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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS IX

DIELECTRIC DISPERSION IN ULTRA-LOW FREQUENCY

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I. Introduction

The presence of a dispersion of the dielectric constant of pure organic solvents in ultra-low frequency band has been already examined for several organic solvents such as benzene and dioxane.1) Recently, we have introduced theoretically a dispersion formula of organic solvent mixture and discussed experimentally on its adaptability to very low frequency band. In these investigations, we have noticed a phenomenon that the observed dielectric constant varies with changing applied voltage. This phenomenon can not be observed in ordinal band of high frequency but observed only in very low frequency band below 1 Hz.

In the present paper, the author has examined experimentally in detailes for the above mentioned dispersion in ultra-low frequency band on the stand-point of voltage dependence. The results obtained in these experiments showed that the observed dispersion clearly related to the applied voltage, and the exterpolation of the curve, dispersion v. s. applied voltage, to zero voltage showed a constant value for the material examined.

II. Experimental

The measurement of the dielectric constant was performed with the use of Ando's TR-4 Type Dielectric Analyser with the conbination of ULO-1 Type Ultra-low Frequency Oscillator, EDC-3 Type Balancing Detector and LE-3 Type Liquid Cell. The measurements of voltage dependence on the dielectric constant were performed by adjusting the out-put power of the oscillator. The applied voltage was recorded on a syncroscope at the imput sides of the dielectric analyser.

The calculation of the dispersion was conveniently performed with the difference of the two dielectric constants which were measured respectively on 0.3 Hz and 3 Hz. The upper frequency, 3 Hz, was selected from the part of the curve on which the dispersion can not be observed as shown in Fig. 1. Before testing samples, the dispersion of a empity cell was measured in varying the applied voltage and no dispersion in the exterpolated value to zero voltage was exactly recognized.

The materials, benzene, toluene, cyclohexane, dioxane and cyclohexene were used for testing materials without further purification from the special grade commercials.

Fig. 2-a shows the relation between the cell constants of the empity cell and the applied voltage on 0.3 Hz and 3 Hz. As shown in this figure, the cell constant measured varies gradually according to the change of applied voltage. The relation between the dispersion of the empity cell, calculated from $D = C_{f1} - C_{f2}$, and the applied voltage was also given in Fig. 2-b. As shown in this figure, the exterpolation of the dispersion to zero voltage shows almost no dispersion. The mean value of the cell constants deduced from the data in Fig. 2-a at zero voltage was 16.939 at 25° C. Figs. 3a, 4a, 5a, 6a and 7a respectively show the plots of dielectric constants of benzene, toluene, cyclohexane, dioxiane and cyclohexene on 0.3 Hz and 3 Hz at 25°C as a function of the applied voltage. Figs. 3b, 4b, 5b, 6b and 7b respectively show the same plots of the dispersion at the same temperature. As shown in the above Figs, the observed dielectric constants and the dispersions are linearly corelated both with applied voltage.

The interesting fact is that each of the exterpolated values of the dispersion of these substances to zero voltage always shows a constant value for each of substances. The exterpolated dispersions thus obtained are

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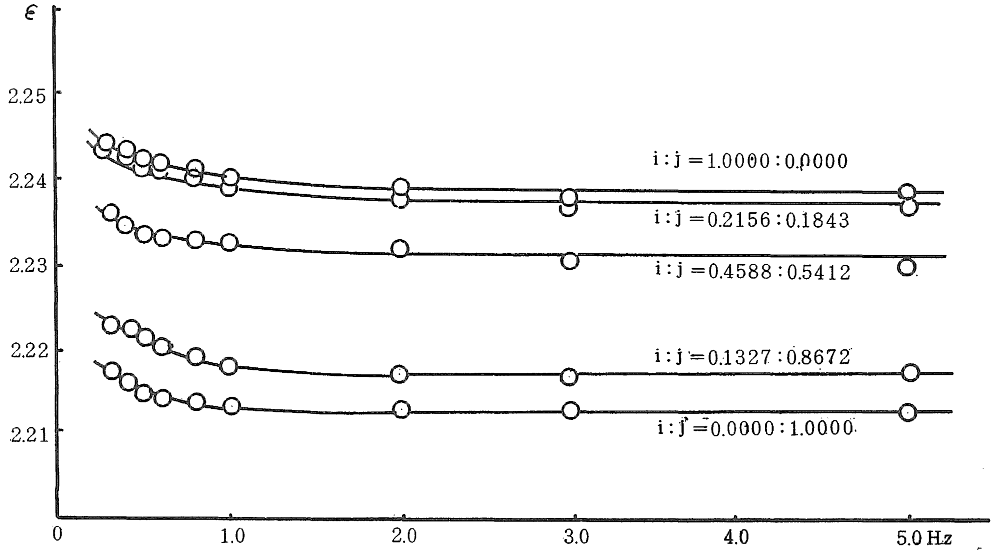

Fig. 1 Relation between the dielectric constant and measured frequency for Benzene (i)-Dioxane (j) mixtures.

