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THERMODYNAMICS OF COUPLED REACTIONS BY THE AMPLITUDES OF CHEMICAL RELAXATION

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Abstract

The amplitudes of the relaxation curves, as obtained by the Temperature-jump method have been used to measure simultaneously equilibrium constant and enthalpy for the reaction of complex formation of Ni^{2+} ion by 2,6-dihydroxobenzoic acid in the presence of a buffer. The experiments have been performed by changing the concentration of metal ion at constant ligand concentration and *pH* as in a complexometric titration. The points of such 'dynamic titrations' have been analysed by means of the concept of 'normal reactions' which enabled us to transform a set of coupled individual steps into a set of kinetically independent reactions. The potentialities of the dynamic titrations are discussed.

Keywords: kinetics, relaxation, thermodynamics

Introduction

Chemical relaxation methods provide a useful tool for the investigation of the kinetic and thermodynamic behaviour of reacting chemical systems [1].

When a set of coupled reactions at equilibrium is perturbed by a sudden external force, such as a change of temperature, pressure or eletric field density, it relaxes toward a new equilibrium position according to a multiexponential function

$$\Delta A_{tot} = \sum_{k=1}^{R} \Delta A_k^o \, e^{-t/\tau_k} \qquad (1)$$

ΔA_{tot} is the time dependent displacement of the whole system from the equilibrium position and therefore represents a concentration variable or a quantity proportional to it. In the present work ΔA_{tot}, and consequently ΔA_k^o, indicate a change of absorbance. R is the number of thermodynamically independent steps, ΔA_k^o is the amplitude of the *kth* relaxational effect and τ_k is the corresponding time constant. The latter parameter encloses information of kinetic nature and its analysis for the present system has been already performed [2].

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The amplitudes, on the other hand, contain information of thermodynamic character.

It should be noted that each *kth* term of the sum in Eq. (1) is not associated to the *kth* individual step but to a suitable combination of all the R thermodynamically independent steps of the system. The result of such a combination is called 'normal reaction' or 'normal mode' by analogy with the normal modes of motion in mechanical and molecular systems. Equation (1) thus describes the behaviour of the system in terms of R normal reactions whose fundamental property is that they are uncoupled, i.e. they relaxe independently.

The complexation of Ni(II) by 2,6-dihydrobenzoic acid in the presence of sodium cacodylate provide an interesting case where the normal reactions take a particularly simple form and therefore the analysis of the amplitudes is quite straightforward.

Experimental

All chemicals were of analytical grade. 2,6-dihydroxobenzoic acid was recrystallised from water. Sodium perchlorate was used to adjust the ionic strength to 0.3 M. The acidity of the solutions was measured by using a combined glass electrode where the usual KCl bridge was replaced by a liquid junction made by 3 M NaCl. The readings of the pH-meter were converted into hydrogen ion concentration with the equation $-\log[H^+] = pH + 0.05$ which was derived by means of an already described calibration procedure [3]. The solution in the T-jump cell, initially kept at 22°C, was subjected to a capacitor discharge providing a jump of temperature of 3°C so that the final temperature was 25(±0.1)°C. The shift of absorbance, ΔA, induced by the perturbation was calculated by the equation $\Delta A = -\Delta I\ /\ (2.3I_o)$ where ΔI is the instrumental signal expressed in mV and I_o = 3000 mV is the total light intensity falling on the photomultipliers. The amplitudes and relaxation times were evaluated with the help of an electronic simulator of exponential curves.

Results

All measurements were performed in the presence of an excess of metal ion ($C_M> >C_L$). These circumstances, besides ensuring the formation only of complexes of molar composition 1:1, offer also the advantage of making simpler the equations necessary to the amplitude analysis. Spectrophotometric measurements [2] enabled us to exclude the presence of noticeable amounts of the protonated complex MH_2L^+. On the other hand, in the investigated range of pH, between 6.0 and 7.0, only the ligand protonated at the phenolic groups, H_2L^-, is present [2]. It was also observed in this and in an other study [4] that the pH

of a solution of ligand decreases after addition of an equimolar amount of nickel perchlorate. According to these results, the reacting system in buffer solution is described by two coupled steps as in the scheme (I–II) (charges are omitted)

$$H + B \rightleftharpoons HB \tag{I}$$

$$M + H_2L \rightleftharpoons MHL + H \tag{II}$$

Step(I) represents a proton transfer process involving the buffer sodium cacodylate-cacodylic acid whose total concentration is $C_B = 3\times10^{-3}$ *M*. Two independent steps give rise to two normal modes [1]. These are obtained by multiplying step(I) and step(II) by C_{1k} and C_{2k} respectively and then by summing the resulting terms [5]. The normal reactions are

$$\left(1 - \frac{C_{2k}}{C_{1k}}\right) H + B + \frac{C_{2k}}{C_{1k}} H_2L + \frac{C_{2k}}{C_{1k}} M \rightleftharpoons HB + \frac{C_{2k}}{C_{1k}} MHL \tag{i}$$

