Bull. Chem. Soc. Jpn., 58, 2456—2460 (1985) [Vol. 58, No. 9

Studies of Collectors. VI.[1] Application of β-Diketone-type Surfactants to Ion Flotation

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(Received February 12, 1985)

β-Diketone-type surfactants(2,4-alkanedione, R_nA) were applied as ion-flotation collectors and as extraction reagents. Fe^{3+}, Ga^{3+}, and Cu^{2+} were floated effectively with R_nA as a 1:1 complex from an acidic solution. From a mixture of metal ions(Fe^{3+}, Ga^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Ca^{2+}), the Cu^{2+} was floated selectively at pH 6 by R_8A or $R_{12}A$. Then, the metal ions were extracted with R_nA into a benzene layer as coordination-saturated species at regions of a neutral pH. The order of selectivity at pH 6.0 was $Fe^{3+} > Cu^{2+} > \cdots$. The difference between the properties of R_nA as an ion-flotation collector and as an extraction reagent was explained using the HLB value and the surface activity based on the composition of R_nA–metal complexes. The metal ions and R_nA could be recovered from the scum.

Ion flotation has been examined as a method of collecting specific metal ions.[2] However, there are few ion-flotation collectors which exert the flotation effect by adding a small amount. In a previous paper[3] it was shown that complexane-type surfactants formed floatable complexes with heavy metal ions when the HLB(hydrophilic-liphophilic balance) values of the complexes were 4—14. Also, only a trace amount of surfactants remained in the residual solution. Consequently, the mechanism regarding ion flotation might be the complex formation (stability constant) and the flotation of the complex(HLB). Even if a surfactant shows a similar stability constant, the selective removal of a specific metal ion may be achieved using a chelating agent bearing a long alkyl group to regulate its HLB. However, there are few reports concerning flotation using such a chelating agent (surfactant) and the floatability of surfactant-metal complexes. Therefore, the HLB values of floatable complexes must be confirmed using various surfactants. Surfactants are considered to be excellent extraction reagents since their distribution coefficients are large due to a long alkyl group.[4–6]

The enol form of acetylacetone, known as an extraction reagent, behaves as a bidentate univalent anion and forms a stable metal chelate.[6] In this study, in order to obtain further information about the HLB effects on floatability and selectivity, and to clarify the characteristic properties of ion-flotation collectors and extraction reagents, β-diketone-type surfactants(2,4-alkanediones,R_nA) were prepared and applied to an ion-flotion collector and compared with other extraction reagents.

Experimental

Materials. R_nA was prepared by the Claisen condensation of methyl alkanoate with acetone in the presence of a sodium hydride.[7] The crude R_nA was purified by the recrystallization of their copper complexes from 50% of a DMF–water solution and by fractionation at reduced pressure after a decomposition process using 20% sulfuric acid. Abbreviations for various forms of R_nA are R_8A(for 2,4-undecanedione), $R_{12}A$(for 2,4-pentadecanedione) and $R_{18}A$(for 2,4-henicosanedione). A further purification of R_nA gave rather low yields (R_8A 24%, $R_{12}A$ 35%, $R_{18}A$ 48%). The structures of the synthesized R_nA were confirmed by means of their melting points,[7] IR spectra (Shimadzu IR-408), NMR spectra (JEOL JMN-MH-100), and elementary analyses(Yanaco CHN Corder MT-3). Mp: $R_{12}A$, 31.5—33.0 °C (lit,[7] 31—32 °C); $R_{18}A$, 56.0—58.0 °C (lit,[8] 52.5 °C). IR(KBr): ν_{CH} 2920 cm^{-1}, $\nu_{C=O}$ 1640 cm^{-1}. NMR (CCl_4) δ=0.9 (3H, t, CH_3–C–C–), 1.3 (methylene in alkane), 2.0 (3H, CH_3COC–), 2.2 (2H, t, –C–C–CH_2COC–), 3.4 (2H, –$CCOCH_2COC$–), 5.4 (H, –CC(–O–)=CHCOC–). R_8A Found: C, 70.82; H, 10.84%; Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94%. $R_{12}A$ Found: C, 74.67; H, 11.82% Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74%. $R_{18}A$ Found: C,77.63; H, 12.59% Calcd for $C_{21}H_{40}O_2$: C, 77.72; H, 12.42%. Acetylacetone(AA) and dibenzoylmethane(DBM) were obtained from Wako Pure Chemical Industries, Ltd., and benzoylacetone(BzA) was obtained from Kishida Chemical Co., Ltd.

