Polarographic Studies on Complexes of Pd(II) & Co(II) with Triethanolamine

MAMDOUH S. MASOUD, T. M. SALEM & R. M. ISSA

Chemistry Department, Faculty of Science, Alexandria, Egypt

The behaviour of Pd(II) and Co(II) complexes with triethanolamine (TEA) has been investigated polarographically. The mechanisms of reduction of Co(II)-TEA and Co(III)-TEA in the presence of NaOH have been discussed and it has been found that 30% of Co(II) is oxidized to Co(III). Different isomeric complexes are formed depending on [cobalt], [TEA], pH and temperature. To get well-defined waves the ratio of Co:TEA should be 1:3 in a solution 0·5M with respect to NaOH and the volume of H_2O_2 must be equivalent to that of cobalt in solution.

SIMPLE tertiary amines have been reported not to form stable complexes with transition metals[1-4]. However, Masoud[5] has shown that the stability of the tertiary amino group increases markedly when incorporated into a chelating ring. Spectral investigations of Pd(II) and Co(II) complexes with triethanolamines have been reported by us[6,7], but no polarographic studies on these are known. It was thought desirable to investigate the reduction of these complexes polarographically with a view to finding optimum conditions for their formation.

Materials and Methods

Stock solution (1%, w/v) of triethanolamine (TEA) was prepared in doubly distilled water. The solution was stable for several months.

Stock solutions of Pd(II) and Co(II) were prepared from the AR grade metal chlorides. To prevent hydrolysis conc. HCl (5 ml per litre) was added. The solutions were standardized according to Vogel[8].

Acetate, borate and universal buffers were used for adjusting the pH[9].

All other reagents used were of AR grade and all the solutions were prepared in doubly distilled water.

A radiometer polarograph was used in the present studies. A Radiometer pH meter was used to record the pH of the solution with an accuracy of ±0·01 pH units.

Results and Discussion

Studies on Palladium(II)-TEA System

Effect of varying [TEA] — On increasing the [TEA] in a solution containing $4 \times 10^{-4}M$ Pd(II) and 0·5M NaOH, the $E_{1/2}$ shifts to more negative values till [TEA] is five times that of Pd(II). If the concentration exceeds this ratio, the polarographic wave becomes less well defined with nearly the same $E_{1/2}$ values (Fig. 1). The shift in $E_{1/2}$ values might be due to the formation of complex compounds or it might be attributed to the polymerization of these complexes, a phenomenon normally encountered with Pd(II)[10,11]. It is known that deprotonation of ethanolic hydroxyl group leads to strong chelate formation[12].

Effect of varying [NaOH] — On increasing [NaOH] from 0·01 to 0·5M for constant concentrations of

Pd(II) $(4 \times 10^{-4}M)$ and TEA $(8 \times 10^{-3}M)$ four well defined waves were obtained. The $E_{1/2}$ values shifted to more negative side on increasing the [NaOH]. $E_{1/2}$ and i_d values attained constancy at [NaOH] > 0·3M. Plot of $E_{1/2}$ versus log [OH⁻] was linear with a slope of 0·05 indicating an irreversible system. The plot of $E_{1/2}$ versus pH, for solutions containing constant [Pd(II)] and [TEA] of $4 \times 10^{-4}M$ and $4 \times 10^{-2}M$ respectively, was linear with a slope of 0·07 suggesting incomplete and irreversible step[13]. In universal buffered media, in the pH range 6-11, the $E_{1/2}$ values shifted to negative potentials (up to −0·71 V). Above this pH, the values recorded coincided with those obtained for NaOH solutions. The shift in $E_{1/2}$ may indicate that the single step moves to more negative values on increasing [NaOH] as a consequence of an increase in stability of the complex.
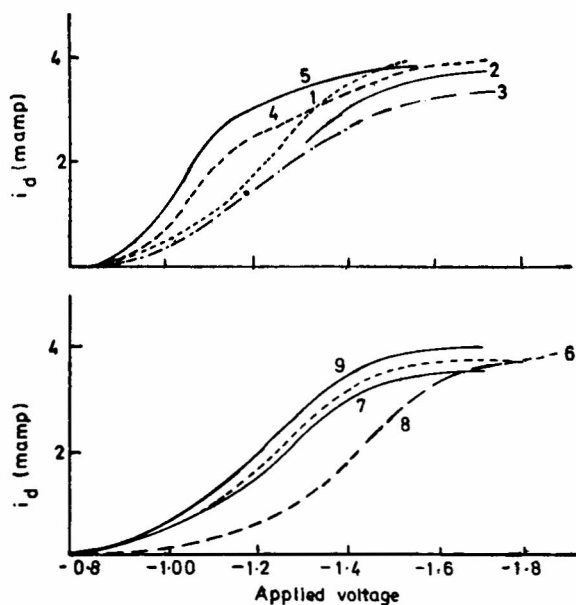