Table 1. The exterpolated dielectric constant and the experpolated dispersion

Material	Dielectric Constant 25°C		Dispersion 25°C.	Dipole Moment	α
	0.3 Hz	3 Hz			
Empity Cell	1.0000	1.0000	0.0000	—	—
Benzene	2.2438	2.2366	0.0070	0.0(g)*	4.154***
Toluene	2.3350	2.3285	0.0061	0.379(g)*	4.932
Cyclohexane	1.9814	1.9814	0.0000	0.6(g)*	4.395
Dioxane	2.2290	2.2105	0.0185	0.45**	—
Cyclohexene	2.1974	2.1953	0.0020	0.75(Hx)	4.293

* McClellan, ** Weisberger, *** Calculated Value.

sumarized in Table 1.

III. Discussion

Owing to the complexity of dielectric measurements and especially to the stray coupling of the bridge circuits, it seems very difficult to distingwish whether the observed phenomena are directly connected with the properties of the testing materials or not. In the case of analysing the data obtained, we must generally consider that the cell contained with testing material acts on electrically as a part of electrical circuits having equivalent impeadance for applied alternating field. The coresponding equivalent circuit may be given as in Fig. 8.

Where C_1 and C_2 are the capacities between the surface of the electrodes of the cell and the adsorped layers of the solvent molecules. C is the capacity eliminated the above mentioned capacities from the whole capacity of the cell. Perphaps C_1 and C_2 would be refered to the structure and the nature of the adsorved layers and, R_1 and R_2 also refered to the movements of the adsorbed molecules in the alternating field. In the case of very low frequency, the movements of the adsorbed molecules due to alternating field would be apparently small and, as a result, it may be presumed that the capacity of the surface

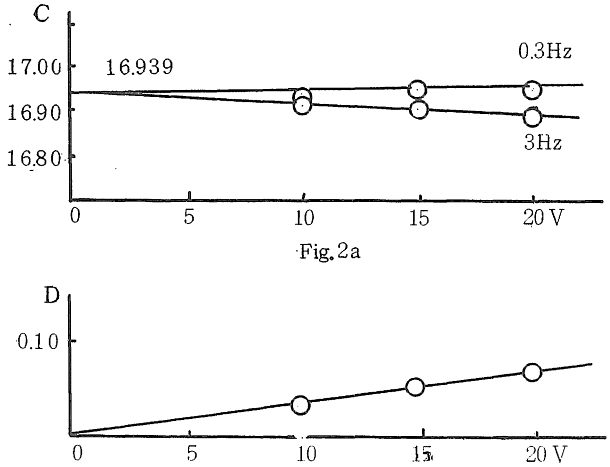

Fig. 2b

Fig. 2 Relationships between the applied voltage and the cell constant (2a), the dispersion D (2b), respectively at 25°C.

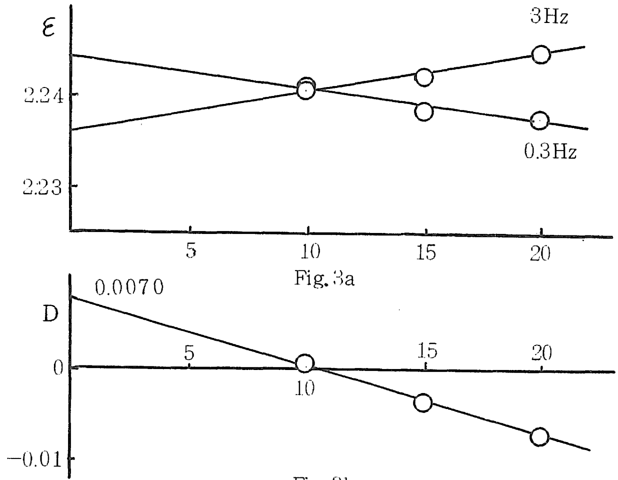

Fig. 3b

Fig. 3 Relationships between the applied voltage and the dielectric constant (3a) and its dispersion D (3b), Benzene at 25°C.

