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Aqueous Co(I) Stabilized Micellar Solution for Catalysis: A Mediated Electrocatalytic Reduction study on Perchloroethylene

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Stabilization and solubilization of electrogenerated $[Co(I)(phen)_3]^{1+}$ and its mediated electrocatalytic reduction on perchloroethylene is primary investigation. High concentrated surfactant (>48 mM) cetyltrimethylammonium bromide (CTAB) is utilized as micellar solution to establish the both stabilization and solubilization of electrogenerated Co(I). Initial cyclic voltammetry studies demonstrates that the electro-generated Co(I) is stabilized effectively in CTAB micellar solution from its decomposition. Also, the solubilization of PCE in CTAB micellar solution reflects clearly by mediated catalytic reduction through micellar stabilized electrogenerated Co(I) aqueous solution. PCE reduction started at same potential of Co(I) and at the cost of Co(I) clearly indicates the formation of $[Co(I)(phen)_3]^{1+}$ and not labile complex $[Co(II)(phen)_2]^{1+}$. The homogeneous rate constant (k_{homo}) between micellar solubilized $[Co(I)(phen)_3]^{1+}$ and PCE is determined by using cyclic voltammetry studies and it found to be 8.9038 $M^{-1}s^{-1}$. Product analysis by GC confirms the PCE reduction in micellar composite solution. The CTAB micellar solution is promising to get active catalyst $[Co(I)(phen)_3]^{1+}$ and for PCE reduction in aqueous medium.

Keywords: Co(I) stabilization, micellar composite solution, CV, VOCs, mediated electrocatalytic reduction

1. INTRODUCTION

Composite solutions are growing domain in various applications like selectivity, stability, and solubilization etc.. Also, the increasing interest in “green chemistry” has encouraged chemists to use water as a solvent instead of organic media [1]. Micellar solutions suits very well into the said fields. Though, it has been established that micelles can cause an acceleration or inhibition of a given reaction relative to the equivalent reaction in aqueous media [2-6], composite solution of micellar solubilized metal complex still should be investigated towards enhanced catalytic reduction of organic pollutants in aqueous medium.

Various transition metals such as copper, platinum, nickel, iron, rhodium, etc., have been used with caps as either catalytic centers or metalloenzyme mimics. Though, cobalt and especially simple cobalt salts of the type CoX_2 (X = Br, Cl and SO_4^{2-}) can be used as catalysts in various chemical, electrochemical synthesis of carbon–carbon coupling reactions from aromatic halides and/or arylzinc compounds and mediated electrochemical oxidation [7–11], cobalt has not received as much attention as those metals yet. Mechanistic investigations demonstrated that most of these syntheses involve a reactive cobalt(I) species which is generated in situ either by electrochemical or chemical reduction of the initial cobalt(II) salt [12,13]. More importantly, it was shown that the success of these cobalt catalyzed reactions relies on the stability/reactivity duality of Co(I) that depends itself on reaction conditions. In the absence of adequate ligand, the cobalt(I) transient species undergoes a very fast disproportionation reaction leading to the loss of the catalyst via the production of inactive cobalt(0). On the other hand, the use simple ligands like bipyridine or salen leads to a stable cobalt(I) species that is unable to efficiently solubilized due to low solubility or insoluble of cobalt(I) [14,15] and non stability due to labile nature of ligand [16,17]. Some organic solvents with suitable ligands have shown stability of Co(I) complex [18,19]. These solvents again give much troublesome in form of toxic to the environment. It is well established that micelles can solubilize and stabilize the low oxidation state of metal complexes with weak ligands [20,21]. $Co(II)(bipy)_3^{2+}$ complex was shown good stability and catalytic activity in CTAB miceller medium [21], but more complications occurred during electroreduction. Also, the rare earth metals like Technetium(III) and rhenium(III) complexes have been stabilized in aqueous surfactants sodiumdodecyl sulfate (SDS), cetrytrimethylammonium bromide(CTAB), and TritonX-100 [22].

