



Electrostatic interactions between viologens and a sulfated β -cyclodextrin; formation of insoluble aggregates with benzyl viologens

Valeria Annibaldi¹ · Tian Yu¹ · Carmel B. Breslin¹

Received: 26 June 2019 / Accepted: 7 November 2019 / Published online: 12 November 2019
© Springer Nature B.V. 2019

Abstract

Viologens are important compounds and are used in several applications. The interactions between viologens and a negatively charged cyclodextrin, sulfated β -cyclodextrin ($s\beta$ -CD), were studied using electrochemistry, ¹H NMR and UV–Vis spectroscopy. Weak electrostatic interactions were found between the dicationic viologens (V^{2+}) and the anionic cyclodextrin. The diffusion coefficient of ethyl viologen (EV^{2+}) was reduced from 5.33×10^{-6} to 1.98×10^{-6} cm² s⁻¹ with an excess of $s\beta$ -CD. More significant electrostatic interactions were found between benzyl viologen (BV^{2+}) and $s\beta$ -CD. The H atoms in the benzyl substituent, which appear as a singlet in the NMR experiment, were split into a multiplet in the presence of the $s\beta$ -CD, while the chemical shift of the H in the β position to the quaternary nitrogen, was shifted by 0.17 ppm in the presence of $s\beta$ -CD. Greater electrostatic interactions were evident between the benzyl radical cation ($BV^{\cdot+}$) and $s\beta$ -CD. Using cyclic voltammetry, reduction of the radical cation to the neutral benzyl viologen (BV^0) was shifted by 230 mV to a lower potential, indicating that the reduction of the radical cation becomes considerably more difficult in the presence of $s\beta$ -CD. This was attributed to the formation of an insoluble $BV^{\cdot+}:s\beta$ -CD aggregate, which was also evident in rotating disc voltammetry, where the typical diffusion-limited currents were not observed and in spectroelectrochemistry experiments, where the deposition of the aggregate at the ITO electrode increased the absorbance of the radical species.

Keywords Sulfated β -cyclodextrin · Viologens · Benzyl viologen · Insoluble aggregate

Introduction

Viologens, also known as 1,1-disubstituted-4,4'-bipyridine ions, are widely used as electron-transfer mediators [1, 2], in electrochromic materials [3, 4], and more recently in the formation of charged polymers [5] and for light-driven hydrogen evolution reactions [6]. Viologens can be easily coupled with linker groups to give polyviologens and these have similar properties to the monomer viologens and are commonly used in biophotovoltaic cells [7]. Viologens are also well known for their herbicidal properties, which are connected to their ability to disrupt electron-transfer in biological systems [8]. Viologens have three main oxidation states and these involve the dicationic, V^{2+} , cationic radical,

$V^{\cdot+}$, and neutral state, V^0 . The V^{2+} is reduced to give the radical species, through a one-electron transfer step [9, 10]. This radical is normally soluble, however with larger substituents bound to the pyridinium nitrogen, insoluble radical species may be formed [9]. A further one electron transfer step gives the neutral reduced viologen and in aqueous solutions this is frequently insoluble. In addition to these reduction steps, the neutral and the dicationic viologen can undergo a comproportionation reaction to generate the radical species ($V^0 + V^{2+} \rightarrow 2 V^{\cdot+}$), while a disproportionation reaction can occur to consume the radical species ($2 V^{\cdot+} \rightarrow V^0 + V^{2+}$) and a dimerization reaction can also take place to form a dimer ($2 V^{\cdot+} \rightarrow (V^{\cdot+})_2$).

The host–guest complexation between viologens and macrocyclic hosts has been extensively reported and includes cucurbiturils [11], pillararenes [12] and calixarenes [13] as hosts. The interactions between viologens and neutral cyclodextrins are also well known [14–20]. It has been shown that the neutral methyl viologen (MV^0) forms an inclusion complex with β -CD [14, 15]. Weaker interactions exist between

✉ Carmel B. Breslin
Carmel.Breslin@mu.ie

¹ Department of Chemistry, Maynooth University, Maynooth, Kildare, Ireland

the charged viologens and the cyclodextrin cavity, however the radical species is more hydrophobic and binds more strongly than the dicationic viologen to the cyclodextrin cavity [16]. It has also been shown that long alkyl chains on the viologen enhance the formation of an inclusion complex by insertion of the alkyl chain within the cyclodextrin cavity [17]. Furthermore, the position of the monomer–dimer equilibrium is influenced by the addition of cyclodextrins. This depends on the viologen substituents and on the cavity size of the cyclodextrins. It is generally accepted that the smaller cyclodextrins, α -CD and β -CD, suppress the formation of the dimer through the formation of an inclusion complex between the CD and the viologen, being facilitated by the alkyl chains of the viologen [18, 19]. On the other hand, it has been suggested that the γ -CD favours the formation of the dimer and this has been explained in terms of the inclusion of the bipyridine rings of the viologen radical dimer within the CD cavity [20]. It appears that the cavity size of the γ -CD is sufficiently large to accommodate the dimer. The formation of a complex between benzyl viologen and β -CD in a mixed water and DMF solvent system has also been reported [21]. In this case, it was concluded that the fully reduced form, BV^0 , did not form an inclusion complex with the β -CD, but instead an inclusion complex was observed between the mono-cationic species, BV^+ , and β -CD. While the size of the cyclodextrin cavity, the substituents on the viologens and a water–organic solvent system have all been varied in several papers, there are very few studies devoted to modification of the pendants on the cyclodextrin cavity. Mirzoain and Kaifer have replaced some of the OH groups on the rim of the CD cavity with O–CH₃ groups to give a heptakis-(2,6-O-dimethyl) analogue and have shown that it forms more stable complexes with viologens [16].

In this study, a sulfated β -CD ($s\beta$ -CD) is employed, where the SO_3^- groups provide a negative charge. The interactions between this sulfated β -CD and methyl, ethyl or benzyl viologens are investigated using a combination of cyclic voltammetry, rotating disc voltammetry, spectroelectrochemistry, ¹H NMR and UV–Vis spectroscopy. To the best of our knowledge, there are no published reports on the complexation or interactions between an anionic $s\beta$ -CD and viologens. The anionic cyclodextrin provides both a cavity and anionic pendants and the combination of these two elements on the interactions with three viologens, is studied.

Experimental

All chemicals were obtained from Sigma-Aldrich. The sulfated β -CD ($s\beta$ -CD) sodium salt was purified further by dissolving the sample in a small volume of deionised water. The solution was then connected to a Schlenk line and dried under vacuum at 70 °C for 12 h to remove the main impurity,

which was identified as pyridine. All other chemicals were of analytical reagent grade and used without further purification. Deionised water was used for the preparation of all solutions and these were deoxygenated with nitrogen for a 3 h period, before any electrochemical experiments, as it is well known that the viologen radical cations react with oxygen to give the dications [22].

The electrochemical measurements were carried out using a Solartron 1287 potentiostat. A three-electrode cell was used with a saturated calomel reference electrode and a high surface area platinum wire counter electrode. Glassy carbon and gold electrodes encased in Teflon, with an exposed diameter of 3 mm, were used as the working electrodes. An EG&G rotating 636 ring disc assembly, with a glassy carbon disc electrode, was used to perform the rotating disc voltammetry experiments. The working electrodes were polished using 1.0 μ m diamond polish (Buehler MetaDi monocrySTALLINE diamond suspension) on a Buehler micro-cloth and washed with distilled water and sonicated to remove any polishing residue. An indium tin oxide (ITO) electrode was employed for the spectro-electrochemistry experiments. A thin copper wire was attached to the ITO electrode using a conducting epoxy resin to give electrical contact. The ITO electrode, a platinum wire and a silver wire pseudo reference were placed in a quartz cell and an appropriate potential was applied to generate the radical cations. All UV–Vis spectroscopy measurements were carried out using a Cary 50 UV–Vis spectrometer, while ¹H NMR data were collected using a Bruker 500 MHz NMR spectrometer in D₂O.

