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## ETHERIFICATION OF STARCH WITH BUTYL ACRYLATE

تفاعل النشا مع البيوتيل اكريلات عن طريق الأثر في وسط قاعدي

by

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### الملخص العربي

تم التفاعل بين نشا الذرة والبيوتيل اكريلات في وجود هيدروكسيد الصوديوم كعامل مساعد وكان ناتج التفاعل يحتوي على كل من اكريلات النشا (الايثر) وكربوكسي ايثيل النشا (ناتج عن التحول الجزئي للبيوتيل اكريلات تحت تأثير الوسط القلوي) لذلك تم تعيين كل من نسبة الايثره والمحتوى الكربوكسيلي لتحديد كمية ايثر النشا المتكون وأيضا تعيين مدى تحويله إلى كربوكسي ايثيل النشا. تضمن هذا البحث تأثير درجة تركيز هيدروكسيد الصوديوم ودرجة تركيز البيوتيل اكريلات ودرجة حرارة وزمن التفاعل ووسط التفاعل على درجة تكوين ايثر النشا ببيوتيل اكريلات. خلصت دراسة هذه العوامل إلى أن أنسب ظروف التفاعل هي كالاتي: درجة تكوين المركب الإيثيري تصل إلى نهاية عظمى عندما يكون تركيز هيدروكسيد الصوديوم إلى النشا 1 مول / 1مول وتركيز البيوتيل اكريلات 60% وأن أنسب زمن للتفاعل 20 ساعة أما عن درجة الحرارة فتمثل 55 °م الدرجة المثلى لتكوين مركب النشا الإيثيري، في حين أنه أعلى أو أقل من درجة 55 °م يصبحه انخفاض في درجة تكوين المركب الإيثيري. أما بالنسبة لتأثير درجة الحرارة على تكوين كربوكسي ايثيل النشا فوجد انه يزداد بازدياد درجة الحرارة عن 60 °م . وكذلك أوضحت هذه الدراسة أن مزيج من الماء مع المذيب العضوي (الكحول الأيزوبروبيلي) بنسبة 4 مللي / 4 مللي يمثل الوسط الأمثل لتكوين المركب الإيثيري.

### Summary

Maize starch was reacted with butyl acrylate (BuA) in presence of NaOH as a catalyst. The reaction products consists essentially of mixed starch ethers namely starch butyl acrylate i.e. starch bearing BuA moieties and carboxyethyl starch. Hence, they were monitored for ether % to bring into focus the extent of reaction of starch with BuA to yield starch butyl acrylate and; for carboxyl content expressed as DS to find out to what extent was the starch butyl acrylate converted to carboxyethyl starch. Dependence of the extent of the

etherification reaction expressed as ether % and DS on conditions of the reaction was studied. Results obtained indicate that the extent of the reaction attains the highest values at NaOH and BuA concentrations of 1 mole/1 mole starch and 60 % w/w, respectively, temperature of 55° C and reaction time of 20 hrs. The reaction occurs easily using water/solvent ratio 4ml/4ml. A tentative mechanism for the reactions involved is also reported.

## 1. INTRODUCTION

Starch occupies a significant position in all known thickeners used in textile warp sizing, finishing and printing <sup>(1,2)</sup>. To bring about modified starches with variable improved properties, it is a must to change the physical and/or the chemical structure of starch. This could be achieved by subjecting starch to acid treatment <sup>(3)</sup> oxidation, <sup>(4)</sup>, etherification and esterification <sup>(5,6)</sup> as well as grafting <sup>(7,11)</sup>.

Chemical modifications of starch through etherification are carried out using numerous methods <sup>(12,13)</sup>; and many starch ethers are commercially available and other are suggested for commercial use. Among these starch ethers mention was made of the following: cationic starch, hydroxy ethyl starch, cyanoethyl starch, carbamoyl ethyl starch and carboxymethyl starch

The present work is undertaken with a view to establish the most appropriate conditions for preparation of starch ethers based on reaction of maize starch with butyl acrylate in presence of sodium hydroxide. The work is further extended to include rheological properties of the starch ethers obtained.

