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

Continuous Foam Fractionation of Phosphate by a Cationic Surfactant

S. Primiani[a]; Y. V. Nguyen[a]; C. R. Phillips[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, APPLIED CHEMISTRY UNIVERSITY OF TORONTO, TORONTO, ONTARIO, CANADA

To cite this Article Primiani, S. , Nguyen, Y. V. and Phillips, C. R.(1974) 'Continuous Foam Fractionation of Phosphate by a Cationic Surfactant', Separation Science and Technology, 9: 3, 211 — 226
To link to this Article: DOI: 10.1080/00372367408057058
URL: http://dx.doi.org/10.1080/00372367408057058

SEPARATION SCIENCE, 9(3), pp. 211–226, 1974

Continuous Foam Fractionation of Phosphate by a Cationic Surfactant

S. PRIMIANI, Y. V. NGUYEN, and C. R. PHILLIPS

DEPARTMENT OF CHEMICAL ENGINEERING AND APPLIED CHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO M5S 1A4, CANADA

Abstract

Continuous foam fractionation experiments in one equilibrium stage were performed using ethylhexadecyldimethylammonium bromide and potassium dihydrogen phosphate. The pH of the solution was maintained at 5.4 at which only $H_2PO_4^-$ was present. The effects of surfactant and phosphate concentrations and liquid and gas flow rates on the percent stripping of phosphate and the distribution factor of phosphate were studied. Equilibria between surface and bulk liquid phases were found to be adequate to explain the inverse relationship between the distribution factor of phosphate and the phosphate and surfactant concentrations.

For optimum separation of phosphate, defined as percent stripping, $[100(c_f - c_w)/c_f]$, low liquid and high gas flow rates must be used with dilute solutions of both surfactant and phosphate. Further, multiple equilibrium stages should be employed.

INTRODUCTION

Foam fractionation has been used successfully to remove many different ions from solution (*1*). Radioactive cations such as strontium, cesium, and ruthenium have been removed and concentrated from nuclear wastes (*2–5*). Phenol, phosphate, and bacteria have also been separated from contaminated water (*1*, *6–8*). The process relies on the tendency for accumulation of the unsymmetrical molecule, namely, surfactant, at the gas–liquid interface. The advantages of the process are that a large transfer area is easily created by a dispersed aeration technique and that the volume of the collapsed foam is small.

The objective of this investigation was to establish the effects of the parameters surfactant and phosphate concentrations, and liquid and gas flow rates on the removal of phosphate in continuous operation. Other parameters which could affect the removal of phosphate are depth of the liquid pool, pH of the bulk solution, nature of the gas phase, temperature of the solution, feed distribution, and column dimensions. Some of these effects were studied elsewhere (*9*).

Depth of liquid pool: According to previous work (*10*), a depth of 170 cm for the liquid pool is more than sufficient for one equilibrium stage. Depth was fixed at this value.

pH: In all experiments the pH was 5.4 ± 0.05. At this pH, phosphate is present only in the form $H_2PO_4^-$ (*11*).

Nature of the gas phase: The permeability of the gas through the foam lamellae affects the nature of the foam. Nitrogen produces a stable foam (*12–14*) and was used here.

Temperature: Temperature affects equilibria and surface parameters such as critical micelle concentration and surface excess. The temperature was held at 25 ± 2°C.

Feed distributor and column dimensions: The arrangement used (see Fig. 1) produced good mixing. A coarse fritted glass disk was used as gas inlet.

BASIC CONCEPTS

Surface Excess Calculation

In continuous flow foam fractionation, the surface excess of colligend can be evaluated from the relationship

$$\Gamma_f = (c_{ft} - c_w)QD_m/6G \tag{1}$$

where c_{ft} and c_w are the concentrations of colligend (i.e., $H_2PO_4^-$) in the collapsed foam and in the bulk solution, respectively. Q is the collapsed foam flow rate, D_m is the volume-to-surface mean diameter, and G is the gas flow rate. This relation results from the Gibbs and Guggenheim concepts of surface adsorption in foam separation (*15*). Equation (1) can also be obtained from a mass balance on the collapsed foam,

$$Qc_{ft} = c_w(Q - Q_d) + \Gamma_f^{\alpha}6G/D_m \tag{2}$$

where Q_d represents the surface layer flow rate and Γ_f^{α} is the actual surface concentration of phosphate. Equation (1) can be obtained from Eq. (*2*) by replacing the term $\Gamma_f^{\alpha}6G/D_m - c_w Q_d$, the number of moles of phosphate on the surface in excess of those in the bulk, by its equivalent, $\Gamma_f 6G/D_m$. Note that when $Q \gg Q_d$, $\Gamma_f \sim \Gamma_f^{\alpha}$.

