

Chronopotentiometric study of the dissociation rate constants of some nitrilotriacetic acid complexes

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Abstract. The labile NTA complexes of cadmium, lead and copper have been studied in buffered solutions by the chronopotentiometric method. The rate constants for the dissociation of these NTA complexes have been calculated from the measured transition times of the kinetic waves, at various current densities, by using a modified equation.

Keywords. Chronopotentiometry; NTA; cadmium; lead; copper.

1. Introduction

The polarographic kinetic waves of labile metal complexes have been the subject of much investigation (Koryta 1967; Tamamushi and Sato 1972). Koryta (1959) was the first to study by the polarographic method the kinetic wave of cadmium-nitrilotriacetic acid (NTA) system, in acetic acid—sodium acetate buffer, after taking into account the influence of both free and acetate species of the metal ion on the equilibrium. In contrast, the chronopotentiometric method has received very little attention, although the measurement of transition time is better suited for the study of fast coupled chemical reactions (Tamamushi and Sato 1972; Davis 1966). Tanaka *et al* (1962) have studied the Cd (II)-NTA system in unbuffered solutions, based on the simplified treatment of Delahay and Berzins (1953). They observed an ambiguous separation of the kinetic step, the transition time showing some inaccuracy and also variation due to the ageing of the hanging mercury drop electrode. This paper deals with the chronopotentiometric study of the labile complexes of cadmium, lead and copper with NTA in buffered solutions, using a modified equation which takes into account the effect of the buffer on the dissociation equilibrium.

2. Experimental

A transistorised constant d.c. source with low ripple was used. The electrolysis current was checked by measuring the iR drop across a suitable precision resistor with a Tinsley Potentiometer (type 3184). The chronopotentiograms were recorded either on Elektronik-194 (Honeywell Brown) recorder or on storage oscilloscope DM 64 (Telequipment) and the transition time was obtained by the graphical method. The pH of the solutions was measured with a Beckmann Expandomatic SS-2 pH meter.

The cell set-up was similar to the one described earlier (Radhakrishnan and Sundaram 1972) and a mercury pool electrode in a glass cup served as the cathode. The cup was coated with Beckman desicote and the true electrode area (1.2 cm^2) was determined by measuring the transition time for 4 mM Cd^{2+} in 0.5 M KCl at various current densities. All solutions were deoxygenated by bubbling tank nitrogen and the temperature was kept at $25 \pm 0.1^\circ\text{C}$ by means of Ultra Thermostat, Type NBE.

Stock solutions of cadmium sulphate, copper sulphate and lead nitrate were prepared from AR salts and standardised by EDTA titration. Nitrilotriacetic acid (Matheson Company, New Jersey) was used and the purity was checked by conventional method. Other reagents used were AnalaR grade.

3. Results and discussion

Chronopotentiograms were recorded for 4 mM solutions of cadmium, copper and lead respectively in the presence of 0.04 M NTA . For studies with cadmium and copper, the solutions were buffered with 0.1 M sodium acetate and the pH was

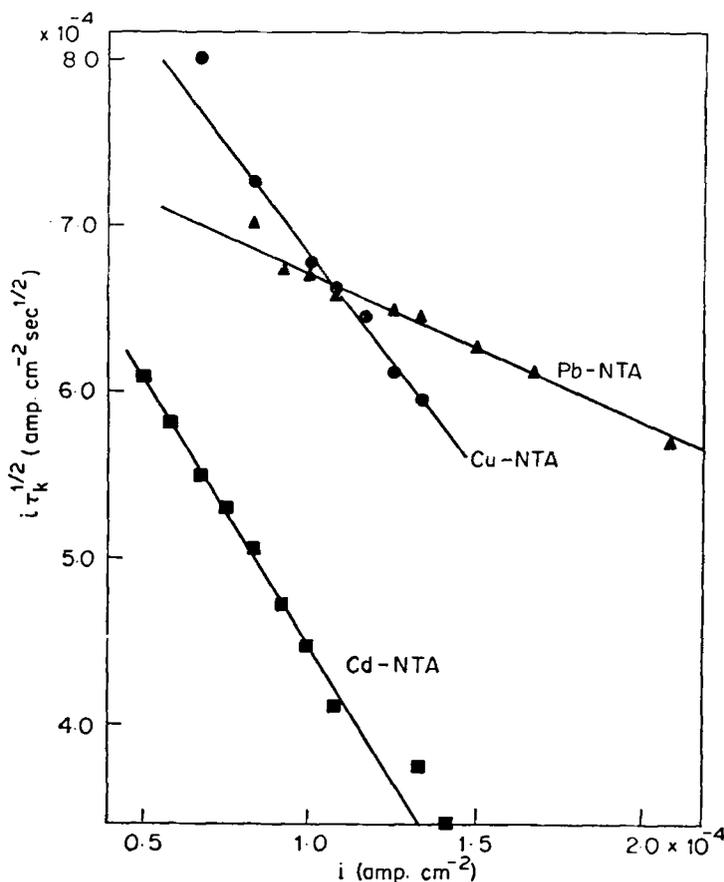
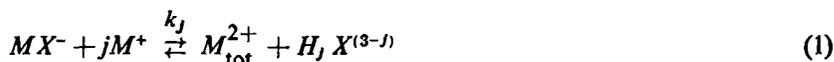


Figure 1. Plot of $i\tau_k^{1/2}$ vs i for Cd, Cu and Pb complexes of NTA

adjusted to 4.05 and 3.45 respectively with acetic acid. For Pb-NTA system, 0.1 M chloroacetic acid was used and the pH was adjusted to 2.6. In all cases, the ionic strength was kept at 0.2 by means of KNO_3 . The chronopotentiograms for these three systems showed two distinct steps, the first wave being kinetic in nature. The dependence of the transition time on current density was studied for the NTA complexes of cadmium, copper and lead and the plot of $i\tau_k^{1/2}$ vs i is shown in figure 1.

