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Galvanostatic electrochemical reduction of pentoses

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Electrochemical reduction of ribose and xylose has been studied in sodium sulphate solution and in phosphate buffers on amalgamated lead cathodes under conditions of galvanostatic electrolysis. The products after peracetylation were determined by gas chromatography. Over the catholyte pH range 8–11 high yields of the pentitols were obtained (84 and 75% for ribose and xylose, respectively). Regardless of the pH, 2-deoxypentitols were also formed in low yields (a few percent). Raising the temperature of the reaction to 45° C intensified the reduction 2 to 3 fold and, with xylose, the yield of xylitol was markedly increased. Large differences were observed between pH readings in the bulk solution and at the cathode. In unbuffered solutions these differences enhanced the rate of reduction of the pentoses autocatalytically.

1. Introduction

Pentoses, like other aldoses, can be reduced to polyhydric alcohols which play an important role in metabolic processes in animals and, with the advances in biochemistry, have attractive worldwide interest [1, 2].

Some of the pentoses are either constituents of bioactive substances [3] or intermediates in glucose metabolism and can be recommended for dietary nutrition as substances inhibiting the growth of microorganisms and enhancing immunity against microbial attack [4–6].

In the laboratory pentoses are usually reduced with complex metal hydrides, while on the industrial scale alditols are currently produced by high pressure catalytic reduction of aldoses over Raney nickel [7].

Electrochemical reduction can provide a competitive method to the high pressure catalytic process. The literature, mostly concerning electrochemical reduction of glucose [8, 9], shows that the process is rather complex since, owing to epimerization, reduction products of the isomers can arise and the cathode-induced splitting of the hydroxyl groups can yield deoxyaldoses and deoxyalditols. In one paper, a hydrodimerisation product was detected arising from the reductive coupling of two aldehyde groups [10].

Both the cathode process and the direction of the reactions can be affected by a number of factors associated with the electrode material, current regime, temperature and composition of the catholyte, primarily by its H^+ ion concentration. The solution acidity is of particular importance here, not only owing to the involvement of the H^+ ions in the cathode process, but also owing to the catalytic effect of both hydrogen and hydroxyl ions on the rate of mutarotation of sugars [11, 12], that after Hudson [13], can be described by the following equation:

$$k_1 + k_2 = A + B[H^+] + C[OH^-]$$

where A, B and C are constants, which for glucose at 20° C are 0.06, 0.18 and 16.00, respectively. According to this equation the mutarotation of glucose for example occurs at its slowest rate at pH 4.6.

Polarographic studies of aldoses [14–16] have shown that only the chain structure, constituting a negligible concentration of the sugar in solution, is active and undergoes reduction at the dropping mercury electrode. According to literature evidence [11], the contributions of aldoses, which can undergo reduction in aqueous solutions at pH 7, expressed as molar percentage of the total sugar concentration are for glucose, mannose, xylose, arabinose, lyxose and ribose 0.024, 0.04, 0.17, 0.28, 0.40 and 8.5, respectively. From the results of studies on electrochemical reduction of monosacharides, mostly glucose, carried out by Creighton [17–19], Brown [20], Hales [21], Wolfram [10, 22] and others the following conclusions can be drawn: (i) reduction of these compounds requires cathode materials of high hydrogen overpotential; (ii) the process should be conducted in a diaphragm-separated electrolysis cell; (iii) raising the temperature over an appropriate range enhances the yield of the process. However, too high a temperature reduces the yield due to the formation of greater amounts of side products.

2. Experimental details

Experiments were carried out galvanostatically in a flow-through diaphragm cell with a vertical system of electrodes, equipped with a magnetic stirrer and thermometer. The cell was made of Plexiglass and the diaphragm was of sintered Al_2O_3. The electrolysis conducted at pH 10–11 did not require circulation of the catholyte. At lower pH values, the solution was circulated by means of a peristaltic pump, placed between the buffering cell, in which the pH was controlled by means of H_2SO_4, and the cathode compartment. The buffering cell with the stirrer and universal silver chloride electrode, connected with a precision pH meter (OP-205, Radeliks, Hungary), was immersed

