

SHORT COMMUNICATION

Electrochemical chlorination of butadiene using $CeCl_3$ -MeCN anolyte

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1. Introduction

Trans-1,4-dichloro-2-butene (trans-1,4-DCB) and 3,4-dichloro-1-butene(3,4-DCB) are important industrial materials for the synthesis of chloroprene ($ClCH=CHCH=CH_2$), which is usually produced from butadiene and chlorine by chemical reaction at about $300^\circ C$. We have proposed that such dichlorobutenes (DCBs) can also be synthesized by electrolysis at high current efficiencies [1, 2]. The main advantages of the electrochemical process are: (a) it does not require the use of expensive and toxic chlorine, (b) the chlorination of butadiene is performed at room temperature. Although studies on the electrolytic chlorination of alkenes have been carried out by many investigators [3–5], those of butadiene have scarcely been reported [6]. In the previous papers [1, 2, 7] $CoCl_2$ was used as the solute of the anolyte because the standard electrode potential of cobalt is high; however, the solute sometimes formed a solid complex with butadiene and water when water entered into the anolyte. With the aim of solving this problem, $CeCl_3$ was examined because its standard electrode potential is adequately high. This investigation has been carried out to examine whether $CeCl_3$ is suitable for the electrochemical chlorination of butadiene as a solute of the anolyte.

2. Experimental details

The potential-current curves for the anodic behaviour of butadiene were measured by use of a conventional beaker-type cell (cell 1), in which the anode and the cathode were a graphite rod (0.5 cm^2) and a platinum plate ($2 \times 3\text{ cm}$), respectively. Potentiostatic electrolyses were

performed by use of two different cells having an anion-exchange membrane separator (Asahi Glass Co., 'Selemion-ASV' made of polystyrene). Graphite plates ($3\text{ cm } \phi$) were used for either the anode and the cathode of cell 2, while a graphite plate cathode ($3.5 \times 3.5\text{ cm}$) and granular graphite anode (particle diameter $\sim 3\text{ mm}$) were used for cell 3 (Fig. 1). Highly purified butadiene was bubbled into the the anolyte (MeCN containing $2.6 \times 10^{-3}\text{ mol dm}^{-3}$ $CeCl_3$ at $25^\circ C$) during electrolyses in order to keep the concentration of butadiene in the anolyte at a constant value ($\sim 2\text{ mol dm}^{-3}$). The catholyte was an aqueous solution of NH_4Cl . Butadiene and its derivatives were determined by gas chromatography (TCD, Silicone Gum SE-30 chromosorb WAW; He).

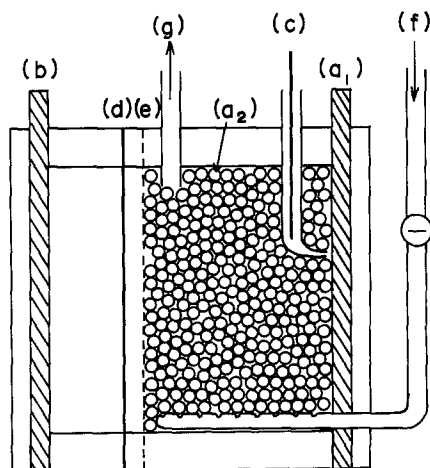


Fig. 1. Schematic diagram of the packed electrode cell, cell 3. a_1 and a_2 , anode (a_1 , graphite plate; a_2 , granular graphite with $\sim 3\text{ mm}$ in diameter); b , cathode (graphite plate); c , reference electrode (Ag/AgCl); d , anion-exchange membrane; e , separator (glass-wool paper); f , C_4H_6 inlet; g , C_4H_6 outlet.

3. Results and discussion

The solubility of CeCl_3 in MeCN (measured by the Volhard method) and the electrolytic conductivity of the saturated solution at 25°C were $2.6 \times 10^{-3} \text{ mol dm}^{-3}$ and $6.3 \times 10^{-6} \text{ S cm}^{-1}$, respectively. Fig. 2 shows the quasi-potentiostatic i - V curves of CeCl_3 -MeCN with or without C_4H_6 on the carbon rod anode using cell 1. The anodic current of curve (a) is due to the oxidation of chloride ions. By the introduction of C_4H_6 into the electrolyte the current density increased in the region below $\sim 0.8 \text{ V}$ versus Ag/AgCl (the electrode potential of Ag/AgCl was 0.222 V versus NHE in aqueous electrolyte). This must be due to the reaction of C_4H_6 with the anodically formed chlorine radical on or near the anode and the subsequent removal of the products to the bulk of the electrolyte, promoting the anodic formation of the chlorine radical [2]. On the other hand, the current density of curve (b) is weaker than that of curve (a), between 0.8 V and 1.3 V , suggesting that the adsorption of C_4H_6 or its intermediates occurred.

