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Short communication

Determination of the degree of the substitution of hydroxyethyl guar gum

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Abstract

An improved chemical method for the determination of the degree of the substitution of hydroxyethyl guar gum by mixed *p*-toluenesulfonic-acetic anhydride has been described. The hydroxyethyl groups are cleaved from modified galactomannans at 130 °C in the presence of excess mixed *p*-toluenesulfonic-acetic anhydride for 14 h, and then the products hydrolyzed into ethylene glycol at pH 11 for an hour. Quantifying the mass of reaction products derived from the hydroxyethyl group, the degree of the substitution of hydroxyethyl guar gum can be precisely estimated.

Keywords: Degree of the substitution; Hydroxyethyl guar gum; Mixed *p*-toluenesulfonic-acetic anhydride

1. Introduction

As a nonionic viscosifier derived from natural guar gum, hydroxyethyl guar gum (HEG) shows good dispersibility in water, and high compatibility with anionic, cationic and nonionic surfactants. With its excellent electrolyte resistance, viscosity stability and good shear stability, HEG can be used in fabric printing and fracture fluids, etc.

HEG is made from guar gum by reaction with ethylene oxide. As with other synthetic polymers, HEG is a heterogeneous group of molecules. Its chemical, physical and pharmacological properties are primarily dependent on molecular weight, molecular weight distribution, the amount of hydroxyethyl substituents, and the pattern of that substitution.

The ability to rapidly and accurately determine the degree of the substitution is a critical factor in proper control of chemical, physical, and biological properties of HEG.

Guar gum and HEG are composed of the same elements and functional groups so that the contents of C, H and O are changed slightly. The chemical shifts of carbons and protons on C_2, C_3, C_4 and C_6 in guar gum are very close to those of hydroxyethyl group in HEG. So it is difficult to determine the degree of the substitution of HEG by physical methods, such as ^{1}H NMR, ^{13}C NMR, EA and FT-IR.

Several analytical methods have been developed over the years for the determination of the degree of the substitution of the hydroxyethyl group. Most of them are based on the cleavage of ether bonds in refluxing hydriodic acid. The reaction products derived from the hydroxyethyl group are then quantitated. They are all based on the method developed by Morgan (1946) for ethers and esters of ethylene glycol and applied to (hydroxyethy1) cellulose. The method was subsequently modified by Lortz (1956) for use with low-substituted starch ethers. The products are ethyl iodide and ethylene which are quantitated by reaction with silver nitrate and bromine in acetic acid, respectively. The amount of silver nitrate and bromine consumed by reaction with the liberated hydroxyethyl residues is determined by back-titration with ammonium thiocyanate and sodium thiosulfate, respectively. This procedure is still widely employed as the standard method of testing even though it is laborious, imprecise, requires specialized glassware, and cannot be automated.

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The powerful acylating ability of mixed *p*-toluenesulfonic-acetic anhydride is demonstrated by their ready cleavage of ethers without labile hydrogen (Karger & Mazur, 1971, 1968). The reason for the high reactivity of mixed anhydride is the powerful electron-withdrawing nature of the sulfonate group. So the presence of labile hydrogen will affect the cleavage rate of ethers containing labile hydrogen. The reaction of mixed anhydride with ethers containing labile hydrogen has been only sparsely investigated, although it had already been pointed out that the mixed anhydride is a highly reactive acylating agents.

Our results have shown the acylating ability of the system to be extremely high and we described a general method for determination of the degree of the substitution of HEG by treatment with mixed *p*-toluenesulfonic-acetic anhydride.

2. Materials and methods

2.1. Materials

p-Toluenesulfonic acid-acetic anhydride, ethylene glycol(EG), diethylene glycol (d-EG), barium hydroxide octahydrate, isopropyl alcohol, diethyl ether, are all analytical reagents. HEG and guar gum used in this investigation were obtained from Jingkun Oilfield Chemistry Company, Jiangsu, China.

2.2. Preparation of mixed *p*-toluenesulfonic-acetic anhydride (T-A Anh)

Anhydrous *p*-toluenesulfonic acid (66 g, 0.38 mol) was dissolved in an excess of acetic anhydride (94 g, 0.92 mol) and the mixture was heated to 130 °C for 30 min (Karger & Mazur, 1971). Excess acetic anhydride together with acetic acid formed in the reaction were removed by distillation under high vacuum at a temperature less than 70 °C.The residual oil, on cooling, solidified to 78 g (96%) of a red crystalline mass.

