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# Flotation Separation of Soluble and Colloidal Indium from Aqueous Solution

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**ABSTRACT:** This work investigated the speciation and solubility of indium (In) and its flotation separation from aqueous solution. Lowest theoretical In solubility was predicted for pH 5.5–8.5, and the solubility increased as it became more acidic or more alkaline. Experimentally, 20 mg/L of In completely dissolved at pH < 3.0, which agreed with theoretical prediction. At pH 3.6–9.9, In showed slightly higher solubility than predictions. There was good agreement at pH > 9.9. Flotation reaction was described by pseudo-first-order kinetic model and its reaction rate increased with increasing nitrogen flow rate. The results indicated that pH played a key for the flotation process. As pH increased from 4.0 to 6.8, removal efficiency rose from 65.0% to 95.8% when applying surfactant SDS as collector. The efficiency decreased to 56.7% at pH 9.9. Lower removal efficiency was found once using CTAB. Electrostatic interaction between collector with both soluble and colloidal In was the main mechanism for In flotation.

## 1. INTRODUCTION

In recent years, indium (In) has been extensively used in semiconductors, thin film transistor liquid crystal display (TFT-LCD), solar cells, and numerous industrial applications.<sup>1</sup> With increasing importance of photovoltaic systems as a source of electricity supply in the world, the use of In will likely increase.<sup>2</sup> However, In is widely distributed and has no individual reserve.<sup>3</sup> The existence of In in the earth's crust is estimated to be 0.05 mg/kg for the continental and 0.072 mg/kg for the oceanic crust.<sup>4</sup> It is a byproduct commodity from primary ones of aluminum and zinc, and the annual world refinery production of In was 570 tons.<sup>2</sup> Production of indium tin oxide (ITO), which is used in a variety of flat panel devices such as TFT-LCDs, continues to be the major end use of In and it accounts for most global In consumption.<sup>1</sup> Annual consumption of In in 2010 in the US was estimated at 120 tons.<sup>1</sup> As the demand for this metal increases, concern about the sustainable use and the lack of effective recovery from low-level wastes and end-of-life products has been raised.<sup>5</sup> Recovery of In could become a significant source of future supply, and a secondary In industry with a focus on recycling electronic wastes (e-wastes) is likely to emerge under favorable market conditions and will potentially play a role.<sup>2</sup> A study shows that the ITO film of waste LCD can be largely recycled if done carefully.<sup>6</sup>

The environmental risks associated with In need to be assessed. Recently, distribution of In among a water environment in Japan has been examined, and it is recommended to be monitored continuously.<sup>7</sup> The embryo-toxicity of In of cultured rat embryos has been indicated,<sup>8</sup> though it is mostly related to lung illness through respiratory ways.<sup>9,10</sup>

It is important as well to develop effective treatment methods for removing In from industrial wastewater. Rare elements and transition metals are often correlated with heavy metals. Even though the removal of heavy metals from wastewater has been extensively studied, reports on the removal and separation of In were few until recently. Indium could be separated from

wastewaters via various technologies, such as chemical precipitation,<sup>11</sup> solvent extraction,<sup>12</sup> adsorption,<sup>13</sup> and ion exchange.<sup>14</sup> Among these methods, solvent extraction has played an important role, especially in the metallurgical industry. Some new treatment technologies have been examined, such as supercritical fluid extraction,<sup>15</sup> and electro-coagulation.<sup>16,17</sup> However, speciation of In has rarely been discussed in detail in these works, not to mention being correlated to removal mechanisms of In from aqueous solutions. Indium is a post-transition metal and it forms anionic complexes or may exist in ionic form in solutions.<sup>18</sup> Wood and Samson<sup>19</sup> reviewed the geochemistry of several elements, including In, and indicated that the stable oxidation state in aqueous phase is In(III). The high charge contributes to its preferable complexes form with hydroxide, fluoride, sulfate, and phosphate. It may also form complexes with chloride and bisulfide due to its soft acid properties. However, limited information is available on the aqueous chemistry of In, such as its solubility and speciation as affected by pH.

Flotation separation is a feasible method for removing and recovering metals from dilute wastewater at large volumes.<sup>20</sup> It has been recognized as an effective and solvent-free method in removing and concentrating various compounds from water. There are some works published on the application of flotation separation of In.<sup>21–23</sup> This paper aims to assess the speciation and equilibrium solubility of In as affected by pH and to study flotation separation of In from aqueous solution. We would closely examine the correlation between flotation separation of In with its speciation and solubility.

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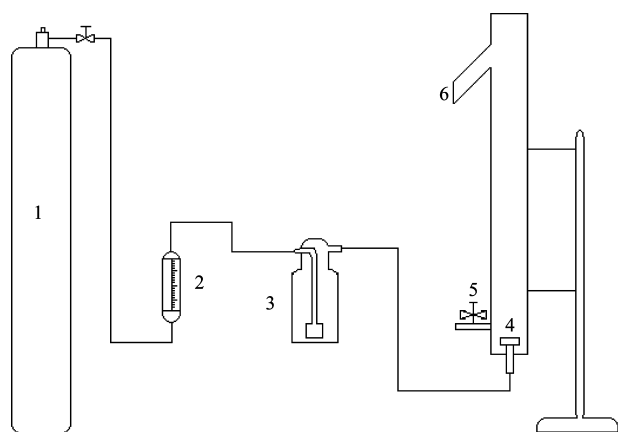
## 2. MATERIALS AND METHODS

