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R. B. Grieves[a]; R. L. Drahushuk[a]; W. Walkowiak[ab]; D. Bhattacharyya[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, THE UNIVERSITY OF KENTUCKY, LEXINGTON, KENTUCKY [b] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, Wroclaw, Poland

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Selectivity Coefficients for Divalent Oxyanions from the Continuous Foam Fractionation of a Quaternary Ammonium Surfactant

R. B. GRIEVES, R. L. DRAHUSHUK, W. WALKOWIAK,* and D. BHATTACHARYYA

DEPARTMENT OF CHEMICAL ENGINEERING
THE UNIVERSITY OF KENTUCKY
LEXINGTON, KENTUCKY 40506

Abstract

An experimental investigation is presented of the continuous, single equilibrium stage foam fractionation of chromate (CrO_4^{2-}) and of thiosulfate ($S_2O_3^{2-}$) from 0.4 to 3.0 × 10^{-4} *M* aqueous solutions. The cationic surfactant, ethylhexadecyldimethylammonium bromide (EHDA-Br), is modeled as a soluble ion exchanger, considering the exchange of CrO_4^{2-} and $S_2O_3^{2-}$ or EHDA-CrO_4^- and EHDA-$S_2O_3^-$ for Br^-. The data indicate that EHDA-CrO_4^- or EHDA-$S_2O_3^-$ is exchanged with Br^-. The selectivity coefficient for chromate is 3.90 and that for thiosulfate is 16.8.

INTRODUCTION

Foam separation processes are effective for the concentration and selective removal of inorganic ions from dilute aqueous solution: an ionic surfactant of charge opposite to the ion of interest (colligend) is utilized which interacts preferentially with the colligend compared to competing

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*Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, Wroclaw, Poland.

ions of like charge. The interaction may occur in the bulk solution and/or at the air–solution interfaces of the generated gas bubbles, and the surfactant–colligend ion pairs or soluble complexes are concentrated in the foam which is formed atop the bulk solution. In the absence of particles formed between the surfactant–colligend pairs, the process is termed foam fractionation. Three recent reviews have included ion separations achieved by foam fractionation (*1–3*), and all foam fractionations reported in the world literature from 1970–1974 have been summarized (*4*).

To establish the feasibility of foam fractionation to effect the separation of a specified colligend from one or more ions of like charge (including the surfactant counterion), a selectivity coefficient must be determined in a manner similar to that for a solid ion exchanger or liquid ion exchanger. Several investigators have discussed the analogy between foam fractionation and ion exchange (*5–8*). A model has been proposed to determine monovalent anion selectivities by a cationic surfactant, utilizing data obtained from a continuous-flow, single equilibrium stage foam fractionation unit (*9*), and selectivity coefficients have been reported for $SCN^- > I^- > ClO_3^- > NO_3^- > BrO_3^- > NO_2^-$, each versus Br^- (*10, 11*).

The objective of this study is the extension of the "surfactant as a soluble ion exchanger" model to divalent anions, considering chromate (CrO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$), each versus Br^-. Experimental data over the concentration range 1.4 to 3.0×10^{-4} *M* in the cationic surfactant ethylhexadecyldimethylammonium bromide (EHDA-Br), and 0.4 to 3.0×10^{-4} *M* in CrO_4^{2-} or 0.5 to 1.2×10^{-4} *M* in $S_2O_3^{2-}$, are presented for a single equilibrium stage separation. Models are proposed and tested with the experimental data for the exchange of either the divalent CrO_4^{2-} (or $S_2O_3^{2-}$) or the monovalent ion pair EHDA-CrO_4^- (or EHDA-$S_2O_3^-$), each with Br^-.

