# Foam Fractionation of Anions with a Cationic Surfactant: Orthophosphate

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## Abstract

An experimental study has been conducted for the first time of the foam fractionation of orthophosphate using a cationic surfactant. For feed solutions $2.63 \times 10^{-4}$ molar in phosphate and three surfactant concentrations, pH has a pronounced effect on residual concentrations of phosphate. A comparison with the ion flotation of dichromate and with the foam fractionation of phenolate shows dichromate flotation to be the most efficient.

FOAM SEPARATION processes have been used successfully by chemists, biologists and engineers for the removal from aqueous solution of a number of inorganic and organic compounds and ions (1). Although extensive studies have been made on several inorganic cations, work on anions is much more limited. Hexavalent chromium in the form of the dichromate anion has been floated in particulate form (2,3). The process relies on the formation of an insoluble complex between divalent dichromate anions and monovalent cations provided by the surface-active agent. Excess surfactant produces a stable foam, at the gas-liquid interfaces of which the particulate complex is preferentially adsorbed. Phenol in the ionized form phenolate ($C_6H_5O^-$) has been foam fractionated with a cationic surfactant (4,5) with optimum separations obtained at pH 11.5. The process involves either the formation of a soluble phenolate-surfactant complex which is then adsorbed at the gas-liquid, bubble interfaces or the electrostatic attraction of the phenolate anions to the surfactant cations already adsorbed at the interfaces. There is some evidence that the surface-activity of phenolate, although weak, has a beneficial effect on the separation process. Orthophosphate has been foam fractionated (6), including the determination of the effects of several independent variables.

The object of this study was to investigate for the first time the foam fractionation of an inorganic anion which would remain soluble when contacted with a cationic surfactant. Orthophosphate was selected for two reasons: first, the separation process should be strongly pH dependent due to the interconversion of the mono-, di-, and trivalent forms with variations in hydrogen ion concentration; second, a new method for phosphate removal from wastewaters is being sought to prevent the formation of algal blooms on lakes and reservoirs.

The experimental apparatus used herein is similar to that in which phenolate was foam fractionated (4). The batch foaming column was cylindrical, made of Pyrex, and was 9.5 cm in diameter and 52 cm in height. For each experiment, two liters of feed solution in distilled water were prepared containing $2.63 \times 10^{-4}$ molar orthophosphate; monobasic potassium phosphate, $KH_2PO_4$, was the reagent. Ethylhexadecyldimethylammonium bromide (EHDA-Br), a cationic surfactant, was added in a concentration of either $5.28 \times 10^{-4}$ (200 mg/l) or $10.56 \times 10^{-4}$ (400 mg/l) or $15.84 \times 10^{-4}$ (600 mg/l) molar. The pH was adjusted to the required value with $8.93 \times 10^{-2}$ molar KOH, or in a few cases with KOH pellets.

The two liters of feed solution were placed in the foaming column and the nitrogen gas flow was begun. The filtered nitrogen gas was saturated with water, metered with a calibrated flowmeter and passed through a sintered glass diffuser, 3 cm in diameter and of 50 $\mu$ porosity. The nitrogen flow was 400 ml/min at 25C and one atmosphere. As the experiment progressed, foam was collected continuously at a port located 44.5 cm above the base of the column, 16.3 cm above the feed solution level. Each experiment was terminated after all foaming had ceased, which required from 2–3 hr; temperature was maintained at 25C throughout. After termination, the volume of residual solution was measured, and the concentration of EHDA-Br in the residual solution was determined by a two phase titration technique (7,8). The concentration of orthophosphate was determined by the *Amino Naphthol Sulfonic Acid Method* (9), modified by the addition of sodium lauryl sulfate to complex the residual EHDA-Br and thereby to prevent the reaction of EHDA-Br with ammonium molybdate.

Results of 32 individual experiments are presented in Figure 1, in which the fractional residual, $z_r/z_i$, of orthophosphate is related to pH for the three feed concentrations of EHDA-Br. The fractional residual is the concentration of phosphate in the residual solution after foaming divided by that in the feed solution (alway $2.63 \times 10^{-4}$ molar). At constant pH, the fractional residual clearly decreases with an increasing feed concentration of surface-active agent, reaching a minimum value of 0.13 at pH 8 and a feed concentration of EHDA-Br of $15.84 \times 10^{-4}$ molar.

In order to understand the effect of pH on the fractional residuals, Table I gives the concentrations of the various anions in the *feed* solutions as functions of pH. The fractional residuals of phosphate include, of course, all three phosphate forms; however, the predominant form affects the magnitude of the fractional residual. As the feed solution pH is elevated

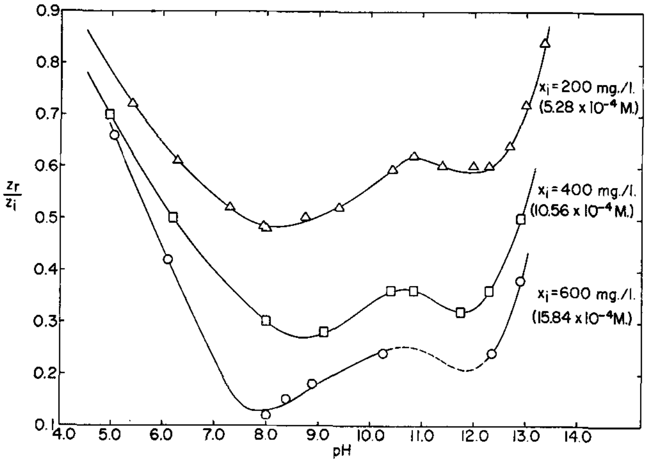

FIG. 1. Data for fractional residuals of phosphate and pH, with three feed surfactant concentrations ($x_i$).

