ABSORPTION OF U. H. F. WAVES IN SALT SOLUTIONS

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ABSTRACT Percentages of absorption of u h f waves (300-500 Mc s) in aqueous solution of sodium chloride for different concentrations have been measured by optical method. Attenuation coefficients and hence absorption indices have been calculated for different frequencies. Values of reflexion coefficients at different frequencies have also been calculated. Values of ionic relaxation time as obtained experimentally for different concentrations of the solution have been compared with the values calculated from Debye-Falkenhagen theory. Values of dielectric constant and loss tangent, as deduced from experimental results, have been compared with those calculated theoretically from Debye-Falkenhagen theory Values of dipole conductivity and molar conductivity have been calculated from experimental results and their variation with frequency studied. it has been found that the position of maximum absorption shifts towards higher concentration for higher frequencies The product of wavelength corresponding to maximum absorption and the normality of the solution expressed in gm equivalent per litre has been found to be 1 61 a constant

INTRODUCTION

The greater part of wireless communication being conducted over sea, an exact determination of the absorption coefficient of sea-water and its variation with frequency is important. Conductivity of different samples of sea-water has been measured by Hill (1907) in the audio frequency range and by Van der Pol (1918) in the medium and long wave band. Electrical properties of sea-water has been studied by Smith-Rose (1933-34) up to 10 Mc/s and by Drysdale (1920) up to 1 Mc/s. For u.h.f. waves transmitted over sea, the absorption of energy by sea-water being considerable and field intensity measurements over sea being difficult, it has been thought worth-while to carry out the measurement in the laboratory in order that the effect of sea water on the propagation of u.h.f. waves, may be more definitely ascertained. Chemical composition of sea-water being liable to variation in its salt content from 0.18 to 4.15, it has been decided to study first the absorption and other associated properties of individual salt solutions that compose average sea-water (Dorsey, 1940) and then the solution as a whole, over a frequency range of 300-500 Mc/s. Electrical properties of potassium chloride solution has been measured at lower radio frequencies by Drake,

Pierce and Dow (1930) and of sodium chloride solution by Cooper (1946), over a frequency range of 0.95-13 Mc/s and 690-4320 Mc/s.

Besides the interest of wave propagation, the absorption of u.h.f. waves in salt solutions is of basic impoitance in the study of the problems of molecular structure. With liquids or solutions, the tendency of an applied e.m. field to orient molecular dipoles is resisted by moleculai inertia and by the viscous forces of the environment, resulting in a lag between the application of the field and the rotation with consequent absorption of energy. The maximum loss takes place at an angular frequency ω given by the reciprocal of the relaxation time τ of the molecule or polar group, where the relaxation time is a function of molecular dimensions, viscosity and absolute temperature. In the case of salt solution, if an ion moves through the solution on the application of an e.m. field, the ions surrounding it will be continually changing their distribution to maintain equilibrium distribution. The result is that in the neighbourhood of the ion there exists an excess of ions of opposite sign. The variation of electric intensity within the ionic atmosphere during its formation is characteiised by a relaxation time Θ accoiding to the well known Debye-Falkenhagen theory (Falkenhagen, 1934).

$$\Theta = \frac{8.85 \times 10^{-11}.D_0}{\Delta_\sigma . \gamma^*} \qquad \dots \quad (1)$$

wheic $\Delta_\sigma =$ equivalent conductivity of solution

$D_0 =$ dielectric constant of water $= 80$

$\gamma^* =$ concentration of solution expressed in gm. equiv. per litre.

The object of the present paper is to study the absorption and reflexion of e.m. waves over a frequency range of 300-500 Mc/s., by aqueous solution of sodium chloride of different concentrations.

