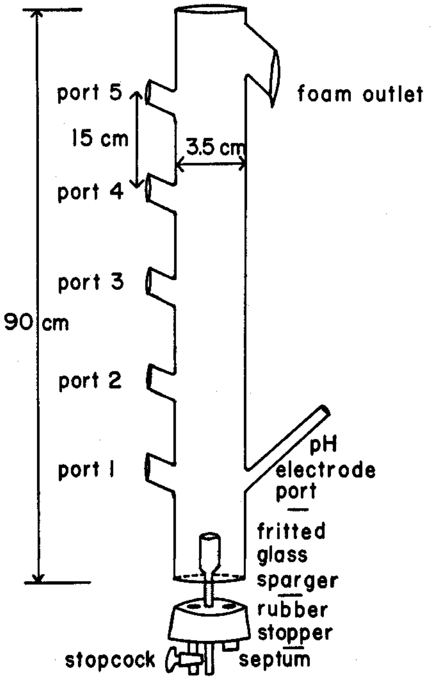

FIG. 1. The foaming column used. The column was made of Pyrex, with dimensions as indicated.

lowed by a microvalve with vernier control. The air was then passed through concentrated sulfuric acid and silica gel to remove oils, water, etc.; ascarite to remove acid; deionized water for controlled rehumidification; and glass wool to remove any remaining particulates. Flow rates were taken with a soap film flowmeter connected into the system directly after the column.

The preparation of highly concentrated HTA solutions was facilitated by initially dissolving the HTA in 1 or 2 ml of ethanol (for a final volume of 1 liter). The solution of NLS, even at concentrations of 3500 ppm, posed no problems. The NLS, however, was first washed with ether in a Soxhlet apparatus for approximately 8 hr at a rate of 6 min/cycle to remove possible lauryl alcohol contamination.

A total volume of 100 ml of solution was poured in from the top of the column in each run. The foam rose and when it completely filled the ports where the measuring electrodes (identical calomel electrodes) were located, a reading was taken as quickly as possible. Then the electrodes were quickly moved to the next pair of ports and the vacated ports sealed with ground glass stoppers. For electrodes not fitted with ground glass points, rubber septa of appropriate size were fitted onto the electrodes to make the apparatus foam- and watertight when the electrodes were seated in the sidearms. With a little practice, there is minimal loss due to removal and replacement of electrodes in regions filled with foam. This loss, under normal operating conditions, does not affect the data or their reproducibility. The column was rinsed thoroughly with deionized water and drained after each run.

RESULTS

Our model predicts that the streaming potential is directly proportional to the static head pressure or to height. Therefore, we would anticipate the potential difference obtained between Ports 1 and 3 (see Fig. 1) to be twice that obtained between 1 and 2; that obtained between Ports 1 and 4 to be three times that between 1 and 2, and so on, since the ports are equally spaced. The theoretical ratios of potential differences are therefore, 1: 2.0: 3.0: 4.0. When HTA was used as the surfactant, the experimental ratio was 1: 1.9: 2.9: 4.0. (Each potential was an average of 12 values.) When NLS was used as the surfactant, the experimental ratio was 1: 2.0: 3.0: 4.2. (Each potential was an average of 18 sets of values.) One also predicts that the sum of the potentials between Ports 1 and 2, 2 and 3, 3 and 4, and 4 and 5 would be equal to the potential developed between Ports 1 and 5. When HTA was the surfactant, the results of 17 runs showed the $V_{12} + V_{23} + V_{34} + V_{45}$ values to be 96.7% of those recorded for the corresponding V_{15} readings. The potential difference range was 30 to 350 mV. When NLS was used (24 runs), this percentage was 97.5% and the potential difference range was 60 to 250 mV. Theoretically, in both cases we should have found 100%.

If the concentration of surfactant is in a range where the surface potential is not varying much with concentration, but where the critical micelle concentration is not exceeded, increasing the surfactant concentration simply increases the concentration of electrolyte in the bulk solution. For this, the model predicts an inverse relationship between the surfactant concentration used and the streaming potential produced. We looked at three different concentrations of HTA, in the ratios of 1: 1.5: 2.0, at a fixed gas flow rate. We would expect the potential difference ratios (for a given port separation) to be 2.0: 1.5: 1. The experimental ratios (average of 32 values for each potential) were 2.0: 1.4: 1, and the streaming potential per unit length, v_s, ranged from 2.9 to 6.4 mV/cm. For NLS the surfactant concentrations were in ratios of 1: 2.0: 4.0. The resulting experimental ratios of the streaming potential were 3.6: 1.8: 1 (average of four values for each potential). The range v_s was 1.3 to 4.7 mV/cm. Two additonal NLS concentrations in a ratio of 1: 1.3 were run, yielding a potential difference ratio of 1.3: 1, and values of v_s of 0.89 and 1.05 mV/cm.