Distribution Factor of Phosphate

The effect of surfactant on the distribution factor of phosphate, Γ_f/c_w, can be obtained by considering the following equilibria at the surface:

$$(\mathrm{EHDABr})_s \rightleftarrows \mathrm{EHDA}^+ + \mathrm{Br}^-$$

$$(\mathrm{EHDAH_2PO_4})_s \rightleftarrows \mathrm{EHDA}^+ + \mathrm{H_2PO_4}^-$$

with equilibrium constants

$$K_1 = [\mathrm{EHDA}^+][\mathrm{Br}^-]/[(\mathrm{EHDABr})]_s \tag{3}$$

$$K_2 = [\mathrm{EHDA}^+][\mathrm{H_2PO_4}^-]/[(\mathrm{EHDAH_2PO_4})]_s \tag{4}$$

Such equilibria were used successfully by Grieves (*20*) for the system EHDABr, I^-, and $\mathrm{NO_3}^-$. Upon rearranging and using the surface neutrality condition

$$\Gamma_{\mathrm{EHDA}^+} = \Gamma_{\mathrm{Br}^-} + \Gamma_{\mathrm{H_2PO_4}^-}$$

Eqs. (3) and (4) reduce to

$$\Gamma_{\mathrm{H_2PO_4}^-} = \frac{\dfrac{K_1}{K_2}[\mathrm{H_2PO_4}^-]\,\Gamma_{\mathrm{EHDA}^+}/[\mathrm{Br}^-]}{1 + \dfrac{K_1}{K_2}[\mathrm{H_2PO_4}^-]/[\mathrm{Br}^-]} \tag{5}$$

For dilute solutions, the distribution factor of phosphate is proportional to the surface excess of surfactant,

$$\Gamma_f/c_w = \Gamma_{\mathrm{H_2PO_4}^-}/[\mathrm{H_2PO_4}^-] = \frac{K_1}{K_2}\Gamma_{\mathrm{EHDA}^+}/[\mathrm{Br}^-] \tag{6}$$

Removal Efficiency

In continuous foam fractionation, the "best" description for the removal of colligend is in terms of percent stripping, R_f, defined as

$$R_f = \frac{c_f - c_w}{c_f} \times 100 \tag{7}$$

This parameter is superior to the other parameters, enrichment ratio

(c_{ft}/c_w) and removal ratio $[(Fc_f - (F - Q)c_w)/Fc_f]$, because it is free from the effects of collapsed foam flow rate and foam drainage. The removal ratio would be free from the mentioned effects only if the interstitial liquid were allowed to drain completely back to the bulk solution. In the limit of complete drainage, the removal ratio will approach the percent stripping since $F \gg Q$. The percent stripping has been shown to correlate well with experimental conditions in the continuous separation of cationic and anionic surfactants (*16*). Here, the effects of the operating conditions on the percent stripping of phosphate can be obtained from the mass balance of phosphate:

$$c_w = c_f - 6G\Gamma_f/D_mF \tag{8}$$

Combining Eqs. (7) and (8) gives

$$R_f = \frac{6G}{D_mF}\frac{\Gamma_f}{c_f} \times 100 \tag{9}$$

Since $c_f \gg c_w$, Eq. (9) can be written in terms of the distribution factor of phosphate,

$$R_f \leqslant \frac{6G}{D_mF}\frac{\Gamma_f}{c_w} \times 100 \tag{10}$$

EXPERIMENTAL

A schematic diagram of the experimental apparatus is shown in Fig. 1. Nitrogen was first humidified and then passed into the foam column through a rotameter and a gas sparger. The foam column had an internal diameter of 6 cm and was 178 cm high. A premixed solution of surfactant, ethylhexadecyldimethylammonium bromide (EHDABr), and phosphate in the form of KH_2PO_4 was introduced to the column through a central feed distributor. The central feed distributor was located so as to facilitate the change in feed height and to ensure good mixing in the column. Foam was removed through the foam port and collapsed in a centrifugal foam breaker consisting of a wire basket rotated by a 1/50 hp motor. The concentration of phosphate in the feed, bottom, and collapsed foam streams was determined by the aminonaphthol sulfonic acid method (*17*), accurate to within 0.02 mg/l. For the surfactant EHDABr, a two-phase titration technique (*18*) was used with an accuracy of 1 mg/l.

Average bubble size was determined photographically. Photographs of bubbles were taken at various places along the foaming column. To