## 2. EXPERIMENTAL

### 2.1. Materials:

Maize starch was supplied by the Egyptian Starch and Glucose Manufacturing Company, Cairo, Egypt. Butyl acrylate (BuA), (Merck) with 0.01 % hydroquinone was freshly distilled under vacuum. Sodium hydroxide, isopropyl alcohol, hydrochloric acid, acetic acid, potassium hydroxide, and acetone, were reagent grade chemicals. Ethyl alcohol was of technical grade chemicals.

### 2.2. Procedure:

Unless otherwise indicated, the reaction was carried out in 250 ml stoppered bottle. The starch was slurred in the required amount of BuA and

isopropyl alcohol, then certain amount of freshly prepared NaOH of known concentration was added. At this end the contents were mixed very well using electric stirrer. The etherification reaction was allowed to proceed at a certain temperature for different time intervals. The contents were stirred very well before heating. After the desired reaction time the reaction products were neutralized by alcoholic acetic acid then filtered and the precipitate was dried in an oven at 600C for 10 hours.

The ether % was measured by making use of hydrolysis according to the following method (5,8). 1 gm of the so obtained etherified starch along with 25 ml 1N alcoholic isopropanol KOH were introduced in a round quick fit flask. The flask contents were boiled under reflux for 3 hours. The flask was then cooled and titrated against 0.1 N HCl using Ph.Ph. indicator. Blank titration was also carried out. The Ether % was calculated according to the following equation.

$$\text{Ether \%} = \frac{V \times N \times 100 \times \text{Mol.Wt. of Monomer}}{\text{Dry weight of sample} \times 1000}$$

$$\text{Carboxyl \%} = \frac{V \times N \times 0.045 \times 100}{\text{Dry weight of sample}}$$

where

V= is the difference of ml of HCl consumed in the titration process of the blank and sample solutions.

N=Normality of HCl.

Degree of substitution:

The degree of substitution was calculated according to the following equation:

$$\text{Carboxyl\%} = \frac{M1 \times DS \times 100}{M1 \times DS + M2}$$

Where

DS =Degree of substitution

M1 = Molecular weight of Butyl acrylate

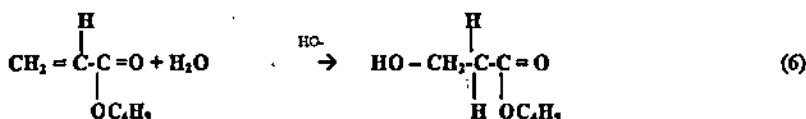
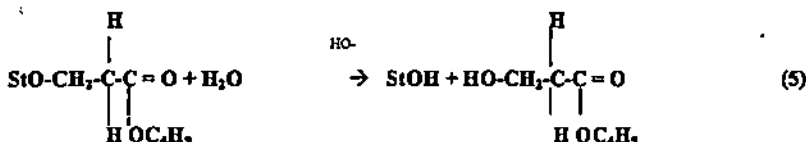
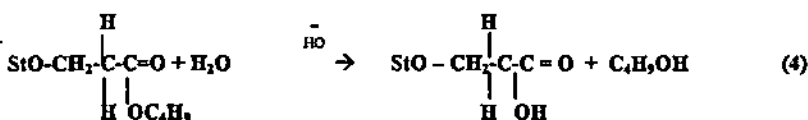
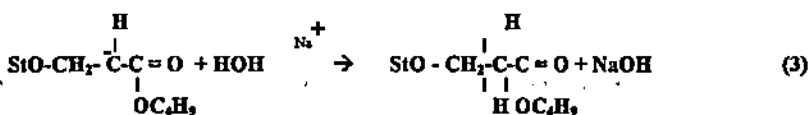
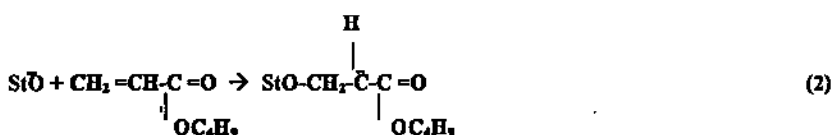
M2 = Molecular weight of starch

