



## ORIGINAL ARTICLE

# Synthesis, spectral characterization, thermal investigation and electrochemical evaluation of benzilbis(carbohydrazone) as Cd(II) ion selective electrode



Sulekh Chandra <sup>a,\*</sup>, Deepshikha <sup>a,b</sup>, Anjana Sarkar <sup>b</sup>

<sup>a</sup> Department of Chemistry, Zakir Husain Delhi College, University of Delhi, New Delhi 110002, India

<sup>b</sup> School of Applied Sciences, Netaji Subhas Institute of Technology, University of Delhi, New Delhi 110075, India

Received 22 August 2012; accepted 15 March 2013  
Available online 29 March 2013

## KEYWORDS

Benzil bis(carbohydrazone);  
Interaction mechanism;  
Electrochemical sensor;  
Selectivity;  
Cadmium(II) selective electrode;  
Electrochemical impedance spectroscopy

**Abstract** Benzil bis(carbohydrazone) (BBC) has been synthesized and structurally characterized on the basis of IR, <sup>1</sup>H NMR, mass, UV spectra and thermogravimetric analyses. BBC has been analysed electrochemically and explored as new N, N Schiff base. It plays the role of an excellent ion carrier in the construction of cadmium(II) ion selective membrane sensor. This sensor shows very good selectivity and sensitivity towards cadmium ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The response mechanism was discussed in the view of UV-spectroscopy and Electrochemical impedance spectroscopy (EIS). The proposed sensor was successfully used for the determination of cadmium in different chocolate samples.

© 2013 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

## 1. Introduction

Schiff base derived from carbohydrazide is a ramification of hydrazine, which has more function groups. So, it has been used in the field of intermediate (Kurzer and Wilkinson, 1970; Para-

shar et al., 2009; Terzioglu and Gursoy, 2003; Thompson et al., 1999) of the organic synthesis for the fine chemicals and medicine, and an effective oxygen scavenger (Cosper and Kowalski, 1990) to prevent corrosion especially in boiler feed system. Carbohydrazone is an azotic ligand with lone electron pairs. It may coordinate with many metal ions as monodentate or multidentate (Akiyoshi et al., 2000; Zhang et al., 2008; Konkova et al., 1995; Talawar et al., 2004). Because it possesses relatively strong reduction ability, it has been used to design a variety of energetic coordination compounds with explosive properties. This kind of compounds of carbohydrazide aroused great interest especially in recent years in primary explosives, propellants, and high explosives (Zhang et al., 2001; Yongxu et al., 2005). Such types of ligand systems are capable to show keto and enol tautomerism which results in the coordination of ligand in deprotonated

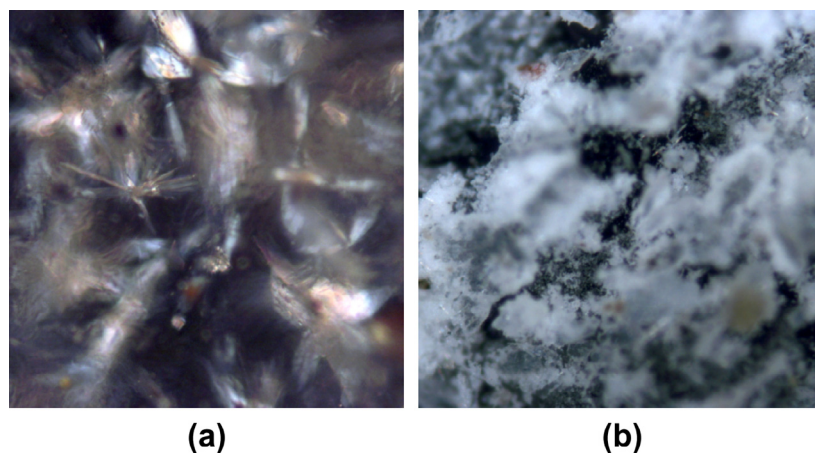
\* Corresponding author. Tel.: +91 1122911267; fax: +91 1123215906.

E-mail addresses: [schandra\\_00@yahoo.com](mailto:schandra_00@yahoo.com) (S. Chandra), [deepshikha.research@gmail.com](mailto:deepshikha.research@gmail.com) (Deepshikha).

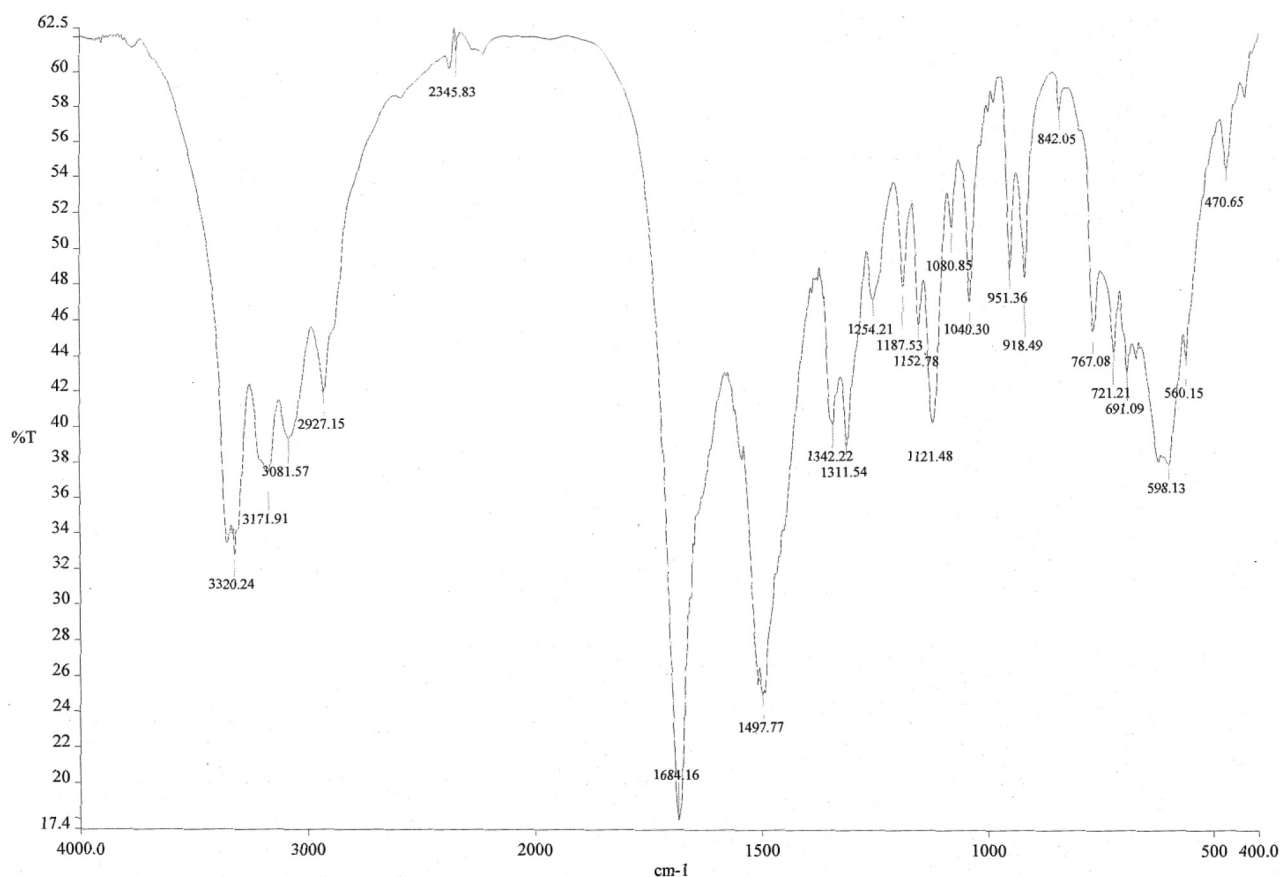
Peer review under responsibility of King Saud University.



