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Electrochemical studies of *p*-sulfonatocalix[4]arene in ionic liquid as supporting electrolyte

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ABSTRACT The electrochemical behaviour of sodium *p*-sulfonatocalix[4]arene (s-*p*sc$_4$) was studied. In this study ionic liquid/water mixtures were used as electrolyte, namely, [BMIM][BF$_4$]/water mixture and [BMIM][OTf]/water mixture ([BMIM] = 1-butyl 3-methyl imidazolium, BF$_4$ = tetrafluoroborate, OTf = trifluoromethanesulfonate). S-*p*sc$_4$ can be oxidised at 0.84 V and 0.83 V in [BMIM][BF$_4$]/water and [BMIM][OTf]/water respectively. The reaction is an irreversible process for both systems. The number of electron transferred in this electrochemical process is one electron and the diffusion coefficient, (D) for both systems was 1.15×10^{-8} cm^2 s^{-1} and 1.67×10^{-8} cm^2 s^{-1} respectively. The anodic potentials were affected by temperature and the activation energy, (E_d) was 18.18 kJ mol^{-1} and 18.78 kJ mol^{-1} in [BMIM][BF$_4$]/water mixture and [BMIM][OTf]/water mixture respectively.

INTRODUCTION

Sodium *p*-sulfonatocalix[4]arene is a water-soluble electroactive species. The unique arrangement of sodium *p*-sulfonatocalix[4]arene and the ability to do a self-assembly chemistry with other metals had attracted researchers to study and understand the behaviour and characteristic of calixarene in different conditions and structural modifications.

The electrochemical study of calixarene particularly sulfonated calixarene has been undertaken previously in aqueous solution and organic solvent[1,2,3,4]. The important of understanding the electrochemical behaviour of the inclusion compounds formed by sodium *p*-sulfonatocalix[4]arene has lead to the study on the electrochemical characteristics of the supramolecule itself. Ionic liquid is widely study as a replacement of the organic and aqueous solutions in the electrochemistry field.

The small electrochemical window provided by the aqueous solution and organic solvent has limited the full picture of the species formed. Moreover, the study in aqueous solution is always complicated by the presence of the hydrogen[5] and the study at high temperature is very limited in organic solvent. Ionic liquid essentially composed of ions and therefore can stabilised unusual species which cannot be observed in molecular solvent or aqueous solution. It has wide electrochemical window to study full picture of the species formed in the solution and has high thermal stability. [BMIM][BF$_4$] and [BMM][OTf] were used in this study as these two common ionic liquids soluble in water and it is interesting to understand the behaviour observed and the effect of the anions.

Therefore this work specifically carried out and focused on the electrochemical behaviour of the sodium *p*-sulfonatocalix[4]arene and (N$_{1444}$)SO$_3$calix[4]arene using [BMIM][BF$_4$] and [BMIM][OTf] as electrolyte.

Experimental

0.01 g of s-*p*sc$_4$ was dissolved in 1 ml of H$_2$O. To the solution 1 ml of ionic liquid was added. The mixture was stirred at room temperature until a homogeneous solution formed. The sample was deoxygenated by bubbling in nitrogen gas for 5 to 10 minutes prior to perform the electrochemical measurements. All the samples are treated in the same way. For the temperature dependence study, the temperature was control using thermo couple and oil bath was used to get a consistent heating.

The electrochemical experiments were carried out in an AUTOLAB (PGSTAT12/30/302) with a three-electrode cell. A glassy carbon disc electrode (diameter: 3 mm) was used as working electrode. Platinum wire was used as the counter electrode.

The reference electrode was an IL reference electrode. The glassy carbon working electrode was polished to a mirror with diamond slurry and rinsed with acetone before use. Then, the ionic liquids ([BMIM][BF$_4$] and [BMIM][OTf]) were scan at glassy carbon between -3 V and 3 V (versus ILRE) respectively.

