

ABSTRACTS

Inductive Effect of Substituents on the Symmetrical Methyl Deformation Frequencies of Aliphatic Hydrocarbons

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*Nippon Kagaku Zasshi (Journal of the Chemical Society of
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In order to discuss the inductive effect of polar group upon methyl group in a molecule, the symmetrical methyl deformation frequencies δ_{CH_3} of $\text{CH}_3(\text{CH}_2)_{n-1}\text{XH}_{m-1}$ molecules were measured, where X represents an atom in groups IV~VII of the periodic table, m the valence of X atom and n the carbon number of the molecule.

For $\text{CH}_3\text{XH}_{m-1}$ molecules ($n=1$), a linear relationship was found to exist between the frequency and logarithm of the electronegativity x_X of X atom for each row and column of the periodic table. These frequency variations are ascribed to change in the deformation force constants, and can be expressed as

$$\delta_{\text{CH}_3} = 375 \log \left(\frac{x_X}{r_{\text{CX}}^2} \right) + 1366$$

where r_{CX} is the C-X bond length. This equation holds not only for $\text{CH}_3\text{XH}_{m-1}$ molecules but also for the series $(\text{CH}_3)_2\text{XH}_{m-2}, \dots, (\text{CH}_3)_m\text{X}$ within the error of $\pm 1\%$.

Frequency variations due to the change of the carbon number of $\text{CH}_3(\text{CH}_2)_{n-1}\text{XH}_{m-1}$ molecule ($n \geq 2$) can be interpreted by a modified equation in which the factor $\{(x_{\text{C}} + 0.40\varepsilon_X\sigma^{n-2})/r_{\text{CC}}^2\}$ is used instead of (x_X/r_{CX}^2) in the above equation. Here, r_{CC} is the C-C bond length, x_{C} the electronegativity of carbon atom, ε_X the induced charge on the carbon atom adjacent to X atom, and σ the ratio of the induced charges at any two adjacent carbon atoms in the alkyl chain.

Dielectric Properties of Emulsions. (III)

Dielectric Behavior of W/O Emulsions

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Dielectric constants and electrical conductivities of W/O emulsions at rest and under shear were measured over a wide range of concentration and at frequencies ranging from 20 cps. to 5 mc.

Striking dielectric dispersions due to the interfacial polarization were observed at high frequency range above 100 kc., while the electrode polarization was found below 1 kc.

It was found that the dielectric dispersions due to the interfacial polarization

ABSTRACTS

are represented approximately by the circular-arc rule. Both the limiting dielectric constants at low frequencies and the conductivities at higher frequencies decreased on application of shearing stress. It is considered that these changes in the dielectric properties of emulsions under shear may be caused by the breaking up of particle agglomerates. The limiting dielectric constants at high frequencies were subjected to no shearing effect, and are expressed best by the Bruggeman equation over the whole range of concentration. The data are discussed in the light of the previous theory on the interfacial polarization.

(d, α) Reactions on O^{16} , N^{14} and C^{12} by 14.7 MeV Deutrons

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Angular distributions of α particles resulting from $O^{16}(d, \alpha_0)N^{14}$ (ground state), $N^{14}(d, \alpha_0)C^{12}$ (ground state), $N^{14}(d, \alpha_1)C^{12}$ (first excited state), $C^{12}(d, \alpha_0)B^{10}$ (ground state) and $C^{12}(d, \alpha_1)B^{10}$ (first excited state) reactions were studied. α particles from the $O^{16}(d, \alpha_0)N^{14}$, $C^{12}(d, \alpha_0)B^{10}$ and $C^{12}(d, \alpha_1)B^{10}$ reactions exhibited forward peaks and backward peaks simultaneously, while α particles from $N^{14}(d, \alpha_0)C^{12}$ reaction showed forward peaks and oscillatory behavior.

α particles leaving N^{14} and C^{12} nuclei in their $T=1$ state were also observed in the forward angle, and the isotopic spin conservation rule seemed to be violated.

The reaction mechanism is then discussed on the basis of the surface direct reaction, the compound nucleus formation and α particle clustering in the target nucleus. It is concluded that α clustering may play an important role in the (d, α) reaction.

Effects of the Addition of Various Oxides on the Crystallization of Lithia-Silica Glass

Sumio SAKKA and Megumi TASHIRO

Yogyo Kyokaishi (Journal of the Ceramic Association, Japan), **69**, 67 (1961)

Generally, on the reheating of lithia-silica glass, it starts to crystallize at the temperatures near or below the softening point to convert into the polycrystalline material without deformation (M. A. Matveev, V. V. Velya, *Steklo i Keramika*, **16** [10] 14 (1959)).

In the present study, various oxides were added as the third component to a lithia-silica glass of the composition, Li_2O 25, SiO_2 75 mol%, and their effects on the crystallization of the base glass on reheating were investigated.

It was found that there is a limit in the amount for each oxide, and the addition over the limit inhibits the crystallization of the glass giving rise to the