

The electrochemical hypochlorination of allyl chloride in dilute HCl solution

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The electrochemical hypochlorination of allyl chloride has been studied. It was found that the reaction is best effected using 1 to 1.5 N HCl as the electrolyte, introducing allyl chloride as an emulsion and working at low current density ($< 150 \text{ mA cm}^{-2}$).

1. Introduction

Alkene oxides are produced commercially by the chlorohydrin process [1]. The alkene is first reacted with chlorine in the presence of water to form chlorohydrin which is then treated with calcium hydroxide to form an alkene oxide plus calcium chloride. This method has, however, at least two disadvantages:

- (a) Molecular chlorine is used;
- (b) Calcium chloride is formed as a by-product.

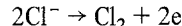
The electrochemical method of alkene oxide preparation may overcome these disadvantages; in this process a two compartment cell containing an aqueous solution of dilute NaCl (5%) is used. The alkene is introduced into the anodic compartment during electrolysis and is transformed to chlorohydrin. The later trickles into the cathode compartment where it is saponified to alkene oxide by a cathodically generated base. This method has been described essentially for the production of ethylene and propylene oxides and gives high current efficiencies [2, 3].

It has been found [4] that when the electrochemical method is used for the production of epichlorohydrin, this compound is obtained only with a low current efficiency (50-60%). This is due to the slow rate of addition of hypochlorous acid to allyl chloride (reaction time 15-30 min) in NaCl solution (pH = 3-6) which leads to the formation of by-products.

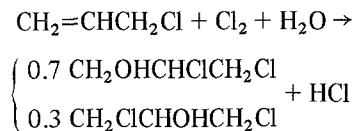
It has been found that in acidic solution (pH = 0-1) the addition of hypochlorous acid to allyl chloride is a fast reaction and can be coupled to the electrogeneration of chlorine.

A procedure for the electrochemical hypochlorination of allyl chloride in dilute HCl solution, using an undivided cell, is described. In this system allyl chloride is introduced into the cell where it reacts with chlorine formed at the anode; hydrogen is evolved at the cathode.

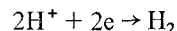
Anode reaction



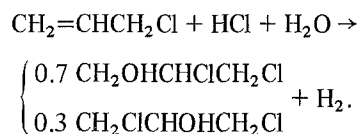
Chemical reaction



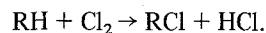
Cathode reaction



Total reaction



The process has a particular interest if HCl is available as a by-product formed from the chlorination of organic compounds



This process has been studied in dilute HCl solution ($< 1.5 \text{ N}$) and using DSA (CWC 2112 III Conradty, Nurnberg) anodes.

2. Experimental procedure

2.1. Chemicals

The chemicals used in this work were hydrochloric acid G.R. ($d = 1.14$), allyl chloride (purum), sodium hypochlorite (14%) and polyoxyethylene sorbitan monolaurate (Atlas-Tween 20 SD, HLB = 16.7, from ICI) which is a non-ionic emulsifier.

2.2. Kinetic measurements

The reaction of chlorine water with allyl chloride in acidic solution is a fast reaction. For this reason the kinetics were studied by continuous potentiometric determination of unreacted chlorine using platinum as the indicator electrode and Ag/AgCl (sat. KCl) as the reference electrode. A 150 cm³ batch reactor thermostated at 20° C and stirred by a magnetic bar was used.

2.3. Preparation of emulsions

The emulsion of allyl chloride in water was prepared using a laboratory dispersion mixer

(ILADO $\times 10/20$). Thus, water (70 vol %), allyl chloride (30 vol %) and emulsifier (0.8 vol %) are mixed for 1–2 min. The emulsion thus obtained is stable for several hours and allyl chloride is dispersed as 2–5 μm particles.

Dilution of the emulsion with HCl solution does not modify its stability.

