# Disposal of cuprous chloride waste water

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**Abstract:** The waste water system generated in the process of production of cuprous chloride was studied. The existing forms of copper in the system and the influence of temperature and pH on the existing forms of copper ion were analyzed and determined through calculating the coefficients of copper complex distribution. In the waste water system, the main forms of copper are $CuSO_4$, $Cu^{2+}$, $CuCl^+$, $CuCl_2^-$, and $CuCl_3^{2-}$. Temperature has little influence on the distribution coefficient of Cu(　), but has significant influence on distribution coefficient of Cu(　). With the increase of temperature, the distribution coefficient of $CuCl_2^-$, increases significantly while the distribution coefficient of $CuCl_3^{2-}$ decreases. The pH has nearly no influence on the distribution coefficients of various Cu(　)-compounds, but has sizable influence on the distribution coefficients of Cu(　)-compounds. With the increase of pH, the distribution coefficient of $CuSO_4(aq)$ increases while the distribution coefficients of $Cu^{2+}$ and $CuCl^+$ decrease. According to these results, the anion resin of $201\times 7\ OH^-$ and the cation resin of 732 Na were chosen to dispose the waste water solution of cuprous chloride. Finally, 97.9% copper in the waste water is recovered.

**Key words:** waste water solution; cuprous chloride; copper complex; coefficient of distribution; ion-exchange

## 1 Introduction

Due to the unique physical and chemical properties, CuCl has been widely used. For example, it has been used as the catalyzer in organic synthesis, the reducer in lipid chemical industry, the discolorant, desulfurizer and deviator in oil chemical industry. In addition, it has also been widely used in the industry of dyes, metallurgy, plating as well as medicine and pesticide[1−2]. The production methods of CuCl are mainly bluestone deoxidization, direct oxidation of waste copper chlorine, bras wire oxidation and the waste copper hydrochloric acid, etc[3]. The waste water generated in the production process often contains copper of 2−3 g/L, which should be recycled. Currently, the widely used recycling method is first reverting bivalent copper into univalent copper by using industrial waste scrap iron, then removing the bivalent iron from the solution by using anti-infiltration membrane method and finally returning the disposed solution to production for recycling utilization. However, this method has some shortcomings, such as the complex working procedure, the poor disposal efficiency and the disturbing ions

introduced into the solution. Therefore, this method has a bad economical efficiency and a bad environmental efficiency[4−5].

In order to find a better disposal method for CuCl waste water, which has a simple process and high recycling rate of copper, in this work, the compound bond theory was used to explain the reason why the CuCl solubility in water solution is low, and to study the structure and stability of the compound formed by $Cl^-$ with Cu(　) and Cu(　). From the solution thermo-dynamics and multi-ion balance theory, the distribution coefficients for the particles of different forms in the CuCl waste water system were calculated and analyzed, and the influence of the concentration of $Cl^-$ in the solution, the temperature and the pH value on the distribution coefficients of Cu compounds was studied.

## 2 Theory of Cu(　)-Cl⁻ and Cu(　)-Cl⁻ compound bond

Because the copper atom has the structure of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$, $Cu^+$ with outermost layer electron structure of $3d^{10}$ is formed when the atom loses an electron. Here, the outermost layer is filled

with electrons and thus $Cu^+$ compound has some different structures and properties with other transition metal ion compounds. The solid CuCl has a similar ion distance with NaCl, whereas CuCl has a larger experimental crystal lattice energy. About the variation of hydration heat with ion radius, for non-transition elements, the ion radius and hydration heat have an inverse ratio; but for transition metal ions Cu(  ) and Na(  ), which have the same radius and electric charge, the hydration heat of copper is larger than that of natrium by 40% and their ionization potentials are also different (496.04 kJ for Na and 745.1 kJ for Cu(I))[6]. The main reason for the property difference between Cu(  ) and Na(  ) is the difference of 8 electrons from 18 electrons in the outermost layer. For the spherically symmetric distribution of electric charge, the electric charge locates outside at one point (relatively far from the charge center), which generates a lower static electric potential compared with the case that the electric charge locates at this point. Therefore, in a transition system, the increased positive electric potential caused by the increase of the nuclear electric charge is not possibly balanced by the added electron negative potential. This is called non-complete screening of nuclear electric charge. So, for a large distance Cu(  ) and Na(  ) have the same electric potential, while for a bond distance the copper has a larger effective ion charge. This is because the electrons on d-orbit tend to appear at a distance larger than bond distance from the copper nucleus. Cu(  ) has an effective charge $q'$ larger than +1. Even for ion bonding, this large charge can obviously affect the bonding energy. If the bonding element (say $Cl^-$) is low electrically negative, the energy is in favor of the transition of the electron from the bonding element to the metal. Such transferred electric charge still obtains a large effective charge. In a word, the d-electron of the spherical $d^{10}$ ion has non-complete screening for nucleus and results in the tendency of covalent bonding when it bonds with some low negatively charged element. This makes $Cu^+$ and $Cl^-$ easily separate out from water solution($K_{sp}^{\ominus}$ is $1.7\times 10^{-7}$ for CuCl).

