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Models for Interactions between Ionic Surfactants and Nonsurface-Active Ions in Foam Fractionation Processes

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Abstract

Interactions are analyzed between an ionic surfactant and nonsurface-active ions (colligends) of opposite charge being separated in foam fractionations. Surfactant selectivity for competing colligends is determined in terms of models based on surfactant–colligend ion pair formation in the feed solution to a foam fractionation unit, based on colligend–surfactant counterion exchange at the gas–solution, bubble interfaces, and based on surface exchange coupled with ion pair formation in the bulk solution. Accurate, continuous-flow, single-equilibrium-stage foam fractionation data for NO_3^-, BrO_3^-, ClO_3^-, and I^-, each versus Br^-, the counterion of the ethylhexadecyldimethylammonium cation, are used to discriminate among the models. Based on a detailed statistical analysis of the selectivity coefficients determined by two interaction models for each of the four colligends, the hypothesis of colligend–counterion exchange at the gas-solution interface is shown to be valid and that of solution ion pair formation is not substantiated. The surface exchange model provides selectivity coefficients which are quite constant over a tenfold concentration range and yet which are very sensitive to data inaccuracies.

INTRODUCTION

Foam separation processes are quite effective for the concentration and selective removal of nonsurface-active ions from dilute (10^{-6}–10^{-3} M) aqueous solutions. An ionic surface-active agent of charge opposite to the ion of interest, which is termed the colligend, is utilized. The surfactant interacts preferentially with the colligend(s) compared to competing ions of like charge (including the surfactant's counterion). The interaction may occur in the bulk solution and/or at the gas–solution interfaces of the gas bubbles generated to effect the separation. The surfactant–colligend ion pairs or soluble complexes are concentrated in the foam which is formed atop the bulk solution: in the absence of the formation of particles by further interaction of the surfactant–colligend pairs, the process is called foam fractionation. To analyze foam fractionation data for the separation of a specified colligend from one or more ions of like charge, a selectivity coefficient may be defined in an analogous fashion to those for ion exchange; the definition will depend on the mode of surfactant–colligend interaction.

Two recent reviews (*1, 2*) have referenced a substantive number of foam fractionations of nonsurface-active ions, updating earlier reviews of foam separation processes (*3–6*). Of the large number of experimental studies reported, three investigations have established cationic surfactant selectivities for anionic colligends from solutions containing five or more colligends: the oxyanions of Re(VII), Mo(VI), Cr(VI), W(VI), and V(V), and chloride (*7*); the cyanide complex anions of Au(III), Zn(II), Cd(II), and Hg(II), and cyanide and chloride (*8*); and the chloride complex anions of Au(III), Zn(II), Cd(II), and Hg(II), and chloride (*9*).

The most direct and probably the most accurate method of establishing a surfactant's selectivity for competing colligends is with a continuous-flow, single-equilibrium-stage foam fractionation unit (*10–14*). However, even in this rather simple and straightforward device, different selectivities may be defined and determined, depending on the model of surfactant–colligend interaction which is utilized. Accurate single-equilibrium-stage foam fractionation data may be used to discriminate between surfactant–colligend interaction models and to establish the most consistent method of determining and presenting selectivities.

The objectives of this investigation are (a) the careful development of the several possible surfactant–monovalent colligend interaction models, based on ion pairing in the feed solution, on an exchange reaction at the bubble interfaces, and on surface exchange–bulk solution ion pairing; (b) the discrimination between the models by analyzing and comparing the selectivity coefficients determined from single-equilibrium-stage foam fractionation data for nitrate, chlorate, bromate, and iodide, each versus bromide, with the cationic surfactant ethylhexadecyldimethylammonium bromide; and (c) further validation of the optimum model on the basis of consistency and data sensitivity.

THE FOAM FRACTIONATION UNIT, NOMENCLATURE, AND MASS BALANCE EQUATIONS

A schematic diagram of a continuous-flow, single-equilibrium-stage foam fractionation unit is presented in Fig. 1. The feed stream from the mix tank to the column contains concentrations e_i of the surfactant (in this case, the ethylhexadecyldimethylammonium ion), b_i of the surfactant counterion (in this case, bromide), n_i of the cation of the colligend salt (in this case, sodium), and c_i of the colligend anion (either nitrate, bromate, chlorate, or iodide), with all concentrations in mole/liter. The flow rate of the feed stream is L (L/min), and the flow rate of the gas stream is A (cm^3/min). The steady-state foam stream (collapsed, as liquid) contains the concentrations e_f, b_f, n_f, and c_f of the four ionic species, respectively, and similarly for the residual or bulk stream, the steady-state concentrations are e_r, b_r, n_r, and c_r. The surfactant rapidly diffuses to the gas–solution interfaces of the rising gas bubbles, with an equilibrium being established between the surface excess of the surfactant, Γ_e, and the bulk solution or residual stream concentration of surfactant, e_r. The following assumptions, which have been validated experimentally (*10*), may be made about the operation of the column: (a) steady-state operation is achieved; (b) the bulk solution is completely mixed and thus at steady state the bulk solution and the residual stream are of the same concentration, e_r; (c) the bubbles, of average diameter D_b (cm), are approximately spherical in shape; (d) there is equilibrium adsorption of surfactant and either the colligend or bromide as counterions before each bubble reaches the exit port; (e) there is minimum foam breakage before the foam reaches the exit port.

