Research Article

Electrochemical Investigations of Some Semicarbazones and Thiosemicarbazones at Glassy Carbon Electrode

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Abstract

Semicarbazones and thiosemicarbazones used in these studies have been synthesized by the condensation of 9-anthracenecarboxaldehyde or 9-Acetylanthracene with semicarbazide hydrochloride or thiosemicarbazide using alcohol as the reaction medium. The comprehensive study of electrochemical behavior of these compounds have been studied in two different medium (DMF & CH_3OH) on glassy carbon electrode (GCE) using cyclic voltammetric technique. The kinetic parameters like cathodic peak potential E_{pc}, cathodic peak current I_{pc}, charge-transfer coefficient α_n, diffusion coefficient $D_0^{1/2}$ and rate constant $K^{\circ}_{f,h}$ have been evaluated. Single irreversible reduction wave was observed due to the reduction of semicarbazone/thiosemicarbazone moiety. The effect of sweep rate, pH, change in medium (DMF & CH_3OH), concentration of electroactive species and variation of acid concentration were evaluated. The electrode process was shown to be diffusion controlled and irreversible.

Ipc = 0.2059v^{1/2} + 0.2356
R^2 = 0.9897

Keywords: Semicarbazones, Thiosemicarbazones, Electrochemical investigations, Kinetic parameters, Irreversible reduction
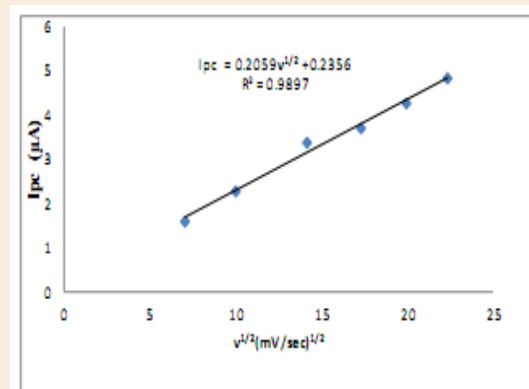
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Introduction

Semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulphur donor ligands. They have been a subject of interest in recent decades due to their biological activity, good complexing properties and analytical applications [1-5]. Systematic perusal of earlier literature reveals that inspite of the variegated importance associated with semicarbazone and thiosemicarbazone compounds, relatively few reports exist on their electrochemical behavior [6-14]. Hence, efforts have been laid down to undertake cyclicvoltammetric studies on some semicarbazones and thiosemicarbazones of 9-anthracenecarboxaldehyde and 9-acetylanthracene. Keeping this in mind and to broaden the knowledge of the electrochemistry and possibility of electrochemical assays, it was considered worthwhile to study critically the electrochemical behavior of these compounds. They have been studied at glassy carbon electrode using cyclic voltammetric technique with a view to investigate some important aspects as mechanism of electrode process and effect of varying condition on redox behavior of these compounds. The effect of substituent is interpreted. The kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K^{\circ}_{f,h}$) have been calculated and their interpretations have been incorporated in this paper.

Experimental

All chemicals employed were of analytical grade. Methanol was freshly distilled prior to use. Semicarbazones and thiosemicabazones were synthesized by standard procedure available in literature [15,16]. The stock solutions of the

compounds (1×10^{-2}M) were prepared in dimethyl formamide (AR) and methanol. Britton-Robinson buffer, phosphate buffer and 0.5M $HClO_4$ were prepared in doubly distilled water. In the typical cyclic voltammetric experiment, reaction mixture consisted of compound solution, solvent (the minimum volume necessary to keep the compound in the solution) and buffer solution (keeping the overall volume constant 10 ml). A stream of nitrogen gas was passed over the reaction mixture. The three electrodes(Glassy carbon electrode-working electrode, Ag/AgCl-reference electrode and a Pt wire-auxiliary electrode.) were connected to the electrochemical cell. Required potential, scan rates, current sensitivity, initial potential and final potential were applied and resulting current was measured as a function of applied potential. In DMF media, the electrochemical behavior was also observed by varying the concentration of $HClO_4$.

