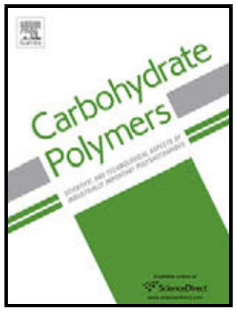

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β-CD assisted aqueous dissolution of Cetylpicolinium dichromates (CPDC) – Evolution of a class of green water compatible lipopathic Cr(VI) oxidants

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Highlights

1. β-CD-assisted transference of dichromate with hydrophobic cleft to aqueous phase
2. B_s type Phase solubility curve
3. Solubility of CPDCs upto a β-CD concentration of 7.5mM
4. Aggregation of β-CD with and without CPDC from DLS study
5. Green and mild Cr(VI) oxidant in aqueous medium

A B S T R A C T

Water-insoluble lipopathic dichromates have been successfully solubilized in aqueous phase by the entrapment of their hydrophobic tails in *β*-cyclodextrin (*β*-CD) non-polar cavity. Aqueous solubility of *α*-, *β*-, and *γ*- cetylpicolinium dichromate (CPDC) molecules, synthesized in our lab, has been studied to find their suitability for Cr(VI) oxidation purposes in water medium. The analysis of phase solubility shows the existence of a B_s type curve and its significance has been fully deciphered through dynamic light scattering (DLS) analysis. The limiting concentration of *β*-CD up to which it can induce 1:1 host-guest complexation with the CPDC entities, has been determined and the stoichiometry has been confirmed from Job's plot. The binding constant and complexation efficiency of the *β*-CD-CPDC complexes have been determined and temperature effect on these parameters has been discussed through thermodynamic calculations. Analyses of viscosity variation of the aqueous solutions of the complexes have been done and correlated with the solubilization phenomenon.

Key Words: solubility analysis; inclusion complexation; cyclodextrin; cetylpicolinium dichromate; oxidant; dynamic light scattering

1. Introduction

Chromium oxidants with lipopathic carriers are well established. Anionic oxidants having onium ion as the counter ion possess oxidation potential different than those without such counter ions and thus are considered to be a different class of oxidizing systems. Such counter ions make the oxidant mild, oil soluble, and many a times chemoselective. Organic mediated oxidation reactions using such oxidants such as cetyltrimethylammonium dichromate (Patel & Mishra, 2006), and various heterocyclic oniums as the counterions containing pyridine (Antonioletti, D'Auria, Piancatelle & Scettri, 1981; Still & Galynker, 1982; D'Auria, Mico, D'Onofrio & Scettri, 1985; Cossio, Aizpurua & Palomo, 1986; Banerji, 1988; Yli-Kauhaluoma, Harwig, Wentworth & Janda, 1998; Maki, Ishihara & Nakanishi, 2000; Alcudia, Arrayas & Liebeskind, 2002; Tajbakhsh, Hosseinzadeh & Shakoori, 2004), quinoline (Dey & Mahanti, 1990; Chaubey, Das & Mahanti, 2003; Kuotsu, Tiewsoh, Debroy & Mahanti, 1996), caffeine (Shirini, Mohammadpoor-Baltrok, Hejazi & Heravi, 2003), imidazole (Agarwal, Tiwari & Sharma, 1990), and nicotine (Cossio, Lopez & Palomo, 1987; Sekar, 2002) systems have been reported. The counter ions in many reaction media form various types of organized assemblies providing micro-heterogeneous domains with variable pockets of solubilization (Patel & Mishra, 2006). In case of lipopathic dichormates such as cetyltrimethylammonium dichromate, it is generally observed that during the oxidation reactions, a reverse micellization phenomenon comes into force due to which a reaction having negative order with respect to the oxidant is generally obtained. Such an aggregation of the onium dichromate may be adversely affecting the efficiency of the oxidant.

Solubilization of some cetylpicolinium dichromates (CPDC) molecules in water medium assisted by β-cyclodextrin (β-CD) has been studied in the present work which will provide a new

functionalized oxidant system without any reverse micellization phenomenon of the lipopathic oxidants so that their oxidation efficiency can be enhanced. Besides, harmful organic solvents can be replaced by water, which ensures a greener protocol during oxidation reactions by lipopathic Cr(VI) oxidants.