The present investigation aims the micellar solubilized $[Co(I)(phen)_3]^{1+}$, as micellar composite solution, for reduction for PCE. Because of its carcinogenic effect to human due to its high use of dry cleaning and persistent contaminant found in many terrestrial and groundwater environments [23,24]. The $[Co(II)(phen)_3]^{2+}$ taken as catalyst, which is used as catalyst for organic compounds reduction [25]. In this work, through CV studies, CTAB surfactant's concentration were optimized towards stability of **[**$Co(I)(phen)_3]^{1+}$ in 0.1 M Na_2SO_4 medium. Mediated electrocatalytic reduction of PCE in micellar solubiliszed $[Co(I)(phen)_3]^{1+}$ conducted and confirmed using CV and GC results. Solution phase electron transfer rate constant was derived for this composite solution.

2. EXPERIMENTAL

All chemicals CTAB, Na_2SO_4, $CoCl_2{\cdot}6H_2O$, 1,10- phenanthroline, and $NaClO_4$ used were of fine grade. Tris-cobalt(II)-phenantroline perchlorate complex was prepared following the literature procedure [26] and its formation was confirmed by UV–visible spectroscopy. In brief, A 0.5014 g sample of 1 ,10-phenanthroline monohydrate(2.53 X10^{-3} mole) was dissolved in 50 ml of water heated to about 80°C. Then, 1.178 g (0.495 X 10^{-3} mole) of cobalt(I1) chloride hexahydrate in 5 ml of water was added to the 1,10-phenanonthroline monohydrate solution. The solution was allowed to come to room temperature by standing in air and then chilled in an ice bath. The cobalt(1I) complex of chloride salts was precipitated. The yield of tris(1,10-phenanthroline)cobalt(II) perchlorate dihydrate was 0.4405 g (95.50 of theoretical) by addition of 5 ml of a solution of sodium perchlorate and chilling in an ice bath.

Cyclic voltammetric experiments were carried out using a BASi Epsilon-EC, Bioanalytical Inc., USA. A Pt wire and an Ag/AgCl were used as counter and reference electrodes, respectively. Glassy carbon electrode (GCE) was used as a working electrode: 0.198 cm^2 geometric area electrode for CV studies and 1.2 cm^2 area massive electrode for bulk electrolysis. GC electrode surface was pretreated by metallographic polishing with alumina on a velvet cloth, followed by ultrasonic cleaning in double-distilled water and washing with methanol. Solutions were made using double-distilled water. All experiments have done at 24 ±0.5 ◦C (This is equal to the lab temperature, which is keep maintained by centralized controlled system).

A Shimadzu model (GCMS-QP2010) was used for gas chromatography/mass spectrometry experiments. It consisted of a ZB 5 msi capillary column (30 cm × 0.25 mm × 0.25 μm). Helium as carrier gas at a flow rate of 1.0 ml/min and an oven programmed between 25 and 200°C at a rate of 10°C/min were used.

