

ANILINE DERIVATIVES AS INHIBITORS FOR CEMENTATION REACTION

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ABSTRACT

The rates of copper(II)/zinc cementation in CuSO_4 solution were measured in absence and in presence of aniline derivatives. It was found that the rate of cementation decreases by increasing the concentration of inhibitors. For para substituent, the order of decreasing cementation was as follow :

p-bromo aniline > p-chloro aniline > p-amino-benzoic > p-amino acetophenone

For bromo aniline the order of decreasing cementation :

p-bromo aniline > o-bromo aniline > m-bromo aniline

INTRODUCTION

The types and amounts of chemical used by man in industry, agriculture and transport have increased greatly in the last half century. When chemicals are absorbed or inhaled in large amounts through direct industrial exposure, several toxic effects upon workers can result unless effective control measures are introduced and maintained [1].

Elements that may cause environmental health hazards have been classified by Wood [2] into three groups, described as "non-critical", "very toxic and relatively accessible" and "toxic, but very insoluble" [3]. The first, non-critical group contain Fe, Si, Al, Na, K, Mg, Ca, P, S, Cl, Br, F, Li, and Sr. The second, very toxic and relatively accessible group comprises, Be, Co, Ni, Cu, Zn, Sn, As, Se, Te, Pd, Ag, Cd, Pt, Au, Hg, Ti, Pb, Sb, and Bi, while the elements Ti, Hf, Zr, Re, W, Nb, Ta, Ga, La, Ir, Os, Rs, Ru, and Ba, are considered to be toxic but very insoluble.

Since copper metal is insoluble, then most copper enters the water system by copper salts. Such salts are used in the electroplating industry, engraving, and photography, while wastes from rinses tanks and filter cleanouts also find their way into the sanitary system [2].

Copper ions, as a pollutant do not accumulate in the human body in massive amounts, though, copper can cause illness or even death. So copper and heavy metals which may be present in many industrial waste

waters must be removed prior to discharge. Various methods are available for removal including neutralization precipitation, sorption and ion exchange. Because copper does not decompose when discharged, and because of its detrimental effects on bacteria, it is usually removed by precipitation and this is carried out by a cementation process, where, the cementation is one of the most effective and economic techniques for recovering toxic or heavy metals from industrial waste solution [3].

Previous studies have established that many of the common cementation reaction are indeed diffusion controlled. Some work [4-7]. has been done on the factors affecting the rate of cementation such as geometry of the less noble metal surface, temperature, concentration of the metal ions and stirring. These studies have revealed that cementation is a diffusion controlled reaction. The object of the present work is to study the effect of aniline derivatives on the rate of cementation of copper from copper sulphate solution.

EXPERIMENTAL & TECHNIQUE

The apparatus consist of 250 ml glass beaker containing 300 ml copper sulphate solution or copper sulphate-organic substance mixture. In which zinc rod of length 7 cm and width 3.2 cm is immersed. Four different solutions of copper sulphate has concentration 0.01, 0.05, 0.1 and 0.15 mol l^{-1} used, 0.1 ml is taken

from CuSO_4 solution every twenty minute and diluted to 10 ml, this step is repeated for time intervals 40, 60, 80, 120 and 140 minutes.

The aniline derivative is added to CuSO_4 solution where the concentrations used are 4×10^{-4} , 6×10^{-4} , 8×10^{-4} , 12×10^{-4} , 13×10^{-4} and 16×10^{-4} mol l^{-1} , 0.1 ml is taken from this solution at interval 20, 40, 60, 80, 100, 120 and 140 minutes and diluted to 10 ml, All these experiments are carried out at 25°C .

All chemical analysis were carried out using PERKING ELMER. ATOMIC ABSORPTION SPECTROPHOTOMETER.