Based upon these assumptions, the following mass balance equations may be written for the column:

$$\Gamma_e = \frac{D_b L}{6A}(e_i - e_r) = k'(e_i - e_r) \tag{1}$$

$$\Gamma_b = \frac{D_b L}{6A}(b_i - b_r) = k'(b_i - b_r) \tag{2}$$

$$\Gamma_c = \frac{D_b L}{6A}(c_i - c_r) = k'(c_i - c_r) \tag{3}$$

in which Γ_e, Γ_b, and Γ_c are the surface excesses of surfactant, bromide, and colligend, respectively, in mole/cm^2, and k' is a procedure dependent "constant" which will be detailed in a later section. Experiments have shown clearly (*10, 11*) that sodium is neither positively nor negatively adsorbed at the gas–solution interface and therefore Γ_n, the surface excess of sodium, is zero. Accordingly, by an ion balance on the interfacial "stream" and from Eq. (1)–(3),

$$\Gamma_e = \Gamma_b + \Gamma_c \tag{4}$$

$$(e_i - e_r) = (b_i - b_r) + (c_i - c_r) \tag{5}$$

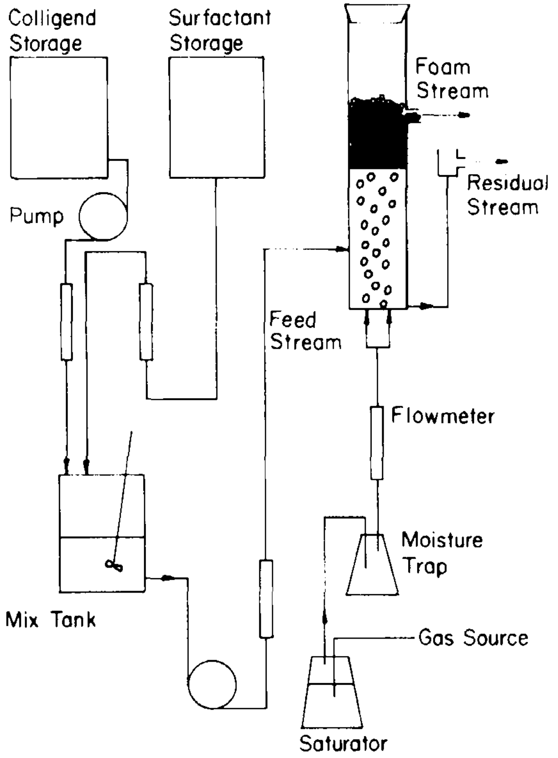

FIG. 1. Schematic diagram of continuous-flow, single-equilibrium-stage foam fractionation unit.

SURFACTANT–COLLIGEND INTERACTION MODELS

Several models can be developed in an effort to describe the interaction between the surfactant cation and the competing anions and to establish the most valid and consistent method of defining and determining surfactant selectivity.

Several investigators have modeled colligend separation as a coadsorption process, utilizing a surface adsorption equation analogous to that for the surfactant (*2, 3*). This approach cannot be used, however, if the surfactant and colligend concentrations are approximately of the same order of magnitude, because of competition between the surfactant counterion and the colligend. This fact is demonstrated clearly in Fig. 2 in which single-equilibrium-stage data for sodium bromate and ethylhexadecyldimethylammonium bromide (EHDA-Br) are presented by plotting $(c_i - c_r)/(e_i - e_r)$, the moles of bromate at the gas–solution interface per mole of surfactant at

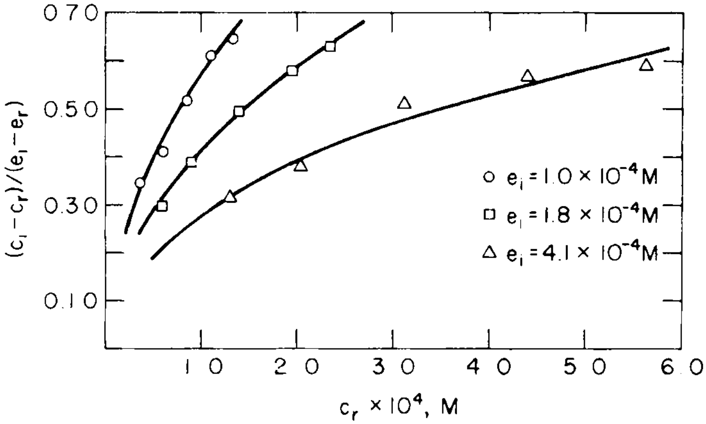

FIG. 2. Relationships between $(c_i - c_r)/(e_i - e_r)$ and c_r for BrO_3^- at three values of e_i.

the interface (analogous to the moles of adsorbate per mole of adsorbent), versus c_r, the bulk solution and residual stream bromate concentration. If there were no ion competition of Br^- with the BrO_3^-, a single curve should result (an adsorption isotherm) for all values of e_i (and thus b_i). The fact that $(c_i - c_r)/(e_i - e_r)$ declines as e_i increases (and thus b_i increases) at constant c_r clearly evidences ion competition.

