ELECTROOPTICAL METHOD OF DETERMINATION OF THE PERMANENT DIPOLE MOMENT OF COLLOIDAL PARTICLES

A Thesis

Presented to

The School of Graduate Studies

Addis Ababa University

In Partial Fulfillment

of the requirements for the Degree

Master of Science in Physics

by

ABRAHAM FELEKE

June, 1984

DEDICATION

to

SEBLEWONGIEL KASSA

ACKNOWLEDGEMENT

Profound gratitude is expressed to Dr. A.A. Spartakov, my advisor who sacrificed his time, energy and advice with no reservation.

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Electrooptical method of determination of the permanent dipole moment of colloidal particles

by

ABRAHAM FELEKE

Advisor: Dr. A.A. Spartakov

Two types of rectangular electric fields (R_1- and R_2-field) are produced by a specially constructed generator. When R_1-field acts on the capacitor plates between which is the solution to be investigated, the colloidal particles rotate and modulate the intensity of light that passes through the solution. The electric dipole moment is given by the expression

$$\frac{6KT\tau \; \ln\{(\frac{2}{b} - 1) + 2 \mid \frac{1}{b}(\frac{1}{b} - 1)\mid^{\frac{1}{2}}\}}{E\tau_o}$$

R_2-field is used for the determination of the time of relaxation τ. The electric field E is choosen and the parameters b and τ_o are measured. Although specimens of different chemical and physical nature are investigated the dipole moment per unit area μ_o is almost the same for all specimens, μ_o lies in the range $(1.4 - 2.0) \times 10^{-4}$ CGSE.

C O N T E N T S

INTRODUCTION

Extremely widespread in nature, colloidal systems are very important in modern engineering, agriculture, pharmaceutical industry, meteorological phenomena and national economy.

Some examples showing the role of colloidal systems and colloidal processes in man's everyday life and his environment are given below.

Colloidal systems and processes are very important in meteorological phenomena, the formation of rocks and minerals.

Clouds and mists are colloidal systems, and their particles often carry and electric change. Rain, lightening, and other meteorological phenomena are connected with colloidal processes.

As a result of thorough investigations of aerosol properties, there are now techniques of counteracting dusts, smokes and mists, and techniques of artificially causing rain, extremely important in agriculture.

Colloidal chemistry is very important in agriculture. Soil for example is an extremely complex colloidal system. The nature, size and form of soil particles determine the water permeability which in turn influence crop yields. Wide use is now made of what are called structuralizing agents based on polymers whose introduction into the soil prevents erosion and gives the soil desirable properties.

In the national economy, all industries are more or less connected with colloidal systems and processes. For example, paper making techniques which give valuable properties to paper include the granulation of plant fibre unitl it is highly dispersed, the preparation of dispersions of various pasting agents (colophony, artificial resins, raw rubber), and the deposition of the particles of these dispersions on the surface of the ground fibre as a result of the coagulating action of electrolytes.

Many more natural, technical and analytical applications of colloids can be sited and still many more colloidal systems and processes are unknown to man. Therefore, better knowledge of the behavior of colloids and their mode of formation is useful for man's progress in the economic and scientific fields.

The aim of the thesis is to determine the value of the permanent electrical dipole moment characteristic of colloidal particles in polar dispersion medium.

When alternating rectangular electric field is applied to a sol, the particles rotate absorbing light which passes through the sol anisotropically and we have a modulation curve of the intensity of transmitted light. From this modulation curve μ , the value of the permanent electrical dipole moment, can be determined.

CHAPTER 1

.1 Colloidal Systems and their properties

A preparatory discussion of the basic ideas of colloidal chemistry is necessary and we start our discussion with what colloids and colloidal systems are.

Man has been acquainted with natural colloidal systems from time immemorial but it was comparatively recently that they began to be studied. In the 1840's the Italian Scientist Francesco Selmi drew attention to the anomalous properties of some solutions which, according to modern concepts, are typical colloidal systems. These solutions strongly scatter light; substances dissolved in them precipitate, dissolution of a substance and its precipitation are not accompanied with a change in temperature. Selmi called such solutions pseudo-solutions in order to distinguish them from the ordinary ones. Later, they became known as soles.

In the 1860's the English chemist Thomas Graham thoroughly studied the properties of those solutions which interested Selmi. Graham termed these solutions, and the substances which form them, colloids. The specific characteristics of colloidal solutions are the following[1].

1. All colloidal solutions are capable of scattering light or, in other words, opalescing. Opalescence becomes especially noticeable if a beam of converging

rays is passed through a colloidal solution, by putting a lens between the light source and the cell containing the solution, as Tyndal had done. Under these conditions, a bright glowing cone (The Tyndal cone) is seen in the colloidal solution when looking at it sideways. Opalescence undoubtedly indicates heterogeneity of colloidal solutions.

2. Diffusion of particles in colloidal solutions is very slow.

3. Colloidal solutions have very low osmotic pressure, which is often even difficult to detect.

4. Colloidal solutions are capable of undergoing dialysis, ie. they can be separated, by means of a semi-permeable partition (membrane), from the impurities of low molecular weight substances dissolved in them. During dialysis the molecules of a low molecular solute pass through the semipermeable membrane while the colloidal particles which are incapable of passing through the membrane (dialyzing) remain behind it as purified colloidal solution.

The last three properties indicate that colloidal solutions contain relatively large particles of the solute. Indeed, diffusion is affected by the size of particles because, as they grow in size, greater friction makes it more and more difficult for them to move in the solution. Osmotic pressure is a colligative property, ie. at constant temperature, it depends only on the number of particles in the volume, its small value indicates the large size of particles because at the same gravemetric concentration and the same density of the solute, the larger the particles, the smaller is their amount in the solution.

5. Unlike true solutions, which are stable systems, colloidal solutions are aggregatively unstable (labile), ie. a colloid is capable of being separated from a solution (to coagulate) rather readily under the action of inconsiderable extraneous effects. As a result, a precipitate consisting of aggregates of aggromerated primary particles is formed in the colloidal solution. The aggregative instability of colloidal systems is usually greater, the larger their concentration is. Among the effects that cause coagulation are heating, freezing, intensive stirring and especially introduction of very small quantities of electrolytes into a solution.

6. Colloidal solutions can be subjected to electrophoresis. Discovered by F. Reiss in Russia in 1808, this phenomena consists in the transfer of colloidal par-

ticles to one of the electrodes in the electric field. Consequently, colloidal particles, like ions, can carry an electric charge. Contrary to electrolysis where its products are deposited on electrodes in equivalent quantities, in electrophoresis substances are transfered only in one direction.

How does a colloidal system differe from a non colloidal one? Decades of extensive research have shown that the colloidal state of a substance is a highly dispersed (greately disintegrated) state in which separate particles are not molecules but aggregates consisting of numerous molecules as a result of the action of intermolecular forces. In accepting this definition of the colloidal state (colloidal system), we may formulate the basic feature which distinguish colloidal systems from true solutions.

In a colloidal system the colloidal particles form one phase, disperged phase, and the molecules of the medium in which colloidal particles are dispersed form another phase, dispersion medium. Consequently, unlike true solutions which are homogeneous systems, any colloidal solution is a heterogeneous, multiphase system and a prerequisite of its formation is the insolubility (or very slow solubility) of a substance of one phase in a substance of another one.

The definition of colloids is confirmed by the aforementioned properties of colloidal solutions. It is precisely such heterogeneous systems that strongly scatter light, possess low diffusibility, are capable of dialysis, and can be aggregatively unstable. The cross sectional size of a colloidal particle (for spherical particles, the diameter d) is within the limits of 1 - 100 nm.

1.2 Optics of Colloidal Particles.

The optical properties of a sol are determined by the properties of colloidal particles, and therefore, the size, shape and structure of particles invisible under the ordinary microscope can be established by studying the optical properties of a system. The study of optical properties has helped to quantitatively interpret such processes as diffusion, brownian motion, sedimentation and coagulation.

In this introduction is presented the principal phenomena and patterns observed when a light beam falls on a colloidal system, and attention is mainly given to application of these regularities to solving practical problems of colloid chemistry.

The following phenomena may be observed when a light beam falls on a disperse system:

1. passage of light through the system;

2. refraction of light by particles of the dispersed phase;

3. reflection of light by particles of the dispersed phase;

4. light scattering (this phenomena is manifested in the form of opalescence);

   The process of scattering resembles fluorescence. That one is not dealing with fluorescence in this case is seen, however, in the fact that the wavelength of the scattered light is always the same as that of the incident light, but fluorescence is an intra-molecular phenomenon, which consists in the selective absorption of light quanta and emission of a longer wavelength.

5. Absorption of light by the dispersed phase with the conversion of light energy into thermal energy.

Light scattering and absorption of light are considered further, because the other three phenomena are subjects already familiar to us and because colloidal systems are mainly characterized by the scattering and absorption of light.

1.2.1 Light Scattering.

Attention was drawn to opalescence resulting from light scattering first by Faraday (1857); and then by Tyndal (1869) who observed the formation of a glowing cone when a light beam was passed through colloidal solution.

Light is scattered only when a light wavelength is greater than the size of a particle of the dispersed phase. If the light wavelength is far smaller than the particle diameter, light is reflected. A distinction should be made between the light scattering by particles which conduct electric current and that by particles which do not.

The theory of the connection between particle size and light scattering is as follows [2].

In a perfectly homogeneous medium the light is not scattered. With the passage of a light wave all the particles of the medium undergo a polarization alternating with the frequency of the light. As a result dipoles are produced with an alternating moment which again radiate light but through interference of the radiation from all the dipoles, the result is that the light is propagated in the original direction with undiminished intensity. If however the refractive index is changed locally by a disturbance, a dipole moment of a different size is induced at this place and its radiation does not quite fit in with the rest of the medium. The result is that the extra dipole moment, which can be positive or negative, emits a radiation which is not compensated and which we observe as scattered light. The disturbance can be by the presence of foreign particles with a greater or smaller polarizability than the medium or by density fluctuations.

Scattered light spreads in all directions, its intensity differing according to the direction. If the particles are very small in comparison with the wavelength, light is scattered to the greatest extent at angles of 0° and 180° to the ray incident on a particle. If the particles are comparatively large (but still smaller than the light wavelength), the greatest amount of light is scattered in the direction of the incident ray (forward). Scattered ray is always polarized. For small particles light scattered at angles of 0° and 180° is not polarized at all; while light scattered at an angle of 90° is completely polarized; for large particles, maximum polarization is observed at an angle which differs from 90°.

It is convenient to represent light scattering in the form of a vector diagram proposed by G. Mie[3]. To obtain such a diagram, the intensity of non-polarized and polarized light expressed in certain units is plotted in the form of radii-vectors in all directions from the point representing a particle, and the terminals of the vectors are connected by a continuous line. Mie's diagrams for light scattering by a very small particle and a comparatively large one are given in Fig. 1 below (the arrow shows the direction of light incident on the particle).

The external curves on the diagrams connect the terminals of radii-vectors which correspond to the total intensity of scattered light, the internal curves limit the segments of vectors which correspond to the intensity of non-polarized light. Hence the external shaded part of the diagram represents the polarized part of the scattered light while the internal part of the diagram represents the non-polarized part of light. The given diagrams relate light scattering by spherical particles.

For spherical particles which do not conduct electric current, are small in comparison with the wavelength of the incident light, and are separated by a rather large distance from one another (dilute system), Rayleigh derived the following equation which connects I_o, the intensity of incident light; I_s, the intensity of scattered light per unit volume of a system:

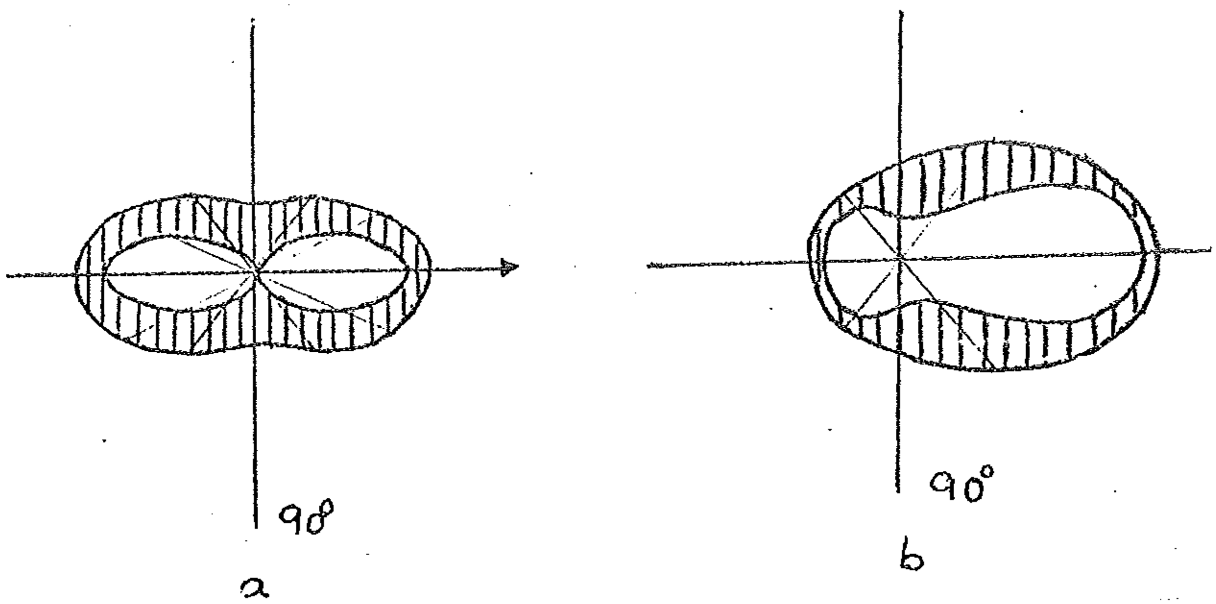


Fig. 1: Mie's diagram characterizing the scattering of light of a very small particle (a) and a large particle (b)