In the theory of soft-hard acid alkali[7], $Cu^+$ belongs to soft acid and its bonding with $Cl^-$ results in a high polarization rate, which corresponds to a low ionization potential and makes for the strong transfer of electrons to $Cu^+$ form $Cu^+$-$Cl^-$ compound with obvious covalence stability. The bonding form of soft acid $Cu^+$ with $Cl^-$ can be explained by π-bonding theory[6]. $Cu^+$ has an electronic layer structure of $1s^2\,2s^22p^63s^23p^63d^{10}$, whose feature is the existence of the loosely bound outer d-orbit electrons. Since $Cl^-$ has an electronic layer structure of $1s^22s^22p^63s^23p^63d^{10}$, the d-electrons of $Cu^+$ can easily form into π-bond on the empty d-orbit of $Cl^-$. In other words, in the formation of π-bond, $Cu^+$ is the potential

d-electron provider while $Cl^-$ is the accepter. In this way, the binding of $Cu^+$ and $Cl^-$ not only forms σ-bond on the mixed orbit, but also leads to the tendency for the binding of feedback π-bond of d-electron of $Cu^+$, as shown in Fig.1.
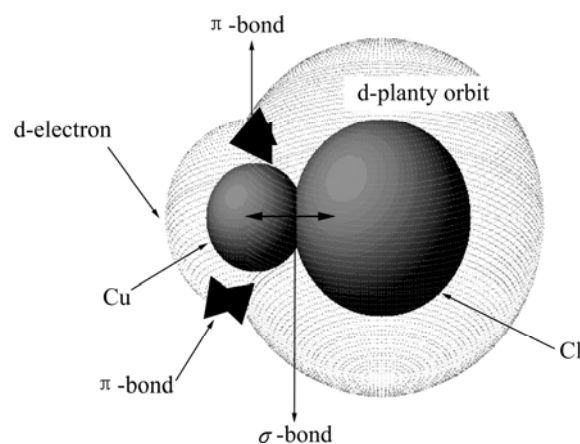


**Fig.1** Bonding mode of coordinated complex of Cu(  )-$Cl^-$

$Cu^{2+}$ has an electronic layer structure of $1s^22s^22p^63s^23p^63d^9$ and belongs to medium acid in the theory of soft-hard acid alkali. When it binds with $Cl^-$, unlike the case of $Cu^+$, it cannot obtain extra stability. Therefore, although in the theory of valence the binding of both $Cu^{2+}$ and $Cu^+$ with two or three $Cl^-$ results in sp hybridization and $sp^2$ hybridization, which forms the compound of linear type and plane triangle structure, their stabilities have much difference in the solution: $CuCl_2^-$ and $CuCl_3^{2-}$ have obviously higher stability $(K^{\ominus}(CuCl_2^-)=5.299\,6,\ K^{\ominus}(CuCl_3^{2-})=5.699\,9,$ $K^{\ominus}(CuCl_2)=-3.730\,8,\ K^{\ominus}(CuCl_3^-)=-2.289\,9\,)$.

Among the compounds formed by Cu(  ) and Cu(  ) with $Cl^-$, besides the existence of CuCl, $CuCl_2^-$, $CuCl_3^{2-}$, $CuCl_2^-$, $CuCl_2$ and $CuCl_3^-$, Cu(  ) can also bind with $Cl^-$ to form $CuCl_4^{2-}$ $(K^{\ominus}(CuCl_4^{2-})=$ $-4.590\,1\,[8-9])$ with plane square structure. These compounds are hard to explain in terms of valence theory. In the crystal lattice theory, unlike in the valence theory, $d^9$ orbital Cu(  ) ion cannot form tetrahedron or octahedron compound. Due to John-Teller effect, the four radicals locate at one plane and close to Cu(  ) ion while other two radicals are perpendicular to the plane and far from the ion, which finally forms $CuCl_4^{2-}$ with a square structure, as shown in Fig.2[8].