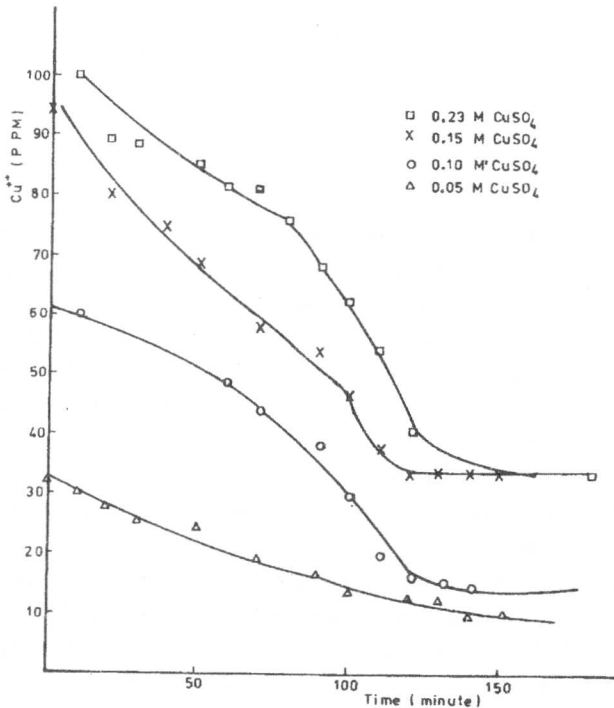


Figure 1. The relation between concentration of Cu^{++} remained (in PPM) and time (in minute) at 25°C for different CuSO_4 concentration.

RESULT AND DISCUSSION

Figure (1) shows that the concentration expressed in ppm (part per million) of Cu^{++} is decreased by increasing the time, while; Figure (2) shows the same above relation between ppm of Cu^{++} and time for m-bromo aniline at 25°C as example

The cementation reaction is as follows:

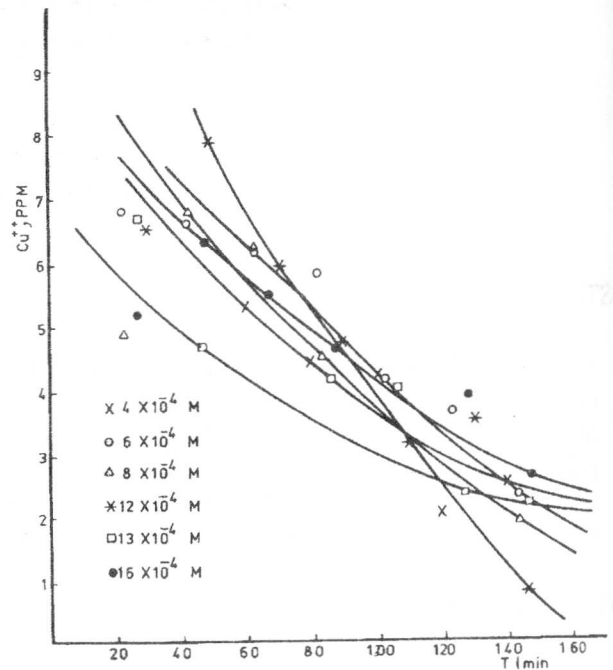
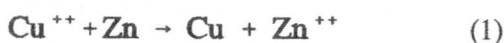


Figure 2. The relation between concentration expressed in PPM of m-bromoaniline and time in minute at 25°C .

This reaction is a diffusion controlled reaction whose rate in a batch reactor can be represented by the following equation (8)

$$-v \frac{dc}{dt} = KAC \quad (2)$$

which upon integration yields

$$v \ln \frac{a-x}{a} = KAt \quad (3)$$

Where v is the volume of the solution containing copper ions, a , is the initial concentration of copper ion and x , is the concentration of copper ion at time t ; K is the mass transfer coefficient and t is the time of cementation. Equation (3) was used to calculate the mass transfer coefficient of copper cementation of zinc under different conditions.

Figure (3) shows the relation between

$\log \frac{a-x}{a}$ against time for cementation of Cu^{++} in different copper sulphate concentration, from

which the mass transfer coefficient is calculated and given in Table (1). The above curve shows that the cementation reaction is a first order reaction which is verified by other authors [7,8,9].

Table (1). Value of K in different copper sulphate solution at 25°C.

| concentration mol l ⁻¹ | 0.01 | 0.05 | 0.10 | 0.15 |
|--|-------|-------|-------|-------|
| K x 10 ² cm min ⁻¹ | 1.106 | 1.547 | 1.857 | 2.322 |