Equation (1) does not predict a dependence of the streaming potential on the flow rate of the gas generating the foam. We looked at six different flow rates (range 153 to 294 ml/min) and three different concentrations of HTA (155, 235, and 315 ppm), expecting that at a given surfactant concentration and port spacing the streaming potential would be essentially independent of the gas flow rate. The results (12 meaurements per ratio) are given in Table 1.

For NLS, four gas flow rates (range 76 to 247 ml/min) and one surfactant concentration (125 ppm) were investigated. The average v_s value was 3.5 mV/cm, and the results, an average of four determinations for each streaming potential, are given in Table 2.

The theory predicts an inverse relationship between the electrical conductivity of the solution and the streaming potential. To test this, varying amounts of reagent grade sodium nitrate were added to solutions having a given surfactant concentration. In a solution 0.009 *M* in HTA, sodium nitrate concentrations as low as 0.05 *M* essentially short out the system, reducing the potential differences to immeasurably small values. Table 3 describes the four HTA–$NaNO_3$ systems investigated. The total inverse

TABLE 1

Effect of Variation of Gas Flow Rate–HTA Surfactant

Flow rate ratio	1: 1.1: 1.5: 1.6: 1.8: 1.9
v_s ratio (exptl)	1: 1.0: 1.1: 0.9[a]: 1.1: 1.2
v_s ratio (theoret)	1: 1.0: 1.0: 1.0: 1.0: 1.0

[a] Average of eight values.

TABLE 2

Effect of Variation of Gas Flow Rate–NLS Surfactant

Flow rate ratio	1: 1.3: 2.0: 3.2
v_s ratio (exptl)	1: 1.0: 1.0: 1.0
v_s ratio (theoret)	1: 1.0: 1.0: 1.0

TABLE 3

Results for HTA/$NaNO_3$ Systems

	Solution I	Solution II	Solution III	Solution IV
Concentration of HTA (*M*)	0.0089	0.0089	0.0087	0.0087
Concentration of $NaNO_3$ (*M*)	0.0072	0.0050	0.0030	0.0016
Total conductivity	1.733	1.466	1.203	1.033
TIC	0.577	0.682	0.831	0.968
v_s (mV/cm)	0.43	0.52	0.62	0.78

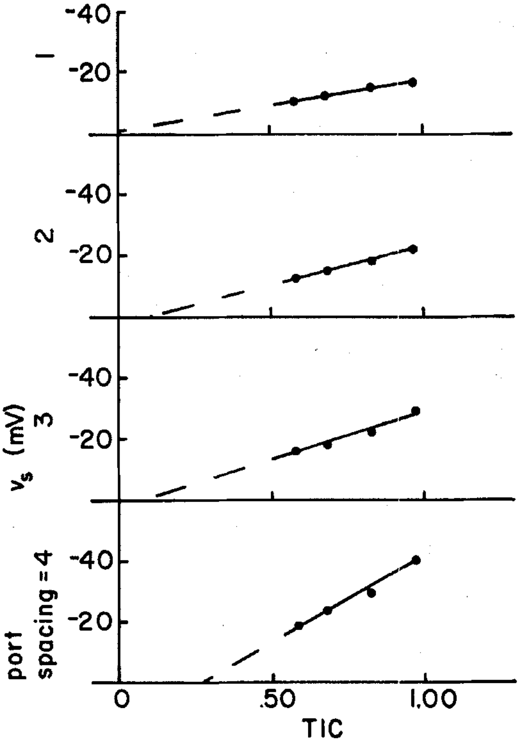

FIG. 2. Dependence of streaming potential on TIC (see text) and electrode port spacing. HTA is the surfactant, $NaNO_3$ the added inert salt.

conductivity (TIC) for each system was calculated according to

$$\begin{aligned} \mathrm{TIC} = 1/[&c(\mathrm{surfactant})(\lambda_0(S^+) + \lambda_0(S^-)) \\ &+ c(\mathrm{NaNO_3})(\lambda_0(\mathrm{Na^+}) + \lambda_0(\mathrm{NO_3}^-))] \end{aligned} \tag{2}$$

The equivalent conductivities at 25°C which were used are

$$\lambda_0(\mathrm{Na^+}) = 50.1 \quad (11)$$

$$\lambda_0(\mathrm{NO_3}^-) = 71.4 \quad (11)$$

$$\lambda_0(\mathrm{Br^-}) = 78.4 \quad (11)$$

$$\lambda_0(\mathrm{LS^-}) = 25 \quad (12)$$

$$\lambda_0(\mathrm{HTA^+}) = 18 \quad (13)$$

The value for $\lambda_0(\mathrm{HTA^+})$ is an approximation suggested by data in the reference indicated.

