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ORIGINAL ARTICLE

A simple conductometric method for trace level determination of brilliant green in water based on β-cyclodextrin and silver nitrate and determination of their thermodynamic parameters

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Abstract A gravimetric and complexometric titration method based on conductometric technique is presented for the quantitative determination of brilliant green (BG) in water. The equilibrium constants and the thermodynamic parameters for the complex formation of β-cyclodextrin (β-CD) with brilliant green (BG) and precipitation of silver nitrate with BG have been determined by conductivity measurements in water. The results suggest that stable 1:1 complex is formed between BG and β-cyclodextrin and the thermodynamic parameters (ΔH_c°, ΔS_c°) for this complexation reaction have been determined from temperature dependence of the stability constant using the van't Hoff plots. Based on the obtained results, the conductometric method for the determination of BG in the presence of β-CD at 25 °C was developed in the range of 10^{-8}–10^{-3} mol L^{-1} and with $AgNO_3$ is 10^{-3}–10^{-5} mol L^{-1}.

1. Introduction

Brilliant green (Fig. 1) is a triphenylmethane dye that has been used in fish farming industry during many decades because of its broad anti-microbial, anti-parasitic and anti-fungal spectrum, its high efficiency in the prevention and treatment of certain fish diseases and its low cost. BG dye is toxic and has mutagenic and carcinogenic effects that affect aquatic biota and humans (Seshadri et al., 1994; McKay and Otterburn, 1985; Dutta and Indian, 1994; Gregory et al., 1991; Krishna and Bhattacharyya, 2003). It causes especially eye burns, which may be responsible for permanent injury to the eyes of humans and animals. It is also used extensively in textile dying (Janos et al., 2003; Mall et al., 1996; Srivastava et al., 2005) and for the production of cover paper in the paper industry. Therefore, developing sensitive and simple method for the determination of BG is of great importance and interest in chemical analysis. Since today some techniques for the

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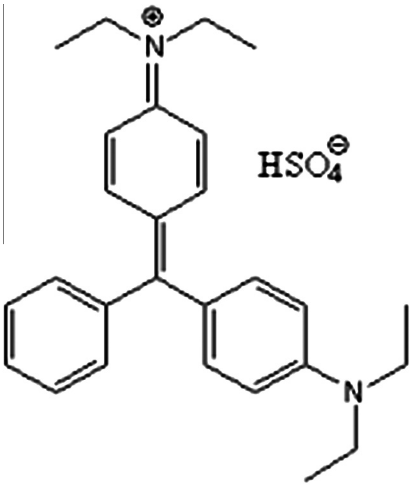

Figure 1 Structure of brilliant green.

determination of trace amounts of malachite green (MG) have been reported (Halme and Lindfors, 2004; Pourreza and Elhami, 2007; Afkhami et al., 2010; Nicolle et al., 2011; Cheng, 2009; Lee et al., 2006; Jesús Martínez Bueno, 2010; Bahram, 2011), but the reports for the determination of BG are very scarce. Some of these techniques are spectrophotometry (Es'haghi, 2011), dosimetry (Khan, 2002); but these techniques are expensive and time consuming. Conductometric method is a very simple, sensitive and low cost method.

The most important uses of conductance in analytical chemistry are related to conductometric titrations which exhibit excellent features. Instrumentation required are simple where a low cost conductance apparatus is adequate. Titration of weak acids and bases that are otherwise impossible to titrate or acid–base system for which no suitable indicators are available are well suited to conductometric titrations. Conductance will be minimal at the equivalence point while high values before and after titrations or at either extreme allow easy location of the equivalence point. Examples of the importance of conductometric titrations are the precipitation and complexometric titrations. Since the conductance of a sparingly soluble compound is minimal, the equivalence point can be easily located. This is significantly important for the precipitation titrations of some systems that have no suitable indicators, or complex forming reactions. Conductometric titrations can also be used for mixture analysis where a separate end point is obtained for each component.