Production and hosting by Elsevier



**Figure 1** Membrane picture under polarized optical microscope (a) before use as long tubular structure (b) after use with blocked capturing sites.



**Figure 2** IR spectra of ligand BBC.

form. These ligand systems have been proved to be a fruitful source to stabilize the unusual oxidation states of metal ions and to give neutral complexes (Bart et al., 2006; Chandra and Sharma, 2009a,b).

Based on the above considerations, the aim of the present work is to synthesize a neutral Schiff base ligand benzil bis(carbohydrazone) (BBC) and characterize it on the basis of spectral and thermal techniques. The Schiff base BBC was used to construct cadmium(II) ion selective sensor. As highly toxic

element cadmium is responsible for several cases of ailments including fever, muscle ache and inflammation that can ultimately lead to respiratory and kidney damage (Matza and Krone, 2007; Pretto et al., 2010). Medical researchers have also revealed that cadmium may cause lung and prostate cancers (Verougstraete et al., 2003).

Therefore, there is an urgent need to design such compounds which can monitor the level of cadmium in the environment.

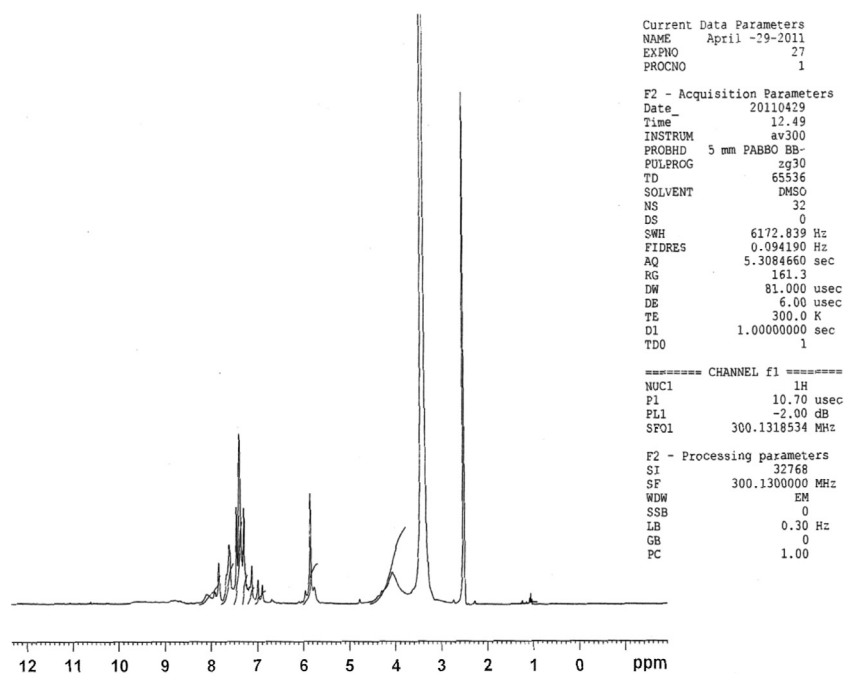


Figure 3  $^1\text{H}$  NMR spectra of ligand BBC.

## 2. Experimental

### 2.1. Materials

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. Benzil, carbohydrazide, high molecular weight poly (vinylchloride) powder (PVC), dibutyl phthalate (DBP), dioctyl phthalate (DOP) and tetrahydrofuran (THF) were obtained from Sigma. Tetradodecylammoniumtetrakis(4-chlorophenyl) borate (ETH 500), tris(2-ethylhexyl)phosphate and 2-nitrophenyl octyl ether (NPOE), were obtained from Fluka. Salts of metal nitrates or chlorides and solvents like methanol, ethanol, acetone, dioxane, nitric acid and hydrogen peroxide (all from Merck) were of the highest purity available and used without any further purification. All the metal nitrate solutions were freshly prepared by accurate dilution from their stock solution of 0.1 M, with distilled, de-ionized water.

### 2.2. Synthesis of benzil bis(carbohydrazone) (BBC)

An aqueous ethanolic solution of carbohydrazide (0.02 mol, 1.8 g) was treated with 1 ml glacial acetic acid followed by slow addition of a solution of benzil (0.01 mol, 2.1 g) in 20 ml ethanol. The resulting mixture was heated under reflux for about 12 h. On cooling overnight at 0 °C, white crystalline precipitate of BBC was separated out, which was filtered, washed with cold ethanol and dried under vacuum. Yield 78%, m.p. 210 °C. Elemental analysis:  $\text{C}_{16}\text{H}_{18}\text{N}_8\text{O}_2$ , Found (Calc.) C: 53.78 (54.23), H: 4.78 (5.08), N: 31.29 (31.64).

### 2.3. Fabrication of electrodes with ligand BBC

For analytical application, the membranes have been fabricated as suggested by Craggs et al. (1974) and others (Chandra

et al., 2010, 2012). The PVC-based membranes have been prepared by dissolving appropriate amounts of BBC, anionic additive and plasticizers TEHP, DBP, *o*-NPOE, DOP and PVC in THF (~5 mL). The components were added in terms of weight percentages. The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and it has been poured into polyacrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform thickness otherwise the response of the membrane sensors has shown a significant variation. Membranes of 0.4-mm thickness were removed carefully from the glass plate and glued to one end of a "Pyrex" glass tube. The membrane was studied under a polarized optical microscope (Fig. 1).