SELECTIVITY COEFFICIENTS

Consider the continuous-flow, foam fractionation unit shown schematically in Fig. 1 with the feed stream to the foam fractionation column containing Na_2CrO_4 of concentration c_i (colligend) in CrO_4^{2-} and the quaternary ammonium surfactant EHDA-Br of concentration e_i (exchanger) in $EHDA^+$ and b_i in Br^-. Some NaBr may also be added to the feed so that b_i may not always be equal to e_i. After foam fractionation, the residual stream, lean in surfactant, contains CrO_4^{2-} of concentration c_r, $EHDA^+$ of concentration e_r, and Br^- of concentration b_r. The assumption can be made (*9*) that the foam stream consists of entrained bulk liquid (of

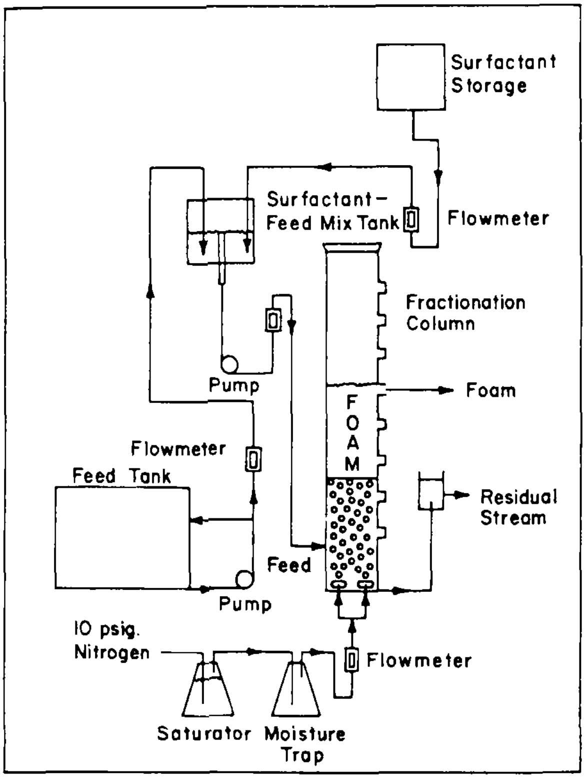

FIG. 1. Schematic diagram of experimental foam fractionation unit.

the same concentration as both the residual stream and the bulk liquid in the column), in equilibrium with surface liquid containing the surface excess of surfactant of surface concentration Γ_e in EHDA$^+$, plus the fixed and diffuse layers of counterions of surface concentrations Γ_c (CrO_4^{2-}) and Γ_b (Br^-).

As each bubble rises through the bulk solution in the column, there may occur an exchange reaction,

$$2(\text{EHDA-Br})_s + (CrO_4^{2-})_r \rightleftarrows (\text{EHDA}_2\text{-CrO}_4)_s + 2(Br^-)_r$$

in which the subscript s designates the surface layer or phase. The selectivity coefficient is defined by

$$K' = (\Gamma_c/c_r)/(\Gamma_b/b_r)^2 \qquad (1)$$

Assuming equilibrium exchange and that the ratios of the activity coefficients both in the bulk solution and in the surface phase are unity, $K' = K$, the thermodynamic equilibrium constant, and K' should be constant over the experimental range. The constancy of K' has been validated for a series of monovalent anions (*9–11*) for which K' was rather independent of ionic strength (over a narrow ionic strength range) and of the fraction of the exchanger occupied by the preferred anion. In the cases of NO_3^- vs Br^- and I^- vs Br^-, liquid height in the column had virtually no effect on K'. Either the surface exchange reaction occurs rapidly and equilibrium is reached at a short distance above the gas diffusers, or no surface exchange occurs and the selectivity is established by ion pair formation in the bulk solution. For CrO_4^{2-} vs Br^-,

$$K' = K'' = (\text{EHDA}_2\text{-CrO}_4)_r(\text{Br}^-)_r^2/(\text{EHDA-Br})_r^2(\text{CrO}_4^{2-})_r \qquad (2)$$

in which K'' is the ratio of the ion pair formation constants of $\text{EHDA}_2\text{-CrO}_4$ and EHDA-Br in the bulk solution.