We used $AgNO_3$ for the precipitation titration and cyclodextrin for complexometric determination of brilliant green in water. Cyclodextrins (CD) (Fig. 2) are a family of cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic central cavity. Cyclodextrin molecules are relatively large with a number of hydrogen donors and acceptors and thus, in general they do not permeate lipophilic membranes. Cyclodextrins are widely used as ‘‘molecular cages’’ in the pharmaceutical, agrochemical, food and cosmetic industries (Roux and Perly, 2007). Cyclodextrin inclusion complexes are of interest for scientific research, because they exist in aqueous solution and can be used to study the hydrophobic interactions which are so important in the biological systems. Cyclodextrins can catalyze several chemical reactions and therefore they and their functionalized derivatives (modified cyclodextrins) provide useful enzyme models. Of particular interest are the water-soluble hosts with hydrophobic cavities, which mimic these biochemical interactions. They catalyze reactions by supramolecular catalysis involving reversible formation of host–guest complexes. Complexation depends on the size, shape and hydrophobicity of the guest molecule.

In this work we used a conductometric method for the determination of BG in water and also simultaneous determination of MG and BG in natural water. Also we investigated on the thermodynamic properties of the BG–CD complex and BG–Ag precipitate.

2. Experimental

β-Cyclodextrin (CD) and BG were purchased from Aldrich. All reagents were of analytical grade, and the solutions were prepared using deionized water. The stock solutions of 1×10^{-2} mol L^{-1} β-cyclodextrin and $AgNO_3$ were prepared by dissolving an appropriate mass of these reagents in deionized

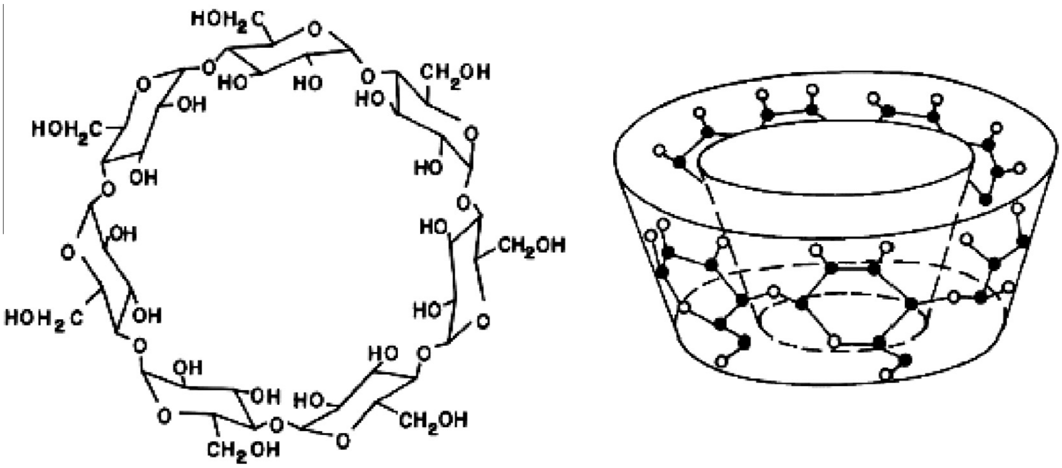

Figure 2 Structure of cyclodexterine.

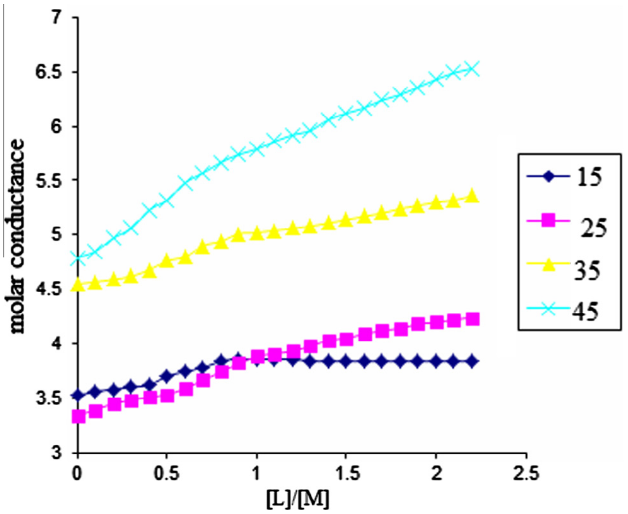

Figure 3 Molar conductance-mole ratio plots for (CD–BG) complex at different temperatures: (♦15 °C, ■25 °C, ▲35 °C, ×45 °C).

water. The solutions of CD and $AgNO_3$ in various concentrations were obtained by adequate dilution of the stock solution.

