This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

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

Foam Fractionation of Orthophosphate with a Cationic Surfactant

Robert B. Grieves[a]; Dibakar Bhattacharyya[a]
[a] Illinois Institute of Technology, Chicago, Illinois

To cite this Article Grieves, Robert B. and Bhattacharyya, Dibakar(1966) 'Foam Fractionation of Orthophosphate with a Cationic Surfactant', Separation Science and Technology, 1: 1, 81 — 94

To link to this Article: DOI: 10.1080/01496396608049436

URL: http://dx.doi.org/10.1080/01496396608049436

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE, 1(1), 81–94 (1966)

Foam Fractionation of Orthophosphate with a Cationic Surfactant

---

ROBERT B. GRIEVES and DIBAKAR BHATTACHARYYA
ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILLINOIS

Downloaded At: 14:52 25 January 2011

Summary

An experimental investigation is presented of the foam fractionation of orthophosphate from aqueous solution using a cationic surface-active agent, ethylhexadecyldimethylammonium bromide. The effects of initial concentration of phosphate, of initial concentration of surfactant, of pH, and of the presence of competing anions are established. Initial concentrations of phosphate range from 12.5 to 150 mg/liter (as PO_4), initial concentrations of surfactant range from 50 to 600 mg/liter, and the pH is varied from 5.0 to 13.4. Results are discussed in terms of the residual concentration of phosphate, the collapsed foam volume, the phosphate removal ratio, and the "relative fractionation" of the phosphate and surfactant into the surface layers of the foam-producing bubbles.

Optimum results are achieved between pH 8 and 9 and in the total absence of competing divalent anions. The removal of 99 per cent of 9.0 mg/liter phosphate can be accomplished with 100 mg/liter of surfactant; the removal of 99 per cent of 24.2 mg/liter phosphate can be accomplished with 600 mg/liter of surfactant. Results are compared with previous work on the foam fractionation of phenolate.

INTRODUCTION

Foam-separation processes have been used successfully for the removal from aqueous solution of fatty acids and detergents, of proteins and enzymes including albumin and catalase, of dyes including bromthymol blue, Congo red, and methyl orange, of cations such as strontium, magnesium, and calcium, and of anions including picrate, gallate, and 1- and 2-naphthoic acid (*1*). For non- or weakly surface-active materials, foaming agents have been added. Extensive engineering studies have been conducted on the foam separation of radioactive cations from nuclear-waste streams (*2,3*), but work on the separation of inorganic and organic anions is more limited. Recently, experimental studies have been reported on the ion flotation of dichromate in particulate form (*4,5*) and on the foam fractionation of phenolate (*6,7*). A few preliminary studies have been made on orthophosphate, together with comparisons with other anion-separation experiments (*8*).

For the foam fractionation of inorganic and organic cations and anions, various mechanisms have been postulated by which the ions together with the surface-active additive are carried into the foam phase. These include the formation in solution of a surfactant-ion complex which is then adsorbed at the air-aqueous solution interfaces of the foam-producing bubbles; and the adsorption of the surfactant at the interfaces followed by the electrostatic attraction between the surfactant and the ions of opposite charge. Both mechanisms apply to a system consisting of two phases-aqueous solution and air. The process is distinct from froth flotation and ion flotation (*9*), which involves a third, solid (particulate) phase.

Phosphates are of particular interest to water and waste-treatment engineers. Phosphates present in effluents and fertilizer leachings provide difficulties in the treatment of surface waters by flocculation and sedimentation. Traces of phosphates promote the growth of algae in reservoirs and lakes; the prevention of algal blooms is a prime cause for the development of new techniques for phosphate removal from waste waters. Methods of phosphate separation have included chemical coagulation (*10,11*), biological treatment (*12*), separation beds (*13*), activated carbon columns (*13*), and electrodialysis (*14*).

The objective of this investigation is the establishment of the feasibility of foam fractionation for the removal and concentration of orthophosphate from aqueous solution. A cationic surface-active agent, ethylhexadecyldimethylammonium bromide, is used and attention is focused on the residual phosphate concentration, the residual surfactant concentration, the collapsed foam volume, and the phosphate removal ratio. Independent variables include pH, the initial phosphate concentration, and the initial surfactant concentration; possible interferences from sulfate and chloride are considered.

