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Electrochemical Investigations of Sydnone Derivatives at Glassy Carbon Electrode

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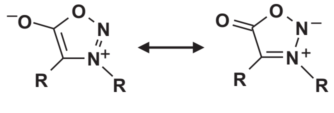
Electrochemical reduction of the –N=N– moiety of sydnone derivatives, like 3-phenyl sydnone, tolyl sydnone and anisyl sydnone, was studied using cyclic voltammetry at a glassy carbon electrode. In acid medium, the above compounds were found to show irreversible electrochemical charge transfer in the pH range studied. Electrochemical studies of these sydnones were carried out in partially aqueous media containing organic co-solvents such as acetonitrile, dimethylformamide, methanol and dimethylsulphoxide. Physical parameters such as the charge transfer coefficient and diffusion coefficient, as well as the effects of variation of the electroactive species concentration, sweep rate, organic solvents, and pH on peak parameters were studied. The reduced products were characterized by IR, NMR and mass spectral studies. The effect of surfactants on the electrochemical reduction of 3-phenyl sydnone was studied using cationic, anionic and non-ionic surfactants.

INTRODUCTION

Sydnones constitute a well-defined class of mesoionic compounds obtained by the action of acetic anhydride on nitroso derivatives.[1,2] These compounds are of interest because of the varied types of biological activity displayed by some of them.[3–5] Sydnones contain a mesoionic aromatic system, which can be depicted with polar resonance structures as shown below:[6]



Many derivatives of sydnones are reported to posses various biological activities such as anticancer, antimalarial and anti-inflammatory activities.[6–10]

Apart from this, sydnones are known to undergo 1,3-dipolar addition reactions with alkynes, resulting in the formation of pyrazoles; 1,5-diarylpyrazoles and 3,4-diaryl gamma-lactones (Celecoxib and Rofecoxib) have shown selective inhibition of the human COX–2 enzyme, acting as stimulators of the central nervous system.[11]

N-methyl sydnone, which is found to have a high dielectric constant, has been used as a solvent for lithium battery electrolyte.[12]

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The electrochemical reduction mechanism of five derivatives of 4-cyano-3-sydnones was investigated at a hanging mercury drop electrode by cyclic, linear sweep and differential pulse voltammetric methods in Britton-Robinson buffer,[13] and square wave voltammetry studies of 4-cyano-3-substituted sydnone have also been reported.[14] The glassy carbon electrode surface was found to catalyze electroreduction of 4-cyano-3-(*p*-tolyl) sydnone. A one electron reductive dimerization mechanism has been proposed at the mercury electrode.[15] Reduction of 3-phenyl-4-nitrosydnone in acetonitrile using differential pulse polarography and cyclic voltammetry has been reported.[16] Polarographic behavior of 3-substituted 4-acetyl- and 4-diazoacetylsydnones has also been reported.[15]

These observations prompted us to study the electrochemical reduction of the following sydnones, the detailed studies of which were so far not reported in the literature. The sydnones selected were: 3-phenyl sydnone **1**, 3-(*p*-anisyl) sydnone **2** and 3-(*p*-tolyl) sydnone **3**. These sydnones were prepared by the procedure reported in literature.[16,17]

EXPERIMENTAL

Reagents and Chemicals

All the compounds used in the preparation of 3-phenyl sydnones and substituted sydnones were of very high purity. 3-Phenyl sydnones used in our study were prepared in the laboratory and purified by previously published methods.[18,19] The solvents used were: acetonitrile, DMSO and DMF (Fluka AR, Switzerland) and methanol (Merck), all A.R. grade. Britton-Robinson buffer, which was used as a supporting electrolyte, was prepared by mixing acetic acid (ultra pure), H_3PO_4 and H_3BO_3, 0.04 mol dm^{-3} each. NaOH and HCl were used to get the required pH. Tetradecyl trimethyl ammonium bromide (TDTAB), and sodium dodecylsulphate (SDS) and Triton X-100 were used as anionic, cationic and non-ionic surfactants (extra pure), respectively. All solutions were prepared with doubly distilled deionized water.

