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Selectivity Coefficients for $Ag(CN)_2^-$ and $Au(CN)_2^-$ from Continuous Foam Fractionation with a Quaternary Ammonium Surfactant

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Abstract

An experimental study is presented of the continuous flow, foam fractionation of cyanide complex anions: $Ag(CN)_2^-$ and $Au(CN)_2^-$ from 1.0 to 8.0 × 10^{-5} *M* aqueous solutions. The quaternary ammonium surfactant, hexadecyltriethylammonium iodide, is modeled as a soluble ion exchanger. The selectivity coefficients were determined for $Ag(CN)_2^-$ vs I^- equal to 2.71, and for $Au(CN)_2^-$ vs I^- equal to 10.85. These coefficients are discussed in terms of the physicochemical properties of cyanide complex anions.

INTRODUCTION

Foam fractionation relies on the interaction of an anionic surfactant with oppositely charged ions in solution and at solution–gas bubble interfaces. The surfactant-colligend ion pair or soluble complex is concentrated in the foam which is formed atop the bulk solution. The principles of foam fractionation have been detailed in several reviews (*1–6*).

The effectiveness of the foam fractionation method is principally governed by its selectivity. The selectivity of cationic surfactants for anions has been determined in several foam fractionation investigations including Cl^-, Br^-, I^-, CN^-, SCN^-, NO_2^-, NO_3^-, ClO_3^-, BrO_3^-, $S_2O_3^{2-}$, CrO_4^{2-}, MoO_4^{2-}, WO_4^{2-}, and ReO_4^- ions (*6–11*). These investigations have also tried to predict selectivity for anions, principally on the basis of the thermodynamic properties of the hydrated anions (*6*, *12–14*).

An original approach to the selectivity problem was presented by Grieves (*8*). A cationic surfactant concentrated from dilute aqueous solution at solution–air 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^-, NO_2^-, $S_2O_3^{2-}$, and CrO_4^{2-}, each versus Br^- (*8*, *9*, *11*, *15*).

Limited data are reported on the foam fractionation selectivity of complex anions. The batch foam fractionation experiments concerned the selectivity of cyanide and chloride complex anions: $Ag(CN)_2^-$, $Au(CN)_2^-$, $PdCl_4^{2-}$, $PtCl_6^{2-}$, $Au(CN)_4^-$, $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ (*10*, *16*, *17*).

The objective of this investigation was the experimental determination of selectivity coefficients for $Ag(CN)_2^-$ and $Au(CN)_2^-$ vs I^- with a quaternary ammonium salt as the soluble ion-exchanger. The selectivity sequence for these cyanide complex anions is discussed in terms of the physicochemical properties of these anions and previous batch foam fractionation experiments.

THE SELECTIVITY COEFFICIENTS OF MONO- AND DIVALENT ANIONS

Steady-state, single equilibrium stage experiments can be conducted in the foam fractionation unit shown in Fig. 1. Consider the continuous flow with the feed stream containing X^- ion, of the concentration c_i, and the quaternary ammonium surfactant, $Surf^+Y^-$, of concentration e_i in $Surf^+$ and b_i in Y^-. When the system reaches an equilibrium, the residual stream contains X^- of concentration c_r, surfactant of concentration e_r, and Y^- of concentration b_r. The assumption can be made that the foam consists of entrained bulk liquid containing the surface excess of surfactant of the surface concentration Γ_e plus the fixed and diffuse layers of counterions of surface concentration Γ_c and Γ_b, respectively.

When each bubble goes through the bulk solution, there may occur an exchange reaction

$$(\text{Surf-Y})_s + (X^-)_r \rightleftarrows (\text{Surf-X})_s + (Y^-)_r \tag{1}$$

