Interaction of Dialdehyde Starch on Platinum Electrodes

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The electrochemical nature and behaviour of dialdehyde starch was investigated using platinum electrode. The open circuit decay of potential obtained with platinized-platinum electrode had suggested the existence of dehydrogenative chemisorption of the reaction product of dialdehyde starch. The existence of the chemisorbed organic intermediate had been suggested by the electron paramagnetic resonance studies with the films formed on platinum electrode. The potentiodynamic transients obtained for dialdehyde starch have shown the existence of chemisorbed carbonaceous intermediates.

The enormous reducing ability(1) of dildehyde starch (DAS) aroused profound interest in utilising this material gainfully. It was thought worthwhile to investigate extensively the nature and the electrochemical behaviour of the electrochemically oxidised topioca starches at mercurry(2) and solid electrodes. The results of a through investigation made with mercury and amlagam electrodes were already communicated(3). Some of the salient features of a study of a open circuit adsorption, the potentiodynamic investigations and the e.p.r. studies at platinum are reported here.

EXPERIMENTAL

METHODS AND MATERIALS

Electrolytically oxidised dialdehyde starch(3) was used as such in our studies. A 2 w/v % solution of DAS in 1 N NaOH was prepared and was used the same day.

All the reagents were of AR grade and were used only after the necessary purification and pretreatment. Open circuit adsorption and the e.p.r. sample preparation were made with an experimental set up which was nearly the same as described earlier(4,5). The preparation of the platinized-platinum electrode, the cell used and the type of pretreatment given to the electrodes were also described(4,5).

A major portion of the studies were made with a reversible hydrogen electrode (RHE) in the same experimental electrolyte at a partial pressure of hydrogen of 1 atmosphere and at 26 $\pm$ 1°C.

The platinum wire electrodes for the e.p.r. studies were very carefully designed. To the tip of the platinum wire which emerged out of the sealed glass tube, three to five wire pieces of the required diameter and length were spot welded. These electrodes have the additional benefit that simultaneously as many as 3 to 5 wires could be prepared. The platinum wire electrodes (5 cm length and 6 mm o.d.) were platinised(5) with 2 mA geom. cm^2 for 3 hours. After the plating, it was pretreated in 0.1M H_2SO_4 solution first anodically and then cathodically and finally it was allowed to age for 4 weeks before use. Maintaining the electrode at about 450 mV with reference to RHE in the clean double layer region of potentials, the absorbate was allowed to interact. As anticipated, the potential decayed with time. The electrode was completely washed free for the dissolved organic by deoxygenated experimental electrolyte (1m NaOH solution).

While the electrode was still inside the experimental electrolyte, the wire electrode were so carefully pressed against the glass wall of the cell, that it got detached at the previously partly-cut portion of platinum wire electrode. It was carefully transferred into the stoppered holders containing the same deoxygenated supporting electrolyte. These samples were further subjected to e.p.r. studies with a Varian Spectroscope.

OPEN CIRCUIT STUDIES

A known value of the 2 w/v % solution of DAS in 1.0N NaOH was initially dearated for 1 hour, and was allowed to come into contact with the platinized-platinum sheet electrode (2 cm x 1 cm x 0.1 cm) which was maintained at 450 mV with reference to RHE. The potential decay was followed as a function of time.

POTENTIODYNAMIC INVESTIGATIONS

Smooth platinum working electrode a palladized palladium reference electrode, and a platinized-platinum counter electrode, a low frequency function generator (Type 202A), a locally

fabricated potentiostat, a Tektronix oscilloscope (Type 531A) with a Tektronix Camera were used in this study. A decade resistance box (General Radio Company) was used for the accurate measurement of current. Potentiodynamic transients were obtained at a triangular sweep rate of 3cps at various temperatures.

RESULTS AND DISCUSSION

It is well-recognised(6-8) that at the platinized-platinum electrode, the adsorbates suffered dehydrogenative chemisorption and this consequently resulted in the decay of open circuit potential. In the current study, the potential fell from 450 mV to a value in the range of 200-250mV. This decay strongly suggested the existence of the stronger attractive interaction(6) between electrode and DAS itself or one of the fragments of the anaerobically depolymerized intermediate product of the DAS. The decay in this case was, however, not so remarkable as in the case of methanol, formaldehyde or ethanol. The absence of a sharp potential decay presumably be due to one or both of the following plausible reasons:

i) DAS being a polymeric material, it could not tunnel through the microcrystallites present on the electrocatlyst(9). Even many of the depolymerized fragments might not be interacting. The most likely candidate of chemisorpiton is formaldehyde which had been proposed earlier by one of us(10) from the polarographic investigations. The quantity of formaldehyde formed would be very small.

ii) Depolymerization reaction leading to the formation of fragmented electro active intermediate could be kinetically controlled. Thus the amount of the intermediate formed would be necessarily small.

