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ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X
CODEN: OJCHEG
2019, Vol. 35, No.(3):
Pg. 1117-1124

Cyclic Voltammetric Studies of Biologically Active Azomethine 2'-Hydroxyacetophenone Sulfamethoxazole

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http://dx.doi.org/10.13005/ojc/350327

(Received: February 26, 2019; Accepted: May 09, 2019)

ABSTRACT

The cyclic voltammetric behavior of newly synthesized biologically active azomethine 2'-hydroxyacetophenone sulfamethoxazole (2'-HyAcPhSM) was examined at glassy carbon electrode in acetonitrile, acetone, methanol and DMF solvents using phosphate buffer and Britton-Robinson (BR) buffer. The effect of solvents, buffers, sweep rates and pH were calculated on peak potential and peak current. The cyclic voltammograms of 2'-HyAcPhSM exhibited two electronic, irreversible and diffusion-controlled single cathodic peak within the entire pH range which is attributed to the reduction of the azomethine group (–CH=N–) to amine group (–CH_2–NH–). The biological activity of synthesized 2'-HyAcPhSM compound were carried out against various bacteria and fungi.

Keywords: 2'-Hydroxyacetophenone sulfamethoxazole, Cyclic voltammetry, Biological activity.

INTRODUCTION

Schiff bases termed as anils, imines or azomethines and are first reported by Hugo Schiff in 1864. Schiff bases and their transition metal complexes exhibit a wide range of biological activity[1-4], corrosion inhibition effects[5-8] and analytical applications[9-13] have been prepared by condensing carbonyl compounds with amines in different conditions and in different solvents with the elimination of water molecule[14-19]. The electrochemical behavior of Schiff bases have been also drawn the attention of many workers[20-24]. However, insuffcient informations are available in the literature regarding the electrochemical behavior of the Schiff bases of sulfa drugs and their transition metal complexes.

The present work emphasized on electrochemical behavior of 2'-HyAcPhSM with a view to investigate some important aspects such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K^o_{f,h}$) by altering scan rate, solvent, buffer solution and pH of the electrochemical solution.

EXPERIMENTAL

Synthesis of 2'-hydroxyacetophenone sulfamethoxazole

All chemicals were analytical grade and of the highest available purity, and used without further purification. 2'-hydroxyacetophenone and

sulfamethoxazole were obtained from Sigma-Aldrich. To synthesize 2'-hydroxyacetophenone sulfamethoxazole (2'-HyAcPhSM), 0.1 M solution of 2'-hydroxyacetophenone added to 0.1 M solution of sulfamethoxazole in ethanol and then reaction mixture was refluxed about two and half hour at 70°C. The product thus obtained was purified by washing with distilled water and then with ethanol. The brown solid crystals were obtained after recrystallization in ethanol. Melting point and yield were found 139°C and 68% respectively.

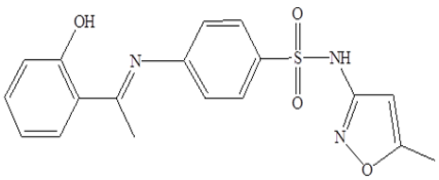


Fig. 1. Synthesized 2'-hydroxyacetophenone sulfamethoxazole Schiff base

Elemental analysis

Elemental analysis of 2'-HyAcPhSM were carried out using micro analytical technique on C, H, N, S, O elemental analyzer. Analytical data were found (Cal.): M. Wt.; 371.09 (371.41), C; 58.22 (58.21), H; 4.11 (4.61), N; 11.17 (11.31), O; 16.96 (17.23) and S; 8.55 (8.63).