2.3. Exploring the feasibility of the chemical method by model molecule

Anhydrous d-EG (1.0 g) was reacted at a temperature (20–140 °C) with a large excess of mixed anhydride (4.0–10.0 g) for a certain time (2–24 h) (Lee, Baaske, & Carter, 1983, 1982). To the reactants barium hydroxide octahydrate (6.4–16.0 g) and water (60 ml) were added and the pH of mixture rose to above 11. Then reactants were kept boiling for an hour. The mixture was extracted with isopropyl alcohol and diethyl ether.

2.4. Determination of the substitution degree of HEG

In place of d-EG, anhydrous HEG (2.0 g) was reacted with mixed anhydride (10.3–24.0 g) at 130 °C for a certain time (4–24 h). And then the reactants hydrolyzed in the same way described in Section 2.3. EG was also collected via extraction with isopropyl alcohol and diethyl ether.

3. Results and discussion

3.1. The cleavage of model ether

Because of the comparability of the structure, it is necessary to make use of model molecules such as d-EG in place of HEG to explore the feasibility of this chemical method in advance. The cleavage rate of ethers (Eq. (1)) and the recovery rate of product (Eq. (2)) are two important parameters to reflect the process of model reaction.

According to ^{1}H NMR spectra of EG and d-EG, the chemical shifts of protons are depicted as follows:

$$\text{HO–CH}_2(a)\text{–CH}_2\text{–OH}, \text{HO–CH}_2(a)\text{–CH}_2(b)\text{–O–CH}_2\text{–CH}_2\text{–OH}; \quad \delta a = 3.66, \delta b = 3.71.$$

$$\text{The cleavage rate of ethers (\%)} = \frac{S_{3.66} - S_{3.71}}{S_{3.66}} \times 100\% \tag{1}$$

($S_{3.66}$ and $S_{3.71}$ are the integrals of protons at 3.66 and 3.71, respectively.)

$$\text{The recovery rate of product (\%)} = \frac{m_2}{m_1} \times 100\% \tag{2}$$

(m_1 is the calculated weight of the product; m_2 is the found weight of the product.)

Tables 1–3 show effect of temperature on the model reaction, effect of ratio of T-A Anh on the model reaction, effect of reaction time on the model reaction, respectively.

The cleavage rate of ether and the recovery data of product in the experiments are close to 100% from Tables 2 and 3, so we consider that the cleavage rate of ether

Table 1
Effect of temperature on the model reaction

Temperature (°C)	Cleavage rate of ether (%)	Recovery rate of product (%)
20	16.7	99.5–100.5
65	84.5	99.5–100.5
130	99.0–100	99.5–100.5
140	Carbonized $\leqslant$100%	

Reaction time = 24 h; d-EG:T-A Anh = 1:5 mol.

Table 2
Effect of ratio of T-A Anh on the model reaction

d-EG:T-A Anh (mol)	Cleavage rate of ether (%)	Recovery rate of product (%)
1:5	99.0–100	99.5–100.5
1:3	99.0–100	99.5–100.5
1:2	99.0–100	99.5–100.5

Reaction time = 24 h; temperature = 130 °C.

Table 3
Effect of reaction time on the model reaction

Reaction time (h)	Cleavage rate of ether (%)	Recovery rate of product (%)
24	99.0–100	99.5–100.5
14	99.0–100	99.5–100.5
4	99.0–100	99.5–100.5

Temperature = 130 °C, d-EG:T-A anh = 1:5 mol.

and the recovery data of product are 100% and the uncertainty around the values is the error of our experiments, and that is considered when estimating the precision of the method.

From the results shown in Tables 1–3, when temperature = 130 °C, reaction time = 4 h and d-EG:T-A Anh = 1:2 in mol, the recovery rate of the product and the cleavage rate of the ether can both approach to 100%. So we believe that hydroxyethyl groups in HEG where the chain length of hydroxyethyl unit linked to HEG equals to 1 can also be cleaved by mixed *p*-toluenesulfonic-acetic anhydride at 130 °C for a certain time and according to a ratio of OH/T-A Anh.

3.2. The cleavage of HEG

The ratio of galactose to mannan (G/M = 2:3, Scheme 1. According to the ratio of the integrals of respective protons on C_1 from ^{1}H NMR spectra) and the degree of the substitution of hydroxyethyl groups in the modified galactomannans are assumed as *a*/*b* and MS, respectively, the moles of OH (N_{OH}) in HEG is calculated by Eq. (3):

$$N_{OH}\ (\text{mol}) = \frac{3 \times (a+b) \times m_{HEG}}{M_{\text{repeated structure}} + 44 \times MS \times (a+b)}, \quad (3)$$

where m_{HEG} is the mass of HEG and $M_{\text{repeating structure}}$ is the molecular weight of repeating structure of guar gum.