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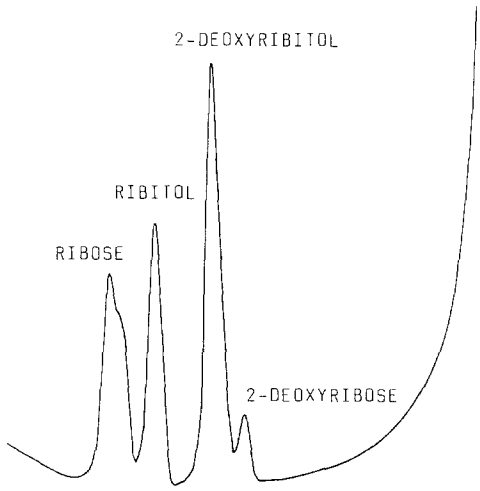

Fig. 1. Chromatogram of standards of the acetyl derivatives of ribose, ribitol, 2-deoxyribose and 2-deoxyribitol.

in a water bath thermostatted with an ultrathermostat. The pH of the solution was also monitored in the cathode compartment of the electrolysis cell. The cell was fed through a stabilised power supply type 5372, Unitra-Cemi, Szczytno).

At this stage of investigation the reduction products were directly determined from catholyte solution by gas chromatography in a packed column after acetylation of the products and of the non-reduced aldoses. Thus, a 0.1 ml sample of the catholyte was pipetted from the cathode compartment into a glass ampoule and evaporated to dryness under nitrogen. To the residue, 6 mg of anhydrous sodium acetate and 0.6 ml of acetic anhydride were added, the ampoule was sealed and maintained at 100° C for 1 h. This sample was then analysed by gas chromatography. The instrument used was a PYE UNICAM Model 104 chromatograph equipped with a flame ionization detector (FID). Argon was used as a carrier gas with a linear flow rate of 60 cm min^{-1}.

The analysis of the electroreduction products of ribose could be carried out with high accuracy by using a Silar 10 C chromatographic phase where differences in the retention times of acetylated ribitol, 2-deoxyribitol and ribose isomers were sufficiently large (Fig. 1).

With xylose, however, only xylitol and the sum of xylose and the deoxy-compounds could be determined because the retention time of one of the acetylated xylose isomers overlapped that of the 2-deoxyxylitol derivative on the OV 225 phase used for analytical purposes.

The results of chromatographic analysis of the product of electroreduction of ribose have been interpreted as follows. First, the peak surface areas corresponding to the reaction products and to the nonreduced ribose were measured. The location of these peaks was established on the basis of a chromatogram run with standard substances. Then the molar percentage of particular compounds was calculated using correction factors [23, 24]. The molar percentage of ribitol was

$$f_p = \frac{100 A_p \operatorname{ctg} \alpha_p}{A_p \operatorname{ctg} \alpha_p + A_b \operatorname{ctg} \alpha_b + A_s \operatorname{ctg} \alpha_s}$$

where f is the molar contribution of ribitol (in %), $A_{p,b,s}$ is the peak area of ribitol, 2-deoxyribitol and ribose, respectively, and ctg $\alpha_{p,b,s}$ is the absolute correction factor for ribitol, 2-deoxyribitol and ribose, respectively. Percentages of the remaining compounds were calculated in the same manner.

The absolute molar correction factors, ctg α, were derived from the chromatographic analysis of a solution comprising equimolar quantities of the analysed compounds (FLUKA A9) after converting them to the acetyl derivatives. The alditol and 2-deoxyalditol standards were also prepared by reducing the pentoses (FLUKA A9) with sodium borohydride (SERVA Feinbiochemika, Heidelberg).

3. Discussion

The results of electrochemical reduction of ribose and xylose are presented in the form of a relationship between the material yield and the quantity of electricity passing through the system. Selection of the material yield, η, as the principal indicator of the process, in place of the commonly used current efficiency, facilitated the determination of conditions under which maximum reduction of the reactant present in the catholyte was attained. Again, replacing the time parameter by the quantity of electricity, Q, expressed as the percentage of the theoretical value $Q_t = 2Fm$ (that corresponding to complete reduction of the mass of reactant m [mol] present in catholyte) enabled comparison of the effectivity of electrolysis conducted at various current densities.

The effect of temperature was studied in an alkaline Na_2SO_4 solution at pH 11 as the most stable value under conditions of the experiments. The effect of pH was investigated both in the Na_2SO_4 solution and in phosphate buffer solutions. The concentration of the reactant was 0.2 or 0.02 M.

