Ion Flotation of Dichromate and of Complexed Cyanide: Surfactants for Qualitative Analysis

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Abstract

Ion flotation studies have shown that a surface-active agent is useful for qualitative analysis of complex ions in dilute aqueous solution, with the surfactant forming a particulate complex with the complex ion of concern. Experiments with a monovalent, cationic surfactant have established the prevalence of $Cr_2O_7^{2-}$ ($HCrO_4^-$) and not CrO_4^{2-}; of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5H_2O]^{3-}$; and of $[FeFe(CN)_6]^{2-}$ and not $[FeFe(CN)_6]^-$ or $[Fe(CN)_6]^{3-}$. The results can be contrasted to those with ions that do not form particulate complexes with the surfactant, such as HPO_4^{2-} and phenolate; with the latter, no qualitative analytical information can be gained. Ion flotation appears to be a promising technique in general for the determination of ionic species present in aqueous solution; the surfactant must react with the ion of significance to form a particulate complex and the initial surfactant concentration must be controlled carefully.

Introduction

SURFACE-ACTIVE AGENTS have been utilized to foam-separate a number of organic and inorganic ions from aqueous solution. Applications have ranged from a laboratory scale, including the concentration of ions from very dilute solution into a concentrated foam for analytical purposes, to practically an industrial scale, including tertiary radioactive waste treatment. Ion flotation has been applied as a technique for the quantitative analysis of cationic and anionic surfactants below the critical micelle concentration (1). The process also has considerable promise for the elucidation of the structure and charge of complex ions, using the foam-separation potential of surface-active agents as a technique of qualitative analysis.

The ion flotation process involves addition to the solution of a surface-active agent of opposite charge to the ion to be separated. The resultant surface-active complex, generally a colloidal suspension of particulates produced by reaction between the surfactant and the ion to be separated, may be floated to the surface of the suspension by gas bubbles at the interfaces of which it is adsorbed, and a froth is formed. In some cases the ion to be separated may itself be a complex ion and may form colloidal, polynucleated species. In other cases, the particulate complex may be formed only in the presence of the high surfactant concentrations at the bubble interfaces, with the primary step being the migration of the surfactant ions to the interfaces. Examples of ion flotation include strontium (2), copper and iron (3), dichromate (4,5), and complexed cyanide (6,7).

The objective of this investigation is to determine the feasibility of ion flotation with a cationic surfactant for qualitative analysis. Three anions are determined, $Cr_2O_7^{2-}$ (or $HCrO_4^-$), $[Fe(CN)_6]^{4-}$, and $[FeFe(CN)_6]^{2-}$, using the molar ratios of surfactant to Cr or to CN in the foam to establish the ions that are actually present. The results of about 40 individual experiments are analyzed, correcting for entrained bulk solution to establish the molar ratios at the bubble-solution interfaces.

Experimental Procedures

The experimental apparatus used herein is similar to that used in the foam fractionation of phenol and of orthophosphate (8,9). The foam column was 9.6 cm in diameter and was made of Pyrex. For each experiment, 2 liters of feed (initial) solution was prepared, containing 0.463 mmolar or 0.926 mmolar hexavalent chromium, as Cr ($Na_2Cr_2O_7$), with the pH adjusted to 4.2 with HCl; or containing from 1.54 to 3.08 mmolar cyanide, as CN (NaCN), complexed with ferrous iron ($FeSO_4 \cdot 7\,H_2O$) with Fe/CN molar ratios of 0.206 and 0.351 and the pH adjusted to 7.0 with NaOH. The surfactant used was cationic, a quaternary ammonium salt, ethylhexadecyldimethylammonium bromide (EHDA-Br). It was added to the initial solutions in concentrations ranging from 0.198 to 1.59 mmolar, with premixing times of 5 or 15 min.

The 2 liters of initial solution was placed in the foaming column. The solution was ion floated for times ranging from 7.5 to 25 min with foam removal from a port located 9.0 cm (7.0 cm for complexed cyanide) above the initial solution level. Filtered nitrogen gas was the flotation medium. It was saturated with water, metered with a calibrated rotameter, and passed through twin sintered glass diffusers of 50 μ porosity at a rate of 1,440 ml/min, metered at 25C and one atmosphere. The rate was 1,300 ml/min for the experiments with complexed cyanide. Temperature was maintained at 25C throughout. After the termination of each experiment, the volume of the residual solution was measured, and the concentration of surfactant in the residual solution determined by a two-phase titration technique, using sodium tetraphenylboron as the titrant and bromophenol blue as the indicator (10). The residual concentration of complexed cyanide was determined by volumetric analysis and that of hexavalent chromium by a colorimetric technique (11).

