

Short Communications

Sorption of Carbon Disulfide onto Ion Exchange Resins

INGEMAR DOLBY and OLOF SAMUELSON

*Department of Engineering Chemistry,
Chalmers Tekniska Högskola, Göteborg,
Sweden*

The net reaction which occurs during the storage of concentrated solutions of cellulose xanthate (ripening of viscose) is a decrease in the degree of xanthation. There is also a formation of new xanthate groups, however. This rexanthation reaction can be eliminated when the ripening is carried out in the presence of an anion exchange resin in its hydroxide form.¹ By using this technique it is possible to determine the content of primary and secondary xanthate groups by a kinetic method and to determine the rate constants of the actual dexanthation reactions.²

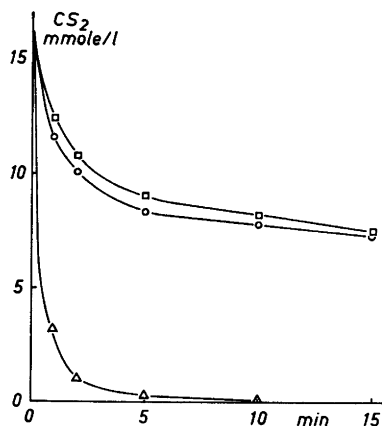


Fig. 1. Remaining carbon disulfide in solution after treatment with Dowex 1 in various ionic forms. □ ClO₄⁻; ○ Cl⁻; △ OH⁻.

There are several indications that the primary product formed during the dexanthation is carbon disulfide^{3,4} although several authors have stated that the primary products are dithiocarbonate and other ions. In several discussions the observation that the rexanthation is eliminated by the presence of an anion exchanger has been used as an argument for the validity of the latter mechanism. For this reason it was deemed important to investigate the adsorption of carbon disulfide from aqueous solution onto ion exchange resins.

Some results obtained with a strongly basic anion exchange resin of the styrene-divinylbenzene type are reported in Fig. 1. It is seen that with the hydroxide form of the resin the uptake of carbon disulfide is complete within 10 min. Carbon disulfide is also taken up in appreciable amounts by the chloride and perchlorate forms of the resin. In the experiment with the chloride resin no chloride could be detected in the external solution indicating that the sorption mechanism is a non-ionic one.

This result was confirmed in experiments in which the chloride resin was extracted with a mixture of ethanol and ether after the sorption step. About 95 % of the adsorbed carbon disulfide was recovered in the eluate.

The influence of sodium chloride upon the sorption is demonstrated by the results presented in Fig. 2. In an ion exchange reaction the uptake should be lowered by the presence of salt but here an addition of electrolyte results in an increased uptake. Similar effects have earlier been observed with other non-electrolytes and have been ascribed to interaction forces with the non-polar resin matrix.⁵ If this explanation also holds true with carbon disulfide, it can be expected that an anion exchanger with a more polar matrix should be less effective than the styrene-divinylbenzene resin. This is confirmed by the results given in Fig. 3 which show the

sorption of carbon disulfide onto a strongly basic anion exchanger with a matrix of cross-linked dextran. It is seen that both the chloride and hydroxide forms are less effective than the styrene-divinylbenzene resin.

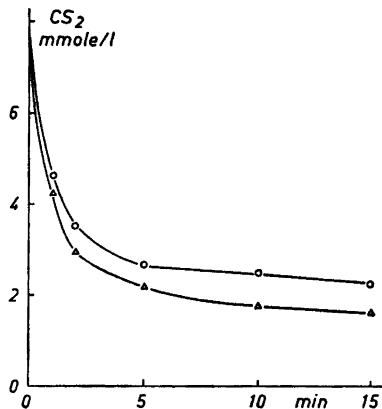


Fig. 2. Remaining carbon disulfide in solution after treatment with Dowex 1 in the chloride form. O in water; Δ in 2 M sodium chloride.

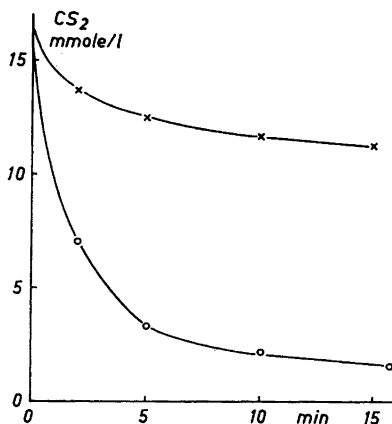


Fig. 3. Remaining carbon disulfide in solution after treatment with a strongly basic anion exchanger prepared from cross-linked dextran. \times Cl^- -form; O OH^- -form.

