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Foam Separation of Anions from Aqueous Solution: Selectivity of Cationic Surfactants

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Abstract

Anions are selectively separated and concentrated from dilute aqueous solution by foam fractionation. Selectivity coefficients are established from steady-state equilibrium data (solution concentrations 10^{-4} to 10^{-3} *M*) for SCN^-, I^-, ClO_3^-, NO_3^-, BrO_3^-, and NO_2^-, each vs Br^-, with the quaternary ammonium surfactant modeled as a soluble anion exchanger. Studies are reviewed on the foam separation of Re(VII), Mo(VI), and V(V) oxyanions; Au(I), Ag(I), Ni(II), and Co(III) cyanide complexes; and Pt(IV), Pd(II), and Au(III) chloro complexes. In a five-component system, the oxyanions of Re(VII), Mo(VI), Cr(VI), W(VI), and V(V) are foam fractionated from 10^{-6} *M* solutions with the cationic surfactant, hexadecyldimethylbenzylammonium chloride. In the batch, time-dependent experiments, the metals are monitored by radiotracers and gamma radiation spectrometry. At pH 6.0 and a chloride (NaCl) concentration of 10^{-2} *M*, and at pH 2.0, adjusted with HCl, Re(VII) and Mo(VI) oxyanions can be separated completely from Cr(VI), W(VI), and V(V) oxyanions. The selectivity sequences are discussed in terms of acid-base equilibria and in terms of the absolute partial molal entropy of each anion in aqueous solution, as a measure of surfactant cation–anion interaction.

INTRODUCTION

Foam separation processes have been used to separate and concentrate inorganic anions from dilute aqueous solution; a cationic surfactant is utilized which interacts preferentially with one or more anions (colligends)

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compared to competing anions. The effectiveness of the process is determined by the selectivity of the surfactant toward the colligend(s). The surfactant–colligend interaction may occur in the bulk solution and/or at the air–solution interfaces of generated gas bubbles. The surfactant–colligend ion pair or soluble complex is concentrated in the foam which is produced atop the bulk solution. In the absence of particles formed among the surfactant–colligend pairs, the process is termed foam fractionation (*1*).

The principles of foam fractionation have been detailed in several reviews (*1–12*) which have included references to a great number of specific separations, generally from dilute aqueous solutions (and involving the discussion of a considerable amount of solution chemistry). In these studies, effects have been enumerated of solution variables such as concentrations of surfactant and colligend, pH, ionic strength, and the presence of specific ionic species which may modify the charge and structure of the colligend or compete with the colligend for the surfactant; of operational variables such as aeration rate, gas bubble size, foaming time, and foam column geometry; and of the mode of operation: batch or continuous flow, with various schemes of foam recycle, feed position modification, etc.

Recently, a cationic surfactant concentrated from dilute aqueous solution at air–solution bubble interfaces has been modeled as a soluble ion exchanger, and selectivity coefficients have been established for SCN^-, I^-, ClO_3^-, NO_3^-, BrO_3^-, and NO_2^-, each vs Br^- (*13*, *14*). Several investigations have been conducted to determine the selectivity of cationic surfactants for transition metal oxyanions (*15–21*), leading to the successful separation and fractionation of as many as five transition metals from a dilute (1.0×10^{-6} *M*) solution of their oxygen compounds (*22*, *23*). Efforts have been made at selectivity prediction, based on the thermodynamic properties of the anions (*14*, *19*, *20*, *24*).

SELECTIVITY COEFFICIENTS OF EACH OF A SERIES OF ANIONS VS BROMIDE FROM CONTINUOUS FLOW STUDIES

Steady-state, single equilibrium stage experiments were conducted in the foam fractionation unit shown schematically in Fig. 1 (*13*, *14*). For a feed stream containing, for example, NaI of concentration c_i in I^- and the quaternary ammonium surfactant, ethylhexadecyldimethylammonium bromide (EHDA–Br), of concentration e_i in $EHDA^+$ and b_i in Br^- (NaBr also was present in some experiments), there were produced by aeration of the bulk solution a steady-state residual stream lean in surfactant and a steady-state foam stream rich in surfactant. The residual stream concentrations are designated c_r in I^-, e_r in $EHDA^+$, and b_r in Br^-. The as-