PRINCIPLE OF THE METHOD

A small aciial connected to an u. h. f. oscillator (G. R. Type No. 857A) and placed at the principal focus of a cylindrical parabolic reflector A serves as a source of radiation giving out a parallel beam. The beam after being reflected by a plane aluminium reflector B passes thiough the liquid contained in the glass cell E, (15 cms × 7.5 cm × 7.5 cms.) and then strikes the detector aciial D which is placed hoiizontally underneath the glass cell. The detector unit C is enclosed completely by means of a thick aluminium box, excepting for a small hole at the top through which the detector aerial is taken out. This scieen reduces to minimum the stray reflection pick-up by the detector unit, as it is desired that the detector should pick-up only the beam which has passed through the cell. The detector microammeter placed just outside the screened box, is connected to the detectoi with a short twisted screened flex. The arrangement is shown in Fig. 1.
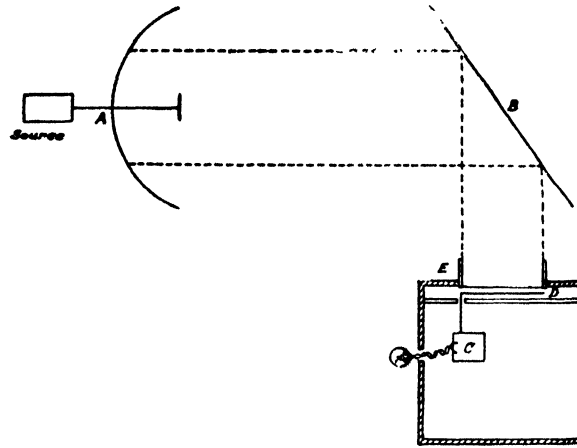
Fig. 1

Initial intensity I received by the detector in absence of the cell is measured. Then placing the cell with liquid of uniform thickness x in the path of the beam, transmitted intensity I_{t} is measured. Changing the thickness of the liquid to a new value x' and keeping the cell in the same position, the transmitted intensity I'_{t} is measured. Assuming that the reflected intensities remain the same in both cases, and also assuming that the attenuation of the glass cell itself remains unchanged, in the presence of the liquid the attenuation coefficient α can be deduced as follows

$$T = \text{Transmission factor} = \frac{\text{Power transmitted}}{\text{Power received}} = \frac{I_{t\,r}}{I} = e^{-\alpha x}$$

Similarly,

$$\frac{I'_{t}}{I} = e^{-\alpha x'}$$

So,

$$\alpha = \frac{1}{2.3(x' - x)} \cdot \log_{10}\frac{I_{t\,r}}{I'_{t}} \qquad \cdots \quad (2)$$

The absorption index k can be found from the following relation.

$$\alpha = \frac{2\pi n k}{\lambda} \qquad \cdots \quad (3)$$

involving refractive index n and wavelength λ. The reflexion coefficient R has been calculated from the following relation (Baz, 1939)

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \qquad \cdots \quad (4)$$

EXPERIMENTAL

Detector deflexion is a measure of the energy incident on it, so it is desirable that the detector plate current change should bear a linear relation

with energy incident on it. Detector used is of resonant line type (Fig. 2).
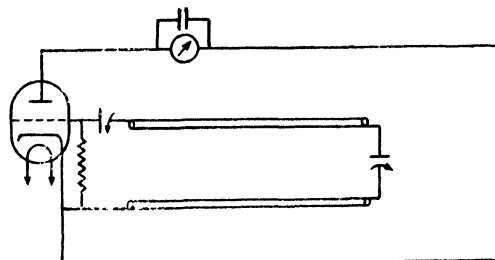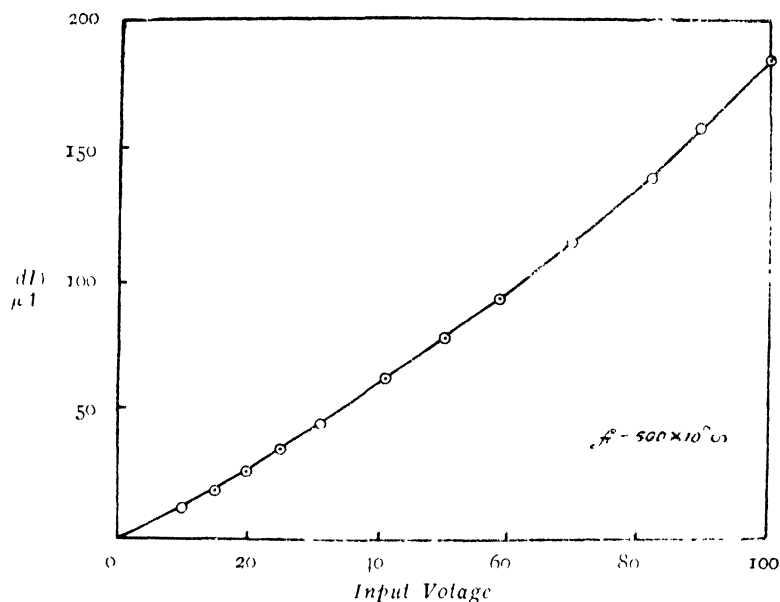Characteristics of detector is shown in Fig. 3.

