

Spectroscopic and electrochemical study of Rose Bengal in aqueous solutions of cyclodextrins

P. Fini^{a,*}, F. Longobardi^b, L. Catucci^{a,b}, P. Cosma^{a,b}, A. Agostiano^{a,b}

^a*Istituto per i Processi Chimico Fisici (IPCF) CNR, sez. Bari, Via Orabona 4, 70126 Bari, Italy*

^b*Dipartimento di Chimica, Università di Bari, Via Orabona 4, 70126 Bari, Italy*

Received 23 June 2003; received in revised form 18 September 2003; accepted 24 September 2003

Abstract

The interaction of Rose Bengal (RB) in aqueous solution of LiClO₄ 0.1 M with α -cyclodextrin (α -CD), hydroxypropyl- β -cyclodextrins (HP- β -CD) and hydroxypropyl- γ -cyclodextrins (HP- γ -CD) were studied by spectrophotometric measurements. The presence of Induced Circular Signals and the results of the analysis of the modifications in the absorbance spectra of RB produced by the presence of CDs in solution indicate that RB forms inclusion complexes only with HP- β -CD and with HP- γ -CD.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Rose Bengal; Aqueous solutions; Cyclodextrins

1. Introduction

The use of Rose Bengal (RB) as photosensitizer in dye sensitizer photochemical cells has been subject to extensive studies [1,2].

This molecule, belonging to the class of xanthenes, is characterised by peculiar spectroscopic and photochemical properties, such as a high absorption coefficient in the visible region of the spectrum and a tendency to transfer electrons from its excited triplet state producing long-lived radicals, which make it particularly suitable as a photosensitizer in area such as conversion and storage of light energy and photocatalysis [3,4].

The tendency of this bis-anionic dye to aggregate in solution at high concentration restricts the widespread use of RB in solution, because the formation of aggregate impairs the photochemical response [5–7]. The formation of aggregates is particularly important in salt solution; in fact, it is well known that the maximum concentration at which RB can be considered as monomer significantly decrease upon the addition of salt. A strategy to prevent the dye self aggregation can be its introduction in solution of cyclodextrins, cyclic oligosaccharides which have the ability to include molecules of organic compounds into their cavity. As previously

evidenced [8,9], these macrocycles, interacting selectively with monomer RB, can shift the equilibrium monomer-aggregates towards the formation of the monomeric form; the result is an increase of the dye efficiency also produced by the protective action of CD against possible photooxidation processes of the dye.

In this note, the results of a study on the aggregation and electrochemical properties of RB in LiClO₄ 0.1 M solution in presence of some cyclodextrins having cavities of different size are reported.

2. Experimental

α -Cyclodextrin (α -CD), hydroxypropyl- β -cyclodextrin (HP- β -CD) DS = 5.6, hydroxypropyl- γ -cyclodextrin (HP- γ -CD) DS = 4.8 were purchased from ALDRICH. RPE ACS D(+)-glucose, Rose Bengal (RB) and LiClO₄ were purchased from Carlo Erba and Fluka, respectively. All chemicals were used as received. A solution of LiClO₄ 0.1 M was prepared with doubly distilled water and used as solvent in the preparation of the RB stock solutions.

Visible absorption and circular dichroism were recorded using a Varian CARY/3 spectrophotometer and a JASCO J810 spectropolarimeter, respectively.

Electrochemical experiments were performed in a standard three electrode cells using as working electrode a MFE

* Corresponding author. Tel.: +39-80-5442060; fax: +39-80-5442129.
E-mail address: p.fini@area.ba.cnr.it (P. Fini).

(Mercury Film Electrode). Voltammograms were recorded by using the AUTOLAB PGSTAT10 potentiostat interfaced with a personal computer.

