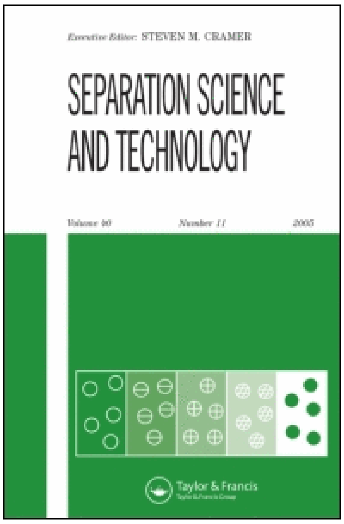


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# Selectivity Coefficients for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ from Continuous Foam Fractionation with a Quaternary Ammonium Surfactant

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# NOTE

# Selectivity Coefficients for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ from Continuous Foam Fractionation with a Quaternary Ammonium Surfactant

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## Abstract

An experimental study is presented on the continuous flow, foam fractionation of cyanide complex anions. $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ form $7.5 \times 10^{-6}$ to $1.5 \times 10^{-5}$ $M$ aqueous solutions with the quaternary ammonium surfactant, hexadecyltrimethylammonium iodide. The selectivity coefficients were determined for $Zn(CN)_4^{2-}$ vs $I^-$ equal to 8.86. for $Cd(CN)_4^{2-}$ vs $I^-$ equal to 21.79 and for $Hg(CN)_4^{2-}$ vs $I^-$ equal to 25.12. The surfactant ion-exchange reaction with the studied complex ions was also suggested.

## INTRODUCTION

The selectivity of cationic surfactants for anions has been determined in several foam fractionation investigations including $Cl^-$, $Br^-$, $I^-$, $CN^-$, $SCN^-$, $NO_2^-$, $NO_3^-$, $ClO_3^-$, $BrO_3^-$, $S_2O_3^{2-}$, $CrO_4^{2-}$, $Au(CN)_2^-$, and $Ag(CN)_2^-$ ions (*1–6*). These investigations include some attempts to predict the selectivity for the anions on the basis of the thermodynamic properties of the hydrated anions (*7–11*), but despite the small number of experimental data the more general thermodynamic criterion for selective action of a cationic surfactant has not been formulated. Especially limited data are reported on foam fractionation of complex anions.

The objective of this investigation, as a part of a research project on selective foam fractionation of complex cyanide anions of transition metals, was the experimental determination of selectivity coefficients for

$Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ vs $I^-$ with a quaternary ammonium salt.

## EXPERIMENTAL

The previously described (*6*) foam fractionation column and the experimental procedure were used with a nitrogen flow rate of 17 $cm^3$/min and a temperature held at 294 ± 1.5°K. The surfactant, 99.5% hexadecyltrimethylammonium iodide, was used as a 0.02 *M* standard solution in analytical grade ethanol. The gamma radioactive isotopes $^{65}Zn$, $^{109}Cd$, $^{131}I$, and $^{203}Hg$ were used either carrier free ($^{109}Cd$, $^{131}I$) or of sufficiently high specific activity to neglect the effect of carrier concentration (0.9 Ci/g for $^{65}Zn$ and 1.2 Ci/g for $^{203}Hg$).

The feed concentrations of cyanide complex anions of Zn(II), Cd(II), and Hg(II) ranged from 0.75 to $1.5 \times 10^{-5}$ *M*, and the surfactant concentrations varied form 1.5 to $3.0 \times 10^{-5}$ *M*. These concentrations for potassium cyanide and potassium hydroxide were kept constant and equal to $5.0 \times 10^{-2}$ and $1.0 \times 10^{-3}$ *M*, respectively.

## RESULTS AND DISCUSSION

The selectivity coefficients ($K'$) were defined according to the original approach to the selectivity of foam fractionation first presented by Grieves (*2, 3*), where a cationic surfactant adsorbed at solution–air bubble interfaces has been modeled as a soluble ion exchanger.

A total of 63 steady-state, single equilibrium foam fractionation experiments were conducted with $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ anions, using the cationic surfactant hexadecyltrimethylammonium iodide.

The experimental data points were then treated according to the standard statistical procedure (*5, 6*). The selectivity coefficients were found equal to 8.86, 21.79, and 25.12 for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$, respectively. The 95% confidence limits for selectivity coefficients are as follows:

$$Zn(CN)_4^{2-}: \quad K' = 8.86 \pm 2.086 \times 0.3080 = 8.22 - 9.50$$
$$Cd(CN)_4^{2-}: \quad K' = 21.79 \pm 2.086 \times 0.5623 = 20.62 - 22.96$$
$$Hg(CN)_4^{2-}: \quad K' = 25.12 \pm 2.086 \times 0.6416 = 23.78 - 26.45$$

For the total of 21 points for each complex anion, the correlation coefficients, $r$, were 0.83, 0.91, and 0.91 for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and

$Hg(CN)_4^{2-}$, respectively. From the above data and according to the applied model, it appears that the selectivity coefficient for the anions studied is defined by

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

where $c$ is the concentration of the complex anion, $b$ is the concentration of the iodide anion, and subscripts $i$ and $r$ refer to initial and final concentrations, respectively.

## CONCLUSIONS

From continuous, single equilibrium stage foam fractionation experiments with a strongly basic, quaternary ammonium surfactant acting as a soluble ion exchanger, the ion-exchange mechanism for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ complex anions was recognized as

$$(R—Y)_s + (R—X)_r^- \leftrightarrows (R_2—X)_s + (Y^-)_r$$

where R describes the surfactant cation, X and Y are the complex anion and iodide anion, respectively, and $s$ and $r$ refer to bubble surface and final bulk solution, respectively. This mechanism is similar to that determined for chromate and thiosulfate anions (*5*).

The selectivity coefficients for $Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, and $Hg(CN)_4^{2-}$ vs $I^-$ were 8.86, 21.79, and 25.12, respectively. It appears from the above data that the affinity of the complex anions studied to the hexadecyltrimethylammonium iodide follows the order $Hg(CN)_4^{2-} > Cd(CN)_4^{2-} > Zn(CN)_4^{2-}$.

A similar trend was observed in batch-type foam fractionation studies with a quaternary ammonium salt (*4*).

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