All chemicals used in the experiments were analytical reagent grade. The synthetic stock solution of In (500 mg/L) was prepared by dissolving  $\text{InCl}_3$  (Acros) in ultrapure water. The stock solution was acidified to pH 2.0–2.5 by adding a certain amount of 3 M  $\text{HNO}_3$  (Acros) to prevent precipitation. For the equilibrium solubility experiment, samples of 40 mL of In solution (20 mg/L) were prepared using a stock solution. They were adjusted to different pH from 2.5 to 11.5 by using 1 M NaOH (Acros) and 1 M  $\text{HNO}_3$  (Acros), placed on a shaker and being shaken for 60 h. The equilibrium pH was measured by using a pH meter (Orion 4–Star Plus pH/Conductivity meters, Thermo Fisher Scientific), and samples were filtered by a 13 mm syringe with a 0.45  $\mu\text{m}$  PVDF membrane (Advantec). The concentration of each sample was measured using inductively coupled plasma–atomic emission spectrometer (ICP–AES JY2000, Horiba Scientific) at wavelength of 230.606 nm. All samples were triplicated and the average value was taken. The residual In concentration was used to calculate the percentage of In precipitation as follows:

$$\text{In precipitation (\%)} = [1 - (C_{\text{res}}/C_0)] \times 100\% \quad (1)$$

where  $C_0$  and  $C_{\text{res}}$  is the initial and residual In concentrations in the solution, respectively. Computer software, PHREEQC Version 2, was used for assessing theoretical equilibrium solubility predictions. It is a computer program that can be used for computing chemical reactions of an element in natural water and wastewater.<sup>24</sup>

The flotation separation of In was carried out by using a bench-scale apparatus<sup>25</sup> of dispersed air flotation (DiAF) (Figure 1). The flotation column, with inner diameter of 4



**Figure 1.** The apparatus of flotation experiment. (1)  $\text{N}_2$  cylinder, (2) rotameter, (3) humidifier, (4) sparger, (5) side arm with stopcock, (6) froth collection).

and 55 cm in height, is equipped with a gas sparger (pore size 10–16  $\mu\text{m}$ , Merck) at the bottom of the flotation column, and a side arm with stopcock for sampling. The synthetic In-containing wastewater with initial concentration of 20 mg/L was prepared from stock solution. It was adjusted to a pH 4.0–9.9 by using 1 M NaOH and 1 M  $\text{HNO}_3$ . After pH adjustment, the solution was kept for 45 min before adding a different dose of collector. Two kinds of collectors were used in the study, namely sodium dodecyl sulfate (SDS, Acros) and cetyl trimethyl ammonium bromide (CTAB, Merck). The solution was stirred for 1 min using magnetic stirrer before being

transferred to the flotation column. It was sampled at different time intervals to assess reaction rate of flotation separation. Samples were filtered with 0.45  $\mu\text{m}$  PVDF membrane (Advantech) to determine the residual soluble In concentration in the solution. Meanwhile, residual In concentration after flotation separation without filtration was analyzed as well to assess the significance of colloidal In. The sample was acidified by 50  $\mu\text{L}$  of concentrated  $\text{HNO}_3$  (3 M) to dissolve all colloidal In completely and then analyzed by ICP–AES. All data from flotation separation experiments were triplicated and the average value was taken. Samples from solubility experiments were used for  $\zeta$  potential measurement, which was done by using a  $\zeta$  meter (Zeta PALS, Brookhaven Instruments). Each sample was measured 3 times.<sup>26</sup>

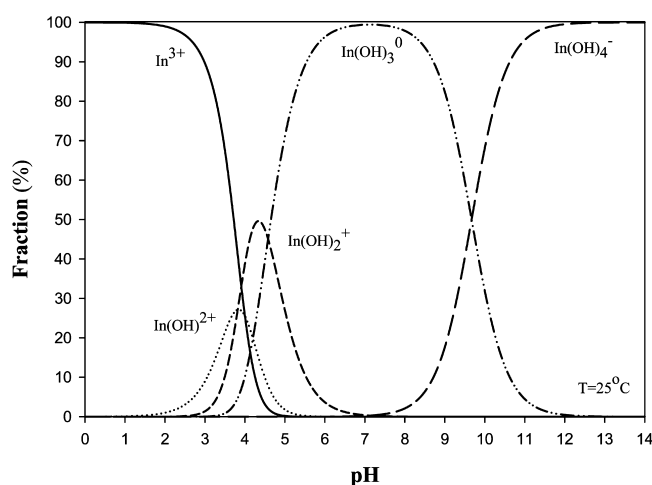
## 3. RESULTS AND DISCUSSION

### 3.1. Speciation and Solubility of Indium in Water.

Speciation of metals has a strong effect on metal removal.<sup>27</sup> For flotation separation of metal, a suitable collector can be selected at a certain pH as long as its speciation is known. The hydrolysis constants of In are shown in Table 1.<sup>28</sup> Figure 2

**Table 1.** Hydrolysis Reactions of In and Their Equilibrium Constants<sup>28</sup>

reaction	log K
$\text{In}^{3+}_{(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{In}(\text{OH})^{2+}_{(\text{aq})} + \text{H}_3\text{O}^+$	−4.0
$\text{In}(\text{OH})^{2+}_{(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{In}(\text{OH})^{+}_{(\text{aq})} + \text{H}_3\text{O}^+$	−3.82
$\text{In}(\text{OH})^{+}_{(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{In}(\text{OH})^0_{(\text{aq})} + \text{H}_3\text{O}^+$	−4.58
$\text{In}(\text{OH})^0_{(\text{aq})} + \text{H}_2\text{O} \leftrightarrow \text{In}(\text{OH})^{-}_{(\text{aq})} + \text{H}_3\text{O}^+$	−9.67
$\text{In}(\text{OH})^{-}_{(\text{aq})} + 3\text{H}_3\text{O}^+ \leftrightarrow \text{In}^{3+}_{(\text{aq})} + 3\text{H}_2\text{O}$	−36.9



