

THE TACHI LABORATORY

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The works that have been done in our laboratory for the past 15 years may be divided into two parts, i. e. the theory and application of electromagnetic absorption and studies on surface electricity. In the following we shall describe them.

Part I. Studies on the Theory and Application of Electromagnetic Absorption¹⁾

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1. Theoretical

1. On the behavior of dipole molecules in the electric field.
 - (i) Dipole molecules in the electrostatic field.
 - (ii) Electric force acting on the molecule.
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 - (iv) Absorption due to the rotation of dipole molecules.
2. On the measurement of dielectric losses.
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3. On adsorbed water in the dispersed system of polysaccharides, especially of cellulose and starch particles.
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 - (ii) The absorption spectrum of wood-cellulose in a low temperature region.
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2. Application

1. On electromagnetic absorption and cellulose chemistry.
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2. On biological water considered from dielectric loss.
 - (i) Manchurian Kaoliang.
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3. On the influence of a high frequency electric field on seeds.

The first chapter treats the theoretical study, in which the behaviors of dipole molecules in various electric fields are examined electrophysically and mathematically in detail. We consider that the dielectric loss measurements are most fitted to research in the mechanism of water adsorption at polysaccharides.

In general, water in cellulose materials exists in two forms; fixed (chemically bound) water and free water. It is also said that it exists in the form of solid solution. Anyway, we may consider that there is dipole orientation of water on the free surface of cellulose. Accordingly we can measure water adsorption by expressing in some measure the behavior of water dipole in an electric field. We adopted the dielectric loss angle $\text{tg } \delta$ and relaxation time τ for it. As a result of examination the A. C. bridge method with equivalent series resistance was proved to be best, which we used in our experiment. In this we used the suspension of various cellulose materials and starch particles in benzene or liquid paraffin as samples, and measured the residual current and electromagnetic absorption spectrum. As the electrical properties of dry cellulose or starch and solvent resemble each other, the electrical property of this system depends almost entirely on the distribution of the water molecules whose electrical property is prominent. Consequently, we could assume the distribution and form of water by electric measurement—residual current and electromagnetic absorption measurements.

As a result we proved that the water adsorption of these samples could be described with their dielectric properties, and the differences between the forms of adsorbed water of various samples could be determined by their dielectric properties.

We could also determine the amount of the chemically adsorbed portion of the water adsorbed by polysaccharide, by treating three component system, i. e. cellulose-sodium thiosulphate-water.

The second chapter treats applications, and is divided into three sections.

The first section is on application to cellulose chemistry, and emphasis is laid on the "determination of chemically bound water". The results obtained from experiments are as follows:

With regard to substances having the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_2 \cdot \text{H}_2\text{O}$, one of the hydroxyl radicals in cellobiose constituting cellulose is in the free state, and if also binds with one molecule of water (chemically bound water), the rest having saturated forms and making side chains. The examples of this are cotton cellulose, linnen cellulose, etc. These have, however, the constitution formula $(\text{C}_6\text{H}_{10}\text{O}_5) \cdot \text{H}_2\text{O}$ by mercerization. This seems to be due to the mechanism that, besides one free hydroxyl radical of cellobiose, another saturated hydroxyl radical becomes free by this treatment and adsorbs another molecule of water. Rayon fibre also belongs to this category.

It is very significant for us to research into the state of hydroxyl radical of glucose residue in cellulose by this electric method. We also obtained various results in the problem on the nature of water-proof property of fibre.

The second section is devoted to biological water. We used Manchurian Kaoliang, Barley and Japanese rye, barley and wheat as samples. The object of our study was to probe the influence of temperature of growing districts on the form of the adsorbed water in them. For this purpose we measured low frequency

electromagnetic absorption below 6,000~ by the A.C. bridge method. As the result we found that the lower the temperature, the larger the relaxation time τ , and so was the adsorbing force. Besides, the change of relaxation time was prominent at measuring temperature below 0°C., and a striking difference in the change of relaxation time was noticed in the case where the minimum of the monthly average of temperature of the growing district was near 0°C.

The explanation is as follows: the tightly combined water of hydrophilic colloid acts as a natural protector against the destruction of cells and the withering of protoplasm due to the freezing of biological water in winter, and the lower the temperature of the growing district, the stronger this function becomes.

The third section deals with the influence of high frequency electric field on seeds, and we discuss seeds as dielectrics. From the $\text{tg } \delta$ - ρ curves we found the following facts. If we properly controlled the water content of seeds, their absorption of high frequency wave would become maximum, and so we would have a good harvest. We are now examining this effect in detail.

Besides the above studies, we are going on with studies on the vulcanization of rubber by high frequency treatment.