Figure 2 shows the behavior of the streaming potential as a function of TIC graphically. The plots are indeed linear over the rather narrow range studied, and generally extrapolate near the origin, as they should.

Solutions in which NLS was the surfactant were studied in similar fashion, and the results are summarized in Table 4. The results are graphed in Fig. 3. It is readily seen that the plots are reasonably linear and that they extrapolate through the origin, as expected.

A copper wire the length of the column was inserted inside the column from one end to the other, and two runs were made at different HTA concentrations (315 and 237 ppm). The streaming potential was essentially shorted out, as expected. The potential differences averaged less than 0.10 of those obtained for regular runs under similar conditions but without the wire present; e.g., the potential differences on a run with the wire ranged

TABLE 4

Results for NLS/NaNO$_3$ Systems

	Solution I	Solution II	Solution III	Solution IV	Solution V
Concentration of NLS (*M*)	0.00043	0.00043	0.00043	0.00043	0.00043
Concentration of NaNO$_3$ (*M*)	0.0007	0.0004	0.0003	0.0001	0
Total conductivity	0.117	0.081	0.068	0.044	0.032
TIC	8.55	12.3	14.7	22.7	31.3
v_s (mV/cm)	1.00	1.21	1.78	2.72	3.34

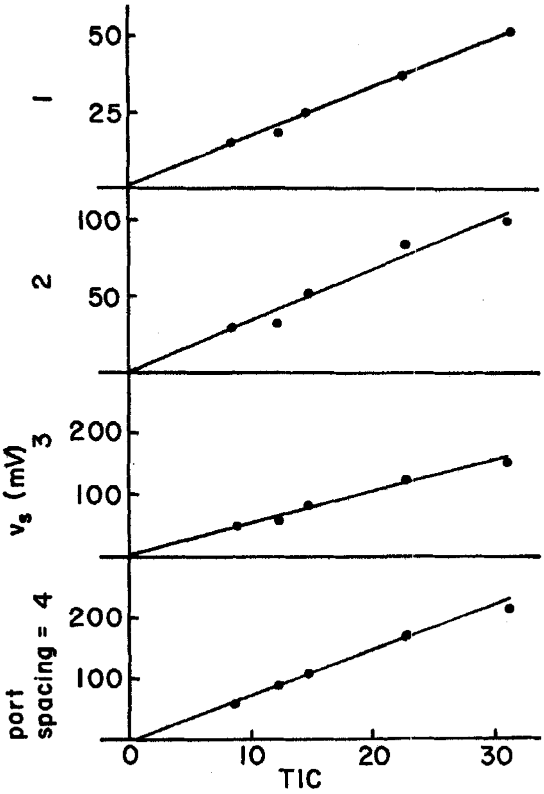

FIG. 3. Dependence of streaming potential on TIC and electrode port spacing. NLS is the surfactant, $NaNO_3$ the added inert salt.

TABLE 5

Streaming Potential Ratios Above and Below the cmc–HTA and –NLS

	HTA	NLS
Above cmc		
Concentration ratio	1: 1.5: 2.0	1: 1.5: 2.0
v_s ratio (exptl)	1.1: 1.0: 1	1.1: 0.9: 1
v_s ratio (theoret)	1.0: 1.0: 1	1.0: 1.0: 1
Below cmc		
Concentration ratio	1: 1.5: 2.0	1: 2.0: 4.0
v_s ratio (exptl)	2.0: 1.4: 1	3.6: 1.8: 1
v_s ratio (theoret)	2.0: 1.5: 1	4.0: 2.0: 1

from +23 to −13 mV compared to a range of −29 to −206 mV for a similar run made without the wire.

We were interested in whether or not the potential differences were affected by surfactant concentrations at levels above the critical micelle concentration (cmc) of the surfactant. The cmc of HTA is 365 ppm at room temperature (*14–16*). The concentrations investigated were 562, 844, and 1175 ppm, standing in the ratio of 1: 1.5: 2.0. In view of the fact that the activities of surfactant film components are very slowly varying functions of bulk concentration above the cmc (*17–19*), one would expect that the streaming potential would remain essentially constant as surfactant concentrations are raised above the cmc. Theory therefore predicts that the ratios of the streaming potentials for these systems should be 1: 1.0: 1.0. The experimental values of the ratios were 1: 1.0: 1.1 (an average of four determinations for each value). The average value of v_s was 2.4 mV/cm. See Table 5 for a comparison with the results for the streaming potential ratios below the cmc.