Fig. 1 — Effect of varying [TEA] on the plot of i_d versus voltage at [Pd(II)] = $4 \times 10^{-4}M$ and [NaOH] = 0·5M; {Curve 1, [TEA] = $4 \times 10^{-3}M$; curve 2, [TEA] = $12 \times 10^{-3}M$; curve 3, [TEA] = $2 \times 10^{-2}M$; curve 4, [TEA] = $3·6 \times 10^{-2}M$; curve 5, [TEA] = $4 \times 10^{-2}M$; curve 6, [TEA] = $4 \times 10^{-4}M$; curve 7, [TEA] = $2 \times 10^{-3}M$; curve 8, [TEA] = $2·8 \times 10^{-3}M$; curve 9, [TEA] = $4 \times 10^{-3}M$}

sign of splitting. The height of the second wave was 4·275 or 2·138 mamp for one electron transfer.

chim. Acta, **17** (1957), 434; *Analyst*, **47** (1958), 88.
20. RAO, A. L. & PURI, B. K., *Analyst*, **96** (1971), 364.

The number of H+ ions liberated in the reaction (Z_{H^+}) was calculated using the relation (1).

$$\frac{\delta E_{1/2}}{p\mathrm{H}} = \frac{0.059}{\alpha_n} Z_{H^+} \qquad \ldots(1)$$

Since the electrode reaction represents only the reduction Pd(II)→Pd(0), and the waves are irreversible (slope = −0.015 V; α_n = 0.375 at pH 11 universal buffer), the Z_{H^+} was found to be 0.094. Thus, H+ ions were not involved in the electrode reaction·in the pH range 9.5-11.5. In the acid range, the Z_{H^+} value was 0.06 indicating that one electron was involved in the rate determining step of the reduction of Pd(II)-TEA complex.

Effect of varying [Pd(II)] — At pH 10.85 and [TEA] = 0.4M and varying Pd(II) concentrations (from 0.2 to 3.8×10⁻³M), the reduction current increased steadily. The reduction current constants were calculated to be 1.35 and 1.14 respectively in the two media studied. So, under these conditions Pd(II) could be estimated with fair accuracy within the concentration range given above.

Analysis of the waves — The plot of wave height against square-root of the effective height of mercury column was linear passing through the origin, indicating that the limiting current is diffusion-controlled. The zero adsorption of the reducible species could be traced from the electrocapillary curve. The plots of $\ln(i/i_d-i)$ versus E showed high irreversibility of the electrode reaction. It has been reported that two molecules of tetramethylenediamine chelate with Pd(II) in a square-planar configuration[14]. Also, Pd(II) forms planar complexes of the type tri-PdL²⁺ (L = triaminopropane) and PdL²⁺ (L = triethylenetetramine) in *trans*-configuration[15]. Pd(II) complex with triethanolamine could thus be assumed to be in planar configuration with the usual chromophore N_2O_2.

