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CATALYTIC–THERMOMETRIC DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES USING THE IODINE–AZIDE REACTION

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ABSTRACT

A catalytic–thermometric method for the determination of the stoichiometry and stability constants of complexes with sulphur-containing ligands is proposed. The method is based on the inhibition of the catalytic activity of the ligands on the iodine–azide reaction when a metallic ion is present. A study of the errors associated with the method has been performed and used to improve experimental design. The conclusions have been applied to the determination of the stoichiometry and the stability constants of the Ni(II)–DDTC and Ni(II)–PDTC complexes.

INTRODUCTION

The iodine–azide reaction is selectively catalyzed by sulphur-containing compounds. In their presence the reaction proceeds rapidly, but stops suddenly when the divalent sulphur has been irreversibly oxidized by iodine. Under suitable experimental conditions, the extent of the reaction is proportional to the concentration of the catalyst, having been extensively applied to analytical chemistry. The determinations can be carried out by titration of the unconsumed iodine [1–4], or by a colorimetric [5] or a thermometric method [6–8].

The reaction has been also applied to the indirect determination of metal ions which inhibit the activity of the catalysts by complex formation. Methods based on this inhibition effect have been described for the determination of Co(II) with diethyldithiocarbamate (DDTC) [9], pyrrolidinedithiocarbamate (PDTC) [10] and 6-mercaptopurine [11]; Ni(II) with DDTC [8,12] and 6-mercaptopurine [11]; Cu(II) with thiopental [13], thioammeline [14] and 8-mercaptopurine [15] and Bi(III) with bismuthiol [16].

In this work, an inhibition-based catalytic–thermometric method is proposed for the determination of the stoichiometry and the stability constants

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of complexes with sulphur-containing ligands. This method provides direct measurement of the free ligand concentration, what is not always achieved by other methods.

Although the method can be applied to all kinds of sulphur-ligand complexes, this work is limited to systems where only one complex of a given stoichiometry, ML_n, is formed in a significant concentration.

A study of the errors associated to the method has been performed and used to improve experimental design. The conclusions have been applied to the determination of the stoichiometry and the stability constants of the Ni(II)–DDTC and Ni(II)–PDTC complexes.

THEORETICAL TREATMENT

In the presence of an excess of azide and small concentrations of a metallic ion and a sulphur-containing ligand, a temperature rise is produced when a certain volume of iodine solution is injected into the thermometric cell. The temperature pulse is usually proportional to the free ligand concentration, l, that may be expressed in the form

$$\Delta T = kl \tag{1}$$

where k is the slope of the ligand calibration straight line. The value of k is proportional to the induction coefficient of the catalyst, which is defined as moles of iodine consumed per mole of sulphur(-II) initially present [17].

The relationship between the stability constants of the complexes and the free ligand concentration is given by the metal and ligand mass-balances. When only one complex, ML_n, is present at significant concentration levels, the balance equations are

$$C_M = m' + [ML_n] = m' + \beta_n' m' l^n \tag{2}$$

$$C_L = l + n[ML_n] = l + n\beta_n' m' l^n \tag{3}$$

where C_M and C_L are the analytical concentrations of metal and ligand and β_n' the conditional stability constant of the complex. From these equations the value of β_n' is obtained

$$\beta_n' = \frac{l - C_L}{l^n(C_L - l - nC_M)} \tag{4}$$

The constant β_n is calculated from β'_n making use of the stability constants of the side-reactions.

Study of the error and experimental design

The determination of stability constants may be performed with minimum error if suitable sets of experiments are designed. In this way, the application of the theory of propagation of errors can be very useful to improve experimental design [18].

Relative errors affecting C_L and C_M are negligible with respect to the error associated to l because the values of the two former arise directly from the dilution of standardized solutions, whereas l is obtained from the thermometric measurements, whose relative standard deviation, σ_l/l, will always be significantly larger.