The open circuit adsorption pattern presented a definitive clue to demonstrate that dehydrogenative chemisorption indeed occured with atleast one of the fragments of the DAS and thus the decay of the potential was noticed. The non-occurance of the characteristic minimum in the open circuit decay curves suggested that either hydrogenation of the chemisorbed radical was absent or if at all it prevailed, it should occur that a rate much lower than that of the dehydrogenative chemisorption(6).

In an attempt to charactrise that the electro active carbonaceous radical, the e.p.r. studies were carried out at 296° K and at 77° K using a field strength of 9.483 GHz. The spectrum at the 296° K indicating that a peak with a separation of about 23 Gauss and the g value was 2.0995. The spectra on liquid nitrogen temperature did not show any such peaks very clearly. This study had given a good route to show the existence of the chemisorbed radicals although the exact nature of the radicals was not established.

The potentiodynamic transients obtained with platinum electrode in the presence and absence of DAS has been presented in the Fig.1. This clearly

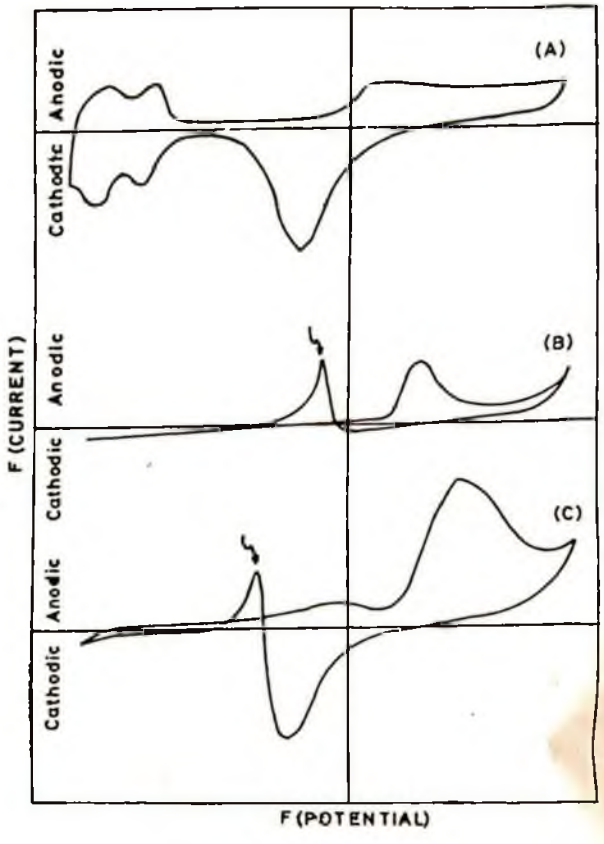


Fig.1 Potentio-dynamic transients obtained
(A) With platinized - platinum electrode for hydrogen
(B) With platinized - platinum electrode for the intermediate of DAS.
(C) With palladium electrode for the intermediate of DAS.

had suggested the existance of chemisorbed radicals on the electrode matrix. Similar potentiodynamic transists were obtained with formaldehyde testifying evidence to out proposed mechanism(10). Palladium electrodes also gave the characteristics peak representing the existance of the intermediate. Here the quantity of the intermediate present was comparatively small.

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REFERENCES

1. S. Balagopal, S. Chidambaram, M.S.V. Pathy and H.V.K. Udupa, Proc. of the 12th Seminar on Electrochemistry held at the Central Electro-Chemical Research Institute, Karaikudi-6(1972).
2. R. Ramaswamy, M.S.V. Pathy and H.V.K. Udupa, Indian J. of Tech. 1 (1963) 115.
3. C.J. Indira, R. Chandrasekharan, P. Sidheswaran, V.K. Venkatesan and H.V.K. Udupa, J. Electroanal. Chem., 64 (1975) 233.
4. P. Sidheswaran, J. Electroanal. Chem., 38 (1972) 101.
5. P. Sidheswaran. "Anodic oxidation of chemisorbed formaldehyde and related studies", Ph.D. Thesis, Indian Institute of Technology, Bombay 1971.
6. P. Sidheswaran, Indian J. Chem. 11 (1973) 960.
7. P. Sidheswaran, in "Technology of Electro-organic Processes", A short-term course conducted at I.I.T., Bombay in 1980 under Q.I.P.
8. B.B. Damaskin, O.A. Petrii and V.V. Batrakov, "Adsorption of organic compounds on electrodes" (Nauka Press, Moscow) 1968.
9. P. Sidheswaran, Indian J.Chem. 17A (1980) 334.
10. P. Sidheswaran, Indian J. Chem. 13 (1975) 630.