1960

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Recommended Citation

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Mic 61–441

CHURCHILL, Donald. INVESTIGATION OF ABSORPTION SPECTRA OF ADSORBED FILMS ON METALS BY MEANS OF A POLARIZATION SPECTROMETER.

Iowa State University of Science and Technology
Ph.D., 1960
Chemistry, physical

University Microfilms, Inc., Ann Arbor, Michigan

INVESTIGATION OF ABSORPTION SPECTRA OF ADSORBED FILMS ON METALS BY MEANS OF A POLARIZATION SPECTROMETER

by

Donald Churchill

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

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I. INTRODUCTION

The investigation of the absorption spectra of adsorbed films is of interest in both theoretical and practical applications. The absorption spectra could be expected to furnish information about interactions between the adsorbed species and the substrate. Such information would contribute to the understanding of the nature of electronic interactions responsible for adsorption forces and lead to a better understanding of catalysis, corrosion inhibition, lubrication and other surface phenomena.

The experimental detection of the absorption spectra of adsorbed films is difficult due to the small amount of material in such films. This problem has been circumvented by several investigators by using substrates having a large surface area or by studying films several molecular layers thick. In the latter case, the spectra are characteristic of the bulk material and do not yield direct information about interactions of the adsorbate with the substrate.

de Boer (1) obtained electronic absorption spectra of molecules adsorbed on transparent films of inorganic salts. The salt films had a laminar structure which had the effect of placing several surfaces in sequence, one behind the other. The additive absorption of radiation by molecules adsorbed on surfaces of the laminae permitted the spectra to be measured by standard transmission techniques. de Boer found that the spectra of the first few molecules adsorbed on these surfaces exhibited shifts in the absorption maxima. As the surface coverage was increased, the absorption spectra became more characteristic of the spectra of the bulk material. de Boer suggested that the shift in the absorption bands was due to a difference in the adsorption energy between the molecule in its ground state and the molecule in its excited state.

Similar results were obtained by Kortüm et al. (2) when molecules of strongly absorbing compounds were chemisorbed on inorganic salts. In this work, a very large surface area was obtained by using powdered salts. The intensity of the light reflected from the powdered sample was measured. Kortüm postulated a Lewis acid-base electron transfer between the surface and the adsorbate to explain the shift in the absorption bands of the chemisorbed molecules. The direction of the electron flow is a function of the relative electron affinities of the adsorbed molecule and the atoms in the salt lattice.

The experimental techniques used by de Boer and Kortüm limit the investigations to molecules adsorbed on transparent substrates.

The absorption spectra of thick films of strongly absorbing dyes have been investigated by standard intensity measurements. These spectra have shown a general broadening of the absorption bands and shifts of the absorption maxima relative to the solution spectra. Weigl (3) also describes a splitting of the long wavelength absorption band in films of several cationic dyes. These effects are characteristic of the solid dyes and do not necessarily indicate interaction between the adsorbed films and the substrates.

Eischens et al. (4,5) have developed techniques for obtaining the infrared spectra of monolayers adsorbed on metal particles supported on a transparent matrix. Francis and Ellison (6) have succeeded in obtaining infrared spectra of monolayers adsorbed on reflecting mirrors by a system of multiple reflections. The infrared spectra of adsorbed molecules yields information about the species adsorbed and the orientation of the molecules on the surface. The vibrational absorption bands of infrared spectra are easier to detect than the electronic absorption bands because of the relative sharpness of the former. Similar techniques have failed in the study of electronic absorption spectra.*

Recently, Bartell (7) has shown that spectroscopic information in the visible and ultraviolet range for films of monolayer thickness adsorbed on opaque substrates may be inferred by analysis of polarized light reflected from the surface. With further development, this technique promises to furnish much information about adsorption phenomena.

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*Hackerman, N., Austin, Texas. Unpublished experimental results. Private communication. 1958.

II. THEORY

According to the electromagnetic theory, light consists of transverse waves. The state of polarization of a light beam may be defined by two vectors describing the resultant oscillation of a wave along two orthogonal axes perpendicular to the direction of propagation. When light is reflected from a surface, the axes are most conveniently chosen to lie in the plane of incidence (p component) and perpendicular to the plane of incidence (s component). If the resultant vibrations along the two axes are in phase, the light is plane polarized. If the components are out of phase, the vector sum of the resultant vibrations describes an ellipse when the beam travels a distance of one wavelength and the light is elliptically polarized.

On reflection from a nonabsorbing surface, the amplitudes of the component vibrations of the light are diminished by different amounts. The ratio of the amplitude of the reflected light to that of the incident beam is given by the Fresnel reflection coefficient:

$$\frac{R_{s,p}}{A_{s,p}} = f_{s,p}(n,\phi,\phi') \qquad (1)$$

where

R = the amplitude of the reflected component
A = the amplitude of the incident component
n = the refractive index of the surface
ϕ = the angle of incidence
ϕ' = the angle of refraction.

If the incoming light is plane polarized at 45 degrees to the plane of incidence, the amplitudes of the incident light along the p and s axes are equal and the ratio of the amplitudes of the reflected components, R_p/R_s, is equal to tan ψ where ψ is the azimuth of the plane of polarization of the reflected light measured from the axis of the s component.

An absorbing substance such as a metal has a complex index of refraction, $\bar{n} = n - ik$, where k is the absorption coefficient. Plane polarized light reflected from a metal surface suffers a phase change as well as an amplitude change and becomes elliptically polarized. The amplitude of the reflected wave is given by the complex reflection coefficient:

$$\bar{R}_{s,p} = R_{s,p} \exp i\,\delta_{s,p}. \tag{2}$$

The ratio of the reflected amplitudes becomes:

$$\frac{\bar{R}_p}{\bar{R}_s} = \tan\psi \exp i(\delta_p - \delta_s) = \tan\psi \exp i\Delta \tag{3}$$

where Δ is the phase difference between the two components of reflected light. Measurement of ψ and Δ for a given angle of incidence allows one to calculate the complex refractive index of the metal (8).

A thin film on the surface of a metal will cause a small change in the effective optical constants of the surface. Expressions for this change have been derived by

Drude (9) and Born (10) subject to the condition that the film thickness is small compared to the wavelength of the light, and cast into the form:

$$\frac{\tan\psi}{\tan\psi'}\ \exp i(\Delta - \Delta') = 1 + i\sigma \qquad (4)$$

where the primed quantities refer to the bare surface, the unprimed quantities refer to the surface with a film, and is a correction factor which is a function of the film thickness, the optical constants of the film and of the bare surface, and the wavelength of the incident light. This expression has been expanded by Lucy (11) to give:

$$\rho\left[\cos\,(\Delta - \Delta') + i\,\sin\,(\Delta - \Delta')\right] = 1 + i\sigma \qquad (5)$$

where

$$\sigma = \frac{4\pi L}{\lambda}\ \sin\phi\ \tan\phi\ \frac{\epsilon - 1}{\epsilon} \cdot \frac{\epsilon'[\epsilon - \epsilon']}{[\epsilon' - 1]\ [\epsilon' - \tan^2\phi]} \qquad (6)$$

$$\rho = \frac{\tan\psi}{\tan\psi'}$$

ϵ = the film dielectric constant
ϵ' = the dielectric constant of the substrate
L = the film thickness
λ = the wavelength of the incident light
ϕ = the angle of incidence.

The dielectric constant is a complex function of the refractive index and the absorption coefficient:

$$\epsilon = n^2 - k^2 - 2\,ink. \qquad (7)$$

The optical parameters characterizing an adsorbed film are the thickness, the refractive index, and the absorption coefficient. Equation 5 may be separated into its real and imaginary parts allowing any two of the film parameters to be expressed as a function of the third and the experimental observables ψ, ψ', Δ, Δ', λ, and ϕ where the dielectric constant of the substrate is explicitly determined by Δ', ψ', and ϕ. At a wavelength where there is no absorption of light by the film, it is possible to determine independently the film thickness and refractive index. Since the thickness of a given film may be considered to be a constant function of the wavelength, the number of variable film parameters is reduced to two and the optical constants of the film can be found as a function of the wavelength.

The separation of equation 5 gives the following two equations:

$$\rho \sin (\Delta - \Delta') = R(\sigma)$$

$$\rho \cos (\Delta - \Delta') - 1 = -I(\sigma)$$

where $R(\sigma)$ and $I(\sigma)$ refer to the real and imaginary parts of σ. Expansion of σ yields the following expressions for $R(\sigma)$ and $I(\sigma)$ in terms of the optical properties of the film.

$$R(\sigma) = \frac{4\pi L}{\lambda} \cdot \frac{\sin\phi \cos\phi}{r^2 + s^2} \cdot \frac{px + qy}{n^4 + 2n^2k^2 + k^4}$$

$$I(\sigma) = \frac{4\pi L}{\lambda} \cdot \frac{\sin\phi \cos\phi}{r^2 + s^2} \cdot \frac{qx + py}{n^4 + 2n^2k^2 + k^4}$$

where

n = the refractive index of the film
k = the absorption coefficient of the film
$a = n'^2 - k'^2$
$b = 2n'k'$
$r = a^2 - a - a\tan^2\phi + \tan^2\phi$
$s = b(2a - 1 - \tan^2\phi)$
$p = ar + bs$
$q = as - br$
$x = n^6 + n^4(k^2 - 1 - a) + n^2(-k^4 - 2k^2 - 2ak^2 + a) + 2bnk$
$\quad + k^6 - k^4 - ak^4 - ak^2$
$y = -2kn^5 + bn^4 - 4n^3k^3 + n^2(2bk^2 - b) + n(-2k^5 + 2ak)$
$\quad + bk^4 + bk^2$.

Curves representing the functions $R(\frac{\sigma}{L})$ and $I(\frac{\sigma}{L})$ are shown in Figure 4.

In the case of weakly absorbing films, the film dielectric constant is approximately equal to the square of the refractive index of the film. In such a case it may be impossible to obtain an accurate value for the absorption coefficient by the solution of equation 5 but the positions of absorption bands and the magnitude of their absorption coefficients may be inferred by a consideration of the anomalous dispersion of the refractive index associated with absorption.

The refractive index of nonabsorbing materials is generally found to decrease with increasing wavelength. This property is known as normal dispersion. At the position of an absorption band, however, the refractive index deviates markedly from normal dispersion. The refractive index falls off rapidly as the absorption band is approached from the short wavelength side, rises abruptly at the position of maximum absorption, and then gradually falls off again to the normal dispersion curve. This effect is known as anomalous dispersion. Graphical representations of these types of dispersion are shown in Figure 1.

A mechanical analogue has been proposed to explain this phenomenon. Let it be assumed that the medium contains particles which have a natural frequency of vibration, ν_0 . When the frequency of the light in the medium is different from ν_0 , the amplitudes of induced vibrations of the particles are small. As the frequency of the light approaches the natural frequency of the particle vibrations, the amplitudes of the vibrations become much greater due to resonance. These vibrations act on the light wave to change its velocity. On the basis of this model, Sellmeier derived the relationship between the index of refraction and the wavelength (12):

$$n^2 = 1 + \frac{A\,\lambda^2}{\lambda^2 - \lambda_o^2} \quad . \tag{8}$$

This equation exhibits a discontinuity in the refractive index at the position of the natural frequency which is not in agreement with experimental results. Sellmeier's formula was modified by Helmholtz to take into account the damping action associated with the absorption of energy by the medium as follows (12):

$$n^2 - k^2 = 1 + \sum_i \frac{A_i \lambda^2}{(\lambda^2 - \lambda_i^2) + \frac{g_i \lambda^2}{(\lambda^2 - \lambda_i^2)}} \qquad (9a)$$

$$2nk = \sum_i \frac{A_i \sqrt{g_i} \lambda^3}{(\lambda^2 - \lambda_i^2)^2 + g_i \lambda^2} \qquad (9b)$$

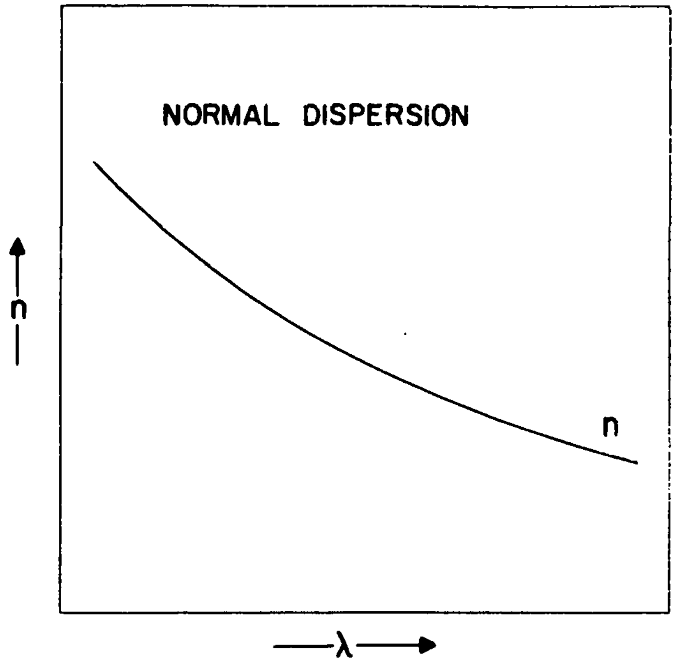
where A is a constant and g is a measure of the resistance to vibration of the particle.

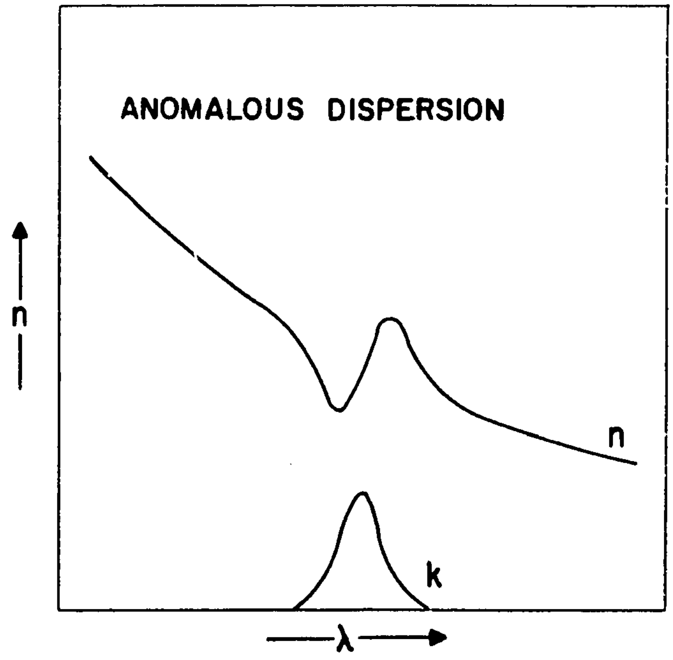
For an absorption where the damping action is small, the peaks of the anomalous break in the refractive index fall at the positions of half maximum absorption and the center of the anomalous break is at the position of maximum absorption.

Pflüger confirmed the Helmholtz relation by direct measurements of the refractive indices and absorption coefficients of solid fuschin and cyanine dyes (13, 14, 15, 16).

The amplitude ratio, ρ , for a thin adsorbed film with weak absorption is nearly unity and the change in the phase difference for readings of the clean surface and the surface with a film is small so that sin $(\Delta - \Delta')$ is approximately equal to $\Delta - \Delta'$. The change in the phase difference is then approximately equal to the real part of σ . Thus, anomalous features in the refractive index of the film alter the value of $\Delta - \Delta'$ and it is possible to ascertain the existence and the position of weak absorption bands in a film from anomalies in the plot of $\Delta - \Delta'$ versus the wavelength. Such plots

Figure 1. Graphical representation of normal dispersion and anomalous dispersion.


NORMAL DISPERSION
n
n
λ


ANOMALOUS DISPERSION
n
n
k
λ

will be called phase dispersion curves in this work.

Drude (17, 18, 19) was the first investigator to use a reflection technique to study the properties of thin films. Since his initial investigation, many workers have applied this technique to investigations of thin films of metals, metal oxides, and organic materials with varying degrees of success. For the most part, these investigations were made at a single wavelength. No attempt has been made to obtain spectral information about thin films.

III. OBJECTIVES

Preliminary investigations have shown that it may be possible to obtain information on the refractive indices and optical absorption coefficients of films of monolayer thickness adsorbed on reflecting substrates by the analysis of polarized light reflected from the surface. The present investigation was undertaken with the following objectives:

1. To design and construct a polarization spectrometer for the accurate determination of the state of polarization of reflected light throughout a wide range of the visible and ultraviolet spectrum;

2. To investigate the relation between polarization measurements and the optical properties of adsorbed films, and to determine the sensitivity of this technique in the determination of absorption spectra;

3. To study films of Lewis bases adsorbed on metal substrates for the purpose of studying the electronic absorption spectra postulated by some investigators to be associated with complex formation between the adsorbate and the substrate.

IV. EXPERIMENTAL

A. Apparatus

1. Polarization spectrometer

The polarization of a light beam impinging on a surface and the subsequent analysis of the reflected light are accomplished by means of a polarization spectrometer. The instrument used in this study was designed to utilize light throughout the visible and near ultraviolet range. The basic components for an instrument of this type are listed below.

1. A powerful light source, preferably a point source.
2. A monochromator.
3. A polarizer.
4. An adjustable stage to hold the sample.
5. A compensator.
6. An analyzing prism.

The instrument was constructed to make use of the analyzer of a Model 80-200 Photoelectric Polarimeter manufactured by O. C. Rudolph and Sons. The polarimeter head was equipped with interchangeable analyzer prisms of calcite and quartz. The azimuth of the analyzer could be read directly to one one-thousandth of a degree.

The polarimeter was also equipped with an interchangeable telescope and search unit of a Photovolt Model 520-M Multiplier Photometer. This arrangement allowed either visual or photoelectric determination of the settings of the analyzer for maximum extinction of the light being analyzed.

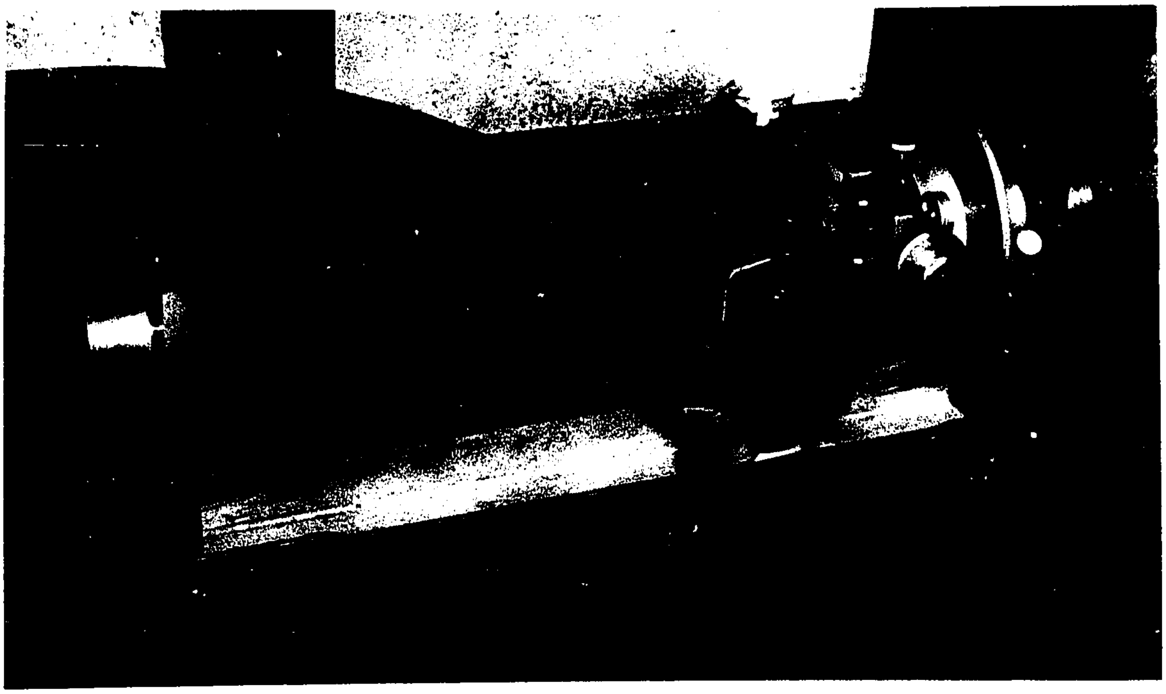
A sturdy brass frame was attached to the polarimeter at the trough supports. The specimen stage and the compensator were mounted on this frame. These components are shown in Figure 2.