The surface tensions of R_nA solutions were measured on a Du nouy surface-tension balance. R_nA in an alkaline solution lowered the surface tension: 46 dyn (10^{-5}N) cm^{-1} for 10^{-3} mol dm^{-3} of R_8A{critical micelle concentration (cmc) was not observed at below 10^{-3} mol dm^{-3}}, 36 dyn cm^{-1} for $R_{12}A$(cmc 5×10^{-4} mol dm^{-3}), and 47 dyn cm^{-1} for $R_{18}A$(cmc 3×10^{-4} mol dm^{-3}). BzA and DBM, known as extraction reagents, scarcely lowered the surface tension. Therefore, the concentration of R_nA in the following ion flotations were always kept below their cmc.

Apparatus and Procedures. The removal of eight kinds of metal ions (Fe^{3+}, Ga^{3+}, Al^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Ca^{2+}) was examined by the method of ion flotation and extraction. The concentrations of these metal ions were determined using an atomic absorption spectrophotometer (Hitachi 170—30). The flotation apparatus and procedures were the same as that previously reported.[1] The floatability(%) of a metal ion was calculated using:

$$F = \frac{a_0 - a_1}{a_0} \times 100$$

where a_0 and a_1 denote the initial and final metal-ion concentrations in solution. Extraction was carried out using a general operation; 100 cm^3 of benzene was added to the 100 cm^3 of metal solution in a separating funnel, and the funnel was shaken for 30 min. The extractability was calculated using the same formula as that regarding floatability.

Results and Discussion

Ion Flotation. The eight kinds of metal ions dissolved in 300 cm^3 of water were floated with a small amount of R$_n$A, especially R$_{12}$A. The floatable pH ranges for a 10^{-5}mol dm^{-3} solution of specific metal ions using 3X10^{-5} mol dm^{-3} of aqueous R$_{12}$A were as follows: for Fe^{3+}, pH 4—8; for Ga^{3+}, 4—8; for Al^{3+}, 7—9; for Cu^{2+}, 4—8; for Zn^{2+}, 7—9; for Pb^{2+}, 6—11; for Cd^{2+}, 10—13; and for Ca^{2+}, 12—13. The flotation data for Fe^{3+}, Ga^{3+}, and Cu^{2+} are shown in Fig. 1. The optimum pH for the Cu^{2+} and Fe^{3+} flotations shifted to a lower pH with an increase in the length of the alkyl group, and R$_{12}$A showed the highest floatability in the series of R$_n$A. However, DBM(having two phenyl groups) was not so effective and AA(having no long alkyl group) was wholly ineffective. The HLB value of the metal complex is affected by pH since the composition varies with pH.

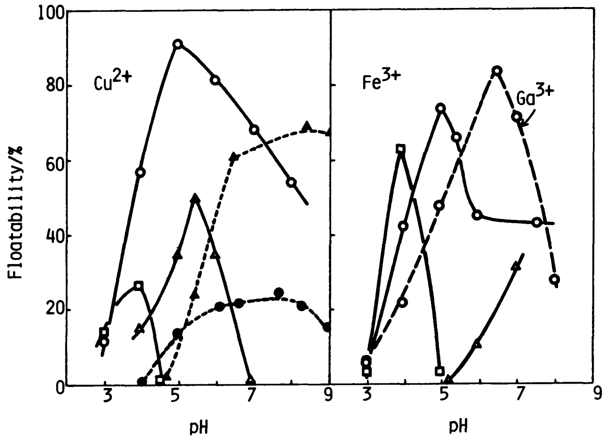

Fig. 1. Flotations for Cu^{2+}, Fe^{3+}, and Ga^{3+}.
Cu^{2+}: 10^{-5} mol dm^{-3}; Fe^{3+}: 10^{-5} mol dm^{-3}; Ga^{3+}: 2.87 × 10^{-4} mol dm^{-3}; [R$_n$A]/[M] = 3. △: R$_8$A, ○: R$_{12}$A, □: R$_{18}$A, ▲: BzA, ●: DBM.