Instrumentation and Apparatus

Measurements were done with a potentiostat/galvanostat AUTOLAB-100 (Eco-Chemie, Utrecht) and the analyses were made using GPES software. Experiments were performed using a one compartment three electrode system in which glassy carbon electrode (GCE) was the working electrode, saturated calomel electrode (SCE) was the reference and platinum was the auxiliary electrode.

Pretreatment of Glassy Carbon Electrode

Before each measurement, the glassy carbon surface was polished with alumina (BAS CF-1050) on an alumina polish pad (BAS MF-1040) for 50 s and then rinsed with purified water.

Effective Electrode Area

The effective electrode area was determined by chronoamperometry with a 4.0×10^{-3} mol dm^{-3} potassium hexacyanoferrate(III) solution (1 e$^-$ exchange) in 0.1 mol dm^{-3} potassium nitrate at 25° C ($D_o = 7.63 \times 10^{-6}$ cm s^{-1}). The area obtained for the glassy carbon electrode was 0.069 cm^2.

Cyclic Voltammetry

Blank cyclic voltammograms were recorded in solutions of 50×10^{-3} mol dm^{-3} of H_2SO_4 and also in 0.04 mol dm^{-3} Britton-Robinson buffer, separately, in different partially aqueous media prepared by mixing acetonitrile, methanol, DMF or DMSO with water.

All samples were purged well with nitrogen for 10 minutes to remove any dissolved oxygen before voltammetric measurements were recorded. The solutions were blanketed with a stream of nitrogen and the mixture was thermostated.

Determination of the Number of Electrons

This was carried out by controlled potential coulometry using 1.0×10^{-2} mol dm^{-3} substituted sydnone solution in 0.1 mol dm^{-3} H_2SO_4 as well as in 0.04 mol dm^{-3} Britton--Robinson buffer. The net charge was obtained by subtracting the charge of the blank from the total charge of the substituted sydnones solutions. Cyclic voltammetry and spectrophotometry were employed to monitor the coulometric experiments.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammogram of 3-phenyl sydnone at a concentration of 1×10^{-3} mol dm^{-3} in the mixed acetonitrile:water (20:80 *v*/*v*) medium using 50×10^{-3} mol dm^{-3} H_2SO_4 supporting electrolyte, at a sweep rate of 0.05 Vs^{-1}. The reduction peak of 3-phenyl sydnone was observed at –0.962 V. It was found to undergo a two-electron irreversible electrochemical reduc-

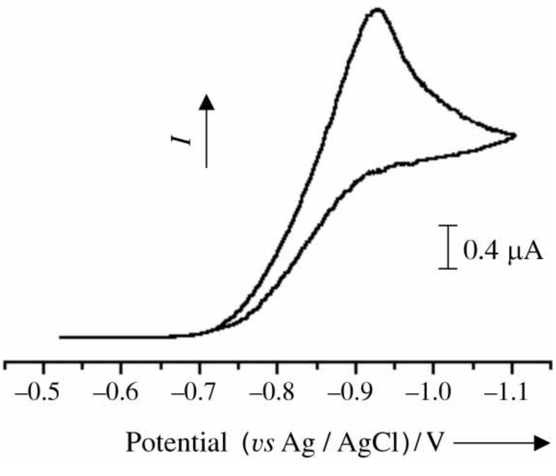
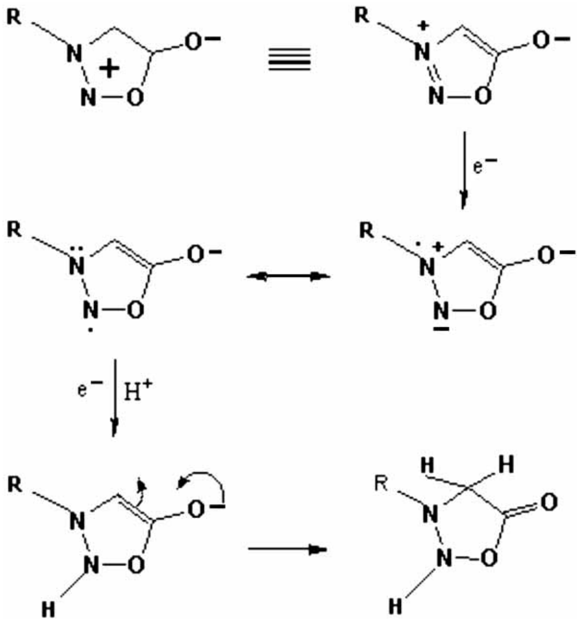


