

Article

# Electrochemical Analysis of Aqueous Benzalkonium Chloride Micellar Solution and Its Mediated Electrocatalytic De-Chlorination Application

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**Abstract:** The physicochemical properties of biologically important benzalkonium chlorides (BKC) and the effects of its structure on the de-chlorination of allyl chloride was studied by electrogenerated [Co(I)(bipyridine)<sub>3</sub>]<sup>+</sup> (Co(I)) using an electrochemical technique. The results of [Co(II)(bipyridine)<sub>3</sub>]<sup>2+</sup> (Co(II)) cyclic voltammetry in the presence of BKC demonstrates Co(II)/Co(III) redox couple for physicochemical analysis of BKC and Co(II)/Co(I) redox couple for catalytic application. Cyclic voltammetry over a range of scan rates and BKC concentrations revealed the BKC-bound Co(II)/Co(III) micelles showed that the identification of *cmc* and association of the probe Co(II) species, associated more in the hydrophobic region. In addition, change in diffusion coefficient value of Co(II)/Co(III) with BKC concentration demonstrates the association of Co(II) in micellar hydrophobic region. The beneficial effects of BKC could be accounted for by considering the benzyl headgroup-Co (II) precatalyst-volatile organic compounds (VOCs) (allyl chloride here) substrate interaction. Chromatography/mass spectroscopy (GC/MS) revealed 100% complete de-chlorination of allyl chloride accompanied by three non-chloro products. This is the first report of benzyl headgroup-induced micellar enhancement by an electrochemical method, showing that it is possible to use hydrophobic benzyl headgroup-substitution to tune the properties of micelles for various applications.

**Keywords:** BKC; micellar association; *cmc*; mediation by electrocatalysts; VOCs

## 1. Introduction

Benzalkonium chloride (BKC) is used primarily as a preservative and antimicrobial agent, as well as a surfactant. The compound has potent biocidal activity, killing microorganisms, and inhibiting their growth [1,2], but is friendlier to human skin, which is why it is used as an ingredient in antibacterial hand wipes, antiseptic creams, and anti-itch ointments. Other than the medicinal field, BKC has a beneficiary role as a surfactant particularly in the corrosion resistance of carbon steel because of its strong adsorption and hydrophobicity [3]. To stabilize and increase the porosity during the preparation of porous carbon, BKC is used greatly as porosity stabilizer [4]. In solubilized media, BKC is used as the supporting electrolyte during the electrochemical reduction of CO<sub>2</sub> reduction in methanol at room temperature [5,6]. Benzalkonium chloride has been applied to remove biofilms on marine-based sensors or optical components [7,8], which highlights the need to determine the diffusion coefficient for BKC in water. Smith et al. [9] developed a membrane diffusion method and derived the diffusion coefficient for BKC with C12 and C14 in water. Ultrafiltration or ultracentrifugation methods have been adopted to determine the partition coefficient of BKC and the free BKC surfactant concentration

in micellar solutions [10,11]. In the biological and chemical fields, both solubilization and stabilization play important roles in their specific applications. A detailed mechanistic aspect to understanding BKC micelles is still lacking, particularly in the electrochemical field.

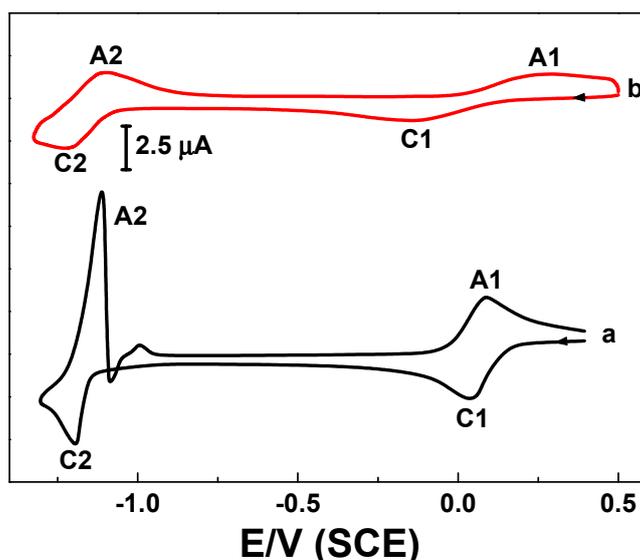
With the exception of BKC, many other self-aggregated surfactant monomers have been used to solubilize redox species in solution, and they have been analyzed by the electrode surface [12,13]. Advantageous of this phenomena used to harvest the physicochemical properties of the various surfactant solutions by single potential step chronoamperometry [14,15] and diffusion limiting current at micro-electrodes techniques [16,17]. Despite the interesting physicochemical identification of surfactants in electrochemistry, the mediated catalytic reduction of halo compounds, such as 4-bromobiphenyl, 4,4'-dichlorobiphenyl, allyl chloride, and PCB (Polychlorinated biphenyls) mixtures, catalyzed by different organic and inorganic mediators, e.g., 9-phenylanthracene [18],  $[\text{Co}(\text{bpy})_3]^{2+}$  (where bpy = 2,2'-bipyridine) [19,20], zinc phthalocyanine [21], etc., have been observed in aqueous solutions of various surfactants, such as CTAB (Cetyltrimethylammonium bromide), SDS (Sodiumdodecyl sulfate), and film-forming dodecyl dimethyl ammonium bromide. In a recent study, the cobalt polypyridine complex-mediated de-chlorination of several chlorinated pesticides with significantly enhanced catalytic rates was achieved in a surfactant-containing aqueous solution [22]. In addition, our previous study reported the electrocatalytic dehalogenation of allyl chloride and its methyl-substituted derivative  $\beta$ -methyl allylchloride mediated by electrogenerated  $[\text{Co}(\text{I})(\text{bpy})_3]^+$  at a glassy carbon electrode in aqueous solutions of cationic micelles [23–25].