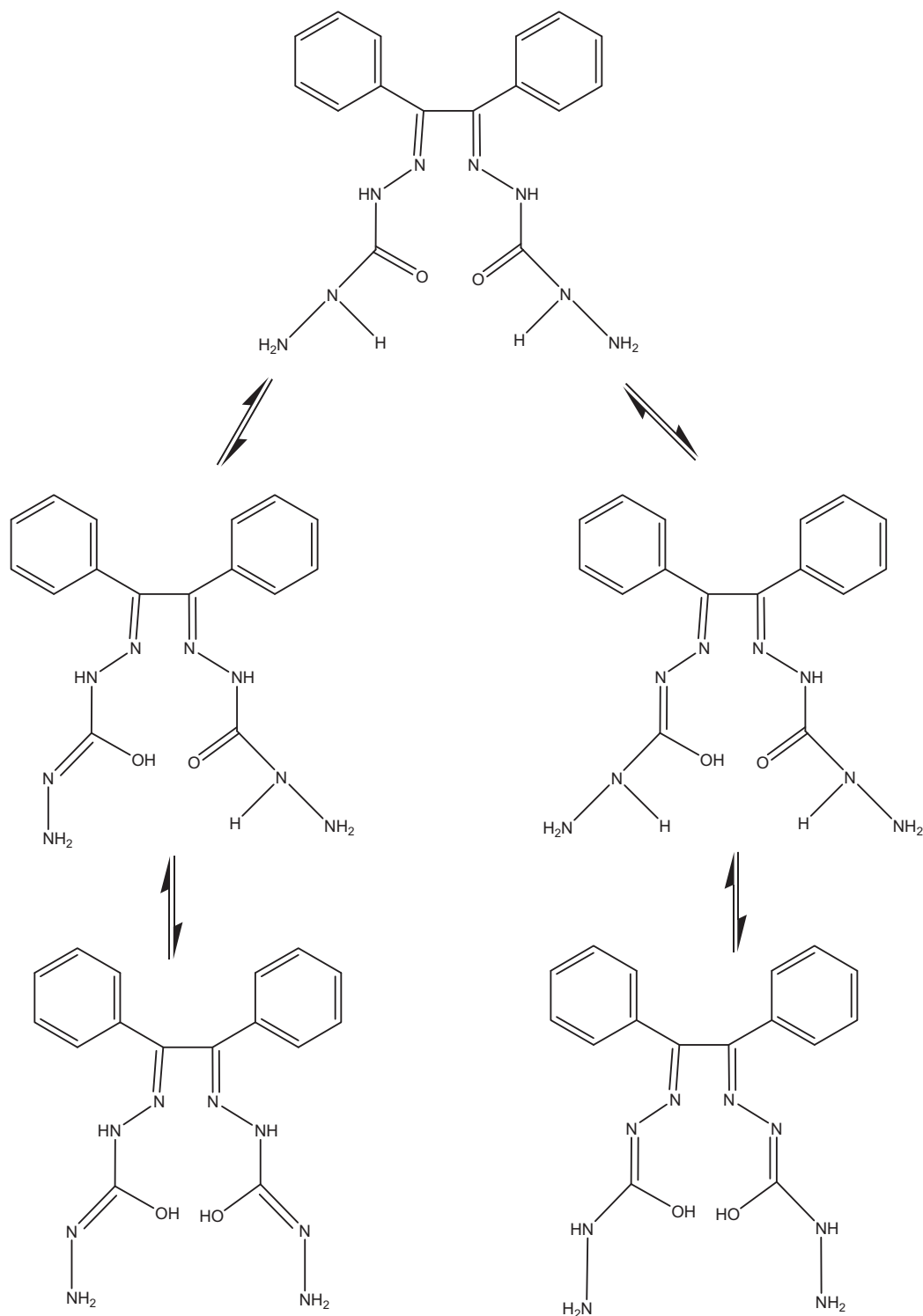
### 2.4. Equilibration of membrane and potential measurement

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potential at relatively short response time.

The polymeric membrane electrode was equilibrated for ~2 days in  $1.0 \times 10^{-1}$  M  $\text{Cd}(\text{NO}_3)_2$  solution. The potentials were measured by varying the concentration of  $\text{Cd}(\text{NO}_3)_2$  in test solution in the range of  $1 \times 10^{-9}$  M– $1.0 \times 10^{-1}$  M. Standard  $\text{Cd}(\text{NO}_3)_2$  solutions were obtained by gradual dilution of  $10^{-1}$  M  $\text{Cd}(\text{NO}_3)_2$  solution.

The emf measurements with the polymeric membrane electrode were carried out on a digital potentiometer at  $25 \pm 1$  °C using saturated calomel electrode (SCE) as reference electrode with the following cell assemblies:

$\text{Hg-Hg}_2\text{Cl}_2$ , KCl (sat.) || internal solution  $1.0 \times 10^{-1}$  M  $\text{Cd}^{2+}$  | PVC membrane | test solution ||  $\text{Hg}_2\text{Cl}_2$ -Hg, KCl (sat.).



**Figure 4** Five possible isomeric forms of ligand BBC.

### 3. Physical measurements

IR spectra (KBr pellets) were recorded in the region  $4000\text{--}400\text{ cm}^{-1}$  on a FT-IR spectrum BX-II spectrophotometer.  $^1\text{H}$  NMR spectrum was recorded with a model Bruker Advance DPX-300 spectrometer operating at 300 MHz using  $\text{DMSO-}d_6$  as a solvent and TMS as an internal standard. Elec-

tron impact mass spectrum was recorded on JEOL, JMS, DX-303 mass spectrometer. Electronic spectra were recorded on a Shimadzu UV mini-1240 spectrophotometer using DMSO as a solvent. Elemental analyses were carried out on a Carlo-Erba EA 1106 analyser. The emf measurements with the polymeric membrane electrode were carried out on a digital potentiometer (Equiptronic Model No. EQ-609) at  $25 \pm 1\text{ }^\circ\text{C}$  using satu-

rated calomel electrode (SCE) as reference electrode. Electrochemical impedance measurements were carried out using a potentiostat/galvanostat instrument (Autolab PGSTAT 302).

#### 4. Results and discussion

The analytically pure ligand BBC was readily synthesized with very good yield (78%) by Schiff base condensation of benzil with two equivalents of carbohydrazide in water-ethanol. The existence of nitrogen and oxygen as donor atoms in the ligand with high lipophilic character, sufficient insolubility in water, low molecular weight was expected to act as suitable ion carriers.

##### 4.1. IR spectra

The assignments of the main IR absorption bands of the ligand are shown in Fig. 2. The ligand displays IR bands at 3391, 3320, 3171 and 3081  $\text{cm}^{-1}$  corresponding to the  $\nu_{\text{as}}(\text{NH}_2)$ ,  $\nu_{\text{s}}(\text{NH}_2)$ ,  $\nu_{\text{as}}(\text{NH})$  and  $\nu_{\text{s}}(\text{NH})$  stretching vibrations, respectively. The spectrum exhibits the IR bands at 1684 and 1497  $\text{cm}^{-1}$  which may be assigned to the amide I [ $\nu(\text{C}=\text{O})$ ] and amide II [ $\nu(\text{C}=\text{N}) + \delta(\text{NH})$ ] stretching vibrations (Chandra et al., 2010; Kataria et al., 2010).

##### 4.2. $^1\text{H}$ NMR spectra

The  $^1\text{H}$  NMR spectrum of ligand was recorded in deuterated DMSO ( $\text{DMSO-}d_6$ ) at 300 MHz. The spectrum (Fig. 3) shows that different non-equivalent protons resonate at different values of applied field which are discussed below:

- I. A distorted singlet at  $\delta$  4.0 ppm appears in the spectrum which is assigned to the four protons of two amino groups. The appearance of signal as a broad peak may be due to the nuclear quadrupole broadening by nitrogen (Mohan, 2001).
- II. Another distorted singlet at  $\delta$  5.8 ppm corresponding to the 2H appeared due to the amide protons.
- III. The spectrum exhibits a multiplet between  $\delta$  6.8 and  $\delta$  7.9 ppm equivalent to the 10H of two phenyl groups.
- IV. The spectrum displays a sharp singlet at  $\delta$  8.1 ppm equivalent to 2H representing the enolic protons of ligand in solution (Tamboura et al., 2004).