# 3 Calculation of distribution coefficient of Cu compound in cuprous chloride waste water

## 3.1 Calculation and analysis of distribution coefficient of Cu compound in Cu-$Cl^-$-$H_2O$ system

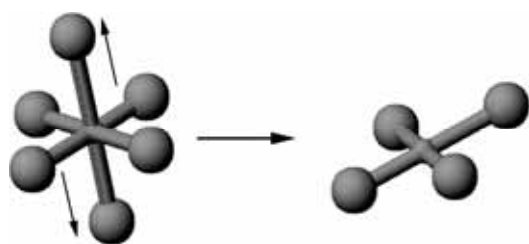In the water solution $Cu^+$ can be easily oxidized to

**Fig.2** Structure of plane square coordinated complex formed by John-Teller effect

$Cu^{2+}$ and is unstable. Due to the strong binding power of $Cu^+$ and $Cl^-$[9−10], $Cu^+$ can exist stably in the solution containing $Cl^-$. Neglecting the oxidation of $Cu^+$, the binding reactions between $Cu^{2+}$ and $Cl^-$ and $Cu^+$ and $Cl^-$ exist in the Cu-Cl⁻-H₂O solution. Such binding reactions and the balance constants at 25    and 60    are shown in Table 1.

**Table 1** Bonding reaction balance constants for Cu(  )-Cl⁻ and Cu(  )-Cl⁻ at 25    and 60    [8−9]

| No. | Bonding reaction | Balance constants | |
|---|---|---|---|
| | | 25 | 60 |
| 1 | $Cu^{2+}+Cl^-=CuCl^+$ | $K_1=10^{0.400\,2}$ | $K_1^*=10^{0.501\,8}$ |
| 2 | $Cu^{2+}+2Cl^-=CuCl_2(aq)$ | $K_2=10^{-0.689\,8}$ | $K_2^*=10^{-0.553\,2}$ |
| 3 | $Cu^{2+}+3Cl^-=CuCl_3^-$ | $K_3=10^{-2.289\,9}$ | $K_3^*=10^{-2.309\,5}$ |
| 4 | $Cu^{2+}+4Cl^-=CuCl_4^{2-}$ | $K_4=10^{-4.590\,1}$ | $K_4^*=10^{-5.005\,1}$ |
| 5 | $Cu^++Cl^-=CuCl(aq)$ | $K_1'=10^{2.330\,2}$ | $K_1'^*=10^{2.100\,1}$ |
| 6 | $Cu^++2Cl^-=CuCl_2^-$ | $K_2'=10^{5.299\,6}$ | $K_2'^*=10^{4.608\,9}$ |
| 7 | $Cu^++3Cl^-=CuCl_3^{2-}$ | $K_3'=10^{5.699\,9}$ | $K_3'^*=10^{4.63}$ |

From Eqs.(1)−(7) the contents of Cu(  ), Cu(  ) and $Cl^-$ in the solution can be obtained as:

$$[Cl^-]_T =[Cl^-]+[Cu^{2+}]\{K_1[Cl^-]+2K_2[Cl^-]^2+$$
$$3K_3[Cl^-]^3+4K_4[Cl^-]^4\}+[Cu^+]\{K_1'[Cl^-]+$$
$$2K_2'[Cl^-]^2+3K_3'[Cl^-]^3\} \qquad (8)$$

$$[Cu(  )]_T =[Cu^{2+}]\{1+K_1[Cl^-]+K_2[Cl^-]^2+$$
$$K_3[Cl^-]^3+K_4[Cl^-]^4\} \qquad (9)$$

$$[Cu(  )]_T =[Cu^+]\{1+K_1'[Cl^-]+K_2'[Cl^-]^2+K_3'[Cl^-]^3\} \qquad (10)$$

From the definition of distribution coefficient [11−12], with only two values of $[Cl^-]_T$, $[Cu(  )]_T$ and $[Cu(  )]_T$, the relation for the other value was obtained with the distribution coefficient. In this work, the common deoxidation method[13] was used to make out cuprous chloride powder to obtain waste water solution through one experiment. Then the state-standard analysis