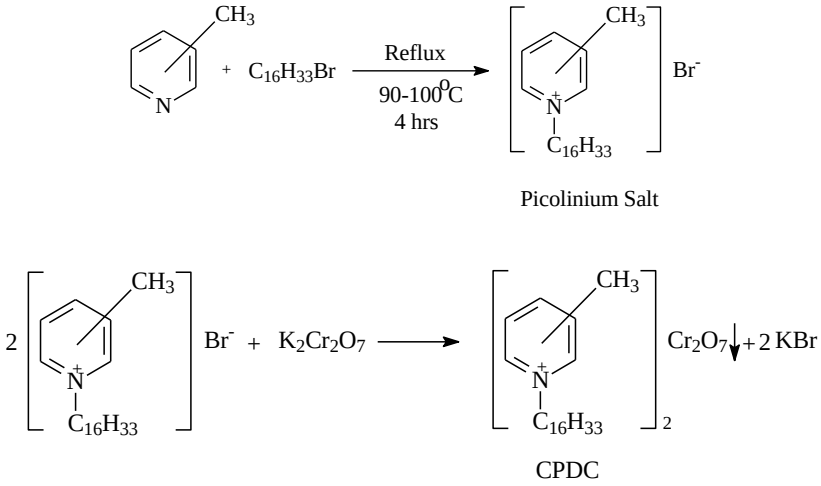
Cyclodextrins are a class of polysaccharides possessing interior hydrophobic cavity capable of encapsulating lipophilic foreign molecules (Martin Del Valle, 2003). They can induce host–guest complexation with various suitable molecules with the help of non-covalent interactions leading to inclusion complex formation (Loftsson & Brewster, 1996). As a consequence, even hydrophobic molecules can be solubilized and stabilized in water medium with the assistance of cyclodextrin molecules without the involvement of any hydrogen bonds (Singh, Sharma & Banerjee, 2002). Sometimes cyclodextrin molecules form some types of micellar organization in aqueous medium, thus helping solubilization of lipophilic entitites in water (Loftsson, Jarho, Masson & Jarvinen, 2005). During complexation between cyclodextrin and hydrophobic molecules, enthalpy-rich water molecules are released from the non-polar cavity of cyclodextrin decreasing its ring strain and complexation is achieved (Loftsson, Jarho, Masson & Jarvinen, 2005).The host-guest binding is a dynamic phenmomen.

In the present work the solution behaviour of three isomeric cetylpicolinium dichromates (CPDC) such as α-, β-, and γ- CPDC in aqueous phase in presence of β-CD have been studied to understand the phenomenon of inclusion complexation between the β-CD and CPDC molecules and to understand their stability and aggregation properties in that medium. Though the β-CD host molecule possesses large number of hydroxyl groups, dichromate does not cause any notable oxidation of the host (Kumar & Khan, 2011).

2. Materials and Methods

2.1. Materials

Cetylpicolinium bromide (CPB) was purchased from Merck, India. It was recrystallized from methanol and purity was checked from melting point determination. *β*-CD (Merck, India) was used as received. Throughout the experiments triple distilled water was used. The lipopathic oxidants such as *α*-, *β*-, and *γ*-CPDC were synthesized as per the reported procedures (Scheme 1) (Chidambaram, Sonavane, Zerda & Sasson, 2007).



Scheme 1. Synthetic route of *α*-, *β*-, and *γ*- CPDC.

Purity of each dichromate is checked through ^{1}H NMR analysis (Supplementary Fig. 1) and the melting points are recorded using open capillary method (Table 1).

Table 1

Melting point and ^{1}H NMR of CPDC oxidants.

Sl No.	CPDC	MP (^{o}C)	^{1}H NMR
1	α-CPDC	103	0.87 (6H, t, J = 7.2Hz), 1.21-1.30(52H, m), 1.84-1.94 (4H, m), 2.95 (6H, s), 4.89-4.91(4H, m), 7.82-7.83(2H, m), 8.09-8.11(2H, m), 8.31-8.32(2H, m), 9.25-9.26(2H, m)
2	β-CPDC	75	0.871 (6H, t, J = 6.8Hz), 1.231-1.307 (52H, m), 1.849-2.010 (4H,m), 2.659 (6H, s), 4.85-4.87 (4H, m), 8.10-8.24 (4H, m), 8.97-8.99 (4H, m)
3	γ-CPDC	70	0.86 (6H, t, J = 8.0Hz), 1.21- 1.28 (52H, m), 1.98-2.20(4H, m), 2.65 (6H, s), 4.76-4.78 (4H, m), 8.01-8.20 (4H, m), 9.03-9.20 (4H, m)

The solubility of all the CPDC molecules has been checked in 15 different solvents (Table 2).

Table 2

Solubility studies of α-, β-, and γ-CPDC in various solvents.