In the present investigation, physicochemical analysis of BKC with an alkyl chain length of C16 was analyzed using an electrochemical method. For this purpose, in the first part of the study, the  $[\text{Co}(\text{II})(\text{bpy})_3]^{2+}/[\text{Co}(\text{III})(\text{bpy})_3]^{3+}$  redox reaction in BKC surfactant was studied by CV (Cyclic voltammetry) and some key parameters, such as the *cmc* (critical micellar concentration), micellar diffusion coefficient, and relative association constants of the oxidized species were estimated, as done for other surfactants [26–31]. Following this, the effects of BKC on allyl chloride catalysis were examined by product analysis and discussed.

## 2. Results and Discussion

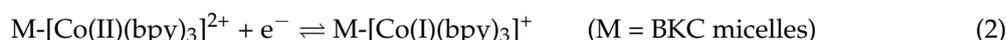
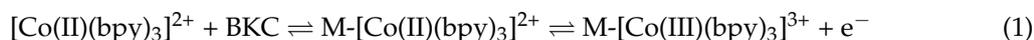
### 2.1. Selection of Redox Couple

According to Figure 1, two redox couples for  $[\text{Co}(\text{II})(\text{bpy})_3]^{2+}$  redox system were found. One was related to Co(II) to Co(III) oxidation and another one was for Co(II) to Co(I) reduction. One mM of  $[\text{Co}(\text{II})(\text{bpy})_3]^{2+}$  in 0.1 M  $\text{Na}_2\text{SO}_4$  medium shows highly reversible redox behavior of Co(II) to Co(III) (A1 and C1) oxidation (Figure1, curve a), but complicated redox peaks were observed in the case of Co(II) to Co(I) reduction (C2 and A2). At the same time, addition of 10 mM BKC led to the reversible Co(II)/Co(III) redox couple becoming quasi-reversible or diminished according to the BKC concentration. Surprisingly, the reduction couple Co(II)/Co(I) became reversible without any complications (Figure1, curve b).



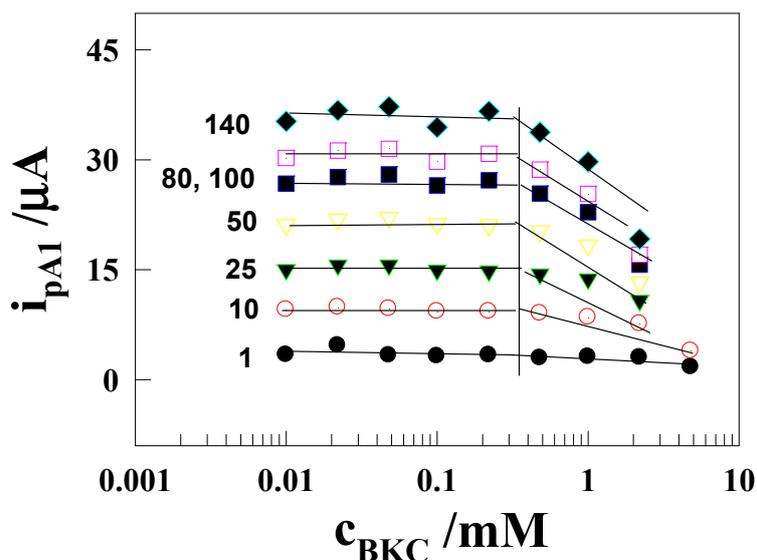
**Figure 1.** Voltammetry responses of 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  on a GCE (Glassy carbon electrode) in 0.1 M  $\text{Na}_2\text{SO}_4$  without (a) benzalkonium chloride (BKC) and (b) with 10 mM BKC at scan rate of  $25 \text{ mVs}^{-1}$ .