FIG. 2

FIG. 3

Characteristic of the Detector

Percentages of transmission for different normalities (N/2 to N/16) of the solution at different frequencies and for different depths of liquids have been measured, and the results for 2 mm. depth of liquid have been reported in Table I.

In order to calculate the attenuation coefficient, at different frequencies, relation (2) may be used, if the transmission takes place directly, *i.e.*, without suffering any reflexion within the liquid which may be considered true, if the liquid depth is very small compared to the wavelength used. To be more accurate, attenuation coefficients have been determined from the slope of the average of the envelopes of the curves, one of which is represented in Fig. 4.
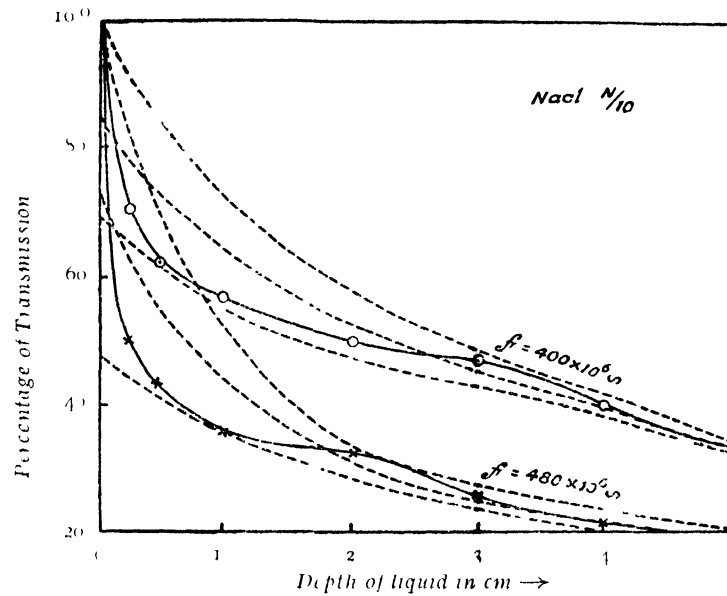
FIG 4

Values calculated from different portions of the average curve will be different So two values of attenuation coefficients α_1 and α_2 corresponding to two different slopes $1-2$ cms and $2-3$ cms have been calculated for different frequencies and normalities, out of which values for three different normalities have been represented in Tables II, III and IV

TABLE I

Frequency in Mc/s	of transmission through a depth of mms of liquid						
	N 2	N 3	N 4	N 5	N 6	N 8	N 10
3 10	9	1	93	81	6 3	85 3	88 8
3 1	83 3	1	9 9	91 6	93 2	85 2	90 0
34	77	50	75 5	58 3	55 3	76 6	75 0
38 0		87 5		66 3	9 6	51 4	1 00 0
400	71 4	88 0	1 3 0	52 3	96 4	98 5	100 0
420	79 4	96 3	76 4			90 9	
460	79 4	62 0	70 0	89 3		88 8	
48 0	78 9	51 4	56 3	63 0	0	56 8	75 4
5 0	61 7	51 5	57 5	56		65 7	75 0

Substituting values of n from Tables VIII to X in column 3 values of k_1 and k_2 have been calculated With the values of n and k_2, values for reflexion

coefficients have been calculated from Eq. 4..The values of k_2 corresponding to α_2 have been selected, as it has been found that they agree more closely with the values calculated theoretically. Variation of percentages of absorption with different normalities for different frequencies have been shown in Fig. 5 for 2 mms depth of liquid.