Sl. No	Solvents	α-CPDC	β-CPDC	γ-CPDC
1	DCM	Soluble	Soluble	Soluble
2	DMF	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot
3	Hexane	Insoluble	Insoluble	Insoluble
4	Ethyl Acetate	Insoluble	Insoluble	Insoluble
5	CCl_4	Sparingly soluble	Sparingly soluble	Sparingly soluble
6	$CHCl_3$	Soluble	Soluble	Soluble
7	Benzene	Insoluble	Insoluble	Insoluble
8	Acetonitrile	Insoluble	Insoluble	Insoluble
9	Toluene	Insoluble	Insoluble	Insoluble
10	1,4-Dioxane	Sparingly soluble in	Sparingly soluble in	Sparingly soluble

		cold/ Soluble in hot	cold/ Soluble in hot	in cold/ Soluble in hot
11	DMS	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot
12	Chloro-benzene	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot	Sparingly soluble in cold/ Soluble in hot
13	Methanol	Soluble	Soluble	Soluble
14	Ethanol	Soluble	Soluble	Soluble
15	THF	Insoluble	Insoluble	Insoluble

2.2. Methods

2.2.1. Preparation of solutions and absorption spectral analysis

1.8gm of β-cyclodextrin was solubilized in 100 ml triple distilled water followed by slight warming. The solution was filtered through a cotton plug resulting in a stock solution of β-CD with a concentration of 15 mM. The stock solution was further used for the preparation of a range of solutions of β-CD of concentrations 1.5–15 mM. Solutions of α-, β-, and γ-CPDC were made with aqueous β-CD medium in a concentration range of 0.5–1.0 mM.

CPDC solutions in aqueous β-CD medium with appropriate concentrations were taken in a sample cuvette of a pair of matched quartz cells and the optical densities (*OD*) were measured at different concentrations of both the components using a Hitachi U-3010 double beam UV-vis spectrophotometer thermostated at 20.0 ± 1^{o}C. The *OD* of each solution was measured at a wavelength (λ_{max}) of 360 nm. The results are averaged values of three runs with an error of (±) 4.0%.

2.2.2. Instrumentation

The formation of host-guest complexes has been characterized using dynamic light scattering (DLS), transmission electron microscopy (TEM), ^{1}H NMR and FTIR spectral methods.

A fixed scattering angle Zetasizer Nano-ZS system (Malvern, UK) attached with a He-Ne laser beam at 658 nm has been used for sizing (dynamic light scattering, DLS) to record the z-average molecular "size (r)" obtained from the hydrodynamic diameter (d_H) within the solution. This parameter is related to the z-average translational diffusion coefficient (D) as shown in the Eq 1:

$$D = \frac{kBT}{3\pi\eta dH} \quad (1)$$

For each sample, measurements were done for 2 minutes at 20.0±1 ºC with a scattering angle of 173º.

Transmission electron micrograph (TEM) of the β-CD-β-CPDC complex was measured on a Phillips Tecnai 12 instrument operating at 120 kV. The specimen was prepared by drop casting technique on a carbon coated copper grid.

Fourier Transform Infrared (FTIR) spectra of the samples were measured on a Bruker Eco-ATR instrument. For carrying out ^{1}H-NMR measurements, a Bruker Avance 400 NMR spectrometer was used with tetramethylsilane (TMS) as an internal standard.

2.2.3. Phase solubility analysis

Spectrophotometric determination of variation in the molar concentration of CPDC with the molar concentration of β-CD at 20^{o}C and plotting the values gives a a phase-solubility diagram. The profile of the graphs shows the type of complexation (Higuchi & Connors, 1965)

and helps in determination of binding constant ($K_{y:x}$) as well as the complexation efficiency (CE) of the host and guest molecules.

The graph consists of linear and non-linear parts where the former is due to 1:1 complexation (Eq 2). The slopes of the plots give the values of the binding constant for 1:1 complexation ($K_{1:1}$) (Eq 3).

$$\text{Guest} + \beta - \text{CD} = \text{Guest} - \beta - \text{CD} \quad (2)$$

$$\text{K1:1} = \frac{\text{slope}}{\text{So}(1-\text{slope})} \quad (3)$$

where, S_o = Intrinsic solubility (i.e. solubility of guest at zero cyclodextrin content)

CE for 1:1 complexation is estimated using the Eq 4.

$$\text{CE} = \frac{[\text{Guest}-\beta-\text{CD}]}{[\beta-\text{CD}]} = \text{So.K1:1} = \frac{\text{slope}}{(1-\text{slope})} \quad (4)$$

3. Results and Discussion

3.1. Analysis of Phase-solubility and Stoichiometry

As per Higuchi and Cornor (Higuchi & Cornor, 1965), the phase solubility profiles are found to be of B_s type, indicating the formation of complexes of limited solubility (Fig. 1).