method [14] was used to measure the concentration of $[Cu(  )]_T$. atom absorption method(AA-6800 atom absorption spectrophotometer) was used to measure the concentration of Cu. The AgNO₃ method[12] was used to measure the concentration of $Cl^-$. Through the calculation using Math-cad[15], the relation of the distribution coefficient for $[Cl^-]_T$ and Cu(  )-$Cl^-$, Cu(  )-$Cl^-$ at 25    and 60    with $[Cu(  )]_T=0.007\,6$ mol/L and $[Cu(  )]_T=0.024$ mol/L, are shown in Figs.3−6.



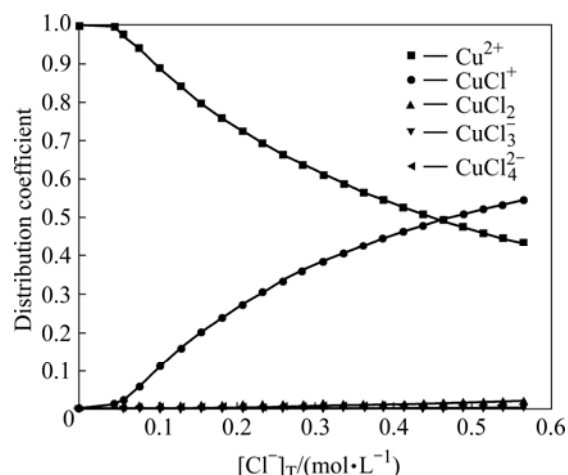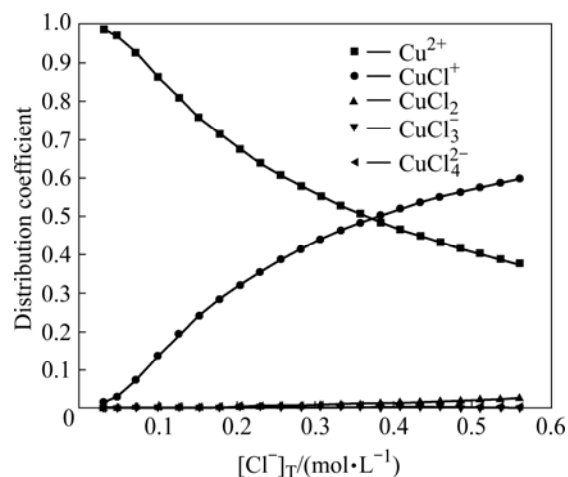**Fig.3** Effect of total concentration of $Cl^-$ on distribution coefficients of coordinated complexes of Cu(  )-$Cl^-$ at 25



**Fig.4** Effect of total concentration of $Cl^-$ on distribution coefficients of coordinated complexes of Cu(  )-$Cl^-$ at 60

From Figs.3 and 4, it can be seen that at 25    , when $[Cu(  )]_T$ is 0.024 mol/L, $[Cu(  )]_T$ is 0.007 6 mol/L and when $[Cl^-]_T$ is in the range of 0−0.566 mol/L, the distribution coefficient of $Cu^{2+}$ drops with $[Cl^-]_T$ increasing and is 0.58 at $[Cl^-]_T=0.345\,2$ mol/L. The distribution coefficient of $CuCl^+$ increases with $[Cl^-]_T$ increasing and is about 0.41 at $[Cl^-]_T=0.345\,2$ mol/L. In addition, the distribution coefficients of $CuCl_2$ is very small in the whole range, slowly going up with $[Cl^-]_T$ increasing, and is 0.01 when $[Cl^-]_T=0.345\,2$ mol/L; while
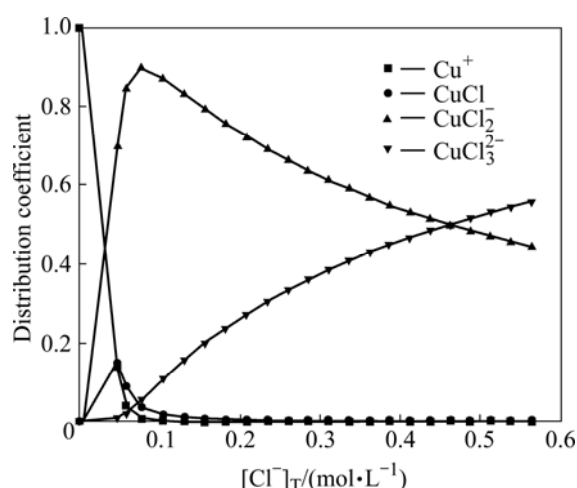
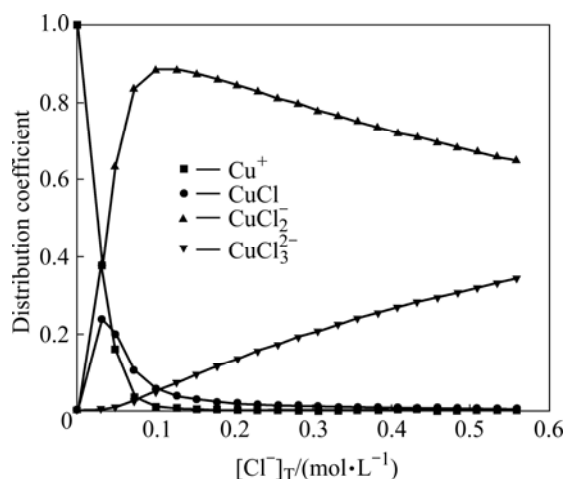**Fig.5** Effect of total concentration of Cl⁻ on distribution coefficient of coordinated complexes of Cu(    )-Cl⁻ at 25