TABLE II

Normality = N/2

Frequency in Mc/s	α_1	α_2	n	k_1	k_2	R
360	0 084	0 101	9 063	0.1238	0.1523	0 6127
400	0 099	0 062	9 059	0.238 0	0 0842	0.6419
140	0 089	0 078	9.055	0 1023	0 0943	0.6414
480	0.045	0 015	9 051	0.0186	0.0169	0 6119

TABLE III

Normality = N/5

Frequency in Mc/s	α_1	α_2	n	k_1	k_2	R
360	0.118	0.180	8 986	0 175	0.266	0.6397
400	0.183	0 108	8.980	0 213	0.111	0 6393
440	0 177	0 118	8.976	0 213	0 178	0 6393
480	0 163	0 052	8 973	0 181	0 057	0.6395

TABLE IV

Normality = N/10

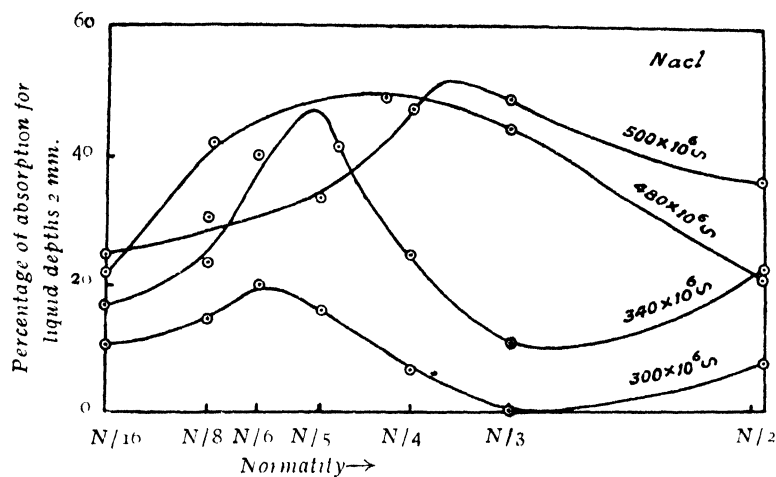| Frequency in Mc/s	α_1	α_2	n	k_1	k_2	R
360	0.1503	0 1057	8 956	0.2224	0 1568	0.6387
400	0,0936	0 045	8.954	0.0991	0.0675	0 6386
440	0.1039	0.082	8.952	0.1260	0.0997	0.6386
480	0.182	0.113	8.952	0.2032	0.1234	0.6386

FIG. 5

DISCUSSION

It will be observed from Fig. 5 that the normalities for which the absorption is maximum for frequencies 300, 340 and 480 Mc/s are 0.166 N, 0.20 N, 0.25N respectively. The product of the normality γ expressed in gm. eq. per litre and the wavelength λ_{max}, corresponding to the frequency of maximum absorption is found to be a constant equal to 16. 64 for aqueous solution of sodium chloride as shown in Table V.

TABLE V

γ in gm. eq per litre	λ_{max} cms	$\gamma \times \lambda_{max}$	Average
0 166 N	100 0	16 66	
0 20 N	88 2	17 64	16 64
0 25 N	62 5	15 62	

This value agrees fairly with 16 45, the value given by Forman and Crisps (1046).

From Tabels II, III and IV it will be observed that reflection coefficients for different cases do not vary much.

Several mathematical theories have been postulated to explain the frequency dependence of dielectric properties. Though different theories present different mechanisms of absorption, they all suggest some form of relaxation function. Therefore the relaxation time corresponding to the frequency of maximum absorption is of interest. From Debye's (1929)

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expression for the generalised dielectric constant

$$\iota = \epsilon' - j\epsilon''$$ ... (5)

it may be deduced that ϵ'' is a maximum, when

$$\omega\tau = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2}$$ ... (6)

For solutions of normalities o. 166 N, o. 20 N, o. 25 N, ϵ_∞ may be assumed to be equal to the dielectric constant of water at u. h. f. which is 80. Values of dielectric constant (ϵ_0) at the audio frequencies for sodium chloride solution, for different concentrations have been calculated from the following relation (Falkenhagen,) loc. cit and the result is given in Table VI.

$$\epsilon_{\omega=0} - \epsilon_s = \frac{1.97 \times 10^6 |\neg_1 z_- \{|z_1| + |z_2|\}^{1/2}}{2\epsilon_s^{1/2} T^{1/2} (1 \pm 1/\sqrt{q})^2} .(q \gamma^*)^{1/2}$$ ... (7)

where, z_1 = valence of Na ion = 1

z_2 = valence of Cl ion = 1

$T = 300°$ A

ϵ_s = dielectric constant of water = 80

$q = 0.5$ for Nacl.