Spectral studies

Infrared studies

The infrared spectra of 2'-HyAcPhSM were scanned in the range 4000-667 cm^{-1} using FT-IR spectrometer (Model 8400S, Schimadzu) in KBr pallets. The Schiff base compound contains five potential donor sites (i) phenolic oxygen, (ii) azomethine nitrogen, (iii) sulphonamide oxygen, (iv) sulphonamide nitrogen, and (v) ring nitrogen. The features observable in the infrared spectra of the compound is the intense and broad band at 3055 cm^{-1}, showing the existence of intramolecular H-bonding between phenolic oxygen and azomethine nitrogen (υOH…N). The broad band at 3355 cm^{-1} due to phenolic –OH group and a sharp band at 1630 cm^{-1} assignable to the azomethine group (υC=N)[25] are also appeared in this spectrum. The strong band at 1276 cm^{-1} indicates the presence of phenolic C-O stretching[26], in addition to other typical bands of phenyl ring vibrations at 1485 cm^{-1} and 754 cm^{-1}. The bands at 1340 cm^{-1} and 1145 cm^{-1} are assigned to asymmetric and symmetric SO_2 vibrations respectively.

^{1}H NMR studies

The ^{1}HNMR spectra of compound was recorded on 300.4 MHz FT-NMR spectrometer (Model Jeol AL 300) in $CDCl_3$ using TMS as internal standard. The compound exhibit multiplet signals corresponding to aromatic protons which occurs between δ 7.20-7.50 ppm. The resonance signals due to methyl protons (–C(CH_3)=N–) are observed at δ 1.80 ppm. The sharp low field signal for the phenolic proton occur at δ 5.25 ppm which shows the presence of intramolecular hydrogen bond involving the phenolic proton and the azomethine nitrogen atom, thus implying a phenol-iminic structure.

Cyclic voltammetric studies of 2'-hydroxyaceto -phenone sulfamethoxazole

The cyclic voltammetric experiments were carried out using *"ECDA–001 Basic Electrochemistry System*". A three electrode combination system which consisted of a working glassy carbon electrode, an Ag/AgCl reference electrode and Pt wire auxiliary electrode was used. To study the effect of solvents, buffers, scan rates and pH on redox behavior of compound, cyclic voltammograms were recorded in acetonitrile, acetone, methanol and DMF solvents using phosphate buffer (mixture of 0.2 M monobasic sodium phosphate, 0.2 M dibasic sodium phosphate and 0.1 M HCl/NaOH) and BR buffer (mixture of 0.04 M boric acid, 0.04 M phosphoric acid, 0.04 M acetic acid and 0.2 M sodium hydroxide) at different pH values. For this, 10 ml of 1 mM concentration solution (containing 1 ml of 0.01 M stock solution of compound in appropriate solvent and remaining 9 ml of phosphate/BR buffer solution of desired pH) were employed in voltammetric experiment on 50, 100, 150, 200 and 250 mV/s sweep rates, +1000 mV to -1800 mV potential range, and at 0.1 mA current sensitivity. All cyclic voltammograms were obtained, exhibits one irreversible reduction peak in the cathodic direction and no anodic peak in reverse scan (Fig. 2 to 4). Thus, to explain irreversible electrochemical reduction nature of 2'-HyAcPhSM,

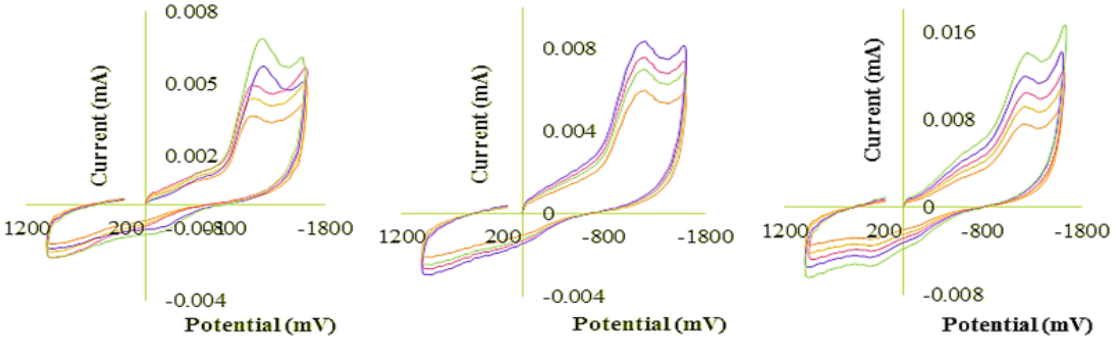
kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($k°_{f,h}$) have been evaluated using equations[27-30] 1 to 3 and are reported in tables 1 to 3.

