

THE PHYSICAL BEHAVIOR OF WATER-SOLUBLE CELLULOSE POLYMERS

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ABSTRACT

The commercially available ionic and nonionic water-soluble cellulose polymers are sodium carboxymethylcellulose, hydroxyethylcellulose and methylcellulose. These polymers impart varying degrees of non-Newtonian behavior to solutions. The physical properties of aqueous and mixed aqueous solutions of these cellulose ethers are governed by the chemical nature of their solubilizing substituents and are discussed with special emphasis on molecular structure.

From a modest start in the early 1920's, water-soluble cellulose ethers now make an important contribution to modern industry. Today, the commercial product line is formidable, and new products are constantly being added. The manufacturing process for each of these derivatives usually involves:

1. Formation of alkali cellulose
2. Reaction with suitable organic reagent
3. Neutralization
4. Purification
5. Drying

Typical reactions and products are shown in Fig. 1.

Small amounts of water-soluble cellulose ethers dispersed in water greatly modify its over-all properties. The most obvious immediate change is an increase in the viscosity of the water. An interesting aspect of this viscosity increase is the fact that a single solution will appear to have a wide range of viscosities when different conditions of physical force are imposed on the solution.

These conditions of physical force may be conveniently referred to as high, intermediate or low stress. For example, rolling or spreading a liquid as if it were an ointment or lotion would be high stress. On the other hand, after the liquid has been applied, gravity and surface tension control flow. These forces are conditions of low stress. Intermediate stress can be typified by pouring a liquid out of a bottle. Thus, if a solution of a water-

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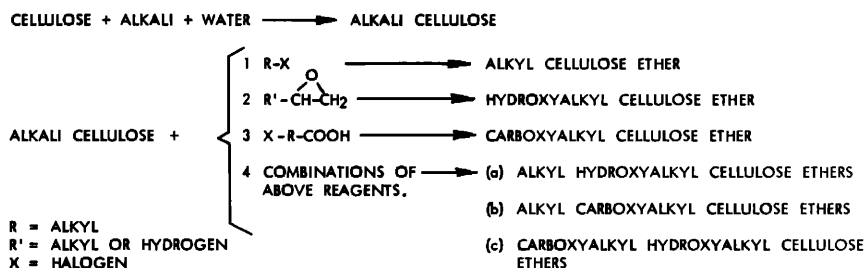


Figure 1.—Manufacture of cellulose ethers.

soluble cellulose ether appears to be a viscous syrup as it is poured from a bottle, it will behave as a runny liquid when applied as a lotion; yet, when high stress is removed it will instantly revert to a “molasses in January” consistency. These variations are pictured in Fig. 2. This type of flow behavior is referred to as pseudoplastic or non-Newtonian. There may also be a time-dependent consistency change usually called thixotropy. A different molecular weight or viscosity grade of polymer will behave in a similar fashion but to a different degree. The lower the molecular weight, the less change in viscosity will occur as stress conditions are varied. If viscosity does not change with stress, the solution is classified as Newtonian. Low molecular weight cellulose ether solutions are less pseudoplastic or non-