**Fig.6** Effect of total concentration Cl⁻ on distribution coefficient of coordinated complexes of Cu(    )-Cl⁻ at 60

the distribution coefficients of $CuCl_3^+$ and $CuCl_4^+$ are almost zero in the whole range. At 60    , the distribution coefficients have no much difference with those at 25    , which is slightly higher for $CuCl^+$ and slightly lower for $Cu^{2+}$. This indicates that as temperature goes up, it is easier for $Cu^{2+}$ to bind with $Cl^-$ to form $CuCl^+$. From these analyses, Cu(    ) mainly exists in the forms of $Cu^{2+}$ and $CuCl^+$ at 25 −60    .

From Figs.5 and 6, it can be seen that, at 25    , when [Cu(   )]$_T$ is 0.024 mol/L, [Cu(   )]$_T$ is 0.007 6 mol/L, Cl⁻ starts to appear in the solution, and $Cu^+$ binds with $Cl^-$ immediately. When [Cl⁻]$_T$ is 0.345 2 mol/L, the distribution coefficient of $Cu^+$ is almost zero. The distribution coefficient of CuCl(aq) increases with [Cl⁻]$_T$ increasing, goes up at first (reaches 0.15 when [Cl⁻]$_T$ is 0.04 mol/L) and then drops and finally tends to zero gradually. When [Cl⁻]$_T$ is 0.345 2 mol/L, CuCl(aq) has a distribution ratio of 0.002. The distribution ratio of $CuCl_2^-$ first increases rapidly with [Cl⁻]$_T$ increasing

(reaches 0.898 when the Cl⁻ concentration is 0.074 mol/L), then drops down and becomes 0.58 when [Cl⁻]$_T$ is 0.345 2 mol/L. The distribution coefficient of $CuCl_3^{2-}$ increases gradually with the [Cl⁻]$_T$ concentration and reaches 0.418 when [Cl⁻]$_T$ is 0.345 2. The distribution coefficient at 60    show little difference with the values at 25    . When [Cl⁻]$_T$ is low, as the temperature goes up, the distribution coefficient of CuCl(aq) increases. When [Cl⁻]$_T$ is smaller than 0.1 mol/L, $CuCl_2^-$ has a slightly larger distribution coefficient at 25    than at 60    . When [Cl⁻]$_T$ is larger than 0.1 mol/L, $CuCl_2^-$ has a much smaller distribution coefficient at 25    than at 60    . In the whole range of [Cl⁻]$_T$, $CuCl_3^{2-}$ has an obviously larger distribution coefficient at 25    than at 60    . So, from above results, it can be seen that Cu(I) exists in the forms of $CuCl_2^-$ and $CuCl_3^{2-}$ in the waster water at 25−60    .

