

# *Effect of 2-mercaptoethanol on the electrodeposition of lead*

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The morphology and the electro-kinetic parameters of lead electrodeposits on polycrystalline lead have been studied in a fluoborate bath at several current densities in the presence of known concentrations of 2-mercaptoethanol. It was observed that there was a notable decrease in the grain-size at low concentrations of the addition agent and the critical concentration varied with the current density. The growth habit modification and the changes in the kinetic parameters with increasing concentrations of the addition agent and current density, were investigated. Suitable transport mechanisms were proposed with the help of IR and X-ray studies.

## 1. Introduction

Lead is commercially electroplated from a fluoborate [1] bath although it can be deposited from perchlorate [2], sulphamate [3], fluosilicate [4], acetate [5] and sulphonate [6] solutions. The effect of various addition agents such as glue, gelatin, pyragallol, resorcinol, saligenin, hydroquinone etc., in the electrodeposition of lead have been studied [7-11]. However, there are very few systematic studies to elucidate the exact transport mechanism and to explain the resulting electro-kinetic parameters [12] and the growth habit modification [13] of the deposit in the presence of addition agents [14-17].

In the present investigation of the electrodeposition of lead on lead, morphological and electrochemical changes have been found with increasing concentrations of the addition agent. Investigations were made on the degradation products formed during the electrodeposition using X-ray and IR studies [18].

## 2. Experimental procedure

Polycrystalline lead (99.99% pure) in the form of a cylinder of about one centimetre long and 0.8 cm in diameter was used as cathode for electrodeposition. The polycrystalline lead surface was first mechanically polished on 2/0 and 4/0 emery

papers using ethyl alcohol as a lubricant and then electropolished [19] in a solution containing 60 g anhydrous sodium acetate, 315 cm<sup>3</sup> glacial acetic acid and 80 cm<sup>3</sup> water. In the electropolishing cell, the polycrystalline lead was made the anode and a platinum foil the cathode. The electropolishing current density range was 50-100 mA cm<sup>-2</sup>. After electropolishing, the crystal was washed well with conductivity water and immediately transferred to the electrodeposition cell.

The electrolytic bath for the deposition of lead was prepared by using the following composition [20]: AR fluoboric acid, 320 g dm<sup>-3</sup>; AR basic lead carbonate, 130 g dm<sup>-3</sup>; AR 2-mercaptoethanol,  $x$  mol dm<sup>-3</sup>. A known amount ( $x$ ) of freshly prepared solution of AR 2-mercaptoethanol was added to the electrolytic bath whenever required.

The electrodeposition cell consists of three compartments. The electropolished cathode surface was placed in the middle compartment. A pure lead foil of area about fifty times greater than the cathode surface was placed in the anode compartment. A reference electrode was prepared by depositing lead on a platinum wire from the same bath at a current density of 10 mA cm<sup>-2</sup>, for about 30 min and was placed in the reference compartment which was connected to the middle compartment by a Luggin capillary. For each experiment, a fresh electrode was prepared. The galvanostatic

condition was maintained by using a 90 V dry battery across resistors. The deposition was carried out to a deposit thickness corresponding to 10 C cm<sup>-2</sup> (3.6 μm). The electrodeposition was carried out at 2, 5, 10, 15, 20, 30 and 40 mA cm<sup>-2</sup> at room temperature. The overpotential was recorded using a digital pH/microvoltmeter (Elico, Model LI 120) with an accuracy of ± 2 mV. The surface appearance of the electrodeposit was examined under phase-contrast and bright illumination microscopy and photomicrographs were taken at a magnification of 625 ×.

The solid obtained when a 2-mercaptoethanol solution of high concentration was added to the electrolytic bath was separated, purified, and Infra-red and X-ray studies were undertaken.

### 3. Results

#### 3.1. Morphology

**3.1.1. Pure solution.** A characteristic type of deposit was observed when the electrodeposition of lead was carried out from the bath without additive, at all current densities (Fig. 1). Big grains were observed at lower current densities (2, 5 and 10 mA cm<sup>-2</sup>) and small grains at higher current densities (15, 20, 30 and 40 mA cm<sup>-2</sup>). With the increase in current density the grain size decreases and the number of grains per unit area increases. At 40 mA cm<sup>-2</sup> the surface appeared dull and the deposit was loose, nodular, powdery and porous.

