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REFERENCES

1. P. Monnartz, *Metallurgie*, **8**, 161 (1911).
2. H.-J. Rocha and G. Lennartz, *Arch. Eisenhüttenwes.*, **26**, 117 (1955).
3. H. H. Uhlig and G. E. Woodside, *J. Phys. Chem.*, **57**, 280 (1953).
4. K. Osozawa and H. J. Engell, *Corros. Sci.*, **6**, 389 (1966).
5. S. Fujimoto, R. C. Newman, G. S. Smith, S. P. Kaye, H. Kheyrandish, and J. S. Colligon, *ibid.*, **35**, 51 (1993).
6. K. Sieradzki and R. C. Newman, *This Journal*, **133**, 1979 (1986).
7. S. Qian, R. C. Newman, R. A. Cottis, and K. Sieradzki, *ibid.*, **137**, 435 (1990).
8. K. Asami, K. Hashimoto, and S. Shimodaira, *Corros. Sci.*, **18**, 551 (1978).
9. P. Marcus and I. Olefjord, *ibid.*, **28**, 589 (1988).
10. S. Haupt and H.-H. Strehblow, *ibid.*, **29**, 163 (1989).
11. R. Kirchheim, B. Heine, H. Fischmeister, S. Hofmann, H. Knote, and U. Stolz, *ibid.*, **29**, 899 (1989).
12. J. E. Castle and J. H. Qiu, *ibid.*, **29**, 591 (1989).
13. I. Olefjord and L. Wegrelius, *ibid.*, **31**, 89 (1990).
14. S. Mischler, A. Vogel, H. J. Mathieu, and D. Landolt, *ibid*, **32**, 925 (1991).
15. D. Landolt, in *Advances in Localized Corrosion*, H. Isaacs, U. Bertocci, J. Kruger, and S. Smialowska, Editors, NACE, Houston, TX (1990).
16. P. Schmuki, S. Virtanen, A. J. Davenport, and C. M. Vitus, *This Journal*, **143**, 574 (1996).
17. P. Schmuki, S. Virtanen, A. J. Davenport, and C. M. Vitus, *ibid.*, **143**, 3997 (1996).
18. S. Virtanen, P. Schmuki, A. J. Davenport, and C. M. Vitus, *ibid.*, **144**, 198 (1997).
19. K. Sugimoto, M. Seto, S. Tanaka, and N. Hara, *ibid.*, **140**, 1586 (1993).
20. S. Tanaka, N. Hara, and K. Sugimoto, *Mater. Sci. Eng.*, **A198**, 63 (1995).
21. P. Vuoristo, Ph.D. Thesis, Tampere University of Technology, Tampere, Finland (1991).
22. T. Stenberg, J. Keränen, P. Vuoristo, and T. Mäntylä, Paper presented at *EUROMAT 97*, 1996.
23. T. Stenberg, P. Vuoristo, J. Keränen, T. Mäntylä, M. Büchler, S. Virtanen, P. Schmuki, and H. Böhni, *Thin Solid Films*, Submitted.
24. A. J. Davenport and M. Sansone, *This Journal*, **142**, 725 (1995).
25. M. Kerkar, J. Robinson, and A. J. Forty, *Faraday Discuss. Chem. Soc.*, **89**, 31 (1990).
26. A. J. Davenport, H. S. Isaacs, J. A. Bardwell, B. MacDougall, G. S. Frankel, and A. G. Schrott, *Corros. Sci.*, **35**, 19 (1993).
27. J. Yahalom and L. K. Ives, in *Passivity and Its Breakdown on Iron and Iron-Base Alloys, USA-Japan Seminar*, R. W. Staehle and H. Okada, Editors, p. 69, NACE, Houston, TX (1976).
28. A. G. Revesz and J. Kruger, in *Passivity of Metals*, R. P. Frankenthal and J. Kruger, Editors, p. 137, The Electrochemical Society Corrosion Series, Princeton, NJ (1978).
29. D. Stauffer, *Introduction to Percolation Theory*, Taylor & Francis, London (1985).

The Effect of Several Benzyl Alcohols and Electron Bridging Anions on the Current Efficiency for Deposition of Cadmium

Thomas C. Franklin,* T. S. N. Sankara Narayanan, and Michael Jackson**

Department of Chemistry, Baylor University, Waco, Texas 76798-7348, USA

ABSTRACT

Because of the ability of millimolar concentrations of substituted benzyl alcohols to block hydrogen evolution and to form complexes with the cadmium ions, their addition to cadmium sulfate and chloride plating baths increased the current efficiency for depositing cadmium. In sulfate baths there was generally a linear correlation between the concentration of the cadmium-alcohol complex and the current efficiency. In the cadmium-chloride system, in which the alcohol could not displace chloride and form a complex, the current efficiency was primarily related to the blocking of hydrogen evolution. Addition of electron bridging anions also catalyzes the deposition of cadmium, and this mechanism of catalysis does not change upon addition of the alcohol. The catalysis decreases in a very regular fashion as the size of the bridging anion increases, indicating that the electron bridging occurred through holes in the alcohol film. Addition of millimolar nonbridging strong complexing agents inhibits metal deposition and decreases current efficiency. Addition of millimolar surfactants increases the current efficiency by blocking hydrogen evolution.

