Fig. 1 — Plots of $F_j[x]$ versus ligand concentration {(A) Cd(II)-DHP system; (B) Pb(II)-DHP system}
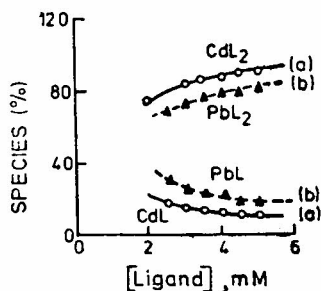

Fig. 2 — Plots of percentage distribution of species versus ligand concentration {(a) Cd(II)-DHP system; (b) Pb-DHP system}

The proportions of the uncomplexed metal ion and the various complex species as a function of the [ligand] can be calculated by means of Eqs. (1) and (2)

$$\frac{M}{C_M} = \frac{1}{F_0[x]} \qquad \qquad \ldots(1)$$

$$\frac{Mx_j}{C_M} = \frac{\beta_j[x]_j}{F_0[x]} \qquad \qquad \ldots(2)$$

where M denotes the concentration of the uncomplexed metal ions, Mx_j is the concentration of jth complex and C is the [total metal ion] added to the system. Percentage distribution of Cd^{2+} and Pb^{2+} in various forms as a function of the [ligand] are plotted in Fig. 2. As expected, the proportion of higher species increases with increasing [ligand]. For both the metal ions reduction at the electrode is reversible which makes it impossible to determine which of the species actually reacts with the electrode in the electron transfer process.

References

1. MOUGHTON, C., WRIGHT, K. A. & CAIN, R. B., Biochem. J., 106 (1968), 51.
2. KATYAL, M., GOEL, D. P. & SINGH, R. P., Talanta, 15 (1968), 711.
3. CURTIS, K. E. & ATKINSON, G. F., Can. J. Chem., 50 (1972), 1649.
4. GOEL, D. P., DUTT, Y. & SINGH, R. P., J. inorg. nucl. Chem., 32 (1970), 3119.
5. CURTIS, K. E., THOMSON, J. A. & ATKINSON, G. F., Analytica chim. Acta, 49 (1970), 351.
6. KUSHWAHA, V., SINGH, R. P. & KATYAL, M., Mikrochim. Acta, (1972), 807.
7. GOEL, D. P. & SINGH, R. P., Analyst, 96 (1971), 123.
8. LINGANE, J. J., Chem. Rev., 29 (1940), 1.
9. DEFORD, D. D. & HUME, D. N., J. Am. chem. Soc., 73 (1951), 5221.
10. IRVING, H., Adv. Polarog., 1 (1960), 42.

Complexes of La(III), Pr(III) & Nd(III) with Nitrilotriacetic Acid as Primary Ligand & Hydroxy Acids as Secondary Ligands

H. S. RANA & J. P. TANDON

Department of Chemistry, University of Rajasthan, Jaipur

The formation constants of mixed ligand complexes of La(III), Pr(III) and Nd(III) with nitrilotriacetic acid as primary ligand and pyrocatechol, disodium salts of 1,2-dihydroxybenzene-3,5-disulphonic acid and 1,8-dihydroxynaphthalene-3,6-disulphonic acid as secondary ligands have been evaluated pH-metrically at $30° \pm 1°$ and $\mu = 0.1M$ (KNO$_3$). These values are lower than the corresponding $K_{M.NTA}$ values. The differences have been explained on the basis of electrostatic attraction and the basicity of the ligand involved. The values of $K_{M.NTA.L}$ follows the order: La <Pr <Nd.

NITRILOTRIACETIC acid is known to form quite stable complexes with a number of metal ions[1-3] even at higher[4] pH. In the present note, $K^{M.NTA}_{M.NTA.L}$ values, where M = La, Pr or Nd, NTA = nitrilotriacetic acid, L = pyrocatechol (PY) or disodium salts of 1,2-dihydroxybenzene-3,5-disulphonic acid (Tiron) or 1,8-dihydroxynapthalene-3,6-disulphonic acid (CS) have been determined using Thompson and Loraas method at $30°\pm1°$, which are not reported earlier in the literature.

The chemicals used were of AR grade. The rare-earth oxides were of spectral grade and a stock solution was prepared and standardized as described earlier[5]. The dipotassium salt of NTA (Koch Light, England) was prepared by dissolving its known amount in the required volume of $0.1M$ potassium hydroxide. The solutions of PY (E. Merck), Tiron (E. Merck) and CS (Fluka) were prepared by dissolving their calculated amounts in doubly distilled water and standardized potentiometrically.

