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침출제로 황산과 메탄술폰산의 화학적 반응성 비교

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Comparison of the Chemical Reactivity between Sulfuric and Methanesulfonic Acids as a Leaching Agent

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요   약

메탄술폰산은 우수한 물리화학적 특성을 지니고 있어 금속의 침출에 효과적이다. 분자구조 및 코발트와 니켈 금속의 침출자료를 이용하여 메탄술폰산과 황산의 화학적 반응성을 비교하였다. 유발과 공명효과는 두 산의 반응성에 큰 영향을 미쳤다. 동일한 침출조건에서 코발트와 니켈의 침출률은 메탄술폰산보다 황산에서 높았다. 메탄술폰산의 강한 산도와 금속염의 높은 용해도를 고려하면 메탄술폰산을 금속회수시 침출제로 이용하는 것이 가능하다.

주제어 : 메탄술폰산, 황산, 화학적 반응성, 침출제

Abstract

Methanesulfonic acid (MSA) can be considered effective in the leaching of metals because of its advantageous physical and chemical properties. The chemical reactivities of MSA and sulfuric acid were compared based on their structures and the dissolution data of Co and Ni metal. The inductive and resonance effects play a vital role in the chemical reactivities of these two acids. The dissolution percentages of Co and Ni in the sulfuric acid solution were higher than those in the MSA solution under the same experimental conditions. Considering the strong acidity of MSA and the high solubility of its metal salts, MSA can be employed as a leaching agent for the recovery of metals.

Key words : methanesulfonic acid, sulfuric acid, chemical reactivity, leaching agent

1. Introduction

In hydrometallurgical processes, aqueous lixiviants play a critical role for dissolving metals from ores or concentrates into aqueous solutions. Mineral acid solutions such as H_2SO_4, HCl, and HNO_3 are the most widely used as lixiviants due to their advantages such as aggressiveness, low price and availability[1]. However, there are

Table 1. Some reported literatures for using MSA in the leaching of metals[13,16,20-24]

Resources	Condition	Leaching percentage of metals, %
Chalcopyrite	30 g/L MSA and 5 g/L ferric at 75°C for 96h	47% Cu
Synthetic alloy containing Co, Ni, and Cu	2.0 mol/L MSA + 10% (v/v) H_2O_2 solution at liquid/solid ratio: ~22.2 g/L at 20°C for 30 min with 300 rpm stirring speed	~100% Co and below 5.0% Cu
Malachite	0.36 mol/L MSA with liquid/solid ratio: 10 g/L 218K (~45°C), 60 min, and 500 rpm stirring speed.	92.41 % Cu
Smithsonite	0.4 mol/L MSA with liquid/solid ratio: 10 g/L at 323K (~50°C), 60 min, and 450 rpm stirring speed.	92.58% Zn
Chacopyrite	0.05 mol/L MSA + 1.5 mol/L $FeCl_3$ with liquid/solid ratio: 100 g/L for 24h at 90°C.	~100% Cu
Zinc ore mineral hemimorphite	0.15 mol/L MSA with liquid/solid ratio: 10 g/L at 25°C, 750 rpm stirring speed for 5 min.	89.78% Zn
Residue of the Hydro WEEE process for lamp phosphor waste	Concentrated MSA with liquid/solid ratio: ~66.7 g/L at 473K (~200°C) 60 min	74.3% Tb, 78.3% Ce, 82.7% Y, 58.2% Eu, 51.8% Gd and 94.7% La

some drawbacks in the use of these acidic lixiviants for the leaching of metals from various resources. For instance, the leaching kinetics of copper from sulfidic ore minerals such as chalcopyrite, bornite, chalcocite, and digenite by H_2SO_4 solution is slow and the formation of passive film on the surface of chalcopyrite like solid sulfur hinders the progress of leaching in the absence of pitting agents like chloride ions[2-4]. Although the leaching rate in chloride media is faster than that of sulfate media due to the high solubility of chloride salts, HCl solution has some disadvantages like the corrosion of the reactors and difficulty of electrowinning of high grade metal[5]. Due to its highly oxidizing characteristics, nitric acid solutions can oxidize both metals and nonmetal elements like sulfide to sulfur or sulfate[6] and produce noxious and corrosive gas products like NO_x in the leaching process, resulting in an increase in reagent consumption[7,8].

