

The Effect of Some Binary Additive Systems in the Electrodeposition of Cadmium

Kyung Ho Lee

Department of Chemistry, Baylor University, U.S.A

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카드뮴 전해석출에서의 이성분첨가물계의 효과

이경호

미국 베일러대학교 화학과

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요약 : 이성분계 첨가물을 이용한 카드뮴 석출과 수소 생성의 상대적인 속도를 조절할 수 있는 가능한 방법에 대하여 조사하였다. 수소를 발생하는 물의 전기환원을 억제하는 소수성 필름을 형성할 수 있는 벤질 알코올을 첨가제 중의 하나로 선택하였다. 다른 한 가지 첨가제는 카드뮴(II) 이온의 친수성을 약화시킴으로써 소수성 벤질 알코올 필름층을 쉽게 가로질러 환원극에 전착시킬 수 있는 것을 선택하였다. 전압 전류 효율 연구로부터 이온쌍과 착물 첨가제가 벤질 알코올 필름 존재하에서 카드뮴의 환원을 촉진시킬 수 있다는 것을 확인하였다. 벤질 알코올 필름은 나트륨 이온과 카드뮴의 염화착물을 형성하는 이온쌍을 얻기에 충분하도록 전극 주위의 유전상수를 낮추고, 카드뮴의 환원을 촉진시킨다. 이러한 환원의 촉진은 염화물이 존재하지 않는 황산염 용액에서는 일어나지 않는다. 왜냐하면 카드뮴은 본래 아쿠아 착물과 이온쌍으로 존재하여 카드뮴의 환원을 촉진시키지 못하고 환원을 방해시키기 때문이다.

Abstract : An investigation was made of possible ways in which one could control the relative rates of cadmium deposition and hydrogen evolution by binary additive systems. Benzyl alcohol was employed as an additives due to its ability to form a hydrophobic film which inhibit the electroreduction of water to form hydrogen. The second additive was chosen to make the cadmium(II) ion less hydrophilic and increase its ability to cross the hydrophobic benzyl alcohol film and be electrodeposited at the cathode. It was shown by voltammetric and current efficiency studies that ion pairing and complexing additives could be used to accelerate the reduction of cadmium in the presence of the benzyl alcohol film. It was also shown that the benzyl alcohol film lowered the dielectric constant of the solution near the electrode enough to obtain ion pairing between the sodium ion and the negative chloride complex of cadmium and accelerate the reduction of the cadmium. This acceleration did not occur in the sulfate solution in the absence of chloride since cadmium(II) is primarily present as a positive aquo complex and ion pairing, if it occurred, would not accelerate but would hinder reduction of cadmium.

Key words : electrodeposition, ion pairing, additive, complexing agent, current efficiency

1. Introduction

A series of studies have been made on the mechanism of action of additives in electrochemical processes in aqueous system. These mechanisms have been summarized in several reviews.¹⁻⁵ The basic model used in these studies is based on the fact that the electrolysis involves at least two competing processes. Oxidation of organic compounds competes with that of water, while electrodeposition of metals competes with the evolution of hydrogen. The additives have been employed as selective catalysts and inhibitors of these competing processes to enhance the electrolysis efficiency. It has been shown that one can inhibit the oxidation of water by the formation of hydrophobic film⁶⁻⁹ and the reduction of water by the formation of insoluble films of inorganic compounds.¹⁰⁻¹³ In addition it has been shown that one can catalyze the electrodeposition of metals by a various techniques.^{1,5} Catalytic effects of additives could cause either decrease of the reduction potential of metal or increase of limiting current.¹⁴⁻¹⁶

The use of hydrophobic organic films in the oxidation experiments was shown to increase the oxygen evolution potential by 0.9V and under some circumstances by 1.7V^{6,7}. This allows one to oxidize various organic compounds in aqueous systems that could not normally be oxidized in the absence of these additives. The use of these hydrophobic additives has not been very successful in the electrodeposition of metals. The normal brighteners and related additives generally shift the hydrogen evolution potential by only 0.2 to 0.3V¹⁷, and additives that cause large shift in the hydrogen reduction potential also cause large shift of the cadmium reduction potential. It is expected that the metal ion in the aqueous system is bonded to water or a hydrophilic ligand so that any hydrophobic layer on the electrode will inhibit not only the water but also the hydrophilic metal ion from approaching to the electrode.