The cmc of NLS at 25 °C is 1758 ppm (*20–22*). The surfactant concentrations used were 1796, 2694, and 3592 ppm, in the ratio of 1: 1.5: 2.0. The experimentally observed ratios of the streaming potentials were 1.1: 0.9: 1, with four determinations being averaged for each result. The average v_s value was 0.28 mV/cm. At surfactant concentrations below the cmc, the streaming potential exhibited the expected inverse dependence on surfactant concentration. The results for HTA and NLS above and below the cmc are summarized in Table 5.

Dodecyltrimethylammonium chloride (DTA), a cationic surfactant, was briefly investigated. DTA yielded streaming potential values of the same sign as HTA, as expected. Although good foams were hard to maintain with this surfactant, the trends observed did agree with the results obtained for NLS and HTA. Specifically, the streaming potential decreased with increasing DTA concentration below the cmc and increased with increased port separation.

CONCLUSIONS

The results reported here are in agreement with Eq. (1), derived from the Gouy-Chapman model. The magnitude of the streaming potential is directly proportional to solution conductivity, and independent of gas flow rate, as predicted by Eq. (1); also, the sign of the streaming potential changes with the sign of the ionic surfactant's charge, as predicted. Constancy of the streaming potential as surfactant concentrations are raised above the cmc is consistent with the fact that the activities of surfactant film components are very slowly changing functions of bulk nominal concentration above the cmc.

Further studies of the streaming potential phenomenon in foams suggest themselves: (a) The predicted inverse viscosity dependence should be verified. (b) The inverse dependence on $\lambda_0^+ + \lambda_0^-$ should be tested by using electrolytes having values of this quantity markedly different from sodium nitrate. (c) Studies should be made at temperatures above and below the foam drainage transition temperature (*23*) to see if this phenomenon affects the streaming potential.

REFERENCES

1. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. R. Lemlich, in "Recent Developments in Separation Science," Vol. 1 (N. N. Li, ed.), CRC Press, Cleveland, Ohio, 1972.
3. P. Somasundaran, *Separ. Purif. Methods*, *1*, 1 (1972).
4. A. J. Rubin and W. L. Lapp, *Separ. Sci.*, *6*, 357 (1971).
5. R. B. Grieves and D. Bhattacharyya, *Ibid.*, *4*, 301 (1969).
6. I. Sheiham and T. A. Pinfold, *J. Appl. Chem.*, *18*, 217 (1968).
7. B. B. Ferguson, C. Hinkle, and D. J. Wilson, *Separ. Sci.*, *9*, 125 (1974).
8. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
9. J. W. Wilson and D. J. Wilson, *Separ. Sci.*, *9*, 381 (1974).
10. J. Jorné and E. Rubin, *Ibid.*, *4*, 313 (1969).
11. W. J. Moore, *Physical Chemistry*, 3rd ed., Prentice-Hall, Englewood Cliffs, New Jersey, 1962, p. 337.
12. A. Lottermoser and F. Puschel, *Kolloid-Z.*, *63*, 175 (1933).
13. A. W. Ralston and C. W. Hoerr, *J. Amer. Chem. Soc.*, *64*, 772 (1942).
14. L. I. Osipow, *Surface Chemistry*, Reinhold, New York, 1962, p. 165.
15. C. A. Burton, E. J. Fendler, L. Sepulveda, and K.-U. Yang, *J. Amer. Chem. Soc.*, *90*, 5512 (1968).
16. A. B. Scott and H. V. Tartar, *Ibid.*, *65*, 692 (1943).
17. A. E. Alexander, *Trans. Faraday Soc.*, *38*, 54 (1942).
18. K. Shinoda and E. Hutchinson, *J. Phys. Chem.*, *66*, 577 (1962).
19. P. H. Elworthy and K. J. Mysels, *J. Colloid Interface Sci.*, *21*, 331 (1966).
20. J. T. Davies and E. R. Rideal, *Interfacial Phenomena*, 2nd ed., Academic, New York, 1963.
21. W. D. Harkins, *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952.
22. F. Franks, M. J. Quickenden, J. R. Ravenhill, and H. T. Smith, *J. Phys. Chem.*, *72*, 2668 (1968).
23. L. Shedlovsky, in *Chemistry and Physics of Interfaces*, Vol. 2 (D. E. Gushee, ed.), American Chemical Society, Washington, D.C., 1971, p. 63.

Received by editor August 9, 1974