Model for Selectivity Controlled by Ion Pair Formation in the Feed Solution

Consider the following ion pairing reaction which could occur in the feed solution before it enters the foam fractionation column (Fig. 1). For the sake of model development, it will be assumed that the feed solution and stream contain ethylhexadecyldimethylammonium bromide (EHDA-Br) and sodium nitrate,

$$\text{EHDA-Br})_i + NO_3^-)_i \rightleftharpoons \text{EHDA-NO}_3)_i + Br^-)_i$$

It is hypothesized that in the feed solution *all* of the large, hydrophobic $EHDA^+$ is ion paired with either NO_3^- or Br^-, leaving the concentrations c_i^* and b_i^* of "free" or unpaired NO_3^- and Br^-, respectively. The ion pair formation constant may now be written in terms of concentrations, assuming the activity coefficient ratios are unity in these dilute solutions,

$$K_{ip} = \frac{[\mathrm{EHDA\text{-}NO_3}]_i[\mathrm{Br^-}]_i}{[\mathrm{EHDA\text{-}Br^-}]_i[\mathrm{NO_3^-}]_i} = \frac{(c_i - c_i^*)(b_i^*)}{[e_i - (c_i - c_i^*)](c_i)^*} \tag{6}$$

The "constant," K_{ip}, is also a measure of the selectivity (or selectivity coefficient) of the surfactant cation for interacting with NO_3^- relative to Br^-. By the requirement for electroneutrality, assuming that all of the $EHDA^+$ is paired,

$$c_i^* + b_i^* = n_i = c_i \tag{7}$$

and from Eqs. (6) and (7),

$$K_{ip} = \frac{(c_i - c_i^*)(c_i - c_i^*)}{[e_i - (c_i - c_i^*)](c_i^*)} \tag{8}$$

The assumption is now made that the ratio of the numbers of EHDA-NO_3 and EHDA-Br pairs which are adsorbed at the gas–solution interfaces of the rising bubbles in the foam fractionation column is the same as $[\mathrm{EHDA\text{-}NO_3}]_i/[\mathrm{EHDA\text{-}Br}]_i$, the ratio of the pairs in the feed stream. This should be valid (particularly for species which are all monovalent) because no preference for interfacial adsorption should be given to one $EHDA^+$ over another by the anion with which it is paired. The fraction of EHDA-NO_3 plus EHDA-Br in the feed stream "picked up" by the bubbles in the single-equilibrium-stage foam fractionation is designated as P, resulting in the interfacial adsorption of $P(c_i - c_i^*)$ and $P[e_i - (c_i - c_i^*)]$ EHDA-NO_3 and EHDA-Br, respectively, and leaving $(1 - P)(c_i - c_i^*)$ and $(1 - P)[e_i - (c_i - c_i^*)]$ in the residual stream. From Eqs. (3) and (2),

$$\frac{\Gamma_c}{\Gamma_b} = \frac{(c_i - c_r)}{(b_i - b_r)} = \frac{P(c_i - c_i^*)}{P[e_i - (c_i - c_i^*)]} = \frac{(c_i - c_i^*)}{[e_i - (c_i - c_i^*)]} \tag{9}$$

From Eqs. (3) and (1),

$$\frac{\Gamma_c}{\Gamma_e} = \frac{(c_i - c_r)}{(e_i - e_r)} = \frac{P(c_i - c_i^*)}{P(e_i)} = \frac{(c_i - c_i^*)}{(e_i)} \tag{10}$$

which can be solved for c_i^*,

$$c_i^* = \frac{(e_i c_r - c_i e_r)}{(e_i - e_r)} \tag{11}$$

By substituting Eq. (9) into Eq. (8) and by replacing c_i^* in the resultant equation with its equivalent from Eq. (11), one obtains,

$$K_{ip} = \frac{(c_i - c_r)(e_i c_i - e_i c_r)}{(b_i - b_r)(e_i c_r - e_r c_i)} \tag{12}$$

Because $e_i = b_i$ (only EHDA-Br and $NaNO_3$ are present in the feed stream), Eq. (5) simplifies to

$$e_r = c_r + b_r - c_i \tag{13}$$

which is substituted into Eq. (12) to give, upon rearrangement,

$$\begin{aligned} K_{ip} &= \frac{(c_i - c_r)}{(b_i - b_r)} \Big/ \frac{[b_i c_r - c_i(c_r - c_i + b_r)]}{b_i(c_i - c_r)} \\ &= \frac{(c_i - c_r)}{(b_i - b_r)} \Big/ M \end{aligned} \tag{14}$$

All terms in Eq. (14) are feed stream or residual stream concentrations of colligend and surfactant counterion and can be measured readily in a single-equilibrum-stage foam fractionation.

If the sodium salt of the counterion, NaBr, is added to the feed solution (in order to vary the feed stream ratio of colligend to surfactant counterion), then $e_i \neq b_i$ and Eq. (7), the requirement for electroneutrality in the feed solution, becomes

$$c_i^* + b_i^* = c_i + b_i - e_i = n_i - e_i \tag{15}$$

and Eq. (8) becomes

$$K_{ip} = \frac{(c_i - c_i^*)(c_i - c_i^* + b_i - e_i)}{[e_i - (c_i - c_i^*)](c_i^*)} \tag{16}$$

The substitution of Eqs. (9), (11), and (5) into Eq. (16) yields

$$\begin{aligned} K_{ip} &= \frac{(c_i - c_r)}{(b_i - b_r)} \Big/ \frac{[c_i(b_i - b_r) - c_i(e_i - c_i + c_r) + e_i c_r]}{[b_i(c_i - c_r) + b_i(b_i - b_r) - e_i(b_i - b_r)]} \\ &= \frac{(c_i - c_r)}{(b_i - b_r)} \Big/ Q \end{aligned} \tag{17}$$

Equation (17) will reduce to Eq. (14) for the base of $b_i = e_i$.

