

Quantitative determination of metal ions and anions in aqueous solution by using pH-responsive redox-active receptors

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The redox-active polyazacycloalkane 1,4,8,11-ferrocenylmethyl-1,4,8,11-tetraazacyclotetradecane L¹ is a versatile receptor for the quantitative electrochemical determination of metal ions (Cu²⁺, Zn²⁺, Cd²⁺) and ATP in aqueous solution.

In recent years a number of work has been devoted to the development of new receptors containing binding sites and redox-active groups.¹ Two properties are common to those new molecules; their electroactive character and the ability to bind substrates. Some of those receptors bearing different redox-active groups (able to be reduced or oxidized), can electrochemically recognize alkali-metal and alkaline-earth-metal cations,² anions³ and neutral species.⁴ Additionally it has recently been reported that transition-metal ions can also adequately be recognised by using ferrocene-functionalised polyamines as receptors.^{5,6} That approach leads to pH-responsive redox-active molecules where the shift of the oxidation potential in the presence of transition-metal ions is a function of the pH.⁵ Additionally the functionalisation of polyaza molecules with redox groups are good candidates to electrochemically recognize anion coordination based on the property of those systems to act as polybases.⁶ To further advance the use of redox-active receptors as practical electrochemical sensors we have performed electrochemical studies, using the redox-functionalised polyazacycloalkane 1,4,8,11-ferrocenylmethyl-1,4,8,11-tetraazacyclotetradecane L¹,⁷ with the aim of quantitatively determining the concentration of cations and anions in solution.

Fig. 1 shows the variation of the oxidation potential ($E_{1/2}$, from rotating disk electrode techniques) vs. pH for the systems L¹-H⁺-M²⁺ (M = Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, ligand-to-metal ratio = 1:1) in thf-water (70:30 v/v) mixtures. The oxidation potential of L¹ shifts to more anodic potentials when the pH is reduced as a consequence of the successive protonation of the amino groups. In the presence of stoichiometric amounts (M²⁺/L¹ = 1) of metal ions different curves are found. Some of them are quite different (for Cu²⁺, Zn²⁺, Cd²⁺) and some quite similar (for Pb²⁺ and Ni²⁺) to that of the free receptor (see Fig. 1). We have also found that for ligand-to-metal ratios <1, curves between that of L¹ and that with M²⁺/L¹ = 1 are obtained. At a fixed pH, $E_{1/2}$ for a determined M²⁺/L¹ ratio is $E_{1/2} = x_L E_{1/2}^L + x_{ML} E_{1/2}^{ML}$ where x_L and x_{ML} are the molar fractions of the free receptor and the metal complex, respectively; whereas $E_{1/2}^L$ and $E_{1/2}^{ML}$ are the oxidation potential of L¹ and the oxidation potential of a 1:1

ligand-to-metal molar ratio. Knowing the amount of receptor used in the electrochemical experiments it is possible to determine the concentration of metal ions in solution. In a typical experiment we measured $E_{1/2}$ for an unknown M²⁺/L¹ ratio at at least five different pH values and have determined an average concentration of the metal and the standard deviation. Working with L¹ concentrations in the range (4–5) × 10⁻⁴ mol dm⁻³ we have been able to determine metal ion concentrations from 5 × 10⁻⁵ to 4 × 10⁻⁴ mol dm⁻³. Probably lower limits of detection could be reached by using lower concentrations of receptor L¹. Table 1 shows the concentration of Cu²⁺, Zn²⁺ and Cd²⁺ found and compared with the concentration by standard atomic absorption analysis. We have also developed studies on the quantitative determination of two metal ions showing different L¹-H⁺-M²⁺ curves to that of L¹ and have found that the simultaneous determination of Cu²⁺, Cd²⁺ and Cu²⁺, Zn²⁺ in mixtures containing both ions is possible if [L¹] = [Cu²⁺] + [Zn²⁺] or [L¹] = [Cu²⁺] + [Cd²⁺], whereas the method seems not to be accurate enough if the total concentration of the metals is unknown. Additionally the existence of some metal ions, as Ni²⁺ and Pb²⁺, with L¹-H⁺-M²⁺ curves close to that of L¹ suggests that the concentration of Cu²⁺ (which probably has a higher stability constant with L¹ than Ni²⁺ or Pb²⁺) could be determined in the presence of those metal ions. Data in Table 1 confirm that [Cu²⁺] can be selectively determined in the presence of Ni²⁺ or Pb²⁺. Even with large amounts of Pb²⁺ copper(II) can be quite accurately determined {[Cu²⁺] = 4.9 × 10⁻⁵, 2.33 × 10⁻⁴ and 3.32 × 10⁻⁴ mol dm⁻³ found in the presence of [Pb²⁺] = 2.23 × 10⁻³ for copper concentrations of 1.33 × 10⁻⁴, 2.66 × 10⁻⁴ and 3.33