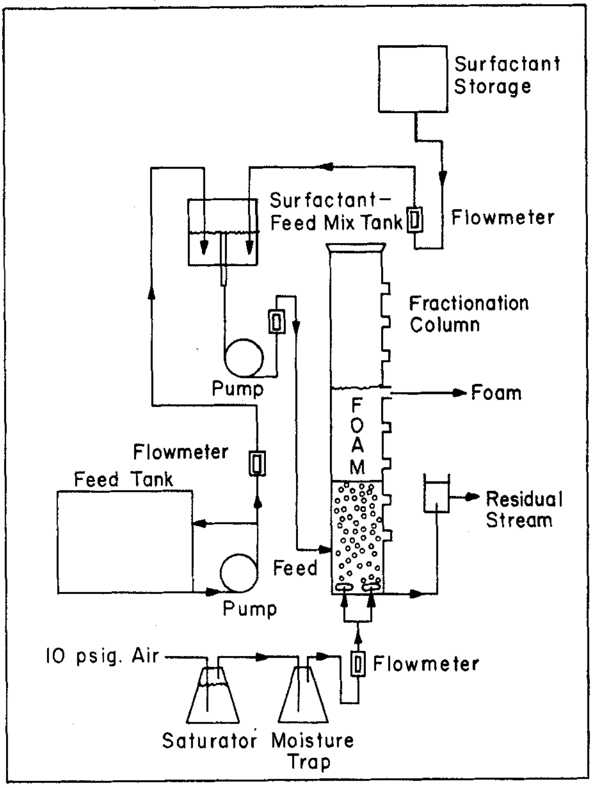

FIG. 1. Schematic diagram of continuous flow, single equilibrium stage foam separation unit.

sumption could be made (*13*) that the foam consisted of entrained bulk liquid (of concentration c_r, e_r, and b_r) in equilibrium with surface liquid containing surfactant of surface concentration Γ_e, plus the fixed and diffuse layers of counterions, of surface concentrations $\Gamma_c(I^-)$ and $\Gamma_b(Br^-)$.

As each bubble rose through the bulk solution, there may have occurred an exchange reaction

$$(\text{EHDA–Br})_s + (I^-)_r \rightleftarrows (\text{EHDA–I})_s + (Br^-)_r$$

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

$$K' = \Gamma_c b_r / \Gamma_b c_r \tag{1}$$

and it was shown that the liquid height in the column had no effect on

K' (*13*). Either the surface exchange reaction occurred rapidly and reached equilibrium at a short distance above the air diffusers, or no surface exchange occurred and the selectivity was determined by ion pair formation in the bulk solution:

$$K' = K'' = (\text{EHDA–I})_r(\text{Br}^-)_r/(\text{EHDA–Br})_r(\text{I}^-)_r \qquad (2)$$

The ratio of Γ_c/Γ_b in Eq. (1) can be replaced by $(c_i - c_r)/(b_i - b_r)$ to enable the direct experimental determination of K'.

Experimental details have been presented previously (*13*, *14*). The feed concentration of the surfactant EHDA–Br, e_i, ranged from 1.0 to 4.0 × 10^{-4} M, and that of each of the salts NaSCN, NaI, $NaClO_3$, $NaNO_3$, $NaBrO_3$, or $NaNO_2$ was within the range 0.4 to 6.6 × 10^{-4} M. In some experiments, NaBr was added to the feed stream in concentrations from 1.0 to 7.8 × 10^{-4} M in order to reduce the c_r/b_r ratio to values lower than could be achieved only by maneuvering the feed concentrations of the colligend salt and of EHDA–Br. The feed stream was within the pH range 5.6 to 5.8. The Pyrex foam fractionation column was 89.5 cm high and 9.7 cm in diameter. The feed rate was maintained at 0.056 liter/min, the air rate through the twin sintered glass diffusers of 50 μm porosity was held at 0.4 liter/min, and the temperature was 24 ± 1.0°C. The surfactant was analyzed by two-phase titration and the various anions by UV absorption (*14*).

Experimental results for each of the anionic colligends are presented in Fig. 2, in which the ratio of the colligend to bromide in the surface phase is related to that ratio in the residual stream. All data points are presented for SCN^-, I^-, and NO_2^-, while for ClO_3^-, NO_3^-, and BrO_3^-, due to crowding, points are given only at $e_i = 1.8 \times 10^{-4}$ M. For ClO_3^- and BrO_3^-, data were also taken at $e_i = 1.0 \times 10^{-4}$ M and 4.0×10^{-4} M and for NO_3^- at 1.4, 1.6, and 2.0 × 10^{-4} M. All data were used to establish the straight lines, and K' was independent of e_i. The resultant values of K', together with statistical indicators of the goodness of fit, are given in Table 1. The last column in Table 1 is discussed in a later section.