Introduction

A variety of additives have been used to obtain brightness, throwing power, or related desired effects in electrodeposition. Although the effects have been explained in several different ways,[1,2] they have been most commonly explained in terms of adsorption of the organic compounds on the metal and the blocking of different steps in the electrode crystallization process.[3-12] Brown[13] synthesized a number of additives with different structures and studied their effect on electrodeposition processes. Leidheiser and Roth[14] made a study of a number of brighteners in nickel plating and the observed potential shifts caused by adsorption of the brighteners. There have been many other narrow studies of different types of additives. Adsorption of organic compounds on metals and electrodes and developing and testing various adsorption isotherms have been widely studied.[15-17] However, the simple blocking mechanism does not lend itself to a method by which different classes of organic compounds and types of structures can control different processes.

Part of the difficulty in understanding the additive effects lies in the fact that all electrodeposition processes involve a competition between at least two processes, the reduction and crystallization of the metal and the reduction of the solvent, or, in the case of alloy plating, the reduction of two or more metals plus reduction of the solvent. Each of these processes involve loss of complexing ligands involving a series of competitive rate processes.

It has been recognized that organic compounds are adsorbed on the metal surfaces, inhibiting the rates of reaction,[16,17] changing the concentration of reactive species,[18-20] and shifting equilibrium potentials at the electrode.[21-22] Quaternary ammonium ions can accelerate deposition of certain metals by ion pairing with negatively charged complexes,[23,24] and electron bridging anions[25] can accelerate the reduction of metal ions with which they can complex.[26-28] In blocking models[3-14] the organic additive adsorbs on the metal electrode surface and blocks or hinders certain electrode processes. Many papers have been written about the steps

* Electrochemical Society Active Member.
** Electrochemical Society Student Member.

occurring in adsorption of organic compounds and ions on the surface of metals[15-17] and an appreciable number have focused on their adsorption on electrodes.

In the early models they were regarded as general blocking agents, with only a question of whether the additive followed Freundlich, Langmuir, or Frumkin isotherms. As more understanding was obtained of the effect of the application of electricity and solid-state theory on adsorption, more sophisticated models discussed the role of potential, current density, kink sites, and various defects in selectively controlling the adsorption sites. These compounds were then visualized as selectively blocking separate steps in electrodeposition and electrocrystallization on the metal.

In the present study an investigation was made of a system containing two competing types of additives, a blocking additive and an electron bridging catalyst. Studies had previously been made on the competition between the blocking additive and ion pairing catalysts.[29-30] The blocking additives studied were benzyl alcohol and a series of substituted benzyl alcohols. These were chosen because, by the shift in the voltammetric potential of evolution of hydrogen in the cathodic direction, they were shown to significantly block the evolution of hydrogen.[29] The initial investigation on ion pairing catalysts involved a comparison of the effect of the blocking alcohols on the current efficiencies for deposition of cadmium and zinc.[29,30] Cadmium and zinc were chosen because they could form a variety of complexes and could be plated out of both negative and positive complexes.

The blocking additive study was then followed by a study of the effect of electron bridging anions and a group of nonbridging surfactants and complexing agents in the presence of the blocking agent. In this study no investigation was made of the effect of the additive on the physical properties of the deposit. However, previous work[31] had shown that the appearance of the deposit was closely related to the amount of codeposited hydrogen so it was assumed that some properties of deposit would be related to the amount of the secondary reaction.

Experimental

Voltammetric measurements made with a BAS voltammograph (CV-27) were used to determine the effect of the additives on the rate of evolution of hydrogen and on the limiting rate of deposition of cadmium. The voltammetric studies were followed with constant current measurements of current efficiency. The voltammetric studies gave information on the effect of the additives on the processes occurring within the electrode interface over short periods of time, while the current efficiency measurements served as a simple way to determine the composite effect of the additive on the relative rates of reduction of hydrogen and cadmium over a longer period of time (1 h).

The current voltage measurements were made with platinum wire cathodes and anodes. The current efficiency measurements were made by weighing the deposits after depositing the metal on copper cathodes at a current density of 0.89 A/dm^2 for 1 h using platinum anodes. In both cases the surface was covered with cadmium after a short time period so that all of the results were essentially obtained on cadmium plated electrodes. This was checked in some voltammetric experiments by comparing platinum electrodes with platinum electrodes preplated with cadmium, and it was found that the results in the region of cadmium deposition were, within experimental error, the same. In the voltammetric experiments the measurements were made with a saturated calomel reference electrode, and all voltages are referenced to this electrode. The conditions for each experiment are given with the data. Each point is the average of at least five experimental points. The average deviation from the means for the current efficiencies measured in the absence of the alcohol, which was the measurement showing the most deviation, was 1.2%.

