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A THERMOMETRIC TITRATION STUDY OF THE INTERACTION OF Co^{2+} WITH METALLOCHROMIC INDICATORS

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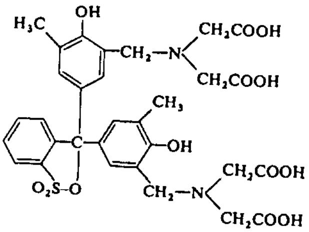
SUMMARY

A thermometric titrimetry study of the interaction in aqueous solution of Co^{2+} with xylenol orange, eriochrome black T and catechol violet at a specified pH, has revealed in each case a linear reaction heat/[Co^{2+}] relationship, thereby suggesting the potential of metallochromic indicators for the determination of macro trace levels of cobalt in water. The relevant complexation enthalpies are rationalized in terms of a combination of ligand steric effect, cobalt-ligand bond energies and chelate effect.

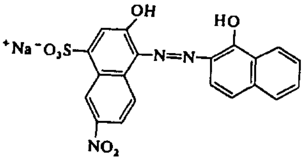
INTRODUCTION

Considerable interest is focussed on the analytical determination of cobalt in industrial, biochemical and environmental samples. Cobalt may be determined in a variety of ways, depending on the presence of interfering elements, the quantity of the metal in the sample and the precision required in the analysis. Cobalt may be determined gravimetrically as the oxide Co_3O_4, as the free metal by electrolysis in ammoniacal solution, potentiometrically via oxidation to cobalt(III) in ammoniacal solution with potassium ferricyanide, titrimetrically with potassium cyanide and colorimetrically using ammonium thiocyanate or a nitroso-alkyl salt as complexing agent. In certain cases, cobalt may be determined polarographically or spectrographically. Also, cobalt together with many other metals, has been determined by thermometric titration with ethylenediaminetetraacetic acid (EDTA) (ref. 1). In the majority of these analyses, it is necessary to separate cobalt principally from iron and nickel prior to determination.

In the conventional volumetric analysis of cobalt in aqueous solution using, for example, EDTA as titrant (ref. 2), a variety of metallochromic indicators such as xylenol orange (I), eriochrome black T (II) and catechol violet (III) are used for the visual determination of the end-point. It is difficult to determine Co^{2+} using EDTA with catechol violet as indicator, since the end-point is defined by an indecisive violet to blue colour change (ref. 2).



(I)



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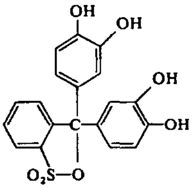

(III)

These metallochromic indicators are strong chelating agents for a variety of metal ions in aqueous solution and hence it appears that a thermometric titrimetric determination of cobalt is feasible using the 1:1, metal:indicator reaction as the basis of analysis.

EXPERIMENTAL

Calorimeter and Accessories. The thermometric titrimetric system employed and associated data analysis procedures have been described in detail by bin Ahmad *et al.* (refs. 3,4). All derived thermochemical data refer to 298K and the relevant uncertainty is quoted as the standard deviation from the mean.

Analytical Procedures. Reaction heat Q_R and molar reaction enthalpy $\Delta_R H^o_m$ (kJ mol^{-1}) are calculated on the basis of the determined temperature variation, ΔT(mV) for the relevant quantitative calorimetric reaction and the associated average heat capacity, Cp_A (kJ mV^{-1}), determined from the measured heat capacities of the calorimeter and contents before and after the thermometric titration.

$$Q_R = -Cp_A \; \Delta T = n_p \Delta_R H^o_m$$

where n_p = number of moles of product formed. $\Delta_R H^o_m$ is determined on the assumption of a 1:1 titrant:titrate reaction. Titrant dilution heats, as determined by titration of metallochromic indicator into titrate solutions minus metal were found to be less than the overall experimental error of $\pm 5\times10^{-5}$ mV in ΔT determination.

Titrants and Titrates. The titrant was a metallochromic indicator: xylenol orange (0.05M) (xylenol orange tetrasodium salt, BDH), eriochrome black T (0.1M) (Difco Labs.), catechol violet (0.05M) (BDH). The burette delivery rate was 1.0355 ± 0.00011 cm^3 min^{-1}.

The titrate was a Co^{2+} aqueous solution ($CoSO_4$, $7H_2O$, BDH), prepared using deionised, distilled water. A 0.1 M stock solution was stored under nitrogen and diluted to the required concentration prior to use. Adjustment of the pH of titrate solutions in the case of xylenol orange titrations was effected using an acetate buffer, (pH 4.45) and for other titrations, an ammonia buffer (pH 10) was used - adjustment to the required pH was effected by adding H^+ or OH^- as necessary. The pH of titrate solutions was determined using a Labmos pH Electrometer-standardised using pH 4 and 7 (Radiometer) standard buffer solutions. The titrate volume throughout was 90.00 cm^3.

