

Ionic Liquid as an Alternative Greener Sensing Medium for the Chemical Warfare Agent

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Abstract

Greener electrochemical detection method developed for chemical warfare agent (CWA) nitrogen mustard-2 (NM-2) using room temperature ionic liquid (RTIL). The diffusion coefficient calculated for NM-2 in acetonitrile and RTIL was $1.57 \times 10^{-4} \text{ cm}^2/\text{s}$ and $1.82 \times 10^{-10} \text{ cm}^2/\text{s}$, respectively. NM-2 addition to RTIL enhanced RTIL conductivity. Moreover, heterogeneous rate constant (0.192 s^{-1}), transfer coefficient (0.231) and the number of electron involved (1.0) were deduced for NM-2 in RTIL. The calibration plot showed linearity between 2.94×10^{-5} and $1.17 \times 10^{-3} \text{ M}$ with detection limit $1.47 \times 10^{-5} \text{ M}$ ($S/N=3$). The large number of available RTIL can be used for greener detection of toxic CWAs.

Keywords: Chemical warfare agent, RTIL, Electrochemical sensor, Nitrogen mustard-2, DPSCA, Ionic liquids, Sensors

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1. Introduction

Room temperature ionic liquids (RTILs) are identified as one of the new class of solvent those offer opportunity to move away from traditional chemical processes to new, clean and green technologies in which waste stream are minimized with the goals of atom efficiency in resulting environment and cost benefits. The RTILs have the potential to provide environmentally friendly solvent for the sensing, catalytic as well as synthetic applications. The RTILs environment is very different to that of normal polar and nonpolar organic solvents; hence, both the thermodynamics and the kinetics of chemical reaction are different, and so the outcome of reaction may also be different.

RTILs typically consist of two asymmetrical ions of opposite charges that only loosely fit together (usually bulky organic cations and smaller anions). Recently, novel ion selective sensors, gas sensors and biosensors based on RTILs are reported. In addition, RTIL gels were found to have good biocompatibility with enzymes, proteins and even living cells [1–3].

The entire ionic composition of RTILs eliminates the need to add supporting electrolyte. Moreover, their intrinsic conductivity, huge electrochemical potential window and negligible vapor pressure made RTILs as unique medium to use in the development of stable electrochemical sensing methodologies for gaseous analytes such as O_2 , CO_2 , and NH_3 [4–10]. Compared to conventional organic solvents, the use of RTILs for sensing medium has a number of advantages as determined by the unique combination of their properties. RTILs comprising of fully quarternized

nitrogen cations have negligible vapor pressure along with nonflammability. These properties are significant when addressing the health and safety concerns associated with many molecular solvent applications. The novel features of RTILs make them as good sensing medium, in addition, it is also possible to design an appropriate RTIL depending on specific application; hence, the term “designer solvents” also given to them. It is also possible to fine tune the properties of a RTIL by the variation of the length and branching of the alkyl group incorporated into the cation.

Numerous applications of RTILs are reported in the literature; however, the electrochemistry group led by Compton very extensively characterized many RTILs and suggested their utility as an alternative medium for the electrochemical sensing of gases and other compounds [11–22]. So far no electrochemical report is available for the detection of a chemical warfare agent using RTIL as sensing medium. Hence, in the present work we report the utilization of RTIL triethyl sulfonium bis (trifluoromethyl sulfonyl) imide (TSBTSI) first time for the sensing of chemical warfare agent nitrogen mustard-2 (NM-2) as its determination is vital due to its ill effects on the human beings as it falls in the schedule-1A of chemical weapons convention [23]. In this study, RTIL with and without NM-2 was characterized electrochemically using cyclic voltammetry (CV), double potential step chronoampermetry (DPSCA), fast scan linear sweep voltammetry (FSLSV) and electrochemical impedance spectroscopy (EIS) so as to develop a simple, field deployable and long term continuously usable detection methodology for NM-2. In addition to above, electrochemical studies of ferrocene and water are

also conducted in order to know the stability of the quasi reference electrode and effect of water on the detection with RTIL. In this work RTIL was used to avoid the shortcomings those are associated with conventional organic solvents such as using supporting electrolyte, lower electrochemical potential window, frequent change of sensing medium due to more volatility, inflammability etc.