and thus the selectivity coefficient can be defined by

$$K' = \Gamma_c b_r / \Gamma_b c_r \tag{2}$$

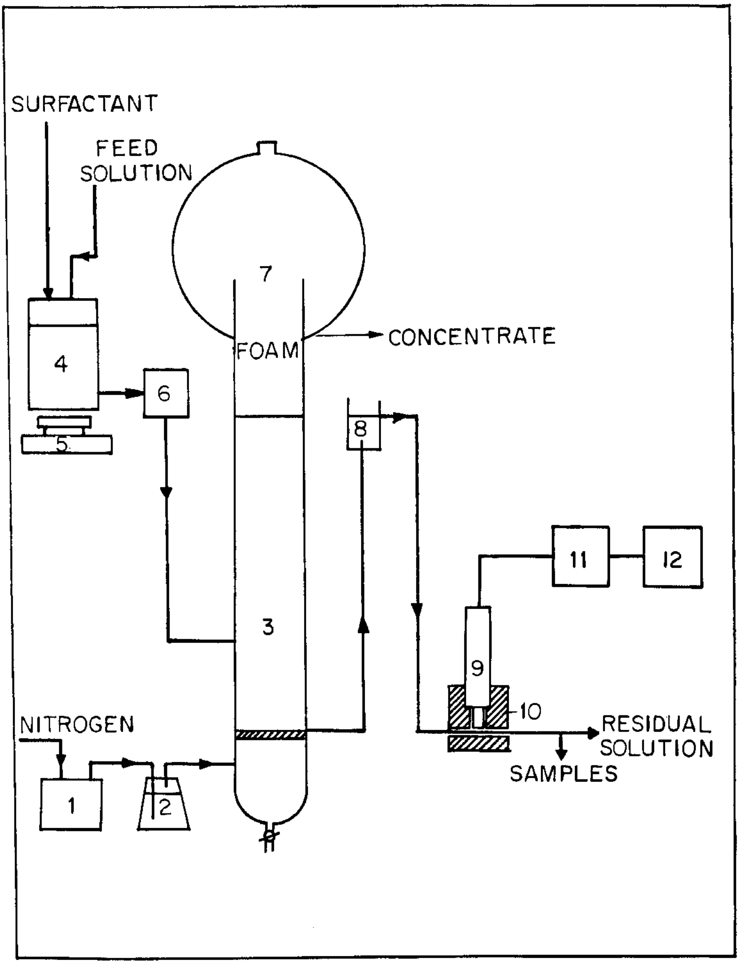

FIG. 1. Schematic diagram of experimental foam fractionation unit: (1) flow and pressure control unit, (2) humidifier, (3) fractionation column, (4) feed tank, (5) magnetic stirrer, (6) dosing pump, (7) foam receiver, (8) overflow, (9) spectrometric scintillation probe, (10) lead screen, (11) gamma spectrometer, and (12) recorder.

It was shown that the liquid height in the column had no influence on K' (*8*). This indicates that either the surface ion exchange reaction is rapid and reaches equilibrium at a short distance above the gas sparger or no surface ion exchange occurs and then the selectivity is determined by ion pair formation in the bulk solution:

$$K' = K'' = (\text{Surf-X})_r(\text{Y}^-)_r/(\text{Surf-Y})_r(\text{X})_r \tag{3}$$

A possible cause for an ion exchange reaction at the surface can be the attraction of the less hydrated anion to the surface in preference to the more hydrated anion. The concentration of the colligend in the surface phase, Γ_c, is proportional to $(c_i - c_r)$:

$$\Gamma_c = (c_i - c_r)\frac{LD}{6A} \tag{4}$$

in which D is the average bubble diameter, L is the feed flow rate, and A is the gas flow rate. A similar expression can be written for Γ_b. The ratio of Γ_c/Γ_b in Eq. (2) can be replaced by $(c_i - c_r)/(b_i - b_r)$. It leads to the simple and direct experimental determination of K':

$$K' = K'' = (c_i - c_r)b_r/(b_i - b_r)c_r \tag{5}$$

For divalent anions an exchange reaction can be expressed as

$$2(\text{Surf-Y})_s + (\text{X}^{2-})_r \rightleftarrows (\text{Surf}_2\text{-X})_s + 2(\text{Y}^-)_r \tag{6}$$

and the selectivity coefficient is consequently

$$K' = K'' = (c_i - c_r)b_r^2/(b_i - b_r)^2c_r \tag{7}$$

An alternative exchange reaction is also possible. For divalent anions and quaternary ammonium surfactant when all of the X^{2-} anions are instantly paired as $(\text{Surf-Y})^-$, the surface ion exchange reaction is defined as

$$(\text{Surf-Y})_s + (\text{Surf-X})_r^- \rightleftarrows (\text{Surf}_2\text{-X})_s + (\text{Y}^-)_r \tag{8}$$

For this case the selectivity coefficient is determined according to Eq. (5). For a chromate and thiosulfate, the expression for the selectivity coefficient given by Eq. (5) fits the data rathei well, considerably better than a second-order relation between Γ_c/c_r and Γ_b/b_r. It indicates that $(\text{Surf-X})^-$ ion is exchanged with counterion Y^-.

