On the Electrochemistry of Lead in Acid Alchohols and their Corresponding Salts

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The study of lead in tartaric, malic, succinic and lactic acids and their corresponding sodium salts showed unhindered dissolution to partial passivation. Two types of films form in the anodic half-cycle; the one formed at lower potentials is more susceptible to attack by the anions. A single (broad to multiple) cathodic peak was indicative of the reduction of the surface film and ions in the nearby solution. The mechanism suggested is based on the involvement of bidentate and bridged anions and accounts for the entire results. Electrochemical Impedance Spectroscopy (EIS) studies exhibited two overlapping semi-circles of various diameters terminating to a large semi-circle or a segment of a straight line *viz* a small inductive loop indicating impedance characteristics of the partially passivating film, interfacial resistance, anions adsorption and transport in the solution layer near the surface.

The electrochemistry of lead in acid solutions have extensively been studied due to its technological importance of lead-acid batteries [1,2,3]. In sulphuric acid, a multitude of anodic peaks appear due to formation of $PbSO_4$, PbO, PbO_x and PbO_2 (overlapping with the anodic evolution of oxygen but very well resolvable under special cycling regime); they are accompanied by the cathodic peaks due to the reduction of PbO_2 to PbO and $PbSO_4$, and then to Pb [4,5] in the cyclic voltammograms.

Lead in acetic and oxalic acids [6,7] show no passivation; the surface remains oxide-free below pH 6 [8]. A recent study in tartaric acid [9] claims that the corrosion of lead increases with pH and the slope of E_{corr} *vs* pH is 30 mV pH^{-1}. The dissolution of lead is attributed to the formation of lead-acid alcohol complex of unidentified structure.

The purpose of the present work is to study the electro-dissolution and possible passivation of lead in acid alcohols and corresponding sodium salts aiming at the elucidation of the nature of the interfacial processes. Methods of cyclic voltammetry and electrochemical impedance spectroscopy have been employed for the purpose.

EXPERIMENTAL

Lead of 99.99% purity and L-tartaric (TH_2), malic (MH_2), succinic (SH_2) and lactic (LH) acids were of Merck AR grade. Water was doubly distilled. Studies were carried out in acid solution and also in the

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corresponding salt solution at pH 8. The solutions were purged and kept under nitrogen throughout the studies.

Cyclic voltammetry was carried out in a three electrode cell; working electrode was a lead disc housed in a teflon holder exposing a circular area of 0.283 cm^2. A large platinum foil was the counter electrode. The cell was powered by a Beckman Electroscan 30 and the potential was monitored against SCE using a SM201 high impedance digital voltmeter. An EG & G model RDE612 rotating disc assembly was used in the rotating studies. Electrode rotation speeds of 0 to 1000 rpm were employed.

Impedance spectroscopy was carried out in the same cell using a EG & G model 387A impedance spectrometer comprising a 273 potentiostat/galvanostat, a 5210 lock-in amplifier and run by a IBM ps/ valuepoint computer through M398 software. In all studies, the CV's were run in the range of -2.5 to 2.5 V/SCE with potential sweep rates of 5 to 100 $mV.s^{-1}$. The figures in the results and discussion refer to 50 mVs^{-1} sweep rates unless otherwise stated. EIS studies were carried out in the frequency range of 100 kHZ to 10 mHz and ac-signal amplitude of 5 mV.

RESULTS

Lactic acid & Sodium lactate (pH=8)

In both acid and basic media, the anodic half cycles are dominated by a steady rise in dissolution current starting at *ca.* -0.7 V and rising continuously upto 2.0 V/SCE limitlessly. The cathodic current follows the anodic path except that a small cathodic peak appears in the range -1.2 to -1.7 V/SCE - the peak position depending on the pH; its size decreases with increase in the rotational speed and has no correspondence to the charge consumed in the anodic half cycles.

Succinic acid & Sodium succinate (pH=8)

The behaviour in acid solution is almost the same as in lactic acid. But in neutralized solution, a relatively sharp anodic peak is observed at 0.25 V and this is accompanied by its corresponding sharp