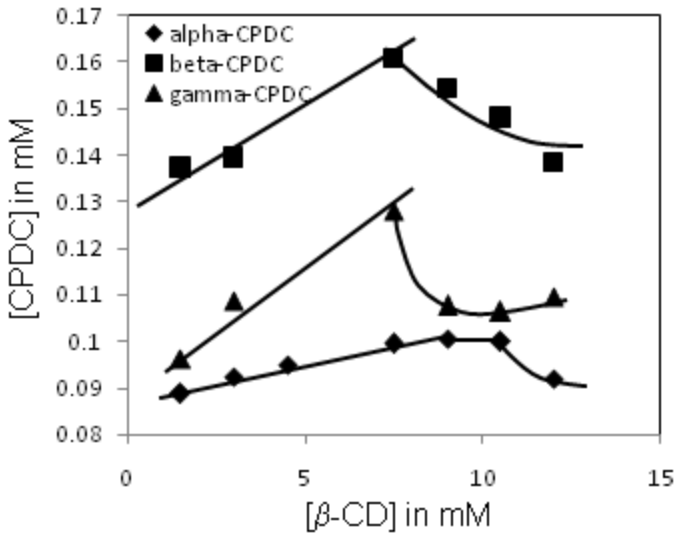


Fig. 1. Plots of [β-CD] versus [CPDC] in aqueous medium at 20.0 ± 1◦C.

The linear part of the plots indicates a proportionate increase in the dichromate solubility due to an increase in the inclusion complexation with the β-CD host suggesting a typical 1:1 type complexation. Hence, the initial linear portion of the solubility diagram suggests the involvement of 1:1 inclusion complexation between the host and the guest molecules and is used for the calculation of $K_{1:1}$ values. However, beyond a concentration of 7.5 mM of β-CD, the solubility decreases in all the β-CD-CPDC interactions (Fig. 1).

A short plateau obtained beyond the ascending part of the B_s type curve indicates the formation of complex with different stoichiometry, when the concentration of β-CD becomes very high.

Beyond the linear part of the plot a decrease in the solubility is observed, which can be attributed to the unavailability of the β-CD molecules for inclusion complex formation (Loftsson & Brewster, 2011). At a β-CD concentration of 7.5 mM, the cyclodextrin molecules finds no interest in inclusion complex formation, rather they prefer to self-assemble with each other, where the wider rim of two cyclodextrin moiety coordinate with each other by means of

hydrogen boding. Cyclodextrins mostly prefer a head-to-head alignment in order to avail maximum hydrogen bonding (Loftsson, Hreinsd´ottir & M´asson, 2010). Interest in self-assembly of β-CD molecules rather than complex formation with the dichromate guest molecules can be visualized from the small binding constant values (at a range of 12 to 93) and small complexation efficiency values (at a range of 0.001 – 0.0065) that are found to be very low. Quantification of β-CD molecule that potentially forms inclusion complex with the number of substrate molecules have been done form the CE value (Loftsson, Hreinsd´ottir & M´asson, 2005) (Supplementary Table 1).

The stoichiometry of the complex was determined using Job method (Job, 1928; Huang, 1982; Vosburgh & Cooper, 1941) by plotting the volume fractions of the β-CD guest molecule against the optical densities of the CPDC molecules. The concentration of the β-CD solutions were maintained within an upper limit of 7.5 mM since 1:1 complexation does not occur beyond this concentration as observed from the Higuchi-Corner plot (Fig. 1). The 1:1 stoichiometry during the complexation of β-CD and CPDC molecules is confirmed from the curve maximum at a volume fraction value of 0.55 (Supplementary Fig. 2).

The observation in case of β-CD-CPDC complexation is in contrast to that reported during the complexation of CTAP with β-CD molecules (Bank, Guru & Dash, 2014) where the cetyltrimethylammonium permanganate (CTAP) molecules form 1:1 complexation with β-CD host molecules at all concentrations representing an A_L type plot with a $K_{1:1}$ value of 100.5 and CE value of 0.017. These values are sufficiently higher than those of the CPDC molecules. A difference in the pattern of complexation, may thus be due to the difference in the type of counter ion and consequent steric influence in the inclusion complex formation.

In order to counter balance the bivalent negative charge on the dichromate ion two numbers of cetylpicolinium ions are needed and proximity of both the clefts in the immediate vicinity of the dichromate ions might cause some steric hindrance to be comfortably encapsulated within the cyclodextrin non-polar cavities. Besides, among the CPDC molecules, the values of the binding constant ($K_{1:1}$) and complexation efficiency decrease in the order, γ-CPDC > β-CPDC > α-CPDC, clearly showing the impact of steric factor on the complexation within the β-CD cavity (Supplementary Table 1). It is prudent here to mention that out of all the CPDC, there lies a steric enactment in case of α-CPDC making it somewhat different from the rest three. When the inclusion complex formation in terms of solubility at a fixed dichromate and cyclodextrin concentration is compared it has been observed that the solubility in case of α-CPDC is less with respect to the other two. This anomaly in behaviour of α-CPDC may be due to the existence of ortho-effect making it sterically more crowded.