2. Experimental

2.1. Chemicals and Reagents

RTIL triethyl sulfonium bis (trifluoromethyl sulfonyl) imide (TSBTSI) and Ferrocene are received from Sigma-Aldrich and used as received. Chemical warfare agent NM-2 ($C_5H_{11}Cl_2N$) was synthesized in our establishment by the trained chemist and all other chemicals and reagents used were AR grade.

2.2. Instruments and Electrochemical Studies

Electrochemical studies were performed using Potentiostat/Galvanostat with frequency response analyzer (Autolab-302 with FRA-II, The Netherlands) at a temperature of $25 \pm 2^\circ C$ in a three electrode cell system consisting of a platinum working; platinum quasi reference and platinum spiral counter electrodes. It is note worthy to mention here about the use of platinum as quasi reference electrode in many earlier studies [13, 24]. Moreover, in this study redox behavior of ferrocene was also performed in RTIL in the potential window between -0.5 and 0.7 V. CVs were performed using 50 mV/s as scan rate in RTIL between 0 and $+2.0$ V for oxidation and between 0 V and -2.2 V for reduction studies.

For all experiments, before each voltammetric scan the electrode was preanodized for 30s at $+2.0$ V. Here, degassing of RTIL was not performed, as the present developed methodology is to be adopted for the sensing of NM-2 in the field condition, moreover, the RTIL used here is air and water stable and it is also insoluble in water. The electrochemical studies are performed in the declared facility with appropriate protective measures in a fume hood (*Caution: NM-2 is a chemical warfare agent and proper care should be taken while handling*). Appropriate decontamination was done to avoid toxicity after every experiment with NM-2. EIS studies with and without NM-2 in the RTIL was performed with same electrochemical cell setup used for CV studies. EIS study was performed in the frequency range between 0.1 Hz and $10\ 000$ Hz. DPSCA experiments are performed in the potential window of $+2.0$ V to -2.2 V for reduction studies. Moreover, FLSV experiments also conducted using the same electrode configuration and cell so as to sense NM-2 instantly at a scan rate of 1 V/s from $+2.0$ V to -2.0 V. After performing the experiments, electrodes are washed thoroughly with Mill-Q water, dried in hot air and sonicated for two minutes and again dried before using them for next work in the RTIL.

3. Results and Discussion

3.1. Redox Behavior of Ferrocene in RTIL

To our knowledge no report is available in the literature for the redox behavior of ferrocene in the RTIL used in this study. Hence, we have conducted electrochemical experiments in order to know the redox behavior of ferrocene (20 mM) in this RTIL against quasi platinum reference electrode with a platinum working electrode. The resultant CV for the scan rate 50 mV/s is presented as inset figure of Figure 1A. In the inset figure indicated as Figure 1a, in the forward scan a peak for the oxidation of ferrocene is observed at 0.26 V and in the reverse scan its reduction peak is observed at 0.19 V, indicating involvement of one electron transfer in the redox behavior. Moreover, scan rate variation study showed a diffusion controlled process for the oxidation of ferrocene in the potential window studied and the calculated diffusion coefficient from chronoamperometric study was 0.920×10^{-8} cm²/s and this value is one order lesser than with an earlier report [16] and this may be due to the use of different RTIL in the present study.