The Job's plots were performed using 2.50×10^{-5} M viologen and 2.5×10^{-5} M $s\beta$ -CD stock solutions prepared in 0.1 M NaCl. This chloride solution was employed to maintain a near constant ionic strength as the $s\beta$ -CD has 7–11 mol of sulfate per mol of β -CD, as reported by the vendor. Different amounts of the two stock solutions were mixed to give viologen mole fractions ranging from 0.0 to 1.0. The cyclic voltammetry experiments were carried out at a scan rate of 50 mV s⁻¹, while the rotating disc voltammetry was performed with rotation rates from 250 to 2000 rpm and at 5 mV s⁻¹ in a supporting 0.1 M NaCl solution.

Results and discussion

The potential interactions between the viologens, as V^{2+} and V^+ , and the $s\beta$ -CD were studied using a combination of cyclic voltammetry, ¹H NMR, rotating disc voltammetry, spectroelectrochemistry and UV–Vis spectroscopy.

Interactions between V^{2+} and $s\beta$ -CD

The stoichiometry of the interaction between the three viologens, as dications, and the $s\beta$ -CD was determined by

applying the well-known Job's plot method. This continuous variation method was employed using UV–Vis spectroscopy and NMR measurements. A typical Job's plot for BV^{2+} in the β -CD solution is shown in Fig. 1a, where the UV data were recorded at 260 nm and the chemical shifts were followed using the methylene protons of the benzyl substituents (H_c) and the protons in position β to the quaternary nitrogen atoms (H_b), identified in Fig. 1b. All measurements were repeated three times ($n=3$) and the average values are plotted with error bars. A schematic of the β -CD is provided in Fig. 1c, where the R groups correspond to SO_3^- groups. Approximately 7–11 of the R groups are sulfated to give a solution conductivity of 5 mS cm^{-1} for a 0.01 M β -CD aqueous solution. It is clear from this plot that the maximum absorbance value and maximum chemical shifts were observed at a mole fraction of 0.5, indicating a 1:1 BV^{2+} : β -CD stoichiometry. Similar data were obtained using EV^{2+} and MV^{2+} , again being consistent with a complex or ion pair with a 1:1 ratio between the viologen and β -CD.

Titration curves were carried out using UV–Vis spectroscopy where the concentration of the viologen was maintained at $2.5 \times 10^{-5} \text{ M}$, and the concentration of the β -CD was varied from 2.5×10^{-5} to $5.0 \times 10^{-4} \text{ M}$. Typical data are presented in Fig. 2 for MV^{2+} , EV^{2+} and BV^{2+} . It is clear from this figure that there is little change in the absorbance of the MV^{2+} and EV^{2+} on the addition of increasing amounts of β -CD. For example, the absorbance of the free MV^{2+} is 0.416 at 257 nm and with a 20-fold excess of β -CD it decreases to 0.405. This is consistent with a weak interaction. However, a stronger interaction is evident with BV^{2+} , where a

small red shift is seen and a more significant decrease in the absorbance is evident with an excess of β -CD. These data are consistent with variations in the electron density on the nitrogen atoms. The electron donating properties of the methyl and ethyl groups are slightly higher than the benzyl substituents, and as a result, the nitrogen atoms have more electropositive character in BV . This facilitates a stronger interaction between the BV^{2+} and the anionic sulfate groups on the β -CD.

NMR data were recorded for 1.0 mM MV^{2+} , EV^{2+} and BV^{2+} in 0.1 M NaCl in D_2O in the absence and presence of a 20-fold excess of β -CD (20 mM) and the corresponding spectra are shown in Fig. 3, while the chemical shifts observed on addition of the β -CD are summarised in Table 1. For comparative purposes, the spectra recorded on adding a 15-fold excess of the neutral β -CD are also presented in Fig. 3. The 1H NMR spectrum of the β -CD was complex and the signals were broad as a consequence of the varying degree of substitution. Consequently, the chemical shifts of the viologens were followed and this was possible without any interference from the β -CD, as the CD signals were all confined between 3.50 and 5.50 ppm. A 20-fold excess of β -CD induces a downfield shift in the aromatic protons for all three viologens, however the downfield shift is small ranging from 0.02 to 0.07 ppm for MV^{2+} and EV^{2+} . Larger changes were observed with BV^{2+} , where the downfield shift in H_b is 0.17 ppm and a somewhat lower change of 0.10 ppm is evident with H_c , Table 1. In addition, the singlet at 7.44 ppm, due to the presence of the benzyl substituent, appears as a multiplet in the presence of the

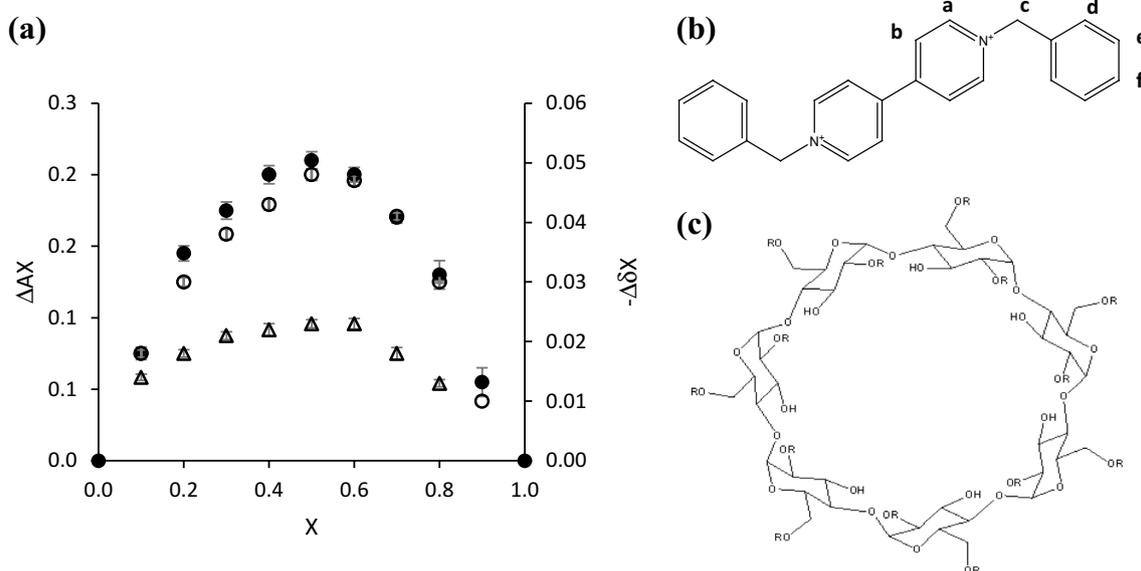


Fig. 1 a Jobs plot titration curves with different β -CD and BV mole fractions plotted with filled circle the absorbance change at 260 nm, open circle NMR chemical shifts of H_b and chemical shift changes of

H_c with repeated measurements, $n=3$, b structure of BV with protons identified, c representation of β -CD, where R represents $-SO_3^-$