The course of reduction of ribose at a current density of 4 A dm^{-2} at 2, 22 and 45° C is shown in Fig. 2. At 22 and 45° C, the maximum material yield of ribitol (80 and 84%, respectively) was obtained during the electrolysis corresponding to $Q \simeq 300\%$. At $Q = 200\%$ the respective yields were 70 and 81%.

At 2° C there was distinct drop in the rate of formation of ribitol. Also the shape of the curve was changed. The yield of ribitol formation did not attain the aforementioned yields even during the time corresponding to double the Q value. In all cases the formation of 2-deoxyribitol was also observed, reaching a few percent.

Figure 3 shows that the current density at which the maximum yield is obtained depends not only on the concentration of reactant, but also on the temperature. There is a relationship between optimum values of these parameters. Consequently, raising the temperature intensifies the process and reduces its

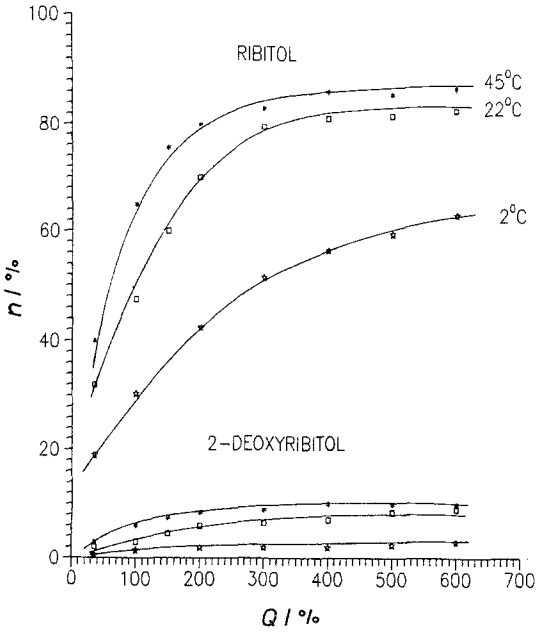

Fig. 2. Yield, η, of ribitol and 2-deoxyribitol against the quantity of electricity, Q, at 2, 22 and 45° C. Current density 4 A dm^{-2}; concentration of ribose 0.2 M; pH 11.

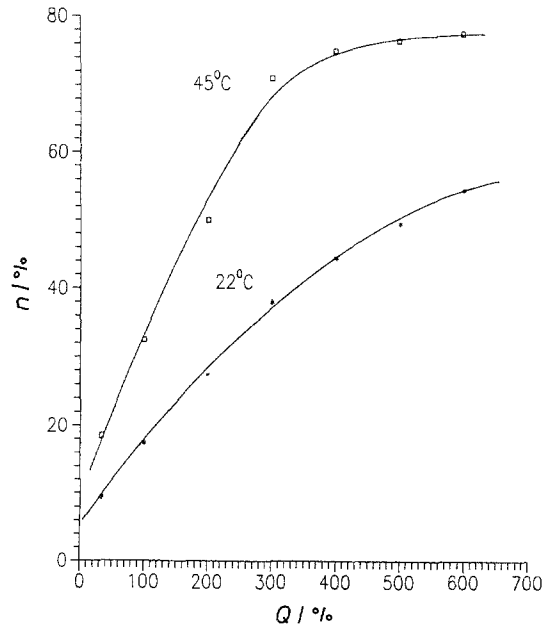

Fig. 4. Yield, η, of xylitol against the quantity of electricity, Q, at a current density of 4 A dm^{-2} at 22 and 45° C. Concentration of xylose 0.2 M; pH 11.

duration. At 45° C the maximum yield of ribitol is obtained at a 2–3 times higher current density.

Raising the temperature from 22 to 45° C considerably affects the yield of electrochemical reduction of xylose (Figs 4 and 5), as compared to ribose. This is obviously due to the much lower concentration of the electrochemically active acyclic form of that monosacharide in solution. Attaining the maximum yield of xylitol ($\simeq$ 75%) at two current densities (4 A dm^{-2}, Fig. 4 and 2 A dm^{-2}, Fig. 5) is possible only at elevated temperature.