##### 4.3. Keto-enol tautomerism

The ligand may show keto-enol tautomerism (Fig. 4) because it contains the amide bonds. The IR spectrum does not show a  $\nu(\text{OH})$  band at ca. 3550  $\text{cm}^{-1}$  but shows the bands at 3391 and 3081  $\text{cm}^{-1}$  corresponding to  $\nu_{\text{as}}(\text{NH})$  and  $\nu_{\text{s}}(\text{NH})$ , indicating that in solid state, the ligand exists in the keto form. However, the  $^1\text{H}$  NMR spectrum of ligand exhibits a sharp singlet at  $\delta$  8.1 ppm due to enolic -OH which indicates that the amide groups are transformed into iminol groups in solution.

##### 4.4. Mass spectra

The mass spectrum of ligand is given in Fig. 5. The spectrum shows the molecular ion peak ( $\text{M}^+$ ) at  $m/z = 354$  (78%) and a weak peak at  $m/z = 355$  due to  $^{13}\text{C}$  isotope. The amide characteristic peak appears at  $m/z = 59$  and the moderate high intense peak (81%) at  $m/z = 177$  appears in the spectrum due to

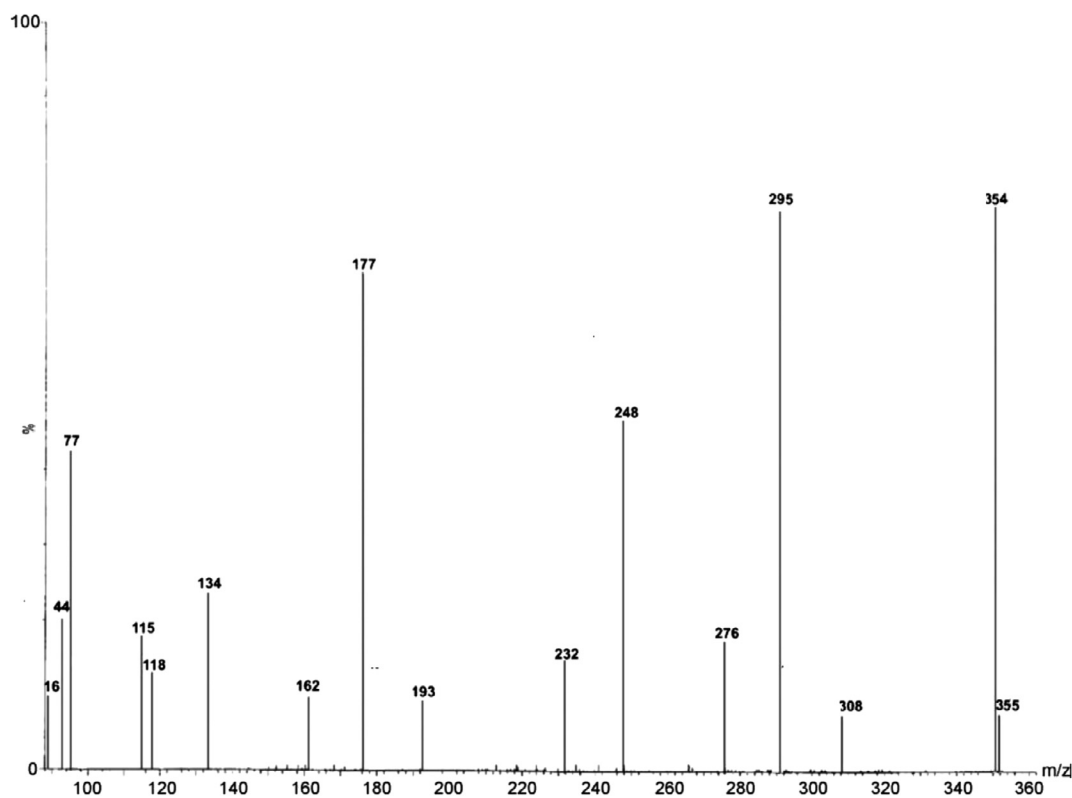
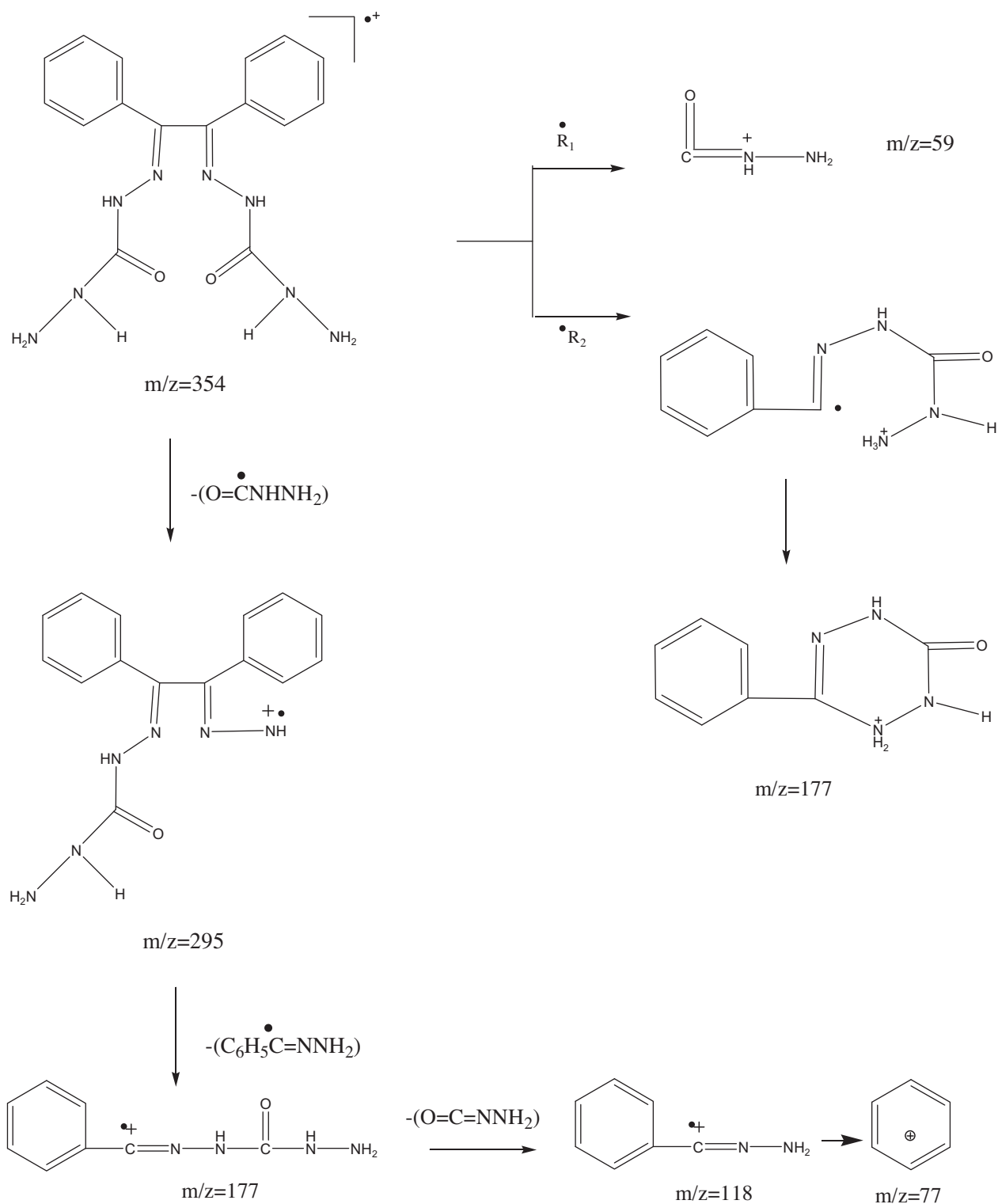


