Reports of the Academy of Sciences of the USSR

E. F. NEKRYACH and Corresponding Member of the Academy of Sciences of the USSR A. V. DUMANSKII

1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 121, No. 1

PHYSICAL CHEMISTRY

E. F. NEKRYACH and Corresponding Member of the Academy of Sciences of the USSR A. V. DUMANSKII

HEATS OF WETTING OF ETHERIFIED CELLULOSE BY WATER

The possibility of rupture and re-formation of the hydrogen bonds present in cellulose determines a number of important properties of cellulose materials (hygroscopicity, rate of dissolution, and others). Bond rupture may result from mechanical and chemical dispersion, solvation, or etherification of hydroxyl groups.

Very interesting results obtained in studying the properties of low-substituted cellulose ethers could be explained only by taking into account the possibility that new free hydroxyl groups arise as a result of the rupture of hydrogen bonds between cellulose macromolecules.

In recent years it has been established that, when a small number of acetyl (1), methoxyl, or ethoxyl (2) groups—considerably less hydrophilic than hydroxyl groups—are introduced into the cellulose molecule, the hygroscopicity of the cellulose material not only does not decrease but even increases. This unexpected fact is explained by the circumstance that, when ether groups are introduced into the cellulose molecule, the distance between macromolecules increases and hydrogen bonds are ruptured; moreover, the number of hydroxyl groups thereby appearing that are capable of binding water exceeds the number of etherified hydroxyl groups. With further etherification, the hydrophilicity of cellulose materials, after reaching a definite maximum, decreases, and products with a high degree of etherification become hydrophobic.

The number of works devoted to the study of the hydrophilic properties of low-substituted cellulose ethers is very small, and the methods of investigation were often very imperfect. It was therefore of interest to carry out such a study, applying, for the quantitative evaluation of the hydrophilicity of cellulose and its derivatives, the method of measuring heats of wetting, which is the most well-founded from the theoretical point of view (3).

In the present work, in addition to studying the influence of the degree of etherification of cellulose on its hydrophilicity, the influence of the chemical nature

Fig. 1. Heats of wetting of dry samples. 1 –methylcellulose from cotton linters, 2 –methylcellulose from viscose silk, 3 –ethylcellulose from cotton linters, 4 –oxyethylcellulose from cotton linters

Figure 1: Fig. 1. Heats of wetting of dry samples. 1 –methylcellulose from cotton linters, 2 –methylcellulose from viscose silk, 3 –ethylcellulose from cotton linters, 4 –oxyethylcellulose from cotton linters

of the substituting groups and of preliminary treatment of the cellulose was also investigated. Samples of methyl-, ethyl-, and oxyethylcellulose obtained from cotton linters, and methylcellulose from viscose silk, were examined. The method for measuring heats of wetting in an adiabatic calorimeter has been described previously (4). The results obtained are shown graphically in Fig. 1. As can be seen from the figure, the nature of the change in the heats of wetting of all the cellulose materials studied as a function of the degree of etherification is completely identical: at first the heats of wetting increase, at a certain degree of etherification reach a maximum, and then decrease.

The absolute values of the heats of wetting of ethers depend on two factors: the chemical nature of the ether group and the structure of the initial cellulose material. A comparison of the curves $Q = f(\gamma)$ for methyl-, ethyl-, and oxyethyl celluloses obtained from cotton linters shows that introducing into the cellulose macromolecule a radical with a larger number of carbon atoms makes the substitution product more hydrophilic. It is very interesting that the maxima of the heats of wetting for these samples are observed at one and the same degree of etherification, namely about 8%.

The treatment of cellulose before etherification has a great effect on the hydrophilicity of cellulose ethers. Curves 1 and 2 refer to methylated cellulose: the first to methylcellulose obtained from cotton linters, and the second to that obtained from viscose silk. According to the available literature data, the heat of wetting by water of viscose silk is considerably higher than the heat of wetting of cotton and ranges from 20 to 22.5 cal/g (5). As a consequence, the maximum hydrophilicity of the methylcellulose obtained from it is also higher than the maximum for methylcellulose from cotton; moreover, the differences between the maximum values of the heats of wetting of the etherified samples and the heats of wetting of the starting materials are fairly close to one another (6–9 cal/g and 6 cal/g). In addition to the difference in the absolute value of the maxima of the heats of wetting, a difference is also observed among the methylcellulose samples in the position of the maxima: the highest heat values for methylcellulose from viscose silk are observed at a substantially higher degree of substitution (about 22%).

Fig. 1. Heats of wetting of dry samples. 1 –methylcellulose from cotton linters, 2 –methylcellulose from viscose silk, 3 –ethylcellulose from cotton linters, 4 –oxyethylcellulose from cotton linters.

Institute of General and Inorganic Chemistry
Academy of Sciences of the Ukrainian SSR

Received
27 II 1958

REFERENCES

1. J. C. Bletzinger, *Ind. and Eng. Chem.*, **35**, 474 (1943); W. H. Aicken, *Ind. and Eng. Chem.*, **35**, 1206 (1943); N. I. Nikitin, *Bumazhn. prom.*, No. 1–5 (1947).
2. N. I. Nikitin, N. I. Klenkova, *Collection: Studies in the Field of High-Molecular Compounds*, Publishing House of the Academy of Sciences of the USSR, 1949, p. 138; N. I. Klenkova, N. I. Nikitin, *ZhPKh*, **27**, 171 (1954).
3. A. G. Pasynskii, *Koll. zhurn.*, **8**, 53 (1946); A. Tager, *Solutions of High-Molecular Compounds*, Moscow-Leningrad, 1951, p. 147.
4. A. V. Dumanskii, E. F. Nekryach, *Koll. zhurn.*, **15**, 91 (1953); E. F. Nekryach, *Zav. lab.*, **21**, 12448 (1955).
5. H. J. White, H. Eyring, *Text. Res. J.*, **17**, 529 (1947); M. Wahba, *J. Phys. and Coll. Chem.*, **52**, 1197 (1948).

Note: Figure translations are in progress. See original paper for figures.