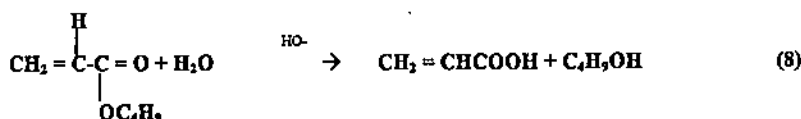
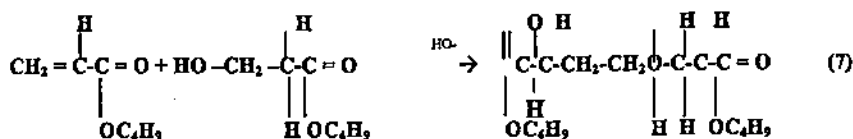
### 3. RESULTS AND DISCUSSION

In a previous study<sup>(14)</sup> the detailed mechanism of the reaction of starch and methyl methacrylate ( $\text{CH}_2 = \text{C} - \overset{\text{CH}_3}{\underset{\text{OCH}_3}{\text{C}}} = \text{O}$ ) in presence of

$\text{NaOH}$  as a base was reported. The reaction is considered as a typical nucleophilic addition reaction of a nucleophil on unsaturated ester. Here the presence of  $\text{C} = \text{C}$  in conjugation with groups having electron attracting effect ( $-\text{R}$ ) permit the nucleophil addition reaction of  $\text{C} = \text{C}$ .<sup>(15-20)</sup> Similarly, reaction between starch and BuA would follow the same reaction mechanism.

It is stated above that the present research deals with a system consisting of starch, BuA,  $\text{NaOH}$  and isopropanol / water. In such a complex system several reactions take place, the major of which are shown under:





This reaction scheme implies that starch may react with BuA in presence of NaOH to yield ultimately an ether, namely, starch butyl acrylate (reaction 3). Starch-butyl acrylate may undergo partial alkaline hydrolysis to give rise to carboxyethyl starch (reaction 4). Partial alkaline hydrolysis of starch butyl acrylate may also lead to de-etherification. (reaction 5). It is further envisioned that BuA undergoes other reactions (reaction 6-8) under the influence of NaOH.

With the above in mind, the system under investigation was studied under a variety of conditions. Factors examined embrace concentrations of NaOH and BuA, etherification time and temperature as well as reaction medium. This is done to discover the most appropriate conditions for etherification. The latter is expressed as ether %, that is monomer reacted as ether in the butyl form and, carboxyl content, expressed as degree of substitution (DS), that is the part of the ether, which is converted to carboxyl groups via partial alkaline hydrolysis of starch butyrate. Results obtained along with appropriate discussion are given below.

### 3.1. Sodium Hydroxide Concentration

Starch (10 g) was reacted with BuA (60% ows) in a reaction medium of water/isopropanol (4ml/4ml) mixture in presence of different amounts of NaOH at 55°C for 20 hours. Figure 1 shows the extent of etherification, expressed as ether % and DS as a function of NaOH concentration. The etherification seems to attain the highest values at NaOH concentration of 1mole/ 1mole starch. Above this concentration, the extent of etherification decreases sharply by increasing NaOH concentration. Higher NaOH concentrations seem to promote de-etherification (reaction 4) and /or inactivation of BuA by side reactions (reactions 6-8) including formation of acrylic acid (reaction 8). These reactions lead certainly to decreased etherification. It is understandable that acrylic acid does not react with starch

under the condition used as proved experimentally. Trials were made to prepare carboxyethyl starch through reaction of starch with acrylic acid in presence of NaOH were not successful.