Model for Selectivity Controlled by Colligend–Counterion Exchange at Gas–Solution Interfaces of Rising Gas Bubbles

The second model focuses on the bubbles rising from the gas diffusers through the completely mixed bulk solution. The surfactant cations ($EHDA^+$), which very rapidly diffuse to and are adsorbed at the gas–solution interfaces, are modeled as mobile ion exchangers according to the reaction

$$EHDA\text{-}Br)_s + NO_3^-)_r \rightleftharpoons EHDA\text{-}NO_3)_s + Br^-)_r$$

where the subscripts "s" and "r" indicate the interfacial or surface "stream" and residual stream (bulk solution), respectively. For a single-equilibrium-stage foam fractionation, the "concentration" of NO_3^- in the interfacial "stream" is Γ_c, which from Eq. (3) is proportional to $c_i - c_r$; similarly for Br^-, Γ_b and $b_i - b_r$; and the residual stream (bulk solution) concentrations are c_r and b_r. The surface exchange reaction equilibrium constant, which is also a surfactant selectivity coefficient, may be written in terms of concentrations, with the neglect of activity coefficient contributions validated in Ref. *10* and *11*,

$$K_{se} = \frac{[EHDA\text{-}NO_3]_s[Br^-]_r}{[EHDA\text{-}Br]_s[NO_3^-]_r} = \frac{(\Gamma_c)(b_r)}{(\Gamma_b)(c_r)} \tag{18}$$

Substitution of Eqs. (2) and (3) into Eq. (18) yields

$$K_{se} = \frac{(c_i - c_r)}{(b_i - b_r)} \Bigg/ \frac{(c_r)}{(b_r)} \tag{19}$$

In a similar fashion to Eqs. (14) and (17), all of the terms on the right-hand side of Eq. (19) can be found from single-equilibrium-stage foam fractionation data. It should be noted here that it had been hypothesized (*10–14*) that the assumption of selectivity control by ion pair formation in the feed solution and the assumption of selectivity control by a surface exchange reaction at the gas–solution interfaces yielded identical models. A comparison of Eqs. (14) or (17) and (19), together with the data analysis presented below, shows that hypothesis to be in error.

Model for Selectivity Controlled Both by Colligend–Counterion Exchange at Gas–Solution Interfaces and by Ion Pair Formation in the Bulk Solution (Residual Stream)

A third model combines in a sense the first two, hypothesizing that surfactant selectivity is determined both by surface exchange,

$$\mathrm{EHDA\text{-}Br})_s + \mathrm{NO_3^-})_r \rightleftharpoons \mathrm{EHDA\text{-}NO_3})_s + \mathrm{Br^-})_r$$

and by ion pairing in the bulk solution (of the same concentrations as the residual stream) which is in equilibrium with the gas bubbles as they rise through the column,

$$\mathrm{EHDA\text{-}Br})_r + \mathrm{NO_3^-})_r \rightleftharpoons \mathrm{EHDA\text{-}NO_3})_r + Br^-)_r$$

Subtraction of the above equations yields

$$\mathrm{EHDA\text{-}Br})_s + \mathrm{EHDA\text{-}NO_3})_r \rightleftharpoons \mathrm{EHDA\text{-}NO_3})_s + \mathrm{EHDA\text{-}Br})_r$$

At equilibrium, the reaction "constant" or selectivity coefficient is

$$K_{s-p} = \frac{[\mathrm{EHDA\text{-}NO_3}]_s[\mathrm{EHDA\text{-}Br}]_r}{[\mathrm{EHDA\text{-}Br}]_s[\mathrm{EHDA\text{-}NO_3}]_r} = \frac{(c_i - c_r)(b_r - b_r^*)}{(b_i - b_r)(c_r - c_r^*)} \qquad (20)$$

in which c_r^* and b_r^* are the concentrations in the residual stream of the "free" or unpaired anions. Because of the electroneutrality requirement for the residual stream,

$$c_r^* + b_r^* = n_r = n_i = c_i \qquad (21)$$

and substituting in Eq. (20),

$$K_{s-p} = \frac{(c_i - c_r)}{(b_i - b_r)} \Bigg/ \frac{(c_r - c_r^*)}{(b_r - c_i + c_r^*)} \qquad (22)$$

Unfortunately, this analysis can be developed no further. The key assumption needed to write the right-hand sides of Eqs. (9) and (10) cannot be made in this case, and from experimental data there is no way to distinguish directly paired anions from unpaired anions.

A final observation can be made from a comparison of Eqs. (14), (19), and (22). In each equation the ratio of colligend to counterion at the gas–solution interfaces, $(c_i - c_r)/(b_i - b_r)$, appears, and thus each "K" is a selectivity coefficient. The denominator of the right hand of each equation represents: the ratio of *unpaired* colligend to *unpaired* counterion (Eq. 14); the ratio of *total* colligend to *total* counterion (Eq. 19); and the ratio of *paired* colligend to *paired* counterion (Eq. 22).

