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# Effect of inhibitors on corrosion behavior of copper-nickel in concentrated lithium bromide solution at high temperature<sup>①</sup>

HUANG Nai-bao(黄乃宝), LIANG Cheng-hao(梁成浩), TONG Da-wei(佟大维)  
(School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China)

**[Abstract]** The conventional mass-loss tests and the electrochemical techniques were used to study the inhibition action of LiOH and Na<sub>2</sub>MoO<sub>4</sub> either individually or in different combination for copper-nickel alloy in boiling 65% LiBr solution. It indicates that the corrosion rate of copper-nickel is decreased when LiOH or Na<sub>2</sub>MoO<sub>4</sub> is added to the solution individually. LiOH concentration has a double-effect on the corrosion behavior of copper-nickel. Low concentration is benefit to forming oxide film. High concentration results in dissolution of oxide film. The optimal concentration of LiOH is 0.15 mol/L. The dissolution of copper-nickel is effectively prevented when adding 200 mg/L Na<sub>2</sub>MoO<sub>4</sub> to boiling 65% LiBr solution with 0.15 mol/L LiOH. The inhibition mechanism is considered that the films of Cu, Ni, Mo oxides and deposited nonprotective in soluble CuBr on the surface of metal could prevent Br<sup>-</sup> ion from absorption, which prevent alloy dissolving.

**[Key words]** inhibitor; copper-nickel; lithium bromide; corrosion

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## 1 INTRODUCTION

With the increasing of consciousness of environmental protection, more and more products are required not to pollute environment. Lithium bromide absorption chiller, which uses LiBr-H<sub>2</sub>O as work substance, is gradually substituted for refrigerator making use of freon as refrigerant and is applied in the whole world. Lithium bromide solution, which is a highly corrosive substance, attacks stainless steel, carbon steel, and copper alloy. The corrosion of copper-nickel alloy affects not only the service life of the machine but also its refrigerating efficiency. In industry, the most effective and economic method is to add different inhibitors to the system, such as LiOH, Li<sub>2</sub>MoO<sub>4</sub>, Li<sub>2</sub>CrO<sub>4</sub>, Na<sub>2</sub>MoO<sub>4</sub>, LiNO<sub>3</sub>, PMA/Sb etc. The study of corrosion behavior of carbon steel in lithium bromide heavy brine has been documented by many authors<sup>[1-6]</sup>. Refs. [7-10] to corrosion caused by LiBr on copper-nickel alloy have been reported. The objective of the present work is to study the corrosion behavior of copper-nickel in 65% LiBr heavy brine solution at 173 °C with different concentrations of LiOH, Na<sub>2</sub>MoO<sub>4</sub> by means of electrochemical measurements and mass-loss tests. The effect and the inhibition mechanism of LiOH, Na<sub>2</sub>MoO<sub>4</sub> are also discussed.

## 2 EXPERIMENTAL

The material tested was copper-nickel, its chemical composition is shown in Table 1. Test solutions were prepared from a reagent grade LiBr and deionized water. LiOH and Na<sub>2</sub>MoO<sub>4</sub> were analytical

reagents.

**Table 1** Chemical compositions of specimens (%)

Ni	Fe	Mn	Pb	Zn	Cu
9.5	1.3	0.70	0.033	0.037	Bal.

Cylinder specimens were used for mass-loss tests (15.84 mm O D, 14.20 mm I D, 13 mm length), and rectangular specimens were utilized in electrochemical measurements. All specimens were abraded with 1000-grit SiC papers, and rinsed with deionized water and acetone. 1 cm<sup>2</sup> was exposed to the solution in electrochemical measurements, and the other was covered with Shir-Etsu Silicone coating.

With a polytetrafluoroethylene (PTFE) cylinder bush (50 mm I D, 65 mm length), stainless steel autoclaves were used in immersion experiments. The 80 cm<sup>3</sup> of 65% LiBr solution, containing different concentration of LiOH, Na<sub>2</sub>MoO<sub>4</sub>, was deoxygenated for 1 h. The autoclave was then held at predetermined temperature (173 °C) for 200 h in a thermostat (Kosumosu AT-S13). The specimens were cleaned by 5% HCl for 3 min at room temperature, and then the corrosion rate was determined from the mass changes of the specimens.