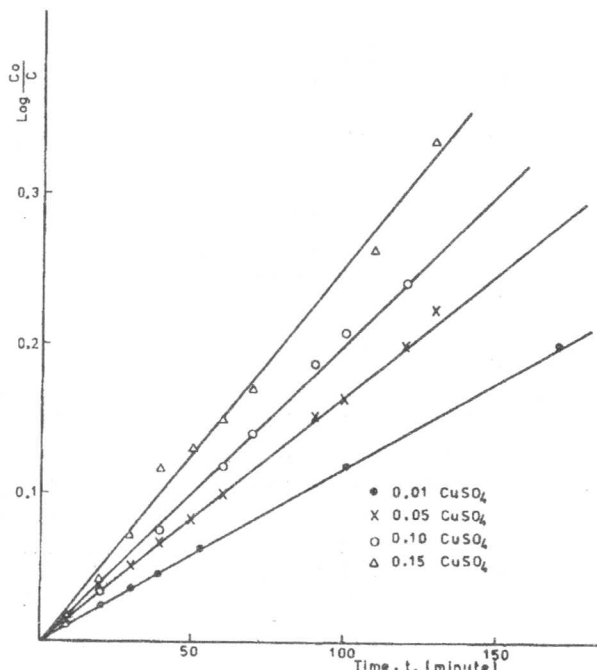


Figure 3. First order relation of cementation at different copper sulphate concentration at 25°C.

From Table (1) it is obvious that the rate of mass transfer is increased by increasing concentration i.e. cementation rate increases in this direction.

Figure (4) shows the relation between

$$\log \frac{a-x}{a} \text{ against time for p-amino-benzoic}$$

at constant CuSO₄ concentration (0.15M). The data fit the equation

$$\log \frac{a}{a-x} = B + \frac{KA}{2.30v}t \quad (4)$$

where B is the intercept.

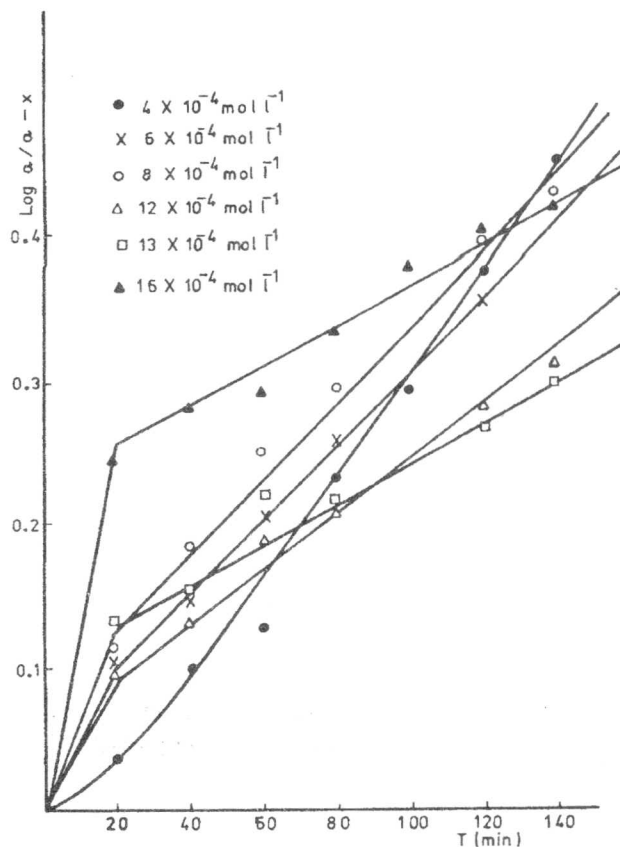


Figure 4. The relation between Log a/a-x and t, for p-amino benzoic acid at 25°C.

This equation is a second order one which is different from equation (3) (first order equation). This may be explained by the fact that at first, at the beginning of cementation, the rate is very high and a rough surface of zinc is formed i.e. the rate of diffusion of Cu to the zinc surface faces two resistances is namely, the liquid diffusion layer and a porous layer of copper deposit.

Figure (5), and Table (2) give the relation between K and concentration of p-aniline derivatives at 25°C the following order is obtained for increasing rate of cementation.

p-bromo aniline > p-chloro aniline > p-amino benzoic > p-amino acetophenone

Figure (6), and Table (2) give the relation between K and concentration of bromo aniline derivatives at 25°C the following order is obtained for increasing rate of cementation.

p-bromo aniline > o-bromo aniline > m-bromo aniline.
The percentage of inhibition for cementation reaction is calculated from the following relation

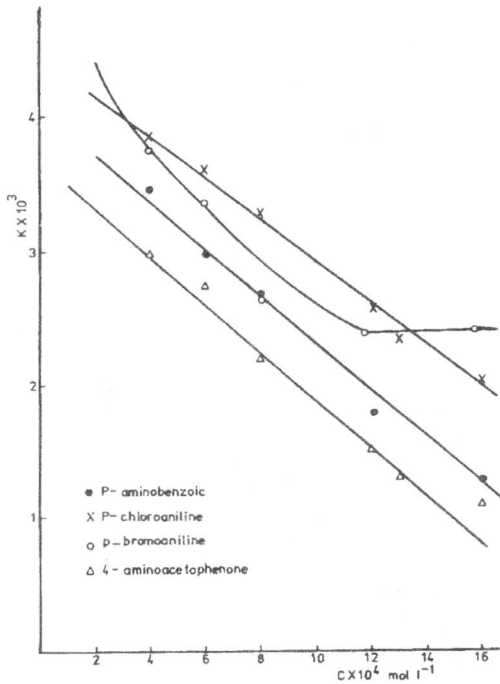


Figure 5. The relation between mass transfer (K) and concentration of 4-substituted aniline at 25°C.