Downloaded At: 14:52 25 January 2011

EXPERIMENTAL

A schematic diagram of the experimental apparatus is presented in Fig. 1. The cylindrical, foaming column was made of Pyrex and was 9.5 cm in diameter and 52 cm in height. The filtered nitrogen gas was saturated with water, metered with a calibrated rotameter, and passed through a sintered glass diffuser 3 cm in diameter and of 50-μ porosity. The nitrogen flow rate was 400 ml/min (at 25°C and 1 atm). For each experiment 2 liters of feed (initial) solution in distilled water were prepared containing from 12.5 to 150 mg/liter orthophosphate (1.32×10^{-4} to 1.58×10^{-3} *M*). All weight concentrations of phosphate in this study are given in terms of PO_4; monobasic potassium phosphate, KH_2PO_4, primary standard, was the reagent. From 50 to 600 mg/liter (1.32×10^{-4} to 1.58×10^{-3} *M*) ethylhexadecyldimethylammonium bromide (EHDA-Br), a cationic surfactant, were added, and the pH was adjusted to the required value with 8.93×10^{-2} *M* KOH (reagent grade), or in a few cases with KOH pellets. In some of the runs, varying quantities of reagent-grade sodium sulfate and sodium chloride were added to the initial solutions.

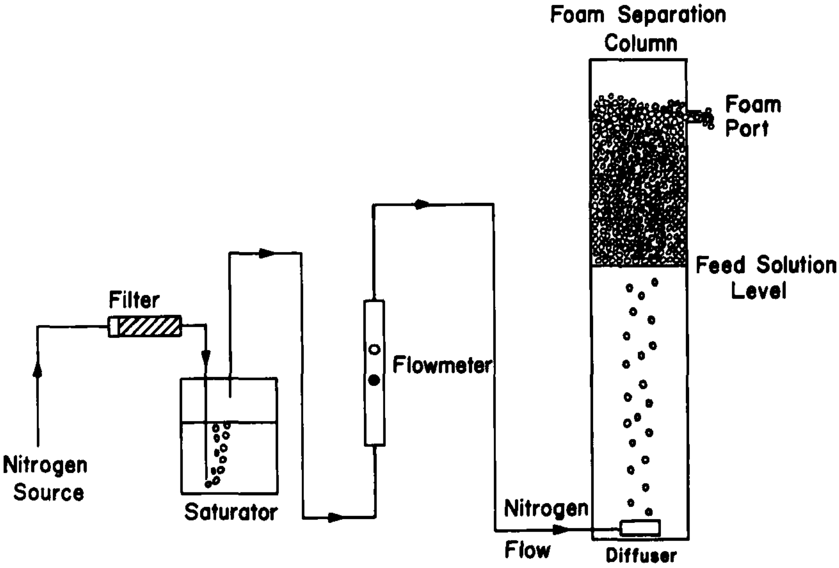

FIG. 1. Schematic diagram of experimental foam-fractionation apparatus.

Downloaded At: 14:52 25 January 2011

Downloaded At: 14:52 25 January 2011

The 2 liters of initial solution were placed in the foaming column and the nitrogen flow was begun. Foam was collected continuously at a port located 44.5 cm above the base of the column, 16.3 cm above the initial solution level, and each experiment was terminated after all foaming had ceased, which required from 2 to 3 hours. Temperature was maintained at 25°C. After completion, the volume of the residual solution was measured, the residual concentration of EHDA-Br was determined by a two-phase titration technique (*15,16*), which was accurate to within 1 mg/liter, and the residual concentration of orthophosphate was determined by the amino naphthol sulfonic acid method (*17*), which was accurate to within 0.02 mg/liter. A slight modification of the standard orthophosphate analysis was necessitated due to the reaction of EHDA-Br with ammonium molybdate. The addition of an excess (more than that required to react the EHDA-Br completely) of dodecyl sodium sulfate, an anionic surfactant, prior to the addition of the ammonium molybdate, completely eliminated any interference. The presence of the dodecyl sodium sulfate had no effect on the analysis.