Studies on Cobalt-TEA System

The Co(II)-TEA complex shows different colours depending on the concentrations of cobalt, TEA and the alkali electrolytes. The change in colour may be due to the formation of different isomeric complexes or due to the partial oxidation of the Co(II) to the corresponding Co(III) complex[1]. The Co(III)-TEA complex was prepared by bubbling oxygen in Co(II)-TEA solution and using H_2O_2 as an oxidant. Excess H_2O_2 was removed by gentle warming for 20 min or by allowing the solution to stand overnight.

Co(II)-TEA *system* — The polarograms were recorded when three moles of the amine were mixed with one mole of cobalt. Fig. (2) shows an increase in i_d with an increase in [TEA]. In non-complexing solutions, the reduction of the strongly hydrated Co(II) ion at the d.m.e. required a large overvoltage with the result that highly irreversible waves were obtained at much more negative potentials than would be expected from the reversible standard potential of the Co/Co(II) couple[16]. The overvoltage required for the reduction of the hydrated ion was attributed to their slow rate of electro-reaction. When sodium hydroxide concentrations were varied from 0.1M to 2.0M, the polarograms recorded showed two waves which were more developed at
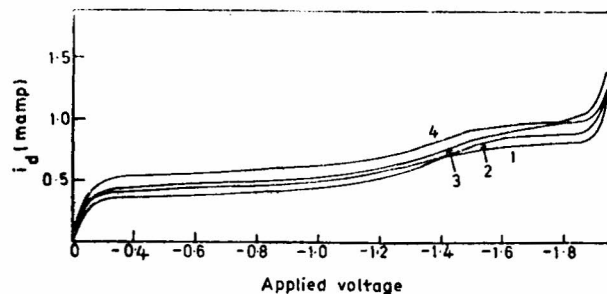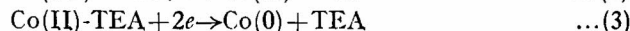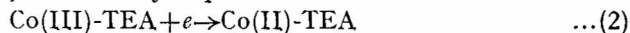

Fig. 2 — Effect of varying [TEA] on the plot of i_d versus voltage at [Co(II)] = 1 mM and NaOH = 0.5M {Curve 1, [TEA] = 1 mM; curve 2, [TEA] = 3 mM; curve 3, [TEA] = 4 mM; curve 4, [TEA] = 6 mM}

[NaOH] = 1.0 and 2.0M. The first wave might be attributed to the reduction of Co(III)-TEA complex which could be formed in the alkaline medium due to the instability of the Co(II) complex in this medium[17]. The second wave is ill-defined and lies at a negative potential (−1.5 V vs SCE) representing the reduction of Co(II)-TEA complex. According to the number of electrons consumed, the probable mechanism of the reaction can be represented by Eqs 2 and 3.

$$\text{Co(III)-TEA} + e \rightarrow \text{Co(II)-TEA} \qquad \ldots(2)$$
$$\text{Co(II)-TEA} + 2e \rightarrow \text{Co(0)} + \text{TEA} \qquad \ldots(3)$$

Subrahmanya[18] found in a series of papers that all the waves are well-defined for NaOH concentrations higher than 0.1M.

However, the ill-defined second wave was expected as Co(II)-TEA complex would either be a weakly bonded complex or exist in a colloidal form which is not readily reduced at d.m.e. But, our spectrophotometric investigation of this complex showed that Beer's law was obeyed over a wide range of concentrations and at different pH values[7]. This observation is opposed to the latter view. On plotting i_d in 0.5M NaOH against different concentrations of TEA, the extrapolated lines intersected at 2 mM TEA per 1 mM Co(II) proving the formation of 1:2 complex, (Fig. 3). The first part of the curve representing the first wave did not pass through the origin indicating that the oxidation of Co(II) to Co(III) was not complete on decreasing the concentration of alkali and the amine. A similar behaviour was observed for Mn[19]. On passing a stream of air through a solution of Co(II) (5×10⁻³M) and TEA (2×10⁻²M) for one hour and analysing for cobalt content, it was found that about 30% of Co(II) was oxidized to Co(III).