γ^* = concentration in gms. eq. per litre.

Substituting proper values Eq. (7) reduces to

$$\epsilon_{\iota=0} - \epsilon_s = 3.536\sqrt{\gamma^*}$$ ... (8)

TABLE VI

Concentration	$\epsilon_{\omega=0} - \epsilon_s$	$\epsilon_{\omega=0}$	Concentration	$\epsilon_{\omega=0} - \epsilon_s$	$\epsilon_{\omega=0}$
N	3 536	83 536	N/8	1 250	81 250
N/2	2 497	82 497	N/10	1.116	81.116
N/3	2.028	82.028	N/16	0 884	80.884
N/4	1 768	81 768	N/32	0 625	80 625
N/5	1 581	81 581	N/64	0 412	80 442
N/6	1 443	81 443	N/128	0 313	80 313

From Table VI and Eq. (6), values of τ for three different concentrations have been calculated and given in Table VII. Values of τ for the same concentrations have also been calculated by using Deby-Falkenhagen relation (Eq.1) and given in the same table for comparison.

In the expression for ϵ (Eq.5), values of ϵ' and ϵ'' may be evaluated from the following relation

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2} \qquad \dots \quad (9)$$

$$\epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{1 + x^2} x \qquad \dots \quad (10)$$

where, x given by

$$x = \omega\tau \left[\frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \right]$$

varies with frequency as well as τ. When the concentration is varied, dielectric constant varies and there is a variation of τ also in accordance with Falkenhagen theory. It is only when the dielectric constant is assumed to remain constant, independent of concentration, and only τ varies, the relation $x = 1$, gives the frequency of maximum absorption. For ϵ'' to have maximum value, $\dfrac{\partial \epsilon''}{\partial x} = 0$

But,

$$\frac{\partial \epsilon''}{\partial x} = (\epsilon_0 - \epsilon_\infty) \frac{\partial}{\partial x} \left(\frac{x}{1 + x^2} \right) + \frac{x}{1 + x^2} \frac{\partial}{\partial x} (\epsilon_0 - \epsilon_\infty) \qquad \dots \quad (11)$$

It is only when second term (Eq. 11) is assumed to be zero, that ϵ'' is a maximum, when $x = 1$. But when the variation of the dielectric constant is taken into consideration, it is extremely difficult to determine the value of x for which ϵ'' is a maximum. While we have assumed, the constancy of the dielectric constant for determining the frequency of maximum absorption, the variation of dielectric constant has been taken into consideration, in calculating the values of ϵ'' for different frequencies and concentrations (Tables VIII-IX). It follows, therefore, that the frequency of maximum absorption, for a particular concentration, as determined by :

1) keeping the frequency constant and varying the concentration, or

2) keeping the concentration constant and varying the frequency is not the same.

In both cases ω_{max} is given by

$$\omega_{max} = x \cdot \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \cdot 1/\tau$$

where ϵ_0, ϵ_∞ and τ are the same in both cases, but in the first case $x \neq 1$ and, in the second case, $x = 1$. Hence, for determining τ, for a particular frequency, it is preferable, to keep the concentration constant and vary the frequency, since in that case x is unity. But in following this method there are certain experimental drawbacks, viz:

(i) It is more difficult to have a wide range of frequency variation than concentration.

(ii) It is difficult to have constant intensity of oscillation for all frequencies. Apart from this consideration, the higher observed values of τ in

Table VII

Concentration	Cal τ in secs. $\times 10^{10}$	Obs. τ in secs. $\times 10^{10}$
0.25 N	2.632	3.21
0.20 N	3.291	4.591
9.166 N	3.967	5.21