The electrochemical reduction behavior of all the synthesized semicarbazone and thiosemicarbazone compounds were studied at glassy carbon electrode in DMF and CH_3OH media using phosphate buffer- $HClO_4$ and B-R buffer respectively, at various sweep rates, pH values, varied concentration of the electroactive species. Voltammograms were also recorded by varying the concentration of $HClO_4$ in DMF-phosphate-buffer media. All the compounds exhibit one irreversible reduction peak in the cathodic direction and no anodic peak was observed in reverse scan. Thus, the kinetic parameters such as charge-transfer coefficient (α_n), diffusion coefficient ($D_0^{1/2}$) and rate constant ($K^{\circ}_{f,h}$) have been calculated for irreversible and diffusion controlled reduction by using following equations [17-20] and reported in **Tables** (1-8).

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

$$I_P = 3.01 \times 10^5 \, n \, (\alpha_n)^{1/2} \, A \, C \, D_0^{1/2} \, v^{1/2} \quad (2)$$

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

Results and Discussions

Table 1 Effect of sweep rate on voltammetric parameters of 1mM 9-anthracenecarboxaldehyde semicarbazone in DMF-phosphate buffer-$HClO_4$ at different pH (5, 7& 9)

pH	v mVs^{-1}.	E_{pc} mV	I_{pc} μA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$ x10^3 cm^2. s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-620	1.61	-507	-565	0.2277	0.4222	1.10	8.14×10^{-8}
	100	-637	2.28	-510	-572	0.228	0.3756	1.17	2.77×10^{-7}
	200	-642	3.39	-521	-585	0.2397	0.3943	1.20	2.40×10^{-7}
	300	-653	3.72	-525	-590	0.2147	0.4078	1.06	1.58×10^{-7}
	400	-659	4.29	-533	-596	0.213	0.4185	1.04	1.26×10^{-7}
	500	-667	4.84	-543	-601	0.2155	0.3268	1.19	1.35×10^{-7}
7	50	-677	1.56	-528	-612	0.2206	0.3202	1.23	4.55×10^{-7}
	100	-692	2.42	-513	-617	0.242	0.2511	1.52	3.77×10^{-6}

	200	-699	3.98	-376	-615	0.2814	0.1477	2.30	9.67×10^{-5}
	300	-713	3.75	-490	-626	0.2165	0.2056	1.50	1.68×10^{-5}
	400	-717	4.45	-503	-633	0.2225	0.2120	1.52	1.62×10^{-5}
	500	-717	4.93	-439	-651	0.2204	0.1668	1.70	6.01×10^{-5}
9	50	-699	1.36	-569	-630	0.1923	0.367	1.00	8.43×10^{-8}
	100	-701	2.25	-521	-639	0.225	0.2650	1.37	2.19×10^{-6}
	200	-719	2.97	-547	-643	0.2100	0.2774	1.25	1.70×10^{-6}
	300	-737	3.70	-570	-656	0.2136	0.2857	1.26	1.37×10^{-6}
	400	-749	4.21	-502	-661	0.2105	0.1932	1.51	2.03×10^{-5}
	500	-752	4.78	-336	-667	0.2133	0.1147	2.02	2.30×10^{-4}

Table 2 Effect of sweep rate on voltammetric parameters of 9-anthracenecarboxaldehyde semicarbazone in CH$_3$OH-B-R buffer at different pH (5,7 & 9)

pH	v mV/s	E_{pc} mV	I_{pc} µA	$E_{1/2}$ mV	$E_{p/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2} \times 10^3$ cm^2.s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-1058	2.61	-942	-992	0.3691	0.4112	1.81	1.54×10^{-10}
	100	-1069	3.62	-949	-998	0.362	0.3975	1.807	3.18×10^{-10}
	200	-1091	5.24	-970	-1020	0.3705	0.4376	1.76	5.9×10^{-11}
	300	-1115	6.56	-976	-1035	0.3787	0.3431	2.03	2.99×10^{-9}
	400	-1131	7.62	-991	-1050	0.381	0.3407	2.05	3.12×10^{-9}
	500	-1145	8.44	-1005	-1058	0.3774	0.3407	2.04	2.88×10^{-9}
7	50	-1133	2.21	-1043	-1078	0.3125	0.5300	1.35	2.08×10^{-13}
	100	-1146	3.20	-1046	-1086	0.320	0.477	1.46	2.46×10^{-12}
	200	-1167	5.18	-1063	-1094	0.3663	0.4586	1.70	6.2×10^{-12}
	300	-1184	6.36	-1074	-1114	0.3672	0.4336	1.75	1.77×10^{-11}
	400	-1200	7.35	-1089	-1130	0.3675	0.4297	1.76	1.88×10^{-11}
	500	-1215	8.02	-1098	-1141	0.3586	0.4076	1.77	2.09×10^{-11}
9	100	-1182	3.12	-1091	-1123	0.312	0.5241	1.36	1.4×10^{-13}
	200	-1205	5.37	-1114	-1146	0.3797	0.5241	1.65	1.51×10^{-13}
	300	-1210	6.22	-1120	-1149	0.3591	0.5300	1.55	1.19×10^{-13}
	400	-1221	7.00	-1129	-1161	0.35	0.5184	1.53	2.21×10^{-13}
	500	-1234	7.88	-1138	-1170	0.3524	0.4968	1.57	4.54×10^{-13}