Figure 1. Cyclic voltammogram of 1×10^{-3} mol dm^{-3} 3-phenyl sydnone in acetonitrile:water (20:80 *v*/*v*). Supporting electrolyte: 50×10^{-3} mol dm^{-3} H_2SO_4; sweep rate: 0.05 Vs^{-1}.

tion since no oxidation peak was observed in the reverse scan. We propose the following mechanism for the electrochemical reduction of 3-phenyl substituted sydnone derivatives.

Mechanism



2,4 – dihydro-3-substituted 1,2,3-oxadiazole-5-one

Effect of Concentration

The concentration of 3-phenyl substituted sydnone was increased from 0.5 × 10^{-3} mol dm^{-3} to 2.5 × 10^{-3} mol dm^{-3} in 50 × 10^{-3} mol dm^{-3} H_2SO_4, with a sweep rate of 0.05 Vs^{-1}, in aqueous acetonitrile medium. The cathodic peak current increased linearly with the concentration of sydnone, indicating that the process is diffusion controlled.

Effect of Scan Rate

Effects of scan rate on electroreduction of 3-phenyl substituted sydnones were examined in different mixed aqueous:organic solvents like DMF, DMSO, methanol and acetonitrile, in a scan rate range from 0.01 to 0.5 V sec^{-1}. In all cases, the cathodic peak current was proportional to the square root of the scan rate. Under these conditions, the currents were diffusion controlled.[20, 21]

Effect of Solvents

Electrochemical reductions of 3-phenyl substituted sydnones were studied in four different partially aqueous solvents: DMSO, DMF, acetonitrile and methanol mixed with water. The supporting electrolyte was of 50 × 10^{-3} mol dm^{-3} H_2SO_4. Substituted sydnones were reduced at –0.951, –0.975, –0.993, and –1.040 V in methanol, acetonitrile, DMF and DMSO, respectively.

Variations of peak characteristics in different organic solvents are represented in Table I. The easier reduction in methanol may be due to the formation of extensive hydrogen bonding as compared to other solvents. In all other cases, the general trend is due to an increase in dielectric constant, which has the highest value in DMSO. The peak current values generally decrease in the order of acetonitrile, DMF and DMSO, as reported in the literature,[22] which is in agreement with the observed values.

Effect of Sulphuric Acid Concentration

Substituted sydnones were studied by varying the supporting electrolyte H_2SO_4, in four different organic co-solvents. The concentration of 3-phenyl sydnone was kept constant at 1 × 10^{-3} mol dm^{-3}. The concentration of sulphuric acid was varied from 16 × 10^{-3} mol dm^{-3} to 80 × 10^{-3} mol dm^{-3}. The cathodic peak potential was found to shift towards a more positive value, thereby showing the involvement of protonation in the reduction process. The standard heterogeneous rate constant values are found to increase with an increase in sulphuric acid concentration, indicating that the reduction process becomes easier at a higher concentration of sulphuric acid.

Effect of pH

The effect of pH was studied by varying the pH from 1.5 to 8.8 in BR buffer. As the pH increased from 1.5 to 8.8, the cathodic peak potential was found to shift toward a more negative potential; also, a slight decrease in peak current was observed, confirming that the substituted sydnones are more electrochemically active at pH 2.4 (Figure 2). Peak currents also decreased drastically above pH 3.5. This implies that as the pH increases, the reduction becomes more difficult, which points to proton involvement in the reduction process. Figure 2 depicts the voltammograms of 3-phenyl sydnones at different pH.