Methanesulfonic acid (CH_3SO_3H, MSA) has been widely used as an electrolyte for electrochemical processes (especially for tin and lead)[9] and can be applied in the synthesis of catalysis[10] and polymer[11]. In recent years, the use of MSA for the leaching of metals in hydrometallurgical processes has attracted many interests due to its excellent chemical and physical properties such as high acidity, solubility of metal salts, high conductivity, high boiling point and less corrosiveness compared to commercially available inorganic acids[12]. Some studies have pointed out that some metals such as Cu, Ni, Pb, Zn, and rare earth elements can be effectively leached by employing either dilute or concentrated MSA solutions in the presence and absence of oxidizing agents such as H_2O_2 and ferric chlorides (see Table 1). The leaching efficiency of Cu by the mixture of MSA and H_2O_2 from chalcopyrite is better than that of sulfuric acid[13]. Besides, MSA is also known as a green acid owing to no production of dangerous volatile compounds, low toxicity, readily biodegradable[14,15]. With its characteristics, MSA can be considered as a potential lixiviant for the recovery of valuable metals from the primary and secondary resources.

In this study, the chemical reactivity of MSA was compared with that of sulfuric acid on the basis of analysis of their structure and the dissolution behavior of Co and Ni metal. The dissolution data was obtained from our previously published data[16]. These obtained results can contribute to provide further information on the application of MSA in hydrometallurgical processes.

2. Results and discussion

2.1. Chemical reactivity of acids

MSA is a strong organic (CH_3SO_3H, $pK_a = -1.19$) and non-oxidizing acid. The acidity of MSA is close to some inorganic acids such as nitric acid (HNO_3, $pK_a = -1.3$) and sulfuric acid (H_2SO_4, $pK_{a1} = -3$) and higher than others such as phosphoric acid (H_3PO_4, $pK_{a1} = 2.12$), acetic acid (CH_3COOH, $pK_a = 4.76$) and maleic acid ($C_2H_2(COOH)_2$, $pK_{a1} = 1.83$). MSA can be completely ionized into proton and methanesulfonate anions ($CH_3SO_3^-$) at 0.1 M in aqueous solution as represented in Eq. (1)[17]. Meanwhile, sulfuric acid is strong inorganic acid with two protons and strong oxidizing agent at concentrated solutions and SO_2 gas can be produced at high temperature, which can act as a reducing agent[18]. The dissociation of sulfuric acid in water depends on solution acidity. When solution acidity is high, the first dissociation of sulfuric acid occurs completely, while the second dissociation can occur in dilute acid solution. The first and second dissociation of sulfuric acid is represented as Eqs. (2) and (3).

$$CH_3SO_3H + H_2O = H_3O^+ + CH_3SO_3^- \quad pK_a = -1.19 \quad (1)$$
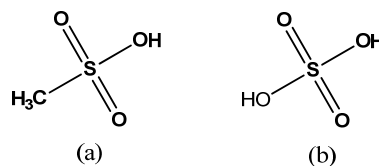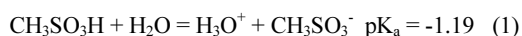
| Density: | 1539 g/L at 298 K | 1840 g/L at 298 K |
| Boiling point: | 256 °C | 317 °C |

Fig. 1. Structure of MSA and sulfuric acid.