The experimental procedure to determine the stability constants of BG–CD complex and BG–Ag precipitate is as follows: a solution of BG (1×10^{-4} M) was placed in a titration cell, thermostated at a given temperature and the conductance of solution was measured. Then a step-by-step increase of the titrant solution (1×10^{-3} M) was carried out by a rapid transfer to the titration cell using a microburett and the conductance of the solution in the cell was measured after each transfer at the desired temperature.

The conductance measurements were performed using a digital AMEL conductivity apparatus, model 60, in a water bath thermostated at a constant temperature which maintained within ±0.03 °C .The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. The cell constant was 0.73 cm^{-1}.

3. Results and discussion

The changes of molar conductivity (Λ_m) versus the $[L]/[M]$ of titrant for the complexation of β-cyclodextrin with BG and precipitation of $AgNO_3$ with BG were measured in water. Fig. 3 presents a characteristic conductometric curve obtained for conductometric titration of the 1.0×10^{-3} mol L^{-1} BG solution using a 1.0×10^{-2} mol L^{-1} CD solution in various temperatures. Also a typical titration of BG with $AgNO_3$ at 25 °C is shown in Fig. 4. As can be seen from these figures, the slope of the curves changes sharply at $[L]_t/[M]_t$ about 1, which is an evidence for the formation of a stable 1:1 product.

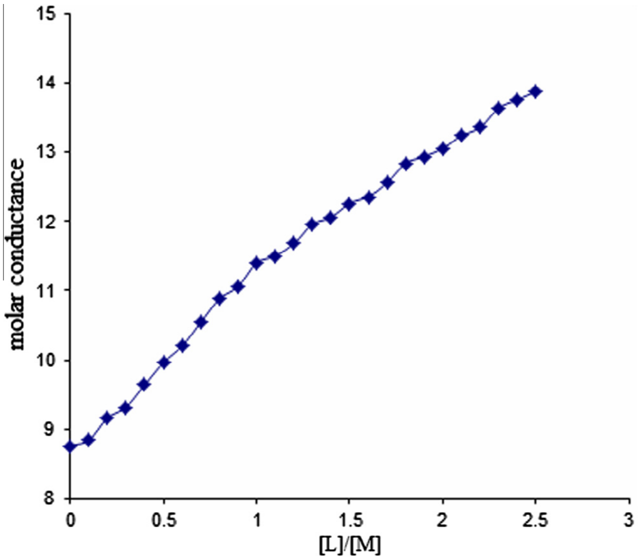

Figure 4 Molar conductance–mole ratio plots for (Ag–BG) precipitate.

3.1. Determination of BG with gravimetric titration method

In the present article, the conductometric titration of BG in water using silver nitrate as titrant is described. The method is based on the formation of an Ag–BG compound between the titrants $AgNO_3$ and the brilliant green. The concentration range of 10^{-3}–10^{-5} mol L^{-1} of BG was determined with this reagent and the detection limit was 1×10^{-5} M

3.2. Determination of BG with complexometric titration method

For the BG concentrations less than 1×10^{-8} mol L^{-1}, the addition of the titrant caused small variations in the conductance, making the determination of the final point of the titration unreliable. So, the determination of the equivalence point can be determined until a content minimum of 1×10^{-8} mol L^{-1} BG also the linear range was 10^{-8}–10^{-3} mol L^{-1} and the detection limit was 1×10^{-8} M.

3.3. Thermodynamic parameters of CD–BG complex and Ag–BG precipitate

For the determination of thermodynamic parameters of CD–BG, the changes of molar conductivity (Λ_m) versus the ligand to the cation molar ratio for the complexation of β-cyclodextrin and BG were measured at different temperatures (Fig. 3). This curve shows an increase in molar conductivity with an increase in ligand concentration. This indicates that the CD–BG complex is more mobile than the free solvated BG in this binary solution.