Effect of Substituents

Electron-withdrawing group accelerates reduction whereas the electron-donating group lowers it.[23] Accordingly, phenyl, tolyl and anisyl sydnone undergo reduction at –0.945, –0.958 and –0.975 V (*vs.* SCE), respectively. Both methyl and methoxy groups stabilize the positive charge. Methyl has a +I effect and a hyper conjugative effect whereas methoxy donates electrons by resonance *i.e.,* +R (or +M) effect, and the dipole associated with it operates in the opposite direction, *i.e.,* the –I effect. The hyper conjugation effect of the methyl group operates through the framework of the benzene ring. The –I effect of methoxy substantially decreases with distance but its +M effect is strongly felt by the aromatic ring as well as

TABLE I. Effect of scan rate on cyclic voltammetric parameters of the reduction of 1 × 10^{-3} mol dm^{-3} 3-phenyl sydnone at GCE in different solvents mixed with water

Scan rate V/sec.	Methanol, 20 % (v/v)		Acetonitrile, 20 % (v/v)		DMF, 20 % (v/v)		DMSO, 20 % (v/v)	
	i_{pc} / μA	$-E_{pc}$ / V	i_{pc} / μA	$-E_{pc}$ / V	i_{pc} / μA	$-E_{pc}$ / V	i_{pc} / μA	$-E_{pc}$ / V
0.01	88.8	0.902	74.5	0.945	83.1	0.967	98.7	0.985
0.02	95.4	0.923	87.1	0.951	95.1	0.975	105.6	1.016
0.05	119.2	0.940	95.0	0.968	101.6	0.990	115.6	1.038
0.10	151.4	0.961	114.0	0.981	148.9	1.009	124.7	1.065
0.20	178.1	0.998	126.1	1.009	161.5	1.035	156.7	1.115
0.50	197.4	0.1025	149.1	1.035	180.4	1.085	178.1	1.156

TABLE II. Effect of substituents on cyclic voltammetric parameters for the reduction of 1 × 10^{-3} mol dm^{-3} substituted sydnones at GCE in aqueous acetonitrile medium

Substituents	$-E_{pc}$ / V	i_{pc} / μA	D_o / 10^{-6} cm^2 s^{-1}	k_0 / 10^{-5} cm s^{-1}
3-phenyl sydnone	0.968	96.6	29.3	16.0
3-(*p*-tolyl) sydnone	0.955	98.2	26.4	17.1
3-(*p*-anisyl) sydnone	0.940	93.8	29.1	18.3

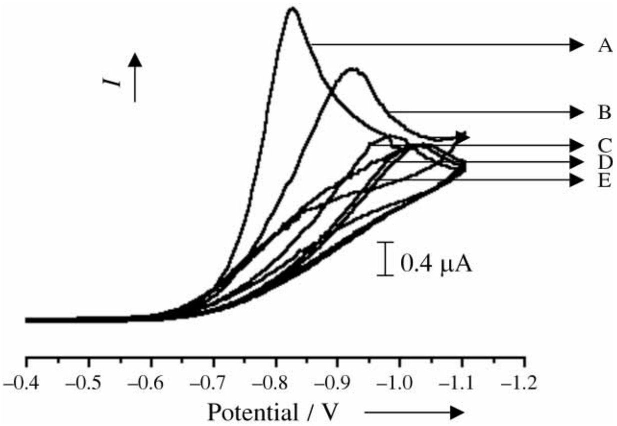


Figure 2. Cyclic voltammograms of 1 × 10^{-3} mol dm^{-3} 3-phenyl sydnone in BR buffer pH 1.5 (A), 2.4 (B), 4.8 (C), 6.5 (D) and 8.8 (E). Other experimental conditions are as in Figure 1.

the heterocyclic ring conjugated with it. Therefore, the methoxy group increases electron density in the aromatic ring even more than methyl does, which is observed in the reactivity and spectral characteristics of such substituted systems. Therefore, it will be more difficult to reduce the methoxy substituted sydnone compared to the methyl substituted one, as it is evident from the reduction potentials.

