Metal-Metal Sulphide Electrodes IV : Thermodynamic Behaviour in Presence of Thio Compounds

Miss Pushpa Sharma and Mukhthar Singh

Department of Chemistry, Agra College Agra

The potentials of $As-As_2S_3$, $Sb-Sb_2S_3$ and $Mo-MoS_2$ electrodes have been determined in the presence of some sulphur containing organic compounds viz., thiourea (TU) thiosemicarbazide (TSC) and diethyldithiocarbamate (DEDTC), with a view to determining the thermodynamic functions (ΔG° , ΔH° and ΔS°) of the electrode reactions in respect of each electrode

In continuation of earlier publications(1) we now report the results of our investigations on the thermodynamic behaviour of $As-As_2S_3$, $Sb-Sb_2S_3$ and $Mo-MoS_2$ electrodes in presence of sulpnur containing organic compounds thiourea (Tu), thiosemicarbazide (TSC) and diethyldithiocarbamate (DEDTC) in different media .

EXPERIMENTAL

$As-As_2S_3$, $Sb-Sb_2S_3$ and $Mo-MoS_2$ electrodes were prepared by the method as reported in earlier publication(1). The potentials of the electrodes were measured as described(1).

RESULTS AND DISCUSSION

The potential of $As-As_2S_3$, $Sb-Sb_2S_3$ and $Mo-MoS_2$ electrodes as a function of the concentrations of thiourea (TU), thiosemicarbazide (TSC) and diethyldithiocarbamate (DEDTC) at different temperatures in aqueous, aquo-alcholic and alkaline media were used to evaluate E° and this is presented in Table.1

The values of temperature coefficient $(\partial E^\circ/\partial T)p$ in various media have been determined from the linear plots of E° (volts) vs $T(^\circ K)$. The temperature coefficient follows the following order in various media:

$$Sb-Sb_2S_3 > Mo-MoS_2 > As-As_2S_3$$

The values of $T(\partial E^\circ/\partial T)p$ for $As-As_2S_3$ electrode have been calculated and the relationship between $T(\partial E^\circ/\partial T)p$ and E° in different media containing TU or TSC or DEDTC, has been shown in Fig .1 This has been found to be linear in all the cases in accordance with the theoretical equation :

$$E^\circ = -\Delta H^\circ/nF + T(\partial E^\circ/\partial T)p \quad ...(1)$$

DETERMINATION OF THERMODYNAMIC FUNCTIONS OF $As-As_2S_3$ ELECTRODE IN AQUEOUS AQUO-ALCOHOLIC (50% v/v) AND ALKALINE MEDIA CONTAINING TU, TSC AND DEDTC AT 25 ± 0.1°C

The thermodynamic functions(3) (ΔG°, ΔH° and ΔS°) for $As-As_2S_3$ electrode as a typical case, have been calculated in different media containing TU,TSC and DEDTC at 25 ± 0.1°C.

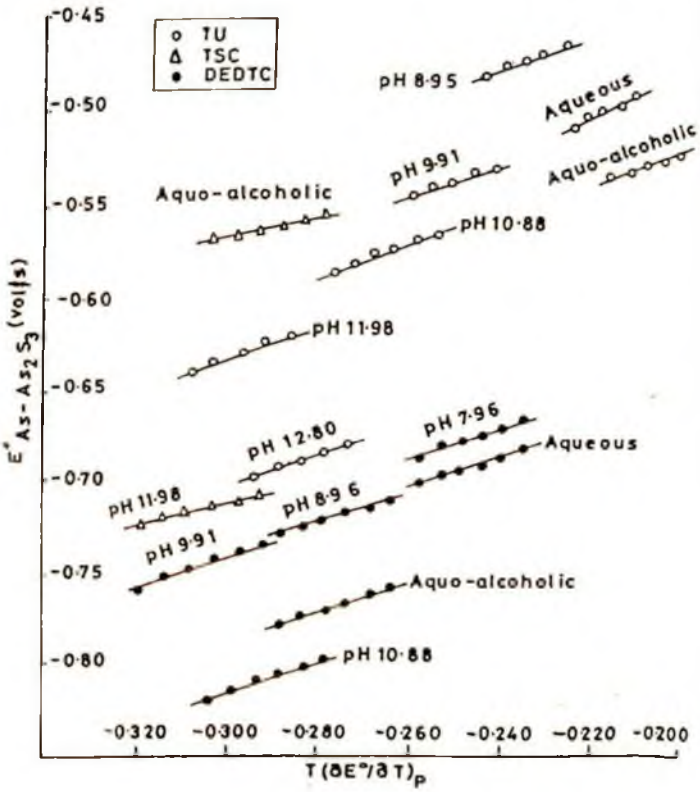


Fig. 1 Plots of $E^\circ_{As-As_2S_3}$ (Volts) Vs. $T(E'/T)p$ in aqueous, aquo-alcoholic and alkaline solutions of TU, TSC and DEDTC