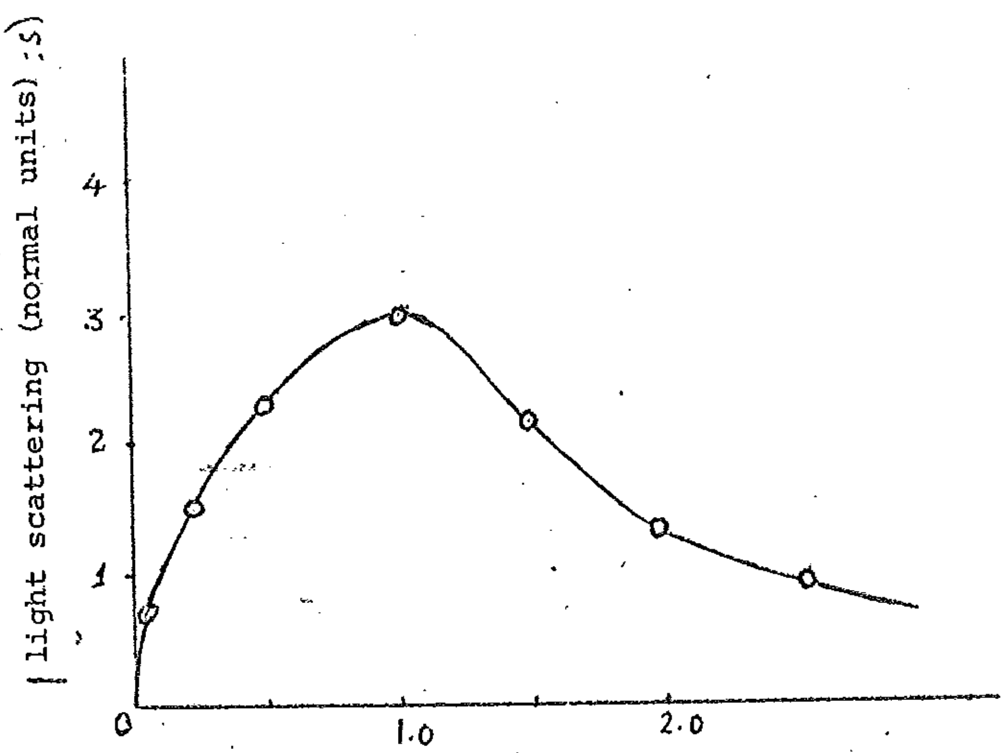


Fig. 2 Particle size, µm

$$I_s = 24\pi^3 \left(\frac{n_1^2 - n_o^2}{n_1^2 + 2n_o^2}\right) \frac{\nu v^2 I_o}{\lambda^4} \qquad (1.1)$$

where n_1 and n_o = indices of refraction of the dispersed phase and the dispersion medium

ν = numerical concentration, the number of particles contained in 1 cc of the system

v = volume of one particle

λ = light wavelength.

Rayleigh's equation is valid for particles whose size is not more than 0.1 of the light wavelength, or 40 - 70 nm. For larger particles, I_s changes in inverse proportion not to the fourth, but to a smaller power of λ. Of course, this increases light scattering.

When the size of particles becomes considerably greater than λ, light is no more scattered but reflected, regardless of the light wavelength. If the particles are too large, light reflection from them increases, and this reduces the intensity of scattered light. At the same time, as we shall see from Rayleigh's equation, the intensity of light scattering also diminishes as the particle size decreases. Therefore, colloidal particles scatter light to the greatest extent.

The following conclusions can be drawn from Rayleigh's equation:

1. For particles of a given size, the intensity of scattered light is directly proportional to the sol concentration. This principle can be used to determine the concentration of the dispersed phase by measuring the light scattering of the sol. However, since multiple scattering occurs at very high concentration, corrections should be made in Rayleigh's equation.

2. The intensity of scattered light is proportional to the square of the particle volume or, for spherical particles, to the six power of their radii. In the Rayleigh region a decrease of the particle size, concentration remaining unchanged, causes a corresponding diminution of light scattering.

Rayleigh's equation can be expressed as

$$I_s = K\nu v^2 I_o \tag{1.2}$$

Suppose the particle volume diminishes by X times as a result of disintegration while the gravimetric concentration of the dispersed phase remains constant. Then, the numerical concentration will increase by X times, and we will have

$$I_S^1 = KX\nu\left(\frac{v}{X}\right)^2 I_O = \frac{K\nu v^2 I_O}{X} \qquad (1.3)$$

ie. light scattering will diminish by X times. This result coincides with the experimental results which show that the higher the dispersion of a sol, the less does it scatter light.

When the size of particles is considerably larger than the light wavelength, light is not scattered, as we have seen, but reflected, the intensity of scattered light diminishes as the particles grow in size[4]. Fig.2 shows the light scattering of a general suspension as a function of the dispersion of a system (at constant gravimetric concentration).

Light scattering is characterized by the initial ascending part of the curve. Since maximum light scattering corresponds to the colloidal extent of dispersion of a system, the observation of opalescence is among the extremely sensitive methods of detecting the colloidal nature of a system.

In opalescence under the action of white light with side illumination, colourless colloidal systems exhibit a dark bluish color. Since the quantity I_S is inversely proportional to λ^4 dark blue (short) waves are the ones mainly scattered. Conversely, these colloidal systems have a reddish color in transmitted light because the rays of dark blue light go out of the spectrum as a result of scattering when they pass through the colloidal solution. If the system is illuminated by monochromatic light, this phenomenon is naturally not observed since in this case scattered light contains only the same wave as that of the incident light.

Opalescence of sols (especially metallic ones) is more intensive than that of solutions of high molecular weight compounds owing to the greater density and, consequently, the higher refractive index of the dispersed phase of the former systems. It is very convenient to observe the effect of the relationship between refractive indices of the dispersed phase and the dispersion medium on light scattering of the disperse systems by taking emulsions.

Opalescence of true solutions is very slight because the expression νv^2 in the numerator of Rayleigh's equation is very small owing to the low volume of particles (molecules).

The foregoing relates to light scattering by colourless colloidal particles which do not conduct electric current In the specific absorption of some rays, the dependence of the intensity of light scattering on λ^4 and v^2 , according to Rayleigh's equation, is upset, the degree of polarization of scattered light changes, and so forth. In a particle which conducts electricity, the electromagnetic field of the light waves induces the electromotive force. As a result, alternating electric current originates in the conductor (particle), just as in the electromagnetic field. Consequently, electric energy is transformed into thermal energy. Under such conditions, short electromagnetic waves (100 - 1000 nm) are absorbed almost completely. This property of conductors which include metals is the cause of their opacity.

1.2.2 Light Absorption

In 1760, J. Lambert, and still earlier P. Bougeur, in studying light scattering, established the following relationships between the intensity of transmitted light and the thickness of the medium through which it was transmitted.

$$I_t = I_o e^{-kx} \tag{1.4}$$

where I_t = intensity of transmitted light;

I_o = intensity of incident light;

k = absorption coefficient

x = thickness of the absorbing layer.

A. Beer showed that the absorption coefficient of solutions with an absolutely colorless and transparent solvent is proportional to the molar concentration C of the solute ie. $k = \varepsilon C$. Increase of concentration should be equivalent to increase of the layer thickness. Introducing the value of the molar coefficient of absorption ε into the Bongeur-Lambert equation we obtain the Bougeur-Lambert-Beer law

$$I_t = I_o \, e^{-\varepsilon c x} \quad (1.5)$$

which establishes the dependence of the intensity of transmitted light on the layer thickness and concentration of the solute. Taking the logarithm of the equation above, we have

$$\ell n \; I_o/I_t = \varepsilon c x \quad (1.6)$$

$\ell n \; I_o/I_t$ is called the optical density D of the solution. In working with monochromatic light, it is always necessary to indicate the wavelength at which optical density was determined and to denote this density by $D\lambda$. I_t/I_o is known as the relative transparency of the solution

From eq. (1.5), we have

$$\frac{I_o - I_t}{I_o} = 1 - e^{-\varepsilon c x} \quad (1.7)$$

$\frac{I_o - I_t}{I_o}$ is known as the relative absorption.

If C = 1 and X = 1 then the molar coefficient of absorption ε will be

$$\varepsilon = \ln I_o/I_t \qquad (1.8)$$

If $\varepsilon = 0$ the solution does not absorb light, and there Boungeur-Lambert-Beer equation will assume the form

$$I_t = I_o \qquad (1.9)$$

ie. the intensity of transmitted light will be equal to that of incident light.

Many attempts have been made to apply the Bougeur-Lambert-Beer law derived for homogeneous systems to colloidal solutions. Experiment have shown that it is quite applicable to sols having a high extent of dispersion if the liquid layer is not too thick and the concentration of a solution is not very high.

The size of particles of a dispersed phase is not included in the Bougeur-Lambert-Beer equation, and therefore it would seem at first sight that the extent of dispersion of a sol should not affect its ability to absorb light. However, the size of colloidal particles affects light absorption indirectly through light scattering, as a result of which the white light which passes through loses some radiation (mainly short wave length radiation) and this can be mistaken for absorption. Such absorption caused by light scattering is called imaginary absorption.

1.3 Electrooptical Properties of Colloidal Systems.

Macroscopically all liquids are isotropic substances. It is only when we turn to the problem of the molecular structure of liquids that we are convinced of the anisotropic character of the particles of which they are formed: In the great majority of cases the molecules do not posses spherical symmetry in their physical and chemical properties (geometrical, electrical, optical, structural, etc.). The macroscopic isotropy of liquids is a result of the disordered orientation of its anisotropic elements, ie. the statistical averaging brought about by thermal motion which "smears out" all the elementary anisotropic properties[5].

Since the microscopic molecular characteristic of matter are of primary interest, several methods of investigation have been developed, based on the following idea: the liquid is subjected to an external action which to some extent orders the orientation of the particles, as a result of which the liquid as a whole acquires an anisotropy. This anisotropy is an induced one.

The role of Brownian motion: The appearance of optical anisotropy in the case of a colloidal solution in a field is determined by the orientation of the particles. Thermal motion (rotational Brownian motion) tends to destroy this orientation. In contrast with the case of molecular liquids, for which the energy of thermal motion is much larger than the energy acquired by the molecule in the electric field, in the case of colloidal liquids these energies can be comparable. Moreover, for sufficiently strong (but completely reasonable) fields and not-too-small particles the energy of a particle in the field can considerably exceed KT. This leads to two results:

1. The orientation of the particles can approach the state of saturation, ie.; can be "almost total". 2. In investigating the kinetics of orientation (ie.; studying the process of establishing the orientation in an alternating electric field) we are correct in considering the motion of a colloidal particle to a considerable degree to be mechanical, ie. in using the equations of motion of a macroscopic body in a viscous medium. We note in passing that for particles of colloidal dimensions we can at the same time neglect the effect of mechanical inertia because of the small moment of inertia of the particles. Physi-

cally this means that the motion will always take on a relaxational rather than an oscillational character; mathematically this means that the motion will be described by first-order differential equation.

The Role of Interactions. Considering a colloidal particle as a small, but macroscopic body we can treat the behavior of colloidal particles in a field as the behavior of independent bodies (for sufficient dilution of the colloid solution). Here the effect of the medium is taken into account through macroscopic parameters (viscosity, dielectric strength, index of refraction, etc.).

The Electric Fields. Let's ask two questions:
1. What sort of electric fields can be created with expedience in colloidal solutions? 2. What kind of optical anisotropy can be studied with expedience as a basic electrooptical phenomenon?

The answers to these two questions to a considerable degree predetermine the choice of the method of investigation as well as the apparatus for its accomplishment.

In the investigation of very many physical phenomena it is customary to study first the simpler laws of stationary phenomena caused by the constant action of disturbing force and then the more complex laws of relaxation phenomena caused by varying disturbances. In our case one troublesome circumstance obstructs this natural course: Colloids possess an ample electrical conductivity, and with the application of a constant electric field the constant current which arises disrupts the colloidal system. Thus, only alternating fields remain at our disposal, and therefore, it would seem, we are forced to begin with the study of nonstationary, very complex phenomena. This difficulty, however, is at a maximum only if, following the example of previous investigators, we produce the alternating field using a sinusoidal voltage, which is the most convenient from the standpoint of its practical production but very complex with regard to the mechanism of its effect on the colloidal system. If we give up sinusoidal voltages and manage to overcome certain technical difficulties creating electric field of a special form, then it is possible to economize substantially in the simplicity of the physical conditions of the experiment. We shall indicate two forms of electric fields which are favorable for the study of colloids.

