

# Influence of some organic additives on the electrochemical behaviour of lead in sulphuric acid - Quarternary ammonium salts-I

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The effect of addition of CTAB (Cetyl Trimethyl Ammonium Bromide) to Pb/PbSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> (8.9N) system is investigated by cyclic voltammetric (CV) technique. The potential region is scanned between 0 mV and -1800 mV vs Hg/Hg<sub>2</sub>SO<sub>4</sub>. It is found that the addition of CTAB increased the overpotential for H<sub>2</sub> evolution by 30 - 50 mV. The effect of cycling is also studied. The *i<sub>p</sub>* values are reduced for both oxidation and reduction reactions in the presence of CTAB. The differential capacitance measurement confirms the adsorption of CTAB on Pb/PbSO<sub>4</sub>.

**Key words:** Cyclic voltammetry, CTAB, impedance studies

## INTRODUCTION

Recently some patents have been issued [1-2] reporting that the addition of quarternary ammonium compound increased the cycle life and reduced the topping up problems in lead acid battery. To study in detail, a long chain alkyl group containing compound (CTAB) is chosen and its effects are investigated on Pb/PbSO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> (8.9 N) smooth electrode system.

## EXPERIMENTAL

Machined cylindrical lead electrodes (4N BHAS) of 0.50 cm<sup>2</sup> (for CV) and 0.20 cm<sup>2</sup> (for impedance studies) are polished by a conventional mechanical method. Electrolyte is prepared from Analar grade reagents and tridistilled water. BAS-100-A & PAR (Model 378) systems are used for CV and impedance measurements respectively with three electrode cell assembly. The concentration of CTAB is 40 ppm w/o H<sub>2</sub>SO<sub>4</sub>. The experiments are carried out at sweep rates (V) viz. 20 and 50.

## RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammogram of Pb electrode in pure H<sub>2</sub>SO<sub>4</sub> electrolyte. The electrode is subjected to 15 cycles to find its behaviour on cycling. The *i<sub>pa</sub>* (Pb → PbSO<sub>4</sub>) and *i<sub>pc</sub>* (PbSO<sub>4</sub> → Pb) are increasing on further cycles because of pitting [3] of the surface due to hydrogen evolution. But in the presence of CTAB, the tendency of increase in *i<sub>p</sub>* or *q* (for both oxidation and reduction reactions) is completely retarded; reflected

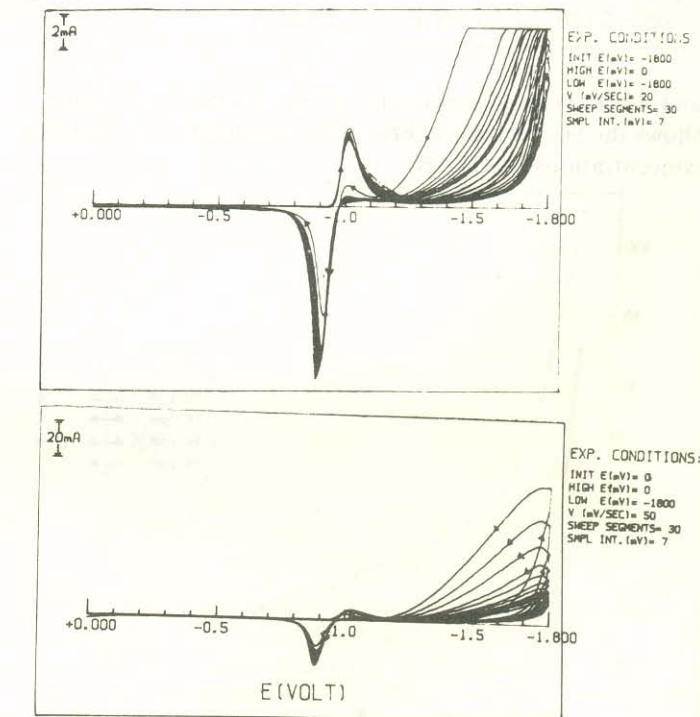


Fig. 1: Lead electrode voltammograms in 8.9N H<sub>2</sub>SO<sub>4</sub> without CTAB. (a) 20 mV s<sup>-1</sup> (b) 50 mV s<sup>-1</sup>

in the reduction in their values (Fig. 2). The hydrogen evolution potential also increases on cycling but in the presence of CTAB the effect is pronounced. Ultimately the current due to the H<sub>2</sub> evolution decreases (at -1800 mV) (the current is 91.66 mA and 12.5 mA in the 1st and 15th cycles respectively in pure electrolyte while in CTAB-containing electrolyte is 42.91 mA and 0.8 mA in 1st