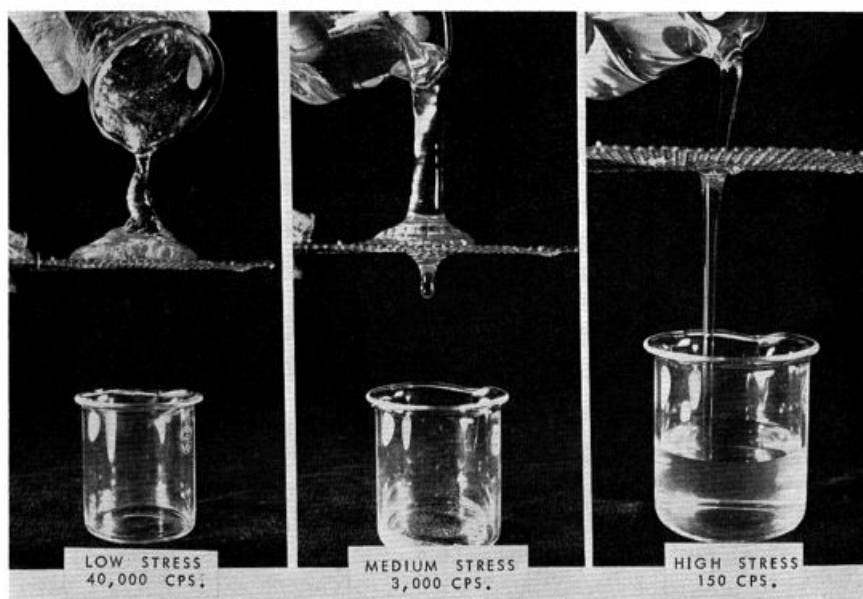


Figure 2.—A single pseudoplastic fluid acts differently under different conditions of stress.

Newtonian than the high molecular weight polymer solutions. These differences in viscosity-stress properties are shown in Fig. 3.

The foregoing discussion briefly shows how water-soluble cellulose polymers can impart divergent flow characteristics to water. Many of them also impart varied thickening properties to solvent systems other than plain water. Behavior of well-dispersed derivatives in these mixed solvent systems is similar to their behavior in water. However, the viscosity of the solvent must be taken into account. For example, if sucrose-water is the solvent and if this solvent is 50 times thicker than water, the

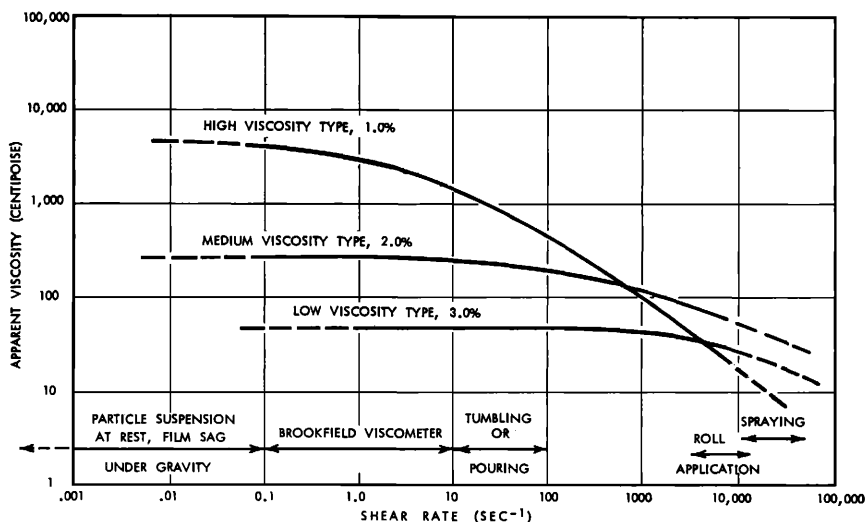


Figure 3.—Typical flow behavior of hydroxyethylcellulose.

resulting cellulose ether solution in the mixed solvent will be 50 times thicker than it will be in water. This behavior is predictable for many solvent-water mixtures, and is shown in Fig. 4.

In order to render cellulose soluble in solvent, chemical groups must be added. These substituents impart solvent attracting characteristics to the cellulose and act as wedges to force the cellulose molecule apart and break its inherent physical bonds. Some of the groups which make cellulose hydrophilic (water attracting) are shown in Fig. 5. Also shown are representations of how water is believed to interact with these groups. The ionic groups, which separate into positive and negative components, provide a strong dissolving force. The components with positive charges migrate away from the cellulose chain, leaving only negative charges. Since like charges repel, the cellulose chain expands and exposes hydrophilic sites to the solvent. The nonionic groups provide dissolving power