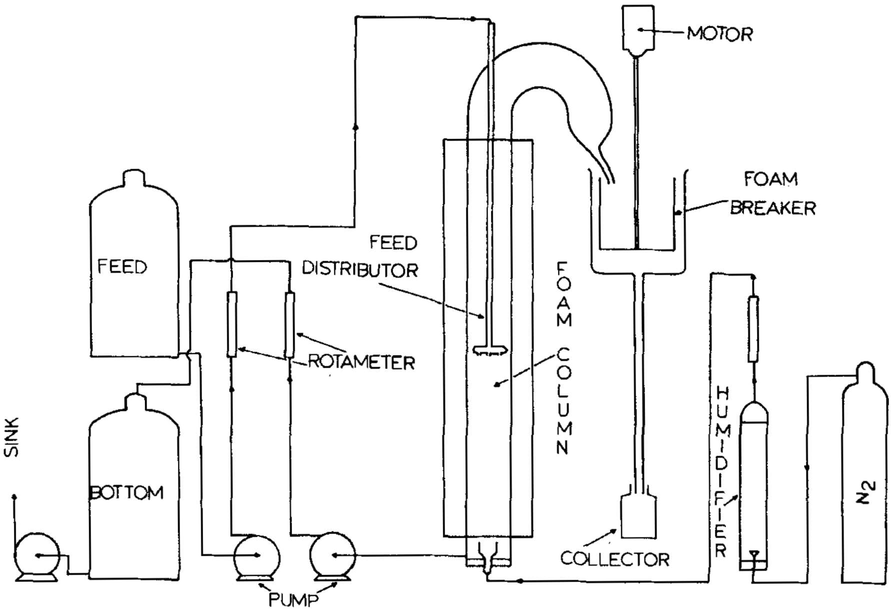

FIG. 1. Diagram of the experimental equipment.

prevent distortion, a rectangular Plexiglas jacket filled with distilled water surrounded the column. Bubble diameters were then obtained with an electronic graph digitizer (Ruscon Logics Ltd.) which gave a magnification ratio of 13 to 23 times.

RESULTS AND DISCUSSION

Critical Micelle Concentration

The cationic surfactant used in this investigation was EHDABr. The concentration of EHDABr was maintained below the critical micelle concentration (cmc), since above this level micelles tend to attract the counterions ($H_2PO_4^-$) and decrease the removal of phosphate. The cmc of EHDABr in distilled water was found by surface tension measurements to be about 300 mg/l or 0.79×10^{-3} g mole/l at 24 ± 1 °C (see Fig. 2). The shape of the surface tension-concentration curve indicated that the adsorption was caused by long chain ions (*19*). The presence of electrolytes decreases the cmc. For example, Grieves (*20*) found the cmc of EHDABr to be about 0.48×10^{-3} g mole/l in an aqueous solution of 2.0×10^{-4}

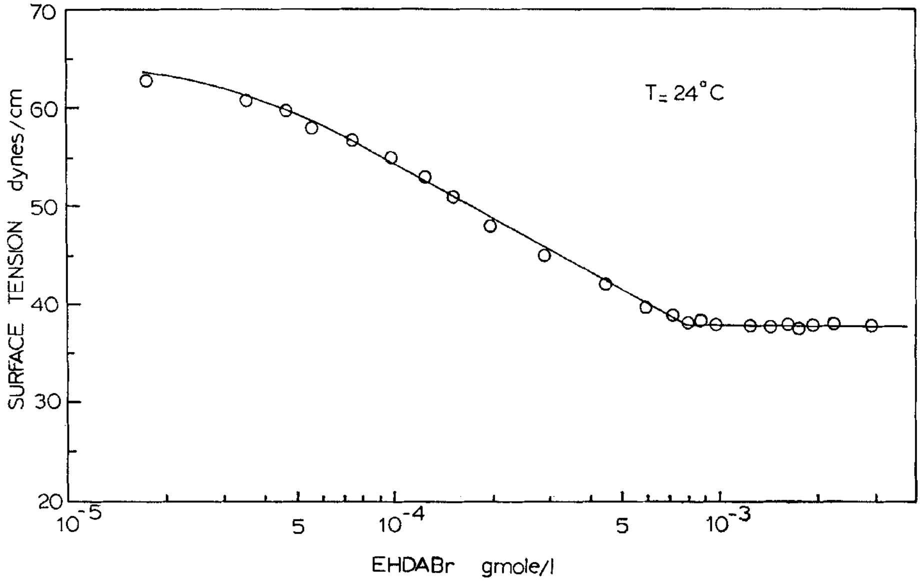

FIG. 2. Surface tension vs surfactant concentration.

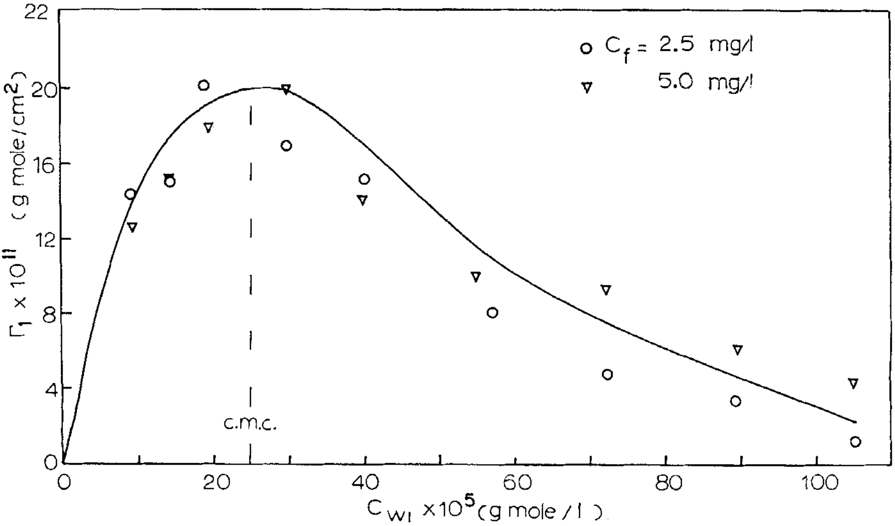

Fig. 3. Effect of surfactant concentration on its surface excess at phosphate bulk concentrations of 2.5 and 5.0 mg/l.

