

Separation of Hg(II) by foam fractionation in the acidic range: Effect of complexation

Mohsen Moussavi*, Maryam Javidnejad

Department of Chemical Engineering, School of Engineering, Shiraz University, Shiraz, Iran

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Abstract

Foam fractionation is a proven technique for separation of heavy metals. This technique was used for separation of mercury from aqueous solutions. It was found that knowledge of mercury-containing species is essential for this process. A rigorous method is presented for estimating the distribution of free and complex mercury-containing species in aqueous solutions. The chelates of Hg^{2+} with ligands such as Cl^- and OH^- are quite stable leading to conclude that poor or no separation results when the pH is reduced by HCl or held alkaline.

Experimental results indicated that the efficiency of mercury removal closely correlates with pH as well as the concentration of positively charged mercury-containing species. They also indicated that this efficiency is higher at lower Hg concentrations. A removal efficiency of ~80% was resulted for solutions containing 2.5×10^{-5} M Hg in highly acidic media. It was noticed that this efficiency would drop almost to zero as pH was raised to around 5.5. The theoretical findings were in close agreement with the experimental results.

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1. Introduction

Foam fractionation is a cost effective and simple separation process which is ideal for removal of heavy metals from contaminated sites. This process works better when the metal ions concentration is low. Almost all of a metal ion will be removed from the reactor by this process if proper surfactant (collector) is employed and if the molar concentration ratio of metal ion (colligend) to surfactant is $\ll 1$. For separation of mercury, however, this process is hampered by formation of stable Hg-containing complexes. Ligands have shown that can mask the presence of mercury in natural waters up to two orders of magnitude thus causing severe errors in analytical calculations [1]. Mercury compounds differ greatly in their toxicity and environmental mobility. Thus the total Hg concentration measurement is a poor indicator of a toxicological and environmental hazard associated with an Hg-contaminated site. Recently attention has been paid to the point that the trace metal analysis must involve true metal speciation in addition to total metal analysis. There is

evidence indicating that the toxicological behavior of mercury-containing species is widely different. Being lipid soluble certain mercury salts, such as HgCl_2 diffuse through the biological cell membrane where methyl mercury may form [2,3]. As a general rule mercury should be in a complex form to prevent formation of organomercury compounds that may cross the biological cell membrane. So, the potential bioavailability, transport behavior [3,4] as well as designing an effective process for treatment of a mercury contaminated waste can be strongly related to the chemical speciation of the available mercury compounds. It is known that only reactive mercury (or reducible mercury), which is not chelated, will form methyl mercury. Nevertheless there are indications that chelated mercury species with low stability can also form methyl mercury [5].

Complexes resulting from the reactions between mercury ions and common ligands in water such as OH^- and Cl^- are highly stable. Therefore, these mercury compounds will not participate in the reactions that transfer them into the foam phase. Consequently, the efficiency of removal is lowered. The separation of mercury-containing species by foam fractionation takes place selectively. It is expected that those surface active mercury compounds, which are more stable separate first. Labile ligands are replaced by stronger non-labile ligands [6].

* Corresponding author. Fax: +98 711 628 7294.

E-mail address: moussavi@shirazu.ac.ir (M. Moussavi).

Nomenclature

A	chelating agent (number of valences = m)
B	chelating agent (number of valences = n)
C	total concentration of Hg-containing species (M)
[HgL ⁺]	total concentration of positively charged Hg-containing complexes (M)
L	ligand
M	metal ion (number of valences = $m + n$)
R	lauryl sulfate ion (C ₁₂ H ₂₅ SO ₄ ⁻)
X	sample-specific coefficient for calculation of Hg materials balance (dimensionless)
Y	sample-specific coefficient for calculation of Cl ⁻ materials balance

Greek letter

η	efficiency of mercury removal
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Table 1

Important chemical reactions of Hg²⁺ with available ligands in the system and their stability constants [31–33,35,36]