Figure 5 Mass spectra of ligand BBC.



where  $\text{R}_1 = \text{C}_6\text{H}_5\text{C}(\text{NNHCONH}_2)\text{C}(\text{=NNH})\text{C}_6\text{H}_5$   
 $\text{R}_2 = \text{C}_6\text{H}_5\text{C}(\text{NNHCONH}_2)$

**Figure 6** Mass fragmentation pattern of ligand BBC.



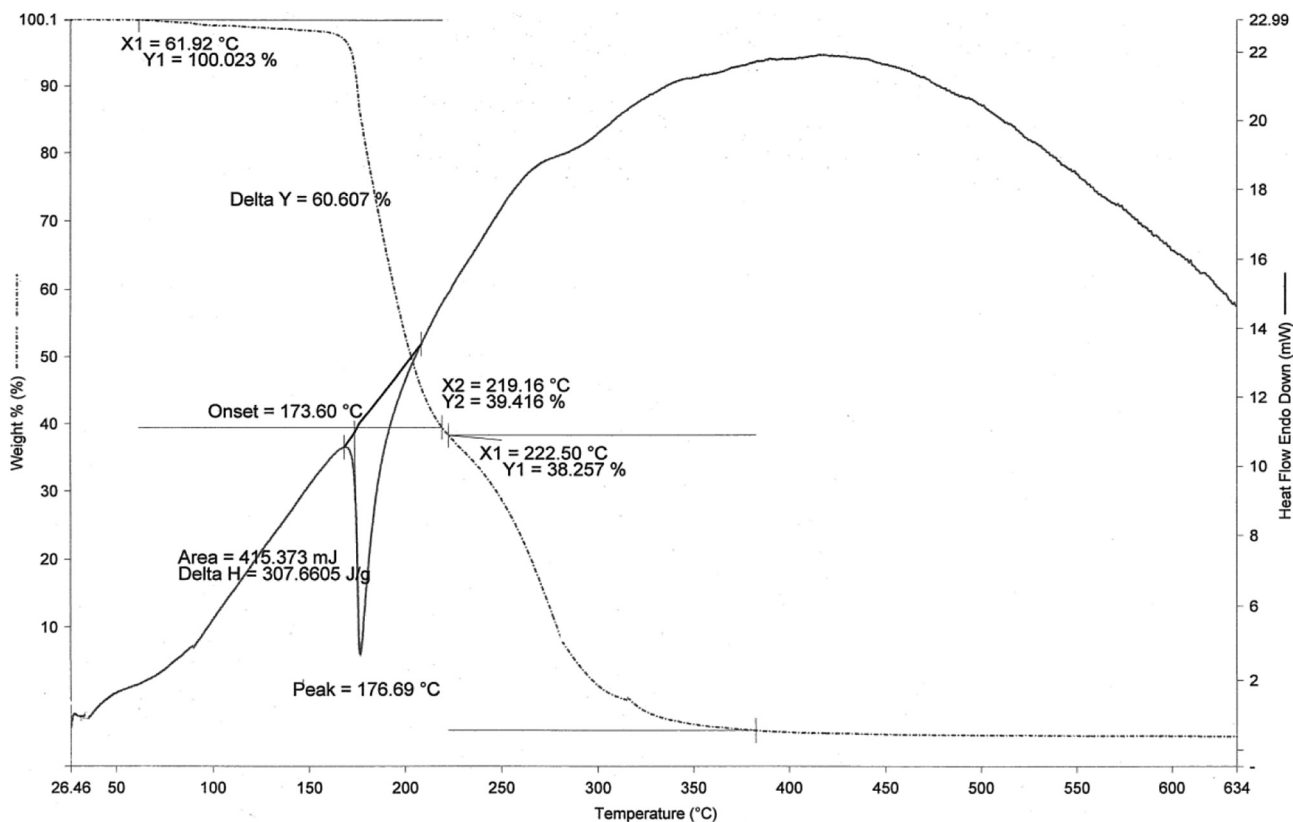


Figure 7 TG-DTA Curve for benzil bis(carbohydrazone).

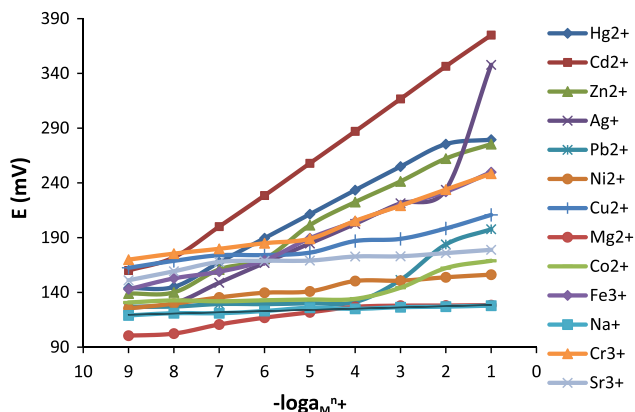


Figure 8 Potential response of ligand BBC to  $M^{n+}$  ion.

the six membered cyclic positive ion which results from  $\gamma$   $\delta$  C–C bond cleavage and followed by cyclization. The other different ions give the peaks of different mass numbers like 295, 134, 118, 44 and 16. The intensities of peaks are in accordance with the abundance of the ions (Chandra and Sharma, 2009a,b; Chandra et al., 2011). The fragmentation path of ligand is given in Fig. 6.