Table 1 Log K_f values of β-cyclodextrine–brilliant green complex at different temperatures.

$\log K_f$ ± SD[a]			
15 °C	25 °C	35 °C	45 °C
3.85 ± 0.06	3.55 ± 0.03	3.73 ± 0.03	3.78 ± 0.03

[a] SD = Standard deviation.

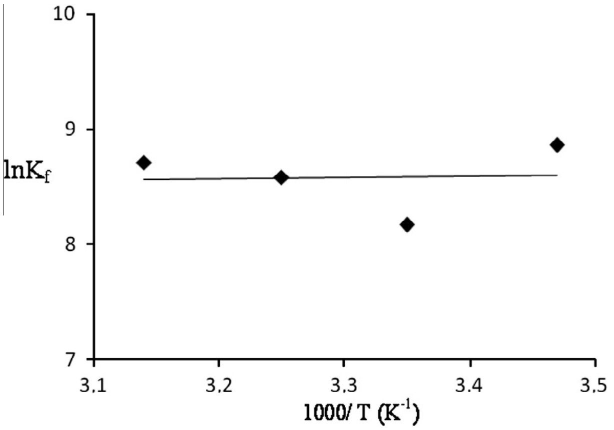

Figure 5 van't Hoff plot for CD–BG.

The 1:1 complexation of a CD (L) with BG is represented by the following equilibrium:

$$M^{n+} + L \leftrightarrows ML^{n+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by:

$$K_f = [ML^{n+}]/[M^{n+}][L] \times f^{n+}_{ML} / \cdot f^{n+}_{M} \cdot f_L \tag{2}$$

where $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f, represent the equilibrium molar concentration of the complex, free BG, free CD and the activity coefficient of the species indicated, respectively.Under the highly dilute condition which we used, in this investigation, the activity coefficient of the uncharged ligand, f_L can be reasonably assumed as unity. By using the Deby–Huckel limiting law, we can assume that the f^{+}_{M}, f^{+}_{ML} values are unity in Eq. (2). Thus the complex formation constant in terms of the molar conductance can be expressed as:

$$K_f = [ML^{n+}]/[M^{n+}][L] = \wedge_M - \wedge_{\text{obs}}/\wedge_{\text{obs}} - \wedge_{ML[L]} \tag{3}$$

where

$$[L] = C_L = C_M(\wedge_M - \wedge_{\text{obs}})/(\wedge_M - \wedge_{ML}) \tag{4}$$

Here Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal cation. The complex formation constant, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by the computer fitting of Eqs. (3) and (4) to molar conductance as a function of ligand/metal cation mole ratio data, using a non-linear least-squares program GENPLOT (Genplot, 1989). All the calculated stability constants are summarized in Table 1. The details of calculation of the stability constants of metal ion complexes by the conductometric method have been described elsewhere (Rounaghi et al., 1997).

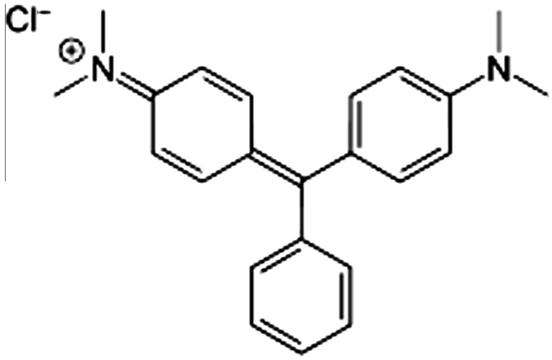

Figure 6 Structure of malachite green.