### 3.2. Butyl Acrylate Concentration:

Different concentrations of butyl acrylate (20,30,40,50 and 60% based on weight of starch ,ows) were independently reacted with starch (10g) in presence of sodium hydroxide at a concentration of one mole /one mole of starch. The reaction was conducted in a medium consisting of 55°C for 20 hours. The resultant etherified product was analyzed for the ether % and DS and the results obtained are shown in Figure 2.

It is seen (Fig.2) that the extent of the etherification reaction, expressed as ether % and DS increases significantly with the increase in the BuA concentrations within the range studied. This could be interpreted in terms of greater availability of BuA molecules in the vicinity of starch hydroxyls at higher BuA concentration. Needless to say that the starch hydroxyls are immobile and their reaction rely largely on the BuA molecules in their proximity, a situation, which is, fulfilled at higher BuA concentrations.

### 3.3. Duration of Etherification:

Figure 3 shows the extent of etherification of starch with butyl acrylate (BuA) as a function of reaction time. The ether % and the DS of the etherified product were taken as a measure of the extent of etherification reaction. The latter was performed using starch (10g), BuA(50% ows), NaOH (1mole/1mole starch) and isopropyl alcohol/water (4ml /4ml). The reaction was carried out at 55°C for varying lengths of time as indicated in the figure.

The results (Fig.3) indicate that the extent of etherification is directly related to the reaction time within the range studied. Prolonging the duration of the reaction from 5 to 20 hours causes significant enhancement in the extent of etherification. This is unequivocally due to the favorable effect of time on provision of better contact among reactants with subsequent faster diffusion and adsorption of these reactants thereby leading to increased etherification.

### 3.4. Etherification Temperature:

Figure 4 shows the effect of temperature on the extent of etherification of starch with butyl acrylate (BuA). The etherification conditions used was

similar to those described above for the duration expect that the latter was 20 hours. The extent of the etherification reaction was expressed as ether % where the etherified starch bears butyl acrylate moieties and as carboxyl groups (DS) where the butyl acrylate moieties were converted into carboxyethyl groups under the catalytic influence of sodium hydroxide.

It is evident (Fig.4) that the extent of etherification, expressed as ether % , increases substantially by raising the reaction temperature from 45 to 55°C, then decreases sharply at 70°C then remains constant at 85°C. Different situation is encountered when the extent of etherification is expressed as DS. Here, the extent of etherification increases by raising the temperature from 45°C to 85°C. These findings are a manifestation of the ultimate result of two essential reactions occurring during etherification of starch with butyl acrylate. The two reactions are shown above in equations 3 and 4. The first reaction gives rise to starch butyl acrylate whereas the second reaction yields carboxyethyl starch through the alkaline hydrolysis of butyl acrylate moieties. Current data signify that the etherification temperature acts in favor of starch butyl acrylate formation provided that the temperature does not exceed 60°C. This temperature seems to supply the starch BuA-NaOH-isopropyl alcohol/water system with the energy required for inducing formation of starch-butyl acrylate through proper diffusion of the etherifying agents into starch along with better reaction collision. Higher temperature, on the other hand, favors alkaline hydrolysis which brings about carboxyethyl starch on the charge of starch butyl acrylate. However, the effect of de-etherification on the decrement in ether % at higher temperatures cannot be ruled out. In combination with this is the inactivation of butyl acrylate by reactions 6,7 and 8; these reactions are anticipated to be more pronounced at higher temperatures.

