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# Introduction

Ionic liquids (ILs) are low-melting salts that are liquid at room temperature and have emerged as potential alternatives to traditional solvents, ligands, and efficient catalysts.<sup>1–3</sup> Their low vapour pressure, high thermal stability, excellent conductivity, unique structural properties, high gas solubility, and flexibility in terms of structural modification have made them a special class of solvents.<sup>4–6</sup> Due to the thermal and electrochemical stability of ILs along with their excellent conductivity, they can be used as an ideal electrolytic media. The initial focus on the electrochemical investigations involving ILs was to evaluate their structural–property relationship to achieve a wider electrochemical potential window.<sup>6</sup> In addition to excellent solvent characteristics, ILs are reported to be a convenient carbene source.<sup>7–9</sup> The highly reactive nature of carbene has broadened the application spectrum of ILs to metal-free organocatalysts, ligand in metal

# Water-assisted stability of carbene: cyclic voltammetric investigation of 1-ethyl-3- methylimidazolium ethylsulfate ionic liquid<sup>†</sup>

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In this work, we report electrochemical studies on imidazolium-based ionic liquids with an objective to explore the possibility of carbene formation in their dilute aqueous solutions. Conventionally, water plays a detrimental role during investigations involving ionic liquids, and this role has been investigated *via* electrochemical studies in aqueous ionic liquid solutions. There are varying opinions regarding the influence of water on the physicochemical behaviour of ionic liquids that require an in-depth understanding. To eludicate the role of water, we attempted to evaluate the electrochemical performance of ionic liquids in water as a solvent, and the influence of water on ionic liquids was explored through feasibility and stability studies on carbene formed in an aqueous imidazolium-based ionic liquid solution. The electrochemical investigation of an aqueous solution of 1-ethyl-3-methylimidazolium ethylsulfate ([EMIM][EtSO<sub>4</sub>]) revealed a redox couple. Detailed investigations suggest that reduction of the imidazolium cation occurs at the C2 position, with subsequent formation of carbene. The coulometric process associated with the anodic peaks indicated that the two-electron oxidation of carbene occurred. The stability of carbene in water was evaluated through the use of different protic and aprotic solvents. The hydrogen bond-forming ability of carbene with water seems to be responsible for its improved stability in water.

complexes, and inversion of polarity (umpolung properties) that play important roles in modern organic synthesis.<sup>10</sup>

The generation of carbenes has been reported as a result of the structure-induced destabilization of ILs.<sup>11,12</sup> However, the formation and stability of the carbene primarily depends on the type of IL and the combinations of its ion pairs.<sup>8,11</sup> The stability of carbene has also been noted to be important for governing its organo-catalytic efficiency, which has been investigated from carbene-catalysed reactions.<sup>8,13,14</sup> The stability of carbene in pure IL has been increased through different combinations of ion pairs or use of organic solvents. Chiarotto et al. have explored the relationship between the nature of the anion and catalytic efficiency of carbene formation.<sup>13</sup> Furthermore, Feroci et al. have demonstrated that the nature of solvent and anion have remarkable effects on the stability and catalytic efficiency of electrogenerated carbenes.<sup>14</sup> They proposed that the carbene is stabilized due to the hydrogen bond with either the cation or anion of IL, and it also forms in organic solvents. However, their study lacks an elaborative mechanism explaining how organic solvents mediate the stabilization of carbenes.

The possible role of water as a solvent in carbene formation is of interest because of its economical and industrial relevance. However, there are varying opinions regarding the effect of IL–water combinations on carbene formation and stability.

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It has been reported that carbene formation is based on the strength of anion basicity, which accelerates carbene formation. However, the presence of water in an IL preferentially interacts with the anion, thereby reducing its charge density, and therefore, decreasing the probability of carbene formation. In other words, engagement of the anion in H-bond formation with any protic source such as water can decrease the probability of carbene formation through a chemical route.<sup>11,15,16</sup>

To the best of our knowledge, this is the first report that emphasizes the formation and stabilization of a carbene in aqueous IL systems. On the contrary, the electrochemical investigations of imidazolium-based ILs have shown that the addition of small amounts of water resulted in the increased electrochemical stability of ILs.17 This water-assisted formation of reactive species adsorbed on an electrode surface has circumvented the electrochemical destabilization of ILs.<sup>17</sup> Although the authors did not comment on the nature of the reactive species formed upon the addition of water, carbene formation could be rationalized by the H<sup>+</sup> ion generation. The presence of water was further explored by Oldamur et al., who studied the hydrolysis of carbene.<sup>18</sup> The authors demonstrated that carbene could be stabilized through the formation of a water-carbene complex at low water content, and its stability was governed by the amount of water present. Although the authors demonstrated the existence of a carbene-water complex, they used a water:THF mixture instead of a pure aqueous system.

