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Foam Fractionation of Mercury(II) Nitro Complexes

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Summary

Using a recycle foam separation apparatus, the foam fractionation distribution factor, Γ/C, of the anionic metal nitro complexes of mercury(II) with the cationic surfactant, hexadecyltrimethylammonium bromide, was determined. The distribution factor was measured as a function of nitric acid concentration. The maximum occurred at 0.1 N nitric acid, which is in agreement with the anionic ion-exchange column distribution coefficient. Total reflux foam fractionation experiments yielded a 150-fold increase in the enrichment factor with a 20% recovery of the mercury(II) ion.

INTRODUCTION

A number of metals form anionic nitro complexes in solutions of nitric acid (*1*). Differences among the formation constants of these metals make it possible to produce complexes selectively by varying the nitric acid concentration. Ichikawa (*2*) conducted a detailed study of the volume distribution factors of metal ions in nitric acid media on anion exchange resins (*2*). Of the metal ions studied by Ichikawa et al. (*2*), mercury(II) was selected to illustrate separations by foam fractionation (*3*). Karger and Miller (*3*) demonstrated that for the foam fractionation of the mercury(II) chloro complexes and iron(III) chloro

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complexes, the values of the distribution factor determined the optimum conditions for the separation of mixtures of metal ion chloro complexes. Using the cationic surfactant hexadecyltrimethylammonium bromide (HDT), a detailed study was made to determine the distribution factor, Γ/C, for mercury(II) as a function of the normality of nitric acid. This communication reports the application of ion exchange data to the removal of mercury(II) nitro complexes by foam fractionation.

EXPERIMENTAL

A recycle foam fractionation apparatus similar to the apparatus of Karger and Miller (*3*) was used to determine the distribution factor of the mercury(II) nitro complexes at steady state. The solution capacity of the column was increased from 500 to 1500 ml by adding a 1-liter reservoir to the base of the column. The achievement of steady state was insured by recycling the collapsed foam liquid for 90 min before taking samples of the foam liquid and bulk solution. The reproducibility of the collapsed foam liquid flow rate was improved by using a high speed spinning polyethylene basket to break the foam. The speed was adjusted to prevent buildup of foam in the basket and refoaming of the liquid striking the sides of the Teflon coated funnel.

The total collection time and volume of the collapsed foam liquid were kept to a minimum to prevent a large displacement of steady-state conditions. The concentration of the mercury(II) ion in the aqueous samples was determined by isotopic dilution analysis using a Packard Model 300 autogamma spectrometer The distribution factors were calculated using the following equation (*5*):

$$\Gamma/C = (E - 1)(L\bar{D}/6.59G)$$

where E = the enrichment ratio (concentration in collapsed foam liquid/concentration in bulk solution), L = collapsed foam liquid flow rate (ml/min), $\bar{D}$ = effective average bubble diameter (volume to surface area average), and G = gas flow rate (ml/min).

The foam bubble diameter was measured by photographing the foam using a Honeywell Pentax 35 mm reflex camera model H3 and a measuring magnifier (Edmund Scientific Co., magnifying power 12X) attached directly to the 50-mm camera lens. The foam column was illuminated at a right angle to the camera with an electronic flash unit (ultrablitz, cornet VS). The photographic negatives were projected with a 35-mm film strip projector (Graflex, School Master) and the sides of the polyhedra measured.

The total reflux foam fractionation apparatus was of the basic design of Karger, Poncha, and Miller (*6*). The foam was broken by circulating steam through a Friedrich's reflux condenser mounted at the top of the column. The condenser could be rapidly cooled to collect the foam by circulating cold water through the condenser in place of the steam. The solution capacity of the apparatus was increased from 500 to 1500 ml by mounting a 1-liter container at the bottom of the column.

The surfactant, hexadecyltrimethylammonium bromide (HDT) (Matheson, Coleman, Bell), was recrystallized three times from acetone–water solvent. All other chemicals were Fisher reagent grade.