Two types of supporting electrolytes were used. Sodium chloride was used as an example of an electrolyte that formed complexes with the cadmium(II) that led to the formation of negatively charged cadmium chloride complexes. Sodium sulfate was selected as an electrolyte which formed only very weak complexes with cadmium. In this system cadmium(II) was primarily present as a positively charged complex with water. In the voltammetric experiments the electrolytes used were 5 mM $CdCl_2$ and 0.01 M NaCl for the chloride system and 5 mM $CdSO_4$ and 0.05 M H_2SO_4 for the sulfate system. In the current efficiency measurements the chloride system was 0.01 M $CdCl_2$ and 0.10 M NaCl while the sulfate system was 0.01 M $CdSO_4$, 0.1 M Na_2SO_4, and 0.2 M H_2SO_4. In the study of the ion bridging and nonbridging additives the electrolytes used are listed with the figures.

Results and Discussion

The effect of blocking agents.—As more recognition has been made of the known chemistry of the processes it has become steadily more obvious that one needs to modify, at least qualitatively, our picture of what is occurring at the electrode. As the organic compound is adsorbed on the electrode, because of its hydrophobic nature and its low dielectric constant, the electrode becomes more hydrophobic, and the dielectric constant in the neighborhood of the electrode becomes much lower than that of water. This is a coarse effect, probably extending for several layers into the aqueous solution and is in addition to the recognized[15] decrease in dielectric constant caused by the electrical field at the electrode surface. It should be recognized that the decrease in dielectric constant causes an appreciable change in equilibrium and rate constants[32] so that the normal constants available as bulk solution properties cannot be accurately used for electrode reactions in the presence of organic additives.

In addition, the picture of having a layer of a hydrophobic substance between the bulk solution and the electrode surface raises questions about the ability of the hydrophilic ions to be transported freely to the point where they can be reduced and the effect of the additive on the adsorption of the reacting compounds on the electrode surface. Previous studies have shown that the adsorbed additive, because it changes the concentration of adsorbed reactive substances, causes shifts in equilibrium potentials[18-20] and in the potentials of deposition of metals.[14]

A series of substituted benzyl alcohols were chosen as examples of blocking agents because they cause appreciable shifts in the potential of evolution of hydrogen in the presence or absence of cadmium(II) on either platinum or cadmium electrodes.

The fact that benzyl alcohol is a blocking agent for the deposition of hydrogen may be because of a mechanical blocking effect or because the hydrophobic, low dielectric constant layer at the surface inhibits migration of the hydronium ions to the electrode surface. It would be expected that a simple blocking agent would also inhibit migration of the aquated cadmium ions. However, in aqueous sulfate systems, in which the cadmium is predominantly present as aquo complexes, it was also observed that the cadmium formed a complex with the benzyl alcohols as can be seen by the presence of a second reduction wave in the voltammetric curve (Fig. 1). It is known[33] that alcohols form complexes with cadmium, but normally these complexes are not observed in water because the water reacts with them. However, it is evident that they are stable at the electrode surface at the concentration of alcohol adsorbed on the electrode. In a system containing chloride ions, the chloride ions form complexes stronger than the alcohol complexes, and one observes (Fig. 2) only a shift in the reduction potential of the cadmium chloride complex as one changes the concentration of the alcohol and thus changes the dielectric constant of the surface layer.

The catalysis of the electrodeposition of the cadmium is further indicated in Fig. 3. It can be seen that in the majority of the experiments the current efficiency is linearly proportional to the concentration of the complex, as measured by the height of the peak observed for reduction of

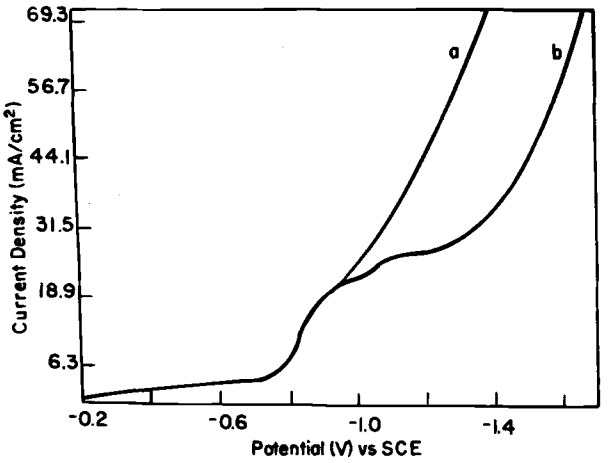

Fig. 1. The effect of *p*-methylbenzyl alcohol (5 mM) on the current–voltage curve for the reduction of Cd(II) ions in a H_2SO_4 solution (cathode, platinum; voltage sweep rate, 20 mV/s); (a) 5 mM $CdSO_4$, 0.05 M H_2SO_4; and (b) A + 5 mM *p*-methylbenzyl alcohol.

the cadmium-alcohol complex. This indicates that, in these cases, the primary effect of the alcohol is the formation of the complex. There are two points which are not on the straight line. This departure from the line indicates the complexity of the process. The additive can increase the current efficiency by hindering hydrogen evolution or by catalyzing cadmium deposition. The electronegativity of the trifluoromethyl derivative, as shown by the Hammett Sigma value,[34] is the highest of any of the additives used and thus it probably inhibits the hydrogen evolution as well as forming a complex with the cadmium, causing a very high current efficiency. On the other hand, the bromo derivative is larger than the other substituents, which may cause a lower complexation of the cadmium. This departure from the straight line could also be caused by the fact that these two compounds have a second electronegative group capable of forming complexes. There are other effects that might cause these two points to be off the line, but the majority of the data lies on the straight line, indicating that the formation and reduction of the complex is the major reason for the increase in current efficiency.