**3.1.2. 10<sup>-10</sup>–10<sup>-8</sup> mol dm<sup>-3</sup> 2-mercaptoethanol.** When the concentration of the addition agent, 2-mercaptoethanol in the electrolytic bath

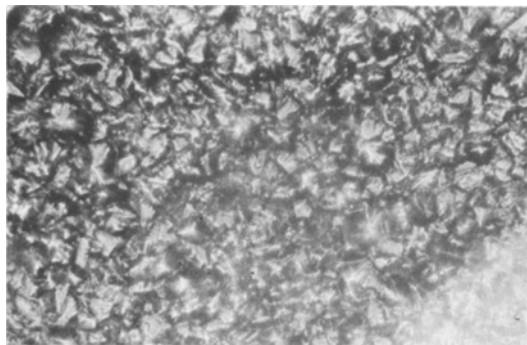


Fig. 1. A characteristic type of deposit of lead on lead from fluoborate bath at 2 mA cm<sup>-2</sup> (X 525).

was gradually increased from 10<sup>-10</sup> mol dm<sup>-3</sup> to 10<sup>-8</sup> mol dm<sup>-3</sup>, there was no significant change in the type of morphology, surface appearance, brightness and other characteristics of the deposit.

**3.1.3. 10<sup>-7</sup> mol dm<sup>-3</sup> 2-mercaptoethanol.** At 2, 5, and 10 mA cm<sup>-2</sup>, the big-grained polycrystalline deposits started spreading and the deposit appears more uniform. The surface coverage and brightness of the deposit increases. At 15, 20, 30 and 40 mA cm<sup>-2</sup> smaller-grained deposit (Fig. 2) was observed. The deposit was uniform, less nodular and less powdery than that of the lower concentration of the addition agent. The brightness of the deposit decreases with increase in current density.

**3.1.4. 10<sup>-6</sup> mol dm<sup>-3</sup> 2-mercaptoethanol.** At this concentration of 2-mercaptoethanol in the bath, at 2, 5, and 10 mA cm<sup>-2</sup>, a further refinement in the grain size occurs. However, the refinement is greater at 10 mA cm<sup>-2</sup>. The surface coverage and brightness were relatively better than the deposits obtained at lower concentrations. At higher current densities, the nodular and powdery deposit changes to a less refined polycrystalline deposit showing occasional outward growth (Fig. 3).

**3.1.5. 10<sup>-5</sup> mol dm<sup>-3</sup> 2-mercaptoethanol.** A fine-grained polycrystalline deposit was observed at low current densities. The surface appears very bright, uniform and smooth at 10 mA cm<sup>-2</sup> compared with 2 and 5 mA cm<sup>-2</sup>. At higher current densities the powdery, nodular and outward

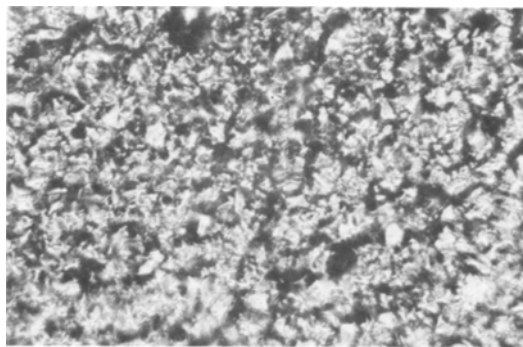


Fig. 2. Big-grained polycrystalline deposit of lead on lead with 10<sup>-7</sup> mol dm<sup>-3</sup> 2-mercaptoethanol at 2 mA cm<sup>-2</sup> (X 525).

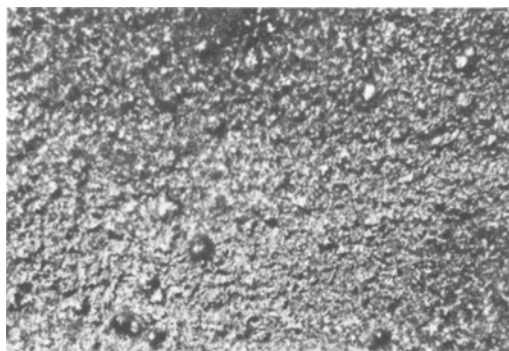


Fig. 3. Occasional outward growth on refined polycrystalline deposit of lead on lead with  $10^{-6} \text{ mol dm}^{-3}$  2-mercaptoethanol at  $20 \text{ mA cm}^{-2}$  ( $\times 525$ ).

growth completely disappears leading to a fine-grained polycrystalline deposit (Fig. 4).