THE EFFECT OF pH

The first series of experiments was conducted to establish the influence of the hydrogen-ion concentration of the initial solution on the foam fractionation of phosphate. For these studies, the initial phosphate concentration was held at 25 mg/liter, and EHDA-Br concentrations of 200, 400, and 600 mg/liter were used. The pH was varied from 5.0 to 13.4. For each experiment the following material balances can be written:

$$V_i = V_r + V_f \tag{1}$$

$$z_i V_i = z_r V_r + z_f V_f \tag{2}$$

$$x_i V_i = x_r V_r + x_f V_f \tag{3}$$

V_i, V_r, and V_f are the volumes in liters of initial solution (always 2.0 liters), residual solution, and collapsed foam, respectively. z_i, z_r, and z_f are the concentrations of phosphate in milligrams per liter in the initial solution, residual solution, and collapsed foam, respectively. The concentration of ethylhexadecyldimethylammonium bromide (EHDA-Br), in milligrams per liter, is denoted by x. Equations (1), (2), and (3) may be used to calculate the concentrations of phosphate and EHDA-Br in the collapsed foam stream from the collapsed foam volume and analyses of the residual solution. The concentration of phosphate in the foam, z_f, is particularly useful, since the parameter z_fV_f/z_iV_i, the removal ratio which represents the weight of phosphate foam fractionated per unit weight of phosphate in the feed, is valuable in establishing the efficiency of the foam-fractionation process.

Relations between the phosphate removal ratio and pH for the three initial concentrations of EHDA-Br are presented in Fig. 2 for 32 individual experiments. At constant pH, the removal clearly increases with a higher dosage of surfactant, reaching a value of 0.9 at pH 8.0 with $x_i = 600$ mg/liter. The maxima in the curves in the range pH 8.0 to 9.0 are brought about by two effects. At fixed initial concentrations of phosphate and surfactant, as the pH is increased from 6 toward 8, the monovalent $H_2PO_4^-$ ion is converted to the divalent $HPO_4^=$ ion (at pH 6, 94 mole % of the phosphate is in the monovalent form, while at pH 8, 86 mole % of the phosphate is in the divalent form). Since the mechanism of the foam-fractionation process either involves complex formation between phosphate anions and EHDA cations or electrostatic attraction of the phosphate anions to the EHDA cations adsorbed at bubble interfaces, the divalent form is more readily separated. It would be expected that further pH elevation would improve the efficiency of the process and would produce higher values of the removal ratio; however, there is a competition between hydroxide ions and phosphate ions for the EHDA cations, which is the second effect mentioned above. Thus as the pH is elevated above 8 and more phosphate is converted into the divalent form (at pH 10, 99^+% of the phosphate is in the $HPO_4^=$ form), which should increase the removal ratio, the presence of higher and higher concentrations of hydroxide ion begins to have an appreciable influence. As the pH is elevated further, the interference by hydroxide increases until trivalent phosphate (PO_4^{3-}) begins to appear in significant quantities (at pH 11, 2.3 mole % of the phosphate is in the trivalent form and at pH 12, 17.5 mole % is in the trivalent form). The effect of increasing hydroxide-ion concentration appears to be partly overcome by the trivalent phosphate in the pH range 11 to 12.2; but, above pH 12.2, the molar concentrations of hydroxide become large in comparison with that of phosphate and sharp decreases

Downloaded At: 14:52 25 January 2011

Downloaded At: 14:52 25 January 2011

in the removal ratio are observed. It is also conceivable that high concentrations of hydroxide depress the ionization of EHDA-Br, bringing about the formation of EHDA-OH. It should be noted that the maxima and minima in the pH range 8 to 12 are not sharp and may have been created in part by experimental inaccuracies. However, several of the points in this range reproduced quite well after considerable time lapses.

Results for the residual concentrations of phosphate have been reported previously (8). Minima for all three initial surfactant concentrations and $z_i = 25$ mg/liter were obtained in the pH range 7.9 to 9.0. With $x_i = 200$ mg/liter, the minimum residual phosphate concentration was 12.2 mg/liter at pH 8.3; with $x_i = 400$ mg/liter, $z_r = 6.9$ mg/liter at pH 9.0; and with $x_i = 600$ mg/liter, $z_r = 3.0$ mg/liter at pH 7.9. In these experiments, collapsed foam volumes were very insensitive to pH and were a function only of the initial surfactant concentration. For $x_i = 200$ mg/liter, the collapsed foam volume, V_f, ranged from 0.15 to 0.24 liter in a random manner with pH; for $x_i = 400$ mg/liter, V_f ranged from 0.36 to 0.47 liter; and for $x_i = 600$ mg/liter, V_f ranged from 0.53 to 0.63 liter. (In each experiment V_i was held constant at 2.0 liters.) The residual concentrations of surfactant were also quite insensitive to pH: for $x_i = 200$ mg/liter, x_r varied randomly from 11.2 to 17.8 mg/liter over the pH range 5.0 to 13.4; for $x_i = 400$ mg/liter, x_r varied from 17.2 to 22.8 mg/liter, and for $x_i = 600$ mg/liter, x_r varied from 21.6 to 28.4 mg/liter.