Reaction	Log K
1. With Cl ⁻	
Hg ²⁺ + Cl ⁻ = HgCl ⁺ , K_1	(1) 6.62
Hg ²⁺ + 2Cl ⁻ = HgCl ₂ , K_2	(2) 12.98
Hg ²⁺ + 3Cl ⁻ = HgCl ₃ ⁻ , K_3	(3) 14.1
Hg ²⁺ + 4Cl ⁻ = HgCl ₄ ²⁻ , K_4	(4) 15.1
2. With OH ⁻	
Hg ²⁺ + OH ⁻ = Hg(OH) ⁺ , K_5	(5) 10.0
Hg ²⁺ + 2OH ⁻ = Hg(OH) ₂ , K_6	(6) 21.0
Hg ²⁺ + 3OH ⁻ = Hg(OH) ₃ ⁻ , K_7	(7) 20.9
3. With Cl ⁻ and OH ⁻	
Hg ²⁺ + OH ⁻ + Cl ⁻ = Hg(OH)Cl, K_8	(8) 17.21
Hg ²⁺ + 2OH ⁻ + Cl ⁻ = Hg(OH) ₂ Cl ⁻ , K_9	(9) 19.11
Hg ²⁺ + OH ⁻ + 2Cl ⁻ = Hg(OH)Cl ₂ ⁻ , K_{10}	(10) 17.07

For solutions with pH ranging from 3 to 11 the activity coefficients of ions can be estimated by following the Debye–Huckel limitation law [20,21]. According to this law these coefficients are >0.917 and thus K may be replaced by K' denoting the conditional equilibrium constant, $K' = \frac{\prod [\text{products}]^{n_i}}{\prod [\text{reactants}]^{n_i}}$. Here, the brackets show the molar concentration of ionic species. Out of this range the ionic strength is too high (close to 1). The effect of high ionic strength on K is dealt with elsewhere in further details [22].

A materials balance relation established at equilibrium between the Hg-bearing species gives:

$$C = [\text{Hg}^{2+}] + \sum [\text{HgL}] = (1 + \sum K[\text{L}])[\text{Hg}^{2+}] = X[\text{Hg}^{2+}] \quad (11)$$

C is the molar concentration of total mercury in the solution, $[\text{Hg}^{2+}]$ the molar concentration of the free mercury ions and $[\text{HgL}]$ is the molar concentration of Hg-containing complexes:

$$X = K_1[\text{Cl}^-] + K_2[\text{Cl}^-]^2 + K_3[\text{Cl}^-]^3 + K_4[\text{Cl}^-]^4 + K_5[\text{OH}^-] + K_6[\text{OH}^-]^2 + K_7[\text{OH}^-]^3 + K_8[\text{OH}^-][\text{Cl}^-] + K_9[\text{OH}^-]^2[\text{Cl}^-] + K_{10}[\text{OH}^-][\text{Cl}^-]^2 + 1 \quad (12)$$

By a similar approach a materials balance relation may be established between the Cl⁻ bearing species (HgCl₂ is the only source of Cl⁻):

$$2C = [\text{Hg}^{2+}]Y + [\text{Cl}^-] \quad (13)$$

and

$$C = 1/2([\text{Hg}^{2+}]Y + [\text{Cl}^-]) \quad (14)$$

$[\text{Cl}^-]$ is the molar concentration of free chloride ion and

$$Y = K_1[\text{Cl}^-] + 2K_2[\text{Cl}^-]^2 + 3K_3[\text{Cl}^-]^3 + 4K_4[\text{Cl}^-]^4 + K_8[\text{OH}^-][\text{Cl}^-] + K_9[\text{OH}^-]^2[\text{Cl}^-] \quad (15)$$

Numerous techniques are applied to remove mercury from a stream. The most commonly used processes for this purpose include precipitation, cementation, ion exchange, reduction, adsorption and solvent extraction [7–10]. Through bioaccumulation processes biota is recently finding a growing application for mercury separation [11–13].

Mercury speciation and complexation play a major role in the effectiveness of all these processes. Foam fractionation, as an adsorption process, is an effective tool for the removal of heavy metals, including mercury, at low concentrations. Further details about this process are provided by Darton et al. [14] and Moussavi and Carleson [15]. The United States Environmental Protection Agency has adopted this technique as a potentially effective tool for control of mercury in the environment [16]. It was recently reported that the presence of proper chelating agents enhances the separation of certain heavy metal ions by the process of foam fractionation [17]. However, little has been known about the physics and the chemistry of the foams [18]. Without removal of those speciated mercury ions, which are toxic effective mercury removal may not be achieved.