**3.1.6.  $10^{-4} \text{ mol dm}^{-3}$  2-mercaptoethanol.** At this concentration of 2-mercaptoethanol in the bath the deposit becomes rough. Big irregular, pyramidal growths on a polycrystalline background were observed at 2, 5 and  $10 \text{ mA cm}^{-2}$ . At higher current densities more irregular pyramids with greater non-uniformity and nodular and outward growth appears (Fig. 5). The surface becomes dull.

At still higher concentrations of the addition agent a coarse, powdery, patchy, non-uniform and dull deposit was observed.

### 3.2. Overpotentials

The overpotential in solutions without additive initially decreases at all current densities studied

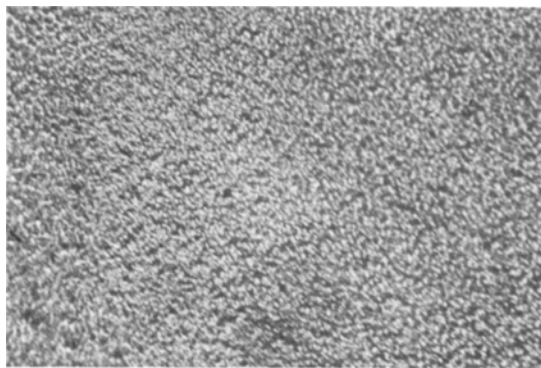


Fig. 4. Fine-grained polycrystalline deposit of lead on lead with  $10^{-5} \text{ mol dm}^{-3}$  2-mercaptoethanol at  $20 \text{ mA cm}^{-2}$  ( $\times 525$ ).

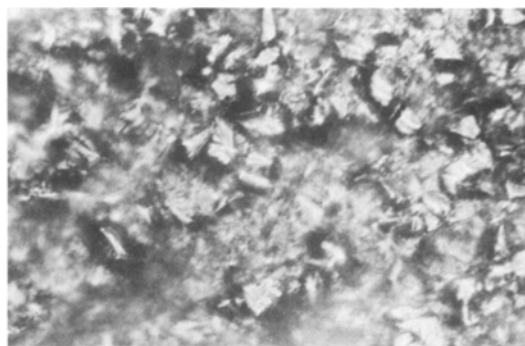


Fig. 5. Non-uniform irregular pyramidal growth of lead on lead with  $10^{-4} \text{ mol dm}^{-3}$  2-mercaptoethanol at  $20 \text{ mA cm}^{-2}$  ( $\times 525$ ).

and then attains a steady value. However, the initial value of the overpotential increases with the increase of current density. This trend in the values of the overpotential continues up to a concentration of  $10^{-8} \text{ mol dm}^{-3}$  of 2-mercaptoethanol. When the concentration of 2-mercaptoethanol was increased to  $10^{-7} \text{ mol dm}^{-3}$ , the overpotential increases (Fig. 6) and this trend increases until at  $10^{-4} \text{ mol dm}^{-3}$ , the overpotential suddenly increases.

The Tafel lines (Fig. 7) was found to hold good at all concentrations of the addition agent studied. The values of kinetic parameters for the electro-deposition process with different concentrations of 2-mercaptoethanol in the bath indicates a decrease in the exchange current density ( $i_0$ ) values, when the concentration of 2-mercaptoethanol was increased from  $10^{-8} \text{ mol dm}^{-3}$  to  $10^{-5} \text{ mol dm}^{-3}$ . However, the value of the Tafel

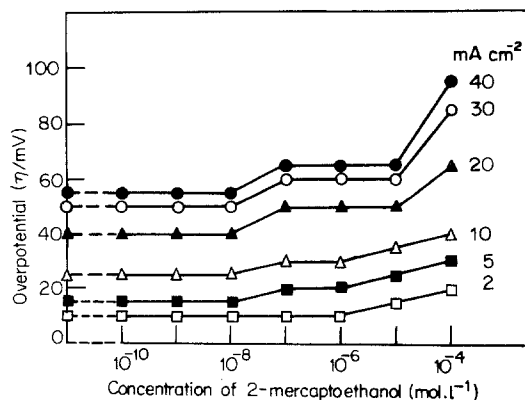


Fig. 6. Overpotential versus concentration of 2-mercaptoethanol.