The ratios C_{2k}/C_{1k} were evaluated as previously described [5]. In all the investigated range of concentrations it was found that, for $k = 1$, $C_{21}/C_{11} = 0$ whereas, for $k=2$, $C_{22}/C_{12}=1$. These results are quite surprising since the above ratios are in general fractional and concentration dependent. Introduction of $C_{21}/C_{11}=0$ in Eq. (i) shows that the first normal reaction coincides with the elementary step(I) whereas introduction of $C_{22}/C_{12} = 1$ in Eq. (i) reduces the second normal reaction to the simple form

$$B + H_2L + M \rightleftharpoons HB + MHL \tag{ii}$$

The amplitude of the *kth* normal mode is given by the relationship [6]

$$\Delta A_k^o = \Delta\varepsilon_k \, \Delta H_k \, \Gamma_k \frac{\Delta T}{RT^2} \tag{2}$$

where $\Delta\varepsilon_k$ is the difference of the extinction coefficients, ΔH_k is the reaction enthalpy and Γ_k is an amplitude factor. Under the circumstances $C_M >> C_L$ and [B], [HB] >> [H_2L], [MHL] the amplitude factor of the normal reaction (ii) is [6]

$$\Gamma_{ii} = \frac{KC_MC_L}{(1 + KC_M)^2} \tag{3}$$

where *K* is an 'apparent equilibrium constant' related to the equilibrium constant of the individual reaction (II). Introduction of Eq. (3) in Eq. (2) yields the linear relationship

$$\left|\frac{C_M C_L}{\Delta A^\circ}\right|^{1/2} = \frac{1}{B} + \frac{K}{B}C_M \qquad (4)$$

where $B = |\Delta\varepsilon K \Delta H \Delta T / RT^2|^{1/2}$.

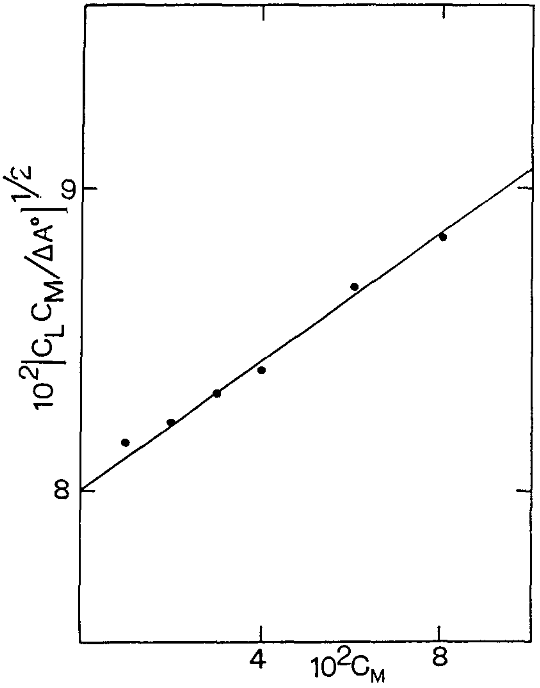

Fig. 1 Dynamic titration of the Ni(II)-2,6-dihydroxobenzoic acid system. $C_L = 4\times10^{-4}$ M, $C_B = 3\times10^{-3}$ M, $pH = 6.0$, $I = 0.3$ M, $T = 25$°C, $\lambda = 332$ nm

An example of analysis according to Eq. (4) is shown in Fig. 1. The ratio of slope to intercept yields K whereas ΔH is derived from the intercept with a measured value for $\Delta\varepsilon$ of 1250 M^{-1} cm^{-1}. As in classical titrations the amplitudes have been measured for different values of C_M at costant C_L and pH. We shall therefore refer to the experiment of Fig. 1 as to a 'dynamic titration'. The values of the thermodynamic parameters derived from dynamic titrations carried out at different pH values are given in Table 1. Note that K increases with pH. This can be explained by considering that in deriving Eq. (3) the contribution of the buffer concentration to the amplitude factor is small and therefore it has been neglected [6]. At constant pH the system behaves as being formed only by the species M, H_2L, MHL. This situation complies with the concept of 'apparent reaction' introduced by Schwarzenbach in its theory of complexometric titrations [7]. The apparent reaction can be written as [2]

$$M_f + L_f \rightleftharpoons ML_T \tag{III}$$

where M_f and L_f indicate all forms of uncomplexed metal and ligand respectively whereas ML_T represents all possible 1:1 complexes. As outlined before [2], in the present system is $[M_f] = [Ni^{2+}]$, $[L_f] = [H_2L]$ and $[ML_T] = [MHL]$. The equilibrium constant of the apparent reaction (III) is then reduced to

$$K_{app} = \frac{[MHL]}{[M]\,[H_2L]} \tag{5}$$

A comparison of Eq. (5) with the equilibrium constant of reaction (II) leads to the relationship

$$K_{app} = \frac{K_{II}}{[H]} \tag{6}$$

which accounts for the observed dependence of K_{app} on the hydrogen ion concentration. Introduction of the data of Table 1 in Eq. (6) yields $K_{II} = (1.0 \pm 0.1) \times 10^{-6}$.