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha_n F} = \left(\frac{47.7}{\alpha_n}\right) mV \quad (1)$$

$$I_P = 3.01\times10^5\, n(\alpha_n)^{1/2} A\, C\, D_0^{1/2}\, v^{1/2} \quad (2)$$

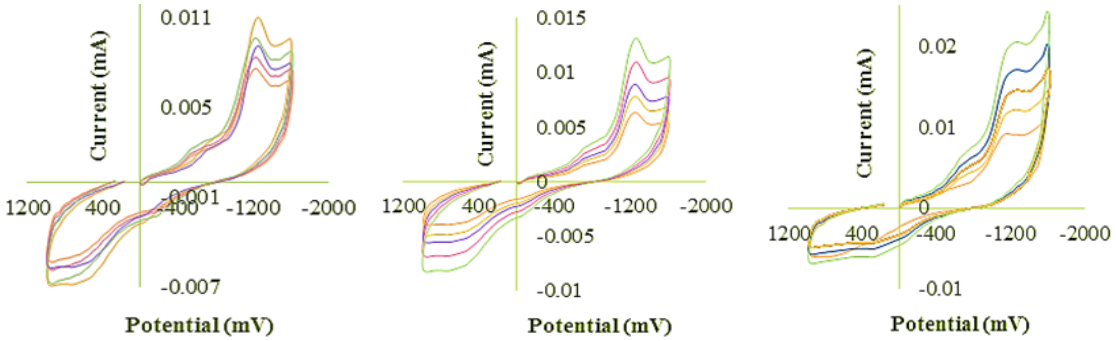
$$E_P = -\frac{RT}{\alpha_n F}\left[0.78 + \ln\left(\frac{D_0^{1/2}}{k^{\circ}_{f,h}}\right) + \ln\left(\frac{\alpha_n F v}{RT}\right)^{1/2}\right] \quad (3)$$

Where E_p, $E_{p/2}$, I_p, ν, *A*, *n* and *C* are peak potential, half peak potential, peak current, scan rate, electrode surface area, number of electrons involved in electrode process and concentration of the electrolytic solution. All other symbols have their usual significance.



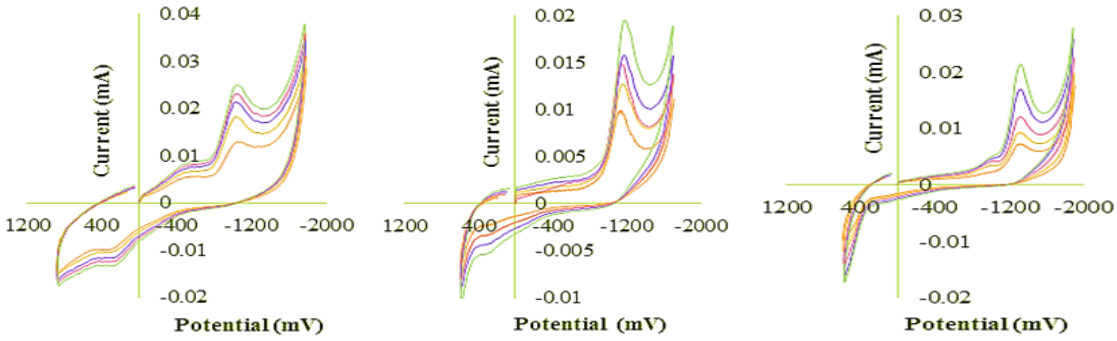
(A) (B) (C)

Fig. 2. Cyclic voltammograms of 1 mM 2'-HyAcPhSM in methanol–phosphate buffer at (A) pH 5 (B) pH 7 and (C) pH 9



(A) (B) (C)

Fig. 3. Cyclic voltammograms of 1 mM 2'-HyAcPhSM in methanol–BR buffer at (A) pH 5 (B) pH 7 and (C) pH 9