RESULTS AND DISCUSSION

Electrochemical behaviour of sodium p-sulfonatocalix[4]arene (s-psc$_4$)

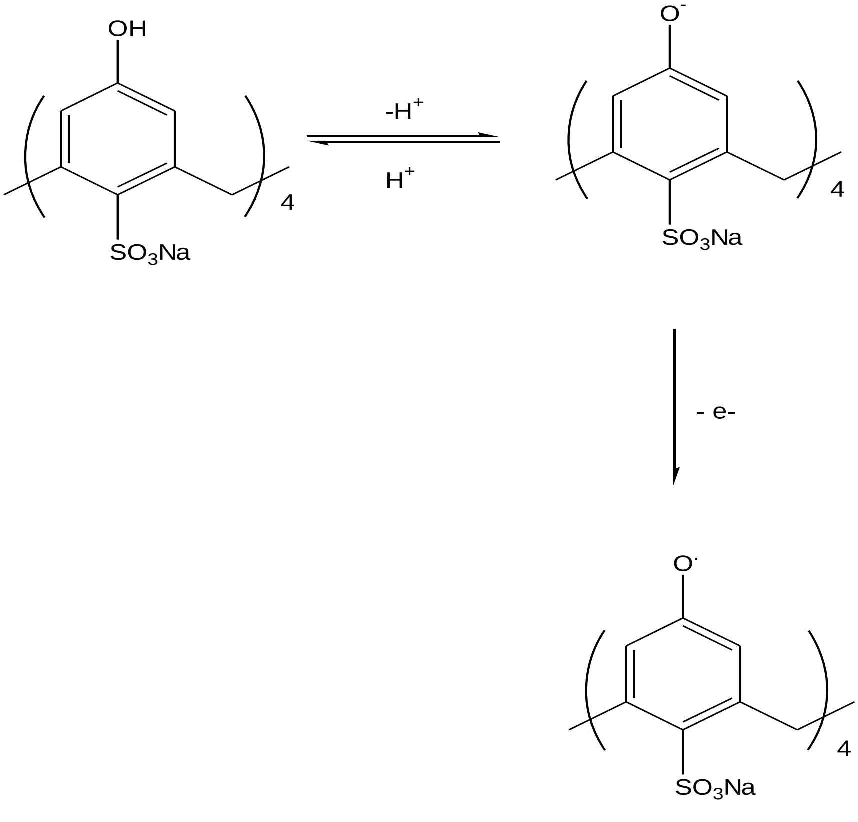
The cyclic voltammogram of a solution containing 0.12 M of s-*p*sc$_4$ in [BMIM][BF$_4$]/water mixture by using GC as WE and SCE as RE at 100 mV/s is shown in Figure 1 (a). There is one oxidation peak observed at 0.84 V and no cathodic peak was detected at the reversed scan. When the scans were repeated for few cycles, the current was decrease to a steady value, zero.

This behaviour was expected where the electroactive species undergoing oxidation was depleted in concentration at the electrode surface and indicated that the electrochemical reaction was passivating the working electrode[3]. Therefore, the surface of working electrode was polished for every single scan.

The same behaviour of s-*p*sc$_4$ was observed in [BMIM][OTf]/water mixture as one oxidation peak observed at 0.83 V and no cathodic peak detected on reversed scan (Figure (b)). Therefore the same explanation was suggested for s-*p*sc$_4$ in different electrolyte system of [BMIM][OTf]/water.

The oxidation peak observed was attributed to the oxidation on the GC surface[3], which is well known and leads to the introduction of oxygen functionality to the surface and often used for the activation of such electrodes prior to electroanalysis. It has been shown that sodium *p*-sulfonatocalix[4]arene solutions can give rise one oxidation peak corresponding to the phenol[6]. Therefore, the peak was assigned to the oxidation of phenolic unit of the calixarene.

Such electrochemical oxidation are produced by *para* coupling of the phenolate radicals generated at the electrode surface leading to the deposition of polyphenol or polyphenylene oxide on the electrode[7]. Scheme 1 shows the proposed electrochemical oxidation reaction of s-*p*sc$_4$ in ionic liquid/water mixture.



Scheme 1: Proposed electrochemical oxidation of s-*p*sc$_4$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water.