Taking into account that $\sigma_l = \sigma_{\Delta T}/k$, the application of the theory of propagation of errors to eqn. (4) gives

$$\sigma_{\log\beta'_n} = \left(\frac{1+\beta'_n l^n}{C_L - l} + \frac{n}{l}\right) \cdot \frac{\log e}{k} \cdot \sigma_{\Delta T} \tag{5}$$

The error, $\sigma_{\log\beta'_n}$ is linearly related to the precision associated with the temperature rise, $\sigma_{\Delta T}$, and can be obtained from the C_M, C_L and β'_n set of values corresponding to a given experiment. The value of l may be obtained solving eqn. (4) by an iterative calculation.

A suitable study of the influence of the variables involved may easily be performed if a constant value of C_L is assumed. Being ΔT_0 the temperature rise corresponding to C_L in the absence of the metallic ion, the substitution of k by the ratio $\Delta T_0/C_L$ in eqn. (5) leads to

$$\frac{\sigma_{\log\beta'_n}}{\sigma_{\Delta T}/\Delta T_0} = \left(\frac{1+\beta'_n l^n}{C_L - l} + \frac{n}{l}\right) C_L \log e \tag{6}$$

Equation (6) is plotted in Fig. 1 as a function of the ratio nC_M/C_L and for complexes of 1 : 1, 1 : 2 and 1 : 4 stoichiometries. A curve is obtained for each value of the parameter $a = C_L\beta_n'^{1/n}$. Optimal precision is attained when the value of the parameter is $a \simeq 1$. On the other hand, if $a \leqslant 1$, it is preferable that the experiments be carried out with C_M/C_L ratios larger than the stoichiometric value, whereas if $a > 1$, C_M/C_L ratios close to the stoichiometric value must be used in order to minimize the errors in the determination of $\log \beta'_n$.

Furthermore, the side-reactions, such as the formation of the metallic ion–azide complexes can be used to modify the value of β'_n. Nevertheless, a change in the concentration of azide not only modifies β'_n, but also the sensitivity, k [8], and therefore the value of C_L that must be used to obtain a certain value of ΔT_0. Both changes affect the parameter a in the same way, making it closer to the optimum value.

Figure 2 shows a plot of the ratio $l/C_L = \Delta T/\Delta T_0$ as a function of C_M/C_L for 1 : 2 complexes. The best range of a values $(0.1 < a < 100)$ corresponds to well separated lines on the figure. Similar diagrams are obtained for complexes of other stoichiometries.

When $a \geqslant 10$ a straight segment is observed for the lower values of C_M/C_L. The stoichiometry of the complex can be derived either from the

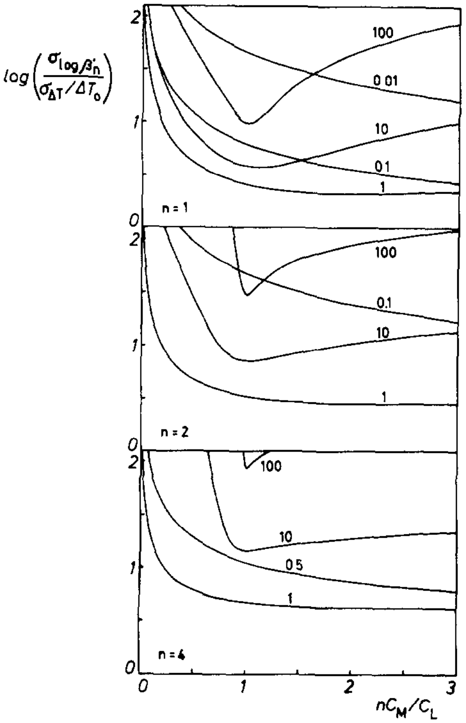

Fig. 1. Plot of eqn. (6) as a function of nC_M/C_L. The parameter on the curves is $a = C_L\beta'^{1/n}_n$.

slope of the straight segment or from the intersection of the extrapolated straight line with the X-axis. Thus, when $10 < a < 100$, both stoichiometry and stability constant can be obtained from a single series of experiments.