(A) (B) (C)

Fig. 4. Cyclic voltammograms of 1 mM 2'-HyAcPhSM at pH 7 using phosphate buffer in (A) acetone (B) acetonitrile, and (C) DMF

Table 1: Effect of sweep rate on voltammetric parameters of 1 mM 2'-HyAcPhSM in methanol-phosphate buffer at pH 5, 7 and 9 (Fig. 2-A, B and C)

pH	v (mVs^{-1})	E_{pc} (mV)	I_{pc} (μA)	$E_{p/2}$ (mV)	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ (cm^2s^{-1})	$k°_{f,h}$ ($cm.s^{-1}$)
	50	-1097	3.49	-904	0.4935	0.2471	6.2493	2.46×10^{-07}
	100	-1124	4.89	-921	0.489	0.2349	6.35	4.52×10^{-07}
5	150	-1145	5.64	-945	0.4605	0.2385	5.9356	3.68×10^{-07}
	200	-1164	5.99	-958	0.4235	0.2315	5.5406	4.49×10^{-07}
	250	-1181	7.64	-978	0.4831	0.2349	6.2746	4.19×10^{-07}
	50	-1112	5.77	-921	0.816	0.2497	10.2784	3.14×10^{-07}
	100	-1138	6.12	-936	0.612	0.2361	7.9276	4.73×10^{-07}
7	150	-1178	6.58	-957	0.5372	0.2158	7.2793	8.93×10^{-07}
	200	-1204	7.25	-984	0.5126	0.2168	6.9303	7.55×10^{-07}
	250	-1234	8.01	-999	0.5065	0.2218	6.7701	5.08×10^{-07}
	50	-1124	6.25	-953	0.8838	0.2789	10.5344	8.43×10^{-08}
	100	-1138	8.78	-964	0.878	0.2741	10.5557	1.26×10^{-07}
9	150	-1178	10.21	-975	0.8336	0.2349	10.8254	5.76×10^{-07}
	200	-1204	11.97	-986	0.8464	0.2188	11.39	1.14×10^{-06}
	250	-1280	13.98	-1005	0.8841	0.1697	13.5085	8.01×10^{-06}

Table 2: Effect of sweep rate on voltammetric parameters of 1 mM 2'-HyAcPhSM in methanol-BR buffer at pH 5, 7 and 9 (Fig. 3-A, B and C)

pH	v (mVs^{-1})	E_{pc} (mV)	I_{pc} (μA)	$E_{p/2}$ (mV)	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ (cm^2s^{-1})	$k°_{f,h}$ ($cm.s^{-1}$)
	50	-1153	6.24	-968	0.8824	0.2578	10.9396	1.59×10^{-07}
	100	-1168	7.77	-975	0.777	0.2471	9.8382	2.76×10^{-07}
	150	-1187	8.79	-984	0.7177	0.2349	9.3198	4.57×10^{-07}
	200	-1212	10.02	-998	0.7085	0.2228	9.4466	7.32×10^{-07}
5	250	-1234	10.91	-1017	0.69	0.2198	9.264	7.64×10^{-07}
	50	-1175	5.24	-981	0.741	0.2458	9.4073	1.85×10^{-07}
	100	-1199	7.56	-992	0.756	0.2304	9.9134	4.35×10^{-07}
7	150	-1221	9.25	-1001	0.7552	0.2168	10.2099	8.35×10^{-07}
	200	-1240	10.45	-1016	0.7389	0.2129	10.0796	9.69×10^{-07}
	250	-1264	12.01	-1028	0.7595	0.2021	10.6352	1.55×10^{-06}
	50	-1212	6.91	-1012	0.9772	0.2385	12.5958	2.42×10^{-07}
	100	-1234	7.89	-1024	0.789	0.2271	10.4208	3.89×10^{-07}
9	150	-1256	9.25	-1035	0.7552	0.2158	10.2331	6.52×10^{-07}
	200	-1274	10.45	-1051	0.7389	0.2139	10.057	6.97×10^{-07}
	250	-1298	12.01	-1079	0.7595	0.2178	10.245	5.38×10^{-07}