Electrochemical measurements were conducted by using a three-electrode system and HA-501 potentiostat/galvanostat. The specimen was placed in a glass vessel with a platinum counter electrode and an Ag/AgCl reference electrode. The solution was deoxygenated with nitrogen during the measurement. After the solution was boiled and the mixture poten-

tial was stable, the anodic polarization curve was measured with a scan rate of 20 mV/min.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of LiOH concentration on corrosion behavior of copper-nickel

Fig. 1 and Fig. 2 show the effect of LiOH concentration on immersion corrosion rate and anodic polarization characteristic respectively. According to Fig. 1, the corrosion rate is gradually decreased with increasing LiOH concentration. The minimum of corrosion rate is obtained, which is  $54.6348 \mu\text{m}\cdot\text{a}^{-1}$ , when LiOH concentration is increased to 0.15 mol/L. Moreover, the dissolution of copper-nickel is accelerated when the concentration of LiOH is more than 0.15 mol/L. In Fig. 2, it indicates that copper-nickel is in active dissolution when there is no LiOH in boiling 65% LiBr solution. Corrosion potential moves towards positive direction, and there occurs passive region when LiOH is added to 65% LiBr solution. Furthermore, the passive

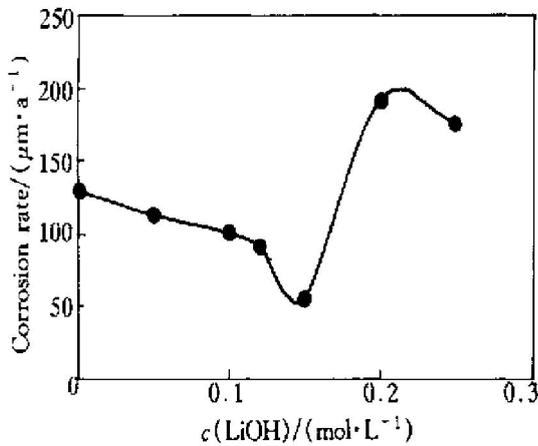


Fig. 1 Effect of LiOH concentration on corrosion rate of copper-nickel in 65% LiBr solution at 173 °C

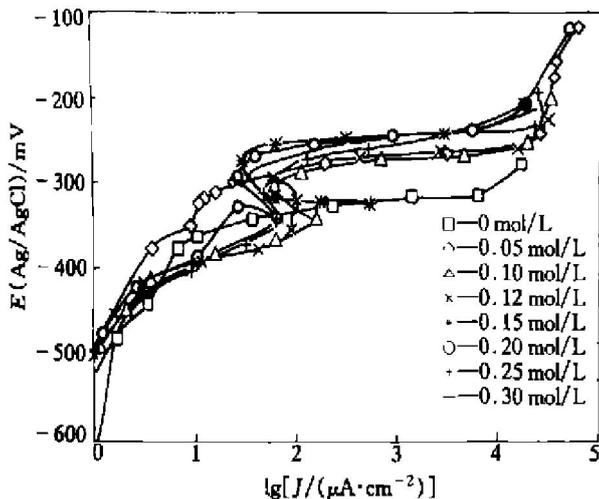
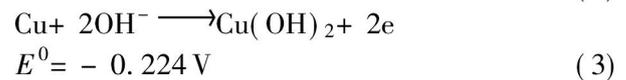
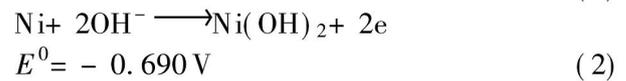
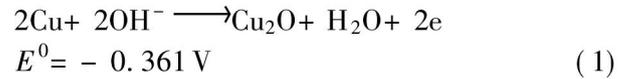


Fig. 2 Effect of LiOH concentration on anodic polarization curves of copper-nickel in 65% LiBr solution at 173 °C

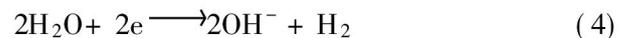
region is broadened with increasing LiOH concentration. It is increased to 49 mV, which is the maximum, when the concentration is raised to 0.15 mol/L. And then, the passive region is decreased after the concentration of LiOH is raised more than that value. The result is in accordance with that of Fig. 1.

