

At the mercury/electrolyte interphase, the HOTMI behaviour varies greatly with the nature and pH of the medium (4). In aqueous solution it was found that HOTMI adsorbs strongly in neutral medium on the mercury electrode in the potential interval -0,20-0,80 V since the C vs E curves show two sharp peaks, characteristic for adsorption-desorption phenomena (Fig.8).

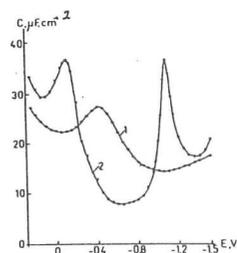


Fig.8. Differential capacity curves for Hg at sweep rate  $3 \text{ mV.s}^{-1}$  and frequency 130 Hz in  $0,2 \text{ M NaClO}_4$  (1) and  $0,01 \text{ M HOTMI}$ .

These results lead to the conclusion, that the electrooxidation of HOTMI on mercury, gold and platinum electrodes are joined with the adsorption-desorption phenomena.

IR-spectroscopy, NMR and H-MS analyses allowed the identification of the main HOTMI electrooxidation products, which in water were diacetylmonoxime and in dichloromethane: dimethylglyoxime and 2-ketoxiimino-3-oximin butanone.

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## AN ELECTROCHEMICAL APPROACH TO THE STUDY OF DYNAMIC PROCESSES AT THE INSULATOR/LIQUID INTERFACE

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### ABSTRACT

A novel flow cell is described which allows the determination of the heterogeneous kinetics of calcite dissolution to be quantified.

### INTRODUCTION

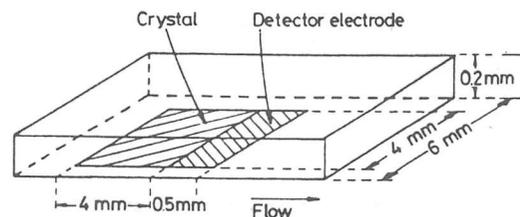
Heterogeneous reactions between a liquid phase reactant (R) and a solid (S) may be regarded as proceeding via a sequence of elementary steps involving, for example, (i) mass transport of R to the Outer Helmholtz Plane of the double layer of S, (ii) adsorption of R, (iii) surface diffusion of adsorbed R to a reaction site on the solid surface, (iv) heterogeneous reaction with the formation of adsorbed product (P), (v) desorption of P and (vi) transport of P into bulk solution. The kinetics of the process may be characterised with a heterogeneous rate law,

$$\text{flux, } j/\text{mol.cm}^{-2}\text{s}^{-1} = k_n[\text{R}]_{\text{ohp}}^n \quad (1)$$

where  $k_n$  is the nth order heterogeneous rate constant and  $[\text{R}]_{\text{ohp}}$  relates to the Outer Helmholtz Plane. In the case when S is a metal then a diverse range of electrochemical methods have been developed to characterise reactions and their kinetics within the framework given above and this has been possible since the current flowing provides a direct measure of  $j$ . However for insulators no ready analogue exists. Accordingly we have developed a novel channel flow cell method to characterise the kinetics and mechanisms of processes at the insulator/liquid interface [1-3]. In this paper we illustrate its use in the quantification of the kinetics of calcite ( $\text{CaCO}_3$ ) dissolution.

The technique uses a cell (figure 1) through which solution is pumped, under laminar flow conditions, along a rectangular duct. A block of calcite (in this application) forms part of one wall of the channel. Material consumed or released by calcite dissolution is detected

immediately downstream of the dissolving surface by an appropriate electrochemical sensor. The well defined hydrodynamic flow within the cell permits the deduction of the concentration profiles of  $\text{Ca}^{2+}$ ,  $\text{H}^+$  and other kinetically significant species within the cell using candidate rate equations as a boundary condition for the relevant mass transport equations. In this way the observed readings at the sensor and their dependence on solution flow rate is used to identify the correct rate equation and hence to provide mechanistic information.



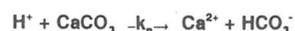
**Figure 1** Schematic flow cell strategy for calcite dissolution kinetics. Amperometric detection is depicted. The platinum detector electrode may be replaced by a flat membrane pH electrode.

**EXPERIMENTAL**

Full experimental details appear in references [1-3]. In low pH experiments solutions of HCl in 1.0M KCl flow past a calcite crystal (exposed dimensions ca. 4x4 mm) and an adjacent 0.5 mm platinum electrode is held at a potential such that all  $\text{H}^+$  reaching it is reduced. All experiments were conducted at 25°C.