It is important to understand the exact nature of carbene formation in a pure aqueous solution of IL. In the present study, we examined carbene formation through the electrochemical reduction of 1-ethyl-3-methylimidazolium ethylsulfate [EMIM][EtSO<sub>4</sub>] in aqueous solution. [EMIM][EtSO<sub>4</sub>] (Fig. 1) was selected as the IL system due to the moderate basicity of the  $[EtSO_4]^-$  anion that can minimize the probability of endogenous carbene formation.11 The solvent-assisted stability of carbene was also evaluated through the use of different protic and aprotic solvents. The mechanism of carbene stabilization and its electrochemical behavior in aqueous solution is interesting and opens up many possibilities to tailor its properties and application in an eco-friendly environment. Water as a solvent plays an important role in improving the stability and hence detection feasibility of carbene. Therefore, our main objectives are (i) to investigate the exact electro-oxidation behavior of the carbene and (ii) to understand the reason behind its enhanced aqueous phase stability.

## **Results and discussion**

As stated earlier, the choice of  $[EMIM][EtSO_4]$  is based on the appropriate basicity of the  $[EtSO_4]^-$  anion to avoid the possibility



Fig. 1 Chemical structure of the [EMIM][EtSO<sub>4</sub>] ionic liquid.



Fig. 2 (A) CV scans recorded using 0.17 M aqueous solution of [EMIM][EtSO<sub>4</sub>], (B) first and second CV scan recorded using 0.17 M aqueous solution of [EMIM][EtSO<sub>4</sub>]. Arrows in the figure indicate the direction of potential scans. Scan rate -100 mV s<sup>-1</sup>.

of endogenous carbene formation. For the cyclic voltammetry (CV) investigations, 0.17 M aqueous solution of  $[EMIM][EtSO_4]$  was used, and an inert atmosphere was maintained during the scans. Fig. 2A shows CV scans recorded using aqueous solution of  $[EMIM][EtSO_4]$ . During the cathodic potential scan, a reduction peak was observed at -0.57 V. Interestingly, upon scan reversal, an anodic peak was also observed at -0.25 V. When we started the CV in the anodic scan direction (Fig. 2B), no anodic peak was observed in the first cycle and it appeared only after the cathodic scan, which suggests that the anodic peak is associated with the electrogenerated species formed at -0.57 V. ILs are known to produce carbene species upon one electron reduction at the C2 position of the imidazolium cation ring.<sup>7</sup>

There are reports on the possibilities of carbene formation at the remaining two carbon positions.<sup>19</sup> To confirm the active reducible site at the cation, we performed an alternative experiment using a 0.17 M aqueous solution of 1-ethyl-2,3-dimethylimidazolium ethylsulfate, [EMMIM][EtSO4] which differs to [EMIM][EtSO4] only at the C2 position, where instead of a hydrogen atom, a methyl group is present. The CV scans recorded using [EMMIM][EtSO4] are depicted in Fig. 3A. Expediently, no electrochemical peaks were observed for [EMMIM][EtSO<sub>4</sub>], which supports our hypothesis that the cation is reduced at the C2 position, and that the one electron electroreduction of imidazolium cation produces a carbene. The C2-H between the two nitrogen atoms is acidic in nature, and its acidity is further enhanced due to electroreduction, which results in a cation that undergoes deprotonation to generate a highly reactive nucleophilic carbene.<sup>20</sup> To characterize an electrogenerated species via spectroscopic techniques, electrolysis was performed in constant potential



**Fig. 3** (A) CV scans recorded using a 0.17 M aqueous solution of [EMIM][EtSO<sub>4</sub>] and [EMMIM][EtSO<sub>4</sub>], (B) CV scans recorded using a 0.17 M aqueous solution of [EMIM][EtSO<sub>4</sub>] in the presence and absence of metal carbonyl ([bromopentacarbonylmanganese(i)] = 0.17 M). Scan rate  $-100 \text{ mV s}^{-1}$ .

mode using similar electrolytic conditions, and the electrolyzed solution was subjected to <sup>1</sup>H-NMR spectroscopy.