The values of Γ_c/Γ_b for SCN^- at $c_r/b_r > 0.35$ and for I^- at $c_r/b_r > 1.0$ (for $e_i \doteq 1.8 \times 10^{-4}$ M) began to rise sharply. For both of these systems, fine particles were observed in the foam at the foam removal port; K' would not be constant if EHDA–SCN or EHDA–I were precipitated in the surface phase (*14*). The effect on K' of the activity coefficient ratio in the concentrated surface layer or phase for each of the anionic colligends was determined by relating K' to Γ_c/Γ_e, the fraction of the exchanger occupied by the preferred ion. K' was found to be independent of Γ_c/Γ_e, indicating a constant activity coefficient ratio, and was found to be rela-

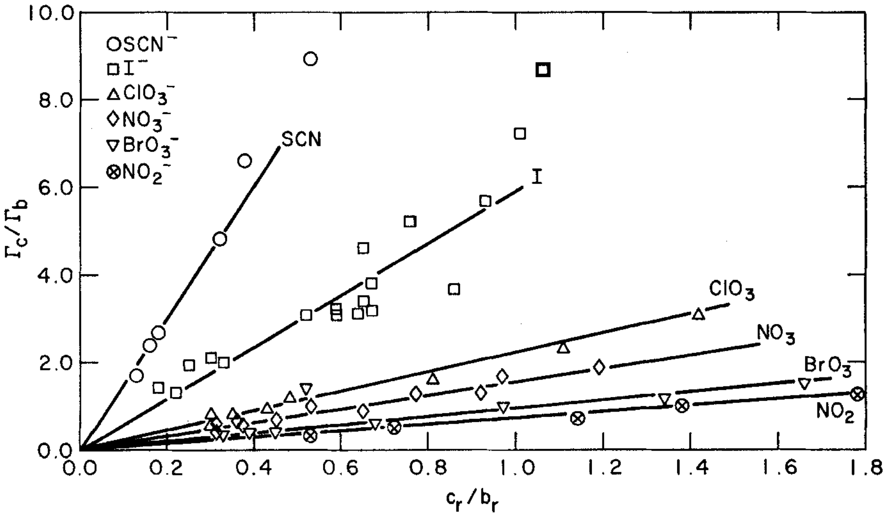

FIG. 2. Establishment of selectivity coefficients for SCN^-, I^-, ClO_3^-, NO_3^-, BrO_3^-, and NO_2^- vs Br^-.

TABLE 1

Determination of Selectivity Coefficients of Anionic Colligends vs Bromide

Anionic colligend	K'	Total number of data points	95% Confidence limits for K'	Correlation coefficient, r, for K'	$\bar{S}^\circ_{298}$ abs (eu)
SCN^-	15.1	4	15.1 (1.0 ± 0.29)	0.98	41.5
I^-	5.85	17	5.85 (1.0 ± 0.31)	0.87	31.6
ClO_3^-	2.21	25	2.21 (1.0 ± 0.058)	0.98	44.5
NO_3^-	1.56	23	1.56 (1.0 ± 0.18)	0.93	40.5
Br^-	1.00				24.8
BrO_3^-	0.95	21	0.95 (1.0 ± 0.084)	0.98	44.0
NO_2^-	0.73	5	0.73 (1.0 ± 0.33)	0.98	35.4

tively independent of ionic strength (*14*). Based on a limited amount of data, K' for NO_3^-/Br^- was found to increase with decreasing surfactant chain length for C_{14}, C_{16}, and C_{18} trimethylammonium bromides (*14*).

REVIEW OF FOAM SEPARATION STUDIES IN POLAND: ANIONIC COLLIGENDS AND CATIONIC SURFACTANTS

Among the known elements, some of the transition metals occupy a peculiar position due to their value, recently increasing demands, and the lack of sufficiently rich mineral resources. In Poland, particular emphasis has been placed on foam separation processes to separate and concentrate Re(VII), Mo(VI), and V(V) oxyanions; Au(I), Ag(I), Ni(II), and Co(III) cyanide complexes; and Pt(IV), Pd(II), and Au(III) chloro complexes. Table 2 presents a review of pertinent references on Re(VII), Mo(VI), and V(V) oxygen compounds: this work is of particular interest due to the separation study of the five-colligend-system detailed in the next section. Utilizing two different surfactants, ReO_4^- could be separated rather completely from $HMoO_4^-$ in 1.0×10^{-2} *M* H_2SO_4 solution (*17*, *19*). V(V) oxygen compounds, in 1.0×10^{-6} *M* solution, could be effectively foam separated with both an anionic and a cationic surfactant, depending on the H_2SO_4 concentration (*18*).