**RESULTS AND DISCUSSION**

We consider first low pH experiments (pH<4) where dissolution occurs overwhelmingly as a result of reaction with  $\text{H}^+$  rather than with  $\text{H}_2\text{O}$  [4]. Detector electrode currents were measured over a wide range of flow rates ( $10^{-3}$ - $0.3 \text{ cm}^3\text{s}^{-1}$ ) and for different bulk proton concentrations in the range  $0.25 < [\text{H}^+]/\text{mM} < 1.0$ . Data was modelled using the following kinetic scheme:



where  $k_{oh}=20 \text{ s}^{-1}$  [5] and  $K=a(\text{H}^+).a(\text{HCO}_3^-)/a(\text{H}_2\text{CO}_3)=1.74 \times 10^{-4} \text{ M}$  [6] together with equation (1) with  $R=\text{H}^+$  as a heterogeneous rate law. A satisfactory fit over the entire flow rate and bulk pH range

employed was only found for first order heterogeneous kinetics with  $k_r=0.043 \text{ cm s}^{-1}$ . Previous studies of calcite dissolution, generally employing particulate material with low rates of mass transport have concluded the process to be mass transport controlled [7-9]. Our determination, using the flow cell with its fast mass transport, has thus probed the rate of the interfacial reaction of  $\text{H}^+$  with calcite for the first time.

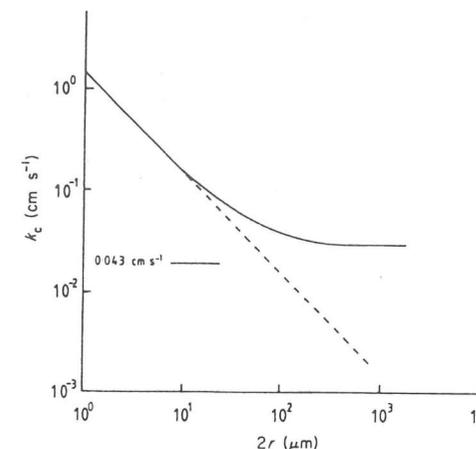
The observation of finite heterogeneous kinetics for the acid induced dissolution of calcium carbonate has serious implications for modelling lake liming strategies aimed at countering the effects of 'acid rain' [10-12]. The rate of mass transport to a falling calcite particle may be estimated from the bulk  $\text{H}^+$  concentration via a mass transport coefficient,  $k_c$ ,

$$j_{\text{H}^+}/\text{mol.cm}^{-2}\text{s}^{-1} = k_c[\text{H}^+]_{\text{bulk}} \tag{2}$$

$k_c$  depends on the slip velocity of the particle. This may be estimated [13] from the terminal velocity of a sphere falling under gravity and hence the Reynolds Number,  $Re$ , of the particle found. Established chemical engineering correlations then give

$$k_c = (D/r)(1 + 0.3Re^{1/2}Sc^{1/3}) \tag{3}$$

where  $r$  is the particle radius and  $Sc$  is the Schmidt Number. Figure 2 shows the mass transfer



**Figure 2** The calculated rate of mass transfer to falling calcite particles as a function of particle radius. Also shown (horizontal line) is the rate of the surface reaction calculated from our flow cell measurements. The dotted line is the equation  $k_c=D/r$  which is the limit of equation (3) for small particle sizes. Notice the logarithmic scales.

coefficient for calcite calculated using the following parameters:  $H^+$  diffusion coefficient =  $7.46 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , kinematic viscosity of water =  $0.01 \text{ cm}^2 \text{ s}^{-1}$ , density of calcite =  $3.0 \text{ g cm}^{-3}$ . The rate of the surface

proton reaction is shown by means of the horizontal line. It can be seen that for small particles the rates of mass transport and interfacial kinetics are approximately equal. However for the small particles ( $<100 \mu$ ) used in lake-liming it can be seen that the rate-determining step will be dissolution as opposed to mass transport as hitherto assumed [7-12].

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### ELECTROCHEMICAL OXIDATION OF BISCYCLOPENTADIENYLMOLYBDENUM COMPLEXES. EFFECT OF COORDINATED AMIDINES.

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In recent years, much attention has been paid to mechanisms of oxidation-reduction of transition metal and organometallic compounds [1]. The 17- electron species resulting from oxidation are important as catalysts or proposed intermediates in many catalytic processes [2]. They also can undergo a wide variety of reactions, including dimerization, disproportionation, reductive elimination of ligands and activation of ligands after electron transfer to the metal.

In this work we report results of the electrochemical oxidation of two types of complexes, both containing the  $\text{MoCp}_2$  moiety, with chelated  $N,N'$ -diarylacetamidinato ligands (I) and monocoordinated amidines (II)