Table 3 Effect of sweep rate on voltammetric parameters of 1mM 9-acetylanthracene semicarbazone in in DMF-phosphate buffer-HClO$_4$ at different pH (5, 7& 9)

pH	v mVs^{-1}.	E_{pc} mV	I_{pc} μA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$ x10³ cm². s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-797	1.85	-656	-709	0.2616	0.3383	1.416	6.87x10^{-8}
	100	-799	2.56	-662	-712	0.256	0.3481	1.37	6.86x10^{-8}
	200	-805	3.84	-674	-716	0.2715	0.3641	1.42	5.74x10^{-8}
	300	-823	4.72	-688	-733	0.2725	0.3533	1.44	7.7x10^{-8}
	400	-835	5.36	-700	-744	0.268	0.3533	1.42	7.4x10^{-8}
	500	-829	5.96	-687	-749	0.2665	0.3614	1.39	6.8x10^{-8}
7	50	-811	1.95	-692	-733	0.2758	0.4008	1.37	8.38x10^{-9}
	100	-809	2.9	-674	-739	0.290	0.3533	1.54	5.76x10^{-8}
	300	-833	5.09	-704	-756	0.2938	0.3697	1.52	4.25x10^{-8}
	400	-855	5.8	-727	-773	0.29	0.3726	1.50	3.22x10^{-8}
	500	-854	6.63	-733	-776	0.2965	0.3942	1.49	1.81x10^{-8}
9	50	-881	1.74	-732	-791	0.2461	0.3335	1.34	2.52x10^{-8}
	100	-908	2.85	-730	-803	0.284	0.2679	1.73	2.95x10^{-7}
	200	-918	4.17	-739	-812	0.249	0.2178	1.99	2.34x10^{-6}
	300	-940	4.70	-754	-819	0.2707	0.2564	1.69	5.34x10^{-7}
	400	-945	5.27	-761	-830	0.2635	0.2592	1.63	5.13x10^{-7}
	500	-967	5.80	-767	-836	0.2589	0.2385	1.76	9.85x10^{-7}

Table 4 Effect of sweep rate on Voltammetric parameters of 1 mM 9-acetylanthracene semicarbazone in CH$_3$OH-B-R buffer at different pH (5,7 & 9)

pH	v mV/s	E_{pc} mV	I_{pc} μA	$E_{1/2}$ mV	$E_{p/2}$ mV	$I_{pc}/v^{1/2}$	α_n	$D_0^{1/2}$ x10³ cm². s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	20	-1172	1.30	-1112	-999	0.2906	0.2758	1.74	6.01x10^{-9}
	50	-1184	1.86	-1121	-967	0.2616	0.2199	1.76	9.96x10^{-8}
	100	-1203	2.53	-1123	-591	0.253	0.0779	2.85	8.88x10^{-5}
	200	-1206	4.21	-1133	-734	0.2977	0.1011	2.95	4.95x10^{-5}
	300	-1224	4.96	-1145	-626	0.2863	0.0798	3.19	1.50x10^{-4}
	500	-1266	6.19	-1170	-636	0.2768	0.0757	3.17	2.00x10^{-4}
7	50	-1208	2.29	-1150	-1063	0.3238	0.3290	1.78	5.87x10^{-10}
	100	-1224	3.08	-1165	-825	0.308	0.1196	2.80	1.39x10^{-5}
	200	-1261	5.44	-1151	-966	0.3842	0.1617	3.01	2.62x10^{-6}
	300	-1295	5.98	-1169	-869	0.3452	0.1120	3.25	2.85x10^{-5}
	400	-1348	6.91	-1201	-805	0.3455	0.0879	3.67	9.29x10^{-5}
	500	-1347	7.60	-1212	-667	0.380	0.0702	4.04	2.59x10^{-4}
9	50	-1198	2.26	-1147	-1067	0.3196	0.3642	1.67	1.28x10^{-10}
	100	-1211	2.82	-1151	-1041	0.282	0.2806	1.67	6.81x10^{-9}
	200	-1314	4.36	-1152	-878	0.3005	0.1094	2.93	2.18x10^{-5}
	300	-1354	5.32	-1178	-858	0.2950	0.0962	3.12	4.52x10^{-5}