For each experiment the following material balances can be written:

$$V_i = V_r + V_f \qquad [1]$$

$$Z_iV_i = Z_rV_r + Z_fV_f \qquad [2]$$

$$X_iV_i = X_rV_r + X_fV_f \qquad [3]$$

The volumes in liters of initial solution, residual solution, and collapsed foam are represented by V_i, V_r, and V_f, respectively. V_i was always maintained at 2.0 liters. The same subscripts apply also to the surfactant concentration, X, mmolar, and to the hexavalent chromium concentration or complexed cyanide concentration, Z, mmolar Cr or CN.

To utilize ion flotation as a qualitative analysis technique, fundamental attention must be focused on

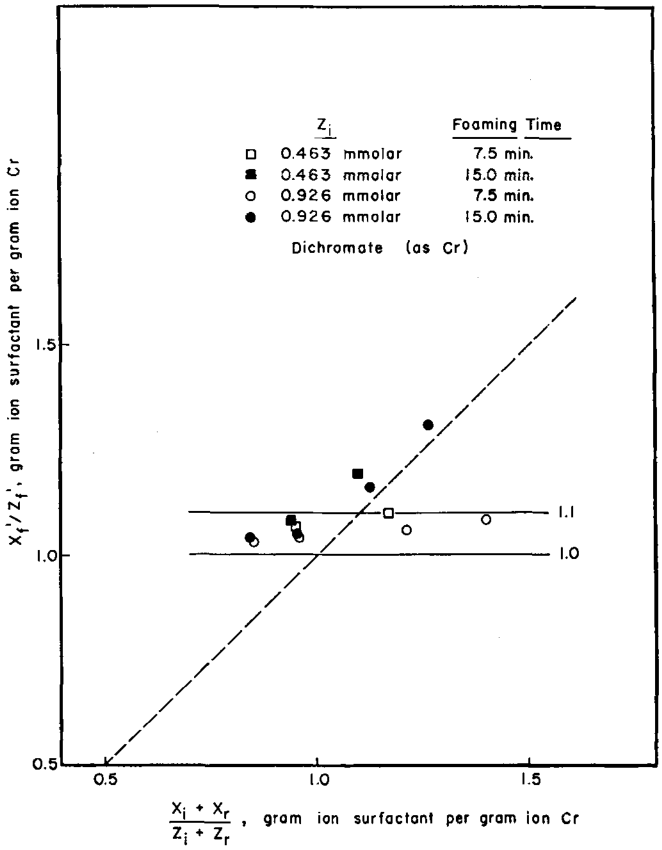

FIG. 1. Relative fractionation parameter for the ion flotation of dichromate.

the collapsed foam accumulated during the course of an experiment. The foam can be collapsed readily using thermal or mechanical means. Some information can be gained from the molar foam ratio, X_f/Z_f, relating the gram ions of surfactant to the gram ions of the complex ion whose charge or structure, or both, is to be established. However, the foam stream includes surfactant and dichromate or complexed cyanide contained in the bulk liquid entrained with the rising foam. Although a sufficient column height may be used to enable adequate foam drainage, most of the liquid volume in the foam consists of entrained liquid. A more accurate foam ratio is defined X_f'/Z_f', the relative fractionation parameter developed in previous studies (8,9). The concentration of surfactant at the bubble-solution interfaces (in the surface layers) is calculated from,

$$X_f'V_f = X_iV_i - X_rV_r - \left(\frac{X_i + X_r}{2}\right)(V_i - V_r) = V_f\left(X_f - \frac{X_i + X_r}{2}\right) \qquad [4]$$

In using Eq. 4, it is assumed that the volume of entrained bulk liquid is equal to the total liquid volume of collapsed foam (and that the volume of the bubble-solution interfaces is negligible); also that the average bulk solution concentration during the course of an experiment can be represented by the arithmetic average. Both of these assumptions have been validated approximately (8). Considering the dichromate or complexed cyanide, or both, a similar relation is used to calculate Z_f':

$$Z_f'V_f = Z_iV_i - Z_rV_r - \left(\frac{Z_i + Z_r}{2}\right)(V_i - V_r) = V_f\left(Z_f - \frac{Z_i + Z_r}{2}\right) \qquad [5]$$

The ratio is then computed using both Equations 4 and 5.