Then, the metal–ligand ratio of a R$_{12}$A–copper complex was examined. The scum(resulting at pH 5.0 upon adding R$_{12}$A) decomposed with 10% sulfuric acid and the resulting R$_{12}$A was extracted using chloroform. The amount of R$_{12}$A was determined by spectrophotometry{Hitachi model 101; ε^{276}, 8360 M^{-1} cm^{-1} (1 M=1 mol dm^{-3}); λ, 276 nm in chloroform}. The mole ratio of R$_{12}$A and Cu^{2+} was 1 : 1. The obtained ratio was equal to that obtained by conductometry(Toa CM-7B). For R$_n$A–copper complex, a 1 : 1 complex would be present at a lower pH and the complex would be hydrolyzed above pH 5—6 since the hydrolysis constant of a copper(II) ion (pK_1, I>0) is 5.4 to 5.8.[9] The HLB values of these complexes calculated using the Oda equation[3,10] are shown in Table 1. High floatabilities were observed over a pH range of 3—4 for hydrophobic R$_{18}$A, 4—6 for less hydrophobic R$_{12}$A, and 5—6 for least hyrophobic R$_8$A. From these data, it is considered that the floatable complexes are R$_8$A-CuOH, R$_{12}$A-Cu$^+$, R$_{12}$A-CuOH, and R$_{18}$A-Cu$^+$. Their HLB values are in a range of 4—8. Furthermore, the relation between floatability and surface activity at pH 5 is shown in Table 2. The surface tension of 10^{-4} mol dm^{-3} R$_{12}$A solution was 54 dyn cm^{-1}, and the value in the presence of 3X10^{-4} mol dm^{-3} Cu^{2+}, Fe^{3+}, or Ca^{2+} ion was 65 dyn cm^{-1}, 61 dyn cm^{-1}, or

TABLE 1. HLB VALUES CALCD FOR R$_n$A-COPPER COMPLEXES

	R$_n$A-Cu$^+$	R$_n$A-CuOH
R$_8$A	11	6
R$_{12}$A	8	4
R$_{18}$A	6	3
DBM	9	5

TABLE 2. RELATION BETWEEN FLOATABILITY AND SURFACE ACTIVITY AT pH 5

Collector	Metal ion	Floatability[a)] %	Surface activity: Surface tension[b)] dyn cm^{-1}	Surface activity: HLB[c)]
R$_{12}$A	none	—	54	5
R$_{12}$A	Cu^{2+}	91	65	8, 4*
R$_{12}$A	Fe^{3+}	74	61	10, 8*
R$_{12}$A	Ca^{2+}	0	54	8
DBM	none	—	68	6
DBM	Cu^{2+}	5	69	9, 5
DBM	Fe^{3+}	24	69	11, 9*
DBM	Ca^{2+}	0	68	9

a) Collector 3 × 10^{-5} mol dm^{-3}, metal ion 10^{-5} mol dm^{-3}. b) Collector 10^{-4} mol dm^{-3}, metal ion 3 × 10^{-4} mol dm^{-3}. c) Calculated by the Oda equation.[10)] * Hydroxo-metal complex.

54 dyn cm^{-1}, respectively. The copper and iron complexes were considered to be weakly surface-active, and the copper complex would be more hydrophobic than the other. However, the floatability of copper using DBM(having a suitable HLB value) was not so high. The surface tension of a 10^{-4} mol dm^{-3} DBM solution was 68 dyn cm^{-1} and this value was not altered even if metal ions were added. DBM and its complex are presumably surface inactive because of their structural characteristics.

The floatability varies with the concentration of metal ions and the collector. The floatabilities at pH 6.5 for a 2.8×10^{-4} mol dm^{-3} Ga^{3+} solution changed as a function of the $R_{12}A$ concentration and were as follows: 38% with 2.8×10^{-4}mol dm^{-3} $R_{12}A$, 60% with 5.7×10^{-4} mol dm^{-3}$R_{12}A$, 82% with 8.2×10^{-4} mol dm^{-3} $R_{12}A$, and 64% with 14.3×10^{-4} mol dm^{-3} $R_{12}A$, respectively.