It is more realistic that the  $\text{Co(II)/Co(III)}$  redox couple can be considered for the BKC aggregates and its physicochemical analysis due to effective change in peak current and potential with BKC concentration, Equation (1). Because of the reversible redox behavior in presence of BKC, the  $\text{Co(II)/Co(I)}$  redox couple can be considered for catalytic reduction analysis, as the reversibility is one of the mediated electrocatalytic processes [32] and solubilities of the VOCs in the micellar medium (Equation (2)).



## 2.2. *cmc* and Solubilization Constant Evaluation of BKC by CV using $[\text{Co(II)(bpy)}_3]^{2+}/[\text{Co(III)(bpy)}_3]^{3+}$ Redox Couple

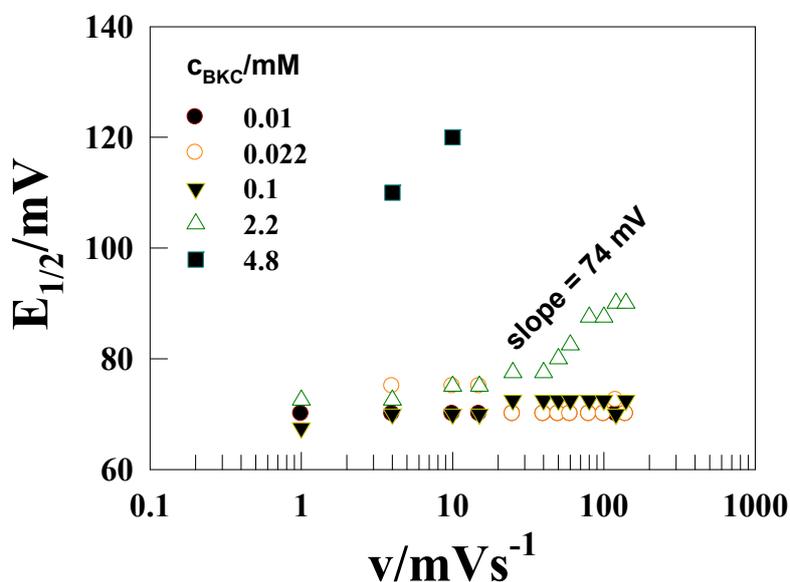
In Figure 2, the peak current initially shows constant from 0.01 mM up to 0.48 mM, then there is a sudden drop in current when the concentration of BKC ( $c_{\text{BKC}}$ ) is increased to 10 mM. A similar trend is followed at all scan rates studied. This sudden variation in  $i_{\text{pA1}}$  with  $c_{\text{BKC}}$  may identify the aggregation of monomer amphiphiles forming higher oligomers of BKC, which in turn predicts the *cmc* values for BKC. The break point value ca. 0.48 mM is near to the *cmc* of BKC observed in water from surface tension measurements, viz. 0.35 mM [33], and from light scattering measurements, viz. 0.4 mM [34]. The light scattering study also reports a value 0.02 mM for the *cmc* of BKC in 0.04 M NaCl [34]. The present study almost correlates with *cmc* of the light scattering measurements.



**Figure 2.** Anodic peak (A1) current as a function of BKC concentration for the oxidation of 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  on a GCE in 0.1 M  $\text{Na}_2\text{SO}_4$  solution at various scan rates.

According to Figure 3, there is almost no change in  $E_{1/2}$  (difference in A1 and C1 peak potential) values with increasing BKC concentration up to 0.48 mM, but there is a positive  $E_{1/2}$  value shift in subsequent concentrations from 1 to 4.8 mM of BKC (Figure 3 shows a definite  $E_{1/2}$  value of 2.2 mM). The shifts in potential can be correlated directly with the relative extent of the solubilization of the redox components within the micelles [26,27,30,31] using Equation (3):

$$E_{1/2,M-W}^r = E_W^{0r} + (RT/nF)\ln(K_R/K_O) \quad (3)$$



**Figure 3.**  $E_{1/2}$  versus  $\log(v)$  plots for the oxidation of 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  on a GCE in 0.1 M  $\text{Na}_2\text{SO}_4$  at various concentrations of BKC.