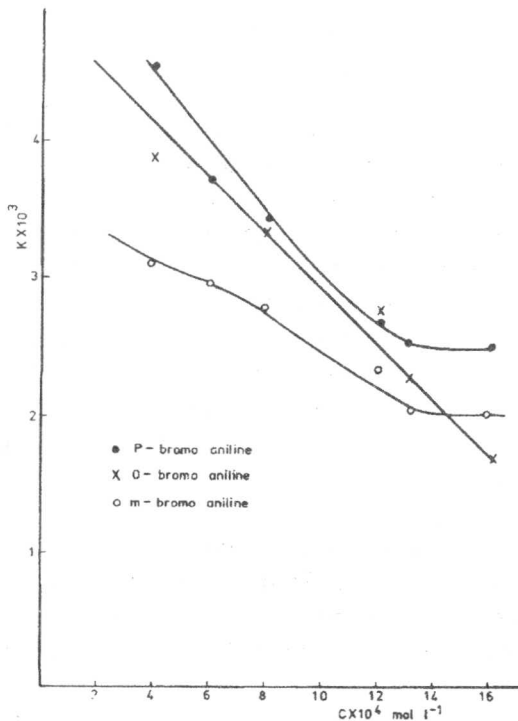


Figure 6. The relation between mass transfer coefficient (K) and concentration of bromoaniline derivatives at 25°C.

$$\% \text{ inhibition} = \frac{\bar{k} - K}{K} \times 1000$$

where K is the mass transfer coefficient when 0.15 M CuSO_4 is used only in absence of organic substance, while \bar{k} , is the mass transfer coefficient when we added organic substance to 0.15 M CuSO_4 .

Table 2. Values of K in 0.15M CuSO_4 solution at 25°C in presence of different aniline derivatives.

[1] p-amino acetophenone.

| Concentration (mol l ⁻¹) 10 ⁻⁴ | 4 | 6 | 8 | 12 | 13 | 16 |
|---|---|-------|-------|------|------|-------|
| (K * 10 ⁻³) cm min ⁻¹ | 3 | 2.778 | 2.174 | 1.43 | 1.25 | 1.111 |

[2] o-bromo aniline.

| Concentration (mol l ⁻¹) 10 ⁻⁴ | 4 | 6 | 8 | 12 | 13 | 16 |
|---|------|-------|-------|------|------|-------|
| (K * 10 ⁻³) cm min ⁻¹ | 3.85 | 2.778 | 2.174 | 1.43 | 1.25 | 1.111 |

[3] p-bromo aniline.

| Concentration (mol l ⁻¹) 10 ⁻⁴ | 4 | 6 | 8 | 12 | 13 | 16 |
|---|------|------|-------|------|------|-----|
| (K * 10 ⁻³) cm mm ⁻¹ | 4.54 | 3.66 | 3.332 | 2.63 | 2.50 | 2.5 |

[4] p-chloro aniline.

| Concentration (mol l ⁻¹) 10 ⁻⁴ | 4 | 6 | 8 | 12 | 13 | 16 |
|---|---|------|------|------|-----|-------|
| (K * 10 ⁻³) cm min ⁻¹ | 2 | 3.57 | 3.85 | 3.33 | 2.5 | 2.222 |

[5] m-bromo aniline.

| Concentration (mol l ⁻¹) 10 ⁻⁴ | 4 | 6 | 8 | 12 | 13 | 16 |
|---|-------------------------|------|-------|--------|------|--------------------|
| (K * 10 ⁻³) cm min ⁻¹ | (3.125)10 ⁻³ | 2.94 | 2.772 | 12.174 | 2.04 | 2*10 ⁻³ |

Figure (7) gives the relation between the percentage of inhibition in mass transfer and concentration in case of aniline derivatives. The order of decreasing mass transfer is as before

p-bromo aniline > p-chloro aniline > p-amino benzoic acid > p-amino acetophenone.