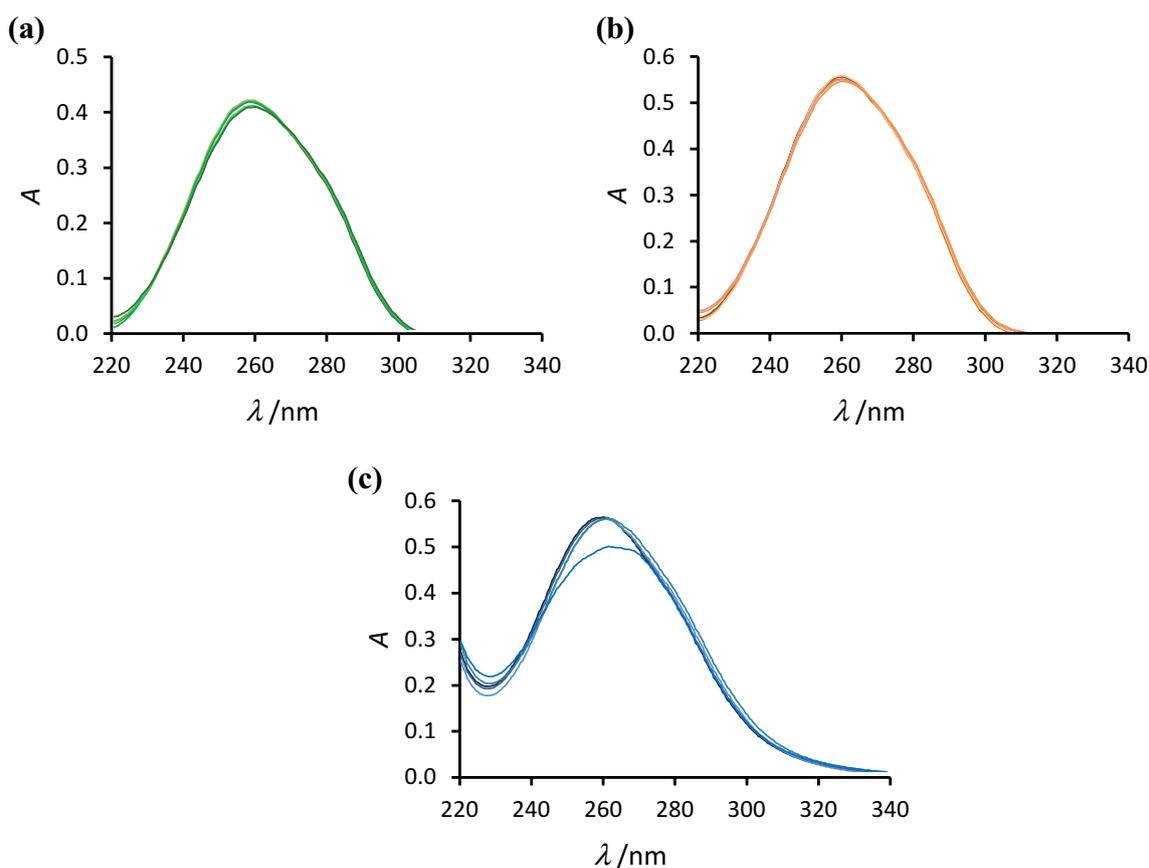


Fig. 2 UV spectra of 2.50×10^{-5} M viologen in 0.1 M NaCl **a** MV, **b** EV and **c** BV in the absence and presence of varying amounts, from 2.50×10^{-5} to 5×10^{-4} M β -CD

β -CD, suggesting a change in the environment of the benzyl group protons. This may indicate that the benzyl substituent is partially included within the CD cavity. However, it is well documented in the literature that an upfield shift is observed when a host molecule is included within a cyclodextrin cavity to form an inclusion complex. The protons of the included guest are shielded to give an upfield shift. Ion pairing interactions are often associated with de-shielding of the protons in the vicinity of the cationic species and this suggests that the interactions between the β -CD and viologens are electrostatic in nature with the formation of an ion pair where the two quaternary nitrogen atoms from the viologen molecule form an ion pair with two of the sulfate groups on the same CD cavity to give a 1.1 stoichiometry. It is clear from these data that stronger electrostatic interactions exist between BV^{2+} and β -CD and this is in good agreement with the UV–Vis titrations, Fig. 2. In contrast, the addition of an excess of the neutral β -CD, has very little effect on the NMR signals, which is in good agreement with previous studies, which show only weak interactions between the charged viologens and the neutral β -CD [14–16]. In order to determine if the interactions observed

were unique to the β -CD, the NMR data were recorded on the addition of 0.15 M Na_2SO_4 to the viologen containing chloride solution. Although a very small downfield shift (H_B was shifted from 8.43 to 8.45 ppm for BV^{2+}) was observed being consistent with the displacement of the chloride by the sulfate anions, a more significant downfield shift was observed on addition of the β -CD, Table 1.

Electrochemistry studies

The electrochemistry of viologens is well known [22–24], with reduction of the dication to the radical cation, Eq. 1, followed by further reduction to give the neutral viologen, Eq. 2, which has poor solubility. The corresponding oxidation reactions are summarised in Eqs. 3–5. These reduction reactions were studied in the absence and presence of β -CD and for comparison purposes, the neutral β -CD was also employed. Cyclic voltammograms are shown for the BV system in Fig. 4 and in Fig. 5, the corresponding data are presented for EV. In Fig. 4a, the typical electrochemistry of BV is evident, where the first reduction peak, corresponding to Eq. 1, occurs at -0.58 V vs SCE and the second

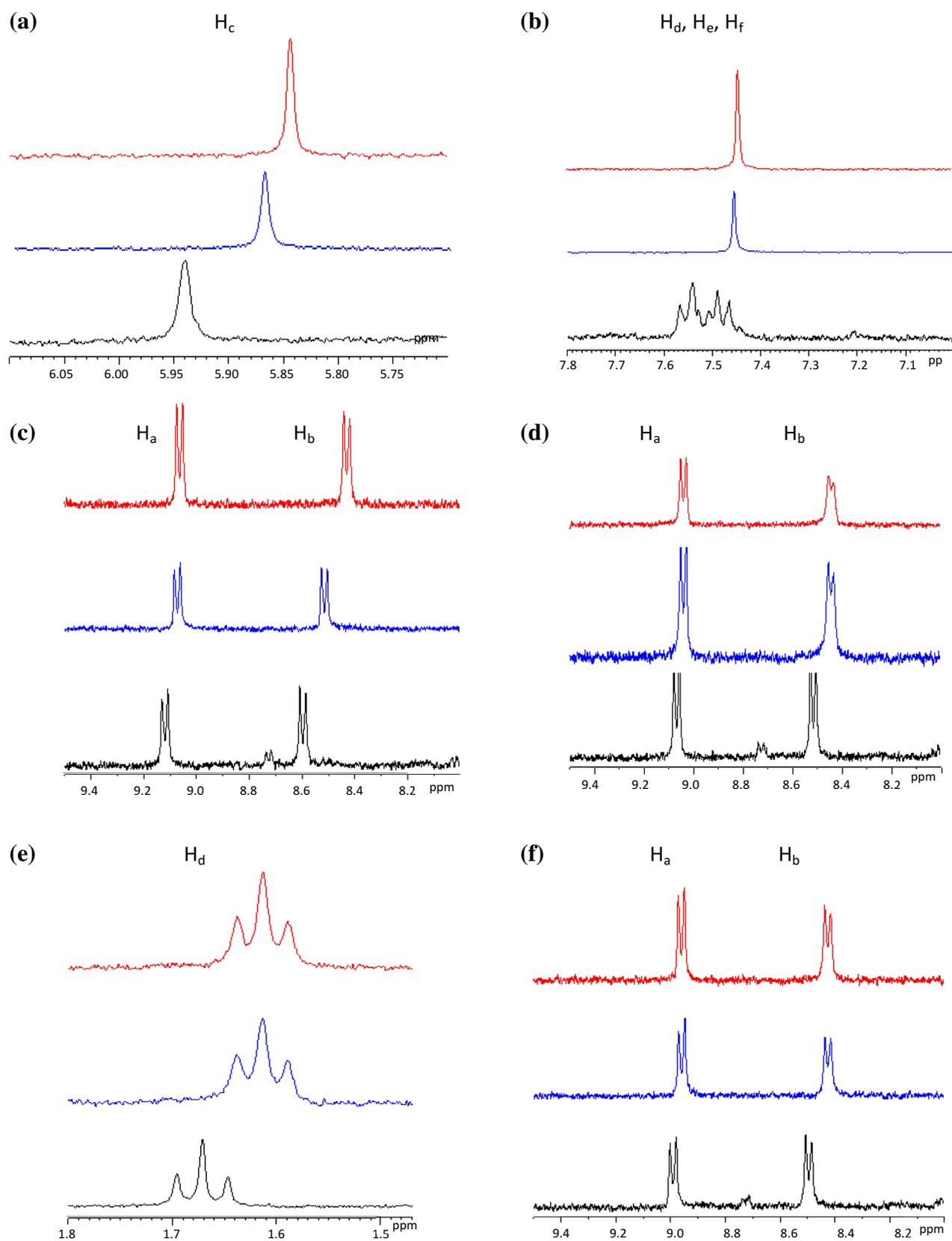
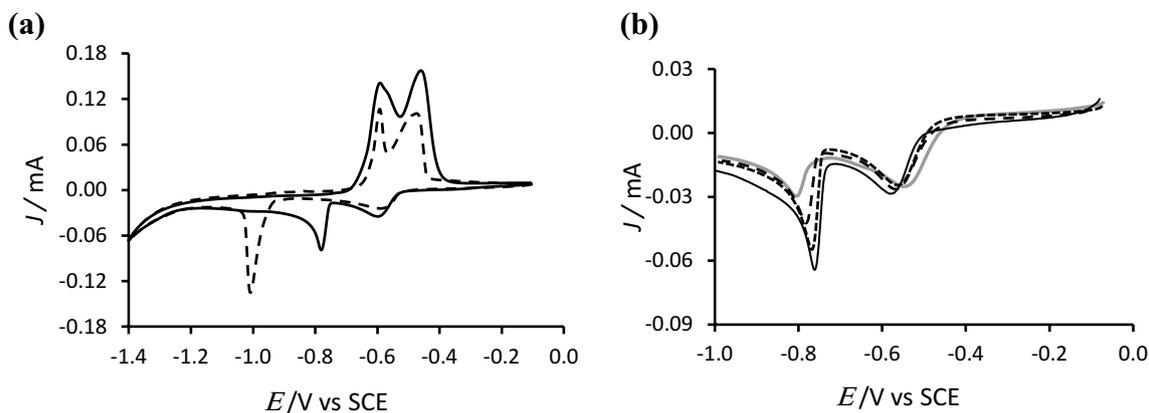
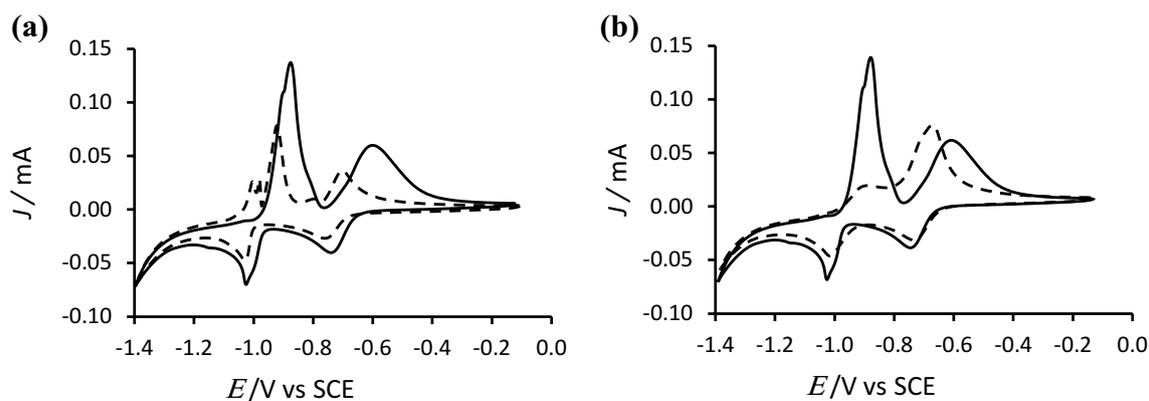