Additional, specific investigations have been made of the foam separa-

TABLE 2

Studies of Foam Separation of Re(VII), Mo(VI), and V(V) Oxygen Compounds

Solution composition	Transition metal oxygen compound concentration (*M*)	Surfactant	Surfactant concentration (*M*)	Ref.
ReO_4^-	1.0×10^{-4}	Hexadecyldiethylammonium hydrochloride (HDEAHCl)	5.0×10^{-4}	*25*
MoO_4^{2-}	1.0×10^{-4}	HDEAHCl	3.0×10^{-4}	*26*
Mo(VI) oxygen compounds	1.0×10^{-6} to 1.4×10^{-3}	HDEAHCl	5.0×10^{-5} to 4.0×10^{-4}	*15*
ReO_4^-	1.0×10^{-5} to 3.0×10^{-4}	HDEAHCl	5.0×10^{-5} to 2.0×10^{-4}	*16*
$ReO_4^- + MoO_4^{2-} + H_2SO_4$	1.9×10^{-4}	Dodecyldimethylbenzylammonium bromide (DDMBABr)	6.0×10^{-4}	*17*
V(V) oxygen compounds + H_2SO_4	1.0×10^{-6} to 1.0×10^{-4}	Hexadecyltrimethylammonium bromide (HTMABr) (also anionic surfactants)	5.0×10^{-4} to 7.5×10^{-4}	*18*
$ReO_4^- + MoO_4^{2-}$	2.0×10^{-5}	DDMBABr	2.0×10^{-4}	*19*
$ReO_4 + HPO_4^{2-}$	5.0×10^{-5}	HDEAHCl	8.0×10^{-4}	*19*
Re(VII), Mo(VI), and P(V) oxygen compounds	1.0×10^{-5} to 1.0×10^{-4}	DDMBABr	8.0×10^{-4}	*20*
ReO_4^-, MoO_4^{2-}	5.0×10^{-5}	HDEAHCl	2.0×10^{-4}	*21*

tion of $AuCl_4^-$ (*27*, *28*); $PtCl_6^{2-}$, $PtCl_4^{2-}$, and $Pt(CN)_4^{2-}$ (*29*, *30*); $Au(CN)_2^-$ and $Ag(CN)_2^-$ (*31*); $PdCl_4^{-2}$ (*32*); $Co(CN)_6^{3-}$ (*33*); $Co(SCN)_4^{2-}$ and $Ni(SCN)_4^{2-}$ (*34*); and anionic complexes of Ni(II), Th(IV), Pa(V), U(VI), Am(III), Cm(III), Eu(III), Tm(III), and Yb(III) (*35–37*). A solvent sublation process has been applied to ReO_4^- and MoO_4^{2-} (*38*). These investigations, almost entirely conducted in batch, time-dependent-based foam separation units, have included experimental methodology, effects of process-controlling variables, solution chemistry aspects, the determination of selectivity, and direct applications of the process to hydrometallurgy.

FOAM FRACTIONATION OF A FIVE COLLIGEND SYSTEM: OXYANIONS OF Re(VII), Mo(VI), Cr(VI), W(VI), AND V(V)

From a dilute (10^{-6} *M*) aqueous solution of the oxygen compounds of Re(VII), Mo(VI), Cr(VI), W(VI), and V(V), the foam separation selectivity should be established by two factors: first, acid-base equilibria in solution which can cause the increase in charge, the neutralization, and even the reversal of charge of the oxyanion, together with the modification of its structure. For these transition metal oxygen compounds, generally in acidic or neutral solution, the following equilibria can be written,

$$H_nMeO_m \overset{K_1}{\rightleftarrows} H^+ + H_{n-1}MeO_m^-$$

$$H_{n-1}MeO_m \overset{K_2}{\rightleftarrows} H^+ + H_{n-2}MeO_m^{2-}$$

for Mo(VI), Cr(VI), and W(VI), $n = 2$ and $m = 4$; for Re(VII), $n = 1$ and $m = 4$; and for V(V), $n = 3$ or 1 and $m = 4$ or 3.

Based upon literature references, selected values of pK_1 and pK_2 are presented in Table 3. In the 10^{-6} *M* solutions involved, complex anions and polynuclear species are neglected except for anionic chloro complexes of Mo(VI) which have been extensively reported (*46*, *57*, *58*). For V(V) the cation VO_2^+ has been reported in dilute acid solutions (*54*, *59*, *60*).

