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INFLUENCE OF ETHANOL ON THE AMYLOSE VISCOSITY IN SOLUTIONS

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In this paper changes of the intrinsic viscosity, $[\eta]$, of amylose in the function of ethanol (EtOH) concentration in water solutions were determined. It was found that in solutions of EtOH concentration lower than 12% and higher than 16% an increase in EtOH concentration brought about an increase in $[\eta]$ value, that was related with the increase in the end-to-end length of amylose chain. Moreover time changes of specific viscosity, η_{sp} , in the studied solutions were determined and they indicated on the stiffening of amylose chain with time.

INTRODUCTION

In works [2, 5, 8, 11] on retrogradation and gelation of amylose it was proposed that the rate of crystallization was largely dependent on the chain conformation. Introduction to largely dependent on the chain conformation. Introduction to the water solution of amylose a low molecular complexing molecule is responsible for the ordering of the structure [9, 10] and for increase in the contribution of single helix forms in the chain [6, 7]. The spiralization and ordering of the structure are related with the change in the length and stiffness of the chain [4, 10, 11], which should be reflected in different viscosity of the analyzed system. The aim of this paper is to determine the viscosity of amylose in water-ethanol solutions depending on the concentration of ethanol and to give the characteristic of time kinetics of viscosity in the analyzed systems.

MATERIAL AND METHODS

The experimental material was amylose from potato obtained from Poland Chemical Reagents. Amylose powder was dissolved in double distilled water, then slowly heated to the temperature of 100° C and boiled for 30 minutes. Then the solution was cooled to room temperature and the appropriate volume of EtOH was added. In this way we obtained amylose-water-EtOH mixtures of different EtOH concentrations (X_{EtOH}) varying from 3% to 22% (V/V). Amylose concentration in water-EtOH mixtures ranged within (1-5) 10^{-2} g/ml. Viscosity

was measured by the Ubbelotte viscosimeter at room temperature. The viscosimeter was scaled each time an appropriate solvent.

RESULTS AND DISCUSSION

The specific viscosity, η_{sp} , of the amylose-water-EtOH solution was determined using the following relation:

$$\eta_{sp} = \frac{\eta_a - \eta_s}{\eta_s}$$

where: η_a is the viscosity of amylose solution and η_s is the viscosity of the solvent. The intrinsic viscosity, $[\eta]$, was obtained via graphic way using the Huggins (2) and Kraemer (3) equations [12]:

$$\frac{\eta_{sp}}{c} [\eta] + k_H [\eta]^2 c \quad (2)$$

$$\frac{\ln(1 + \eta_{sp})}{c} = [\eta] + (k_H - 0.5) [\eta]^2 c \quad (3)$$

where: c — is amylose concentration, k_H — Huggins constantant.

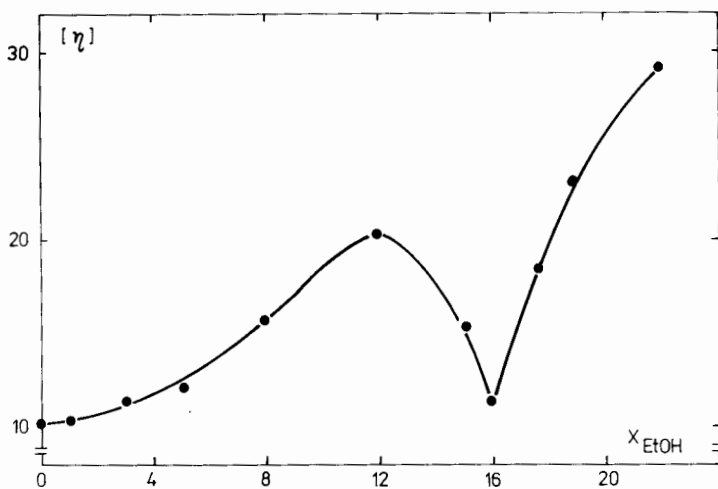


Fig. 1. Intrinsic viscosity, $[\eta]$, (in ml/g) of amylose vs the EtOH concentration (in % V) in solutions

The values of $[\eta]$ calculated as the function of EtOH concentration are presented in Fig. 1. The observed changes in viscosity indicate on the specific properties of the about 16% water solution of EtOH as a amylose solvent. This anomalous behavior of amylose in the about 16% solution of EtOH results from the fact that this particular concentration range for the water-EtOH system corresponds to the critical micelle concentration, CMC [1, 3]. At EtOH

concentration in water solution which corresponds to the CMC value, the probability of ethanol-ethanol interaction is higher than of the ethanol-polymer interaction, therefore within this concentration range ethanol should not be incorporated into amylose helices. The above theoretical assumption was confirmed by the obtained values of intrinsic viscosity $[\eta]$ of amylose in water-EtOH solutions. The value for amylose in 16% EtOH is almost equal to the intrinsic viscosity of amylose in water.

Moreover, in order to determine the kinetics of viscosity of amylose-water-EtOH solutions, a specific viscosity, (η_{sp}), was measured in the time interval 0-5 hours (every 0.5 h) after the preparation of the solutions. The obtained values of η_{sp} for amylose in water and selected water-EtOH mixtures are shown in Fig. 2.