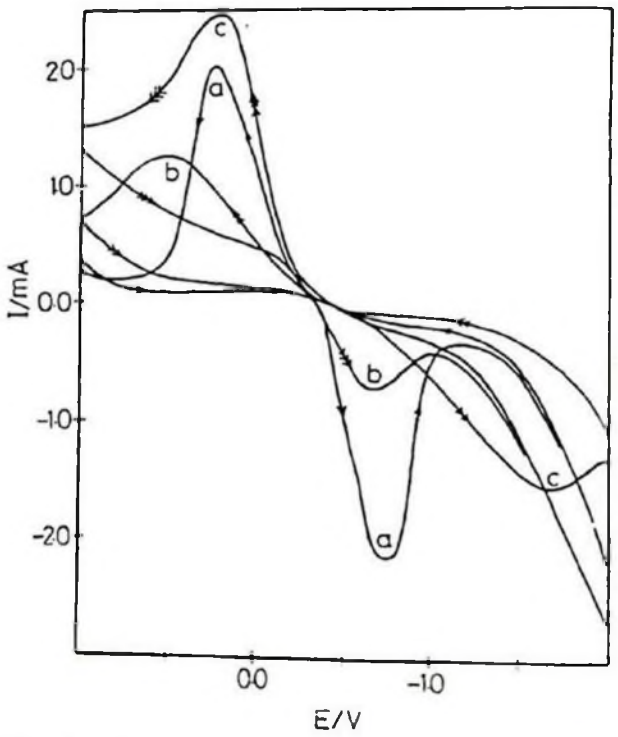


Fig. 1. Cyclic voltammograms for succinate/Pb at pH=8
Pb electrode rotates at 200 rpm.
Scan rate 50 $mV.s^{-1}$
(a) 0.5 M, (b) 0.1 M and (c) 0.5 M;

cathodic peak at -0.75 V/SCE (Curve a in the Fig 1). Both peaks broadened with decreasing concentrations with a shift of the anodic peak to 1.2 V. The cathodic peak appeared as overlapping peaks (rather broad) at -0.75 V/SCE. Increasing the rotational speed converted the anodic peak to almost a plateau; the size of cathodic peak dramatically decreased and was converted to small and well resolved peaks (curve c in fig 1).

Malic acid & Sodium malate (pH=8)

In acid solution, the steady dissolution current in the anodic sweep terminates to a very broad peak (almost a plateau) at about 1.0 V. But a multitude of peaks (at least two) are observed around -1.25 V in the cathodic half cycle (Fig.2). Decreasing the concentration removes the plateau and the cathodic peaks become smaller and structureless. Delays and reversal of the anodic sweep at -0.5 V/SCE amplifies the cathodic structure revealing two distinct peaks at -0.9 and -1.25 V/SCE.

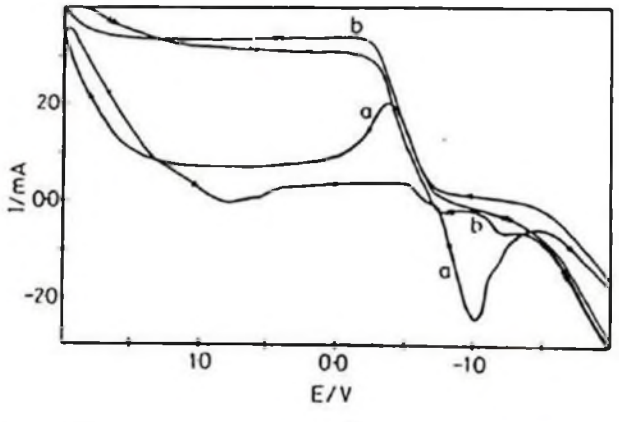


Fig. 2-Cyclic voltammograms for malite/Pb at pH=8
conc. 0.5 M; Scan rate 50 mV.s^{-1}
(a) stationary (b) rotated at 2000 rpm.

At pH = 8 where almost one H^+ is neutralized, a pair of peaks at -0.25 and +0.25 V/SCE in the anodic half cycle and a single cathodic peak at -1.25 V/SCE were observed. Further increase in pH tends to increase the first and diminish the second anodic peak while the cathodic peak remains at its position. Interestingly enough, in malate (and to a much lesser extent in succinic solutions) extending the anodic half cycle to +2.0 V causes the appearance of two broad cathodic peaks around +0.5 V/SCE and an additional broad cathodic peak centered around -1.75 V/SCE. Cyclicing the potential in the range of -0.5 to +2.0 V intensifies the peaks around +0.5 V/SCE.

Tartaric acid & Sodium tartarate

In acid solutions, the steady dissolution currents in the anodic half cycle terminates to a broad peak under both steady and rotating regims - its potential strongly dependent on the rate of potential sweep (Fig. 3). In the cathodic half cycle, a similar broad peak was observed; the ratio of the corresponding anodic/cathodic charges decreased and approahced unity as the sweep rate decreased. The effect was more pronounced in more concentrated solutions.