Electrochemical reactions of copper-nickel in concentrated LiBr solution at high temperature are as follows, and the standard electrode potential<sup>[11]</sup> of these reactions are also shown in the follows.

Anode:



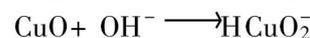
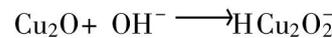
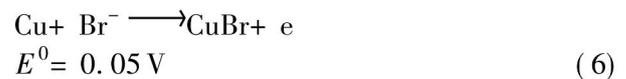
Cathode:



There are reducing reaction of trace amount of oxygen and oxidation reactions of iron, aluminum, etc.



Because  $\text{Br}^-$  ion is more aggressive in concentrated LiBr at high temperature, and the adsorption of  $\text{OH}^-$ ,  $\text{Br}^-$  ion on the surface of electrode are prior to other ions, and the following reactions can be found<sup>[12]</sup>.



It indicates that LiOH concentration has a double-effect on the corrosion behavior of copper-nickel in concentrated LiBr solution at high temperature. Low concentration is of benefit to forming oxide film, high concentration results in the dissolution of oxide film, so, there exists optimal concentration of LiOH.  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{NiO}$  and  $\text{CuBr}$  may be coexisted on the surface of metal for the reason why the reactions ((1), (2), (3), (6)) compete with the others. On the other hand, the corrosion resistance of copper alloy is improved by adding nickel. We can find that the passive region is increased with increasing LiOH concentration. On the contrary, it is decreased when the concentration of LiOH exceeds one value. The reason is that concentrated LiOH accelerates the dissolve of oxide films of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ . Moreover, the nonprotective insoluble  $\text{CuBr}$  film is a loosely adherent corrosion product which is thought to be incapable of protecting the copper-nickel surface from the attack of bromine ion and hindering the dissolution of the metal

to soluble species<sup>[10]</sup>.

### 3.2 Effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on corrosion resistance of copper-nickel

The effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on the corrosion resistance of copper-nickel is shown in Fig. 3 and Fig. 4. It is seen that the corrosion rate of copper-nickel is gradually reduced with the increasing of Na<sub>2</sub>MoO<sub>4</sub> when its concentration is less than 200 mg/L. The least corrosion rate is 86.175 μm•a<sup>-1</sup> when the concentration of Na<sub>2</sub>MoO<sub>4</sub> is 200 mg/L. The value of corrosion rate changes a little after the concentration of Na<sub>2</sub>MoO<sub>4</sub> is greater than 200 mg/L. The above-mentioned results show that the adding of Na<sub>2</sub>MoO<sub>4</sub> efficiently improves the corrosion resistance of copper-nickel. The rule of passive region in anodic polarization is the same as that of corrosion rate mentioned above. Since the solubility of Na<sub>2</sub>MoO<sub>4</sub> reaches its limit when its concentration is more than 200 mg/L, concentrated Na<sub>2</sub>MoO<sub>4</sub> has no effect on the passive region and reducing corrosion

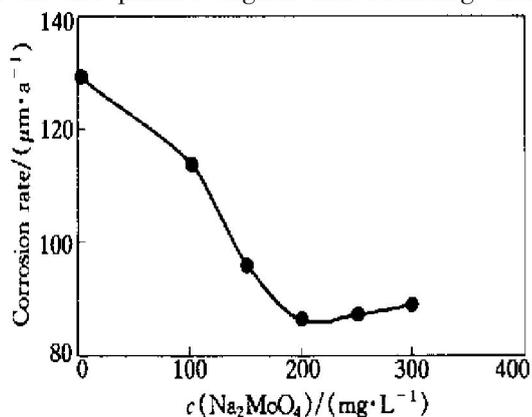


Fig. 3 Effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on corrosion rate of copper-nickel in 65% LiBr solution at 173 °C

