

Electrochemical behaviour of metal complexes of salicylic acid hydrazide

Salisilik asit hidrazürün metal komplekslerinin elektrokimyasal davranışı

Research Article

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ABSTRACT

The present article deals with the electrochemical investigations of salicylic acid hydrazide (SAH) and its complexes of cadmium(II), copper(II), manganese(II), nickel(II), zinc(II), cobalt(III) and iron(III). The results obtained in polarography are compared with that in cyclic voltammetric studies. The effect of height of the mercury column on wave height, the effect of concentration of the complex on the wave height and half wave potential and the effect of temperature etc were studied in detail and the sites susceptible for reduction were explored and presented.

Key Words

Salicylic acid hydrazide, metal complexes, polarography, cyclic voltammetry.

ÖZET

Sunulan çalışma, salisilik asit hidrazürün (SAH) ve kadmiyum(II), bakır(II), mangan(II), nikel(II), çinko(II), kobalt(III) ve demir(III) komplekslerinin elektrokimyasal incelenmesini içermektedir. Polarografiden elde edilen sonuçlar, dönüşümlü voltmetre sonuçlarıyla karşılaştırılmıştır. Civa kolon yüksekliğinin dalga yüksekliğine etkisi; kompleks derişiminin dalga yüksekliğine ve yarı-dalga potansiyeline etkisi ve sıcaklığın etkisi vb. değişkenler ayrıntılı olarak incelenmiş ve indirgenme bölge duyarlılığı sunulmuştur.

Anahtar Kelimeler

Salisilik asit hidrazür, metal kompleksler, polarografi, dönüşümlü voltmetre.

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INTRODUCTION

The physico-chemical properties and potentially therapeutic properties [1-4] of metal complexes have attracted the considerable attention of chemists. In particular electrochemical studies have been used to explore the therapeutic properties of the complexes [5]. Literature survey reveals that polarographic studies have been exploited to predict the behavior of ligand and their complexes in biochemistry and medicine [6]. Polarography proved to be useful for determination of oxidation state of metals, both in the ionic form and in complexes [7,8]. The lower costs, faster results, better accuracy are the powerful advantages to employ polarographic methods for analyses [8]. The concept of complexation is also extensively utilized for the trace analysis of pollutants [9,10]. In earlier studies [11], the authors exploited general methods i.e. elemental analysis, spectroscopy, magnetic moment measurements, molar conductivity measurements to study the physico-chemical aspects the complexes of SAH under study. In this article, the authors reported the electrochemical studies of the complexes of SAH.

MATERIALS AND METHODS

All the chemicals used were of analytical reagent grade obtained from Merck India Limited. The complexes under study were synthesized and characterized by the procedures reported in the literature [11]. pH measurements were made using ELICO pH meter Model L1-10, ELICO Private Limited, Hyderabad, India. ELICO DC Recording Polarograph manufactured by ELICO Private Limited, Hyderabad, India was used for polarographic studies. The mercury flow rate of dropping mercury electrode was found to be 1.80 mg/cm² at a height of 80 cm and zero applied voltage. Cyclic voltammetric unit consists of X-Y recorder (Model RE. 0074), PAR 173 potentiostat, PAR 175 universal programmer. A single compartment cell model 303 HMDE supplied by PAR with silver wire as reference electrode and platinum wire as counter electrode was used in the studies. A static mercury (HMDE 303) drop electrode with a drop area 0.0096 cm² was used as the working cathode. A circulating type thermostat, supplied by Toshniwal, Bombay, India with water as the thermostatic liquid was employed to maintain a constant temperature.

General experimental procedure

10 mL of buffer solution and 2.5 mL of metal complex solution (1 x 10⁻² M), 10 mL of dimethylformamide and remaining volume of distilled water to make the total volume to 25 mL were taken into a polarographic/cyclic voltammetric cell. Polarograms/cyclic voltammograms were recorded after deaeration of the solution with nitrogen gas. The polarographic maxima in all the cases were suppressed by the addition of two drops of 0.001% gelatin.

RESULTS AND DISCUSSION

General polarographic behaviour

All the metal complexes under investigation have shown a single reduction wave in the pH range 2.1 - 10.1. The reagent when present alone did not give any polarographic wave. The half wave potentials of the waves were found to be more negative when compared to the simple metal ions. The change in half wave potential ($E_{1/2}$) with the concentration of the complex may be attributed to the irreversible electrochemical behaviour of the complex [12]. The same was further confirmed from the non integral values of n obtained from the plots of $\log \frac{\bar{i}}{\bar{i}_d - \bar{i}}$ vs

$E_{1/2}$ (Figure 1). The values of $H/h^{1/2}$ were fairly constant. A plot of concentration of the complex versus wave height was linear (Figure 2). All these facts reveal that the complexes undergo a diffusion controlled irreversible reduction. The half wave potentials were shifted to more negative values with the increase of pH of the media. However there was no change in the half wave potential beyond 8.1. The shift of half wave potentials to more negative values with increase in pH suggests that the protons (P) were involved in the reduction process. Further the non integer value of P (Tables 1 and 2) confirms the surface protonation. However the wave height remains constant beyond pH 8.1. The decrease in wave height upto pH 8.1 may be due to the electroactive nature of the protonated form of the depolarizer. Beyond pH 8.1, both forms of the depolarizer were electroactive and were reduced at the same potential.