g mole/l of NaI. Since the cmc is affected by concentrations of other ions, it was determined from actual foam separation experiments with aqueous solutions of 2.5 to 5 mg/l of KH_2PO_4. Figure 3 indicates that the surface excess of $EHDA^+$ passes through a maximum at an $EHDA^+$ concentration of approximately 0.25×10^{-3} g mole/l. The maximum in the $EHDA^+$ concentration is the result of competition between adsorption of $EHDA^+$ at the air–water interface and solubilization of $EHDA^+$ in the micelles. Increasing the surfactant concentration in the bulk solution would increase the surface excess of the long chain ion $EHDA^+$, as can be seen from (*19*)

$$\Gamma_{EHDA^+} = \frac{B_1}{B_2} \times EHDA^+ \exp\left(\frac{W - ze\psi_0}{kT}\right) \tag{11}$$

When micelles are present, however, the surface excess decreases because of preferential "solubilization" in the micelles (*19, 21*). This result indicates that for best separation of the counterion $H_2PO_4^-$, experiments must be carried out at or below the cmc of the surfactant.

Batch Experiments

For exploratory studies of the foam fractionation of phosphate with EHDABr, batch experiments were carried out.

A volume of 3.85 l of the premixed solution of EHDABr and KH_2PO_4 was used to fill the column to a level of 170 cm liquid pool depth, to ensure that one equilibrium stage was achieved. The foaming process ceased after 3 hr, 20 min when the collapsed foam flow rate was almost zero. Results are presented in Fig. 4. Figure 4 shows that the percent stripping of phosphate, defined as $100(c_f - c_w)/c_f$, decreases when the initial phosphate concentration increases. This is probably due to the fact that the amount of phosphate in the solution increases faster than the concentration of phosphate on the surface of bubbles at the same surfactant concentration. This result is in agreement with that of Grieves (*1*), where the percent stripping of phosphate in batch operation was related to the initial phosphate concentration via the empirical equation

$$(c_f - c_w)/c_f = aC_1 + cC_1^{0.5}/c_f$$

where *a* and *c* are empirical constants.

Although the percent stripping is high in these batch experiments—for example, 98% stripping was obtained with initial concentration of phosphate equal to 2.5 mg/l—the amount of treated solution in batch operation is extremely small (3.85 l of solution for 3 hr, 20 min operation). For any practical application of the process, continuous operation must be employed.

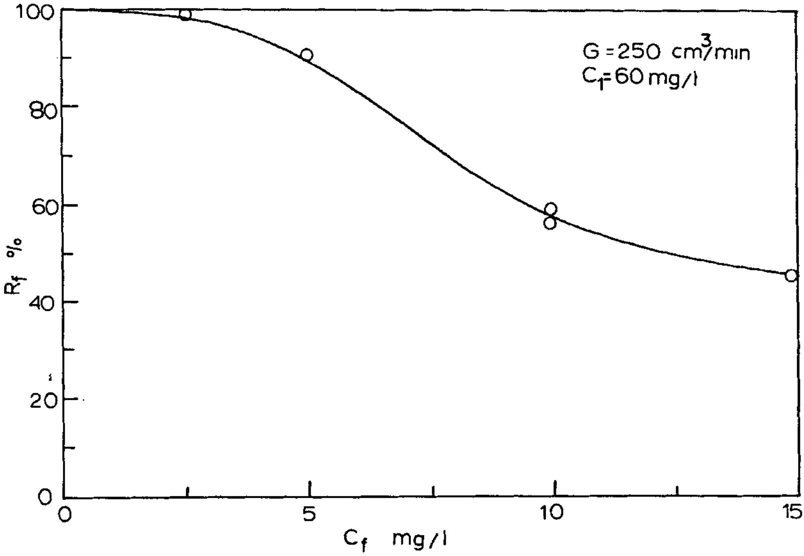

FIG. 4. Percent stripping of phosphate vs initial phosphate concentration in batch operation.

Phosphate Removal in Continuous Operation

In the following experiments the removal of phosphate was investigated over a wide range of surfactant concentration (40 to 400 mg/l) with liquid and gas flow rates up to 355 and 600 cm^3/min, respectively. Increasing the surfactant concentration decreased the surface tension of the solution (see Fig. 2), thus favoring smaller bubbles. For a gas flow rate of 250 cm^3/min, the mean bubble diameter, D_m, was found to correlate well (within 95% confidence limit) with surfactant concentration as follows:

$$D_m = 0.020/C_1^{0.30}$$

where C_1 is surfactant concentration in grams/liter and and D_m is in centimeters. At a constant gas flow rate, the number of bubbles then increased with surfactant concentration; more plateau borders were created and more interstitial liquid was carried over which in turn resulted in an increase in the collapsed foam flow rate (see Fig. 5). The increase in interstitial liquid consequently led to a lower enrichment ratio (see Fig. 6). The enrichment ratio, although of practical value, does not show the extent of separation and is subject to error due to fluctuation in col-