Results and Discussion

The relative fractionation parameter, X_f'/Z_f', is calculated from experimental data for 12 individual experiments with dichromate shown in Fig. 1. The parameter is related to the average bulk solution concentration ratio occurring during the course of an experiment. This ratio, $(X_i + X_r)/(Z_i + Z_r)$, is used instead of the feed ratio, X_i/Z_i, as being more representative of the actual concentrations involved over an entire ion flotation experiment. The dotted 45° line on Fig. 1 indicates equality between values of the relative fractionation parameter and the average bulk concentration ratio and is shown only as a reference. With the exception of three values corresponding to the 15-min foaming time, all values of X_f'/Z_f' lie between 1.0 and 1.1 g ions $EHDA^+$ per gram ion of Cr. For qualitative analysis, the shorter time of 7.5 min is more representative, because significant concentrations of both surfactant (EHDA-Br) and dichromate are still present in the residual solution. At 15 min, the concentrations of surfactant and of dichromate are very low (foaming has ceased) and surfactant not associated with the "stoichiometric" quantity of dichromate may have been foam separated for several minutes, giving high values of X_f'/Z_f'.

The data in Fig. 1 establish clearly that the prevalent species in the initial solutions are $HCrO_4^-$, or $Cr_2O_7^{2-}$, or both, and not CrO_4^{2-}. The particulate complexes formed between the surfactant and the chromium are EHDA-$HCrO_4$, or $(EHDA)_2$–Cr_2O_7, or both; both correspond to X_f'/Z_f' values of 1.0. The flotation of $(EHDA)_2$–CrO_4 would yield ratios of 2.0. The ratios of 1.0–1.1 may have been due to the presence of a very small amount of CrO_4^{2-}. In the pH range 2–6, it has been reported that $HCrO_4^-$, and $Cr_2O_7^{2-}$ are the prevalent species, with CrO_4^{2-} present in negligible concentrations (12,13).

The dichromate study validates information in the literature. Considerably less is reported with certainty on cyanide complexed with iron. At a molar iron-to-cyanide ratio of 0.206, before surfactant addition the initial solution was clear yellow, with $[Fe(CN)_6]^{4-}$ being the predominant species, together with a small quantity of $[Fe(CN)_5H_2O]^{3-}$ (6,14,15). Results of 8 individual ion flotation experiments are shown in the top half of Fig. 2. Only complexed cyanide is considered because the extent of flotation of noncomplexed cyanide was very small (6). Except for one point, the relative fractionation parameter ranges between 0.60 and 0.66 g ion $EHDA^+$ per gram ion CN. These values establish clearly that the dominant species is $[Fe(CN)_6]^{4-}$, with $[Fe(CN)_5H_2O]^{3-}$ also being present. It is of interest that over the average bulk concentration ratio range of 0.14 to 0.65, the relative fractionation parameter ranged only between 0.60 and 0.66. The particulates that were ion floated were definitely a combination of $(EHDA)_4$–$[Fe(CN)_6]$ and $(EHDA)_3$–$[Fe(CN)_5H_2O]$.

At a molar iron-to-cyanide ratio of 0.351, before surfactant addition a blue suspension of polynucleated species was formed consisting of what is known as soluble Prussian blue. The predominant species was probably polynucleated $[FeFe(CN)_6]^{2-}$, with some $[Fe(CN)_6]^{3-}$ and polynucleated $[FeFe(CN)_6]^-$ also being present (6,16,17). Results of 19 individual ion flotation experiments are shown in the lower half of Fig. 2. Some points represent averages of several experiments. Except for 4 points, the relative fractionation parameter ranges from 0.27 to 0.37 g ions $EHDA^+$ per gram ion CN. The points corresponding to foaming times of 8, 12, or 15 min are again the most representative, because of the presence of significant concentrations of both surfactant and complexed cyanide, and are more useful for qualitative analysis. The values 0.27–0.37 establish clearly that the dominant species is $[FeFe(CN)_6]^{2-}$ with lesser concentrations of $[FeFe(CN)_6]^-$ and $[Fe(CN)_6]^{3-}$ also being present.