The following solutions (total vol. 50 ml) were titrated pH-metrically for Ln-NTA-PY (where Ln = La, Pr or Nd) system at $30°\pm1°$ under oxygen-free

nitrogen atmosphere using a Cambridge pH-meter, standardized against $0.05M$ potassium hydrogen phthalate solution:

(i) 10 ml ($0.025M$) PY.

(ii) 10 ml ($0.025M$) dipotassium salt of NTA in presence of 10 ml ($0.025M$) Ln-nitrate [Ln-NTA, 1:1].

(iii) 10 ml ($0.025M$) dipotassium salt of NTA in presence of 10 ml ($0.025M$) Ln-nitrate and 10 ml ($0.025M$) PY [Ln-NTA-PY, 1:1:1].

Similar sets of titrations were carried out for Ln-NTA-tiron and Ln-NTA-CS systems respectively. The ionic strength of all the solutions was kept constant by adding $0.1M$ KNO$_3$ solution.

Titration curves for La(III)-NTA-L system are shown in Fig. 1. Similar curves (not shown) were obtained for Pr(III)-NTA-L and Nd(III)-NTA-L systems. The values of acid dissociation constants of hydroxy acids were taken from the literature[6,7]. The titration curves corresponding to the binary mixtures (1:1) Ln-NTA showing inflexions at $m = 1$ ($m =$ moles of base added per mole of metal ion, Fig. 1, curves b, b' and b"), indicate the formation of 1:1, M-NTA complexes due to the neutralization of the free proton of the carboxylic group of NTA. The superimposable nature of the theoretical composite curve[8] in the lower buffer region supports the stepwise formation of the mixed complexes in each case and the secondary ligand is attached only after the complete formation of 1:1, M-NTA binary chelate. Their formation constants K_{MAL} have been calculated[9] and are listed in Table 1.

Solutions containing equimolar concentrations of M-NTA-PY or M-NTA-Tiron on titration (Fig. 1, curve d and d') give two inflexions. The first inflexion at $m = 1$ may be due to the formation of 1:1 M-NTA binary complex. Further addition of the alkali neutralizes the hydroxylic protons of PY or of Tiron and an inflexion at $m = 3$ may be ascribed[10] to the formation of the mixed complex (MAL). The appearance of the green colour in the case of PY and yellow colour in the case of Tiron after $m = 1$ clearly indicates the existence of new species. After $m = 1$ a lower buffer region starts clearly showing the formation of the mixed complex between $m = 1$ and $m = 3$ and this can be further substantiated by comparing the curve d and d' with the corresponding composite curves c and c', drawn by adding the horizontal distance of the secondary ligand curve to the horizontal distance of Ln-NTA curve at the same pH.

On titrating 1:1:1 M-NTA-CS systems (Fig. 1, curve d") three inflexions at $m = 1$, $m = 2$ and $m = 3$
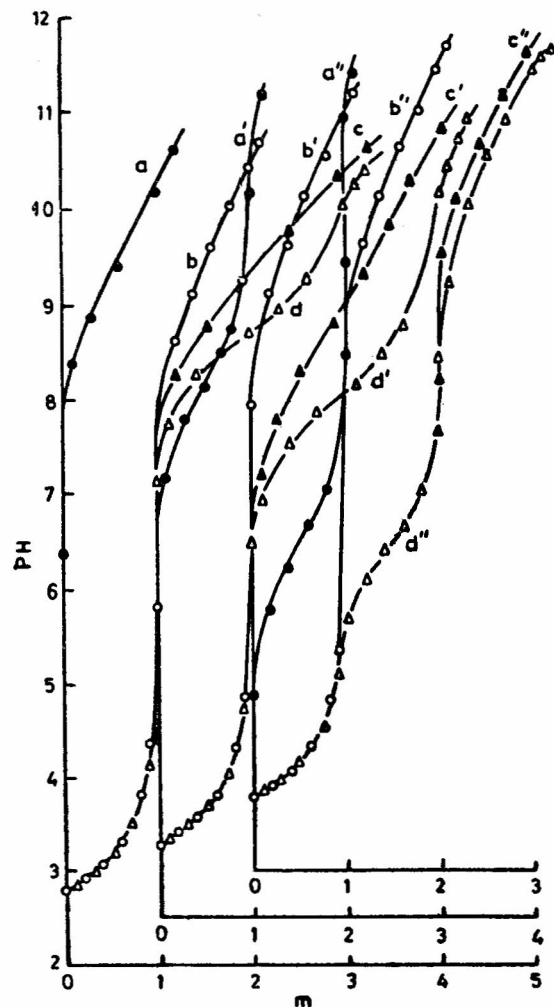