Effect of temperature

To study the effect of temperature on half wave potential and the diffusion current, the polarograms of the metal complexes were recorded at 303, 313, 323 and 333 K at pH 4.1. The data is presented

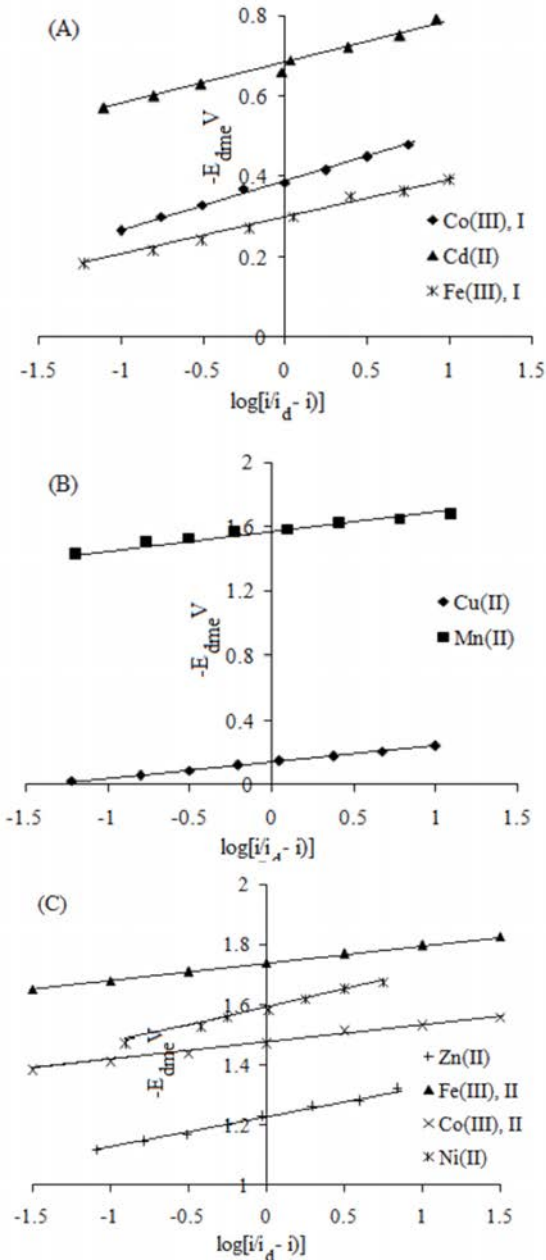


Figure 1. Semi log plots of M-SAH complexes under study; pH = 4.1; Medium = Dimethylformamide (50% by volume)

in Table 3. The complexes exhibit a well defined single wave at all temperatures studied. At all temperatures the ratio of wave height (H) and $h^{1/2}$ values was almost constant. The diffusion current increases with increase in temperature and the value of temperature coefficient for the diffusion current [13] was in the range 0.7-1.4% deg^{-1} .

Tomes criteria [14] was employed to determine

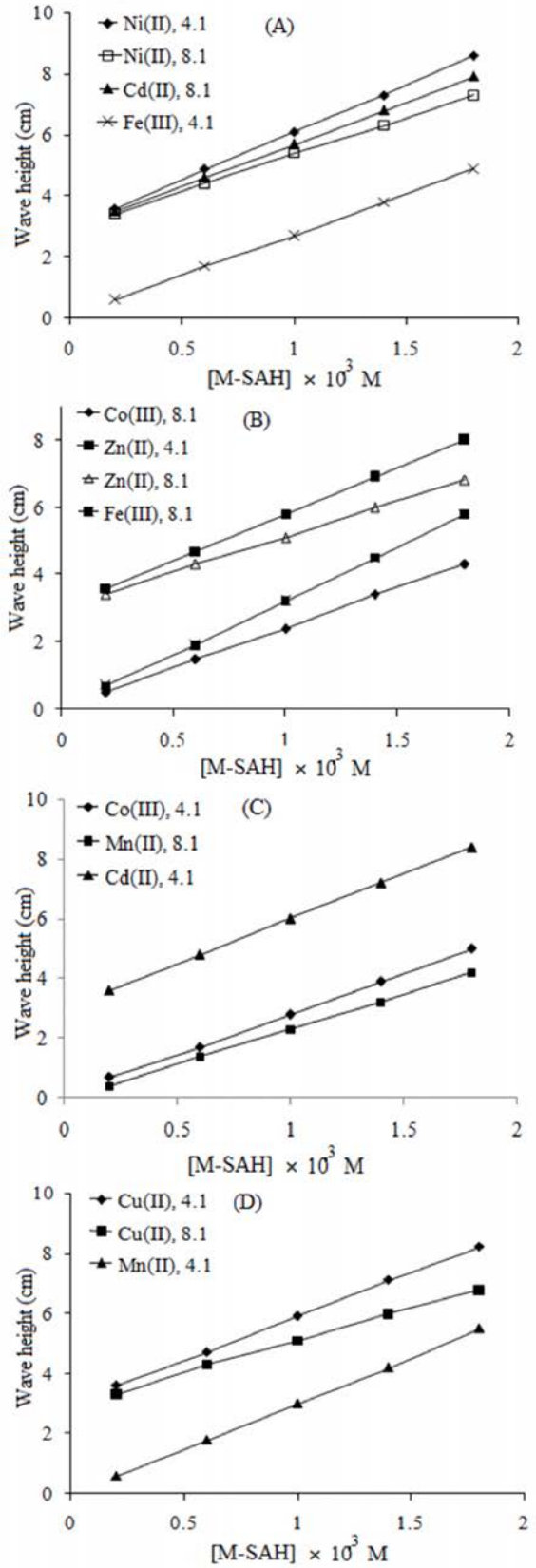


Figure 2. Effect of concentration of M-SAH on its limiting current; Medium = Dimethylformamide (50% by volume).