Part II. Studies on Surface Electricity²⁾

Although many attempts have been made to study on electrical phenomena at interfaces, it is a difficult and unsolved problem yet to elucidate the structure of the electrical double layer at interfaces, and to clarify the situation of ions and molecules there.

During our studies on the electrical double layers at interfaces described above, we discovered a new phenomenon concerning these problems. We called it "U-effect". We shall make a slight description on it.

I. U-Effect

1. Definition

When we mechanically vibrate various kinds of double layers in glass capillaries by a definite vibration source, e. g., sonic or supersonic wave, etc., periodical changes of charge of the same wave character as the original source occur at the two ends of the glass capillaries. This was discovered for the first time in our laboratory using U-tube, and we may call it "U-effect". In our experimental devices we adopted two kinds of electrical double layers, i. e. those of glass-liquid interfaces and those of mercury-electrolyte solution interfaces. The former case is called "U-effect I", and the latter "U-effect II".

2. U-Effect I

(i) Experimental. We attached a glass capillary filled with dilute salt solution of concentration ca. 0.001 norm. (we call it "vibrating element" or simply "element", Fig. 1) to a vibrator. The vibrator used was one of moving coil type or a unit of Rochelle salt. When the vibrator began to operate, the element vibrated with it, and the electrical double layer at the glass-liquid interface was disturbed because of the inertia of the liquid. By this disturbance alternating voltage occurred at the electrodes

ee' , and we amplified it, and observed it with a cathode ray oscillograph system. As a means of experimental verification we used sine wave only. In some cases, we delivered the vibration of sonic or supersonic wave through medium (here, water) to a diaphragm to which the element was attached vertically.

In every case it was proved that the voltage generated in the element was of the same character with the original wave.

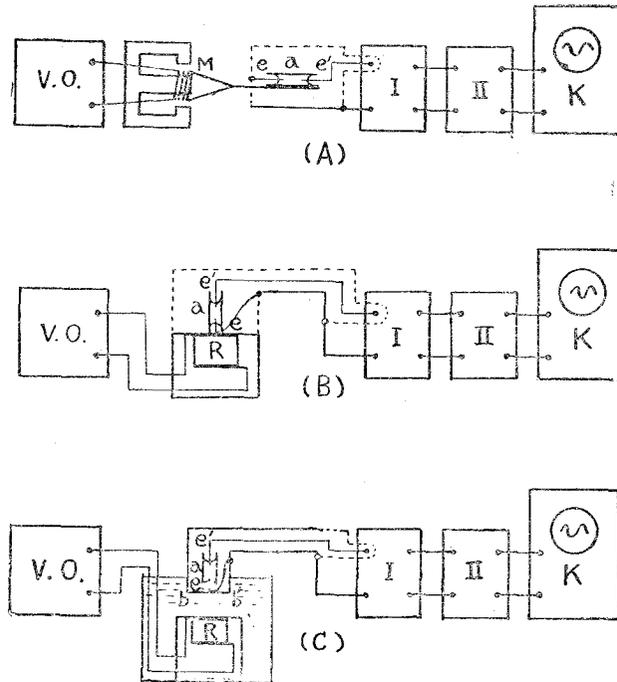


Fig. 1.

V. O. :	Oscillator	a :	element
M :	Moving coil vibrator	ee' :	electrodes
I :	1st amplifier	bb' :	diaphragm
II :	2nd „	W :	Water tank
K :	Cathode ray Oscillograph	R :	Rochelle salt vibrator

(ii) Theoretical. Let us consider for the sake of simplicity that the interface is made up with two layers of positive and negative charges of distance δ , i. e. Helmholtz's double layer model, which is equivalent to an electrostatic condenser. The electrical charge density of this condenser σ is given by

$$\sigma = D\zeta/4\pi\delta \quad (1)$$

where D is the dielectric constant of the medium, and ζ the ζ -potential. Take x -axis in the direction of tangent at the interface, and describe the relative motion at interface in

$$x = x_0 \sin \omega t + \text{const.} \quad (2)$$

where x_0 is the amplitude of vibration, ω is 2π times frequency, and t is time. The instantaneous quantity of transfer of electric charge due to this motion is given by

$$2\pi r\sigma \frac{dx}{dt} = \frac{D\zeta r x_0 \omega}{2\delta} \cos \omega t \quad (3)$$

where r is the radius of the capillary.

On the other hand, from Ohm's law this quantity is given by

$$E\lambda\pi r^2/l \quad (4)$$

where E is the potential difference between two electrodes whose distance is l , and λ is the specific conductivity of the liquid. Equating (3) and (4), we obtain the following formula which represents the alternating voltage generated by U-effect I and shows the same wave character as the original one

$$E = \frac{D\zeta l x_0 \omega}{2\pi\delta\lambda r} \cos \omega t \quad (5)$$

3. U-Effect II

(i) Experimental. The method of experiment and its devices are quite same with those in U-effect I, except that the element is filled with mercury and solution, and contains about 40 interfaces (Fig. 2).