3.2. Characterization of host-guest complexes

The average of mean intensity percent at various size ranges for the aqueous solutions of neat β-CD at different concentrations and in presence of CPDC molecules were studied using dynamic light scattering (DLS) method (Table 3).

β-CD molecules undergo self-aggregation in neat aqueous medium as well as in presence of CPDC molecules within a size of 100-600 nm (Supplementary Fig. 3), which is also corroborated by the phase solubility curve (Fig. 1). The phenomenon of self-aggregation is responsible for the decrease in the complexation between β-CD and CPDC molecules. It is of general observation that with the increase in the size of the aggregation, the mean intensity decreases. Increasing order of average size of aggregation (r) in nm is "neat β-CD (215.3) < β-

CD in presence of β-CPDC (303.7) < β-CD in presence of γ-CPDC (311.4) < β-CD in presence of α-CPDC (337.9) and the mean intensity decreases in the reverse order.

Table 3

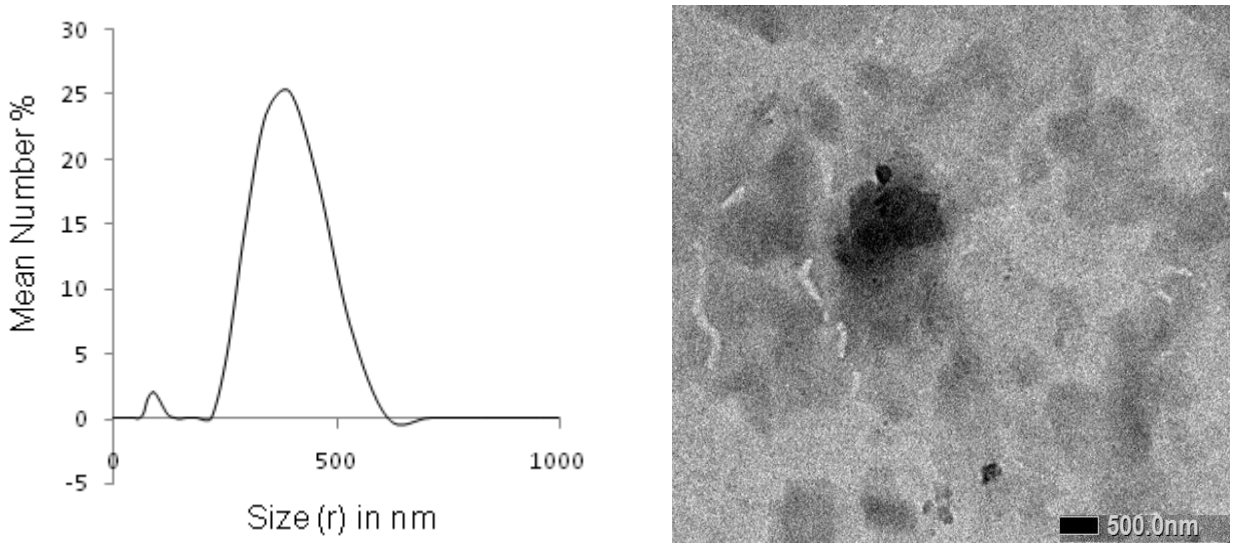
Size distribution of β-CD and β-CD in presence of various CPDC isomers in aqueous medium, [β-CD] = 1.5-12 mM, [CPDC] = 8×10^{-4}M, T = 25^{o}C.

Solutes	Average of Mean intensity percent at various size range (nm)							
	100-150	150-200	200-250	250-300	300-350	350-400	400-500	500-600
β-CD neat	48.1	40.7, 26.4	31.7,29.7	34.9,39.4, 36.5	---	---	---	---
β-CD in presence of α-CPDC	---	---	---	39.7	28.2,32.8, 27.9,34.8, 29.9,29.8	25.2	---	---
β-CD in presence of β-CPDC	---	---	---	42.6,41.3, 32.5,38.5, 34.9,34.8	27.8	25.2	---	---
β-CD in presence of γ-CPDC	42.7	---	---	23.3,31.5, 36.1,31.4, 36.1	30.8	---	---	29.9

The observation of maximum mean intensity with smallest average size of β-CD indicates its compact aggregation in aqueous medium. However, in presence of CPDC molecules, the aggregation phenomenon of β-CD starts diminishing. On the other hand, the average size of the aggregates increased in the presence of CPDC, which may be due to the formation of β-CD-CPDC aggregates. The self-aggregations of the β-CD is the root cause of observation of B_s type curve where beyond a certain concentration, a platue is observed

representing the self-aggregation phenomenon along with a decrease in the complexation phenomenon.