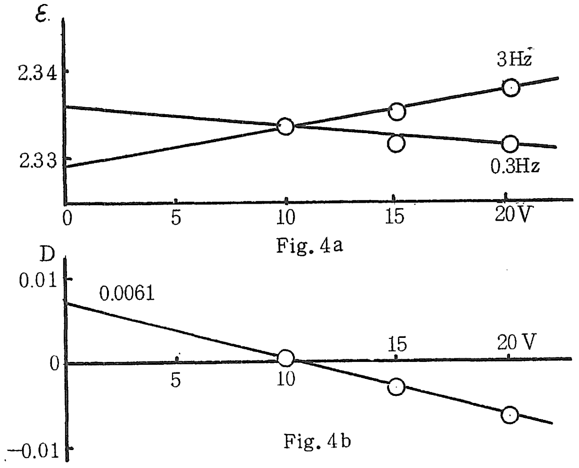

Fig. 4 The same relationships, Toluene at 25°C.

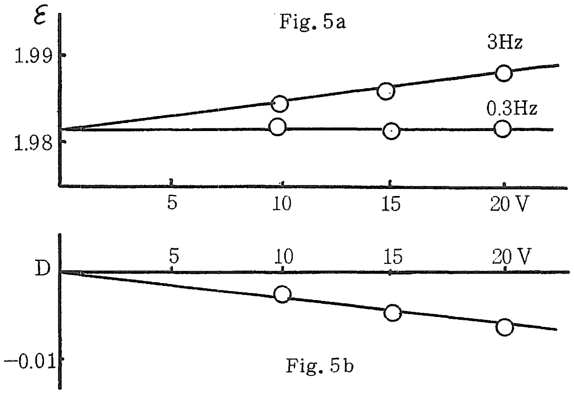

Fig. 5 The same relationships. cyclohexane at 25°C.

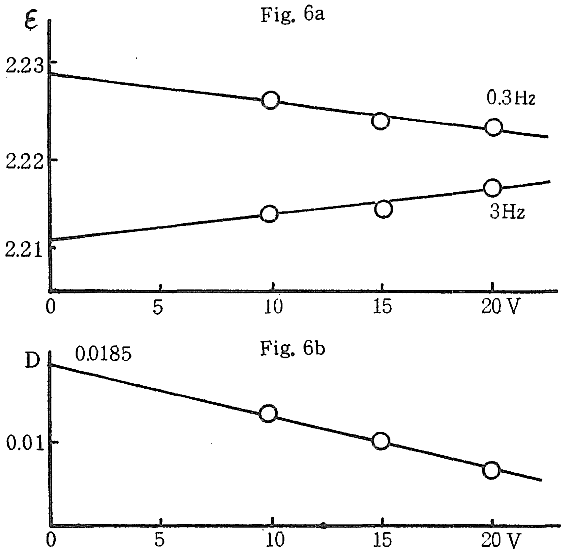

Fig. 6 The same relationships. Dioxane at 25°C.

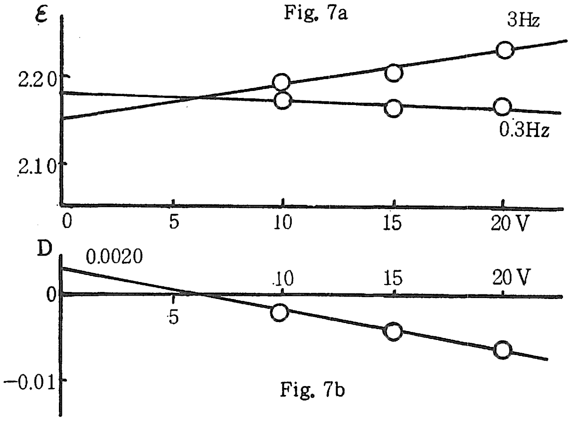

Fig. 7 The same relationships. Cyclohexene at 25°C.

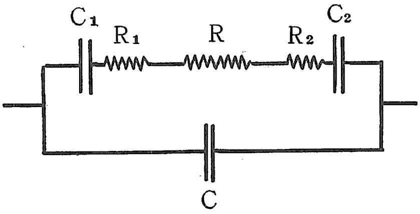

Fig. 8 The equivalent circut of cell.

must be incresed with decresing field strength.