Number of electron (n) and diffusion coefficient (D)

In order to investigate the behaviour of s-*p*sc$_4$ in IL/water mixture further, the scan rate dependent studies were done. When the potential scan rate ranged from 10 mV/s to 400 mV/s, both anodic peak potential, E_p and peak current, I_p are affected by scan rate as shown in Figure 1 (a) and (b). As the scan rate increase, the peak currents increase and the potential shifted to more positive potential.

According to Nicholson for an irreversible anodic reaction, the relationship between E_p and ν is

$$E_p = E° + (RT/\alpha n_a F)\ [0.780 + \ln (D^{1/2} / k°) + \ln (\alpha n_a F\nu / RT)^{1/2}] \qquad \text{Equation 1}$$

By plotting E_p versus ln ν (Figure 2 (a) and (b)), the plot show a linear graph for s-*p*sc$_4$ in both [BMIM][BF$_4$] and [BMIM][OTf] in water mixture. This behaviour obeys the Nicholson's equation and confirmed that the electrochemical oxidation of s-*p*sc$_4$ in ILs/water mixture in this experimental condition is totally irreversible.

According to the slope of the straight line of E_p against ln ν the product of αn_a can be evaluated. Plot E_p versus ln ν (a) show the slope is 1.3×10^{-3} while (b) show the slope is 1.1×10^{-3}. After simplifying the equation, the slope is $RT/2\alpha n_a F$. Therefore, the value of αn_a is 0.99 in [BMIM][BF$_4$]/water mixture and 1.17 in [BMIM][OTf]/water mixture.