Table 1. Polarographic characteristics and kinetic parameters of Metal - SAH complex; Medium: Aqueous DMF (40% V/V); [Metal-SAH]: 1×10^{-3} M.

	pH	$-E_{1/2}$ V vs SCE		Wave height H (cm)	$\Delta E_{1/2}/\Delta pH$ (mV)	αn_a	Number of protons (P)	Dx 10^6 (cm ² sec ⁻¹)	I* x 10 ³	K ^o _{th} (cm sec ⁻¹)	ΔG^* K cal mole ⁻¹
		Simple metal ion	M(II)- SAH								
Mn(II)- SAH	2.1	1.32	1.49	3.2	0.04533	0.52	0.3985	2.144	1.778	1.141×10^{14}	11.349
	4.1	1.42	1.59	3.0		0.50	0.3832	1.885	1.667	4.037×10^{15}	11.619
	6.1	1.51	1.68	2.7		0.48	0.3679	1.527	1.500	1.932×10^{15}	11.927
	8.1	1.59	1.76	2.3		0.46	0.3448	1.108	1.278	1.204×10^{15}	12.051
	10.1	1.59	1.76	2.3		0.43	0.3295	1.108	1.278	1.204×10^{15}	12.051
Ni(II) - SAH	2.1	0.49	0.61	6.4	0.03333	0.71	0.4001	8.579	3.56	8.126×10^8	7.265
	4.1	0.56	0.69	6.1		0.69	0.3888	7.793	3.39	1.203×10^8	7.759
	6.1	0.63	0.76	5.7		0.67	0.3775	6.804	3.17	2.569×10^9	8.159
	8.1	0.71	0.84	5.4		0.65	0.3663	6.107	3.00	4.778×10^{10}	8.594
	10.1	0.71	0.84	5.4		0.63	0.3550	6.107	3.00	4.778×10^{10}	8.594
Cu(II)-SAH	2.1	0.03	0.11	6.2	0.07451	0.73	0.919	8.050	3.444	1.500×10^0	2.933
	4.1	0.14	0.26	5.9		0.71	0.894	7.290	3.278	1.809×10^2	4.077
	6.1	0.19	0.31	5.5		0.69	0.869	6.335	3.056	2.940×10^{-4}	5.143
	8.1	0.24	0.36	5.1		0.67	0.844	5.447	2.833	7.806×10^{-5}	5.487
	10.1	0.24	0.36	5.1		0.65	0.844	5.447	2.833	7.806×10^{-5}	5.487
Zn(II)- SAH	2.1	0.89	1.17	6.1	0.03658	0.71	0.4391	7.792	3.389	1.469×10^{14}	11.284
	4.1	0.95	1.23	5.8		0.69	0.4267	7.045	3.222	5.745×10^{15}	11.527
	6.1	1.02	1.30	5.5		0.67	0.4143	6.335	3.056	1.895×10^{15}	11.814
	8.1	1.09	1.38	5.1		0.65	0.4020	5.447	2.833	5.294×10^{16}	12.144
	10.1	1.09	1.38	5.1		0.63	0.4020	5.447	2.833	5.294×10^{16}	12.144
Cd(II)- SAH	2.1	0.50	0.60	6.2	0.03854	0.52	0.3388	8.050	3.444	1.474×10^6	6.514
	4.1	0.58	0.68	6.0		0.50	0.3258	7.539	3.333	3.976×10^7	6.854
	6.1	0.64	0.74	5.9		0.48	0.3128	7.290	3.278	2.677×10^7	6.956
	8.1	0.72	0.82	5.7		0.46	0.2997	6.804	3.167	6.096×10^8	7.339
	10.1	0.72	0.82	5.7		0.44	0.2997	6.804	3.167	6.096×10^8	7.339

Table 3. Effect of temperature on the polarographic characteristics of Metal-SAH complex; Medium : Aqueous DMF (40% V/V); [Mn(II)-SAH]: 1×10^{-3} M; pH:4.1

Temperature K	Half wave potential, $-E_{1/2}$ V vs SCE	Wave Height, H (cm)	Temperature coefficient % (deg^{-1})	αn_a	$D \times 10^6$ ($\text{cm}^2 \text{sec}^{-1}$)
Mn(II)- SAH					
303	1.54	2.7	-	0.51	1.527
313	1.59	3.0	1.054	0.49	1.885
323	1.65	3.4	1.252	0.47	2.421
333	1.71	3.8	1.112	0.45	3.024
Ni(II) - SAH					
303	0.65	5.4	-	0.75	6.107
313	0.69	6.1	1.219	0.72	7.793
323	0.74	6.8	1.233	0.69	9.684
333	0.79	7.6	1.112	0.67	12.096
Cu(II) - SAH					
303	0.12	5.3	-	0.76	5.881
313	0.15	5.9	1.072	0.74	7.290
323	0.19	6.6	1.121	0.71	9.122
333	0.23	7.3	1.008	0.69	11.160
Zn(II) - SAH					
303	1.18	5.2	-	0.73	5.663
313	1.23	5.8	1.092	0.71	7.045
323	1.29	6.5	1.139	0.69	8.848
333	1.35	7.3	1.161	0.67	11.160
Cd(II) - SAH					
303	0.62	5.3	-	0.57	5.883
313	0.68	6.0	1.241	0.53	7.539
323	0.75	6.8	1.252	0.50	9.684
333	0.82	7.6	1.112	0.47	12.096
Fe(III) - SAH					
303	0.27	2.6	-	0.67	5.659
313	0.30	2.9	1.092	0.64	7.045
323	0.34	3.2	0.984	0.60	8.578
333	0.38	3.6	1.178	0.57	10.856
Co(III) - SAH					
303	0.36	2.4	-	0.74	4.825
313	0.39	2.7	1.178	0.70	6.107
323	0.43	3.0	1.054	0.66	7.539
333	0.49	3.3	0.953	0.64	9.122

Polarographic behaviour of SAH complexes of iron (III) and cobalt (III)

The polarographic behaviour of iron(III) and cobalt(III) complexes of SAH have been studied in the pH range 2.1 to 10.1. The complexes of iron(III) and cobalt(III) have resulted in two waves.

First wave

A single well defined wave observed in the pH range 2.1 to 4.1 may be attributed to one electron reduction of the metal complex. The half wave potential values of the metal complexes were shifted to more negative values compared to the half wave

Table 4. Kinetic and thermodynamic parameters of polarographic reduction of M(III)-SAH complex (1×10^{-3} M) at pH 4.1.