### 3. 5. Reaction Medium:

Starch (10 g ) was reacted with BuA (50% ows)in presence of NaOH (1mole / 1mole starch) in a reaction medium consisting of water/organic solvent (4ml/4ml) at 55°C for 20 hours. Organic solvents used were n-butanol, cyclo hexanol, ethanol, n-propanol, acetone, isopropanol. In this context, it should be emphasized that the etherification reaction did not occur neither in complete aqueous medium nor in complete non-aqueous medium. This was also the case where water/solvent ratio (v/v) higher than 4ml/4ml were used. Higher ratios causes very high degree of swelling of starch and results in almost solid



mass which diminishes the mobility and probability of reactants collision thereby preventing the etherification reaction to occur.

Figure 5 shows the dependence of the extent of etherification (expressed as ether %) of starch with butyl acrylate under the conditions indicated above on the reaction medium. The diagram depicts that the use of iso propanol/ water mixture (4ml/4ml) brings about the highest extent of etherification whereas similar n-butanol /water mixture the least. Based on the results of ether % the following decreasing order may be drawn: Iso propanol > acetone > n-propanol > ethanol > cyclo hexanol > n-butanol.

Similar trend is observed when the extent of etherification is expressed as DS. This is shown in Figure 6.

Differences in effecting etherification among the solvents used could be associated with differences in (a) miscibility, (b) ability to dissolve BuA and to swell starch, (c) some physical constants such as dipole moment and dielectric constant.

### 3.6. Rheology:

Figure 7 shows the apparent viscosity of starch-butyl acrylate ether at concentrations of 5% and 10% versus rate of shear. Obviously the apparent viscosity decreases by increasing the rate of shear irrespective of the concentration of the etherified starch under investigation. However, the decrease is more significant at 5% than 10% concentration.

By increasing the rate of shear entangled rod likes and/or looping etherified starch molecules are turned lengthwise into the direction of the flow. Chain type molecules can disentangle, stretch and orient parallel to the deriving force. Particles or molecular alignment allow particles and molecules to slip past each other more early. This shows up as decreased viscosity. Current data suggest that at lower etherified starch concentration occurrence of shear thinning phenomenon is more significant at higher concentration. The degree of molecular alignment seems to be better. Hence it is not largely affected by increasing the rate of shear.

