Determination of Ammonia Based on the Electrochemical Oxidation of *N,N'*-Diphenyl-1,4-phenylenediamine in Propylene Carbonate

Xiaobo Ji and Richard G. COMPTON[†]

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

The oxidation of *N,N'*-diphenyl-1,4-phenylenediamine (DPPD) has been studied by cyclic voltammetry at glassy carbon electrodes in propylene carbonate. Next, the reaction between ammonia and DPPD was similarly investigated. It has been shown that ammonia reversibly removes protons from oxidized DPPD molecules, thus facilitating the oxidative process with the emergence of a new wave at less positive potentials. The results suggest a novel methodology for the electrochemical determination of ammonia based on its interaction with DPPD in propylene carbonate. The measurement of the current of the new wave is shown to scale linearly with the ammonia concentration up to *ca.* 200 ppm and above.

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Introduction

Given its high toxicity, the determination of ammonia is essential to a number of applications including environmental protection, clinical diagnosis, industrial processes, food processing and power plants.^{1,2} Ammonia detection is also important for the diagnosis of diseases such as renal inadequacy and diabetes.³ Another important arena for ammonia determination is in water samples where it indicates organic material decomposition, which can be harmful to human health, whilst higher ammonia levels are of analytical interest in industrial operations such as refrigeration or fertilizer manufacture.^{4,5}

Chemical sensors provide vital sensing platforms for monitoring in a large plethora of technologies and applications, which include safety, pollution, medical engineering and industrial processes.⁶ Sensors need to be fast, specific, reliable, sensitive, low cost and have the possibility for miniaturisation.^{2,6,7} For such sensor designs, electrochemical strategies are advantageous due to their rapid response and their inherent low cost but high sensitivity.^{8–11}

Generally in the above sensor designs, including those for ammonia, the electrolyte employed is water based. The appreciable water vapour pressure inevitably means that the sensor will dry out over time so limiting the lifetime at typical operating temperatures and restricting the sensor reliability. The volatility of the water can be reduced by the use of high concentrations of sulphuric acid as an electrolyte but this places significant constraints on the voltammetry possible. In the context of ammonia sensing, the ammonia will be converted into the electro inactive NH_4^+ ion: alternatives are clearly desirable. In particular, to the best of our knowledge, there are very few studies exploring the oxidation of ammonia in non-aqueous

systems where there is scope for low volatility solvents to be employed in an attempt to overcome the sensitivity of sensor to moisture and humidity.

In the present report, we have investigated the electrochemical oxidation of *N,N'*-diphenyl-1,4-phenylenediamine (DPPD) in propylene carbonate (PC) at glassy carbon (GC) electrodes. Next the reaction between ammonia and DPPD has been explored and a new oxidation wave was formed at *ca.* +0.3 V (vs. Ag wire). We report the effect of ammonia as a proton acceptor species on the anodic oxidation of DPPD in the aprotic solvent PC. The aim of this work was to investigate whether the acid-base equilibrium between ammonia and either DPPD or its oxidized form could be used for ammonia sensing. Ammonia removes protons from oxidized DPPD, thus making the oxidative process occur at lower oxidizing potentials. It was found that the oxidation peak current of the new voltammetric response was linearly dependent on the concentration of ammonia, over the range up to *ca.* 200 ppm, provided sufficient excess DPPD was present, exhibiting its analytical utility for ammonia sensing.

Experimental

Chemical reagents

Propylene carbonate (Aldrich, 99.7%), *tetra-n*-butylammonium perchlorate (TBAP, Fluka), and *N,N'*-diphenyl-1,4-phenylenediamine (DPPD, Aldrich, 99%) were purchased at the highest grade available and used directly without further purification. Pure ammonia and nitrogen gas (BOC, Guildford, Surrey, UK) were used for electrochemical experiments as described below. All the solutions were vigorously degassed with oxygen-free nitrogen until oxygen was not electrochemically detectable. All experiments were carried out at a temperature of 295 ± 3 K.