3.2. Oxidation of NM-2 on Platinum

Figure 1A shows CVs obtained with a platinum electrode in the RTIL TSBTSI between 0 and $+2.0$ V without (Figure 1Aa) and with NM-2 of 5.88×10^{-4} M (Figure 1Ab). In Figure 1Aa two peaks are observed during the forward scan at 1.14 V (6.5 μ A) and 1.47 V (12.1 μ A) in RTIL and the reverse scan also exhibited one peak at $+0.53$ V (3.4 μ A). These peaks are probably due to the formation of platinum oxide on the electrode surface as reported earlier in a RTIL and aprotic solvent [20, 25]. However, after the addition of 5.88×10^{-4} M NM-2 (Figure 1Ab), three peaks were observed in the forward scan at 1.13 V and 1.47 V as in the case of RTIL and a new peak at 1.68 V with huge peak current. The peak at 1.14 V is shifted to 1.13 V (probably due to the interaction between NM-2 and RTIL) and the peak at 1.47 V is unaltered. The new peak arising at 1.68 V is due to the oxidation of NM-2 as only NM-2 was added to RTIL, probably due to the dechlorination of chloride ions from NM-2. It is note worthy to discuss here about earlier reports [22, 26] where chloride ion oxidation was conducted in other RTILs with different working electrodes. In the reverse scan, three peaks are observed at 1.59 V (18 μ A), 0.98 V (1 μ A) and 0.13 V (18 μ A) and this observation is in agreement with earlier studies [22, 26]. The tentative mechanism of NM-2 oxidation based on earlier reports is given below



In order to know the nature of electrochemical process of RTIL with platinum electrode, scan rate variation studies were carried out from 25 mV/s to 150 mV/s with an increment of 25 mV/s. The resultant CVs are shown in Fig.1B and