FOAM FRACTIONATION DATA BASE

In order to test the validity of the two fully developed models and to compare the selectivity coefficients, accurate single-equilibrium-stage foam fractionation data are necessary. Such data are available for nitrate, chlorate, bromate, and iodide, each foam fractionated with ethylhexadecyldimethylammonium bromide (*10, 11*). In each experiment the feed stream flow rate was 0.056 L/min, the gas rate was 400 cm^3/min, and the average bubble diameter was 0.06 cm. Therefore, k' in Eqs. (1)–(3) is 1.4×10^{-6} L/cm^2. In several of the experiments for each colligend, sodium bromide was added to the feed stream to increase the counterion to colligend ratio. The concentration ranges for all of the experiments are summarized in Table 1.

TABLE 1

Colligend	Number of data points	$e_i \times 10^4$ (M)	$c_i \times 10^4$ (M)	$b_i \times 10^4$ (M)
NO_3^-	23	1.42–2.03	0.81–2.38	1.42–5.35
BrO_3	21	1.02–4.19	0.44–6.63	1.00–11.81
ClO_3^-	23	0.98–4.10	0.42–6.70	1.00–11.79
I^-	15	1.38–1.82	1.49–2.08	1.38–5.30

In each experiment, e_r, c_r, and b_r were determined; the feed stream and residual stream concentrations are used in the model evaluation detailed below.

MODEL EVALUATION AND DISCRIMINATION

Selectivity Controlled by Ion Pair Formation in the Feed Solution

In order to test the validity of Eqs. (14) and (17), Figs. 3–6 present foam fractionation data for nitrate, bromate, chlorate, and iodide, respectively, with $(c_i - c_r)/(b_i - b_r)$ plotted against M (Eq. 14) for $e_i = b_i$ and against Q (Eq. 17) for $e_i \neq b_i$. For each colligend, statistical indications of the goodness of fit of the modeling equations are given in Table 2. In Table 2 for each colligend are presented the number of data points, $t_{\text{calculated}}$ and t_{table}, the least squares slope through (0, 0), K_{ip}, and the 95% confidence limits and correlation coefficient of the linear functional dependence of $(c_i - c_r)/(b_i - b_r)$ on M or Q, for a zero intercept. The $t_{\text{calculated}}$ and t_{table} values refer to Student's t-test analyses of the data: if $t_{\text{calculated}} > t_{\text{table}}$, the hypothesis that the intercept of the best least squares straight line is zero may be rejected with 95% confidence for $N - 2$ degrees of freedom. From Table 2 it is clear that the hypothesis of a zero intercept must be rejected for nitrate, chlorate, and iodide, but can be accepted for bromate.

Assuming that Eqs. (14) and (17) hold, the best values of K_{ip} are given in Table 1: the indicated confidence limits mean that if the assumptions made to

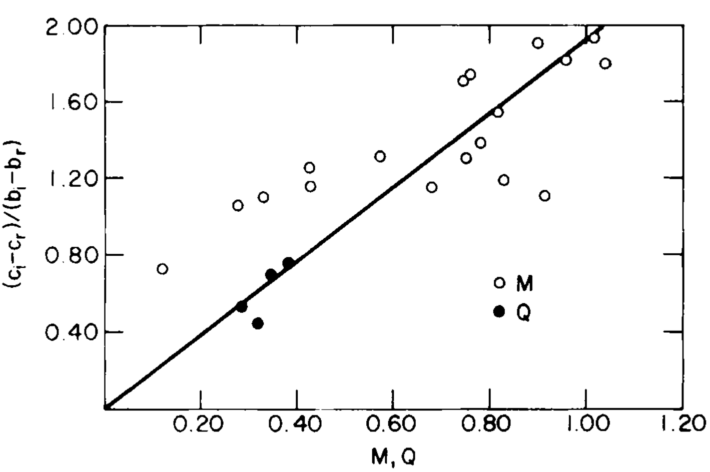

FIG. 3. Relationship between $(c_i - c_r)/(b_i - b_r)$ and M or Q for NO_3^-.

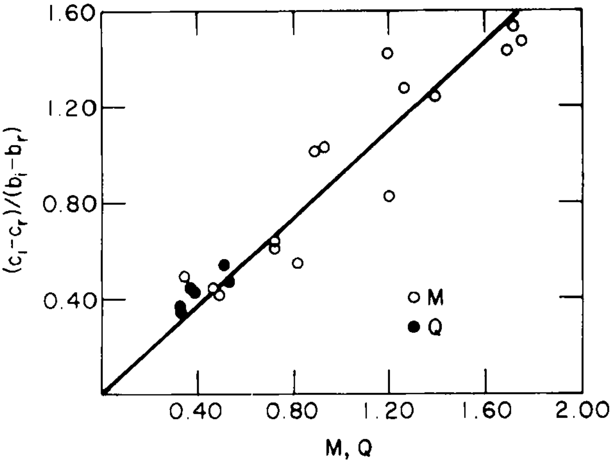

FIG. 4. Relationship between $(c_i - c_r)/(b_i - b_r)$ and M or Q for BrO_3^-.