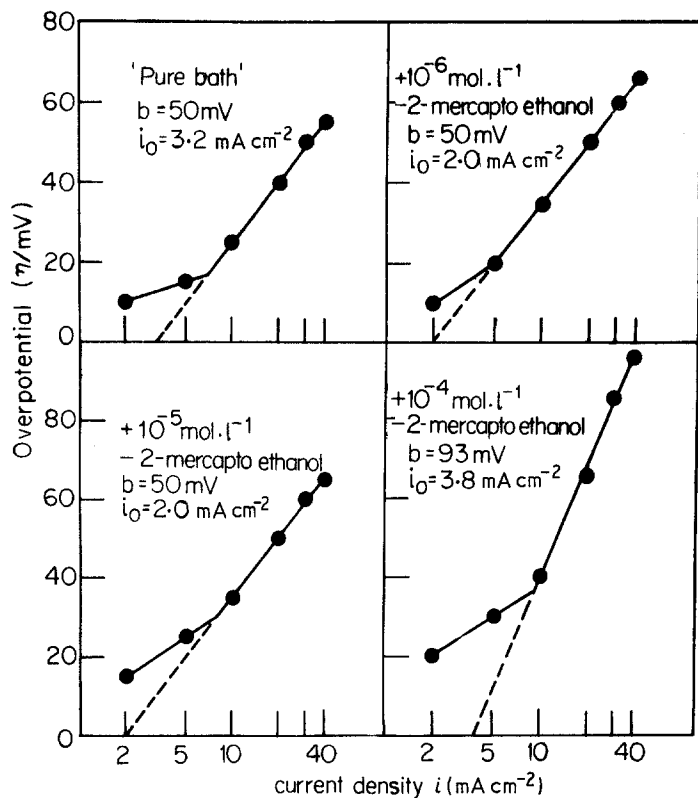


Fig. 7. Tafel relationship of lead on lead.

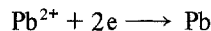
slope ( $b$ ) remains constant up to  $10^{-5} \text{ mol dm}^{-3}$  of 2-mercaptoethanol. At  $10^{-4} \text{ mol dm}^{-3}$  of 2-mercaptoethanol the value increases (Table 1).

#### 4. Discussion

The observed values of the overpotentials in the presence of the addition agent reveals that there is no change in the mechanism of deposition in the presence of 2-mercaptoethanol up to

$10^{-8} \text{ mol dm}^{-3}$ . When the concentration of the 2-mercaptoethanol was increased to  $10^{-7}$ – $10^{-5} \text{ mol dm}^{-3}$  the reaction may proceed through complex formation leading to a decrease in the exchange current density value. At still higher concentrations, the addition agent may undergo degradation.

According to Piontelli [21], the charge transfer reaction for lead from lead fluoborate bath proceeds as follows:



This conforms with the observed higher ionic exchange rate.

When lead was deposited on polycrystalline lead in the presence of 2-mercaptoethanol, one of the following mechanisms may occur as the concentration is progressively increased.

##### 4.1. Mercaptide formation

Through mercaptide formation [22] ( $10^{-7}$ – $10^{-5} \text{ mol dm}^{-3}$  2-mercaptoethanol):

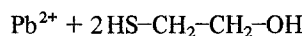
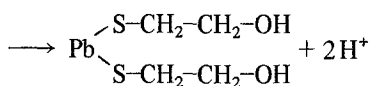


Table 1. Tafel slope and exchange current density values at various concentrations of 2-mercaptoethanol

Concentration of 2-mercaptoethanol in the fluoborate bath ( $\text{mol dm}^{-3}$ )	Tafel slope $b$ (mV)	Exchange current Density $i_0$ ( $\text{mA cm}^{-2}$ )
0	50	3.2
$10^{-10}$	50	3.2
$10^{-9}$	50	3.1
$10^{-8}$	50	3.1
$10^{-7}$	50	2.0
$10^{-6}$	50	2.0
$10^{-5}$	50	2.0
$10^{-4}$	93	3.8

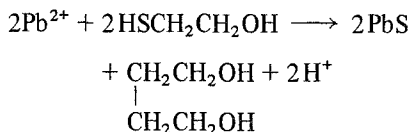


The 2-mercaptoethanol forms a complex with lead ions in solution and may get adsorbed on the surface, at the active sites favouring lateral growth leading to refinement in the deposit.