The purpose of this study was to characterize the mercury bearing species that control the process of separation by foam fractionation.

2. Approach

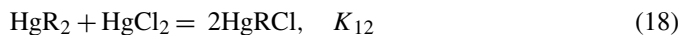
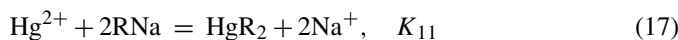
When dissolved in water mercuric chloride forms, besides Hg²⁺, a number of positively charged mercury-containing species. These species react and equilibrate with Cl⁻ and OH⁻ available in the solution. Other anions such as NO₃⁻ and carbonates form weaker complexes with mercury [19] and can be easily ignored. The reactions between mercury and these ligands and their stability constants as used in this work are shown in Table 1. In this table $K = \frac{\prod \{\text{products}\}^{n_i}}{\prod \{\text{reactants}\}^{n_i}}$ where n_i is the stoichiometric coefficient of compound i in the reaction and the braces show the activities.

At equilibrium the Eqs. (11) and (14) are equal. That is

$$X[\text{Hg}^{2+}]/(Y[\text{Hg}^{2+}] + [\text{Cl}^-]) = 1/2 \quad (16)$$

Now the task is to calculate the concentration of all Hg-containing species in the solution. Following an iterative approach $[\text{Cl}^-]$ could be so calculated for a fixed pH to satisfy Eq. (16). The amount of HNO_3 for pH adjustment is estimated by comparing the total positive and total negative ions.

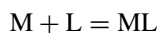
The following three complexes would possibly form in the solution due to addition of sodium lauryl sulfate:



Here $\text{R} = \text{C}_{12}\text{H}_{25}\text{SO}_4^-$.

Further additional terms would be incorporated to X and Y by the above reactions.

Complexes of monodentate ligands are less stable than multidentates. They also dissociate more extensively when the metal concentration is decreased. It follows that the complexes of multidentates are more stable and their relative concentration is increased when the metal concentration is increased. This fact may be represented by:



$$-\text{Log}[\text{M}] = p\text{M} \quad \text{and} \quad -\text{Log}[\text{ML}] = p\text{ML}$$

$$\Delta p\text{ML} = \text{Log} \left(\frac{[\text{M}]_{\text{T}}}{[\text{M}]} \right), \quad [\text{M}]_{\text{T}} = [\text{M}] + [\text{ML}]$$

Here, L is the ligand, M the metal ion and [ML] is the complex concentration. The slope of the curve of $\Delta p\text{ML}$ versus $[\text{M}]_{\text{T}}$ determines the behavior of the complex as depicted in Table 2.

By inspecting the trend of $[\text{Hg}-\text{R}]$ versus $[\text{Hg}]_{\text{T}}$ it is noticed that sodium lauryl sulfate behaves as bidentates when exposed to Hg^{2+} . Having the value of $\Delta p\text{ML}$ and following a trial-and-error technique the closest value for K_{11} is found to equal $10^{5.61}$.

The stability constants for the complexes of certain transition elements with sodium lauryl sulfate (MR_2) were calculated and found to be in the range of 10^5 to $10^{6.4}$ [23].

Once K_{11} is calculated the values of K_{12} and K_{13} could be determined by following the mixed complexes rule [24]. According to this rule when two ligands A and B (here, OH^- and Cl^-) and a metal ion M, are available in a solution they form complex products. In general:

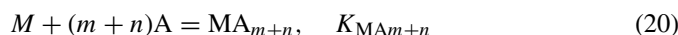


Table 2
Determination of the behavior of the complex [24]

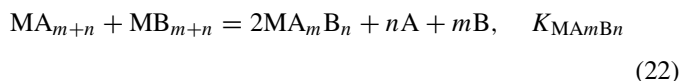
Type of chelating agent	$\Delta p\text{ML}/[\text{M}]_{\text{T}}$ (dm^3/mol)
Monodentates	2
Bidentates	1.5
Multidentates	0.5