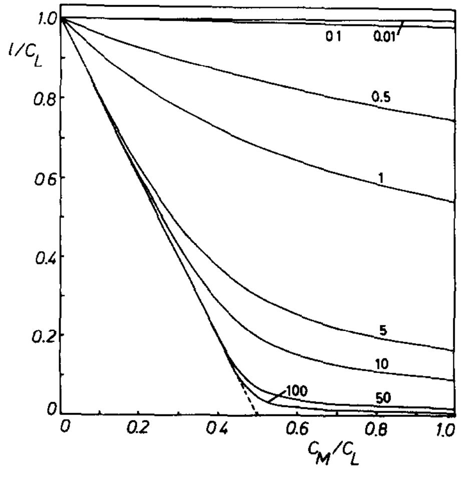

Fig. 2. Influence of the parameter a on l/C_L values for 1 : 2 complexes.

EXPERIMENTAL

Reagents

Iodine solutions 0.1 M in 1.0 M potassium iodide.

Sodium azide solutions 0.6 M prepared containing 1.77 M KCl in order to attain a constant 1 M ionic strength in the experiments and standardized by titration with $NaNO_2$, using $FeCl_3$ as indicator [19]. The concentration of the azide solution was checked to remain unchanged for two days.

Buffer solutions of $KH_2PO_4/NaOH$ (pH 6.6).

Sodium diethyldithiocarbamate and ammonium pyrrolidine-1-dithiocarbamate solutions prepared shortly before use by dissolving the reagents in a buffer solution of HBO_2/BO_2^- (pH 9). At this pH, the solutions remain unchanged at least for 3 h. The solid carbamates were stored at 0°C, in a refrigerator.

Nickel(II) solutions prepared by dilution of a 0.01 M $Ni(NO_3)_2$ stock solution, standardized gravimetrically with dimethylglyoxime.

Apparatus

Constant DC power supply and Wheatstone bridge were built according to Lumbiarres et al. [20]. The temperature-sensing element is a thermistor of 5 kΩ nominal resistance at 25°C. At the sensitivity setting used, a response of 15.27 mV $°C^{-1}$, corresponding to 305.4 mm $°C^{-1}$ pen deflection on the recorder, was obtained.

Triplicate experiments were performed in a thermostatted room at $25.0 \pm 0.1°C$.

Iodine solutions were injected into the cell by means of a Metrohm Multidosimat E-415 apparatus. The solution in the cell was stirred mechanically.

Procedure

The reagents are introduced into the cell in the following order: 5 ml of the ligand solution, 0–5 ml of the Ni(II) solution, 10 ml of the azide–KCl solution and 5 ml of the $KH_2PO_4/NaOH$ buffer. Distilled water is added to make the volume up to 25 ml if necessary. The mixture is allowed to stand for 10 min to assure the establishment of the Ni(II) carbamate–azide equilibrium [8]. Finally, 1 ml of the iodine–iodide solution is injected into the mixture.

The temperature rise produced by oxidation of the carbamates in the absence of azide is negligible at their usual concentration levels. However, blank tests without addition of the catalysts should be carried out because of the dilution heat of the iodine–iodide solution. The value of the blank

($\Delta T = 0.017$°C from five replicates) has been subtracted from all temperature rise values.

RESULTS AND DISCUSSION

The calibration straight lines for DDTC and PDTC, obtained in absence of a metallic ion are shown in Fig. 3. The values of the slopes are $k = 1.817 \times 10^4$°C M^{-1} and 1.537×10^4°C M^{-1}, respectively.

For the determination of the stability constants, two series of experiments with increasing Ni(II) concentrations have been carried out. The values of C_L (2.436×10^{-5} M DDTC and 3.279×10^{-5} M PDTC) have been chosen to get a temperature rise of $\Delta T_0 \simeq 0.5$°C. The results are shown in Fig. 4. The extrapolation of the straight segments intersect the X-axis close to the point $C_M/C_L = 0.5$ in both cases, according to the formation of 1:2 complexes. The same value is obtained from the ratio of the ligand calibration straight lines to the corresponding Ni(II) calibration straight segment slopes.