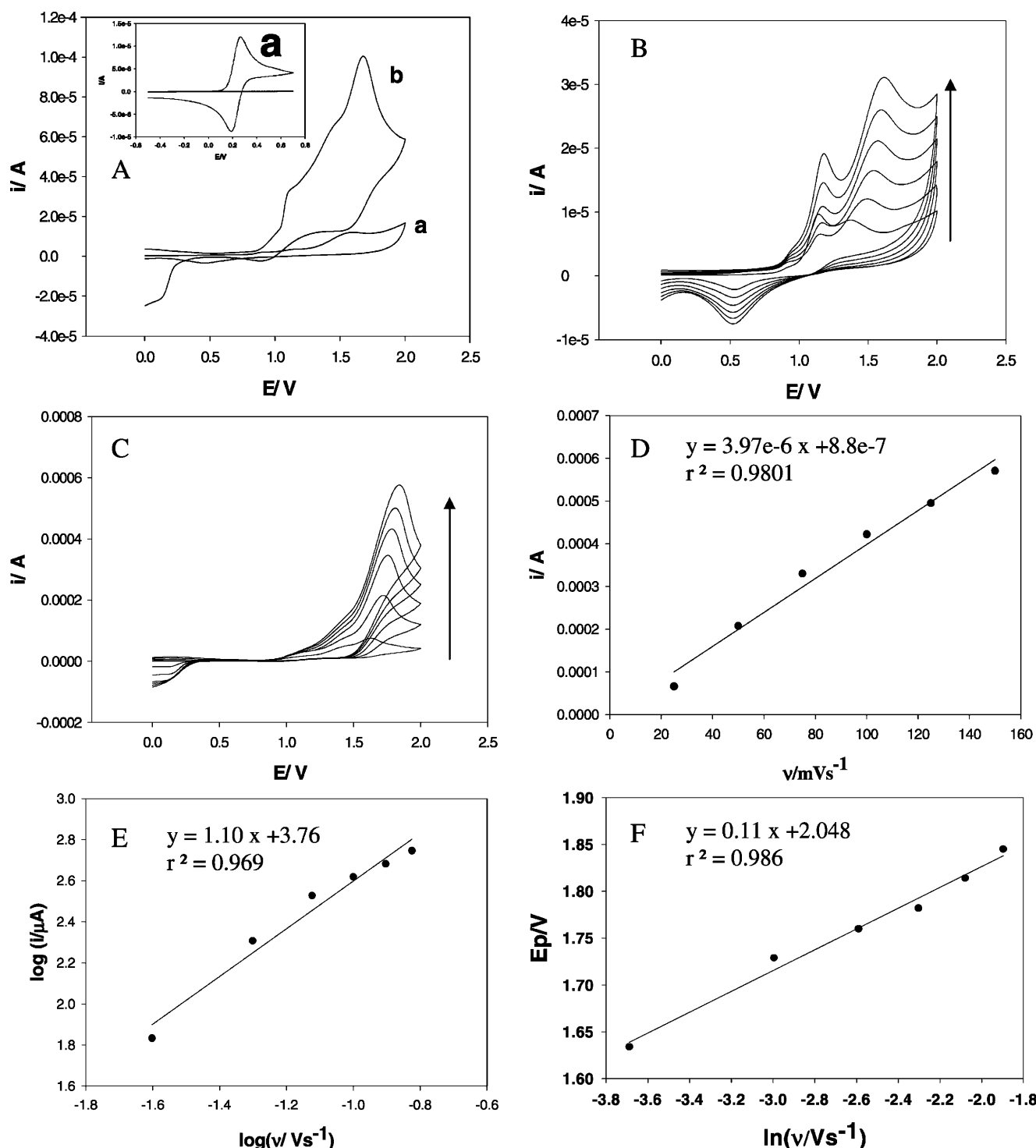


Fig. 1. CVs for (A) (a) RTIL and (b) RTIL with 5.88×10^{-4} M NM-2. Scan rate 50 mV/s vs. Pt quasireference electrode. Inset figure shows the redox behavior of 20 mM Ferrocene. (B) Effect of scan rate on RTIL oxidation (Scan rate: 25 mV/s to 150 mV/s with 25 mV/s increment). (C) Effect of scan rate on NM-2 (5.88×10^{-4} M) oxidation in RTIL (Scan rate: 25 mV/s to 150 mV/s with 25 mV/s increment). (D) Peak current vs. scan rate plot for NM-2 (5.88×10^{-4} M) oxidation in RTIL. (E) $\log i$ vs. $\log v$ plot for NM-2 (5.88×10^{-4} M) oxidation in RTIL. (F) E_p vs. $\ln v$ plot for NM-2 (5.88×10^{-4} M) oxidation in RTIL.

an increase in peak current was observed as scan rate was increased with all the peaks observed in forward and reverse scans. Analysis of the data by plotting the current versus scan rate variation profile exhibited good linearity with all

peaks observed in the forward and reverse scan indicating adsorption controlled processes for all observed peaks. Moreover, the scan rate variation studies (Figure 1C) conducted with NM-2 (5.88×10^{-4} M) in RTIL also exhib-

ited adsorption controlled processes for all peaks similar to RTIL alone (Figure 1D). To further confirm the NM-2 oxidation peak, $\log i$ vs. $\log \nu$ graph was plotted (Figure 1E) and the slope value was found to be 1.10, this confirms involvement of an adsorption controlled process during the oxidation [27].

The plot of E_p versus $\ln \nu$ is exhibiting linear relationship as shown in Figure 1F for the potential scan rate ranging from 25 to 150 mV s⁻¹, with the following linear equation $E_p = 0.11 \ln \nu + 2.048$ ($r^2 = 0.986$), which confirms that the electrochemical oxidation of NM-2 is as irreversible process. According to Laviron theory [28] for an irreversible anodic reaction, the relationship between E_p and ν is described as follows:

$$E_p = E^\circ - RT/\alpha nF \ln RTk_s/\alpha nF + RT/\alpha nF \ln \nu \quad (1)$$

Where E° is the formal standard potential, α is the charge transfer coefficient, n is the number of electrons involved in the oxidation of NM-2, F is the Faraday constant (96485 C/mol), k_s is the heterogeneous reaction rate constant, R is the universal gas constant and T is the temperature. According to the slope of the straight line of E_p against $\ln \nu$, the product of α and n was calculated as 0.231. The value of E° was estimated to be 1.62 V from the intercept of E_p vs. ν plot on the coordinate by extrapolating to $\nu = 0$. Moreover, the value of heterogeneous rate constant (k_s) was calculated from the intercept of the straight line of E_p vs. $\ln \nu$ and it is found to be 0.192 s⁻¹.

On the other hand, for an irreversible adsorption controlled process, according to Laviron's theory [29] a linear relationship between the peak currents and the scan rate is described as follows:

$$i_p = nFAF\nu/4RT = nFQ\nu/4RT \quad (2)$$

Here i_p is expressed in the unit of amperes, Q is the peak area of voltammogram (coulomb), by substituting the respective value in Equation 2, and the number of electron involved in the anodic oxidation of NM-2 was found to be 1.2. This result suggests that the oxidation reaction of NM-2 is approximately as one electron transfer reaction. Therefore the value of α is 0.231.