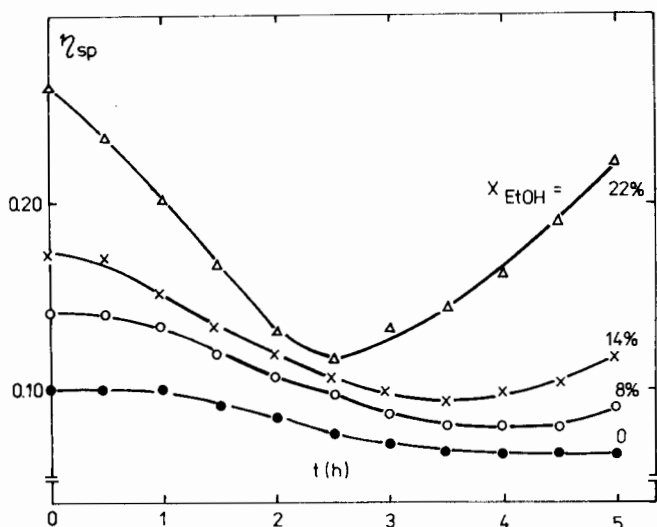


Fig. 2. Dependence of specific viscosity, η_{sp} , on time (in hours) for 1% amylose in water (curve 0) and in selected water-EtOH mixtures

The initial decrease in η_{sp} testifies to the stiffening of amylose chain proceeding with time, whereas the increase in viscosity for a longer time of observation indicates on the aggregation of molecules. Moreover, on analysing the relative changes in viscosity, $\Delta_t \eta_{sp}$, for two limiting times of measurements, $t = 0$ and $t = 5$ hours, which is given by the dependence:

$$\Delta_t \eta_{sp} = [\eta_{t=0} - \eta_{t=5}] x_{\text{EtOH}}, \quad (4)$$

it was found that in solutions of $x_{\text{EtOH}} < 14\%$, the influence of ethanol on changes in the structure of amylose was time dependent (Fig. 3). In contrast, in solutions with ethanol concentrations higher than 16%, ethanol induced changes in the structure of amylose which were immediate and finite.

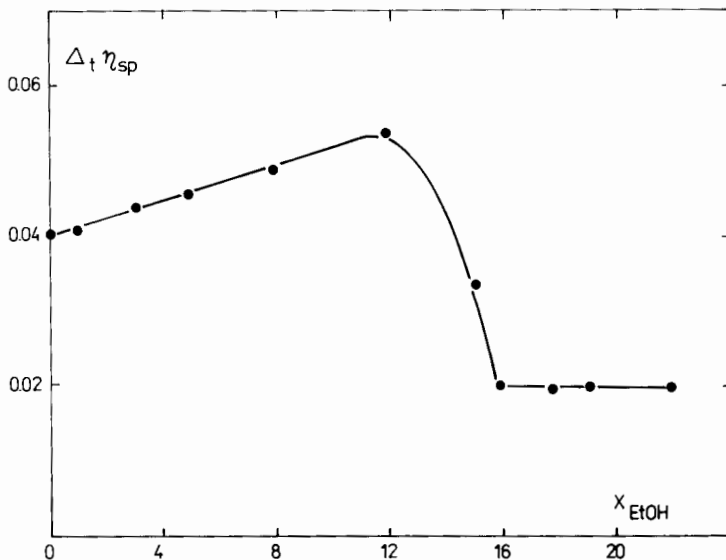


Fig. 3. Dependence of relative changes in viscosity, $\Delta_t \eta_{\text{sp}}$, on EtOH concentration

CONCLUSIONS

The analysis of the results leads to the conclusion that the addition of ethanol to amylose water solutions is responsible for the differences in the viscosities of this solutions. Namely in solutions of $x_{\text{EtOH}} < 12\%$ and $x_{\text{EtOH}} > 16\%$ an increase in EtOH concentration results in an increase in the $[\eta]$ value. It is evidence of the increase in the end-to-end length of amylose chain in these solutions. Studies on kinetics of viscosity proved that in the initial stage, a stiffening of the amylose structure in the studied solutions occurred. As the time passed an increase in viscosity related to the molecule aggregation took place.

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WPLYW ETANOLU NA LEPKOŚĆ ROZTWORÓW AMYLOZY

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Streszczenie

Omówiono wpływ etanolu na lepkość wodnych roztworów amylozy. Wykryto, że w roztworach, w których stężenie etanolu było w granicach 3-12% (v/v) wzrost stężenia etanolu wyrażał się w nieliniowym wzroście lepkości granicznej amylozy, co świadczy o rozciągnięciu się łańcucha amylozowego. Z drugiej strony porównanie lepkości granicznej amylozy w 16% roztworze EtOH z lepkością w roztworze wodnym wskazuje na szczególne właściwości 16% roztworu EtOH jako rozpuszczalnika amylozy. Lepkość ponownie wzrasta w przypadku roztworów alkoholu o stężeniu większym niż 16%. Przyczyną takich zmian lepkości w układach amyloza-woda-etanol może być zmiana w długości i sztywności łańcucha amylozowego. Poza tym, badania nad lepkością amylozy jako funkcji czasu wskazują, że kinetyka lepkości silnie zależy od stężenia EtOH w roztworze. W początkowej fazie eksperymentu zachodził spadek lepkości właściwej, co jest związane ze sztywnością struktury łańcucha amylozy. W szczególności w roztworach etanolowych o stężeniu mniejszym niż 14% zmiany w strukturze amylozy zależą od czasu, podczas gdy w roztworach, w których stężenie EtOH jest większe niż 14%, końcowe zmiany strukturalne skrobi zachodzą bardzo szybko. Z upływem czasu następuje zbijanie się cząsteczek amylozy.