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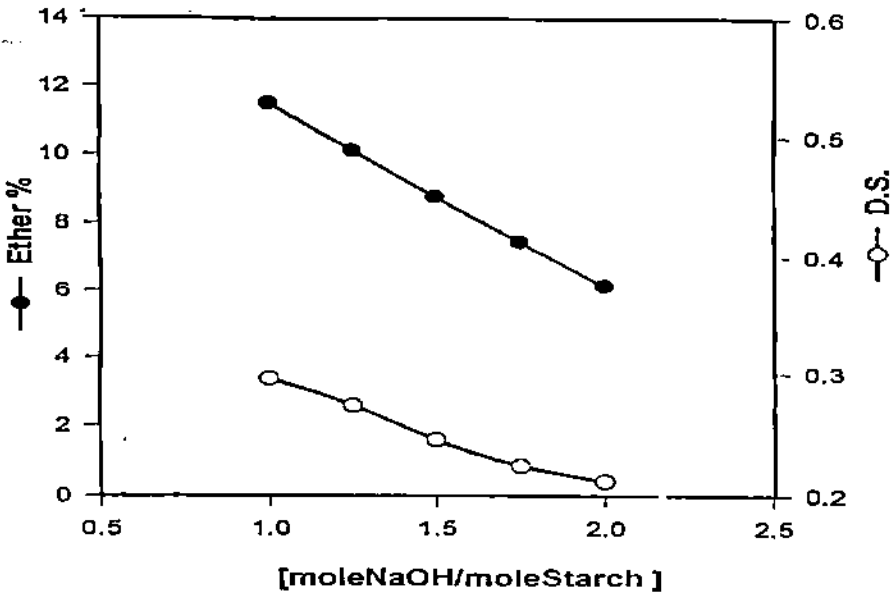
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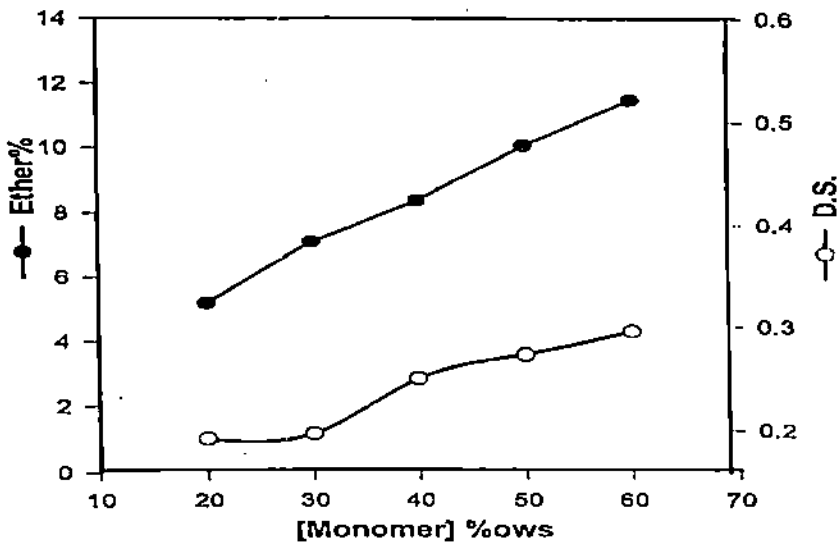
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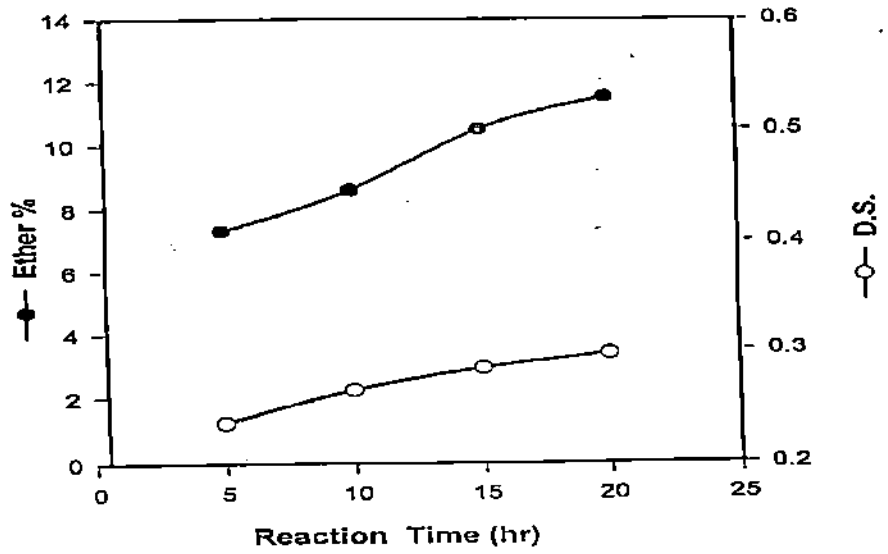
- Fig.1 Effect of sodium hydroxide concentration on the extent of etherification, expressed as Ether % and D.S. [BuA], 60% ows; temp.55<sup>0</sup>C, time 20 hours water/solvent 4ml/4ml
- Fig.2 Dependence of Ether % and D.S on the monomer concentration  
Starch 10 gm 1mole/1mole NaOH; temp.55<sup>0</sup>C, time,20 hours, water/solvent, 4ml/4ml.
- Fig.3 Ether %, and D.S. versus time when starch was etherified with Butyl acrylate.  
Starch 10 gm 1mole/1mole NaOH; temp.55<sup>0</sup>C; water/solvent, 4ml/4ml.
- Fig.4 Variation of Ether %, and D.S. with etherification temperature when BuA was react with starch.  
Starch 10 gm 1mole/1mole NaOH; time, 20 hours; water/solvent, 4ml/4 ml.
- Fig. 5 Dependence of Ether % on reaction medium.  
Starch 10 gm 1mole/1mole NaOH, temp.55<sup>0</sup>C
- Fig.6 Dependence of DS on reaction medium.  
Starch 10 gm 1mole/1mole NaOH; temp; 55<sup>0</sup>C
- Fig.7 The apparent viscosity curve of starch butyl acrylate ether at different concentrations 5%, 10%.