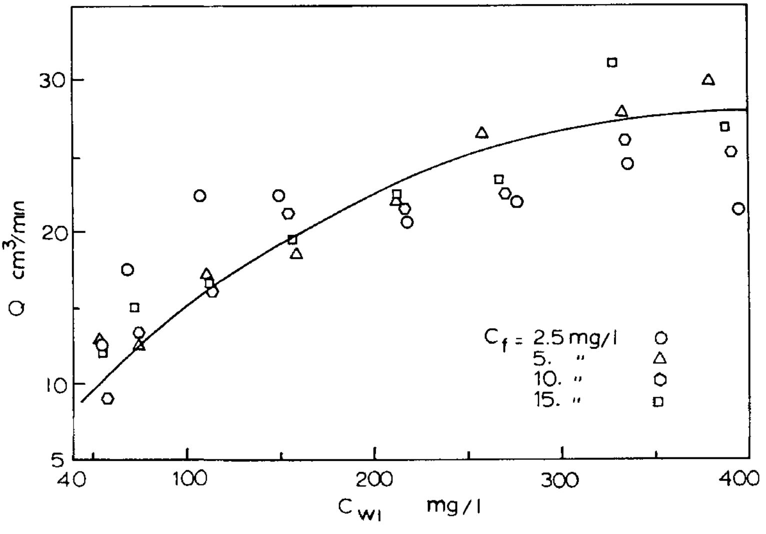

FIG. 5. Collapsed foam flow rate vs surfactant concentration at a gas flow rate of 250 cm^3/min and a liquid flow rate of 355 cm^3/min.

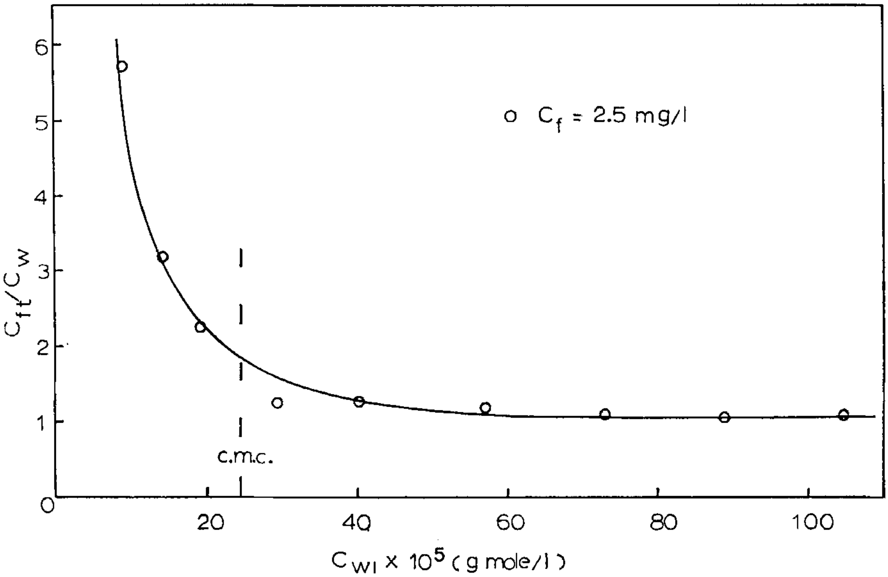

FIG. 6. Phosphate enrichment ratio as a function of surfactant concentration.

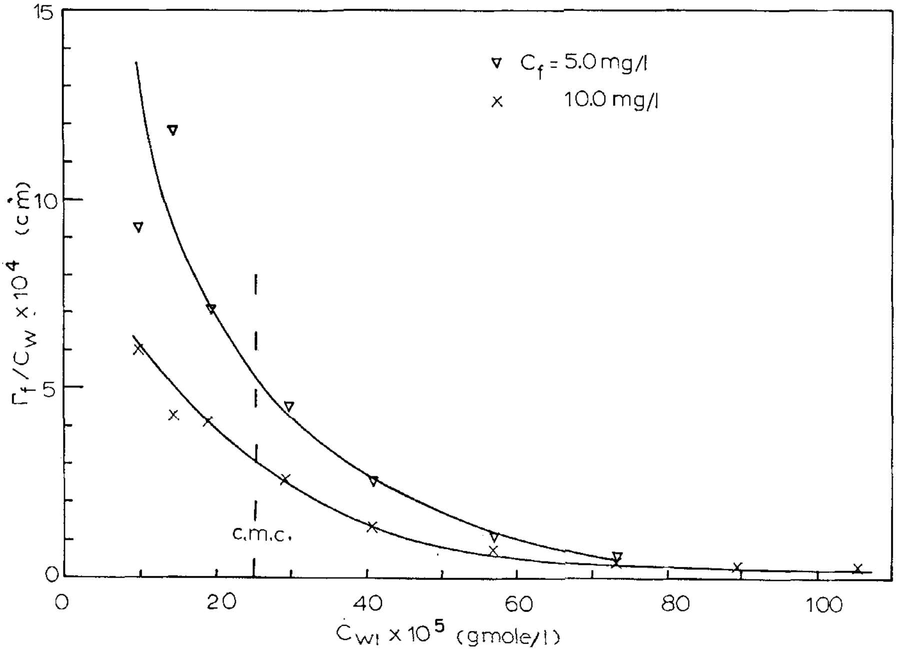

FIG. 7. Effect of surfactant concentration of the distribution factor of phosphate at feed phosphate concentrations of 5.0 and 10.0 mg/l.