For the of *β*-CD-*β*-CPDC complexes, large peaks located at about 400 nm are observed from the DLS study. However, the TEM for the complexes shows the presence of nearly spherical structures with an average radius of 500 nm (Fig. 2).



(a) (b)

Fig. 2. (a) DLS spectrum of the aqueous solutions of *β*-CD-*β*-CPDC complex; (b) TEM image of *β*-CD-*β*-CPDC complex.

The size of aggregations measured by DLS is found to be slightly smaller than that of the TEM result. Such a difference may be due to the difference in the physical states of the complexes during their measurements since dimensions of solid spheres are measured in TEM whereas hydrodynamic radii are measured in DLS methods (Shi & Shen, 2014).

The ^{1}H-NMR spectra of *β*-CD and the complexes of *β*-CD-*α*-CPDC, *β*-CD-*β*-CPDC and *β*-CD-*γ*-CPDC (Supplementary Figure 4) have been compared to account for the shift of the

protons of cyclodextrin before and after complexation (Table 4). *β*-Cyclodextrin protons are named as follows:

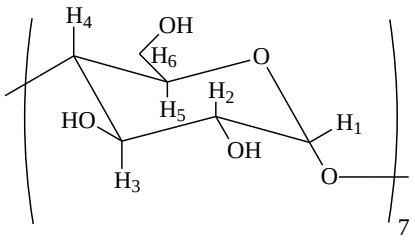


Table 4

Chemical shifts of *β*-CD, *β*-CD-CPDC complexes and their differences ($\Delta\delta = \delta_{complexed} - \delta_{free}$).

H	*β*-CD	*β*-CD : *α*-CPDC		*β*-CD : *β*-CPDC		*β*-CD : *γ*-CPDC	
	$\delta_{\beta\text{-CD}}$	$\delta_{\beta\text{-CD:}\alpha\text{-CPDC}}$	$\Delta\delta_{\beta\text{-CD:}\alpha\text{-CPDC}}$	$\delta_{\beta\text{-CD:}\beta\text{-CPDC}}$	$\Delta\delta_{\beta\text{-CD:}\beta\text{-CPDC}}$	$\delta_{\beta\text{-CD:}\gamma\text{-CPDC}}$	$\Delta\delta_{\beta\text{-CD:}\gamma\text{-CPDC}}$
1	4.98	4.97	0.01	4.97	0.01	4.97	0.01
2	3.57	3.56	0.01	3.55	0.02	3.56	0.01
3	3.87	3.84	0.03	3.84	0.03	3.86	0.01
4	3.48	3.50	-0.02	3.49	-0.01	3.49	-0.01
5	3.78	3.78	0.00	3.77	0.01	3.77	0.01
6	3.75	3.72	0.03	3.74	0.01	3.74	0.01

Comparison of the Δδ values ($\Delta\delta = \delta_{complexed} - \delta_{free}$) of H3 and H5 of all the *β*-CD-CPDC complexes shows a partial inclusion in case of *β*-CD: *α*-CPDC and *β*-CD: *β*-CPDC. Moreover, in case of *β*-CD: *γ*-CPDC the inclusion is total (Schneider, Hacket, Rüdiger & Ikeda, 1998). Geometrical structure of the CPDC molecules show that in case of *γ*-CPDC, there is no steric hindrance between the methyl group on the aromatic ring and the cetyl chain resulting in a comfortable encapsulation of hydrophobic moiety of *γ*-CPDC into the non-polar cavity of *β*-CD.

Besides, among all the CPDC, the values of complexation efficiency and binding constant of γ-CPDC is quite higher than those of α-CPDC and β-CPDC clearly explaining the steric factor.

The complex formation of β-CD and all CPDCs is accompanied by changes in their IR spectra as shown in the Fig. 3.

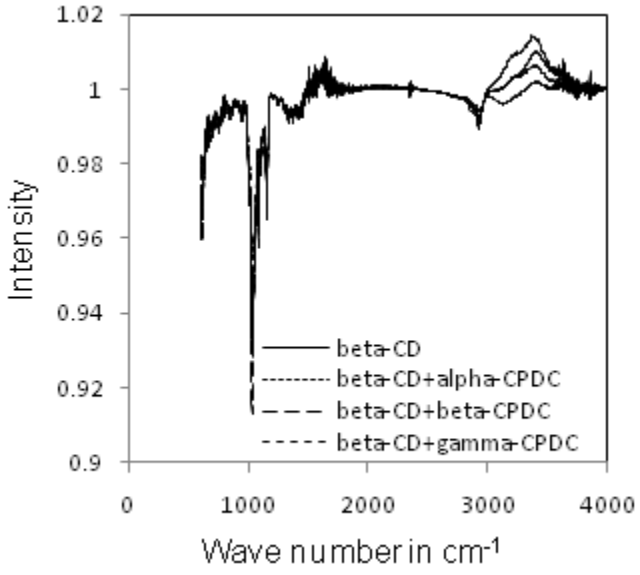


Fig. 3. IR spectra for β-CD and β-CD-CPDC complexes.