Table 3
Calculated stability constants of Hg–SLS complexes

Compound	Stability constants, K	Log K
HgR_2	K_{11}	5.61
HgRCl	K_{12}	9.6
$\text{HgR}(\text{OH})$	K_{13}	13.6



Again the products react with each other to form a complex (mixed complex) MA_mB_n (i.e., $\text{Hg}(\text{OH})\text{Cl}$, $m=n=1$). Here, the valence of M is $(m+n)$, A and B are monovalent:



$K_{\text{MA}_m\text{B}_n}$ is calculated by the following formula:

$$\text{Log } K_{\text{MA}_m\text{B}_n} = \frac{m}{m+n} \text{Log } K_{\text{MA}_{m+n}} + \frac{n}{m+n} \text{Log } K_{\text{MB}_{m+n}} + \text{Log } S \quad (23)$$

$$S = \frac{(m+n)!}{(m!n!)} \quad (\text{here, } S = 2)$$

The accuracy of this technique may be examined by applying the stability constants of $\text{Hg}(\text{OH})_2$ and HgCl_2 in Eq. (23). It yields: $\text{Log } K_{\text{Hg}(\text{OH})\text{Cl}} = 17.3$, which is reasonably close to 17.21 used in this work, Table 1.

The stability constants of HgRCl and $\text{HgR}(\text{OH})$ are calculated based on the above technique and the results appear in Table 3.

3. Materials and methods

3.1. Apparatus

The experiments were conducted in a batch system. The column was a Pyrex cylinder with internal diameter $d_i = 5.0$ cm and the height of the liquid in that column varied from $h_0 = 11.3$ to $h_1 = 7.5$ cm. This was primarily due to the liquid entrainment by rising foam bubbles.

The column was equipped with a sintered glass sparger (ASTM 40–60 type C). The bubbles formed by this type of sparger have diameters that are distributed roughly between 0.5 and 1.5 mm. Through a separate series of experiments the effectiveness of three types of surfactants was studied. The study showed that anionic sodium lauryl sulfate, SLS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$) with critical micelle concentration (CMC) of 8.3×10^{-3} M is a more effective collector than cationic cetyl trimethyl ammonium bromide, CTAB ($\text{C}_{19}\text{H}_{42}\text{NBr}$, $\text{CMC} = 8.12 \times 10^{-4}$ M [25]) and non-ionic Triton X-100 ($\text{C}_{14}\text{H}_{22}(\text{C}_2\text{H}_4\text{O})_n$, $n = 10$, $\text{CMC} = 0.24$ mM [26]). All surfactants were made by BDH and were analytical grade.

Nitrogen, 5N grade (distributed by Iranian Electronic Industries, IEL) was first humidified and was then used as carrier gas. The flow rate of nitrogen was regulated by a rotameter with

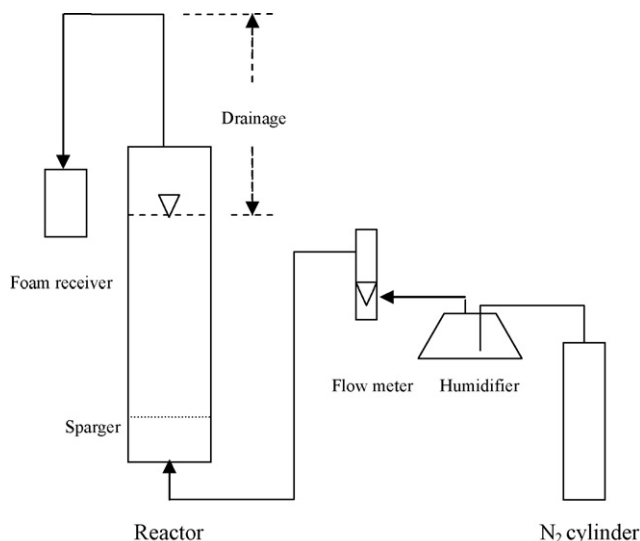


Fig. 1. Flow diagram in foam fractionation unit.

constant flow rate of $1.2 \times 10^{-6} \text{ m}^3/\text{s}$ at standard conditions. Nitrogen was allowed to pass through the column until foam bubbles ceased to form. A vertical glass tubing was installed between the reactor and the foam receiver serving to minimize the liquid entrained by the rising foam (Fig. 1). Further details about the equipment and process are given elsewhere [14,15,27,37].