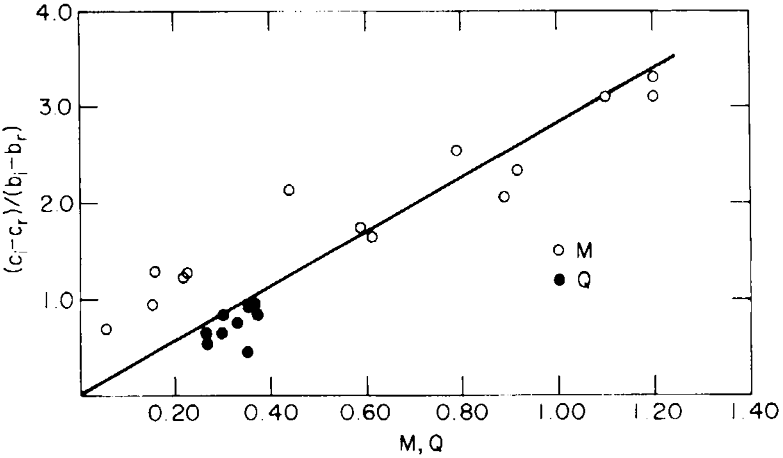

FIG. 5. Relationship between $(c_i - c_r)/(b_i - b_r)$ and M or Q for ClO_3^-.

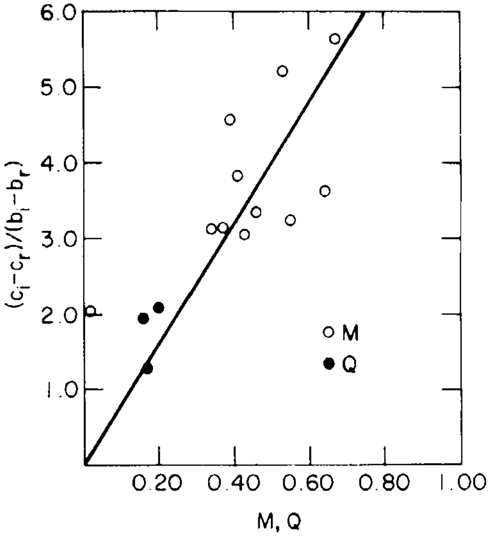

FIG. 6. Relationship between $(c_i - c_r)/(b_i - b_r)$ and M or Q for I^-.

TABLE 2

Statistical Indications of the Goodness of Fit of Eqs. (14) and (17): Figs. 3–6

Colligend	NO_3^-	BrO_3^-	ClO_3^-	I^-
Number of data points	23	21	23	14[a]
$t_{calculated}$	3.52	1.69	2.73	2.36
t_{table}	2.08	2.09	2.08	2.18
Slope through (0, 0)	1.91	0.914	2.82	8.04
95% Confidence	±0.19	±0.06	±0.31	±1.3
Limits of slope	±9.9%	±6.9%	±11%	±16%
r	0.73	0.95	0.88	0.65

[a] One point for I^- was not used because of a negative value of M.

develop the model are correct, it can be stated with 95% confidence that the true value of K_{ip} lies between (slope + limit) and (slope − limit). The least squares correlation coefficient, r, is defined by

$$r = \left[1 - \frac{\Sigma[g_{\text{experimental}} - g_{\text{calculated}}]^2}{\Sigma[g_{\text{experimental}} - g_{\text{mean}}]^2} \right]^{1/2} \tag{23}$$

in which g stands for $(c_i - c_r)/(b_i - b_r)$, and the calculated values are computed from Eq. (14) or (17) using the indicated best values of K_{ip}. The correlation coefficient means that $(r^2 \times 100)\%$ of the variations in $(c_i - c_r)/(b_i - b_r)$ may be explained on the basis of the linear functional dependence on M or Q given by Eq. (14) or (17). In general, the confidence limits are rather broad and the correlation coefficients are rather low for three of the four colligends.

Selectivity Controlled by Colligend–Counterion Exchange at Gas–Solution Interfaces

In order to test the validity of Eq. (19), Figs. 7–10 present foam fractionation data for nitrate, bromate, chlorate, and iodide, respectively, with $(c_i - c_r)/(b_i - b_r)$ plotted against c_r/b_r. For each colligend, statistical indications of the goodness of fit of the modeling equation are given in Table 3. From observation of the Student's t-test analyses of the results, the assumption of a zero intercept is valid for all four colligends. The correlation coefficients are all 0.90 or above, indicating that at least 81% of the variations in $(c_i - c_r)/(b_i - b_r)$ may be explained on the basis of a linear functional dependence on c_r/b_r. The 95% confidence limits have also been

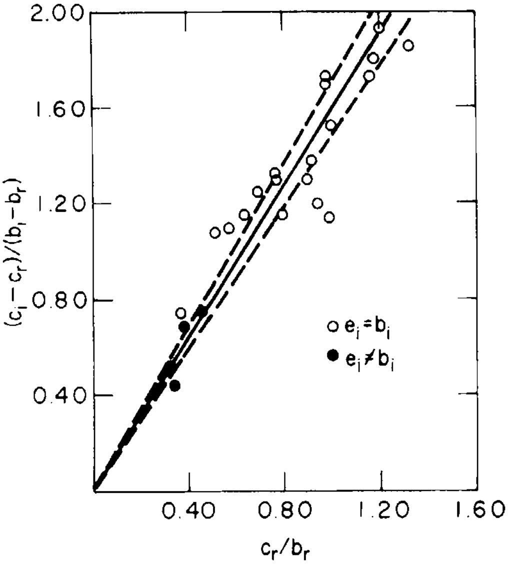

FIG. 7. Relationship between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for NO_3^-.