**Figure 2.** Speciation diagram of In as affected by pH at 25 °C.

shows the speciation of In as affected by pH. It was observed that  $\text{In}^{3+}$  was the dominant species in the highly acidic zone (pH < 3.0). When pH increased to 3.9,  $\text{In}(\text{OH})^{2+}$  reached its highest of 27.15%. When pH was at 4.4,  $\text{In}(\text{OH})^{+}$  accounted for approximate 50% of soluble In, which was at its highest. The neutral species,  $\text{In}(\text{OH})^0$ , was present under a wide pH range from 3.0 to 12.0. More than 95% of soluble In was in this form when in neutral pH range of 5.9 to 8.4. When under alkaline condition, about 70% of soluble In was in anionic form of  $\text{In}(\text{OH})^{-}$  at pH 10.0, and the fraction of  $\text{In}(\text{OH})^{-}$  species increased with increasing of pH. It was noted that both  $\text{In}(\text{OH})^0$  and  $\text{In}(\text{OH})^{-}$  constituted 50% each at pH 9.67.

Similar results of In speciation can be found in the work of Wood and Samson.<sup>19</sup>

The solubility of In as affected by pH is assessed and results are shown in Figure 3. The lowest theoretical solubility of In

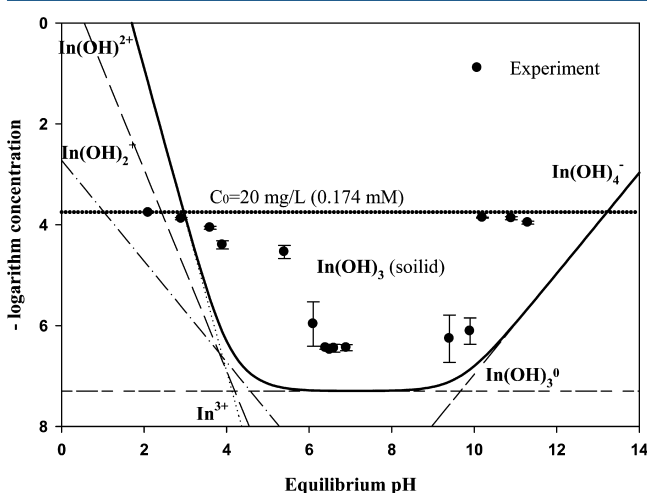


Figure 3. Theoretical and experimental solubility of In(OH)<sub>3</sub> at 25 °C.

( $6.0 \times 10^{-3}$  mg/L,  $0.521 \times 10^{-4}$  mM) existed within pH range of 5.5–8.5, and the solubility increased as it became more acidic or more alkaline. The experimentally derived solubility of In at initial concentration of 20 mg/L (0.174 mM) is also shown. Complete dissolution of In was found at pH < 3.0, which was in agreement with theoretical prediction. In acidic pH zone of 3.6–5.4, In showed higher solubility than predictions as 51.76% of In precipitated at pH 3.6, whereas the theoretical value was 98.15%. Although theoretical prediction showed 99.97% of In should precipitate, the experimental result was 83.28% at pH 5.36. Experimentally derived solubility decreased as pH increased, and about 99.8% of In precipitated in the pH range of 6.0–9.8, which was slightly higher than predictions. A drastic increase of In solubility at pH 10.2 was noted and the fraction of In precipitates decreased from 99.8% at pH 9.8–22.96% at pH 10.2; it then did not change further as pH increased to 11.3.

In this work, three pHs, 4.0, 6.8, and 9.9, were chosen to carry out the flotation separation experiments of In from aqueous solution. At pH 4.0, approximately 77% of In was in colloidal form, while the other 23% was in soluble form. The soluble In consisted of four species, including In<sup>3+</sup>, In(OH)<sup>2+</sup>, In(OH)<sub>2</sub><sup>+</sup>, and In(OH)<sub>3</sub><sup>0</sup>. Among these species, In(OH)<sub>2</sub><sup>+</sup> was the most dominant species and constituted 39%. On the other hand, about 99.8% and 77.01% of In precipitated as colloidal In at pH 6.8 and pH 9.9, respectively. It was different from previous paper, in which 4.7% of In precipitated at pH 3.6 at an initial concentration of 20 mg/L and increased to 59.9% at pH 7.2.<sup>17</sup> The difference could be due to the matrix effect or different experimental conditions in assessing equilibrium solubility of In. However, it was noted that this study was the first study in studying actual In solubility and comparing with theoretical predictions. More systematic approach to the issue is needed in the future.