Rectangular electric impulses of the first kind (R_1-field) are depicted in Fig.3a. The field of these impulses is

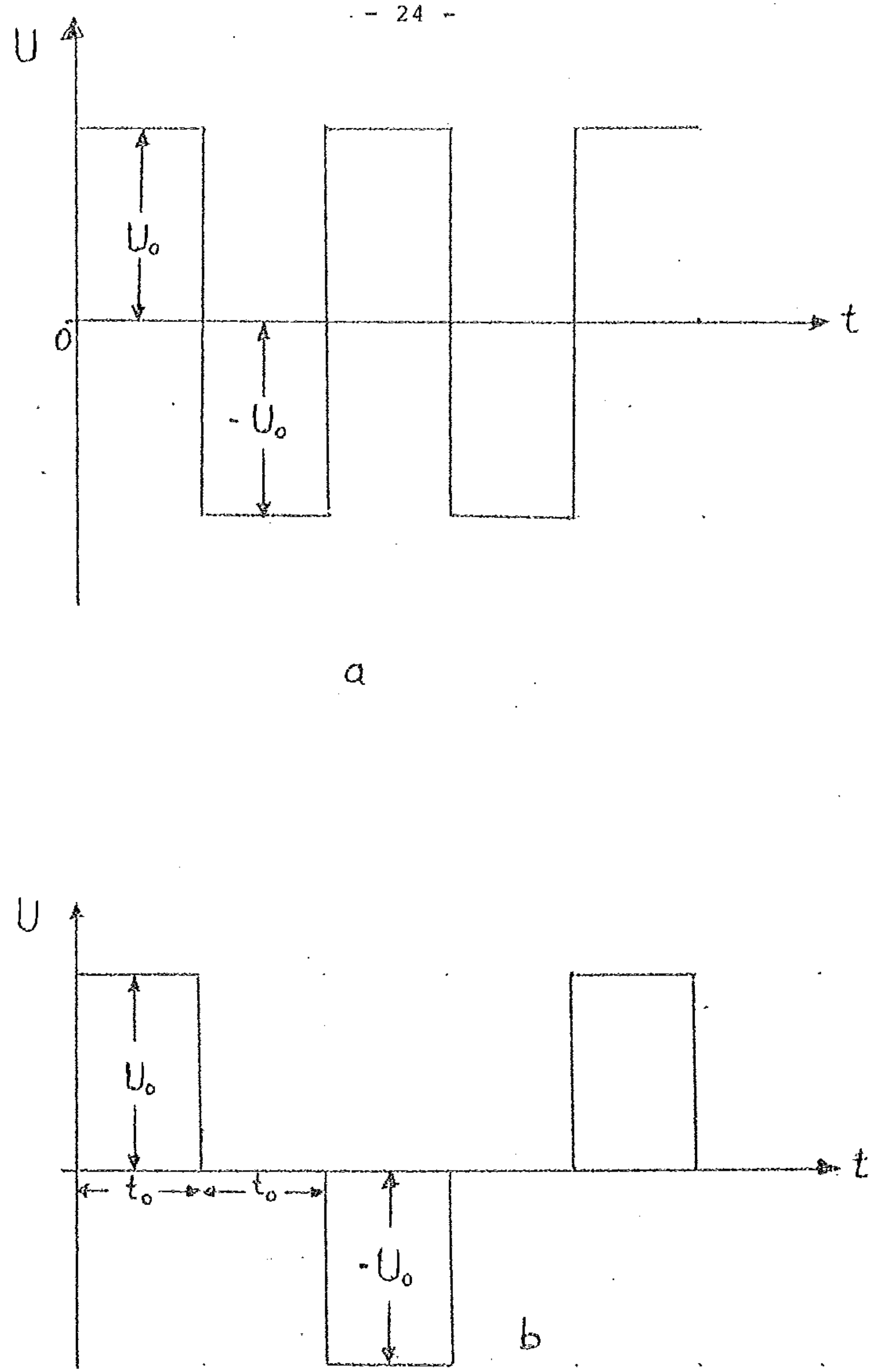


Fig. 3: Rectangular impulses of the first (a) and second (b) type

constant in magnitude but changes sign. The transition time from voltage U_o to $(-U_o)$ can be practically instantaneous ($< 10^{-6}$ sec). It is obvious that for electro-optical phenomena which depend only on the magnitude and not on the direction of the field (we shall call these phenomena nonpolar) the R_1-field does not differ from a constant one. Moreover, the static component of this field is equal to zero.

Rectangular electric impulses of the second kind (R_2-field) are depicted in Fig. 3b. The field of these impulses has a constant magnitude U_o for a time t_o, then it is equal to zero for the same time interval, where upon it has a constant magnitude but the opposite sign $(- U_o)$ for a time t_o, etc. The field R_2 appears to be the most favorable for the investigation of relaxation phenomena. Actually, the establishment of an electro-optical phenomenon is accomplished under the influence of a constant factor, and the relaxation of the electro-optical phenomenon proceeds with the sudden disappearance of this influence. The R_2-field also has no static component.

Let's return to a description of further results of the basic experiment. When R_1-field is applied to the capacitor (Fig. 4a.) the average value of the luminous flux changes, ie., the solution becomes less transparent or more transparent, and a modulation of the light with a period equal to half the period of the R_1-field is observed. Both these effects, stationary and modulated, almost always depend essentially on the orientation of the polaroid P. ie., on wether the light is polarized along or across the field.

The light modulation curves for comparatively high (Fig. 4a.) and comparatively low (Fig. 4b.) field frequencies are given.

As seen from Fig. 4, at the moment at which the field changes sign the light modulation curve not only undergoes a sharp break but the very process of increasing transparency (or opacity) of the solution is quickly replaced by a process of decreasing transparency (or opacity) (Fig. 4c.). If the modulation curve in any way reflects the change in orientation of colloidal particles, then we must conclude that after each change in sign of the field the orientation changes its direction (Fig. 4a.). In other words, if a given colloidal particle is rotated under the action of the field in some direction, then after an instantaneous change in sign of the field it reverses the direction of its rotation. The most important conclusion about the electrical structure of colloidal particles follows directly from this: Colloidal particles in water possess a rigid (permanent) dipole moment of considerable magnitude.

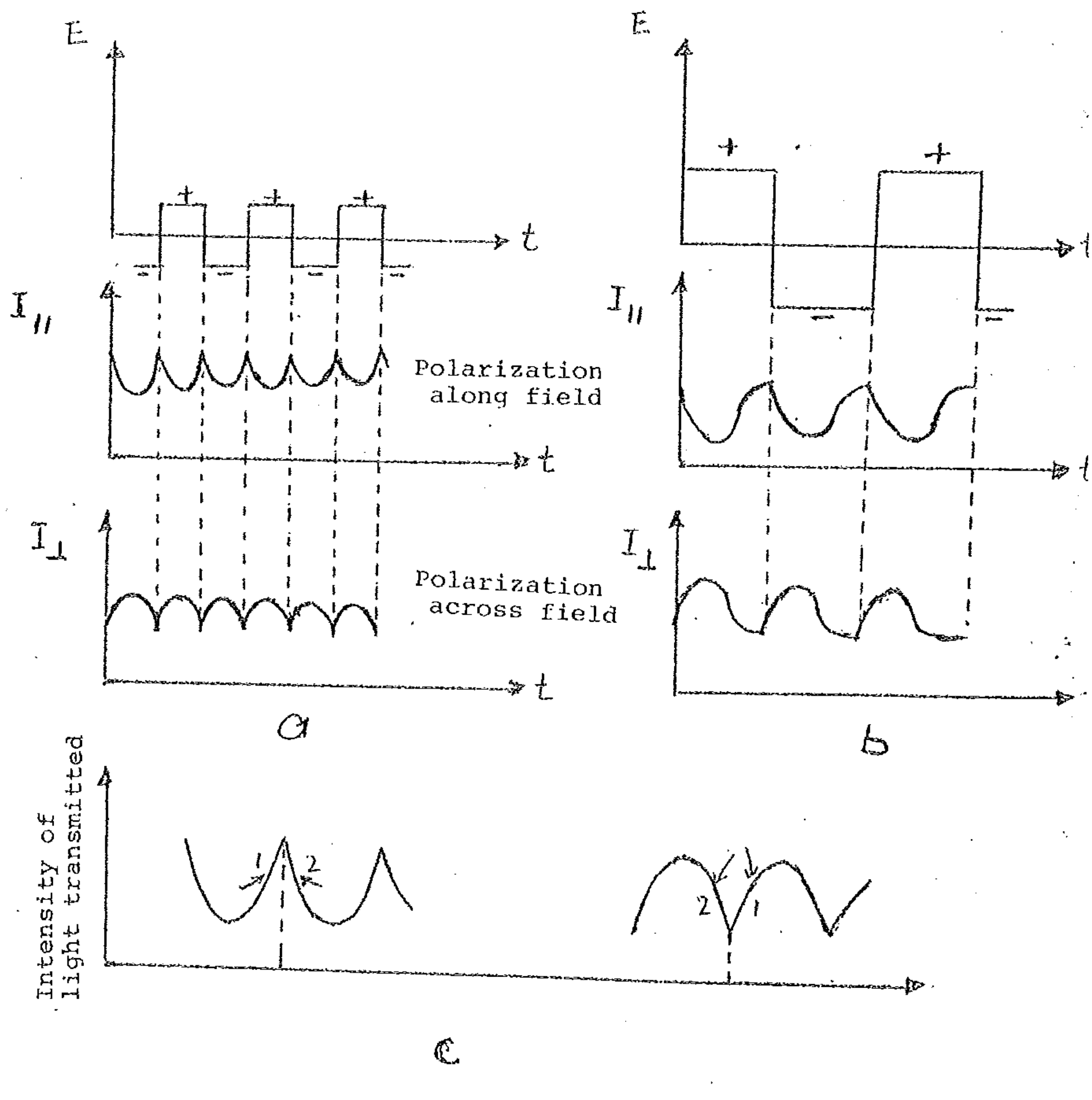


Fig. 4: Light modulation curves in an impulse field F_1
a) Field of comparatively high frequency; field of comparatively low frequency c) time plot of increase (1) and decrease (2) of transparency of a colloidal solution at the instant the field sign.

The torque experienced by a non-spherical particle in an electric field depends on its form and dimensions and on the difference in the dielectric constants of the particle (εp) and the medium (εm).

A particle will always tend to place its longest axis along the line of the field. The torque is proportional to the square of the field intensity E^2, and consequently the direction of the torque will not change when the field changes sign.

The torque may be dependent on the anisotropy of the electric polarizability of the colloidal particle (eg. if it is an electrically anisotropic crystalline particle). In this case the torque is also proportional to E^2 and does not change sign when the field changes sign. The particle tends to place its axis of greatest polarizability parallel to the field.

In all these cases the particle assumes an induced dipole moment in the electric field. When the field changes sign this induced ("soft") dipole also changes sign (practically without inertia), and therefore the direction of the mechanical torque remains unchanged.

Thus, in the electric field of the first kind (R_1-field) all factors of nonpolar orientation can cause only stationary orientation and can't be responsible for the modulation of light, which is associated with a change of orientation. Consequently, the only factor that brings about a reorientation of a particle when the field changes sign can be the rigid dipole moment of a colloidal particle. In this case the sign of the torque changes together with the sign of the field.

CHAPTER 2

THEORY OF THE METHOD OF DETERMINATION OF THE PERMANENT DIPOLE MOMENTS OF COLLOIDAL PARTICLES

The existence of an electric charge of colloidal particles has been known long ago. In 1955 N. Tolstoi and his co-worker[6] advanced the hypothesis about the existence of a permanent electric dipole moment μ of colloidal particles. Lately he and his co-workers developed methods of determination of μ[7,8]. It has been shown that this electric dipole moment is characteristic of colloidal particles of polar dispersion medium on the surface of colloidal particles.

In this chapter, we describe the new method of determination of the permanent electrical dipole moment of colloidal particles.

It is known that a colloidal solution which is subjected to a field of rectangular electric pulses modulates the intensity of light which passes through it. This modulation of light intensity proves the existence of the permanent electric dipole moment of the colloidal particles[5].

Imagine a system of monodisperse and monoshape particles oriented in the field of rectangular electric impulses. The value of this field changes from say a positive value to zero and then to a negative value periodically.

Suppose the particles have ellipsoidal shape and the direction of the electric dipole moment is along the major axis[10].

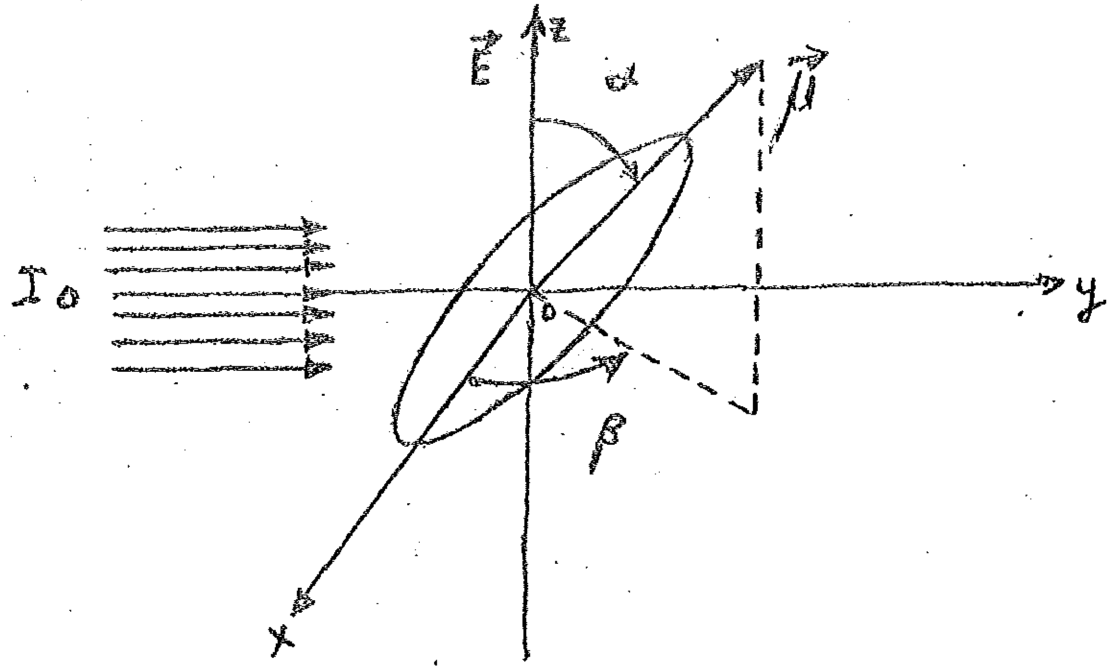
Assume the major axis of all particles make a small average angle α_o with the direction of the electric field. One of the particles is shown in Fig. 5 . If the direction of the electric field changes, the particle will rotate because an ellipsoid whose major axis is oriented along the applied field is in stable equilibrium and the equilibrium position of the minor axis is unstable[11].

