P2.12a. STUDY OF HYDROLYSED HUMIC SUBSTANCES BY ONE AND TWO DIMENSIONAL NMR SPECTROSCOPY

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The composition and structure of products of mild acid hydrolysis (0.2 M HCl) of several humic (HA) and fulvic acids (FA) was studied with quantitative $^{13}$C and homo-
and heteronuclear correlation 2D NMR spectroscopy (HAP and FAP, solid precipitates, HAD and FAD, water-soluble products). The quantitative determination of the carbon content of main humic fragments leads to suggest different types of organization of the main structural moieties in HA and FA. The HA aggregates are build up of a non-hydrolysable polyphenolcarboxylic network with carbohydrate and aliphatic moieties being attached as substituents. The structure of FA can be described as a polycondensate of low-molecular weight phenolic components bridged with hydrolysable bonds with some participation of humic-like structures.

Correlation 2D spectra provide additional information on the partial structures present in humic substances. The HAD of high-land peats show the correlation patterns similar to corresponding FA in homonuclear 2D NMR spectra, in which intact carbohydrates are present together with substantial amounts of methyl sugars. The HAD products of 6 M HCl or H$_2$O$_2$ hydrolysis contain large amounts of amino acids. The FAD of low-land peats contain only minor amounts of carbohydrates, which are nearly absent in corresponding HAD. Instead of sugars and polyols, substantial amounts of methyl ethers and esters give rise to corresponding C,H correlations. Series of peaks correlating with terminal CH$_3$ signal at 0.9 ppm correlating with resonances downfield to 2.5 ppm are also present in the hydrolysates of low-land peats. They are assigned to protons of functionalized aliphatic units, bearing electronegative groups, such as carbonyl derivatives, amino acids and phenyl ring [1].

Aromatic region of the HAD of the low-land peats shows series of prominent homonuclear 2D NMR cross peaks being attributable to ortho-proton disubstituted benzene rings with ranges of chemical shifts which indicate a substantial proportion of oxygen (shielding) and carbonyl derivative (deshielding) substituents. These correlations are nearly absent in HAD of the high-land peat, indicating a higher degree of substitution of benzene rings.


P2.12b. ИЗУЧЕНИЕ ПРОДУКТОВ ГИДРОЛИЗА ГУМУСОВЫХ ВЕЩЕСТВ С ПОМОЩЬЮ 1D И 2D СПЕКТРОСКОПИИ ЯМР

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Состав и строение продуктов мягкого кислотного гидролиза (0.2 M HCl) гуминовых (HA) и фульвокислот (FA) торофор изучен с помощью количественной $^{13}$С и гомо- и гетероядерной корреляционной 2D спектроскопии ЯМР (HAP и FAP, твердые остатки; HAD и FAD, водорастворимые продукты). Количественное определение содержания углерода основных структурных фрагментов позволило предположить, что строение макромолекул HA и FA существенно различается. Молекулы HA состоят из негидролизуемого полиинолкарбоксильного ядра, замещенного карбогидратными и алифатическими остатками. Строение FA может быть представлено в виде поликонденсата низкомолекулярных фенольных фрагментов, объединенных гидролизуемыми связями, с включением гуминоподобных структур.

Двумерные корреляционные спектры предоставляют дополнительную информацию о структурных компонентах гумусовых веществ. COSY-спектры
P2.13a. NMR SPECTROSCOPY INVESTIGATIONS OF POLYVINYLTRIMETHYLSILANE STRUCTURE, CONFORMATION AND MOLECULAR DYNAMICS

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Polyvinyltrimethylsilane (PVTMS) was prepared in Institute of Petrochemical Syntheses and immediately caused the great interest of investigators and experienced specialists because of the high selectivity of gas separation by PVTMS films and the possibility to create membranes permitting to enrich air by oxygen up to 30—40 %.

However, up to date there is insufficient information on PVTMS structure, polymer chain conformation, molecular dynamics, and gas transfer mechanism.

The goal of this study was to receive a maximal possible information on PVTMS by several NMR methods with a partial usage of theoretical calculations. The 1D and 2D methods of 1H, 13C, 20Si, 2D NMR spectroscopy were used. Spectra were obtained at different temperatures, solution concentrations and also in solid state with MAS and Broad Line techniques. The results obtained permitted to propose the model of gas transfer through the “ideal” PVTMS film.

PVTMS obtained by “classic” synthesis has been found to consist of straight and essentially isotactic polymer chains. From relaxation measurements, it follows that 10% of SiMe3 groups are characterized by very short relaxation times.

Experiments on model compounds, calculations and NMR investigation results indicated that there is a possibility of cavities formation inside some polymer chain segments, their volumes being close to O2 molecule “volume”.


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