3. RESULTS AND DISCUSSION

3.1 Stability and solubilization by CTAB composite solution

Fig.1 explains the composite solution effect on cyclic voltammetric reduction of $[Co(II)(phen)_3]^{2+}$ complex in presence of different concentration of CTAB in 0.1 M Na_2SO_4 solution at a scan rate of 10 mVs^{-1}.. At zero and low concentrations (0-0.048 mM) of CTAB, there appears one cathodic reduction peak with diffusion tail around -1028 mV and a sharp anodic peak, like surface bound species behavior, around -985 mV during reverse scan. Similar CV response of $[Co(II)(phen)_3]^{2+}$ reduction continues up to the concentration of 22 mM of CTAB (Fig.1 curves(a-d)) in 0.1M Na_2SO_4 solution. The surface bound species like CV response on reverse scan may be due to the preceding chemical reaction controlled electron transfer phenomena, i.e., chemical decomposition [27,28]. Here, possibly the formation $[Co(I)(phen)_3]^{1+}$ or dissociation of complex by expel of one ligand $[Co(II)(phen)_2]^{1+}$ + (phen), as shown in reaction 1 and 2. The (phen) ligand coordination with Co(II) is similar of bipyridine complex of Co(II), where $[Co(I)(bipy)_3]^{1+}$ is not soluble in aqueous medium [14,29], it is believed that the $[Co(I)(phen)_3]^{1+}$ or $[Co(II)(phen)_2phen^-]^{1+}$ complexes may insoluble in aqueous medium. This preceding chemical complication is minimized completely at high concentration of CTAB (48 mM) and become reasonably reversible electron transfer CV behavior with diffusion tail of both forward and reverse scans, as shown in Fig.1(curve e). Further, the ΔE_p = 88 mV at (E_{pc} = -1028 mV, E_{pa} = -940 mV) 10 mVs^{-1} remain almost invariant within the experimental error with scan rate range 10-150 mVs^{-1} and i_{pc} varies linearly with $v^{1/2}$ (not shown) evidences the diffusion controlled electron transfer behavior of $Co(II)(phen)_3]^{2+/1+}$ at 48 mM CTAB. It is mentioned that the oxidative addition of substrate (R) with $[Co(I)(phen)_3]^{1+}$ complex which is facilitate the reduction process [19]. Note that the reduction peak was not same of $[Co(I)(phen)_3]^{1+}$ and it was higher confirms the formation of $[RCo(III)(phen)_2]^{1+}$ [19]. Here, the PCE reduction starts at the same potential of Co(II) reduction indicates the formation of $[Co(I)(phen)_3]^{1+}$ and not the oxidative addition of complex or expel of ligand from coordination. In other words, one can say that the $[Co(I)(phen)_3]^{1+}$ complex is stabilized from decomposition, preceding chemical reaction, by solubilization of CTAB micelles at high concentrations, as seen in reaction 3. It is well documented that critical micellar concentration (CMC) of CTAB by CV using electrochemical probe was reported 0.6 mM [30]. See that the reported work used high oxidation state(Co(III)/Co(II)) redox couple to elucidate, which is highly reversible in nature. Here, the present study involved in Co(II)/Co(I) redox couple, which is little complicated due to its labile nature, as we seen above. It is to be believed that to stabilize the reduced form of $[Co(I)(phen)_3]^{1+}$ complex, 48 mM of CTAB might have been needed and can be called CMC of CTAB in the present system. Further works will be needed to confirm the above, which are in plan to execute.

$$[Co(II)(phen)_3]^{2+} + e^- \longrightarrow [Co(I)(phen)_3]^{1+}_{(insol)} \text{ or } [Co(II)(phen)_2]^{1+}_{(insol)} + (phen) \quad ...(1)$$

$$CTAB + [Co(II)(phen)_3]^{2+\ -} \longrightarrow CTAB\text{-}[Co(II)(phen)_3]^{2+} \quad ...(2)$$

$$CTAB\text{-}[Co(II)(phen)_3]^{2+} + e^- \longrightarrow CTAB\text{-}[Co(I)(phen)_3]^{1+}_{(sol)} \quad ...(3)$$

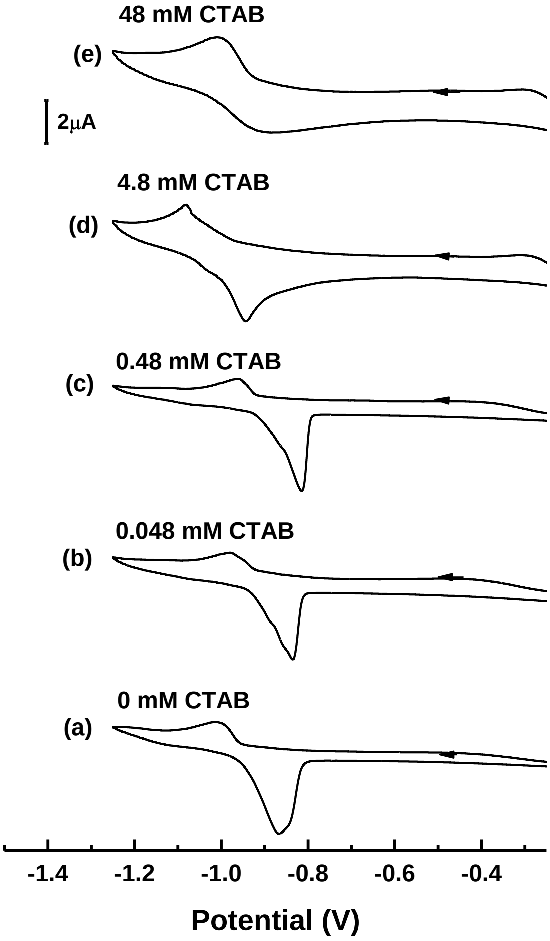

Figure 1. CV response' effect on various concentration of CTAB (mentioned in the figure) in 0.1 M Na_2SO_4 containing 1 mM $[Co(II)(phen)_3]^{2+}$ solution at GCE. Scan rate = 10 mVs^{-1}.