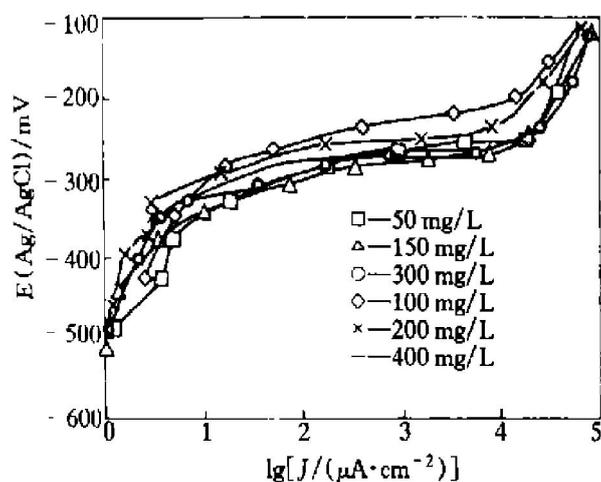
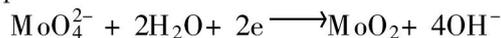


Fig. 4 Effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on anodic polarization curves of copper-nickel in 65% LiBr solution at 173 °C

rate. LiBr solution is an alkaline solution, the reduction of MoO<sub>4</sub><sup>2-</sup> may be emerged on the anodic surface except these reactions mentioned above.



Since MoO<sub>4</sub><sup>2-</sup> ion has larger ionic radius, which hinders the adsorption of Br<sup>-</sup> after being adhered, and the reduction product (MoO<sub>2</sub>) coexists with oxide of copper, the corrosion rate of alloy is decreased by collective effect. The passive region is observed and has the increased trend with increasing Na<sub>2</sub>MoO<sub>4</sub> concentration on anodic polarization curve. The passive region in 65% LiBr solution containing Na<sub>2</sub>MoO<sub>4</sub> is smaller than that containing LiOH. The phenomenon can be explained from the following aspects: the first is the diffusive rate of MoO<sub>4</sub><sup>2-</sup> ion is slower than that of OH<sup>-</sup> ion, the second is the preferential absorption of OH<sup>-</sup> ion which hinders that of MoO<sub>4</sub><sup>2-</sup> ion, the third is OH<sup>-</sup> ion participates in electrode reaction. They result in that OH<sup>-</sup> ion has strong effect on anti-corrosion.

### 3.3 Effect of LiOH combining with Na<sub>2</sub>MoO<sub>4</sub> on characteristic of copper-nickel

Fig. 5 shows the effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on the corrosion behavior of copper-nickel in boiling 65% LiBr solution containing 0.15 mol/L LiOH. The result, as shown in Fig. 5, suggests that the minimum corrosion rate, which is 40.5124 μm•a<sup>-1</sup>, is attained when the concentration of Na<sub>2</sub>MoO<sub>4</sub> is 200 mg/L. The value is smaller than that in Fig. 3. Moreover, it is the smallest among the values obtained in Fig. 1, Fig. 3 and Fig. 5, although the tendency of the curve is the same as that in Fig. 3 and Fig. 5. The result indicates that the corrosion resistance of copper-nickel is notably improved when 0.15 mol/L LiOH was combined with 200 mg/L Na<sub>2</sub>MoO<sub>4</sub>. Fig. 6 shows the SEM surface micrograph of copper-nickel after it was immersed in 65% LiBr solution containing 0.15 mol/L LiOH and 200 mg/L