A colloidal particle in such a field has thermal energy KT and electrostatic potential energy because of the permanent and induced dipole moments. The thermal energy at room temperature is of the order of 10^{-14} ergs while the electrostatic potential energy $\mu E \cos \alpha$ associated with the permanent dipole moment is (taking $\mu \simeq 10^{-12}$ cgs and $E \simeq 10^{-1}$ cgs) of the order of 10^{-13}. The order of the electrostatic potential energy increases with increasing E. Therefore, the thermal energy can be neglected compared with the electrostatic potential energy.

The general equation of motion of the particle is given by the following equation.

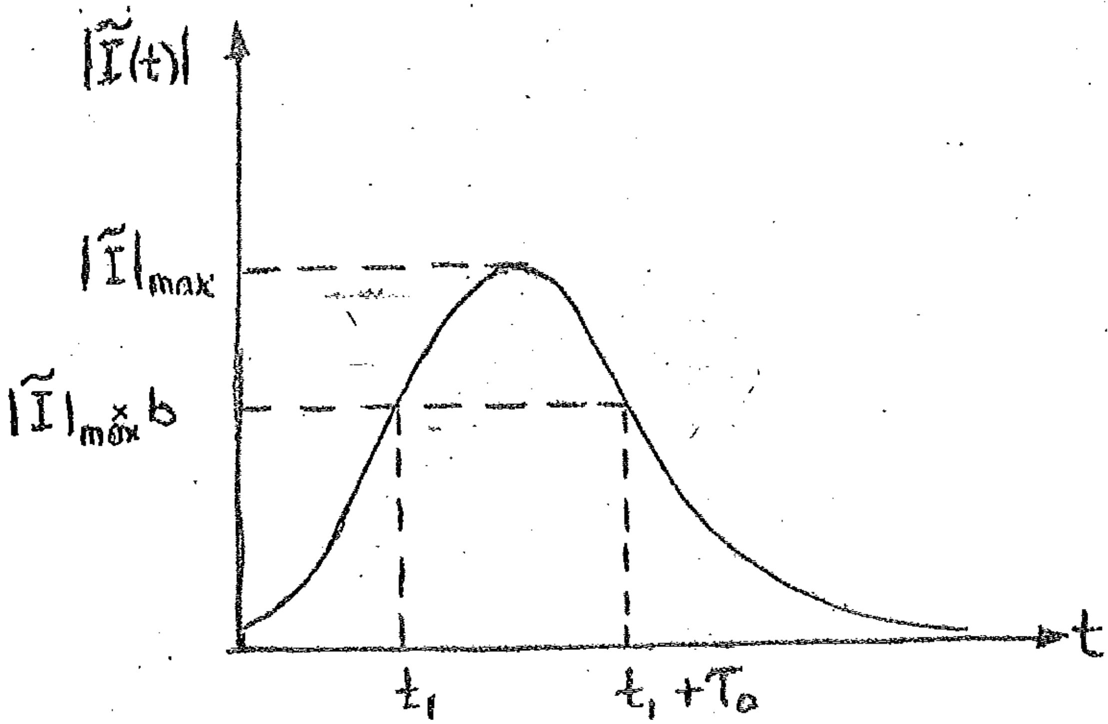
$$\mu E \sin \alpha + \tfrac{1}{2} \Delta\chi \, E^2 \sin 2\alpha = V[P]\eta \frac{d\alpha}{dt} \qquad (1)$$

where $\Delta\chi$ is the difference in the electric polarizability, V



$\vec{E}$
z
α
$\vec{\mu}$
I_0
y
o
β
x

Fig. 5:



$|\tilde{I}(t)|$
$|\tilde{I}|_{max}$
$|\tilde{I}|_{max} b$
t
t_1
$t_1 + \tau_0$

Fig. 6:

is the volume of the particle, $[P]$ is the shape factor of the particle ($[P] = 6$ for a sphere), η is the viscosity of the dispersive medium and E is the intensity of the electric field.

The order of the first term on the left of equation (1) is (taking $\mu \approx 10^{-12}$ and $E \approx 10^{-1}$) 10^{-13} cgs and that of the second term is (taking $\Delta\chi \approx 10^{-13}$; and $E^2 \approx 10^{-2}$ cgs) 10^{-15}. Moreover, the second term is insensitive to the change of sign of the electric field and remains the same when the field changes from one sign to the other. The above proof of the dominant role of the permanent dipole moment provides a route to confident determination of its magnitudes. Therefore, equation (1) with the second term neglected can be written as follows:

$$\mu E \sin\alpha = V[P]\eta \frac{d\alpha}{dt} = \lambda \frac{d\alpha}{dt} \qquad (2)$$

where $\lambda \equiv V[P]\eta$.

From equation (2), we have

$$\frac{d\alpha}{\sin\alpha} = \frac{\mu E\, dt}{\lambda}$$

$$\int_{\alpha_o}^{\alpha} \frac{d\alpha}{\sin\alpha} = \frac{\mu E}{\lambda} \int_{o}^{t} dt$$

and $\ln \tan \frac{\alpha}{2}\Big|_{\alpha_o}^{\alpha} = \frac{\mu E}{\lambda} t$

$$\tan\frac{\alpha(t)}{2} = \tan\frac{\alpha_o}{2}\, e^{\frac{\mu E}{\lambda}t} \qquad (3)$$

Equation (3) is the solution of equation (2).

The intensity I of polarized light passing through the system of colloidal particles in the direction $\vec{OY}$ will change according to:

$$dI = -I(K_1 \cos^2\alpha + K_2\sin^2\alpha \cos^2\beta + K_3\sin^2\alpha\sin^2\beta)cdy \qquad (4)$$

where K_1, K_2 and K_3 are the absorption coefficients of the particle corresponding to the three axes of the particle and c is their concentration. Solution of equation (4) can be obtained with an average β as follows:

$$\int_{I_o}^{I} \frac{dI}{I} = -(K_1 \cos^2\alpha + \frac{K_2+K_3}{2} \sin^2 \alpha)\, c \int_o^{\ell} dy \qquad (5)$$

Let's use the following simplifications and designations

$$\sin^2 \alpha = \frac{\tan^2\alpha}{1+\tan^2\alpha} \quad , \cos^2 \alpha = \frac{1}{1+\tan^2\alpha}$$

$$\sin^2 \alpha = 4 \sin^2\frac{\alpha}{2} \cos^2\frac{\alpha}{2} \text{ and } \cos^2 \alpha = 1-4 \sin^2 \frac{\alpha}{2} \cos^2 \frac{\alpha}{2} \qquad (6)$$

Therefore, $\sin^2 \alpha = \frac{4 \tan^2 \alpha/2}{(1+\tan^2 \alpha/2)^2}$

and $\cos^2 \alpha = 1 - \frac{4 \tan^2 \alpha/2}{(1+\tan^2 \alpha/2)^2}$ (7)

Let $N(t) = \tan^2 \frac{\alpha(t)}{2}$ (8)

and $K_1 \equiv K_{\parallel}$; $\frac{K_2+K_3}{2} \equiv K_{\perp}$ (9)

With the above trignometric identities and designations solution of equation (5) will be:

$$I(t)=I_o \quad e^{-c\ell\{K_{\parallel} + (K_{\perp} - K_{\parallel}) \frac{4N(t)}{[1+N(t)]^2}\}} \tag{10}$$

where ℓ is the thickness of the layer of particles. For small concentration, equation (10) can be approximated by:

$$I(t) = I_o(1-C\ell K_{\parallel}) - I_o C\ell \; (K_{\perp} - K_{\parallel}) \frac{4N(t)}{[1+N(t)]^2} \tag{11}$$

Only the second term of equation (11) depends on time. Designating this part by $\tilde{I}(t)$, we have

$$\tilde{I}(t) = I_o C\ell (K_{\perp} - K_{\parallel}) \frac{4N(t)}{[1+N(t)]^2} \tag{12}$$

The maximum of $|\tilde{I}(t)|$ designated by $|\tilde{I}(t)|_{max}$ occurs when N(t) is unity and equation (12) becomes

$$\tilde{I}(t) = |\tilde{I}(t)|_{max}\, b(t) \tag{13}$$

where $b(t) = \frac{4N(t)}{[1+N(t)]^2}$

$\tilde{I}\ max = I_o C\ell \; (K_{\perp} - K_{\parallel})$ since the maximum occurs when N(t) equals unity. I t is clear that $0<b<1$.

The second part of equation (13) has two roots N_1 and N_2 where

$$N_2 = (\frac{2}{b} - 1) + 2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]^{\frac{1}{2}} = \frac{1}{N_1} \tag{14}$$

The intensity $\tilde{I}(t)$ which characterizes the motion of the particles in the field of rectangular pulses depends on time according to equation (13). The general dependence of the intensity on time is shown in Fig.6 schematically.

The graph of the theoretical curve $\tilde{I}(t)$ for four different values α_o is plotted in Fig.7. The value of $\tilde{I}max$ is arbitrary and is set equal to unity for convenience. In the next chapter the experimental curves are produced for a series of specimens. The proof of the accuracy of the new method of determination of the permanent dipole moment of colloidal particles is the comparison of the experimental and theoretical curves.

Table I

α_o (degrees)	$\lvert\tilde{I}(t)\rvert$
2	$\tilde{I}max \frac{4x3x10^{-4}e^{ct}}{(1+3x10^{-4}e^{ct})^2}$
4	$\tilde{I}max \frac{4x10^{-3}e^{ct}}{(1+10^{-3}e^{ct})^2}$
10	$\tilde{I}max \frac{4x7.5x10^{-3}e^{ct}}{(1+7.5x10^{-3}e^{ct})^2}$
20	$\tilde{I}max \frac{4x3x10^{-2}e^{ct}}{(1+3x10^{-2}e^{ct})^2}$

$C = 1 \ sec^{-1}$

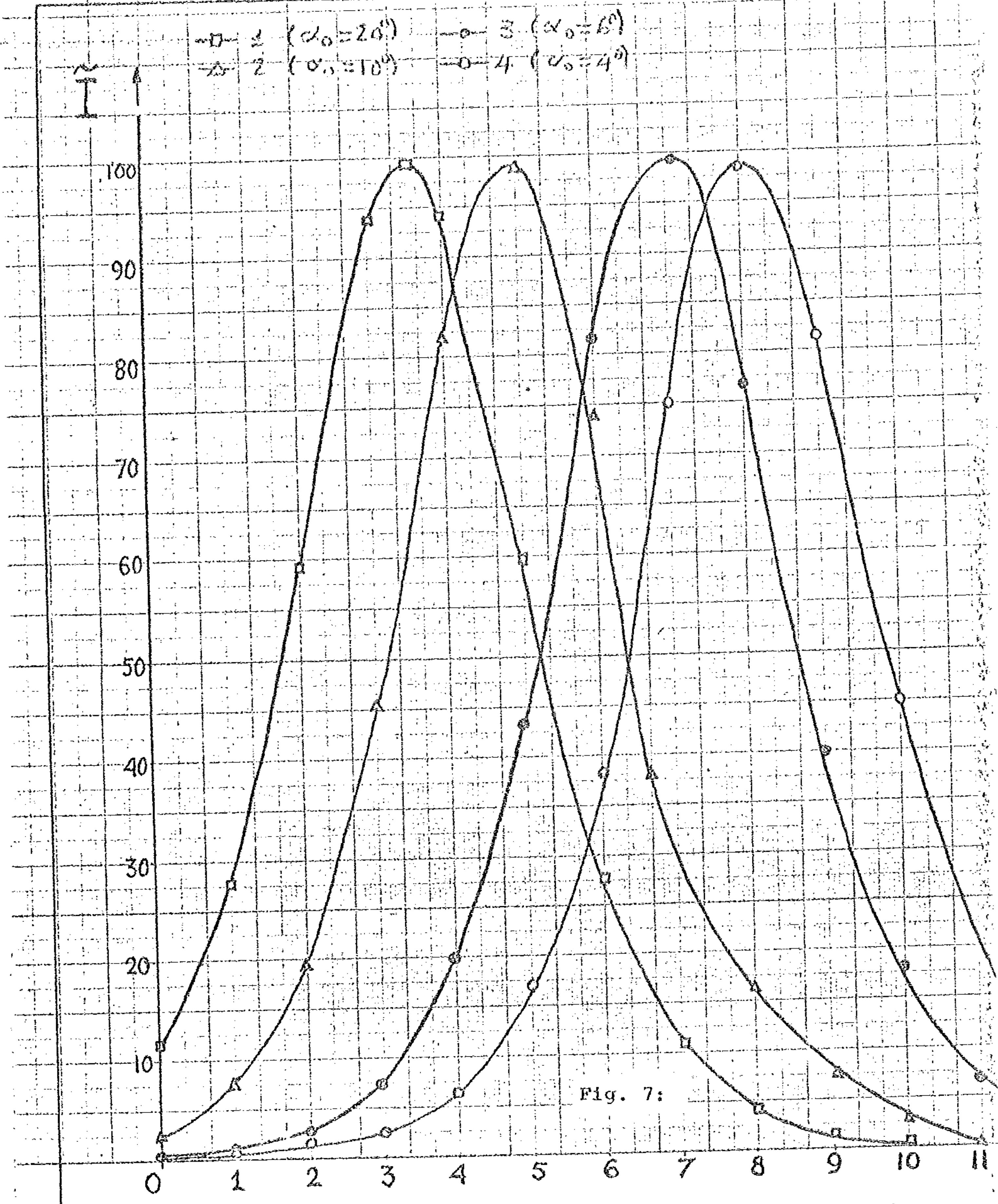

1 ($\alpha_0 = 20°$)
2 ($\alpha_0 = 10°$)
3 ($\alpha_0 = 6°$)
4 ($\alpha_0 = 4°$)
$\tilde{I}$
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11