The experimentally measured  $E_{1/2M-W}$  in the presence of BKC and  $E_{1/2W}$  without BKC difference is 25 mV ( $E_{1/2M-W} = 95$  mV and  $E_W^{0r} = 70$  mV), which is giving rise to the partition coefficient ratio  $K_{\text{Co(III)}/\text{Co(II)}}$  for Co(III)/Co(II) redox couple to be 2.9. This implies a preferential partitioning of  $[\text{Co(II)(bpy)}_3]^{2+}$ , than  $[\text{Co(III)(bpy)}_3]^{3+}$ , into the BKC micellar phase. The larger  $K_{\text{Co(II)}}$  value for the

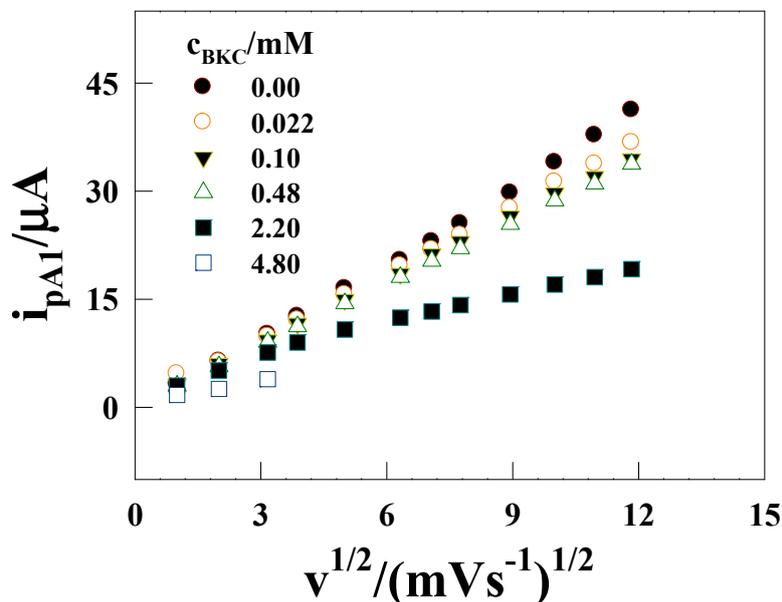
association of complex than for its oxidized counterpart can be attributed to greater hydrophobic nature of the divalent complex, supported by the reduced charge on the cobalt center, which provides electrostatic advantage of the 2+ charge, since its electrostatic repulsion with the cationic micellar entity is smaller. The predominance of hydrophobic interactions has also been observed for  $[\text{Co(III)(phen)}_3]^{3+}/[\text{Co(II)(phen)}_3]^{2+}$  couple by Davies and Hussam [30] in SDS micelles, which collectively tells that BKC solubilize also the cationic counterpart into its micelle.

### 2.3. Partition Coefficient and Association Constant by Diffusion Coefficient of the Co(II)/Co(III) Redox Couple

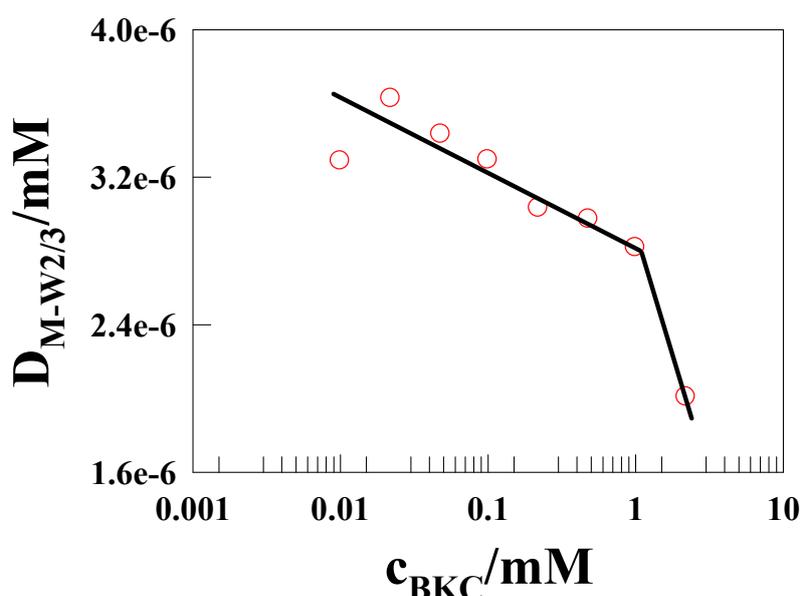
Figure 4 shows the variation of  $i_{pA1}$  with  $v^{1/2}$  for various  $c_{\text{BKC}}$ . The linearity is decreased with increasing the BKC concentration, but at low scan rate, the peak current value obey linearity with passes through the origin. The condition predicted by the Randle–Sevcik equation for a diffusion controlled electron transfer process, namely, peak current passing through the origin and also varying linearly with  $v^{1/2}$  is strictly followed only in the absence of BKC, and at low concentrations of BKC, confirms that BKC allows C(III)/Co(II) via diffusion controlled electron transfer process. The diffusion coefficient of the micelle-solubilized Co(II) complex,  $D_{\text{M-W}2/3}$ , was calculated from  $i_{pA1}$  vs.  $v^{1/2}$  slope using Equation (4), which is valid for an electrode process controlled by diffusion [32]:

$$\frac{\partial(i_{pc})}{\partial(v^{1/2})} = 2.69 \times 10^5 n^{3/2} A_{geo} D_{\text{M-W}2/3}^{1/2} c_{\text{M-W-Co(II)}} \quad (4)$$

where  $n$  is the number of electrons of the redox couple ( $n = 1$  here);  $A_{geo}$  is the electrode area, and  $c_{\text{M-W-Co(II)}}$  is the bulk concentration of  $[\text{Co(II)(bpy)}_3]^{2+}$  in the presence of defined BKC concentration.  $D_{\text{M-W}2/3}$  values slightly decreased with BKC concentration up to 1 mM, as predicted by the linear interaction theory [17], then sharply decreased in additional BKC concentration (Figure 5).



**Figure 4.**  $i_{pA1}$  versus  $v^{1/2}$  plots for the oxidation of 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  on a GCE in 0.1 M  $\text{Na}_2\text{SO}_4$  solution in presence of various concentrations of BKC (mM mentioned in the figure).



**Figure 5.** Diffusion coefficient of surfactant bound- $[\text{Co(II)(bpy)}_3]^{2+}$  from CV as a function of BKC concentration (mM).

A decrease in diffusion coefficient value when the increasing BKC concentration associates with the larger micelle aggregates formation, which means solubilization of the Co(II)/Co(III) within the micellar region. In the present case of the preferably polar head-confined Co(II) complex-bound BKC micelles, their effective size could also increase due to the additional electrostatic repulsion-induced Co(II) among the adjacent surface sites acting along the surface periphery at the micelle head/solution boundary. These larger BKC micelles would allow the slower diffusion of Co(II) probe-solubilized aggregates with smaller diffusion coefficients. In addition, the diffusion coefficient value change with BKC concentration can be used to identify the *cmc* of BKC.

The measured diffusion coefficient of the micelle-bound Co(II) complex in the aqueous/micellar mixture,  $D_{\text{M-W2/3}}$ , is contributed by free complex and the bound complex. Thus, considering the partitioning of the complex between the free and the micelle bound forms,  $D_{\text{M-W2/3}}$  is described by a concentration (mole fraction) weighted average of the two forms [35–38] for a partitioning of  $[\text{Co(II)(bpy)}_3]^{2+}$  between micelle bound ( $S_n \cdot R$ ) and free ( $R_W$ ) form in the BKC micellar medium ( $S_n$ ), which can be written as

$$R_W + S_n \frac{K_{\text{in}} \cdot R}{K_{\text{out}} \cdot R} S_n \cdot R \quad (5)$$

$$D_{\text{M-W2/3}} = F_f \cdot D_{\text{WR}} + F_b \cdot D_{\text{BKC}} \quad (6)$$

Here,  $D_{\text{WR}}$  is the diffusion coefficient of free  $[\text{Co(II)(bpy)}_3]^{2+}$  measured in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution without surfactant.  $D_{\text{BKC}}$  is the diffusion coefficient of BKC micelle.

$$F_f = \text{mole fraction of free } [\text{Co(III)(bpy)}_3]^{2+} = \frac{[R_W]}{[R_W] + [S_n \cdot R]} \quad (7)$$

$$F_b = \text{mole fraction of micelle bound } [\text{Co(II)(bpy)}_3]^{2+} = \frac{[S_n \cdot R]}{[R_W] + [S_n \cdot R]} \quad (8)$$

Since  $F_f + F_b = 1$ , Equation (6) can be expressed in terms of diffusion parameters as

$$F_f = (D_{\text{M-W2/3}} - D_{\text{BKC}}) / (D_{\text{WR}} - D_{\text{BKC}}) \quad (9)$$

$$F_b = (D_{\text{M-W2/3}} - D_{\text{WR}}) / (D_{\text{BKC}} - D_{\text{WR}}) \quad (10)$$

$$K_R = [S_n \cdot R]/[R_W] = F_b/F_f = (D_{M-W2/3} - D_{WR}) / (D_{BKC} - D_{M-W2/3}) \quad (11)$$