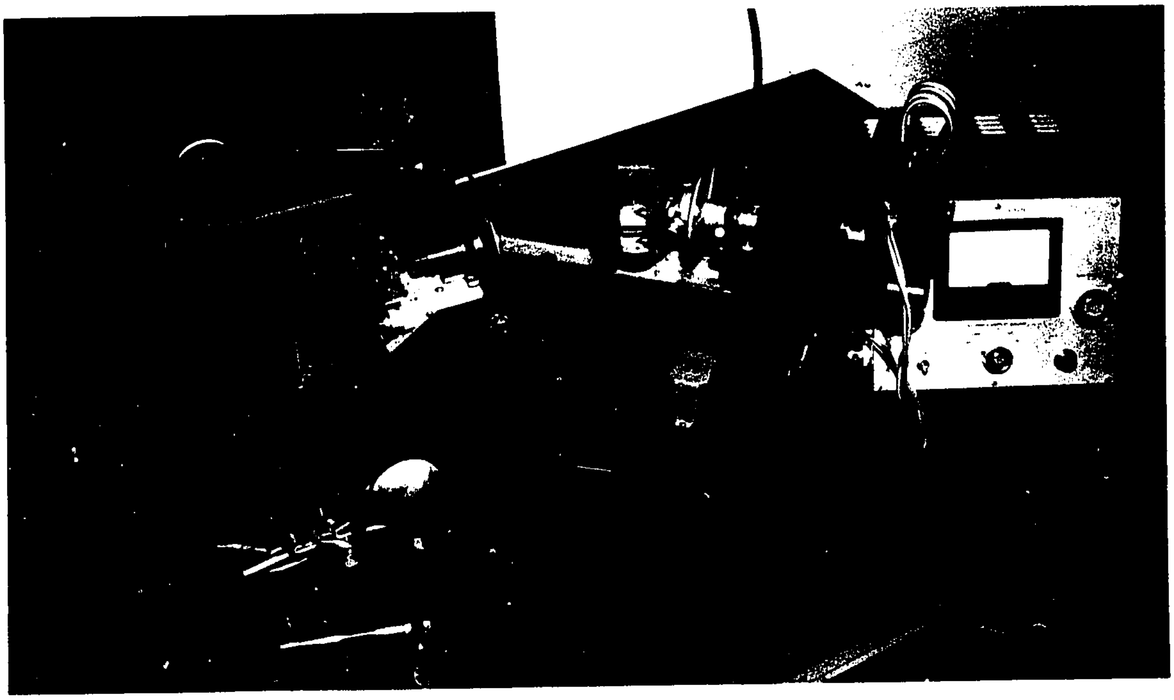
The stage was mounted on a plate supported by three adjustable legs so that the slide could be oriented properly with respect to the plane of incidence of the light beam. A track and screw device made it possible to adjust the position of the slide in a direction perpendicular to the surface of the slide. The stage could also be rotated about its vertical axis. The slide was held to the face of the stage by two brass spring clips.

A Babinet Soleil compensator constructed by Gaertner Scientific Corporation was used with the instrument. This compensator consisted of a quartz parallel plate and two quartz wedges. The crystal axis of the plate was perpendicular to the crystal axes of the wedges. One of the wedges was held stationary with respect to the parallel plate and the other was mounted on a carriage attached to a micrometer screw. Rotation of the screw caused the carriage to move in a direction perpendicular to the apex of the wedge. In this manner, the combined thickness of the wedges was altered. When the combined thickness of the wedges was equal to that of the parallel plate, there was no compensation of the light passing through the compensator. However, when the traveling

Figure 2. Specimen stage and compensator of the polarization spectrometer.

Figure 3. The polarization spectrometer as arranged for experimental measurements. Several light shields used when readings were made are not shown.





wedge was adjusted to make their combined thickness greater than that of the plate, the net effect was equivalent to that of a thin quartz plate with its crystal axis parallel to those of the wedges. This caused a phase change between the components of the transmitted light.

The micrometer screw of the compensator was calibrated to one hundred divisions per turn and could be estimated accurately to within two parts in a thousand.

The compensator was mounted in a rotating object-holder which was calibrated to tenths of a degree.

A Bausch and Lomb Grating Monochromator, Model 33-86-40, was used for selection of the wavelength of light desired. The linear dispersion of the monochromator was 3.3 millimicrons per millimeter. The exit slit was set at 0.45 millimeters. The band width of the transmitted light was 1.5 millimicrons.

The polarizer was a calcite prism of the Glan-Thompson design. It was mounted in a rotating object-holder which was calibrated in tenths of a degree. The object-holder was mounted on a frame attached directly to the monochromator.

A quartz collimating lens was mounted between the monochromator and the polarizer.

Two light sources were used at various times during this investigation. A compact xenon arc lamp was used in the earlier stages of the work. This lamp furnished a very intense source in the region from 200 to 750 millimicrons.

However, the arc was not stable enough for precise work. It was replaced with a tungsten filament projection bulb. This lamp was rated at 1000 watts at 115 volts. It was found that the stability of this source was enhanced by operating at 100 volts.

The power for the amplifier and light source was stabilized with a 2000 watt voltage stabilizer which held voltage fluctuations to within one-half of one percent.

Figure 3 shows the polarization spectrometer as it was set up for experimental measurements.

2. Spectrophotometers

The transmission spectrum of the tetraphenylporphine and tetraphenylchlorine mixture was run on a Cary Model 14 Recording Spectrophotometer.

The transmission spectrum for the Rhodamine B was measured with a Beckman DU Spectrophotometer.

B. Materials

1. Surfaces

The chromium surfaces used in this investigation were cut from commercial chromium plated steel ferrotype plates. The slides were cut in one inch squares. Prior to use, they were polished by hand on a Buehler Ltd. finest quality microcloth impregnated with Linde A alumina. The polishing was done with the cloth immersed in a water bath. The slides were then held under a stream of laboratory supply distilled water while being rubbed with a cotton swab to remove the abrasive. They were then rinsed with doubly distilled water and warmed over the flame of a Meker burner until the water had evaporated after which they were passed through the hottest part of the flame at a rate of two passes per second. The usual flaming time was three seconds. These surfaces gave clear breath figures and readily formed films of n-octadecylamine by adsorption from a 0.08% solution of the amine in purified cetane.

The optical constants of the chromium slides were found to change as the flaming time was increased. This was probably due to the formation of a film of chromium oxide on the surface. The thickness of this film was estimated to be about 10 Ångstroms after a four second flaming time. The film formation was rapid initially after which the rate decreased, perhaps because the oxide film protected the metal from further oxidation.

2. Compounds

a. Octadecylamine Two separate samples of n-octadecylamine were used. One was a product of Armour and Company. Carbon dioxide was removed from this amine by the method described by Zisman *et al.* (20). The sample was held slightly above the melting point in a vacuum for 30 minutes. The melting point of the amine so treated was 52.5-53.5° C.

(Beilstein, 53° C.). This sample of amine was used to make up the solutions in cetane.

The other sample was Matheson Company practical grade. This material was vacuum distilled under nitrogen. The crude material distilled at a temperature range of 145-165° C. at 1.25 mm pressure. The fraction distilling at 155-160° C. was used for preparation of surface films from the melt of the amine. The boiling point at this pressure recorded in the literature was 157° C. (21). This product had a slight yellowish tinge which became more pronounced with successive heating of the sample.

Both samples were stored in dessicators containing sodium hydroxide pellets.

b. <u>Stearonitrile</u> The stearonitrile was isolated from Armour industrial grade material. The crude material contained 90% stearonitrile, 6% palmitonitrile, and 4% of other impurities. Three samples were purified for adsorption studies.

Sample I: Recrystallized from diethyl ether and then from acetone. Melting point, 39.3-41.0° C.

Sample II: Recrystallized from ethanol several times. Melting point, 39.5-41.5° C.

Sample III: Recrystallized from acetone, ethanol, and twice more from acetone. Melting point, 41.0-42.0° C.

The melting point recorded in the Handbook of Chemistry and Physics (22) was 42.5-43.0° C. It is possible that the final product contained appreciable quantities of palmitonitrile.

c. Octadecylthiocyanate n-Octadecylthiocyanate was prepared by heating n-octadecyliodide with potassium thiocyanate in ethanol. The product was recrystallized from methanol and had a melting point of 29.0-29.5° C. The literature value was 27.0° C. (23).

d. Cetane The cetane used as a solvent for the octadecylamine was a product of Eastman Organic Chemicals Company. It was purified in this laboratory according to a method described by Zisman et al. (24). The purified cetane did not spread on a clean surface of water held above pH 10 or below pH 3 indicating the absence of adsorbable impurities.

e. Tetraphenylporphine This material was the product of a reaction of pyrrole with benzaldehyde. The principal reaction products are $\alpha, \beta, \gamma, \delta$ -tetraphenylporphine and $\alpha, \beta, \gamma, \delta$ -tetraphenylchlorine (25). The crude product was dissolved in benzene and percolated through a column of activated alumina to remove the major portion of impurities. No further purification was attempted. In further reference to tetraphenylporphine, it will be understood that the material contained both the porphine and the chlorine.

f. Dyes The Rhodamine B was Hartman-Leddon Company general biological stain. It was used without purification.

g. Stearic acid The stearic acid was Baker and Adamson N. F. grade. No further purification was made.

C. Procedures

1. Adjustment of the polarization spectrometer

In setting up the spectrometer, each component was separately adjusted as it was placed into the system. The light source was first adjusted to focus the filament or arc on the entrance slit to the monochromator. The collimating lens was then put in place and adjusted to focus the exit slit of the monochromator at infinity. The polarizing prism was mounted on the frame attached to the monochromator and set so that the light beam was centered on the prism.

The polarimeter was positioned to place the slide stage in the light beam. A slide was fixed to the stage and the stage was set to reflect the light beam directly back onto the exit slit of the monochromator. The stage was then rotated to reflect the light into the analyzer. The amount of rotation was a measure of the angle of incidence of the light beam. Most of the measurements taken in this work were made at an angle of incidence of 68.45 degrees.

The relative azimuths of the polarizer and analyzer were found by adjusting the polarizer until its electric vector was parallel to the plane of the slide. Light reflected in this manner is plane polarized. The analyzer was set to extinguish the light so reflected. The components were adjusted alternately until a maximum extinction of the light was obtained. At this setting, the electric vector of the analyzer lay in the plane of incidence of the light beam.

The compensator was placed in the system and its wedge set away from the position of no compensation. The compensator was rotated until maximum extinction of the light was again realized. At this setting, the fast axis of the compensator lay in the plane of incidence. The compensator was then rotated until the fast axis was oriented at 45 degrees to the plane of incidence. The micrometer screw was adjusted until maximum extinction of the light was obtained. This was the null setting for the compensator wedge. There was a slight variation in this null position with wavelength. The most consistent value was -0.790.

2. Calibration of the compensator

The compensator was calibrated to determine how many degrees compensation resulted from one turn of the micrometer screw. The fast axis of the compensator was set at 45 degrees to the plane of incidence. The electric vector of the analyzer was set normal to the plane of incidence. At these settings, extinction of the light will occur when the components of polarized light are 180 degrees out of phase.

The number of turns of the micrometer screw, N, for full wave compensation (360 degrees) was found to be a linear function of the wavelength:

$$N = 0.11466\,\lambda - 6.405\ .$$

To find the degrees compensation per turn of the micrometer screw, 360 was divided by N. The wavelength is in millimicrons.

3. Spectrometer readings

The spectrometer readings were made with the polarizer azimuth set at 45 degrees to the plane of incidence and with the fast axis of the compensator in the plane of incidence. The compensator micrometer screw and the analyzer azimuth were adjusted until there was maximum extinction of the light as indicated by the photometer reading. At the extinction point, the elliptically polarized light reflected from the slide was rendered plane polarized by the compensator and the electric vector of the analyzer was perpendicular to the electric vector of the compensated light.

When an analyzer is rotated in a beam of plane polarized light, the intensity of the transmitted light varies as the square of the sine of the angle of rotation except for a small constant background of extraneous light. A plot of the intensity of the transmitted light versus the angle of rotation yields a curve whose slope at the extinction point is zero. As a result, there is considerable uncertainty in determining the setting of the analyzer for the exact extinction position. A more accurate method for determination of the extinction position is by use of the "Method of Symmetric Angles" (26). In this method, the extinction intensity is first found. The analyzer is then rotated away from the approximate extinction position until a predetermined intensity above the extinction intensity is reached. At this position, the intensity curve has a finite slope and the analyzer setting can be made with much greater precision. The analyzer setting for this intensity is recorded and the analyzer is rotated back through the extinction position until the intensity rises again to the same value at which the first setting was recorded. If there is no drift in the light intensity or the photomultiplier sensitivity, the two analyzer settings are an equal number of degrees from the true extinction position and their average determines the extinction position.

In this work, six to ten readings were recorded on alternate sides of the extinction position. The true extinction position was found by taking the average of consecutive pairs of readings, discarding those values which deviated markedly from the others, and finding the average for the sets of pairs. With this technique, errors due to misread settings or sharp fluctuations in the light intensity were eliminated.

The average deviation in the analyzer extinction position was usually less than 0.005 degree when the "Method of Symmetric Angles" was used. When the extinction position was found by adjusting for maximum extinction, the average deviation in a series of readings was found to be about

0.02 degree.

Compensator readings were made in the same manner. The extinction intensity was found and the micrometer screw was adjusted alternately to either side of the extinction position to a setting which resulted in a predetermined intensity above the extinction intensity. Experimental justification for this method of determining the compensator extinction position is given in Table 1. The same extinction position was found for several intensity values. This indicated that the intensity curve was symmetrical about the extinction position.

Table 1. Symmetric intensity settings of the compensator.

Extinction intensity (arbitrary units)	Intensity for compensator settings	Extinction position of compensator
440	540	6.265
440	640	6.270
440	840	6.268

In most of the experiments, ten to fourteen settings of the compensator were made. The extinction position of the compensator was determined by averaging pairs of consecutive readings in the same manner as was done for the analyzer extinction positions. When micrometer settings were converted to degrees, the average deviation within a set of readings was seldom larger than 0.015 degree.

The micrometer screw of the compensator had a slight amount of backlash. Settings of the screw were always made by approaching the desired position with a clockwise rotation of the screw.

When the compensator was set with one of its principal axes in the plane of incidence, the extinction positions of the analyzer and of the compensator were essentially independent of one another (27). Experimental verification of this independence is shown in Table 2.

Table 2. Independence of analyzer and compensator settings (fast axis of compensator in the plane of incidence).

Analyzer setting (degrees)	Extinction position of compensator
56.352	6.272
55.352	6.276
56.352	6.274
57.352	6.272
56.352	6.270

Spectrometer readings were made by first setting the analyzer and compensator for maximum extinction. Several symmetric angle readings were then taken for the analyzer. These readings were averaged directly to find the approximate extinction position. The analyzer was set at this extinction position and the compensator readings were made. After the run was completed, the analyzer extinction position was refined by averaging consecutive pairs of readings.

It was found that the phase change resulting from a film on the surface was a much more sensitive indication of the film properties than was the change in the amplitude ratio. For this reason, the analyzer position was determined first from an approximate setting of the compensator for maximum extinction.

A typical set of spectrometer readings is listed in Table 3.

Table 3. Typical set of spectrometer readings. Readings taken of a clean chromium slide at 420 millimicrons.

Analyzer settings for symmetric angles (degrees)	Average of consecutive pairs (degrees)	Compensator settings	Average of consecutive pairs
58.260	54.980 (discard)	4.355	5.1875
51.700	54.974	6.020	5.1870
58.248	54.9715	4.354	5.1870
51.695	54.9715	6.020	5.1870
58.248	54.9695	4.356	5.1880
51.691		6.020	5.1880
		4.353	5.1865
		6.020	5.1865
		4.353	5.1865
		6.021	5.1870
		4.354	
54.974	54.972		5.1970 ± .0004

4. Spectral determination

The optical constants of the chromium slides were found to vary from slide to slide. For this reason, spectrometer runs had to be made twice for each slide, once for the clean slide or for a slide with a reference film, and again for the film being investigated. Care was taken to use identical procedures of polishing and flaming within this pair of runs.

After polishing and flaming, the clean slide was stored in a test tube for a given length of time, usually about two hours. This was done to allow complete adsorption of gases from the air or evaporation of volatile solvents from the slide before readings were made.

It was found that a clean slide adsorbed impurities from the air to form a film several Angstroms thick. This adsorption was rapid in the first few minutes of exposure to the air, but tapered off after about thirty minutes. After a slide was mounted on the stage, a period of thirty minutes was allowed to pass before readings were made.

After the slide was mounted on the stage, the monochromator was set to 350 millimicrons and the compensator screw was set about five full revolutions away from the extinction position. The slide stage was adjusted to give maximum reflection of the light into the analyzer. The analyzer was then rotated 180 degrees. If the two positions for maximum intensity gave the same reading on the photometer, the slide was presumed to be well centered with respect to the analyzer and polarizer.

The monochromator was then set at the desired wavelength and the extinction positions for the analyzer and compensator were found as described previously. A new wavelength was then selected and the balancing repeated. The measurements were always made in the order of increasing wavelength and at ten minute intervals. This was done to ensure that time dependent changes due to adsorption of material from the air would alter results, at most, in a smooth way.

After the reference readings had been taken over the spectrum, the slide was removed and repolished with a procedure identical to that for the reference run. A film was then adsorbed or deposited on the surface and the procedure for readings was repeated.

6. Film formation

Films of octadecylamine, octadecylthiocyanate, and stearonitrile were formed by adsorption from the melt of the compound. A bulk supply of the compound was melted and the slide was placed in the melt. If an oriented monolayer was formed on the slide, the surface was nonwet by the melt on withdrawal of the slide (20). The films of the thiocyanate and the nitrile were nonwet by the melt except for occasional isolated droplets. These were removed by wiping with facial tissue.

Some difficulty was encountered in the formation of amine films from the melt. On exposure to air, a crystalline film was formed on the surface of the melt which inhibited the pealing back of the melt from the surface of the slide. This film was perhaps the result of a reaction of the amine with carbon dioxide from the air. The amine films were rubbed vigorously with facial tissue to remove the excess amine which remained on the surface. The surface was rubbed until a homogeneous breath figure was obtained. These films were found to have a thickness slightly greater than that of a monolayer of barium stearate.

Some of the amine films were formed by adsorption of the amine from a 0.1% solution of the amine in cetane. The surfaces of the slides with these films were nonwet by the cetane solution when they were withdrawn, indicating that a close packed monolayer had been formed (24).