lapsed foam flow rate and in foam height. For example, the surfactant enrichment ratio of 60 mg/l of feed surfactant solution was found to vary from 5.8 to 10.2 as foam height increased from 3 to 20 cm, and an increase of 1 cm from zero foam height caused a change in collapsed foam rate of about 20% (*22*). To eliminate these errors, a study was made of the effect of surfactant on the surface excess of phosphate. Figure 7 shows that the distribution factor of phosphate, defined as Γ_f/c_w, decreases with increasing surfactant and phosphate concentrations either side of the cmc of EHDABr. This is the result of the equilibria between the surface and bulk liquid phases:

$$(\mathrm{EHDABr})_s + \mathrm{H_2PO_4}^- \rightleftarrows (\mathrm{EHDAH_2PO_4})_s + \mathrm{Br}^-$$

At constant phosphate concentration, increasing the surfactant concentration would bring more Br^- to the solution, thus shifting the equilibrium to the left and lowering the concentration of the surfactant–phosphate complex on the surface phase. Above the cmc, the surface excess of phosphate would be even lower due to the "solubilization" effect of micelles. For dilute solutions of phosphate, the distribution factor of phosphate can be related to the surface excess of surfactant via

$$\Gamma_f/c_w = (K_1/K_2)(\Gamma_1/[\mathrm{Br}^-]) \tag{6}$$

Although data are not available to evaluate K_1/K_2, Fig. 8 substantiates the hypothesis of equilibria between the surface and bulk liquid phases. Figure 8 shows a linear relationship between the distribution factor, Γ_f/c_w, and Γ_1/Br^- at a low concentration of phosphate (5 ppm), in accordance with Eq. (6).

The decrease in the distribution factor of phosphate at higher levels of phosphate (see Fig. 7) is also a consequence of the above equilibria. Higher phosphate concentrations would shift the equilibrium to the right, leading to a higher surface excess of phosphate, as can be seen from

$$\Gamma_f = \frac{\dfrac{K_1}{K_2}(\Gamma_1/[\mathrm{Br}^-])c_w}{1 + \dfrac{K_1}{K_2}\left(\dfrac{c_w}{[\mathrm{Br}^-]}\right)} \tag{5}$$

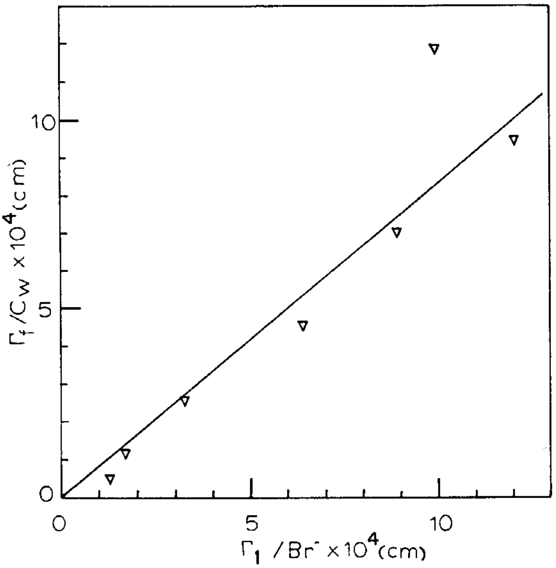

FIG. 8. Relationship between the distribution factor of phosphate and Γ_1/Br^- for a dilute solution of phosphate.

and to a lower distribution factor of phosphate, as can be seen from

$$\frac{\Gamma_f}{c_w} = \frac{(K_1/K_2)\Gamma_1/[\mathrm{Br}^-]}{1 + (K_1/K_2)(c_w/[\mathrm{Br}^-])} \tag{12}$$

In terms of the distribution factor of phosphate, the removal is at its best at low levels of phosphate and surfactant concentrations. This result in consistent with other work on the effect of surfactant on the distribution factor of colligend. Jorne (*23*) investigated the effect of monobutyl biphenyl sodium sulfonate on the distribution factor Sr^{2+} and found that the distribution factor decreased exponentially with surfactant concentration. In terms of degree of stripping, R_f, the same conclusion applies, since R_f can be related to the distribution factor via Eq. (10). Figure 9 shows the percent stripping of phosphate as a function of bulk concentration of surfactant at feed and gas rates of 355 and 250 cm^3/min, respectively, and at feed phosphate concentration of 2.5 mg/l. Separation was found to be low, 10.4%, at a surfactant concentration of 40 ppm. Separation could be improved by increasing the surface flow rate per unit feed rate (6*G*/