If the cleavage rate of ethers equals to 100% and esters entirely hydrolyzed, the mass of EG ($m_{\text{ethylene glycol}}$) and the degree of the substitution of HEG can be calculated according to the Eqs. (4) and (5), respectively.

$$m_{\text{ethylene glycol}}\ (\text{g}) = \frac{62 \times MS \times (a+b) \times m_{HEG}}{M_{\text{repeated structure}} + 44 \times MS \times (a+b)} \quad (4)$$

$$MS = \frac{M_{\text{repeated structure}} \times m_{\text{ethylene glycol}}}{(a+b) \times (62 \times m_{HEG} - 44 \times m_{\text{ethylene glycol}})}, \quad (5)$$

where $m_{\text{ethylene glycol}}$ is the mass of EG extracted with isopropyl alcohol and diethyl ether.

3.2.1. The effect of the ratio of OH/T-A Anh on measurement of the degree of the substitution

Because of the powerful electron-withdrawing property of the sulfonite group, the group may attack the labile hydrogen in advance. Making sure that all ether bonds are ruptured, will reduce the ratio of OH/T-A Anh (Eq. (3)). But there will be great difficult in extracting EG from the reactant because of the large amount of deposition. So we should be explored an appropriate ratio of OH in HEG to T-A Anh.

Data in Fig. 1 show that the effect of ratio of OH/T-A Anh on the degree of the substitution (Eq. (5)) would not be distinctly reflected if the ratio exceeded 1:2.5. According to our experiment in fact, the ratio of 1:2.5 is a good choice.

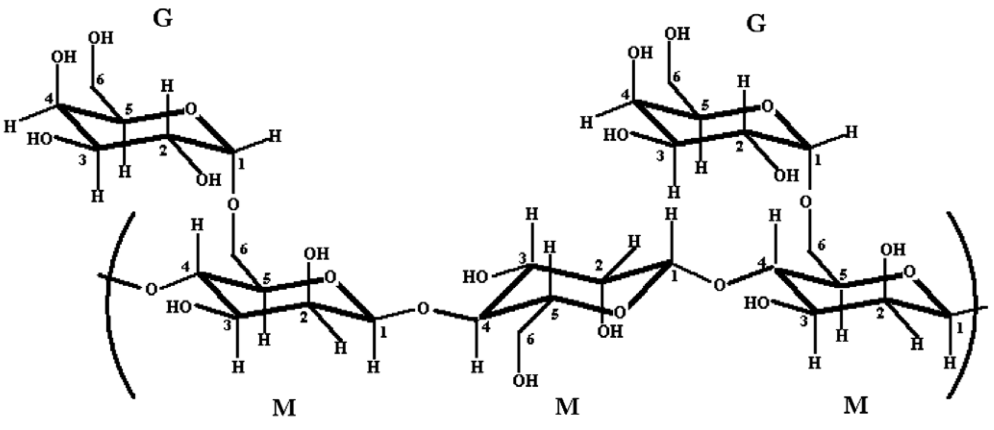
3.2.2. The effect of reaction time on measurement of the degree of the substitution

The data in Fig. 2 shows that the effect of reaction time on the degree of the substitution (Eq. (5)) would not be distinctly reflected if the reaction time exceeded 14 h. According to our experiment in fact, the optima time is 14 h.

3.3. Feasibility and creditability of the chemical method

Determination of the degree of substitution of HEG by mixed *p*-toluenesulfonic-acetic anhydride is aimed to collect EG from cleaved hydroxyethyl groups, and then the degree of the substitution can be calculated by Eq. (5).

The main resonance peak at $\delta = 3.66$ in ^{1}H NMR spectra of extracted products (Fig. 3) shows the existence of EG derived from the hydroxyethyl group and the high purity of EG. The resonance peak around $\delta = 3.71$ from the



Scheme 1. Repeating structure of guar gum.

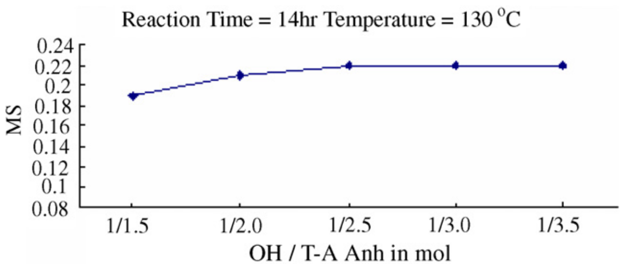


Fig. 1. Effect of ratio of OH/T-A Anh on measurement of the degree of the substitution.