Barium stearate films were formed by the Langmuir-Blodgett technique (28). A condensed monolayer of the acid was formed on the surface of water containing barium ions and buffered to maintain a pH of about 7.0. This film was transferred to the slide by drawing the slide up through the water surface or by touching a wet slide to the surface.

Paraffin films were formed by melting paraffin on the surface of the slide and then rubbing with facial tissue until a homogeneous breath figure was obtained.

Films of Rhodamine B and of tetraphenylporphine were formed by placing a drop of a solution containing the dye on the slide and tilting the slide until a uniform liquid film was formed. The excess liquid was wiped off and the solvent of the remaining film was allowed to evaporate, depositing the dye on the surface. These solutions contained collodion solids which served to keep the dye or porphine randomly oriented on the surface. A few dye films were run with no collodion.

The solvent for the dye was a mixture of ethanol and n-amyl acetate. The acetate was added to retard the rate of evaporation.

7. Breath figures

Breath figures were formed by holding the slide in front of the mouth and slowly exhaling. The moisture from the breath condensed on the slide surface. If the slide were clean, the droplets of condensed moisture coalesced and spread over the surface and the resultant water film was invisible. If the slide had a hydrocarbon film on it, the droplets remained isolated on the surface and a cloudy film could readily be detected. A homogeneous film resulted in a homogeneous breath figure.

V. RESULTS

A. Strongly Absorbing Films

Tables 4 through 7 list the data obtained from spectrometer readings of films containing strongly absorbing materials on chromium. The results are listed for a film containing 50% by weight of tetraphenylporphine dispersed in collodion solids, for films containing 50% and 17% by weight of Rhodamine B dispersed in collodion solids, and for a film of pure Rhodamine B. These data were used to calculate the optical properties of the films as a function of the wavelength in the manner outlined in Section II.

Equation 5 was separated into its real and imaginary parts to give:

$$\rho \sin(\Delta - \Delta') = R(\sigma) \tag{10a}$$

$$\left[\rho \cos(\Delta - \Delta')\right] - 1 = -I(\sigma) \tag{10b}$$

where $R(\sigma)$ and $I(\sigma)$ refer to the real and imaginary parts of σ.

These equations were solved simultaneously for the film thickness and refractive index with the absorption coefficient of the film taken as zero. The film thicknesses found in this manner are listed in the tables with the data. These values for the thickness are valid only at wavelengths where absorption of light by the film is negligible. At positions of absorption, the thickness calculated for zero absorption

Table 4. Data from spectrometer readings of a film containing 50% by weight of tetraphenylporphine in collodion solids adsorbed on chromium ($\phi = 68.45^{\circ}$).

λ mμ	Δ degrees	Δ' degrees	ψ degrees	ψ' degrees	L^a Ång-stroms	n^b	k^b
330	101.170	110.467	35.095	34.062	29.81	-	-
340	102.913	111.977	35.046	34.193	27.21	1.993	.070
350	104.499	113.330	34.832	34.037	26.71	1.977	.082
370	107.581	116.145	34.525	33.745	27.14	1.978	.079
380	109.048	117.304	34.660	33.906	27.81	1.947	.059
390	111.009	118.927	34.726	34.176	24.45	1.895	.133
400	112.718	120.409	34.423	34.157	20.51	1.843	.262
410	114.595	122.317	33.981	34.151	16.37	1.775	.526
415	114.748	122.895	33.921	34.371	14.74	1.892	.942
420	115.054	123.919	34.140	34.511	17.20	2.305	.764
430	115.944	125.414	34.480	34.349	24.30	2.498	.323
440	117.855	126.934	34.394	34.041	26.93	2.410	.200
450	119.750	132.661	34.167	33.715	36.95	-	-
460	121.485	130.078	33.908	33.492	28.08	2.328	.129
470	123.111	131.435	33.720	33.220	29.40	2.262	.066
480	124.484	132.625	33.600	33.032	30.89	2.240	.005
490	125.760	133.640	33.422	32.968	28.90	2.208	.085
500	126.944	134.605	33.511	33.082	28.61	2.170	.097
505	127.900	135.556	32.761	32.350	28.46	2.188	.115
510	128.288	135.768	33.523	33.161	27.66	2.148	.140
515	128.345	135.872	32.653	32.146	30.41	2.178	.023
520	129.177	136.975	32.878	32.509	29.09	2.321	.107
525	128.981	136.371	32.964	32.538	29.24	2.182	.073
530	129.805	137.167	32.188	31.765	29.22	2.185	.079
535	130.571	137.819	33.011	32.565	29.92	2.160	.040
540	130.055	137.219	32.413	31.949	30.11	2.150	.034
545	131.128	138.284	31.949	31.484	30.29	2.155	.030
550	131.552	138.566	32.845	32.387	30.47	2.130	.020
555	130.719	138.038	32.077	31.626	31.01	2.320	0
560	131.778	139.066	31.682	31.258	30.64	2.292	.020
565	132.596	139.393	32.599	32.172	30.01	2.108	.033
575	132.899	139.636	31.447	30.992	30.60	2.113	.015

[a] Film thickness calculated for k = 0.

[b] Index of refraction and absorption coefficient calculated for L = 31.0 Å.

Table 5. Data from spectrometer readings of a film containing 17% by weight of Rhodamine B in collodion solids adsorbed on chromium ($\phi = 68.45^\circ$).

λ mμ	Δ degrees	Δ' degrees	ψ degrees	ψ' degrees	L[a] Ångstroms	n[b]	k[b]
350	107.659	117.325	35.139	34.327	28.06	2.096	.064
400	114.896	123.972	35.397	34.742	28.73	2.12	.055
450	122.773	130.926	35.168	34.558	30.64	2.10	.005
475	126.335	134.273	33.819	33.280	29.80	2.13	.037
500	129.500	136.835	33.705	33.318	27.23	2.025	.223
525	131.531	138.567	32.932	32.767	24.65	1.98	.302
550	132.363	139.318	31.562	31.537	24.35	2.07	.56
575	132.561	139.928	32.269	31.934	30.35	2.43	.03
590	133.342	140.358	32.444	32.039	31.39	2.31	0
625	135.625	141.903	32.371	31.963	31.54	2.122	0
650	139.965	142.050	31.920	31.479	33.34	2.15	0

[a] Film thickness calculated for k = 0.

[b] Index of refraction and absorption coefficient calculated for L = 31.0 Å.

Table 6. Data from spectrometer readings of a film containing 50% by weight of Rhodamine B in collodion solids adsorbed on chromium ($\phi = 68.45$).

λ mμ	Δ degrees	Δ' degrees	ψ degrees	ψ' degrees	L[a] Ångstroms	n[b]	k[b]
450	120.434	128.842	34.563	33.700	37.97	1.765	0
475	125.212	132.344	34.432	33.872	29.49	-	-
500	128.176	134.674	33.487	32.907	31.24	1.545	.075
512	129.263	135.660	32.799	32.796	20.42	1.455	.185
525	129.679	136.503	32.252	32.633	19.24	1.540	.195
537	130.597	137.567	32.343	32.629	20.98	1.490	.364
550	131.094	138.678	31.883	32.416	21.95	1.460	.533
575	130.998	139.827	31.026	31.065	31.37	2.605	.690
600	132.832	140.628	32.436	31.932	36.19	2.070	.050
625	133.830	141.230	31.184	30.601	38.50	2.040	.010
650	135.781	142.722	30.942	30.462	35.86	1.950	0

[a] Film thickness calculated for k = 0.

[b] Index of refraction and absorption coefficient calculated for L = 38.0 Å.

Table 7. Data from spectrometer readings of a film of Rhodamine B adsorbed on chromium (ϕ = 68.45).

λ mμ	Δ degrees	Δ' degrees	ψ degrees	ψ' degrees	L[a] Ångstroms	n[b]	k[b]
425	124.973	126.272	34.059	33.973	5.08	1.554	.051
450	128.695	129.972	33.770	33.657	7.49	1.570	0
475	132.503	133.599	33.761	33.753	3.52	1.430	.120
500	134.698	135.739	32.916	32.985	2.89	1.362	.220
515	135.647	136.894	31.828	32.094	2.67	1.180	.500
525	136.020	137.387	32.270	32.453	3.51	1.339	.5925
535	137.358	138.804	32.165	32.396	3.67	1.2385	.6704
545	137.621	139.205	31.166	31.418	4.28	1.154	.734
555	137.194	138.906	31.271	31.528	4.73	1.055	.832
565	138.525	140.273	31.866	32.074	5.18	3.751	.726
575	138.600	140.469	30.770	30.959	5.97	3.835	.305
585	138.280	140.125	31.458	31.576	6.27	3.555	.160
600	139.516	141.289	31.848	31.910	6.53	3.315	.034
625	140.006	141.721	30.528	30.596	6.63	3.337	0
650	141.591	144.061	30.377	30.347	10.95	-	-

[a] Film thickness calculated for k = 0.

[b] Index of refraction and absorption coefficient calculated for L = 6.6 Å.

was found to be too small. The actual film thickness was estimated from the values obtained at wavelengths where the solution spectra showed little absorption and the calculated thickness approached an upper limit. The calculated thicknesses which were weighted most heavily in this estimate are underlined in the tables. The values calculated from data taken at wavelengths greater than 625 millimicrons were not assigned much weight in this estimation because of the relative insensitivity of the photocell.

The estimated thickness was assumed to be a constant function of the wavelength allowing equations 10 to be solved for the absorption coefficient and refractive index of the film as functions of the wavelength. Algebraic solution of the equations proved to be impractical due to difficulty in separation of the variables so a graphical solution was made. Both sides of the equations 10 were divided by the thickness to give:

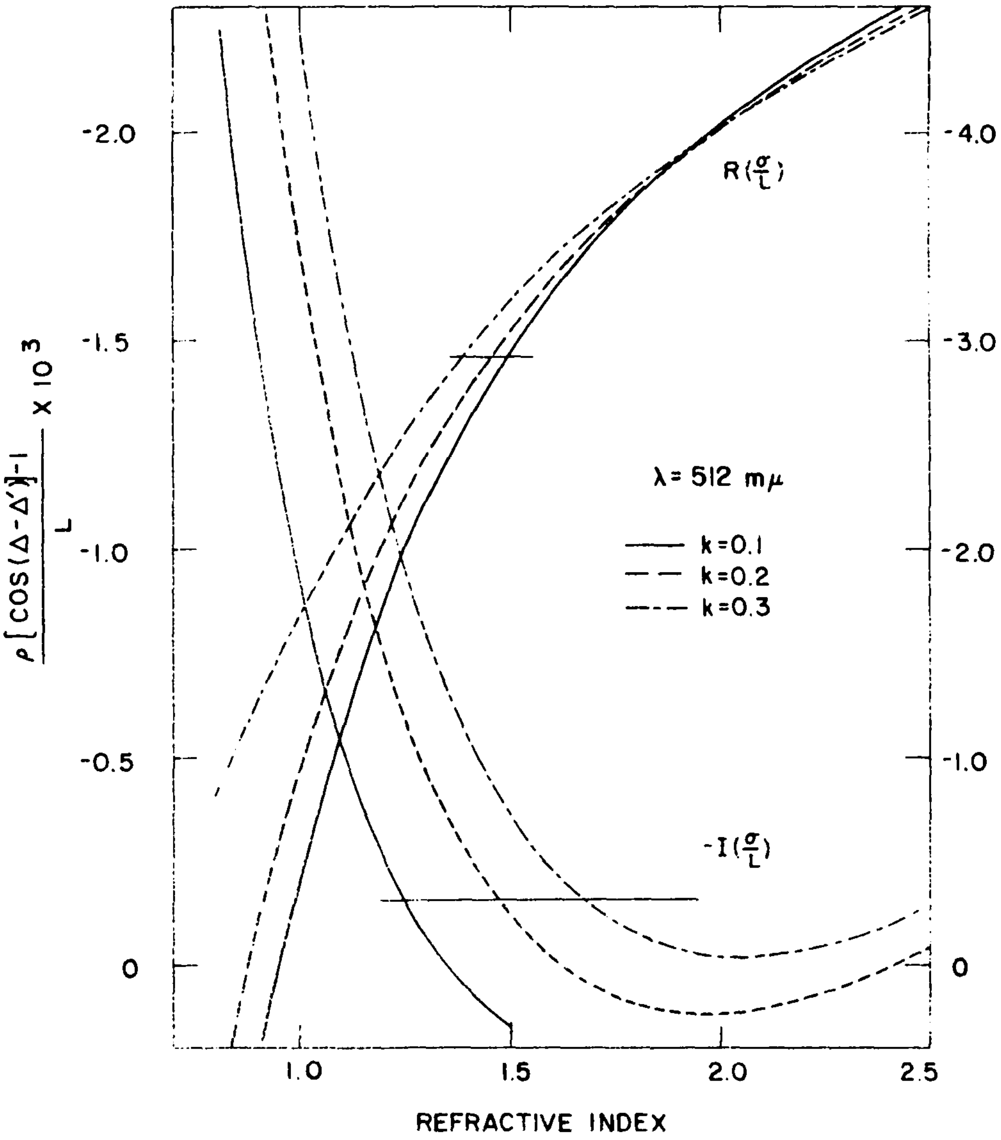
$$\frac{\rho \sin (\Delta' - \Delta')}{L} = R\left(\frac{\sigma}{L}\right) \tag{11a}$$

$$\frac{[\rho \cos (\Delta - \Delta')] - 1}{L} = -I\left(\frac{\sigma}{L}\right) . \tag{11b}$$

The dielectric constants of the substrate were calculated from the spectrometer readings of the clean surface and these values were used to calculate $R(\frac{\sigma}{L})$ and $I(\frac{\sigma}{L})$ as functions of the film refractive index for a series of absorption coefficients. A typical set of curves for these functions is shown in Figure 4. This set of curves was calculated from readings taken at a wavelength of 512 millimicrons for the slide which was used to study a film containing 50% Rhodamine B. A similar set of curves was calculated for every wavelength at which experimental readings were made. These calculations were made with an IBM 650 computer.

Experimental values for $\frac{\rho \sin (\Delta - \Delta')}{L}$ and $\frac{[\rho \cos (\Delta - \Delta')] - 1}{L}$ were calculated and drawn in as horizontal lines on the graphs of $R(\frac{\sigma}{L})$ and $I(\frac{\sigma}{L})$. A series of

Figure 4. Typical set of curves calculated for the graphical solution of the refractive index and absorption coefficient of an adsorbed film. The horizontal lines represent the experimental values. These curves represent calculations made for a film containing 50% by weight of Rhodamine B in collodion solids.


$\frac{\rho[\cos(\Delta-\Delta')]-1}{L} \times 10^3$
-2.0
-1.5
-1.0
-0.5
0
$\frac{\rho \sin(\Delta-\Delta')}{L} \times 10^3$
-4.0
-3.0
-2.0
-1.0
0
$R(\frac{\sigma}{L})$
λ= 512 mμ
k=0.1
k=0.2
k=0.3
$-I(\frac{\sigma}{L})$
1.0
1.5
2.0
2.5
REFRACTIVE INDEX

successive approximations for the refractive index and absorption coefficient was made to obtain the values for which the experimental terms intersected the calculated curves. The optical constants so determined are listed in Tables 4 through 7. Figures 5 through 8 show the absorption coefficients and refractive indices plotted as a function of the wavelength along with the experimental phase dispersion of the film.

In order to estimate the probable error in the determination of the film optical constants, the absorption coefficients and refractive indices were found for values of $\Delta - \Delta'$ which were altered from the experimentally determined values by one-tenth of a degree, which is greater than the normal experimental error. The results of these computations are shown in Table 8 along with the experimentally determined values at the same wavelengths. It was found that an error of this magnitude in the determination of $\Delta - \Delta'$ did not significantly alter the optical constants.

Table 8. Uncertainty in the calculated refractive index and absorption coefficient due to experimental error in the determination of the phase change. (Film of 50% Rhodamine B)

λ	$\Delta - \Delta'$	n	k	$\Delta - \Delta' \pm 0.1$	n	k
512	-6.397	1.455	0.185	-6.497	1.465	0.200
550	-7.584	1.460	0.533	-7.684	1.460	0.550
575	-8.830	2.605	0.690	-8.730	2.580	0.700

Figure 5. Calculated optical constants for a film of tetraphenylporphine adsorbed on chromium. The film contained 50% by weight of the porphine dispersed in collodion solids and was 31 Ångstroms thick. The top curve represents the phase dispersion obtained for this film.

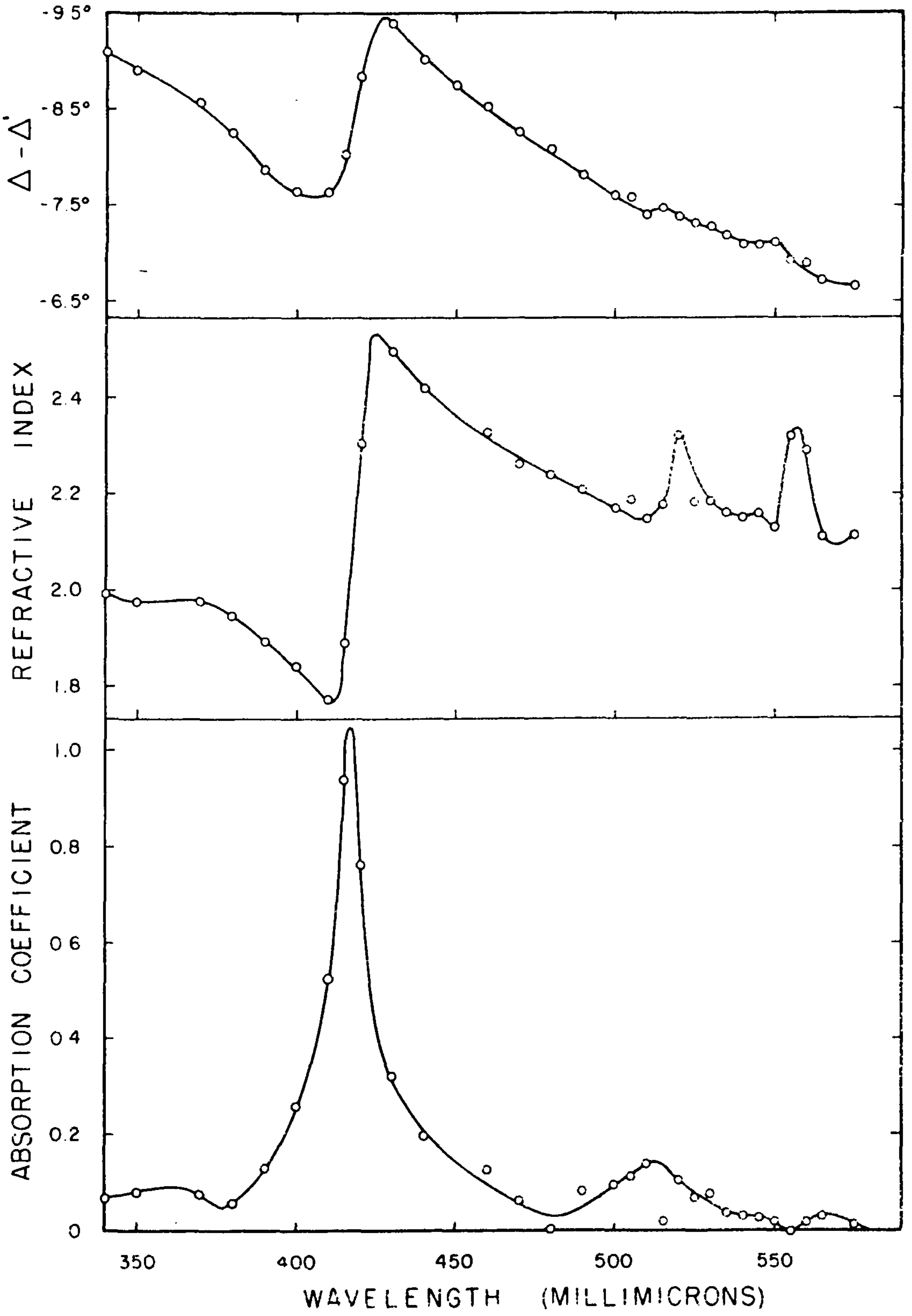

Δ - Δ'
-9.5°
-8.5°
-7.5°
-6.5°
REFRACTIVE INDEX
2.4
2.2
2.0
1.8
ABSORPTION COEFFICIENT
1.0
0.8
0.6
0.4
0.2
0
350
400
450
500
550
WAVELENGTH (MILLIMICRONS)

Figure 6. Calculated optical constants for a film of Rhodamine B adsorbed on chromium. The film contained 17% by weight of the dye dispersed in collodion solids and was 31 Ångstroms thick. The top curve represents the phase dispersion obtained for this film.