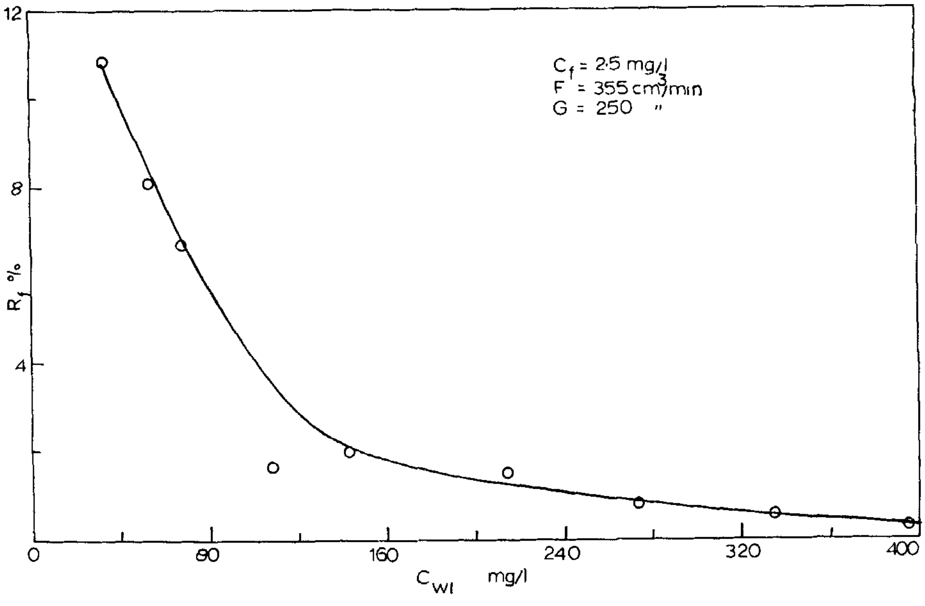

FIG. 9. Effect of surfactant concentration on percent stripping of phosphate at a phosphate feed concentration of 2.5 mg/l.

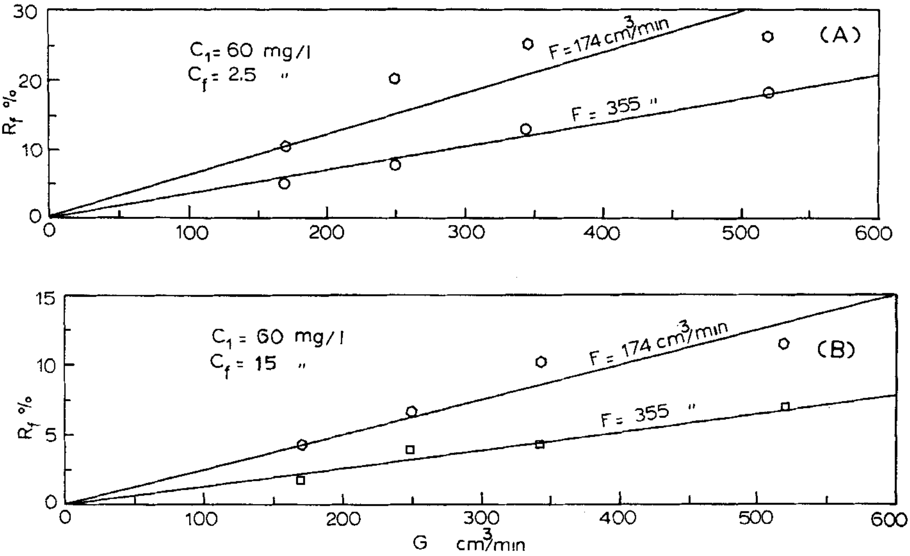

FIG. 10. Effect of gas and liquid flow rates on percent stripping of phosphate. (A) Feed phosphate concentration of 2.5 mg/l. (B) Feed phosphate concentration of 15 mg/l.

(D_mF)], either by increasing gas flow rate or by decreasing liquid flow rate. However, increasing the gas flow rate must be exercised with care to ensure that bubble residence time is long enough for equilibrium surface adsorption. Nguyen and Phillips (*9*) and Grieves et al. (*20*) have examined the approach to equilibrium surface adsorption as bubble residence time increases. In this investigation, gas flow rates were maintained at levels less than 600 cm^3/min for a liquid column length of 174 cm to ensure equilibrium surface adsorption (*9*). Figure 10 shows a linear relationship between percent stripping of phosphate and gas flow rate. This is expected from Eq. (9). Figure 10 also shows a marked increase in percent stripping of phosphate at the lower feed rate. It is clear that the degree of separation could be improved by employing an even lower feed rate and a higher gas flow rate. However, too low a feed rate would lead to small flow rates of treated solution, and is therefore undesirable. Although the removal of about 30% of phosphate at a feed rate of 174 cm^3/min (see Fig. 10) probably would not be adequate in most industrial applications, the removal of phosphate could be greatly improved by the use of multistage column operation since for the succeeding stages the concentration of phosphate and surfactant are lower, and therefore the degree of separation could increase (see Fig. 9). The use of multistage operation is therefore preferred.