It was decided to investigate the use of binary additive systems in the electrodeposition of metals. One additive was selected to form a hydrophobic layer on the cathode hindering the reduction of water. The second additive was selected to interact with the metal ion to form a species that aid in making the metal ion more hydrophobic and thus accelerate its migration through the film to the cathode.

Cadmium(II) was chosen as the metal ion for the study, because it formed a number of complexes, and in neutral solutions it was plated along with appreciable amounts of hydrogen. Thus, changes in the ratio of hydrogen to cadmium deposited could be readily observed. The primary goal was to obtain an understanding of the behavior of systems containing more than one additive. It is hoped that one can eventually extend the hydrogen evolution potential enough to be able to deposit some of the difficultly depositable refractory metals, such as titanium or molybdenum.

2. Experimental

Voltammetric measurements were used as the exploratory technique to determine the effect of the additives on the evolution rate of hydrogen and the deposition rate of cadmium. The voltammetric studies were followed with constant current or constant potential-current efficiency measurements. The current efficiency measurements gave a simple way of showing the composite effect of the additive on the relative reduction rate of hydrogen and cadmium over a longer period of time.

Current-voltage curves were made using a PAR polarographic analyzer. Current efficiency studies were made with constant current power supplies. The initial current-voltage measurements were made with a platinum wire cathode; however, most of the measurements were made using a cadmium plated platinum cathode. Current efficiency measurements were using copper foil cathodes(3.9~

6.6cm²) and platinum, anodes. In the voltammetric experiments a saturated calomel reference electrode was used.

A preliminary study was made on the effect of sulfonates, nitriles and various surfactants on the potential of the hydrogen evolution on a cadmium plated electrode in neutral solutions in order to find additives which would block the cathode surface enough to cause appreciable shifts in the hydrogen evolution potential. In agreement with previous work¹⁶, most of these compounds caused potential shifts of approximately 0.2V. But benzyl alcohol showed an appreciable potential shift of 0.6V in cathodic direction, indicating that this compound formed a hydrophobic barrier to reduction of water. Therefore it was chosen for further investigation as a general blocking agent.

3. Results and Discussions

3.1. Ion Pairing

Negatively charged anionic complexes of cadmium have an energy barrier to adsorption on the cathode. It has been shown^{15,16} that ion pairing of the complexes with positively charged quaternary ammonium ions reduce the repulsion between the anionic complex and cathode and thus accelerated the reduction rate of cadmium(II). The ion pairing also decreases the hydrophilic nature of the cadmium ion and thus would be expected to enhance the solubility of the cadmium chloride complex in the adsorbed benzyl alcohol layer and, as a result, should increase the rate of reduction of the cadmium.

Fig. 1 shows the effect of tetramethylammonium chloride(TMAC) on the current-voltage curve for the reduction of cadmium chloride complex. It can be seen that, in agreement with the observation made in the absence of the film^{15,16}, the limiting current for cadmium reduction was higher in the presence of TMAC. However, when tetrabutyl ammonium chloride(TBAC) was substituted for