3.3. Reduction of NM-2

Reduction of NM-2 was carried out using platinum electrode with RTIL TSBTSI between 0 and -2.2 V without (Figure 2Aa) and with 2.94×10^{-5} M concentration of NM-2 (Figure 2Ab). Three peaks are observed in the forward scan, one peak at -0.41 V (6.2 μ A), second peak at -1.221 V (5.0 μ A) probably due to atmospheric oxygen reduction and third peak starting at -1.82 V is probably due to the reduction of cation and is extending up to -2.2 V (14.2 μ A) in RTIL, in addition, no peak is seen in the reverse scan (Figure 2Aa). However, upon addition of 2.94×10^{-5} M NM-2, two peaks are observed in the forward scan one at

-0.03 V (13 μ A) and another prominent peak is observed starting from -1.54 V and this peak extended up to -2.2 V with huge peak current of 195 μ A and this is due to reduction of NM-2 on Pt electrode along with atmospheric oxygen and RTIL cations reductions. The peak potential of NM-2 reduction observed at -1.54 V shifted towards positive side up on increasing NM-2 concentration with increase in peak current (Figure 2Ac-d). Moreover this peak current is very less in absence of NM-2 in RTIL so it confirms this peak as NM-2 reduction peak. It is note worthy to mention here about the similar kind of reduction peak reported for chloride ion in another RTIL [26]. Here, NM-2 is having two chloride ions and this may be reason for the reduction peak with NM-2. To check further whether this peak is due to moisture, we deliberately added water (0.22 M) with RTIL containing NM-2, we observed a 50 % decrease in this CV peak current (not shown) along with peak shifting towards negative potential (-1.69 V) probably due to the reaction of water with NM-2. However, again we deliberately added water (0.22 M) to blank RTIL, we observed four peaks in the forward scan at -0.1 V (27 μ A), -0.55 V (33 μ A), -1.5 V (23 μ A) and a peak starting from -1.89 V and this peak extended up to -0.2 V with a peak current of 85 μ A (Figure 2Bb) and this may be due to the reduction of water as reported earlier in RTILs [30, 31]. Moreover, in the reverse scan two peaks are observed at -0.5 V and -1.0 V, this may be due to the oxidation of reduced species in the forward scan. From the above results of a peak potential difference of 0.38 V is observed between RTIL-NM-2 (0.0294 mM, 195 μ A) and RTIL-water (0.22 M, 85 μ A) along with current increase at -2.2 V. This again confirms the peak with NM-2 in RTIL as the reduction peak for NM-2 and not due to the reduction of water reported for in another RTIL [32].

3.4. EIS Studies of NM-2 in RTIL

EIS is an effective tool for studying the interface properties of electrodes [33]. The Nyquist plot without (Figure 3a) and with NM-2 (Figure 3b) is presented. Analysis of experimental impedance data was performed by fitting the data in software provided with Autolab FRA-II. Figure 3a, exhibited solution resistance (380 ohm), CPE (constant phase element) ($0.4016 e^{-6}$) and n ($0.9463 e^{+00}$), however, after the addition of NM-2 (Figure 3b), a decreased solution resistance (343 ohm) was observed in addition to an increased CPE ($0.5058 e^{-6}$) and n ($0.9557 e^{+00}$) values when compared to RTIL alone. The changes occurred here is probably due to the interactions between RTIL and NM-2.

3.5. DPSCA Studies with NM-2 in RTIL

Adsorption controlled process is observed for NM-2 redox studies from CV data. It is well known that DPSCA is used to characterize the adsorption controlled process [34]; hence, DPSCA studies are performed with NM-2 reductive