Parameter	Meites-Israel Treatment				Oldham-Parry Treatment				Gaur-Bhargava Treatment			
	303K	313K	323K	333K	303K	313K	323K	333K	303K	313K	323K	333K
$K_o \times 10^6$ (cm sec ⁻¹)	47.805	25.700	12.020	6.153	47.790	25.710	12.034	6.164	70.609	36.900	16.690	8.289
ΔH_p^* (K cal mole ⁻¹)	13.728	13.728	13.728	13.728	13.385	13.385	13.385	13.385	14.405	14.405	14.405	14.405
ΔH_v^* (K cal mole ⁻¹)	13.126	13.106	13.086	13.066	12.783	12.763	12.743	12.723	13.803	13.783	13.763	13.743
ΔG^* (K cal mole ⁻¹)	5.672	6.027	6.432	6.823	5.672	6.027	6.431	6.823	5.570	5.929	6.340	6.737
$-\Delta S^*$ (eu)	24.601	22.617	20.601	18.748	23.468	21.521	19.542	17.718	27.172	25.093	22.981	21.039
$K_o \times 10^7$ (cm sec ⁻¹)	30.520	17.950	8.860	2.493	30.590	18.000	8.890	2.504	40.569	23.272	11.130	2.969
ΔH_p^* (K cal mole ⁻¹)	12.154	12.154	12.154	12.154	12.113	12.113	12.113	12.113	12.392	12.392	12.392	12.392
ΔH_v^* (K cal mole ⁻¹)	11.552	11.532	11.512	11.492	11.511	11.491	11.471	11.451	11.790	11.770	11.750	11.730
ΔG^* (K cal mole ⁻¹)	6.392	6.746	7.158	7.744	6.391	6.745	7.158	7.743	6.317	6.676	7.095	7.694
$-\Delta S^*$ (eu)	17.030	15.291	13.480	11.255	16.897	15.163	13.353	11.135	18.063	16.275	14.412	12.120

potentials of the simple metal ions. The values of $H/h^{1/2}$ were fairly constant (Table 7). The plots of wave height Vs concentration of the complex were linear. These facts reveal that the complexes were undergoing diffusion controlled reduction. The change in half wave potential with the concentration of the complex may be attributed to the irreversible behaviour of the complex. The fractional values of n obtained from the plots of $\log \frac{i}{i_d - i}$ vs $-E_{1/2}$

$$\frac{i}{i_d - i}$$

further confirms this fact. The involvement of protons in the reduction process was revealed by the shift of half wave potentials towards negative values with increase in pH. However, an increase in wave height with increase in pH in the case of Fe(III)-SAH complex may be attributed to the electroactive nature of the unprotonated form of the complex. The wave height remains constant beyond pH 8.1. Whereas in case of Co(III)-SAH complex, the wave height decreases with increase in pH. This suggests that the protonated form of the complex was electroactive.

Second wave

The absence of second wave in the pH range 2.1-4.1 may be ascribed to the formation of a species that can be reduced at more negative potentials. A second wave was observed in the pH range 6.1-10.1 of study. With increase in pH and also with increase in concentration of the complex, the half wave potentials of the second wave were shifted to more negative values. n value was found to be a non-integer. These facts suggest the irreversible nature of the electrode process. A linear relationship observed between $\log \frac{i}{i_d - i}$ vs $-E_{1/2}$

$$\frac{i}{i_d - i}$$

and the constancy of $H/h^{1/2}$ values suggest the diffusion controlled nature of the reduction process. The effect of pH on the half wave potential and the effect of pH on the wave height were similar to that observed for the first wave.

Effect of temperature

The metal complexes exhibit a single wave at temperatures 303, 313, 323 and 333 K in buffer solutions of pH 4.1. The data presented in Tables 3, 4 and 5 concludes following points.

With increase in temperature [22],

- the half wave potential values tend to become more negative, the wave height increases, (the temperature coefficient values for the diffusion current were in the range 0.95-1.18% deg⁻¹).
- α_n values decrease.

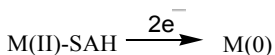
The above facts suggest that the electrode process was irreversible and diffusion controlled. Kinetic parameters data presented in Tables 4 and 5 suggest that the reduction process was becoming increasingly irreversible with increase in pH. This observation was further confirmed by the decrease in $K^o_{f,h}$ and increase in ΔG^* values.

Table 5. Kinetic and thermodynamic parameters of polarographic reduction of M(II)-SAH complex (1 x 10⁻³ M) at pH 4.1.