2.4. The electrolytic cell

The electrolytic cell was made of PVC and contains two groups of electrodes, each group consists of five parallel electrodes (each with a surface area of 96 cm²), three dimensionally stable anodes (DSA) and two cathodes (stainless steel). The distance between the electrodes is 0.8 cm and the electrolyte velocity is 3.8 cm s⁻¹.

A schematic diagram of the electrolyte flow circuit and the electrical assembly of the two groups of electrodes is shown in Fig. 1. The total volume of the system is 2.6 dm³ and it can work as a batch or a continuous reactor.

Allyl chloride is introduced into the cell in excess; a fraction of it (about 60%) reacts with chlorine and the remainder escapes with the hydrogen evolved at the cathode. Three procedures

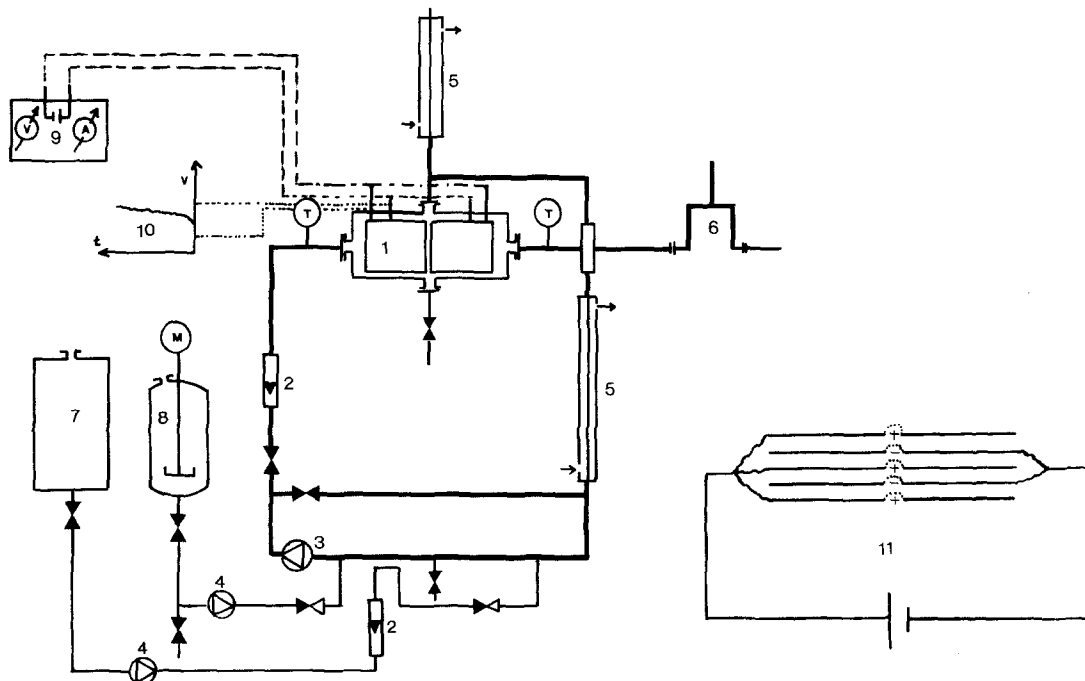


Fig. 1. A schematic diagram of the electrolyte flow circuit: 1. electrolytic cell; 2. flow meter; 3. circulation pump; 4. metering pump; 5. heat exchanger; 6. siphon; 7. HCl tank; 8. Allyl chloride tank; 9. current source (10 V, 400 A); 10. measure and recording the cell potential; 11. electrical assembly of the two electrode groups.

were used depending on the mode of introduction of the allyl chloride. Procedure A: Liquid allyl chloride is introduced into the cell in small fractions during the electrolysis. Procedure B: An emulsion of allyl chloride in water is introduced into the cell at the beginning of the electrolysis. Procedure C: The emulsion of allyl chloride in water is introduced into the cell during the electrolysis in small fractions.