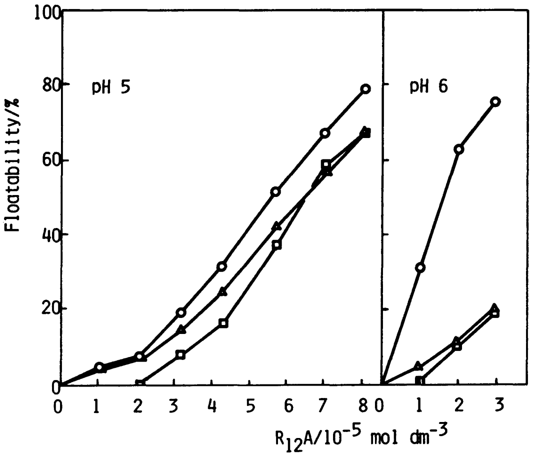

Fig. 2. Selectivity to metal ions.
Mixture of metal ions(Fe^{3+}, Ga^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Ca^{2+}: 10^{-5} mol dm^{-3}, respectively). ○: Cu^{2+}, △: Fe^{3+}, □: Ga^{3+}.

The selectivity of these agents to metal ions was examined at pH 5 and 6. A Cu^{2+} ion could be selectively floated with $R_{12}A$ from a mixture of Fe^{3+}, Ga^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, and Ca^{2+}(each a_0 was 10^{-5} mol dm^{-3}) at pH 6.0 as indicated in Fig. 2. However, the selectivity was not obtained at pH 5.0. Moreover, the selectivity was also examined using a 3×10^{-5} mol dm^{-3} solution of BzA, R_8A, $R_{12}A$, $R_{18}A$, and DBM. The floatabilities for Fe^{3+} and Cu^{2+} are indicated in Fig. 3. The Cu^{2+} ion could be selectively floated with R_8A and $R_{12}A$ at pH 6 (floatabilities were 70% and 75%, respectively). However the Cu^{2+} couldn't be floated with the others. The concentration of R_nA was smaller than that of the total metal ions. Therefore, the mole ratio of a R_nA–metal or a R_nA–hydroxo metal complex must be 1 : 1 at pH 6.0. The HLB values calculated for $R_{12}A$–Cu^+ and $R_{12}A$–CuOH were 8 and 4, as indicated in Table 1. Regarding the complexes of $R_{12}A$–Fe^{2+}, $R_{12}A$–$FeOH^+$, and $R_{12}A$–$Fe(OH)_2$, they were 10, 9, and 8, respectively. Consequently, the more hydrophobic copper complex would be floated selectively.[3] However, the floatabilities of Cu^{2+} using BzA and $R_{18}A$ were very low. The calculated HLB values for the complexes of BzA–Cu^+ and BzA–CuOH were 12 and 7, and for the complexes of $R_{18}A$–Cu^+ and $R_{18}A$–CuOH were 6 and 3 (Table 1), respectively. The BzA complex would be too hydrophilic, while the $R_{18}A$ complex would be too hydrophobic to be floated selectively.

Extraction. Extractability is greatly affected by the distribution coefficient of the extraction reagent corresponding to the HLB value.[4,5] R_nA is expected to be an excellent extraction reagent due to its large distribution coefficent related to its long alkyl group.[4–6] Therefore, extractions for eight kinds of metal ions were examined. The metal ions and the pH range when extracted by benzene (a_0 for 10^{-5} mol dm^{-3} metal ion and 10^{-4}mol dm^{-3} $R_{12}A$) were as follows: for Fe^{3+}, 5.5—11; for Ga^{3+}, 6—8; for