#### 4.5. Thermogravimetric analyses

Benzil bis(carbohydrazone) was studied by thermogravimetric analyses from ambient temperature to 700 °C in nitrogen

atmosphere. The TG curve was redrawn as % mass loss versus the temperature (TG) curve. Typical TG curve is presented in Fig. 7. Thermal techniques, such as thermogravimetric analysis (TGA and DTA), have been successfully employed for the study of the energetic interactions of metal cations with biological species, such as amino acids (Burger, 1973). The weight loss profiles are analysed by the amount or percent of weight loss at any given temperature, and the temperature ranges of the degradation process were determined. Thermal stability domains, melting points, decomposition phenomena and their assignments for the benzil bis(carbohydrazone) are summarized below. The overall loss of mass from the TG curves is 100% for benzil bis(carbohydrazone). In the first step the compound undergoes decomposition with a weight loss exp. 2.52–2.79% (ca. 2.59–2.75%), between 170 and 190 °C due to the loss of  $N_2H_4$  moiety. In the second step decomposition of the compound shows weight loss exp. 60.584–61.743% (ca. 60.877–61.58%) in the temperature range of 210–240 °C due to the organic moiety  $C_9H_{10}N_6O$ . DTG maximum temperature is 176.69 °C.

#### 4.6. Electrochemical sensors

##### 4.6.1. Response of electrode based on $Cd^{2+}$ ions

The existence of nitrogen and oxygen as donor atoms in the ligand with high lipophilic character seems to form strong complexes with transition metal ions (Gupta and Chandra, 2007; Chandra and Gautam, 2009; Chandra et al., 2010). In order to study the potential response and selectivity of the ionophore for different metal ions, BBC was used as neutral carriers to

**Table 1** Optimization of membrane composition.

S. No.	PVC (wt.%)	Plasticizer (wt.%)	Ionophore (wt.%)	ETH 500 (wt.%)	Slope (mV/decade)	Detection limit (M)	Linear range (M)
1.	31	66 (NPOE)	3.0	–	18.8	$1.0 \times 10^{-5}$	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-7}$
2.	31	65 (TEHP)	4.0	–	26.0	$1.6 \times 10^{-5}$	$1.0 \times 10^{-2}$ – $1.0 \times 10^{-5}$
3.	33	65 (DOP)	4.0	–	22.0	$6.0 \times 10^{-5}$	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-6}$
4.	33	64 (DBP)	3.0	–	41.2	$5.0 \times 10^{-5}$	$1.0 \times 10^{-2}$ – $1.0 \times 10^{-6}$
5.	30	65 (NPOE)	3.5	1.5	24.5	$5.0 \times 10^{-7}$	$1.0 \times 10^{-1}$ – $1.0 \times 10^{-7}$
6.	32	63 (DBP)	3.0	2.0	39.8	$1.0 \times 10^6$	$1.0 \times 10^{-4}$ – $1.0 \times 10^{-7}$
7.	30	65 (DOP)	3.5	1.5	27.2	$5.0 \times 10^{-6}$	$1.0 \times 10^{-3}$ – $1.0 \times 10^{-7}$
8.	30	65 (TEHP)	4.0	1.0	24.5	$1.0 \times 10^{-5}$	$1.0 \times 10^{-1}$ – $1.0 \times 10^{-6}$
9.	30	65 (TEHP)	3.5	1.5	29.7	$3.2 \times 10^{-8}$	$1.0 \times 10^{-1}$ – $1.0 \times 10^{-8}$
10.	31	64 (TEHP)	3.0	2.0	35.6	$3.0 \times 10^{-5}$	$1.0 \times 10^{-2}$ – $1.0 \times 10^{-7}$

prepare PVC based membrane electrodes for a variety of metal ions including alkali, alkaline earth, transition and heavy metal ions. The potential responses obtained are shown in Fig. 8. The sensitivities and selectivities obtained for a given membrane depend significantly on the membrane ingredients and the nature of plasticizer and additives used. Therefore, 10 membranes of different compositions (Table 1) have been prepared and their response characteristics were evaluated according to the IUPAC recommendations (Guilbault et al., 1976).

The best performance was obtained with a membrane composition of 30% poly (vinyl chloride), 65% TEHP, 3.5% BBC and 1.5% Tetradodecylammoniumtetrakis(4-chlorophenyl) borate (ETH 500). The electrode exhibits a Nernstian behaviour (with slope of 29.7 mV per decade) over a very wide concentration range of  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-8}$  M with a detection limit of  $3.2 \times 10^{-8}$  M. This sensor shows very good selectivity and sensitivity towards cadmium ion over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. In this work, the selectivity coefficient of the sensor towards different cationic species ( $M^{n+}$ ) was evaluated by using the fixed interference method (FIM) (Gupta et al., 2008; Chandra and Singh, 2009). In FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion ( $1.0 \times 10^{-2}$  M) and varying amount of  $Cd^{2+}$  ions. It is given by the expression.

$$\log K^{pot}_{Cd^{2+}, B} = \log (a_{Cd^{2+}}) - \log (a_B)^{Z_{Cd^{2+}}/Z_B}$$

where,  $Z_{Cd^{2+}}$  and  $Z_B$  are the charge on  $Cd^{2+}$  ion and interfering ion.

The resulting  $K^{pot}_{Cd^{2+}}$  values are summarized in Table 2.

The effect of pH of the test solution on the response of the membrane electrode was examined at two  $Cd^{2+}$  ion concentrations. As illustrated in Fig. 9, the potentials remained constant from pH 2.0 to 9.0. However, outside this range the electrode responses at pH < 2.0 seem ascribable to the competitive binding of proton to the ligand at the surface of the membrane electrode, while the diminished potential at higher pH (>9), the potential change may be due to the hydroxylation of  $Cd^{2+}$  ions.

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by immediately changing the  $Cd^{2+}$  ion concentration from  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-2}$  M. The actual potential-time trace is shown in Fig. 10(a). As is seen, in the

**Table 2** Potentiometric selectivity coefficient  $\log K^{pot}_{Cd^{2+}, B}$  for interfering ions.

Interfering ion	$\log K^{pot}_{Cd^{2+}, B}$	Interfering ion	$\log K^{pot}_{Cd^{2+}, B}$
$K^+$	–2.98	$Cr^{3+}$	–2.82
$NH_4^+$	–2.01	$Ag^+$	–2.98
$Na^+$	–3.41	$Zn^{2+}$	–3.45
$Ni^{2+}$	–3.09	$Pb^{2+}$	–3.29
$Cu^{2+}$	–2.93	$Sr^{2+}$	–3.33
$Co^{2+}$	–3.72	$Hg^{2+}$	–3.62
$Mn^{2+}$	–3.98	$Ce^{3+}$	3.99
$Fe^{3+}$	–3.96	$Ca^{2+}$	–3.84
$Cr^{2+}$	–2.13	$Mg^{2+}$	–3.59

whole concentration range, the sensor reaches the equilibrium response in a very short time (~8 s).

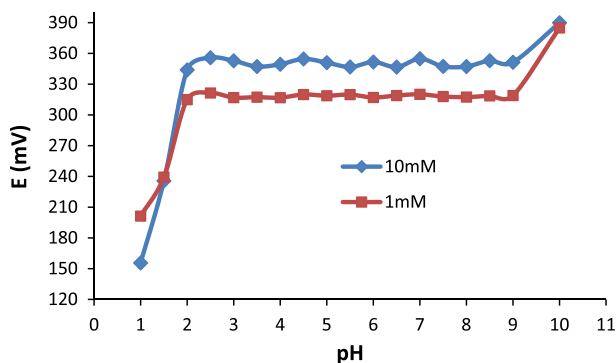
To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from ( $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-8}$  M) sample concentrations. The results (Fig. 10(b)) showed that, the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (40 s) was longer than that of low-to high sample concentrations.