2.5. Analysis

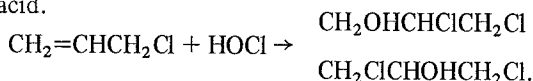
Allyl chloride was determined by potentiometric titration in acidic solution ($\text{pH} \leq 0$) with NaOCl. The reaction products are extracted with ether and analysed by gas chromatography.

3. Results

3.1. Study of the chemical reaction

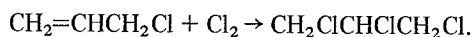
The selectivity and kinetics of addition of hypochlorous acid to allyl chloride has been studied to determine the conditions under which this reaction is fast (reaction occurs in a few seconds) and when it can be coupled to the electrogeneration of chlorine.

3.1.1. Selectivity of the reaction. Allyl chloride is converted to a mixture of two isomers of glycerol dichlorohydrin by the addition of hypochlorous acid.



The isomer 2,3-dichloro-1-propanol constitutes 65–70% of the total chlorohydrin product, while the remainder is the 1,3-dichloro-2-propanol isomer (30–35%).

The main side reaction in this process is the addition of chlorine to the double bond of allyl chloride to form 1,2,3-trichloropropane.

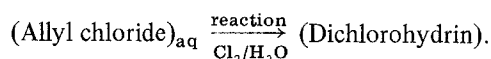
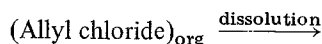


Another secondary reaction is the oxidation of dichlorohydrins to form either chlorinated aldehydes or ketones.

It has been found that the temperature (20–60°C) does not influence the selectivity of the reaction. This selectivity is mainly determined by the concentration of the chloride ion in the

medium; high chloride concentration (i.e. HCl concentration) favours the formation of trichloropropane. If the reaction is carried out in dilute HCl ($< 1.4 \text{ N}$), high selectivity can be obtained ($> 90\%$).

3.1.2. Kinetics of the reaction. Allyl chloride is slightly soluble in water (0.06 M at 20°C) and as its reaction with chlorine is carried out in the aqueous phase, allyl chloride must be dissolving in the water before its reaction with the chlorine.



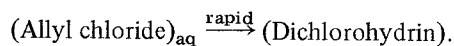
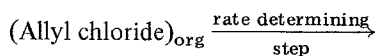
Thus the rate of dissolution of allyl chloride and the rate of its chemical reaction with chlorine water have been studied separately under different operating conditions.

(a) Chemical reaction of allyl chloride with chlorine

To study this reaction a solution of allyl chloride in HCl solution was prepared and a stoichiometric amount of NaOCl was added to this solution. The degree of conversion as a function of time was calculated from the potentiometric curve. The order and the rate constant were evaluated under different operating conditions. In the pH range studied (0–4), it was found that the reaction is first order with respect to hypochlorous acid, and its activation energy is 50.24 kJ mol⁻¹ (12 kcal mol⁻¹). The chloride concentration (0–1.4 M) has little influence on the rate of the reaction but the pH of the solution (or the concentration of HCl) influences the rate of reaction very strongly as shown in Fig. 2.

(b) Dissolution of allyl chloride in the aqueous phase

The dissolution rate of allyl chloride has been studied in acidic solution (1.4 N HCl). Under these conditions the chemical reaction of allyl chloride with hypochlorous acid is fast and the dissolution of allyl chloride is the rate determining step.