Thus, Equations (9)–(11) are a method to calculate  $F_f$ ,  $F_b$ , and  $K_R$ , respectively, from diffusion coefficient values. Mandal and Nair [39] have adopted this method to calculate the partition parameters and the mole fractions in the micellar phase for three redox forms of  $[\text{Co}(\text{en})_3](\text{ClO}_4)_3$  in CTAB and CPC (Cetylpyridinium chloride) micellar solution. By substituting experimentally measured diffusion coefficient values in Equations (7)–(9), the micellar solubilization constant,  $K_{\text{Co(II)}}$ , fractions of solubilized and free probe molecules are calculated to be  $3.8 \times 10^4 \text{ M}^{-1}$  using the values of  $D_{WR} = 3.42 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  and  $D_{BKC} = 0.39 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [40]. The calculated thermodynamic parameters are presented in Table 1. The micelle solubilized fraction of Co(II) species is negligible up to 0.1 mM of BKC, and gradually increases up to 2.2 mM, where Co(II) is partitioned equally into the micellar phase. The partition coefficient,  $K_{\text{Co(II)}}$ , increases with  $c_{\text{BKC}}$  and shows linear segment with slope (Figure 4)  $\{K_{\text{Co(II)}} / [\text{BKC}]\} = 3.8 \times 10^2 \text{ M}^{-1}$ . The corresponding association constant is, therefore,  $3.9 \times 10^4 \text{ M}^{-1}$  ( $K_{\text{Co(II)}} \times n$ ,  $n = 102$  for BKC), which confirms the BKC allows the probe molecule (Co(II)) equally distributed in the micellar system.

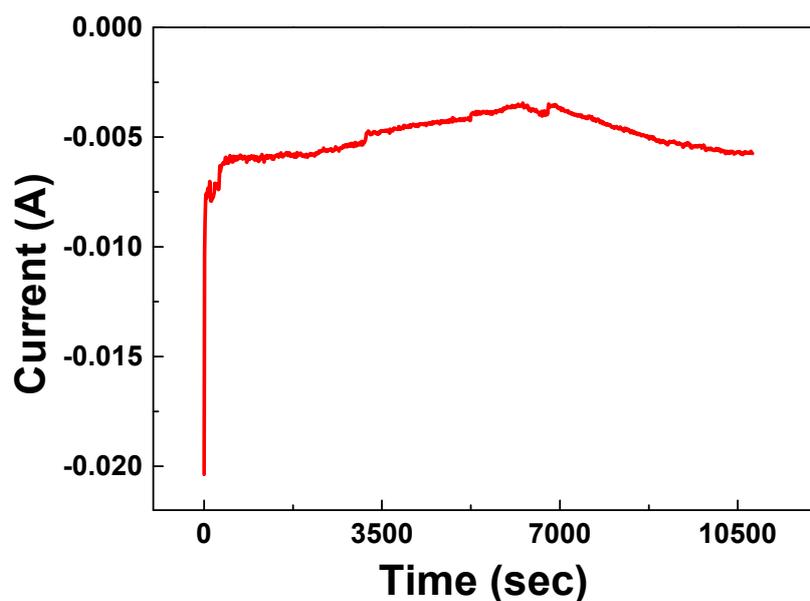
**Table 1.** Experimentally measured diffusion coefficient of  $[\text{Co(II)}(\text{bpy})_3]^{2+}$  complex in micellar solutions by CV ( $D_{M-W2/3}$ ), mole fraction of micellar bound Co(II) complex ( $F_b$ ), mole fraction of unbound Co(II) complex ( $F_f$ ), and partition coefficient of Co(II) complex ( $K_{\text{Co(II)}}$ ) in 0.1 M  $\text{Na}_2\text{SO}_4$  containing different concentrations of BKC.

$c_{\text{BKC}}/\text{mM}$	$D_{M-W2/3}/10^{-6} \text{ cm}^2 \text{ s}^{-1}$	$F_b^a$	$F_f^b$	$K_{\text{Co(II)}}^c$
0.00	3.42	-	-	-
0.01	3.29	0.05	0.96	0.04
0.022	3.63	-0.07	1.07	-0.06
0.048	3.43	-0.04	1.00	-0.04
0.10	3.29	0.04	0.96	0.04
0.22	3.03	0.12	0.88	0.14
0.48	2.97	0.14	0.86	0.17
1.00	2.82	0.19	0.81	0.24
2.20	2.01	0.45	0.55	0.83

