

Some Views on the Gelation of Aqueous Solutions of Ethyl Cellulose on Heating

SVEN SÖNNERSKOG

Mo and Domsjö AB, Örnsköldsvik, Sweden

Ethyl cellulose, containing 1.2—1.4 ethoxy groups per anhydroglucose residue, dissolves in cold water (below 20° C) to a clear viscous solution. Maximum clarity is obtained by cooling the solution until freezing. The viscosity increases with decreasing temperature, but a range of irregularity is observed just when the main part of the sample has passed into solution. The following diagram shows some measurements of the viscosity of a 2 per cent solution on cooling from 25 to 5° C.

The long horizontal part of the curve arises the question whether the dissolution involves some *special* kind of interaction between solvent and solute. Below this part the slope indicates no irregularities. Only the range between the two knees diverges from what could be considered as a standard.

If we compare the rapid increase in viscosity above the right knee-point with the comparatively small gradient at lower temperatures, we establish that some kind of immobilization of solvent molecules takes place simultaneously with a more regular association. The dissolution should therefore

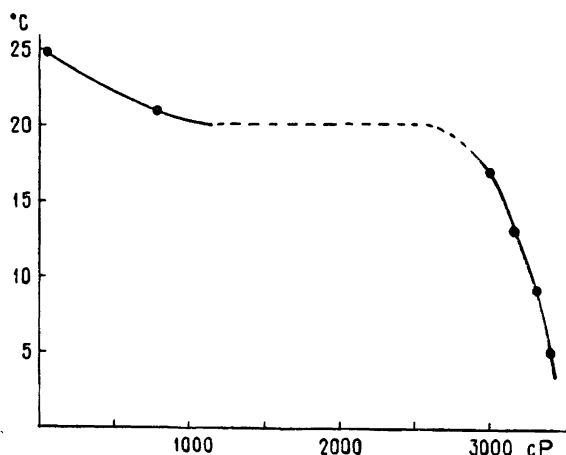
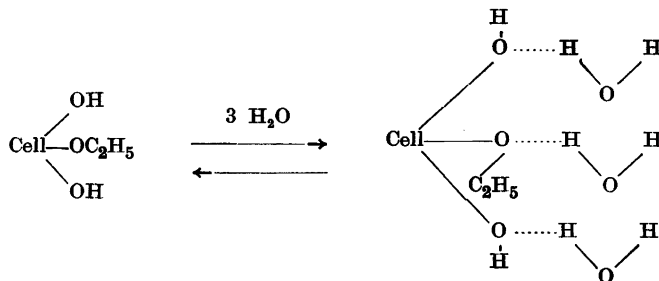


Fig. 1. The relation between temperature and viscosity for water soluble ethyl cellulose between 5 and 25° C.

be considered as a superposition of two processes, firstly a solvation of the hydroxyl groups by the water dipoles, secondly *an aggregate formation* between the layers of hydrated cellulose chains. The first phenomenon takes place at all temperatures, while the second mainly is localized to the neighbourhood of the range of irregularity.

What is stated above can be readily understood if we consider that dissolution of the cellulose ether implies an orientation by dipole forces between the water molecules and the hydroxyls or ethoxy radicals in the cellulose chains. The degree of orientation is depending on the temperature and increases with the ratio $1/T^1$. (T = temp. in °K.) When the dipole forces are in equilibrium with the thermal movement energy of water molecules, a parallel or an antiparallel orientation might occur. The hydration may be symbolized as follows:



Such a molecule, however, would be able to contribute to an aggregate formation, for instance by further dipole interaction or simply a cross linkage formation by secondary valence forces. If two hydrated chains form an aggregate, the result is a network where the distance between adjacent chains roughly is determined by the sum of two hydrogen bridges (5.5 Å). Secondary valence lattices of noticeable stability do not show higher distances between their net planes than 4.5 Å¹. The state represented by the formula must therefore be considered as a fairly supersaturated one which tends to contract, for instance by splitting off some immobilized water molecules. In fact, if a 3 % solution is heated in a test tube until complete gelation takes place, water is gradually liberated until the solid gel is made free from the glass walls. This phenomenon should not be confused with the first period in the gelation process, where the volume increases^{2, 3} thanks to the removal of highly compressed water molecules who have taken part in the dissolution but not in the aggregate formation.

It should be noticed that this immobilization of water molecules is analogous to the arrangement of crystal water in certain organic molecules, for instance in oxalic acid dihydrate⁴. The cohesion forces which are involved in aggregate formation there are the same as in the case of ethyl cellulose.