We did not observe any additional characteristic features for the reactive species by <sup>1</sup>H-NMR, perhaps due to its unstable nature. We further investigated this with the aim to trap the electrogenerated species with a metal complex.<sup>3</sup> To confirm the formation of a carbene, we developed a scheme based on Fig. 2 with the assumption that the metal carbonyl will trap the carbene, *i.e.*, the electrogenerated species at 'c'. This will result in the unavailability of carbene for the electrochemical oxidation at 'a', which was confirmed by the absence of an anodic peak at 'a'. Using this scheme, we recorded the CV an using aqueous solution of [EMIM][EtSO<sub>4</sub>] in the presence of bromopentacarbonylmanganese(1) (Fig. 3B). We noted that the anodic peak 'a' disappeared, and only a cathodic peak was observed after the addition of metal carbonyl. In addition, a hump was also observed at a more positive potential that could be attributed to a carbene complex with metal carbonyl. We performed an identical experiment in pure IL, and a CV was recorded using pure [EMIM] [EtSO<sub>4</sub>]; as shown in Fig. 4. An anodic peak was not observed during these experiments. Only a cathodic peak was seen at a comparatively higher negative potential, which could possibly be due to the high viscosity of pure IL compared to aqueous solution.

Therefore, based on the above sets of experiments, it is inferred that [EMIM][EtSO<sub>4</sub>] undergoes one electron reduction at the C2 position, which results in carbene formation. Because the carbene in aqueous solution undergoes oxidation at 'a', it is oxidatively detectable.<sup>7,13,14,20,21</sup> To date, carbenes have been detected through catalyzed chemical reactions, electrochemical techniques, or a combination of spectroscopy and electrochemical techniques.<sup>8,11,13,14,19,21,22</sup> However, the exact electrochemical behavior of carbenes is still unclear due to their high reactivity towards an electroanalytical probe, which makes the coulometric investigation of ILs difficult.<sup>23</sup>

We used ferrocene, which is an established electrochemical internal standard, to determine the charges of the oxidative process. However, deviation in its behavior was observed due to its probable interactions with the IL.<sup>23</sup> We then decided to use a cathodic peak as a reference point because its electrochemical behavior is now almost established, *i.e.*, a one-electron reduction process.<sup>7</sup> Rate-dependent CV scans were recorded for the aqueous



We followed the scan rate-dependent variation in the charge ratio under anodic to cathodic (Ca/Cc) peaks, as plotted in Fig. 5. The Ca/Cc ratio initially increased and was then saturated at higher scan rates. The saturation point is the time frame in which we can trace the exact concentrations of the formed carbene before it decays, and therefore, charges at that point can be correlated with the cathodic peak. Interestingly, the Ca/Cc ratio at the saturation point is close to two, and by considering the one-electron reduction process associated with the cathodic peak, it can be rationalized that carbene electrooxidation can be a two-electron process. It is clear that the carbene is a strong ligand and has a lone pair of electrons at the C2 position that can be easily oxidized.<sup>24,25</sup>

However, this is contradictory to the single electron oxidation reported for carbene.<sup>23,26</sup> One-electron oxidation of carbene therein can be justified based on the stability provided to oxidize species with what is available in their surroundings, such as the  $CO_2$  radical. The current study further focuses on the effect of the surrounding medium on stability and the mechanism of carbene oxidation. Because no extra trapping agent has been used in this study, the electrochemical performance observed here can be comparable to nascent carbene. This infers that carbene electrooxidation is a two-electron process.

Previous reports have emphasized the influence of water on the formation and stability of carbene.<sup>11,16–18,27</sup> To elucidate the role of water in stabilizing the carbene, we performed identical experiments with pure IL. In the case of pure [EMIM][EtSO<sub>4</sub>], the anodic peak disappeared, suggesting that the carbene that formed due to the reduction of [EMIM][EtSO<sub>4</sub>] is highly reactive and is immediately replaced. Carbene formation occurs in pure ionic liquid with H-bonded and networked



Fig. 4 CV scan recorded using pure [EMIM][EtSO<sub>4</sub>]. Scan rate –100 mV s<sup>-1</sup>.



**Fig. 5** (A) Scan rate-dependent variation of the anodic to cathodic charge ratio (Ca/Cc) for [EMIM][EtSO<sub>4</sub>] in aqueous solution. (B) Variation of anodic and cathodic current with scan rate for [EMIM][EtSO<sub>4</sub>] in aqueous solution.

cation–anion interactions. The highly basic nature of anions weakens the C2–H bond, and the subsequent proton abstraction results in carbene formation. Addition of water disturbs the cation–anion network and solvates these anions so that there is a reduced probability of carbene formation.