Table VIII

Normality $= \dfrac{N}{4}$; $(\epsilon_0)_{N/4} = 81.768$; $\epsilon_\infty = 80.0$, $\tau = 3.245 \times 10^{-10}$ sec ;

$$\epsilon_0 - \epsilon_\infty = 1.768$$

Frequency in Mc/s	$\omega\tau$	$\epsilon' = n^2$	ϵ''	tan δ	Δk (mho/cm.)$\times 10^4$
300	0.6117	81.272	0.795	9.781×10^3	1.324
360	0.7315	18.132	0.819	1.02×10^2	1.697
420	0.8565	81.020	0.876	1.08×10^2	2.015
480	0.9959	80.884	0.884	1.093×10^2	2.357
500	1.020	80.847	0.881	1.091×10^{-2}	2.417
600	1.221	80.690	0.862	1.069×10^2	2.876

Table IX

Normality $= \dfrac{N}{5}$; $(\epsilon_0)_{N/5} = 81.581$; $\epsilon_\sigma = 80$, $\epsilon_0 - \epsilon_\infty = 1.581$;

$$\tau = 4.591 \times 10^{-10} \text{ sec.}$$

Frequency in Mc/s	$\omega\tau$	$\epsilon' - n^2$	ϵ''	tan $\delta \times 10^3$	Δk mho/cm.
200	0.5769	81.176	0.6908	8.59	7.674×10^{-4}
250	0.7211	81.029	0.7548	9.31	1.048×10^{-4}
300	0.8654	80.889	0.7843	9.696	1.307×10^{-4}
340	0.9855	80.790	0.7905	9.783	1.493×10^{-4}
400	1.154	80.664	0.7800	9.672	1.734×10^{-4}
500	1.442	80.499	0.7350	9.131	2.042×10^{-4}

Table VII, may be ascribed to the fact that Falkenhagen expression for τ is based on the assumption of Debye's, theory, which is primarily applicable to more dilute solutions, than those employed in the present investigation. The change of conductivity and viscosity of the solutions, if there is a temperature rise due to passing of e.m. wave, along with the first cause, may be responsible for the observed higher values of τ. But the temperature change being negligible, in the present experiment, due to very weak source employed, the possibility of second cause is ruled out.

In order to determine the frequency dependence of dielectric constant ϵ' and loss tangent $\tan \delta = \epsilon''/\epsilon'$ for the above three concentrations, Eqns. (9) and (10) and values of τ from Table VII have been utilised. The results are given in Tables VIII to X.

TABLE X

Normality $= \dfrac{N}{6}$; $(\epsilon_0)_{N/6} = 81.443$; $\epsilon_\infty = 80.0$, $(\epsilon_0 - \epsilon_8) = 1.443$

$\tau = 5.212 \times 10^{-10}$ sec.

Frequency in Mc/s	$\omega\tau$	$\epsilon' - n^2$	ϵ''	$\tan \delta \times 10^3$	$\dfrac{\Delta k}{\text{mho}/\text{cm}}$
200	0 655	80 99	0 656	8 22	7 401 × 10⁵
250	0.819	80 85	0 709	8 77	9 849 × 10⁻⁵
300	0.982	80 721	0 7-15	8 91	1 202 × 10⁻⁴
360	1 118	80 591	0 7098	8 81	1.419 × 10⁻⁴
400	1 311	80 520	0 6920	8 60	1 539 × 10 ⁴
500	1 629	80.382	0 6365	7 92	1 768 × 10⁻⁴

Values for absorption conductivities Δk for different frequencies and concentrations have been calculated from the following relations (Sharbaugh, etc., 1947)

$$\Delta k = \frac{(\epsilon_0 - \epsilon_\infty) v^2 / v_c^2}{(1 + v^2/v_c^2) \times 1.80 \times 10^{11}}$$ (12)

where,

$$v_c = \text{critical frequency} = \frac{\epsilon_f + 2}{\omega\tau(\epsilon_0 + 2)}$$