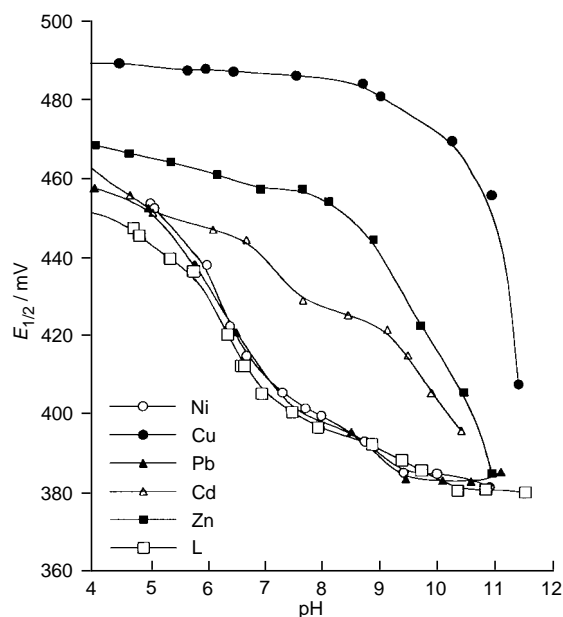
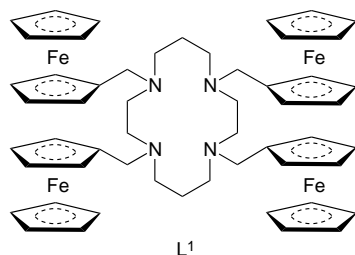


Fig. 1 Plot of $E_{1/2}$ vs. pH for L¹-H⁺ and L¹-H⁺-M²⁺ (M²⁺ = Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺)

Table 1 Comparison between the determination of the concentration of metal ions by using electrochemical (L^1 as receptor) and standard atomic absorption methods

| $10^5 [Cu^{2+}]$ | $10^5 [Zn^{2+}]$ | $10^5 [Cd^{2+}]$ | $10^5 [Cu^{2+}] + [Cd^{2+}]^a$ | $10^5 [Cu^{2+}] + [Zn^{2+}]^d$ | $10^5 [Cu^{2+}]^e$ | $10^5 [Cu^{2+}]^f$ |
|--|------------------|------------------|--------------------------------|--------------------------------|--------------------|--------------------|
| 8.8(6) ^a [9.1] ^b | 5.2(9) [5.9] | 10.6(7) [11.1] | 13(2), 27(3) [12.9, 26.6] | 14(1), 26(1) [13.4, 26.1] | 11(4) [9.6] | 11(1) [9.7] |
| 17(1) [18.7] | 27(1) [28.4] | 19(1) [22.4] | 19(2), 20(3) [20.1, 19.5] | 20(1), 20(1) [20.1, 19.7] | 25(4) [19.3] | 20(1) [19.4] |
| 29(1) [28.0] | 18(1) [17.9] | 31(2) [33.6] | 28(1), 12(2) [26.9, 12.9] | 28(1), 12(1) [26.7, 13.2] | 30(3) [28.9] | 28(1) [28.9] |