$$H_2SO_4 + H_2O = H_3O^+ + HSO_4^- \qquad pK_{a1} = -3 \quad (2)$$

$$HSO_4^- + H_2O = H_3O^+ + SO_4^{2-} \qquad pK_{a2} = 2.0 \quad (3)$$
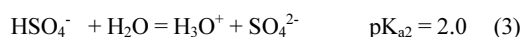
Fig. 1 shows the similarity (-SO_2OH group) and difference (CH_3- and -OH groups) in the chemical structure of MSA and sulfuric acids, which relates to their chemical reactivity. In their structure, $HOSO_2$- and CH_3SO_2- groups attached to -OH groups are quite strong electron withdrawing groups owing to the presence of highly electronegative oxygen atoms and the moderately sulfur atom (see Fig. 2. A1&B1). The inductive effect increases the polarity of O-H bonds, resulting in the easy liberation of protons. Besides, resonance effects (see Fig. 2. A2&B2) also contribute to an increase in these polarity. The strong polarity of O-H bonds can explain for the strong
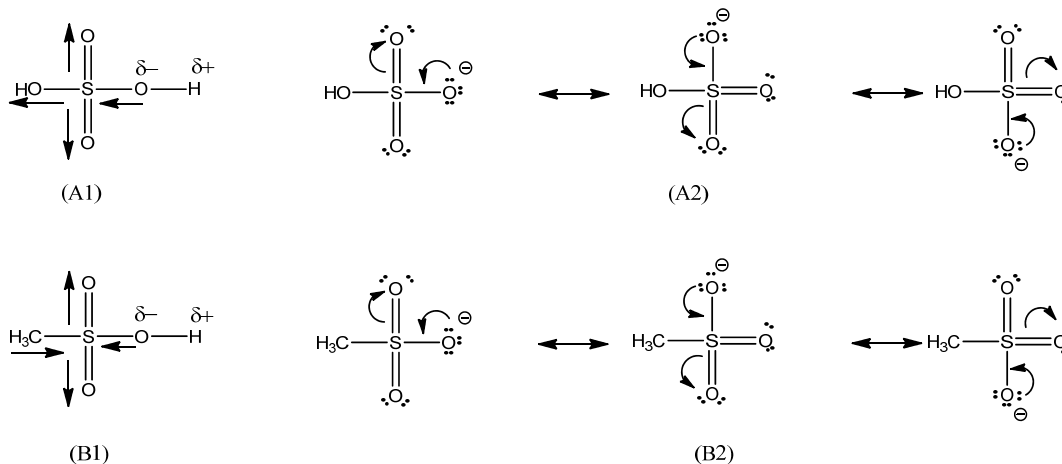
Fig. 2. Inductive and resonance effects of sulfuric acid (A1&A2) and MSA (B1&B2).

Table 2. The equivalent conductance (S·cm^2/mol) of aqueous solutions of sulfuric acid and MSA[14]

Acid	2 N	1 N	0.5 N	0.1 N	0.05 N	0.01 N
Sulfuric	413.84	444.88	464.12	529.08	572.76	699.40
Methanesulfonic	232.97	299.60	336.47	372.74	381.76	391.78

acidic properties of sulfuric acid and MSA. The higher acidity of sulfuric acid compared to MSA was ascribed to the positive inductive effect due to electron donating group of methyl group (CH$_3$-) in MSA. Moreover, these inductive and resonance effects lead to the stability of hydrogen sulfate (HSO$_4^-$) and methane sulfonate (CH$_3$SO$_3^-$) ions due to the stabilization of the negative charge on the oxygen atom after being deprotonated[19]. This can be shown in the solubility of their metal salts (see Table 2). Most metal methanesulfonates and hydrogen sulfates are highly soluble in aqueous solutions. Only some metal sulfates such as Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag$^+$, and Pb^{2+} are sparingly soluble in water. On the other hand, some studies have pointed out that MSA aqueous solutions can suppress the oxidation of metal ions to their high valence states[13,14]. For instance, Sn(II) in the aqueous MSA solution can exist at the lower valence state and the oxidation to Sn(IV) would not occur. The oxidative stability of metal ions in MSA solution is ascribed to the formation of highly stable metal complexes[12,24]. Thus, MSA will bring many advantages to extractive metallurgy as well as electrochemical processes in the production of metals from their solutions.