Table 5 Effect of sweep rate on voltammetric parameters of 1mM 9-anthracenecarboxaldehyde thiosemicarbazone in in DMF-phosphate buffer-HClO$_4$ at different pH (5, 7& 9)

pH	v mV/s	$E_{p,c}$ mV	$I_{p,c}$ µA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2}$ x10^3 cm^2. s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-713	162	-615	-655	0.2291	.4867	1.03	2.98x10^{-9}
	100	-730	241	-604	-667	0.241	.3785	1.23	6.9x10^{-8}
	200	-735	353	-616	-678	0.2496	.4008	1.24	4.97x10^{-8}
	300	-743	439	-619	-681	0.2534	.3846	1.29	8.75x10^{-8}
	400	-750	517	-624	-695	0.2585	.3785	1.32	1.10x10^{-7}
	500	-770	584	-629	-709	0.2611	.3382	1.42	1.43x10^{-7}
7	50	-846	154	-686	-760	0.2178	.2981	1.26	1.13x10^{-7}
	100	-847	224	-668	-762	0.224	.2664	1.37	4.64x10^{-7}
	200	-864	337	-467	-778	0.2383	.1201	2.16	8.0x10^{-5}
	300	-873	400	-662	-788	0.2309	.2064	1.61	4.88x10^{-6}
	400	-890	464	-690	-801	0.232	0.2385	1.94	2.09x10^{-6}
	500	-890	523	-685	-809	0.2338	0.2326	1.53	2.02x10^{-6}
9	50	-878	1.54	-641	-739	0.2178	0.2013	1.53	2.14x10^{-6}
	100	-898	2.21	-601	-760	0.221	0.1606	1.73	1.09x10^{-5}
	200	-910	4.50	-615	-779	0.3182	0.1617	2.49	1.97x10^{-5}
	300	-934	4.57	-575	-822	0.2638	0.1329	2.28	4.92x10^{-5}
	400	-948	5.46	-619	-832	0.273	0.1450	2.26	3.50x10^{-5}
	500	-953	6.04	-644	-836	0.2701	0.1544	2.16	2.65x10^{-5}

Table 6 Effect of sweep rate on Voltammetric parameters of 1 mM 9-anthracenecarboxaldehyde thiosemicarbazone in CH$_3$OH-B-R buffer at different pH (5,7 & 9)

pH	v mV/s	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2}$ x10^3 cm^2. s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-1006	2.42	-942	-833	0.3422	0.2758	2.05	6.65x10^{-8}
	100	-1028	3.44	-958	-808	0.344	0.2169	2.32	7.89x10^{-7}
	200	-1053	4.75	-969	-756	0.3359	0.1606	2.64	8.86x10^{-6}
	300	-1067	6.02	-978	-770	0.3463	0.1606	2.73	7.51x10^{-6}
	400	-1076	7.38	-987	-736	0.3685	0.1403	3.10	2.79x10^{-5}
	500	-1038	7.79	-931	-526	0.3483	0.0932	3.59	2.44x 0^{-4}
7	50	-1148	230	-1028	-1083	0.3253	0.3975	1.62	5.92x10^{-11}
	100	-1163	330	-1045	-1102	0.330	0.4042	1.63	1.36x10^{-10}
	200	-1179	515	-1037	-1108	0.3642	0.3359	1.98	1.39x10^{-9}
	300	-1195	623	-1055	-1127	0.3596	0.318	2.01	2.78x10^{-9}
	400	-1221	705	-1067	-1149	0.3525	0.3097	1.99	3.8x10^{-9}
	500	-1224	782	-1089	-1161	0.3497	0.3267	1.92	1.58x10^{-9}
9	50	-1165	243	-1087	-1109	0.3437	0.3942	1.72	5.60x10^{-11}
	200	-1191	518	-1087	-1130	0.3663	0.4586	1.70	4.04x10^{-12}
	300	-1212	621	-1111	-1151	0.3585	0.4722	1.64	1.75x10^{-12}
	400	-1222	728	-1120	-1162	0.364	0.4676	1.67	2.0x10^{-12}