3. Results and discussion

The absorption spectra in the range between 450 and 600 nm of RB in water is characterised by a maximum at 548.10 nm and a shoulder at about 510 nm whose relative intensity is usually used as a measure of the aggregation of RB in solution [5,10]. The presence of LiClO₄ 0.1 M in solution produces a shift of the bands of about 0.5 nm and alters the relative intensity of the shoulder to the peak evidencing the presence of a greater amount of dimer compared to water in agreement with other studies on RB in salt solutions [7,11]. The addition of CD to water and to aqueous solution of LiClO₄ causes a bathochromic shift of the RB spectra similar to that obtained in solvent less polar than water [10], suggesting the formation of inclusion complexes between RB and CDs; in fact the observed shift may be the result of changes in the polarity of the chromophore environment produced by its transfer from the polar aqueous media to the apolar cyclodextrin cavity [12]. Furthermore, it is also important to note that the λ_{\max} shift may also be caused by the changes in the solvent properties produced by the addition of CDs and/or by the presence of interactions between RB and CDs different from those involved in the formation of inclusion complexes [13]. In order to discriminate between the formation of inclusion complexes and different effects, we performed the same set of experiments substituting the CDs by comparable amounts of D-(+)-glucose. The wavelengths corresponding to the maximum absorbance of RB in LiClO₄ 0.1 M aqueous solutions of different CDs and D-(+)-glucose as a function of CD and of D-(+)-glucose concentration expressed as grams of saccharide dissolved in 1 ml of solution are reported in Fig. 1. These data show that the addition of increasing amounts of both glucose and CD gives rise to an increase of the red shift and that the entity of the shift depends on the nature of the saccharide. In particular, the glucose produces only a small red shift which is slightly lower than that observed in presence of α -CDs and much lower than that observed in presence of the HP-CDs. These results indicate that, in the case of the α -CD, the observed spectral modifications of RB are mainly due to effects similar to those produced by glucose and therefore not associated to the formation of inclusion complexes in agreement with the results of a study on the interaction between α -CD and RB in water [13]. On the contrary, in the case of HP-CDs, the observed λ_{\max} shift is mainly caused by the formation of inclusion complexes having a higher stability. Evidences of the formation of inclusion complexes between RB and HP- β -CD and HP- γ -CD were also obtained in water [14].

In addition we have also observed that the relative intensity of the shoulder to the peak of RB does not change

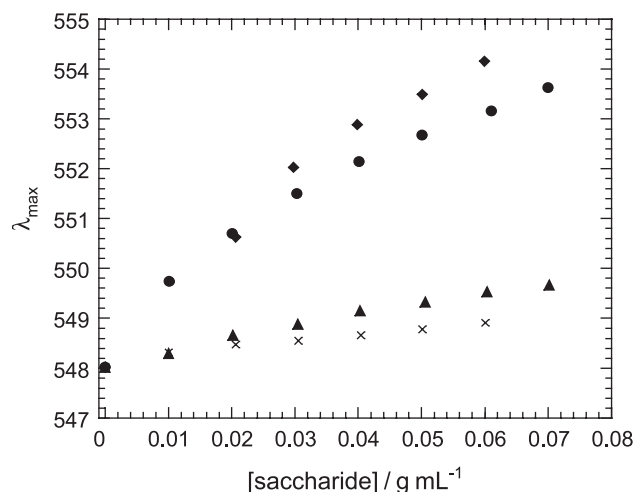


Fig. 1. Experimental wavelengths of the absorption maximum, in the spectral range 450–600 nm, of RB 1.9×10^{-5} M as a function of the concentration (g/ml) of (x) D-(+)-glucose, (▲) α -CD, (●) HP- β -CD and (◆) HP- γ -CD.

in the presence of different amounts of glucose or α -CD while it decreases at increasing of HP-CDs concentration (data not shown). This result can be considered a proof of the inclusion of RB in HP-CDs. In fact, due to the molecular dimensions, CD are able to include only RB monomer, therefore, the formation of complexes, promoted by an increase of the CD concentration, is expected to give rise to a shift of the equilibrium monomer/aggregate of RB towards the monomeric form.

The comparison between the dependence of λ_{\max} on HP- β -CD and HP- γ -CD molarity in water [14] and in LiClO₄ 0.1 M aqueous solution points out that, in general, inclusion complexes formed between RB and HP- γ -CD are characterised by an higher stability constant than those formed with HP- β -CD and that the presence of salt in solution, differently from what was previously observed studying the formation of inclusion complexes between CD and alcohols, reduces the stability of the complexes [15].