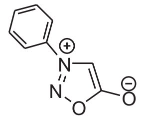
TABLE III. Effect of pH variation on the peak current and peak potentials of 3-phenyl sydnone (1 × 10^{-3} mol dm^{-3}) at a scan rate of 0.05 Vs^{-1} at GCE in aqueous acetonitrile medium

pH	$-E_{pc}$ / V	i_{pc} / μA	D_o /10^{-5} cm^2 s^{-1}
1.50	0.851	109.08	18.67
2.15	0.887	98.0	17.32
2.4	0.930	94.85	17.36
3.3	0.956	85.05	16.42
4.5	0.971	76.68	14.01
5.2	0.996	67.70	11.16
6.0	1.017	54.7	10.61
6.8	1.038	45.8	10.23
7.5	1.063	32.5	9.81
8.8	1.094	27.6	8.20

Identification of Products of Electrolysis Using Spectral Data

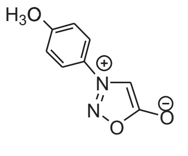
Controlled Potential Electrolysis. – Controlled potential electrolysis (CPE) was carried out using an H type cell separating the anodic and cathodic compartments by a fine glass sinter. The rate of electrolysis was enhanced by using a GCE with a larger surface area as the working electrode in the cathodic compartment and a potential of –1.35 V *vs.* SCE was applied. The potential is usually fixed slightly higher than that obtained in CV experiments. Pt gauze acted as an anode in the other compartment. SCE, used as a reference electrode, was placed in the same compartment along with GCE. CPE of sydnone compounds were carried out for 12 hours for complete reduction, using 1 × 10^{-3} mol dm^{-3} H_2SO_4 as the supporting electrolyte under hydrodynamic conditions in order to speed up the mass transport. All measurements were carried out at laboratory ambient temperature controlled at 25 ± 0.5 °C. Reduced products were isolated and separated in a column with methanol solvent and the fractions were evaporated in rotary vapor. The reduced products were characterized by IR, NMR and mass spectral studies. The reduction product was identified as 2,4-dihydro-3-substituted-1,2,3-oxadiazole-5-one by spectral data.

PARENT COMPOUNDS:



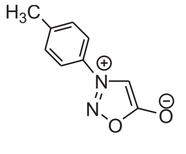
3-phenyl sydnone

1



3-(*p*-anisyl) sydnone

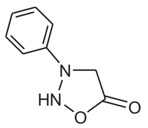
2



3-(*p*-tolyl) sydnone

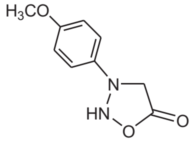
3

ELECTROCHEMICALLY REDUCED ANALOGUES:



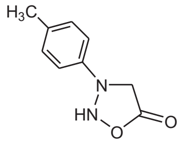
3-phenyl-1,2,3-
oxadiazolidin-5-one

4



3-(4-methoxyphenyl)-1,2,3-
oxadiazolidin-5-one

5



3-*p*-tolyl-1,2,3-
oxadiazolidin-5-one

6

*3-Phenyl-1,2,3-oxadiazole-5-one (**1**)*

Brown crystalline, m.p. 122 °C, Yield: 0.172 g (86 %); IR (KBr) $\nu_{\max}$/cm^{-1}: 3126 (s), 1756 (s); ^{1}H NMR, 400 MHz (MeOD), δ/ppm: 3.32 (s, 2H), 7.42 (s, 1H), 7.67–7.92 (m, 5H); MS *m*/*z* (rel. intensity): 164 (M$^+$, 18), 103 (10); 60 (10).

Anal. Calcd. for $C_8H_8N_2O_2$: C 48.53, H 4.91, N 17.06, O 19.49 %; found: C 48.49, H 4.83, N 17.02, O 19.41 %.