Table 7 Effect of sweep rate on voltammetric parameters of 1mM 9-acetylanthracene thiosemicarbazone in DMF-phosphate buffer-HClO$_4$ at different pH (5, 7& 9)

pH	v mV/s	$E_{p,c}$ mV	$I_{p,c}$ µA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2}$ x10^3 cm^{2}s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-736	1.71	-581	-658	0.2418	.3078	1.37	3.41x10^{-7}
	100	-767	2.53	-554	-672	0.253	.2240	1.68	4.26x10^{-6}
	200	-791	3.79	-531	-691	0.268	.1835	1.97	1.8x10^{-5}
	300	-865	5.20	-494	-736	0.302	.1286	2.63	9.25x10^{-5}
	400	-861	5.91	-525	-720	0.2955	.1420	2.47	6.85x10^{-5}
	500	-873	6.91	-557	-736	0.3081	.1510	2.50	5.52x10^{-5}
7	50	-816	1.73	-622	-727	0.2446	.2459	1.55	9.45x10^{-7}
	100	-851	2.63	-609	-755	0.263	.1971	1.86	5.17x10^{-6}
	200	-900	4.36	-535	-792	0.3076	.1307	2.68	6.05x10^{-5}
	300	-918	6.07	-572	-812	0.3498	.1379	2.97	5.94x10^{-5}
	400	-921	6.41	-586	-847	0.3205	0.1424	2.67	5.25x10^{-5}
	500	-926	7.25	-599	-846	0.3233	0.1459	2.67	5.09x10^{-5}
9	50	-1048	169	-943	-990	0.2390	0.4542	1.11	2.02x10^{-11}
	100	-1034	231	-919	-972	0.231	0.3816	1.18	5.72x10^{-10}
	200	-1044	345	-896	-978	0.2439	0.3229	1.35	9.2x10^{-9}
	300	-1076	428	-960	-1012	0.2471	0.4112	1.21	1.89x10^{-10}
	400	-1096	492	-982	-1023	0.246	0.4185	1.20	1.16x10^{-10}
	500	-1106	574	-991	-1039	0.2567	0.4145	1.25	1.35x10^{-10}

Table 8 Effect of sweep rate on voltammetric parameters of 1 mM 9-acetylanthracene thiosemicarbazone in CH$_3$OH-B-R buffer at different pH (5,7 & 9)

pH	v mV/s	E_{pc} mV	I_{pc} µA	$E_{p/2}$ mV	$E_{1/2}$ mV	$I_{p,c}/v^{1/2}$	α_n	$D_0^{1/2}$ x10^3 cm^2.s^{-1}	$K^{\bullet}_{f,h}$ cm.s^{-1}
5	50	-1046	232	-912	-988	0.3281	0.3559	1.73	1.58x10^{-9}
	100	-1063	321	-922	-1001	0.321	0.3382	1.74	3.61x10^{-9}
	200	-1078	491	-946	-1019	0.3472	0.3335	1.90	4.8x10^{-9}
	300	-1104	609	-955	-1034	0.3516	0.3201	1.96	8.7x10^{-9}
	400	-1118	705	-949	-1050	0.3525	0.2822	2.09	4.40x10^{-8}
	500	-1131	792	-972	-1065	0.3542	0.2805	2.11	4.1x 0^{-8}
7	50	-1243	2.77	-1201	-907	0.3903	0.1420	3.27	3.88x10^{-6}
	100	-1265	3.75	-1216	-897	0.375	0.1296	3.28	8.55x10^{-6}
	200	-1277	6.26	-1227	-934	0.4227	0.1391	3.73	8.39x10^{-6}
	400	-1323	8.61	-1263	-951	0.4305	0.1282	3.78	1.57x10^{-5}
	500	-1341	9.50	-1279	-971	0.4248	0.1289	3.72	1.53x10^{-5}
9	50	-1205	2.20	-1167	-634	0.3111	0.0835	3.39	5.90x10^{-5}
	100	-1212	3.07	-1172	-652	0.307	0.0852	3.31	7.45x10^{-5}
	200	-1230	4.65	-1177	-720	0.3274	0.0935	3.38	7.13x10^{-5}
	300	-1305	6.53	-1237	-809	0.377	0.0962	3.83	6.66x10^{-5}
	400	-1364	6.85	-1258	-814	0.342	0.0867	3.66	9.25x10^{-5}
	500	-1368	7.60	-1272	-826	0.3399	0.0852	3.66	1.03 x10^{-4}