An alternative exchange reaction is also possible. For a solution containing divalent anions and long-chain quaternary ammonium cations, it is possible that all of the CrO_4^{2-} are instantly paired as EHDA-CrO_4^-. The surface exchange reaction which then occurs is

$$(\text{EHDA-Br})_s + (\text{EHDA-CrO}_4^-)_r \rightleftarrows (\text{EHDA}_2\text{-CrO}_4)_s + (\text{Br}^-)_r.$$

and the selectivity coefficient is

$$K' = (\Gamma_c/c_r)/(\Gamma_b/b_r) \qquad (3)$$

In this instance the "colligend" is EHDA-CrO_4^-. If ion pair formation in the bulk solution controls,

$$K' = K'' = (\text{EHDA}_2\text{-CrO}_4)_r(\text{Br}^-)_r/(\text{EHDA-Br})_r(\text{EHDA-CrO}_4^-)_r \qquad (4)$$

Equations (1) and (3) can be contrasted on the basis that, for a constant K', the ratio Γ_c/c_r is a second-order function of Γ_b/b_r in the first case, and a linear function, identical to that for the exchange of two monovalent anions, in the second case.

EXPERIMENTAL

The feed solutions to the foam fractionation column were prepared with double distilled water of conductivity 6 μmho/cm at 25°C and with Analytical Reagent Grade sodium dichromate, sodium thiosulfate, sodium bromide, and sodium hydroxide for pH adjustment. The surfactant was ethylhexadecyldimethylammonium bromide, which analyzed 97 ± 3% on a Br^- basis and 93 ± 3% on a carbon basis. The feed concentration of the surfactant was either 1.4, 2.0, or 3.0×10^{-4} *M*, and that of the salts ranged from 0.4 to 3.0×10^{-4} *M* for CrO_4^{2-}, from 0.5 to 1.2×10^{-4} *M* for $S_3O_2^{2-}$, and from 3.0 to 9.0×10^{-4} *M* added Br^-. The feed surfactant concentration was always below the critical micelle concentration in the presence of each colligend (*12*). The pH of the feed in the case of $S_2O_3^{2-}$ was the unadjusted value of pH 6.3, with $S_2O_3^{2-}$ as the dominant species (*13*). For CrO_4^{2-} the pH was adjusted to 10.3 ± 0.3 to insure the presence of no other chromate species (*14*). The pH of the residual stream was consistently identical to that of the feed stream, indicating no foam fractionation of OH^-.

The Pyrex foam fractionation column in Fig. 1 was 89.5 cm high and 9.7 cm in diameter. The entire apparatus and procedure have been described in detail (*9*, *10*). The feed rate to the column was 0.056 l/min. The liquid level height was maintained at 32.5 cm and the foam height at 11.5 cm (above the liquid level). Temperature was held at 24 ± 1 °C. The flow rate of the residual stream was rather constant over the range of the experiments at 0.055 l/min. Nitrogen gas was saturated with water and was metered through twin, sintered glass diffusers of 50 μm porosity at 0.40 l/min (at 24 °C and 1 atm). The average bubble diameter, determined by a photographic technique, was rather constant over the range of the experiments at 600 μm (*9*, *12*).

Steady-state operation was consistently obtained in 2.5 to 3.5 hr as indicated by the constancy of the colligend concentration in three consecutive samples. The chromate concentrations in the feed and residual streams were analyzed by atomic absorption spectrophotometry at a wavelength of 358 nm; the thiosulfate concentrations in the feed and residual streams were analyzed by UV spectrophotometry at a wavelength of 234 nm (with no Br^- interference). The surfactant concentrations in the feed and residual streams were determined by a two-phase titration procedure (*15*) and with a Beckman Total Organic Carbon Analyzer.

The bromide concentrations in the feed and residual streams were established by ion balance. Atomic absorption spectrophotometry at a wavelength of 589 nm determined that the concentrations of sodium in the feed and residual streams were consistently identical and that there was no positive or negative adsorption of sodium in the surface phase. The ion balance could thus be used as an accurate measure of the bromide concentration.

RESULTS AND DISCUSSION

A total of 41 steady-state, single equilibrium stage foam fractionation experiments was carried out with CrO_4^{2-} or $S_2O_3^{2-}$ and EHDA-Br as the surfactant. For CrO_4^{2-}, over the feed concentration range 0.4 to 3.0×10^{-4} M, the concentration of CrO_4^{2-} in the residual stream could be related to the feed concentration by a power function:

$$c_r = 8.67 c_i^{1.29} \tag{5}$$

Equation (5) was derived for feed surfactant concentrations, $e_i = 2.0 \times 10^{-4}$ and 3.0×10^{-4} M. The correlation coefficient,

$$r = \left[1 - \frac{\sum(c_{r\ \mathrm{exptl}} - c_{r\ \mathrm{calc}})^2}{\sum(c_{r\ \mathrm{exptl}} - c_{r\ \mathrm{mean}})^2}\right]^{1/2}$$

was 0.99+ for the 18 data points, meaning that 99% (r^2) of the variations in c_r could be explained on the basis of a power function dependence on c_i.