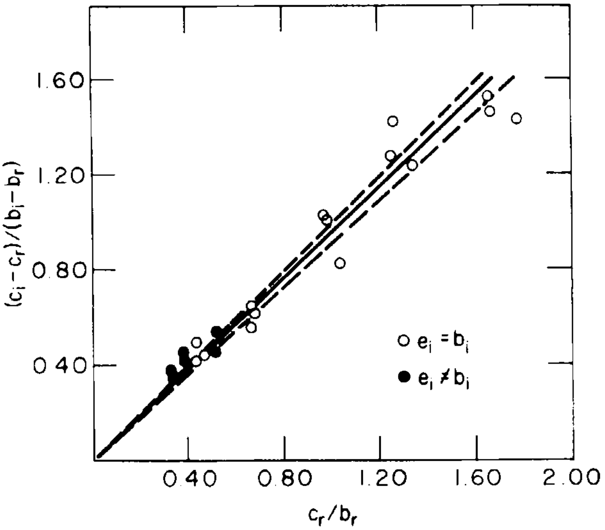

FIG. 8. Relationship between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for BrO_3^-.

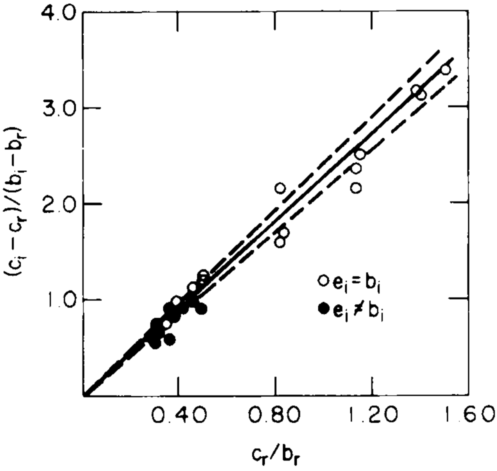

FIG. 9. Relationship between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for ClO_3^-.

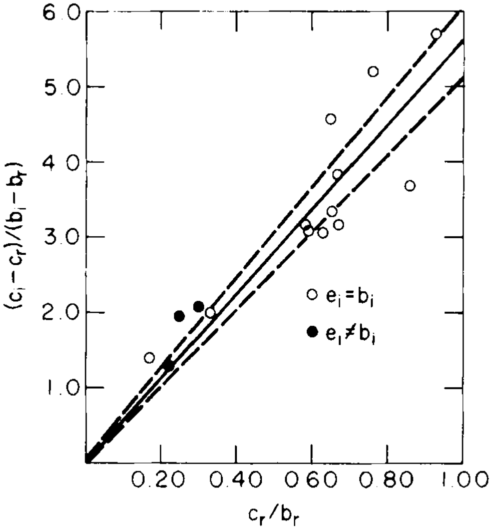

FIG. 10. Relationship between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for I^-.

TABLE 3

Statistical Indications of the Goodness of Fit of Eq. (19): Figs. 7–10

Colligend	NO_3^-	BrO_3^-	ClO_3	I^-
Number of data points	23	21	23	15
$t_{\text{calculated}}$	1.59	0.415	0.303	1.19
t_{table}	2.08	2.09	2.08	2.16
Slope through (0, 0)	1.59	0.94	2.21	5.64
95% Confidence	±0.08	±0.05	±0.07	±0.53
Limits of slope	±5.0%	±4.8%	±3.2%	±9.4%
r	0.93	0.97	0.99	0.90

drawn on Figs. 7–10: the bounds on K_{se} are generally rather narrow, indicative of good correlations.

A further test of Eq. (19) was made by plotting $(c_i - c_r)/c_r$ vs $(b_i - b_r)/b_r$ and making a least squares analysis of the results, which is presented in Table 4. For each colligend the slope of the best line through (0, 0) and the data is also K_{se}. The purpose of this analysis, which appears to duplicate that of Table 3, is to give greater weight to the points in Figs. 7–10 which are close to (0, 0): generally, points with large values of $(c_i - c_r)/(b_i - b_r)$ and of c_r/b_r have small values of $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$, and vice versa. The results in Table 4 shows that the hypothesis of a zero intercept may be accepted for all four colligends ($t_{\text{calculated}} < t_{\text{table}}$) and that the correlation coefficients and confidence limits, although slighly poorer than those in Table 3, are still quite good. The best values of the selectivity coefficient K_{se} are the averages of the values in Tables 3 and 4: nitrate, 1.62; bromate, 0.95; chlorate, 2.25; iodide, 5.80.

TABLE 4

Statistical Indications of the Goodness of Fit of Eq. (19) from Relations of $(c_i - c_r)/c_r$ vs $(b_i - b_r)/b_r$

Colligend	NO_3^-	BrO_3	ClO_3^-	I^-
Number of data points	23	21	23	15
$t_{\text{calculated}}$	0.701	0.681	1.09	1.89
t_{table}	2.08	2.09	2.08	2.16
Slope through (0, 0)	1.64	0.98	2.28	5.95
95% Confidence	±0.11	±0.04	±0.11	±0.66
Limits of slope	±6.7%	±4.1%	±4.8%	±11%
r	0.83	0.94	0.96	0.84

A Comparison of Models

The colligend–counterion exchange model (Figs. 7–10 and Tables 3 and 4) appears to be quite superior to the feed solution ion pairing model (Figs. 3–6 and Table 2). For the latter, a zero intercept cannot be assumed in three of the four cases, and when it is assumed, the predicted linear relationship is not validated well by the data. For the former, all of the statistical tests indicate a good correlation.