Cobalt(III)-TEA system — The colour of the solution was found to be green or violet depending on the molar ratio of TEA/Co. A plot of i_d versus potential is shown in Fig. 4 for the green solution containing Co(III) (2 mM) and TEA (6-12 mM) in 0.5M NaOH. It was noticed that i_d decreased with the increase in [amine]. There are two waves; the E potential of the second was recorded at the same value (−1.5 V) as that of the wave in the case of Co(II)-TEA system. The height of the second wave was double that of the first one. The second wave was well pronounced when the concentration of cobalt was 4 mM. Fig. 5 shows the effect of varying [TEA] on Co(III) (4 mM) dissolved in 0.5M
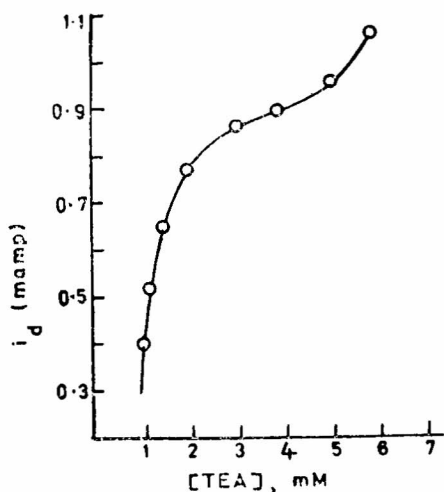
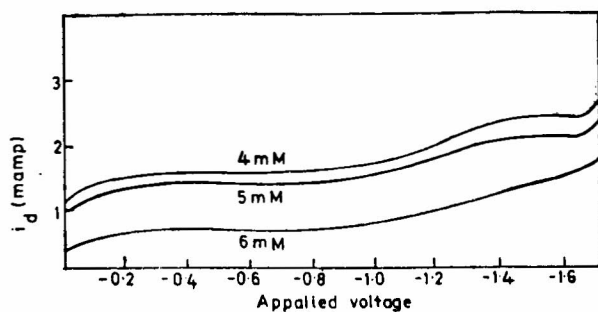Fig. 3 — Plot of [TEA] against i_d at [Co(II)] = 1 mM and [NaOH] = 0.5M

Fig. 4 — Effect of varying [TEA] on the plot of i_d versus voltage for the green species [Co(III)] = 2 mM and [NaOH] = 0.5M

NaOH, where the first wave split into two. The first one appeared at i_d of ∼2.5 mamp, similar to the position of the first wave of the green complex (Fig. 4). The height of the second wave increased proportionally with the [ligand]. But, on increasing the pH of the solution, the height of the wave decreased due to the formation of the green form. At 0.1M NaOH the solution acquired a violet colour, at 2M NaOH the colour changed to green, but from 0.5 to 1.0M NaOH an intermediate colour between violet and blue was obtained. The transformation of the violet to the green form was achieved by heating the solution; such a change was reversible. This might denote the existence of different isomeric complexes. Also, at 0.1M NaOH, the diffusion current of the first wave (violet species) was of considerable value but the splitting into two waves was not observed. The reduction of the Co(II) to Co(0) was only apparent at 1M NaOH but the height of the first wave was lowered. At 2M NaOH, the height of the second wave decreased with the precipitation of colloidal particles. It was found that solutions containing 2 mM cobalt and 6 mM TEA in 0.5M NaOH when allowed to stand for 16 hr mixed with H_2O_2 did not show any change in the reduction current on the formation of a green colour. The first wave was a simple one with no sign of splitting. The height of the second wave was 4.275 or 2.138 mamp for one electron transfer.
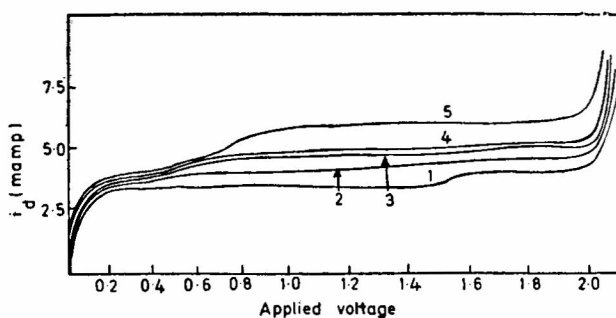