RESULTS AND DISCUSSION

The results of the effect of nitric acid concentration on the distribution factor of mercury(II) nitro complexes are shown in Fig. 1. The initial conditions were: $Hg(NO_3)_2$, 5×10^{-7} *M*; ^{203}Hg tracer, 0.1 μCi; HDT, 1×10^{-3} *M*; total volume, 1500 ml; and nitrogen gas flow rate, 90 ml/min. The results indicate that the distribution factor is strongly dependent on the HNO_3 acid concentration with the maximum occurring at approximately 0.1 *M* nitric acid; the surfactant, HDT, forms an ion pair with the $Hg(NO_3)_3^-$ complex and at 0.1 *M* the fraction of mercury(II) ion in the $Hg(NO_3)_3^-$ form is presumably at a maximum. At higher concentrations of nitric acid, the distribution factor decreases due to the increasing fraction of mercury(II) ion in the $Hg(NO_3)_4^{2-}$ form. This behavior is similar to the behavior of the mercury(II) ion in nitric acid media on an anion exchange resin (*2*, *7*). The decrease in the foam fractionation distribution factor at low nitric acid concentrations is due to the formation of nonabsorbed nitro and hydroxide complexes.

The magnitude of the foam fractionation distribution factor for the $Hg(NO_3)_3^-$ complex, 26×10^{-4} cm, can be compared with the results obtained in the foam fractionation of the mercury(II) chloro complexes (*3*). The maximum value obtained for the $HgCl_3^-$ complex, 56×10^{-4} cm, was two times larger than the maximum value obtained for the $Hg(NO_3)_3^-$ complex. In the anion exchange studies of mercury(II) chloro and nitro complexes tabulated by Kraus and Nelson (*4*), the volume distribution coefficient for the chloro complex was 100 times