To study the dissolution rate a stoichiometric amount of allyl chloride was introduced into a

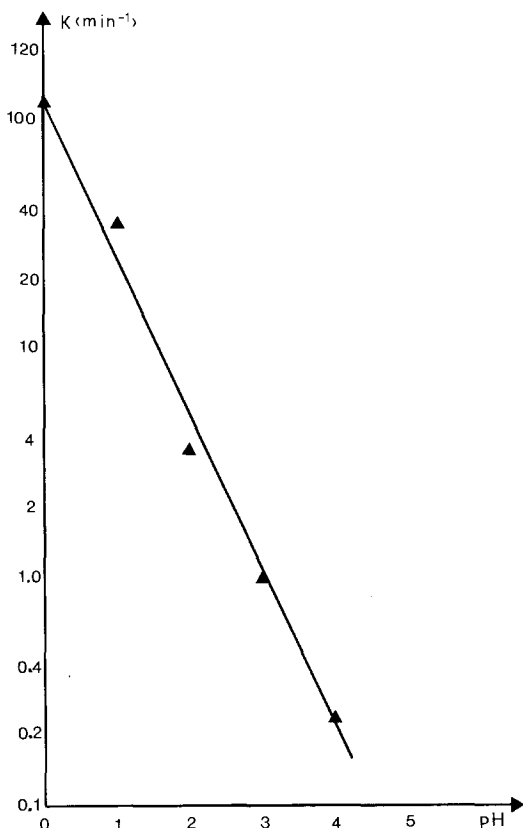


Fig. 2. Influence of pH on the reaction rate constant for the hypochlorination of allyl chloride, $T = 20^\circ \text{C}$.

solution of hypochlorous acid (0.028 M) dissolved in 1.4 N HCl. The dissolution rate was calculated from the potentiometric curve.

It was found that the dissolution rate increased with stirring and with emulsifier concentration, but it remains low still ($2.5\text{--}7.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$).

Table 1. Dissolution rate of allyl chloride in the aqueous phase at different operating conditions, $T = 20^\circ \text{C}$

Conditions	Dissolution rate ($\text{mole dm}^{-3} \text{ s}^{-1}$)	Relative dissolution rate
Moderate stirring	2.5×10^{-4}	1.0
Vigorous stirring	3.8×10^{-4}	1.5
Moderate stirring in the presence of emulsifier ($0.8\text{--}1 \text{ g dm}^{-3}$)	7.2×10^{-4}	2.9
Moderate stirring using an emulsion	4.5×10^{-2}	180.0

To increase the dissolution rate, allyl chloride was introduced into the hypochlorous acid solution in the form of emulsion in water; Table 1 shows the dissolution rate obtained under different conditions. A remarkable increase in dissolution rate is obtained using an emulsion of allyl chloride.

3.2. Electrochemical preparation of dichlorohydrin

To find the optimal conditions for the electrochemical hypochlorination of allyl chloride, some preparative electrolyses have been effected under different operating conditions. The current efficiencies of dichlorohydrin and trichloropropane formation have been determined.

3.2.1. Characterization of the electrochemical reactor. Depending on the recycling ratio, R , the reactor can operate as a batch reactor, as a plug flow reactor ($R = 1$), as mixed reactor ($R = \infty$) or in a mode between plug flow and a mixed reactor ($0 < R < \infty$).

In this work the reactor has been used as a batch cell and as a mixed reactor ($R = 127$).

The relationship between the cell potential, E , and the current density (kA m^{-2}) using 1.5 N HCl as the electrolyte is

$$E = 1.65 + 0.5538i.$$

3.2.2. Influence of the current concentration. The maximum current concentration (current/unit volume) in the cell can be obtained by equalizing the rate of chlorine formation at the anode with the rate of its consumption by chemical reaction with allyl chloride

$$\frac{I}{ZF} = V \frac{dC}{dt}$$

or

$$\frac{I}{V} = ZF \frac{dC}{dt}$$

where (dC/dt) is the rate of change of chlorine throughout the reaction with allyl chloride, I is the current and V is the volume of the system (2.6 dm^3).