Effect of scan rate

The cyclic voltammograms were recorded by varying the scan rate (50-500 mV/s), keeping the pH and the concentration of solution constant. The data show one irreversible reduction peak at all scan rates. The peak potential value shifted in the more negative direction with an increase in the scan rate indicating the electrochemical process was irreversible. The peak potential shift was higher when the scan rate increased. This means that under these conditions the electrochemical process is more irreversible. Peak current also increases as the scan rate increased for all the compounds. Data obtained were used in the plotting of current function ($I_{pc}/v^{1/2}$) against the scan rate (v) in order to apply the Nicholson-Shain criteria to elucidate the reduction mechanism. **Figure 1** show the linear relationship between the square root of scan rate ($v^{1/2}$) and cathodic peak current (I_p), indicating the irreversible nature of charge transfer process. The current function ($I_{pc}/v^{1/2}$) has been found to be fairly constant with respect to sweep rate indicating that the electrode process is diffusion controlled [17-20].
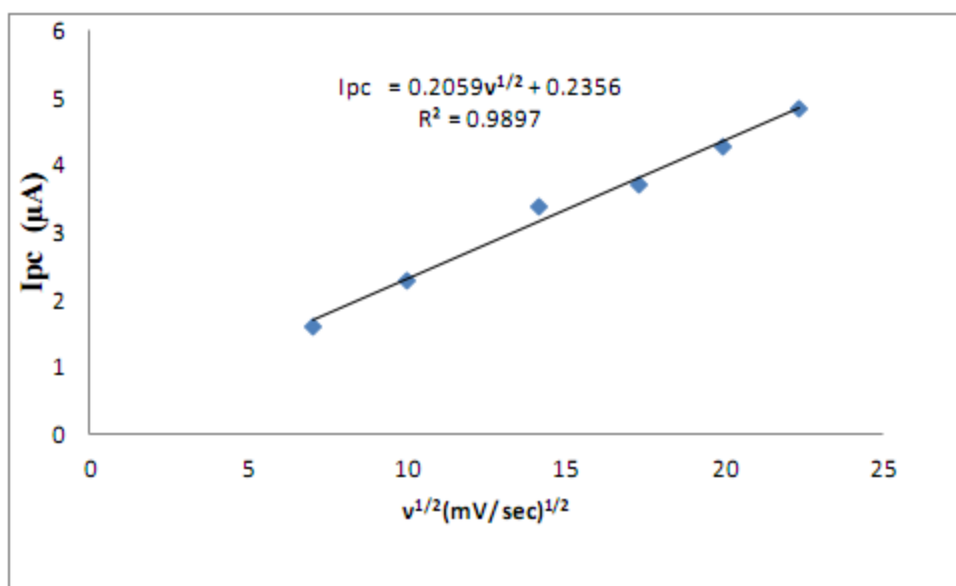
Figure 1 Variation of cathodic peak current (I_{pc}) versus $v^{1/2}$ for 1 mM 9-anthracenecarboxaldehyde semicarbazone in DMF-phosphate buffer-HClO$_4$ (pH5)

Effect of concentration of electroactive species

Table 9 Values of cathodic peak potential and peak current for 9-anthracenecarboxaldehyde semicarbazone in DMF-phosphate buffer-HClO$_4$ (pH5) at different concentration

v (mVs^{-1})	Concentration(mM)					
	1mM		2mM		3mM	
	E_{pc} (mV)	I_{pc} (µA)	E_{pc} (mV)	I_{pc} (µA)	E_{pc} (mV)	I_{pc} (µA)
50	-620	1.61	-661	2.16	-724	2.95
100	-637	2.28	-695	2.64	-731	3.59
200	-642	3.39	-708	4.26	-761	5.54
300	-653	3.72	-706	4.59	-775	6.42
400	-659	4.29	-733	5.52	-797	7.37
500	-667	4.84	-742	6.24	-814	8.24