Water molecules preferentially interact strongly with the anion of ILs.<sup>28</sup> Water can also interact with the cation (H2, H4, and H5) through H-bonding as well as ion pairs. However, the order of the interaction of water increases according to the order of the ion pair < cation < anion. The amount of water in the mixture significantly affects the rates and selectivity of reactions.<sup>11,16,27,29</sup> It has been further proposed that addition of a proton donor such as water can protonate the carbene and stabilize the IL by shifting the equilibrium towards the ion pair.<sup>11,15,16</sup> Therefore, the presence of water molecules reduces the probability and stability of the carbene formed. Contradictorily, increased stability of carbene in pure IL was observed and attributed to hydrogen bond formation between the carbene and protonated anion or cation.<sup>30</sup> However, all these investigations involved the influence of water on the anion basicity, where water modifies the anion basicity, and hence, the driving force of carbene formation.

Oldamur et al. systematically demonstrated the nature of the reactive species and the role of water towards the stability of the reactive species formed.<sup>18</sup> It was proposed that carbene interacts with water through H-bonds, and a stable carbene-water bridging complex is subsequently formed. Interestingly, the stability of the water-associated carbene complex depends on the amount of water. At a higher water content, the bridging complex is converted into a hydrolysed ring open product.<sup>18</sup> Migliorini et al. observed the influence of water on the reactive species formed, the stability of which depends upon the amount of water present.<sup>17</sup> However, the authors did not explain the exact nature of the reactive species formed in the presence of water or the role of water. Recently, Feroci et al. demonstrated the possible stability of a carbene formed in organic solution.<sup>14</sup> They proposed that not only is the hydrogen bond formation ability involved, but the nature of anion and solvent polarity also play an important role in stabilizing the carbene. However, a study showed that the formation of the carbene in polar medium is unfavourable.<sup>31</sup>

We determined the effect of solvent polarity on carbene formation and stability by using water and methanol (hydrogen bond donor solvents), and DMSO and acetonitrile (hydrogen bond acceptor solvents). The CV scans recorded using [EMIM][EtSO<sub>4</sub>] in the above solvent systems are depicted in Fig. 6. Anodic peaks were noted with water and methanol used as solvents, while we did not observe any peaks for the DMSO and acetonitrile systems. This implies that the polar protic solvent provides stability to the carbene formed. We developed a possible mechanism for hydrogen bond formation (see Fig. 7) as (1) protonated anion (EtSO<sub>4</sub>H) forms H-bonds with carbene, and (2) all the solvents chosen here also have the capability to develop H-bonds. We ruled out the possibility of mode (1) because if it had been operative, then it would have also been effective with pure [EMIM][EtSO<sub>4</sub>]. Secondly, preferential interaction of anion with solvent and low concentration of IL reduces the possibility of anion-carbene interaction.<sup>25</sup> In mode (2), all the solvents are H-bond acceptors. Polar solvents



Fig. 6 CV scans recorded using 0.17 M [EMIM][EtSO\_4] in different solvent medium with a scan rate of 100 mV  $s^{-1}\!.$ 



Fig. 7 Possible interactions between the carbene and anion in different solvents.

favour the formation of ion pairs more than neutral species, and therefore, they avoid carbene formation, despite the polar nature of water and the methanol that stabilized the carbene.

Hence, the stabilization of carbene can be understood by the development of H-bonds (donor) with water and methanol. Both water and methanol establish H-bonds with the carbene and reduce its effective electron density on hypovalent carbon. Due to the involvement of a lone pair of carbene in H-bond, its reactivity was also decreased, and hence, comparatively more stable. Therefore, [EMIM][EtSO<sub>4</sub>] IL can produce a stable carbene in aqueous solution. Other imidazolium-based ILs may also show similar behavior, provided that their structural aspects and ion pair combination favours the redox process and induces carbene formation.

To confirm this prospect, we performed CV investigations on another two ILs with the same cation but different anion by varying their basicity, *i.e.*, [EMIM][HSO<sub>4</sub>] and [EMIM][BF<sub>4</sub>], and compared them with [EMIM][EtSO<sub>4</sub>]. Fig. S2 (ESI<sup>†</sup>) depicts the comparative CV scans recorded using these three ILs in their aqueous solutions. As can be seen, similar to [EMIM][EtSO<sub>4</sub>], [EMIM][HSO<sub>4</sub>] also shows similar electrochemical behaviour, whereas for [EMIM][BF<sub>4</sub>], no redox characteristics were exhibited for carbene formation or for its oxidation. This may be due to less basicity as compared to the [EtSO<sub>4</sub>]<sup>-</sup> and [HSO<sub>4</sub>]<sup>-</sup> anions, and hence, it was unable to produce the carbene. However, considering the CV of [EMIM][HSO<sub>4</sub>], the appearance of cathodic

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and anodic peaks clearly confirmed that the ILs can produce relatively stable carbenes in their dilute aqueous solutions. Further study to explore the comparative catalytic activity of carbene generated in aqueous solution is in process.