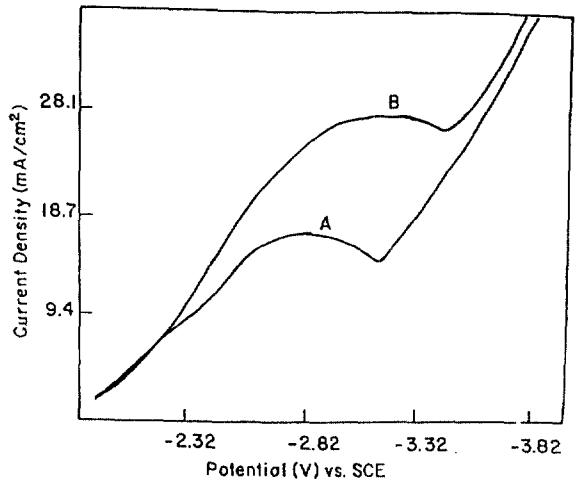


Fig. 1. Current-voltage curves for the reduction of 5mM cadmium nitrate in 0.1M sodium chloride in the presence of (A) 5.8mM benzyl alcohol and (B) 5.8mM benzyl alcohol plus 0.12mM tetramethyl ammonium chloride(TMAC).

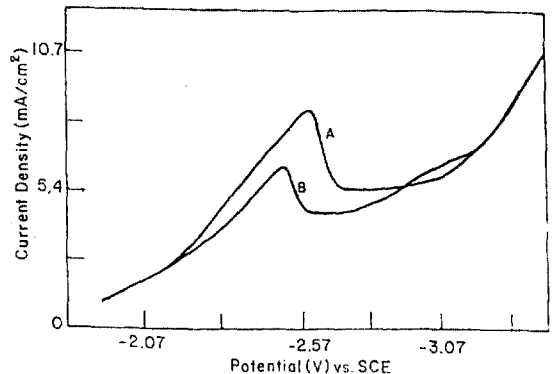


Fig. 2. Current-voltage curves for the reduction of 5mM cadmium nitrate in 0.1M sodium chloride on a cadmium plated platinum cathode in the presence of (A) 5.8mM benzyl alcohol and (B) 5.8mM benzyl alcohol plus 22mM TBAB.

TMAC a distinct difference was observed. In the absence of the film it had been observed that tetramethylammonium(TMA), tetrabutylammonium(TBA), and tetraethylammonium(TEA) ions accelerated the reduction of negatively charged complexes of cadmium^{15,16}; however, in the presence of the film, tetrabutylammonium ion did not accelerate

Table 1. The Effect of Quarternary Ammonium Salts on the Current Efficiencies for Electrodeposition of Cadmium on Copper in a 100mL 5mM Cadmium Nitrate Solution in 0.01M Sodium Chloride at 50mM for 1hr.

Amts. of Additives Present (10^{-4} mol)	Current Efficiency(%)
0.048 BzOH	48.9
0.048-BzOH, 0.01 TBAB*	43.7
0.048-BzOH, 0.01TMAC**	54.3

* TBAB : Tetrabutylammonium bromide

** TMAC : Tetramethylammonium chloride

the reduction of cadmium ion. In fact, as indicated by the decrease in the reduction current in Fig. 2, it inhibits the reduction of the metal ion.

Similar results were observed in the current efficiency measurements. Table 1 shows that addition of TMAC increases the current efficiency while addition of TBAB causes decreases in the current efficiency. Apparently, the benzyl alcohol film blocks the migration of the larger TBA-cadmium chloride ion pair to the electrode while the smaller TMA-cadmium chloride ion pair migrates readily to the electrode.

3.2. The effect of the benzyl alcohol on ion pairing

The attraction force involved in ion pairing is generally treated as a coulombic interaction in which the force of attraction is inversely proportional to the dielectric constant. One can increase the force of attraction between the ions by a low dielectric constant medium. The effect of the lowering of the dielectric constant of the solvent on ion pairing effects in electrodeposition has been demonstrated.¹⁵ Even though benzyl alcohol is treated as an inert hydrophobic filming agent it also causes a decrease in the dielectric constant near the electrode. In Fig. 3 one can see from the current-voltage curve that the formation of benzyl alcohol film in the cad-