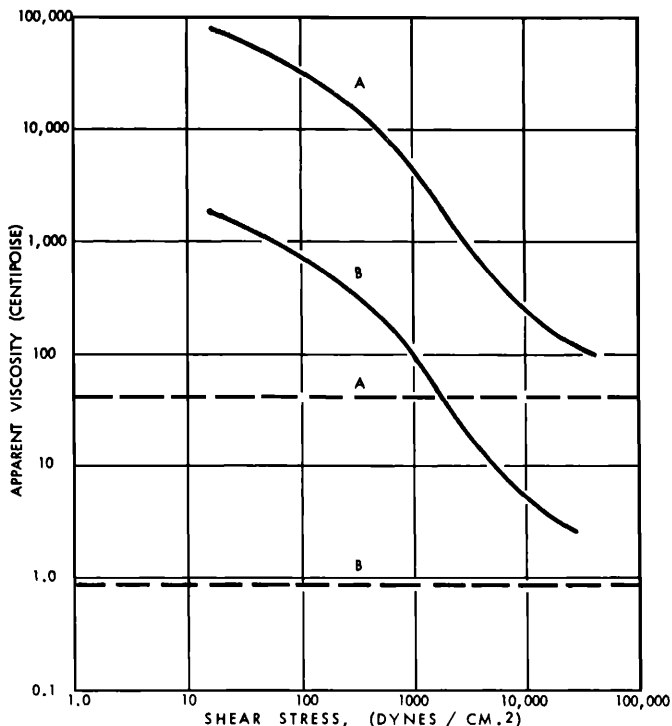


Figure 4.—Flow behavior of well-dispersed carboxyalkyl- and hydroxyalkylcellulose ethers in (A) sucrose-water and (B) water solid; curves are solutions; broken curves are solvents.

mainly by hydrogen bonding with the solvent. The oxygen and hydrogen of the solvent interact with like groups in the polymer. Figure 6 summarizes the hydrophobic (or water-repelling) and the hydrophilic groups of typical ionic and nonionic water-soluble polymers.

Many of the physical properties imparted to aqueous solutions by hydroxyalkylcellulose are governed by the chemical nature of its solubilizing substituent. When ethylene oxide is added to cellulose, no hydroxyl groups are lost. They are merely transferred to the end of the substituent. Such a derivative is more hydrophilic than alkyl cellulose derivatives, which have far fewer hydroxyl groups. This fact can be used to explain why alkyl celluloses precipitate at elevated temperature, whereas hydroxyethylcellulose does not. Figure 7 depicts the solvent water interacting with hydrophilic ether and hydroxyl groups. These hydrophilic groups are separated by hydrophobic ethylene groups ($-\text{CH}_2-\text{CH}_2-$). At normal room temperature, it is suggested that these chains are relatively motionless, as depicted by the uppermost structure in the figure. However, as the temperature increases, the hydrophobic group becomes excited and begins to vibrate between the ether linkages in some-

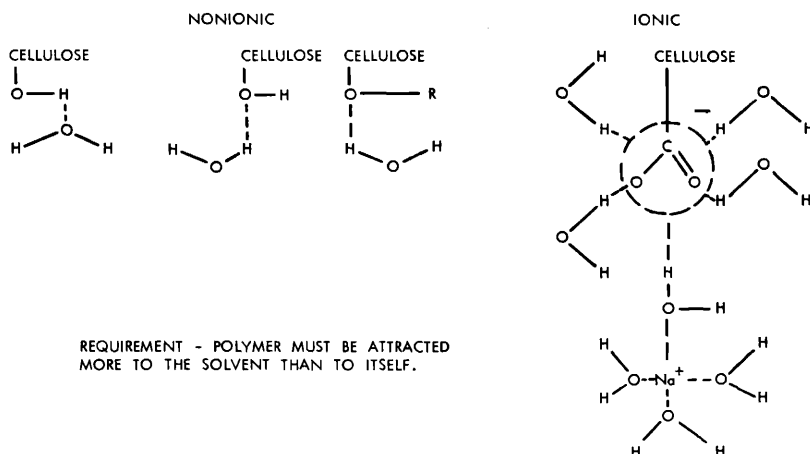


Figure 5.—Forces for dissolving hydrocolloids in water.

what the same manner as a jumping rope. In essence, the hydrophobic volume increases, causing the hydrophilic ether linkages to become less accessible to the water solvent. A similar mechanism is shown at the bottom of Fig. 7 for an alkyl cellulose ether. Since the hydroxyethylcellulose has terminal hydroxyl groups which are not affected by this increased hydrophobic sphere, it remains soluble even at the boiling point of water. In the alkyl cellulose ether, insufficient terminal hydroxyls are available to keep the polymer soluble as the hydrophobic volume of the alkyl substituent increases. At some point (or temperature) the derivative precipitates from water. If the water is made a poorer solvent, for instance by adding salt to it, we can demonstrate the same phenomenon with hydroxyethylcellulose as is exhibited with alkyl cellulose in plain water.

