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INVESTIGATIONS ON MAGNETIC LOSS FACTORS OF COLLOIDAL AGAR SOLUTIONS

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ABSTRACT

In the present work the pure salt solutions and salt-added colloidal solutions were investigated in a magnetic field produced by a LRC circuit. The magnetic loss factor which is imaginary part of a complex permeability, was stutied as a function of salt ions and colloidal macroion concentrations. KCl, NaCl, $CaCl_2$,$MgCl_2$ and $BaCl_2$ were used as salts and the solutions of agar were used as colloidal solutions. The main parameters were calculated and the conditions of maximum energy absorptions were discussed for each solution. It was observed that the maximum energy absorption was frequency and concentration dependent at constant temperature.

INTRODUCTION

According to Deby-Hückel theory in the study of simple electrolytes a fundamental assumption is the presence of two kinds of ions in the solution. If any particular charged ion is chosen as the central ion, it is well known that an ionic atmosphere that consists of counter ions is formed around it. These ionic atmospheres cannot set up or vanish in an infinitely short time interval. If suddenly the central ions are taken out of the solution, the initial ionic distribution cannot continue because the field of central ion will not be present in the latter case. The ions forming the ionic atmospheres will penetrate gradually into the solution and finally ions will be distributed randomly throughout the solution. The time required for the nonuniform ionic distribution to decay back to the random distribution is called the relaxation time for the ionic atmosphere. It is given by

$$\tau = k / C \tag{1}$$

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where C is the concetration of the solution, in terms of mol per liter, and k is a constant which is in the order of 10^{-10} (Falkenhagen, 1929).

If we study a mixture of polyelectrolytes and simple electrolytes we may expect that similar ionic distributions must be formed around polyions like simple ions. The term polyelectrolyte describes all polymers containing many dissociable groups such as carboxyle, sulfonic, amino etc. (Conway 1966, Ling 1962).In general introduction of a charged colloidal particle into a homogeneous electrolyte causes a redistribution of the ions (Moore, 1964). Colloidal particles are charged by fixing or absorbing the ions on their surfaces (Schwarz, 1962). Suppose that the particle is spherical and carries a negative charge. Then there will be a concentration of positive ions in the region surrounding the particle in order to make the total charge zero. In the case of presence of macroions we expect that a second relaxation process decribing the ionic atmosphere around the macroion must be present in the suspension.

The aim of the present study is to observe these two relaxation phenomena. So we investigated the absorbed energy, from alternating radio frequency field, by the solution. Since the charge density of ionic atmospheres in polyelectrolytes much greather than that of simple electrolytes we expect that the relaxation times of ionic atmospheres surrounding small and macroions must be quite different. The absorbed energy is frequency-dependent. Maximum energy absorption is obtained when the frequency of the field is nearly equal to the relaxation rate.

MATERIALS AND METHODS

In the present work $NaCl$, KCl, $CaCl_2$, $BaCl_2$ and $MgCl_2$ were used as simple electrolytes and the suspensions of agar as colloidal solutions. Agar is a sulfuric acid ester of the complex galactose polysaccharide (Wes, 1966). It is ordinarily combined with metal ions such as Na^+, K^+, Ca^{++} and Mg^{++}. The metals are combined with the sulfuric acid groups of the agar molecule.

The agar used in this work is "Difco Bacto Agar", production of Difco Laboratory, Michigan U.S.A. The preparation of agar shows that the dispersion of agar in water can be brought about by heating. The important factor causing this dispersion is the strong affinity of the agar micelles for water (Krishnamurti, 1929). The water tries to penetrate through the pores of solid agar, and causes it to split up into separate micelles. The higher the temperature, the greather the facility with which this subdivision of agar takes place. When the whole process is completed a dispersion will be obtained in which each micelle is surrounded by a hydration layer. These micelles need not all be of the same type. Some may be monomolecular and others polymolecular. That is, a part of agar is probably in the molecularly-dispersed condition and the rest in the form of colloidal micelles.