Fig. 3 NMR spectra recorded for the viologens (1.0 mM) in 0.1 M NaCl in D_2O (top, red), in the presence of 15 mM $\beta\text{-CD}$ (middle, blue) and in the presence of 20 mM $s\beta\text{-CD}$ (bottom, black) for **a–c**

BV $^{2+}$, d, e EV $^{2+}$ (where H_d represents the methyl protons) and **f MV $^{2+}$** . (Color figure online)

Table 1 Chemical shifts of viologen protons in the absence and presence of β -CD, with multiplicity assigned as doublet (d), singlet (s) and multiplet (m)

Protons	MV		EV		BV	
	Free	β -CD	Free	β -CD	Free	β -CD
H _A (ppm)	8.95 (d)	8.97 (d)	9.04 (d)	9.07 (d)	9.06 (d)	9.13 (d)
H _B (ppm)	8.43 (d)	8.50 (d)	8.45 (d)	8.50 (d)	8.43 (d)	8.60 (d)
H _C (ppm)					5.84 (s)	5.94 (s)
H _D H _E H _F (ppm)			1.61 (t)	1.67 (t)	7.44 (s)	7.52 (m)

**Fig. 4** Cyclic voltammograms recorded in 2.5 mM BV in 0.1 M NaCl at 50 mV s^{-1} for **a** black solid lines in the absence and long dashed line presence of 10 mM β -CD and **b** black solid lines in the absenceand presence of β -CD at short dashed line 2.5 mM, long dashed line 5.0 mM and grey solid lines 10 mM**Fig. 5** Cyclic voltammograms recorded in 2.5 mM EV in 0.1 M NaCl at 50 mV s^{-1} for **a** black solid lines in the absence and long dashed line presence of 10 mM β -CD and **b** black solid lines in the absence and long dashed line presence of 10 mM β -CD

electron–transfer step occurs at about -0.77 V vs SCE, to generate BV^0 . On the reverse cycle, the adsorption wave, at about -0.60 V vs SCE, reflects the oxidation of the poorly soluble BV^0 , Eq. 4 and soluble BV^0 , Eq. 3, while the peak at -0.47 V vs SCE corresponds to the oxidation of the radical cation back to the original BV^{2+} , Eq. 5. The electrochemistry of BV in the presence of β -CD is very different. There is a considerable shift, of about 230 mV, in the position of the second reduction wave on addition of 10 mM β -CD.

Reduction of the BV^+ becomes considerably more difficult in the presence of a slight excess of β -CD, indicating a significant interaction between the BV^+ radical and the anionic β -CD. The first reduction wave, observed at about -0.58 V vs SCE, becomes progressively broader on addition of increasing concentrations of β -CD, which may indicate a decrease in the rate of the electron transfer reaction and/or a decrease in the rate of diffusion to the electrode surface, and this is consistent with the weak interaction between BV^{2+}

and β -CD, evident in Figs. 2, 3 and Table 1. The presence of the β -CD has less influence on the oxidation processes. However, the first oxidation wave, corresponding to Eqs. 3 and 4, is sharper in the presence of β -CD and this may indicate a change in the contributions of Eqs. 3 and 4 to the observed peak. In this case the reduced viologens are the insoluble BV^0 , insoluble $BV^0:\beta$ -CD and soluble BV^0 which are formed through the reduction of BV^{+} and $BV^{+}:\beta$ -CD. While the interactions between BV^{+} and β -CD appear to be significant, the sharp oxidation peak observed is consistent with the insoluble species BV^0 and $BV^0:\beta$ -CD having very similar oxidation potentials.

In Fig. 4b, the reduction waves are shown in the absence and presence of the neutral β -CD and in this case, it is clear that while there are small changes in the peak potential and peak current on the addition of increasing concentrations of the neutral β -CD, the second reduction wave remains at approximately -0.80 V vs SCE, which is very different to that observed in Fig. 4a.



Similar data recorded for EV in the absence and presence of β -CD are shown in Fig. 5a. In this case, the peak currents for both reduction waves are lower in the presence of β -CD. With an equimolar concentration of β -CD, a clear drop in the peak current was evident and the currents decreased further with an excess of the β -CD. On considering the first reduction wave, it is evident that the lower peak current is accompanied by a shift in the peak potential to more negative values and this is consistent with the formation of an inclusion complex or some other interaction between the EV^{2+} and β -CD. As a reduction in the current associated with the first wave is seen, this will also give rise to lower peak currents for the second wave and this suggests that the main interactions are between the V^{2+} and the β -CD. The oxidation profiles of the electrogenerated EV^0 and EV^{+} species are considerably more complex in the presence of β -CD. Three separate signals are evident reflecting a different environment at the electrode-solution interface. The largest peak centred at about -0.90 V vs SCE corresponds to the oxidation

of the adsorbed EV^0 species, while the preceding peaks may be due to co-adsorbed EV^0 and β -CD on the gold substrate. Indeed, these signals increased with increasing β -CD concentration. Kostela et al. [25] have observed similar effects with micelles and have postulated the possibility of co-adsorption of viologens with micelles on the electrode surface.

In the presence of the neutral β -CD, Fig. 5b, the oxidation peak centred at -0.85 V vs SCE is considerably smaller. Moreover, a larger oxidation peak, corresponding to the oxidation of the radical cation, is observed. It appears that complexation of the neutral EV^0 , which is normally poorly soluble, by the β -CD increases its solubility and the anodic peak at -0.85 V vs SCE, which is due to the oxidation of the adsorbed insoluble viologen is lowered considerably. The solubilised EV^0 can undergo a comproportionation reaction [22] to generate EV^{+} and this is consistent with an increase in the second oxidation wave. Clearly these data are again very different to that observed in the presence of β -CD, Fig. 5a.