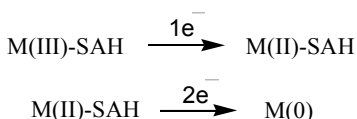
Parameter	Meites-Israel Treatment				Oldham-Parry Treatment				Gaur-Bhargava Treatment			
	303K	313K	323K	333K	303K	313K	323K	333K	303K	313K	323K	333K
Mn(II)-SAH												
$K^o_{f,h} \times 10^{16}$ (cm sec ⁻¹)	3.333	3.846	4.103	4.688	3.404	3.940	4.191	4.829	1.829	2.122	2.254	2.601
ΔH^*_p (K cal mole ⁻¹)	2.361	2.361	2.361	2.361	2.362	2.362	2.362	2.362	2.479	2.479	2.479	2.479
ΔH^*_v (K cal mole ⁻¹)	1.759	1.739	1.719	1.699	1.760	1.740	1.720	1.700	1.876	1.857	1.837	1.817
ΔG^* (K cal mole ⁻¹)	12.389	12.760	13.149	13.518	12.384	12.753	13.143	13.509	12.546	12.920	13.316	13.687
$-\Delta S^*$ (eu)	35.08	35.21	35.39	35.49	35.06	35.19	35.37	35.46	35.21	35.35	35.54	35.65
Cu(II)-SAH												
$K^o_{f,h} \times 10^{10}$ (cm sec ⁻¹)	24.640	6.804	1.088	0.155	24.840	6.868	1.100	0.157	24.580	6.428	0.929	0.244
ΔH^*_p (K cal mole ⁻¹)	33.392	33.392	33.392	33.392	30.509	30.509	30.509	30.509	33.048	33.048	33.048	33.048
ΔH^*_v (K cal mole ⁻¹)	32.790	33.770	32.750	32.730	29.907	29.887	29.867	29.847	32.446	32.426	32.406	32.386
ΔG^* (K cal mole ⁻¹)	8.254	8.874	9.668	10.528	8.251	8.871	9.665	10.524	8.255	8.889	9.712	10.397
$-\Delta S^*$ (eu)	80.970	79.540	71.461	66.673	71.470	67.140	62.545	58.027	79.838	75.198	70.260	66.033
Zn(II)-SAH												
$K^o_{f,h} \times 10^3$ (cm sec ⁻¹)	2.678	1.391	0.544	0.189	2.669	1.387	0.543	0.189	4.635	2.434	0.879	0.243
ΔH^*_p (K cal mole ⁻¹)	20.020	20.020	20.020	20.020	20.469	20.469	20.469	20.469	22.880	22.880	22.880	22.880
ΔH^*_v (K cal mole ⁻¹)	19.418	19.398	19.378	19.358	19.867	19.847	19.827	19.807	22.278	22.258	22.238	22.218
ΔG^* (K cal mole ⁻¹)	4.620	4.949	5.369	5.839	4.621	4.950	5.370	5.839	4.476	4.798	5.235	5.767
$-\Delta S^*$ (eu)	48.838	46.160	43.370	40.597	50.317	47.594	44.758	41.946	58.752	55.783	52.641	49.402
$K^o_{f,h} \times 10^{16}$ (cm sec ⁻¹)	23.540	3.250	0.320	0.030	24.010	3.320	0.360	0.030	13.600	1.730	0.150	0.012
ΔH^*_p (K cal mole ⁻¹)	48.048	48.048	48.048	48.048	48.049	48.049	48.049	48.049	51.481	51.481	51.481	51.481
ΔH^*_v (K cal mole ⁻¹)	47.446	47.426	47.406	47.368	47.447	47.427	47.407	47.387	50.879	50.859	50.839	50.819
ΔG^* (K cal mole ⁻¹)	11.878	12.805	13.860	14.969	11.873	12.799	13.827	14.970	12.022	12.975	14.071	15.285
$-\Delta S^*$ (eu)	117.386	110.610	103.857	97.348	117.406	110.632	103.963	97.348	128.241	121.035	113.833	106.709

Reduction Pattern

The millicoulometric data is presented in Table 6. For M(II)-SAH complexes (M= Ni, Mn, Cu, Zn, Cd), the single wave indicated the two electron reduction process as shown below.



Whereas for M(III)-SAH complexes (M= Fe & Co) indicate that the reduction process involve one electron in the case of first wave and two electrons in the case of second wave. The wave height of the second wave was two times to that of the first wave. Hence the sequence of the reduction process may be represented as



Cyclic voltammetric studies

The cyclic voltammograms for all the complexes were recorded in solutions of pH 4.1 and 8.1 at the scan rates of 10, 20, 50, 100, 200 mV/sec using HMDE as the indicator electrode.

Cyclic voltammetric behaviour of Cd(II)-SAH, Mn(II)-SAH and Zn(II)-SAH complexes

The results obtained in the cyclic voltammetric studies on SAH complexes of Cd(II), Mn(II) and Zn(II) and are presented in Table 8.

The cyclic voltammograms of the three metal complexes contain a cathodic peak at all scan rates. The absence of anodic peak in the reverse scan indicates the irreversible nature [23] of the reduction process. The presence of single cathodic peak in all cases suggests that the reduction process involves two electrons as observed in polarographic studies. The peak potentials and the peak currents increase with increase in the scan rate. Further, increase in peak potential was more pronounced at pH 8.1 compared to that at pH 4.1. The increase in peak current values with increase in scan rate indicates that no chemical reaction was taking place at the vicinity of the electrode [24].

Nature of the electrode process

The electrode process was found to be irreversible and diffusion controlled under experimental

conditions of study. The diffusion controlled nature of the electrode process was confirmed by the following facts.

1. linearity of i_{pc} vs $v^{1/2}$ plots [25],
2. unaltered $i_{pc}/v^{1/2}$ values [26],
3. the increase of peak current with increase in the concentration of the depolarizer [26].

The irreversible nature of the reduction process was confirmed by the following facts.

1. The $i_{pc}/v^{1/2}$ vs v plots were not parallel to the scan rate axis and may be related to the case III of Nicholson-Shain criteria [27].
2. The anodic peak was absent in the reverse scan [26].
3. The value of $(E_{pc/2} - E_{pc})$ was greater than 56.5/n mV [26].
4. The shift of E_{pc} towards more negative potentials [26].

Ni(II)-SAH complex

The results presented in Table 9 indicate that a single cathodic peak was observed at low scan rates. Two cathodic peaks and one anodic peak were observed at high scan rates.

The electrode process was found to be diffusion controlled. The first cathodic cyclic voltammetric peak may be due to the one electron reduction of Ni(II)-SAH complex to the Ni(I)-SAH complex. The second cathodic peak may be due to the one electron reduction of Ni(I)-SAH complex. The peak currents increase with increase in scan rates. The peak current values were almost the same for the two peaks indicating that the reduction involves one electron in each step. An anodic peak was noticed in reverse scan at high scan rates.

Two possible explanations may be offered to explain the formation of anodic peak.

- i. Oxidation of Ni(I)-SAH to Ni(II)-SAH.
- ii. Oxidation of Ni(O) - Ni(I).

However, the anodic peak obtained by the application of potential below the peak potential of the second cathodic peak confirms that the first option i.e., oxidation of Ni(I)-SAH to Ni(II)-SAH. ΔE_p , the difference between the anodic and the cathodic peaks at 25°C in the present investigation was

found to be 60 mV. Further it was noticed that the ratio of cathodic to anodic peak currents (i_{pc}/i_{pa}) was almost equal to one [26]. Hence the electrode process may be termed as quasi reversible.