^a Concentration (mol dm^{-3}). Values in parentheses are the standard deviations in the last significant digit. ^b Metal concentration (mol dm^{-3}) found using standard atomic absorption methods. ^c Determination under the condition $[L^1] = [Cu^{2+}] + [Cd^{2+}]$. ^d Determination under the condition $[L^1] = [Cu^{2+}] + [Zn^{2+}]$. ^e $[Cu^{2+}]$ determined in the presence of Ni^{2+} , $[Ni^{2+}] = 20 \times 10^{-5} \text{ mol dm}^{-3}$. ^f $[Cu^{2+}]$ determined in the presence of Pb^{2+} , $[Pb^{2+}] = 20 \times 10^{-5} \text{ mol dm}^{-3}$.

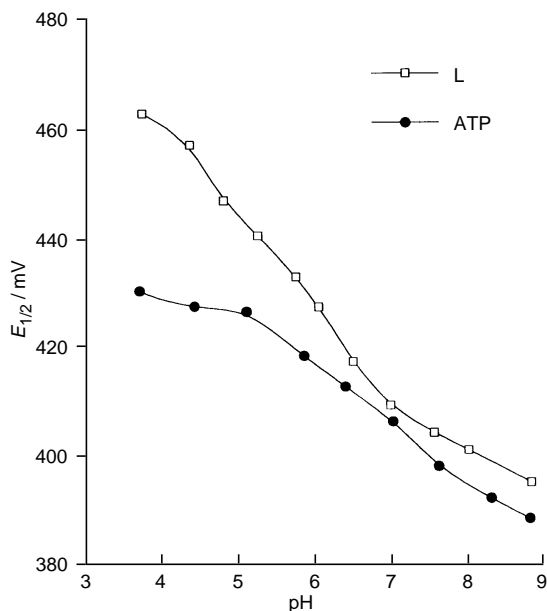


Fig. 2 Plot of $E_{1/2}$ vs. pH for L^1-H^+ and L^1-H^+-ATP

$\times 10^{-4} \text{ mol dm}^{-3}$, respectively, from standard atomic absorption analysis).

Finally Fig. 2 displays the $E_{1/2}$ -pH curve obtained for receptor L^1 with ATP. The presence of the anion, as expected, does not change significantly the $E_{1/2}$ -pH curve of L^1 when the pH is basic, but if the pH is reduced a steady shift to more cathodic potentials is observed. Based on that difference between the two L^1-H^+ and L^1-H^+-ATP systems and following a similar method to that used above we have determined ATP concentrations in aqueous solution (see Table 2). The results, which are as accurate as when metal ions are determined, although there is a small difference between L^1-H^+ and L^1-H^+-ATP curves, suggest that the method may prove useful in the determination of ATP or other anions using similar systems containing larger numbers of amino groups.

To our knowledge this is a new method for the quantitative determination of metal ions and anions in aqueous solution by using pH-responsive redox-active receptors. As an example molecule L^1 has proved to be a versatile receptor which can be used to quantitatively determine metal ions (Cu^{2+} , Zn^{2+} or Cd^{2+} ; mixtures of Cu^{2+} , Cd^{2+} and Cu^{2+} , Zn^{2+} ; Cu^{2+} selectively in the presence of Ni^{2+} or Pb^{2+}) and anions (ATP). The development

Table 2 Determination of the concentration of ATP by using electrochemical methods and L^1 as receptor^a

| $10^5 [ATP]$ |
|---------------------------|
| 17(2) ^b [16.4] |
| 21(1) [18.9] |
| 40(2) [41.1] |

^a Data for the ATP determination have been taken from pH 3.5 to 5. ^b Concentration (mol dm^{-3}). Values in parentheses are the standard deviations in the last significant digit.

of new sensors for quantitative recognition is now being carried out.

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Footnote

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