Further evidence of the formation of complexes between RB and HP-CDs is also given by the Induced Circular Dichroism spectra reported in Fig. 2. The interaction between the chiral environment provided by CDs and the achiral molecule of RB gives rise an induced circular dichroism signal whose intensity increases at increasing of the value of the binding constant [16]. Therefore, the different intensity of the induced circular dichroism spectra of Fig. 2 indicates that the complexes formed in water are more stable than those formed in salt solution. Furthermore, the opposite sign of the induced circular dichroism signals obtained in the presence of the two HP-CD having different size suggests a different orientation of the electric transition moment of RB with respect to the axis of the cavity of the two HP-CDs [17].

A further confirmation of the inclusion complex formation was obtained by using Cyclic Voltammetry, an analytical technique completely independent. The voltammograms recorded for a 2×10^{-4} M RB solution containing different

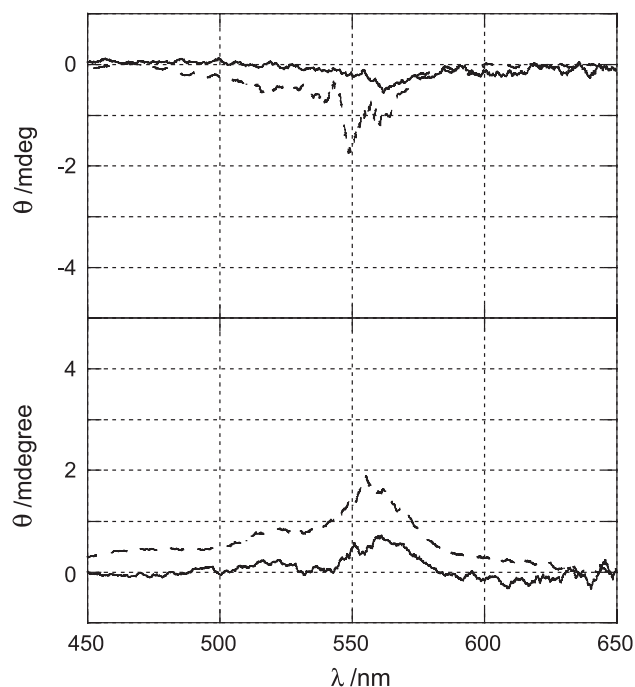


Fig. 2. Induced circular dichroism spectra of RB (1.9×10^{-5} M) in water (—) and in aqueous solution of LiClO_4 0.1 M (---) containing HP- β -CD 0.034 M (top) and HP- γ -CD 0.031 M (bottom).

CDs are shown in Fig. 3, compared with the simple aqueous solution. The solutions containing the included RB yield the same electrochemical characteristics of the

free aqueous RB, presenting two reduction peaks due to the furan and pyrone rings [18]. It is necessary to point out that the RB electrochemistry is particularly complicated because it involves not well-known irreversible chemical reactions following the electron transfer [18–21]. The two reduction peaks (I and II) present in the voltammograms are affected by the presence of cyclodextrine. In particular, it is possible to note that the presence of β -HP-CD and γ -HP-CD determines a shift of the peak II potential toward positive potential (from -0.984 to -0.946 V for β -HP-CD and to -0.945 V γ -HP-CD) with a contemporarily peak current decrease. Whereas the α -CD presence does not alter the electrochemical behaviour of the dye. Further, it is possible to note that the reduction is strongly influenced by adsorption phenomena as it is evidenced by linear dependence of the wave II peak current in function of the scan rate (inset of Fig. 3) [22]. The current intensity decrease of the CD-RB solution, with respect to the free RB, can be ascribed to the minor exposure of the RB molecule to the electrode surface due to the CD-RB inclusion complex formation. As widely shown in the literature [23,24], changes in the peak position and intensity are indicative of the inclusion complex formation.