The values of K', together with statistical indicators of the goodness of fit, are given in Table 1 (*8*, *9*, *11*).

TABLE 1

Selectivity Coefficients for Anions from the Continuous Foam Fractionation of a Cationic Surfactant, Ethylhexadecyldimethylammonium Bromide

Anion	*K'*	Total number of data points	95% confidence limits for *K'*	Correlation coefficient, *r*, for *K'*
SCN^-	15.1	4	±4.35	0.98
I^-	5.85	17	±1.85	0.87
ClO_3^-	2.21	25	±0.128	0.98
NO_3^-	1.56	23	±0.281	0.93
BrO_3^-	0.95	21	±0.080	0.98
NO_2^-	0.73	5	±0.24	0.98
$S_2O_3^{2-}$	16.8	18	±3.36	0.89
CrO_4^{2-}	3.90	21	±0.82	0.89

EXPERIMENTAL

The initial aqueous solutions subjected to foam separation were prepared with double distilled water of conductivity 1.4 $\mu\Omega^{-1}cm^{-1}$ at 25°C, and the salts $KAg(CN)_2$, $KAu(CN)_2$, and KOH (analytical reagent grade). The surfactant, hexadecyltriethylammonium iodide, 98% active on a carbon basis, was used as a 0.05 *M* standard solution in analytical grade ethanol. The gamma radioactive isotopes Ag-110 m, I-131, and Au-198 were in the form of $Ag(CN)_2^-$, I^-, and $Au(CN)_2^-$, respectively. They were either carrier free (I-131) or of sufficiently high specific activity to neglect the effect of carrier concentration (1 Ci/g for Ag-110 m and 72 Ci/g for Au-198).

The feed concentrations of cyanide complex anions of Ag(I) and Au(I) ranged from 1.0 to 8.0×10^{-5} *M*, and the surfactant concentrations varied from 5.0 to 8.0×10^{-5} *M*. The feed surfactant concentrations were always below its critical micelle concentration (*18*). Known amounts of the cyanide complex salts [$KAg(CN)_2$ or $KAu(CN)_2$] and 10 to 20 μCi of the respective isotopes were added, then NaCN, and then, to prevent hydrolysis of the cyanide anions, 20 mmoles of KOH was added to 1.0 liter of the initial solution. The pH of the initial solutions was in the range of 11.5 to 12.2. The total cyanide ion concentration was always equal to 0.050 *M*. To establish an ionic equilibrium, the initial solutions were aged for 24 hr before being foam fractionated.

The foam fractionation column (Fig. 1) was 36 cm high and 6.5 cm in diameter. The feed solution flow rate was 4.1 cm^3/min, and the feed entered the column 10 cm above the gas sparger. The liquid level height was maintained at 26 cm and the foam height at 12 cm (above the liquid level). The nitrogen was saturated with water and its flow rate was maintained at 12.2 cm^3/min (at 25°C and 760 mmHg). The gas diffusers were of 40 to 50 μm porosity. The volume of each initial solution was 0.25 liter and the temperature was held at 21 ± 2°C.

The floated complex anions solution and the surfactant alcoholic solution were mixed before the flotation process. Then this mixture was introduced to the flotation column by a dosing pump. Steady-state equilibrium was achieved in 3 to 4 hr. The flotation runs were carried out up to the moment when the indications of a single-channel gamma radiation spectrometer recorder were constant (*19*). Activities of the initial and residual streams were analyzed by the measuring set which consisted of a Ge–Li semiconductor detector and multichannel gamma radiation spectrometer (1202 Nuclear Data Model). Solution activities of cyanide complex anions of silver(I) and gold(I) and iodide anions were determined as an arithmetic mean from four reproducible determinations using 4 cm^3 samples. The surfactant concentrations in the feed and residual streams were analyzed by a two-phase titration technique using bromophenol blue as the indicator and sodium tetraphenylboron as the titrant (*20*). Cyanides were determined by an argentometric method using 0.01 *M* $AgNO_3$ as the titrant (*21*).