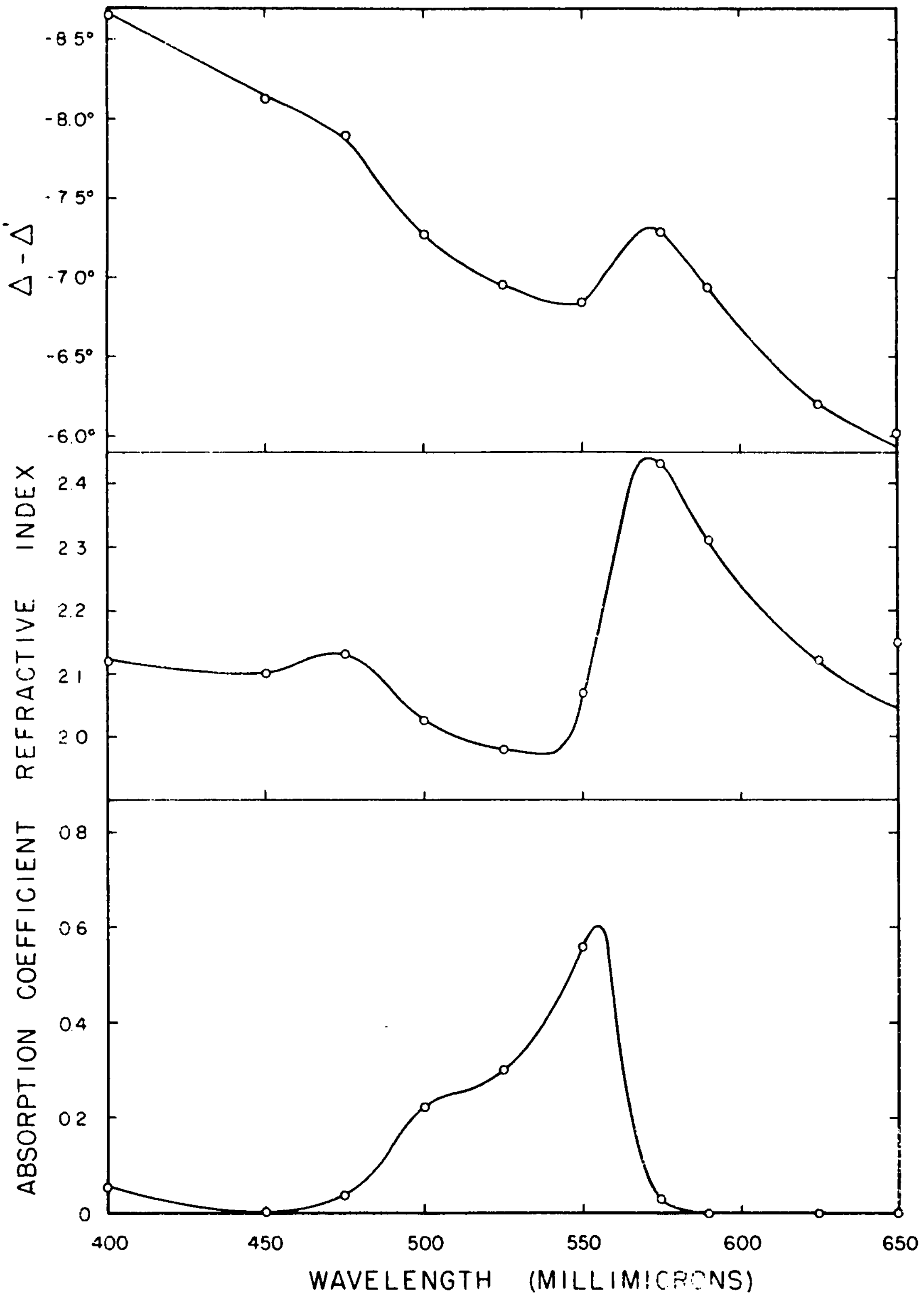

Δ - Δ'
-8.5°
-8.0°
-7.5°
-7.0°
-6.5°
-6.0°
REFRACTIVE INDEX
2.4
2.3
2.2
2.1
2.0
ABSORPTION COEFFICIENT
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
WAVELENGTH (MILLIMICRONS)

Figure 7. Calculated optical constants for a film of Rhodamine B adsorbed on chromium. The film contained 50% by weight of the dye dispersed in collodion solids and was 38 Ångstroms thick. The top curve represents the phase dispersion obtained for this film.

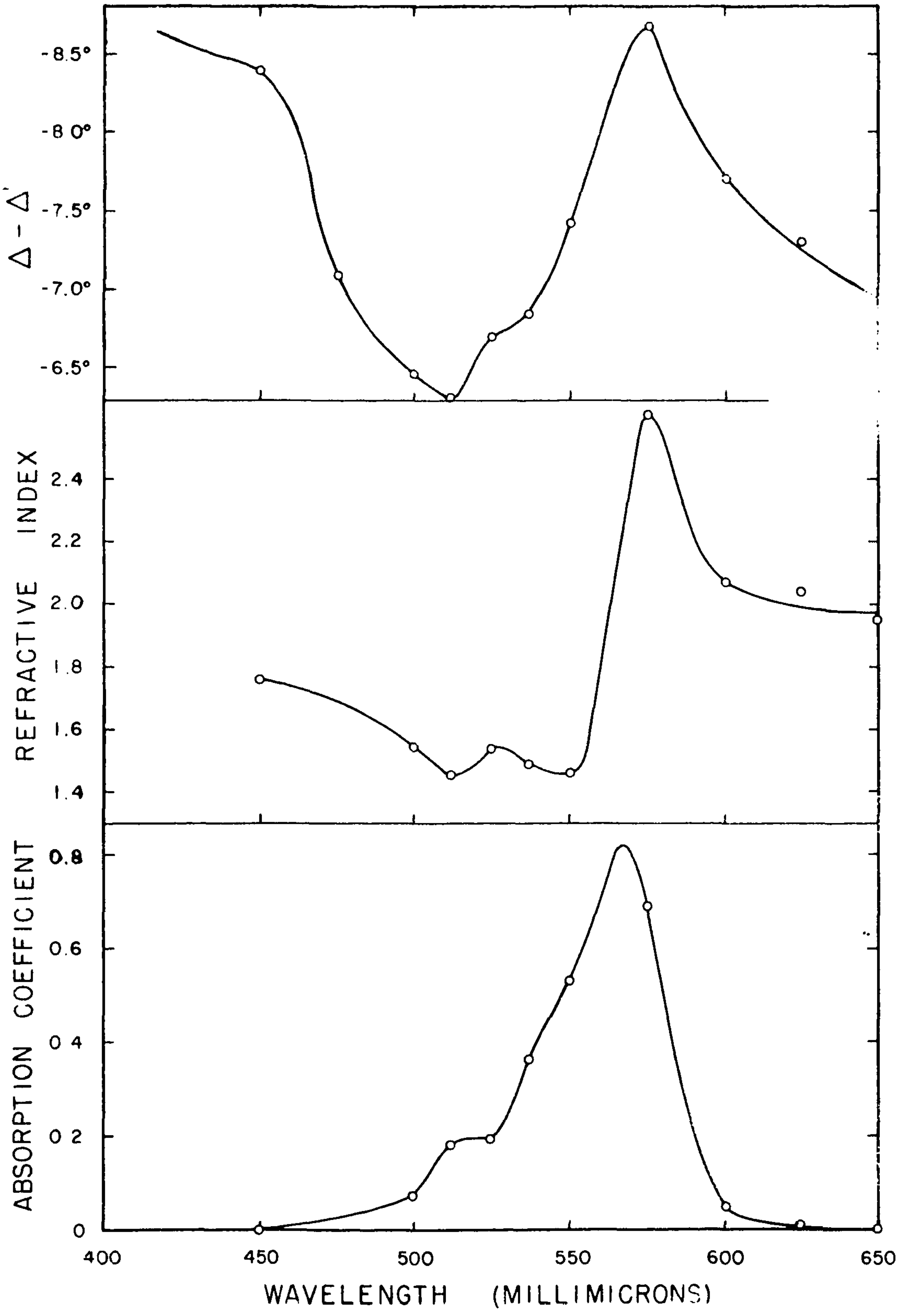
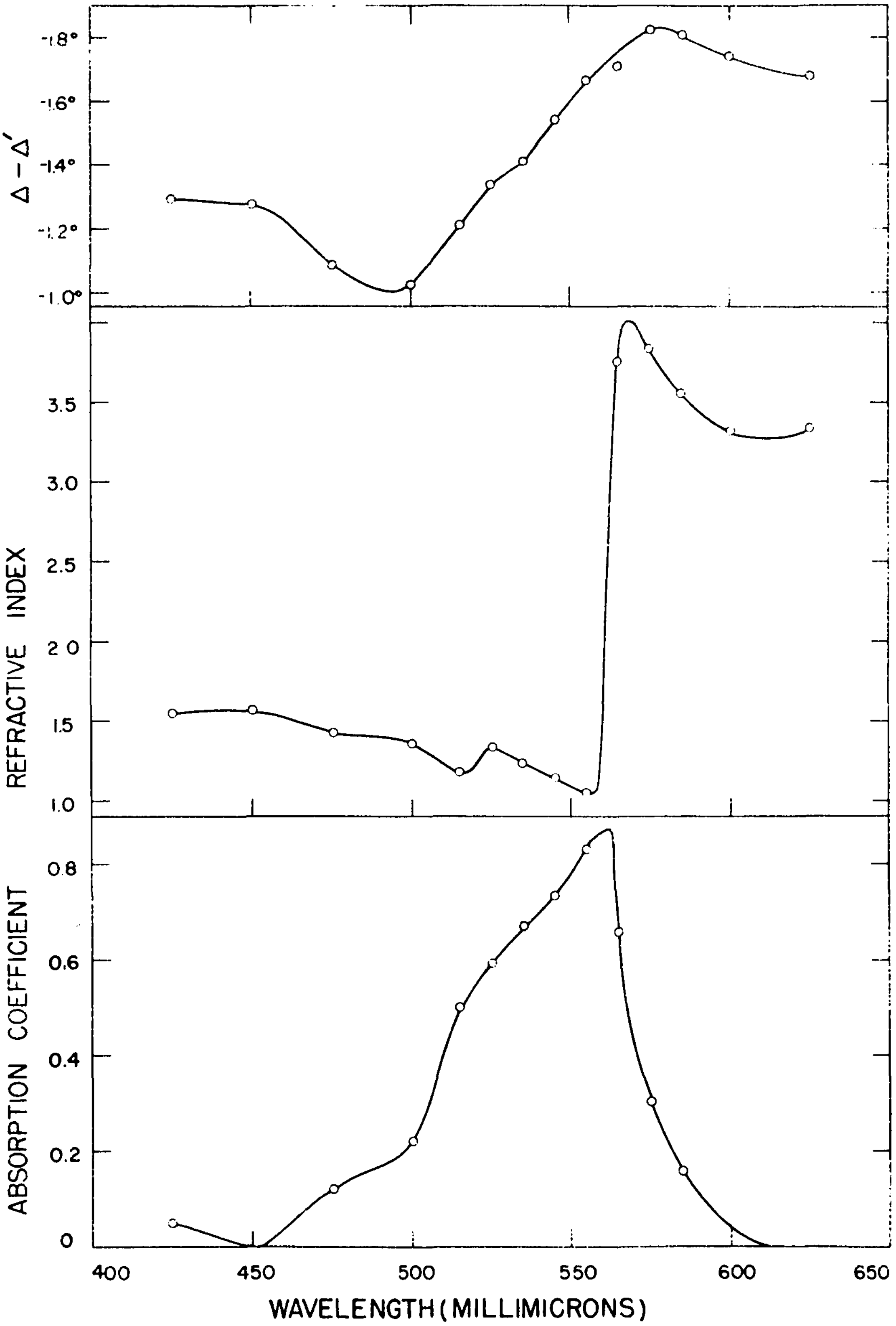

-8.5°
-8.0°
-7.5°
-7.0°
-6.5°
Δ - Δ'
2.4
2.2
2.0
1.8
1.6
1.4
REFRACTIVE INDEX
0.8
0.6
0.4
0.2
0
ABSORPTION COEFFICIENT
400
450
500
550
600
650
WAVELENGTH (MILLIMICRONS)

Figure 8. Calculated optical constants for a film of pure Rhodamine B adsorbed on chromium. The film thickness was 6.6 Ångstroms. The top curve represents the phase dispersion obtained for this film.


Δ − Δ′
-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
REFRACTIVE INDEX
3.5
3.0
2.5
2.0
1.5
1.0
ABSORPTION COEFFICIENT
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
WAVELENGTH (MILLIMICRONS)

The absorption coefficients for the films were converted to their equivalent molar extinction coefficients, E, for convenience of comparison of the absorption by the films to that in solution. These two quantities are defined as follows:

$$\ln \frac{I_o}{I} = \frac{4\pi kL}{\lambda} \tag{11a}$$

$$\log \frac{I_o}{I} = ECd \,. \tag{11b}$$

I_o = the intensity of incident light
I = the intensity of transmitted light
L = the thickness of the film in the same units as the wavelength
C = concentration of solution in moles per liter
d = thickness of the absorption cell in centimeters.

If the thickness and wavelength are expressed in Angstrom units, the relation between the absorption coefficient and the molar extinction coefficient is as follows:

$$E = \frac{4\pi k}{2.303\,\lambda C} \times 10^8 = 5.46 \times 10^8 \times \frac{k}{\lambda C} \,. \tag{12}$$

It was necessary to know the density of the film components in order to calculate the concentration of the films. The density of Rhodamine B was estimated by placing crystals of the dye in organic liquids in which the dye was insoluble. The crystals floated on the surface of chloroform (density 1.50) and sank in dichloromethane (density 1.34). Collodion solids are composed of nitrocellulose which has a density of 1.27-1.61 (22). A value of 1.4 grams/cm^3 was used for the density of these materials. The density of tetraphenylporphine was not listed in the literature but a value of 1.445 was found (29) for phthalocyanine which has a similar structure. This value was used for the density of the porphine. The molecular weight of the porphine is 614 and that of the Rhodamine B is 479.

Table 9 lists the molar concentrations of the tetraphenylporphine and Rhodamine B in the films, the wavelengths of the absorption bands, and the molar extinction coefficients of these bands. Table 10 lists the positions and molar extinction coefficients of the absorption bands of these compounds in solution. Figure 9 shows the absorption spectra of the dilute solutions of Rhodamine B and of tetraphenylporphine.

B. Films of Polar Hydrocarbon Derivatives

1. n-Octadecylamine

Figures 10 through 14 represent the phase dispersion obtained for films of n-octadecylamine adsorbed on chromium. The experimental runs are listed in chronological order. The average deviation in the determination of the phase difference is shown for the earlier runs. The experimental technique improved as more runs were made and the average deviation for run A-5 and subsequent runs was seldom greater than 0.015 degree.

Table 9. Positions and molar extinction coefficients of absorption bands in films containing tetraphenylporphine and Rhodamine B.

Film	Concentration moles/liter	λ max millimicrons	k	Molar extinction coefficient
50% tetraphenylporphine	1.16	417	1.047	11.8×10^{4}
		513	0.141	1.3×10^{4}
		546	0.030	0.3×10^{4}
		566	0.033	0.3×10^{4}
17% Rhodamine B	0.497	555	0.606	12.0×10^{4}
50% Rhodamine B	1.461	567	0.820	5.4×10^{4}
100% Rhodamine B	2.922	562	0.873	2.9×10^{4}

Table 10. Positions and molar extinction coefficients of absorption bands for dilute solutions of tetraphenylporphine and Rhodamine B.

Compound	Solvent	Concentration moles/liter	λ max millimicrons	Molar extinction coefficient
Tetraphenylporphine	benzene	6.5×10^{-5}	418	26.0×10^{4}
			514	1.3×10^{4}
			547	0.9×10^{4}
Rhodamine B	water	8.5×10^{-6}	556	10.6×10^{4}

Figure 9. Solution spectra for tetraphenylporphine and Rhodamine B. The porphine was 6.5×10^{-6} molar in benzene and the Rhodamine B was 8.5×10^{-6} molar in water.

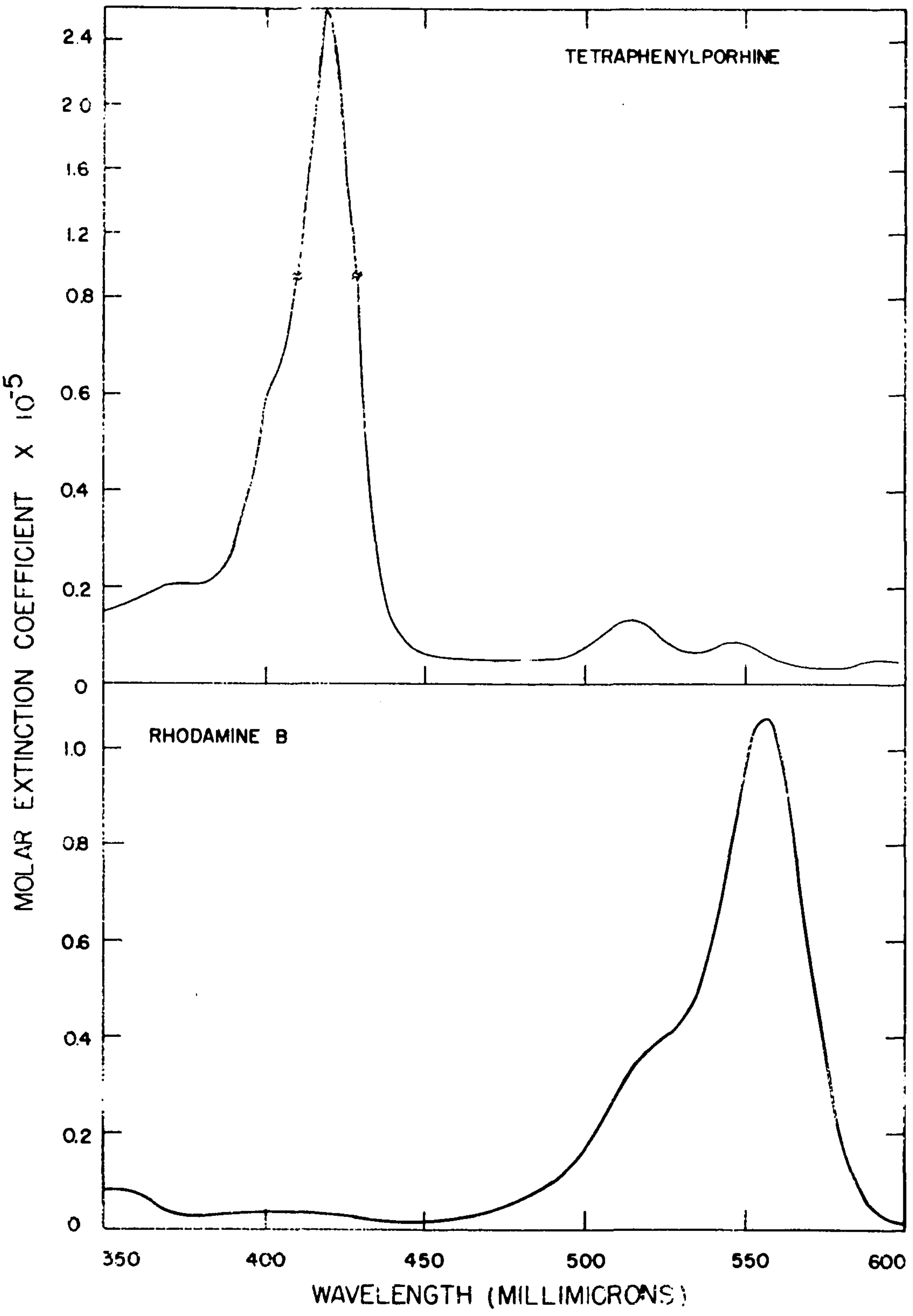

TETRAPHENYLPORHINE
RHODAMINE B
MOLAR EXTINCTION COEFFICIENT X 10^-5
2.4
2.0
1.6
1.2
0.8
0.6
0.4
0.2
0
1.0
0.8
0.6
0.4
0.2
0
350
400
450
500
550
600
WAVELENGTH (MILLIMICRONS)

Figure 10. Phase dispersion of octadecylamine adsorbed on chromium. The points denote the phase change of the amine film relative to the clean surface. In run A-1, the polarity of the xenon arc light source was reversed at 312 millimicrons. In run A-2, the slide was flamed heavily prior to adsorption of the amine film.