Fig. 7:

In Fig. 6 the intensity at an arbitrary time t_1 and $t_1+\tau_o$ is the same

$$N_2(t_1+\tau_o) = \tan^2 \frac{\alpha_o}{2} \; e^{\frac{2\mu E}{\lambda}(t_1+\tau_o)} \tag{15}$$

$$N_1(t_1) = \tan^2 \frac{\alpha_o}{2} \; e^{\frac{2\mu E}{\lambda}t_1} \tag{16}$$

Dividing equation (15) by equation (16), we have

$$\frac{N_2}{N_1} = e^{\frac{2\mu E}{\lambda}\tau_o} \tag{17}$$

Since $N_2/N_1 = N_2{}^2$(Eq.14); we have

$$2 \ \ell n \ N_2 = \frac{2\mu E}{\lambda} \ \tau_o$$

and $$\mu = \frac{\lambda \ell n \ N_2}{E\tau_o}2 \tag{18}$$

Substituting the value of N_2 from equation (14) into equation (18); we have

$$\mu = \frac{\lambda \ \ell n\{(\frac{2}{b} - 1)+2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]^{\frac{1}{2}}\}}{E\tau_o} \tag{19}$$

To calculate μ, we choose b ($0<b<1$) using the experimental curve of $|\tilde{I}(t)|$ and find the corresponding time interval τ_o (Fig. 6). For example if b = 0.5, then

$$\mu = \frac{\lambda \ 1.76}{E\tau_o}$$

$$\mu = \frac{V[P]\,\eta\ell n \ \{(\frac{2}{b} - 1)+2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]\}^{\frac{1}{2}}}{E\tau_o} \tag{20}$$

In experiment it is possible to choose E and measure τ_o. To calculate μ we must know V, [P] and η separately. But another convenient way is to find the combined value of V[P].

From the theory of rotational motion of colloidal particles in viscous medium, the time of relaxation τ is connected with the diffusion coefficient D by the following equation .

$$\tau = \frac{1}{6D} = \frac{V[P]\eta}{6KT} \tag{21}$$

and $$V[P]\eta = 6KT\tau \tag{22}$$

Using equation (22), equation (20) can be written as:

$$\mu = \frac{6KT\tau \ \ln \{(\frac{2}{b} - 1) + 2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]^{\frac{1}{2}}\}}{E\tau_o} \tag{23}$$

For the determination of the value of the permanent dipole moment of colloidal particles τ is the only unknown parameter. The method of determination of τ experimentally will be explained in chapter 4 .

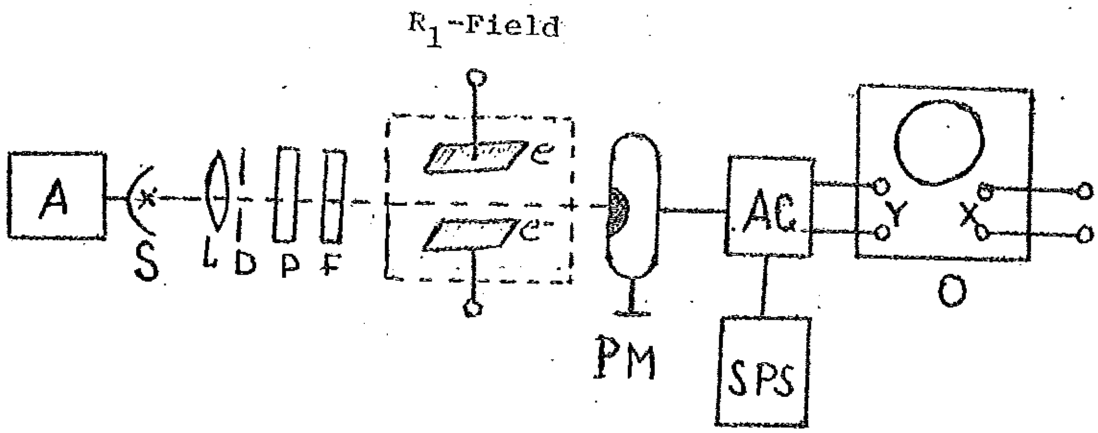
CHAPTER 3

EXPERIMENTAL INSTALLATION

:his chapter is devoted to the description of the basic method ›f investigation of colloidal solution in the field of rectan- ular pulses and to the description of the methods of prepara- :ion of colloidal solution[13].

}.1 Block-scheme of the installation for the investigation of electrooptical effect of colloidal solution is shown in Fig. 8

The source of light, S is a lamp with special filament which gives light of very high intensity in the visible spectrum. The lamp should give very high intensity of light with very high stability for correct experimental results without hindrance. Therefore, it is not possible to use electronic power supply without special high quality current stabilization. To have large stabilized current of 8 to 10 amperes is a difficult problem. Therefore, battery accumulators connected to any high current supplying power supply is used. The current from the electronic power supply is not stabilized but has oscillations. As the current passes through the accumulator, the oscillations are damped and one gets a constant large current of high stability which is supplied to the light source. In this manner, the lamp gives light in the visible



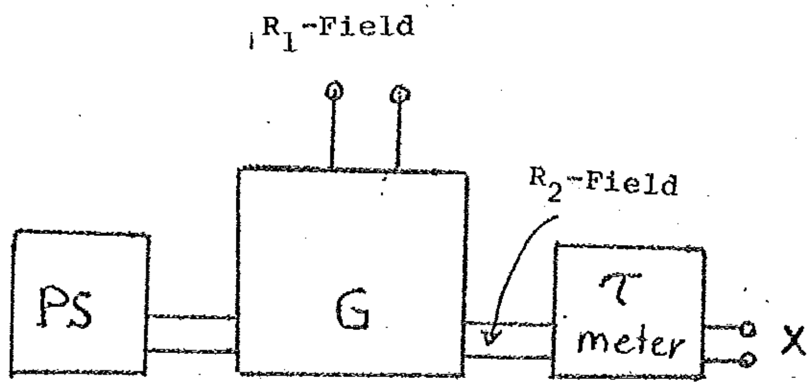


Fig. 8: Black-scheme of the installation for the investigation of electrooptical effect

spectrum of very high intensity and stability. The light from the source is focussed by a long focusing lens L in the middle of the cell with the solution to be investigated. Before it reaches the solution the light is polarized and filtered by the polarizer and interferometer filter F.

The plane parallel electrodes (e) create the electric field in the solution. The light transmitted through the solution reaches the photomultiplier PM or photo-cell, The light that reaches it has two components, a constant intensity and an oscillating part because of the dispersive medium and the colloidal particles respectively. The oscillating component is the useful part to our investigation.

If the light intensity is very weak, it is not possible to see the electrooptical effect using a photocell because of its low sensitivity. In this case a photomultiplier is used since its sensitivity is very high. If the intensity of light is very high, the oscillating useful component is very high and good electrooptical effect is produced. But photomultipliers, although they have good sensitivity, are destroyed by high intensity light. On the other hand photo cells can tolerate high intensity light and can be used for such cases. Photo cells or photo multipliers use drycells.

Electric signals from the photomultipliers or photo cells are fed into the current amplifier (Ac) for amplification. This current amplifier is run by a stability power supply (SPS). All these last parts of the installation should be carefully shielded to avoid even the smallest electric field obstruction.

The Ac current amplifier amplifies the useful signal about hundred times. This amplified signal from Ac is fed into the Y channel of the oscilloscope O which amplifies it by some thousands. The useful signal is therefore, altogether amplified by about hundred thousand times.

The generator of rectangular electric impulses, G, produces the field applied on the plates of the capacitor with electrodes (e) placed in the cell with solution. In the space between the electrodes, uniform electric field is established. This field acts on the colloidal particles oscillating them periodically. This periodic oscillation causes the modulation of the light intensity. Power supply PS connected to the generator operates the power lamps inside the generator. From one pair of terminals of the generator, electric pulses of the first kind (R_1-field) are directed to the cell containing colloidal solution, from the other pair of terminals, electric pulses of the second kind (R_2-field) are directed to the electrooptical τ-meter and after that to the X-channel of the oscilloscope O. The second type of rectangular pulses is used for the determination of the dimensions of colloidal particles observing electrooptical effects in exponential sweep obtained by the τ-meter.

3.2 Method of obtaining the electric field of special forms for the investigation of dispersion systems.

The generator produces two kinds of electrical pulses which are needed for the decision of different problems in the investigation of the physical properties of different kinds of dispersion systems such as colloidal solutions, airosols[14]. The general wire diagram of the generator is shown in Fig. 9.

The most important part of the scheme is the lamp 6H7 called the multi vibrator which produces the special form of electric pulses which makes 6H8 function. Electric pulses from the multivibrator cross the differential circuit and lamps $6x6_1$ and $6x6_2$ and reach the anodes of the trigger lamps ($6H8_1$ and $6H8_2$). The part of the scheme which is connected to the lamps $6H8_4$ and $6H8_3$ are cathode repeaters.

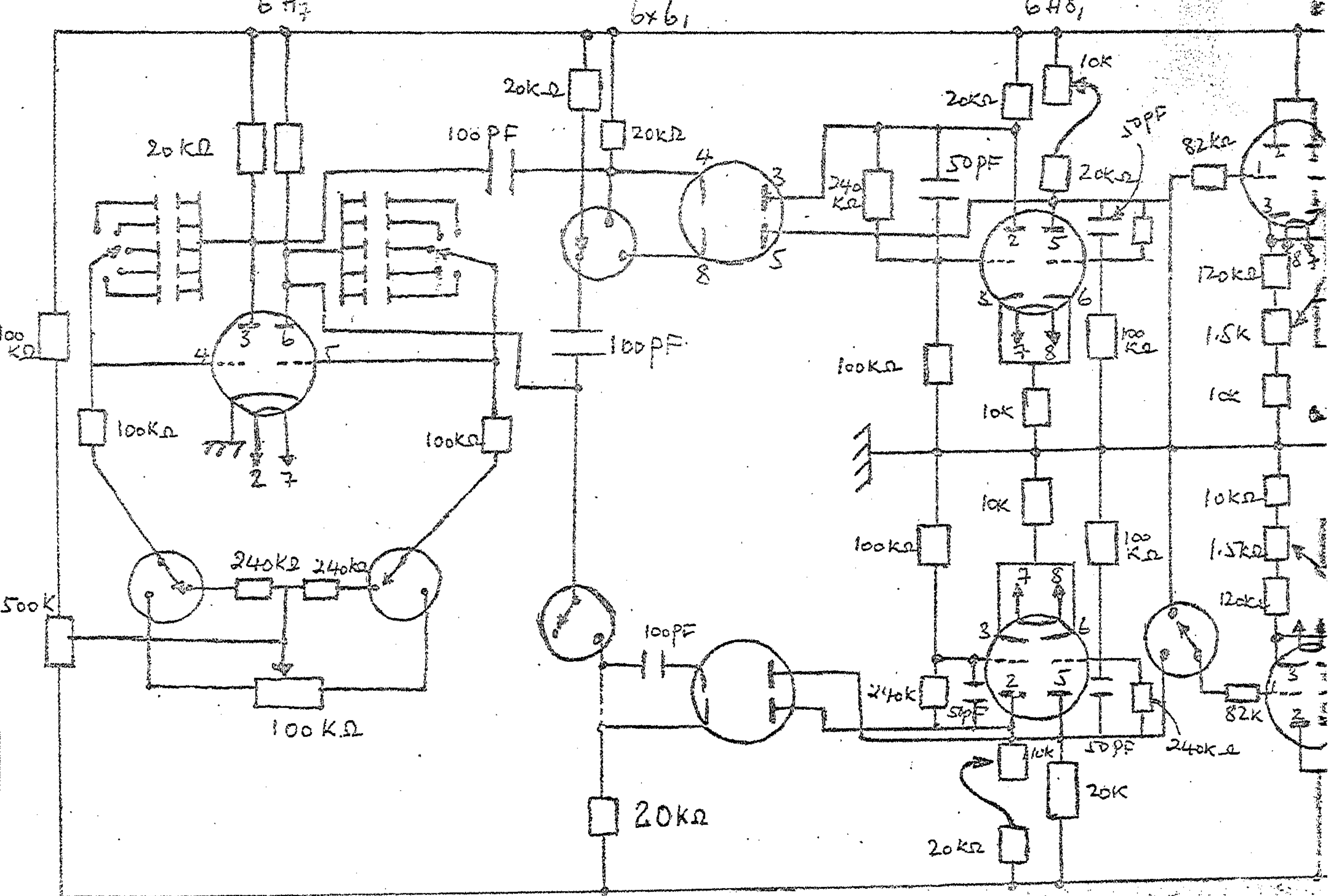

6H7
6Ж6
6Н8
20KΩ
100PF
20kΩ
20kΩ
4
3
8
5
240 KΩ
50PF
20kΩ
10K
50PF
82kΩ
120kΩ
1.5K
10K
10kΩ
1.5kΩ
120kΩ
100KΩ
100 KΩ
10K
10K
100kΩ
100 KΩ
100kΩ
100kΩ
2 7
240KΩ
240kΩ
500K
100 KΩ
100PF
240k
50pF
50PF
240kΩ
82K
10K
20K
20kΩ

Fig. 9:

This generator can work in two ways. In one way it produces symmetrical rectangular pulses of the first kind (Fig. 10 a) and in the second way non symmetrical electric field of the second kind (Fig. 10 b).