A solution in a magnetic field produced by an alternating current of the coil of LRC circuit absorbs energy from the magnetic field. In order to express magnetic loss in the coil, it is necessary to obtain complex magnetic permeability $\mu = \mu' - j\mu''$ for the solution. For this purpose we have used a parallel LRC resonant circuit within the coil of which the electrolytic solutions to be investigated. The solution introduced into the resonant coil interacts with the electromagnetic field within the coil. Due to the circular induction currents created in the bulk of the electrolytic solution, a magnetization $\vec{M}$ may be defined for the solution. This magnetization, of course, oscillates with the frequency of the applied external electromagnetic field. It was observed that the resonant conditions of the circuit depend on the concentrations of the solutions. Due to the finite relaxation times of the ionic atmospheres of the individual ions within the solution there occurs an absorption of electromagnetic energy by the solution. The rate of energy absorption from the field depends on several factors, such as, the concentration and the temperature of the solution and the frequency of the electromagnetic field (Çetin, 1976; Forman, 1946).

The complex magnetic permaebility of a material medium is given by

$$\mu^{+} = \mu' - j\mu'' \tag{2}$$

where μ' and μ'' are magnetic permeability and magnetic loss factor of the medium (Condon 1967). A useful expression relating the magnetic loss factor μ'' to the relaxation time τ of the ionic atmosphere and to the field frequency ω has been given as follows (Çetin, 1976):

$$\mu'' = \omega k' \frac{\omega\tau}{1 + \omega^2 \tau^2} \tag{3}$$

Here k' is a constant. It can easily be shown that μ'' has a maximum value for $\omega\tau = 1$. At this condition Eq. (3) becomes

$$\mu'' = \omega k'/2 \tag{4}$$

Since we have no information about k′ we could not estimate the absolute value of μ''. So we expressed μ'' as a relative value by dividing Eq. (3) to Eq. (4). Therefore we obtained an expression for μ_r'' as follows:

$$\mu''_r = \mu''/\mu''_{max} = \frac{2\,\omega\,\tau}{1+\omega^2\,\tau^2} \tag{5}$$

Eq. (5) can be expressed in terms of concentration C by using Debye-Falkenhagen relaxation time, i.e. by using Eq. (1):

$$\mu''_r = 2\,\frac{C_{op}/C}{1+(C_{op}/C)^2} \tag{6}$$

Here C_{op} is the concentration value corresponding to the maximum absorption, i.e. corresponding to the value of $\mu'' = 1$. If we rewrite Eq. (1) in the form of $\omega\,\tau = \omega k/C$, at the maximum absorption condition (i.e. $\omega\tau = 1$ and $C = C_{op}$) we obtain the relation

$$C_{op} = \omega k \tag{7}$$

$$\omega\tau = C_{op}/C \tag{8}$$

If we can determine C_{op} experimentally for a given field frequency we may estimate the constant k and therefore the relaxation time τ of the solution corresponding to each concentration.

On the other hand it is possible to express the μ'' in terms of experimental circuit elements. A detailed analysis of the LRC circuit including a material media (i.e. electrolytic solution) gives the relations between the experimentally measured quantities, namely, the frequency of the field and the amplitude V_r of the potential across the parallel LRC circuit and μ''. These relations can be summarized as follows (Çetin, 1976).

$$\mu'' = A_o\,(V_{ro}/V_r - 1) \tag{9}$$

Here A_o is a constant for fixed frequency, V_{ro} is the amplitude of the resonance voltage when the coil is empty and V_r is the same amplitude when it is full.

The block diagram of the experimental circuit used in this work is shown in Fig. 1. The C element of the LRC circuit is a variable condencer with metal plates having air among its plates as dielectric matter. A capacitance of this type doesn't cause magnetic loss at high frequency and therefore the total loss occurs in the coil element of the circuit (Brophy, 1972).

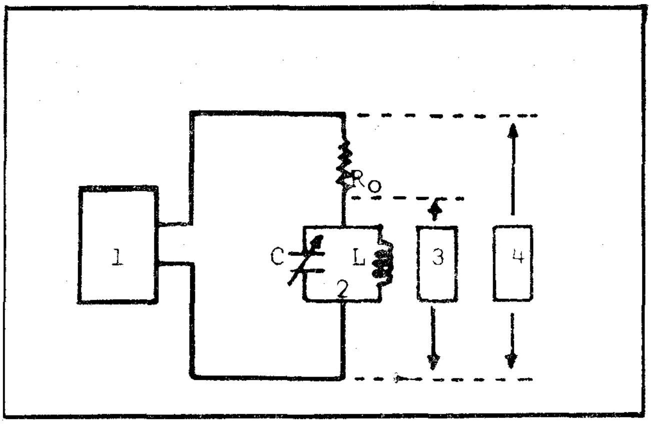

Fig. 1. The block diagram of the measurement circuit

1 Signal generator: 10 Hz – 10 MHz Breitbandgenerator Typ 2016a VEB FUNKWERT ERFURT - DDR.

2 The LRC resonance circuit

3, 4 Oscilloscopes: Nordmende Universal Oszillograph U0963

All the experiments were accomplished at fixed frequency, 2 MHz, and fixed temperature, 37 °C. The reason for choise of this temperature is to avoid the gelation of agar solution. Because the agar solutions become gell states below 37 °C.