Because of the competitive nature of the reactions, the current efficiency can be raised in two ways, blocking of hydrogen evolution and catalysis of cadmium deposition.

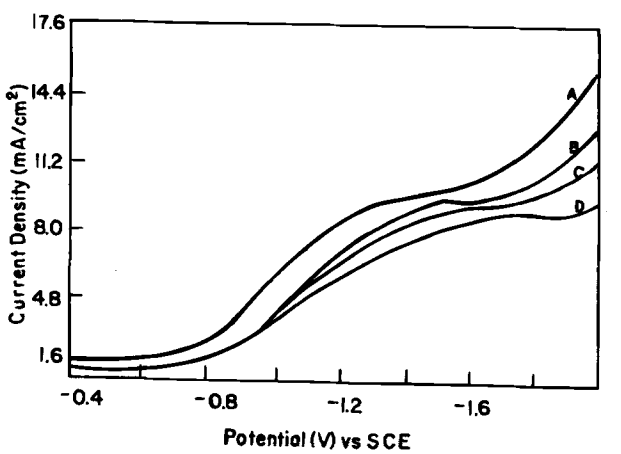

Fig. 2. The effect of *m*-methylbenzyl alcohol on the current–voltage curves for the reduction of Cd(II) in a chloride solution using a platinum cathode and a voltage sweep rate 20 mV/s; A: 5 mM $CdCl_2$, 0.01 M NaCl; B: A + 1 mM *m*-methylbenzyl alcohol; C: A + 5 mM *m*-methylbenzyl alcohol; D: A + 10 mM *m*-methylbenzyl alcohol.

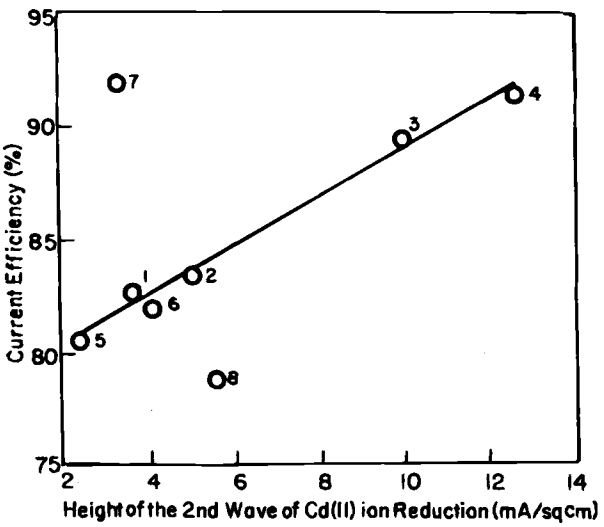

Fig. 3. The relation between the current efficiency for deposition of cadmium and the height of the wave for reduction of the cadmium-alcohol complex in the sulfate system; 1, benzyl alcohol; 2, *p*-methylbenzyl alcohol; 3, *m*-methylbenzyl alcohol; 4, *m*-methoxybenzyl alcohol; 5, *o*-chlorobenzyl alcohol; 6, *p*-chlorobenzyl alcohol; 7, *p*-trifluoromethylbenzyl alcohol; and 8, *p*-bromobenzyl alcohol.

The end result of both processes is that addition of the benzyl alcohols in sulfuric acid or chloride media caused increases of the current efficiency (Fig. 4).