Table 3: Effect of sweep rate on voltammetric parameters of 1 mM 2'-HyAcPhSM in different solvents with phosphate buffer at pH 7 (Fig. 4-A, B and C)

Solvent	v (mVs^{-1})	E_{pc} (mV)	I_{pc} (μA)	$E_{p/2}$ (mV)	$I_{pc}/\nu^{1/2}$	α_n	$D_0^{1/2}$ (cm^2s^{-1})	$k°_{f,h}$ ($cm.s^{-1}$)
	50	-914	10.56	-742	1.4934	0.2773	17.8509	1.48×10^{-06}
	100	-942	14.78	-751	1.478	0.2497	18.6169	4.21×10^{-06}
Acetone	150	-988	17.45	-769	1.4247	0.2178	19.2171	1.08×10^{-05}
	200	-1016	20.56	-794	1.4538	0.2148	19.7425	1.13×10^{-05}
	250	-1055	23.68	-812	1.4976	0.1962	21.2781	2.02×10^{-05}
	50	-1056	9.04	-935	1.2784	0.3942	12.8172	2.23×10^{-09}
	100	-1098	12.79	-971	1.279	0.3755	13.1368	3.67×10^{-09}
Acetonitrile	150	-1132	15.65	-1012	1.2778	0.3975	12.7578	1.04×10^{-09}
	200	-1164	18.05	-1035	1.2763	0.3697	13.2122	2.57×10^{-09}
	250	-1197	19.97	-1063	1.263	0.3559	13.3253	3.36×10^{-09}
	50	-1218	8.34	-1078	1.1794	0.3407	12.7193	2.16×10^{-09}
	100	-1231	12.45	-1089	1.245	0.3359	13.5217	3.42×10^{-09}
DMF	150	-1256	15.42	-1101	1.259	0.3077	14.2863	1.21×10^{-08}
	200	-1289	17.98	-1112	1.2713	0.2694	15.4162	6.50×10^{-08}
	250	-1307	20.01	-1125	1.2655	0.262	15.5607	8.72×10^{-08}

RESULTS AND DISCUSSION

Effect of scan rate

Effect of scan rate on the cathodic peak potential of 1 mM 2'-HyAcPhSM were examined in acetonitrile, acetone and DMF solvents using phosphate buffer at pH 7, methanol-phosphate buffer and methanol-BR buffer at pH 5,7 and 9. All cyclic voltammograms were taken by varying the scan rate from 50 mV/s to 250 mV/s in all cases. The peak potential shifted to more negative value with an increase in the scan rate, implying that electrochemical process was irreversible[31] in nature. The irreversibility of reduction process is confirmed from the linear dependence of the cathodic peak potential (E_{pc}) with ln v (Fig. 5 to 8). The peak potential shift is larger at high scan rates. This implies that under these conditions the electrochemical processes are more irreversible. In all the cases the cathodic peak current (I_{pc}) is proportional to the square root of the scan rate ($v^{1/2}$) (tables 1 to 3), which infer that under these conditions, the electrochemical processes are diffusion controlled[27,32].

Effect of solvent

The effect of solvent on electrochemical properties can't be explained by any single chemical or physical property of the solvent or by a single unified theory. It can be explained by viscosity, dielectric constant, steric factor and polarity of the solvent[33-34]. In this work cyclic voltammograms of 2'-HyAcPhSM were recorded in acetone, acetonitrile, methanol and DMF solvents with phosphate buffer. It was observed that, the peak potential has maximum negative potential in presence of DMF and minimum in presence of acetone. This trend is parallel to the trend in viscosity, dielectric constant and polarity of these solvents[35-36].