The agar solutions were prepared in salt and water mixtures. While the agar contents were kept constant the salt contents were decreased step by step from saturated concentrations to very dilute ones. For each experiment the saturated salt concentrations were accepted as unity and were diluted by half. So obtained concentrations were diluted by half again and so on.

In order to eliminate the quantity A_o in Eq. (9) all values of μ'' were normalized to unity, i.e. all values of μ'' corresponding to V_r were divided to its maximum value for each concentration. So the magnetic loss axis in the figures was expressed as relative magnetic loss factor μ_r''. On the other hand the salt concentration axes were taken as $-\text{Log}_2 (C/C_o)$. C_o represents the saturated value of salt concentration and Log_2 is the logarithm with respect to the base 2.

RESULTS AND DISCUSSION

The variation of relative magnetic loss factors μ_r'' versus Log_2 C/C_o are shown in Figs. 2, 3, 4, 5, 6, 7, 8 and 9 for different samples. The interpretation of results as follows:

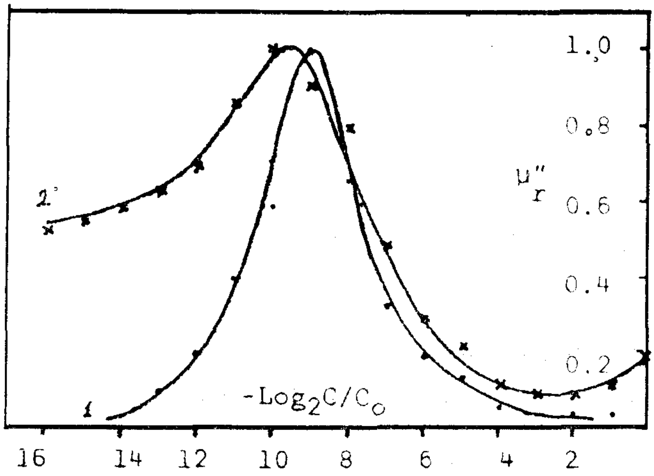

Fig. 2. μ_r'' vs Log_2 C/C_0 for NaCl (1) and NaCl + 0.004 wt/vol Agar (2)

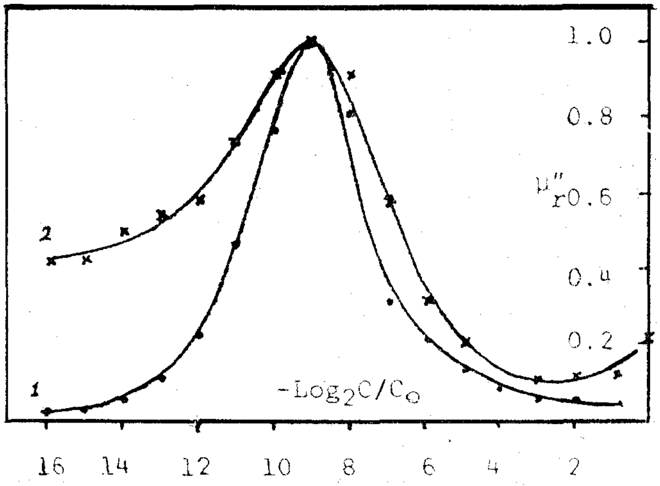

Fig. 3. μ_r'' vs Log_2 C/C_0 for KCl (1) and KCl + 0.004 wt/vol Agar (2)