RESULTS AND DISCUSSION

A total of 40 steady-state, single equilibrium foam fractionation experiments were conducted with $Ag(CN)_2^-$ and $Au(CN)_2^-$ anions, using the cationic surfactant hexadecyltriethylammonium iodide. Assuming that floated complex anions are monovalent, the relationship between the concentration of these anions and the counterion concentration can be described by the linear equation

$$y = bx + a \tag{9}$$

in which y is equal to $(c_i - c_r)/c_r$ and x is equal to $(b_i - b_r)/b_r$. By using the method of least squares the values of a and b regression coefficients were calculated for $Ag(CN)_2^-$ and $Au(CN)_2^-$ anions (22). The results are given in Table 2. In this table the standard deviation values of coefficients a and b have been also summarized. There are various hypotheses that

TABLE 2

Data for Linear Regression

	$Ag(CN)_2^-$	$Au(CN)_2^-$
$\sum x$	1.4325	1.4664
$\sum y$	3.9020	16.021
$\sum x^2$	0.1287	0.1109
$\sum y^2$	0.9646	13.151
$\sum xy$	0.3493	1.2037
$\sum' x^2 = \sum x^2 - \frac{(\sum x)^2}{N}$	7.99×10^{-3}	1.7407×10^{-2}
$\sum' y^2 = \sum y^2 - \frac{(\sum y)^2}{N}$	6.892×10^{-2}	1.9913
$\sum' xy = \sum xy - \frac{\sum x \sum y}{N}$	2.05×10^{-2}	0.1823
$b = \frac{\sum' xy}{\sum' x^2}$	2.57	10.47
$a = \frac{\sum y}{N} - b\frac{\sum x}{N}$	0.0129	0.0291
$\sum' \hat{y}^2 = \sum' y^2 - \frac{(\sum' xy)^2}{\sum' x^2}$	1.638×10^{-2}	8.262×10^{-2}
$S^2(\hat{y}) = \frac{\sum' y^2}{N-2}$	1.092×10^{-3}	3.934×10^{-3}
$S(b) = \left(\frac{S^2(\hat{y})}{\sum' x^2}\right)^{1/2}$	0.370	0.475
$S(a) = S(b)\left(\frac{\sum x^2}{N}\right)^{1/2}$	3.22×10^{-2}	3.30×10^{-2}

are of interest in relation to the simple linear regression model. One of these is H_0: $a = 0$, which can be checked by the Student's test:

$$t = \frac{|a|}{S(a)} \tag{10}$$

The t-value was computed from the data given in Table 2; this value is equal to 0.401. The tabular value of t with 15 degrees of freedom at a 0.05 significance level is 2.131. Since the calculated value of t is less than the tabular t-value, the hypothesis that $a = 0$ is accepted. The computed t-value for $Au(CN)_2^-$ anions is equal to 0.967; the tabular value of t for these anions with 21 degrees of freedom at a 95% confidence interval is 2.080. In this manner, the hypothesis that $a = 0$ for $Au(CN)_2^-$ anions is also accepted. This gives irrefutable proof of a simple linear regression:

$$y = b_0 x \tag{11}$$

Assuming that $b_0 = K'$, the linear equation leads to

$$(c_i - c_r)/c_r = K'(b_i - b_r)/b_r \tag{12}$$

These considerations indicate that the selectivity coefficients of $Ag(CN)_2^-$ and $Au(CN)_2^-$ anions with hexadecyltriethylammonium iodide can be calculated from the slopes of the straight line passing through the origin of the coordinates. The slope coefficients and their standard deviations are summarized in Table 3. The selectivity coefficient is equal to 2.71 for $Ag(CN)_2^-$ and 10.85 for $Au(CN)_2^-$. Figures 2 and 3 present the relationship between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ for $Ag(CN)_2^-$ vs I^-, and for $Au(CN)_2^-$ vs I^-, respectively.