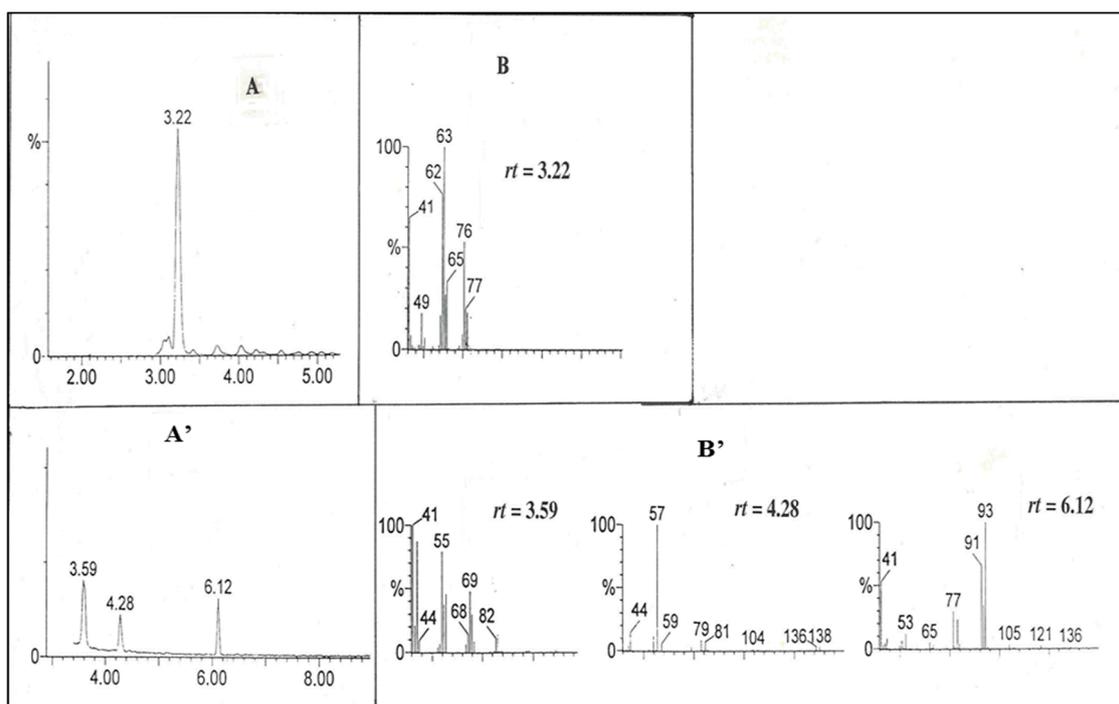
$$^a F_b = (D_{M-W2/3} - D_{WR}) / (D_{BKC} - D_{WR}); ^b F_f = (D_{BKC} - D_{M-W2/3}) / (D_{BKC} - D_{WR}); ^c K_{\text{Co(II)}} = (D_{WR} - D_{M-W2/3}) / (D_{M-W2/3} - D_{BKC}).$$

#### 2.4. BKC Effect on Catalysis by Product Analysis

As shown in Figure 1, curve b, the C2 and A2 redox couple in the presence of 0.1 M BKC was adopted to check the catalytic reduction of allyl chloride (a model VOC solution). The CV of  $[\text{Co(II)}(\text{bpy})_3]^{2+}$  in different surfactant with various substrates proved its mediated catalytic reduction [19,23–25]. The product identification may lead to the effectiveness of BKC in catalytic reaction on allyl chloride. Figure 6 shows the current response during the bulk electrolysis of allyl chloride (5 mM),  $[\text{Co(II)}(\text{bpy})_3]^{2+}$  (1 mM, the 5:1 ratio of allylchloride to cobalt enables to follow pseudo first order condition), and BKC (100 mM) in 0.1 M  $\text{Na}_2\text{SO}_4$  solution. The current sharply increased and reached to 4 mA in 2 h and started to decrease a little, which indicates the reduction reaction was enabled without blocking and the reaction was completed in 2 h. Figure 7A',B' presents GC/MS data of the reduction products collected from a 3-h electrolyzed solution of allyl chloride. They show three GC peaks at three different *rt* (3.59, 4.28, and 6.12) (Figure 7A') corresponding to the fragment ions at  $m/z = 82$ , 138, and 136 in their respective mass spectrum (Figure 7B'). The three compounds predicted by these fragment ions at the above  $m/z$  are likely to be 1,5-hexadiene (**3**) ( $m/z = 82$ ), 1,4,8-nonatriene (**4**) ( $m/z = 138$ ), and 1,8-nonadiene (**5**) ( $m/z = 136$ ). The absence of an allyl chloride substrate GC peak (*rt* = 3.22) in the GC spectrum for the electrolyzed solution confirms the complete degradation of allyl chloride by the BKC micelle solubilized Co(I) mediation process. Scheme 1 presents the possible allyl chloride reduction mechanism based on the results of both CV and bulk electrolysis, accounting for these three reduction products.