As mentioned above, the effect of pH on the electrochemical reduction of pentoses is due to the catalytic influence of the H^+ and OH^- ions on the mutarotation of the reactant in the catholyte during the electrolysis, as well as to the mechanism of the electrode process and the possibility of simultaneous evolution of hydrogen or deposition of the alkali metal on the cathode. Obviously, the pH measured in the cathode compartment is lower than that in the neighbourhood of the cathode during electrolysis, i.e. within the zone of electrode reaction. This difference depends on the current density and conditions of the mass exchange within this zone.

A comparison of the effect of pH on the reduction of ribose in experiments conducted in the sodium sulphate solution and in the phosphate buffers of various buffer capacities (0.66, 0.33 and 0.16 mol PO_4^{3-} dm^{-3}) over a

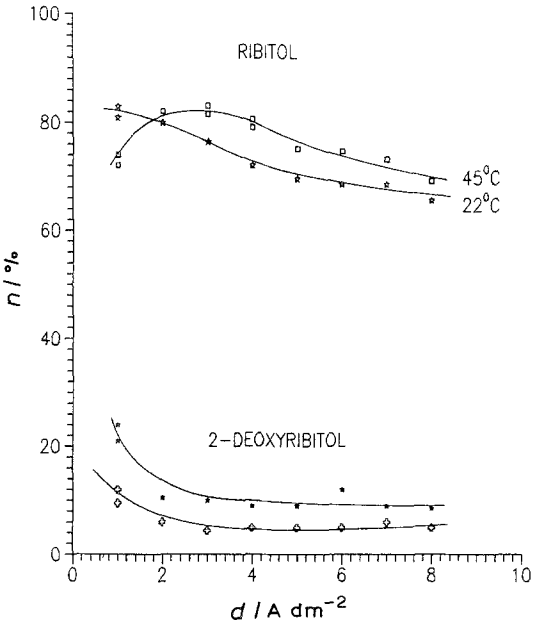

Fig. 3. Yield, η, of ribitol against current density, d, at 22 and 45° C. Q 200%; concentration of ribose 0.2 M; pH 11.

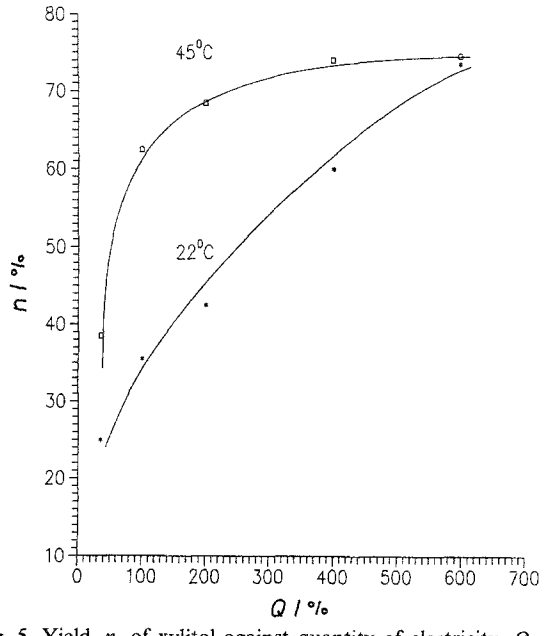

Fig. 5. Yield, η, of xylitol against quantity of electricity, Q, at a current density of 2 A dm^{-2}, at 22 and 45° C. Concentration of xylose 0.2 M; pH 11.

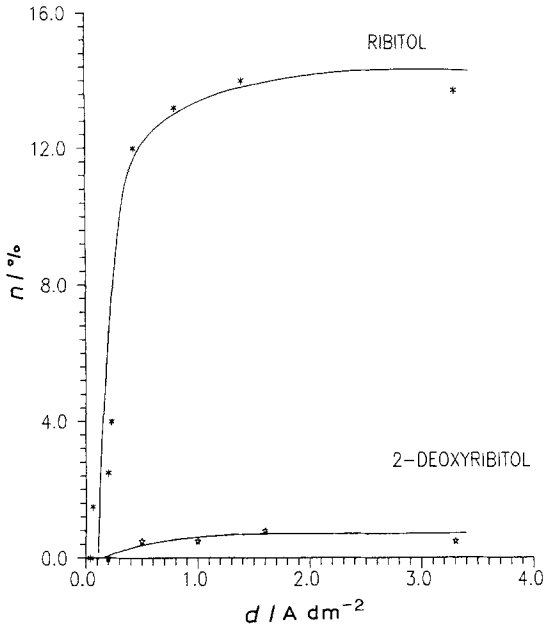

Fig. 6. Yield, η, of ribitol and 2-deoxyribitol against current density, d, in sodium sulphate solution at ribose concentration C_R 0.02 M, τ 80 min; t 20° C; pH 11.