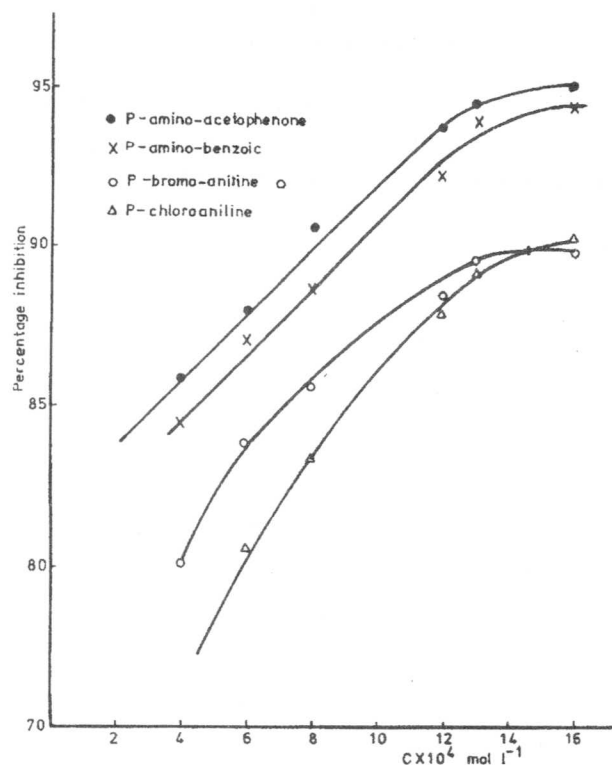


Figure 7. The relation between percentage inhibition and concentration of 4-substituted aniline at 25°C.

Figure (8) gives the above relation for bromo-aniline derivatives which decreases as follow

p-bromo aniline > o-bromo aniline > m-bromo aniline. Structural effect of organic compounds. The N atom of the amino groups is considered as an adsorbed center of the organic molecules on the surface of Zn metal. The basicity of an aromatic amine is affected by the substituent on the ring, it is known that an electron releasing substituent, increases the basicity of the amino group. i.e. the electron density at the nitrogen atom is increased by those substituents. On the other hand an electron with drawing group decreases the basicity of the amino group. i.e. it decreases the electron density at the nitrogen atom. As inductive effect of the substituent decreases then more electron density will be present at nitrogen atom and the compound can be easily adsorbed at Zn surface. This can explain the order of decreasing inhibition of 4-substituted aniline.

p-aminoacetophenone < p-aminobenzoic acid < p-chloroaniline < p-bromoaniline.

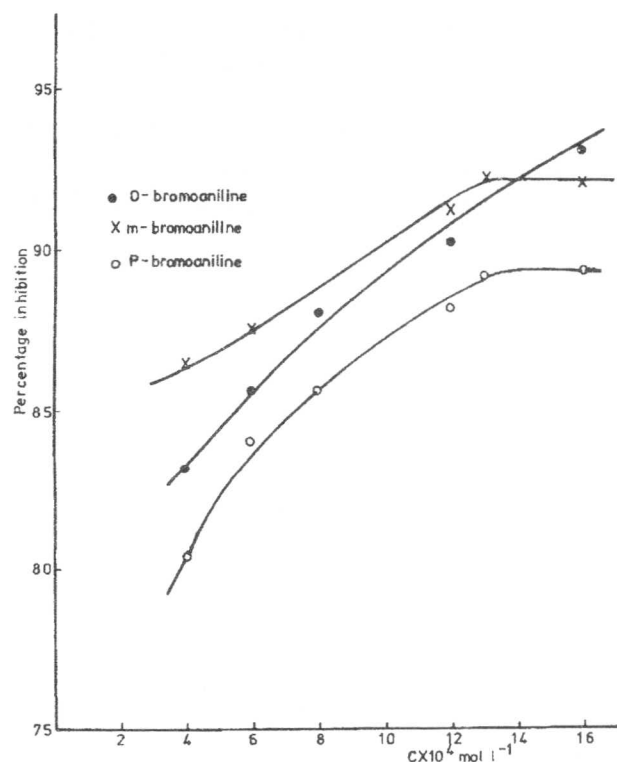


Figure 8. The relation between percentage inhibition and concentration of bromo aniline derivatives at 25°C.

Figure (8) shows that for bromo aniline derivatives the inhibition efficiency increase in the following order



There are two factors controlling the reactivity of the amino group, the first factor is the conjugation, which is found for o-Br and p-Br, but there is no conjugation effect for m-substrntuent. The second factor is the inductive effect which is smaller at the p-position than at the m-position.

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