From the expression $\Delta S^\circ = nF(\partial E^\circ/\partial T)p$, the value of ΔS° can be calculated. The value of ΔG° has been obtained from the equation, $\Delta G^\circ = -nFE^\circ$ The value of ΔH° has been calculated from equation 1. The calculated values of ΔG°, ΔH° and ΔS° for $As-As_2S_3$/TU or TSC or DEDTC electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline media at 25 ± 0.1°c have been presented in Table 2

TABLE 1

VALUES OF STANDARD ELECTRODE POTENTIAL (E°) AND TEMPERATURE COEFFICIENT OF AS-As_2S_3 Sb-Sb_2S_3 AND Mo-MoS ELECTRODES IN AQUEOUS, AQUO-ALCOHOLIC (50% V/V) AND ALKALINE SOLUTIONS OF Tu, TSC AND DEDTC

Solution	Medium	-E° (mv) at different temperatures						$(-\partial E/\partial T)p$
	pH	278	283	288	293	298	303°	(V/°K)
	As-As_2S_3							
TU	Aqueous	495	498	501	504	509	-	7.0×10^{-4}
	Aquo-alcoholic (50% V/V)							
		513	518	523	525	528	-	7.5×10^{-4}
	Alkaline							
	8.95	463	468	471	475	480	-	8.5×10^{-4}
	9.91	528	533	537	541	546	-	9.0×10^{-4}
	10.88	565	568	573	579	584	-	9.5×10^{-4}
	11.98	617	622	626	633	638	-	10.5×10^{-4}
	12.80	677	684	689	692	697	-	10.0×10^{-4}
TSC	Aqueous	508	515	520	523	526	532	9.5×10^{-4}
	Aquo- alcoholic (50% V/V)							
		556	562	567	572	578	581	10.0×10^{-4}
	Alkaline							
	7.96	475	480	484	488	491	495	8.0×10^{-4}
	8.95	512	517	520	524	529	533	8.5×10^{-4}
	9.91	544	549	554	558	562	568	9.5×10^{-4}
	10.88	634	640	644	648	653	659	10.0×10^{-4}
	11.98	708	712	718	723	728	734	10.5×10^{-4}
DEDTC	Aqueous	680	684	689	692	696	701	8.5×10^{-4}
	Aquo- alcoholic (50% V/V)							
		759	764	769	773	777	783	9.5×10^{-4}
	Alkaline							
	7.96	666	670	673	677	681	687	8.5×10^{-4}
	8.95	707	712	716	721	725	731	9.5×10^{-4}
	9.91	736	741	745	750	755	762	10.5×10^{-4}
	10.88	799	805	809	813	818	824	10.0×10^{-4}
	11.98	814	819	823	828	833	838	9.5×10^{-4}
	Sb-Sb_2S_3							
TU	Aqueous	405	410	419	430	439	447	1.68×10^{-3}
	Aquo- alcoholic (50% V/V)							
		412	418	426	439	447	455	1.72×10^{-3}

Table 1 (contd.)

