Bull. Inst. Chem. Res., Kyoto Univ., Vol. 54, No. 6, 1976

LABORATORY OF DIELECTRICS

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This laboratory deals with basic research and applications of dielectrics. The subjects of researches which have been conducted for recent ten years are as in the following: (1) dielectric polarization and relaxation of polar liquids; (2) dielectric relaxations and molecular motions in polymers; (3) dielectric properties of heterogeneous systems; (4) dielectric approach to biological suspensions; (5) data analysis and technique in dielectric measurements.

1. Dielectric Polarization and Relaxation of Polar Liquids

Dielectric behavior of polar liquids has been studied for some diols, ethanolamines, and ethylenediamine oligomers. Dielectric relaxations in 2-methyl 2,4-pentanediol, 2-ethyl 1,3-hexanediol, dipropylene glycol at low temperatures were fitted by the Davidson-Cole relaxation characteristic of strongly hydrogen-bonded liquids. Introduction of the amino group into molecules reduces the intermolecular hydrogen bonding. This effect was confirmed with the Kirkwood correlation factor evaluated from the dielectric constants of ethanolamines and ethylenediamine oligomers. Relaxations found for those molecules having the amino group as aminoethyl ethanolamine, diethylenetriamine *etc.* were not expressed by the Davidson-Cole relaxation, but interpreted as superposition of the Cole-Cole and the Davidson-Cole relaxations. The equilibrium dielectric constant of these hydrogen-bonded liquids varied linearly with the reciprocal of the thermodynamic temperature.

2. Dielectric Relaxations and Molecular Motions in Polymers

Dielectric behavior of a variety of fluorocarbon polymers has been investigated over wide ranges of frequency and temperature and discussed in terms of molecular motions and other physical properties.

Precision measurements of poly(tetrafluoroethylene) PTFE were carried out over a frequency range of 10 Hz to 300 kHz at temperatures of -195 to 170°C. The dielectric constant of PTFE was about 2 over the entire range of frequency studied, being slightly dependent on the degree of crystallinity and temperature. The dielectric constant showed an abrupt change at the crystalline transition of 19°C in highly crystalline PTFE. The dielectric loss was very low, showing a small loss peak of the γ relaxation near -80°C at 1 kHz. Copolymers of tetrafluoroethylene and hexafluoropropylene, FEP, are also non-polar polymers. FEP, however, exhibited three small loss peaks, α, β, and γ, which appeared near 100, -50, and -170°C at 1 kHz, respectively. The glass transition was found at 60°C. The α and β relaxations were assigned to micro-Brownian motions of backbone chains and local motions of short

molecular segments, respectively. Poly(vinylidene fluoride) PVDF showed three relaxations, the α relaxation near 130°C, the β near 0°C, and the γ near −30°C at 100 kHz. In the α relaxation the loss peak and the relaxation time increased not only with increasing lamellar thickness but also with crystal defects in crystalline regions. This relaxation was attributed to molecular motions in crystalline regions. The β relaxation was ascribed to conformational rearrangements of backbone molecular chains. Effects of orientation of molecular chains by drawing were reflected on dielectric relaxations of PVDF. Dielectric behavior of another copolymer has been studied for copolymers of vinylidene fluoride VDF and hexafluoropropylene HFP with different comonomer contents. A copolymer with low HFP contents showed the α relaxation similar to that in PVDF. Copolymers with high HFP contents were amorphous, showing relaxations associated with conformational rearrangements of molecular chains and local motions of molecules below the glass transition.

3 Dielectric Properties of Heterogeneous Systems

As the integral parts of dielectric approaches to colloidal disperse systems, a number of dielectric investigations have been carried out on diphasic systems such as emulsions in oil-in-water and water-in-oil types theoretically as well as experimentally.

On the basis of the Wagner theory of the interfacial polarization, a new theory was developed which is expected to be applicable to spherical disperse systems in higher concentrations. The dielectric behavior observed for the oil-in-water emulsions was understood quantitatively with this new theory. Striking dielectric relaxations were observed for the water-in-oil emulsions in accordance with the theoretical prediction. The data on the dielectric relaxations were in satisfactory agreement with the new theory for the preparations by the minimal use of emulsifiers.

