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[Lab. of Pharm. Physical Chemistry]

Mechanolytic Analysis of Glucose-Based Polysaccharides As Studied by Electron Spin Resonance.

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We report the detailed study of mechanically induced free radical (Mechanoradical) formation of glucose-based polysaccharides such as cellulose and amylose based on electron spin resonance (ESR) on its comparison with plasma-induced radicals of polysaccharides. The systematic computer simulations disclosed that the observed spectra of cellulose consist of three kinds of spectral components, while those of amylose consist of two kinds of spectral components. One of the most intriguing facts is that the component radicals are all glucose-derived mid-chain alkyl-type radicals as in the case of plasma irradiation, although it is known that mechanoradicals are produced by the polymer main-chain scission. It can be reasonably assumed, therefore, that the mechanoradicals primarily formed by 1,4-glucosidic bond cleavage of polysaccharides at room temperature underwent a hydrogen abstraction from the glucose units to give rise to the glucose-derived mid-chain alkyl-type radicals. Furthermore, it was suggested that cross-linking reactions simultaneously occur accompanied by a decrease in the molecular weight in the course of vibratory milling.

[*Yakugaku Zasshi*, **119**, 929-935 (1999)]

[Lab. of Pharm. Physical Chemistry]

Effect of Plasma-Treatment on Suppression of Drug Adsorption to the Surface of Plastic Infusion Bag.

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Plastics has been widely used at the hospitals and dominates the field of the manufacture of infusion bag sets and packaging materials as a disposable product. Recently, it has been reported, however, that expected drug effects could not be obtained owing mainly to the drug adsorption to the surface of plastic bags observed when several injection drugs such as nitroglycerin, isosorbide dinitrate, diazepam, and insulin were injected mixedly into a certain plastic intravenous bags. And there is a possibility of the occurrence of chemical reactions between the added drugs and the surface of plastic bags. We also can not deny the possibility of the dissolution of softener from the plastic bags. We have been working on the nature of plasma treatment of polymer surfaces by irradiation of low temperature plasma and its pharmaceutical application studies. In this study, we obtained the data concerning the effect of plasma treatment on the reduction of adsorption of insulin to the surface of ethylene-vinylacetate (EVA) bag.

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[Lab. of Pharm. Anal. Chemistry]

Electronic Spectra of the Electrogenerated 1,4-Benzoquinone π -Dianion and the Strongly Hydrogen-Bonded Charge-Transfer Complex with Methanol.

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Electronic spectra of the active π -electronic dianion of 1,4-benzoquinone and its hydrogen-bonded complex with CH_3OH , generated at sequential electroreduction steps, have been discussed from the points of view of the observation techniques and n - σ charge-transfer interaction of the dianion with a weak hydrogen donor. The improvement method involving rapid circulation of the electrolyzed solution via a photodiode array detector to avoid comproportionation and side reactions was applied to successful measurements of the clear spectra resulting from the dianion generation. CNDO/S-CI calculations well reproduced the longest-wavelength band observed for the dianion, assigning to the benzenoid ${}^1\text{B}_{3u} \leftarrow {}^1\text{A}_g$ band under D_{2h} symmetry. Hydrogen-bonding interaction of the 1,4-benzoquinone dianion with CH_3OH allows the ${}^1\text{B}_{3u} \leftarrow {}^1\text{A}_g$ band to be blue-shifted. This behavior has been well explained in terms of the strong n - σ type charge-transfer interaction of the dianion with CH_3OH . These results have been extensively discussed with regard to coupled electron and proton transfer reactions in the quinone-hydroquinone redox system.

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[Lab. of Pharm. Anal. Chemistry]

The D_{2d} Structure and Easy Rotation around the C=C Bond of the Tetracyanoethylene Dianion.

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The structural and spectral characteristics of the tetracyanoethylene dianion (TCNE^{2-}) have been investigated. The two-electron addition to the antibonding LUMO of TCNE causes the easy rotation around the C=C bond characterized by the formal single bond. The spectral measurements and MO calculations gives results that TCNE^{2-} preferentially adopts the D_{2d} and D_{2h} structures in CH_3CN and CH_2Cl_2 , respectively.