Apparatus

Electrochemical experiments were performed using a

[†] To whom correspondence should be addressed.
E-mail: Richard.Compton@chemistry.oxford.ac.uk

Fig. 1 Cyclic voltammetric responses of 0.5 mM DPPD in 0.1 M TBAP with PC as the solvent using a 3-mm diameter GC electrode. Scans were run at 100 mV s⁻¹.

Fig. 2 Cyclic voltammetric responses of 0.5 mM DPPD in 0.1 M TBAP with PC as the solvent using a 3-mm diameter GC electrode at scan rates between 10 and 1 V s⁻¹.

μ -Autolab Type II potentiostat (Eco-Chemie, Utrecht, Netherlands) controlled by General Purpose Electrochemical Systems Ver. 4.7 software. For electrochemical experiments, the working electrode used was glassy carbon (GC), together with a platinum wire counter electrode, and a silver wire reference electrode. The GC was polished using diamond-lapping compounds (Kemet, UK). The electrochemical cell used was a septum sealed three-necked flask which was always held under a nitrogen atmosphere. In experiments where ammonia was utilised, the gas was directly introduced from a cylinder containing volume percentages (0.004, 0.01, 0.02, 0.1, and 1 vol% BOC Gases, Guildford, Surrey, UK) by bubbling the ammonia directly into the solution (nitrogen comprises the remaining part of all the gas mixtures).

Results and Discussion

Electrochemical study of *N,N'*-diphenyl-1,4-phenylenediamine in PC

The electrochemical oxidation of *N,N'*-diphenyl-1,4-phenylenediamine (DPPD) was first investigated by recording the cyclic voltammetry of 0.5 mM DPPD in a propylene carbonate (PC) solution supported with 0.1 M TBAP using a 3-mm diameter glassy carbon (GC) electrode.

The voltammetric response is shown in Fig. 1, where two quasi-reversible waves are clearly discernable as seen in other non-aqueous solvents.¹²⁻¹⁷

The first oxidation wave, E_p at ca. +0.53 V (vs. Ag wire), is attributed to the one electron oxidation of DPPD and at more positive potentials a further one-electron oxidation becomes favorable leading to a second oxidative wave, E_p at ca. +0.91 V (vs. Ag wire). The stability of this di-cation in the aprotic solvent, PC, was proved by continuous cyclic voltammetric scans. It was found that no new waves, either oxidation or reduction, appear on the second or subsequent scans, demonstrating that the oxidation product of DPPD is stable in PC in the experimental time scale.

Fig. 3 Cyclic voltammetric responses of 1 mM DPPD with bubbling 1 vol% ammonia for 60 s (dashed line) and without ammonia (solid line) in PC with 1 M TBAP at GC. Note that peaks I and VI only appear in the presence of ammonia.

Figure 2 shows cyclic voltammetric responses at a range of scan rates from 10 mV s⁻¹ to 1 V s⁻¹. Excellent linear relationships from the plot of the oxidative and reductive peak currents against the square root of scan rate suggest that the electrochemical processes involved solution based processes rather than surface-controlled at these scan rates.

Kinetic analysis of DPPD in the presence of ammonia in PC

Ammonia gas (1%) was bubbled into the voltammetric cell containing 2 mM DPPD in PC solution with 0.1 M TBAP for 60 s, the consequent voltammetric response was overlaid as solid line in Fig. 3.

It was found that there are three redox peaks appearing in the potential range. The electrode reaction of DPPD again appears as two one-electron steps corresponding to peaks II, III, IV, and V. In comparison with the oxidation of DPPD (shown as solid line), it was clear that after bubbling the ammonia a new pair of oxidation peaks (shown as dotted line), I and VI, appear at less positive potentials (+0.31 V vs. Ag wire and -0.15 V vs. Ag wire, respectively). In this case, on adding of ammonia to DPPD in PC, it is interesting to note that the new redox potential is not the same as that of DPPD, suggesting that the electrochemical oxidation of DPPD likely proceeds at the first place via the following electrochemical step mechanism of the EC type.

Fig. 4 Linear sweep voltammetric responses of 10 mM DPPD to increasing ammonia concentration (40, 100, 200, 400, 600 ppm) in PC (0.1 M TBAP) at GC. Insert graph: a plot of the anodic peak current at +0.3 V against concentration of ammonia (40, 100, 200 ppm). Note that the forward scan is shown in the voltammetry; if the reverse scans are made, peak VI is then visible.

