

pH Responsive Resin Electrode

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Quinhydrone electrode, after its introduction by Bilman¹ and, Granger and Nelson² in 1921 has been extensively used as a substitute for the hydrogen electrode in the low pH range. However, the most severe limitation of the quinhydrone electrode is that it can not be used above pH 7 due to the secondary oxidation by the atmosphere, and also due to the dissociation of hydroquinone forming salts. This electrode is also sensitive to the presence of salts in the solution.

Miyamoto and Sasaki³ have reported the preparation of a pH responsive polymer prepared from hydroquinone and formaldehyde. The resin was subjected to 50% oxidation in acetic acid solution, and a thin film was formed on the flat platinum surface. They found a linear relationship between the potential determined by means of this electrode and the pH in the range 0.5 to 8.0.

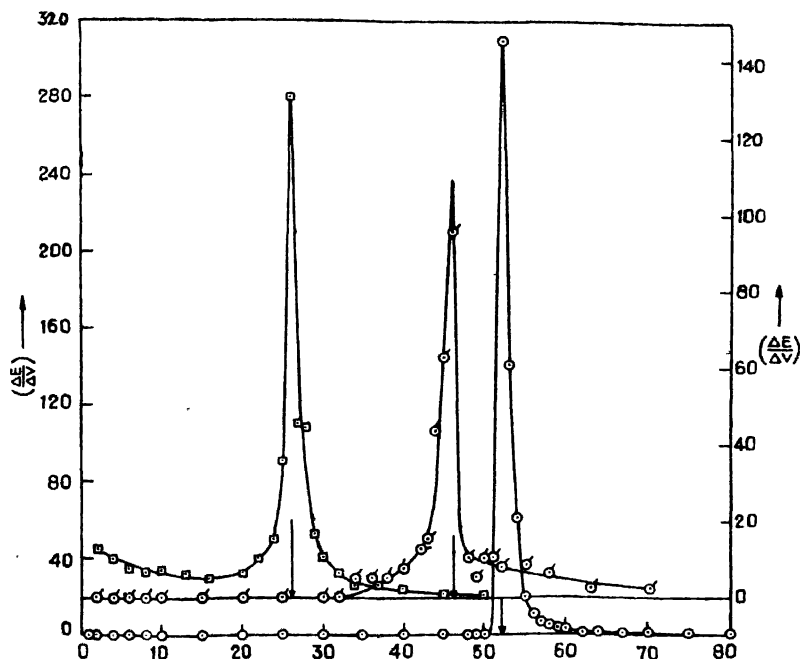


Fig. 1. $\Delta E/\Delta V$ vs DROPS of Alkali Added

\circ ---0.097 N HCl; ϕ ---0.0017 N HCl; \square ---0.046 N Acetic Acid.

The present note deals with the interesting properties of a condensation polymer prepared from quinhydrone and formaldehyde. This resin, QFR (quinhydrone-formaldehyde resin) has been found to respond as a hydrogen ion reversible electrode like quinhydrone itself. Interesting results have been observed in our studies of acid-base titrations. In the titrations of strong acids with strong bases, the nature of the titration curves is almost the same as those obtained with quinhydrone electrode. The most prominent feature of this observation is the extreme stability of the polymer even at high pH maintaining its reversibility as electrode. Another distinct advantage of QFR is that unlike quinhydrone it does not impart any colour to the solution even when sufficient amount of alkali is added after neutralisation. This special property, i.e. its stability at high pH , has helped in the estimation of a very weak acid like boric acid, which can not be titrated by quinhydrone electrode.

Figure 1 illustrates the titration curves of hydrochloric and acetic acids of different strengths with sodium hydroxide, and Figure 2 represents that of boric acid. The different amounts of alkali needed for the complete neutralisation of these acids have been calculated from the graphs and the results quantitatively agree with the values obtained by direct titrations within 1 to 2%.

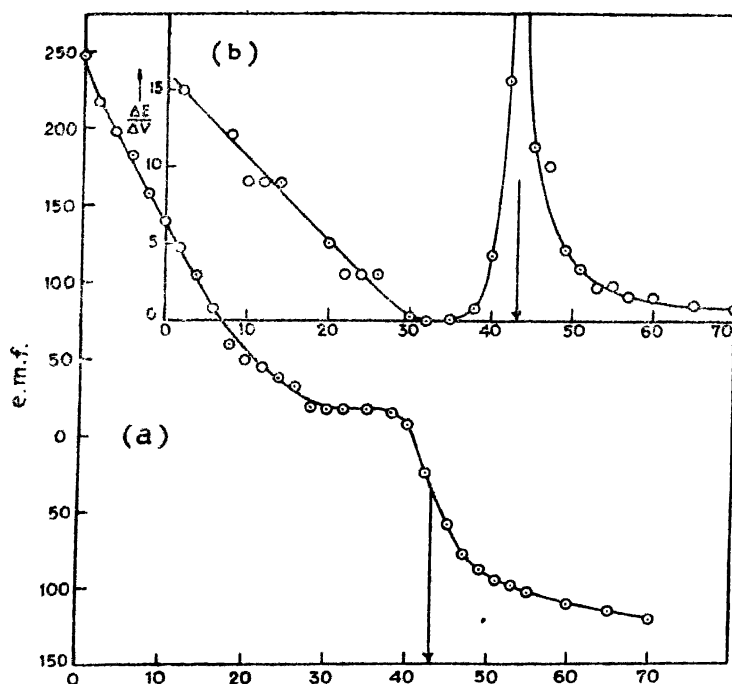


Fig. 2 Titration curves of 0.0932 N Boric Acid using QFR Resin
(a) EMF. vs. DROPS of Alkali Added; (b) $\Delta E/\Delta V$ vs DROPS
of Alkali Added.

The disadvantage observed with this resin electrode is that unlike quinhydrone, it requires a longer time for the attainment of equilibrium if the polymer is added to the solution

immediately before the titrations. However, the fluctuation in the observed potentials, which is a common characteristic of the redox and electron exchange polymers⁴, diminishes during the course of the titrations. This has also been found that in the case of QFR the equilibrium can be hastened if the polymer is pre-soaked in the titrant for about one hour or more before the titration. Preliminary studies with buffer solutions show a linear relationship between the observed e.m.f. values and the pH. Further work in this line is in progress.

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