In pure sodium tartarate solutions, two anodic peaks were obsedved (in the range of -0.8 to +1.0 V/SCE) and a broad cathodic peak (or two overlapping peaks) appeared in the range of -0.1 to -1.7 V/SCE. Rotating the electrode tends to increase the size of the second anodic peak substantially, while the cathodic peak remains unchanged (Fig. 4A). Two

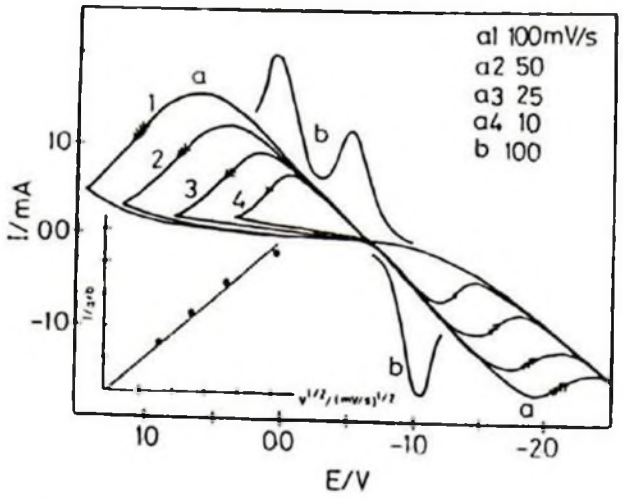


Fig. 3 - Cyclic voltammograms at various potential sweep rates
(a) 0.1M tarataric acid/Pb and
(b) 0.1M sodium-di-tartarate/Pb

overlapping anodic peaks around 0.0 V/ SCE and a single cathodic peak at -1.5 V/SCE dominated the voltammograme at pH = 8 (Fig. 4B).

DISCUSSION

The results can be explained on the basis of structure, the extent of the dissociations of the acid alcohols and also on the solubilities /dissociations of the salts /complexes containing lead and acid alcohols. Lactic acid is not chelating and succinic acid is weakly chelating. In these, lead dissolves under anodic polarization. Malic acid is a strong acid compared to salicyclic; in this case, a limited surface film is formed. Tartaric acid is a considerably stronger acid (2< pK <3) and chelating. In this case, cathodic/anodic peak increases and approaches unity as the potential sweep rate is decreased. No passivation is observed in case of nonchelating lactic acid even in alkaline solutions (pH=8), while other three systems show partial

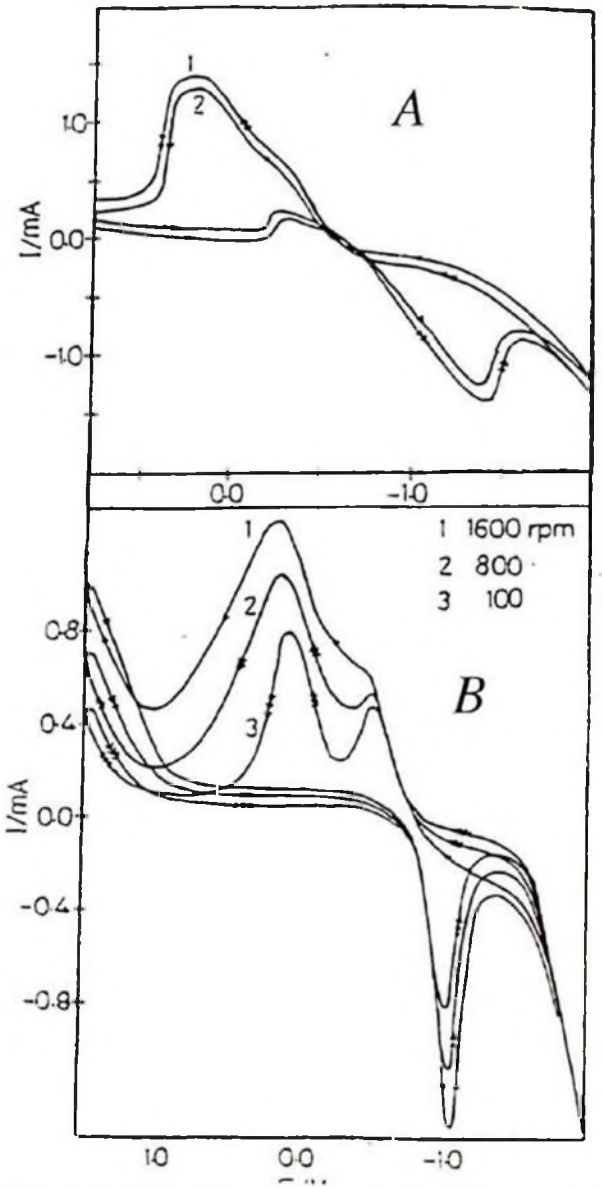
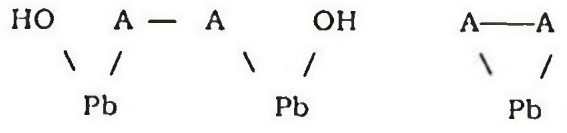


Fig. 4 - Cyclic voltammograms at various rotating speeds.
A - 0.1 M tartaric acid /Pb
B - 0.1 M tartaric acid /tartarate/Pb, pH=8
Scan rate 50 mVs^{-1}

passivation at considerably lower anodic potentials. This points to the importance of the chelating ability of the anions.