## Experimental

#### Materials

1-Methylimidazole, 1,2-dimethylimidazole, diethyl sulfate, sodium tetrafluoroborate, and sodium bisulfate were procured from Sigma-Aldrich Co. 1-Methylimidazole and diethyl sulfate were distilled, and sodium tetrafluoroborate and sodium bisulfate were dried in an oven prior to their use in experiments. Toluene, ethyl acetate, methanol, DMSO, and acetonitrile were obtained from Merck Co. and used as procured. Deionised water (with resistivity 18.2 M $\Omega$  cm<sup>-1</sup>) was used throughout the work.

#### Synthesis of ionic liquids

All ILs employed in this study were synthesized by following the established procedures reported in the literature.<sup>32–34</sup>

(1) [EMIM][EtSO<sub>4</sub>] and [EMMIM][EtSO<sub>4</sub>]. 1-Methylimidazole/ 1,2-dimethylimidazole (1 mol  $L^{-1}$ ) was placed in an ice-cold bath containing 10 ml of toluene followed by the drop-wise addition of diethyl sulfate (1 mol  $L^{-1}$ ). Following continuous stirring for 4 h, the upper organic layer was carefully decanted. Furthermore, the liquid layer was dried in a rotary evaporator under vacuum at 343.15 K.

(2) **[EMIM][HSO<sub>4</sub>] and [EMIM][BF<sub>4</sub>].** These ILs were synthesized using two steps: quarterisation reaction and metathesis. In the quarterisation reaction, 1-methylimidazole was added to excess haloalkane (1-bromoethane) (1:1.2) in a round-bottom flask. This mixture was maintained at 343.15 K with a reflux condenser for 12 h. Thereafter, unreacted starting material was removed from the mixture by washing it with ethyl acetate several times. The quaternized product was used for the metathesis process after drying it under vacuum for 12 h at 343.15 K.

In the metathesis, for [EMIM][BF<sub>4</sub>], tetrafluoroboric acid (48 wt% in water, 1 mol) was added to the stirred solution of quaternized product (1 mol) obtained from the first step in acetonitrile. For [EMIM][HSO<sub>4</sub>], sulphuric acid (99%, 1.07 mol) was added in a dropwise manner to the stirred solution of quaternized product (1 mol) obtained from the first step in acetonitrile. The reaction mixture was then refluxed for 48 h at 343.15 K. Excess solvent was removed by drying the reaction mixture in a rotary evaporator at 343.15 K.

Finally, the obtained products were dried under high vacuum for 24 h at 343.15 K prior to each experiment. The water content of the ionic liquids was measured by a Karl–Fischer coulometer and was observed below to 50 ppm. The purity of all the synthesised ionic liquids was ensured by analysis of <sup>1</sup>H-NMR spectra (given in the ESI<sup>†</sup>).

#### Cyclic voltammetric investigations

Cyclic voltammetric (CV) investigations were performed using a CHI 660E (compliance voltage:  $\pm 13$  V) electrochemical workstation in an airtight glass cell composed of three electrode systems, with a Pt disc (2 mm diameter) as the working electrode, and Ag/AgCl (3 M KCl) and Pt mesh as the reference and counter electrodes, respectively. The Pt disc electrode was cleaned by sequentially polishing on 0.3  $\mu$ m and 0.05  $\mu$ m alumina powder followed by electrochemical cycling at 1 V s<sup>-1</sup> scan rate in 0.1 M H<sub>2</sub>SO<sub>4</sub> solution until stable characteristic features for Pt were obtained. Then, the electrode was washed with copious amounts of de-ionized water, acetone, and methanol, and dried under vacuum. Initially, argon gas was bubbled through solutions for 30 minutes, which were also jacketed during the scans. All the potentials reported here are against the Ag/AgCl reference electrodes unless specified.

# Conclusions

The electrochemical reduction of aqueous solution of [EMIM][EtSO<sub>4</sub>] yielded relatively stable carbene. It was then followed by electrooxidation. The electrooxidation behavior of the carbene formed in aqueous solution was investigated by using the cation reduction peak as the reference process. This procedure was found to be a twoelectron process based on the charge ratio under anodic to cathodic (Ca/Cc) peaks at the saturation point. Furthermore, the relative stability of the carbene in an aqueous system was evaluated through the use of different polar solvents, which specified that the stability of water. This investigation demonstrates a novel method that can be used to stabilize the carbene in the universal solvent 'water', and hence opens up the possibilities for diverse applications.

# Conflicts of interest

There are no conflicts to declare.

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