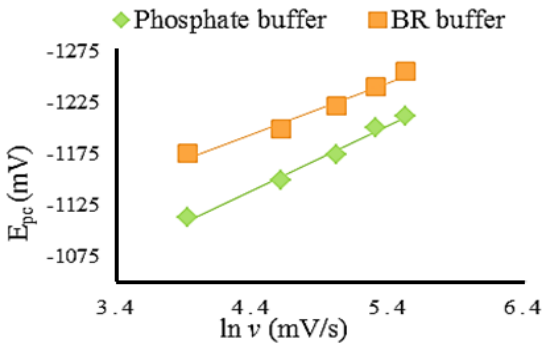


Fig. 5. E_{pc} vs ln v for 1 mM 2'-HyAcPhSM in methanol-phosphate and methanol-BR buffer at pH 7 solvent

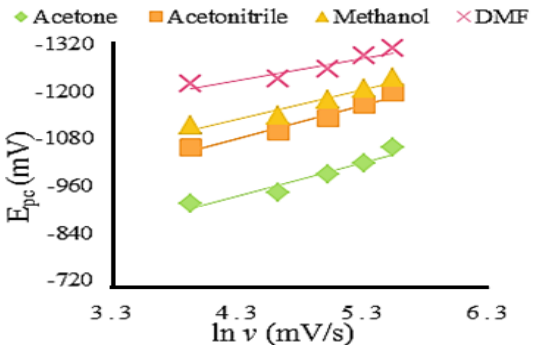


Fig. 6. E_{pc} vs ln v for 1 mM 2'-HyAcPhSM in acetone, acetonitrile, methanol and DMF using phosphate buffer at pH 7

Effect of pH

The effect of pH on electrochemical reduction behavior of 2'-HyAcPhSM were studied in acidic, neutral and alkaline media at pH 5, 7 and 9 in methanol-phosphate buffer and methanol-BR buffer. The reported cyclic voltammograms, shows that cathodic peak potentials have negative shift with the increase of the pH, suggesting that the reduction process involves protons[30]. The relationship between the peak potentials (E_{pc}) and the pH of the electrochemical solution were investigated (Fig. 7 and 8). The $E_{p/2}$ values are also found to be pH dependent and shift towards more negative potential that indicates the involvement of protons in the electrode process. The increase in the pH value increases the dissociation constant of protonated species which affects the protonation rate, and consequently $E_{p/2}$ value of the reduction wave shifts towards more negative value. These phenomena appear to have the same results in methanol-phosphate buffer as well as in methanol-BR buffer systems (Tables 1 and 2).