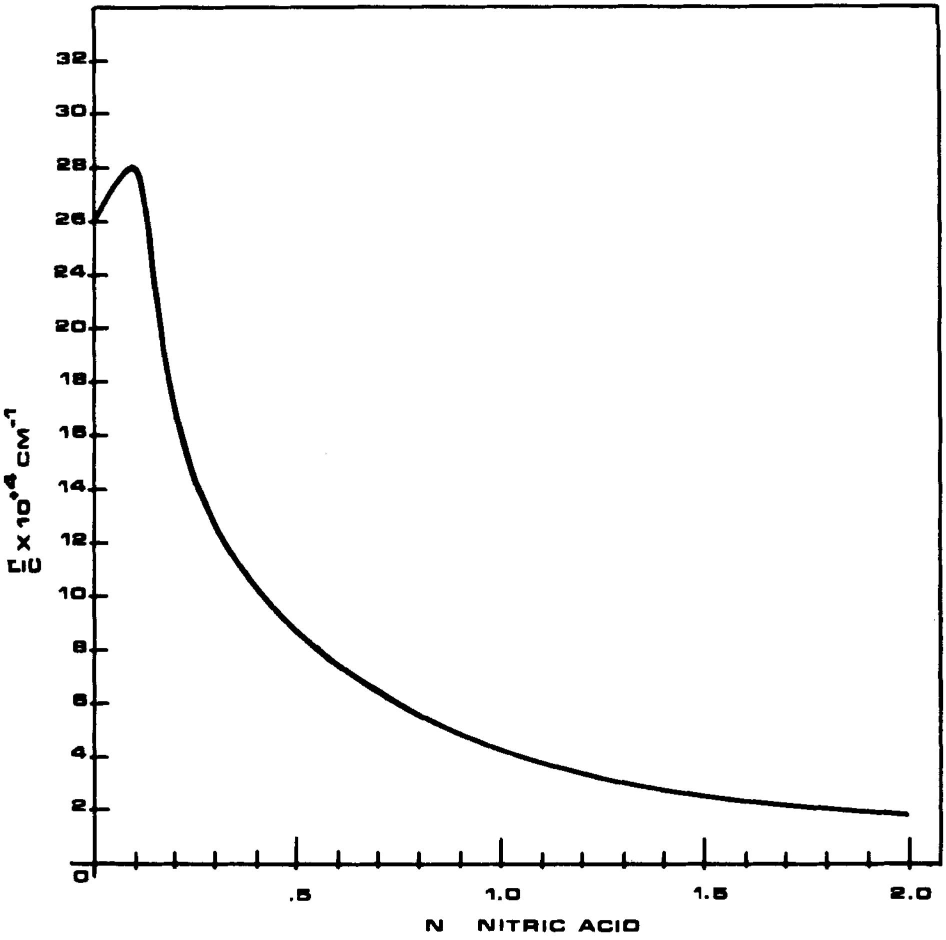

FIG. 1. Distribution factor of mercury(II) nitro complexes as a function of nitric acid concentration.

larger than that of the nitro complex. The smaller stability constants for the formation of the nitro complexes account for the difference between the values of the nitro and chloro complexes. The extractable nitro complex, therefore, represents a smaller fraction of mercury(II) ion species than the extractable chloro complex. The magnitude of the stability constant has a greater effect on the value of the anion exchange volume distribution coefficient than on the foam fractionation distribution factor.

Karger and Miller (*3*) have shown that total reflux foam fractionation is an efficient means of concentrating and separating solutes at trace concentration levels. In this method the foam is thermally broken at the top of the column during the total reflux period and the more concentrated collapsed foam liquid displaces the less concentrated bulk liquid from the interstices between the gas bubbles at the top of the column. After total reflux the hot zone is cooled, the foam travels out of the column to be collapsed, and the liquid is collected.

Total reflux experiments were performed to concentrate mercury(II) nitro complexes. Using a 1-liter reservoir, 20 cm high liquid pool, and 45 cm high foam column, the Friedrich's condenser total reflux apparatus previously described was employed. The conditions chosen for total reflux were identical with those used in the study of mercury(II) chloro complex recovery by Karger and Miller (*3*). The enrichment ratio, E (concentration in the foam/concentration in the bulk), and per cent recovery, $\%R$ (moles in foam/moles in original $\times 10^2$), decontamination factor, D_f (concentration bulk/concentration original), were determined for mercury(II) nitro complexes using a 60-min total reflux time, 90 ml/min gas flow, and 1500 ml of 5×10^{-7} M mercury(II) nitrate solution, 0.05 M in nitric acid. Table 1 compares the data for the total reflux foam fractionation of mercury(II) chloro (*3*) and mercury(II) nitro complexes. The values of the enrichment ratio, per cent recovery, and decontamination factor for the nitro complexes are lower than the values for the chloro complexes. The smaller values are to be expected due to the lower distribution factor for the nitro complexes. The enrichment ratio, per cent recovery, and decontamination factor can be increased by increasing the reflux time (*3*). The per cent recovery can

TABLE 1

Comparison of Total Reflux Foam Fractionation of Mercury(II) Nitro and Chloro Complexes

	Normality of acid	E	$\%R$	D_f	Volume collected (ml)	Γ/c (cm^{-1})
Nitro complex	0.1	157	21	1.5	3.0	26×10^4
Chloro complex	1.0	710	79	24	4.1	48×10^4

be increased by collecting a larger volume of collapsed foam liquid. The latter leads to a decrease in the enrichment ratio because the concentration of the collapsed foam liquid decreases with increasing collection volume.

CONCLUSIONS

Foam fractionation and ion exchange studies of mercury(II) nitro complexes resulted in similar separation parameters as maxima for the ion exchange volume distribution factor and the foam fractionation distribution factor at the same nitric acid concentration. The correct nitric acid concentration for the removal of one or more metal ions in nitro complex form can be determined from the ion exchange volume distribution factor maxima reported by Ichikawa et al. (*2*).

The removal of trace levels of mercury(II) nitro complexes demonstrated that foam fractionation is an effective method of removal for trace amounts of complexes which form soluble ion pairs with a surfactant.

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