Table 6. Millicoulometric data of Mn(II)-SAH complex; Medium: Aqueous DMF (40% V/V); [M-SAHI]: 1×10^{-3} M.

pH	t	Mn(II)		Ni(II)		Cu(II)		Zn(II)		Cd(II)		Fe(III)		Co(III)	
		H	n	H	n	H	n	H	n	H	n	I wave	II wave	I wave	II wave
4.1	0	3.0	-	6.1	-	5.9	-	5.8	-	6.0	-	2.9	-	2.8	-
	7200	2.9	1.9	4.6	1.7	4.5	1.8	4.4	1.8	4.6	1.9	2.3	-	2.7	-
	10800	2.4	1.8	4.0	1.8	4.0	1.9	3.9	1.8	4.1	1.9	2.1	-	2.0	-
8.1	0	2.3	-	5.4	-	5.1	-	5.1	-	5.7	-	3.5	7.1	2.4	4.6
	7200	2.1	1.9	4.2	1.8	4.1	1.9	4.1	1.9	4.4	1.8	2.6	5.4	2.0	3.8
	10800	2.0	1.8	3.6	1.7	3.6	1.9	3.7	1.9	3.8	1.7	2.3	4.8	1.8	3.5

Wave height (H cm); Time (t Sec); no. of electrons (n).

Table 7. Effect of mercury column height (h, cm) on wave height (H, cm), Medium: Aqueous DMF (40% V/V), [M-SAHI]: 1×10^{-3} M.

h	pH 4.1		pH 8.1		pH 4.1		pH 8.1		pH 4.1		pH 8.1		pH 4.1		pH 8.1		
	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	H	H/h ^{1/2}	
Mn(II)-SAH	Mn(II)-SAH		Ni(II)-SAH		Cu(II)-SAH		Zn(II)-SAH		Co(II)-SAH		Fe(III)-SAH		Cd(II)-SAH		Co(III)-SAH		
	80	3.1	0.35	2.5	0.28	6.4	0.72	5.8	0.65	6.3	0.70	5.5	0.61	6.1	0.68	5.5	0.62
	70	3.0	0.36	2.3	0.27	6.1	0.73	5.4	0.64	5.9	0.70	5.1	0.61	5.8	0.69	5.1	0.61
	60	2.8	0.36	2.1	0.27	5.6	0.73	5.0	0.64	5.5	0.71	4.6	0.60	5.3	0.68	4.7	0.61
	50	2.5	0.35	2.0	0.28	5.1	0.72	4.6	0.65	5.0	0.71	4.2	0.60	4.8	0.69	4.4	0.62
40	2.2	0.35	1.8	0.28	4.5	0.72	4.1	0.65	4.5	0.71	3.9	0.61	4.4	0.69	3.8	0.60	
Cd(II)-SAH	Cd(II)-SAH		Fe(III)-SAH		Ni(II)-SAH		Cu(II)-SAH		Zn(II)-SAH		Co(II)-SAH		Fe(III)-SAH		Cd(II)-SAH		
	80	6.4	0.71	6.2	0.69	3.2	0.36	3.8	0.42	3.0	0.34	2.6	0.29				
	70	6.0	0.72	5.7	0.68	2.9	0.35	3.5	0.42	2.8	0.33	2.4	0.29				
	60	5.6	0.72	5.3	0.68	2.7	0.35	3.3	0.43	2.6	0.34	2.2	0.28				
	50	5.0	0.71	4.7	0.67	2.5	0.35	3.1	0.44	2.3	0.33	2.0	0.28				
40	4.4	0.70	4.2	0.67	2.2	0.35	2.8	0.44	2.1	0.33	1.8	0.28					

Table 8. The effect of scan rate on peak potentials and peak currents at different pH values of M(II)-SAH complex.

Scan rate	pH 4.1		pH 8.1		pH 4.1		pH 8.1		pH 4.1		pH 8.1	
	E_{PC} (V)	i_{PC} (cm)	E_{PC} (V)	i_{PC} (cm)	E_{PC} (V)	i_{PC} (cm)	E_{PC} (V)	i_{PC} (cm)	E_{PC} (V)	i_{PC} (cm)	E_{PC} (V)	i_{PC} (cm)
	Mn(II)-SAH						Cd(II)-SAH					
0.010	1.63	3.2	1.71	2.4	1.27	3.4	1.42	3.0	0.72	2.8	0.86	2.5
0.020	1.63	3.7	1.71	2.6	1.27	4.0	1.42	3.4	0.72	3.2	0.86	2.7
0.050	1.66	4.6	1.74	2.8	1.30	5.1	1.45	4.2	0.75	3.8	0.89	3.1
0.100	1.69	5.8	1.77	3.2	1.33	6.5	1.48	5.2	0.78	4.6	0.92	3.6
0.200	1.72	7.3	1.80	3.7	1.36	8.4	1.51	6.4	0.81	5.7	0.95	4.3

Table 9. The effect of scan rate on peak potentials and peak currents at different pH values of Ni(II)-SAH complex.

Scan rate	pH 4.1							pH 8.1						
	E_{PC} (V)	E_{Pa} (V)	$E_{1/2}$ (V)	ΔE (mV)	i_{PC} (cm)	i_{PC}^{II} (cm)	i_{Pa} (cm)	E_{PC} (V)	E_{Pa} (V)	$E_{1/2}$ (V)	ΔE (mV)	i_{PC} (cm)	i_{PC}^{II} (cm)	i_{Pa} (cm)
	Ni(II)-SAH													
0.010	-	-	-	-	-	2.5	-	-	-	-	-	-	2.4	-
0.020	-	-	-	-	-	2.8	-	-	-	-	-	-	2.6	-
0.050	0.63	0.69	0.66	60	3.2	3.3	3.1	0.74	0.80	0.77	60	3.0	3.0	2.7
0.100	0.66	0.72	0.69	60	3.8	3.9	3.5	0.77	0.83	0.80	60	3.5	3.4	3.0
0.200	0.69	0.75	0.72	60	4.5	4.4	4.1	0.80	0.86	0.83	60	4.1	3.9	3.4