*3-(4-Methoxyphenyl)-1,2,3-oxadiazole-5-one (**2**)*

Brown crystalline solid, m.p. 128 °C, Yield: 0.165 g (82.5 %); IR (KBr) $\nu_{\max}$/cm^{-1}: 3151(s), 3072(w), 1742 (s); ^{1}H NMR, 400 MHz (DMSO-d_6) δ/ppm: 3.87 (s, 3H), 3.35 (s, 2H), 7.22 (d, J = 15.8 Hz, 2H), 7.7 (s, 1H), 7.88 (d, J = 15.8 Hz, 2H); MS *m*/*z* (rel. intensity): 194(M$^+$, 10) 193 (60), 132 (10).

Anal. Calcd. for $C_9H_{10}N_2O_3$: C 55.67, H 5.91, N 14.43, O 24.72 %; found: C 55.10 H 5.89, N 14.12, O 24.61 %.

*3-*p*-Tolyl-1,2,3-oxadiazole-5-one (**3**)*

Pale brown needle-shaped solid, m.p. 115 °C, Yield: 0.175 g (87.5 %); IR (KBr) $\nu_{\max}$/cm^{-1}: 3137(s), 1749(s); ^{1}H NMR, 400 MHz (MeOD) δ/ppm: 2.49 (s, 3H), 3.32 (s, 2H), 7.37 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H); MS *m*/*z* (rel. intensity): 178 (M$^+$, 5), 177 (55), 116 (10).

Anal. Calcd. for $C_9H_{10}N_2O_2$: C 60.66, H 5.66, N 15.72, O 17.96 %; found: C 59.96, H 5.58, N 15.22, O 17.71 %.

Yield Calculation

The molecular weight of compound **1** is 163 and the reduced compound **4** has a molecular weight of 164.

100×10^{-3} g (*i.e.,* 0.1 g) of compound **1** was taken for electrolysis (M_r 163):

100×10^{-3} g / 163 g mol^{-1} = 0.613 mol, is the no. of moles of the starting compound.

The final product obtained was dried and weighed and the weight was found to be 86×10^{-3} g (M_r 164).

Therefore, 86×10^{-3} g / 164 g mol^{-1} = 0.524 mol, is the no. of moles of the product obtained after electrolysis.

Therefore, the % yield = 0.524 mol / 0.613 mol × 100 = 85.48 %.

In the same way, compound **2** reduces to compound **5**, with a yield of 83.59 %, and compound **3** reduces to compound **6**, with a yield of 86.54 %.

Behavior in Surfactant Media

Keeping the concentration of sydnone at 1×10^{-3} mol dm^{-3}, pH 2.3 in BR buffer and at a scan rate of 0.05 Vs^{-1}, voltammograms were recorded by increasing the surfactant concentration from 1×10^{-3} mol dm^{-3} to 6.0×10^{-3} mol dm^{-3}. In the case of anionic surfactant (SDS), the peak current decreased with increased addition of SDS and peak potentials were shifted in the negative direction. Different factors affect surfactant adsorption on the solid/liquid interface.[24] Apart from this, it is also claimed that at higher concentrations of the surfactant SDS, repulsive forces between the surfactant molecules adsorbed at the solid (adsorbent)/solution interface are more effective.[25] By increasing the concentration of the surfactant, more and more of the anionic part of the surfactant gets adsorbed at the surface of the electrode, resulting in a decrease in the cathodic current. The reductive group of sydnones now requires more potential on account of adsorption of the surfactant and hence the potential shifts towards a more negative region and the current decreases. Heterogeneous kinetic process of the transfer of electrons between the electrode surface and molecules in the interfacial region can be significantly affected by the microstructure and blocking of active sites on the electrode surface by adsorbed materials. Reduction was markedly suppressed as the concentration of SDS increased and the peak disappeared beyond 4×10^{-3} mol dm^{-3} of SDS.