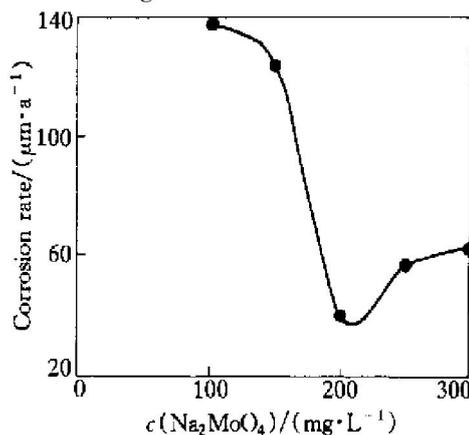
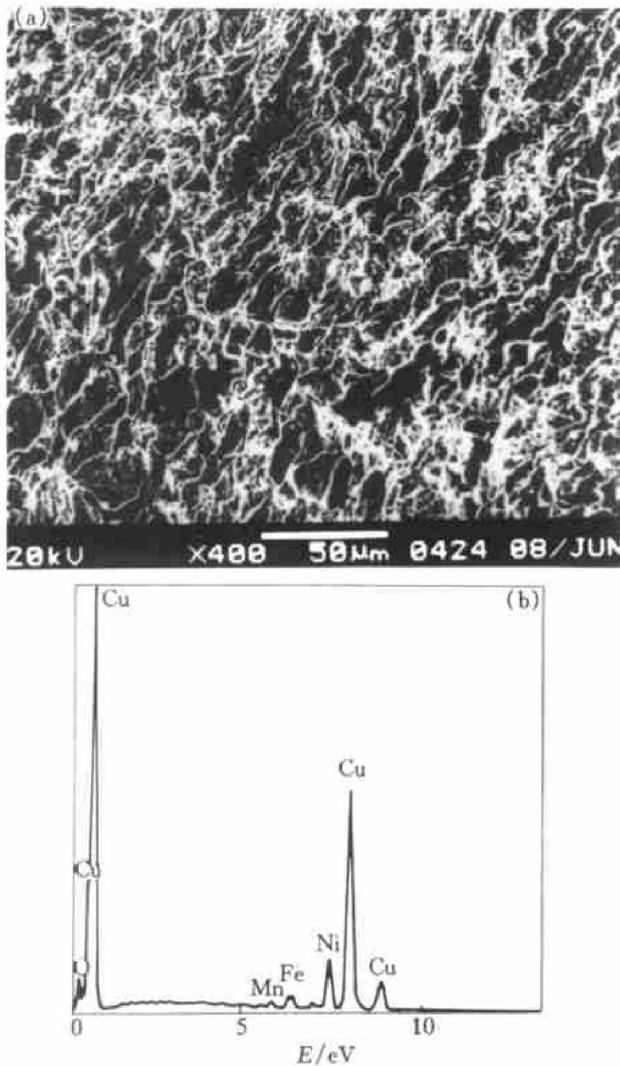


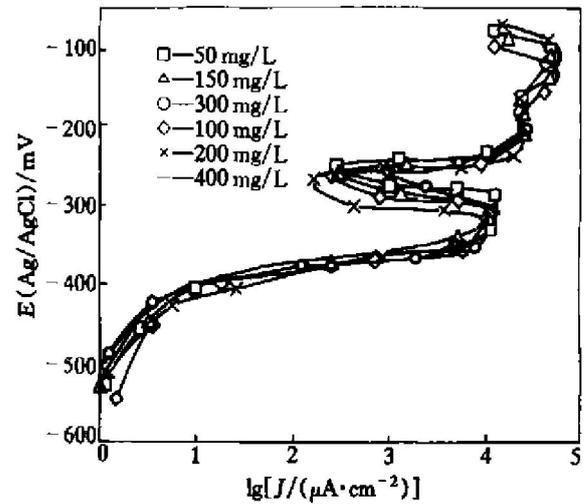
Fig. 5 Effect of Na<sub>2</sub>MoO<sub>4</sub> concentration on corrosion rate of copper-nickel in 65% LiBr+ 0.15mol/L LiOH solution at 173 °C



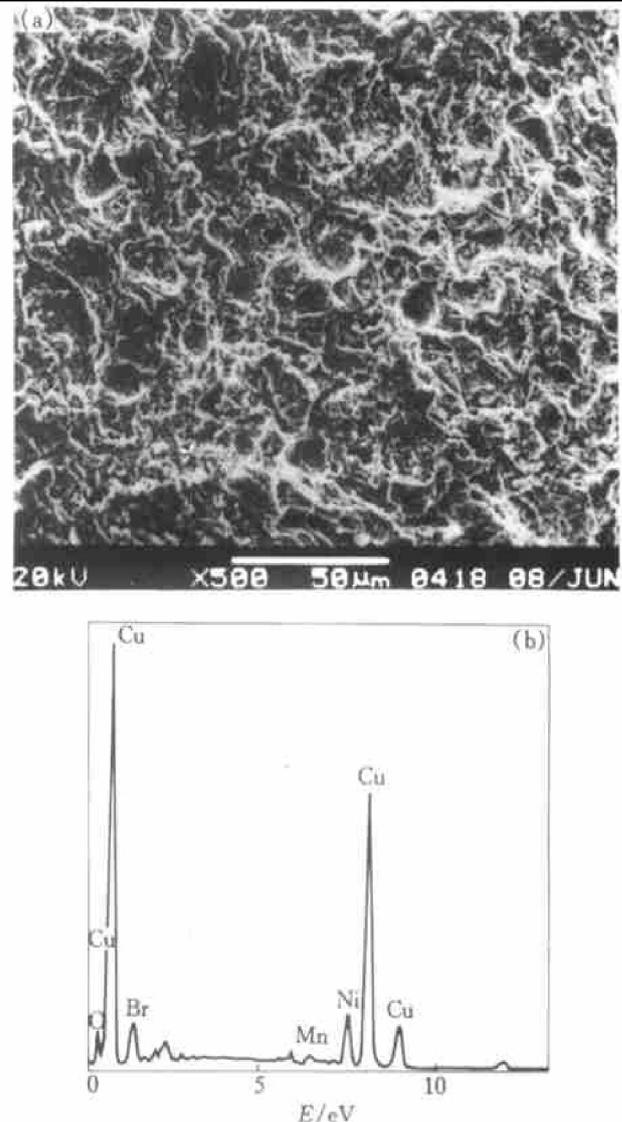
**Fig. 6** SEM surface micrograph (a) and EDX spectrum (b) of copper-nickel