**3.2. Kinetics and Effects of Nitrogen Flow Rate.** The flotation mechanism essentially involves the target compounds, such as charged or noncharged species, soluble or insoluble, to interact with the collector, usually a surfactant, and then are adsorbed on the surface of bubbles.<sup>29</sup> The bubbles created by

gas and surfactant go through bulk solution to the surface, and the target compounds are separated from the solution.<sup>30</sup> Gas plays an important role for transporting target compounds to the liquid–gas interface, and it also acts as a mixing agent. To evaluate reaction kinetics, simplified models based upon certain assumptions are usually adopted.<sup>31,32</sup> Figure 4 shows the effect

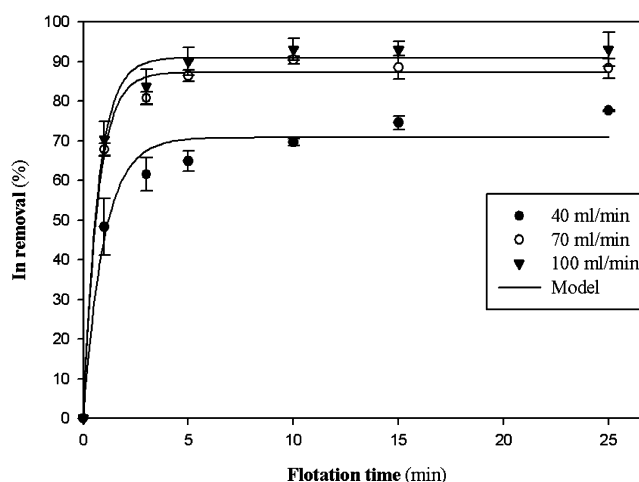


Figure 4. Effects of N<sub>2</sub> flow rate on separation of In at pH 4.0 ( $C_0 = 20$  mg/L; [SDS] = 80 mg/L;  $I = 0.02$  M of NaNO<sub>3</sub>; without filtration).

of nitrogen flow rate on separation efficiency of In. The removal efficiency of In increased from approximately 70% to 90% as nitrogen flow rate increased from 40 to 70 mL/min. When nitrogen flow rate further increased to 100 mL/min, there was a slight increase in removal efficiency of In from 90% to 93%. The flotation separation could be described by a pseudo-first-order kinetic model<sup>33</sup>

$$f = A(1 - e^{-kt}) \quad (2)$$

where  $f$  is removal efficiency of In (%),  $k$  considered as the overall rate constant ( $\text{min}^{-1}$ ),  $t$  the flotation time (min), and  $A$  the constant. Parameters of kinetic model are shown in Table 2

Table 2. Parameters of Pseudo-First-Order Kinetic Model for In ( $C_0 = 20$  mg/L) Removal at Different N<sub>2</sub> Flow Rates

nitrogen flow rate (mL/min)	parameters		
	$k$ ( $\text{min}^{-1}$ )	$A$	$R^2$
40	1.03	70.82	0.969
70	1.46	87.29	0.993
100	1.44	91.01	0.992

for In removal at different nitrogen flow rates. The rate constant increased from 1.03 to 1.46 as nitrogen flow rate increased from 40 to 70 mL/min. It slightly decreased once nitrogen flow rate increased to 100 mL/min. The overall flotation process could be described well by the model. There was no significant change in separation efficiency after reaction time of 10 min. Thus, 10 min was chosen for following experiments.

Bubble size is an important parameter that influences the flotation separation efficiency and flotation rate. A smaller bubble could result in larger surface area or solid–gas interface and higher removal efficiency.<sup>34</sup> Ahmed and Jameson<sup>35</sup> reported that the flotation rate was very strongly affected by the bubble size, and it increased significantly when the bubble

size was reduced from 655 to 75  $\mu\text{m}$ . However, it does not necessarily mean that the smallest size is correlated to the highest separation efficiency. Dobby and Finch<sup>36</sup> illustrated that generation of very small gas bubbles (<0.08 cm diameter) will not always yield higher rate constants in conventional column operation. Experimental and theoretical investigation into the effect of bubble size on particle separation may be affected by many factors.<sup>37</sup> The average diameter of bubbles in this work was assumed to be in the range of <500  $\mu\text{m}$ .<sup>37,38</sup>

**3.3. Effects of pH.** It is well known that pH is an important factor affecting the interactions of collector and metal ions in flotation separation process.<sup>39</sup> As shown in the solubility of In (Figure 3), the percentage of colloidal In ( $\text{In}(\text{OH})_3(\text{s})$ ) increased from 77% to more than 99% when pH increased from 4.0 to 6.8 and decreased to 77% as pH further increased to 9.9. Thus, pH determines speciation and phase of In of the system as well. That is to say, depending upon pH, both foam fractionation and precipitate flotation were involved in flotation separation of In. Results of flotation separation of In at three different pHs are shown in Table 3. A total of 65.0% of In was

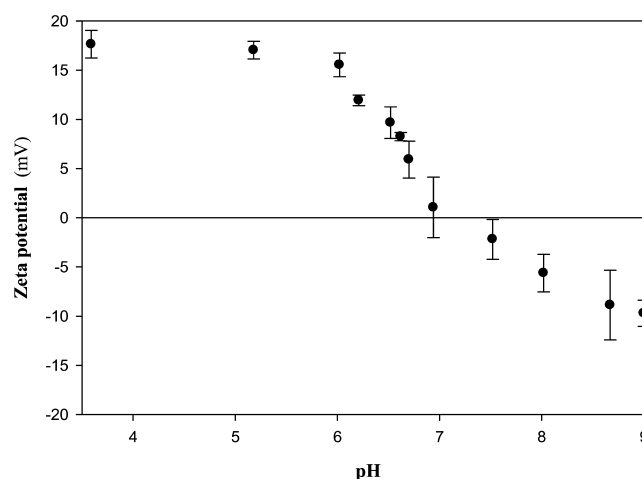
**Table 3. Flotation Separation of In under Different pHs<sup>a</sup>**

collector dose	In removal (%)		
	pH 4.0	pH 6.8	pH 9.9
40 mg/L of SDS	65.0 $\pm$ 7.6	95.8 $\pm$ 1.1	56.7 $\pm$ 1.2
40 mg/L of CTAB	12.9 $\pm$ 3.7	42.6 $\pm$ 4.5	48.9 $\pm$ 4.9

<sup>a</sup> $C_0 = 20 \text{ mg/L}$ ,  $I = 0.02 \text{ M}$  of  $\text{NaNO}_3$ , 70 mL/min of  $\text{N}_2$ .