The second factor determining the selectivity should be specific, metal oxyanion–surfactant cation interaction (ion pair formation) in solution. For the system described, ReO_4^-, for example, must compete for the surfactant cations with the other four transition metal oxyanions and with other anions, such as Cl^- or SO_4^{2-}, which may be present in concentrations several orders of magnitude greater than that of ReO_4^-. The relative competitiveness of the various anionic species is determined by their charges, degrees of hydration, and structures.

TABLE 3

Selected Acid-Base Dissociation Constants for Transition Metal Oxyacids

Metal	Constants	Refs.
Re(VII)	$pK_1 = -1.2$	*39–41*
Mo(VI)	$pK_1 = 1.4$	*39, 42, 43*
	$pK_2 = 4.0$	*39, 42, 44, 45*
Cr(VI)	$pK_1 = -0.9$	*39, 41, 47–49*
	$pK_2 = 6.5$	*39, 41, 48, 49*
W(VI)	$pK_1 = 2.2\text{–}3.5$	*39, 50, 51*
	$pK_2 = 3.8\text{–}4.6$	*50–52*
V(V)	$pK_1 = 3.6$	*39, 53–55*
	$pK_2 = 8.2$	*39, 41, 53, 55, 56*
	$pK_3 = 13.5$	*41, 55, 56*

Experimental

A Pyrex batch flotation cell, 45.7 cm high and 2.4 cm in diameter, was employed in the five-colligend-system study. Experimental details have been reported previously (*22*, *23*). All of the experiments were carried out at constant 1.0×10^{-6} *M* initial concentration (z_i) of each metal [Analytical Reagent Grade NH_4ReO_4, $(NH_4)_6Mo_7O_{24}$, $(NH_4)_2CrO_4$, Na_2WO_4, and NH_4VO_3], with all five metals always present, and at constant 5.0×10^{-5} *M* surfactant (hexadecyldimethylbenzylammonium chloride, 97–99% active) concentration. The pH was adjusted with HCl and the ionic strength with NaCl. The initial solution volume was 0.10 liter, the air flow rate was 0.01 liter/min, and the temperature was 22.5 ± 1.0°C.

The time dependence of the concentration (z_t) of each metal in the bulk solution was recorded continuously during the experiments by means of radioactive analytical tracers and gamma radiation spectrometry (*22*, *23*). At each initial HCl or NaCl concentration, five identical experiments were carried out: in each of the five a different radiotracer was used and thus a different metal oxyanion was monitored, yielding five z_t vs time curves. These curves enabled the calculation of the maximum flotation at foam cease, $1 - z_r/z_i$ (for complete flotation, $z_r = 0$ and $1 - z_r/z_i = 1.0$), and of the first-order flotation rate constant, k, min^{-1} (*20*).

Results

Two distinct series of experiments were carried out, one at constant pH = 6.0 ± 0.2, with the ionic strength varied from 9.0×10^{-5} to 3.0×10^{-1} *M* with NaCl (*23*); and the other with the pH varied from 4.5 to 0.7

with HCl, and ionic strength variable (*22*). In both series the Cl^- concentration should be expected to play a significant role; the equilibrium position of the ion pair formation reaction between surfactant cations and Cl^- should determine the quantity of surfactant cations available to the five metal oxyanions. The cessation of metal oxyanion–surfactant cation ion pair formation should be expected at a certain high Cl^- concentration, and thus flotation should cease.

Figures 3 and 4 give the flotation results at pH 6.0 as a function of *p*[NaCl], the negative log of the activity of the NaCl in the initial solution. From Fig. 3, at low chloride concentrations, all five metal oxyanions were floated completely, due to the excess surfactant present; at *p*[NaCl] = 3.5, the residual solution contained only V(V), with the other four metal oxyanions entirely in the foam; and at *p*[NaCl] $\leq$ 1.5, Re(VII) and Mo(VI) were separated completely from Cr(VI), W(VI), and V(V). Figure 4 indicates that the order of the first-order flotation rates of the metal oxyanions was similar to that of the maximum flotations ($1 - z_r/z_i$) in Fig. 3. The flotation rate of Mo(VI) fell off at lower chloride concentrations, indicating that the very efficient flotation of Mo(VI) at higher chloride concentrations was produced by the presence of anionic chloro complexes.

