Metal-Metal Sulphide Electrodes III: Application in the Quantitative Determination of Thio Compounds

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As - As_2S_3, Sb- Sb_2S_3 and Mo-MoS_2 electrodes have been prepared and successfully used in the quantitative determination of thiourea (Tu), thio semicarbazide (TSC) and diethyl dithio carbamate (DE DTC). The role of pH in these determinations is examined. The electrodes show Nernstian response to pH (above pH 8) and to concentration of Tu, TSC and DEDTC (conc $<10^{-2}$ M). The effect of the medium & temperature on the behaviour of the electrode and the exact concentration dependence have been investigated.

Ag-Ag_2S electrode has been used in the determination of sulphur containing organic compounds, viz., thiols(1), thioacetamide(2), thiourea(3). Recently Gurtu(4), Agarwal(5) and Bhargava(6) have prepared a number of metal-metal sulphide electrodes, viz., Cu-Cu_2S, Ag-Ag_2S, Zn-ZnS, Cd-CdS, Hg-HgS; Cr-Cr_2S_3, Mn-MnS, Fe-FeS, Co-CoS, Ni-NiS; Pb-PbS, Sn-SnS and Ge-GeS, and studied their utility in the quantitative determination of sulphur containing organic compounds dithiocarbamate and thiosemicarbazide. However, no work has been reported so far on As-As_2S_3, Sb-Sb_2S_3 and Mo-MoS_2 electrodes with regard to their utility in the quantitative determination of sulphur containing organic compounds. In continuation of earlier publications(7,8) on these electrodes, we now report the results of investigation on the electrochemical behaviour of these electrodes in the presence of thiourea (Tu: $NH_2.CS.NH_2$), thiosemicarbazide (TSC: $NH_2.CS.NH.NH_2$) and diethyldithiocarbamate, DEDTC: $(C_2H_5)_2$ N.CS.SNa), under different experimental conditions.

EXPERIMENTAL

All the chemicals used were of analytical reagent grade. The solutions of varying concentrations of thiourea, thiosemicarbazide and diethyldithiocarbamate have been prepared in double distilled water.

The other experimental details were the same as already reported(7).

The potentials of the electrodes were measured by setting up the following type of cell.

Metal, Metal sulphide/solution of Thio compound/SCE

RESULTS AND DISCUSSION

As-As_2S_3, Sb-Sb_2S_3 and Mo-MoS_2 electrodes were found to be stable if handled with care without jerks for 6,8 and 3 months respectively provided they are preserved in double distilled water after use. It was found that the potential of the As-As_2S_3 electrode became constant within 1 mt in well stirred solutions of Tu, TSC and DEDTC, while in the other two electrodes the potential became steady within three minutes.

The plots of the potentials of a given electrode vs logarithm of [Tu], [TSC] and [DEDTC] are found to be linear. The slopes were not necessarily Nernstian. The values of E°and slope are presented in Table 1. The following relation represents the potential concentrations of different electrodes in aqueous medium at 25±0.1°C.

(i) Tu Solutions

$E_{As\ As_2S_3}$ = - 0.268 - 0.057 log [Tu] in the range 0.032-23 mM

$E_{Sb\ Sb_2S_3}$ = - 0.198 - 0.046 log [Tu] in the range 0.064-46 mM

$E_{Mo\ MoS_2}$ = - 0.350 - 0.050 log [Tu] in the range 0.032-23 mM

(ii) TSC Solutions

$E_{As\text{-}As_2S_3}$ = - 0.285 - 0.043 log [TSC] in the range 0.032-9.9 mM

$E_{Sb\text{-}Sb_2S_3}$ = - 0.178 - 0.020 log [TSC] in the range 0.064-46 mM

$E_{Mo\text{-}MoS_2}$ = - 0.391 - 0.047 log [TSC] in the range 0.032-23 mM

(iii) DEDTC Solutions

$E_{As\text{-}As_2S_3}$ = - 0.455 - 0.063 log [DEDTC] in the range 0.19-13 mM

$E_{Sb\text{-}Sb_2S_2}$ = - 0.250 - 0.043 log [DEDTC] in the range 0.0032-2.3 mM

$E_{Mo\text{-}MoS_2}$ = - 0.376 - 0.053 log [DEDTC] in the range 0.32 to 23 mM

Statistical analysis of the data reveals that variance and standard deviation for As-As_2S_3 electrode are 2.6×10^{-5} and 0.5% for Sb-Sb_2S_3