The scheme allows us to change the amplitude of both kinds of electric pulses from 100 to 260 volts and the frequency from 0.2 H_z to 2000 H_z. The time interval t and t_o can be varvied over a wide range of values. This is especially necessary for investigations such as processess of orientation and disorientation of colloidal particles and determination of the dimensions of dispersion particles. This scheme also allows one to change the frequency of the pulses without changing the amplitudes. This ability is very important in the process of investigation.

As was mentioned earlier, the two types of rectangular pulses R_1 and R_2 fields can be applied for different purposes. If R_1-field is applied to a colloidal solution, polarized light which passes between the plates of the capacitor C becomes modulated. The variation of the intensity of the transmitted light with time is shown in Fig.10 When R_2-field is applied the intensity of the transmitted light changes in accordance with Fig. 10 d.

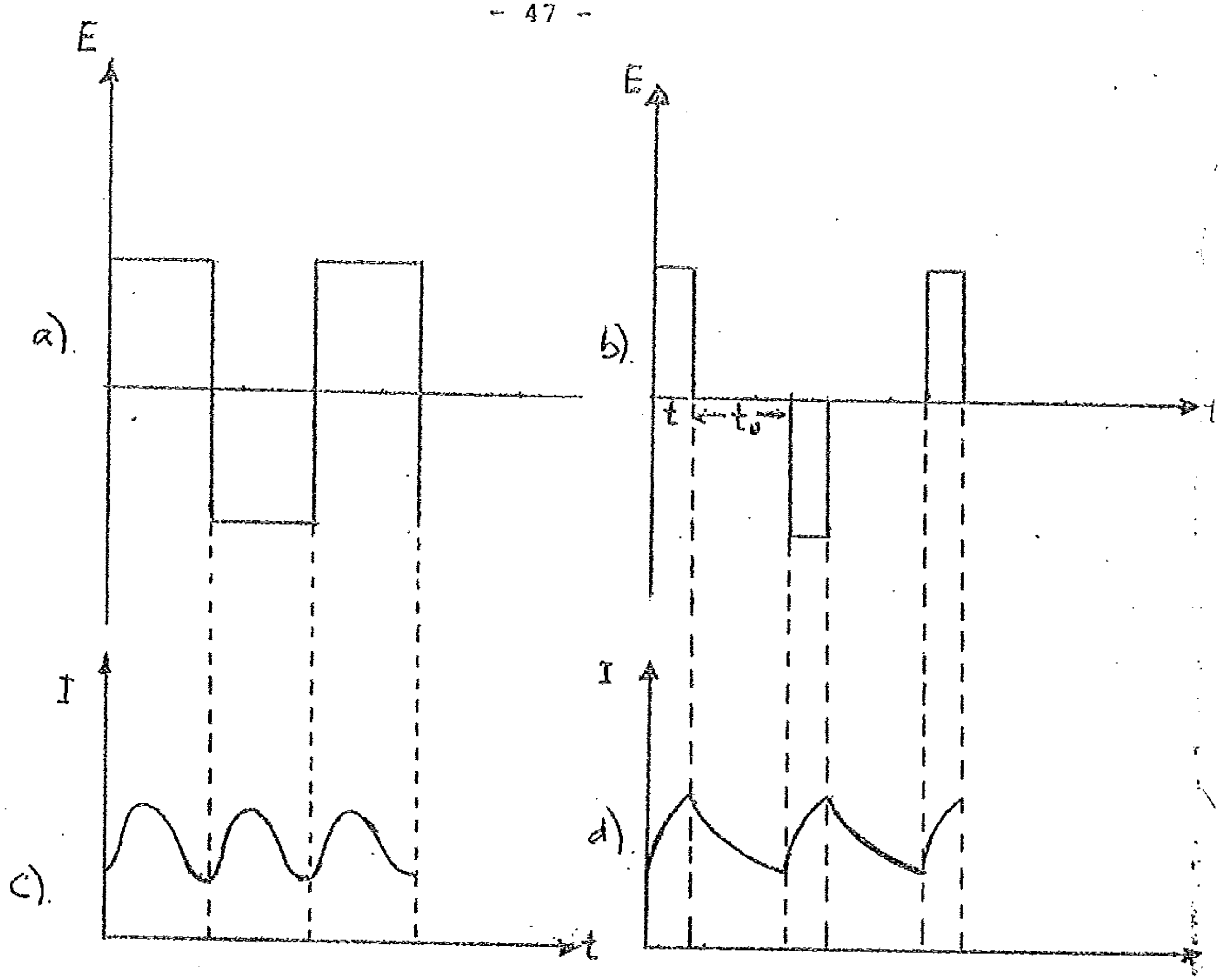


Fig. 10:

CHAPTER 4

EXPERIMENTAL RESULTS

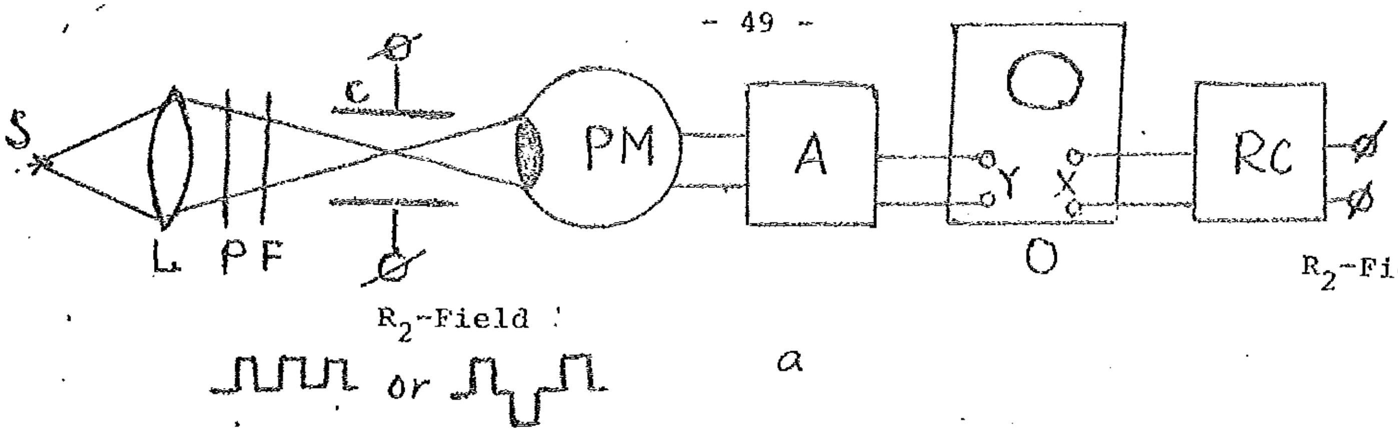
4.1 Measurement of the time of disorientation τ of colloidal particles.

The determination of the time of disorientation τ of colloidal particles can be done in a number of different ways. Out of the different methods of determination of the time of disorientation, the τ-meter method, described below is chosen because of the availability of the necessary equipment[10].

When rectangular electric pulses of the second kind R_2-field are applied to a colloidal solution (the apparatus is shown schematically in Fig. 11a, the form of the pulses in Fig. 11 b) polarized light passing between the plates of the flat capacitor C with the solution becomes modulated. During the time of action of the pulses (t_+ or t_- in Fig. 11 c), the particles are oriented in the field; relaxation of orientation occurs in the interval between pulses t_o. During the period t_o the intensity I of the polarized light either decreases or increases in accordance with the expressions:

$$I(t) = I_o e^{-t/\tau} \quad \text{or} \quad I(t) = I_o(1-e^{-t/\tau}) \qquad (4.1.1)$$

dependent on the sign of the electrooptical effect in the given colloidal solution.



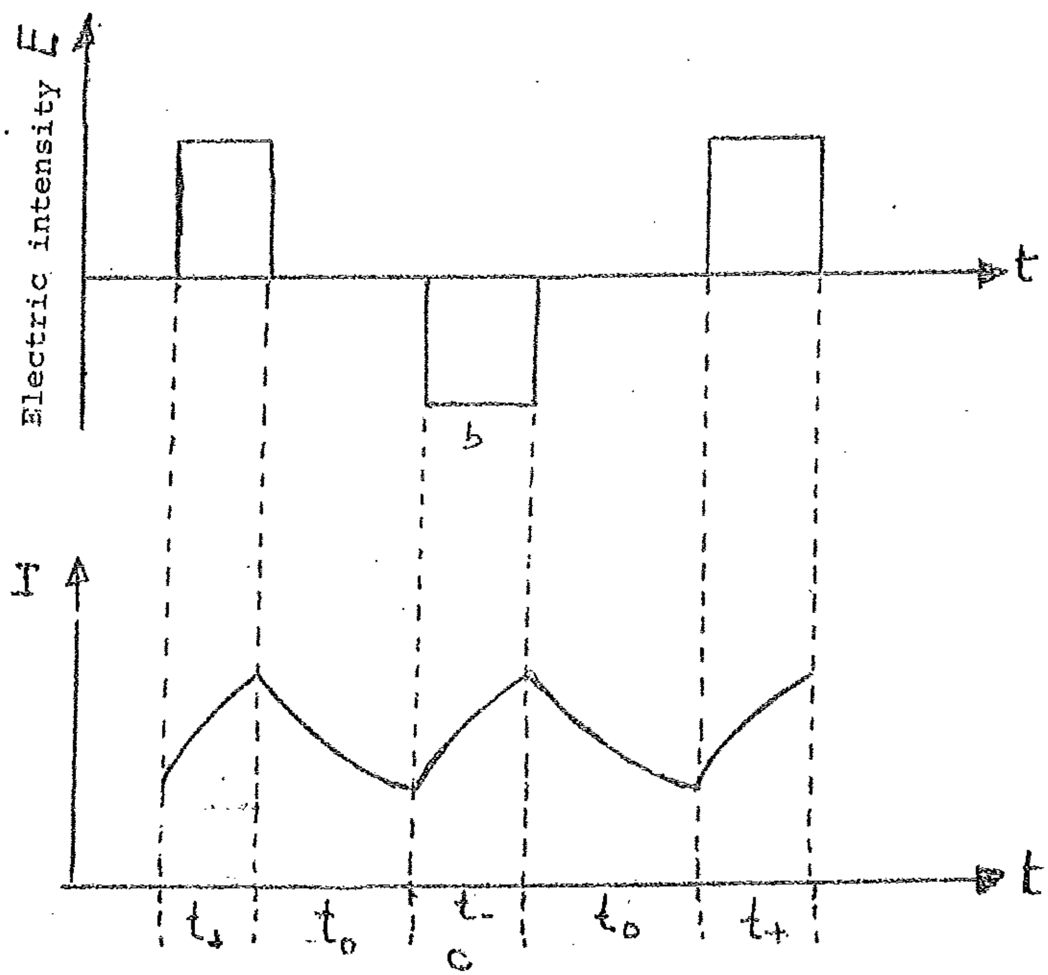


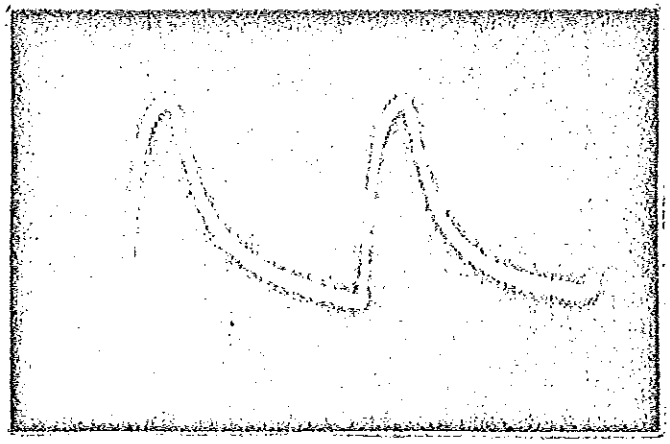
Fig.11 :

Diagram of apparatus for investigation of the orientation of relaxation curve for measuring τ by the rectangular electric field of the second kind (R_2-Field) a) S Light source; P. Polaroid; F filter; C cell with electrodes; PM Photomultiplier; A dc amplifier; O oscilloscope; Rc τ-m form of rectangular electric pulses of the second kind b) Modulation curve for light passed through a solution c) t_+ and t_- period field action ; t_0 interuption period (relaxation of orientation).