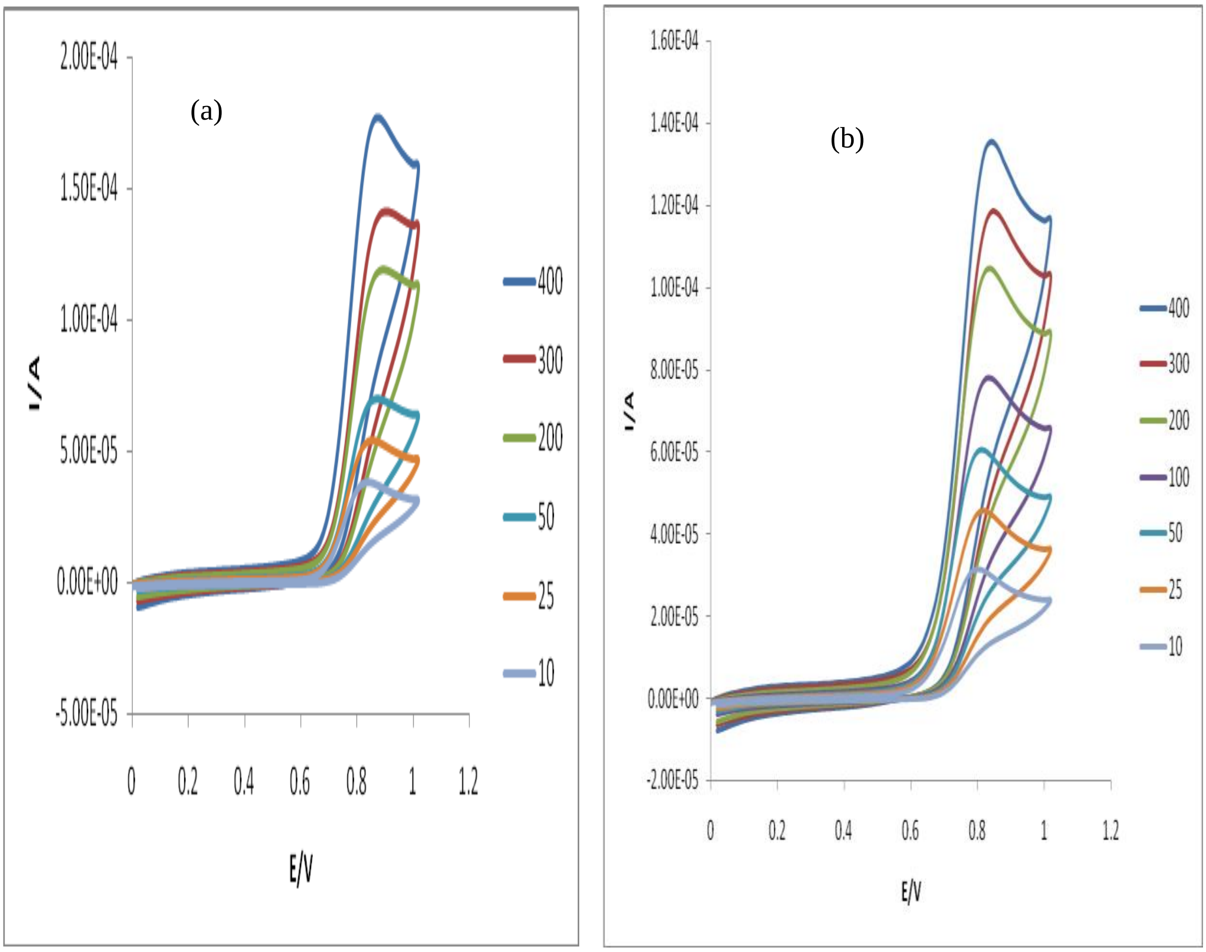


Figure 1: At 25°C, the voltammogram of 0.12 M of s-*p*sc$_4$ in **(a)** [BMIM][BF$_4$]/water mixture and **(b)** [BMIM][OTf]/water mixture at scan rate ranged from 10 mV/s to 400 mV/s, GC versus SCE.

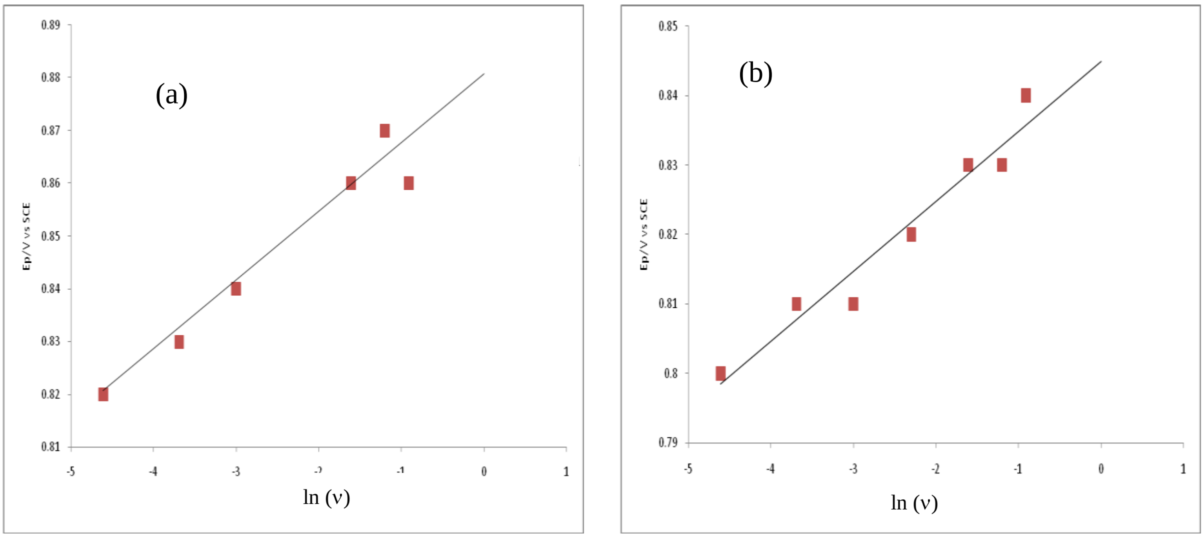


Figure 2: At 25°C, the plot of E_p versus ln (ν) of 0.12 M of s-*p*sc$_4$ in **(a)** [BMIM][BF$_4$]/water mixture and **(b)** [BMIM][OTf]/water mixture.