Table 10. The effect of scan rate on peak potentials and peak currents at different pH values of M-SA-H complex

Scan Rate (Vs ⁻¹)	pH 4.1										pH 8.1										
	E _{pc} ^I (V)	i _{pc} ^{II} cm	E _{pc} ^I (V)	E _{pc} ^{II} (V)	E _{pa} (V)	E _{1/2} (V)	ΔE (mV)	i _{pc} ^I (cm)	i _{pc} ^{II} (cm)	i _{pa} (cm)	E _{pc} ^I (V)	i _{pc} ^{II} cm	E _{pc} ^I (V)	E _{pc} ^{II} (V)	E _{pa} (V)	E _{1/2} (V)	ΔE (mV)	i _{pc} ^I (cm)	i _{pc} ^{II} (cm)	i _{pa} (cm)	
Cu(II)-SAH																					
0.010	0.21	1.7	-	0.45	-	-	-	-	-	-	1.6	-	-	-	-	-	-	-	-	-	
0.020	0.21	2.0	-	0.45	-	-	-	-	-	-	1.7	-	-	-	-	-	-	-	-	-	
0.050	0.24	2.5	0.36	0.48	0.42	0.39	60	1.9	2.3	2.1	2.3	2.3	1.9	2.3	2.8	60	2.3	2.8	2.6	2.6	
0.100	0.27	3.3	0.39	0.51	0.45	0.42	60	2.3	2.8	2.6	2.8	2.8	2.3	2.8	3.5	60	2.7	3.5	3.2	3.2	
0.200	0.30	4.1	0.42	0.54	0.48	0.45	60	2.7	3.5	3.2	3.5	3.5	2.7	3.5	4.7	60	2.7	3.5	3.2	3.2	
Scan Rate																					
pH 4.1																					
pH 8.1																					
Fe(III)-SAH																					
0.010	0.36	0.35	0.355	10	1.0	0.9	1.27	1.78	0.8	1.8	0.8	0.8	1.78	0.8	0.9	1.27	1.78	0.8	1.8	1.8	
0.020	0.36	0.35	0.355	10	1.4	1.3	1.27	1.78	1.1	2.3	1.1	1.1	1.78	1.1	1.3	1.27	1.78	1.1	2.3	2.3	
0.050	0.39	0.40	0.395	10	2.0	1.9	1.30	1.81	1.7	3.5	1.7	1.7	1.81	1.7	1.9	1.30	1.81	1.7	3.5	3.5	
0.100	0.42	0.43	0.425	10	3.1	2.9	1.33	1.84	2.6	3.5	2.6	2.6	1.84	2.6	2.9	1.33	1.84	2.6	3.5	3.5	
0.200	0.45	0.46	0.455	10	4.2	3.9	1.36	1.87	3.5	7.2	3.5	3.5	1.87	3.5	3.9	1.36	1.87	3.5	7.2	7.2	
Co(III)-SAH																					
0.010	0.42				1.3		0.57	1.47	1.1	2.2	1.1	1.1	1.47	1.1		0.57	1.47	1.1	2.2	2.2	
0.020	0.42				1.9		0.57	1.47	1.4	3.0	1.4	1.4	1.47	1.4		0.57	1.47	1.4	3.0	3.0	
0.050	0.45				2.9		0.60	1.50	2.3	4.7	2.3	2.3	1.50	2.3		0.60	1.50	2.3	4.7	4.7	
0.100	0.48				4.3		0.63	1.53	3.5	6.9	3.5	3.5	1.53	3.5		0.63	1.53	3.5	6.9	6.9	
0.200	0.51				5.9		0.66	1.56	4.7	9.5	4.7	4.7	1.56	4.7		0.66	1.56	4.7	9.5	9.5	

Cu(II)-SAH complex

The results pertaining to cyclic voltammetric behaviour of Cu(II)-SAH complex are presented in Table 10. The polarogram and the cyclic voltammogram are shown in the Figure 3 and 4. Cyclic voltammograms at pH 4.1 and 8.1 contain a single cathodic peak and two cathodic peaks followed by an anodic peak in the reverse scan in solutions of pH 8.1 at high scan rates. In contrast only a single polarographic wave was observed at pH 4.1 and 8.1 in polarographic studies. An inspection of the cyclic voltammogram as well as the polarogram of the complex in solutions of pH 4.1 suggest that the polarographic reduction wave seems to manifest itself as a cathodic peak in cyclic voltammetric studies. This was attributed to the reduction of Cu(II)-SAH complex to the metal. The two cathodic peaks observed in solutions of pH 8.1 at high scan rates suggest that the reduction was taking place in two steps. At high scan rates, the formation of two cathodic peaks involves a rapid exchange of electrons in the electrode process. The first cathodic peak was attributed to the one electron reduction of Cu(II)-SAH complex to the Cu(I)-SAH complex and the second cathodic peak was due to the reduction of Cu(I)-SAH complex to the metal. The peak current values were almost same. The reduction process involves two steps each involving one electron. An anodic peak was noticed in the reverse scan at high scan rates. This

behaviour is similar to that observed in the case of Ni(II)-SAH complex at pH 8.1. The potential of separation DE_p between the anodic and the cathodic peak was 0.060 V and value of the ratio i_{pc}/i_{pa} (one) suggests that the electrode process was quasi reversible.

Fe(III)-SAH complex

The results pertaining to Fe(III)-SAH complex are presented in Table 10. In solutions of pH 4.1, the complex produces a single cathodic peak and an anodic peak in the reverse scan.