Next, potentiostatic electrolyses were performed as a function of the electrode potential using cell 2 and the results are shown in Fig. 3. The current efficiency for each dichlorobutene, 3,4-DCB and trans-1,4-DCB, was defined as the percentage of the quantity of electricity that passed through the cell, and was calculated by assuming that the chlorination was a two-electron reaction. The influence of the electrode potential on the current efficiencies were not so large. The ratio of the 3,4-DCB to trans-1,4-DCB formed was about 1.1–1.5, analogous to the case in which CoCl_2 -MeCN anolyte was used, while the current efficiencies were somewhat lower than those of the CoCl_2 -MeCN system [1, 2]. It is notable that the dichlorobutenes were produced at high current efficiencies even at low electrode potential (e.g. 1.2 V). Since butadiene seems not to be oxidized at 1.2 V versus Ag/AgCl [2], the DCBs can be formed without the oxidation of butadiene. However, the bubbling of the mixed gas of chlorine and butadiene into the solution without electrolysis did not form any appreciable amount of DCB. Therefore, the anodically formed chlorine

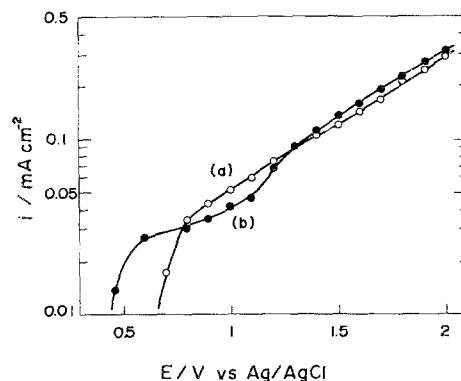


Fig. 2. Anodic current-potential curves obtained quasi-potentiostatically at a graphite rod electrode in CeCl_3 -MeCN solution with or without C_4H_6 using cell 1. [CeCl_3], $2.6 \times 10^{-3} \text{ mol dm}^{-3}$; [C_4H_6], 2 mol dm^{-3} ; temperature, 25°C ; \circ , CeCl_3 -MeCN; \bullet , CeCl_3 -MeCN- C_4H_6 .

radical seems to react with butadiene to form DCBs. The disadvantage of the electrolysis is that a high cell voltage is needed due to the low electrolytic conductivity of the CeCl_3 -MeCN solution. In order to reduce the cell voltage the packed electrode cell, cell 3, was adopted for the electrolysis. Table 1 presents the current efficiencies for the formation of DCBs. As shown in this table, the cell voltage was substantially reduced by use of the granular graphite anode. The quantity of electricity passed in these runs (200 C) was that required to convert $\sim 2\%$ of butadiene initially dissolved in the anolyte into DCBs. The current efficiencies were

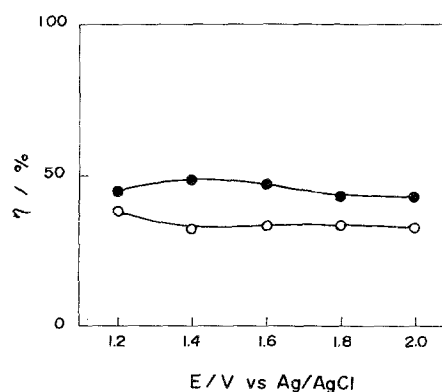


Fig. 3. Effect of anode potential on the current efficiency for the formation of dichlorobutenes using cell 2. Anode and cathode, graphite plate; anolyte, CeCl_3 -MeCN ([CeCl_3], $2.6 \times 10^{-3} \text{ mol dm}^{-3}$; [C_4H_6], 2 mol dm^{-3}); catholyte, NH_4Cl - H_2O ([NH_4Cl], 1.0 mol dm^{-3}); temperature, 25°C ; quantity of electricity passed, 200 C; \circ , 3,4-DCB; \bullet , trans-1,4-DCB.

Table 1. Electrolytic conditions and current efficiencies for the formation of dichlorobutenes by using cell 3

Anode	Current density (mA cm ⁻²)	Cell voltage (V)	Current efficiency (%)		
			3,4-DCB	Trans-1,4-DCB	Total
Graphite plate without granular graphite particles	3.3	46	35	39	74
Graphite plate with granular graphite particles	3.3	3.7	36	42	78
	42	6.5	38	41	79

Cathode, graphite plate; anolyte, CeCl₃-MeCN ([CeCl₃], 2.6×10^{-3} mol dm⁻³, 0.026 dm³; [C₄H₆], 2 mol dm⁻³); catholyte, NH₄Cl-H₂O ([NH₄Cl], 1.0 mol dm⁻³); electrode potential, 1.6 V versus Ag/AgCl; temperature: 25°C; quantity of electricity passed, 200 C.

sustained at similar levels after prolonged electrolysis using cell 3, e.g. for 2000 C. The addition of a small amount of water to the anolyte (1 vol %) reduced the total current efficiency to 65% when cell 3 was used. Although the electrolytic conductivity of this anolyte is low, cerium ions do not form a solid complex with butadiene and water. Therefore, this anolyte is a possible candidate for the electrolytic chlorination of butadiene, especially if the cell voltage can be reduced further.

References

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