In addition, the peak current I_p for an irreversible electrochemical reaction can be described by the following formula

$$I_p = (2.99x10^5)n(\alpha n_a)^{1/2}AC^*_RD^{1/2}\ \nu^{1/2}$$

ln (ν)

Equation 2

According to Equation 2, at a given concentration of s-*p*sc$_4$, the plot of peak current, I_p versus square root of the scan, $\nu^{1/2}$ should be linear passing through the origin. From the slope of the straight line, the value of $[n(\alpha n_a)^{1/2}AC^*_RD^{1/2}]$ can be evaluated (Figures 3 (a) and (b)). Linear plots of I_p versus $\nu^{1/2}$ was obtained and the parameter of $[n(\alpha n_a)^{1/2}D^{1/2}]$ was calculated as 9.03 x 10^{-5} cms^{-1} for [BMIM][BF$_4$] and 6.99 x 10^{-5} cms^{-1} for [BMIM][OTf].

Combining the two parameters of αn_a and $[n(\alpha n_a)^{1/2}D^{1/2}]$, the value of $nD^{1/2}$ can be evaluated as 9.07 x 10^5 cms$^{-1/2}$ and 6.46 x 10^{-5} cms$^{-1/2}$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water respectively .

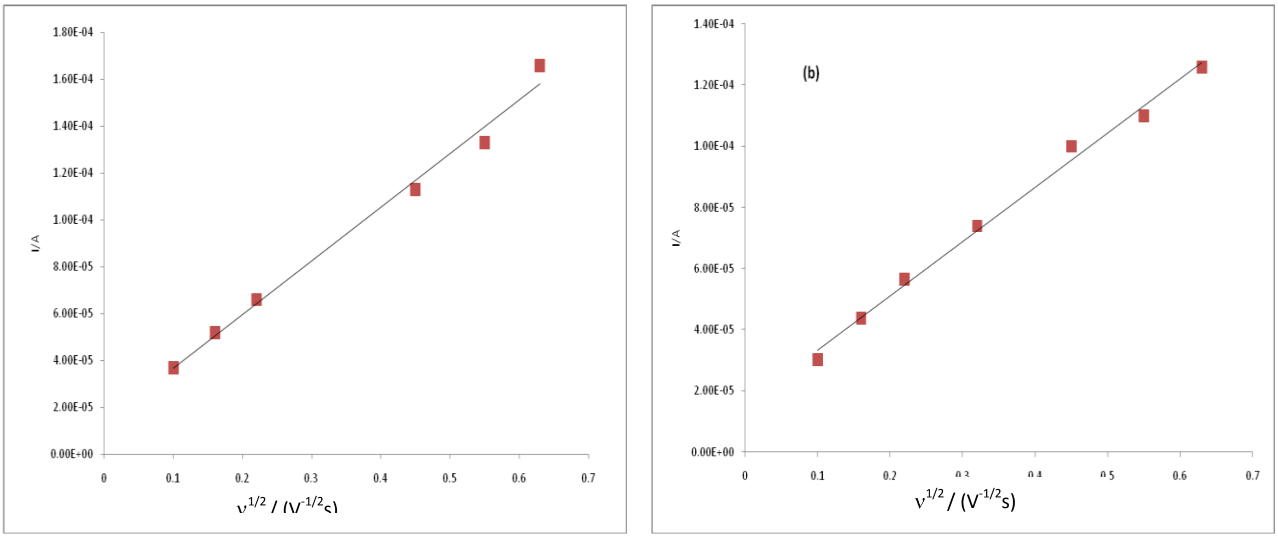


Figure 3; Plot of I_p versus $\nu^{1/2}$ for (a) s-*p*sc$_4$ in [BMIM][BF$_4$]/water mixture, (b) s-*p*sc$_4$ in [BMIM][OTf]/water mixture.

To get the value of *n* and *D*, a steady voltammetry of 0.1 M of s-*p*sc$_4$ in [BMIM][BF$_4$]/water and [BMIM][OTf]/water on the same electrode was determined. The limitation diffusion current, I_l is 8.38 x 10^{-11} A and 5.80 x 10^{-11} A respectively. Therefore the value of *nD* can be calculated as 1.20 x 10^{-8} cm^{2}s^{-1} in [BMIM][BF$_4$]/water mixture and 8.35 x 10^{-9} cm^{2}s^{-1} in [BMIM][OTf]/water mixture by using the following formula;