3.2 Mediated electrocatalytic reduction in CTAB composite solution.

Though the perchloroetylene is slightly soluble in aqueous solution, PCE is not directly reduced on activated GCE in 0.1M Na_2SO_4 solution, but in 50 mM CTAB containing 0.1M Na_2SO_4 solution shows slight increase in cathodic reduction going cycle, as shown in Fig.2a(curve c).

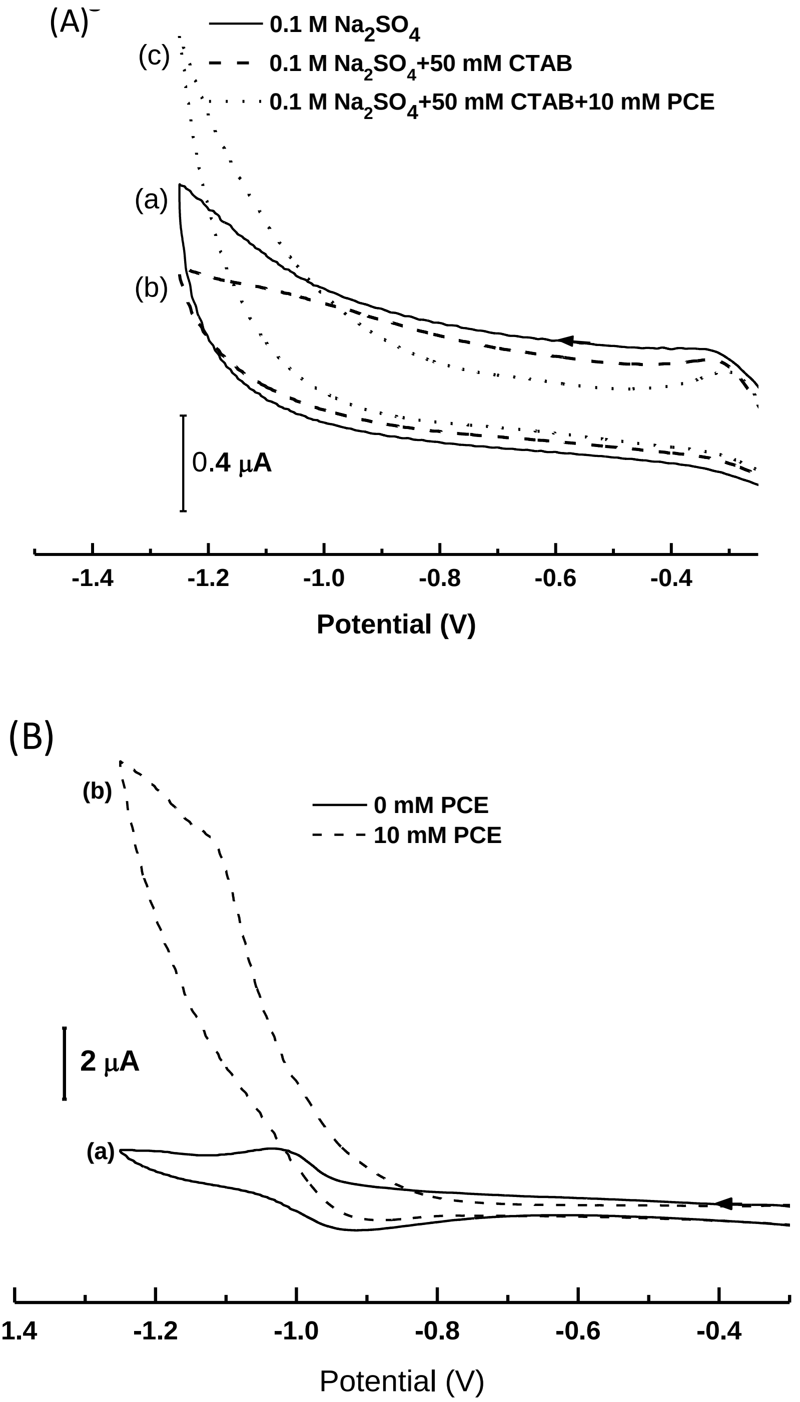

Figure 2. (A) CV response on GCE at a scan rate of 10 mVs^{-1}(solution conditions given in figure);

(B) CV response of micelle (50 mM CTAB) solubilized 1 mM [Co(II)(phen)$_3$]$^{2+}$ at GCE in 0.1 M Na_2SO_4 containing two different solutions (mentioned in the figure). Scan rate = 10 mVs^{-1}.