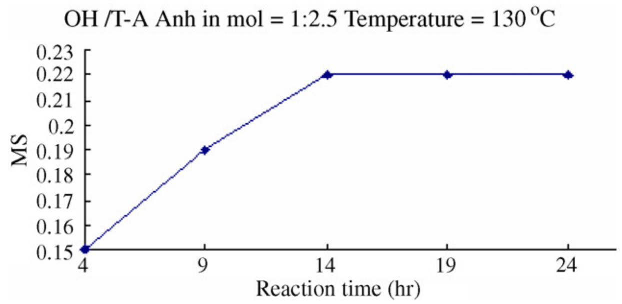


Fig. 2. Effect of reaction time on measurement of the degree of the substitution.

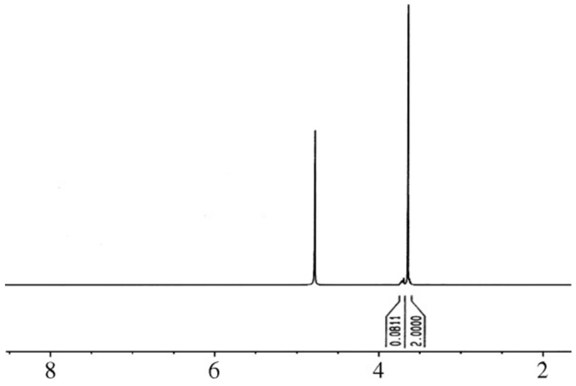


Fig. 3. ^{1}H NMR spectra of extracted products.

hydroxyethyl group is taken into account in further investigation. The other solo resonance peak comes from the D$_2$O.

In experiment of the model molecule of d-EG, the ether bond can be cleaved totally by mixed anhydride and EG can be entirely extracted by organic solvent. So hydroxyethyl groups in HEG have also be cleaved by mixed anhydride (Figs. 1 and 2). According to the recovery rate of EG in the blank reaction (when reaction time = 14 h, temperature = 130 °C and OH/T-A Anh = 1:2.5, the mixture of guar gum with EG was reacted with mixed anhydride, and the recovery rate of EG approached 100%), it was found that HEG does not have effect on EG derived from cleaved hydroxyethyl groups. So EG from cleaved hydroxyethyl groups can be entirely extracted like a model molecule.

All the experiment of exploring the effect of different factors and determination of the degree of the substitution of HEG show good agreements.

Considering merely d-EG as model molecule, a good result can be got for the time being when this method is applied to HEG, where the chain length of the hydroxyethyl unit linked to HEG equals to 1.

The errors of the method mainly come from the influences of the recovery data and the cleavage rate. According to the Eq. (5), the error in the recovery data is around 2.5%. The error in the cleavage rate is around 1.0%. So the precision of the method can reach to 96.5% at least.

Above all, the method of determination of the degree of the substitution of HEG by mixed *p*-toluenesulfonic-acetic anhydride is feasible and creditable, where the chain length of hydroxyethyl unit linked to HEG equals to 1.

4. Concluding remarks

In terms of reaction time = 14 h, temperature = 130 °C and OH/T-A Anh = 1:2.5, the method of determination of the degree of the substitution of HEG by mixed *p*-toluenesulfonic-acetic anhydride is feasible and creditable, and the precision of the method can reach to 96.5% at least, where the chain length of hydroxyethyl unit linked to HEG equals to 1.

References

Harry-O'Kuru, R. E., Moser, K. B., & Gordon, S. H. (1982). Colorimetric determination of the molar substitution of 2-hydroxybutyl and related starch ethers. *Carbohydrate Polymers, 17*(4), 313–318.

Karger, Michael Haward, & Mazur, Yehuda (1968). The clearage of ethers by mixed sulfonic-carboxylic anhydrides. *Journal of the American Chemical Society, 90*(14), 3878–3879.

Karger, Michael Haward, & Mazur, Yehuda (1971). Mixed sulfonic-carboxylic anhydrides. II. Reaction with aliphatic ethers and amines. *Journal of Organic Chemistry, 36*(4), 532–540.

Karger, M. H., & Mazur, Yehuda (1971). Mixed sulfonic-carboxylic anhydrides. I. Synthesis and thermal stability new synthesis of sulfonic anhydrides. *Journal of Organic Chemistry, 36*(4), 528–531.

Lee, Ying-Chi, Baaske, David M., & Carter, James E. (1983). Determination of the molar substitution ratio of hydroxyethyl starches by gas chromatography. *Analytical Chemistry, 55*(2), 334–338.

Lortz, Harlan J. (1956). Determination of the molar substitution ratio of low-substituted hydroxyethyl starch ethers. *Analytical Chemistry, 28*, 892–895.

Morgan, Paul W. (1946). Determination of ethers and ethers of ethylene glyol a modified alkoxl analysis. *Industrial Engineering Chemistry, Analytical Edition, 18*, 500–504.