Fig. 5 — Effect of varying [TEA] on the plot of i_d versus voltage for the violet species at [Co(III)] = 4 mM and NaOH = 0.5M {Curve 1, [TEA] = 4 mM; curve 2, [TEA] = 8 mM; curve 3, [TEA] = 12 mM; curve 4, [TEA] = 16 mM; curve 5, [TEA] = 20 mM}

On the addition of H_2O_2 to a solution containing 4 mM cobalt and 12 mM TEA in 0.5M NaOH, the reduction current increased till 80% of H_2O_2 was added. Maximum i_d for complete reduction was 8.74 mamp and the colour of the solution turned bluish-violet indicating that the violet form of Co(III)-TEA complex was predominant. Rao and Puri[20] have stated that Co-monoethanolamine complex at pH 11 in 0.1M KCl behaved in an irreversible manner.

So, in order to get well-defined waves, the ratio of Co/TEA should be 1 : 3 in 0.5M NaOH and the volume of H_2O_2 added must be equivalent to that of cobalt in solution. On increasing the concentration of cobalt from 0.4 to 2.0 mM, the diffusion current varied linearly with concentration. The number of electrons calculated was less than a single electron transfer.

References

1. MANN, G. F. & POPER, J. W., J. chem. Soc., (1926), 489.
2. GAUSS, W., MOSEN, P. & SCHWARZENBACH, G., Helv. chim. Acta, 35 (1952), 2359.
3. SCHWARZENBACH, G. & MOSEN, P., Helv. chim. Acta, 36 (1953), 581.
4. MANN, G. F. & WATSON, R. H., J. chem. Soc., (1957), 3950.
5. MASOUD, M. S., Physicochemical studies on ethanolamines and their complexes, Ph.D. thesis, Alexandria University, 1970.
6. SALEM, T. M., ISSA, R. M. & MASOUD, M. S., Egypt. J. Chem., 16 (1973), 283.
7. MASOUD, M. S., SALEM, T. M. & ISSA, R. M., Egypt. J. Chem., 17 (1974), 415.
8. VOGEL, A. I., Quantitative inorganic analysis (Pergamon Press, London), 1966.
9. BRITTON, H. T., Hydrogen ions, Vol. 1 (Chapman & Hall, London), 1955, 365.
10. HARRIS, C. M., LIVINGSTONE, E. & LEESE, I. H., J. chem. Soc., (1959), 1505.
11. JICHA, D. C. & BUSCH, D. H., Inorg. Chem., 1 (1962), 872.
12. MARSHELL, A. E. & CHABERCK, Organic sequestering agents (John Wiley, New York), 1959.
13. HIROTA, M., UMEZAWA, T., NAKAMUA, M. & JIWARA, S. F., J. inorg. nucl. Chem., 33 (1971), 2617.
14. MANN, F. G. & WASTON, H. R., J. chem. Soc., (1958), 2772.
15. JØRGENSEN, C. K., Acta chem. scand., 10 (1956), 887.
16. SPACUE, P. & SCHERZER, I., Z. anorg. Chem., (1962), 319.
17. GAUR, J. N. & GOSWAMI, N. K., Electrochim. Acta, 15 (1970), 519.
18. SUBYAHMANYA, R. S., Proc. Indian Acad. Sci., 43A (1956), 133, 383; 54A (1957), 184, 195; 46A (1957), 377, 433, 443.
19. ISSA, I. M., ISSA, R. M. & HAWAIDY, I. F., Analyt. chim. Acta, 17 (1957), 434; Analyst, 47 (1958), 88.
20. RAO, A. L. & PURI, B. K., Analyst, 96 (1971), 364.