4. Conclusions

The result of this study indicates that HP- β and γ -CDs are able to include RB in water and in salt solution. In

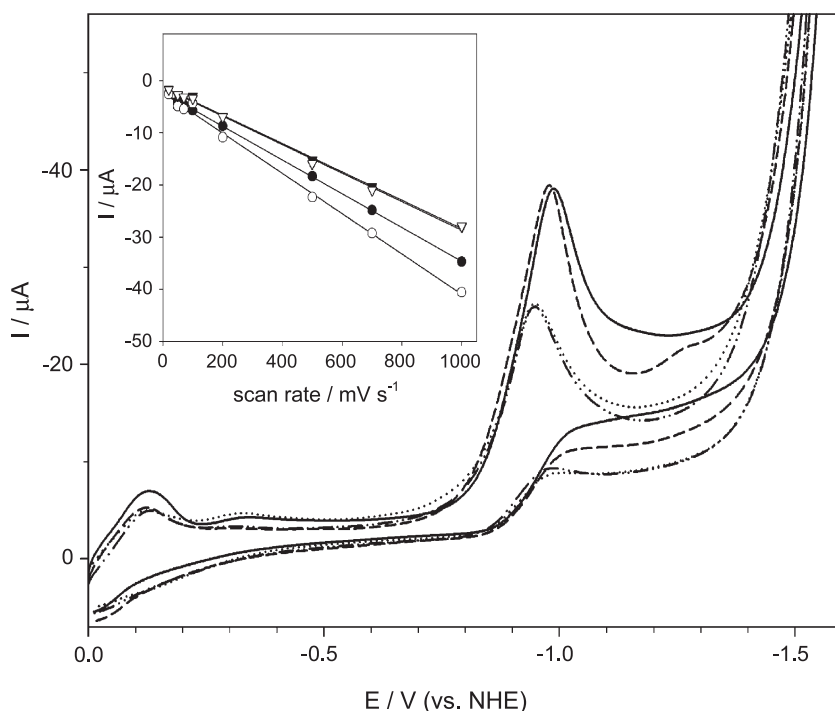


Fig. 3. Cyclic Voltammograms of a RB (2×10^{-4} M) solution in aqueous 0.1 M LiClO_4 containing different CDs: (—) water, (---) 0.052 M α -CD, (.....) 0.034 M HP- β -CD, (-·-·-) 0.029 M HP- γ -CD. Inset: Current intensity of peak II vs. scan rate of RB solution with the different CDs: (●) water, (○) α -CD, (▼) HP- β -CD, (▽) HP- γ -CD.

particular, it was observed that, although the salt presence reduces the stability of the complexes, the inclusion in CDs shifts the RB monomer-aggregate equilibrium towards the RB monomer.

Acknowledgements

This work was made possible because of the financial support of the “Organizzazione sopramolecolare di porfirine naturali e sintetiche” COFIN-MIUR 2002 grants.