The broad peak of OH group in β-CD is found to be in the range 3157.197 cm^{-1}. This peak starts diminishing after complexation with CPDC molecules, which may be due to the effect of inner cavity interaction of β-CD hydroxy groups and the hydrophobic tails of the CPDC molecules. Moreover, after fitting of the hydrophobic tail into the cavity of β-CD, restriction of hydroxy vibration may be occurring, leading to the decrease in the peak intensity (Mangolim, Moriwaki, Nugeira, Sato, Baesso, Neto & Matioli, 2014; Zhang, Liao, Liu & Ma, 2001).

3.3. Variation of CPDC concentration in fixed β-CD concentration

Maintaining the concentration of β-CD at an optimum value of 7.5 mM, up to which the complexation of β-CD-CPDC molecules have been observed, the molar concentrations of CPDC have been varied in the range of 0.5 – 1.0 mM and plotted against the corresponding

optical density values in aqueous medium. The optical density (*OD*) values are found to increase linearly with [CPDC] (Fig. 4) with hypothetical optical densities of 0.240, 0.275 and 0.118 for α-, β-, and γ-CPDC respectively, when there is no presence of β-CD.

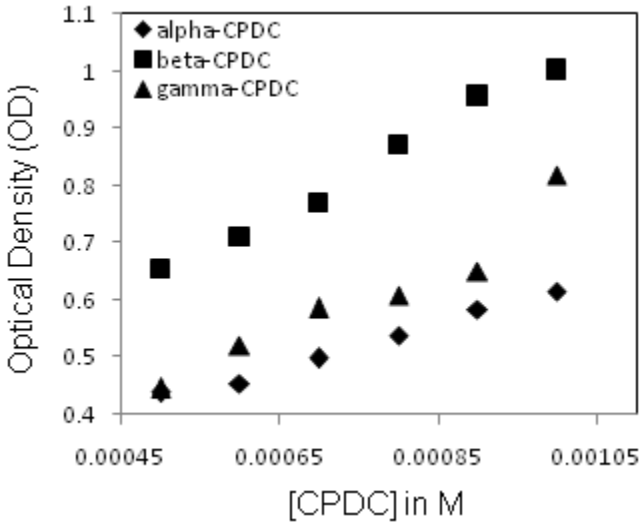


Fig. 4. Variation of [CPDC] with *OD* at a fixed β-CD concentration in aqueous medium at 20.0 ± 1◦C.

Such linear increase in the *OD* values with the increase in the concentration of CPDC eliminates the possibility of any micellar aggregation of the lipopathic dichromates; on the other hand, inclusion of the molecules within the non-polar cavity of β-CD molecules is a possible reason. The possibility of micellar aggregation of free CPDC molecules in the above range of concentration is thus remote; rather there is perfect dominance of inclusion complexation with β-CD.

3.4. Thermodynamics of host-guest complexation

Various thermodynamic parameters for host-guest complexation, such as the enthalpy change (ΔH), the entropy change (ΔS), and the free energy change (ΔG) have been calculated from the variation of temperature with the stability constant ($K_{1:1}$) of the β-CD-CPDC complexes (Martin, 1993) (Eqs 5-7).

$\ln K_{1:1} = \ln A - \Delta H / RT$ (5)

where, A = frequency factor = constant, the slope provides the enthalpy data.

$\Delta S = \ln A - \ln (k_B/h)] \times R$ (6)

where, k_B = Boltzmanns constant, h = Planck's constant and R = gas constant

$\Delta G = \Delta H - T\Delta S$ (7)

Values of the thermodynamic parameters of the host-guest complexation measured in the present case (Table 5) suggest an influence of the molecular structure of the CPDC guest molecules.

Table 5

Thermodynamic parameters (ΔH, ΔS and ΔG) and binding constants at various temperatures for host-guest complexation of β-CD with CPDC molecules.