This slightly increased charging current like CV response evidenced the solubility of PCE in CTAB micellar solution. Further, Co(II)(phen)$_3$]$^{2+/1+}$ is not able to electrocatalytically reduce PCE when the absence of surfactant (not shown). Composite solution containing both 50 mM of CTAB and 1 mM [Co(II)(phen)$_3$]$^{2+}$, in which micellar stabilized by solubilization of [Co(II)(phen)$_3$]$^{2+/1+}$, in 0.1 M Na_2SO_4 solution, PCE reduction is occurred with many fold while the anodic peak eventually disappears, as shown in Fig.2b(curve b). This is a similar case of mediated electrocatalytic reduction of target substrate [31,32], PCE in the present study. Because of chemical reaction between reduced mediator [Co(I)(phen)$_3$]$^{1+}$ and PCE, Co(II)(phen)$_3$]$^{2+}$ is formed more and more, which enhances cathodic peak current and reason for reduced anodic peak current at the same time. At the same time, solubilization of PCE and stabilization–cum-solubilization of [Co(I)(phen)$_3$]$^{1+}$ in micellar hydrophobic region believed to pave the way to react both the reactants effectively.

3.3 Kinetics of mediated catalysis

The composite solution's homogeneity and rate controlling step have further proved by a simple current function plot. The current function ($i_{CAT}/v^{1/2}\, c_{Co(II)}$) in presence of PCE decreases with log(v) approaching the value obtained for the micellar solubilized mediator reduction in absence of target PCE(Fig.3a curve b), typical of mediation reaction with homogenous chemical reaction as the slowest step [33]. The second order rate constant for homogeneous electron transfer reactions are measured by the CV technique according to the method suggested by Saveant and Vianello [33] for catalytic current under pseudo first order conditions (excess of target substrate. The cathodic peak current in absence (i_{pc}) and presence (i_{CAT}) were calculated from CV of micellar solubilized mediator alone and presence of 30 mM of PCE, respectively. Here, the mediator to target substrate ratio is 1:30, which obeys the pseudo first order conditions. The second order rate constant (k_{homo}) for the homogeneous reaction is calculated using the following equation:

$$i_{CAT}/i_{pc} = (1/0.447)(RT/nF)^{1/2}\,(\sigma\, k_{homo}\, c_z/v)^{1/2} \qquad \text{---(4)}$$

where c_z is the concentration of the target substrate(PCE here), v(Vs^{-1}), k_{homo} (M^{-1}s^{-1}) and σ the stoichiometric coefficient and other parameters has usual meanings. If n and σ are known prior, k_{homo} can be calculated from the slope of the plot i_{CAT}/i_{pc} versus $v^{-1/2}$, according to the equation (4). The obtained plot (Fig.3b) is reasonably linear ($R^2 = 0.9625$) with a slope (57.8167 (mVs^{-1})$^{1/2}$) at studied scan rates. Using the slope value 57.8167 (mVs^{-1})$^{1/2}$, k_{homo} is calculated with the help of eqn.(4) with n = 1 and the σ as 4 because 4 mole of Co(II) complex is needed to reduce 1 mole of PCE. The found k_{homo} is 8.904 M^{-1}s^{-1}.

3.4 Product analysis

In order to confirm the composite solution's effect of mediated catalysis, bulk electrolysis were carried out for 20 mM PCE in presence of 50 mM CTAB in 0.1 M Na_2SO_4 aqueous solution. A big carbon electrode (1.2 cm^2) as cathode, Pt and Ag/AgCl as counter and reference electrode, respectively were used to carry out constant potential electrolysis, at the potential of -1250 mV in one hour duration. The ether extracted samples from bulk electrolysis were analyzed with GC, which is depicted in Fig.4.