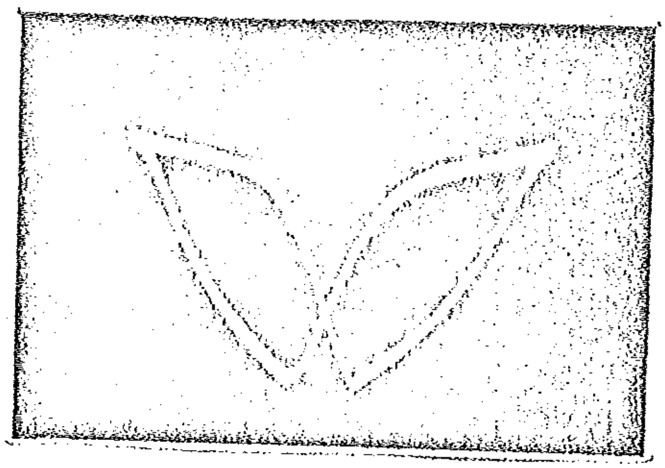
Formula 4.1.1 is valid for monodisperse colloid with particles of the same shape, with a single rotary diffusion coefficient D[10] and therefore a single τ. We describe the corresponding relaxation as monoexponential. Real solutions in general, exhibit poly-exponential relaxation, but the degree of deviation from monoexponentiality and the consequent degree of uncertainity which this introduces into the interpretation can be estimated only from experimental data. Therefore, a rapid and reliable technique for studying relaxation curves of real solutions is of particular importance.

For the measurement of the time of disorientation τ by the rectangular electric field of the second kind with the aid of τ-meter, the instrument is adapted for electrooptical effects. The light modulation curves are observed on the oscilloscope (photo a) with an exponential time scale, triggered by the rectangular electric field of the second kind pulses themselves, passing through the integrating RC circuit. When the selected value of RC is not equal to τ a straight line is not obtained (photo b). The values of R and C are changed until the selected value of RC becomes equal to τ for monoexponential relaxation of the colloid at which a straight line appears on the screen (photo c).

a)



b)



c)

Using this method, the time of disorientation τ for our specimens are obtained. Table II contains the time of disoriéntation for the specimens under investigation.

Table II

	Specimen	$\tau x10^{-3}$ sec
1	chrysene	1.4
2	azoxyanisole	1.4
3	terfenile	3.0
4	anisaldazine	1.2
5	anisyliden benzidine	1.1
6	antracene	26.0
7	diamond (ACM-0.5)	36.0

Calculation of an average dimension $\bar{d}$ of colloidal particles.

For rotating colloidal particles in the field of rectangular pulses of the second kind, the relation between τ and the rotary diffusion coefficient D is given by the following equation.

$$\tau = \frac{1}{6D} = \frac{V[P]\eta}{6KT} \qquad (4.2.1)$$

where K is Boltzman's constant, T is the absolute temperature, V is the volume of a particle, [P] is the shape factor ([P] = 6 for a sphere) and η is the viscosity of the dispersive medium.

From the above relation, we can find the diameter of an equivalent spherical particle whose volume is the same as a colloidal particle whose shape is not necessarily spherical.

From equation 4.2.1 , we have for V

$$V = \frac{6KT\tau}{[P]\eta} \qquad (4.2.2)$$

But volume of a sphere with radius r is $\frac{4}{3}\pi r^3$, and since the shape factor [P] for a sphere is 6, we have:

$$r = \left[\frac{3KT\tau}{4\pi\eta}\right]^{1/3} \qquad (4.2.3)$$

and $\bar{d} = 2r$

Table III contains the dimensions of the particles of the specimens under investigation.

Table III

No.	Specimens	$\bar{d}$ (μm)
1	chrysene	0.22
2	azoxyanisole	0.29
3	terfenile	0.29
4	anisaldazine	0.21
5	anisyliden bezidine	0.22
6	antracene	0.43
7	diamond (ACM-0.5)	0.54

Special specimen diamond (ACM-0.5) was prepared with very narrow distribution of dimensions of particles. Electromicroscopic studies show that the average dimension of diamond (ACM-0.5) is 0.5μm, and our investigation shows an average dimension of 0.54μm making a 10% (0.04) deviation only. This specimen shows the correctness of our method.

4.3 Determination of the dipole moment μ and the dipole moment per unit area μ_o.

The accepted view of the nature of the permanent dipole moment is associated with unipolar orientation of polar molecules of the dispersive medium (H_2O in our case) adsorbed in the form of a monomolecular layer on the surface of colloidal particles and therefore the dipole moment has a surface nature . Fig. 12 shows two kinds of adsorption of polar molecules on the surface of a colloidal particle.

The dipole moment μ for any of the specimens can be calculated from the intensity curve $\tilde{I}(t)$ as a function of time from which we choose five values of b with their corresponding values of τ_o. These values of b and τ_o with τ from table II are substituted into equation (23) reproduced below for convenience

$$\mu = \frac{6KT\tau \, \ln \{(\frac{2}{b} - 1) + 2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]^{\frac{1}{2}}\}}{E\,\tau_o} \qquad (4.3.1)$$

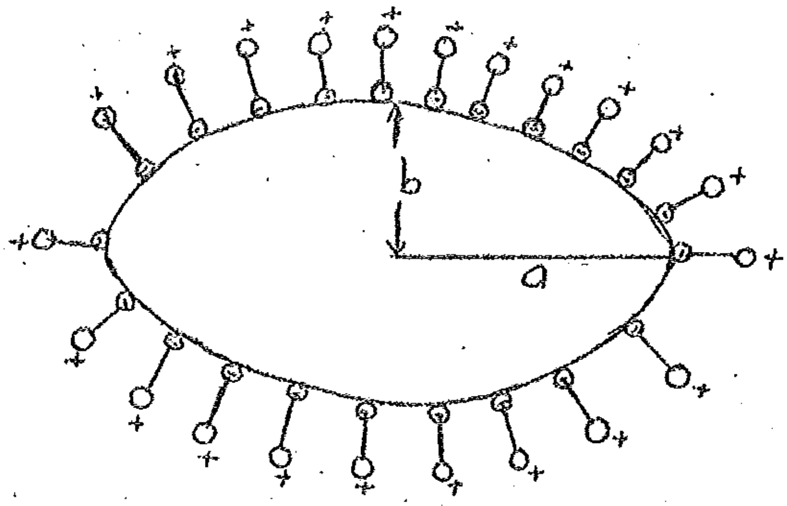
The selected five values of b and τ_o give us five values of μ and an average permanent dipole moment is obtained for each of our specimens. In table IV a-g are tabulated five values of b, τ_o, λ and μ for each of the specimens ,

Table IV

a) Chrysene

No.	b	τ_o (m sec)	λ=6KTτ	μx10^{13}CGS	$\bar{\mu}$x10^{13}CGS
1	0.4	41.0	3.4x10^{-16}	1.85	
2	0.5	37.0		1.75	1.75$\pm$0.02
3	0.6	31.5		1.75	
4	0.7	25.5		1.75	
5	0.8	21.5		1.65	

a).



b).

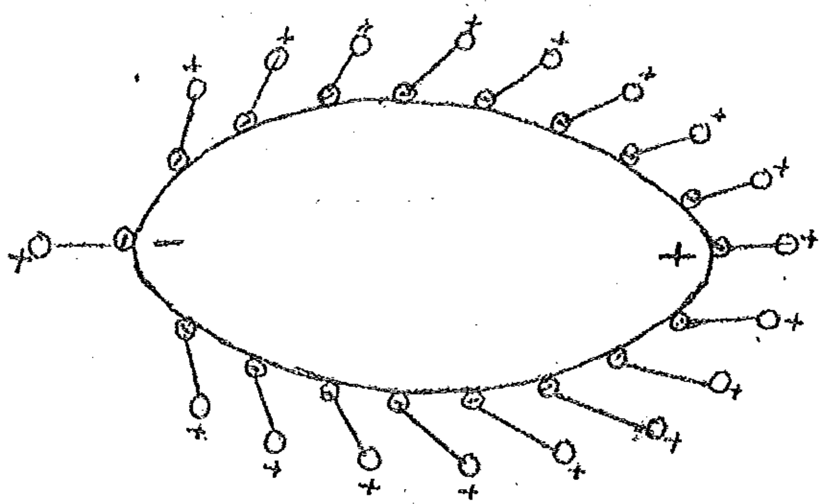


Fig. 12: Schematic diagram of a colloidal particle with a monomolecular film of water or other polar molecules adsorbed on its surface.
a) molecular dipoles normal to the surface, $\mu = 0$; b) molecular dipoles inclined to the particle surface, and the latter as a whole acquires the dipole moment μ.

b) Azoxyanisole

No.	b	τ_o (m sec)	$\lambda=6KT\tau$	$\mu x 10^{13}$ CGS	$\bar{\mu} x 10^{13}$ CGS
1	0.4	29.0	$9.94x10^{-16}$	7.50	
2	0.5	24.5		7.50	7.50$\pm$0.2
3	0.6	20.0		8.00	
4	0.7	17.0		7.50	
5	0.8	15.0		7.00	

c) Terfenile

No.	b	τ_o (m sec)	$\lambda=6KT\tau$	$\mu x 10^{13}$ CGS	$\bar{\mu} x 10^{13}$ CGS
1	0.4	41.0	$7.45x10^{-16}$	3.95	
2	0.5	40.0		3.45	3.62$\pm$0.2
3	0.6	31.0		3.80	
4	0.7	28.0		3.45	
5	0.8	22.0		3.45	

d) Anisaldazine

No.	b	τ_o (m sec)	$\lambda=6KT\tau$	$\mu x 10^{13}$ CGS	$\bar{\mu} x 10^{13}$ CGS
1	0.4	16.5	$2.98x10^{-16}$	3.95	
2	0.5	14.5		3.85	3.7$\pm$0.2
3	0.6	12.5		3.80	
4	0.7	10.5		3.70	
5	0.8	9.5		3.20	

e) Antracene

No.	b	τ_o (m sec)	λ=6KTτ	$\mu.10^{13}$CGS	$\bar{\mu}.10^{13}$CGS
1	0.4	32	$3.23x10^{-15}$	3.45	
2	0.5	26		3.65	3.21±0.33
3	0.6	24		3.35	
4	0.7	22		3.00	
5	0.8	20		2.60	

f) Diamond (ACM-0.5)

No.	b	τ_o (m sec)	λ=6KTτ	$\mu.10^{12}$CGS	$\bar{\mu}.10^{12}$CGS
1	0.4	43	$4.97x10^{-15}$	3.95	
2	0.5	38		3.85	4.25±0.20
3	0.6	30		4.45	
4	0.7	23		4.00	
5	0.8	14		5.00	

g) Aniziladen benzilden

No.	b	τ_o (m sec)	λ=6KTτ	$\mu.10^{13}$CGS	$\bar{\mu}.10^{13}$CGS
1	0.4	25	$2.65x10^{-16}$	2.75	
2	0.5	22		2.65	2.54±0.55
3	0.6	19		2.60	
4	0.7	17		2.40	
5	0.8	14		2.30	

It is also known from the theory of rotational motion of particles in viscous medium that P (P = a/b where a and b are the major and minor half axes of an ellipsoidal particle is related to the shape factor [P] according to table V [10,15] for some values of a and b.

Table V

P	1	1.5	2	3	4	5	6	8	10
[P]	6	7.5	9.0	14.0	20.1	27.7	35.8	56.1	80.5

Data of electromicroscopic studies gives the shape factor [P] and P of a host of specimens among which are the ones we are interested in.

The resultant dipole moment μ of a particle in the form of an ellipsoid of revolution with half axes a and b will depend on the dipole moment/cm^2 , μ_o. If the ellipsoid is characterized by the volume V and ratio P = a/b calculation gives

$$\mu_o = \frac{\mu}{3.8\left[V^2 P\right]^{1/3}} \qquad (4.3.2)$$

Substituting the value of μ from equation 4.3.1 and V from equation (4.2.2), we have an expression for μ_o as follows.

$$\mu_o = \frac{(6KT\tau)^{1/3}\,[P]^{2/3}\,\eta^{2/3}\,\ln N}{E\tau_o} \qquad (4.3.3$$

Equation 4.3.3 enables to calculate the correct value of μ_o for different kinds of colloidal particles.

Water is used as the dispersive medium , For water at room temperature $\eta = 10^{-2}$ poise. Table VI contains the dipole moment per unit area μ_o of the specimens.

Table VI

No	Specimen	$\mu_o . 10^4$ CGS
1	chrysene	1.4
2	azoxyanisole	1.4
3	terfenile	1.5
4	anisaldazine	2.0
5	anisyliden benzidine	1.9
6	antracene	1.8
7	diamond (ACM-0.5)	1.9

From table VI we note that the values of μ_o are rather close to one another. This is a very noteworthy fact, offering weightly evidence in favor of the view that the permanent dipole moment has surface nature [6]. These values of μ_o are roughly the same as the values of μ_o

obtained by the method of rotating electric field.[12] These comparisons show the correctness of the new method of determination of the permanent dipole moment of colloidal particles using rectangular electric field. μ_o is the most important characteristic of all colloidal particles.

4.4 Comparison of the experimental results with the results obtained by the method of rotating electric field[7,8].

The values of μ and μ_o of colloidal particles are obtained from the theoretical formulas 4.3.1 and 4.3.3 respectively.

The value of b in 4.3.1 can be chosen arbitrarily in the limit $0<b<1$. For a specific specimen we choose b and the corresponding τ_o from the experimentally obtained curve of intensity of light passing through the colloidal solution.

By using equations (2), (7) and (12) of chapter 2, it is not difficult to show that the intensity is given by the following equation

$$\tilde{I}(t) = \frac{Imax \; 4 \tan^2\frac{\alpha_o}{2} \quad e^{\frac{2\mu E}{\lambda}t}}{\left[1 + \tan^2\frac{\alpha_o}{2} \quad e^{\frac{2\mu E}{\lambda}t}\right]^2} \qquad (4.4.1)$$

where α_o is a small average angle with the major axes of all particles make with the direction of the electric field at $t = 0$ and $\lambda = 6KT\tau$.