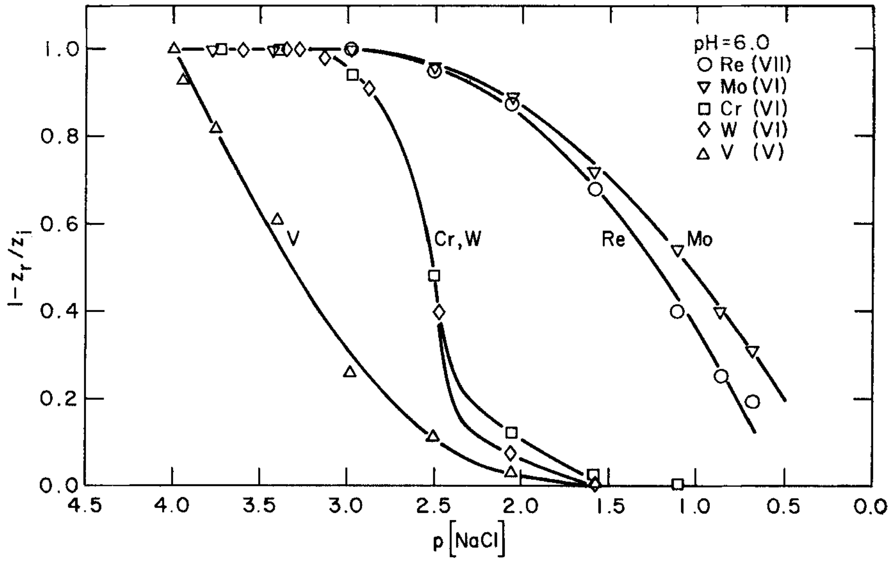

FIG. 3. Maximum flotations of five metal oxyanions vs sodium chloride activity at pH 6.0.

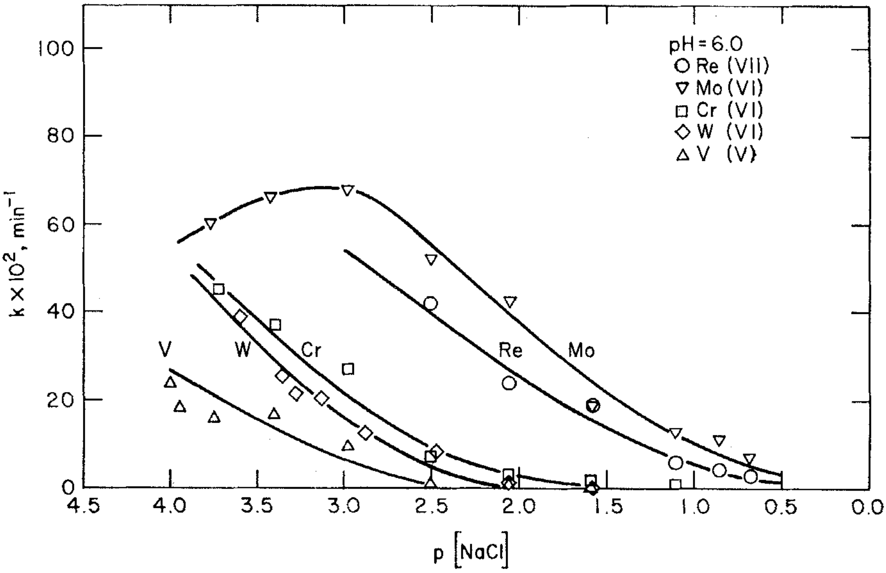

FIG. 4. First-order flotation rate constants of five metal oxyanions vs sodium chloride activity at pH 6.0.