THE EFFECT OF INITIAL CONCENTRATIONS OF PHOSPHATE AND SURFACTANT

The second series of experiments was conducted to establish the influence of variations in the initial concentrations of phosphate and EHDA-Br on the foam-fractionation process. The initial concentration of phosphate was varied from 12.5 to 150 mg/liter and that of EHDA-Br from 50 to 600 mg/liter. In each experiment the pH of the initial solution was adjusted to 8.0 with KOH. Results for one set of experiments are given in Fig. 3 in which the ratios z_r/z_i, x_r/x_i, and V_f/V_i are related to x_i; for these runs, z_i was held constant at 25 mg/liter. The logarithmic ordinate scale is used to present the data more clearly. The fractional residual of phosphate, z_r/z_i, decreased exponentially with x_i, but was always significantly greater than the fractional residual of EHDA-Br.

Downloaded At: 14:52 25 January 2011

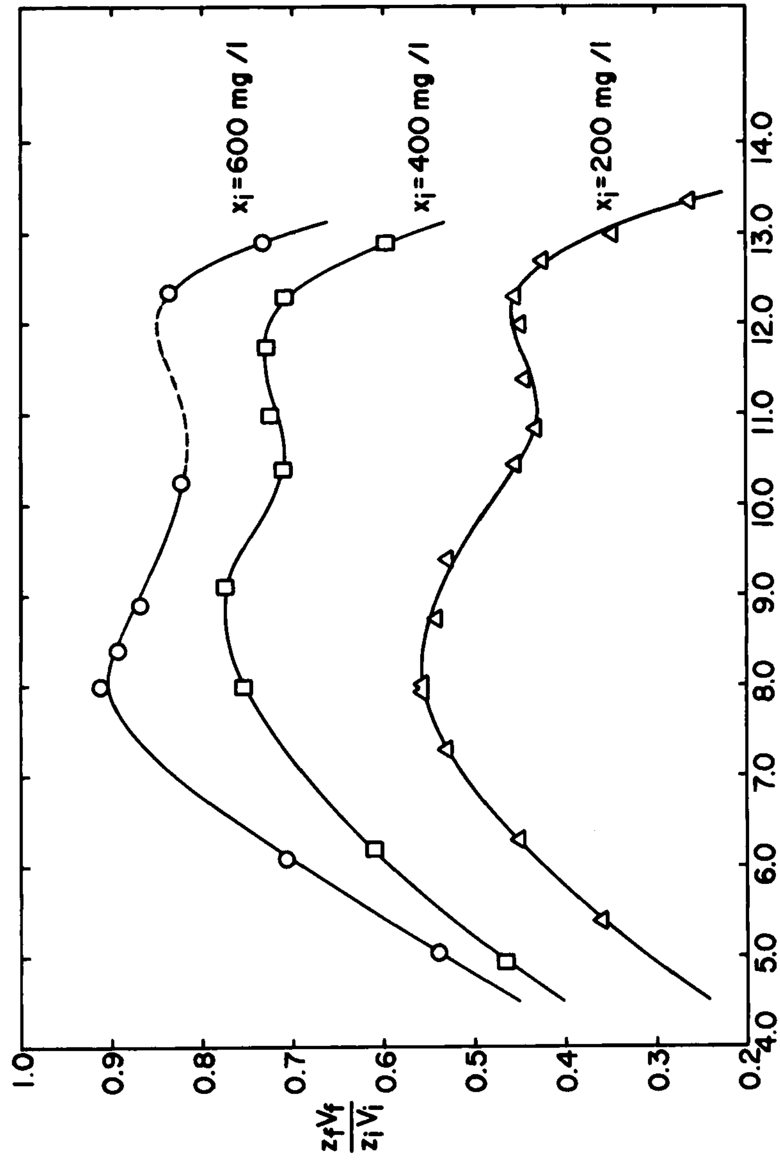

FIG. 2. Relations between phosphate-removal ratios and pH for three initial EHDA-Br concentrations.