$$I_1 = 4nFDC^*_R r$$

Equation 3

Combining with the value of $nD^{1/2}$ as described previously, the value of *D* is calculated as 1.15 x 10^{-8} cm^{2}s^{-1} and 1.67 x 10^{-8} cm^{2}s^{-1} and the value of *n* is calculated as 0.83 and 0.71 respectively. Taking account the error of calculation, it was assuming that the number of electron transfer for s-*p*sc$_4$ in both IL/water mixture is 1. Assuming $n_a = n$, therefore the value of α is 0.99 (in [BMIM][BF$_4$]/water) and 1.17 (in [BMIM][OTf]/water). The value of the diffusion coefficient is small compared to the behaviour in other solvent[1,2] as the ionic liquid has higher viscosity.

Temperature dependence

As shown in Figure 5 (a) and (b), both peak current and peak potential for the electrochemical reaction of s-*p*sc$_4$ were affected by temperature. The anodic peak current increased with temperature. The peak potential shifted in negative direction with the temperature increasing, which tells us that it is easier for the oxidation of s-*p*sc$_4$ at high temperature. This behaviour is due to the viscosity of the ionic liquid. At higher temperature the viscosity of IL will slightly decrease in viscosity[8]. Therefore, it was assumed that the movement of electroactive species of s-*p*sc$_4$ in the solution easier at higher temperature. Taking account of n_a, *α* as independent of *T*, then according to Nicholson, the peak current, I_p at different temperature should be described as follows;

$$I_p = -04985nFA(\alpha n_a F/RT)^{1/2} C^*_R D^{1/2} \nu^{1/2}$$

Equation 4

From Equation 4, the diffusion coefficient, *D* for different temperature can be calculated and the relationship between *D* and temperature is

$$\log D = -E_d/(2.303\,RT) + \log D_0$$

Equation 5

E_d is the active energy of diffusion of s-*p*sc$_4$. By plotting log *D* over 1/*T* (Figure 6) the active energy diffusion of s-*p*sc$_4$ can be evaluated as 18.41 kJ mol^{-1} in [BMIM][BF4]/water and 17.97 kJ mol^{-1} in [BMIM][OTf]/water .By comparing the value of activation energy with reported in the literature[2,4,6], 29.00 kJ mol^{-1} and 18.80 kJ mol^{-1} which is in different solvent, it can be concluded that, in ionic liquid/water mixture, the activation energy of s-*p*sc$_4$ are much lower then in other solvents. Guowang Diao reported that, the diffusion of calixarene in organic solvent is much easier then in aqueous solution[6], however, the study in ionic liquid/water mixture show that it is much difficult to diffuse in ionic liquid due to the viscosity of the ionic liquid although in the presence of water .