If we now proceed from the picture of the dissolved ethyl cellulose as being a framework of hydrated chains partly or totally immobilized by secondary valence forces between the hydroxyl or ethoxy groups, it is easy to understand that the irregularity in viscosity, shown in Fig. 1, as well as the gelation on heating, disappear, when an increasing part of the hydroxyls is displaced from the original position, for instance by introducing ethylene oxide in the ethyl cellulose. When a hydroxyl radical adds ethylene oxide catalytically, the displacement of the hydroxyl group from the original position corresponds to about 3 Å. The hydroxyl is no longer able to take part in the aggregate formation mentioned above and cross linkages with shorter bridging than 4.5 Å are very unlikely if we consider the large energy content which would be involved in a shortening of the linkages with 3 Å. The dehydration of glycol groups in cellulose can be estimated from the viscosity-temperature diagram of glycol cellulose. Fig. 2 shows some values measured on a 2 per cent solution. The curve is a hyperbola $VT = \text{const.}$, which is the same as $V = \text{const. } 1/T$, or in other words the *relation between temperature and the degree of orientation of rigid dipoles*.

If we now introduce various amounts of glycol groups into watersoluble ethyl cellulose, part of the hydroxyls become unsuitable for taking place in the aggregate formation which would imply a lower rigidity of the gel formed on heating a solution. The following diagram shows the gel hardness for a few glycol ethers of ethyl cellulose. The measurements are carried out on 2 per cent solutions at 80° C, using a test tube of stainless steel, fitted with an inlet for a metallic rod ending with a surface of 1 cm². The rod could be loaded with concentric weights on the upper part.

The number of glycol groups are calculated from the total amount of ethylene and ethyl iodide formed by combustion with hydroiodic acid, supposing the ethoxy content known ($DS = 1.2$).

The similarity between the decrease of viscosity of glycol cellulose on heating and the weakening of the gel rigidity of ethyl cellulose by introducing glycol groups allows us to suppose that removal of purely oriented water molecules is the essential change that takes place on gelation. The glycol groups in the modified ethyl cellulose prevent part of the water molecules to join in the aggregate formation resulting in a corresponding decrease of gel hardness. Most of the water molecules fixed at the cellulose chains only by dipole cohesion are sloughed off on heating, causing a sudden increase of rigidity. In pure ethyl cellulose gels the remaining network is strong enough to keep the lattice structure, but when many glycol groups are present, the number of cross linkages is reduced and the lattice breaks down. This might be the reason why ethyl ethers of cellulose containing more than one glycol

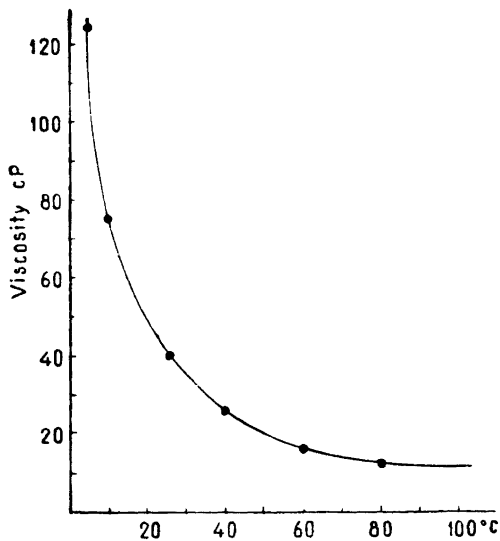


Fig. 2. Relation between temperature and viscosity for glycol cellulose between 5 and 80° C.

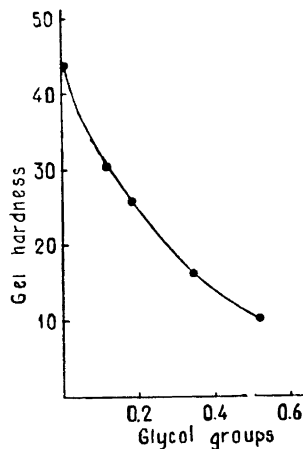


Fig. 3. Gel hardness of ethyl cellulose containing 0.11—0.52 glycol groups per anhydroglucose residue.

group hardly give any gel at all but flocculate very easy on heating to the gelation point.

SUMMARY

Ethyl ethers of cellulose, showing a degree of substitution between 1.2—1.4, dissolve in cold water to a clear, viscous solution. On cooling, a sudden increase in viscosity is observed just when the main part of the ether has passed into solution. The phenomenon is explained by an analysis of the possibilities of cross linking as well as simple orientation of the water dipoles with regard to the hydroxyls of the cellulose chains. The gelation on heating is shown to be essentially due to a removal of purely oriented water molecules.

REFERENCES

1. Mark, H. *High polymers* Vol. II (1940) pp. 91 and 129.
2. Heymann, E. *Trans. Faraday Soc.* 31 (1935) 846.
3. Heymann, E. *Trans. Faraday Soc.* 32 (1936) 462.
4. Hoffman, H., and Mark, H. *Z. Phys. Chem.* 111 (1924) 321.

Received June 6, 1948.