In the case of cationic surfactant TDTAB, the peak potential decreased as the concentration of TDTAB increased up to 6.0×10^{-3} mol dm^{-3}, thereby indicating a higher energy requirement for the reduction process. The

TABLE IV. Effect of the variation of surfactant concentration on the peak potentials and peak currents of 3-phenyl sydnone (1×10^{-3} mol dm^{-3}) at a scan rate of 0.05 Vs^{-1} at GCE in aqueous acetonitrile medium

Concentration × 10^{-3} / mol dm^{-3}	TDTAB		SDS		TX-100	
	$-E_{pc}$ / V	i_{pc} / μA	$-E_{pc}$ / V	i_{pc} / μA	$-E_{pc}$ / V	i_{pc} / μA
1.0	0.958	98.48	0.971	96.48	0.964	89.12
1.5	0.969	91.15	0.963	81.45	0.964	82.56
2.0	0.985	83.26	0.980	70.78	0.963	76.10
2.5	0.999	78.48	0.999	62.76	0.963	71.61
3.0	1.014	63.15	1.023	49.71	0.961	63.32
3.5	1.038	55.10	1.049	30.31	0.960	52.47
4.0	1.054	49.53	1.090	21.10	0.960	45.85
4.5	1.070	35.62	–	–	0.960	36.95
5.0	1.084	21.04	–	–	0.959	21.65

decrease in current could be a result of the slower diffusion of the electroactive species as a result of higher viscosity of the medium. The cathodic peak was not observed at the higher concentration of TDTAB. This could be due to the carbon saturation capacity[26] for adsorption of the cationic surfactant due to the electrostatic interaction between the adsorbent and the surfactant. The reduction was markedly suppressed as the concentration of TDTAB increased and the peak disappeared beyond 5×10^{-3} mol dm^{-3} of TDTAB.

The nonionic surfactant Triton X-100 affected the electrochemical behavior of sydnone compounds in an opposite way, *i.e.*, it did not affect the peak potential, E_{pc}, but the peak current, i_{pa} got affected as it decreased with the increase in surfactant concentration.

The effect of surfactant on the electrochemical behavior of sydnone compounds can be due to the surfactant adsorption at the electrode surface. Ionic surfactants form hydrophilic charged films at the glassy carbon electrode, with the polar head groups directed to the bulk phase.[27]

The fundamental explanation for this kind of behavior observed in non-ionic surfactant media is yet to be established.

CONCLUSIONS

The following conclusions can be drawn from the studies into the electrochemical behavior of sydnones in four different solvents:

i) Peak potential is found to shift to a more positive value with an increase in the volume of sulphuric acid, indicating easier reduction owing to the proton involvement in the reduction;

ii) At a higher concentration of the surfactant (within CMC), the peak current decreases, which is an indication of the reduction process inhibition due to the surface coverage of the surfactants at the surface of the working electrode;

iii) Cathodic peak current was found to increase linearly with square root of the sweep rate and also with the electroactive species concentration. This suggests that the overall electrode process is a diffusion controlled irreversible process;

iv) Reduction potential of sydnone compounds decreases according to the dielectric constant of organic co-solvents, *i.e.*, DMSO>DMF>CH_3CN>CH_3OH;

v) This serves as a new method of preparation of 2,4-dihydro-3-substituted-1,2,3-oxadiazole-5-one, with a high yield of ~82–88 %;

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SAŽETAK

Elektrokemijska istraživanja derivata sidnona na elektrodi od staklastog grafita

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Cikličkom voltametrijom na elektrodi od staklastog grafita proučavana je elektrokemijska redukcija dvostruke veze između atoma dušika u derivatima sidnona poput 3-fenil sidnona, tolil sidnona i anisil sidnona. U kiselom mediju, unutar istraženog opsega pH vrijednosti, elektroredukcija ovih spojeva je ireverzibilna. Istraživanja su provedena u vodi miješanoj sa acetonitrilom, dimetilformamidom, metanolom i dimetilsulfoksidom. Određeni su koeficijenti prijelaza elektrona i difuzijski koeficijenti spojeva, a proučavani su i utjecaji koncentracije reaktanta, brzine promjene potencijala, vrste organskih otapala i pH na njihove odzive. Produkti redukcije su analizirani infracrvenom spektroskopijom, nuklearnom magnetskom rezonancijom i spektroskopijom masa. Utjecaj površinski aktivnih tvari na elektrodnu reakciju 3-fenil sidnona proučavan je korištenjem kationskog, anionskog i neionskog detergenta.