Downloaded At: 14:52 25 January 2011

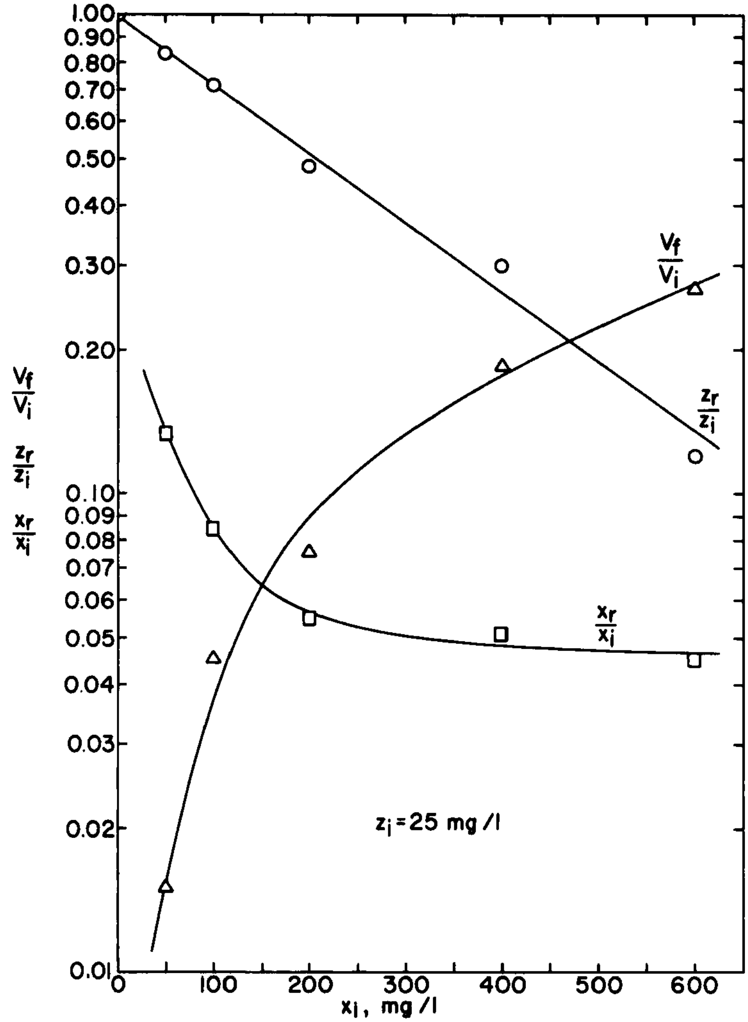

FIG. 3. Fractional residuals of phosphate and EHDA-Br and fractional collapsed foam volumes related to initial EHDA-Br concentrations.

For a total of 16 experiments covering the full ranges of z_i and x_i given above, the fractional residual of phosphate could be readily correlated with initial concentrations by the following equation:

$$z_r/z_i = 1.0 - 1.65 \times 10^{-4}x_i - 0.877x_i^{0.5}/z_i \tag{4}$$

It may readily be shown from Eq. (4) by multiplying through by z_i that for a constant initial concentration of EHDA-Br the residual phosphate concentration is a linear function of the initial phosphate concentration. This behavior is in direct contrast to that observed for the foam fractionation of phenolate with EHDA-Br in a similar apparatus (7), in which the residual phenolate concentration was a more complicated function of the initial phenolate concentration, involving a linear term and a power term.

In these experiments the volume of collapsed foam was independent of the initial phosphate concentration and was practically a linear function of the initial concentration of EHDA-Br:

$$V_f = 7.0 \times 10^{-4} x_i^{1.07} \tag{5}$$

The residual concentration of EHDA-Br decreased as the initial concentration of phosphate was increased at constant initial EHDA-Br, and increased with the initial concentration of EHDA-Br at constant initial phosphate. The range of variation was from 6.7 to 27 mg/liter for the 16 runs. This behavior was similar to that observed for phenolate.