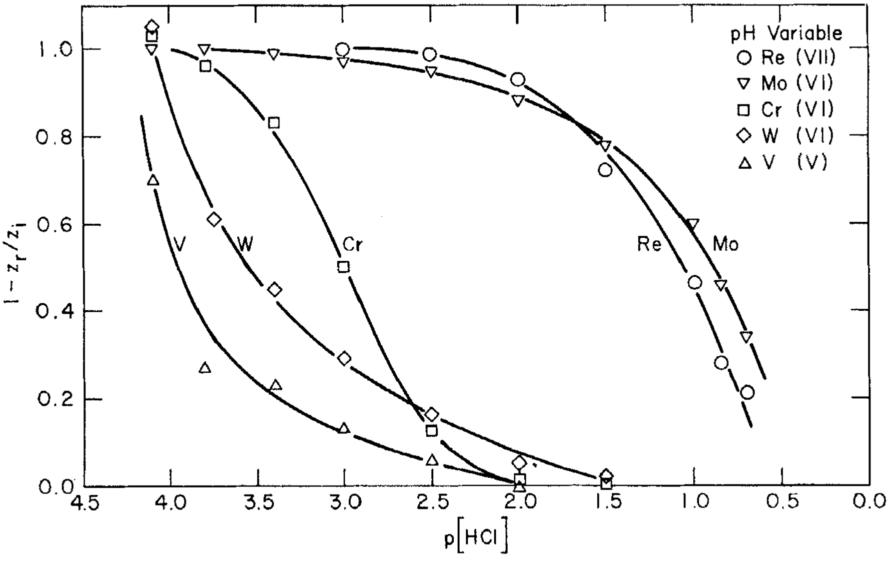

FIG. 5. Maximum flotations of five metal oxyanions in acidic solution vs hydrogen chloride activity.

Figure 5 presents the flotation results at variable, acidic pH (*22*). The parameter *p*[HCl] is the negative log of the activity of HCl in the initial solution and was always quite close to the measured pH value. The separations indicated in Figs. 3 and 5 were quite similar, particularly for Re(VII) and Mo(VI). The flotation of Cr(VI) was reduced in the acidic solutions (making the comparison at constant ionic strength, *p*[HCl] = *p*[NaCl]), perhaps due to the complete conversion of $CrO_4^{2-} \rightarrow HCrO_4^-$. The flotations of W(VI) and V(V) were sharply reduced, probably due to the $WO_4^{2-} \rightarrow HWO_4^- \rightarrow H_2WO_4$ and $H_2VO_4^- \rightarrow H_3VO_4 \rightarrow VO_2^+$ conversions. The role of the transition metal oxyanion species on the flotation behavior is discussed in greater detail below. The effect of *p*[HCl] on the first-order rate constant (*22*) was similar to that of *p*[NaCl], again with reductions in the *k* values for Cr(VI), W(VI), and V(V) in the acidic solutions, making the comparison at values of *p*[HCl] = *p*[NaCl].

For all of the metals in both series of experiments, the collapsed foam volume varied from 2.1 to 0.4% of the initial solution volume of 0.10 liter, providing very rich foams. As would be expected, the foam volume decreased with a decrease in *p*[HCl] or *p*[NaCl] (*22*). For 100% and for 50% flotation of a metal, the ratio of the concentration in the foam to that in the initial solution varied from 50 to 250, and from 25 to 125, respectively, corresponding to the collapsed foam volume values at the extremes of the added electrolyte range.

Discussion

Efforts have been made to predict the selectivity of cationic surfactants for series of anions (*14*, *19*, *24*, *61*, *62*). The extent of interaction is determined by the anion's charge, structure, and degree of hydration. The absolute partial molal entropy of the ion in aqueous solution, $\bar{S}^\circ_{298}$ abs, has been suggested as a possible selectivity criterion (*24*). For ions of like charge, $\bar{S}^\circ_{298}$ abs increases with the size of the crystal radius and has been correlated as a decreasing function of the degree of hydration, as measured by the difference between the hydrated radius and the crystal radius (*24*). An increase in the charge of an ion generally produces a decrease in $\bar{S}^\circ_{298}$ abs unless there is a large increase in the crystal radius, and generally produces an increase in the degree of hydration unless there is a large increase in the crystal radius. For two ions of like charge, the less hydrated (largest value of $\bar{S}^\circ_{298}$ abs) should be floated preferentially. For two ions of different charges, the more highly charged ion should be floated preferentially unless its entropy is very much smaller that that of the ion of lower charge.

The entropy criterion was tested on a series of anions of like charge (*14*), with values reported in the last column of Table 1; a distinction is made between oxyanions and those not containing oxygen. Some trend is evident, but BrO_3^- is out of order. Perchlorate, with $\bar{S}^\circ_{298}$ abs = 48.7 eu, formed particulates with the cationic surfactant, EHDA–Br, indicating a much stronger interaction than with ClO_3^- (*14*), and $H_2PO_4^-$, with $\bar{S}^\circ_{298}$ abs = 33.5, exhibited a selectivity vs Br^- similar to that of NO_2^- (*63*).