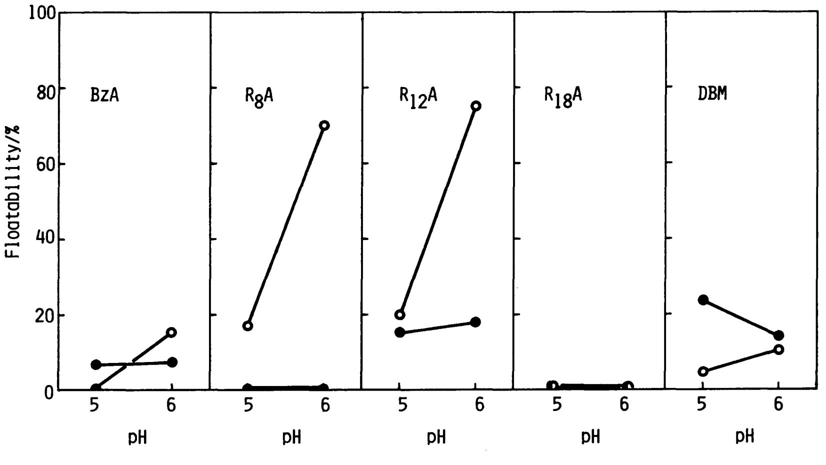

Fig. 3. Selectivity in ion flotation.
Mixture of metal ions(Fe^{3+}, Ga^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Ca^{2+}: 10^{-5} mol dm^{-3}, respectively); R_nA: 3×10^{-5} mol dm^{-3}; BzA: 3×10^{-5} mol dm^{-3}; DBM: 3×10^{-5} mol dm^{-3}. ○: Cu^{2+}, ●: Fe^{3+}.

Cu^{2+}, 5.5—11; for Zn^{2+}, 8—12; for Pb^{2+}, 6—11; for Cd^{2+}, 9—13; and for Ca^{2+}, 11—13. Extractions for Cu^{2+} and Ga^{3+} ions are shown in Fig. 4. The extraction efficiencies with R_nA and BzA were more effective than that with AA. Furthermore, the highest extractability was obtained by DBM. The HLB values* calculated for DBM, $R_{18}A$, $R_{12}A$, R_8A, BzA, and AA were 5, 3, 4, 6, 7, and 13, respectively. However, the distribution coefficient of DBM must be the largest value in these agents.

The selectivity regarding an extraction was examined using $R_{12}A$. The stability constants of the metal acetylacetone complexes (log K_{MA} and log K_{MA_2}) are arranged in the following order: $Fe^{3+} > Ga^{3+} > Cu^{2+} > Zn^{2+} > Pb^{2+} > Cd^{2+} > Ca^{2+}$.[11] The selectivity order regarding an extraction from a mixture of seven metal ions at pH 6.0 was the same as the order regarding their stability constants (Fig. 5). A more selective removal of Fe^{3+} was obtained at pH 5 when DBM was employed. The formed metal complex is thought to be uncharged(neutral) because the complex is soluble in benzene. Furthermore, the concentration effect of $R_{12}A$ on the extraction of a Cu^{2+} ion suggested that the mole ratio of R_nA to copper is 2:1. The calculated HLB value for both the complexes{$(R_{12}A)_2Cu$ and $(R_{12}A)_3Fe$} was 1. Therefore, the selectivity is presumably controlled by the stability constant.

Comparison. Ion flotation by using R_8A or $R_{12}A$ was superior to extraction at a lower pH region and inferior around neutral regarding the separation of Cu^{2+}, Fe^{3+}, or Ga^{3+} ion(Fig. 6). The R_nA-metal complex at a lower pH was a 1:1-complex and the ratio of R_nA to metal ions became maximum around a neutral pH. The 1:1-complex must be slightly hydrophilic(HLB, 4—14) and the 2:1- and 3:1-complexes must be more hydrophobic(HLB, 1). The 1:1-complex(which shows a surface-active property) is presumably suitable for ion flotation. Also, coordination-saturated and uncharged complexes of 2:1 and 3:1 are presumably suitable for extraction.

Especially the selective removal for Cu^{2+} ion by the ion-flotation method using R_nA was superior to that by extraction, in spite of a smaller stability constant compared to Fe^{3+} and Ga^{3+} ions.

Recovery. The ion-flotation collector should be recovered almost completely from the residual solution. The residual concentration of $R_{12}A$ was 0.2 ppm after the flotation of Cu^{2+} ions at pH 5, and was below 0.2 ppm after selective removal by the successive addition of $R_{12}A$ at pH 6. Therefore, the additive, $R_{12}A$, remained in an aqueous solution very little and was floated as a scum. The scum was dispersed in benzene; then, the benzene solution was shaken with a 2 mol dm^{-3} solution of mineral acid.