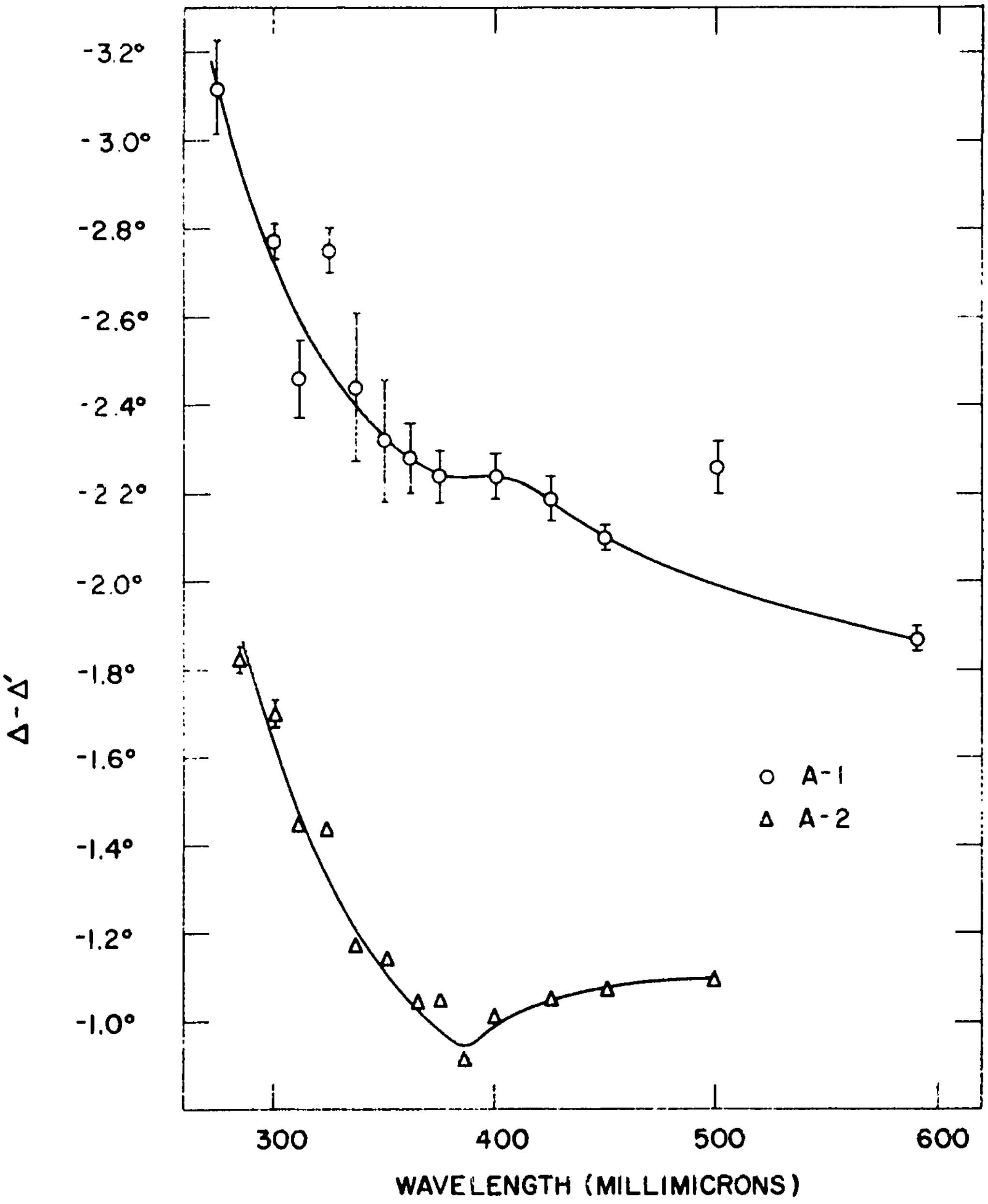
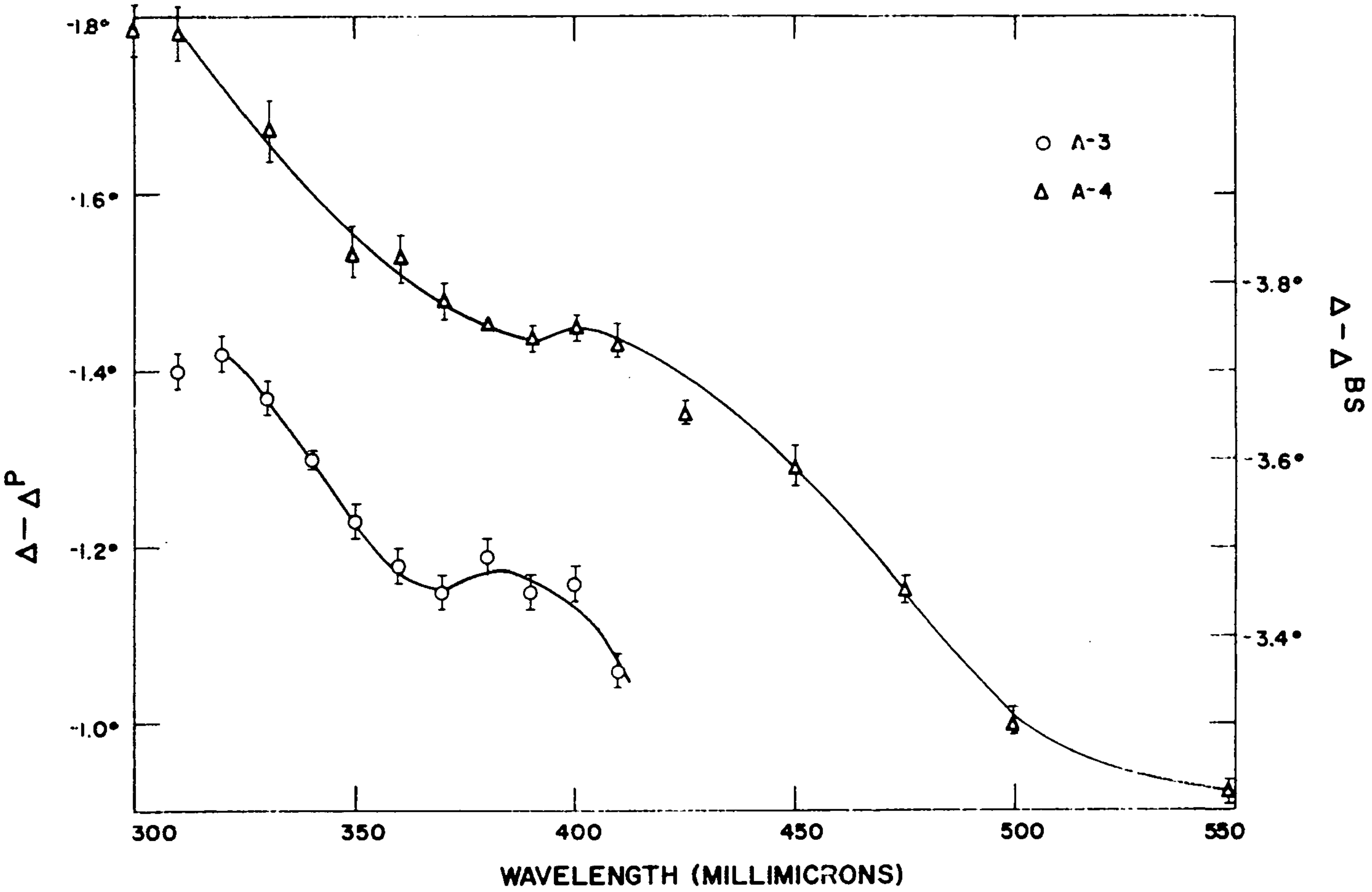

-3.2°
-3.0°
-2.8°
-2.6°
-2.4°
-2.2°
-2.0°
-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
Δ-Δ′
○ A-1
Δ A-2
300
400
500
600
WAVELENGTH (MILLIMICRONS)

Figure 11. Phase dispersion of octadecylamine adsorbed on chromium. The points of run A-3 represent the phase difference between an amine film and a barium stearate monolayer. The points of run A-4 represent the phase difference between an amine film and a paraffin film. The right ordinate refers to run A-3, the left to run A-4.



-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
$\Delta - \Delta^P$
-3.8°
-3.6°
-3.4°
$\Delta - \Delta^{BS}$
○ A-3
Δ A-4
300
350
400
450
500
550
WAVELENGTH (MILLIMICRONS)

Figure 12. Phase dispersion of octadecylamine adsorbed on chromium. The points denote the phase change of the amine films relative to the clean surfaces. Smooth background curves are drawn in for each set of data.

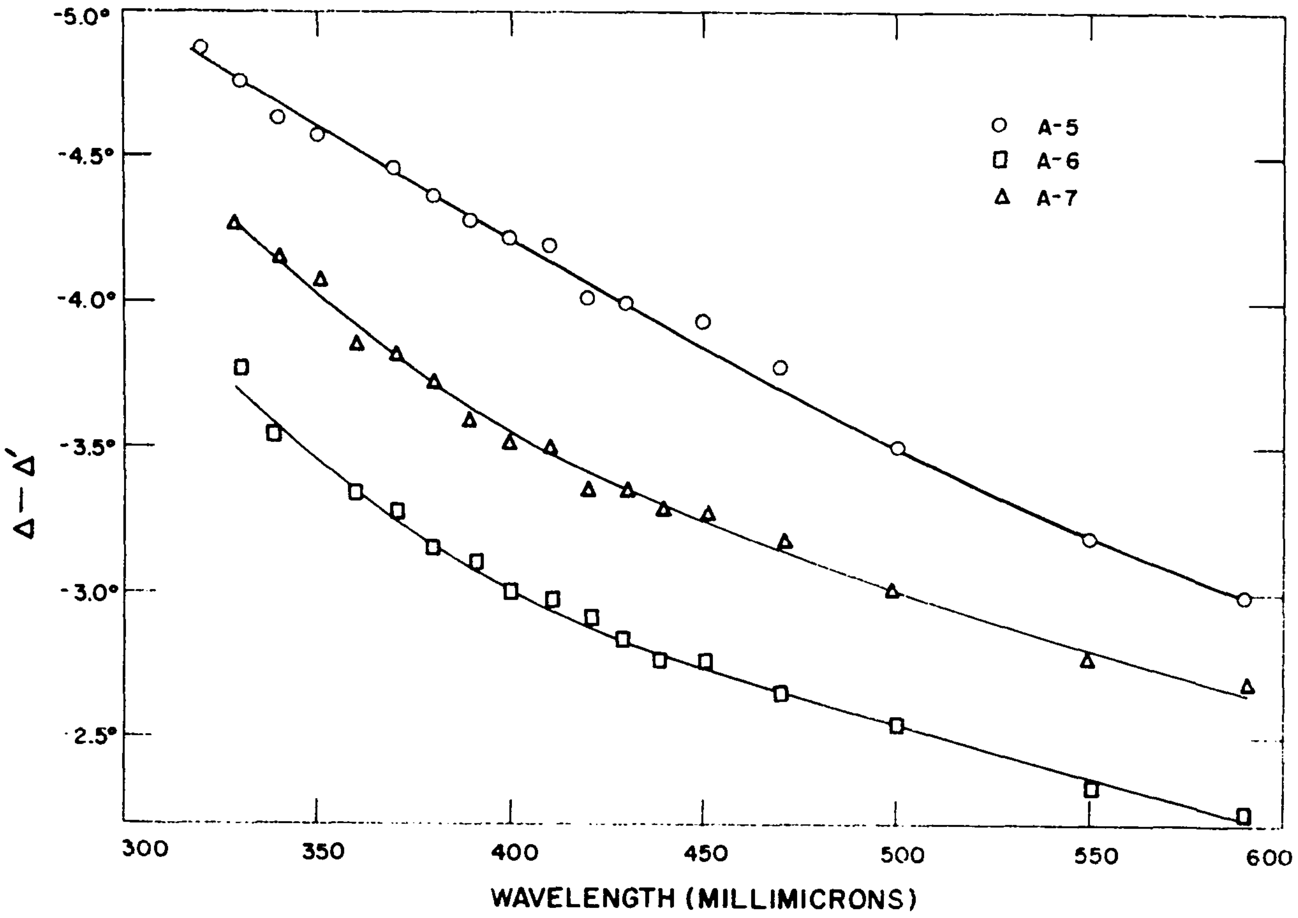

-5.0°
-4.5°
-4.0°
-3.5°
-3.0°
2.5°
Δ — Δ′
300
350
400
450
500
550
600
WAVELENGTH (MILLIMICRONS)
○ A-5
□ A-6
Δ A-7

Figure 13. Phase dispersion of octadecylamine adsorbed on chromium. The films were adsorbed from the melt of the bulk amine. The points denote the phase change of the amine films relative to the clean surfaces.

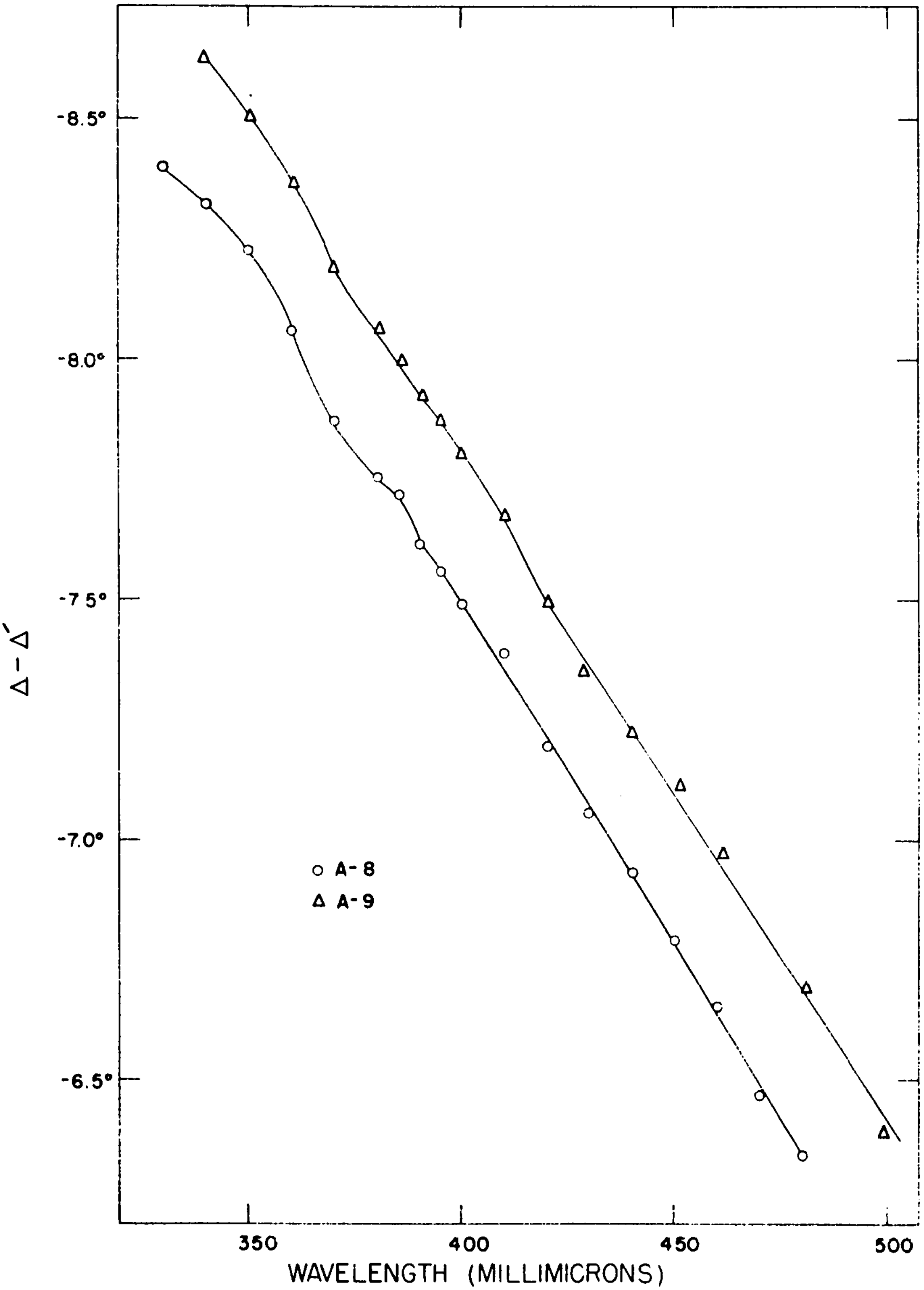

-8.5°
-8.0°
-7.5°
-7.0°
-6.5°
Δ - Δ′
○ A- 8
Δ A- 9
350
400
450
500
WAVELENGTH (MILLIMICRONS)

Figure 14. Phase dispersion of octadecylamine adsorbed on chromium. The triangles denote the phase difference between the clean surface flamed for one-half second and the clean surface flamed four seconds. The open circles denote the phase change of the amine film relative to the clean surface flamed four seconds.