At low current densities the lead-mercaptoethanol complex may get adsorbed favouring growth of small grains rather than big grains by fresh nucleation as observed (cf. Fig. 4). At higher current densities the adions may acquire sufficient energy and may grow in the usual manner leading to less nodular and less powdery deposit.

#### 4.2. Lead sulphide formation

Lead sulphide formation [22] ( $10^{-4}$  mol dm $^{-3}$  2-mercaptoethanol):



At the concentration of  $10^{-4}$  mol dm $^{-3}$  and above, 2-mercaptoethanol may get degraded forming lead sulphide.

The observed variation of overpotentials with the increasing concentration of the added addition agent is not large up to a concentration of  $10^{-5}$  mol dm $^{-3}$ , but increases at  $10^{-4}$  mol dm $^{-3}$  of 2-mercaptoethanol (cf. Fig. 6). This may be due to the precipitation of lead sulphide at the metal solution interface which increases the Tafel slope value by blocking the active sites. This results in

the increase in the exchange current density value. The adsorbed material may bring a change in the properties of the double layer. Further, the free energy of activation for the elementary charge transfer steps may be changed. Hence, the rate constant, rate determining step and the path of the reaction changes due to the precipitation of lead sulphide.

The above mechanisms are in agreement with the observed electro-kinetic parameters, morphology, infra-red and X-ray studies. The IR spectra (Fig. 8) of the compound obtained with electrolytic bath solution and 2-mercaptoethanol indicates that the -SH group (whose absorption peak due to the stretching vibration is at  $2550\text{ cm}^{-1}$ ) is not present in the compound indicating complex formation as proposed. The X-ray studies indicate a change in the lattice parameters (Fig. 9). The minimum interatomic distance of pure lead is  $0.3492\text{ nm}$  and that of the lead-2-mercaptoethanol complex is  $0.3557\text{ nm}$ .

Thus, it could be concluded that at low concentrations of 2-mercaptoethanol no appreciable change occurs either in the morphology or electro-kinetic parameters. At the critical concentrations of 2-mercaptoethanol, an appreciable change in the grain size occurs favouring low ionic exchange transport. At still higher concentrations, the addition agent itself gets degraded and incorporates in the deposit.

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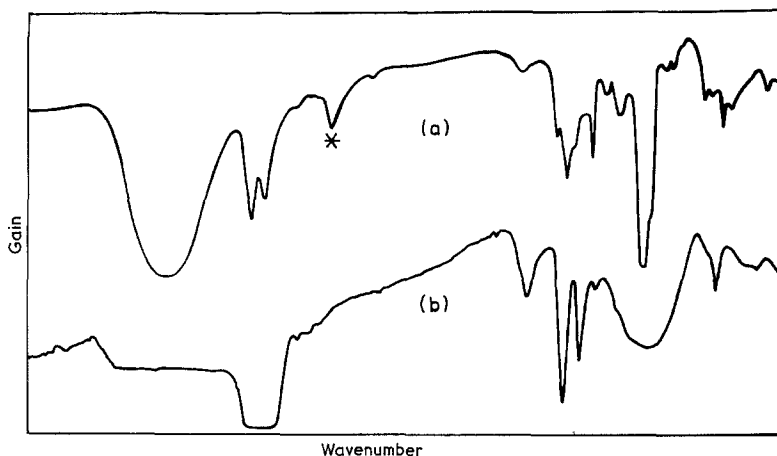


Fig. 8. Infra-red spectra of (a) 2-mercaptoethanol and (b) lead-2-mercaptoethanol complex.