CPDC	T (K)	ΔH (kJ/mol)	ΔS (kJ/mol/K)	ΔG (kJ/mol)	$K_{1:1}$
	293			50.2	22.5
	298			51.9	19.5
α-	303	-49.3	-0.34	53.6	10.4
	308			55.3	7.99
	313			57	6.99
	293			49.4	31.4
	298			51	26.5
β-	303	-45.6	-0.32	52.6	15.1
	308			54.3	13.4
	313			63	9.90
	293			47.6	55.6
	298			49.6	46.2
γ-	303	-67.2	-0.39	51.5	31.2
	308			53.5	18.6
	313			55.5	9.60

Negative enthalpy indicates the process to be exothermic in all cases. This also is reflected from the decrease in the binding constants with the increase in temperature. The entropy in each case shows a negative change. Such a negative entropy change was also observed during the complexation of CTAP (cetyltrimethylammonium permanganate) with β-CD (Bank, Guru & Dash, 2014), which normally is due to the loss of conformational freedom due to host-guest binding. However, there may be reorganization of the salvation shell of both the components resulting in a disorder, which finally leads to a gain in the entropy of the system. Such a gain in entropy may compensate for the entropy loss so that the final entropy change may also be postitive. So, the analysis of entropy change during host-guest complexation is generally not certain from the standpoint of both the host as well as the guest. (Liu, Cao, Chen & He, 2008). During β-CD-CPDC complexation, lower disorderliness and better stabilization can be predicted from the negative entropy change. The free energy of host-guest complexation indicates that the phenomenon takes place more efficiently at a lower temperature condition. Besides, the enthalpy and entropy changes of the three isomers of CPDC give a good correlation ($R^2 = 0.985$) suggesting an isokinetic relationship (Supplementary Fig. 5). From the entropy data it can be concluded that the complex formation is more ordered in case of γ-CPDC and least ordered for β-CPDC. None the less, a higher value for ΔH than TΔS suggests the process to be enthalpy driven. In each of the dichromate the binding constant for the complex formation decreases with the increase in temperature. The CPDC molecules possess both hydrophobic chains as well as aromatic nuclei. Hence, during complexation with the β-CD molecules, both hydrophobic as well as π-π and $\sigma_{C\text{-}H}$-π interactions may be playing significant roles.

3.5. Viscosity measurement

At a fixed *β*-CD concentration, a linear increase in the viscosity of the solution is observed in each case with the increase in the dichromate concentration (Fig. 5); however, at a fixed dichromate concentration, viscosity decreases up to a *β*-CD concentration of 7.5 mM, beyond which it further rises.

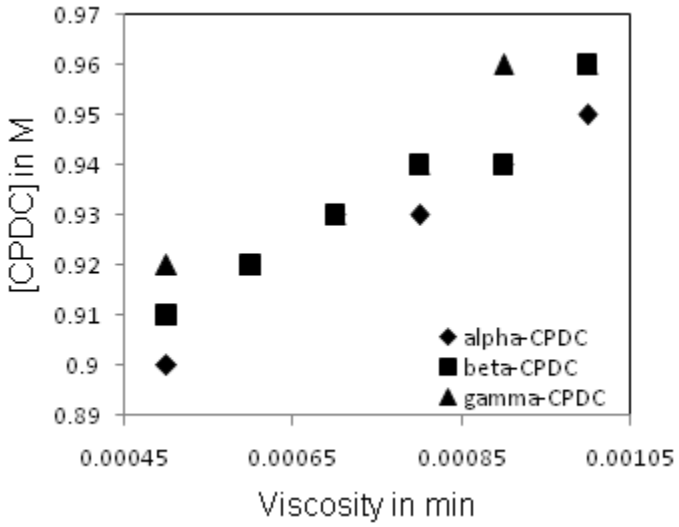


Fig. 5. Variation of viscosity in min with [CPDC] in M for various CPDC molecules in aqueous *β*-CD medium at fixed *β*-CD concentration at 20.0 ± 1◦C.

As observed from the phase solubility profile of CPDC molecules in aqueous *β*-CD medium, B_s type curves indicate the occurrence of complexation up to a *β*-CD concentration of 7.5 mM, beyond which this complexation decreases tremendously. Analysis of viscosity data and its comparison with those of phase-solubility, self-assembling of *β*-CD molecules beyond the concentration of 7.5 mM might be responsible for the increase in the viscosity. Analogous effects have also been reported by earlier workers (Kuperkar, Abezgauz, Prasad & Bahadur, 2010).

4. Conclusions

The present work is an attempt to solubilize lipopathic dichromate molecules in aqueous medium for their utilization as water-mediated oxidants. Inclusion complexation between β-CD and the CPDC molecules drives the solubilization phenomenon upto a limiting concentration of 7.5 mM of β-CD beyond which the extent of complexation diminishes due to the induction of aggregation among the β-CD molecules. The hydrophobic chains and the aromatic nuclei of the CPDC molecules might be responsible for the host-guest complexation phenomena through π-π and $\sigma_{C\text{-}H}$-π interactions. However, the complexation effects of CPDC molecules are found to be remarkably lower compared to quaternary ammonium permanganates within aqueous β-CD medium. The work, however, will be a foot step in conducting Cr(VI) oxidations using mild lipopathic dichromate oxidants in a greener aqueous environment.

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