Rotating the electrode has a dramatic effect on the succinic acid system while marginal effects are observed in the

tartaric acid system. This points to the effects of α-hydroxyl groups in stabilizing the passivating film and also the charge on the carboxylate groups. In all cases, the sharpening of the cathodic peaks and resolution to two distinct peaks of lower intensity points to the reduction of the surface as well as the solution entities. Considering the entire results, two types of surface films are envisaged; their formations are most clearly observed in tartarate solutions as two distinct and relatively sharp peaks in the cyclic voltammograms. The film formed at lower potentials (which involves the dissolution of small amounts of lead) is unstable and quickly dissolved in tartarate solution at the open circuit resulting in the complete disappearing of the cathodic peak. The second film is much thicker and more stable. Also, reversing the cathodic half cycle prior to the reduction peaks resulted in the appearing of the second anodic peak only. This signifies the conversion of the first film to the second type and the involvement of similar lead surface sites. Brief coulomertric studies of film covered electrodes were performed in DMSO and Nitromethane solutions to investigate the tartarate content of the films. Although the studies never produced a unique integral value the ratio of tartarate 2/tartarate 1 per lead atom was always between 1.4 and 2.0. The following structures are proposed for the films. These indeed produce different compactness and stabilities to the film.



Analysis of the I_{peak} *vs* $v^{1/2}$ (v being the potential sweep rate) for the anodic peak observed in tartaric acid gives a straight line passing through the origin (inset in Fig. 3). According to Muller [11] and Calandra [12], the passivation is due to the change in the ohmic resistance and the slope is $(nF\rho k/M)1/2A\ (1-\theta)$ where n=2 is the number of electrons, ρ=2.50 $g.cm^{-3}$ is the density of the film, M=330 is the molecular weight of the film, $k=10^{-4}$ $S.cm^{-1}$ is the solution conductivity, A=1 cm^2 is the electrode's area. The fraction of the surface covered by the film (θ) is obtained as 0.97.

The Nyquist plots for different acid solutions are given in Fig. 5.

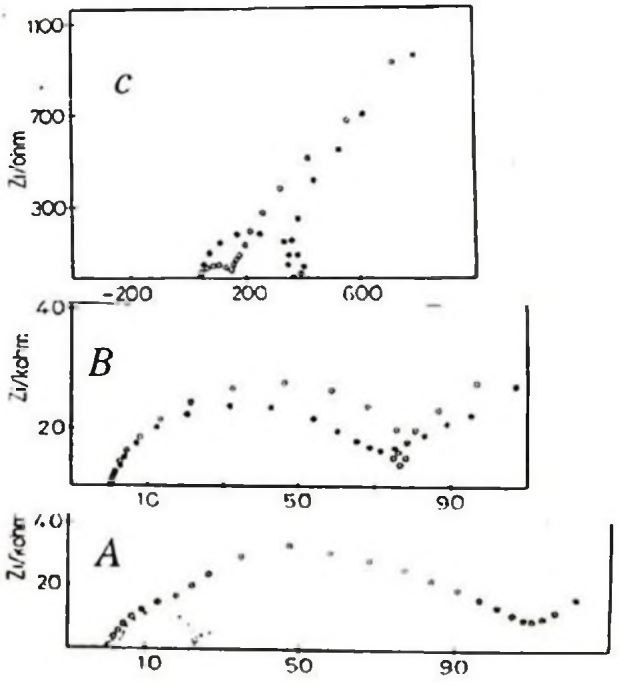
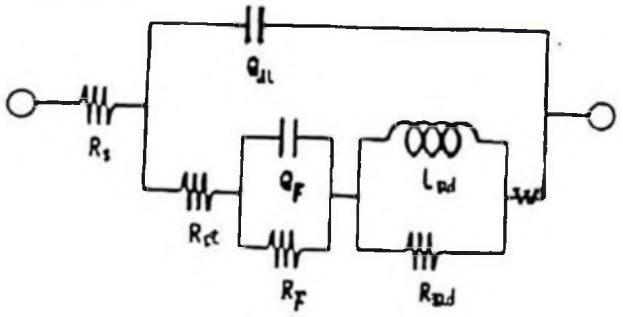


Fig. 5 - Nyquist plots
A for sodium-di-tartarate/Pb, 0.1M 0.6 V/SCE
(o) stationary, (o) rotated at 1400 rpm
B for succinic acid/succinate/Pb, pH=8 and 0.1M.
C for malic acid/malite/Pb at pH=8 and 0.5 M
(o) at -0.4 V/SCE and (o) 0.5 V/SCE dc off - set potentials.