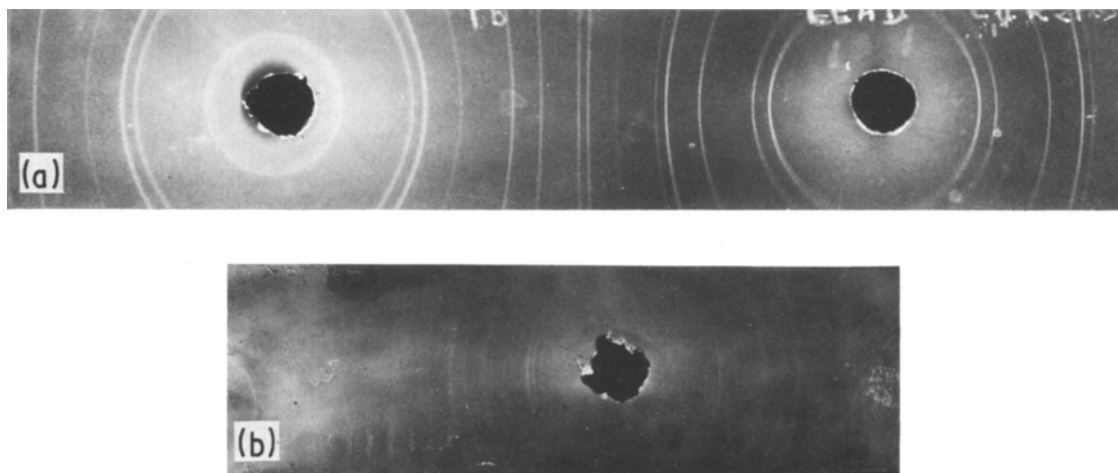


Fig. 9. X-ray diffraction patterns of (a) pure lead and (b) lead-2-mercaptoethanol complex.

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#### References

- [1] W. Blum and G. B. Hogaboom, 'Principles of Electroplating and Electroforming', 3rd edn., McGraw Hill Book Co. Inc., New York (1949).
- [2] F. Mathers and O. R. Overman, *Trans. Am. Electrochem. Soc.* **21** (1912) 313.
- [3] R. Piontelli, *J. Electrochem. Soc.* **94** (1948) 106.
- [4] W. Blum and H. E. Harring, *Trans. Electrochem. Soc.* **40** (1921) 287.
- [5] F. Mathers, *Met. Finish.* **38** (1940) 533.
- [6] F. Mathers and J. Suttle, *J. Electrochem. Soc.* **93** (1948) 47.
- [7] F. Mathers, *Trans. Electrochem. Soc.* **76** (1939) 37.
- [8] W. Blum and H. E. Harring, *Trans. Electrochem. Soc.* **44** (1923) 313.
- [9] S. Venkatachalam and T. L. Ramachar, *Bull. India Sec. Electrochem. Soc.* **8** (1959) 65.
- [10] I. Rajagopalan and K. S. Rajam, *Met. Finish.* **76** (1978) 51.
- [11] W. Blum, F. J. Liscomb, Z. Jencks and W. E. Bailey, *Trans. Am. Electrochem. Soc.* **36** (1919) 243.
- [12] V. I. Chernenko and Yu. E. Udovenko, *Electrokhimiya* **13** (1977) 1311.
- [13] D. Merever and G. Maurin, *Met. Corros. Ind.* **55** (1980) 33.
- [14] P. Renich, *Trans. Kansas Acad. Sci.* **48** (1945) 169.
- [15] P. A. Kohl, 'Extended Abstract Electrochemical Division', Electrochem. Soc. Fall Meeting, (1980) p. 951.
- [16] K. Ohsawa, *Denki Kagaku* **44** (1976) 120.
- [17] *Idem, ibid.* **44** (1976) 183.
- [18] G. Roop Kumar and S. Nageswar, *Surf. Technol.* **10** (1980) 147.
- [19] E. Jones and H. R. Thirsk, *Nature* **171** (1953) 843.
- [20] E. A. Ollard, 'Handbook of Industrial Electroplating', ILIFFE Books Ltd, Elsevier Publishing Co. Ltd., London, New York, Amsterdam (1964) p. 163.
- [21] R. Piontelli, G. Poli and G. Serravalle, 'Transactions of the Symposium on Electrode Processes' (edited by E. Yeager), John Wiley & Sons Inc., New York (1961) p. 67.
- [22] I. L. Finar, 'Organic Chemistry', Vol. 1, 6th edn., Longman Group Ltd., London (1973) p. 399.