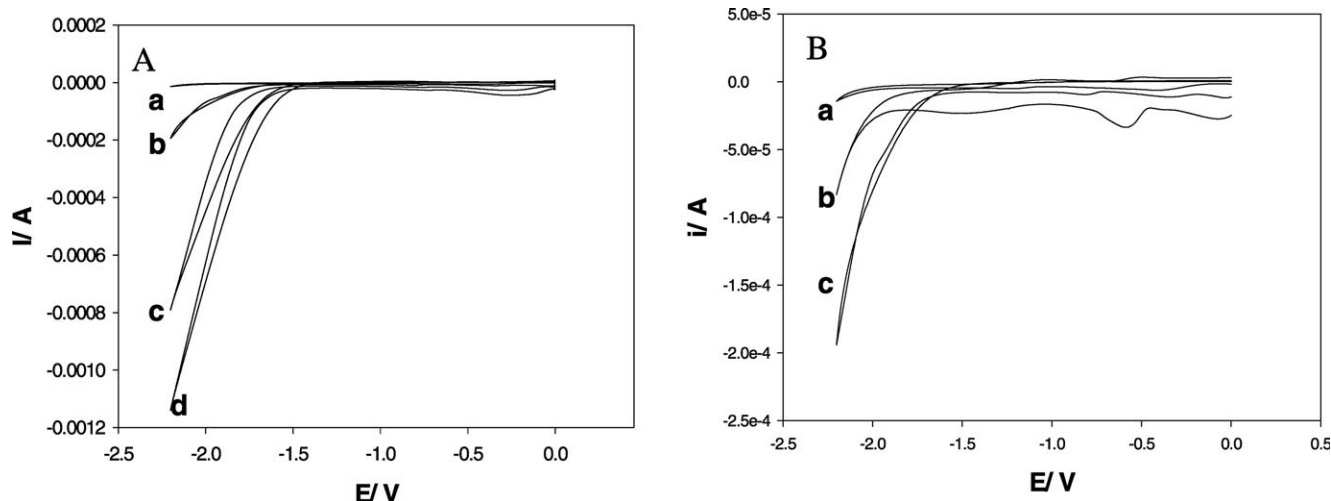


Fig. 2. CVs for (A) (a) RTIL (b) 2.94×10^{-5} M NM-2 (c) 2.94×10^{-4} M NM-2 and (d) 5.88×10^{-4} M NM-2. (B) Effect of water on RTIL (a) RTIL (b) 0.22 M water in RTIL and (c) 2.94×10^{-5} M NM-2 in RTIL.

process and the results of reductive part is used for the diffusion coefficient (D) calculation and for the construction of calibration plot for NM-2.

In order to get more information about the cathodic reduction of NM-2, DPSCA experiment was carried out with NM-2 between 2.94×10^{-5} and 1.17×10^{-3} M and the resultant data is used to calculate the D of NM-2 in RTIL. The results showed an increase in current upon increase of concentration of NM-2 as shown in Figure 4A for a potential step of -2.0 V vs. Pt quasireference electrode. The chronocoulometric method [35, 36] is suitable for determination of diffusion coefficient in adsorption controlled process, according to the following equation:

$$Q = \{2nFAC(Dt)^{1/2}/\pi^{1/2}\} + Q_{dl} + Q_{ads} \quad (3)$$

Where Q is the amount of charge in coulombs that has passed at time t , D and C are diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) and bulk concentration of NM-2, respectively; A is the

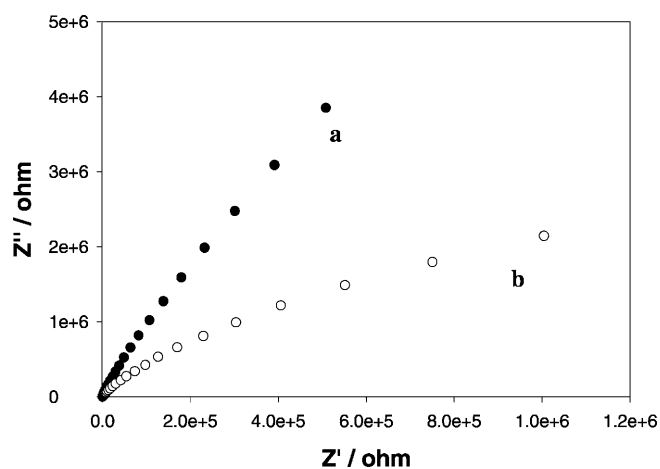


Fig. 3. EIS Nyquist plot for NM-2 (a) RTIL and (b) RTIL with 5.88×10^{-4} M NM-2.

electrode area (0.070 cm^2); Q_{dl} is double-layer charge (integration of charging current), Q_{ads} the faradaic component given to the reduction of adsorbed species. The graph was plotted between Q vs. $t^{1/2}$ for different concentrations. From the slope, the value of diffusion coefficient was determined ($D = 1.82 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$).