RESULTS AND DISCUSSION

Thermochemical data relating to the interaction of Co^{2+} with xylenol orange (0.025M) at pH 4.5, eriochrome black T (0.1M) at pH 10.4 and catechol violet (0.50M) at pH 9.5 are given in Tables 1-3 respectively. The corresponding linear $Q_R/[Co^{2+}]$ plots (Fig. 1), suggest that these metallochromic indicators may be used to determine cobalt within the concentration ranges 2.78×10^{-5} to 2.78×10^{-4}, 1.39×10^{-4} to 1.11×10^{-3} and 6.94×10^{-5} to 5.56×10^{-4} mol dm^{-3}, respectively. A least squares analysis of these data indicates that for the concentration ranges given, the following relationships apply: $Q_R = a[Co^{2+}] + b$: xylenol orange, a = 1.33810, b = 0.00001; eriochrome black T, a = 0.34120, b = 0.00006; catechol violet, a = 0.85150, b = 0.00005. It is noted that the overall reaction of Co^{2+} with xylenol orange at the specified pH is endothermic whereas the corresponding reactions with the other two indicators studied are exothermic. A typical family of thermograms, as related to Co^{2+}/catechol violet thermometric titrations at pH 9.5 is shown in Fig. 2. The first break in these curves corresponds to the commencement of titrant addition to the calorimeter. Essentially linear reaction periods are obtained and sharp single extrapolated end-points are identified, thereby verifying that the Co^{2+}/catechol violet reaction is quantitative within the concentration range investigated. The calculated molar reaction enthalpies, $\Delta_R H_m^o$, are $+14.86\pm0.59$, -3.80 ± 0.07 and -9.46 ± 0.77 kJ mol^{-1} for Co^{2+}/xylenol orange, eriochrome black T and catechol violet interactions respectively in the reaction media defined.

An overall and detailed interpretation of these thermochemical data is difficult due to the variation of the respective reaction media in terms of

TABLE 1

Thermometric Titration of Co^{2+} with Xylenol Orange 0.025 M (pH 4.5)

$[Co^{2+}]x10^{-4}$ (Mol. dm^{-3})	$-\Delta T$ (mV)	Heat capacity (kJ mV^{-1})			$Q_R x10^{-4}$ (kJ)
		before	after	Cp_A	
0.27778	0.00018	0.21416	0.21808	0.21612	0.38902
0.41667	0.00028	0.21564	0.21738	0.21651	0.60612
0.55556	0.00035	0.21297	0.22095	0.21696	0.75937
0.69445	0.00069	2.21319	0.21712	0.21516	1.29096
0.83334	0.00060	2.21156	0.21451	0.21304	1.27825
1.11112	0.00074	0.21158	0.21678	0.21418	1.58495
1.38889	0.00087	0.21663	0.21908	0.21785	1.89534
1.66667	0.00110	0.21016	0.22287	0.21652	2.38172
2.08335	0.00123	0.21832	0.22301	0.22067	2.71426
2.77778	0.00180	0.21394	0.21904	0.21649	3.89683

TABLE 2

Thermometric Titration of Co^{2+} with Eriochrome Black T (0.1 M) (pH 10.4)

$[Co^{2+}] \times 10^{-4}$ (Mol. dm^{-3})	ΔT (mV)	Heat capacity ($kJ\ mV^{-1}$) before	after	Cp_A	$-Q_R \times 10^{-4}$ (kJ)
1.38889	0.00048	0.21700	0.21952	0.21862	1.04765
2.77778	0.00072	0.21552	0.21600	0.21576	1.55350
4.16667	0.00090	0.21709	0.21813	0.21761	1.95852
5.55556	0.00115	0.21504	0.21764	0.21634	2.48797
8.33334	0.00162	0.21453	0.21847	0.21650	3.50736
11.11110	0.00203	0.21320	0.21423	0.21371	4.33845

TABLE 3

Thermometric Titration of Co^{2+} with Catechol Violet (0.05 M) (pH 9.5)

$[Co^{2+}]x10^{-4}$ (Mol. dm^{-3})	ΔT (mV)	Heat capacity ($kJ\ mV^{-1}$)			$-Q_R x10^{-4}$ (kJ)
		before	after	Cp_A	
0.69444	0.00045	0.21276	0.21543	0.21410	0.96345
1.38888	0.00074	0.21567	0.21800	0.21683	1.60460
2.08333	0.00100	0.21453	0.21700	0.21577	2.15770
2.77777	0.00153	0.21625	0.21753	0.21689	3.31846
4.16666	0.00172	0.21705	0.22205	0.21955	3.77634
5.55555	0.00240	0.21654	0.21698	0.21676	5.20231