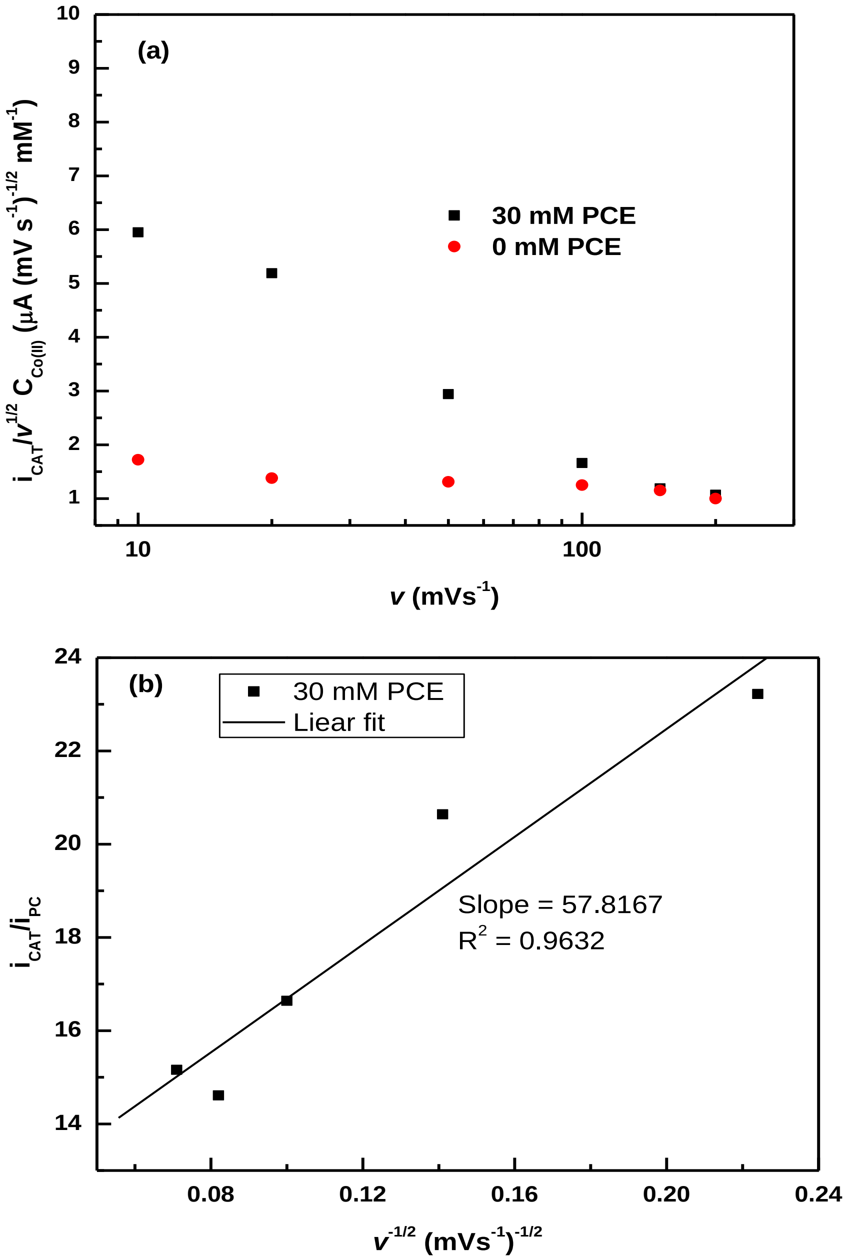

Figure 3. (a) The change of current function with log(v); (b) Effect of catalytic current with $v^{-1/2}$. The data obtained from the CV response of 30 mM PCE in (50 mM CTAB+1 mM $[Co(II)(phen)_3]^{2+}$+0.1M Na_2SO_4) aqueous solution.

