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LABORATORY OF SURFACE CHEMISTRY

Head: Dr. Tohru Takenaka

Gotoh laboratory was established in 1947 for physico-chemical studies of surface and colloid chemistry and officially named "Laboratory of Colloid Chemistry" in 1964. After the retirement of Professor Rempei Gotoh in 1969, Professor Tohru Takenaka succeeded him as the head of the laboratory in 1971. The official name of the laboratory was changed to "Laboratory of Surface Chemistry" in 1975.

Scientific works carried out in this laboratory before 1966 were reviewed in the Special Issue on the Commemoration of the Fortieth Anniversary of the Institute for Chemical Research. Since that time, vibrational spectra of surface thin films and of surface-chemically interesting materials and electrical phenomena at interfaces were studied in collaboration with Assistant Professor Dr. Soichi Hayashi, Dr. Mutsuo Matsumoto, Mr. Junzo Umemura, and Mr. Noriyuki Kimura. A brief description of the works published during these ten years will be given below.

I. Vibrational Spectra of Surface Thin Films

1. Resonance Raman Spectra of Adsorbed Monolayers

Studies of molecular orientation in monolayers adsorbed at the liquid-gas and liquid-liquid interfaces are a subject of much interest in the field of surface chemistry. We have studied the resonance Raman spectra of monolayers of complexes of cationic surfactants and anionic azo dyes adsorbed at the interface between carbon tetrachloride and aqueous solutions using the total reflection method of the exciting light (laser beam) at the interface. From polarization measurements of the Raman spectra, the orientation of the dye molecules in the monolayers was discussed. The same type of studies were also carried out for monolayers of surface-active azo dyes adsorbed at the oil-water and air-water interfaces. It was found that there was good correspondence between the states of monolayers and the molecular orientations and that the planes of the chromophore of the dye molecules had a tendency to subtend an angle with the interface with increasing the amount of the adsorbed molecules.

2. Infrared Spectra of Surface Thin Films

Thin films adsorbed at the gas-solid and liquid-solid interfaces were studied by using the infrared transmission and attenuated total reflection (ATR) methods. Built-up films of long-chain fatty acids transferred from monolayers spread on substrates onto germanium plates were also studied by the ATR method. The use of polarized infrared radiation allowed us discussions about molecular structure and orientation in surface films. It was concluded that the built-up and adsorbed films of the long-chain fatty acids consisted of an assembly of monoclinic crystallites which were uniaxially oriented with respect to the normal axis to the interface.

II. Molecular Orientation

1. Simultaneous Measurements of Stress and Infrared Dichroism of Polymer Films

The method for simultaneous measurements of stress and infrared dichroism of polymer films was devised by using a double beam infrared spectrophotometer. The time dependence of the infrared dichroism was obtained by measuring the intensity change at peak maxima on the differential polarized infrared spectra. The method was applied to studies of continuous elongation and stress relaxation of various polymers such as natural rubber, polyethylene, polychloroprene, and polyvinylchloride containing diethyl phthalate or dioctyl phthalate as plasticizer.

2. Precise Measurements of Dichraic Ratio by Spectropolarimeter

Precise measurements of dichroic ratio close to unity were made with a spectropolarimeter. By this method, slight orientation of small molecules induced by the following methods was investigated; (a) irradiation of polarized monochromatic light to various dyes dispersed in polymer films, (b) stretching of polyvinylchloride films containing the anthracene molecules, and (c) application of high electric field to small molecules having large dipole moments, *p*-nitroaniline and N,N-dimethyl-*p*-nitroaniline, in various solvents.

III. Vibrational Spectra of Molecular Crystals

1. Molecular Structure of Crystalline Fatty Acids

Infrared and Raman spectra of normal fatty acids were studied in the range from room to liquid-helium temperatures. Great temperature dependences were observed at characteristic frequencies of the carboxyl group and in the region of the band progression due to the CH_2 wagging modes. These results suggest that the two distinct configurations, *cis* and *trans* forms for the C_β–C_α–C=0 group, coexist in the crystalline state. Enthalpy and entropy differences between the two forms were obtained from the temperature dependence of band intensities.

2. Vibrational Spectra of Fully Conjugated Tetracyano-Compounds

Fully conjugated tetracyano-compounds such as tetracyanoethylene, 7,7,8,8–tetracyanoquinodimethane and 1,2,4,5-tetracyanobenzene are known to be strong electron acceptors in charge-transfer complexes. Infrared and Raman spectra of these compounds and their deuterated derivatives were examined. From polarization measurements of the infrared and Raman spectra of the crystals, the bands were experimentally classified into respective symmetry species under the assumption of the oriented gas model. The assignments of the observed frequencies to the fundamental modes were carried out with the aid of comparison of the spectral data with those of analogous molecules, application of the product rule and the normal coordinate analysis. The same examinations were also made for thiocyano-compounds such as tetracyano-1,4-dithiin and tetracyanothiophene.

IV. Electrical Phenomena at Interfaces

1. Electrocapillarity at Liquid-Liquid Interfaces

a) The coalescence of liquid droplets in aqueous and non-aqueous solutions in the presence and absence of surfactant was investigated by applying the polarizing potential. The experimental results were explained in the same mechanism as the stability of disperse systems. b) In order to study the double layer structure at oil-water interfaces the electrocapillary curve was measured at different concentrations of various kinds of electrolytes.

2. Double Layer Interactions in Thin Liquid Films

The drainage process of thin liquid films between two phases was measured as a function of time by using the capacitance and optical reflection methods. The disjoining pressure which was experimentally determined from the drainage rate is analysed in terms of electrostatic force and attraction, the characteristic of attraction constant between two phases as well as the mechanism of coagulation of disperse systems being investigated.

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