For $S_2O_3^{2-}$, over the feed concentration range 0.5 to 1.2×10^{-4} M, the residual stream concentration was a stronger power function of the feed stream concentration:

$$c_r = 1.59 \times 10^3 c_i^{1.90} \tag{6}$$

For the total of 11 points, the correlation coefficient was 0.94 with the poorer fit, compared to CrO_4^{2-}, due to some variation in c_r with e_i, at constant c_i; c_r was a stronger power function of c_i at $e_i = 3.0 \times 10^{-4}$ M than at $e_i = 2.0 \times 10^{-4}$ M.

Equations (5) and (6) indicate the existence of significant ion competition, with Br^- competing with chromate or thiosulfate for the $EHDA^+$ cations. If there was little or no competition of Br^- with either chromate or thiosulfate, then c_r would have been a linear function of c_i, as proposed by several investigators (*1*). For the data fit by Eqs. (5) and (6), it should be noted that the only source of Br^- was as surfactant counterions (no NaBr was added).

Further evidence of ion competition is given by Fig. 2 in which the distribution coefficient of each colligend, with the distribution coefficient defined as Γ_c/c_r, the ratio of the colligend concentration in the surface phase to that in the residual solution, is related to the feed Br^- concentration (the surfactant counterion concentration *plus* the added NaBr concentration). The distribution coefficients for both chromate and thiosulfate decreased approximately linearly with b_i. Data are also shown for I^- and NO_3^- (*12*). In the absence of ion competition or exchange, Γ_c/c_r should be rather independent of b_i.

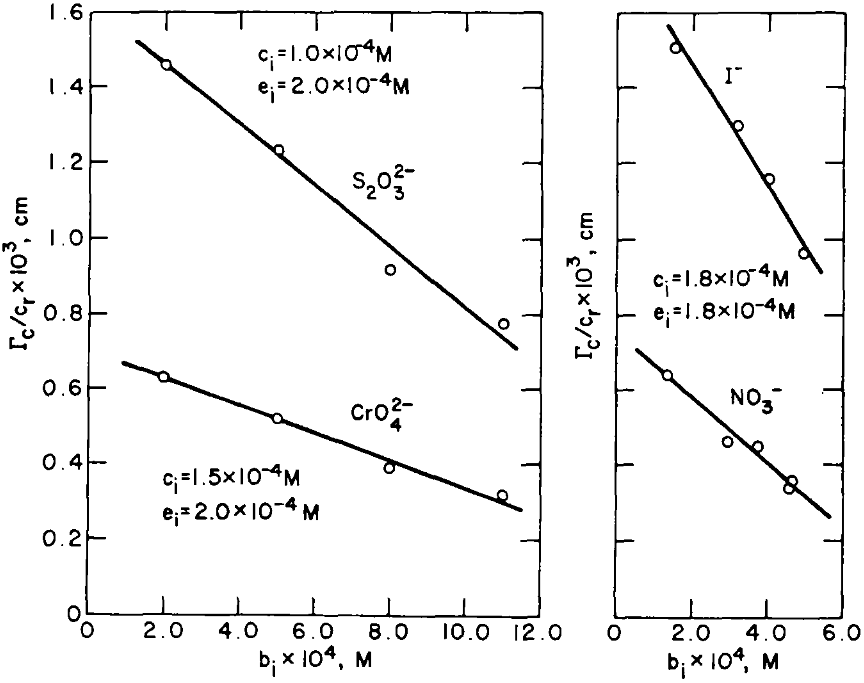

FIG. 2. Effect of the feed bromide concentration on the distribution coefficients for chromate, thiosulfate, nitrate, and iodide.