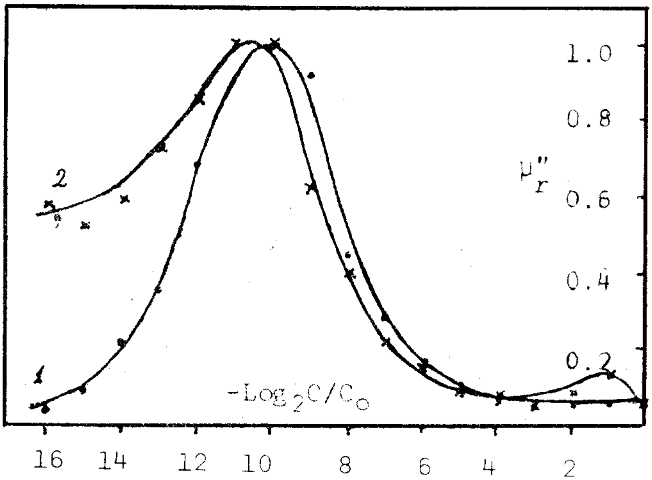

Fig. 4. μ''_r vs Log$_2$ C/C$_0$ for CaCl$_2$ (1) and CaCl$_2$ + 0.004 wt/vol Agar (2)

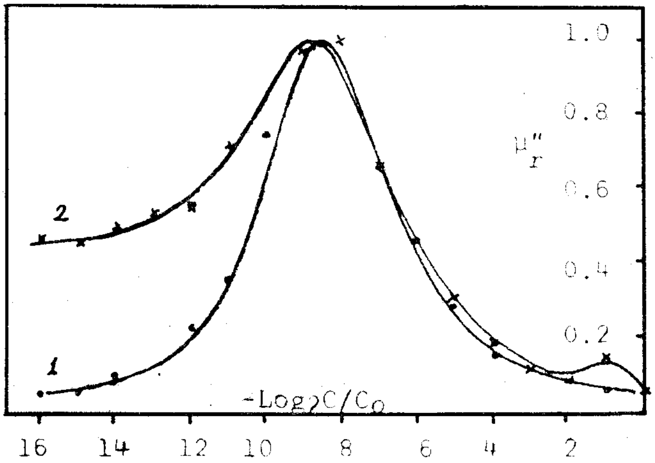

Fig 5. μ''_r vs Log$_2$ C/C$_0$ for BaCl$_2$ (1) and BaCl$_2$ + 0.004 wt/vol Agar (2)

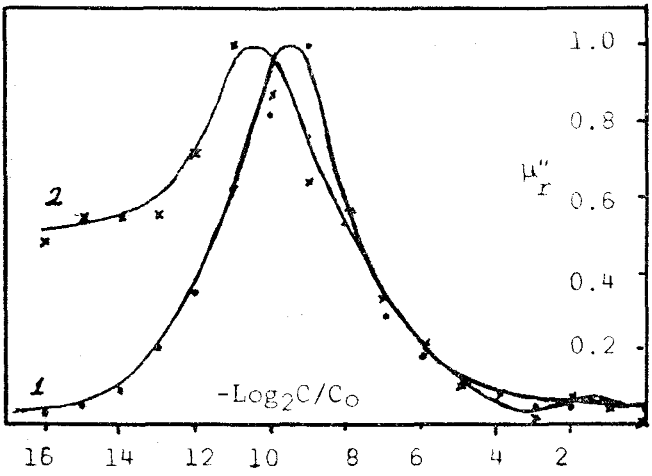

Fig. 6. μ''_r vs Log$_2$ C/C_0 for $MgCl_2$ (1) and $MgCl_2$ + 0.004 wt/vol Agar (2)

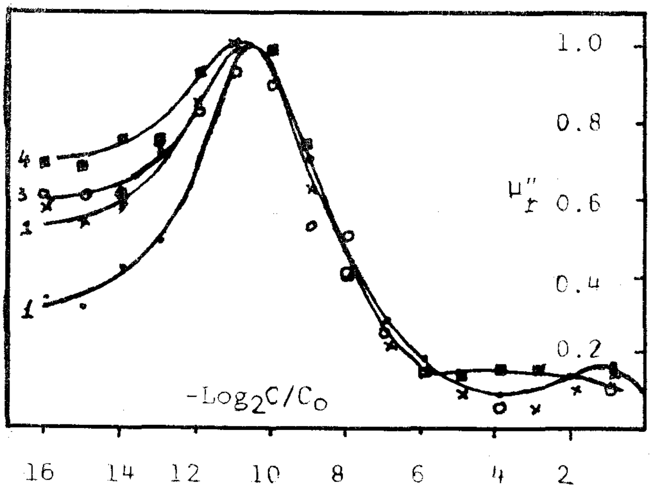

Fig. 7. μ''_r vs Log$_2$ C/C_0 for $CaCl_2$ + Agar (at different contents)
(1) 0.002 wt/vol (2) 0.004 wt/vol (3) 0.006 wt/vol (4) 0.008 wt/vol