Working above this current concentration level leads to accumulation of chlorine in the elec-

Table 2. Maximum current and current concentration at different operating conditions, $T = 20^\circ \text{C}$. $V =$ volume of the system (2.6 dm^3). $Z = \text{eq mol}^{-1}$ [2]

Conditions	Dissolution rate (r_D) ($\text{mol dm}^{-3} \text{ s}^{-1}$)	Maximum current (A) $I_{\text{max}} = ZFVr_D$	Maximum current concentration, I_{max}/V
Moderate stirring	2.5×10^{-4}	125.4	48
Vigorous stirring	3.8×10^{-4}	190.7	73
Moderate stirring in the presence of emulsifier ($0.8\text{--}1.0 \text{ g dm}^{-3}$)	7.2×10^{-4}	361.3	139
Moderate stirring using an emulsion	4.5×10^{-2}	22 581.0	8685

trolyte and loss of current efficiency and selectivity of the reaction.

In acidic solution the rate of hypochlorination of allyl chloride is limited by its dissolution in the electrolyte. This dissolution rate and the maximum current concentration in the cell under different conditions is shown in Table 2.

A remarkable increase in the maximum current concentration is obtained using an emulsion of allyl chloride.

3.2.3. Electrolysis in a batch reactor using Procedure A.

(a) Influence of HCl concentration

The current efficiencies of dichlorohydrin and

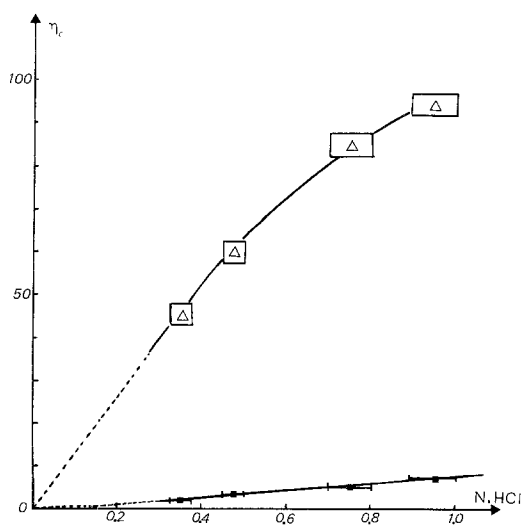


Fig. 3. Variation in current efficiencies of: (Δ) dichlorohydrin (1,3- and 2,3-) and (\blacksquare) trichloropropane (1,2,3-) with HCl concentration using Procedure A. $D = 67 \text{ mA cm}^{-2}$ and $T = 20^\circ \text{C}$.

trichloropropane formation as functions of the HCl concentration at constant current density (67 mA cm^{-2}) and temperature (20°C) are shown in Fig. 3.

At low HCl concentration the current efficiency of dichlorohydrin formation decreases; the decrease is especially rapid below 0.6 N HCl .

3.2.4. Electrolysis in a batch reactor using Procedure B.

(a) Influence of the amount of electricity passed

The current efficiencies for dichlorohydrin and trichloropropane formation as functions of the charge passed (A h) are shown in Fig. 4 for two current densities (39 and 78 mA cm^{-2}).

The current efficiency for dichlorohydrin formation initially increases with the charge passed and then reaches a constant value; the current efficiency of trichloropropane decreases with the charge passed.

(b) Influence of current density

The influence of current density on the current efficiencies for dichlorohydrin and trichloropropane formation is shown in Fig. 5. Increasing the current density results in a considerable decrease in the current efficiency of dichlorohydrin formation.

3.2.5. Continuous electrolysis using Procedure C.

(a) Influence of time

A continuous electrolysis was carried out at constant current density (130 mA cm^{-2}) and HCl concentration (1 N) for 4 h under steady-state conditions to determine the influence of time on the