For all of the experimental data, an effort was made to validate the exchange or competition mechanisms proposed by Eqs. (1) and (2) or (3) and (4). Figures 3 and 4 present relations between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ for $CrO_4{}^{2-}$ vs Br^- and for $S_2O_3{}^{2-}$ vs Br^-, respectively. The concentration of the colligend in the surface phase, Γ_c, is directly proportional to $(c_i - c_r)$:

$$\Gamma_c = (c_i - c_r)\frac{LD_b}{6A} \tag{7}$$

in which D_b is the average bubble diameter (600 μm), L is the feed flow rate (0.056 l/min), A is the gas flow rate (0.40 l/min), and Γ is in units of gmole/cm². The assumptions necessary to write Eq. (7) have been validated experimentally (9). Thus $\Gamma_c = 1.4 \times 10^{-6}\ (c_i - c_r)$, and similarly, $\Gamma_b = 1.4 \times 10^{-6}\ (b_i - b_r)$: if the Γ's had been plotted in Figs. 3 and 4, instead of the actual, measured concentration differences, the scales would have

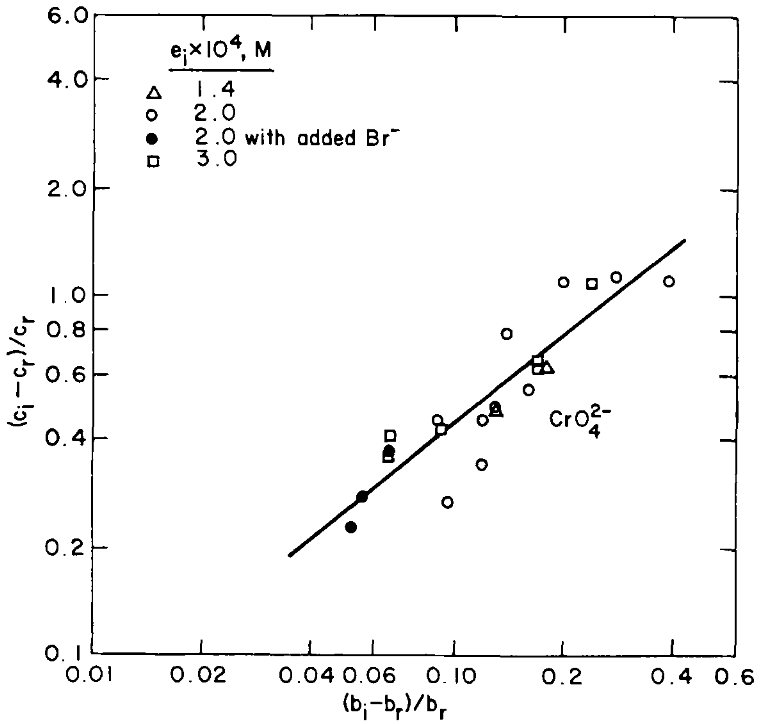

FIG. 3. Relation between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ for chromate.

been different, but the slopes and intercepts of the lines would have been identical.

For Fig. 3 the best least squares fit (log functions) was provided by the line

$$(c_i - c_r)/c_r = 2.78[(b_i - b_r)/b_r]^{0.80} \tag{8}$$

For the total of 21 points, the correlation coefficient r was 0.90. One data point with a value of $(b_i - b_r) < 0.10 \times 10^{-4}$ was not plotted or correlated because the value of $(b_i - b_r)$ was close to the experimental accuracy. For Fig. 4 the best least squares fit (log functions) was provided by the line