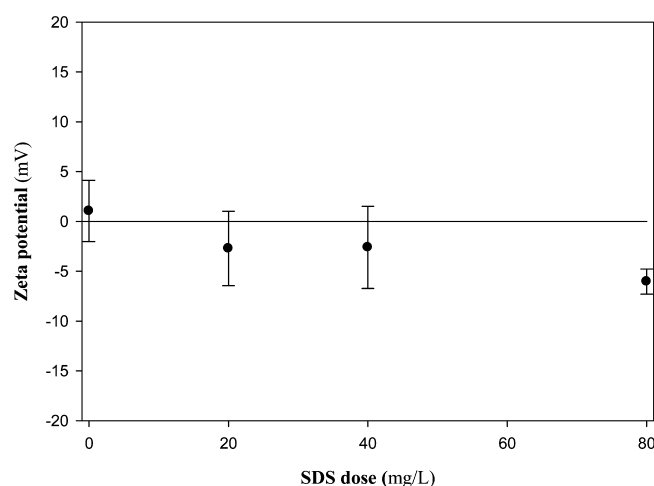
separated at pH 4.0 at SDS dose of 40 mg/L, whereas 95.8% and 56.7% of In were removed at pH 6.8 and 9.9, respectively. It could be explained that major species of soluble In at pH 4.0 included  $\text{In}^{3+}$ ,  $\text{In}(\text{OH})^{2+}$ , and  $\text{In}(\text{OH})_2^+$ . These cationic species could interact with anionic SDS and be separated by foam.<sup>40</sup> Colloidal In ( $\text{In}(\text{OH})_3(\text{s})$ ) was the dominant species at pH 6.8, and it was effectively separated by SDS. However, the separation efficiency decreased as pH approached 9.9. Indium at pH 9.9 mainly existed as colloidal In ( $\text{In}(\text{OH})_3$ ) and  $\text{In}(\text{OH})_4^-$ , which could still be separated by SDS. It was because SDS could become adsorbed onto hydrophilic solid surfaces primarily via electrostatic and hydrogen bonding interactions.<sup>41</sup> There is no sharp break in the adsorption at the isoelectric point ( $\text{pH}_{\text{IEP}}$ ), and a gradual decrease in the adsorption amount as the pH increased.<sup>42</sup>

When 40 mg/L of CTAB was used, a very low separation efficiency of In (12.9%) was found at pH 4.0. It was expected because the electrostatic interaction between CTAB and cationic species of In was not there.<sup>41</sup> The separation efficiency increased to 42.6% and 48.9% as pH increased to 6.8 and 9.9, respectively. It implied that CTAB was generally not as effective as SDS in flotation separation for colloidal In at identical dose.  $\zeta$  potential of colloidal In as affected by pH is shown in Figure 5. The isoelectric point ( $\text{pH}_{\text{IEP}}$ ) was 7.2, and colloidal In was positively charged at  $\text{pH} < 7.2$  and negatively charged at  $\text{pH} > 7.2$ . The positively charged surface of colloidal In at pH 6.8 could explain why SDS performed better at pH 6.8 than 9.9, and why SDS was a better collector than CTAB at pH 6.8. It was noteworthy that colloidal In could aggregate at pH 6.8 as it was close to its  $\text{pH}_{\text{IEP}}$ , which also was beneficial for separation of colloidal In. It was also noted that CTAB was not as effective even for colloidal In and soluble anionic In species ( $\text{In}(\text{OH})_4^-$ ) when at pH 9.9. It was probably because nonelectrostatic interactions were involved in CTAB adsorption onto colloidal



**Figure 5.**  $\zeta$  potential of colloidal In as affected by pH.

In. It has been indicated that both electrostatic and hydrophobic interactions are important for CTAB adsorption onto hydrophilic solid surfaces.<sup>41</sup> The increased hydrophobic interaction, imparted by its long tail groups, may exist between CTAB and the solid surface and also laterally between adsorbed CTAB.<sup>41,43</sup> It was speculated that different adsorption mechanism may affect flotation separation efficiency. However, further study is required to elucidate why CTAB was not very effective under alkaline condition. The adsorption of SDS onto colloidal In was further evidenced in Figure 6, in which  $\zeta$



**Figure 6.**  $\zeta$  potential of colloidal In as affected by SDS dose at pH 6.8.

potential of colloidal In decreased with SDS dose at pH 6.8. It originally carried positive charge when in the absence of SDS, and it gradually decreased with increasing SDS dose, and charge reversal was found due to adsorption of SDS. Hence, the main mechanism for removing colloidal In at pH 6.8 was the adsorption of anionic SDS on the positively charged solid surfaces via electrostatic force. Meanwhile, soluble and colloidal In at pH 9.9 could still be separated by SDS via other intermolecular forces between SDS and In, though not as effectively because colloidal In was negatively charged at pH 9.9. It was expected that CTAB could hardly induce separation of soluble In at pH 4.0. However, colloidal In could be separated by CTAB at pH 6.8, though not as effectively as with SDS. Again, aggregation of colloidal In at pH near its  $\text{pH}_{\text{IEP}}$