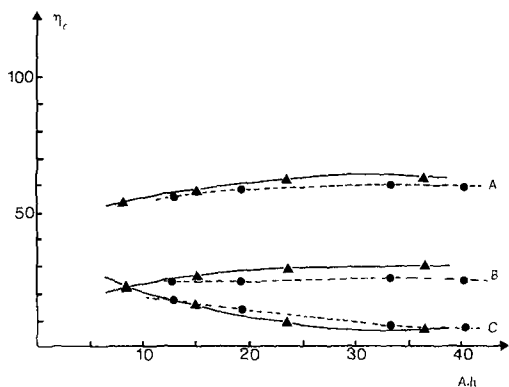


Fig. 4. Variation of current efficiencies of (A) 2,3-dichloro-1-propanol, (B) 1,3-dichloro-2-propanol and (C) 1,2,3-trichloropropane with the charge passed using Procedure B. Average HCl concentration was 1.35 N and $T = 20^\circ \text{C}$. Continuous line: $D = 39 \text{ mA cm}^{-2}$. Dotted line: $D = 78 \text{ mA cm}^{-2}$.

current efficiency of chlorohydrin formation and on the activity of the electrode.

The results obtained show that:

(i) The current efficiency of chlorohydrin formation is not influenced by time, thus an average value of 76% was obtained which is about the same as that obtained in the batch reaction.

(ii) The cell potential remains constant for about 1 h but thereafter it increases with time. This increase in potential is due to the formation of an organic film on the electrode. Fig. 6 shows photomicrographs of the electrode before and after electrolysis.

(iii) The electrode is restored to its initial activity after washing with acetone, due to the dissolution of the organic film.

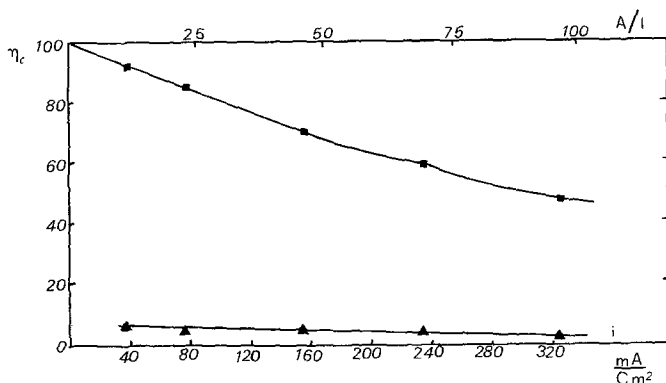
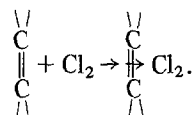


Fig. 5. Variation of current efficiencies of (■) dichlorohydrin (1,3- and 2,3-) and (▲) trichloropropane (1,2,3-) with current density using Procedure B. Average HCl concentration was 1.2 N and $T = 20^\circ \text{C}$.

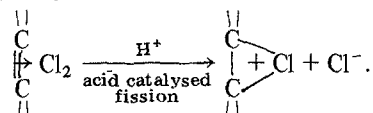
4. Discussion

4.1. Chemical reaction in homogeneous solution

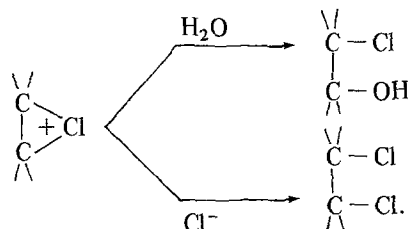
If the hypochlorination of allyl chloride is carried out in homogeneous solution, the rate of the reaction is determined by chemical kinetics alone. In this case the formation of a complex between chlorine and allyl chloride is assumed to be the first step:



Subsequently the acid catalysed fission of the Cl-Cl bond takes place with the formation of an halonium ion:



Water or a chloride ion reacts with the halonium ion with the formation of chlorohydrin or trichloropropane



In dilute HCl solution ($< 1.5 \text{ N}$) the chlorohydrin is the main reaction product.