In the latter process the ammonium ions are formed *via* loss of protons from the DPPD dictation to ammonia. Since DPPD is typically present at much higher level than ammonia, the EC mechanism proceeds until the ammonia local to the electrode is “titrated” away. Note that the mechanism requires the electrochemical oxidation of DPPD at GC electrodes to be an electrochemically reversible or *quasi*-reversible two-electron process.

Analytical use of the homogeneous reaction between DPPD and ammonia in PC

The cyclic voltammetric responses between -0.4 and $+0.5$ V shown were obtained at a GC electrode in a PC solution containing 10 mM DPPD with 0.1 M TBAP in the absence of ammonia and saturated with different concentrations of ammonia gas (40, 100, 200, 400, 600 ppm); the voltammetric responses are shown in Fig. 4.

The new wave indicated that the electrochemical oxidation of DPPD appears at less positive potentials with the removing protons from oxidized form in the presence of ammonia. A plot of this new oxidation peak current *versus* the ammonia concentration (see insert graph in Fig. 4) shows an excellent linear relationship, giving a sensitivity $9.62 \times 10^{-8} \text{ A ppm}^{-1}$ ($r^2 = 0.999$) and limit-of-detection 8 ppm ammonia (based on $3sb$), demonstrating the analytical ability of this homogeneous reaction.

The analytical approach above has shown that the propylene carbonate solution containing DPPD can be beneficially used as the working electrolyte in ammonia gas sensors. Generally in

Fig. 5 Linear sweep voltammetric responses of 10 mM 1,2-dihydroxybenzene to increasing ammonia concentration (20, 40, 50, 60 ppm) in PC (0.1 M TBAP) at GC. Insert graph: a plot of the anodic peak current at +0.33 V against concentration of ammonia (ppm).

the gas sensor design, the electrolyte employed is water based. The appreciable water vapour pressure inevitably means that the sensor will dry out over time so limiting the lifetime at typical operating temperatures and restricting the sensor reliability. The volatility of the water can be reduced by the use of high concentrations of sulphuric acid as an electrolyte but this places significant constraints on the voltammetry possible. In the context of direct amperometric ammonia sensing, the ammonia will be irreversibly converted into the electro-inactive NH_4^+ ion: alternatives are clearly desirable. PC is likely a good choice for use as a solvent in commercial gas sensors given the vapour pressure of PC is 0.03 mm Hg (at 20°C) in contrast to the vapour pressure of water which is 17.5 mm Hg (at 20°C).¹⁸ The consequence is that sensor lifetime maybe greatly extended as the tendency for the sensor to “dry-out” is significantly reduced.

Extension to the reaction between 1,2-dihydroxybenzene and ammonia in PC

In order to explore the specificity, or otherwise, of the chemistry reported, we also examined the voltammetric responses of 10 mM 1,2-dihydroxybenzene in PC (0.1 M TBAP) saturated with 20, 40, 50 and 60 ppm ammonia recorded at a GC electrode by means of cyclic voltammetry. Analogous electrochemical behaviour is observed as that of DPPD in the presence of ammonia and a new wave shown in Fig. 5 generated in the presence of ammonia. The peak oxidation current was found to linearly increase with increased ammonia concentration, giving a LOD 6.5 ppm.

Conclusion

The electrochemical oxidation of *N,N'*-diphenyl-1,4-phenylenediamine (DPPD) has been investigated by cyclic voltammetry at glassy carbon (GC) electrodes in propylene carbonate (PC). Furthermore, the response of DPPD in the presence of ammonia has been examined in the PC. The above results detail a new oxidation wave observed at *ca.* $+0.15$ V (vs. Ag wire) and can be attributed to the basic ammonia removing protons from the oxidized DPPD species. In an EC process with a reversible or *quasi*-reversible E step, its analytical utility for ammonia sensing was examined in the range from 40 to 200

ppm by measuring the peak current of new wave as function of ammonia concentration with a detection limit of 8 ppm.

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