A small difference of 10 mV between the anodic and cathodic peak potentials was observed. The cathodic peak obtained was due to the reduction of Fe(III)-SAH complex to Fe(II)-SAH complex and that of anodic peak formation was due to the oxidation of Fe(II)-SAH complex to Fe(III)-SAH complex. A ratio of cathodic to anodic peak currents i.e. i_{pc}/i_{pa} was nearly one. These arguments suggest that the electrode process was quasi reversible. The nature was further confirmed by the Case I of Nicholson-Shain criteria [27]. Diffusion controlled behaviour is same as explained earlier for other complexes. The stability (electro inactive nature) of Fe(II)-SAH complex under the experimental conditions was confirmed by carrying out the experiment directly with Fe(II)-SAH complex instead of Fe(III)-SAH complex.

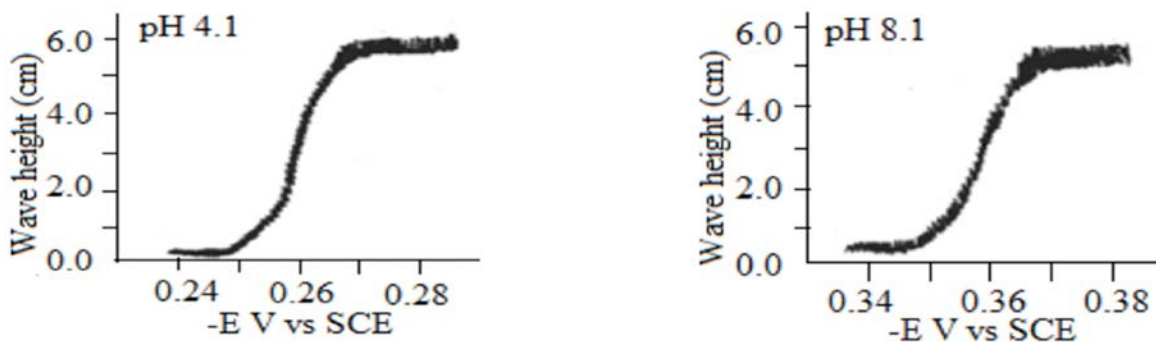


Figure 3. Polarograms of Cu(II)-SAH complex; [Cu(II)-SAH]= 1×10^{-3} M; Medium: 40% DMF.

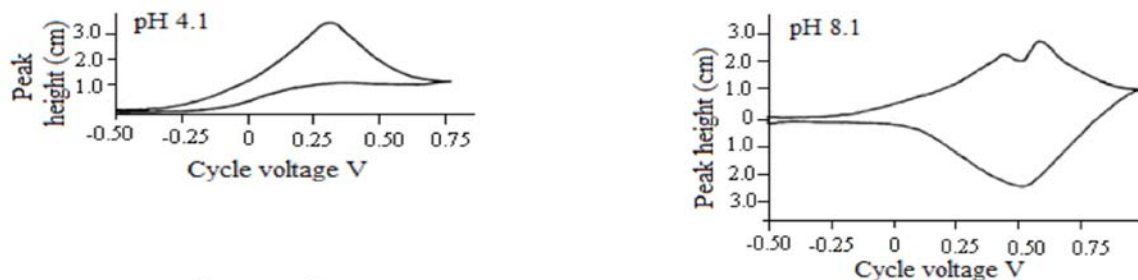


Figure 4. Cyclic voltammograms of Cu(II)-SAH complex; [Cu(II)-SAH]= 1×10^{-3} M; Medium: 40% DMF.

In solutions of pH 8.1, two cathodic peaks were observed. The peak potentials in general increase with increase in scan rate. The factors, cathode peak potentials were independent of scan rate, $E_{pc/2} - E_{pc}$ values were greater than $56.5/n$ mV and the shift of peak potentials to more negative values suggest that the electrode process was irreversible. Increase of peak current with increase in the concentration of depolarizer, a linear plot of i_{pc} vs $n^{1/2}$ and constant values of $i_{pc}/n^{1/2}$ suggest that the electrode process was diffusion controlled.

The total peak current values of $i_{pcI} + i_{pcII}$ at pH 8.1 was almost three times greater than the peak current values for the single cathodic peak obtained at pH 4.1 suggest that the reduction process can be represented as



Co(III)-SAH

The relevant experimental data is presented in Table 10. In solutions of pH 4.1, a single cathodic peak was observed at all scan rates. The peak potential and peak current values increase with increase in scan rate. The irreversible nature of the process was confirmed by the absence of anodic peak in the reverse scan. In solutions of pH 8.1, two cathodic peaks were observed as was shown by Fe(III)-SAH complex. The explanation and reduction mechanism proposed for Fe(III)-SAH complex holds good for Co(III)-SAH complex. The absence of anodic peak in the reverse scan rate and the behaviour similar to that reported in the Case II of Nicholson-Shain criteria confirms the irreversible nature of the electrode process.

CONCLUSION

The detailed electrochemical investigations on seven metal complexes namely Cd(II), Cu(II), Mn(II), Ni(II), Zn(II), Co(III) and Fe(III) with SAH were reported. The conclusions drawn from the above studies are presented in the form of table shown below.

Table 11. Conclusions drawn from the electrochemical studies

M-SAH	pH	Nature	Polarographic studies	Cyclic voltammetric studies	Nature
Cd(II)	Acidic and alkaline	Irreversible, diffusion controlled	One wave	Single cathodic peak and no anodic peak	Irreversible and diffusion controlled
Mn(II)					
Zn(II)				2 cathodic peaks and 1 anodic peak at high scan rates.	Quasi reversible and diffusion controlled
Ni(II)					
Cu(II)				single cathodic peak in acidic media, two cathodic peaks followed by an anodic peak in basic media.	Quasi reversible and diffusion controlled
Fe(III)	Acidic	Irreversible, diffusion controlled	One wave	single cathodic peak and an anodic peak	Quasi reversible and diffusion controlled
Co(III)			One wave	single cathodic peak	Irreversible and diffusion controlled
Fe(III)	Basic		Two waves	two cathodic peaks	Irreversible and diffusion controlled
Co(III)			Two waves	two cathodic peaks	Irreversible and diffusion controlled

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