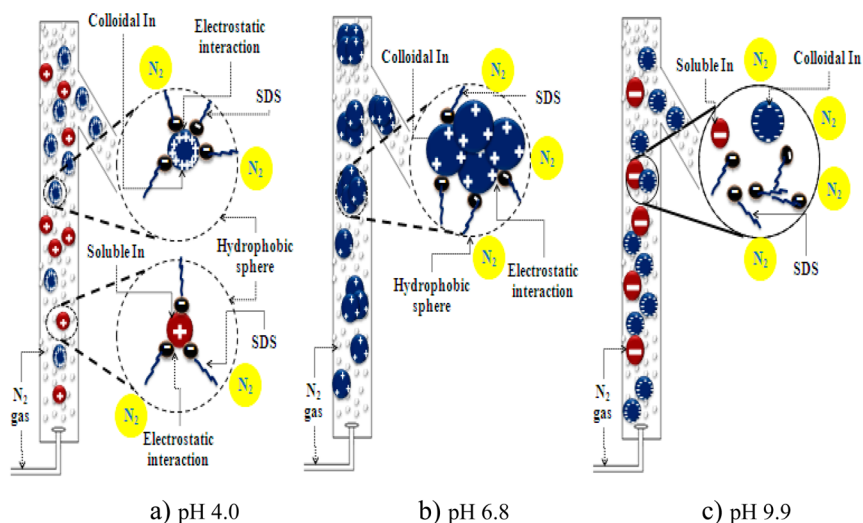


Figure 7. Mechanisms of flotation separation of In using SDS at different pH values.

may be involved for its flotation separation. Similarly, soluble and colloidal In at pH 9.9 could be separated by CTAB. Overall, SDS was a much better collector than CTAB in separating soluble and colloidal In. The mechanisms of In separation by SDS under different pHs are summarized in Figure 7.

**3.4. Effects of Collector Dose.** The effect of collector dose was investigated and results are shown in Table 4. It was found

Table 4. Effects of Surfactant Dose on In Separation at pH 4.0<sup>a</sup>

concentration of SDS (mg/L)	In removal (%)	
	without filtration	filtration
20	26.3 ± 6.8	57.0 ± 2.6
40	65.0 ± 7.6	81.7 ± 6.5
80	90.4 ± 0.9	92.6 ± 0.9

<sup>a</sup> $C_0 = 20$  mg/L,  $I = 0.02$  M of  $\text{NaNO}_3$ , 70 mL/min of  $\text{N}_2$ .

that In separation efficiency at pH 4.0 increased from 26.3% to 65.0% and 90.4% as SDS dose increased from 20 to 40 and 80 mg/L, respectively. Lack of SDS was the reason of low separation efficiency at SDS dose of 20 mg/L.<sup>40</sup> The clear correlation between collector dose and In separation efficiency confirmed that it was the electrostatic interactions that resulted in flotation separation of cationic species of soluble In, such as  $\text{In}^{3+}$ ,  $\text{In}(\text{OH})^{2+}$ , and  $\text{In}(\text{OH})_2^+$ .

Separation efficiency for samples that were filtered before measurement of residual In in the aqueous solution is also illustrated in Table 4. It was found that separation efficiency of In was 57.0, 81.7, and 92.6% at SDS dose of 20, to 40 and 80 mg/L, respectively. All the removal efficiency was higher than those for unfiltered samples. It is because 77% of In was in colloidal form, whereas 23% was in soluble form when at pH 4.0. Some colloidal In that could not be separated via flotation from aqueous solution might be mistakenly included as long as samples were filtered before analysis. Therefore, it is important to delineate how speciation of In is related to its separation from water.

**3.5. Effects of Ionic Strength.** Ionic strength can influence interactions between collector and target compounds as well as foam stability.<sup>44</sup> Experiments with different concentrations of

$\text{NaNO}_3$  as background electrolyte were conducted and results are shown in Table 5. Ionic strength in this study slightly

Table 5. Effects of Ionic Strength on Separation of In at pH 6.8<sup>a</sup>

In removal (%)	concentration of $\text{NaNO}_3$ (M)		
	0.002	0.02	0.2
	94.6 ± 0.8	95.8 ± 1.1	86.5 ± 4.5

<sup>a</sup> $C_0 = 20$  mg/L,  $[\text{SDS}] = 40$  mg/L, 70 mL/min of  $\text{N}_2$ , without filtration.

influenced In separation efficiency. The removal efficiency of In remained unchanged at approximately 95% as  $\text{NaNO}_3$  concentration increased from 0.002 to 0.02 M. However, the separation efficiency of colloidal In slightly decreased to 86.5% as  $\text{NaNO}_3$  concentration increased to 0.2 M. It was because the electrostatic interactions were screened when under higher electrolyte concentration.<sup>43,45</sup> It again confirmed that electrostatic interaction was the main mechanism in flotation separation at pH 6.8, and there was no specific interaction involved. Electrolytes could also weaken the stability of bubbles.<sup>46</sup> Therefore, the rise in electrolyte concentration led to a decrease in separation efficiency, which usually could be overcome by increasing collector dose.

## 4. CONCLUSIONS

The flotation separation of In from aqueous solution in a batch system was investigated. The main findings of this work were summarized as follows:

1. With the initial concentration of 20 mg/L, complete dissolution of In was found at pH <3.0, which was in agreement with the theoretical prediction. In the acidic pH zone of 3.6–5.4, In showed higher solubility than predictions; it then decreased as pH increased and about 99.5% of In precipitated at pH range of 6.0–9.8, which was slightly higher than predictions. There was a drastic increase of In solubility at pH 10.2; it then did not change further as pH increased to 11.3.
2. The highest flotation separation efficiency of In was at pH 6.8 at SDS dose of 40 mg/L. The main mechanism was the adsorption of anionic SDS on the positively

charged colloidal In surfaces via electrostatic force and rendered solids more hydrophobic. Major cationic species of soluble In at pH 4.0, such as  $\text{In}^{3+}$ ,  $\text{In}(\text{OH})^{2+}$ , and  $\text{In}(\text{OH})_2^+$  could interact with anionic SDS and be separated by foam. Both soluble and colloidal In at pH 9.9 could still be separated by SDS, though not as effectively. SDS was an effective collector for removing In ions as well as colloidal In.