Most examples of emulsions reported so far are of a diphasic system in which the conductivities of the constituent phases are several orders of magnitude different from each other. In this instance the approximate expressions of the theory were put to use on application of the theories to the experimental results. For general cases of diphasic systems where the approximation is not allowable, new procedure is being developed for practical use of the Wagner and the new theory.

Dielectric measurements were made on Fe_3O_4 and some ferrites in fine powders precipitated from aqueous solutions and in calcined powders. In the temperature range from 77 to 300 K some ferrites containing Fe^{2+} ions showed dielectric relaxations, which were interpreted as interfacial polarization due to the heterogeneous structure of the oxides. Another type of dielectric relaxations was observed for the same ferrites at temperatures from 77 to 4.2 K. This kind of dielectric relaxation was considered to be caused by the hopping of electrons between Fe^{2+} and Fe^{3+} ions. Magnetic relaxations in the same ferrites were also investigated.

As further extension of the dielectric approaches to the spherical disperse systems, a triphasic system consisting of conducting spheres covered with an insulating shell phase and dispersed in a conducting medium was investigated in connection with an

analysis of biological suspensions. On the basis of a theoretical expression proposed by Pauly and Schwan for a suspension of shell-spheres, fitting procedure was established so that the dielectric constants and the conductivities of the inner spheres and of the shell phase may be determined by means of the fittings of the theoretical curves to dielectric relaxation data observed.

4 Dielectric Approach to Biological Suspensions

The curve-fitting method established was successfully applied to some biological suspensions to obtain the dielectric constants and the conductivities of the inner phase and of the shell phase of the suspending particles from the dielectric relaxation data observed.

It was found for the synaptosome suspensions that the conductivity of the synaptosome interior was about 37% of the outer medium conductivity irrespective of the salt concentration of the outer medium, and that the dielectric constant for the inner phase was about 35. The membrane capacitance was estimated to be 0.7 μF cm^{-2}, remaining constant irrespective of species and concentration of the univalent salts examined.

Dielectric measurements were made on suspensions of intact yeast cells. The suspensions showed typical dielectric relaxations which are caused by the triphasic structure with the cytoplasm, the cell membrane, and the suspending medium. The dielectric relaxation data were subjected to the analysis by the curve-fitting method to deduce the characteristics of the cytoplasm and the cell membrane. The cell membrane capacitance was estimated to be 1.1 μF cm^{-1}. The conductivity of the cytoplasm was almost unchanged with varying salt concentrations of the suspending medium. The dielectric constant of the cytoplasm was estimated to be about 50. The effect of some surfactants on the yeast cell membranes was also examined in connection with bactericidal effect.

5 Data Analysis and Technique in Dielectric Measurements

The expressions of the complex capacitance and conductance were derived for the Cole-Cole relaxation. Numerical values of the normalized complex capacitance and conductance were tabulated as a function of frequency over a wide range of the distribution parameter of relaxation times to facilitate the numerical analysis of relaxation as observed in the frequency domain technique.

The theory of a transient current method in dielectric measurements has been discussed in connection with investigation of relaxation processes using the time domain technique. Numerical values of the response functions and their intergrals in the Debye, Cole-Cole, and Davidson-Cole types of relaxation were compiled over a wide range of the distribution parameter of relaxation times. These data were intended for investigation of relaxation as observed with a transient current method using either step or ramp voltage. In connection with the transient current method the accuracy of the Hamon approximation for evaluating the dielectric loss and the relaxation time was examined with regard to the Cole-Cole, Davidson-Cole, and Williams-Watts relaxations. It was found that the approximation is applicable, with fairly good

accuracy, only to the Cole-Cole relaxation with a broad distribution of relaxation times.

An ultra low-frequency bridge which is usable in a frequency range of 1 mHz to 100 Hz was built for dielectric measurements of slow relaxation processes in polymer solids. The bridge was featured with three-terminal measurements and with capability of the distinction between the capacitive and conductive unbalances in the null detection at low frequencies. The time required for the final balance was greatly reduced in this bridge.

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(*indicates an article published in Japanese)

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