Effect of concentration on the reduction potential was studied by varying the concentration of compound from 1mM to 3mM in the potential range +1300mV to -1300mV, keeping the scan rate constant. The cathodic peak current was found to increase linearly with increase in the concentration of the compound. The plot of I_{pc} vs concentration shows linearity, further indicating the electrode process were diffusion controlled. It was also observed that the peak potential (E_{pc}) were shifted towards more negative values as the compound concentration increased (**Table 9**).

This kind of shift in E_{pc} in the cathodic direction with increasing concentration indicating that the reduction products are adsorbed over the electrode surface, this kind of shift has been predicted theoretically and observed experimentally[21,22].

Effect of pH

The effect of pH upon the reduction of semicarbazones and thiosemicarbazones was investigated (**Tables 1-8**). Peak potential values of the compounds are found to be changed with the pH value of the solution. This dependence of the peak potential on pH indicating that proton transfer also takes place in the electrode reaction. The peak potential shifts in more negative values depending upon the pH of the solution. This means that the reduction is easier in acidic media and difficult in media where the proton concentration is low. The ease of reduction is found to be more in acidic pH than in alkaline pH which may be because of the formation of easily reducible protonated intermediate.

Effect of concentration of HClO$_4$

Cyclic voltammograms were also recorded in DMF-phosphate buffer media by varying the concentration of $HClO_4$ from 5mM to 25mM and data are collected in **Table 10**. Voltammetric data show that as the concentration of $HClO_4$ increases, the cathodic peak potential decreases at all the scan rates studied thereby showing the involvement of proton in the reduction process.

Table 10 Values of cathodic peak potential for 9-anthracenecarboxaldehyde semicarbazone in DMF-phosphate buffer (pH5) at different concentration of $HClO_4$

| ν (mVs^{-1})	Concentration of HClO$_4$(mM)			
	25mM		5mM	
	E_{pc} (mV)	I_{pc} (µA)	E_{pc} (mV)	I_{pc} (µA)
50	-620	1.61	-1093	1.91
100	-637	2.28	-1117	2.34
200	-642	3.39	-1143	3.75
300	-653	3.72	-1153	4.08
400	-659	4.29	-1155	5.21
500	-667	4.84	-1172	6.08

Effect of –CH$_3$

Electron withdrawing groups accelerate the reduction and electrondonating groups lower it [23,24]. Effect of –CH$_3$ group on the reduction of semicarbazone and thiosemicarbazone was studied by running the cyclic voltammograms of semicarbazones and thiosemicarbazones of 9-anthracenecarboxaldehyde and 9-acetylanthracene. In all the cases the single wave was obtained which ascribed to the reduction of protonated semicarbazone/thiosemicarbazone group. When compared to protonated form the reduction becomes easier in case 9- anthracenecarboxaldehyde semicarbazone/ thiosemicarbazone than 9- acetylanthracene semicarbazone/thiosemicarbazone respectively because

in 9- acetylanthracene semicarbazone/thiosemicarbazone, the +I effect of $-CH_3$ group which is directly attached to the semicarbazone/thiosemicarbazone group and its hyperconjugative effect increases the electron density, therefore it will be more difficult to reduce semicarbazone/thiosemicarbazone group of 9- acetylanthracene semicarbazone / thiosemicarbazone as compared to 9-anthracenecarboxaldehyde semicarbazone / thiosemicarbazone respectively. It is evident from the reduction potential values. Besides this the electrondonating +I methyl group hinders the reduction in9- acetylanthracene semicarbazone / thiosemicarbazone.