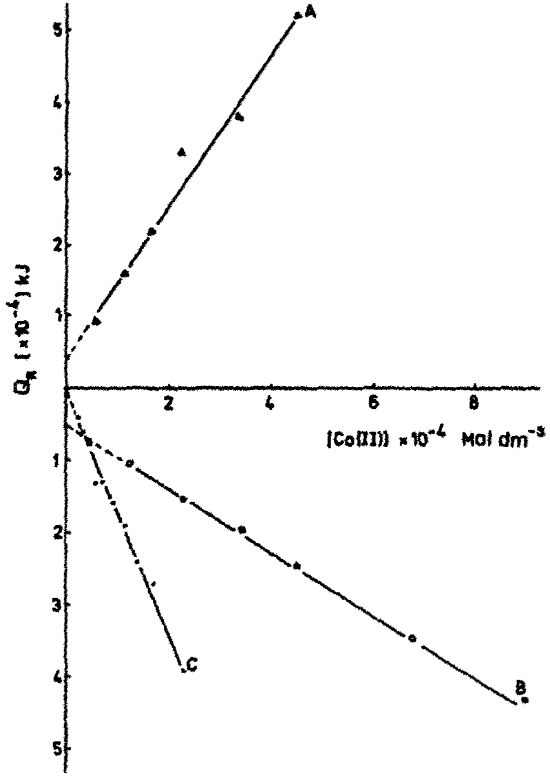

Figure 1 Q_R vs $[Co^{2+}]$; a xylenol orange

b eriochrome black T

c catechol violet

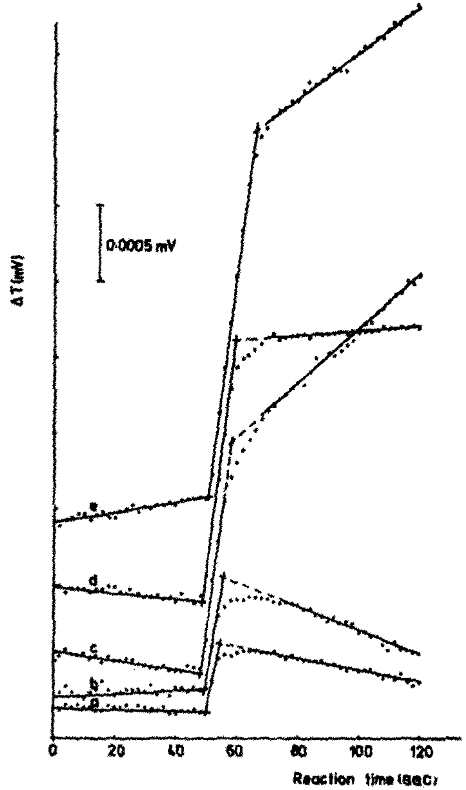

Figure 2 Enthalpograms: Co^{2+}/catechol violet; pH = 9.5; $[Co^{2+}]\times10^{-4}$ mol. dm^{-3}; a = 0.6944, b = 1.3888, c = 2.7776, d = 4.1664, e = 5.5952.

ionic strength and pH and the complexity in behaviour of these multidentate ligands in aqueous solution. However, for each titration type, it is assumed that the ionic strength of the reaction medium remains essentially constant during the thermometric titration as a result of excess buffer present. Also, due primarily to the strong chelate effect associated with these metallochromic indicator ligands, it is inferred that the primary reaction is the Co^{2+}/indicator reaction. Secondary complexation reactions between Co^{2+} and other ligands present in solution, such as NH_3 and OH^-, are neglected. With these assumptions, it is possible to interpret at least the $\Delta_R H_m^o$ data in terms of fundamental metal and ligand properties. According to Bishop (ref. 5), xylenol orange, eriochrome black T and catechol violet function in aqueous solution as hexabasic, tetrabasic and pentabasic acids, respectively. If 1:1, hexacoordinate, tetracoordinate and pentacoordinate complexes are formed by xylenol orange, eriochrome black T and catechol violet respectively with Co^{2+}, the relative stability of these complexes is reflected in the corresponding $\Delta_R H_m^o$ values, if it is assumed that these metal/metallochromic indicator reactions are 'enthalpy controlled'. This assumption is plausible in view of the strong chelate effects operating. The stability sequence in terms of the ligand involved is hence revealed as:

xylenol orange < eriochrome black T < catechol violet.

This sequence is partially rationalised in terms of a combination of three principle factors. Overall, for these complexes, it appears that the cobalt-oxygen coordinate bond strength exceeds that of cobalt-nitrogen and this effect in conjunction with the chelate effect, essentially explains the greater stability of the catechol violet complex compared to the eriochrome black T complex. The relatively low stability of the xylenol orange complex possibly reflects a coordination number of less than six for cobalt in this complex - steric factors associated with the ligand preclude the possibility of existence of the higher, preferred coordination number.

The present thermochemical data have indicated the potential of metallochromic indicators for the determination of cobalt in water by thermometric titrimetry. A further investigation of the effect of pH, indicator concentration and interfering ions is necessary prior to an assessment of the wider analytical significance of the method.

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