The values of μ and condition of experiment E, λ by the method of rotating electric field are substituted in equation 4.4.1 for diamond and anisaldazine from which theoretical curves of the intensity of light as a function of time are plotted. The experimental curves $\tilde{I}(t)$ of the specimens obtained directly from the oscilloscope using our method fit into the curves of $\tilde{I}(t)$ obtained by the other independent method as shown in Fig. 13.

For example for b = 0.5 the difference in the values of μ and μ_o for diamond is not more than 25%. This is the greatest deviation we have encountered and about 17% for anisaldazine.

In Fig. 13 the fitting of the experimental curve with the theoretical one is not as accurate originally as at latter times. This is so because originally the particles have different conditions like different α_o, shape and consequently frictional force, but later on, they have averaged similar conditions. It is not possible to produce similar averaged original conditions in our case.

When the equation of motion of a colloidal particle was set in chapter 2, equation (2), the induced dipole moment, the distribution of the particles dimensions, the shape differences among the particles were neglected. This must be justified. The induced dipole moment was neglected by

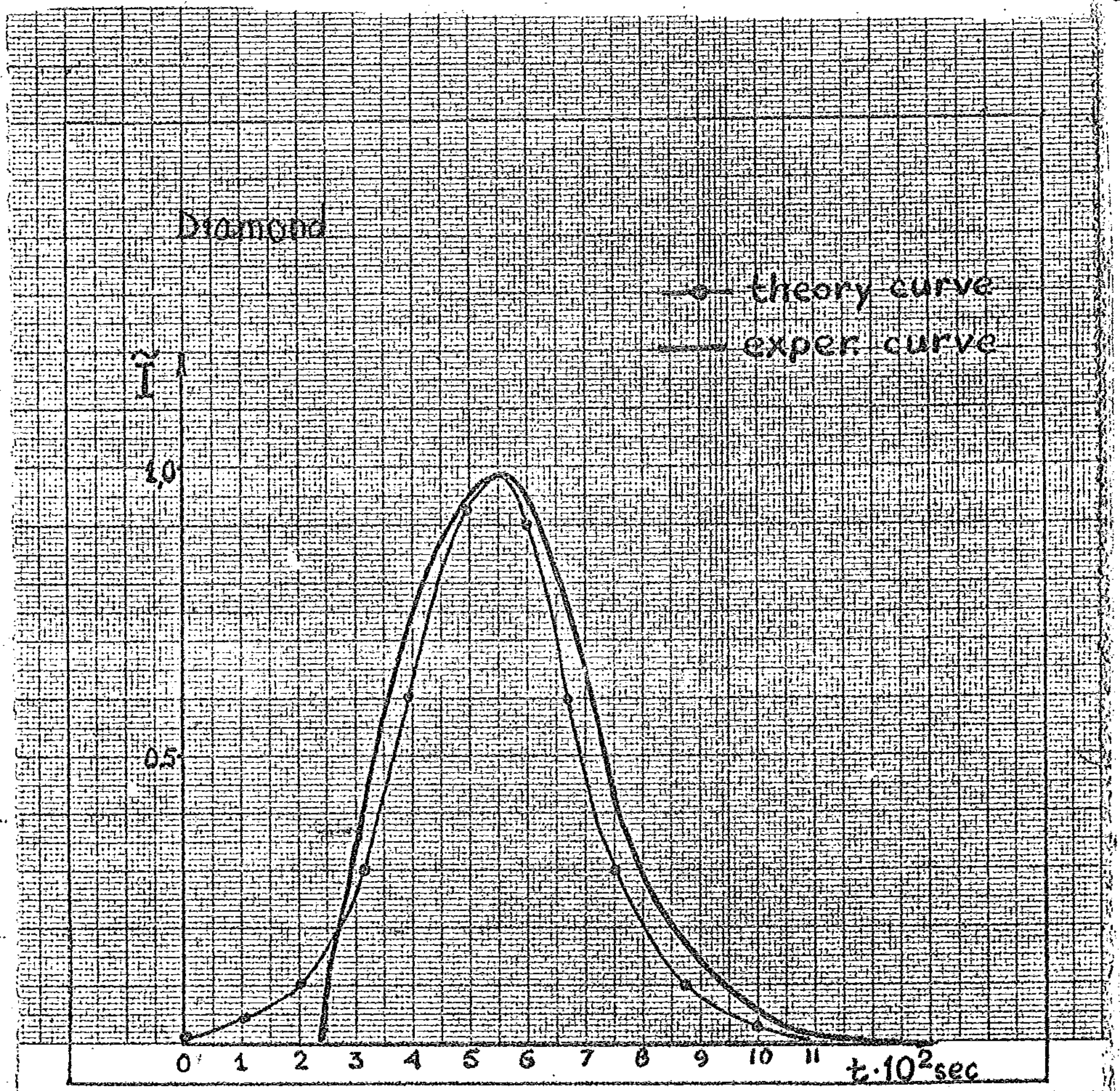

Diamond
theory curve
exper. curve
Ĩ
1,0
0,5
0 1 2 3 4 5 6 7 8 9 10 11
t·10²sec

Fig. 13.a.

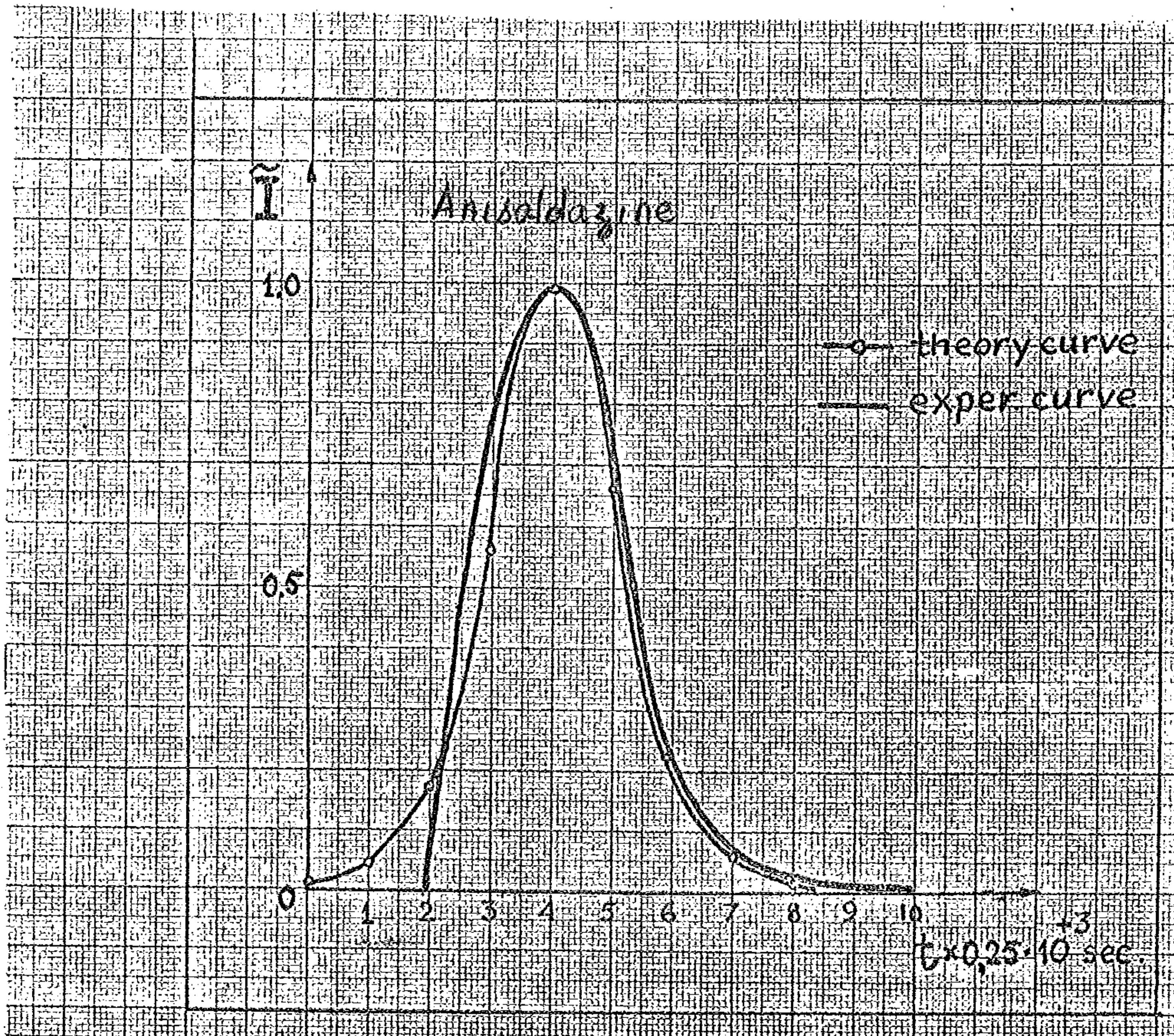

Ĩ
Anisaldazine
1,0
0,5
0
1
2
3
4
5
6
7
8
9
10
theory curve
exper. curve
t×0,25·10^{+3} sec.

Fig. 13.b.:

choosing suitable experimental conditions (selection of the value of E) which enable us to neglect the contribution of the torque because of the induced dipole moment. Uniformity of the dimensions of particles is obtained to a satisfactory degree by repeated fractional centrifuging or other method when the specimens are prepared. The approximation of our particles by ellipsoids gives us correct results as shown by the comparisons of experimental and theoretical curves.

Colloidal solutions were investigated with water as the dispersion medium. The particles have different physical and chemical nature. These colloidal particles are chrysene, antracene, azoxyanisole, anisaldazine, anisildenbenzidene, terfenile and diamond (ACM-0.5). Colloidal solutions are prepared by dissolving the solvent in water directly or by the method of substitution.

Summary

1. The apparatus for the investigation of electrooptical properties of dispersion systems in the field of rectangular electric impulses R_1 and R_2-field is described. The installation for this investigation includes the optical part, the scheme for measuring and observing optical signals which a colloidal solution give by the action of the electric field.

The generator is constructed and built for obtaining rectangular electric impulses (R_1 and R_2-field) and electrooptical τ-meter for the investigation of electrooptical effects in exponential sweeping.

2. The theory of motion of monodisperse and monoshape dispersion particles in the field of rectangular electric pulses is developed.

It is shown, that the intensity $\tilde{I}(t)$ which characterizes the motion of particles in the field of rectangular pulses depends on time according to the equation $|\tilde{I}(t)| = |\tilde{I}(t)|$ max.$b(t)$ where "$b(t)$" is determined by the conditions of experimental and physical properties of the colloidal particles and dispersion medium, and in particular by the value of the permanent electric dipole moment μ.

3. The value of μ can be found from the equation:

$$\mu = \frac{6KT\tau \, \ln \{ (\frac{2}{b} - 1) + 2\left[\frac{1}{b}(\frac{1}{b} - 1)\right]^{\frac{1}{2}} \}}{E\tau_o}$$

where λ, E are experimental parameters and τ_o and b are determined from experimental dependence of intensity of light with respect to time in the process of investigation of electrooptical effect in dispersion systems.

4. Determination of the value of μ requires the knowledge of the time of disorientation τ of particles. The value of τ is determined experimentally by the method of electrooptical τ-meter.

5. Six different colloidal solutions were investigated with water as the dispersion medium. The particles have different physical and chemical nature. These colloidal particles are chrysene, antracene, azoxyanisole, anisaldazine, anisiliden benzidine, terfenile and diamond (ACM-0.5). Colloidal solutions are prepared by dissolving the solvent in water directly or by the method of substitution.

6. The values of μ_o were measured for all of the colloidal particles mentioned (μ_o is the dipole moment per unit area of the colloidal particle). For all particles μ_o lies in the interval (1.4-2.0) 10^{-4}CGSE. These values are in

agreement with the values of μ_o which were obtained before by another independent method and confirm the surface nature of, and the formation of the permanent electric dipole moment of colloidal particles.

7. Dimensions of the particles were determined by the method of electrooptical τ-meter. For different specimens the average dimensions lie in the interval from 0.2 μm for anisaldazine to 0.54 μm for diamond particles.

8. Comparison of the theoretical curve of $\tilde{I}(t)$ with the experimentally determined dependence of $\tilde{I}(t)$ for real colloidal systems gives quite satisfactory fitting. This develops confidence on our new method because the experimental curve of $\tilde{I}(t)$ is used for the determination of the value of μ_o.

REFERENCES

1. Colloid Chemistry, S. Voyutsky. Mirpublishers, 1978.
2. Colloid Science Vol.1 Kruyt. H.R. Elsevier Pub-Co., Amsterdam, 1952.
3. G. Mie, Ann. Phys. 25, 377 (1908).
4. Light Scattering in a Cloudy Medium Shifrin, K.S.,1951.
5. Coll. J. Electrooptical properties of Lyophobic Colloids, N.A. Tolstoi; A.A. Spartakov, and G.I. Khil'ko Vol.22 No6, 1960.
6. Dakl. N.A. Tolstoi AN SSSR, 110, 893, 1955.
7. Coll. J. N.A. Tolstoi; A.A. Spartakov; A.A. Trusov. 22, 705, 1960.
8. Opt. and Spectr. N.A. Tolstoi; A.A. Spartakov; A.A.Trusov. 19, 826, 1955.
9. Coll. J. N.A. Tolstoi and others.
10. Coll. J. N.A. Tolstoi; A.A. Spartakov; A.A. Trusov, and G.I. Khil'ko. Vol.29, 584 (1967).
11. Electromagnetic theory, J. Straton (1941).
12. Coll. J. V.V. Voytilov and others No.1, 107, 1982.

14. J. Technical Physics. A.M. Bonch-Bruevitch 22, 259, 1952.
15. Rev. Mod. Phys. W. Heller, 14, 390 (1942).