The carrier gas flow rate and its total volume were maintained constant in all experiments. The overall mercury removal efficiency was estimated at the end of each experiment by measuring the mercury left in the reactor.

The efficiency of mercury removal (η) could be estimated by considering the ratio of concentrations of final to original. In spite of the presence of the drainage facility the amount of entrained liquid by foam was too significant to be neglected. So, the expression relating these two concentrations was based on variable liquid volume. That is

$$\eta (\%) = 100 \times \frac{C_0 V_0 - C_1 V_1}{C_0 V_0}$$

$$\eta = \left(1 - \frac{C_1 h_1}{C_0 h_0} \right) \times 100 \quad (24)$$

where C_0 and C_1 indicate the original and final concentrations, respectively, and h_0 and h_1 indicate the liquid height under the above conditions.

3.2. Experimental procedures

Stock solutions were prepared with the original Hg concentration ranging from 1.5×10^{-5} to 2.5×10^{-4} M by diluting HgCl_2 stock solutions. The concentration of surfactant (SLS) was always maintained at 10^{-3} M in these solutions, far below the CMC.

A one-hour period was assigned to all solutions prior to beginning the experiments for equilibration considerations [28]. The pH of the stock solutions was adjusted by adding normal solutions of either HNO_3 or NaOH before starting the experiments.

The chemicals used for preparing stock solutions were all analytical grade type and made by BDH. All of the chemical analyses were made in triplicate and were finally analyzed statistically before being reported. The foam bubbles were quite stable with minimal coalescence while rising in the ascending line.

Samples analysis began at the end of each experiment by pipetting aliquots of liquid from the reactor solution (sometimes called raffinate). A sample point is provided on the reactor wall for taking samples. Then each sample was mixed with a highly concentrated SnCl_2 solution. This solution was first acidified by HNO_3 and then the mixture was transferred into the reaction vessel of the equipment. A magnetic stirrer mixed the vessel contents vigorously during the reaction. Under the reaction conditions the reducible mercury (or reactive mercury) is reduced to Hg^0 in the solution and swept by a current of N_2 gas into a detection cell ending by two quartz windows. The emitted 2537Å radiation of a mercury vapor lamp passes through this cell and the amount of mercury is estimated by measuring the absorbance of radiation. A cold vapor atomic absorption spectrophotometer, AA (Varian Aerograph model 7) was used for this measurement. The detection limit for the AA instrument is $0.04 \mu\text{g}/\text{ml}$ at 253.7 nm or, 2 ng absolute. It is anticipated that all Hg-containing species in the solution are reducible (or reactive) and form Hg^0 when treated with acidified Sn(II) [29]. Newer AA and other techniques are used to measure reducible mercury as well as chelated mercury [27,30,34].

4. Results and discussion

The original concentration of Hg and the pH of the solution were the main variables to study the effects on the performance of foam fractionation. All experiments show that the Hg removal efficiency is highest at pH 2.0 and is close to zero around pH 5.5. The results of an experiment are illustrated in Fig. 2 as an example. The method used for estimation of species concentration revealed that the concentration of positively charged Hg-containing species followed for all mercury concentrations very closely a unique pattern. The method showed that the concentration of these species is highest at pH 2.0 and lowest around pH 5.5. All experiments showed that the Hg removal efficiency followed the same pattern as that of positively charged Hg-

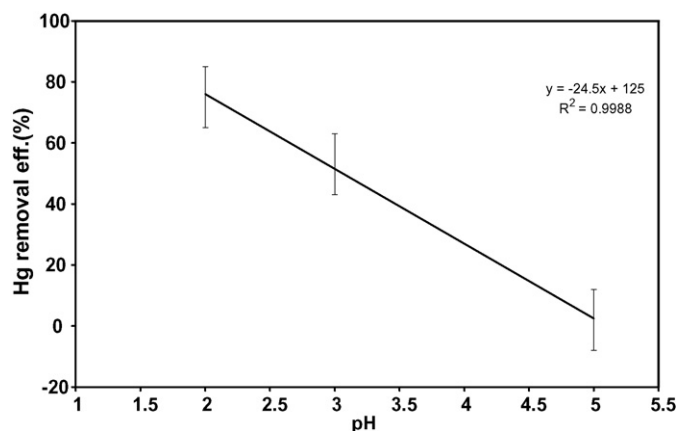


Fig. 2. Statistical representation of experimental results.