wide pH range (1–12) enables estimation of the importance of these differences. The experiments were conducted in solutions of lower concentration of ribose (C_R = 0.02 M), in shorter times corresponding to $Q \simeq 150\%$, under a preliminarily established (Fig. 6) current regime, i.e. at such a current density at which the cathode reduction of ribose was controlled by the diffusion and kinetics of conversion of the reactant into an electrochemically active form.

Figure 7 show that in the strongly acidic buffer solutions (pH 1–6), small quantities of ribitol are formed. The yield increases rapidly over the pH range 6–9. A further increase in pH does not affect the reduction process markedly. In the sodium sulphate solution, however, the yield increases rapidly over the pH range 0–2, attaining at pH 3 a value that does not change appreciably up to pH 11 inclusively (Fig. 8).

A comparison of the shapes of the curves in Fig. 7 and 8 reveals therefore that during the process conducted in the sodium sulphate solution at pH 3, containing 0.02 M of a depolarizer, at a cathodic current density of 1.4 A dm^{-2}, the actual pH within the zone of the electrode reaction is a few pH units higher than that measured in the bulk solution.

It must be born in mind that with buffer solutions, their buffer capacity plays an important role. In the case of a too low capacity, the equilibrium may be disturbed resulting in an increase in the hydroxyl ion concentration in the neighbourhood of the cathode. The shapes of the curves in Fig. 7 show clearly that the influence of the buffer capacity manifests itself distinctly at pH 6–7, since in solution of the lowest buffer concentration (0.16 M) the yield of the reduction distinctly increases, while in the remaining solutions it increases only at higher pH values.

The relationships reveal that during the electrode process the pH in the zone of the electrode reaction

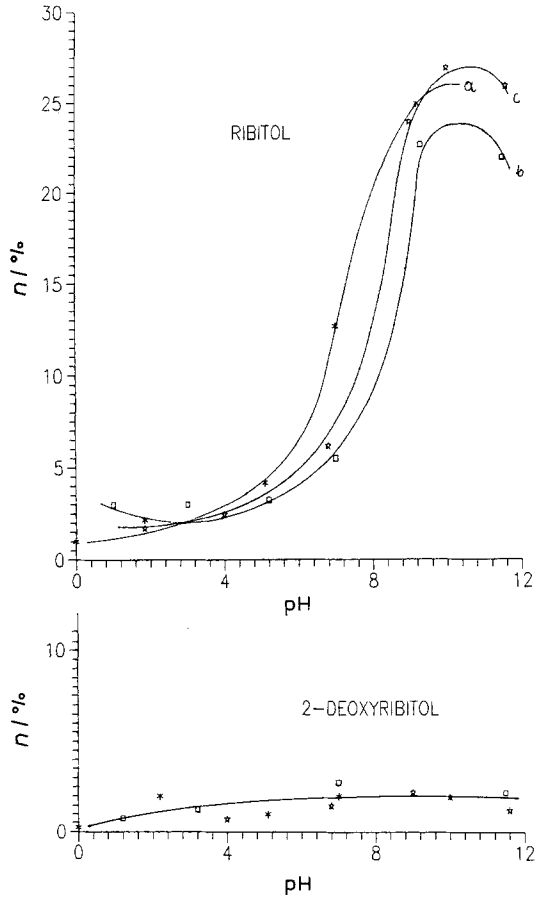

Fig. 7. Yield, η, of ribitol and 2-deoxyribitol against pH in phosphate buffer solutions of capacity: (a) 0.16; (b) 0.33; (c) 0.66 mol PO_3^{-3} dm^{-3} at ribose concentration C_R 0.02 M; d 1.4 A dm^{-3}; t 22° C; Q 150%.

can increase by several units relative to that measured in the bulk solution. This increase depends on a number of factors associated with the current regime