3. Separation efficiency of In at pH 4.0 increased with increasing SDS dose. The separation efficiency of colloidal In slightly decreased to 86.5% as  $\text{NaNO}_3$  concentration increased to 0.2 M. It confirmed that electrostatic interaction was the main mechanism in flotation separation.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Tolcin, A. C. *Indium, Mineral Commodity Summaries*; U.S. Geological Survey: Reston, VA, 2012.
- (2) Bleiwas, D. I. *Byproduct mineral commodities used for the production of photovoltaic cells*, U.S. Geological Survey Circular 1365; U.S. Geological Survey: Reston, VA, 2010.
- (3) Paiva, A. P. Recovery of indium from aqueous solutions by solvent extraction. *Sep. Sci. Technol.* **2001**, 36, 1395.
- (4) Phipps, G.; Mikolajczak, C.; Guckes, T. Indium and gallium: long-term supply. *Renew. Energy Focus* **2008**, 9, 56.
- (5) Izatt, S. R.; Izatt, N. E.; Bruening, R. L. Metal separations of interest to the Chinese metallurgical industrial. *J. Rare Earth* **2010**, 28, 22.
- (6) Juchneski, N. C. F.; Scherer, J.; Grochau, I. H.; Veit, H. M. Disassembly and characterization of liquid crystal screens. *Waste Manage. Res.* **2013**, 31, 549.
- (7) Miyazaki, A.; Kimura, A.; Tao, H. Distribution of indium, thallium and bismuth in the environmental water of Japan. *Bull. Environ. Contam. Toxicol.* **2012**, 89, 1211.
- (8) Usami, M.; Nakajima, M.; Mitsunaga, K.; Miyajima, A.; Sunouchi, M.; Doi, O. Proteomic analysis of indium embryotoxicity in cultured postimplantation rat embryos. *Reprod. Toxicol.* **2009**, 28, 477.
- (9) Tanaka, A.; Hirata, M.; Kiyohara, Y.; Nakano, M.; Omae, K.; Shiratani, M.; Koga, K. Review of pulmonary toxicity of indium compounds to animals and humans. *Thin Solid Films* **2010**, 518, 2934.
- (10) Homma, T.; Ueno, T.; Sekizawa, K.; Tanaka, A.; Hirata, M. Interstitial pneumonia developed in a worker dealing with particles containing indium-tin oxide. *J. Occup. Health* **2003**, 45, 137.
- (11) Minamisawa, H.; Murashima, K.; Minamisawa, M.; Arai, N.; Okutani, T. Determination of indium by graphite furnace atomic absorption spectrometry after co-precipitation with chitosan. *Anal. Sci.* **2003**, 19, 401.
- (12) Nishihama, S.; Hirai, T.; Komasa, I. Separation and recovery of gallium and indium from simulated zinc refinery residue by liquid-liquid extraction. *Ind. Eng. Chem. Res.* **1999**, 38, 1032.
- (13) Li, H. M.; Liu, J. S.; Gao, X. Z.; Liu, C.; Guo, L.; Zhang, S. X.; Liu, X. Y.; Liu, C. P. Adsorption behavior of indium (III) on modified solvent impregnated resins (MSIRs) containing secocetylphenoxy acetic acid. *Hydrometallurgy* **2012**, 60, 121.
- (14) Herdzik, I.; Dembinski, W.; Narbutt, J.; Siekierski, S. Separation of gallium and indium isotopes by cation and anion exchange chromatography. *Solvent Extr. Ion Exch.* **2012**, 30, 593.
- (15) Chou, W. L.; Yang, K. C. Effect of various chelating agents on supercritical carbon dioxide extraction of indium (III) ions from acidic aqueous solution. *J. Hazard. Mater.* **2008**, 154, 498.
- (16) Chou, W. L.; Wang, C. T.; Huang, K. Y. Effect of operating parameters on indium (III) ions removal by iron electro-coagulation and evaluation of specific energy consumption. *J. Hazard. Mater.* **2009**, 167, 467.
- (17) Chou, W. L.; Huang, Y. H. Electrochemical removal of indium ions from aqueous solution using iron electrodes. *J. Hazard. Mater.* **2009**, 172, 46.
- (18) Fortes, M. C. B.; Martins, A. H.; Benedetto, J. S. Indium recovery from acidic aqueous solutions by solvent extraction with D2EHPA: a statistical approach to the experimental design. *Braz. J. Chem. Eng.* **2003**, 24, 287.
- (19) Wood, S. A.; Samson, I. M. The aqueous geochemistry of gallium, germanium, indium and scandium. *Ore Geol. Rev.* **2006**, 28, 57.
- (20) Masuyama, A.; Okano, T.; Okahara, M. Application of surface-active amide oximes to the collectors for gallium ion in an ion-flotation system. *Ind. Eng. Chem. Res.* **1990**, 29, 290.
- (21) Mal'tsev, G. I.; Vershinin, S. V. Concentration and recovery of halide complexes of aluminum subgroup metals by ionic flotation. *Theor. Found. Chem. Eng.* **2012**, 46, 63.
- (22) Sonawane, N. J.; Hiraide, M.; Mizuike, A. Combined use of two surfactants for flotation of metal hydroxide precipitates in sea water. *Anal. Chim. Acta* **1983**, 149, 359.
- (23) Yamashita, H.; Matsumoto, N.; Otsubo, T.; Ochi, H.; Maekawa, T. Ion flotation of metal ions with diphenyl - and diethyl dithiophosphoric acids. *Anal. Sci.* **1992**, 8, 251.
- (24) Parkhurst, D. L.; Appelo, C. A. J. *User's Guide to PHREEQC (Version 2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, Water Resources Investigations Report; Geological Survey: Denver, Colorado, U.S., 1999.
- (25) Huang, C. J.; Liu, J. C. Precipitate flotation of fluoride-containing wastewater from a semiconductor manufacturer. *Water Res.* **1999**, 16, 3403.
- (26) Berger, W.; Simon, F. G.; Weimann, K.; Alsema, E. A. A novel approach for the recycling of thin film photovoltaic modules. *Resour. Conserv. Recycl.* **2010**, 54, 711.
- (27) Matis, K. A.; Zouboulis, A. I. Flotation techniques in water technology for metals recovery: the impact of speciation. *Sep. Sci. Technol.* **2001**, 36, 3777.
- (28) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Krieger Publishing Company: Malabar, FL, 1986.
- (29) Finch, J. A.; Dobby, G. S. Column flotation: A selected review. Part 1. *Int. J. Miner. Process.* **1991**, 33, 343.
- (30) Chen, H. R.; Chen, C. C.; Reddy, A. S.; Chen, C. Y.; Li, W. L.; Tseng, M. J.; Liu, H. T.; Pan, W.; Maity, J. P.; Atla, S. B. Removal of mercury by foam fractionation using surfactin, a biosurfactant. *Int. J. Mol. Sci.* **2011**, 12, 8245.
- (31) Li, Y. F.; Zhao, W. D.; Gui, X. H.; Zhang, X. B. Flotation kinetics and separation selectivity of coal size fraction. *Physicochem. Prob. Miner. Process.* **2013**, 49, 387.
- (32) Polat, M.; Chander, S. First-order flotation kinetics models and methods for estimation of the true distribution of flotation rate constants. *Int. J. Miner. Process.* **2000**, 58, 145.
- (33) Laplante, A. R.; Toguri, J. M.; Smith, H. W. The effect of air flow rate on the kinetics of flotation. Part 1: The transfer of material from the slurry to the froth. *Int. J. Miner. Process.* **1983**, 11, 203.
- (34) Wang, L. K.; Shammass, N. K.; Selke, W. A.; Aulenbach, D. B. Gas dissolution, release, and bubble formation in flotation systems. In *Handbook of Environmental Engineering*, Humana Press: New York, 2010; 12, 49.