Finally, some experiments were carried out with cation exchange resins of the sulfonic acid type with a styrene-divinylbenzene matrix. The resins, which were

used in their potassium form, possessed different exchange capacities and were obtained by careful desulfonation of a commercial resin. As shown in Fig. 4 there is a marked adsorption onto these types of resin also. Expectedly, the sorption increases with a decreased ion exchange capacity.

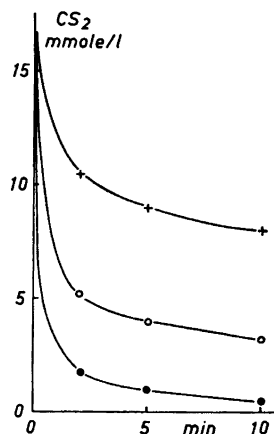


Fig. 4. Remaining carbon disulfide in solution after treatment with sulfonated styrene-divinylbenzene resins of varying exchange capacities. + 4.39 mequiv./g; O 2.74 mequiv./g; \bullet 1.72 mequiv./g.

From these results it can be concluded that carbon disulfide is taken up from an aqueous solution by a non-ionic mechanism and that the interaction forces with the resin matrix are of primary importance. The fact that anion exchange resins in the hydroxide form adsorb more effectively than other resin forms is explained by secondary reactions between carbon disulfide and the hydroxide ions. These reactions give rise to dithiocarbonate, sulfide, carbonate, and trithiocarbonate. Hence, the fact that the reanethation of viscose is eliminated by the presence of an anion exchange resin is consistent with the assumption that carbon disulfide is the primary reaction product in the dexanethation of cellulose xanthate.

Experimental. The strongly basic anion exchange resins used in this work were Dowex 1 X-8 with a particle size of about

0.3 mm and an experimental anion exchange resin kindly put at our disposal by Pharmacia Fine Chemicals, Uppsala, Sweden. This resin had been prepared from cross-linked dextran (Sephadex) by introduction of quaternary ammonium groups. The particle size was about 35 μm and the exchange capacity 2.7 mequiv./g. The cation exchange resins were the same as those used previously.⁴

Aqueous solutions of carbon disulfide were prepared by passing nitrogen saturated with carbon disulfide into a flask with water. Wet anion exchanger (20 g) obtained by careful suction was stirred with 100 ml of the solution at 20°. After various lengths of time the solution was freed from resin and analyzed by passing nitrogen through the solution with subsequent absorption of the carbon disulfide in M sodium ethoxide solution in ethanol. The carbon disulfide was determined spectrophotometrically as ethyl xanthate at 301 nm.⁷ The variations in the water contents of various ionic forms of the same resin⁸ have only a slight influence upon the results and no corrections have, therefore, been applied.

The cation exchange resins were dried before the experiments in which 12 g of dry resin were added.

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Transport of B-Vitamins in Microorganisms

VI. The Non-specificity of the Effect of Exogenous ATP on the Uptake of Labelled Thiamine by Non-proliferating Thiamine Deficient Cells of *L. fermenti*. A Reappraisal

HALINA Y. NEUJAHN

Department of Biochemistry, Royal Institute of Technology, Stockholm 70, Sweden

It was observed earlier¹ that exogenous ATP stimulated, in certain cases, the uptake of ³⁵S-thiamine by thiamine deficient non-proliferating cells of *L. fermenti*, but was without effect on normal cells. The stimulating effect was observed only with severely thiamine deficient cells (thiamine content in the growth medium 1 $\mu\text{g}/\text{ml}$) employing in the incubation mixture 20 mM ATP, 0.01–0.02 M potassium phosphate pH 5.5, 10^8 – 10^{10} cells/ml and certain other components.

Results of comparative studies on the permeability of thiamine depleted and normal cells towards a number of compounds other than thiamine did not indicate any generally increased permeability of the deficient cells.² It did not seem probable, therefore, that ATP had easier access to the thiamine depleted cells than to the normal ones.

It was found, during subsequent studies on thiamine transport in *L. fermenti*, that the effect of ATP did not always take place when the conditions of the incubation with labelled thiamine were different from those employed in the originally reported experiments.¹ For example, changing the pH and/or buffer from the originally employed potassium phosphate pH 5.5 to pH 6.8 or to Tris-HCl pH 6.8 gave variable results with respect to the ATP effect. Experiments were therefore undertaken to investigate whether or not the stimulation by ATP of thiamine uptake was a true energy effect. In these experiments the effect of ATP was compared with that of AMP at equimolar concentrations. Certain representative results are shown in Table I. It can be seen that the effect of ATP varied with the buffer and the pH employed.