

ABSTRACTS

named lower limit and upper limit, and that the viscoelastic behavior appeared markedly between these two limits.

Below the lower limit of stress no deformation was observed. The bentonite in swelling liquids showed the viscoelastic behavior different from that in non-swelling liquids. The upper limit was assumed to be a value above which local breakdown of the structure of paste occurs. This upper limit was compared with the critical value obtained from a uniaxial compression test and that from a direct shear test used in soil mechanics. The upper limit σ_2^* was related to the shear fracture, and was expressed experimentally by the following equation,

$$\sigma_2^* = A \exp(k \cdot C)$$

where C the concentration of bentonite and A and k were constants. σ_2^* takes higher value in swelling liquids than in non-swelling liquids.

Effect of Adjacent Group on the Rocking Frequencies of Methyl Group

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*Nippon Kagaku Zasshi, (Journal of the Chemical Society of
Japan, Pure Chemistry Section) 83, 997 (1962)*

The CH_3 and CD_3 rocking frequencies, γ_{CH_3} and γ_{CD_3} , of $(\text{CH}_3)_n\text{XH}_{m-n}$ molecules and their deuterium derivatives are studied in relation to the type of X atom in groups IV~VII of the periodic table, where m is the valence of X atom and n an integer from 1 to m . The frequency shifts are ascribed to changes in the force constant for the deformation of H-C-X angle, and can be expressed as

$$\gamma_{\text{CH}_3} = 582 \log(x_X/r_{\text{CX}}^2) + 1045$$

$$\gamma_{\text{CD}_3} = 416 \log(x_X/r_{\text{CX}}^2) + 778$$

for all undeuterated and deuterated molecules examined except for some cases where considerable coupling exists between the rocking and other modes of vibrations. Here x_X represents the electronegativity of X atom and r_{CX} the C-X bond length. The relation between two formulae can be theoretically interpreted by taking into consideration the change of the kinetic energy matrix on deuteration of the methyl group.

If these formulae and similar ones previously proposed by one of the authors for the symmetrical deformation frequencies are assumed to hold for the molecules such as CH_3NO_2 and CH_3CCl_3 , the group electronegativity of the radical directly bonded to the methyl group is derived from the frequencies observed for the molecule. The results are compared with other sets of the values obtained empirically from various spectroscopic relations.