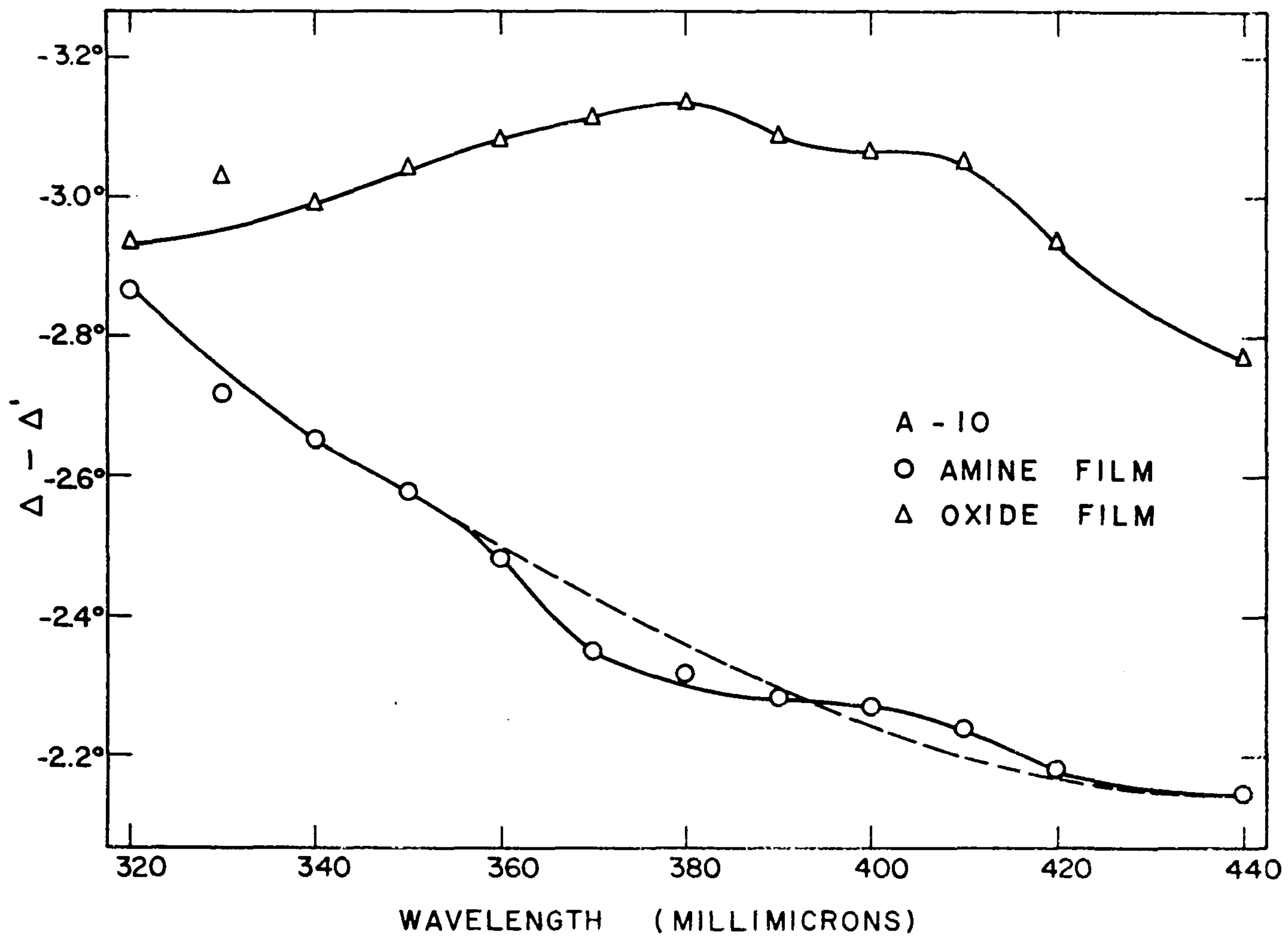

-3.2°
-3.0°
-2.8°
-2.6°
-2.4°
-2.2°
Δ − Δ′
320
340
360
380
400
420
440
WAVELENGTH (MILLIMICRONS)
A - 10
○ AMINE FILM
△ OXIDE FILM

Table 11 lists information about the preparation of the surfaces and films which were studied in this investigation. The second column shows the type of film on the surface of the slide for which readings were made. The same slide was used for all readings in a particular run and the films read in a run are listed in the order in which they were observed. The thickness of the film for run A-7 was determined by the simultaneous solution of equations 10 for the thickness and index of refraction with the absorption coefficient taken to be zero. For a thin, nonabsorbing film, the film thickness is proportional to the phase change, $\Delta - \Delta'$. The thickness of the amine films listed in Table 11 was found from the ratio of $\Delta - \Delta'$ of the film to that of the film of run A-7.

In run A-3 the phase dispersion is plotted as the difference between readings of an amine film and a reference film of barium stearate. A reference film of paraffin was used in run A-4. It was found that clean surfaces adsorbed considerable amounts of material from the air whereas a surface with an organic film on it adsorbed very little additional material from the air (see Appendix). The reference films were used to minimize the effect of this adsorption on the phase dispersion measurements. The dispersion curves for films of paraffin or barium stearate revealed no anomalous behavior within the spectral range of the spectrometer. Anomalous behavior in the phase dispersion for the amine film was evident upon taking the difference between the phase

Table 11. Preparation of surfaces and films in runs made to investigate the phase dispersion of octadecylamine adsorbed on chromium.

Run	Surface and adsorbed film (in order of investigation)	Surface preparation[a] and film formation	Ads. time (hr.)	L[b]
A-1	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from 0.08% cetane solution. Film nonwet by solution on withdrawal.	4	10.2 Å.
A-2	Octadecylamine film	Slide flamed for five seconds after polish. Film adsorbed from 0.08% cetane solution. Film nonwet by solution on withdrawal except for isolated droplets. Rubbed to remove droplets.	3	4.7 Å.
	Clean chromium	Surface polished to remove amine film. Film not completely removed after polishing ten minutes. (Water did not wet surface entirely.)		
A-3	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from 0.08% cetane solution. Film nonwet by solution on withdrawal.	21	12.6 Å.
	Barium stearate film	Transferred from water surface. Slide drawn through the water-film-air interface. Film nonwet by water on withdrawal of slide.		

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[a] Except where noted otherwise, the surfaces were polished with alumina in water until wet by the water and flamed for three seconds prior to film formation.

[b] Film thickness determined from the ratio of $\Delta - \Delta'$ for the film to that for the film of run A-7. Thickness of the film of run A-7 was calculated from equations 10.

Table 11 (Continued).

Run	Surface and adsorbed film (in order of investigation)	Surface preparation^a and film formation	Ads. time (hr.)	L^b
A-4	Octadecylamine film	Adsorbed from 0.1% cetane solution. Film nonwet by solution on withdrawal.	20	
	Paraffin film	Slide polished to remove amine film. Solid paraffin melted on slide and rubbed until a homogeneous breath figure was observed.		
A-5	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from 0.1% cetane solution. Film nonwet by solution on withdrawal.	12	19.6 Å.
A-6	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from 0.1% cetane solution. Film nonwet by solution on withdrawal except for several droplets. Rubbed to remove droplets.	6	14.0 Å.
A-7	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from 0.1% cetane solution. Slide withdrew wet by solution. Repolished and replaced in cetane solution. Film nonwet by solution on withdrawal.	4½ 4½	16.5 Å.
A-8	Clean chromium	Polished and flamed three seconds.		
	Octadecylamine film	Adsorbed from melt of the bulk amine. Film wet by melt on withdrawal. Rubbed until a homogeneous breath figure was obtained.	1½	34.2 Å.

Table 11 (Continued).

Run	Surface and adsorbed film (in order of investigation)	Surface preparation[a] and film formation	Ads. time (hr.)	L[b]
A-9	Clean chromium	Polished and flamed four seconds.		
	Octadecylamine film	Slide repolished and flamed four seconds. Film adsorbed from melt of bulk amine. Film wet by melt on withdrawal. Rubbed until a homogeneous breath figure was obtained.	1½	35.6 Å.
A-10	Clean chromium	Polished and flamed one-half second.		
	Clean chromium	Repolished and flamed four seconds.		
	Octadecylamine film	Slide not repolished or flamed after readings taken of clean slide. Film adsorbed from 0.1% cetane solution.[c] Film nonwet by the solution on withdrawal. Rubbed lightly.	10	10.4 Å.

[c] Fresh solution of amine in cetane. Free from carbon dioxide contamination.

differences for the amine film and the reference film. The use of reference films was discontinued because of the difficulty of removing the first film completely from the surface before adsorbing the second film and because inhomogeniety in the reference films may have caused anomalous points to appear in the phase dispersion curves.

When clean chromium was used as a reference surface, readings were taken at constant time intervals.

Runs A-1 through A-4 revealed evidence of anomalous behavior in the phase dispersion in the region from 375 to 395 millimicrons. Runs A-5 through A-7 (Figure 12) revealed no anomalous breaks which were significantly larger than the normal experimental scatter. The cetane solution of amine used to form the films for these runs had been exposed to air several times in previous work and was probably contaminated by carbon dioxide. Octadecylamine readily reacts with carbon dioxide to form a carbamide. The change in the electronic structure of the amine due to the carbamide formation may have inhibited the transition responsible for the absorption found in other films or shifted it out of the range of investigation.

The amine films studied in runs A-8 and A-9 were adsorbed from the melt of the bulk amine. This amine became discolored when it was heated suggesting that there were impurities in the sample. The anomalous breaks in the phase dispersion curves were smaller for these films than for those adsorbed from cetane but they were found in the same region of the spectrum. These films were thicker than those adsorbed from cetane causing a steeper slope in the phase dispersion curves which tended to obscure the anomalies.

In run A-10, the chromium slide was flamed for only one-half a second for the first reading. It was then repolished and flamed for three seconds, the normal flaming time used in other runs. This was done to determine the effect of the oxide film on the anomalous dispersion of the amine. The amine film was adsorbed on the slide after the oxide film had been read without further polishing or flaming of the slide. The cetane solution of the amine used in this run had been stored over sodium hydroxide and was free from carbon dioxide contamination.

Table 12 lists the positions and magnitudes of the anomalous breaks in the phase dispersion curves for octadecylamine films.

The absorption coefficient for the transition observed in the films of octadecylamine adsorbed on chromium is very small relative to the refractive index. Accordingly, there is little error involved in eliminating from the dielectric constant the terms containing the absorption coefficient in solving for the refractive index of the film. The refractive index for the amine film of run A-10 was calculated from equation 10a for an absorption coefficient of zero and a film thickness of 10.4 Ångstroms. The refractive index was also calculated for a smooth background curve drawn through the dispersion curve (dashed line, Figure 14). The results of these calculations are shown in Figure 15. Also shown in Figure 15 are the optical constants for the clean chromium surface flamed one-half second and four seconds.

Table 12. Position and magnitude of anomalous breaks in the phase dispersion of octadecylamine adsorbed on chromium.

Run	Reference surface	Position of anomaly millimicrons	Magnitude[a] of anomaly in degrees	Film thickness
A-1	Clean chromium	385	0.085	10.2 Å.
A-2	Clean chromium	400	-	4.7 Å.
A-3	Barium stearate	376	0.080	12.6 Å.
A-4	Paraffin	396	0.055	-
A-8	Clean chromium	390	0.050	34.2 Å.
A-9	Clean chromium	380	0.050	35.6 Å.
A-10	Clean chromium	393	0.085	10.4 Å.

[a] The sum of the vertical distance from a smooth background curve to each of the peaks of the anomaly.

2. Stearonitrile

Figures 16 through 18 show the phase dispersion for films of stearonitrile adsorbed on chromium. Table 13 lists information about the surfaces and films studied in this investigation. The clean surfaces of the slides were used

Figure 15. Refractive index for the amine film of run A-10 calculated for the data points and for a smooth background curve. The lower curves show the optical constants for the clean chromium surface. The solid points denote the optical constants after one-half second flaming, the open points denote the optical constants after four seconds flaming.

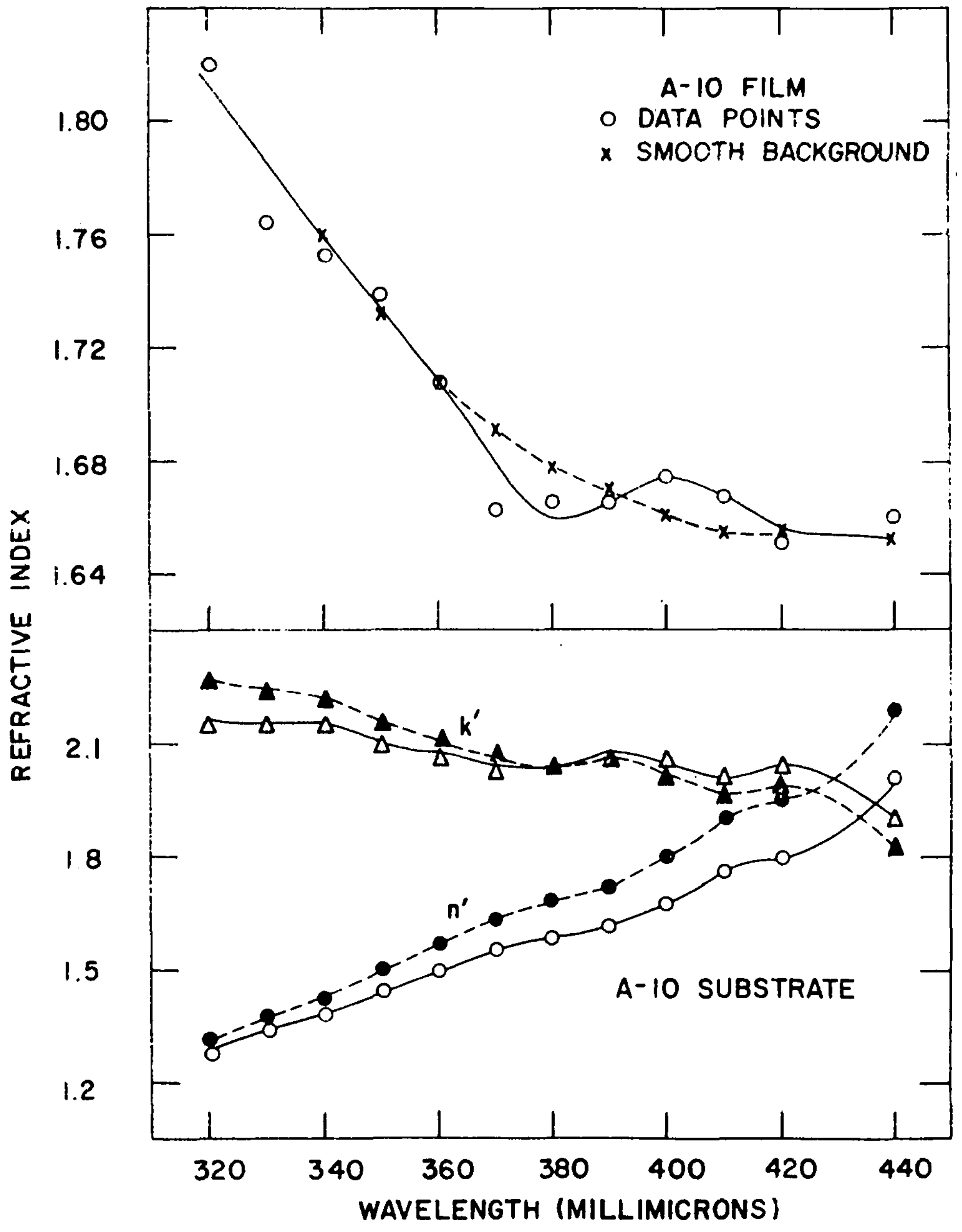
A-10 FILM
○ DATA POINTS
x SMOOTH BACKGROUND
1.80
1.76
1.72
1.68
1.64
REFRACTIVE INDEX
k′
n′
A-10 SUBSTRATE
2.1
1.8
1.5
1.2
320
340
360
380
400
420
440
WAVELENGTH (MILLIMICRONS)

Figure 16. Phase dispersion for films of stearonitrile adsorbed on chromium. The points denote the phase change of the films relative to the clean surfaces.

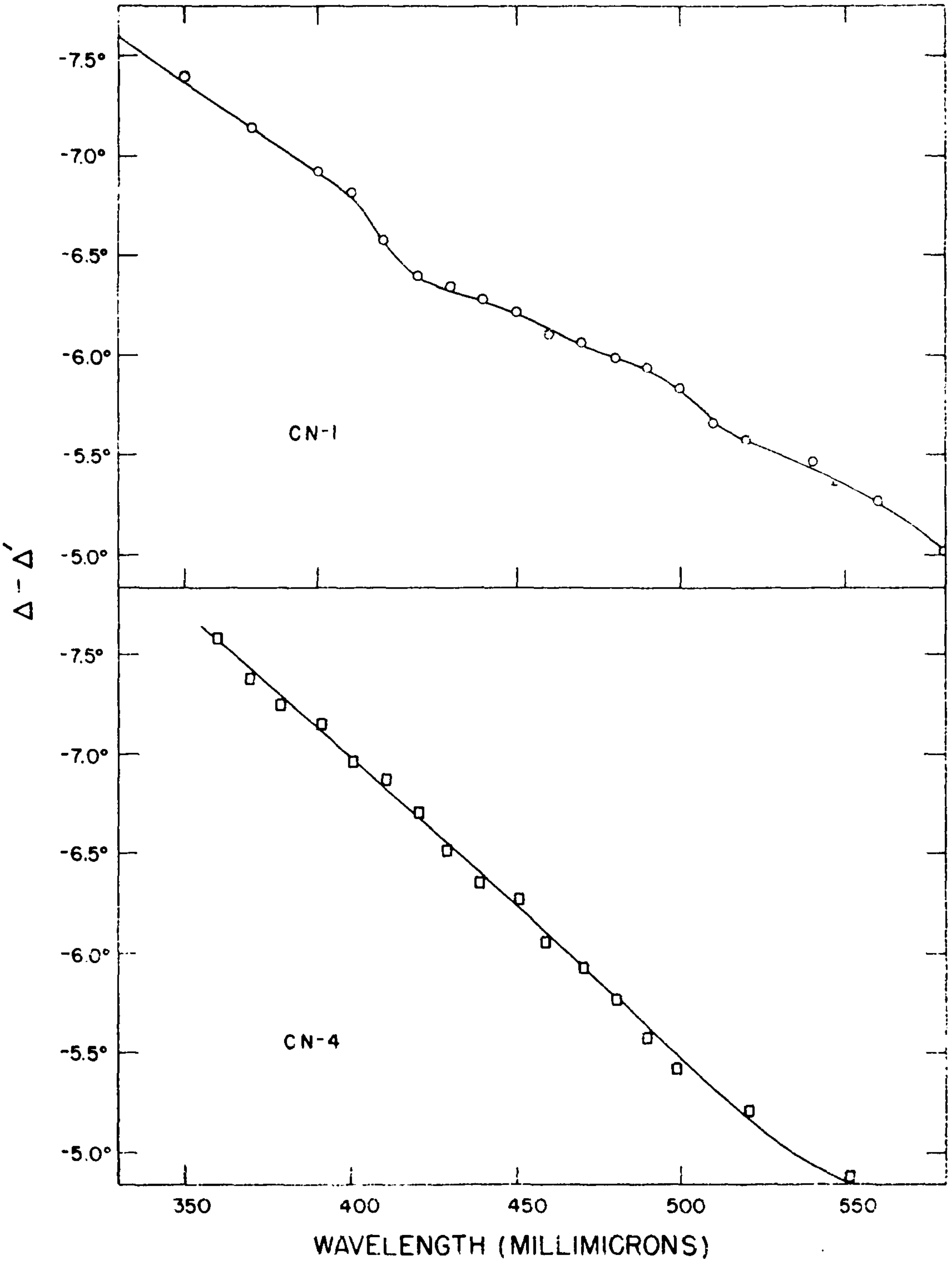
-7.5°
-7.0°
-6.5°
-6.0°
-5.5°
-5.0°
CN-1
CN-4
Δ - Δ'
350
400
450
500
550
WAVELENGTH (MILLIMICRONS)

Figure 17. Phase dispersion for films of stearonitrile adsorbed on chromium. The points denote the phase change of the films relative to the clean surfaces.