These interactions between EV or BV and β -CD were studied further using RDV measurements and these results are presented in Fig. 6. Rotating disc voltammograms are shown in the presence and absence of β -CD for the EV system in Fig. 6a where it is evident that the addition of the β -CD has a significant effect on the reduction of EV. The limiting currents are lower and there is a shift in the half-wave reduction potentials. With a 30-fold excess of β -CD, a negative shift in the half-wave potential, $\Delta E_{1/2}$ of 45 mV vs SCE, is observed for the reduction of the dication to form the radical, $EV^{2+} + e^{-} \rightarrow EV^{+}$. A smaller shift in the half-wave potential of 15 mV vs SCE was observed for the reduction of the radical to the neutral molecule, $EV^{+} + e^{-} \rightarrow EV^0$. The RDV plots are considerably more complex for the BV system in the presence of β -CD, as illustrated in Fig. 6b. Typical limiting currents are not observed. Instead, a sharp reduction peak is evident, which resembles the data observed in Fig. 4a. Again, this is consistent with the formation of an insoluble product between the BV^{+} radical and the β -CD, which is deposited at the surface. As this is an adsorbed species its redox reaction is not influenced by diffusion and reduction of the adsorbed and bound BV^{+} radical appears as a sharp peak at about -1.0 V vs SCE.

The diffusion coefficients and heterogeneous rate constants for EV and MV in the absence and presence of excess β -CD were calculated. However, this was not possible with the BV system as typical limiting currents were not observed, Fig. 6b. The diffusion coefficients were obtained using the Levich equation, Eq. 6, while the Koutecky–Levich equation, Eq. 7, was employed to compute the rate constants. Here, J_L represents the measured limiting current, J_{lev} is the Levich current, F is Faraday's constant, A is the surface area, k is the rate constant, Γ is the surface coverage,

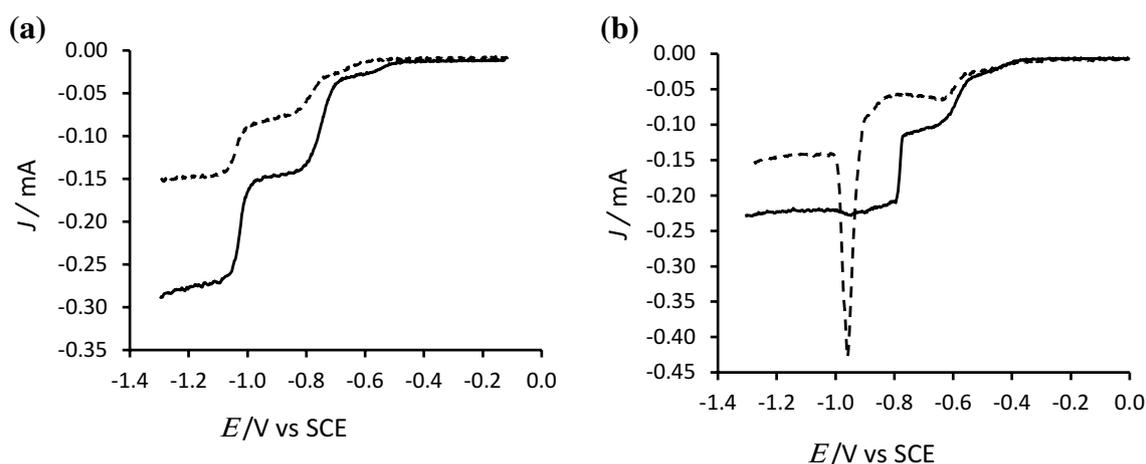


Fig. 6 RDV voltammograms recorded at a GC electrode at 2000 rpm in the black solid lines absence and long dashed line presence of 30 mM sβ-CD in 0.1 M NaCl for **a** 1.0 mM EV and **b** 1.0 mM BV

c is the concentration, D is the diffusion coefficient, ω is the rotational speed and ν is the kinematic viscosity.

$$J_L = 0.621 nFA D^{2/3} \nu^{-1/6} c \omega^{1/2} \quad (6)$$

$$\frac{1}{J_L} = \frac{1}{J_K} + \frac{i}{i_{lev}} = \frac{1}{nFAkc} + \frac{1.61}{nFA \nu^{-1/6} D^{2/3} \omega^{1/2} c} \quad (7)$$

The linear Levich plots are shown for the first reduction wave in Fig. 7a and for the second reduction wave in Fig. 7b for EV free in solution and in the presence of a 30-fold excess of sβ-CD. Using Eq. 6, the diffusion coefficients of the free V^{2+} and V^+ and bound V^{2+} and V^+ species were computed for MV^{2+} , MV^+ , EV^{2+} , EV^+ and BV^{2+} and these data are provided in Table 2. The diffusion coefficient computed for free MV^{2+} was $5.21 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and this is in good agreement with the value of $6.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ reported by Ling et al. [26]. There is a clear decrease in the computed diffusion coefficients on addition of the sβ-CD, indicating interactions between the viologens and the anionic cyclodextrin, being consistent with the slower diffusion of the V^{2+} :sβ-CD. The ratios, D_c/D_f , where D_c represents the bound viologen and D_f signifies the diffusion coefficient of the free viologen, were computed and these are also shown in the table, with the ratios varying between 0.35 and 0.47. The Koutecky–Levich plots for the EV free and in the presence of sβ-CD are shown in Fig. 7c and d, while the corresponding rate constants are summarised in Table 3, for MV^{2+} , MV^+ , EV^{2+} , EV^+ and BV^{2+} . It is clear that the rate constant is influenced by the added sβ-CD and in all cases, the rate constant is reduced in the presence of an excess of the sβ-CD. The influence of the presence of trace amounts of dissolved oxygen in solution is also illustrated in the table. It is well known that dissolved oxygen reacts with the viologen radical cations to give the dications [22] and it is clear

from the data presented in the table that higher rate constants are computed for the viologen cations, but lower rate constants are seen with the radical cations in the presence of trace amounts of dissolved oxygen (where the solutions were only deoxygenated for 20 min). This may be related to the oxygen induced conversion of the radical cation to the dication, Eq. 8. However, in the presence of the sβ-CD, the rate constants appear to be less dependent on the presence of oxygen and this may be associated with the electrostatic interactions between the viologens and sβ-CD, leading to the inhibition of the oxidation reaction, Eq. 8.



The binding constants, K_f , between MV^{2+} , MV^+ , EV^{2+} , EV^+ and BV^{2+} and the sβ-CD were estimated by fitting the voltammetry data to Eq. 9, where j_0 and j represent the peak current densities in the absence and presence of sβ-CD, and A is a proportionally constant. This analysis is valid when the sβ-CD concentration is in excess [27]. The computed binding constants are given in Table 4. In all cases, these K_f values are lower than the typical constants associated with the formation of an inclusion complex. Nevertheless, these values combined with the lower diffusion coefficients and lower rate constants indicate an interaction between the viologen and sβ-CD and this is most likely an electrostatic interaction with the formation of ion pairs.

$$\frac{1}{[s\beta\text{-CD}]} = K_f \frac{1-A}{1-\frac{j}{j_0}} - K_f \quad (9)$$

The K_f value estimated for the BV^{2+} :sβ-CD ion pair is lower than expected, as the NMR analysis, Table 1, showed a more significant interaction between the sβ-CD