Fig. 1 — Potentiometric titrations of La(III)-NTA-L systems {(a), Py, (a') Tiron, (a") CS; (b, b', b"), 1:1 La(III)-NTA; (d), 1:1:1 La(III)-NTA-Py; (d') 1:1:1 La(III)-NTA-Tiron; (d"), 1:1:1 La(III)-NTA-CS; (c, c', c") corresponding composite curves of mixed ligand systems. $m =$ moles of base added per mole of metal ion}

are observed. In the beginning, 1:1, M-NTA simple complex appears to be formed and further addition of the alkali gives a sharp inflexion at $m = 2$ due to the neutralization of one of the phenolic protons of CS. The third inflexion at $m = 3$ may be attributed to the neutralization of the second phenolic proton of CS librated due to its chelation with the simple 1:1 complex. After $m = 2$, a lower buffer region starts clearly indicating the formation of the mixed complex. The formation of the mixed complex (MAL) between $m = 2$ and $m = 3$ may be further substantiated by the appearance of the pink colour and by comparing the curve d" with the corresponding composite curve c". It may, however, be noted that the value of K_{MAL}^{MA} (Table 1) increases from La(III) to Nd(III) and this trend can reasonably be explained[11] on the basis of the increasing complexing power of the rare earth ions as the atomic number increases.

It may further be observed that in all the above cases K_{MAL} has a lower value than K_{MA} (ref. 12). This can reasonably be explained on the basis of the ab-

TABLE 1 — FORMATION CONSTANTS OF MIXED LIGAND COMPLEXES

[$\mu = 0.1M$ (KNO$_3$); t = 30° $\pm$1°]

Log $K_{M.NTA.L}^{M.NTA}$

L	La(III)	Pr(III)	Nd(III)
PY	6.30 ± 0.06	6.98 ± 0.06	7.36 ± 0.04
Tiron	7.40 ± 0.07	8.22 ± 0.06	8.70 ± 0.05
CS	8.65 ± 0.04	9.40 ± 0.05	9.97 ± 0.05

sence of electrostatic attraction between the incoming charged hydroxy acid ion and the neutral M-NTA binary complex and the basicity of the incoming ligand.

In terms of the secondary ligands, the formation constants of the resulting mixed complexes of any particular rare earth ion decrease in the following order:

$$CS > Tiron > PY$$
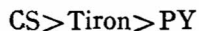
The ternary complexes with pyrocatechol are the least stable and this may be due to the fact that the sulphonic acid groups in the case of Tiron and CS increase the reactivity of the aromatic hydroxyl groups towards coordination with the metal ions[13].

The authors thank Prof. K. C. Joshi for laboratory facilities.

References

1. INTORRE, B. J. & MARTELL, A. E., *J. Am. chem. Soc.*, **83** (1961), 3618.
2. CAREY, G. H., BOGUCKI, R. F. & MARTELL, A. E., *Inorg. Chem.*, **3** (1964), 1288.
3. SHARMA, G. & TANDON, J. P., *J. inorg. nucl. Chem.*, **32** (1970), 1273.
4. HOPGOOD, D. & ANGELICI, R. J., *J. Am. chem. Soc.*, **90** (1968), 2508.
5. RANA, H. S. & TANDON, J. P., *Mh. Chem.*, **106** (1975), 559.
6. L.'HEUREUX, G. A. & MARTELL, A. E., *J. inorg. nucl. Chem.*, **28** (1966), 481.
7. LAL, K. & AGARWAL, R. P., *J. Less-common Metals*, **12** (1967), 269.
8. CAREY, G. H. & MARTELL, A. E., *J. Am. chem. Soc.*, **89** (1967), 2859.
9. THOMPSON, L. C. & LORAAS, J. A., *Inorg. Chem.*, **2** (1963), 89.
10. AFGHAN, B. K. & ISRAELI, J., *Talanta*, **16** (1969), 1601.
11. MOELLER, T., MARTIN, D. E., THOMPSON, L. C., FERRUS, R., FEISTEL, G. R. & RANDALL, W. J., *chem. Revs.*, **65** (1965), 1.
12. SCHWARZENBACH, G. & GUT, R., *Helv. chim. Acta*, **39** (1956), 1599.
13. CAREY, G. H., BOGUCKI, R. F. & MARTELL, A. E., *Inorg. Chem.*, **3** (1964), 1288.