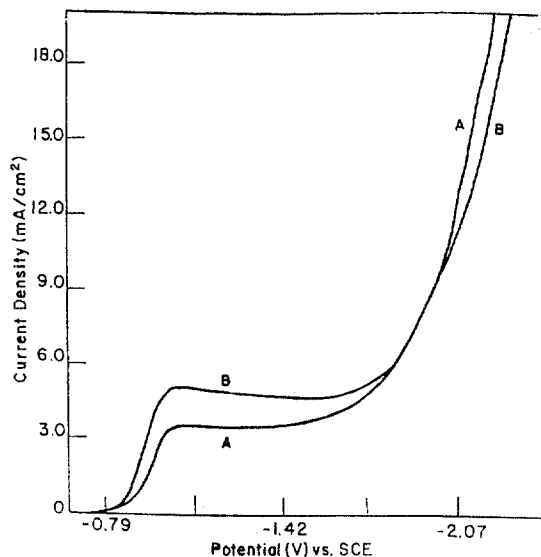


Fig. 3. Current-voltage reduction curves obtained in 0.1M sodium chloride containing (A) 10mM cadmium chloride and (B) 10mM cadmium chloride containing 9.6mM benzyl alcohol.

mium(II)-sodium chloride media causes an increase in the limiting current for deposition of cadmium. It was concluded that this increase occurs because of an increase in ion pairing between the sodium ion and the negative chloride complex in the low dielectric constant benzyl alcohol film, decreasing the repulsion between the cathode and the negative cadmium chloride complex.

Fig. 4 shows the effect of concentration of benzyl alcohol on the current efficiency. Since water is not a charged ion there are no ion pairing effects involved in the reduction of water. Thus one expects to observe an increase in the current efficiency as the amount of benzyl alcohol adsorbed on the cathode increases, and one can see that this is exactly what occurs at low concentrations of the alcohol. At some point the electrode becomes completely covered with the film and begins to block cadmium ions. A decrease in the current efficiency which begins at 7.2mM benzyl alcohol is interpreted as being related to complete coverage; at concentrations higher than 9.6mM the current efficiencies became

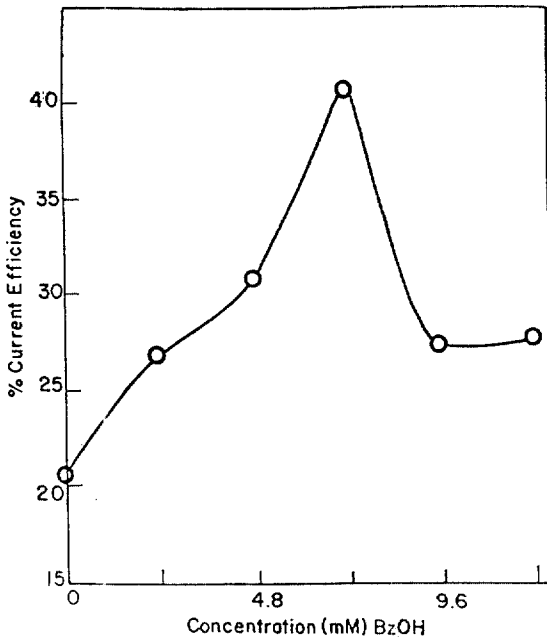


Fig. 4. The effect of benzyl alcohol on the current efficiencies for electrodeposition of cadmium on a copper cathode with a platinum anode from 100ml of a solution containing 0.01M cadmium chloride, and 0.10M sodium chloride at 50mA for 60min.

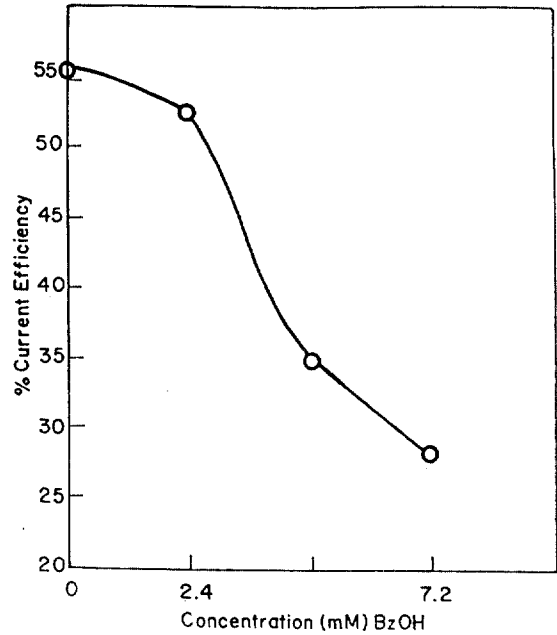


Fig. 5. The effect of benzyl alcohol on the current efficiencies for electrodeposition of cadmium on a copper cathode using a platinum anode from 100ml of a solution containing 0.01M cadmium sulfate and 0.10M sodium sulfate at 50mA for 60min.