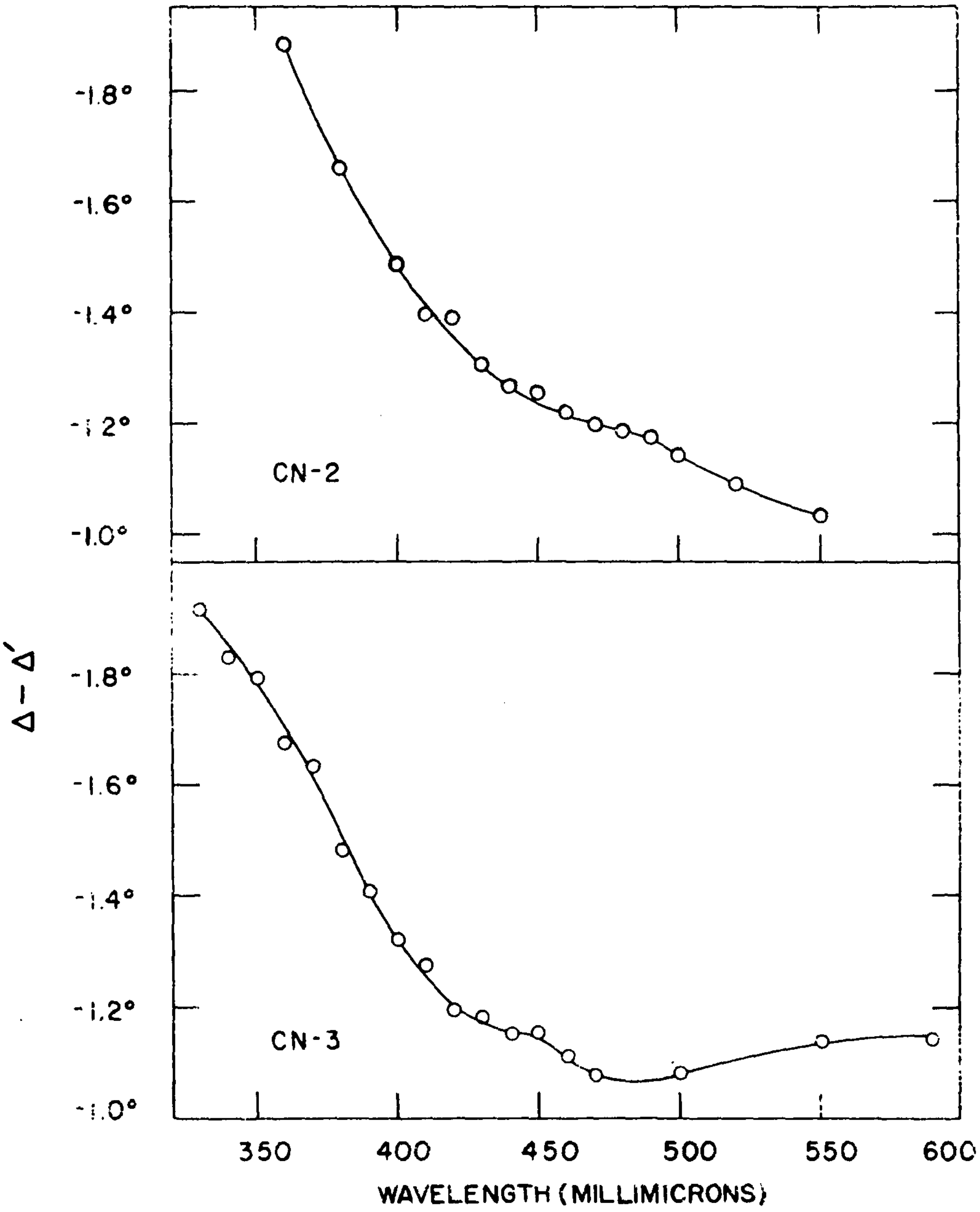
-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
CN-2
-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
CN-3
Δ − Δ′
350
400
450
500
550
600
WAVELENGTH (MILLIMICRONS)

Figure 18. Phase dispersion for films of stearonitrile adsorbed on chromium. The points denote the phase change of the films relative to the clean surfaces.

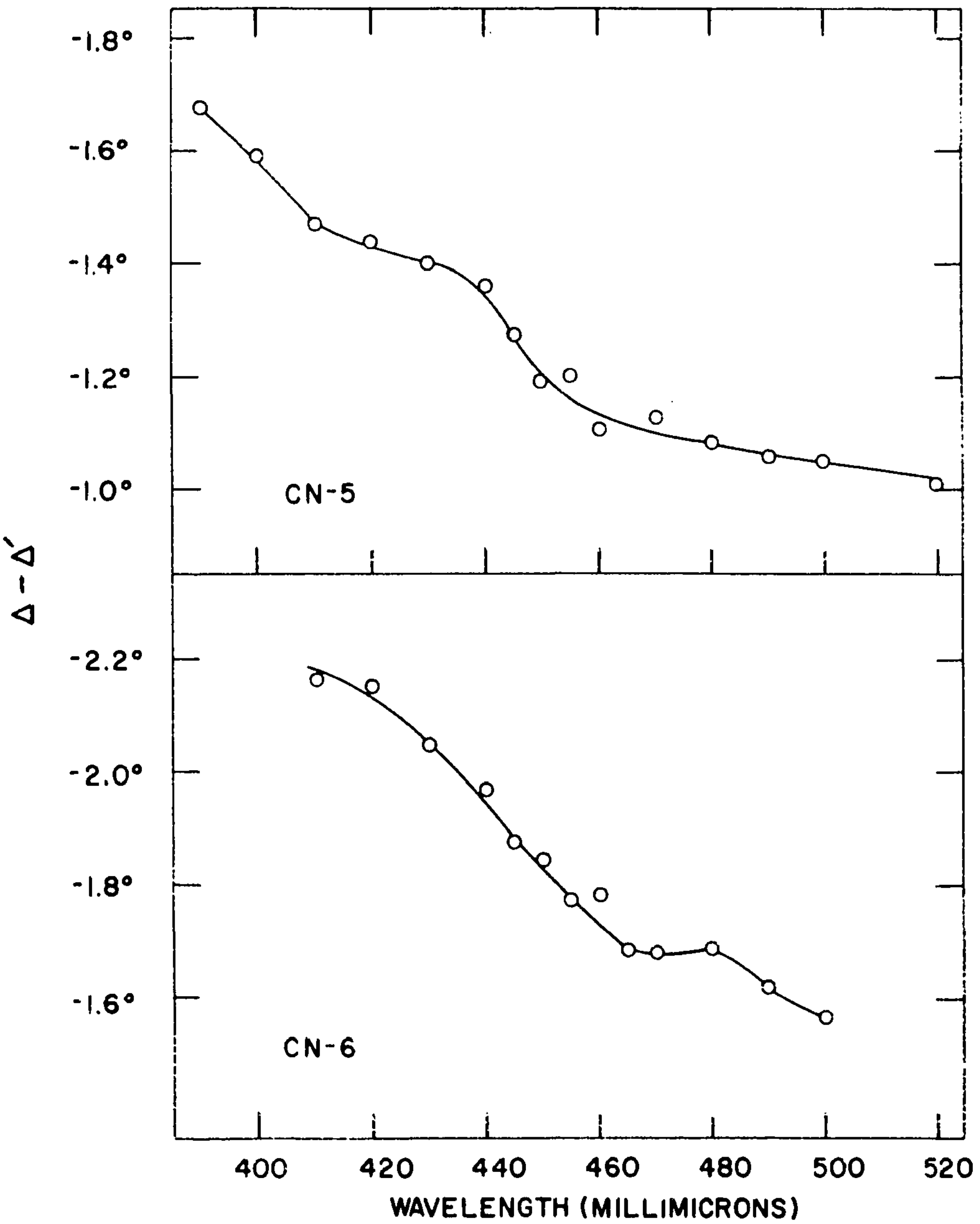
-1.8°
-1.6°
-1.4°
-1.2°
-1.0°
CN-5
Δ - Δ′
-2.2°
-2.0°
-1.8°
-1.6°
CN-6
400
420
440
460
480
500
520
WAVELENGTH (MILLIMICRONS)

Table 13. Preparation of surfaces[a] and films in runs made to study the phase dispersion of stearonitrile adsorbed on chromium.

Run	Surface and adsorbed film (in order of investigation)	Film formation[b]	Ads. time (hr.)	L[c]
CN-1	Clean chromium	Polished and flamed three seconds		
	Stearonitrile film	Ads. from sample I. Surface wet by melt. After standing in air for one hour under a heat lamp, melt began to peal back from the surface. Rubbed until a homogeneous breath figure was obtained.	10	22.0 Å.
CN-2	Clean chromium	Polished and flamed three seconds.		
	Stearonitrile film	Ads. from sample II. Streaks of melt clung to otherwise nonwet surface. Rubbed until a homogeneous breath figure was obtained.	5	4.7 Å.
CN-3	Clean chromium	Polished and flamed three seconds.		
	Stearonitrile film	Ads. from sample III. Film nonwet by melt except for isolated droplets. Rubbed until a homogeneous breath figure was obtained.	$1\frac{1}{2}$	4.3 Å.
CN-4	Clean chromium	Polished and flamed three seconds.		
	Stearonitrile film	Ads. from sample III. Slide placed in warm melt. Melt cooled to crystallization temp. Melt reheated before withdrawal of the slide. Film nonwet by melt.	$1\frac{1}{2}$	21.4 Å.

---

[a] All surfaces were polished with alumina in water until wet by water and flamed for three seconds prior to film formation.

[b] Films of stearonitrile were adsorbed from the melt of the bulk compound.

[c] Film thickness calculated for the stearonitrile film of CN-1. Other thicknesses found from the ratio of $\Delta - \Delta'$ to that of the calculated film.

Table 13 (Continued).

Run	Surface and adsorbed film (in order of investigation)	Film formation[b]	Ads. time (hr.)	L[c]
CN-5	Clean chromium	Polished and flamed three seconds.		
	Stearonitrile film	Ads. from sample III. Film partially wet by melt. Rubbed to obtain a homogeneous breath figure.	1½	4.4 Å.
CN-6	Clean chromium	Polished and flamed three seconds.		
	Stearonitrile film	Ads. from sample III. Film nonwet by melt except for isolated droplets. Rubbed until a homogeneous breath figure was obtained.	1½	6.5 Å.

for the reference surface in all of the nitrile runs.

Stearonitrile films were formed by adsorption from the melt of the bulk material. In most cases the film adsorbed from the melt was largely nonwet by the melt on withdrawal of the slide although the thickness was often much less than that for a monolayer of barium stearate. Several attempts were made to adsorb the nitrile from cetane solutions but the surfaces of the slides were wet by the solution on withdrawal indicating poor film formation. This was true even when the concentration of the nitrile in the cetane was as high as six percent by weight.

The phase dispersion curves for stearonitrile films exhibited anomalous behavior in several runs, but the breaks were less consistent than those found for films of n-octadecylamine. Runs CN-1 and CN-6 showed anomalous dispersion at about 475 millimicrons. The phase dispersion curves for runs CN-2, CN-3, and CN-5 exhibited anomalous behavior but the nature of the breaks made it difficult to assign an exact position to the anomalies. In run CN-5 the anomalous break is opposite to that obtained for absorption bands of strongly absorbing films. The phase dispersion rises above the background at the short wavelength side of the anomaly and falls below on the long wavelength side. Run CN-4 showed no anomalous behavior in the phase dispersion.

The thickness of the nitrile film of run CN-1 was calculated from equations 10 and was found to be 22.0 Å.

The thicknesses of the other films were found from the ratio of the phase differences, $\Delta - \Delta'$, to that for the film of CN-1. Only the films of runs CN-1 and CN-4 approached a thickness expected for a close packed monolayer of the nitrile. The adsorption technique was altered from the normal technique in both of these cases (see Table 13).

3. n-Octadecylthiocyanate

Figure 19 shows the phase dispersion for films of n-octadecylthiocyanate and barium stearate monolayers adsorbed on chromium. Table 14 lists information about the surfaces and the film formation. The thickness of the barium stearate film of run SCN-2 was calculated from equations 10 and was found to be 17.6 Å. The thicknesses of the other films were found from the ratio of the phase differences, $\Delta - \Delta'$, to the phase difference of the film of SCN-2.

The break in the dispersion curve at 365 millimicrons for run SCN-2 was not verified. The most significant feature of these curves is the lack of anomalous behavior in the regions where anomalies were found for films of n-octadecylamine and stearonitrile.

Figure 19. Phase dispersion for films of octadecylthiocyanate and of barium stearate adsorbed on chromium. The points denote the phase change of the films relative to the clean chromium surfaces.

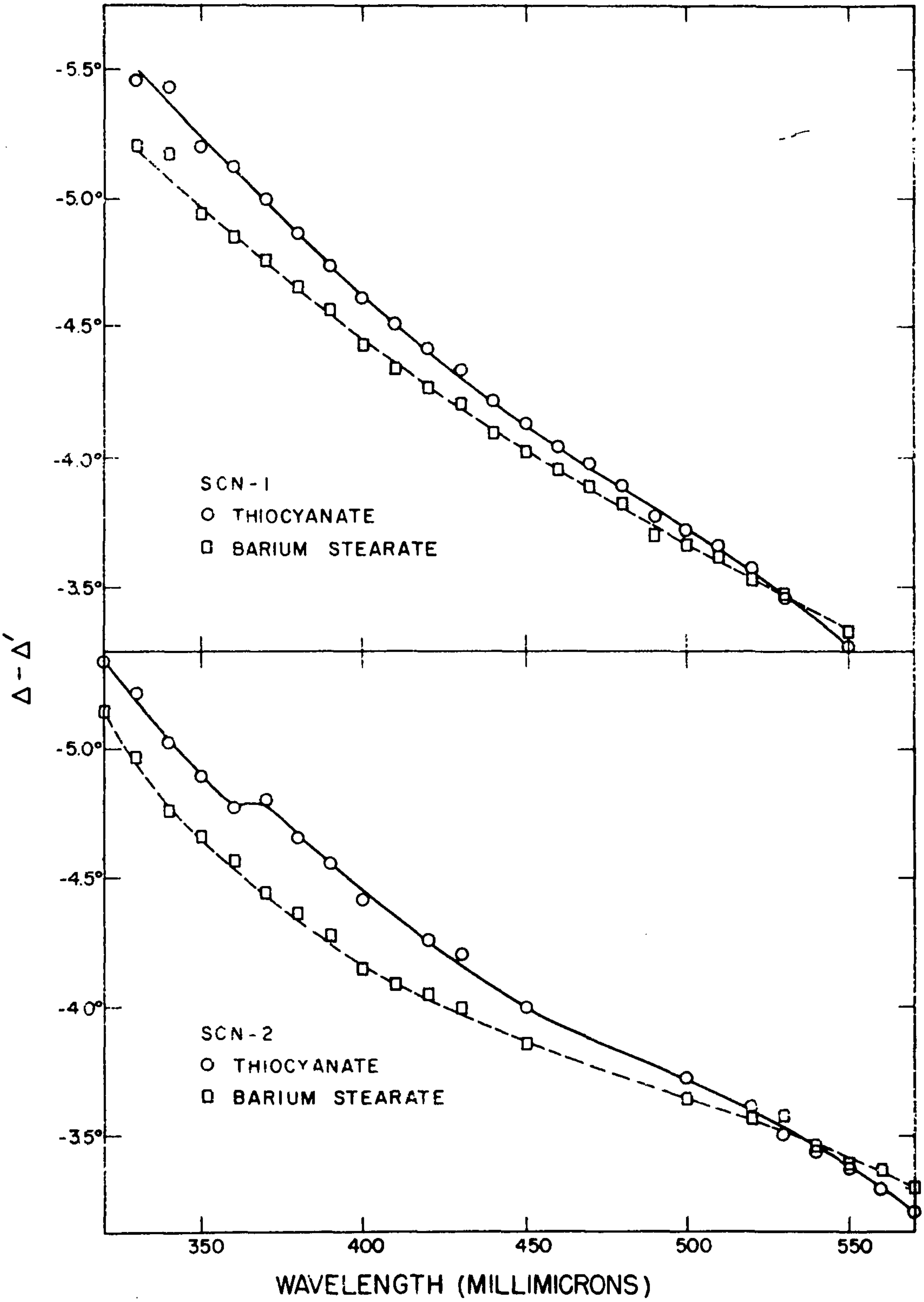
-5.5°
-5.0°
-4.5°
-4.0°
-3.5°
SCN-1
○ THIOCYANATE
□ BARIUM STEARATE
Δ - Δ′
-5.0°
-4.5°
-4.0°
-3.5°
SCN-2
○ THIOCYANATE
□ BARIUM STEARATE
350
400
450
500
550
WAVELENGTH (MILLIMICRONS)

Table 14. Preparation of surfaces[a] and films in runs made to study the phase dispersion of films of n-octadecylthiocyanate adsorbed on chromium.

Run	Surface and adsorbed film (in order of investigation)	Film formation	Ads. time (hr.)	L[b]
SCN-1	Clean chromium	Polished and flamed three seconds.		
	Octadecyl-thiocyanate film	Adsorbed from melt of bulk compound. Film nonwet by melt on withdrawal except for isolated droplets. Rubbed lightly to remove droplets.	12	18.5 Å.
	Barium stearate film	Transferred from water surface by touching wet slide to the surface. Homogeneous breath figure was observed.		18.0 Å.
SCN-2	Clean chromium	Polished and flamed three seconds		
	Octadecyl-thiocyanate film	Similar to film of SCN-1.	12	18.0 Å.
	Barium stearate film	Transferred from water surface by touching wet slide to the surface. Breath figure revealed streaks in film.		17.6 Å.

[a] All surfaces were polished with alumina in water until wet by water and flamed for three seconds prior to film formation.

[b] Film thickness calculated for barium stearate film of SCN-2. Other thicknesses found from ratio of $\Delta - \Delta'$ to that of the calculated film.

VI. DISCUSSION

A. Strongly Absorbing Films

Films containing compounds having strong absorption bands within the spectral range of the spectrometer were studied in order to establish the validity of the reflection technique for determining the electronic absorption spectra of thin films adsorbed on opaque substrates and to determine the sensitivity of this technique. Tetraphenylporphine and Rhodamine B were particularly well suited to this investigation. The former has sharp absorption bands of varied strength which are well separated from one another and the latter has a shoulder on the principal absorption band. These characteristics presented the opportunity for determining the degree of detail in the spectrum which could be defined by this technique.

These compounds have large, flat molecules which would tend to be preferentially oriented on the surface. Most of the films studied in this investigation were formed by dispersing the material in collodion solids which are composed mainly of nitrocellulose. This was done to keep the molecules randomly oriented with respect to the surface and to prevent aggregation of the molecules.

The absorption spectrum for the film containing tetraphenylporphine was in good agreement with the solution spectrum for this compound. Absorption peaks were apparent in the film spectrum at nearly the same positions as the peaks in the solution spectrum. The ratio of the molar extinction coefficients for the absorption peaks in solution at 418, 514 and 547 millimicrons was 20 : 1 : 0.71. In the spectrum for the film, this ratio was 9 : 1 : 0.2. The molar extinction coefficient for the peak at 514 millimicrons was the same in both spectra. Since the concentration of the tetraphenylporphine in the film was considerably greater than that in the solution, and since the solvents were different, it is not to be expected that the spectra should be identical.