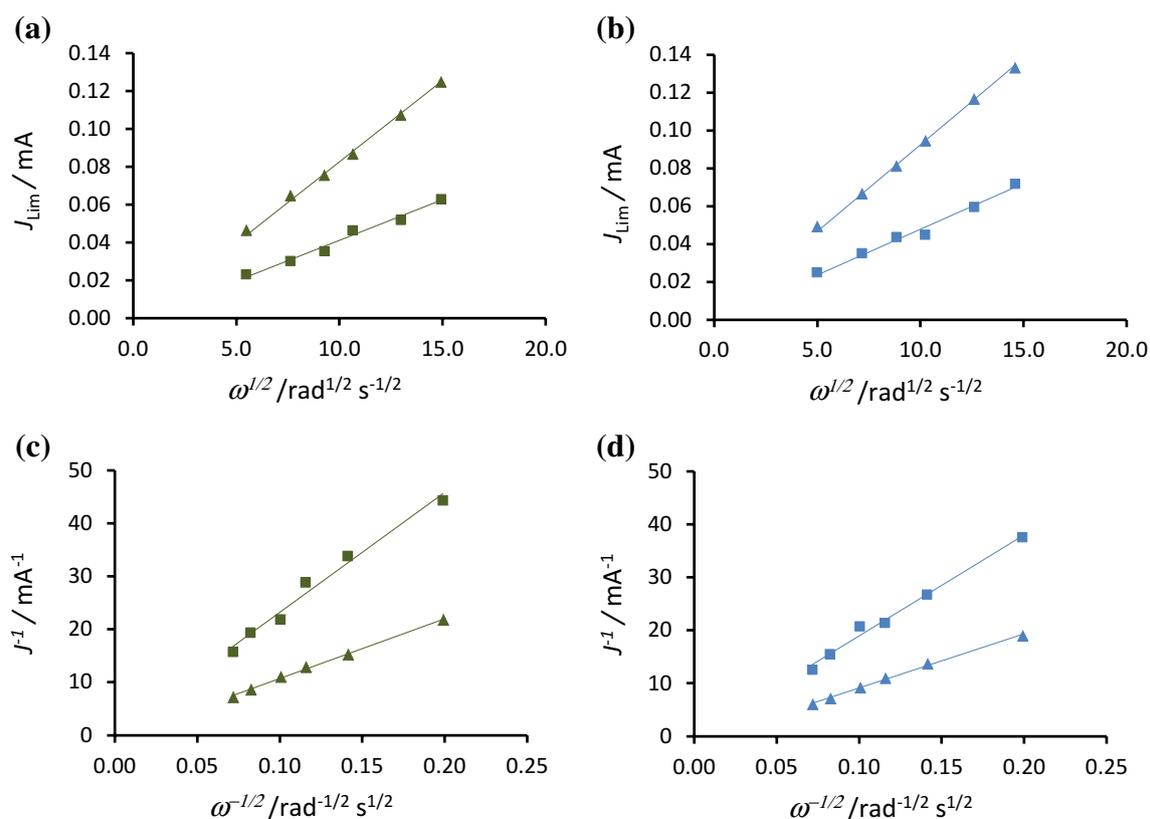


Fig. 7 Levich plots for the limiting currents recorded at 250, 500, 750, 1000, 1500 and 2000 rpm for **a** the first and **b** the second reduction waves and Koutechy–Levich plots recorded for **c** the first and

d the second reduction wave in 1.0 mM EV in 0.1 M NaCl in the absence (filled triangle) and the presence of 30 mM β -CD (filled square)

Table 2 Apparent diffusion coefficients calculated for the free viologens (1.0 mM) and in the presence of increasing concentrations of β -CD

[β -CD]/mM	D (apparent)/cm ² s ⁻¹				
	MV ²⁺	MV ⁺	EV ²⁺	EV ⁺	BV ²⁺
0	5.21×10^{-6}	5.78×10^{-6}	5.33×10^{-6}	5.74×10^{-6}	4.57×10^{-5}
1	4.48×10^{-6}	5.33×10^{-6}	4.80×10^{-6}	5.16×10^{-6}	4.04×10^{-5}
5	3.81×10^{-6}	4.69×10^{-6}	4.21×10^{-6}	4.35×10^{-6}	3.34×10^{-5}
10	2.92×10^{-6}	4.22×10^{-6}	3.71×10^{-6}	3.67×10^{-6}	2.39×10^{-5}
20	2.42×10^{-6}	3.30×10^{-6}	3.08×10^{-6}	3.06×10^{-6}	1.96×10^{-5}
40	2.10×10^{-6}	2.74×10^{-6}	1.98×10^{-6}	2.29×10^{-6}	1.62×10^{-5}
D_d/D_f	0.40	0.47	0.37	0.40	0.35

and BV²⁺. Viologens are well known to adsorb at electrode surfaces and in particular, the benzyl viologen dication can form an organized and ordered adsorbed layer [28, 29]. The reduction of this adsorbed species takes place in the same potential region as the bulk solution species, making it difficult to differentiate between both. Therefore, in this electrochemical method, the peak currents will always contain a contribution from the reduction of the adsorbed BV²⁺ to give an estimated K_f that is lower than the true value.

Spectroelectrochemistry studies

In order to investigate the interactions between the radical species of the viologen compounds and the β -CD, spectroelectrochemical experiments were performed and these data are shown in Figs. 8 and 9, where data are compared for BV and MV with different concentrations of β -CD. For comparative purposes, similar data recorded using the neutral β -CD are shown.

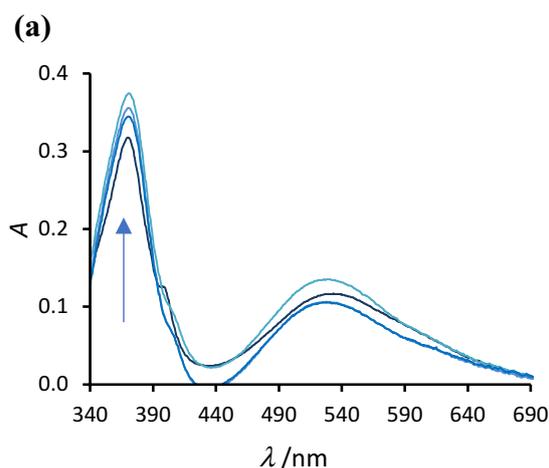
Table 3 Rate constants, k , calculated for the free viologens (1.0 mM) and in the presence of a 30-fold higher β -CD concentration for deoxygenated solution and with traces of oxygen

System	$k/\text{cm s}^{-1}$	
	Free viologen	Viologen with β -CD
Deoxygenated		
MV ²⁺	0.113 ± 0.003	0.024 ± 0.002
MV ⁺	0.046 ± 0.003	0.011 ± 0.003
EV ²⁺	0.048 ± 0.001	0.022 ± 0.002
EV ⁺	0.061 ± 0.003	0.026 ± 0.002
BV ²⁺	0.131 ± 0.002	0.012 ± 0.003
Traces of O ₂		
MV ²⁺	0.161 ± 0.006	0.032 ± 0.005
MV ⁺	0.039 ± 0.005	0.010 ± 0.003
EV ²⁺	0.132 ± 0.005	0.029 ± 0.003
EV ⁺	0.037 ± 0.004	0.029 ± 0.003
BV ²⁺	0.127 ± 0.005	0.039 ± 0.003

Table 4 Formation constants, K_f , calculated for the viologen; β -CD

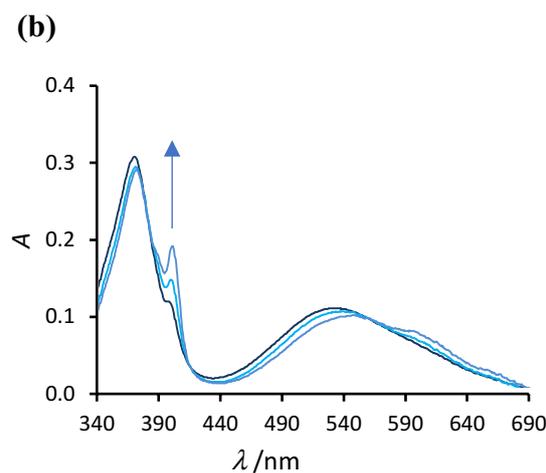
Viologen: β -CD	K_f/M^{-1}
MV ²⁺ : β -CD	743 ± 21
MV ⁺ : β -CD	248 ± 11
EV ²⁺ : β -CD	744 ± 21
EV ⁺ : β -CD	170 ± 6
BV ²⁺ : β -CD	449 ± 7

The UV–Vis spectrum for the radical cation of the benzyl viologen, BV⁺, generated on electrolysis at -0.70 V vs Ag|Ag⁺ is illustrated, in Fig. 8a. The spectrum exhibits a band centered at 370 nm, which corresponds to the dimer

