$T_{c,m}$ was calculated from the slope (γ) of the line in the plot of $\Delta_r H^o$ vs $\Delta_r G^o_{T_{hm}}$ (fig. 2).

$$T_{c,m} = T_{hm} / (1-1/\gamma)$$

where $T_{hm} = n/ \sum_i 1/T_i$, T_i - experimental temperatures and the obtained value was -1046K.

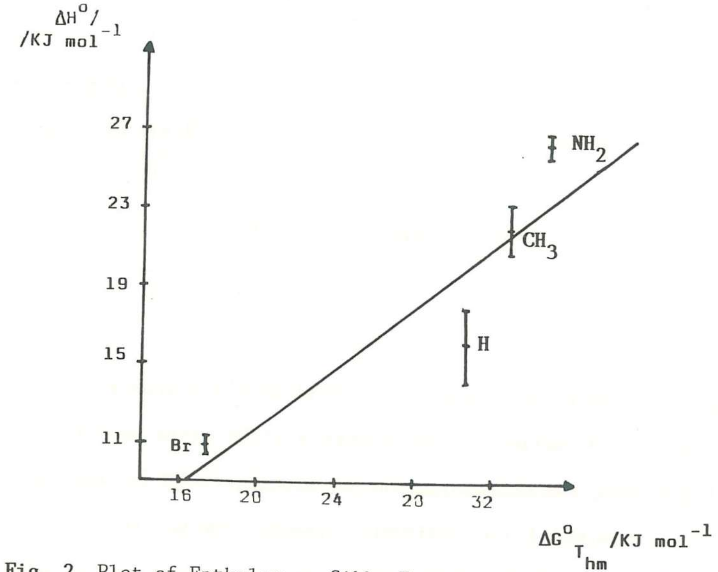

Fig. 2. Plot of Enthalpy vs Gibbs Energy estimates with 50% joint confidence regions.

The line in figure 2 cannot be used to represent the observed relation between $\Delta_r H^o$ and $\Delta_r G^o_{T_{hm}}$ because data do not display a linear compensation effect but do display a nonlinear pattern. We don't present a nonlinear relationship owing to the few number of elements of the studied series.

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A MICROELECTRODE STUDY OF THE METHOXYLATION OF FURAN

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In the conventional synthesis of 2,5-dimethoxy-2,5-dihydrofuran, furan is treated with bromine in a solution of methanol according to the following reaction(1):

The main disadvantage of this method, however, is the formation of halogen by-products. To overcome this problem a method for methoxylation of furan was developed using electrochemical indirect oxidation, in a methanol solution of potassium bromide(2).

Here, we present a study of the catalytic oxidation of furan at finite platinum microdisc electrodes, using conditions very close to industrial practice.

For the determination of the kinetics of the pseudo-first order homogeneous chemical reaction coupled to the heterogeneous electron transfer reaction, a technique involving the recording of steady state current-voltage curves at microelectrodes was used with the assumption that the limiting current can be analysed in terms

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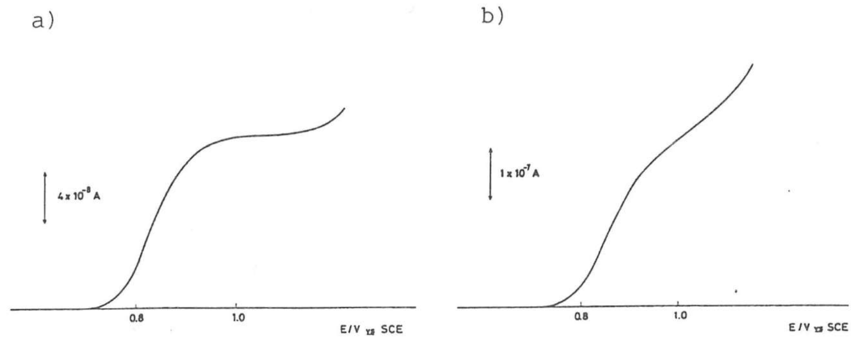

Figure 1: a) I-E curve for the oxidation of a methanol solution of 10^{-2}M NaBr in 0.1M $NaClO_4$.

b) Same as in a) but in the presence of furan 0.14M.