It was also seen that the voltages generated at ee' were of the same wave character as the original mechanical vibration.

(ii) Theoretical. The theory of this phenomenon is closely connected with that of the electrocapillarity. Omitting the detailed discussion of the state of the mercury-solution interface, let us consider it as ideal polarized electrode, which behaves like a static condenser of no leakage. For the sake of simplicity take a single interface. In our case connection is in series, and the electromotive force generated is the sum of the absolute values of each single electrode.

When we put the interfacial charge density $\sigma(\varphi)$, where φ is the polarizing potential, the interfacial charge q is given by

$$q = \sigma(\varphi) \cdot s \quad (6)$$

where s is the interfacial area. Now, when we vibrate this interface, s changes periodically with it and we may put

$$s = s_0 \sin \omega t + \text{const.} \quad (7)$$

Hence

$$q = \sigma(\varphi) \cdot s = \sigma(\varphi) (S_0 \sin \omega t + \text{const.}).$$

Putting the whole resistance of the circuit R , the voltage E generated is

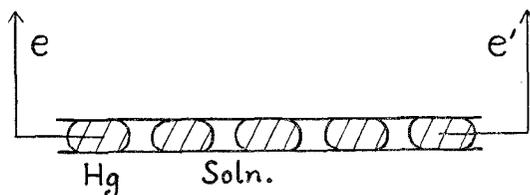


Fig. 2

$$E = R \cdot \frac{dq}{dt} = R\sigma(\varphi) s_0 \omega \cos \omega t. \quad (8)$$

This is the equation which gives the alternating voltage of U-effect II.

II. Applications of U-Effect

U-effect can be applied at every device where the mechanical energy of vibration is converted into electrical energy. For this device many ideas have been proposed, among which the one using the piezo-electricity of Rochelle salt was considered to be the best. As will be shown in the following description, the apparatuses applying our effect are equally matched to those of Rochelle salt at the point of frequency character. Moreover, with regard to resistance against humidity, temperature and mechanical shock as well as the easiness of manufacture, which Rochelle salt lacks, our device is superior. (Patent No. 174570, 1947)

1. Pick-up of Electrophonograph

An element of mercury-sulphuric acid interfaces is attached to the armature of pick-up. When the needle runs along the disque, the vibration is transferred to the element, and alternating voltages are generated, which has the same frequency character as the vibration cut on the disque. This voltage is amplified, and delivered to the speaker. The frequency character curve of this pick-up proved very good. The weight is small, and the mechanical load on the disque can be controlled at will, and, consequently the defacement of the disque can be small.

2. Microphone

When we fix the element of mercury and sulphuric acid vertically to the center of the diaphragm of a microphone, we can convert the vibration of diaphragm produced by sound or voice into electric current, and it is amplified and delivered to the speaker.

3. Fish group detector

A supersonic wave which is sent from one end of a ship is reflected by the school of fish, and received by an element of mercury-sulphuric acid fixed to the other end of it with a heterodyne device. According to our experiments done at the River Yodo in Hirakata, Osaka prefecture, the maximum receivable distance, when the out-put power of the oscillator was ca. 10 KW., was about 3 km. and that of Rochelle salt was about 1.5 km.

4. Other applications

As has already been pointed out, this device is applied in various ways, e. g., cardiographs, stethoscopes, telephone mouth-pieces, etc.

5. Efficiency of conversion from mechanical to electrical energy by U-effect II

As the amplitude of mechanical vibration in our effect was so small that this must be measured by some devices, so we undertook to measure it by the frequency

modulation method. It is now in operation and some results have already been published.

III. Measurement of Streaming Potential by the Vibration Method using U-Effect I

When fluid is forced by pressure through a diaphragm or capillary, an electromotive force, so called "streaming potential", is generated. Hitherto constant pressure was used, and the streaming potential measured by the electrostatic method. But we used periodically changing pressure, e. g. simple harmonic motion of moving coil, and succeeded in measuring it as alternating voltage using U-effect I. The experimental devices were as follows.

(i) Vibrating element. We used an element filled with liquid in which Pt electrodes were inserted vertically from the capillary wall, and a fine glass pole was inserted from one end of the capillary in order to prevent the vibration of liquid with the capillary wall. The glass used was "Telex".

(ii) Amplitude of vibration. The amplitude of mechanical vibration was represented by the measure of the valve voltmeter connected in parallel to the moving coil.

(iii) Amplifier. The frequency character of the amplifier was observed.

(iv) Streaming potential. We made a peak voltmeter (UX 514), and measured the streaming potential with this arrangement.