Effect of solvent

Cyclic voltammograms were recorded in two different DMF-phosphate buffer medium and CH_3OH-BR buffer. It was observed that the peak potential shifted to more negative values in presence of organic co solvent and magnitude of shift depends on the nature of solvent. The order of shift observed in present study is CH_3OH-BR buffer> DMF-phosphate buffer. This trend parallels the trend in dielectric constant of solvent (32.5>37.5) respectively
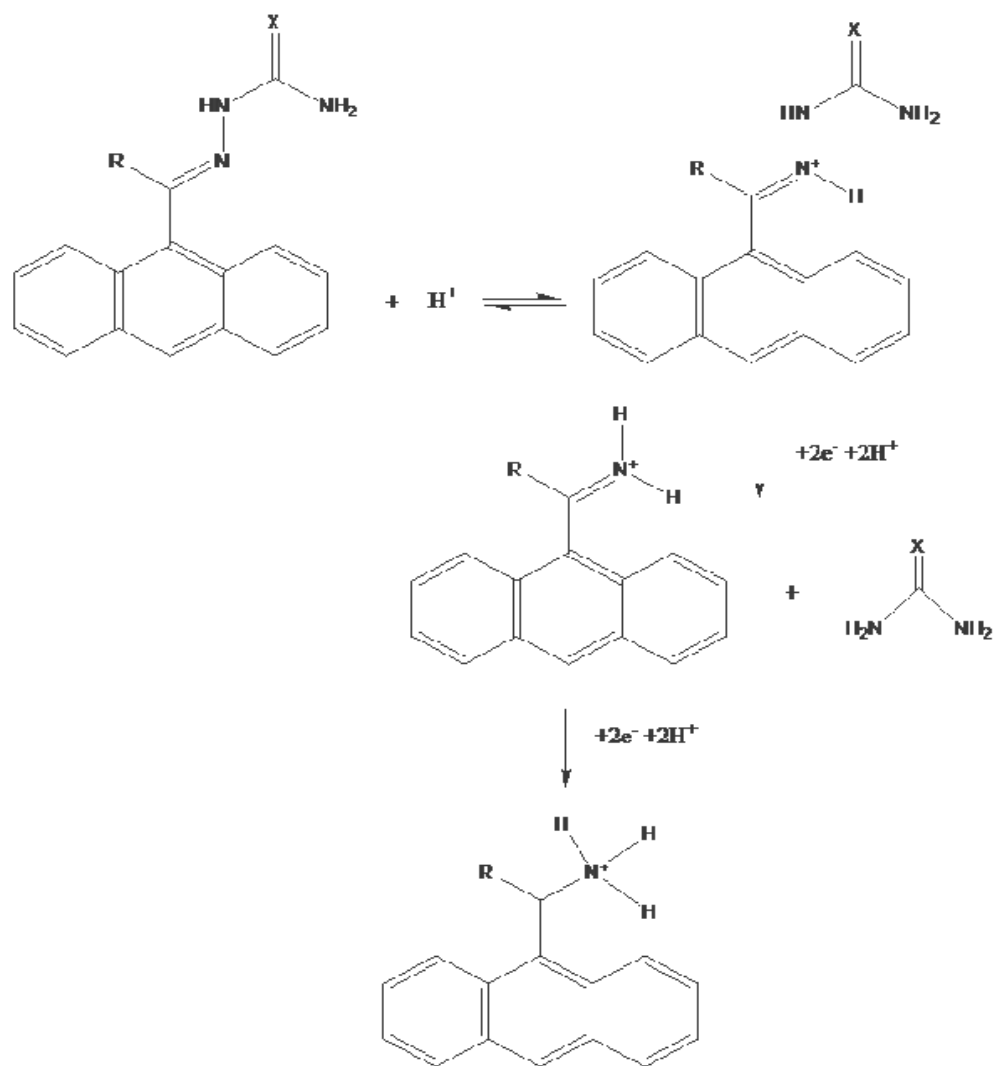
Where R = -H or -CH$_3$
and X = O or S

Scheme 1 Proposed reduction mechanism for semicarbazone / thiosemicarbazone

Conclusion

The result obtained in the present study show that 9-anthracenecarboxaldehyde semicarbazone / thiosemicarbazone presently investigated undergoes easily reduction than 9- acetylanthracene semicarbazone/thiosemicarbazone.Keeping in view of feasibility of the site of reduction and on the basis of cyclic voltammetric results, the reduction mechanism shown in **scheme 1** may be suggested for electroreduction of above studied semicarbazones and thiosemicarbazones, similar that reported in the literature[17-20]. The mechanism finds supports from the E_{pc} and $E_{1/2}$ shifts towards negative potential with pH, as protons are consumed in the reduction.

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