References

- [1] A.K. Jana, Solar cells based on dyes, *J. Photochem. Photobiol. A, Chem.* 132 (2000) 1–17.
- [2] L. Bahadur, L. Roy, A binary mixture of dyes (2-imidazolin-5-one and Rose Bengal) for photosensitization of *n*-ZnO thin film electrodes in aqueous and acetonitrile media, *J. Appl. Electrochem.* 29 (1999) 109–116.
- [3] M.E. Daraio, E. San Román, Aggregation and photophysics of Rose Bengal in alumina-coated colloidal suspensions, *Helv. Chim. Acta* 84 (2001) 2601–2614.
- [4] K. Gurunathan, P. Maruthamathu, M.V.C. Sastri, Photocatalytic hydrogen production by dye-sensitized Pt/SnO₂ and Pt/SnO₂/RuO₂ in aqueous methyl viologen solution, *Int. J. Hydrogen Energy* 22 (1997) 57–62.
- [5] D. Xu, D.C. Neckers, Aggregation of Rose Bengal molecules in solution, *J. Photochem. Photobiol. A, Chem.* 47 (1989) 213–222.
- [6] K.K. Rohatgi, A.K. Mukhopadhyay, Isolation of unique dimer spectra of dyes from the composite spectra of aggregated solutions, *Photochem. Photobiol.* 14 (1971) 551–559.
- [7] O. Valdes-Aguilera, D.C. Neckers, Rose Bengal ethyl ester aggregation in aqueous solution, *J. Phys. Chem.* 92 (1988) 4286–4289.
- [8] A. Agostiano, L. Catucci, P. Cosma, P. Fini, Aggregation processes and photophysical properties of chlorophyll *a* in aqueous solutions modulated by the presence of cyclodextrins, *Phys. Chem. Chem. Phys.* 5 (10) (2003) 2122–2128.
- [9] A. Agostiano, L. Catucci, M. Castagnolo, D. Colangelo, P. Cosma, P. Fini, M. Della Monica, Interaction between chlorophyll *a* and beta-cyclodextrin derivatives in aqueous solutions—spectroscopic and calorimetric study, *J. Therm. Anal. Calorim.* 70 (1) (2002) 115–122.
- [10] S.D.M. Islam, O. Ito, Solvent effects on rates of photochemical reactions of Rose Bengal triple state studied by nanosecond laser photolysis, *J. Photochem. Photobiol. A, Chem.* 123 (1999) 53–59.
- [11] O. Valdes-Aguilera, D.C. Neckers, Aggregation of Rose Bengal ethyl ester induced by alkali metal cations in aqueous solution, *J. Photochem. Photobiol. A, Chem.* 47 (1989) 213–222.
- [12] M. Novakowska, M. Smoluch, D. Sendor, The effect of cyclodextrins on the photochemical stability of 7-amino-4-methylcoumarin in aqueous solution, *J. Incl. Phenom. Macrocycl. Chem.* 40 (2001) 213–219.
- [13] L. Flamigni, Inclusion of fluorescein and halogenated derivatives in α , β and γ -cyclodextrins. A steady state and picosecond time resolved study, *J. Phys. Chem.* 97 (1993) 9566–9572.
- [14] P. Fini, M. Castagnolo, L. Catucci, P. Cosma, A. Agostiano, Inclusion complexes of Rose Bengal and Cyclodextrins, *Thermochimica Acta* (in press).
- [15] P. Fini, M. Castagnolo, L. Catucci, P. Cosma, A. Agostiano, The effects of NaCl concentration on the stability of inclusion complexes in aqueous solutions, *J. Therm. Anal. Calorim.* 73 (2003) 653–659.
- [16] D. Krois, U.H. Brinker, Induced circular dichroism and UV–Vis absorption spectroscopy of cyclodextrin inclusion complexes: structural elucidation of supramolecular azi-adamantane (spiro[adamantane-2, 3' -diazirine]), *J. Am. Chem. Soc.* 120 (1998) 11627–11632.
- [17] M. Kodata, Application of a general rule to induced circular dichroism of naphthalene derivatives complexed with cyclodextrins, *J. Phys. Chem.* 102 (1998) 8101–8103.
- [18] A.M. Hindawey, M.M. Ghoneim, I.M. Issa, R.M. Issa, Polarographic study of the behavior of phloxine and Rose Bengal in solutions of varying pH, *Monatsh. Chem.* 107 (1976) 605–618.
- [19] M.E. Daub, G.B. Leisman, R.A. Clark, E.F. Bowden, Reductive detoxification as mechanism of fungal resistance to singlet oxygen-generating photosensitizers, *Proc. Natl. Acad. Sci.* 89 (1992) 9588–9592.
- [20] N.R. Bannerjee, A.S. Negi, Polarograms of eosin (2,4,5,7-tetrabromo-(*R*)-fluorescein) in aqueous buffers, *Electrochim. Acta* 18 (1973) 335–342.
- [21] I.M. Issa, R.M. Issa, M.M. Ghoneim, Y.M. Temerk, Polarography of eosin and erythrosin in solutions of varying pH at the DME, *Electrochim. Acta* 18 (1973) 265–270.
- [22] A.J. Bard, L.R. Faulkner, Double-layer structure and adsorbed intermediates in electrode processes, *Electrochemical Methods*, Wiley, New York, 1980, pp. 519–538.
- [23] Z. Yuan, M. Zhu, S. Han, Supramolecular inclusion complex formation and application of β -cyclodextrin with heteroanthracene ring cation dyes, *Anal. Chim. Acta* 389 (1999) 291–298.
- [24] V.V. Strelets, I.A. Mamedjarova, M.N. Nefedova, N.I. Pysnograeva, V.I. Sokolov, L. Pospíšil, J. Hanzlík, Electrochemistry of inclusion complexes of organometallics. Complexation of ferrocene and azaferrocene by cyclodextrins, *J. Electroanal. Chem.* 310 (1991) 179–186.