approximately constant indicating that one is forming multilayers, and thus the dielectric constant at the electrode surface did not change appreciably.

In an aqueous sulfate system, the sulfate, which is a weak complexing agent, does not strongly complex with cadmium(II) and, as a result, cadmium(II) is present primarily as a positive aquated complex. There is no repulsive barrier between the cathode and the positive ion. When ion pairing occurs, if it has any effect, it will inhibit the deposition of cadmium¹⁸, and one will observe a decrease in the current efficiency. This is seen in Fig. 5.

3.3. Complexing Agents

Much work has been done on the use of high ion concentrations of complexing agents in plating in aqueous solutions. In these systems the complex ions formed are thermodynamically more stable

than in the aqueous complex. The reduction potential shift in the cathodic direction as the complex is formed indicates the increased barrier to reduction. Complexing agents are especially used in electrodeposition from basic solutions in order to prevent precipitation of metal hydroxides. In addition, many of the complexing agents are organic compounds with hydrophobic groups and it was felt that this increased hydrophobicity might increase transport across the hydrophobic barrier even at very low concentrations.

Ethylene diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (EDA), forms complexes with a number of transition metal ions including cadmium(II) in which the two amine groups replace water ligands. In the case in which both amino groups are bonded to the metal, Fig. 6, it is obvious from the structure that the hydrophobic ethylene groups will make the ion

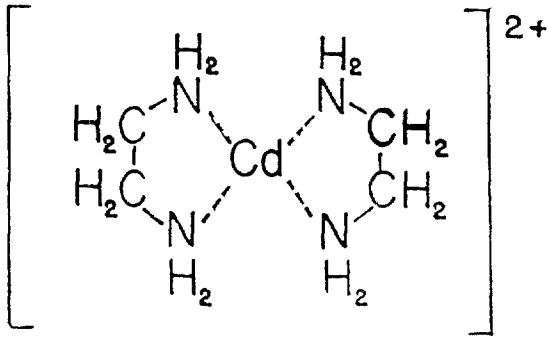


Fig. 6. A sketch of the structure of the complex Cd (EDA)₂(II)

Table 2. The Effect of Benzyl Alcohol on the Current Efficiency for Cadmium Deposition in an Ethylene Diamine Solution (Experimental Conditions : 0.04M H₂SO₄, 5mM Cd(NO₃)₂, 0.12M Ethylene Diamine ; Controlled Potential, -2.04V for 40min., Cd Plated Platinum Cathode(0.4cm²), Pt Anode(5.4cm²) SCE Reference Electrode).

Additive	Current Efficiency(%)
None	24.0%
5.8mM benzyl Alcohol	52.5%

more hydrophobic.

All the current efficiency experiments had to be performed in the presence of the complexing agent, so that the metal ion would not precipitate in the basic solutions. Table 2 shows the effect of benzyl alcohol on the current efficiency in a solution containing amine. It can be seen that benzyl alcohol caused an appreciable rise in the current efficiency, indicating that benzyl alcohol markedly inhibits the evolution of hydrogen but does not appreciably inhibit the rate of reduction of the cadmium(II) ethylene diamine complex.

4. Conclusions

The results presented here indicate that in some binary additive systems one can visualize the ac-

tion of some additives as hydrophobic films that repulse the hydrophilic water and hydrated or ligated metal ions. Other additives can be chosen to interact with the hydrophilic metal ions producing less hydrophilic species that will more readily migrate across the hydrophobic film and thus accelerate the reduction of these ions.

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