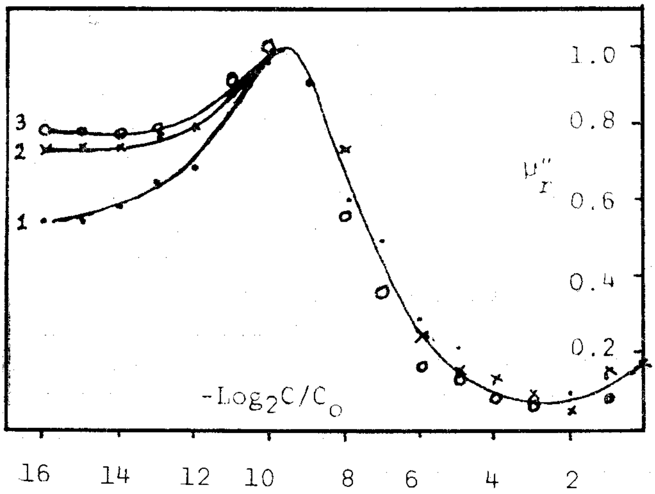

Fig. 8. μ''_r vs Log_2 C/C_0 for NaCl + Agar (at different contents)
(1) 0.004 wt/vol (2) 0.008 wt/vol (3) 0.0016 wt/vol

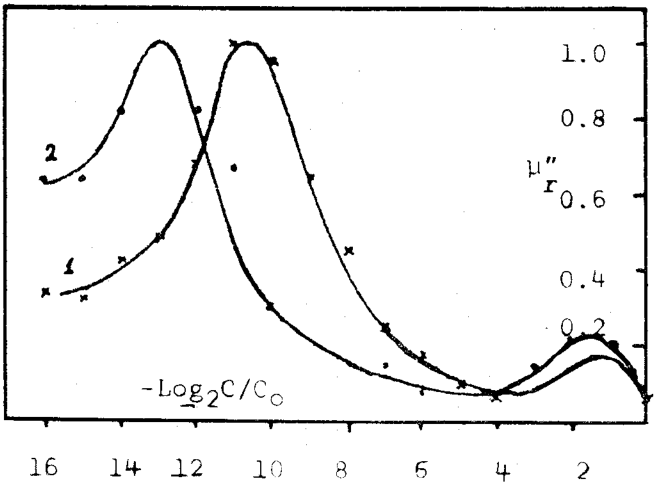

Fig. 9. μ''_r vs Log_2 C/C_0 for $CaCl_2$ + Agar (at different frequencies)
(1) 2.0 MHz (2) 0.5 MHz

(a) General. The shapes of all the figures are in accord with Eq. (3) or Eq. (6). They all have a main peak corresponding to a concentration C_{op}. The C_{op} values were determined for each sample from the figures and they were listed in Table I. The Debye-Falkenhagen constants also were estimated for each sample from Eq. (7). The results are in the order of 10^{-10} (mol/lt) s and agree with the prediction of Falkenhagen. The relaxation times of each solutions have been given in sixth column for $C = 10^{-2}$ mol/lt. In the last column, the total macroion concentrations which are the differences between C_{op} values with and without agar of the solutions, are shown. In the salt-added colloidal solutions, the positions of the main peaks have been drifted with respect to related pure salt solutions. It is evident that maximum absorptions are due to ionic relaxations of pure salt solutions. The drifting of the positions of the main peaks toward dilute salt solutions show that the addition of the agar causes an increase in the total ion number in the sample. It is shown from Table I that as the agar content increases the total macroion concentration increases for the same salt solutions. On the other hand the total macroion concentration in NaCl is greather than in $CaCl_2$ for same agar content.