Variation of loss factor ϵ'' and dipole conductivity with frequency for different concentrations are shown in Figs 6 and 7 respectively. It will be observed that the loss factor maxima shifts towards higher frequencies, as the concentrations become greater. It may also be noted that the rate of variation of dipole conductivity with frequency becomes greater, the higher the concentration.
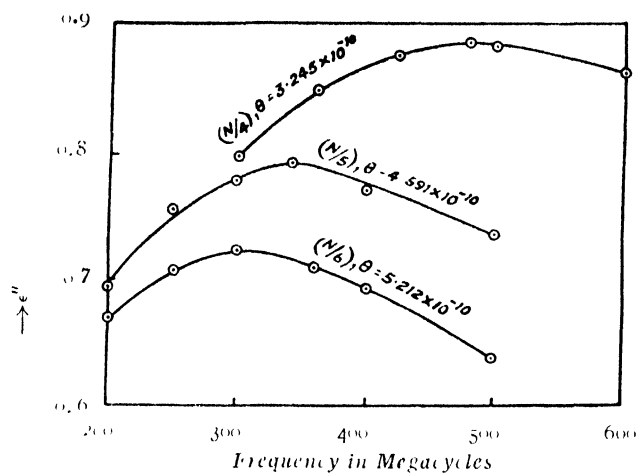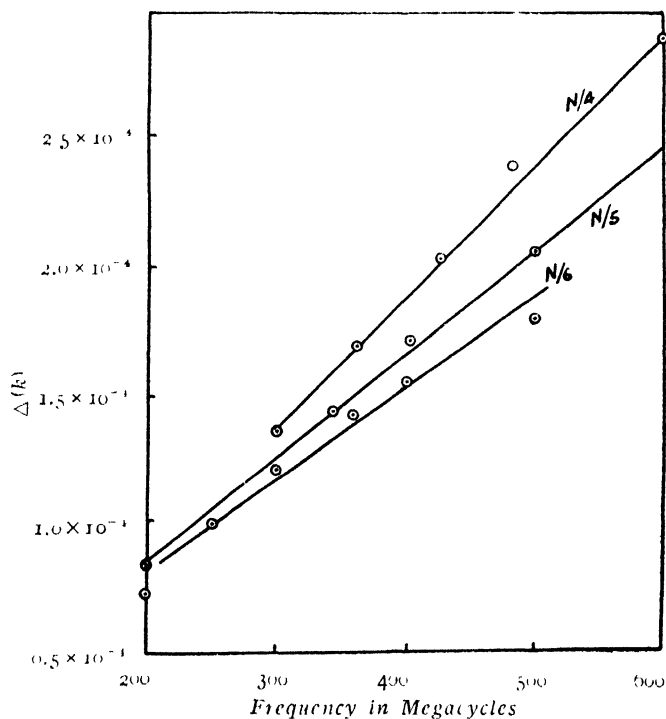
FIG. 6

Variation of ϵ'' with frequency.

FIG 7.

Variation of Dipole Conductivity with frequency.

Dispersion of conductivity with frequency for strong electrolytes, may be explained in the following way (Falkenhagen, *loc. cit*). When an ion moves under the application of a stationary electric field, the charge distribution loses its symmetry. Disappearance of the unsymmetrical charge distribution

in the ionic atmosphere is governed by a law similar to that which determines Θ, the time of relaxation of the whole ionic atmosphere. When an e. m. field of angular frequency ω acts upon the solution, each ion will describe (apart from its Brownian movement) a to-and-fro motion. If $\omega \ll 1/\Theta$ the unsymmetrical charge distribution, in the ionic atmosphere, at any moment will correspond to the instantaneous velocity of the ion $i. e.$ the relaxation force will be the same as in the stationary field case Whereas, if $\omega > 1/\Theta$ there will not be enough time for the formation of any unsymmetrical charge distribution and hence the retarding relaxation force will be reduced to minimum. The conductivity, therefore, increases with frequency. The conductivity at a frequency ν, ($\omega = 2\pi\nu$) may be written as

$$\frac{\Lambda\omega}{\Lambda_{10}}\Lambda_\omega = \Lambda_\infty - \Lambda_{I\omega} - \Lambda_{II} \qquad \qquad \ldots \quad (13)$$

where, Λ_∞ = Conductivity at infinite dilution

$\Lambda_{I\omega}$ = the part due to the relaxation effect.

Λ_{II} = the part due to electrophoretic effect

$= 50.5 \sqrt{\gamma^x}$ for univalent system like NaCl.

The molar conductivity under steady electric field is given by :

$$\Lambda_0 = \Lambda_\infty - \Lambda_{10} - \Lambda_{11} \qquad \qquad \ldots \quad (14)$$

From Eqs. (13 and 14), it may be written

$$\Lambda_\omega - \Lambda_0 = \Lambda_{10} - {}_{1\omega} \qquad \qquad \ldots \quad (15)$$

For sodium chloride solution

$$\Lambda_{10} = 0.224 \Lambda_\infty . \sqrt{\gamma^x}$$

where, $\Lambda_\infty = 108.99$ for NaCl solution.