TABLE I

Concentrations of Various Anions in Feed Solutions Versus pH (Molarity, × $10^4$)

| pH | $PO_4^{3-}$ | $HPO_4^{2-}$ | $H_2PO_4^-$ | $OH^-$ |
|---|---|---|---|---|
| 6 | ...... | 0.15 | 2.48 | ...... |
| 7 | ...... | 1.00 | 1.63 | ...... |
| 8 | ...... | 2.26 | 0.37 | 0.01 |
| 9 | ...... | 2.59 | 0.04 | 0.10 |
| 10 | ...... | 2.62 | ...... | 1.00 |
| 11 | 0.06 | 2.57 | ...... | 10.00 |
| 12 | 0.46 | 2.17 | ...... | 100.00 |
| 13 | 1.79 | 0.84 | ...... | 1000.00 |

Total phosphate = $2.63 \times 10^{-4}$ molar.

from 6 toward 8, the monovalent $H_2PO_4^-$ ion is converted to the divalent $HPO_4^{2-}$ ion: at pH 6, 94 mole per cent of the phosphate is in the monovalent form, while at pH 8, 86 mole per cent of the phosphate is in the divalent form. Since the mechanism of the process 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 should be more readily separated and the fractional residual should be lower at pH 8. Further pH elevation above 8 converts more phosphate to the divalent form but the per cent increase is small, and now begins to produce measurable concentrations of competing hydroxide anions. These two effects produce the minima in all three curves in the pH range 8–9. As the pH is elevated from 9 toward 11, the competition by the increasing number of hydroxide ions becomes more appreciable until trivalent phosphate begins to appear in measurable quantities, producing the slight maxima in the vicinity of pH 11. Further reductions in the residuals from pH 11 to pH 12 with further conversion of phosphate to the trivalent form are overshadowed by the preponderant concentrations of hydroxide. The bromide anion added to the feed solutions as part of the surfactant produces a constant (with pH) competition with the various phosphate species for the EHDA cations ($Br^- = 5.28 \times 10^{-4}$ molar, etc.).

In these experiments, collapsed foam volumes were very insensitive to pH and were a function only of the feed EHDA-Br concentration. For feed EHDA-Br concentrations of $5.28 \times 10^{-4}$, $10.56 \times 10^{-4}$, and $15.84 \times 10^{-4}$ molar, the collapsed foam volumes averaged 0.17 liter, 0.41 liter, and 0.57 liter, respectively. The volume of the feed solution was always 2.0 liters. The residual concentrations of EHDA were also quite insensitive to pH: average values of $0.33 \times 10^{-4}$, $0.53 \times 10^{-4}$, and $0.70 \times 10^{-4}$ molar, residual EHDA were obtained for the three feed concentrations. In each experiment, the fractional residual of EHDA was considerably lower than that of phosphate, clearly indicating the competition with bromide and hydroxide ions. These latter results are similar to those obtained for phenolate (4).

TABLE II

Comparison of Foam Separation Processes (Molarity, × $10^4$)

| Feed conc. of EHDA-Br | Residual conc. of dichromate | Residual conc. of phenolate | Residual conc. of phosphate |
|---|---|---|---|
| 5.28 | 0.56 | 1.03 | 1.20 |
| 7.92 | 0.09 | 0.62 | 0.95 |
| 10.56 | 0.02 | 0.42 | 0.73 |
| 15.84 | ..... | 0.17 | 0.30 |

Feed concentration: $2.50 \times 10^{-4}$ molar.

Results are presented in Table II for the ion flotation of dichromate (3), the foam fractionation of phenolate (4), and the foam fractionation of phosphate. Each feed solution was $2.50 \times 10^{-4}$ molar in the particular ion and the feed concentrations of EHDA-Br are listed in the first column. The pH of the dichromate feed solutions was 3.6, that of the phenolate feed solutions was 12.9, and that of the phosphate feed solutions was 8.0. For dichromate the air rate was 4250 ml/min, and for phenolate and phosphate the nitrogen rates were approximtaely 400 ml/min. The higher gas rate for dichromate was necessitated by the reaction of EHDA with $Cr_2O_7^{2-}$, effectively removing the surfactant from solution and thereby considerably reducing the foamability of the feed solution. Clearly, the best results were achieved with dichromate, indicating that the ion flotation of an insoluble complex is a more efficient process than the foam fractionation of soluble complexes or electrostatically attracted ion pairs. The greater efficiency of phenolate fractionation over phosphate fractionation is apparently produced by the surface activity of the phenolate anions or by the greater tendency of the phenolate to complex with EHDA.

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