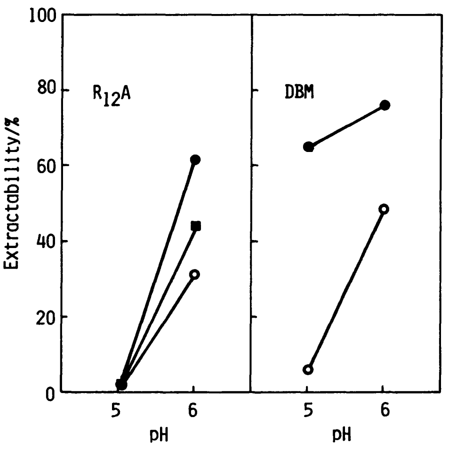

Fig. 5. Selectivity in extraction.
Mixture of metal ions(Fe^{3+}, Ga^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, and Ca^{2+}: 10^{-5} mol dm^{-3}, respectively); $R_{12}A$: 3×10^{-5} mol dm^{-3}; DBM: 3×10^{-5} mol dm^{-3}. ○: Cu^{2+}, ●: Fe^{3+}, □: Ga^{3+}.

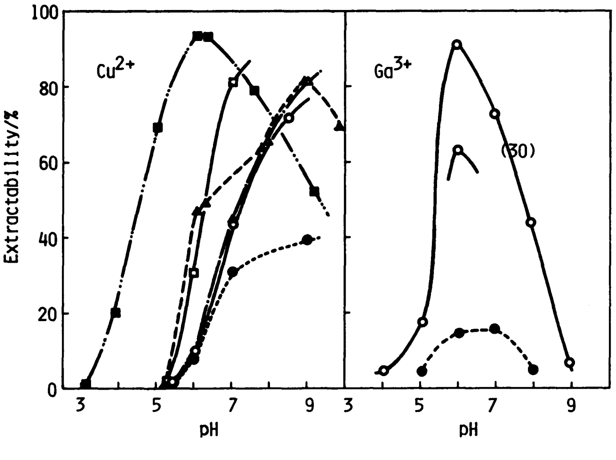

Fig. 4. Extractions for Cu^{2+} and Ga^{3+}.
Cu^{2+}: 10^{-5} mol dm^{-3}; Ga^{3+}: 2.86×10^{-4} mol dm^{-3}; $[R_nA]/[M]=3$, $(=30)$; Solvent: benzene. △: R_8A, ○: $R_{12}A$, □: $R_{18}A$, ●: AA, ▲: BzA, ■: DBM.

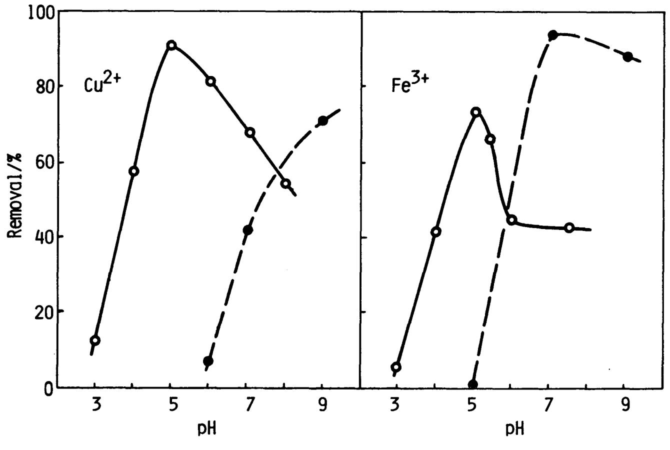

Fig. 6. Removals of Cu^{2+} and Fe^{3+}.
Metal ions: 10^{-5} mol dm^{-3}; $R_{12}A$: 3×10^{-5} mol dm^{-3}. ○: Ion flotation, ●: extraction.

$R_{12}A$ could be quantitatively recovered from the benzene layer, while the Cu^{2+} ions were recovered from an aqueous layer containing a mineral acid.

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