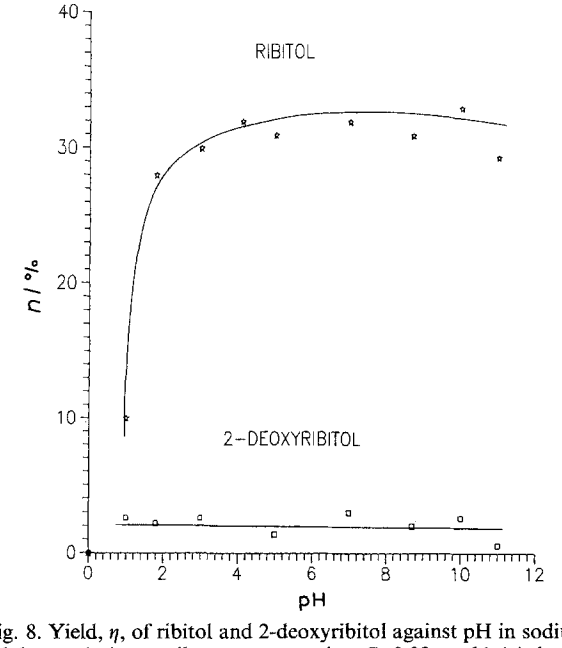

Fig. 8. Yield, η, of ribitol and 2-deoxyribitol against pH in sodium sulphate solution at ribose concentration C_R 0.02 M; d 1.4 A dm^{-2}; t 22° C; Q 150%.

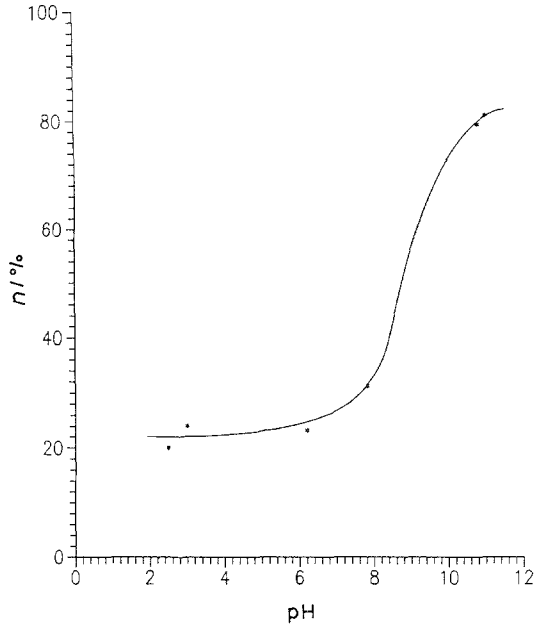

Fig. 9. Yield, η, of ribitol against pH in sodium sulphate solution at ribose concentration, C_R 0.2 M; d 1.4 A dm^{-2}; t 22° C; Q 150%.

and hydrodynamic conditions. Consequently the concentration of the electroactive aldehyde chain structure of reactant at the cathode and its contribution to the electrode process varies considerably.

This autocatalytic increase in the rate of reduction of aldoses is particularly evident when the electrolysis is run under conditions where the rate is controlled exclusively by diffusion and by the kinetics of the mutarotation of the reactant to produce an electroactive form (low reactant concentration, high current density).

However, the results of electrochemical reduction of ribose carried out in Na_2SO_4 solutions at pH 3, 7 and 11 and at a 10 times higher reactant concentration (Fig. 9) match those obtained in the buffered solutions.

So the dependence between the yield and the current efficiency of reduction of the monosacharides and the pH measured in the bulk solution may be different at the beginning of the process when the reactant concentration is high, than in its final stage.

4. Conclusions

1. Electrochemical reduction of pentoses under conditions of galvanostatic electrolysis in sodium sulphate solution at an amalgamated lead cathode over the pH range 8–11 gives pentitiols in high yields (with ribose 84%, with xylose in excess of 75%). Small amounts (a few percent) of 2-deoxyalditols are formed as the side products.

2. Raising the temperature to 45° C allows increase of the current density threefold without lowering the yield of ribitol.

3. Comparison of the results of electrolysis, conducted in buffered and unbuffered solutions shows that, in the latter case, a large difference between the H^+ ion concentration in the bulk solution and in the neighbourhood of the cathode can occur. Alkalization of the layer adhering to the cathode results in an autocatalytic increase in the rate of pentose reduction in unbuffered solutions over the range of low pH values.

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