(v) Results. Having observed change of the potential at various salt solutions of different concentrations at the constant amplitude of vibration, it was proved that the more dilute the solution was, the larger the potential. The potential-concentration curve gave considerable parallelism with the results given by the ordinary electrostatic method in the case of KCl, KI and $K_4Fe(CN)_6$ aq. etc.

We measured also the change of potential with the amplitude of vibration, and compared it with other scientists' results. Contrary to their results, we got linear relation between them. This means that electrokinetic potential is independent of the pressure.

It is worth while to notice that we can well remove the difficulties met with in the electrostatic measurement by this method.

IV. Measurement of the Capacity of Electrical Double Layer at Mercury-Solution Interfaces by the Impedance Matching Method

Various methods of capacity measurement at mercury-solution interfaces have been devised, but we find some points ambiguity in them, though they are important in the structural theory of interfaces.

When we apply the "maximum power transfer theorem" (impedance matching) to U-effect II, a new method for the capacity measurement can be introduced, which is quite different in principle from any others previously proposed.

1. Maximum power transfer theorem

When the angle of load impedance is constant, it is when the moduli of load

and inner-impedances are equal that the power supplied from the source to load has its maximum value.

2. Principles of the new method

When, generating an alternating current by the mechanical vibration of element, we measure the power supplied to (variable) load R , it has its maximum value at a point R^* , when $|R^*| = |Z_i|$, (Maximum power transfer theorem) where Z_i is the inner impedance of the element. Accordingly, we can guess the values of R_i and C by two measurements with different frequencies ω and ω' using formula

$$\begin{cases} R_i^2 + \frac{1}{\omega^2 C^2} = R^{*2} \\ R_i^2 + \frac{1}{\omega'^2 C^2} = R^{*2} \end{cases} \quad (10)$$

where R_i and C are the resistance of solution column and capacitance of the interface respectively.

3. Some of the results obtained

(i) The electrical capacity of mercury-norm. sulphuric acid and mercury-norm. KCl solution interfaces in the non-polarized state were 20.24 and 16.02 $\mu\text{F}/\text{cm}^2$.

(ii) The electrical capacities of mercury-norm. KCl, KNO_3 and KBr aq. at various polarizations were also measured. In general, capacities at positive polarization were larger than those at negative polarization, and there were humps near the electrocapillary maximum.

This voltage is generated by the charging and discharging of the interfacial condenser in our effect, and not caused by periodical polarization of the interface due to the outer source. This is why our method is quite different from others.

- 1) Shikata and Ueda: J. Electrochem. Soc., Japan, **3**, No. 8 (1935).
 Shikata and Ueda: Rep. Inst. Chem. Res., Kyoto Univ., **6**, (1936).
 Shikata and Ueda: J. Electrochem. Soc., Japan, **4**, No. 2 (1936).
 Shikata and Ueda: *Ibid.*, **4**, No. 6 (1936).
 Shikata and Ueda: *Ibid.*, **5**, No. 3 (1937).
 Shikata and Ueda: *Ibid.*, **5**, No. 8 (1937).
 Shikata and Ueda: *Ibid.*, **5**, No. 12 (1937).
 Shikata and Ueda: *Ibid.*, **6**, No. 10 (1938).
 Shikata and Ueda: *Ibid.*, **6**, No. 10 (1938).
 Shikata and Ueda: *Ibid.*, **7**, No. 2 (1939).
 Ueda and Shikata: *Ibid.*, **7**, No. 7 (1939).
 Ueda and Shikata: *Ibid.*, **7**, No. 7 (1939).
 Ueda and Shikata: *Ibid.*, **7**, No. 7 (1939).
 See also the references in these papers.
- 2) Ueda, Tsuji and Watanabe: Rep. Inst. Chem. Res., Kyoto Univ., **18**, 108 (1949).
 Ueda, Tsuji and Watanabe: *Ibid.*, **19**, 44 (1949).
 Ueda, Watanabe and Tsuji: *Ibid.*, **20**, 28 (1950).
 Ueda, Watanabe and Tsuji: *Ibid.*, **22**, 31 (1950).
 Ueda, Watanabe and Tsuji: *Ibid.*, **23**, 23 (1950).

Ueda, Watanabe and Tsuji: *Ibid.*, **24**, 12 (1951).

Ueda, Watanabe and Tsuji: Mem. Coll. Agr., Kyoto Univ., No. 57 (Chem. Series No. 24)
July, 22 (1950).

Ueda, Watanabe and Tsuji: *Ibid.*, No. 60, March, 1 (1951).

Ueda, Watanabe and Tsuji: *Ibid.*, 8.

Ueda, Watanabe and Tsuji: *Ibid.*, 13.

See also the references in these papers.