### 3.2 Influence of other ions in waste water on existing form of Cu

In the waste water of cuprous chloride, besides the existence of $Cu^{2+}$, $Cu^+$, Cl⁻, there are $SO_4^{2-}$, $Na^+$ and $H^+$ with certain concentration which affect the existing forms of Cu(   ) and Cu(   ) in the solution[16]. These six ions have the reactions in Eqs.(1)−(7) and, in addition, have the following balance reactions as shown in Eqs.(11)−(14) with the balance constants at 25    [8−9]. Then, five relations (Eqs.(15−19)) can be obtained. At the same time, assuming no loss of $SO_4^{2-}$ and $Na^+$ in the experimental process, [$SO_4^{2-}$]$_T$=0.261 mol/L and [$Na^+$]$_T$=0.71 mol/L can be obtained through calculation. Through measurement, the initial pH value of the solution is 2.6(PB-10 acidity meter). Then, from the definition of distribution coefficient and through the calculation by Mathcad, the relation graphs shown in Figs.7 and 8 are obtained.

$$Na^+ + Cl^- = NaCl(aq), \quad K(NaCl) = 10^{-0.777} \tag{11}$$

$$Na^+ + SO_4^{2-} = NaSO_4^-, \quad K(NaSO_4^-) = 10^{0.7} \tag{12}$$

$$SO_4^{2-} + Cu^{2+} = CuSO_4(aq), \quad K(CuSO_4) = 10^{2.36} \tag{13}$$

$$SO_4^{2-} + H^+ = HSO_4^-, \quad K_{b1} = 10^2 \tag{14}$$

$$[Cl^-]_T = [Cl^-] + [Cu^{2+}]\{K_1[Cl^-] + 2K_2[Cl^-]^2 +$$
$$3K_3[Cl^-]^3 + 4K_4[Cl^-]^4\} + [Cu^+]\{K_1'[Cl^-] +$$
$$2K_2'[Cl^-]^2 + 3K_3'[Cl^-]^3\} + K(NaCl)[Na^+][Cl^-] \tag{15}$$

$$[SO_4^{2-}]_T = [SO_4^{2-}]\{1 + K_{b1}[H^+] + K(CuSO_4)[Cu^{2+}] +$$
$$K(NaSO_4^-)[Na^+]\} \tag{16}$$

$$[Na^+]_T = [Na^+]\{1 + K(NaCl)[Cl^-] +$$
$$K(NaSO_4^-)[SO_4^{2-}]\} \tag{17}$$

$$[Cu(\ )]_T = [Cu^+]\{1 + K'_1[Cl^-] + K'_2[Cl^-]^2 + K'_3[Cl^-]^3\} \tag{18}$$

$$[Cu(\ )]_T = [Cu^{2+}]\{1 + K_1[Cl^-] + K_2[Cl^-]^2 + K_3[Cl^-]^3 +$$
$$K_4[Cl^-]^4 + K(CuSO_4)[SO_4^{2-}]\} \tag{19}$$

As shown in Fig.7, compared with the system of $Cu-Cl^--H_2O$, two kinds of ions $SO_4^{2-}$ and $Na^+$ have much influence on the distribution coefficients of Cu(  ) compounds. Except for the case with a low pH, in which $Cu^+$ and $CuCl^+$ have large distribution coefficients, Cu(  ) mainly exists in the form of $CuSO_4(aq)$ in the solution. As the pH increases, the distribution coefficient of $CuSO_4(aq)$ increases.
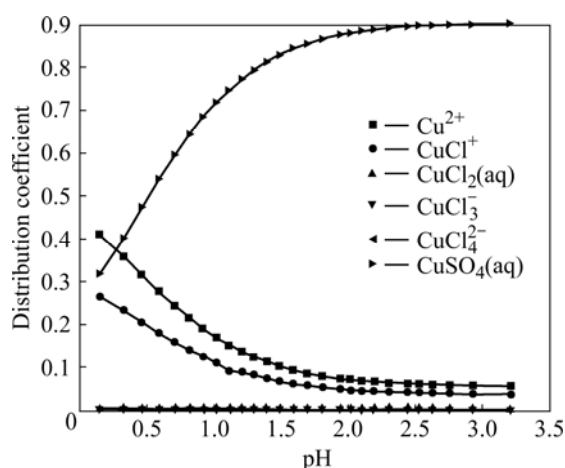


**Fig.7** Effect of pH on distribution coefficients of coordinated complexes of Cu(  )-Cl⁻ at 25

The initial pH is 2.6 and the distribution coefficient of $CuSO_4(aq)$ is 0.9. Under the same condition, the distribution coefficients of $Cu^{2+}$ and $CuCl^+$ which take up 99% in the $Cu-Cl-H_2O$ system, are only 0.1. The main reason is that the binding power of $Cu^{2+}$ and $SO_4^{2-}$ is strong and the concentration of $SO_4^{2-}$ in the solution is high.