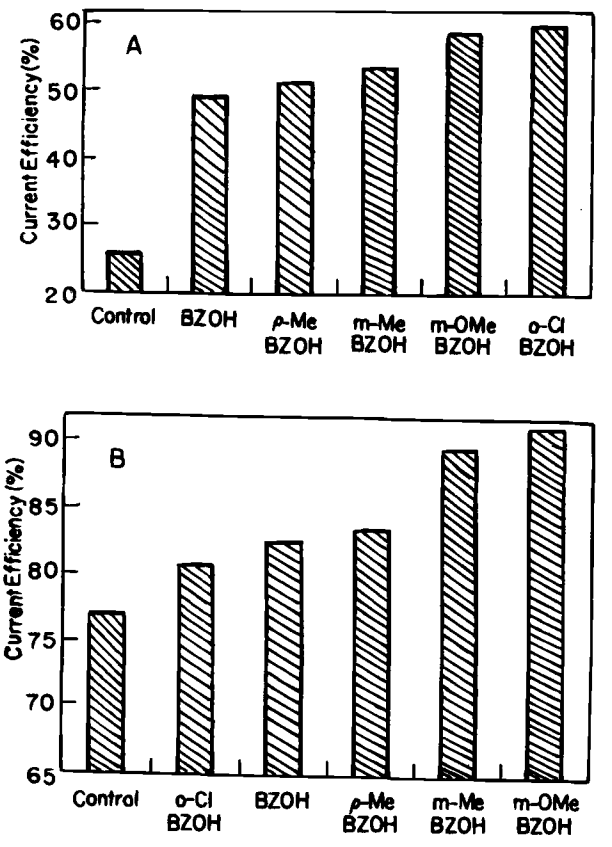

Fig. 4. (A) The effect of various alcohol additives (5 mM) on the current efficiency of cadmium deposition from a 0.01 M $CdCl_2$, 0.01 M NaCl solution (Cu cathodes, 5.6 cm^2; C.D, 0.89 A/dm^2; time, 1 h; (B) the effect of various alcohol additives (5 mM) on the current efficiency of cadmium deposition from a 0.01 M $CdSO_4$, 0.01 M Na_2SO_4, 0.02 M H_2SO_4 solution (Cu cathodes, 5.6 cm^2; C.D, 0.89 A/dm^2; time, 1 h).

The effect of nonelectron bridging anions.—It has been previously shown that electrodeposition of metals can be catalyzed by adding ion bridging anions that form complexes with the metal being deposited.[24] Figure 5 shows the effect of addition of 5 mM alcohol in systems containing a variety of nonbridging additives with some variations in concentration. The additives placed in these two supporting electrolytes contain some complexing agents (benzoic acid, citrates, and catechol) and some sulfonates that are generally regarded as noncomplexing detergents, cleaning the surface. These additives are added in concentrations (1 mM) that are too low to be considered in normal complexation discussions. The sulfosalicylic acid has both a complexing salicylate group and a sulfonate detergent group to increase solubility. The fact that the two lines are approximately straight indicates that the benzyl alcohol causes no changes in the mechanism of action of these additives. This is logical since these are merely blocking agents and addition of the alcohol merely changes the blocking ability. The acid sulfate solution is slightly different in slope from the approximately neutral chloride system (which complexes the cadmium ion). However, it is shown below that the acid has very little effect when both measurements are made in the sulfate system.

In Fig. 5 in the acid sulfate system it can be seen that some points were measured in the presence of additional sodium sulfate raising the ionic strength. The fact that the two ionic strengths lie on the same curve indicates that changes in ionic strength in these concentrations has little effect on the current efficiency.

Nonbridging larger additives.—The ion pairing study[29,30] indicated that the size of the additive was a controlling factor in the catalysis. As one studies the larger blocking additives that are commonly used as additives in electrodeposition, one does not have available sizes to determine precisely the effect of their size on the current efficiency. The only convenient thing related to size that can be used is molecular weight. This is not a direct measure of size because, as these large molecules get larger, they begin to bend, curl, and dimerize because of hydrophobic and hydrogen bonding.

Figure 6 shows the effect of addition of molecular weight on the current efficiency using the surfactants and complexing agents. (Note that these agents are used in the millimolar range rather than in the higher range of concentration use as complexing agents.)

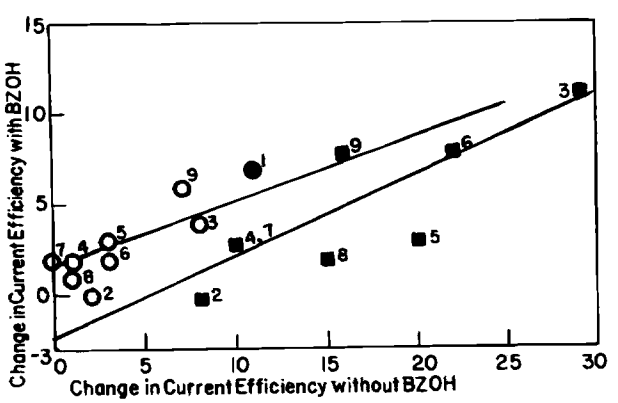

Fig. 5. The effect of a variety of nonbridging additives on the change in current efficiency for deposition of cadmium in the presence (5 mM) and absence of benzyl alcohol (BzOH): (●) 0.03 M $CdSO_4$/0.2 M H_2SO_4; (○) 0.03 M $CdSO_4$/0.2 M H_2SO_4/0.1 M Na_2SO_4; (□) 0.01 M $CdCl_2$/0.1 NaCl. 1, 0.2 M sodium formate; 2, 1 mM catechol; 3, 1 mM benzoic acid; 4, 1 mM 2-propene-1-sulfonic acid; 5, 1 mM 2,4-dimethylbenzene sulfonic acid, 6, 1 mM citrate; 7, 1 mM 1-octane sulfonic acid; 8, 1 mM sulfosalicylic acid; 9, 1 mM 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt. Least square straight lines are shown that include some points that are off the graph. The linear regression correlation coefficient (r) is 0.916 for the sulfate system and 0.842 for the chloride system.