Table I. Some Experimental and Calculated Parameters of the Solutions (f = 2 MHz and t = 37 °C)

Salt Solutions	Agar Content (wt/Vol) x 10^{-3}	C_o (mol/lt)	C_{op} (mol/lt) x 10^{-3}	k x 10^{-10}	τ x 10^{-8} s	Total Macroion Concentration (mol/lt) x 10^{-3}
NaCl	–	5.000	19.50	15.5	15.5	–
NaCl	–	5.000	15.30	12.2	12.2+	–
KCl	–	7.533	18.10	14.4	14.4	–
KCl	–	7.533	11.50	9.2	9.2+	–
NaCl	4	5.000	6.01	4.8	4.8	13.50
NaCl	8	5.000	5.61	4.4	4.4	13.89
NaCl	16	5.000	4.88	3.8	3.8	14.62
KCl	4	7.533	14.71	11.7	11.7	3.39
$MgCl_2$	–	5.697	5.56	4.4	4.4	–
$BaCl_2$	–	1.800	5.71	4.5	4.5	–
$CaCl_2$	–	6.710	6.55	5I2	5.2	–
$CaCl_2$	2	6.710	4.32	3.4	3.4	2.23
$CaCl_2$	4	6.710	4.32	3.4	3.4	2.23
$CaCl_2$	6	6.710	3.76	3.0	3.0	2.79
$MgCl_2$	4	5.697	3.93	3.1	3.1	1.63
$BaCl_2$	4	1.800	4.33	3.4	3.4	1.38

+ At 25 °C (Çetin, 1976).

(b) The Relaxation Times. The relaxation time of each solution was calculated from Eq. (1) for $C = 10^{-2}$ mol/lt. It is shown that the ionic relaxation times have considerable different values for monovalent and divalent pure salt solutions. While it varies from 14.4×10^{-8} s to 15.5×10^{-8} s for KCl and NaCl respectively, in divalent salts this variation occurs in the interval of 4.4×10^{-8} s and 5.2×10^{-8} s. That is the ionic relaxation times of divalent salt solutions shorter than that of monovalent salts. On the other hand the relaxation times of all solutions containing macroions shorter than corresponding salt solutions.

It is also possible to obtain an information about temperature dependence of ionic relaxation times in salt solutions. At 37 °C it has 15.5×10^{-8} s for NaCl and 14.4×10^{-8} s for KCl. At 25 °C these values become 12.2×10^{-8} s and 9.2×10^{-8} s for same results respectively. As the temperature decreases the ionic relaxation time decreases too. This result agrees with temperature dependence of the molecular motion.

(c) The Frequency Dependence of μ_r''. Fig. 9 shows the variation of μ_r'' versus $\text{Log}_2\, C/C_o$ at two different frequencies, 2.0 MHz and 0.5 MHz. C_{op} values for the main peaks were found 4.63×10^{-3} mol/lt and 1.00×10^{-3} mol/lt for 2.0 MHz and 0.5 MHz respectively. These concentration values correspond to $\tau = 7.96 \times 10^{-8}$ s for f = 2.0 MHz and $\tau = 31.84 \times 10^{-8}$ s for f = 0.5 MHz. According to Eq. (8) as the frequency decreases the concentration corresponding to maximum energy absorption must decrease in the same rate. It is obviously shown that our experimental results and the related theory are in perfect agreement.

(d) Macroionic Relaxation. For all salt-added colloidal solutions the plots of μ_r'' versus $\text{Log}_2\, C/C_o$ have not symmetric forms as in the case of pure salt solutions. The differences from related pure salt solutions can be summarized as follows:

1. The Region Corresponding to Dilute Salt Concentration. It is shown from Fig. 2 that μ_r'' goes zero for $-\text{Log}_2\, C/C_o = 16$, namely for $C = 7.6 \times 10^{-5}$ mol/lt in pure NaCl solution. But in the salt-added colloidal solution the value of μ_r'' corresponding to the same salt concentration is 0.52. This absorption must be due to colloidal macroions. Indeed the calculated total macroion concentration in this sample is about 13.50×10^{-3} mol/lt.

2. The Region Corresponding to Saturated Salt Concentration. The ranges of absorption curves of salt-added colloidal solutions correspon-

ding to the saturated salt concentrations are more interesting. In the case of monovalent salts these curves approach a second peak (Figs. 2 and 3). But in the samples containing divalent salts these new peaks are shwon clearly (Figs. 3, 4 and 5). Also these new peaks are frequency dependent as in the case of main peaks mentioned earlier and, we may say that they are due to colloidal macroions. That is at these high concentration ranges another relaxation mechanism must be present belonging to colloidal macro ions. The ionic relaxation times of related salt solutions corresponding to these concentration ranges are in the order of 10^{-10} s and quite smaller than the relaxation time that corresponds to the C_{op}.

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