The 95% confidence limits for selectivity coefficients are as follows:

$$Ag(CN)_2^-: K' = 2.71 \pm 2.131 \times 8.89 \times 10^{-2} = 2.52 - 2.90$$

$$Au(CN)_2^-: K' = 10.85 \pm 2.080 \times 0.188 = 10.45 - 11.24$$

For the total of 17 points, the correlation coefficient, r, was 0.86 for $Ag(CN)_2^-$. This value is higher than the tabular r-value at a 0.01 significance level ($r = 0.611$). This means that there is less than one chance in a hundred of making an error that correlation between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ exists. For the total of 23 points, the correlation coefficient, r, was 0.98 for $Au(CN)_2^-$ anions. This value is much higher than the maximum tabular value of r for 21 degrees of freedom at a 0.01 significance level ($r = 0.527$). According to Eq. (5), the selectivity coefficients, K' should be independent of the initial concentration of cyanide complexes. This hypothesis is confirmed in Fig. 4 where the values of K' are presented versus the initial concentration of floated complex anions.

TABLE 3

Data for Linear Regression Going Through an Origin of Coordinates

	$Ag(CN)_2^-$	$Au(CN)_2^-$
$b_0 = \frac{\sum xy}{\sum x^2}$	2.71	10.85
$\sum \hat{y}_0{}^2 = \sum y^2 - \frac{(\sum xy)^2}{\sum x^2}$	1.63×10^{-3}	8.61×10^{-2}
$S^2(\hat{y}_0) = \frac{\sum \hat{y}_0{}^2}{N-1}$	1.017×10^{-3}	3.914×10^{-3}
$S(b_0) = \left(\frac{S^2(\hat{y}_0)}{\sum x^2}\right)^{1/2}$	8.89×10^{-2}	0.188
$r = \left(\frac{b_0 \sum xy - (\sum y)^2/N}{\sum y^2 - (\sum y)^2/N}\right)^{1/2}$	0.86	0.98

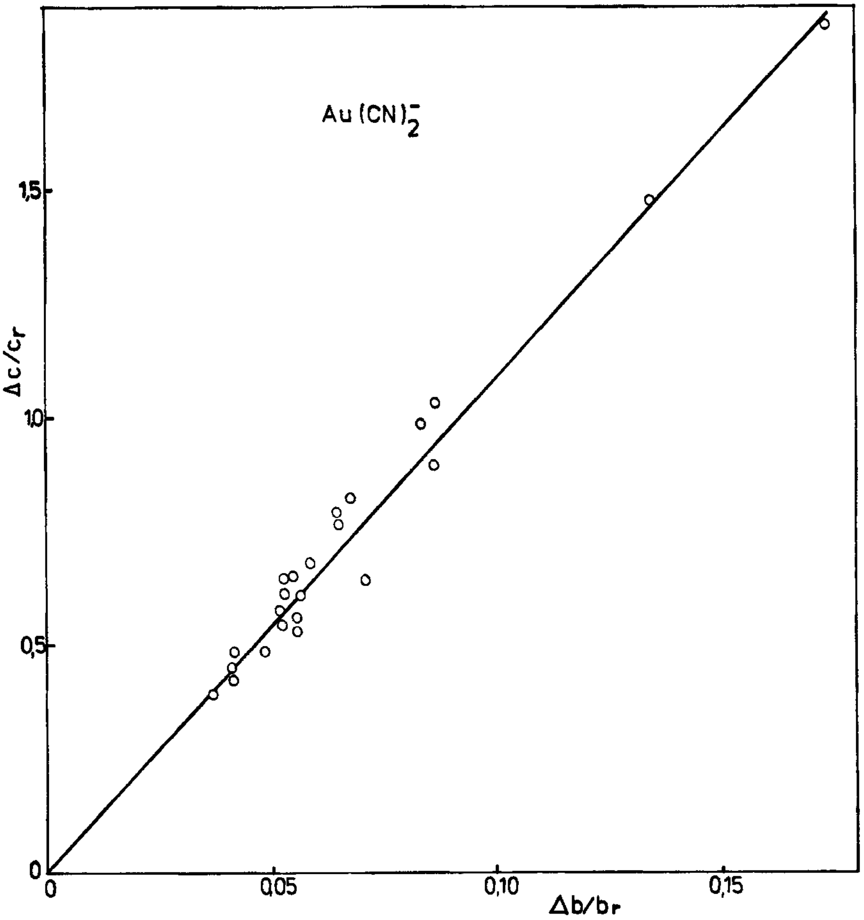

FIG. 2. Relation between $(c_i - c_r)/c_r$ and $(b_i - b_r)/b_r$ for $Au(CN)_2^-$.