Since these are not electron bridging agents they increase the current efficiency primarily by blocking hydrogen evolution. In either supporting electrolyte one obtains the same general form of the curves with or without the benzyl alcohol, leading again to the conclusion that the alcohol does not change the mechanism. The increased

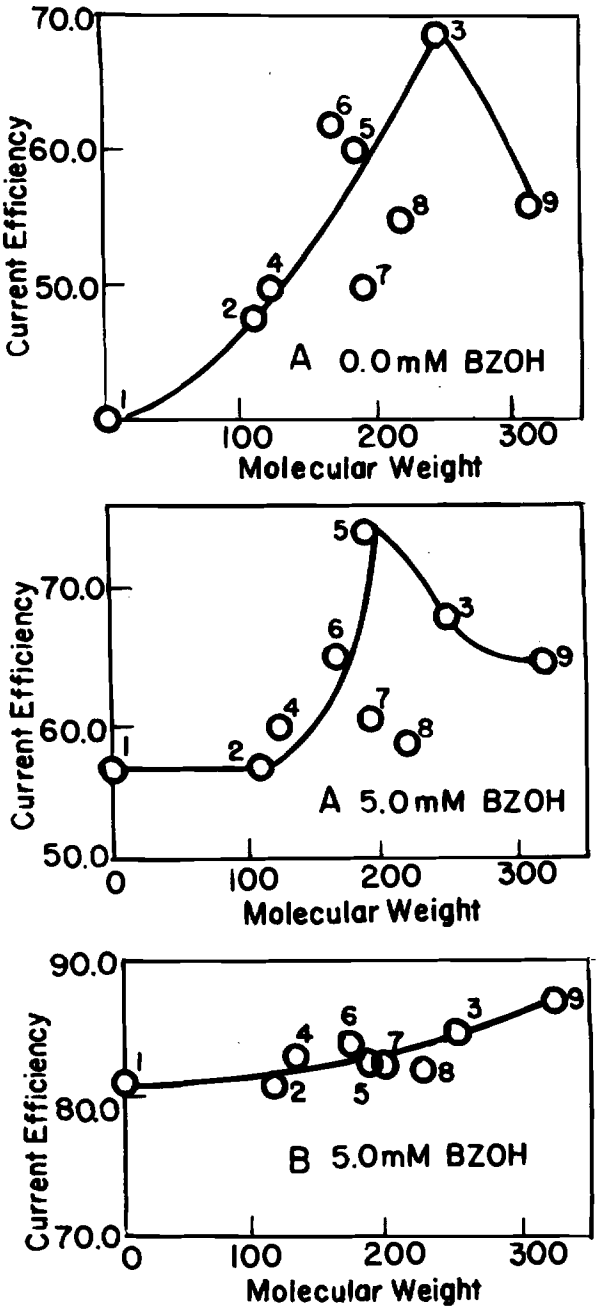

Fig. 6. (A) The effect of the molecular weights of nonbridging additives (1 mM) on the current efficiency for deposition of cadmium in 0.01 M $CdCl_2$, 0.01 M NaCl in the presence (5 mM) and absence of benzyl alcohol (BzOH); (B) the effect of molecular weights of nonbridging additives (1 mM) on the current efficiency for deposition of cadmium in 0.03 M $CdSO_4$, 0.1 M Na_2SO_4, 0.02 M H_2SO_4 in the presence (5 mM) of benzyl alcohol (BzOH). 1, control; 2, catechol; 3, benzoic acid; 4, 2-propene-1-sulfonic acid; 5, 2,4-dimethylbenzene sulfonic acid, sodium salt; 6, citrate; 7, 1-octane sulfonic acid; 8, sulfosalicylic acid; 9, 4,5-dihydroxy-2-7-naphthalenedisulfonic acid, disodium salt.

blocking of hydrogen evolution arises because of the increased size of the blocking agent.

It can be observed (Fig. 6A) that in the chloride system one can see a drop-off in the size effect at around a molecular weight of 200. This decrease is expected because of the bending and hydrophobic bonding of the larger molecules. The benzoic acid (point 3) is made to fall on the curve by assuming that its molecular weight is twice its formula weight. This is logical because it is well known to dimerize. Similar intermolecular bonding causing changes in radius, probably accounts for the fact that points 7 and 8 in Fig. 6A and B lie below the line.

Electron bridging additives.—Questions still exist as to whether electron bridging catalysts are blocked from the electrode by the alcohol film and whether catalyst size controls the inhibition of their action. In the presence of ion pairing catalysis it was concluded that ion paired cadmium and zinc ions were hindered in their migration to the electrode, and the amount of hindrance was related to the size of the ion pair.[29,30] The work on ion pairing indicated that, although the catalyst was not blocked by the alcohol from carrying the metal ion to the electrode, it was inhibited and it was concluded that the migration occurred through holes in the film, and the inhibition was related to the size of the ion pair. It is relatively easy to check precisely the effect of the small electron bridging ions for the effect of the size of the ions on the current efficiency. These ions have had their sizes measured by X-ray or electron diffraction. Figure 7 shows the effect of the size of these ions on the current efficiency for the deposition of cadmium. It can be seen that there is a very good correlation between the current efficiency and the measured size of the anion indicating that, as the size of the ion bridge increases, the catalysis decreases. This is consistent with a model in which the complexed ion migrates through holes in the film. It is also noteworthy that the bromide ion does not lie on the line unless one doubles the size of the bromide ion. This indicates that the bromide complex contains two bromide ions while the other complexes have only one complexing ion.