There appears a reduced (80% reduction in peak area) PCE peak at retention time of 8.8 min in electrolyzed sample (Fig.4 curve b), Where appears at before electrolysis (Fig.4 curve a) evidences the effectiveness of micellar composite solution on mediated reduction of PCE at given experimental conditions. Based on the experimental evidence, we proposed a reaction pathway for the mediated electrocatalytic reduction of PCE in micellar composite solution.

$$3\text{CTAB-}[\text{Co(I)(phen)}_3]^{1+} + \text{Cl}_2\text{C=CCl}_2 \longrightarrow 3\text{CTAB-}[\text{Co(II)(phen)}_3]^{2+} + \text{CH}_2\text{=CHCl} \qquad \text{---(5)}$$

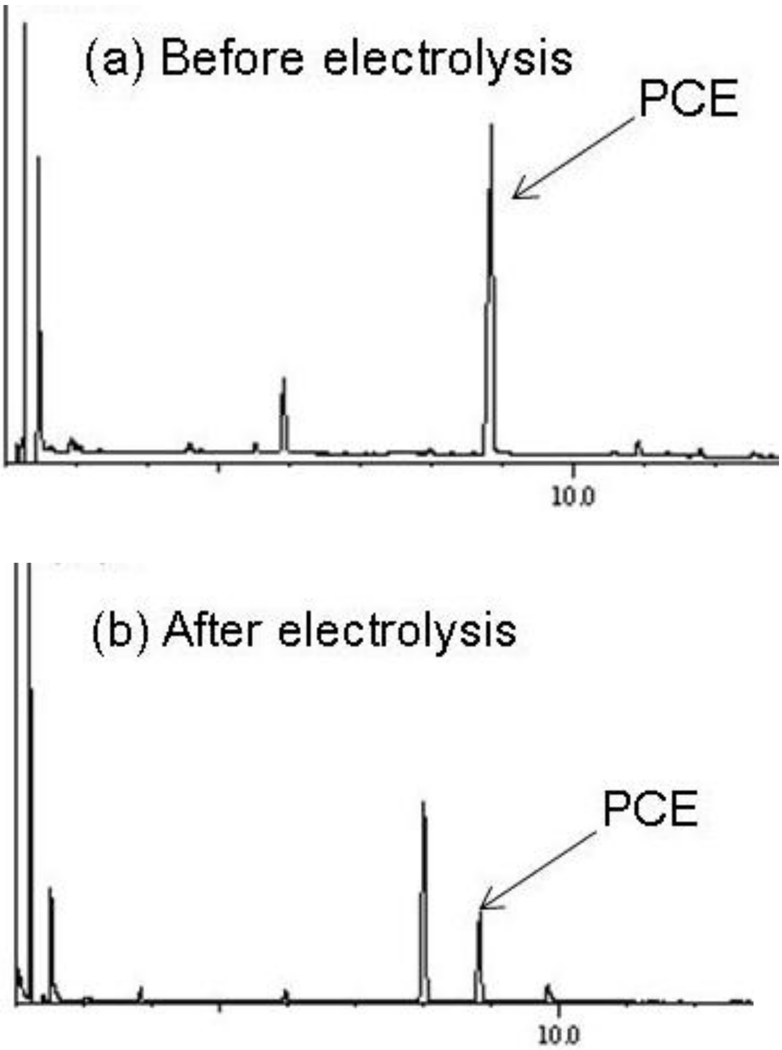

Figure 4. GC of PCE (20 mM) in different conditions: (a) Before electrolysis; (b) after electrolysis. Working solution: 0.1 M Na_2SO_4 + 50 mM CTAB + 1 mM $[Co(II)(phen)_3]^{2+}$

4. CONCLUSIONS

In this study, CTAB micellar composite solution was successfully utilized to stabilize and solubilized the both $[Co(I)(phen)_3]^{1+}$ and PCE. Reversibility of $[Co(II)(phen)_3]^{2+//1+}$CV studies evidence the CTAB micellar composites formation. Mediated catalytic reduction of PCE in micellar stabilized $[Co(I)(phen)_3]^{1+}$ aqueous solution confirms the solubilization of PCE in CTAB micellar solution. Also, CV of micellar solubilized $[Co(I)(phen)_3]^{1+}$ and PCE were used to calculate their homogeneous rate constant ($k_{homo\,=}$ 8.9038 $M^{-1}s^{-1}$). Micellar composite solution effectively reduces the PCE, which is confirmed by GC analysis. Further work is in progress to understand the in-depth of composite solution effect and its utility of VOCs degradation.