In order to find the variation of molar conductivity with frequency for three concentrations (N/4, N/5, N/6), the following procedure has been adopted. Two curves $\Lambda_{1\omega}'/\Lambda_{10}$ against $\omega\Theta$ and $(\epsilon_\omega - \epsilon_x)/(\epsilon_{\omega-0} - \epsilon_x)$ against $\omega\Theta$ have been plotted in Fig. 8 From these two graphs, variation
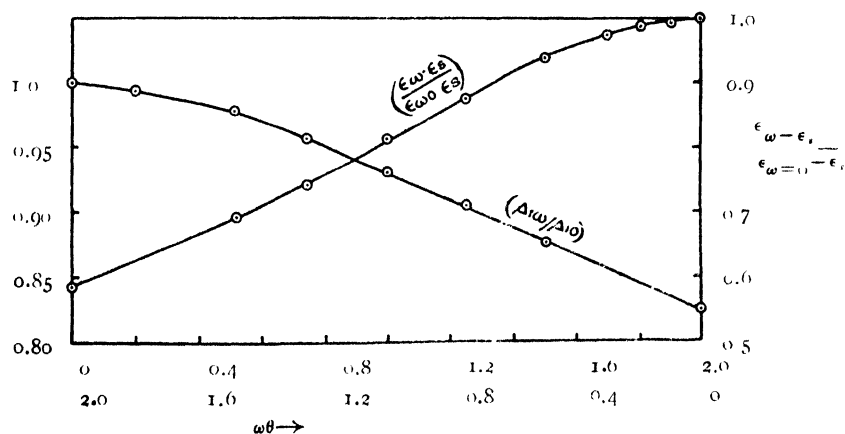

FIG. 8

Variation of conductivity and Dielectric constant with $\omega\Theta$

of $(\epsilon_\omega - \epsilon_s)/(\epsilon_{\omega=0} - \epsilon_s)$ and $\Lambda_{1\omega}/\Lambda_{10}$ with frequencies for different normalities have been prepared (Fig.8- 9). From these latter curves, variation
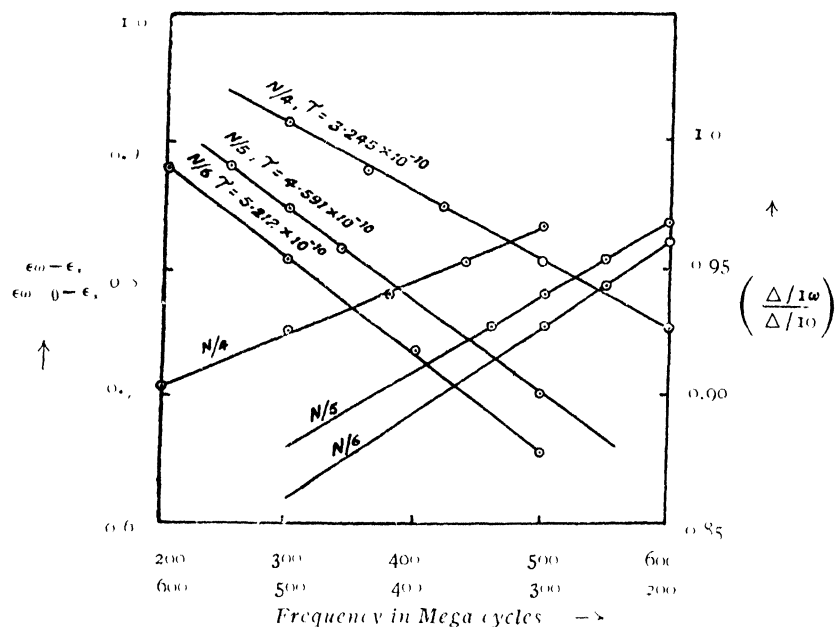

FIG. 9

of molar conductivities with frequency for three normalities have been computed and the results are plotted in Fig 9. It will be observed that the molar conductivity increases with frequency and that the rate of variation with frequency is less with higher concentration.

ACKNOWLEDGMENT

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