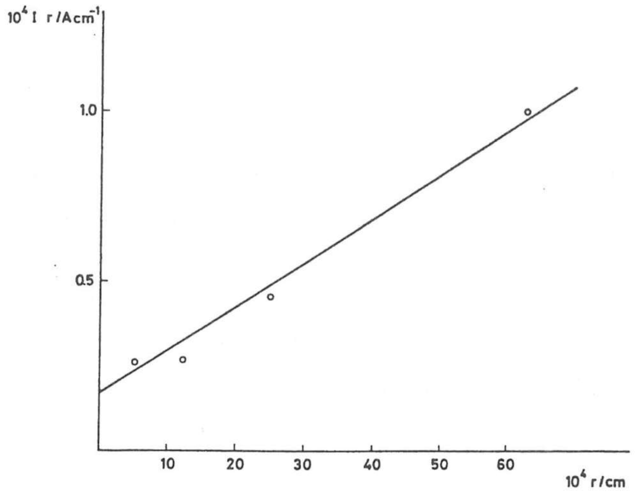

Figure 2. A plot Ir_m as a function of microelectrode radii for a methanol solution of furan 0.14M, NaBr 0.01M in 0.1M $NaClO_4$.

of a sperical diffusion field$^{(3)}$.

The following equations describe a typical catalytic reaction (EC'):

$$R - ne^- \rightleftharpoons O \qquad (1)$$

$$O + Z \xrightarrow{k} R + P \qquad (2)$$

where K is the catalyst and Z the substrate. When the reaction (2) is pseudo-first order, the diffusion limited current density at a microdisc electrode in the steady state is given by:

$$I = (4nFDc_0/\pi r_m)\left[1 + \frac{\pi}{4} r_m (k'/D)^{1/2}\right]$$

where $k' = k[Z]$ is the pseudo-first order rate constant, because the concentration of the substrate is much greater than the concentration of the catalyst, so it is considered constant.

Thus a plot of Ir_m as a function of r_m is linear and from the gradient k' can be obtained.

In order to study the catalytic effect of furan on the oxidation of sodium bromide, we recorded steady state current-voltage curves on the absence of substrate, as shown in figure 1a).

Upon addition of furan the limiting current increases due to the catalytic effect, as shown in figure 1 b).

This experiment was repeated for a series of microelectrodes of different radii and the plot of Ir_m vs r_m is present in figure 2.

From the gradient of the straight line, the pseudo-first order rate constant may be obtained and the second order rate constant derived from this using the equation $k'=k[Z]$.

The data of this experiment and of others with different concentrations of furan and sodium bromide, are in the table I.

TABLE I

[NaBr]/mol dm^{-3}	/mol dm^{-3}	k'/s^{-1}	k/mol^{-1}dm^{3}s^{-1}
0.01	0.14	11	75
0.01	0.28	19	66
0.01	0.70	50	71
0.005	0.14	9	61

It was found that the average value of k is about 68 mol^{-1}dm^{3}s^{-1}

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THE REDUCTION OF FORMALDEHYDE IN CONCENTRATED SOLUTIONS USING MICROELECTRODES

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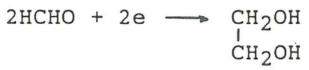
Recently, there has been a considerable interest in the hydrodimerisation of formaldehyde to ethylene glycol (1,2). This process occurs at high concentrations of formaldehyde and the cathodic reaction occurs by the mechanism

$$CH_2(OH)_2 \rightleftharpoons HCHO + H_2O$$



$$2HCHO + 2e \longrightarrow \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

where the dehydration reaction is the rate determining step.

The Electrosynthesis Company has developed a very efficient process (3) and the recommended conditions include a low methanol content formate electrolyte, pH 5-7, containing a tetraalkylammonium salt, a high formaldeyde concentration (40 %), a high temperature (80ºC) and a cathode chosen from a range of carbons.

We have carried out a study of formaldeyde reduction at microelectrodes in conditions as close as possible to the Electrosynthesis Company's process. However, since it is not possible to manufacture carbon microelectrodes with surfaces which can be demonstrated to have the properties necessary for production of ethylene glycol in good yield, most of the experiments have employed mercury microelectrodes.

i-E curves were recorded for a concentration range from 0.04 to 40% in formaldehyde and for a range of temperatures. Figure 1 shows a typical i-E curve for 40% concentration on formaldehyde at room temperature.

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