In the case of labile metal complexes with NTA, the electrochemical reduction is preceded by the chemical reaction



$$(j=0, 1 \dots)$$

where k_j is the rate constant of dissociation for the reaction (1) and X^{3-} denotes a trivalent NTA anion. As the reaction occurs in acetate buffer, M_{tot}^{2+} represents the total free (hydrated) metal ion and the acetate complex in equilibrium.

The reaction



is rapid enough to maintain equilibrium at the electrode, as no kinetic wave was observed for the metal ion in the buffer alone. It is evident that in the potential region of the first step, both M^{2+} and MOAc^+ are reduced whereas MX^- does not undergo reduction.

In the presence of acetate buffer, when NTA is also present in large excess compared to the metal ion, it can be shown that

$$\frac{[MX^-]}{[M_{\text{tot}}^{2+}]} = \frac{K_{MX}[X^{3-}]}{1 + K_{\text{MOAc}}[\text{OAc}^-]} \quad (3)$$

where K_{MX} and K_{MOAc} are the formation constants of the metal-NTA and metal-acetate systems respectively. The concentration of free acetate, $[\text{OAc}^-]$ can be calculated from the pH of the solution and the pK of acetic acid (Harned and Hickey 1937). The free nitrilotriacetate concentration $[X^{3-}]$ is given by

$$[X^{3-}] = \frac{k_1 k_2 k_3 / [H^+]^3}{1 + \frac{k_1}{[H^+]} + \frac{k_1 k_2}{[H^+]^2} + \frac{k_1 k_2 k_3}{[H^+]^3}} \cdot C_x \quad (4)$$

where k_1 , k_2 and k_3 are the successive dissociation constants (Schwarzenbach *et al* 1955) of NTA and C_x is the total NTA concentration

In addition from equation (1)

$$[MX^-]/[M_{\text{tot}}^{2+}] = k_f / k_d \quad (5)$$

and so combining (5) with (3)

$$\frac{k_f}{k_d} = \frac{K_{MX} [X^{3-}]}{1 + K_{MOAc} [OAc^-]} \quad (6)$$

where k_f and k_d are the rate constants for the formation and dissociation respectively of the NTA complex.

Delahay and Berzins (1953) have shown that for systems such as Cd-NTA which exhibit kinetic behaviour, the transition time is given by the relation

$$i \tau_k^{1/2} = i \tau_d^{1/2} - \frac{\pi^{1/2} k_f}{2 k_d^{1/2} \left[1 + \frac{k_f}{k_d} \right]^{1/2}} i \quad (7)$$

where τ_k is the transition time for the kinetic wave, τ_d is the transition which would be observed had there been no kinetic effect and i is the current density. The presence of the buffer and hence the influence of acetate complex on reaction (1) can be taken into account by substituting the value of k_f/k_d from (6) in (7) and the final expression can be written as

$$i \tau_k^{1/2} = i \tau_d^{1/2} - \frac{\pi^{1/2} \left\{ \frac{K_{MX} [X^{3-}]}{1 + K_{MOAc} [OAc^-]} \right\}}{2 k_d^{1/2} \left\{ 1 + \frac{K_{MX} [X^{3-}]}{1 + K_{MOAc} [OAc^-]} \right\}^{1/2}} i \quad (8)$$

i.e.

$$i \tau_d^{1/2} = i \tau_k^{1/2} - \frac{\pi^{1/2} K_{MX} [X^{3-}]}{2 k_d^{1/2} \left\{ (1 + K_{MOAc} [OAc^-]) (1 + K_{MOAc} [OAc^-] + K_{MX} [X^{3-}]) \right\}^{1/2}} i \quad (9)$$

A plot of $i \tau_k^{1/2}$ vs i should be linear at low current densities and from the slope of the plot (figure 1), k_d was calculated. For Cd-NTA (Schwarzenbach *et al* 1955), Pb-NTA (Pryszczewska *et al* 1959) and Cu-NTA (Schwarzenbach and Gut 1956) systems $\log K_{MX}$ was taken as 9.83, 11.78 and 12.96 respectively. For CdOAc⁺ and CuOAc⁺ complexes (Tanaka *et al* 1960; Tanaka and Kato 1960), K_{MOAc} was taken as 16 and 52.5 whereas for Pb-chloroacetate system (Batyrsheva and Toropova 1956), the formation constant was taken as 22.4. The dissociation rate constants were calculated as 29.4 sec⁻¹ for Cd-NTA, 6.7 × 10³ sec⁻¹ for Pb-NTA and 1.4 × 10³ sec⁻¹ for Cu-NTA at the respective pH at 25°C. The dissociation rate constant for Cd-NTA system is comparable with the polarographic value of 30 sec⁻¹ at 25°C reported by Koryta (1959) in acetate buffer at pH 4.05.

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