TABLE 1

VALUES OF EXPERIMENTAL SLOPE OF LOG PLOT AND STANDARD ELECTRODE POTENTIAL (E°) FOR As-AS_2S_3, Sb-Sb_2S_3 AND Mo-MoS_2 ELECTRODES IN DIFFERENT SOLUTIONS OF TU OR TSC OR DEDTC AT 25±0.1°C; ALL POTENTIALS EXPRESSED IN mV.

Electrode	Medium pH	TU Solutions		TSC Solutions		DEDTC Solutions	
		Slope	-E°	Slope V	-E°	Slope	-E°
		Aqueous					
As-As_2S_3		57	509	43	526	63	696
		Aquo-Alcohol(50% V/V)					
		56	528	49	578	50	797
		Alkaline					
	7.54	--	--	--	--	--	--
	7.96	--	--	39	491	55	681
	8.95	54	480	40	529	54	725
	9.91	55	546	40	562	50	755
	10.88	56	584	47	653	54	818
	11.98	54	638	51	728	44	833
	12.80	52	697	--	-	--	-
		Aqueous					
Sb-Sb_2S_3		46	439	20	419	43	491
		Aquo-alcoholic (50% V/V)					
		47	447	19	419	46	514
		Alkaline					
	7.54	--	-	12	376	--	-
	8.69	45	515	14	402	34	430
	9.91	46	555	17	444	39	507
	10.88	44	586	20	476	40	551
	11.98	43	626	16	488	45	623
	12.80	40	642	--	-	43	647
	13.60	42	682	--	-	34	648
		Aqueous					
Mo-MoS_2		50	591	47	632	53	617
		Aquo-alcohol (50% V/V)					
		51	605	45	638	57	652
		Alkaline					
	7.54	--	-	43	539	49	548
	7.96	50	604	45	563	45	558
	8.95	51	649	47	617	48	625
	9.37	49	671	45	634	51	655
	9.91	50	706	48	665	49	664
	10.38	49	713	47	689	53	709
	10.88	48	737	49	719	52	726
	11.20	51	768	--	-	--	-

electrode 5.6×10^{-5} and 0.75% and;for Mo-MoS_2 elec trode 2.0×10^{-5} and 0.45% respectively thereby showing that these electrodes can be successfully used in the quantitative determination of TU, TSC and DEDTC in the given samples.

EFFECT OF MEDIUM

The values of E° of the electrodes in 50% V/V aquo-alcoholic solutions of TU, TSC and DEDTC have also been presented in Table 1.The plots of potential of the electrodes vs logarithm of [Tu], [TSC] and [DEDTC] in these media also are linear thereby showing that these electrodes can be successfully used in the quantitative determination of the compounds in the same concentration again as in aqueous medium. The validity of analysis in aquo-alcoholic medium is justified by the statistical treatment of the data which shows variance and standard error for As-As_2S_3 electrode: 3.6×10^{-5} and 0.6%; for Sb-Sb_2S_3 electrode 4.9×10^{-5} and 0. 7% and for Mo-MoS_2 electrode 2.6×10^{-5} and 0.5%. It would not be out of context to mention here that the electrodes were also tried in 100% alcoholic medium but they failed to respond to [TU], [TSC] and [DEDTC].

EFFECT OF pH

The electrochemical behaviour of the electrodes has also been studied in alkaline buffered solutions (pH 7.54 - 13.60) of TU, TSC and DEDTC at 25 ± 0.1°C. The potentials are reproducible and attains equilibrium rapidly in alkaline buffered solutions. The potential of these electrodes has been measured as a function of [TU], [TSC] and [DEDTC] in the same range as in aqueous and aquo-alcoholic media, at controlled pH values (7.54 - 13.60).