The values of the stability constant ($\log K_f$) complexation of β-cyclodextrin and BG are listed in Table 1. The van't Hoff plots of $\ln K_f$ versus $1/T$ for all of the investigated systems were constructed. A typical example of these plots is shown in Fig. 5. The changes in the standard enthalpy (ΔH°_c) for complexation reactions were obtained from the slope of the van't Hoff plots assuming that ΔC_p is equal to zero over the entire temperature range investigated. The experimental values of ΔH°_c show that the change in enthalpy for the complexation reactions between β-cyclodextrin and BG is negligible, therefore, it seems that the complexation processes in the water is probably athermic. The changes in the standard entropy (ΔS°_c) were calculated from the relationship $\Delta G^\circ_{c,298.15} = \Delta H^\circ_{c,-298.15} \Delta S^\circ_c$. The results are summarized in Table 2.

The values of ΔS°_c for the complexation reactions between β-cyclodextrin and BG in solution is positive, therefore, the complexation reaction is entropy stabilized. It is reasonable to assume that the increase in entropy on complexation is due to the additional solvent molecules which may be released from solvation shell of the studied cation upon complexation. It should be mentioned, however, that the complexation process involves not only a change in solvation of the BG, but also that of the β-cyclodextrin and the change in the flexibility of the β-cyclodextrin upon complexation.

Also we determine the stability constant of Ag^+ with BG in 25 °C and it was $\log K_f = 3 \pm 0.05$.

3.4. Simultaneous determination of MG with BG

One of the most difficult problems is simultaneous determination of MG (Fig. 6) with BG, because these two compounds have similar structure and their UV–Vis peak overlaps with each other. In the present study we used conductometric method for the simultaneous determination of these two compounds with $AgNO_3$ as titrant. One of the differences between MG and BG is their anion. Silver cation has different Ksp with HSO_4^- and Cl^-.We used this characteristic for

Table 2 Thermodynamic parameters for β-cyclodextrine–brilliant green complex.

$\Delta G^\circ_c \pm \text{SD}^a$(25 °C) (KJ mol^{-1})	$\Delta H^\circ_c \pm \text{SD}^a$ (J mol^{-1})	$\Delta S^\circ_c \pm \text{SD}^a$ (J mol^{-1} K^{-1})
−20.3 ± 0.8	10.1 ± 0.1	1 64.7 ± 2.6

[a] SD = Standard deviation.

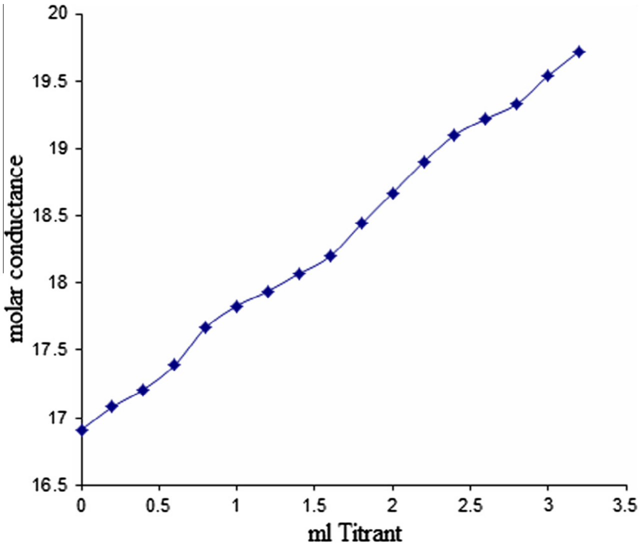

Figure 7 Simultaneous determination of BG and MG (0.001 M) with $AgNO_3$ (0.01 M).

simultaneous determination of these two compounds. Also in Fig 7, a two-step curve has been given. Because of the fact that AgCl has lower Ksp than $AgHSO_4$, therefore the first curve is related to MG and second is related to BG.

4. Conclusions

We used a conductometric gravimetric and complexometric procedure for BG determination in water. The proposed procedure is simple, fast, precise, and inexpensive. The linear range for the determination of BG in the presence of β-CD at 25 °C was 10^{-8}–10^{-3} mol L^{-1} and with $AgNO_3$ was 10^{-3}–10^{-5} mol L^{-1}. Therefore, we can say between these two methods, the complexometric titration is more appropriate for the determination of BG. Also we investigated on thermodynamic parameters of BG–CD complex. In addition a simultaneous determination of BG and MG was also performed. The results show that this method is very suitable for the determination of trace level of BG in water.

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