An expression for the removal ratio, z_fV_f/z_iV_i, may be developed from Eqs. (1), (2), (4), and (5):

$$z_fV_f/z_iV_i = 1.0 - [(1.0 - 3.5 \times 10^{-4} x_i^{1.07}) (1.0 - 1.65 \times 10^{-4} x_i - 0.877 x_i^{0.5}/z_i)] \tag{6}$$

At constant initial EHDA-Br concentration, it may be shown from Eq. (6) that the removal ratio is a linear function of the reciprocal of the initial phosphate concentration. Data for 15 of the 16 experiments (the single point with $x_i = 50$ mg/liter is omitted) are shown in Fig. 4. The straight lines for the four values of x_i ranging from 100 to 600 mg/liter were calculated from Eq. (6). From Fig. 4 100 mg/liter of EHDA-Br are able to provide 99% removal ($z_fV_f/z_iV_i = 0.99$) of 9.0 mg/liter of phosphate, 200 mg/liter to provide 99% removal of 12.7 mg/liter of phosphate, 400 mg/liter to provide 99% removal of 18.8 mg/liter, and 600 mg/liter to provide 99% removal of 24.2 mg/liter. A relation similar to Eq. (6) was developed for phenolate (7); the removals of phenolate by a given quantity of EHDA-Br were generally better than those of phosphate, indicating that any surface activity that the anion which is to be foam-fractionated may

Downloaded At: 14:52 25 January 2011

possess may have a decided influence upon the efficiency of the process.

For the foam fractionation of phenolate, a "relative fractionation" parameter was developed to relate the quantities of phenolate and surfactant removed by foam separation in the surface layers at the air-solution interfaces of the bubbles (7). The use of this parameter eliminated the relative quantities of ion and surfactant carried from solution by mechanical entrainment in the foam. For phosphate fractionation, the parameter may be calculated from the following equation:

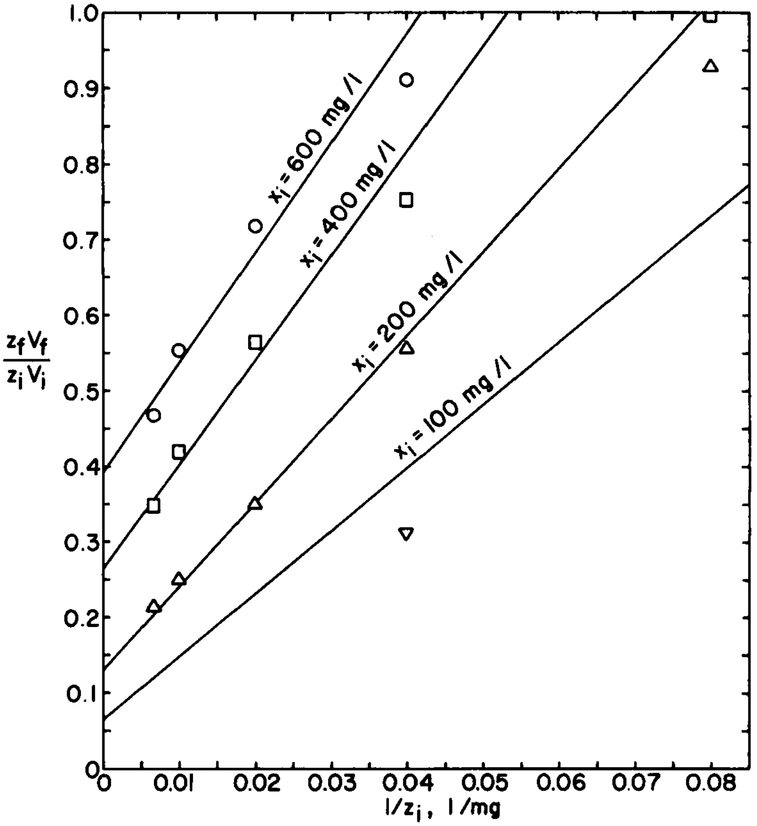

FIG. 4. Relations between removal ratios and reciprocal initial phosphate concentrations with parameters of initial EHDA-Br concentrations.

$$\left.\frac{z_f'}{x_f'}\right]_{RF} = 3.98\,\frac{z_f - \frac{1}{2}(z_i + z_r)}{x_f - \frac{1}{2}(x_i + x_r)} \tag{7}$$