$$(c_i - c_r)/c_r = 18.9[(b_i - b_r)/b_r]^{1.04} \tag{9}$$

For the total of 18 points, the correlation coefficient r was 0.91, again not

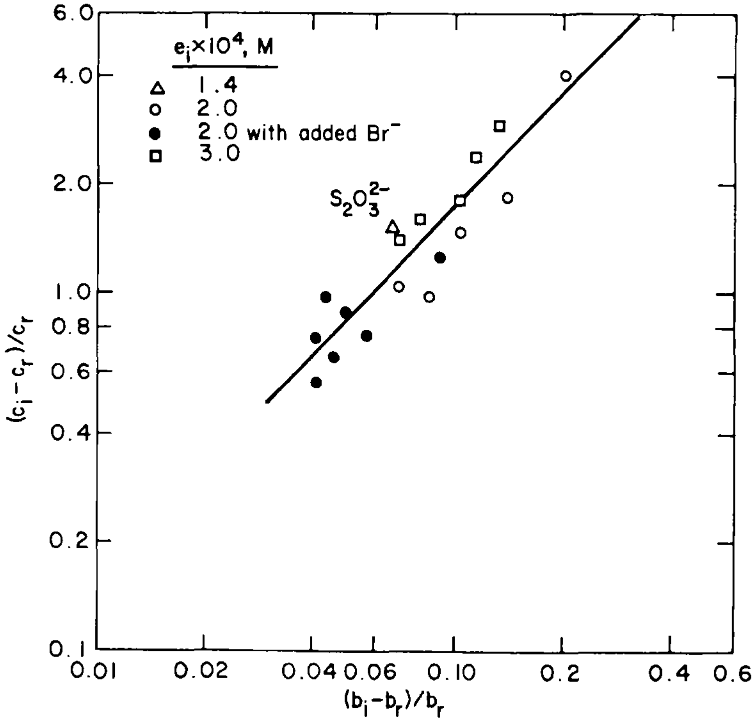

FIG. 4. Relation between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ for thiosulfate.

plotting or correlating one point with a low value of $(b_i - b_r) < 0.10 \times 10^{-4}$ M.

Equations (8) and (9) show that the mechanism described by the linear Eq. (3), with EHDA-CrO_4^- and EHDA-$S_2O_3^-$ as the exchanging or competing species, may have been what occurred, rather than the second-order Eq. (1), with CrO_4^{2-} and $S_2O_3^{2-}$ as the exchanging species.

Other factors may have brought about the linearity, including the adsorption of monovalent ions (Br^-) in the diffuse layer and that of divalent ions (CrO_4^{2-} or $S_2O_3^{2-}$) in the fixed layer, both as counterions to the $EHDA^+$ in the surface layer or phase. Steric effects may also have resulted due to the presence of $EHDA_2$-CrO_4, compared to monovalent ion pairs. Further data would have to be taken to be assured of EHDA-CrO_4^- or EHDA-$S_2O_3^-$ as the exchanging species, including variation in the feed surfactant concentration, e_i, over a wider range.

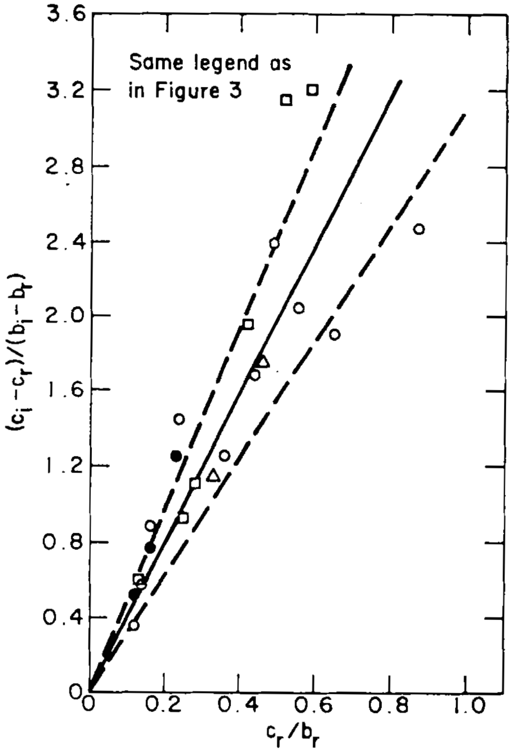

FIG. 5. Relation between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for chromate.

The experimental data in Figs. 3 and 4 were then fit by linear relations:

$$(c_i - c_r)/c_r = K'(b_i - b_r)/b_r$$

$$(c_i - c_r)/(b_i - b_r) = K'(c_r/b_r)$$

with the second relation shown for CrO_4^{2-} and $S_2O_3^{2-}$ in Figs. 5 and 6, respectively. Both of the above relations, which are algrabraic manipulations of Eq. (7) substituted into Eq. (3), were used in order to obtain the most accurate values of K', as shown in Table 1. The 95% confidence limits indicate that, for example for the first entry in the table, if the assumptions concerning the true situation were correct, there is 95% confidence that the true value of K' lay between 3.85 (1.0 + 0.20) and 3.85 (1.0 − 0.20). The 95% confidence limits are plotted as the dashed lines in Figs. 5 and 6.

