

Electroreduction of vanillin in aprotic and protic media on glassy carbon electrode

M Chandrasekaran, M Noel and V Krishnan

Central Electrochemical Research Institute, Karaikudi - 623 006, INDIA

Cyclic voltammetric behaviour of vanillin on a perfectly polished glassy carbon electrode (GCE) both in aprotic and in protic solutions of various pH ranges have been studied. In aprotic solvent (DMF), vanillin undergoes two 1 e, irreversible diffusion controlled reduction. The anion radical formed undergoes a fast dimerisation process. The stability and reactivity of the anion radicals have been studied using protonating agents (H₂O, o-cresol and benzoic acid) ion-pair forming agent (LiClO₄) and redox catalytic reagent (n-butyl bromide). In aqueous media - acidic, neutral and alkaline - vanillin undergoes a single irreversible wave at potentials close to the hydrogen evolution potential. Constant potential electrolysis of vanillin reduction in acidic medium yields vanillyl alcohol. On a partially pretreated/polished GC electrode, a slow time-dependent adsorption prewave is observed. However, in a neutral medium, even a highly polished GC electrode gives a prewave in addition to the main wave. Such prewaves are not observed on Hg surfaces.

Key words: Electroreduction of vanillin, glassy carbon electrode, cyclic voltammetry

INTRODUCTION

Polarographic studies on vanillin reduction both in aprotic [1] and protic media [2] are available. However, voltammetric investigations on glassy carbon electrode (GCE) are not available. Hence detailed investigations in both media were undertaken. The results are discussed with due emphasis on the influence on the electrode surface.

EXPERIMENTAL

Tetra-n-butyl ammonium iodide in dimethylformamide was used as aprotic solution. 50% ethanolic solutions of 0.1M concentration of sulphuric acid (acidic medium), tetra ethyl ammonium p-toluene sulphonate (TEATS, neutral medium) and tetra-n-butyl ammonium hydroxide (TBAH, alkaline medium) were used in aqueous conditions. All experimental details regarding cell, instruments, electrode, pretreatment procedures were discussed elsewhere [3]. In constant potential experiments performed in acidic medium, vanillyl alcohol was isolated and identified by IR spectral analysis. Studies were carried out at 298 ± 1 K.

RESULTS AND DISCUSSION

Voltammetry in DMF

On a perfectly polished GC electrode, vanillin gives two 1 e diffusion controlled waves at slow sweep rates. The first reduction peak noticed around -1.9V is sharp and second wave around -2.7V is diffused and merges with the background reduction. The peak current increases

with sweep rate and concentration. However, the peak current constant slowly decreases with sweep rate and concentration. This is due to some blocking/adsorption of vanillin on GC surface. The appearance of a small anodic wave at high sweep rates as well as the shift of peak potential with sweep rate and concentration suggest that the vanillin reduction follows EC mechanism or more specifically reductive dimerisation. This is further supported by the study of the effect of protonating agents, ion-pair forming agent and redox catalytic reagent. The reduction behaviour on a perfectly polished GC surface is quite similar to the behaviour observed on Hg surface. However, on a partially pretreated GC surface, a slow-time dependent adsorption prewave is observed in addition to the main waves.

Voltammetry in aqueous media

On a perfectly polished GCE, in aqueous acidic and alkaline media, vanillin gives one diffusion controlled wave at potentials close to the background reduction process. However in neutral solution, a slow, time-dependent adsorption prewave (similar to the one observed in DMF) is noticed on a perfectly polished GC surface. The approximate charge in the prewave region is about $43.13 \mu\text{C}\cdot\text{cm}^{-2}$. If 'n' is assumed to be one, the surface coverage of surface bound species is 24.65%.

CONCLUSION

Vanillin reduction behaviour on a perfectly polished GC electrode in DMF is almost similar to the behaviour on Hg surface. A slow time-dependent adsorption prewave in addition to the main waves is observed on a partially

pretreated GC which is not observed on Hg surface. In aqueous solutions, the reduction process merges with the background reduction. Even on a perfectly polished GC, the same prewave is observed for vanillin reduction in aqueous neutral solution.

REFERENCES

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