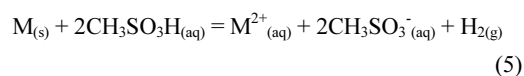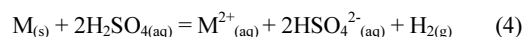## 2.2. Dissolution behavior of individual metals by acid solutions

To compare the reactivity of MSA and sulfuric acid in aqueous solutions, the dissolution of Co and Ni metal is compared under the same experimental conditions. The data was obtained from our previous published data[16]. Concentration of the two acids in the aqueous solutions was fixed at 2.0 mol/L. The experimental leaching conditions were as follows: 60°C temperature, 300 rpm stirring speed, 120 min reaction time, and 50 g/L pulp density. In Fig. 3, the dissolution percentage of
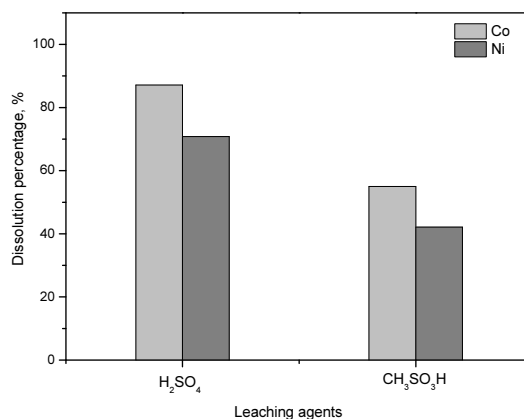
Fig. 3. The dissolution percentage of Co and Ni metal in 2.0 mol/L H$_2$SO$_4$ and MSA with 50 g/L at 60°C for 120 minutes.

Table 3. The aqueous saturation solubility of metal salts at 22°C[14]

Metal ions	Methanesulfonate	Sulfate
Li$^+$	7.06	8.17
Mg^{2+}	1.40	2.63
Ca^{2+}	2.92	0.02
Sr^{2+}	2.55	0.00
Ba^{2+}	1.59	0.00
Mn^{2+}	2.90	3.52
Co^{2+}	2.53	2.16
Ni^{2+}	2.13	2.44
Cu^{2+}	2.00	1.35
Ag$^+$	3.72	0.06
Pb^{2+}	2.60	0.00

Co and Ni by MSA solution were 70.8 and 42.1% and that by H$_2$SO$_4$ solution were 87.1 and 55.0%, respectively. These results showed that the dissolution of metals in sulfuric acid solution was more effective than that of MSA, which can be attributed to the stronger activity of hydrogen ions in sulfuric acid compared to MSA solution. The difference in the effect of the respective anions, CH$_3$SO$_3^-$ and HSO$_4^-$ on the dissolution of metals is negligible. This could be due to the insignificant

difference in the affinity of two anions to Co(II) and Ni(II) ions, which might be recognized in the solubility of their salts in water (see Table 3). Besides, the dissolution percentage of Co was higher than that of Ni in these acids, which was ascribed to the difference in their nature such as crystalline structure, reduction potentials of metals (= -0.28V and = -0.25V) and stable complexes in the solution. Dissolution reactions of metals can be written as

$$M_{(s)} + 2H_2SO_{4(aq)} = M^{2+}_{(aq)} + 2HSO_4^{2-}_{(aq)} + H_{2(g)} \qquad (4)$$

$$M_{(s)} + 2CH_3SO_3H_{(aq)} = M^{2+}_{(aq)} + 2CH_3SO_3^{-}_{(aq)} + H_{2(g)} \qquad (5)$$

where M denotes Co or Ni.

Thus, the dissolution efficiency of Co and Ni metal in the MSA and sulfuric acid solutions mainly depends on the redox potentials of the metals and the activity of hydrogen ions in the solutions.

3. Conclusions

Chemical reactivity between MSA and sulfuric acid was compared on the basis of their structure and dissolution data of metals in their aqueous acidic solutions investigated. The electronic effects such as inductive and resonance have significant contribution for the difference in the chemical properties of these acids such as acidity, solubility of metal salts and affinity to metal ions. The dissolution efficiency of Co and Ni mainly depends on the activity of hydrogen ions in the acid solution, resulting in more effective dissolution by sulfuric acid solution than MSA solution in the same experimental condition. Thus, these data showed MSA can be used as a lixiviant in the recovery of metals from the primary and secondary resources. And, further studies are necessary for the application of MSA in the real operation.

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