**Fig. 8** Spectroelectrochemical data recorded for 1.0 mM BV in 0.1 M NaCl at -0.70 V **a** in the black line absence and presence of blue line 1.0 mM, light blue line 2.5 mM and light blue line 10 mM β -CD

absorption, while the shoulder peak at about 400 nm has been attributed to the radical as a monomeric species. The dimer has an additional band at about 500 nm while the monomer has a band centred at around 600 nm in the visible region [30, 31]. In the presence of excess β -CD the intensity of the band centered at 370 nm, and corresponding to the absorption of the dimer, increases, while the monomer signal at 400 nm is suppressed. Jeon et al. [31] observed similar results in a study on the interactions between methyl viologen and a cucurbituril and explained their results in terms of an inclusion of the dimer species within the cavity of the host. However, when spectroelectrochemical data were obtained for BV⁺ in solution with a sulfated α -CD (α -CD), which does not possess a cavity large enough to host two viologen guests, similar data were obtained, indicating that the inclusion of the dimer within the β -CD is unlikely. Instead, the enhancement of the absorption intensity upon addition of the β -CD seems to be due to the deposition of an insoluble BV⁺: β -CD aggregate on the ITO electrode, which was evident in the electrochemical data, Figs. 4a and 6b. The absorbance at 370 nm increases by about 0.05 on adding an excess of β -CD, while the monomer signal is absent, which may indicate that the deposited aggregates contain the BV⁺ dimer. The corresponding data recorded for the neutral viologen, shown in Fig. 8b, indicate a significant alteration in the monomer–dimer ratio. The monomer absorption is enhanced and this is accompanied by a decrease in the absorption of the dimer. This suggests that the radical cation, as a monomer, is included in the hydrophobic cavity of the neutral β -CD, in agreement with previous studies [19].

The corresponding UV–Vis data recorded for MV are shown in Fig. 9, where the radical was generated at -0.90 V vs Ag|Ag⁺. In this case, the absorbance band at 400 nm,

**and b** in the dark blue line absence and presence of blue line 1.0 mM and light blue 2.5 mM β -CD. Arrows indicate the direction of change with increasing CD concentration. (Color figure online)

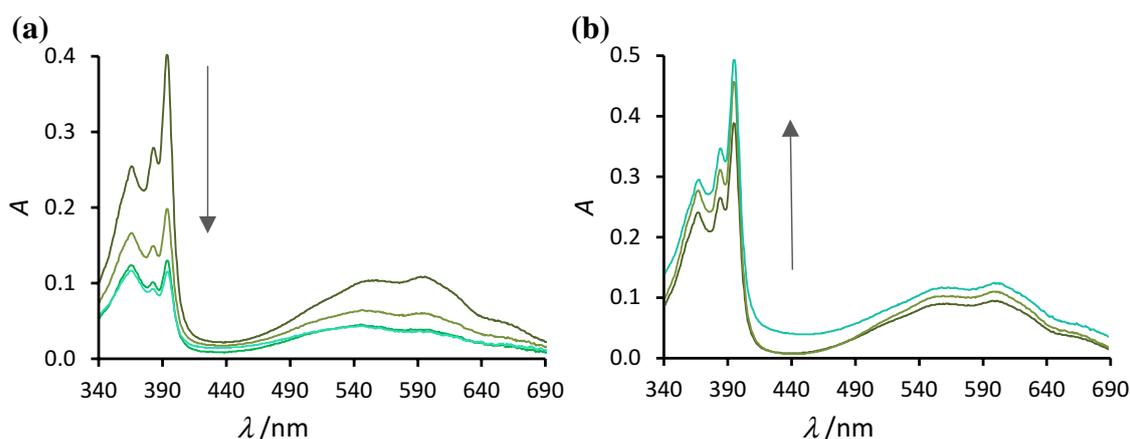


Fig. 9 Spectroelectrochemical data recorded for 1.0 mM MV in 0.1 M NaCl at -0.90 V **a** in the black line absence and presence of grey line 1.0 mM, dark green line 2.5 mM and light green line 10 mM $s\beta$ -CD and **b** in the black line absence and presence of grey

line 1.0 mM and light green line 10 mM β -CD. Arrows indicate the direction of change with increasing CD concentration. (Color figure online)

corresponding to the absorption of the radical monomer, is more pronounced and this can be related to the decreasing tendency to form dimers with the less hydrophobic methyl group. An equi-molar concentration of $s\beta$ -CD is sufficient to give a significant reduction in the absorbance of the radical. It appears that the rate of diffusion of MV^{2+} to the ITO surface, is reduced on addition of the anionic $s\beta$ -CD to give a lower absorbance for the radical species. This is in good agreement with the electrochemical data, where lower diffusion coefficients were obtained to give D_c/D_f ratios close to 0.5. It is also evident that the absorbance of the radical dimer seems to be enhanced in the presence of the $s\beta$ -CD. The $s\beta$ -CD seems to stabilise and promote the dimer over the monomer. For example, the ratio of monomer to dimer varies from 1.57 in the absence of the $s\beta$ -CD to 1.21 with an equimolar ratio of viologen to $s\beta$ -CD to a ratio of 0.95 for a tenfold excess of $s\beta$ -CD. A similar variation in the monomer to dimer ratio was observed by Quintela and Kaifer [32] for MV in the presence of a surfactant. This may indicate the preference for a radical dimer: $s\beta$ -CD ion pair and this is consistent with the more complex cyclic voltammograms shown in Fig. 5, where the first oxidation peak may arise from the oxidation of insoluble V^0 , soluble V^0 and an insoluble dimer: $s\beta$ -CD. The structure of the viologen dimer is not fully elucidated, however there is a general acceptance that it exists in solution in a face-to-face orientation arising from the overlapping π system of the two viologen molecules [33].

In the presence of the neutral β -CD, Fig. 9b, it is evident that the absorbance of MV^{+} increases slightly on increasing the concentration of the cyclodextrin. This phenomenon is usually explained in terms of increasing solubility due to the formation of an inclusion complex [34]. With the neutral β -CD, the ratio of monomer to dimer varies only

slightly from 1.57 for the free viologen to 1.67 with a tenfold excess of the neutral β -CD. This suggests the formation of a very weak inclusion complex between MV^{+} and the neutral cyclodextrin. Similar data were recorded with EV, with the ratio of the monomer to dimer changing from 1.45 for the free species to 1.70 for a tenfold excess of the neutral cyclodextrins.

Clearly, the BV system behaves differently to the MV or EV systems in the presence of the anionic $s\beta$ -CD. The BV system is more complex with the formation of an insoluble product between the radical cation and the $s\beta$ -CD to give an insoluble $BV^{+}:s\beta$ -CD aggregate. The voltammetry, Fig. 4a, RDV, Fig. 6b and spectroelectrochemical data are consistent with the formation of this insoluble aggregate at the electrode–solution interface. There are weak interactions between the dications and the $s\beta$ -CD and this is evident in Fig. 9a, where the absorbance becomes increasingly lower as more of the $s\beta$ -CD is added, as the diffusion coefficient of the V^{2+} is reduced. This reduction in the absorbance is not evident with the BV system, Fig. 8a, as the aggregate is deposited at the ITO electrode. Although the interactions between BV^{2+} and $s\beta$ -CD seem to be stronger, as evidenced from the NMR data, Table 1, and UV–Vis titrations, Fig. 2, the opposing increase in the absorbance due to the deposition of the aggregate, gives an overall increasing absorbance.

Conclusions

Evidence for the deposition of a $BV^{+}:s\beta$ -CD aggregate was obtained using cyclic voltammetry, rotating disc voltammetry and spectroelectrochemistry. Reduction of the radical cation, BV^{+} , to the neutral BV^0 was shifted by 230 mV in

the presence of β -CD, indicating a significant and strong interaction. The complex rotating disc voltammograms, obtained during the reduction of BV^{2+} in the presence of excess β -CD, showed evidence for the reduction of an adsorbed species, consistent with the deposition of the insoluble BV^{+} : β -CD aggregates at the electrode surface. The presence of this insoluble aggregate at the ITO electrode was observed in spectroelectrochemical experiments where the radical species were generated. The absorbance of the dimer increased by about 0.05 on adding an excess of β -CD, which is consistent with the deposition of the aggregate at the ITO electrode and indicates that the aggregates may contain the BV^{+} dimer. Electrostatic interactions were observed between the viologen dications, V^{2+} and the β -CD, with slightly stronger electrostatic interactions between the BV^{2+} and the β -CD.

Acknowledgements The authors would like to thank Science Foundation Ireland (SFI) for funding this work through research grant RFP/EEB006.