Anion structure may have produced some of the discrepancy in the selectivity vs $\bar{S}^\circ_{298}$ abs correlation attempted in Table 1. For oxyanions of similar structure, a summary is presented in Table 4. For ReO_4^-, MoO_4^{2-}, CrO_4^{2-} and WO_4^{2-}, literature values were used (*64–66*), while for the others, in the absence of reported values, an average was taken of values calculated by the methods of Cobble (*67*) and of Couture and Laidler (*68*). A value of 5.5 eu was used for the proton. For oxyanions with the same charge, again a trend is evident. For Mo(VI), anionic chloro complexes undoubtedly enhanced the flotation; in a sulfuric acid solution with $p[H_2SO_4] = 1.0 \rightarrow 2.0$, ReO_4^- was separated completely from $HMoO_4^-$ by preferential (for ReO_4^-) foam separation with a cationic surfactant (*19*). Diamond (*69*) has reported a selectivity sequence

TABLE 4

Oxyanion Selectivities vs Absolute Partial Molal Entropies

	$1 - Z_r/Z_t$ at		k(min^{-1}) at p[NaCl] = 3.0 or p[HCl] = 3.0	Oxyanion from pK_1 and pK_2	$\bar{S}^\circ_{298}$ abs(eu)	
Metal	p[NaCl] = 3.0	p[HCl] = 3.0				
			pH = 6.0			
Re(VII)	0.99		55	ReO_4^-	55	
Mo(VI)	0.99		68	MoO_4^{2-}		25
Cr(VI)	0.96		22	$HCrO_4^-$ (76%)	40	
W(VI)	0.96		16	WO_4^{2-}		26
V(V)	0.31		6	$H_2VO_4^-$ (VO_3^-)	7	
			pH = 3.0			
Re(VII)		0.99	50	ReO_4^-	55	
Mo(VI)		0.97	62	$HMoO_4^-$	45	
Cr(VI)		0.50	14	$HCrO_4^-$	40	
W(VI)		0.29	9	HWO_4^- (H_2WO_4)		
V(V)		0.13	6	$H_3VO_4(HVO_3)$ (VO_2^+)		

TABLE 5

Oxyanion Selectivities at pH 11

Metal	k(min^{-1}) in mixture	k(min^{-1}) for anion alone	Oxyanion present from pK_1 and pK_2	$\bar{S}^\circ_{298}$ abs(eu)
Re(VII)	27	16	ReO_4^-	55
Mo(VI)	6	7	MoO_4^{2-}	25
Cr(VI)	8	5	CrO_4^{2-}	20
W(VI)	5	4	WO_4^{2-}	26
V(V)		2	HVO_4^{2-}	7

$ReO_4^- > CrO_4^{2-} > WO_4^{2-}$ using Dowex–1, a solid anion exchange resin in the Cl^- form.

Additional data were available at pH 11 for a mixture of Re(VII), Mo(VI), Cr(VI), and W(VI), and for each of the five transition metal oxyanions of interest, present by itself in aqueous solution (*70*). The cationic surfactant was hexadecyltrimethylammonium bromide. Results are presented in Table 5. It would appear that $\bar{S}^\circ_{298}$ abs does provide an indication of foam separation selectivity, and thus of oxyanion–surfactant cation interaction, when comparing oxyanions with a wide spread of values of $\bar{S}^\circ_{298}$ abs. For oxyanions with similar entropies, the criterion is not of value.

CONCLUSIONS

The cationic surfactant ethylhexadecyldimethylammonium (bromide) is selective for $SCN^- > I^- > ClO_3^- > Br^- > NO_2^-$ as determined from steady-state, equilibrium foam fractionation experiments. The surfactant is modeled as a soluble ion exchanger, and the selectivity coefficients do not vary with the fraction of the exchanger occupied by the preferred ion and are relatively independent of ionic strength.

The cationic surfactant hexadecyldimethylbenzylammonium chloride is selective for Re(VII) $\geqq$ Mo(VI) > Cr(VI) $\geqq$ W(VI) > V(V) oxyanions in batch, time-dependent foam separation studies from solutions 1.0×10^{-6} M in each metal and containing all five metals. At pH 6.0, with no added NaCl, all five metal oxyanions are floated completely; at p[NaCl] = 3.5, V(V) is the only metal remaining in the bulk solution after foam separation; at p[NaCl] $\leqq$ 1.5, Re(VII) and Mo(VI) can be separated completely from Cr(VI), W(VI), and V(V). Flotation results are similar in acidic solutions, making the comparison at p[HCl] = p[NaCl], except that the flotations of Cr(VI), W(VI), and V(V) are somewhat retarded.

The absolute partial molal entropy in aqueous solution provides an indication of foam separation selectivity by a cationic surfactant when comparing oxyanions with a wide spread of entropy values.

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