Based upon foam fractionation experiments with iodide and nitrate (*10*, *11*) for which the liquid height in the foam fractionation column was varied with all other variables held constant, the hypothesis was made that because the selectivity coefficient, K_{se}, was independent of liquid height, either (a) the exchange reaction occurs very rapidly and is completed when each bubble has risen a short distance above the gas diffusers, or (b) ion pair formation in the feed solution controls the separation. On the basis of the analysis presented herein, it appears that the former explanation is valid and that if feed solution ion pairing does occur, it does not control the selectivity.

DISCUSSION

The selectivity constant, K_{se}, may be used to compute residual stream colligend concentrations versus feed stream concentrations if the surfactant separation can be estimated. For example, for $e_i = b_i$, Eq. (13) can be substituted into Eq. (19) to give

$$K_{se} = \frac{(c_i - c_r)}{(e_i - e_r - c_i + c_r)} \Bigg/ \frac{(c_r)}{(c_i - c_r + e_r)} \tag{24}$$

Experimental foam fractionation data for nitrate (*10*, *11*) indicate that for $e_i = 1.8 \times 10^{-4}$, $e_r = 0.9 \times 10^{-4}$ as an average value for seven runs at variable c_i. These points are plotted on coordinates of c_r versus c_i in Fig. 11. Three values of K_{se} are used in Eq. (24) to calculate curves of c_r versus c_i, at $e_i = 1.8 \times 10^{-4}$ and $e_r = 0.9 \times 10^{-4}$: $K_{se} = 1.59$ (Table 3), a value of K_{se} one order of magnitude greater and a value one order less than the experimental value. There are also drawn two 45° straight lines, corresponding to $c_r = c_i$ (selectivity for nitrate of zero) and to $c_r = c_i - (e_i - e_r)$ (selectivity for bromide of zero).

Three observations can be made from Fig. 11. First, the fit of the curve for $K_{se} = 1.59$, which was determined from all 23 data points for nitrate, is very good for the seven points at $e_i = 1.8 \times 10^{-4}$. Second, c_r is quite insensitive to K_{se}: a large variation in K_{se} results in a small change in c_r. Third and most significant, a small change in c_r necessitates a large change in K_{se}. This fact reflects strongly on the excellent discriminatory ability of the colligend–

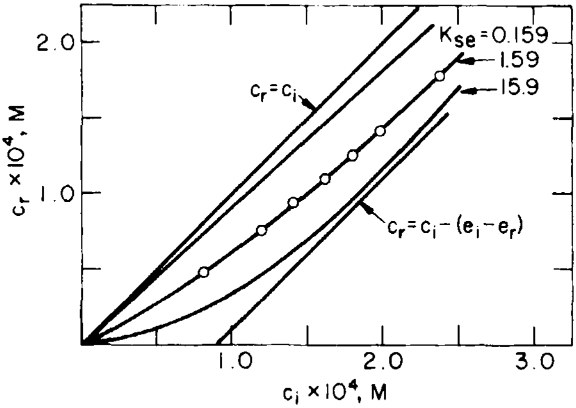

FIG. 11. Relationship between c_r and c_i for NO_3^- at $e_i = 1.8 \times 10^{-4}$ *M* and predicted relationships for three values of K_{se}.

counterion exchange model. For example, from Fig. 7, if for one of the data points the measured value of the nitrate concentration in the residual stream were in error by 5%, which would also mean a 5% change in the residual stream bromide concentration to maintain electroneutrality, the slope (K_{se}) of the line through that point would change by almost 25%! The extreme sensitivity of K_{se} to the measured residual stream concentrations, coupled with the goodness of fit of the correlations shown in Tables 3 and 4, indicates the validity of the model to describe foam fractionation selectivity in terms of a selectivity coefficient which is constant over at least a tenfold concentration range.

CONCLUSIONS

1. Hypotheses of surfactant–colligend ion pair formation in the feed solution, colligend–counterion exchange at the gas–solution interfaces of rising bubbles, and surface exchange coupled with ion pair formation in the bulk solution yield distinct expressions for the selectivity coefficient in the continuous-flow, single-equilibrium-stage foam frationation of nonsurface-active ions.

2. Based on data for the foam fractionation of NO_3^-, BrO_3^-, ClO_3^-, and I^-, each versus Br^-, the counterion of the ethylhexadecyldimethylammonium cation, over the 10^{-4}–10^{-3} *M* concentration range and from a careful statistical analysis of the resultant selectivity coefficients, the colligend–counterion exchange model is valid, the feed solution ion pair formation model is not substantiated, and the surface exchange coupled with ion pair

formation model cannot be developed far enough for analysis, but could have merit.

3. The selectivity coefficients determined with the colligend–counterion exchange model are constant over a tenfold concentration range, are extremely sensitive to data inaccuracies, and provide a consistent and valuable method of reporting foam fractionation data.

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