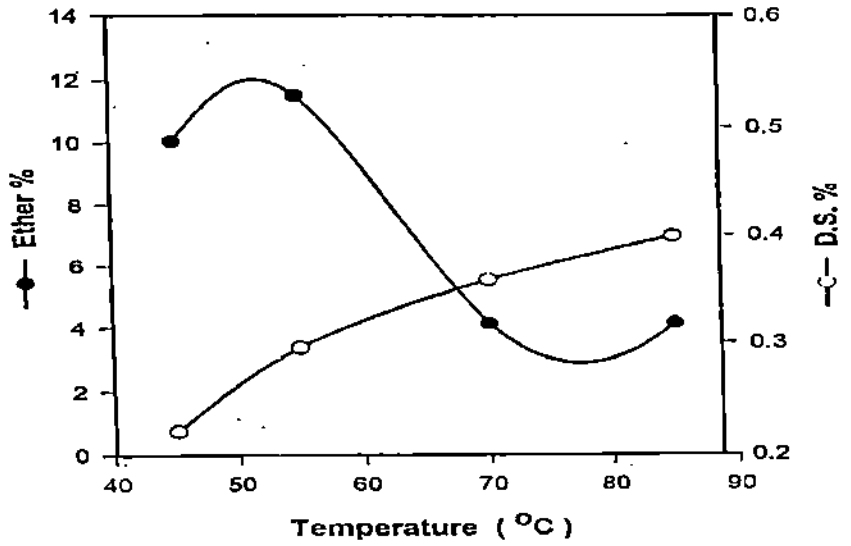
(Fig. 1)



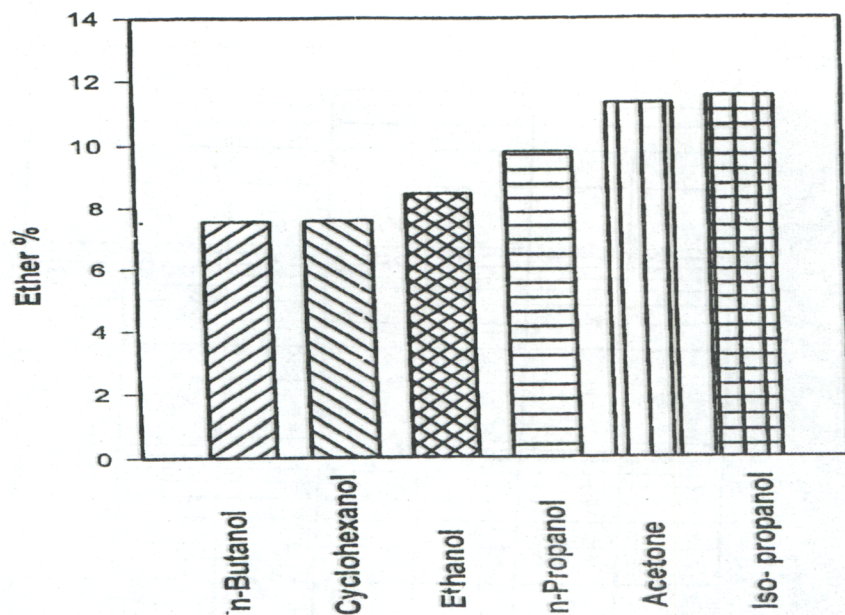
(Fig. 2)