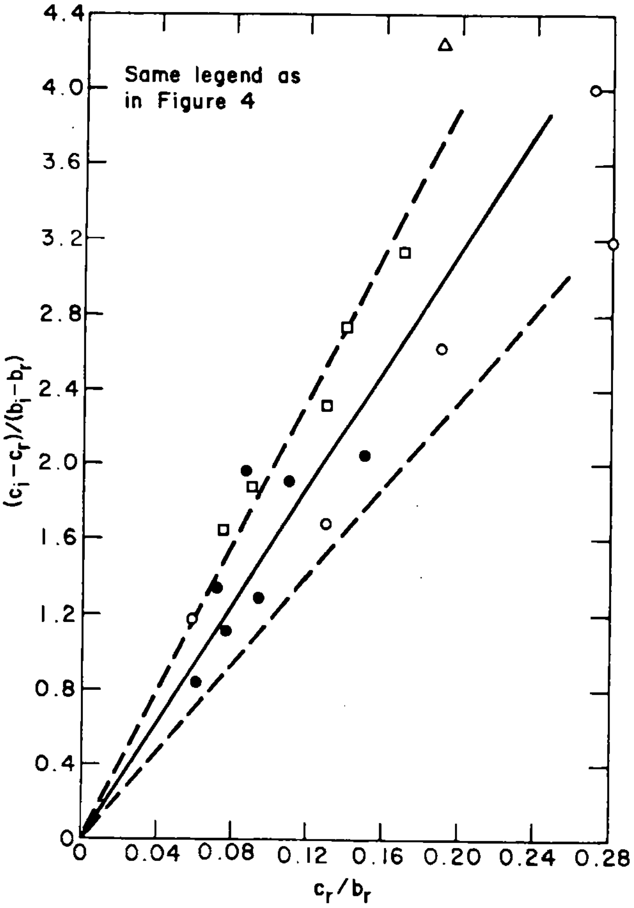

FIG. 6. Relation between $(c_i - c_r)/(b_i - b_r)$ and c_r/b_r for thiosulfate.

TABLE 1

Anion	Figure no.	K'	r	95% Confidence limits
CrO_4^{2-}	3[a]	3.85	0.86	3.85 (1.0 ± 0.20)
CrO_4^{2-}	5	3.96	0.84	3.96 (1.0 ± 0.22)
$S_2O_3^{2-}$	4[a]	17.9	0.92	17.9 (1.0 ± 0.15)
$S_2O_3^{2-}$	6	15.7	0.83	15.7 (1.0 ± 0.25)

[a] Replotted on linear coordinates.

The best value of K' for CrO_4^{2-} should be the average of 3.85 and 3.96, or 3.90, and the best value for $S_2O_3^{2-}$ should be the average of 17.9 and 15.7, or 16.8. The overall accuracy of the correlations is reasonable, considering the fact that K' is based on two concentrations and two concentration differences.

CONCLUSIONS

The continuous, single equilibrium stage foam fractionation of divalent anions was modeled both on the basis of the divalent CrO_4^{2-} or $S_2O_3^{2-}$ as the species exchanging with Br^- onto the surfactant cation $EHDA^+$ and on the basis of the monovalent EHDA-CrO_4^- or EHDA-$S_2O_3^-$ as the species exchanging with Br^-. The experimental data indicated that ion competition was prevalent, with the Br^- concentration producing a linear decrease in the distribution coefficient of chromate and of thiosulfate. For both chromate and thiosulfate a selectivity coefficient expression of the form

$$K' = (\Gamma_c/c_r)/(\Gamma_b/b_r)$$

fit the data rather well; considerably better than a second-order relation between Γ_c/c_r and Γ_b/b_r. It was postulated that EHDA-CrO_4^- or EHDA-$S_2O_3^-$ was the exchanging species. The value of K' for chromate was 3.90, with a correlation coefficient of 0.85, and that for thiosulfate was 16.8, with a correlation coefficient of 0.88.

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