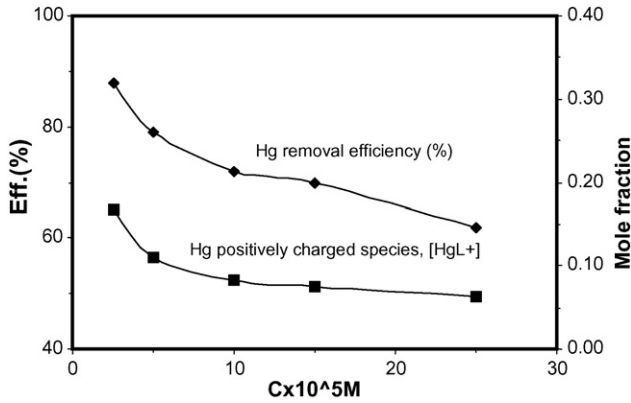


Fig. 3. Effect of C on Hg removal efficiency and [HgL⁺].

containing species did. The two sets of results obtained in the above are compared in Fig. 3.

A series of experiments was conducted to examine the effect of Hg concentration on the efficiency of mercury removal. Solutions containing Hg concentrations from 1.5×10^{-5} to 2.5×10^{-4} M were foam fractionated. The experimental results indicated that the removal efficiency steadily increased, as more dilute reactors were examined. The theoretical results also, indicated that the mole fraction of positively charged Hg containing species is increased as the reaction vessels become diluted. They followed closely a similar pattern (Fig. 4).

It was expected that the chelates resulting from reactions between Cl⁻ and Hg²⁺ would compete with reactions between surfactant and Hg²⁺ and therefore the removal efficiency would eventually be affected. A set of experiments was conducted to study the effect of Cl⁻ on the Hg removal efficiency. The results indicated that the removal efficiency was exponentially dependent on [Cl⁻]. The theoretical method also showed that the concentration of positively charged Hg containing species, similar to experimental results, is exponentially related to [Cl⁻]. The results obtained in the above experiments are compared with the theoretical results in Fig. 5.

HgCl₂ dissociates in aqueous acidic solutions mostly into Hg²⁺ and HgCl⁺. The Hg²⁺ fraction is directly proportional to X⁻¹ Eq. (11) and due to less available chloride X is smaller for

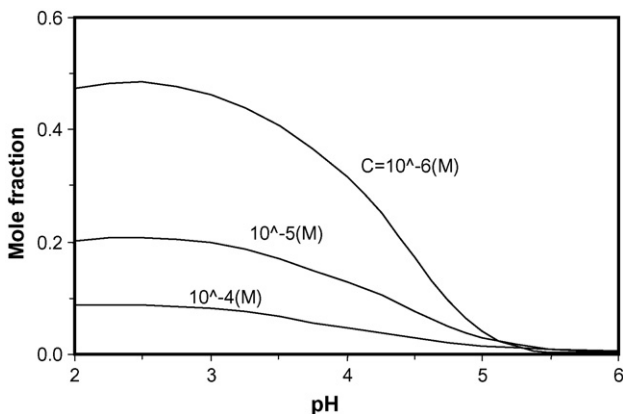


Fig. 4. Effect of C on [HgL⁺].