3.6. Comparison of Molecular Solvent and RTIL as Sensing Medium

In this work an attempt was made to compare the electrochemistry of NM-2 in RTIL and in conventional molecular solvent (Acetonitrile-TBAP) in order to see the differences. In RTIL the value of D is $1.82 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and in molecular solvent it is $1.57 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ and this observation is due to higher viscosity of the RTIL (15–50 cP) when compared to that of water (1.00 cP) and other molecular solvents. Based on the above D values, current response in molecular solvent should be more because D value is more and the same is observed here with CV and DPSCA studies, hence, one can conclude that the molecular solvent as the most suitable medium for sensing purpose. Though molecular solvent exhibited higher D value and current response, one can not use this as sensing medium for longer time duration due to its high volatility, inflammability in addition to its requirement of supporting electrolyte, frequent replacement and lesser potential window. The above shortcomings make it difficult to use the molecular solvents in field condition. RTILs generally overcomes all these drawbacks encountered with molecular solvents due to their high thermal stability, negligible vapor pressure (solvent evaporation is eliminated, reducing the need for respiratory protection and exhaust system) and reusability, makes RTILs very suitable to use as sensing medium in the field condition.

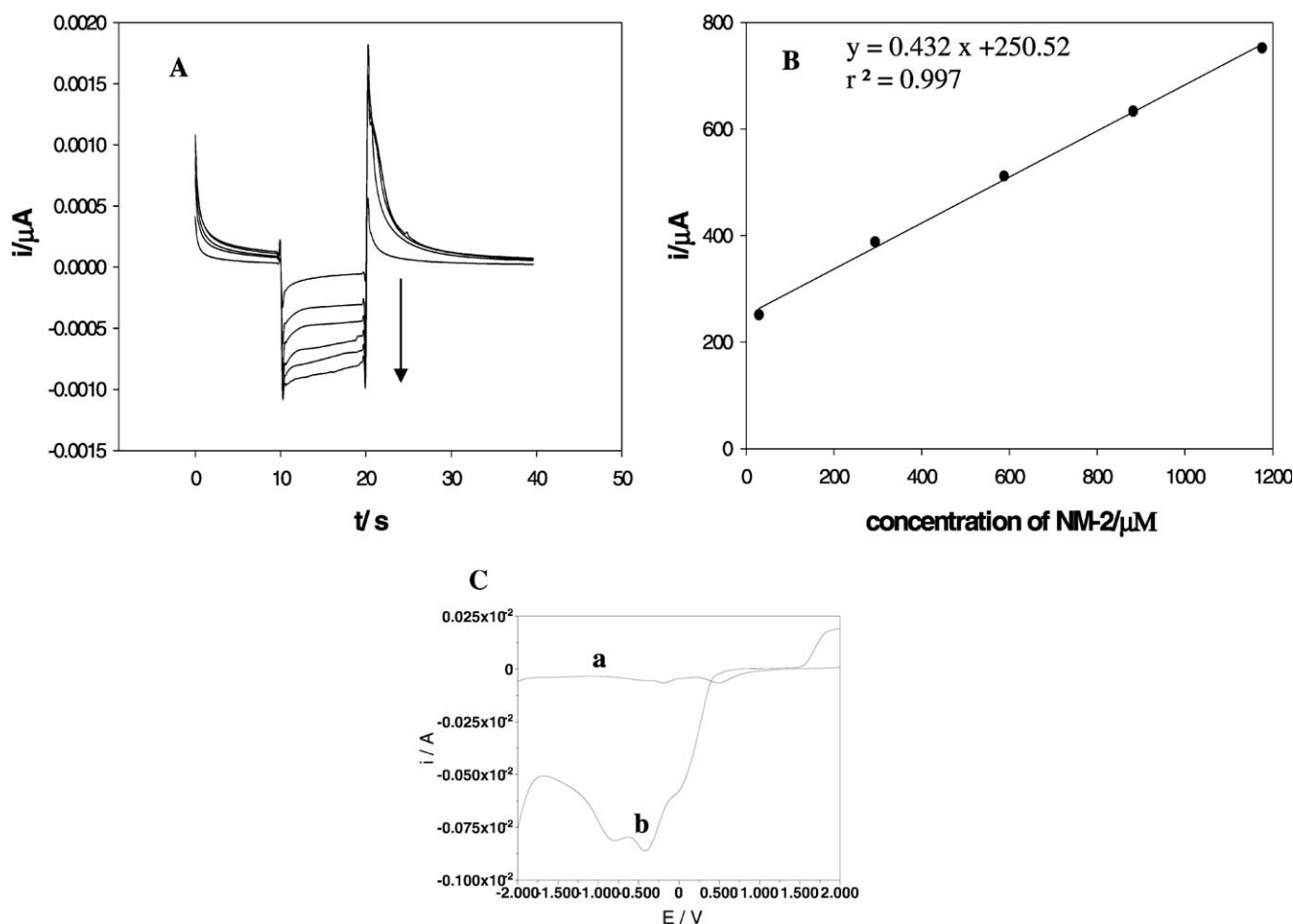


Fig. 4. DPSCA current–time curves obtained for different concentration of NM-2 in RTIL. (A) Reduction current of NM-2 for concentrations: 2.94×10^{-5} M, 2.94×10^{-4} M, 5.80×10^{-4} M, 8.82×10^{-4} M and 1.17×10^{-3} M; (B) DPSCA calibration plot for NM-2 by using the reduction current of Fig. 4A. NM-2 concentration: 2.94×10^{-5} M, 2.94×10^{-4} M, 5.88×10^{-4} M, 8.82×10^{-4} M and 1.17×10^{-3} M. (C) FLSV for (a) RTIL and (b) RTIL- NM-2 (2.94×10^{-4} M).

3.7. Calibration Curve