- (35) Ahmed, N.; Jameson, G. J. The effect of bubble size on the rate of flotation of fine particles. *Int. J. Miner. Process.* **1985**, *14*, 195.
- (36) Dobby, G. S.; Finch, J. A. Particle collection in columns—gas rate and bubble size effects. *Can. Metall. Quart.* **1986**, *25*, 9.
- (37) Gorain, B. K.; Franzidis, J. P.; Manlapig, E. V. Studies on impeller type, impeller speed and air flow rate in an industrial scale flotation cell – Part 1: Effect on bubble size distribution. *Miner. Eng.* **1995**, *6*, 615.
- (38) Lelinski, D.; Bokotko, R.; Hupka, J.; Miller, J. D. Bubble generation in swirl flow during air-sparged hydrocyclone flotation. *Miner. Metall. Proc.* **1996**, *13*, 87.
- (39) Vieira, A. M.; Peres, A. E. C. The effect of amine type, pH, and size range in the flotation of quartz. *Miner. Eng.* **2007**, *20*, 1008.
- (40) Peng, F. F.; Di, P. K. Removal of Arsenic from Aqueous Solution by Adsorbing Colloid Flotation. *Ind. Eng. Chem. Res.* **1994**, *33*, 922.
- (41) Dobson, K. D.; Roddick-Lanzlotta, A. D.; McQuillan, A. J. An in situ infrared spectroscopic investigation of adsorption of sodium dodecylsulfate and of cetylammonium bromide surfactants to  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Ta}_2\text{O}_5$  particle films from aqueous solutions. *Vib. Spectroscopy* **2000**, *24*, 287.
- (42) Li, N.; Thomas, R. K.; Rennie, A. R. Effect of pH, surface and counter-ions on the adsorption for sodium dodecyl sulfate to the sapphire/solution interface. *J. Colloid Interface Sci.* **2012**, *378*, 152.
- (43) Paria, S.; Khilar, K. C. A review on experimental studies of surfactant adsorption at the hydrophilic solid-water interface. *Adv. Colloid Interface Sci.* **2004**, *110*, 75.
- (44) Zouboulis, A. I.; Matis, K. A.; Stalidis, G. A. Parameters influencing flotation in removal of metal ions. *Int. J. Environ. Stud.* **1990**, *35*, 183.
- (45) Pugh, R. J.; Weissenborn, P.; Paulson, O. Flotation in inorganic electrolytes; the relationship between recover of hydrophobic particles, surface tension, bubble coalescence and gas solubility. *Int. J. Miner. Process.* **1997**, *51*, 125.
- (46) Lin, C. S.; Huang, S. D. Removal of Cu(II) from Aqueous Solution with High Ionic Strength by Adsorbing Colloid Flotation. *Environ. Sci. Technol.* **1994**, *28*, 474.