Extraction & Spectrophotometric Determination of Pt(IV) with Benzil-α-monoxime

PRAPHULLA KUMAR PARIA & SANTOSH KUMAR MAJUMDAR

Department of Chemistry, North Bengal University Darjeeling

A method has been developed for the extraction and spectrophotometric determination of Pt(IV) using benzil-α-monoxime. Pt(IV) forms a brown chelate with the reagent which is extractable into chloroform. Quantitative extraction occurs at pH 3·0. Beer's law is valid at 440 nm over a concentration range of 1-22 µg of Pt per ml.

A NUMBER of reagents have earlier[1-11] been suggested for the solvent extraction of Pt(IV). A few of these have been employed for the separation of Pt(IV) and Pd(II). Ueda has employed benzil-α-monoxime for the solvent extraction of cobalt[12]. In the present note we report a method for the extraction and simultaneous spectrophotometric determination of Pt(IV) in microgram quantities using benzil-α-monoxime. The method is based on the fact that aqueous Pt(IV) solution when heated on

a water-bath with the reagent (optimum conc. 2 ml of 1% in acetone) for 80 min, forms a brown colour which is extractable into chloroform. At the room temperature Pt(IV) produces no precipitate or even colour. With lower concentrations of the reagent the colour development is slow.

Examination of the extraction behaviour of the Pt(IV) complex over the pH range 1-7 revealed that the extraction is quantitative at pH 3.

The reagent absorbs strongly below 310 nm but the absorption is not significant above this wavelength. However, the complex absorbs strongly at 440 nm. The optical densities of the chloroform extracts containing different amounts of platinum extracted from the aqueous phase at pH 3 were measured at 440 nm against the reference solution. The results indicate that the coloured system obeys Beer's law at 440 nm over the concentration range 1-22 µg of Pt per ml of the solution.

The colour is extracted within 5 min when shaken with chloroform and is stable for 6 hr. The molar absorptivity of the complex is $6·67 \times 10^3$ at 440 nm (on the basis of platinum content) and sensitivity in terms of Sandell's definition is 0·028 µg.

Beckman spectrophotometer model DU2 with optically matched quartz cells (10 mm path length) was used for optical density measurements.

Benzil-α-monoxime was prepared and purified in the laboratory[13]. A 1% solution of the reagent in acetone was used. Chloroform was distilled before use.

Following buffers of different pH values were prepared by standard procedures: Hydrochloric acid-potassium chloride (pH 1-2·5); hydrochloric acid-potassium hydrogen phthalate (pH 3-4); potassium hydrogen phthalate-sodium hydroxide (pH 4·5-5·5) and potassium hydrogen phosphate-sodium hydroxide (pH 6-8).

Stock solution of Pt(IV) was prepared by dissolving chloroplatinic acid (1 g) in distilled water (50 ml). The solution was standardized by precipitation as ammonium chloroplatinate and subsequent weighing as platinum[14]. A test solution was prepared by suitably diluting a portion of the platinum stock solution so as to contain 380 µg of platinum per ml.

All the other chemicals used were of CP grade unless otherwise mentioned.

Procedure for the determination of Pt(IV) — Buffer solution (15 ml) of desired pH was added to an aliquot containing 380 µg of Pt. Benzil-α-monoxime (2 ml of 1% solution in acetone) was added and the solution heated on a water-bath for 80-90 min when development of the colour was complete. The solution was then cooled to room temperature and extracted with chloroform (10 ml) for 5 min, The organic phase was separated and diluted to 25 ml with chloroform. The optical density of the chloroform extract was measured at 440 nm against a reagent blank and platinum determined from the calibration curve drawn previously.

From six runs with 380 µg Pt, the mean optical density found was $0·515 \pm 0·013$. The relative mean deviation was $\pm 2·5\%$.

Effect of diverse ions — In the estimation of Pt(IV) (380 µg), the following ions did not cause deviation of more than $\pm 3\%$ in absorbance when