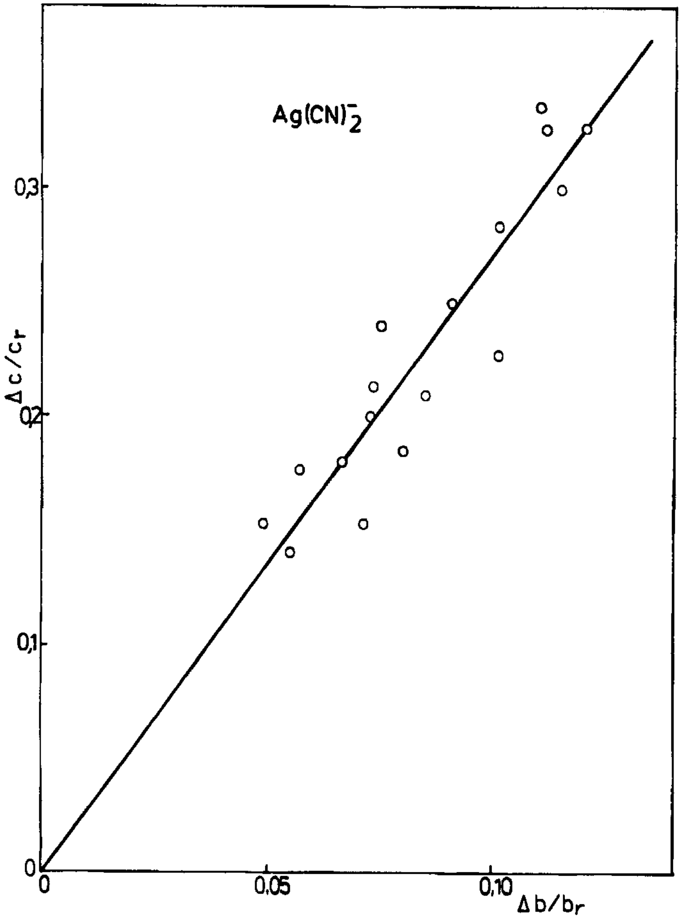

FIG. 3. Relation between $(c_t - c_r)/c_r$ and $(b_t - b_r)/b_r$ for $Ag(CN)_2^-$.