The inclinations of these curves which were illustrated in Figs. 3b, 4b, 5b, 6b, and 7b are very distinctive, and the gradients of these curves are generally positive. The above mentioned facts show us that the capacity between the snrface of the electrodes and the adsorbed layer increases with decreasing applied voltage as we prospected above. Accordingly, the noticiable points are sumarised up as follows : i) the gradients of the dispersion curves ii) the exterpolated values of the dispersion curve to zero voltage. These values are seemed to be both relatad to the refractivity and the polarizability of the testing substances as illustrated in Figs. 10 and 11. iii) the relation between the structure and the exterpolated dispersion. In the case of substances having similar structure, such as benzene, toluene, cyclohexene and cyclohexane, a regularity can be observed between the exterpolated dispersion and the number of π-electrons, and this will be connected to the polarizability and refractivity as mentioned above. These relations are sumarised in Table 2.

Table 2.

Relation between the structure and the Exterpolated polarization

Material	$\left(\frac{dD}{dV}\right)\ V=0$	Number of π electrons
Benzene (C_6H_6)	0.0070	6
Toluene ($C_6H_5\cdot CH_3$)	0.0061	6
Cyclohexene (C_6H_{10})	0.0020	2
Cyclohexane (C_6H_{12})	0.0000	0

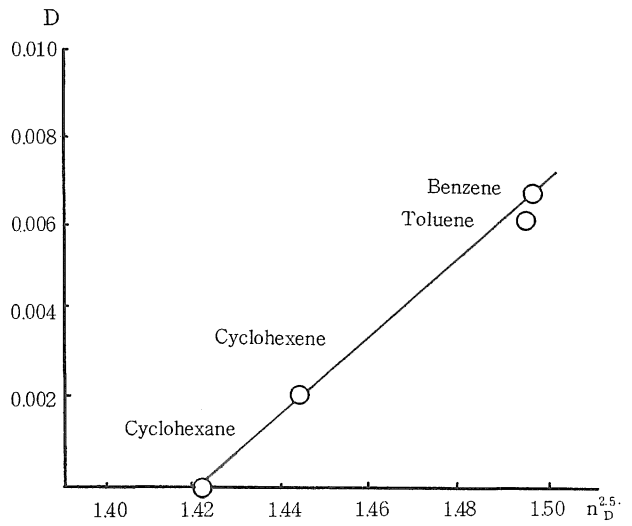

Fig. 9 Relationship between the exterpolated dispersion D and the optical refractivity.

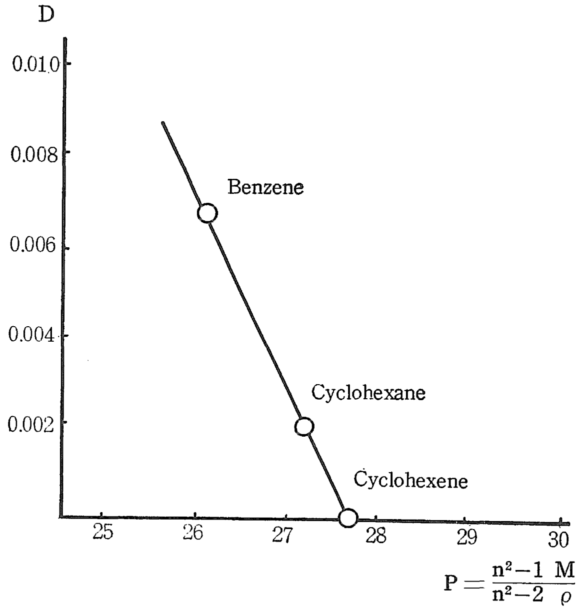

Fig. 10 Relationship between the exterpolated dispersion D and atomic polarization.

From these results of investigstion, it may be concluded that the new form of dielectric dispersion in ultra-low frequency band can essentially be attributed to a surface phenomenon and is connected to the electrical disturbance of the adsorbed molecules on the surface of electrode and is essentially different fromt the ordinal dispersion as observed in very high frequency band.

The outline of this investigation was already opened at the meeting of The Chemical Society of Japan, Okayama University in september 1975. The author wishes to thank Mr. Yukio Kurosaki and Yuzo Hamada for their helpfull participation to the experimental work through this investigation.

Literature

1) Senseki Takano ; Studies on the Dielectric Properties of Organic Solvents 1. Part 1. Mem. Fac. Educ. Shimane Univ., 1, 24 (1967).