References

- Sousa, C.P., Polo, A.S., Torresi, R.M., de Torresi, S.I.C., Alves, W.A.: Chemical modification of a nanocrystalline TiO_2 film for efficient electric connection of glucose oxidase. *J. Colloid Interface Sci.* **346**, 442–447 (2010)
- Chen, L., Lin, C., Compton, R.G.: Single entity electrocatalysis: oxygen reduction mediated via methyl viologen doped Nafion nanoparticles. *Phys. Chem. Chem. Phys.* **20**, 15795–15806 (2018)
- Zhao, S., Huang, W., Guan, Z., Jin, B., Xiao, D.: A novel bis(dihydroxypropyl) viologen-based all-in-one electrochromic device with high cycling stability and coloration efficiency. *Electrochim. Acta* **298**, 533–540 (2019)
- Hoshino, K., Okuma, M., Terashima, K.: Electrochromic properties of metal oxide nanoparticles/viologen composite film electrodes. *J. Phys. Chem. C* **122**, 22577–22587 (2018)
- Li, X., Zhou, M., Jia, J., Jia, Q.: A water-insoluble viologen-based β -cyclodextrin polymer for selective adsorption toward anionic dyes. *React. Funct. Polym.* **126**, 20–26 (2018)
- Li, G., Xu, L., Zhang, W., Zhou, K., Ding, Y., Liu, F., He, X., He, G.: Narrow-bandgap chalcogenoviologens for electrochromism and visible-light-driven hydrogen evolution. *Angew. Chem.* **57**, 4897–4901 (2018)
- Dervishogullari, D., Gizzie, E.A., Jennings, G.K., Cliffl, D.E.: Polyviologen as electron transport material in photosystem I-based biophotovoltaic cells. *Langmuir* **34**, 15658–15664 (2018)
- Palatnik, J.F., Valle, E.M., Carrillo, N.: Oxidative stress causes ferredoxin-NADP⁺ reductase solubilization from the thylakoid membranes in methyl viologen-treated plants. *Plant Physiol.* **115**, 1721–1727 (1997)
- Monk, E.E., Evans, D.H.: Investigation of the nature of electrodeposited neutral viologens formed by reduction of the dications. *J. Electroanal. Chem.* **349**, 141–158 (1993)
- Annibaldi, V., Breslin, C.B.: Electrochemistry of viologens at polypyrrole doped with sulfonated β -cyclodextrins. *J. Electroanal. Chem.* **832**, 399–407 (2019)
- Moon, K., Kaifer, A.E.: Modes of binding interaction between viologen guests and the cucurbit[7]uril host. *Org. Lett.* **6**, 185–188 (2004)
- Li, C.J., Shu, X.Y., Li, J., Chen, S.H., Han, K., Xu, M., Hu, B., Yu, Y.H., Jia, X.S.: Complexation of 1,4-bis(pyridinium) butanes by negatively charged carboxyl-atopillar[5]arene. *J. Org. Chem.* **86**, 8458–8465 (2011)
- Wang, K., Xing, S.Y., Wang, X.G., Dou, H.X.: The effect of terminal groups of viologens on their binding behaviours and thermodynamics upon complexation with sulfonated calixarenes. *Org. Biomol. Chem.* **13**, 5432–5443 (2015)
- Matsue, T., Kato, T., Akiba, U., Osa, T.: Inclusion, solubilization, and stabilization of two-electron reduced species of methyl viologen by cyclodextrins. *Chem. Lett.* **14**, 1825–1828 (1985)
- Lee, C., Kim, C., Park, J.W.: Effect of α - and β -cyclodextrin on the electrochemistry of methylheptylviologen and dibenzylviologen. *J. Electroanal. Chem.* **374**, 115–121 (1994)
- Mirzoian, A., Kaifer, A.E.: Reactive pseudorotaxanes: inclusion complexation of reduced viologens by the hosts β -cyclodextrin and heptakis(2,6-di-O-methyl)- β -cyclodextrins. *Chem. Eur. J.* **3**, 1052–1058 (1997)
- Dias, A., Quintela, P.A., Schuette, J.M., Kaifer, A.E.: Complexation of redox-active surfactants by cyclodextrins. *J. Phys. Chem.* **92**, 3537–3542 (1988)
- Park, J.W., Choi, N.H., Kim, J.H.: Facile dimerization of viologen radical cations covalently bonded to β -cyclodextrin and suppression of the dimerization by β -cyclodextrin and amphiphiles. *J. Phys. Chem.* **100**, 769–774 (1996)
- Ader, E., Degani, Y., Goren, Z., Willner, I.: Photosensitized electron-transfer reactions in β -cyclodextrin aqueous media: effects on dissociation of ground-state complexes, charge separation, and hydrogen evolution. *J. Am. Chem. Soc.* **108**, 4696–4700 (1986)
- Lee, C., Moon, M.S., Park, J.W.: γ -Cyclodextrin-enhanced dimerization of viologen radicals. *J. Incl. Phenom. Mol. Recognit. Chem.* **26**, 219–232 (1996)
- Perveen, S., Naqvi, I.: I: Inclusion complexation of benzyl viologen by β -cyclodextrin in DMF-H₂O mixed solution. *Pak. J. Anal. Environ. Chem.* **17**, 58–64 (2016)
- Bird, C.L., Kuhn, A.T.: Electrochemistry of the viologens. *Chem. Soc. Rev.* **10**, 49–82 (1981)
- Cook, S.K., Horrocks, B.R.: Heterogeneous electron-transfer rates for the reduction of viologen derivatives at platinum and bismuth electrodes in acetonitrile. *ChemElectroChem* **4**, 320–331 (2017)
- Bard, A.J., Ledwith, A., Shine, H.J.: Formation, properties and reactions of cation radicals in solution. *Adv. Phys. Org. Chem.* **13**, 155–278 (1976)
- Kostela, J., Elmgren, M., Hansson, P., Almgren, M.: Electrochemical properties of an amphiphilic viologen in differently charged micelles. *J. Electroanal. Chem.* **536**, 97–107 (2002)
- Ling, Y.H., Mague, J.T., Kaifer, A.E.: Inclusion complexation of diquat and paraquat by the hosts cucurbit[7]uril and cucurbit[8]uril. *Chem. Eur. J.* **13**, 7908–7914 (2007)
- Yanez, C., Nunez-Vergara, L.J., Squella, J.A.: Differential pulse polarographic and UV-Vis spectrophotometric study of inclusion complexes formed by 1,4-dihydropyridine calcium antagonists, nifedipine and nicardipine with β -cyclodextrins. *Electroanalysis* **15**, 1771–1777 (2003)
- Safarowsky, C., Rang, A., Schalley, C.A., Wandelt, K., Broekmann, P.: Formation of 2D supramolecular architectures at electrochemical solid/liquid interfaces. *Electrochim. Acta* **50**, 4257–4268 (2005)
- Akdim, B., Pachter, R., Mou, S.: Theoretical analysis of the combined effects of sulfur vacancies and analyte adsorption on the electronic properties of single-layer MoS_2 . *Nanotechnology* **27**, 185701 (2016)

30. Monk, P.M.S., Hodgkinson, N.M., Ramzan, S.A.: Spin pairing (“dimerisation”) of the viologen radical cation: kinetics and equilibria. *Dyes Pigment*. **43**, 207–217 (1999)
31. Jeon, W.S., Kim, H.J., Lee, C., Kim, K.: Control of the stoichiometry in host–guest complexation by redox chemistry of guests: inclusion of methylviologen in cucurbit[8]uril. *Chem Commun*. **17**, 1828–1829 (2002)
32. Quintela, P.A., Kaifer, A.E.: Electrochemistry of methylviologen in the presence of sodium decyl sulfate. *Langmuir* **3**, 769–773 (1987)
33. Vuckovic, M., Mentus, S.V., Janata, E., Milosavljevic, B.H.: Fast dimerisation of the triparaquat radical dication. *Phys. Chem. Chem. Phys.* **3**, 4310–4315 (2001)
34. Al-Marzouqi, A.H., Shehatta, I., Jobe, B., Dowaidar, A.: Phase solubility and inclusion complex of itraconazole with beta-cyclodextrin using supercritical carbon dioxide. *J. Pharm. Sci.* **95**, 292–304 (2006)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.