The high lipophilicity of ionophore and plasticizer ensures stable potentials and longer lifetime (Chandra et al., 2010) for the membrane. Hence, the lifetime is dependent upon the components of the solution and the measured specimens. The lifetime of the electrode was determined by performing calibrations periodically with standard solutions and calculating the slopes over the concentration ranges of  $1.0 \times 10^{-2}$ – $1.0 \times 10^{-8}$  M  $Cd^{2+}$  solutions. The experimental results showed that the lifetime of the present sensor was over 75 days. During this time, the detection limit and the slope of the electrode remained almost constant. Afterwards, the electrochemical behaviour of the electrode gradually deteriorated, which may be due to ageing of the polymer (PVC), the plasticizers, and leaching of the ionophore. Therefore, the electrode can be used for at least 2 and half months without a considerable change in their response characteristic towards  $Cd^{2+}$ .

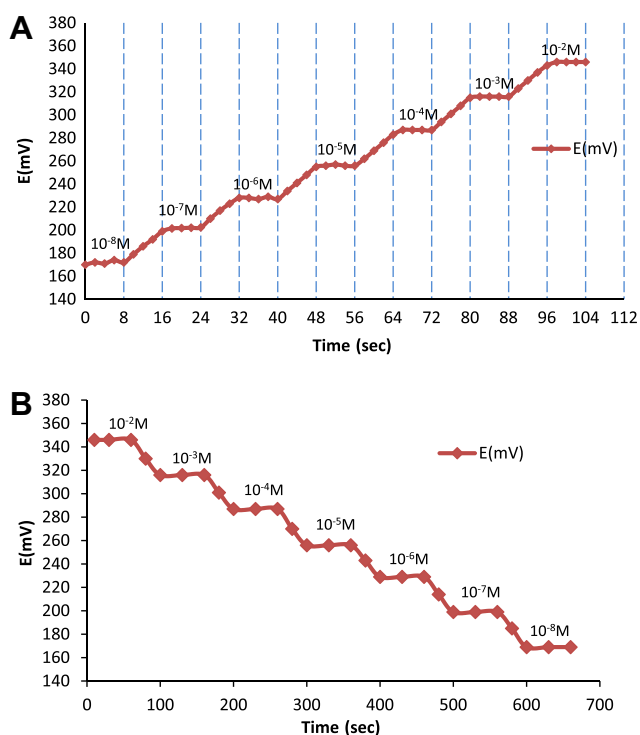
#### 4.6.1.1. Interaction mechanism on the basis of UV spectroscopy.

The interaction mechanism of  $Cd^{2+}$  ion with the ionophore was discussed on the basis of UV–Visible spectrophotometry.



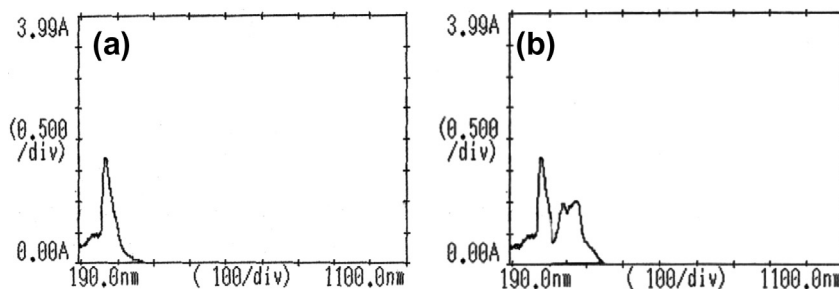


**Figure 9** pH Effect on the response of  $\text{Cd}^{2+}$ -ISE.



**Figure 10** (A) Response time curve for  $\text{Cd}^{2+}$ -ISE at different concentrations. (B) Reversibility study for  $\text{Cd}^{2+}$ -ISE at different concentrations.

Thus, in order to investigate such mechanism UV-visible spectra of carrier without and with cadmium ion were recorded. A UV-visible spectrum of BBC of 0.01 M concentration dissolved in DMSO was recorded first. It was then used for the



**Figure 11** UV-Visible interaction mechanism of (a) BBC ( $1 \times 10^{-2}$  M) in DMSO and (b) BBC with  $\text{Cd}^{2+}$  ( $1 \times 10^{-2}$  M) in DMSO.

quantitative complexation with  $\text{Cd}^{2+}$  ion by adding an increasing amount of the  $\text{Cd}^{2+}$  ion up to 0.01 M concentration. The spectra of the ionophore BBC show the absorption bands at 266 nm (Fig. 11(a)). In Fig. 11(b) shift in the peaks was observed and the new peaks were observed at 329–397 nm with increased absorptivity when  $\text{Cd}^{2+}$  ion interacted with the carrier, which shows that the size of the complex increases on interaction of  $\text{Cd}^{2+}$  with the carrier. The absorption intensity changes as a function of molar ratio  $[\text{Cd}^{2+}]/[\text{BBC}]$  (Rawat et al., 2008).

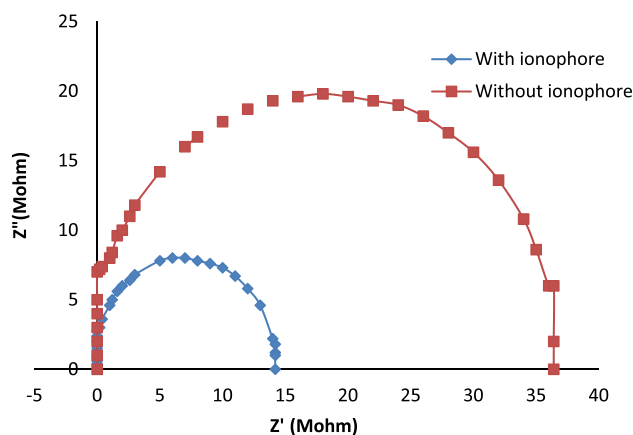
**4.6.1.2. Electrochemical impedance spectroscopy.** Impedance measurements were carried out on the membrane with and without ionophore, and  $1.0 \times 10^{-2}$ – $1.0 \times 10^{-3}$  M solutions of cadmium nitrate as the internal and external solutions of the electrode were used, respectively. Finally their complex plan plots were generated and compared. As shown in Fig. 12, the charge transfer resistance of the membrane without ionophore (36.431 Mohm) is more than that of the membrane with ionophore (14.215 Mohm). These results can be attributed to increasing the electrical conductivity with the available ionophore that can reduce a charge transfer resistance ( $R_{ct}$ ). This explanation confirms the results obtained from the UV-vis and potentiometric studies.