Another interesting fact about the solubility of hydroxyethylcellulose is its relative solubility in solvents containing salts with multiple ionic charges. It has been found that hydroxyethylcellulose is less soluble in solutions containing multiple negative charges than in solutions containing

AQUEOUS SOLUBILITY FACTORS

| POLYMER | NO. OF HYDROPHOBIC GROUPS / UNIT | NO. OF ETHER GROUPS/UNIT | NO. OF -OH GROUPS/UNIT |
|-------------------|---|--------------------------|------------------------|
| CARB. ALKYL CELL. | NONE | 1.0 | 2.0 |
| HYD. ALKYL CELL. | 1.5 -CH ₂ -CH ₂ - | 1.5 | 3.0 |
| HYD. ALKYL CELL. | 2.5 -CH ₂ -CH ₂ | 2.5 | 3.0 |
| ALKYL CELLULOSE | ~ 2 -CH ₃ | ~ 2 | ~ 1 |

DECREASING
THERMAL
STABILITY
IN WATER

Figure 6.—Aqueous solubility factors.

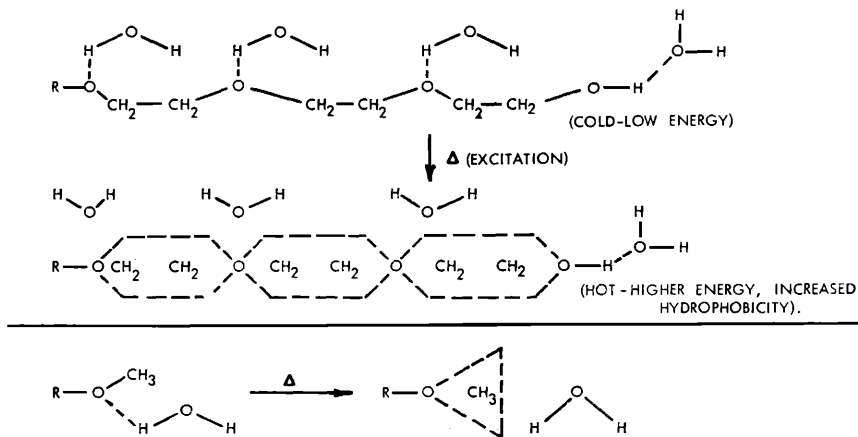


Figure 7.—Factor governing interaction of ether links with water.

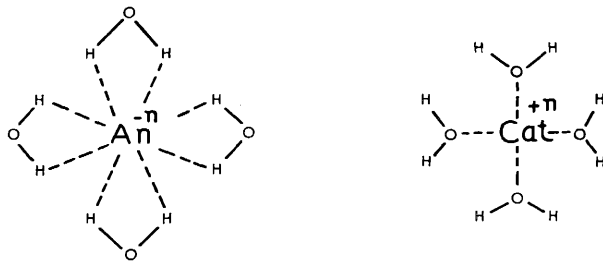


Figure 8.—Suggested action of polyvalent ions.

multiple positive charges. As shown in Fig. 8, it is proposed that the solvent molecules orient themselves so that fewer solvent hydrogens are available for associating with the cellulose molecules through its ether (C—O—C) linkages.

These examples only suggest the versatility and sophistication of the water-soluble cellulose ethers. They serve to suggest that, whereas a single sample may not perform as desired in an end use, many other variations of cellulose ethers exist which may turn the trick. The formulator is advised to seek information and assistance from the manufacturer of the cellulose ether in question before embarking on a program involving complex aqueous systems.

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