CONCLUSIONS

The following conclusions can be drawn for continuous operation: Separation of phosphate in terms of distribution factor increases with lower surfactant and phosphate concentrations. This can be predicted from the assumed equilibria

$$(\mathrm{EHDABr})_s + \mathrm{H_2PO_4^-} \rightleftarrows (\mathrm{EHDAH_2PO_4})_s + \mathrm{Br^-}$$

between the bulk liquid and surface phases.

In terms of percent stripping, the removal of phosphate was found to decrease strongly with increasing surfactant concentration on either side of the cmc. For best removal of phosphate in one equilibrium stage, high gas and low liquid flow rates should be employed with a dilute solution of both phosphate and surfactant. For best overall removal of phosphate, multiple equilibrium stages should be employed.

Acknowledgement

Financial support was provided by the Department of the Environment, Ottawa.

SYMBOLS

B_1, B_2	hydrodynamic constants
C_1	concentration of EHDABr in the feed, mg/l
C_{1t}	concentration of EHDABr in the collapsed foam, mg/l
C_{w_1}	concentration of EHDABr in the bottom, mg/l or g mole/l
c_f	concentration of phosphate in feed as potassium monobasic phosphate, mg/l
c_w	concentration of phosphate in the bottom solution as potassium monobasic phosphate, mg/l
c_{ft}	concentration of phosphate in the collapsed foam as potassium monobasic phosphate, mg/l
D_m	volume-to-surface mean diameter ($= \sum n_i d_i^3 / \sum n_i d_i^2$), cm
e	electronic charge
F	feed flow rate, cm^3/min
G	gas flow rate, cm^3/min

k	Boltzmann constant
K_1, K_2	equilibrium constants
Q	collapsed foam flow rate, cm^3/min
Q_d	surface layer flow rate, cm^3/min
R_f	percent stripping of phosphate $[= (c_f - c_w)/c_f] \times 100$
S	rate of surface flow ($= 6G/D_m$), cm^2/min
T	temperature of the solution, °K
W	energy of desorption of hydrocarbon chain
z	valency of long chain ions
γ	surface tension, dynes/cm
Γ_1	surfactant surface excess, g moles/cm^2
Γ_f	phosphate surface excess, g moles/cm^2
Γ_f^α	actual surface concentration of phosphate, g moles/cm^2
ψ_0	surface potential, mV

Subscript

s	surface phase

REFERNCES

1. R. Lemlich, *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
2. W. Davis, A. H. Hibbey, and E. Schonfeld, Report ORNL 3811, USAEC, October 1965.
3. E. Schonfeld et al., Report NYO 9577, USAEC, July 1963.
4. E. Schonfeld and A. H. Hibbey, *Nuclear Appl.*, *3*, 353 (1967).
5. P. F. Wace and D. L. Banfield, "Foam Separation," Report AERE-R5189, Harwell, United Kingdom, 1966.
6. R. B. Grieves and R. C. Aronica, *Int. J. Air Water Pollution*, *10*, 31 (1966).
7. R. B. Grieves and R. C. Aronica, *Nature*, *210*, 901 (1966).
8. R. B. Grieves, H. W. Bretz, and S. L. Wang, *Appl. Microbiol.*, *14*, 778 (1966).
9. Y. V. Nguyen and C. R. Phillips, *Separ. Sci.*, *8*, 11 (1973).
10. R. Lemlich, in *Progress in Separation and Purification*, Vol. 1 (E. S. Perry, ed.), Wiley (Interscience), New York, 1968, Chap. 1.
11. J. N. Butler, *Solubility and pH Calculations*, Addison-Wesley, Reading, Masschusetts, 1964.
12. R. B. Grieves and D. Bhattacharyya, *Can. J. Chem. Eng.*, *43*, 286 (1965).
13. D. Harper and R. Lemlich, *Ind. Eng. Chem., Process Des. Develop.*, *4*, 13–15 (1965).
14. A. J. Rubin and M. L. Lapp, *Anal. Chem.*, *41*(8), 1133–1135 (1969).
15. H. M. Schoen, *New Chemical Engineering Separation Techniques*, Wiley (Interscience), New York, 1962, Chap. 5.
16. R. B. Grieves, C. J. Crandall, and R. K. Wood, *Int. J. Air Water Pollution*, *8*, 501 (1964).
17. *Standard Methods*, American Public Health Assoc., New York, 1961, p. 199.
18. W. B. Smith, *Analyst*, *84*, 77 (1959).
19. J. T. Davies and E. K. Rideal, *Interfacial Phenomena*, Academic, New York, 1963.

20. R. B. Grieves and D. Bhattacharyya, and P. J. W. The,*Can. J. Chem. Eng.*, *51*, 173 (1973).
21. E. Rubin and J. Jorne, *Ind. Eng. Chem., Fundam.*, *8*, 474 (1969).
22. S. Primiani, "Continuous Foam Fractionation of Phosphate Using a Cationic Surfactant," M.A.Sci. Thesis, University of Toronto, December 1971.
23. J. Jorne and E. Rubin, *Separ. Sci.*, *4*, 313 (1969).

Received by editor December 10, 1973