$\text{Na}_2\text{MoO}_4$  for 200 h. It manifests that general corrosion is observed except a handful of oxide film existing on the surface of metal. In EDX figure, besides the peaks of Cu and Ni, the peaks of O, Mn, Fe are also appeared. Oxide films of  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$  formed on the surface of metal are confirmed by X-ray diffractometer.

In Fig. 7, the maximum passive region, which is 51 mV, is obtained when the concentration of  $\text{Na}_2\text{MoO}_4$  is increased to 200 mg/L. The value is larger than those values we have gotten in 65% LiBr containing either LiOH or  $\text{Na}_2\text{MoO}_4$  individually. We can draw the conclusion that there has combined effect between LiOH and  $\text{Na}_2\text{MoO}_4$ . Second passive region is observed on anodic polarization curve. The SEM surface micrograph of copper-nickel after appearing second passive region, which is rinsed with deionized water and acetone, is shown in Fig. 8. General corrosion is also observed except small quantity of oxide film. Bromide of copper may be existed on the surface of alloy besides oxide of copper, nickel, for the peaks of O, Br, Mo coexist with that of Cu, Ni in EDX figure (see Fig. 8). With

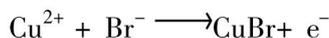


**Fig. 7** Effect of  $\text{Na}_2\text{MoO}_4$  concentration on anodic polarization curve of copper-nickel in 65% LiBr + 0.15 mol/L LiOH solution at 173 °C



**Fig. 8** SEM surface micrograph (a) and EDX spectrum (b) of second passivated copper-nickel

the dissolution of anode, the following reaction is accelerated for the concentration of  $\text{Cu}^{2+}$  is increased in LiBr solution.



Nonprotective insoluble CuBr film sedimentates on the surface of metal and coexists with oxide of Cu, Ni, Mo, whose combined effect hinders the absorption of  $\text{Br}^{-}$  and the dissolution of alloy. It results in second passive region occurred on anodic polarization curve. With increasing current density, second passive region disappears and active dissolution is observed as CuBr film has loosely binding power with metal and easily breaks away from the surface of metal. The phenomena that there are no second passive region on the anodic polarization curves of copper-nickel in 65% LiBr solution with LiOH or  $\text{Na}_2\text{MoO}_4$  individually can confirm the combined effect between LiOH and  $\text{Na}_2\text{MoO}_4$ .

#### 4 CONCLUSIONS

1) Either LiOH or  $\text{Na}_2\text{MoO}_4$  is added to the concentrated LiBr solution at high temperature, the corrosion rate of copper-nickel is decreased. The inhibition efficiency of  $\text{Na}_2\text{MoO}_4$  is less than that of LiOH. LiOH concentration has a double-effect on the corrosion behavior of copper-nickel. Low concentration is of benefit to forming oxide film. High concentration results in dissolution of oxide film. The optimal concentration of LiOH is 0.15 mol/L.

2) The dissolution of copper-nickel is remarkably inhibited when adding 0.15 mol/L LiOH and 200 mg/L  $\text{Na}_2\text{MoO}_4$  to boiling 65% LiBr solution.

3) Since the small quantity oxide films of Cu, Ni, Mo are advantage to the absorption of insoluble CuBr, second passive region is observed on the anodic polarization curve.

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