Triplicate experiments were repeated six times to establish the value $\sigma_{\Delta T} = 0.004$°C. Using eqns. (4) and (5), each experimental point leads to a value of $\log \beta_2' \pm \sigma_{\log \beta_2'}$. From the most significant points (Tables 1 and 2), a weighted mean conditional stability constant has been obtained for each complex, adopting the reciprocal of the variances as the statistical weights

TABLE 1

Determination of $\log \beta_2'$ for the Ni(II)–DDTC complex

$C_{Ni(II)}$ (M)	$\overline{\Delta T}$ (°C)	$\log \beta_2'$	$\sigma_{\log \beta_2'}$
5.602×10^{-6}	0.248	11.074	0.22
6.536×10^{-6}	0.218	11.089	0.16
7.469×10^{-6}	0.186	11.231	0.15
8.403×10^{-6}	0.162	11.156	0.098
9.337×10^{-6}	0.140	11.147	0.078

TABLE 2

Determination of $\log \beta_2'$ for the Ni(II)–PDTC complex

$C_{Ni(II)}$ (M)	$\overline{\Delta T}$ (°C)	$\log \beta_2'$	$\sigma_{\log \beta_2'}$
1.212×10^{-5}	0.147	11.401	0.14
1.327×10^{-5}	0.127	11.243	0.087
1.442×10^{-5}	0.100	11.375	0.082
1.557×10^{-5}	0.088	11.310	0.072
1.672×10^{-5}	0.079	11.255	0.067

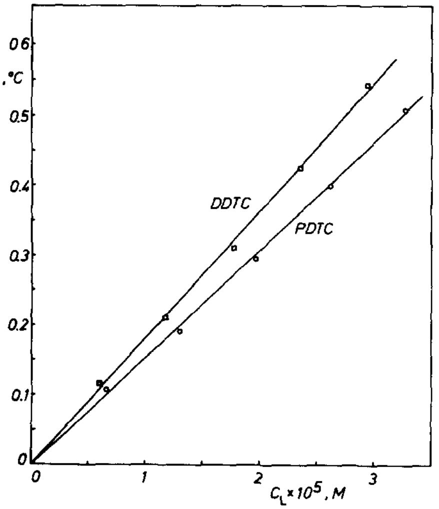

Fig. 3. DDTC and PDTC calibration straight lines.

[18]. The mean values are $\log \beta_2' = 11.148 \pm 0.052$ and 11.301 ± 0.037 for Ni(II)–DDTC and Ni(II)–PDTC, respectively.

The values of the parameter a corresponding to the two series of experiments performed are 9.2 and 14.7 for Ni(II)–DDTC and Ni(II)–PDTC, respectively, in agreement with the shape of the Ni(II) calibration curves (Fig. 4). These values allow the simultaneous determination of the conditional constant and the stoichiometry of the complexes.

The values of $\log \beta_2$ have been calculated taking into account the formation of the Ni(II)–azide complexes ($\log \beta_1 = 0.86$, $\log \beta_2 = \log \beta_3 = 1.3$ at

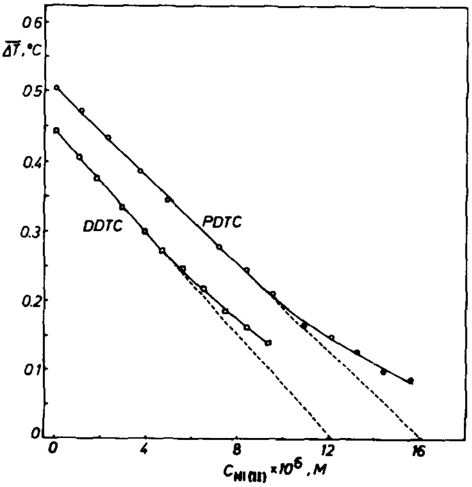

Fig. 4. Ni(II) calibration curves. Determination of the conditional constants. $C_{DDTC} = 2.436 \times 10^{-5}$ M, $C_{PDTC} = 3.279 \times 10^{-5}$ M.

25°C and I = 1 M) [21], the Ni(II)–HPO_4^{2-} complex (log $K = 2.08$ at 25°C and I = 0.1 M) [22] and the protonation of the phosphate system (log K_1 = 11.1, log $K_2 = 6.61$, log $K_3 = 2.36$ at 25°C and I = 1 M) [23]. The results are log $\beta_2 = 12.26$ for Ni(II)–DDTC and 12.41 for Ni(II)–PDTC, which agree satisfactorily with the literature data, 12.1 and 12.4, respectively, obtained by a polarographic method in the same conditions (25°C and I = 1 M) [24].

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