As-As_2S_3 responds linearly in pH range 8.95-12.8 in Tu, and pH range 7.96 - 11.98 in TSC and DEDTC Sb-Sb_2S_3 responds linearly in range 8.69-13.60 in Tu & DEDTC and in the range 7.54 to 11.95 in TSC.

Mo-MoS_2 responds linearly in the range 7.96-11.2 in Tu and in the range 7.54-10.88 in TSC and DEDTC.

Beyond these ranges of pH, the behaviour becomes erratic. The E° and slope values in the case of linear plots are give in Table 1.

A persual of Table 1 indicates that As-AS_2S_3 Sb-Sb_2S_3 and Mo-MoS_2 electrodes can be successfully used at controlled pH values for the quantitative determination of TU, TSC and DEDTC in the concentration range :

For As-As_2S_3

[TU] = 9.9×10^{-5} - 2.3×10^{-2} M pH 8.95 - 12.80

[TSC] = 3.2×10^{-5} - 9.9×10^{-3} M pH 7.96 - 11.98

[DEDTC] = 3.2×10^{-5} - 1.3×10^{-2} M pH 7.96 - 11.98

For Sb-Sb_2S_3

[TU] = 6.4×10^{-5} - 4.6×10^{-2} M pH 8.69 - 13.60

[TSC] = 6.4×10^{-5} - 4.6×10^{-2} M pH 7.54 - 11.98

[DEDTC] = 3.2×10^{-6} - 2.3×10^{-3} M pH 8.69 - 13.60

For Mo-MoS_2

[TU] = 3.2×10^{-5} - 2.3×10^{-2} M pH 7.96 - 11.20

[TSC] & [DEDTC] = 3.2×10^{-5} - 2.3×10^{-2} M pH 7.54 - 10.88

DEPENDENCE ON pH

The pH response of the electrodes in the presen of Tu, TSC and DEDTC has also been studied measuring their potentials as a function of values keeping [TU], [TSC] and [DEDTC] constan The plots of $E_{As\text{-}As_2S_3}$ or $E_{Sb\text{-}Sb_2S_3}$ or Mo-MoS_2 V pH at constant [TU], [TSU] and [DEDTC] are line in the pH range as described above. The resul can be expressed by the following relationships:

(i) TU Solutions:

$E_{As\text{-}As_2S_3}$ = 0.506 - 0.059 pH
[Tu] = 9.9×10^{-5} M

$E_{As\text{-}As_2S_3}$ = 0.459 - 0.058 pH
[Tu] = 5.0×10^{-4} M

$E_{As\text{-}As_2S_3}$ = 0.427 - 0.058 pH
[Tu] = 2.0×10^{-3} M

$E_{As\text{-}As_2S_3}$ = 0.370 - 0.058 pH
[Tu] = 2.3×10^{-2} M

(ii) TSC Solutions:

$E_{As\text{-}As_2S_3}$ = 0.228 - 0.038 pH
[TSC] = 3.2×10^{-5} M

$E_{As\text{-}As_2S_3}$ = 0.254 - 0.046 pH
[TSC] = 2.9×10^{-4} M

$E_{As\text{-}As_2S_3}$ = 0.250 - 0.049 pH
[TSC] = 1.4×10^{-3} M

$E_{As\text{-}As_2S_3}$ = 0.249 - 0.052 pH
[TSC] = 9.9×10^{-3} M

(iii) DEDTC Solutions:

$E_{As-As_2S_3}$ = 0.179 - 0.047 pH
[DEDTC] = 3.2×10^{-5} M

$E_{As-As_2S_3}$ = 0.126 - 0.042 pH
[DEDTC] = 2.9×10^{-4} M

$E_{As-As_2S_3}$ = 0.092 - 0.046 pH
[DEDTC] = 9.9×10^{-4} M

$E_{As-As_2S_3}$ = 0.026 - 0.044 pH
[DEDTC] = 7.4×10^{-3} M

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