Downloaded At: 14:52 25 January 2011

The ratio $z_f'/x_f']_{RF}$ represents the gram ions of phosphate foam-fractionated in the bubble-surface layers per gram ion of EHDA fractionated. The number 3.98 is the ratio of the molecular weight of EHDA-Br to the ionic weight of PO_4. In this study, $z_f'/x_f']_{RF}$ varied from 0.153 to 0.366, for 16 points with the gram-ion ratios in the feed (initial) solution varying from 0.124 to 2.98 gram ion phosphate per gram ion EHDA. At a constant initial concentration of EHDA-Br, $z_f'/x_f']_{RF}$ increased with increasing initial concentration of phosphate; at a constant initial concentration of phosphate, $z_f'/x_f']_{RF}$ decreased with increasing initial concentration of EHDA-Br. At pH 8.0, where these experiments were conducted, 84 mole % of the phosphate would be in the divalent $HPO_4^=$ form and 1 gram ion of phosphate should be removed with every 2 gram ions of EHDA, giving a theoretical value of $z_f'/x_f']_{RF}$ of 0.5. The fact that this value was never achieved indicates that there was competition between bromide and hydroxide (to a lesser extent at this pH) ions with phosphate for the EHDA cations. Although phosphate is complexed or attracted preferentially, the existence of high concentrations of competing anions could cause a substantial interference to the fractionation process.

Downloaded At: 14:52 25 January 2011

THE EFFECT OF CHLORIDE AND SULFATE INTERFERENCES

A final series of experiments was conducted to establish interferences that other anions might provide with the foam fractionation of phosphate. The competition of other anions with phosphate was clearly evidenced in experiments in which sodium chloride and sodium sulfate were added to the initial solutions. The initial concentration of phosphate was 25 mg/liter, the initial concentration of EHDA-Br was 400 mg/liter, and the pH of the initial solutions was adjusted to 8.0. Results for the fractional residuals and removal ratios are presented in Fig. 5, related to the initial concentrations of chloride and sulfate. The interference from the monovalent chloride ion is not too significant, similar to that from hydroxide, as discussed previously. However, the interference from sulfate is most pronounced, indicating that the foam fractionation of phosphate would be seriously impaired by the presence of appreciable concentrations of sulfate anions. For example, for an initial solution containing 25 mg/liter (2.64×10^{-4} *M*) of phosphate, the presence of an equimolar concentration of sulfate would increase the fractional residual of phosphate from 0.3 to 0.7, and would decrease the phosphate removal ratio from 0.76 to 0.47. This difficulty could be overcome, perhaps, through modifications in operating conditions and through the use of higher initial concentrations of surfactant, enabling the efficient foam fractionation

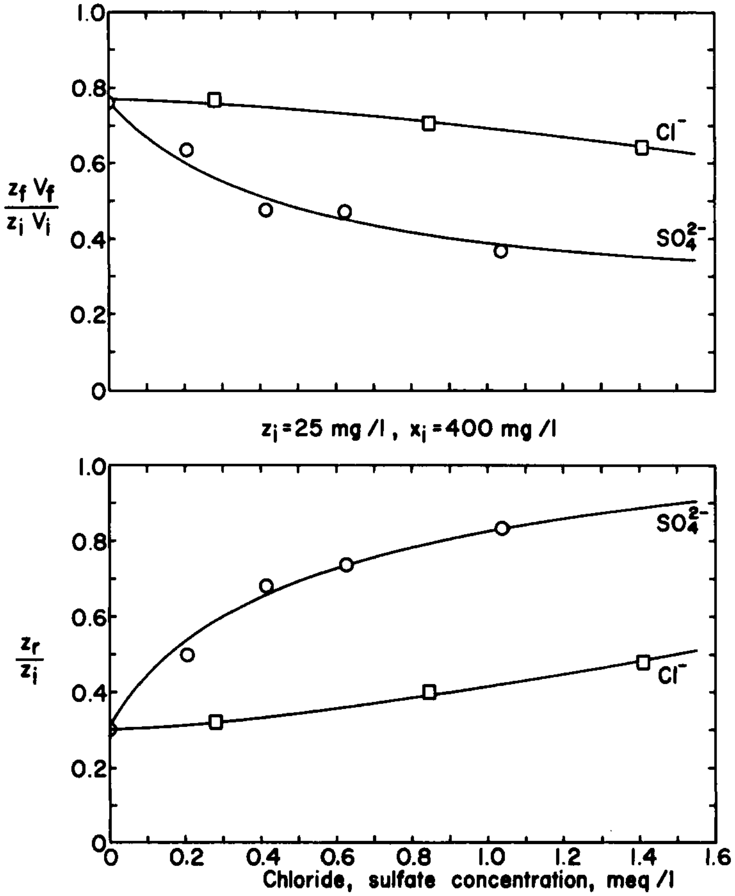

FIG. 5. The effect of competing anions on the foam fractionation of phosphate.

of phosphate and sulfate simultaneously. Although analyses were not run for sulfate on the residual solutions, there is little doubt that sulfate was simultaneously foam-fractionated. This was evidenced in a previous investigation of the ion flotation of dichromate (5). The

Downloaded At: 14:52 25 January 2011

presence of both chloride and sulfate produced increases in the collapsed foam volumes, but had virtually no influence on the residual concentration of EHDA-Br.