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References

1. P.T. Anastas, and J.C. Warner, *In Green Chemistry: Theory and Practice*, Oxford University Press, New York (2000).
2. T. Dwars, E. Paetzold, and G. Oehme, *Angew. Chem. Int*. Ed., 44 (2005) 7174–7199.
3. V.K. Balakrishnan, X. Han, G.W. VanLoon, J.M. Dust, J. Toullec, and E. Buncel, *Langmuir*, 20 (2004) 6586–6593.
4. C.A. Bunton, *Adv. Colloid. Interface. Sci*., 123-126 (2006) 333–343.
5. V. Chechik, *Annu. Rep. Prog. Chem. Sect. B*, 104 (2008) 331–348.
6. L. Dupont-Leclercq, J.J. Delpuech, and B. Henry, *Chem. Phys. Chem*., 9 (2008) 2305–2308.
7. C. Gosmini, Y. Rollin, J.Y. Nédélec, and J. Périchon, *J. Org. Chem*., 65 (2000) 6024-6026.
8. H. Fillon, C. Gosmini, and J. Périchon, *J. Am. Chem. Soc*., 125 (2003) 3867-3870.
9. M. Amatore and C. Gosmini, *Angew. Chem. Int. Ed*., 47 (2008) 2089-2092.
10. M. Matheswaran, S.J. Chung, and I.S. Moon, *Korean. J. Chem. Eng*., 25 (2008) 1031−1035.
11. G. Muthuraman, S.J. Chung, and I.S. Moon, *ACS. Comb. Sci*., 14 (2012) 359-365.
12. S. Seka, O. Buriez, J.Y. Nédélec, and J. Périchon, *Chem. Eur. J*., 8 (2002) 2534-2538.
13. S. Seka, O. Buriez, and J. Périchon, *Chem. Eur. J*., 9 (2003) 3597-3603.
14. A.A. Vleck, Nature, 180 (1957) 753-754.
15. G.M. Waind and B. Martin, *J. Inorg. Nucl. Chem*., 8 (1958) 551-556.
16. B. Brisig, E.C. Constable, and C.E. Housecroft, *New J. Chem*., 31 (2007) 1437–1447.
17. M. Matsumoto and J.H. Espenson, *J. Am. Chem. Soc*., 127 (2005) 11447–11453.
18. S. Margel and F.C. Anson, *J. Electrochem. Soc*., 125 (1978) 241-246.
19. P.L. Fabre and O. Reynes, *Electrochem. Comm*., 12 (2010) 1360–1362.
20. G.N. Kamau and J.F. Rusling, *J. Electroanal. Chem*., 240 (1988) 217-226.
21. G. Muthuraman and K. Chandrasekera Pillai, *J. Colloid. Inter. Sci*., 297 (2006) 687–695.
22. J.R. Kirchoff, W.R. Heineman, E. Deutsch, *Inorg. Chem*., 27 (1988) 3608-3614.
23. R.E. Doherty, *Environ. Forensics*., 1(2000) 69-81.
24. P.J. Squillace, M.J. Moran, W.W. Lapham, C.V. Price, R.M. Clawges, and J.S. Zogorski, *Environ. Sci. Technol*., 33 (1999) 4176-4187.
25. K. Gao and N. Yoshikai, *Angew. Chem. Int. Ed*., 50 (2011) 6888 –6892.
26. C.S. Lee, E.M. Gorton, H.M. Neumann, and H.R. Hunt, *Inorg. Chem*., 5(1966) 1397-1399.

27. N. Tanaka and Y. Sato, *Bull. Chem. Soc. Jpn.*, 41(1968) 2059-2064.
28. B.C. Willett and F.C. Anson, *J. Electrochem. Soc.*, 129 (1982) 1260-1266.
29. S. Margel, F.C. Anson, *J. Electrochem. Soc.*, 125 (1978) 1232-1235.
30. A.B. Mandal and B.U. Nair, *J. Phys. Chem.*, 95 (1991) 9008-9013.
31. R.S. Nicholson and I. Shain, *Anal. Chem.*, 36 (1964) 706-723.
32. A.J. Bard and L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley–Interscience, New York (1980).
33. J.M. Saveant and E. Vianello, *Electrochim. Acta*, 10 (1965) 905-920.