This model is supported by the following experimental facts: (a) hypochlorination of allyl

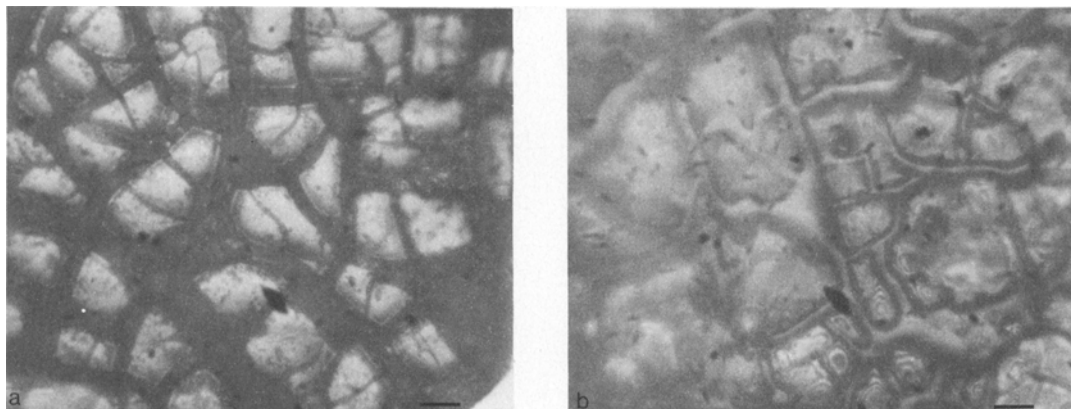


Fig. 6. Photomicrographs of DSA (a) before and (b) after electrolyses. Scale bars: 0.01 mm.

chloride occurs in a pH region (< 4) where Cl_2 is present in solution; (b) the reaction is catalysed by acid and is shown in Fig. 2; (c) the chlorohydrin is formed in a high yield if dilute HCl solution is used.

4.2. Dissolution of allyl chloride

As allyl chloride is slightly soluble in water, it must be dissolved in the aqueous phase before its reaction with chlorine. The dissolution of allyl chloride depends on the mode of dispersion of the two phases. Emulsification greatly increases the surface area of the dispersed phase (allyl chloride). Thus 1 cm^3 of allyl chloride emulsified in the aqueous phase has a total interfacial area of about 1 m^2 compared with 0.006 m^2 in non-emulsified solution.

This large increase of contact area accelerates the dissolution rate of allyl chloride as shown in Table 1.

4.3. Electrochemical preparation of dichlorohydrin

4.3.1. Mode of introduction of allyl chloride. Allyl chloride can be introduced into the reactor as a liquid (Procedure A) or as emulsion in water (Procedures B and C). In the first case the current concentration is the limiting factor of the process (maximum current concentration = 48 A dm^{-3}) and in the second case high current concentration can be achieved (8685 A dm^{-3}) and the current density becomes the limiting factor.

4.3.2. Influence of HCl concentration and current density. The HCl concentration must lie below 1.5 N since above this value a considerable amount of trichloropropane is formed. The decrease in current efficiency for dichlorohydrin formation with decreasing HCl concentration (Fig. 3) is due to simultaneous oxygen evolution, the sum of the current efficiencies for dichlorohydrin and trichloropropane formation is 100% at about 1 N HCl using a current density of 67 mA cm^{-2} . We can conclude that the limiting current for chlorine formation is 67 mA cm^{-2} in 1 N HCl.

Working at current densities above this limiting current decreases the current efficiency of chlorine formation (which is equal to the sum of dichlorohydrin and trichloropropane) due to simultaneous oxygen evolution.

4.3.3. Influence of time. The increase of potential with time is due to the formation of an organic film (dimers or polymers) at the electrode surface which decreases the effective electrode area and increases the resistance of the cell.

5. Conclusions

The electrochemical hypochlorination of allyl chloride must be effected under the following conditions: (a) using dilute HCl solution as electrolyte ($1\text{--}1.5 \text{ N}$); (b) introducing allyl chloride as an emulsion in water; (c) working at low current density ($< 150 \text{ mA cm}^{-2}$). The main problem in this process is the poisoning of the DSA electrodes due to the formation of an organic film at the electrode.

Acknowledgement

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