Two kinds of calibration plots are constructed based on the data of concentration variation studies with CV and DPSCA. DPSCA (Figure 4A) is found to be more sensitive when compared to CV based calibration plot for NM-2. It is probably due to the in-situ electrode cleaning of adsorbed species during the potential step applications. So finally we have chosen DPSCA method to make calibration plot (Figure 4B) for NM-2 determination.

DPSCA recorded with different concentration of NM-2 showed peak current increase as the concentration increased. A calibration plot made (Figure 4B) by using the reduction currents (Figure 4A) against concentration of NM-2 exhibited linearity over the concentration range of 2.94×10^{-5} to 1.17×10^{-3} M with a correlation coefficient of 0.997 and a detection limit of 1.47×10^{-5} M ($S/N=3$). To know the repeatability of proposed method, the coefficient of variation of 4 times measurement of peak current of 2.94×10^{-5} M NM-2 was calculated to be 1.25%, which demonstrates the good repeatability of method.

3.8. FLSV Studies of NM-2 in RTIL

Figure 4C shows the FLSV for the RTIL and NM-2 reduction in RTIL in the potential region from +2.0 V to -2.0 V with a scan rate of 1 V/s. An increase in current after adding 2.94×10^{-5} M NM-2 is observed (Figure 4Cb) as reported earlier for detection of chloride ion in another RTIL [22]. This is the first study which utilizes RTIL as sensing medium for a chemical warfare agent, especially blistering chemical warfare agent (NM-2). Now efforts are going on in our establishment to use this methodology for the sensing of NM-2 and other chemical warfare agents using micro liter volume of this RTIL and other RTILs in addition to the development of field portable sensing system for the detection of chemical warfare agents.

4. Conclusions

The redox studies of NM-2 are performed in RTIL first time. DPSCA and FLSV study were utilized for the sensing of

NM-2. The detection time required for the NM-2 is less than 20 seconds. This study brings a way for the utilization of RTILs as alternative greener medium for the sensing of chemical warfare agents without modifying electrode surface due to the extended potential window and other unique properties of RTILs. Certain RTILs can work under any field condition as sensing medium for years together due to the low volatility and negligible vapor pressure when compared to molecular solvents.

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