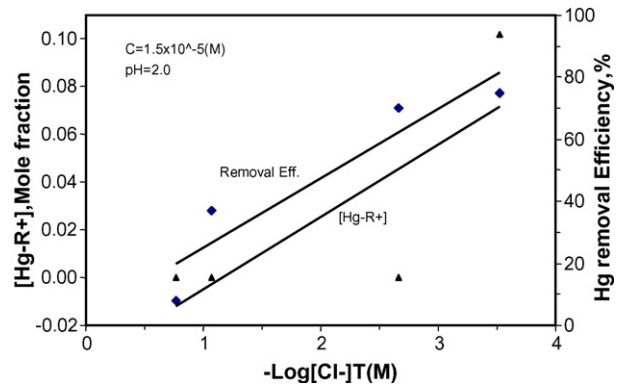
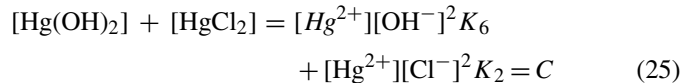


Fig. 5. Effect of [Cl⁻] on Hg removal efficiency (experimental) and [Hg-R⁺].

any given fixed pH in more dilute solutions. Therefore the [Hg²⁺] fraction would be larger in this type of solution. In general, more dilute solutions contain a higher fraction of positively charged Hg-containing species as presented in Fig. 4.

Mercury removal efficiency is negligible for low concentrations of total positively charged mercury-containing species. In such a case the sum of the concentrations of the non-ionic mercuric hydroxide and mercuric chloride is close to the total mercury concentration. That is



Rearranging gives:

$$[\text{OH}^-] = [(C/[\text{Hg}^{2+}] - K_2[\text{Cl}^-]^2)/K_6]^{0.5} = (X - K_2/K_6[\text{Cl}^-]^2)^{0.5} \quad (26)$$

For the mercury concentration range of 1.5×10^{-5} to 2.5×10^{-4} M the values of X and [Cl⁻] were calculated for a pH range of 5–6 to estimate [OH⁻] in Eq. (26). The deviation between the expected and calculated [OH⁻] was found to be between 0.01 and 0.3 pH units. This suggests that the efficiency of mercury removal by foam fractionation is directly correlated to the positively charged Hg-containing species. The experimental results obtained for Hg removal efficiency confirms the finding. Fig. 4 shows the results.

This study shows the composition of the separated mercury rich phase. Sodium lauryl sulfate is a chelating agent. When added to the solutions containing HgCl₂ it will react with free Hg²⁺ by reactions 17–19 to produce mercury-containing surface active complexes. Calculations show that the predominant complex is HgRCl. A smaller fraction appears as HgR₂ and HgR(OH) (Fig. 6).

Being surface active the Hg-bearing surfactant species leave the solution along with the remaining free SLS as a foam phase when nitrogen is bubbled through the solution. A larger fraction of Hg²⁺ is available in more dilute solutions. This explains the higher removal efficiency at lower mercury concentrations.

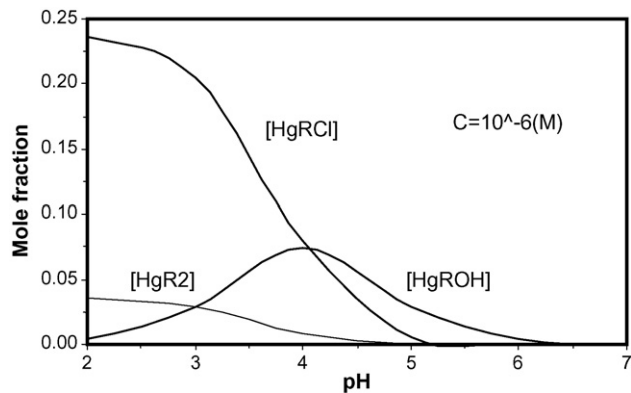


Fig. 6. Effect of pH on [Hg-SLS].

5. Conclusions

The method used in this study estimates the free and complex mercury-containing species even in low concentrations. It shows that the process of foam fractionation is highly sensitive to pH for Hg removal and the ligands present modulate the efficiency of separation through chemical speciation.

This study shows that chloride and other halides (due to their high stability constants), in general, must be removed from the system (particularly from the saline systems) before surfactant is added. The experimental results of this study indicate that the technique of foam fractionation is potentially an effective tool for the separation of dissolved mercury-containing species. It was possible to remove close to 80% of these species. It is expected that still better removal efficiencies can result if a less stable mercury compound, such as mercuric nitrate is used for preparing stock solutions instead of mercuric chloride.

Acknowledgement

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