Effects of concentration of additive.—Since some additives were studied in 0.2 M solution, and others were studied in the millimolar range a brief investigation was made of the effect of concentration on the results. This is shown in Fig. 8. It is difficult to study concentration effects of larger ions because they do not have a wide range of solubilities. Thus, one observes very small changes in current efficiencies over their observed solubility range. The additives shown in Fig. 8 were selected because they were more soluble. The catechol is a strong complexing agent and one observes a steady decrease in the current efficiency effect because of formation of cadmium complexes. This is true whether the experiments are run in acidic or neutral solutions. It should be noted that complexation effects are observed at these low concentrations which are much lower than are usually used in complexation studies. The azide ion begins to precipitate an insoluble cadmium azide species before one reaches the desired concentration (0.2 M). However, it is a known electron bridge[8,9] and, after one gets a high enough concentration to start forming the azide complex one begins to observe a sharp rise in the current efficiency. This type of experiment appears to be a sensitive test of whether a complexing agent is an electron bridge or not.

Conclusion

The benzyl alcohol is not only a blocking additive, but it also forms an alcohol complex with the cadmium which catalyzes the reduction of the cadmium. The benzyl alcohol in sulfuric acid thus raises the current efficiency, both by inhibiting the hydrogen evolution and catalyzing the rate of cadmium deposition.

The addition of an electron bridging ion (0.2 M) to the benzyl alcohol system increases the current efficiency for cadmium deposition, but the amount of the catalysis decreases as the size of the electron bridging agent increases. This data indicates that the benzyl alcohol forms a porous film, and the complexes migrate through these pores to be reduced at the electrode. The alcohol does not block the catalysis. The benzyl alcohol does not change the mechanism of reduction of the metal. However, the low dielectric constant benzyl alcohol, which because of its adsorption lowers the dielectric constant at the electrode interface, increases the equilibrium constants for formation of the complexes. Thus complexation effects are seen at much

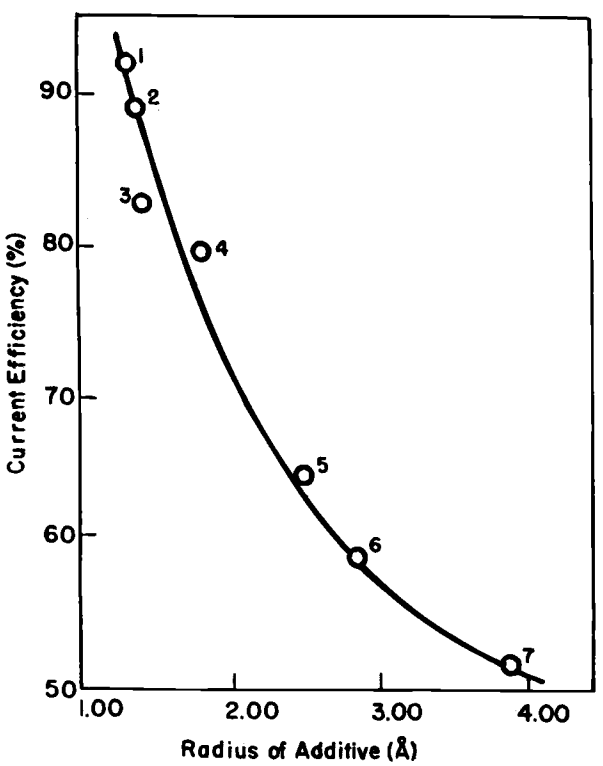

Fig. 7. The effect of the size of the electron bridging anions (0.2 M) on the current efficiency for deposition of cadmium from sulfate solutions containing 5 mM benzyl alcohol (Cu cathodes, 5.6 cm^2; C.D 0.89 A/dm^2; time, 1 h). 1, fluoride; 2, formic acid; 3, thiocyanate; 4, chloride; 5, acetate; 6, acetic acid; 7, bromide.

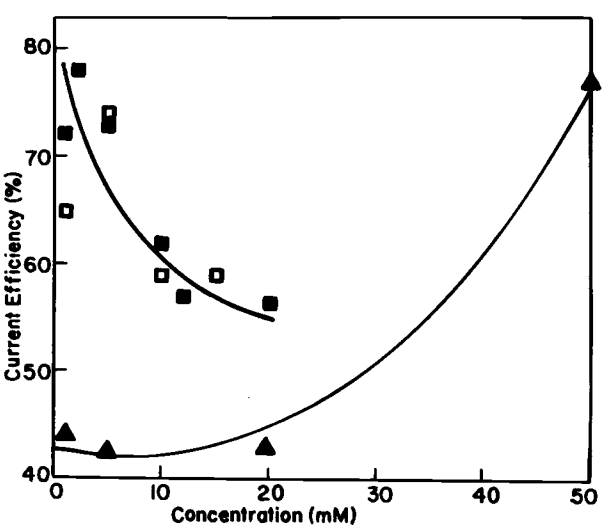

Fig. 8. The effect of concentration of the additive on the current efficiency for deposition of cadmium in the presence of benzyl alcohol (5 mM): (■) catechol in 0.03 M $CdSO_4$/0.1 M Na_2SO_4/0.2 M H_2SO_4; (□) catechol in 0.03 M $CdSO_4$; (▲) sodium azide in 0.03 M $CdSO_4$.

lower concentrations than are usually used in complexation studies.