It has been demonstrated [6] that, when the solution is buffered, the reaction parameters, $\Delta\varepsilon$, Γ and ΔH, of the apparent reaction (III) coincide with those of a suitable normal reaction. Therefore, whereas K_{app} derived from plots as in Fig. 1 is related to Γ_{ii}, the reaction enthalpy evaluated from the same plots coincides with ΔH_{ii}. An inspection of Eq. (ii) shows that the second normal reaction is formed by step (I) plus step (II). Therefore

$$\Delta H_{ii} = \Delta H_I + \Delta H_{II} \tag{7}$$

Being [5] $\Delta H_I = 2.3\,kJ\cdot mol^{-1}$ from the data of Table 1 one obtains $\Delta H_{II} = -(32 \pm 3)\ kJ\cdot mol^{-1}$.

Table 1 Equilibrium constant, K_{app}, of reaction (III) and enthalpy of the normal reaction (ii) for different *pH* values. $T = 25°C$, $I = 0.1\ M$

pH	K_{app} / 1 mol^{-1}	ΔH_{ii} / kJ·mol^{-1}
6.0	1.4	–25
6.3	2.3	–28
6.5	3.2	–32
6.8	7.2	–32
7.0	9.7	–32

Discussion

The value of the equilibrium constant derived from the amplitudes is in fair agreement with those obtained [2] by classical spectrophotometry and from the ratio of rate constants. No data are reported in the literature about ΔH_{II}. From previous studies [5, 6, 8] it has been found that the accuracy of the dynamic titration is similar to that of the classical methods for systems which, as the presently investigated one, exhibit a moderate degree of formation.

The analysis of the amplitudes is in this case particulary easy because the dynamic behaviour of the system is described by only two stoichiometrically simple normal reactions. It should be noted that the additional steps

$$MOH + H \rightleftharpoons M + H_2O \qquad \text{(IV)}$$

$$MOH + H_2L \rightleftharpoons MHL + H_2O \qquad \text{(V)}$$

could in principle contribute to the dynamics of the system. However the exchange rates [9] of step (IV) and step (V) are negligible in comparison with those of steps (I) and step (II) respectively and consequently their contribution to the expressions for C_{2k}/C_{1k} can be disregarded as far as the conditions [M], [B]> >[MOH] hold. Replacing the buffer sodium cacodylate (3×10^{-3} *M*) by the indicator bromothymolblue (3×10^{-5} *M*) the amplitudes could be correctly analyzed only by taking account for the additional step (IV) whereas step (V) could be again neglected. The presence of a suitable buffer can thus simplify the amplitude analysis. Moreover, the buffer addition makes a transformation in the normal reactions of such a nature that measurable amplitudes are often excited in system that, as the present one, in the absence of buffer would be almost insensitive to the external perturbation [6, 8].

The circumstances where the dynamic method becomes superior to the classical techniques have been discussed elsewhere [6, 10]. It will be pointed out here that in classical titrations the information about the equilibrium constants depends on a relative instrumental response and therefore signal amplification cannot provide any improvement of resolution. By contrast, in the dynamic titration the required information is enclosed in the absolute instrumental signal. In this case the electronic amplification can enhance the response to levels that can provide a sensitive measure of the parameter K [10]. A limit to the amplification is set only by the instrumental noise. For this purpose we have recently built [11] a spectrophotometric device for detection of fast transient processes which makes use of lasers as light sources. With a power of 5 mWatt at 633 nm and with a rise time of 2 μsec the signal-to-noise ratio is about 40 times higher than that of one of the best commercial apparatuses. This result enabled us to measure accurately relaxation processes which are too disturbed to be analyzed with conventional *T*-Jump instruments.

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Zusammenfassung — Die Amplitude von Relaxationskurven, wie man sie durch die Temperatursprungmethode erhält, wurde zum simultanen Vermessen der Gleichgewichtskonstante und der Enthalpie für die Reaktion der Komplexbildung des Ni^{2+}-Ions mit 2,6-Dihydroxobenzoesäure in Gegenwart eines Puffers verwendet. Die Experimente wurden – wie in einer komplexometrischen Titration – bei konstanter Ligandenkonzentration und konstantem *pH*-Wert durch Änderung der Metallionenkonzentration durchgeführt. Die Punkte dieser 'dynamischen Titrationen' wurden mit Hilfe des Konzeptes der 'Normalreaktionen' ausgewertet, was uns die Umwandlung eines Satzes von miteinander verbundenen Einzelschritten in einen Satz kinetisch voneinander unabhängigen Reaktionen ermöglichte. Die Möglichkeiten der dynamischen Titrationen werden diskutiert.