To analyse the impedance results, equivalent circuit simulation software developed by Boukamp [13] has been employed. Fig. 6 presents the simulated results. Scheme 1 presents the general equivalent circuit compatible with the results. According to this model, the

Scheme 1



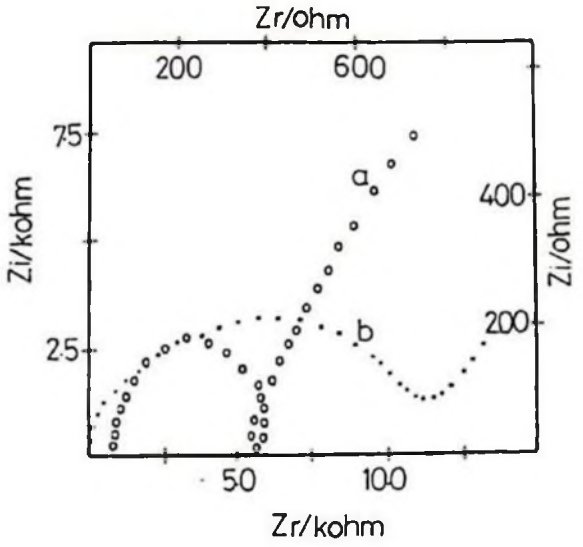


Fig. 6 - Presentation of the simulated results
(a) Malite 0.5 M; pH 8; at -0.4 V
(b) Succinate 0.1 M; pH 8.

Table 1

Magnitude of the equivalent circuit elements presented in scheme 1 and compatible with the experimental results

Magnitude Elements	Tartaric acid R(Q(R(RQ)W)	Succinic acid R(Q(R(RQ)W)	Malic acid (Q(R(RQ)(RL))
R_s(ohm)	65.4	81.9	36.5
Q_{dl}(μfarad)	2.2×10^{-6}, n = 0.7099	2.09×10^{-6}, n=0.7396	8.85×10^{-7}, n=0.6574
R_f(ohm)	4.48×10^{3}	30459	292.1
Q_f(μfarad)	3.92×10^{-6}, n=0.849	5.32×10^{-7}, n=0.764	3.92×10^{-4}, n=0.6574
R_{ct}(ohm)	5.24×10^{3}	15800	5.51×10^{4}
L_{ad}(henri)			0.346
R_{ad}(ohm)			85.3
W(mho)	8.43×10^{-6}	3.44×10^{-4}	

R_s = solution resistance. R_{ct} = charge transfer resistance. R_f = film resistance.
Q_{dl} = double layer capacitance. Q_f = film capacitance.
W = Warburg impedance. R_{ad} = adsorption resistance. L_{ad} = adsorption inductance.

complicated interface exhibiting interfacial reactions, transport through the surface film, adsorption and Warburg impedance show themselves in the form of two overlapping semi circles at the high frequency side of the spectrum an inductive loop signifying adsorption of anions and a segment of a straight line pointing to the Warburg impedance due to the mass transfer near the film. There are chances that at the frequencies below 0.01 HZ (not available to us), the straight line curves drawn in the form of a quarter of a circle signifying diffusion through a gel like layer near the surface.

Table 1 presents the magnitudes of the simulated circuit elements which fit the results best. Rotating of the electrode decreases the steady state thickness of the film and thus the film resistance decreases while the rate of interfacial reaction increases and also the Warburg impedance decreases due to the enhanced mass transfer to the electrode. The assignment of the inductive loop to the adsorption of anions seems to be justified as it is only present at more anodic potentials and films are thinner and more permeable (as that of malic acid). In many cases Q's (Constant phase element) instead of C's (Capacitive elements) has to be employed to achieve the best fit. This indeed points to the roughness of the surface film and it's fractal dimension.

CONCLUSION

On the basis of this study, the following conclusions can be reached :

1. The electrochemical dissolution/ passivation of lead in acid alcohols depends on the structure of the acid and it's acidity strength.
2. The passivation seems to be under ohmic control.
3. The complicated interface can be modeled by an equivalent circuit comprising of serial couples of parallel resistance/capacitance, resistance/inductance and Warburg elements.

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