Examination of the effect of changing concentrations of surfactants or complexing agents shows that their primary effect is on the blocking of hydrogen evolution and one observes a rise in the current efficiency for cadmium deposition which is related to the increase in size of the additive. If one increases the concentration of a complexing agent one observes, even at millimolar concentrations, as a result of the complexation of the metal, a drop in the current efficiency. However, as one increases the concentration of an electron bridging ion one observes a rise in the current efficiency because of the electron bridging catalysis.

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REFERENCES

1. T. C. Franklin, *Surf. Coat. Technol.*, **30,** 415 (1987).
2. T. C. Franklin, *Plat. Surf. Fin.*, **81,** 62 (1994).
3. H. Fischer, *Electrolytische Abscheidung und Electrocrystallization,* Springer, Berlin (1954).
4. H. Fischer, *Electrochim. Acta,* **2,** 50 (1960).
5. H. Fischer, *Electrodeposition Surf. Treat.*, **1,** 239 (1973).
6. H. Fischer, *ibid.*, **1**, 319 (1973).
7. M. Fleischman and H. R. Thirsk, in *Adv. Electrochem. Electrochem. Eng.*, **3,** 123 (1963).
8. O. Kardos and D. G. Foulke, *ibid.*, **2,** 145 (1962).
9. S. E. Beacom and B. J. Riley, *This Journal,* **106,** 309 (1959).
10. S. E. Beacom and B. J. Riley, *ibid.*, **108,** 758 (1961).
11. P. Malathy and B. A. Shenoi, *Met. Finish.*, **75,** 56 (1977).
12. E. H. Lyons, Jr., in *Modern Electroplating,* F. A. Lowenheim, Editor, p. 26, John Wiley & Sons, New York (1974).
13. H. Brown, *Plating,* 1047 (1968).
14. C. C. Roth and H. Leidheiser, Jr., *This Journal,* **100,** 553 (1953).
15. B. E. Conway, *Theory and Principle of Electrode Processes,* Ronald Press, New York (1965).
16. J. O'M. Bockris and A. K. N. Reddy, *Modern Electroplating,* Vol. 2, p. 1222, Plenum Press, New York, (1970).
17. J. O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White, *Comprehensive Treatise of Electrochemistry,* Vol. 2, p. 330, Wiley, New York (1981).
18. T. C. Franklin and S. L. Cooke, Jr., *This Journal,* **107,** 556 (1960).
19. T. C. Franklin and D. H. McClelland, *J. Phys. Chem.*, **67,** 4236 (1963).
20. T. C. Franklin, J. C. Chiu, and N. F. Franklin, *J. Electrochem. Soc. Jpn.*, **37,** 94 (1969).
21. T. C. Franklin and R. Sothern, *J. Phys. Chem.*, **58,** 951 (1954).
22. T. C. Franklin, M. Naito, T. Itoh, and D. H. McClelland, *J. Electroanal. Chem. Interfacial Electrochem.*, **27,** 303 (1970).
23. T. C. Franklin, J. Darlington, and R. Fierro, *This Journal,* **133,** 893 (1986).
24. T. C. Franklin, V. Totten, and A. Aktan, *ibid.*, **135,** 1638 (1988).
25. D. E. Pennington in *Coordination Chemistry,* Vol. 2., A. E. Martell, Editor, Chap. 3, Washington, DC (1978).
26. T. C. Franklin and S. A. Mathew, *This Journal,* **134,** 760 (1987).
27. T. C. Franklin and S. A. Mathew, *ibid.*, **136,** 3627 (1989).
28. T. C. Franklin and S. A. Mathew, *ibid.*, **135,** 2725 (1988).
29. T. C. Franklin and T. S. N. Sankara Narayanan, *ibid.*, **143,** 2759 (1996).
30. T. C. Franklin, T. Williams, T. S. N. Sankara Narayanan, R. Guhl, and G. Hair, *ibid.*, **144,** 3064 (1997).
31. T. C. Franklin and J. Goodwyn, *ibid.*, **109,** 288 (1967).
32. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions,* p. 583, Reinhold, New York, (1950).
33. E. C. Constable, *Coord. Chem. Rev.*, **58,** 1 (1984).
34. J. March, *Advances Organic Chemistry: Reactions, Mechanisms, and Structure,* p. 238, McGraw-Hill Book Co., New York (1968).