CONCLUSIONS

Orthophosphate has been foam-fractionated using a cationic surfactant, ethylhexadecyldimethylammonium bromide, in a batch foaming unit.

1. For initial solutions containing 25 mg/liter of phosphate (as PO_4) and 200 or 400 or 600 mg/liter of surfactant, maximum phosphate removal ratios and minimum phosphate fractional residuals were obtained in the pH range 8 to 9. Poorer results were produced at higher hydrogen-ion concentrations due to the existence of phosphate in the monovalent form, and at lower hydrogen-ion concentrations due to competition with hydroxide. Collapsed foam volumes and residual surfactant concentrations were independent of pH and were functions only of the initial surfactant concentration.

2. For initial solutions at pH 8.0 containing from 12.5 to 150 mg/liter of phosphate and from 50 to 600 mg/liter of surfactant, the phosphate fractional residuals, collapsed foam volumes, and phosphate removal ratios could be related analytically to the initial concentrations. The removal ratio was inversely proportional to the initial phosphate concentration. 100 mg/liter EHDA-Br provided 99% removal of 9.0 mg/liter phosphate, while 600 mg/liter EHDA-Br provided 99% removal of 24.2 mg/liter phosphate. The calculation of a relative fractionation parameter established the competition between bromide (and hydroxide) with phosphate for the EHDA cations.

3. The presence of divalent sulfate anions provided a serious impairment to the foam fractionation of divalent phosphate ($HPO_4^=$). However, this difficulty could possibly be overcome by modifications in operating conditions and through the use of higher surfactant concentrations to produce the simultaneous foam fractionation of phosphate and sulfate.

4. Results indicate that the process has sufficient merit for further study, including modifications in equipment geometry and operation, such as continuous, multicolumn processes with foam reflux.

Downloaded At: 14:52 25 January 2011

Acknowledgment

The authors wish to acknowledge gratefully the support of the Division of Water Supply and Pollution Control of the U.S. Public Health Service through Research Grant No. WP 00702-01.

REFERENCES

1. H. M. Schoen (ed.), *New Chemical Engineering Separation Techniques*, Wiley, New York, 1963, pp. 319–385.
2. E. Schonfeld, U.S. Atomic Energy Commission, Rept. NYO-9577, July 1960.
3. H. M. Schoen, E. Rubin, and D. Ghosh, *J. Water Pollution Control Federation*, **34**, 1026 (1962).
4. R. B. Grieves and T. E. Wilson, *Nature*, **205**, 1066 (1965).
5. R. B. Grieves, T. E. Wilson, and K. Y. Shih, *J. Am. Inst. Chem. Engrs.*, **11**, 820 (1965).
6. R. B. Grieves and R. C. Aronica, *Nature*, in press.
7. R. B. Grieves and R. C. Aronica, *Intern. J. Air Pollution*, in press.
8. R. B. Grieves and D. Bhattacharyya, *Surface Science*, in press.
9. F. Sebba, *Ion Flotation*, Elsevier, Amsterdam, 1962.
10. G. A. Rohlich, *R. A. Taft Sanit. Engr. Center Tech. Rept. W61-3*, pp. 130–135, 1961.
11. A. Henriksen, *Schweiz. Z. Hydrol.*, **24**, 253 (1962).
12. H. E. Klotter and R. Neussel, *Vom Wasser*, **26**, 110 (1959).
13. R. L. Culp, *J. Water Pollution Control Federation*, **35**, 799 (1963).
14. Tsuan Hua Feng, Small scale laboratory units for exploratory electrodialysis experiments, paper presented at American Chemical Society Meeting, Division of Water and Waste Chemistry, Cincinnati, Ohio, Jan. 1963.
15. W. B. Smith, *Analyst*, **84**, 77 (1959).
16. D. C. Cullum, *Proc. World Congr. Surface-Active Agents*, **3**, 42 (1960).
17. *Standard Methods*, American Public Health Association, New York, 1961, p. 199.

Received by editor November 20, 1965
Submitted for publication December 30, 1965

Downloaded At: 14:52 25 January 2011