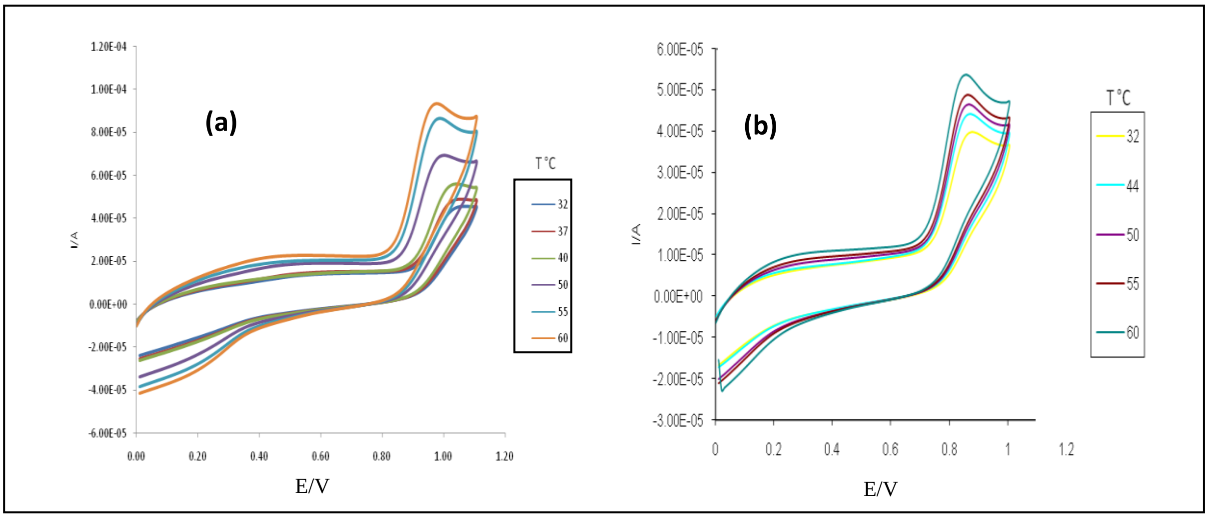


Figure 5 Cyclic voltammograms of s-*p*sc$_4$ in **(a)** 0.12 M [BMIM][BF$_4$]/water mixture **(b)** 0.12 M [BMIM][OTf]/water mixture up to 60°C, 100 mV/s, GC versus SCE.

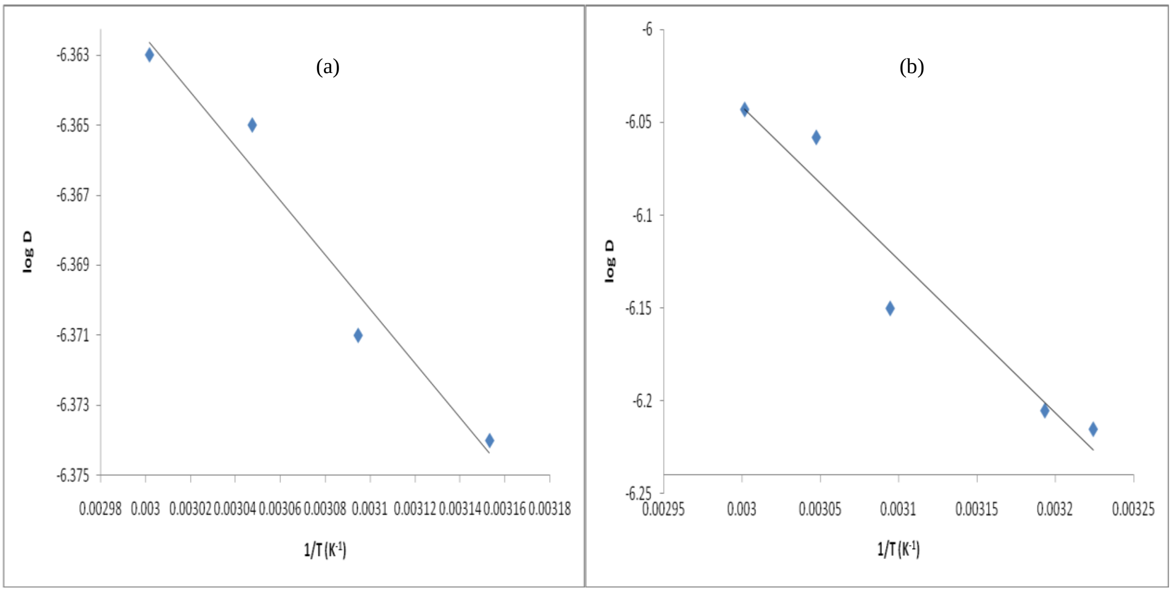


Figure 6: Plot log *D* versus 1/*T* (K^{-1}) (a) 0.12 M [BMIM][BF_4]/water mixture (b) 0.12 M [BMIM][OTf]/water mixture 0.12 M s-*p*sc$_4$ in [BMIM][OTf]/water mixture

CONCLUSION

The electrochemistry of *p*-sulfonatocalix[4]arene in the presence of [BMIM][BF_4] or [BMIM][OTf] as supporting electrolyte shows similar behaviour as reported in aqueous solution[1,8] and/ or organic solvent[2,6,9]. The pathway of oxidation of sodium *p*-sulfonatocalix[4]arene have been discussed which proceed *via* a common one-electron intermediate of phenoxide. Temperature dependence study was carried out and activation energy for different systems are 18.18 kJ mol^{-1} and 18.78 kJ mol^{-1} respectively.

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