#### 4.6.2. Application

The sensor has been applied for the direct determination of cadmium in chocolate samples. Chocolate and chocolate-based sweets and candies are common treats, snacks, or gifts for children and adults alike. The main ingredients in chocolate consist of cocoa, milk and fats, each of which is a potential source of cadmium. The determination of cadmium levels in chocolate is therefore an important issue for chocolate consumers and manufacturers around the globe.

The sample for cadmium determination is prepared by weighing approximately 0.20 g pieces of chocolate (popular global brands of milk and dark variety) accurately and transferred to microwave digestion vessels. 7 ml of nitric acid and 1 ml of hydrogen peroxide were added and left to stand for 5 min, before the vessels were sealed and samples digested in a high pressure microwave digestion system by ramping to 200 °C over 10 min. Samples were maintained at 200 °C for 20 min before being allowed to cool. The contents of the vessels were then quantitatively transferred to 100 ml volumetric flasks with deionized water and made up to a final volume of 100 ml.

A comparison of the results obtained by proposed sensor with the results obtained by atomic absorption spectrometry (AAS) shows good agreement as shown in Table 3.



**Figure 12** Complex plan plots of the membrane with and without ionophore.

**Table 3** Determination of cadmium in chocolate samples using BBC cadmium selective electrode.

Chocolate sample ( $\mu\text{g L}^{-1}$ )	ISE study <sup>a</sup>	AAS study <sup>a</sup>
Milk	0.018	$0.019 \pm 0.002$
Dark	0.065	$0.067 \pm 0.002$

<sup>a</sup> Std. deviation calculation for five measurements.

## 5. Conclusion

On the basis of IR, <sup>1</sup>H NMR and mass spectra, benzyl bis(carbohydrazone) (BBC) has been characterized, thermally analysed and explored as a cadmium(II) ion selective electrode. The interaction mechanism is explained by the UV-spectroscopy. The ligand BBC based membrane exhibits a linear stable response over a wide concentration range with a near Nernstian response of 29.7 mV/decade. The sensor was used for the direct determination of cadmium ion in the given chocolate samples with reproducible results.

## Acknowledgement

The author is thankful to the principal, Zakir Husain Delhi College for providing the laboratory facility and Netaji Subhas Institute of Technology for financial assistance.

## References

- Akiyoshi, M., Nakamura, H., Hara, Y.P., 2000. *Explos. Pyrot.* 25, 41–46.
- Bart, S.C., Chlopek, K., Bill, E., Bouwkamp, M.W., Lobkovsky, E., Neese, F., Wieghardt, K., Chirlik, J., 2006. *J. Am. Chem. Soc.* 128, 13901–13912.
- Burger, K., 1973. *Coordination Chemistry: Experimental Methods.* Akademiai Kiado, Budapest, p. 23.
- Chandra, S., Gautam, A., 2009. *J. Serb. Chem. Soc.* 74, 1413–1422.
- Chandra, S., Sharma, A.K., 2009a. *Spectrochim. Acta Part A* 74, 271–276.
- Chandra, S., Sharma, A.K., 2009b. *Spectrochim. Acta Part A* 72, 851–857.
- Chandra, S., Singh, D.R., 2009. *Mat. Sci. Eng. A* 502, 107–110.
- Chandra, S., Jain, D., Sharma, A.K., Sharma, P., 2009. *Molecules* 14, 174–190.
- Chandra, S., Sharma, K., Kumar, A., 2010. *Anal. Bioanal. Electrochem.* 2, 125–138.
- Chandra, S., Ruchi, Qanungo, K., Sharma, S.K., 2011. *Spectrochim. Acta Part A* 79, 1326–1330.
- Chandra, S., Deepshikha, Sarkar, A., 2012. *Anal. Bioanal. Electrochem.* 4, 45–50.
- Cosper, D.R., Kowalski, D.J., 1990. *Ind. Eng. Chem. Res.* 29, 1130–1136.
- Craggs, A., Moody, G.J., Thomas, J.D.R., 1974. *J. Chem. Educ.* 51, 541–544.
- Guilbault, G.G., Durst, R.A., Frant, M.S., Freiser, H., Hansen, E.H., Light, T.S., Pungor, E., Rechnitz, G., Rice, M.N., Rohm, T.J., Simon, W., Thomas, D.R., 1976. *Pure Appl. Chem.* 48, 127–132.
- Gupta, L.K., Chandra, S., 2007. *Spectrochim. Acta Part A* 68, 839–844.
- Gupta, V.K., Jain, A.K., Ludwig, R., Maheshwaria, G., 2008. *Electrochim. Acta* 53, 2362–2368.
- Kataria, A., Sharma, A.K., Chandra, S., 2010. *J. Chem. Pharm. Res.* 2, 339–344.
- Konkova, T.S., Matyushin, Y.N., Sidiskii, V.P., Fogelzang, A.E., 1995. *Chem. Phys. Rep.* 14, 674–865.
- Kurzer, F., Wilkinson, M., 1970. *Chem. Rev.* 70, 128–138.
- Matza, C.J., Krone, P.H., 2007. *Environ. Sci. Technol.* 41, 5143–5151.
- Mohan, J., 2001. *Organic Spectroscopy, Principles and Applications.* Narosa Publishing House, Delhi.
- Parashar, B., Punjabi, P.B., Gupta, G.D., Sharma, V.K., 2009. *Int. J. Chem. Technol. Res.* 1, 1022–1025.
- Preto, A., Loro, V.L., Morsch, V.M., Moraes, B.S., Menezes, C., Clasen, B., Hoehne, L., Dressler, V., 2010. *Arch. Environ. Contam. Toxicol.* 58, 1008–1014.
- Rawat, A., Chandra, S., Sarkar, A., 2008. *Anal. Lett.* 41, 3058–3073.
- Talawar, M.B., Agrawal, A.P., Chhabra, J.S., Asthana, S.N., 2004. *J. Hazard. Mater.* 113, 57–65.
- Tamboura, F.B., Haba, P.M., Gaye, M., Sall, A.S., Barry, A.H., Jouini, T., 2004. *Polyhedron* 23, 1191–1197.
- Terzioglu, N., Gursoy, A., 2003. *Eur. J. Med. Chem.* 38, 781–786.
- Thompson, S.K., Halbert, S.M., DesJarlais, R.L., Tomaszek, T.A., Levy, M.A., Tew, D.G., Ijames, C.F., Veber, D.F., 1999. *Bioorg. Med. Chem.* 7, 599–605.
- Verougstraete, V., Lison, D., Hotz, P., 2003. *J. Toxicol. Environ. Health B: Crit. Rev.* 6, 227.
- Yongxu, Z., Dabin, L., Chunxu, L., 2005. *Propell. Explos. Pyrotech.* 30, 438–441.
- Zhang, J.G., Zhang, T.L., Wei, Z.R., Yu, K.B., 2001. *Chem. J. Chin. U* 22, 895–897.
- Zhang, J., Feng, L., Zhang, S., Zheng, H., Zhang, T., Yang, L., Zheng, H., 2008. *Intern. J. Quan. Chem.* 108, 1555–1564.