As shown in Fig.8, the variation of pH has little effects on the distribution coefficients of Cu(  ) compounds. When pH is 2.6, the distribution coefficients of $CuCl_2^-$ and $CuCl_3^{2-}$ are 0.599 and 0.398, respectively. As mentioned above, if there are no $SO_4^{2-}$ and $Na^+$ in the solution, $CuCl_2^-$ and $CuCl_3^{2-}$ have distribution coefficients of 0.58 and 0.418, respectively. This indicates that adding $SO_4^{2-}$ and $Na^+$ in the $Cu-Cl-H_2O$ system has little influence on the distribution coefficients of Cu(  ) compounds. The main reason is that the binding power of Cu(  ) with 2 or 3 $Cl^-$ is strong. In the solution Cu(  ) mainly exists in the form of $CuCl_2^-$ and $CuCl_3^{2-}$. The above analytical results are in agreement with the experimental results[17−18].
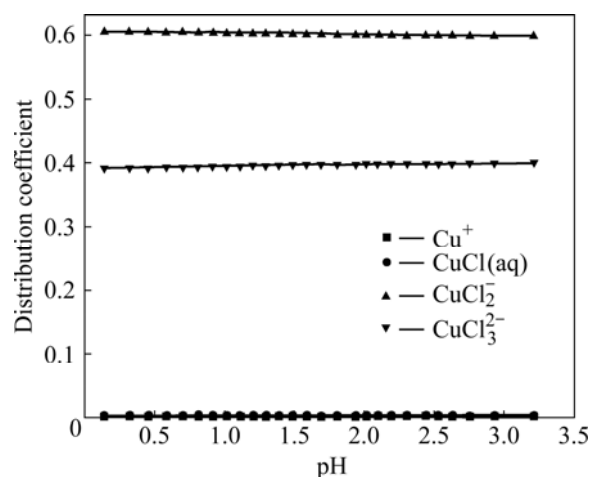


**Fig.8** Effect of pH on distribution coefficients of coordinated complexes of Cu(  )-Cl⁻ at 25

## 4 Conclusions

1) From the study of matching bond theory, the non-complete screening of the d-electrons of the spherical $d^{10}$ structure of Cu(  ) to the nucleus leads to the fact that its binding with low negatively charged $Cl^-$ tends to covalent bond. This makes CuCl have a low solubility and easy to separate out as sedimentation. Because the binding mode of Cu(  ) and $Cl^-$ can form the $\sigma$-bond on the mixing orbit and, at the same time, there exists the tendency of the feedback $\pi$-bond of the d-electron of $Cu^+$, the compounds of Cu(  ) and $Cl^-$ have higher stability than the compounds of Cu(  ) and $Cl^-$.

2) Through the calculation and analysis for the distribution coefficients of Cu compounds in the cuprous chloride waste water, the main existing forms of copper are $SO_4^{2-}(aq)$, $Cu^{2+}$, $CuCl^+$, $CuCl_2^-$, $CuCl_3^{2-}$. As $[Cl^-]_T$ increases, the distribution coefficients of $CuCl^+$ and $CuCl_3^{2-}$ increase while the distribution coefficients of $Cu^{2+}$ and $CuCl_2^-$ decrease. The temperature has little influence on the distribution coefficient of Cu(  ) compounds. As the temperature increases, the distribution coefficient of $CuCl^+$ increases slightly and the distribution coefficient of $Cu^{2+}$ decreases slightly. The temperature has obvious influence on the distribution coefficients of Cu(  ) compounds. As the temperature increases, the distribution coefficient of $CuCl_2^-$ increases sizably and the distribution coefficient of $CuCl_3^{2-}$ decreases sizably. The pH value has almost no influence on the distribution coefficients of Cu(  ) compounds, but has sizable influence on the distribution coefficients of Cu(  ) compounds. As pH increases, the distribution coefficient of $SO_4^{2-}(aq)$ increases while the distribution coefficients of $Cu^{2+}$ and $CuCl^+$ decrease.

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