It should be pointed out that as the average bulk concentration ratio becomes larger than the "stoichiometric" value of the relative fractionation parameter, i.e., the value corresponding to the formula of the species being floated (for example, $(EHDA)_2$–$[FeFe(CN)_6]$), the relative fractionation parameter begins to increase in proportion to the average bulk concentration ratio. This can be observed on the lower half of Fig. 2 as the points begin to follow the 45° line. The high values of X_f'/Z_f' that would be obtained using too high values of $(X_i + X_r)/(Z_i + Z_r)$ can be avoided by careful selection of the initial (feed) surfactant concentration, using a series of preliminary experiments. A very low initial surfactant concentration should be used at first, corresponding to no foam formation ($V_f = 0$); then X_i should be increased gradually to give a moderate amount of foam ($V_f/V_i = 0.05$ to 0.10) at the foam cease point. The determination of X_f'/Z_f' should be made with the X_i that gives this moderate amount of foam; higher values of X_i, corresponding to excessive surfactant, will give high values of X_f'/Z_f'.

The relative fractionation parameter has been considered previously in foam fractionation studies of orthophosphate (9) and phenolate (8); entirely homogeneous systems in which ion competition between OH^- and Br^- with HPO_4^{2-} or phenolate was prevalent. For orthophosphate, X_f'/Z_f' ranged from 2.5 to 7.5 g ion $EHDA^+$ per gram ion HPO_4^{2-} and from 0.62 to 7.2 g ion $EHDA^+$ per gram ion phenolate. The corresponding ranges of the average bulk solution concentration ratio were 0.13 to 12.5 for orthophosphate and 0.025 to 8.3 for phenolate. At $(X_i + X_r)/(Z_i + Z_r) = 2.0$ for HPO_4^{2-}, $X_f'/Z_f' = 4.8$; at $(X_i + X_r)/(Z_i + Z_r) = 1.0$ for phenolate, $X_f'/Z_f' = 3.0$. Both values of X_f'/Z_f' were far greater than the values of 2.0 and 1.0 that would be predicted if all the surfactant were foam separated as $(EHDA)_2$–HPO_4 and EHDA-phenolate.

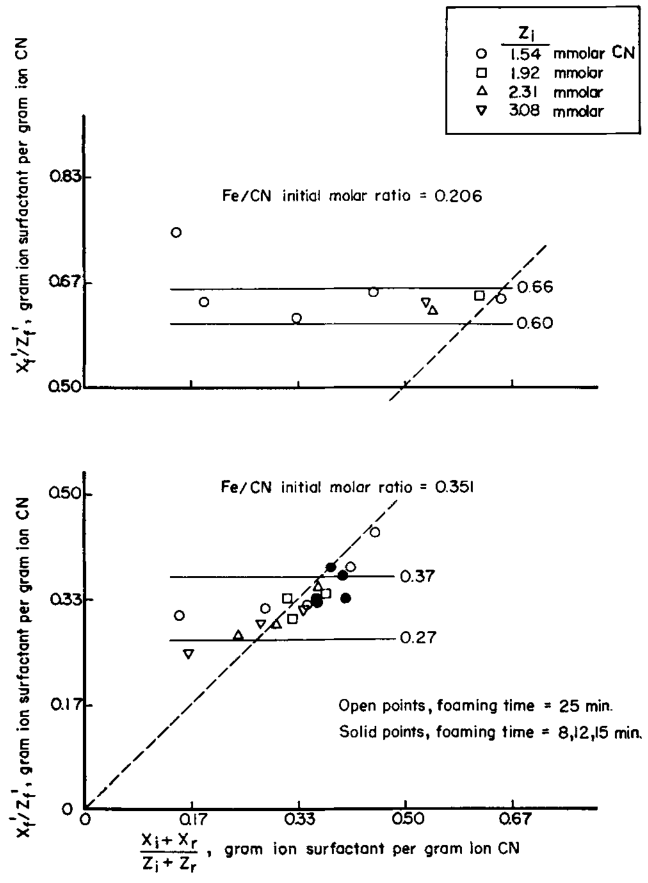

FIG. 2. Relative fractionation parameter for the ion flotation of complexed cyanide.

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