**Figure 6.** Chronoamperometric curve during mediated electrocatalytic reduction of allyl chloride. Conditions: working solution (250 mL) = 5 mM allyl chloride + 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  + 100 mM BKC in 0.1 M  $\text{Na}_2\text{SO}_4$  solution; Electrodes = Carbon cathode and Pt anode; Applied potential =  $-1300$  mV.



**Figure 7.** (A,A') Gas chromatograms and (B,B') mass spectra of different systems: (A,B) pure AC (allyl chloride); (A',B') AC degradation products from constant-potential bulk electrolysis using a carbon plate cathode of 5 mM allyl chloride + 1 mM  $[\text{Co(II)(bpy)}_3]^{2+}$  + 100 mM BKC in a 0.1 M  $\text{Na}_2\text{SO}_4$  aqueous solution. Potential applied =  $-1300$  mV (SCE). Mass spectra are given for different retention times (*rt*) indicated in the figure.



because one mole of mediator is needed to reduce 1 mole of the substrate. On the other hand, the source for OH<sup>•</sup> radical (in Reaction (8)) could not be accounted for, and the reaction intermediates have not been identified or characterized independently.

### 3. Material and methods

#### 3.1. Chemicals

Benzalkonium chloride was purified by repeated washing with anhydrous ether [43]. Allyl chloride was distilled twice (BP = 46 °C) prior to use. The Co(II)-tris-bipyridine perchlorate complex was prepared using the procedure reported elsewhere [44]. All other reagents and solvents were of AR grade and used as received.

#### 3.2. Electrochemical Studies

The CV experiments were carried out using a Wenking potentiostat (ST 72, Gerhard Bank Elektronik, Göttingen, Germany), a Wenking signal generator (VSG 83, Gerhard Bank Elektronik, Göttingen, Germany) and a X-Y-t recorder (WX 2300, Graphtec, Tokyo, Japan) in combination. A conventional gas-tight three-electrode electrolysis cell was used with a glassy carbon disk, a Pt plate, and a dip type saturated calomel electrode (SCE) as the working, counter, and reference electrodes, respectively. Before each experiment, the GCE surface was polished using a fine mesh alumina on a velvet cloth followed by ultrasonic cleaning in double distilled water and washing with methanol. Charcoal-treated double distilled water was used to prepare all experimental solutions. Dry nitrogen was used to degas the solutions and the temperature was maintained at 25 ± 0.2 °C for all experiments.

Bulk electrolysis for the de-chlorination products was carried out using a large-sized carbon plate cathode in a divided cell containing 250 mL of a stirred electrolyte solution under a N<sub>2</sub> atmosphere with Pt as the anode at a constant potential that was 100 mV negative of the reduction peak of the catalyst (−1300 mV) in the presence of the substrate. After approximately 3-h electrolysis, the products from the catholyte were extracted into ether and analyzed using a Perkin-Elmer Auto System XL gas chromatograph with a Turbo Mass Spectrometer (EI.70 eV, Perkin-Elmer, Waltham, MA, USA). A 30 m × 0.25 mm × 1 μm capillary column (Perkin-Elmer Elite series PE-5, Perkin-Elmer, Waltham, MA, USA) with helium as the carrier gas at a flow rate of 1.0 mL min<sup>−1</sup> and an oven temperature programmed between 80 and 250 °C at a rate of 10 °C min<sup>−1</sup>.

### 4. Conclusions

The paper reported that the benzyl headgroup-bearing BKC micelles exerted significantly different effects on the oxidation of [Co(II)(bpy)<sub>3</sub>]<sup>2+</sup> to [Co(III)(bpy)<sub>3</sub>]<sup>3+</sup> as well as on the effect of electrocatalysis by the BKC bound electrogenerated Co(I)(bpy) complex. The CV analysis with different BKC concentrations demonstrates the identification of *cmc* and diffusion coefficient of BKC surfactant. The presence of bulkier hydrophobic benzyl headgroups in BKC led to the preferred solubilization of the Co(II) complex ( $K_{Co(II)}/K_{Co(III)} = 2.9$ ), a more positive onset potential for Co(II) oxidation to Co(III), and considerably larger micellar aggregates with decreasing  $D_{M-W2/3}$  values with concentration. These studies clearly correlated the behavioral differences of the BKC surfactant on the different redox couples of the same mediator. The highly stable micelle-solubilized Co(I) mediator and the total de-chlorination of allyl chloride accompanied by three non-chloro organics as the only de-chlorination products in the BKC solution highlight the efficiency of the hydrophobic benzyl headgroup-bearing surfactant towards the de-chlorination process. This study also highlights the power of the CV technique as the diagnostic electrochemical tool in characterizing the micellar systems as well as in electrocatalytic systems.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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