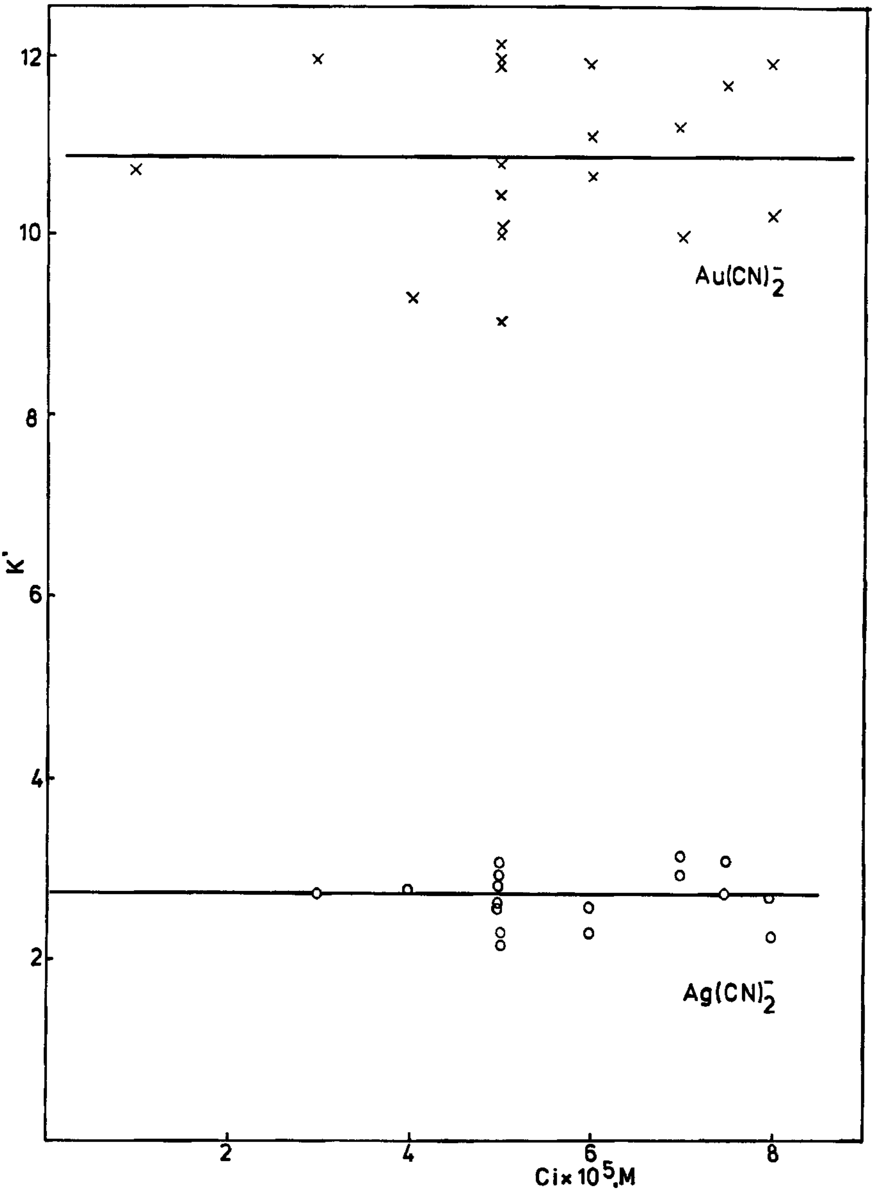

FIG. 4. Effect on K' the initial cyanide complex anion concentration.

The cyanide complex anions of Ag(I) and Au(I) have several common characteristics such as charge, electronic structure, and linear geometric structure. However, these two complex anions have a different affinity to water. Gold has a higher electronegativity than silver. According to Gordy (*23*), the electronegativity value for Au is 2.3 and for Ag is 1.9. Gold, with its higher electronegativity, has less basic complex anions which interact with water less strongly. The lower the extent of hydration, the greater should be the affinity for the surfactant cation. Some indications that this hypothesis is true are the values of water entropy changes created by an ion, which are equal to 3.8 cal/mol·°K for $Ag(CN)_2^-$ and 4.2 cal/mol·°K for $Au(CN)_2^-$ (*24*).

According to Charewicz's criterion (*6*) for the selective flotation of oxyanions, the affinity of oxyanions for a cationic surfactant is mainly dependent on the ion–water interaction in the bulk solution and decreases with the increase in this interaction. The affinity of anions for a cationic surfactant is approximately proportional to the value of the water entropy changes. The results obtained are in good agreement with previous research on batch foam fractionation of $Ag(CN)_2^-$, and $Au(CN)_2^-$ anions (*16*). The separation coefficient of $Au(CN)_2^-$ over $Ag(CN)_2^-$ is about 50. Similar trends were observed for the foam fractionation sequence with a quaternary ammonium surfactant, $Hg(CN)_4^{2-} > Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$ (*10*), and for ion exchange sequences with a strongly basic resin, $Pt(CN)_4^{2-} > Pd(CN)_4^{2-} > Ni(CN)_4^{2-}$, and $Au(CN)_2^- > Ag(CN)_2^-$ (*25, 26*).

CONCLUSIONS

Selectivity coefficients for $Ag(CN)_2^-/I^-$ and $Au(CN)_2^-/I^-$ have been determined from the continuous, single equilibrium stage foam fractionation with a strongly basic, quaternary ammonium surfactant acting as a soluble ion exchanger. For both $Ag(CN)_2^-$ and $Au(CN)_2^-$ anions, a selectivity coefficient expressed by

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

fits the data well. The value of K' for $Ag(CN)_2^-$ was 2.71 ± 0.19, with a correlation coefficient of 0.86, and that for $Au(CN)_2^-$ was 10.85 ± 0.39, with a correlation coefficient of 0.98. The foam fractionation selectivity sequence can be partly predicted from the water entropy changes in the presence of these complex anions.

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