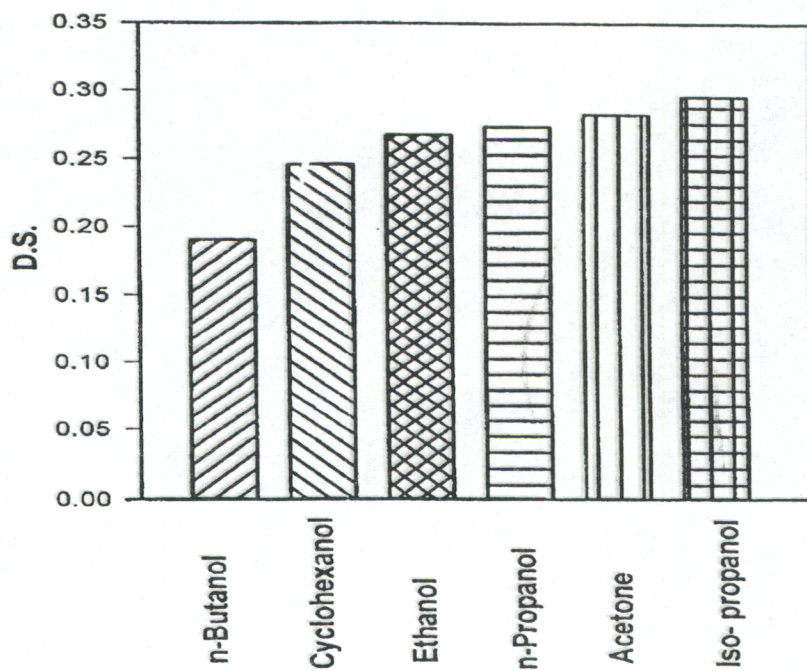
(Fig.3)



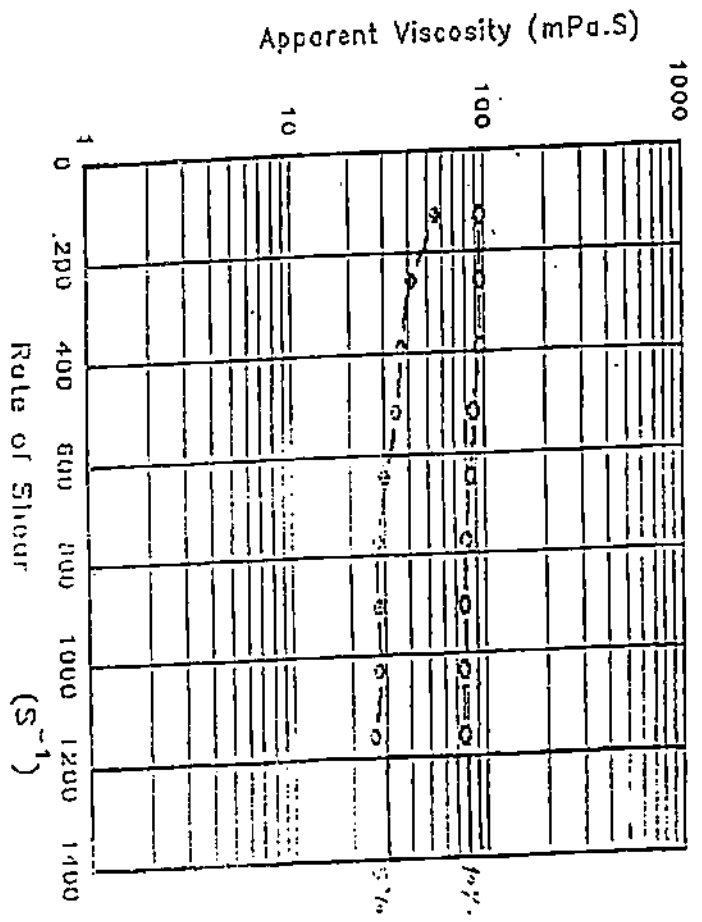
(Fig. 4)



(Fig.5)



(Fig.6)



(Fig.7)