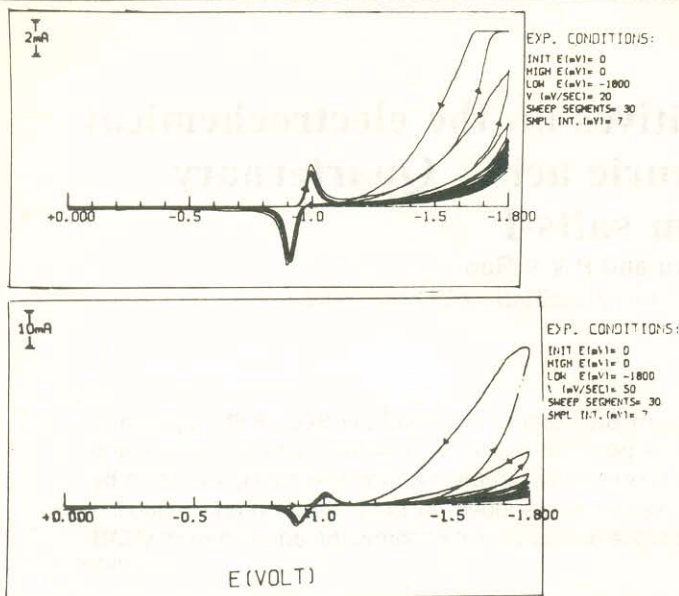


Fig. 2: Lead electrode voltammograms in 8.9N H<sub>2</sub>SO<sub>4</sub> with 40 ppm CTAB. (a) 20 mV s<sup>-1</sup> (b) 50 mV s<sup>-1</sup>

and 15th cycles respectively) (Figs. 1 and 2). Figure 3 shows the H<sub>2</sub> evolution current vs cycle number for various concentrations of CTAB.

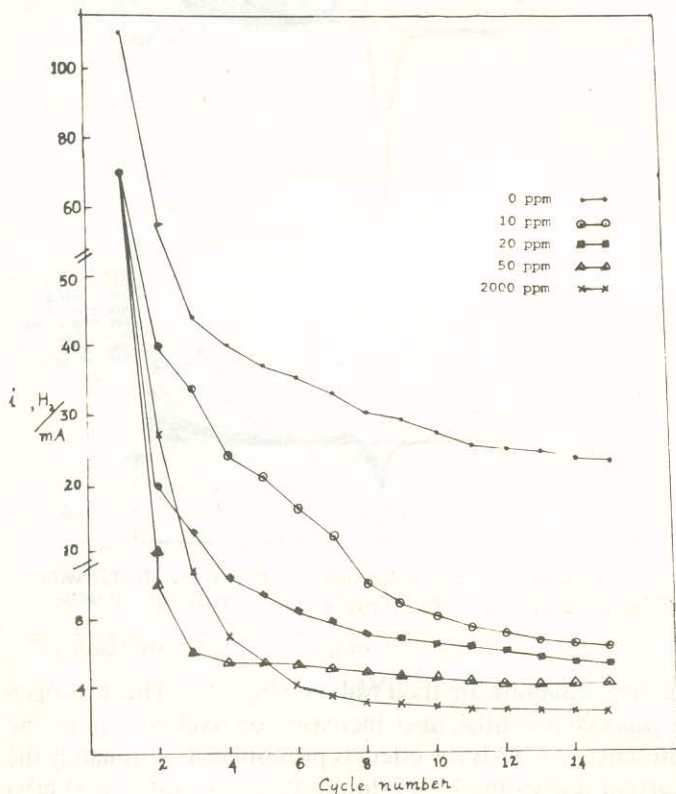


Fig. 3: H<sub>2</sub> evolution current (at -1800 mV). Variations with cycle number for different concentrations of CTAB in 8.9N H<sub>2</sub>SO<sub>4</sub> (at 20 mV s<sup>-1</sup> scan)

The observed effects may be due to the adsorption of CTA<sup>+</sup> onto the electrode surface. The differential capacitance is increased in the potential region -1200 mV to -800 mV at 250 Hz (Fig. 4) by the addition of CTAB. This substantiates the adsorption of CTA<sup>+</sup> onto Pb/PbSO<sub>4</sub>. Similar trend in results has been observed for other surfactants [4].

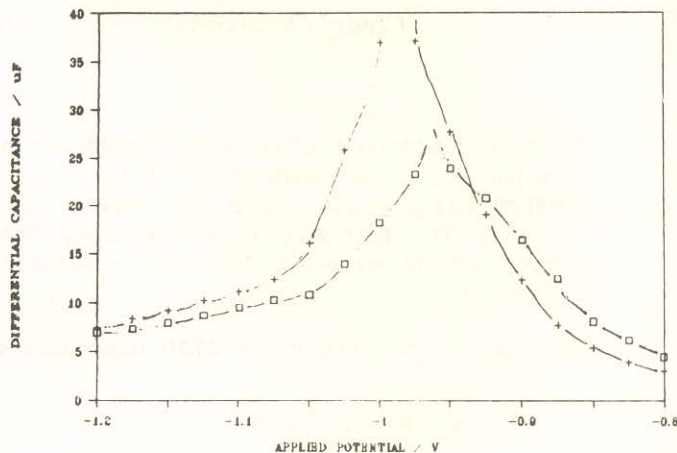


Fig. 4: Differential capacitance of lead electrode in 8.9N H<sub>2</sub>SO<sub>4</sub> □ - □ Without CTAB and + - + with 40 ppm CTAB

## CONCLUSION

CTAB addition reduces the  $i_{pa,c}$  (or  $q_{a,c}$ ) values and increases the overpotential for hydrogen evolution. Detailed studies on impedance behaviour of the electrode reaction in presence of CTAB and performance of the battery are warranted.

## REFERENCES

1. Fukuda Sadao, Okahisa Mitsugu, Ikeda Yutaka, Ohhira Tsukasa, JPN Pat. No.75,136,637 (1975)
2. Lowenstein Hoshea, U.S.Pat.No.3928,066 (1975)
3. S Fletcher and D B Mathews, *J Appl Electrochem*, 11 (1981) 23
4. T F Sharpe, *J Electrochem Soc*, 116 (1969) 1639