	Alkaline							
	8.69	477	483	492	506	515	521	1.76×10^{-3}
	9.91	518	527	538	547	555	563	1.80×10^{-3}
	10.88	548	554	567	578	586	592	1.76×10^{-3}
	11.98	589	595	608	617	626	633	1.76×10^{-3}
	12.80	609	616	623	631	642	652	1.72×10^{-3}
	13.60	646	652	661	673	682	690	1.76×10^{-3}
TSC	Aqueous	386	394	402	410	419	426	1.60×10^{-3}
	Aquo- alcoholic (50% V/V)							
		386	395	403	412	419	427	1.64×10^{-3}
	Alkaline							
	7.54	343	351	359	368	376	382	1.56×10^{-3}
	8.69	369	378	387	394	402	409	1.60×10^{-3}
	9.91	410	417	425	432	444	451	1.64×10^{-3}
	10.88	440	447	456	465	476	482	1.68×10^{-3}
	11.98	454	463	471	480	488	495	1.64×10^{-3}
DEDTC	Aqueous	455	463	472	482	491	498	1.72×10^{-3}
	Aquo- alcoholic (50% V/V)							
		479	487	495	505	514	521	1.68×10^{-3}
	Alkaline							
	8.69	396	404	412	421	430	438	1.68×10^{-3}
	9.91	473	482	490	499	507	516	1.72×10^{-3}
	10.88	516	524	532	543	551	558	1.68×10^{-3}
	11.98	587	596	605	614	623	630	1.72×10^{-3}
	12.80	612	621	632	640	647	656	1.76×10^{-3}
	13.60	613	621	630	637	648	655	1.68×10^{-3}
	$Mo-MoS_2$							
TU	Aqueous	566	571	577	584	591	598	1.28×10^{-3}
	Aquo- alcoholic (50% V/V)							
		576	582	589	596	605	609	1.32×10^{-3}
	Alkaline							
	7.96	579	583	589	596	604	611	1.32×10^{-3}
	8.95	628	632	638	643	649	658	1.28×10^{-3}
	9.37	647	654	662	668	671	680	1.32×10^{-3}
	9.91	680	688	694	699	706	714	1.36×10^{-3}
	10.38	687	693	699	706	713	720	1.32×10^{-3}
	10.88	712	718	724	731	737	745	1.32×10^{-3}
	11.20	742	749	756	761	768	776	1.36×10^{-3}
TSC	Aqueous	606	612	618	625	632	639	1.32×10^{-3}
	Aquo- alcoholic (50% V/V)							
		611	619	626	631	638	645	1.36×10^{-3}

Table 1 (contd.)

Alkaline							
	7.54	513	518	525	531	539	544	1.24×10^{-3}
	7.96	537	545	551	557	563	569	1.28×10^{-3}
	8.95	591	599	607	612	617	624	1.32×10^{-3}
	9.37	607	613	620	626	634	640	1.32×10^{-3}
	9.91	639	646	652	660	665	671	1.28×10^{-3}
	10.38	662	668	674	681	689	695	1.32×10^{-3}
	10.88	691	701	707	714	719	725	1.36×10^{-3}
DEDTC Aqueous		590	597	603	610	617	625	1.40×10^{-3}
Aquo- alcoholic (50% V/V)								
		624	630	638	645	652	660	1.44×10^{-3}
Alkaline								
	7.54	518	525	534	541	548	554	1.36×10^{-3}
	7.96	532	539	546	552	558	565	1.32×10^{-3}
	8.95	597	603	610	618	625	631	1.36×10^{-3}
	9.37	628	634	642	649	655	663	1.40×10^{-3}
	9.91	636	643	650	656	664	672	1.44×10^{-3}
	10.38	680	687	695	701	709	715	1.40×10^{-3}
	10.88	698	705	712	720	727	733	1.40×10^{-3}

TABLE 2

UES OF VARIOUS THERMODYNAMIC FUNCTIONS (ΔG°, ΔH° AND ΔS°) FOR $As\text{-}As_2S_3$ ELECTRODE IN VARIOUS MEDIA CONTAINING THIOUREA (TU) THIOSEMICARBAZIDE (TSC) AND DIETHYLDITHIOCARBAMATE (DEDTC) AT 25 ± 0.1°C.

Medium	TU Solution			TSC Solution			DEDTC Solution		
pH	ΔG° Kcal/mole	ΔH°	ΔS° e.u.	ΔG° Kcal/mole	ΔH°	ΔS° e.u.	ΔG° Kcal/mole	ΔH°	ΔS° e.u.
Aqueous	11.7	6.9	-16.2	-	-	-	16.1	10.2	-19.6
Aquo- alcoholic (50% V/V)									
	12.2	7.0	-17.3	13.3	6.5	-23.1	17.0	11.4	-21.9
Alkaline									
7.96	-	-	-	-	-	-	15.7	9.9	-19.6
8.95	11.1	5.2	-19.6	-	-	-	16.7	10.2	-21.9
9.91	12.6	6.4	-20.8	-	-		17.4	10.2	-24.2
10.88	13.5	6.9	-21.9	16.8	9.6	-24.2	18.9	12.0	-23.1
11.98	14.7	7.5	-24.2	-	-	-	-	-	-
12.80	16.1	9.2	-23.1	-	-	-	-	-	-

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