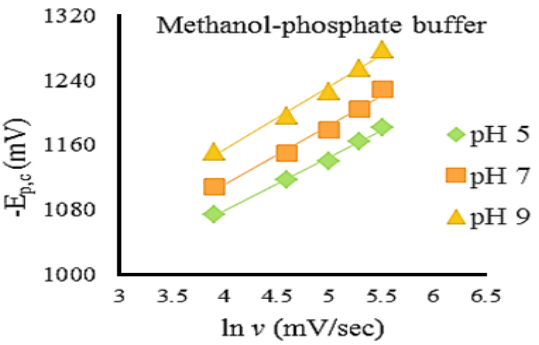


Fig. 7. Effect of pH on E_{pc} for 2'-HyAcPhSM in methanol-phosphate buffer

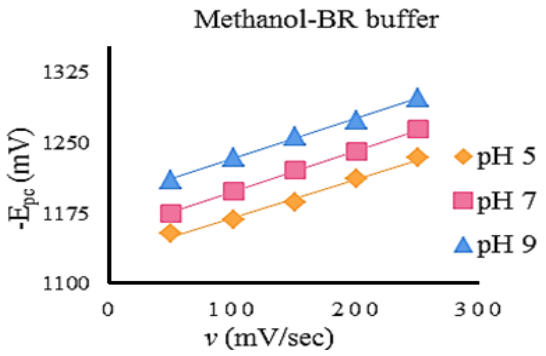


Fig. 8. Effect of pH on E_{pc} for 2'-HyAcPhSM in methanol-BR buffer

Effect of buffer solutions

The effect of buffer solutions on electrochemical behavior of 2'-HyAcPhSM were investigated by taking cyclic voltammograms in phosphate buffer and Britton-Robinson buffer with methanol solvent. Cyclic voltammograms obtained in both buffers with methanol solvent shows that cathodic peak potential (E_{pc}) values of compound are found to be changed with change in buffer solution. The cathodic peak potential shifts to more negative value at all scan rates and on same pH in Briton-Robinson buffer compared to phosphate buffer. This means, that the electrochemical reduction is dependent on polarity of buffer solutions. The E_{pc} value in phosphate buffer at 50 mV/s scan rate is -1112 mV and at 250 mV/s scan rate is -1234 mV while in Briton-Robinson buffer at 50 mV/s is -1175 mV and at 250 mV/s scan rate is -1275 mV which is greater than phosphate buffer. So it can be concluded that reduction is easier in more polar phosphate buffer solution and difficult in less polar Briton-Robinson buffer solution where the ionization is low as evident from the Tables 1 and 2.

Biological studies

The *In vitro* biological screening effects of 2'-HyAcPhSM were tested against bacteria *Staphylococcus aureus*, *Streptococci and Escherichia coli*, and Fungi *Candida albicans* and *Aspergillus niger* by agar well diffusion method[37]. For this purpose, the standard drug *Ciprofloxacin* and *Ketoconazole* were used for antibacterial screening and antifungal screening respectively. The antimicrobial/antifungal spectrum of the experimental compound were determined for the bacterial/fungal species in terms of inhibited zone size around each well. For each bacterial/fungal strain controls were maintained by pure solvents instead of the compound solution[38-39]. The compound is reported to have most antibacterial activity against *Escherichia coli* (activity index 0.9615 at 60 μg/mL concentration) and most antifungal activity against *Candidi albicans* (activity index 1.3529 at 60 μg/mL concentration) (Table 4). In comparison with Ciprofloxacin drug, the compound is less active against all tested bacteria in the compound concentration range 20 μg/mL to 60 μg/mL. However, the compound is more active than standard Ketoconazole drug, against *Candida albicans* in the compound concentration range 40 μg/mL to 60 μg/mL and *Aspergillus niger* at 60 μg/mL compound concentration (Table 4).

Table 4: Antibacterial and antifungal activity of 2'-HyAcPhSM against bacteria *Staphylococcus aureus*, *Streptococci* and *Escherichia coli*, and fungi *Candida albicans* and *Aspergillus niger*

Conc. (μg/mL)	*Staphylococcus Aureus*		*Streptococci*		*Escherichia Coli*		*Candida albicans*		*Aspergillus niger*	
	I. Z. (mm)	Activity Index	I. Z. (mm)	Activity Index	I. Z. (mm)	Activity Index	I. Z. (mm)	Activity Index	I. Z. (mm)	Activity Index
20	13	0.5	10	0.3846	15	0.5759	13	0.7647	9	0.5294
30	15	0.5769	12	0.4615	17	0.6538	15	0.8823	11	0.647
40	16	0.6153	14	0.5384	20	0.7692	18	1.0588	14	0.8235
50	18	0.6923	17	0.6538	22	0.8461	20	1.1764	16	0.9411
60	20	0.7692	19	0.7307	25	0.9615	23	1.3529	19	1.1117

I. Z. = Inhibition zone in mm; Ciprofloxacin=26 mm and Ketoconazole=17 mm

CONCLUSION

It was concluded from the electrochemical data that the electrochemical reduction of 2'-HyAcPhSM is irreversible and diffusion controlled in nature under the pH 5 to 9 and scan rate range

from 50 mV/s to 250 mV/s. The irreversibility of the process was found more at higher scan rates and higher pH values in all applied conditions that indicate the scan rate and pH dependence of the electrode process. It was also found that the reduction process is dependent on the polarity of the medium. The In vitro biological screening studies show sufficient activity against tested microorganisms in the compound concentration range of 20 to 60 mg/mL.

ACKNOWLEDGMENT

The authors express sincere thanks to the Head, Department of Chemistry, University of Rajasthan, Jaipur for providing research facilities. The author Preeti Choudhary is thankful to UGC, New Delhi for financial assistance.

Conflict of Interest

The authors declare no confilict of interest.

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