The refractive index for the film underwent anomalous behavior near each of the absorption positions. The anomalous break associated with the strongest absorption band had its midpoint at the position of maximum absorption as predicted by the Helmholtz relation. The anomalous breaks for the weaker absorption bands were displaced to the long wavelength side of the positions of maximum absorption. This shift amounted to four millimicrons in the case of the absorption peak at 513 millimicrons and six millimicrons for the peak at 546 millimicrons. Considering the early stage of development of the present technique, it is possible that this small shift was due to experimental error or to inadequacies in the interpretation of the data.

A weak absorption band was observed in the film spectrum at about 566 millimicrons. The experimental readings were not carried out far enough to identify an anomalous break in the refractive index associated with this band and confirmation of this absorption will require further investigation.

The absorption spectra obtained for adsorbed films containing Rhodamine B were found to be dependent on the concentration of the dye in the film. The absorption peak in the least concentrated film containing 17% by weight of the dye in collodion solids appeared at the same wavelength as the peak in the dilute aqueous solution of the dye. The molar extinction coefficients for the dye in these two media were of similar magnitude and the size of the shoulder on the absorption band relative to the principal absorption peak was nearly the same in both cases although the shoulder in the film was somewhat broader. The absorption peaks in the more concentrated dye films were shifted to longer wavelengths and the shoulders on the absorption band were altered.

In all of the Rhodamine B films, the center of the anomalous break in the refractive index fell very close to the position of maximum absorption.

The molar extinction coefficient for the dye in the films decreased as the concentration of the dye in the film increased. This discrepancy cannot be assumed to be entirely due to experimental error for Beer's Law cannot be expected to hold for such high concentrations as those found in these solid films. It is probably significant that the molar extinction coefficient for the film of pure Rhodamine B

(2.9×10^4) was similar to the value of 2.13×10^4 reported by Weigl (3) for a thick film of Rhodamine B adsorbed on glass.

As in the case of the porphine, there is some doubt as to the validity of the shifts in the absorption peaks relative to the peak in the solution spectrum. This is particularly true for the Rhodamine B films because the interval between the experimental points was greater and the assignment of the positions of the absorption peaks is subject to the prejudice of the author. It should be mentioned, however, that Weigl (3) observed a shift to a longer wavelength in the absorption peak for a thick film of pure Rhodamine B.

The film in this study which contained the greatest amount of absorbing material was 38 Ångstroms thick and contained 50% of dye in collodion corresponding in amount of absorbing material to a film of pure dye 19 Ångstroms thick. The thickness ranged down to 6.6 Ångstroms for the film of pure Rhodamine B. These films correspond to little more than monomolecular layers of the absorbing material.

It was shown that an experimental error of 0.1 degree in the determination of $\Delta - \Delta'$ had little effect on the calculated optical constants for film containing Rhodamine B (Table 8). This estimation of the error was made for a film 38 Ångstroms thick and it is probable that an error of similar magnitude in the determination of $\Delta - \Delta'$ for a thinner film would make a greater difference in the optical constants. However, since the normal experimental deviation was much smaller than the error taken for the test case cited above, it is safe to assume that the calculated optical constants are valid if the optical properties of the surface are correctly defined by equation 5.

The results of this investigation have conclusively established the feasibility of obtaining spectral information about very thin films adsorbed on opaque substrates. The minor discrepancies between the spectra of the adsorbed films and the dilute solutions are to be expected considering the great differences in the media and in the concentration of the material. It is encouraging to find that the method is sensitive enough to describe such detail in the spectra as the shoulder on the Rhodamine B absorption band.

It was found, as expected, that the refractive index of a film undergoes anomalous dispersion at the position of absorption and in the case of weak absorption bands, the anomalous nature of the refractive index is as sensitive an indication of absorption as is the absorption coefficient.

The phase dispersion for these films exhibited anomalous behavior at the position of maximum absorption in much the same way as the index of refraction. This is fortunate for it allows one to ascertain the existence and the position of absorption bands in adsorbed films directly from the experimental data without carrying out the tedious computations necessary to determine the optical constants of the film.

B. Polar Hydrocarbon Derivatives

The adsorption of Lewis bases on metallic surfaces falls into two types: reversible adsorption in which the adsorbate is easily removed by washing with solvent, and firm adsorption in which the adsorbate can be removed only by repeated washings with hot solvent or by abrasive polishing (30,31). It is probable that the firmly adsorbed portion of the adsorbate interacts electronically with the substrate to form a chemical complex with the substrate. Such a complex might exhibit an absorption spectrum quite different from that of the adsorbate or adsorbent separately. An absorption of sufficient strength could be detected by measurement of the phase dispersion of the film.

Several phase dispersion measurements were made of films of n-octadecylamine adsorbed on chromium surfaces to investigate the possibility of obtaining direct evidence of complex formation between a Lewis base and a metal substrate. This compound was used because amines in general are good adsorbates and because the adsorption characteristics of n-octadecylamine on chromium were well known from previous adsorption studies (31,32). Most of the runs made with the amine revealed anomalous breaks in the phase dispersion curves which intersected the smooth background curve in the region between 380 and 400 millimicrons. The magnitude of these breaks was generally appreciably larger than the random experimental scatter, indicating that they represented a real absorption. The deviation from the background curve was always negative on the short wavelength side of the intersection and positive on the other side. While the exact shape of the anomaly was not reproducible, it is unlikely that such consistent behavior was spurious in origin.

Factors other than surface-adsorbate interaction which could have accounted for the observed anomalous breaks were investigated. The magnitudes of the anomalous breaks listed in Table 12 were relatively constant and independent of the film thickness indicating that the absorption was not the result of the more loosely adsorbed molecules. This showed that the absorption was not due to normal transitions of the amine alone, as did also the fact that the absorption spectrum for the amine in a cetane solution exhibited no absorption in the region of the observed anomalous dispersion.

The optical properties of the chromium substrates were not smooth functions of the wavelength in the region where anomalous phase dispersion was observed (Figure 15). The possibility that this irregularity in the optical properties of the substrate may have been responsible for anomalous behavior in the phase dispersion was investigated in run A-10. The refractive index of the amine film was calculated for the data points and also for phase change values taken from a smooth background curve drawn to best fit the data points. The calculated refractive index for the background curve showed little dependence on the optical constants of the substrate and a smooth curve was obtained which showed normal dispersion. The refractive index calculated from the data points showed anomalous behavior similar to the anomaly in the phase dispersion curve. Thus the irregularity in the optical constants of the substrate had a negligible effect on the dispersion curve for the adsorbed film. This conclusion was supported by the smooth phase dispersion curves obtained for nonabsorbing films such as barium stearate.

The effect of an oxide film on the surface was also investigated in run A-10. Readings were first taken of the clean slide which had been flamed for only one-half a second. The slide was then repolished and flamed four seconds and the readings were repeated. The extended flaming resulted in the formation of a film on the surface which was probably an oxide of the chromium. The phase change between these two sets of readings showed a slight anomaly in the same region where the amine films absorbed but the direction of the deviation from the background curve was opposite to that observed for the amine films. An amine film was then adsorbed onto the surface without further polishing or flaming of the surface. The phase dispersion of the amine film relative to the oxide film showed anomalous dispersion similar to that observed for other amine films.

The optical constants for the surface flamed one-half second and flamed four seconds were plotted as a function of the wavelength. The constants were altered slightly in magnitude but the general behavior of the optical constants was not changed significantly. These results indicated that the anomalous dispersion observed for the amine films was not due to an underlying oxide film. The adsorption of material from the air onto the surface was found to be a smooth function of time. Since the experimental readings were taken at constant time intervals, it is possible that this adsorption caused a smooth variation in the slope of the phase dispersion curve. Anomalous breaks such as those observed could not have been due to adsorption from the air.

We conclude that the anomalous dispersion was almost certainly due to interactions between the adsorbed film and the metal or, more probably, metal oxide of the substrate. The failure to obtain faithful reproducibility of the anomalous breaks was not regarded as serious in view of the many variables involved in this new method.

The optical properties of the chromium surface varied from slide to slide. This variation represented a difference in the substrates which may have affected their relative ability to act as Lewis acids. The polishing of the slides was done by hand and probably was not accomplished with the same degree of vigor for each specimen. The polishing bath was cleaned after every two or three runs, but contamination of the bath and of the polishing cloth was not entirely excluded. Although care was taken to reproduce the position of the slide on the spectrometer stage, it is doubtful that exactly the same portion of a slide was studied for both the reference surface readings and the readings of the slide with a film. The film formation varied from slide to slide. This is evident from the difference in film thicknesses listed in Table 11. Some of the variation can be attributed to differences in adsorption time, but inconsistencies appear which cannot be rationalized by this fact.

The absorption transition in the amine films was too weak to allow accurate determination of the absorption coefficient by the solution of equations 10 as was done for the dye films. In many cases, the absorption coefficient for a solid is approximately equivalent to the height of the anomalous break in the refractive index associated with the absorption. The amplitude from trough to crest of the anomaly with respect to the smooth background curve in the calculated refractive index for the amine film of run A-10 was about 0.03. It is reasonable to assume that the absorption coefficient was of the same magnitude. The height of the anomalous break for the weakest absorption peak in the tetraphenylporphine film was four-fold greater than the absorption coefficient however. Taking this into consideration, it was assumed for the purpose of estimating the molar extinction coefficient that the absorption coefficient was 0.01.

The molar concentration of the bulk amine is about three moles per liter. The concentration of the adsorbed film is probably very close to this. The molar extinction coefficient calculated on the basis of this concentration was approximately 5×10^2. The position of the absorption peak was taken to be at 392 millimicrons where the anomalous break in the refractive index intersected the background curve.

Films of stearonitrile adsorbed on chromium were studied because the nitrile group readily complexes with many metal ions in solution and is known to adsorb readily on a variety of metal surfaces. The films adsorbed from the melt of the bulk nitrile varied widely in thickness. Two runs were made in which the film thickness approached that expected for a close packed monolayer. One of these showed evidence of anomalous dispersion at 475 millimicrons but the other showed no anomalous behavior. The other nitrile films were very thin, being of the order of one-fourth to one-fifth of a monolayer. These films showed some evidence of anomalous behavior but the positions of the anomalous breaks were widely scattered. It is possible that there was absorption by the nitrile but the evidence was not as convincing as that for the amine transition.

Two runs were made with films of n-octadecylthiocyanate. The thickness of these films was very close to that obtained for monolayers of barium stearate. One of these films showed a possible anomalous break at 365 millimicrons but this was not verified by the other.

Two possible explanations for the surface-adsorbate interaction postulated for the films of n-octadecylamine adsorbed on chromium will be discussed. It is possible that a molecular complex was formed between the amine group and a chromium ion or chromium oxide molecule on the surface of the substrate. Many complexes with the chromium ion have been recorded in the literature. The hexamine and hexaquo chromium complexes have weak absorption bands at 350 and 407 millimicrons respectively (33,34) and the hydroxo pentamine chromium ion has been reported with an absorption band at 392 millimicrons (35). It is premature to assume a close relation between these complexes and that indicated by the absorption in the amine film for there are severe steric limitations in an adsorbed film and the media are quite different. The chromium complexes in solution are octahedrally coordinated and quite sensitive to changes in the anion. The molar extinction coefficients of the complexes with the ion are more than an order of magnitude smaller than that estimated for the transition in the film.

The formation of a different type of complex, a charge-transfer complex associated with the adsorbtion of certain molecules on metals, has been suggested by Mulliken (36). This concept was further developed by Matsen, et al. (30) and applied to the adsorption of Lewis bases by metals and metal oxides. Indirect support for such a complex was given by these and other investigators (37,38). The formation of a charge-transfer complex is strongly dependent on the ionization energy of the adsorbate and the work function of the substrate. If the absorption observed in the present investigation were due to such a complex, systematic shifts in the absorption band would be expected if the amine were adsorbed on metals with differing work functions. In this manner it might be possible to test the hypothesis that absorption was due to a charge-transfer complex.

VII. SUMMARY

A polarization spectrometer for measuring the phase differences between the principal components of polarized light reflected from a metal surface and the amplitude ratios of these components was designed and constructed. It was used to measure the change in the state of polarization associated with the formation of adsorbed films on chromium surfaces and the variation in polarization with wavelength.

Data obtained from measurements of adsorbed films of molecular thickness of Rhodamine B and α, β, γ, δ-tetraphenylporphine were used to calculate the absorption coefficients and refractive indices of the films. The absorption spectra for the films were found to be in good agreement with the solution spectra of these compounds and the molar extinction coefficients for the absorption bands in the films were not greatly different from those in solution. The refractive indices for the films exhibited anomalous dispersion at the positions of absorption as expected on the basis of the Sellmeier-Helmholtz model for dispersion. The results obtained from the measurements of strongly absorbing films confirmed the feasibility of obtaining electronic absorption spectra for very thin films adsorbed on reflecting surfaces. The method was shown to be sensitive enough to detect the presence of secondary absorption bands such as that responsible for the shoulder on the Rhodamine B absorption band.

The change in the phase differences for these films showed anomalous behavior at the positions of absorption similar to the anomalous behavior of the refractive index. Similar measurements made for films of n-octadecylamine adsorbed on chromium exhibited anomalous dispersion near 390 millimicrons. While experimental difficulties prevented faithful reproduction of the anomalies, the frequency of occurrence and the similarity among them suggested that they represented a real optical absorption by the film rather than spurious behavior. It was concluded that this absorption was due to the formation of a complex between the amine and the substrate. The molar extinction coefficient of this absorption complex was estimated to be about 5×10^2.

Experimental measurements of films of barium stearate, stearonitrile, and n-octadecylthiocyanate did not reveal anomalous behavior in the same region as that observed for the amine. The nitrile showed evidence of anomalous dispersion near 470 millimicrons but the evidence was less substantial than that for the amine.

A discussion of the nature of adsorption complexes for Lewis bases adsorbed on chromium was presented. Suggestions were made for further investigations to elucidate the type of adsorption complex from the electronic absorption spectra of films.

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IX. ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. L. S. Bartell for suggesting this problem and for the helpful suggestions and the encouragement he offered throughout the course of the investigation.

Appreciation is also extended to Mr. B. L. Carroll for his assistance in running some of the spectra.

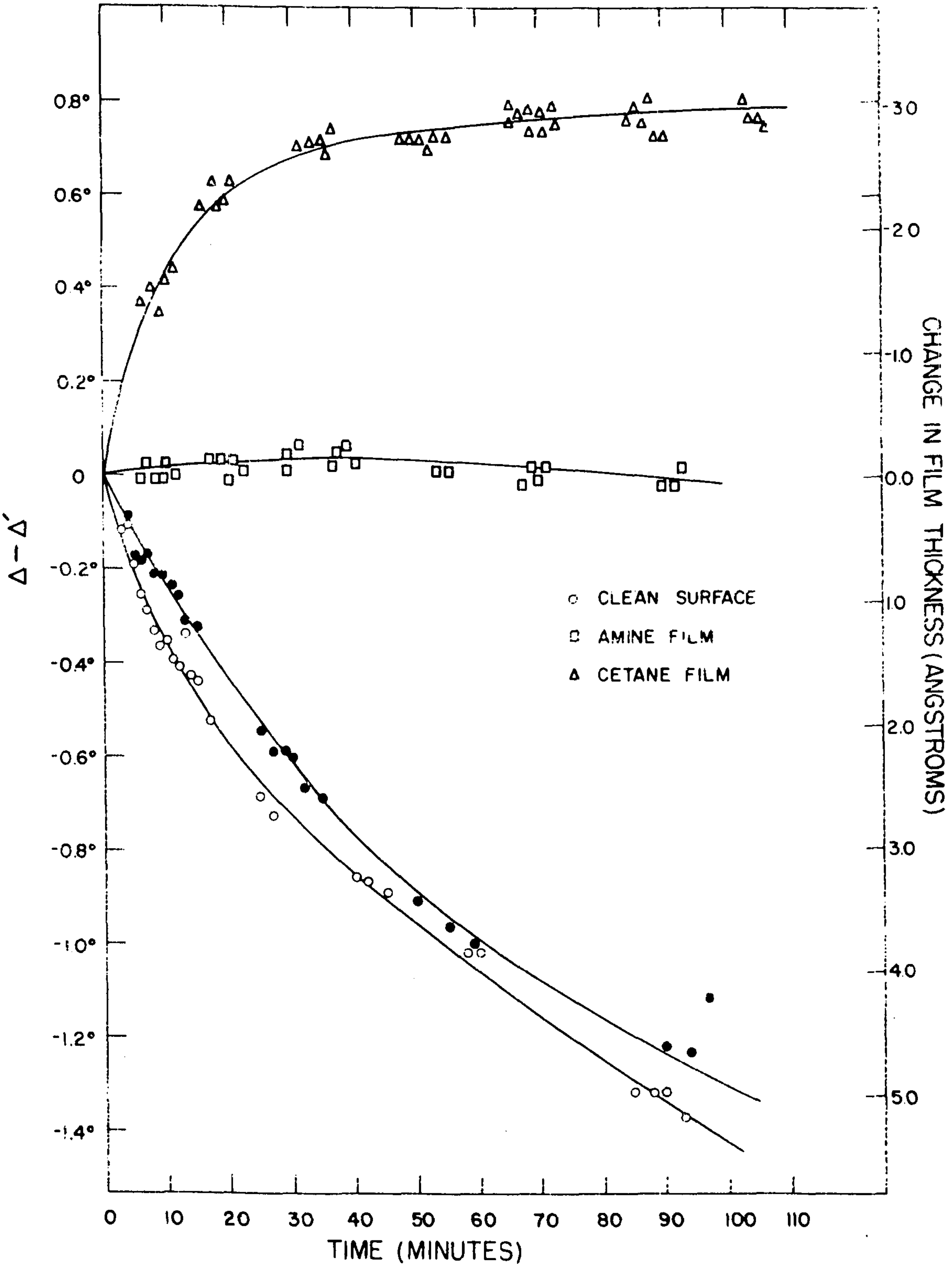
To his wife, Alberta, the author is indebted for her constant faith and encouragement.

X. APPENDIX: ADSORPTION OF MATERIAL ONTO A SURFACE FROM THE AIR

The optical constants of a freshly polished and flamed surface were found to change slightly on exposure of the surface to air. Figure 20 shows the change in the phase difference, Δ , as a function of the time of exposure of a clean platinum slide to laboratory air. Time was recorded from the moment the slide was removed from the flame. The change in the phase difference was rapid initially but decreased to an almost constant value after 30 minutes of exposure. This change is probably the result of adsorption of material from the air onto the surface. The thickness of the film represented by the change in the phase difference is indicated in Figure 20. It is possible that the initial rapid change in the optical constants was due to changes in the structure of the surface following heating.

Readings were also made for films of cetane and n-octadecylamine adsorbed on the surface. The cetane film was formed by placing the clean slide in pure cetane for four hours and wiping off the excess cetane with tissue after removal of the slide. Time was recorded from the moment the slide was wiped. The amine film was adsorbed by immersion of the clean slide for 20 hours in a solution of 0.1% of the amine in cetane. The surface was non-wet by the solution on withdrawal of the slide. Time was recorded from the moment

Figure 20. Change in the film thickness on exposure of a surface to laboratory air. The circles show the adsorption of material from the air onto a clean platinum surface. The triangles refer to a film of cetane on the surface and the squares refer to a monolayer of n-octadecylamine adsorbed from cetane. All readings were made at 350 millimicrons.


0.8°
0.6°
0.4°
0.2°
0
-0.2°
-0.4°
-0.6°
-0.8°
-1.0°
-1.2°
-1.4°
Δ − Δ′
-3.0
-2.0
-1.0
0.0
1.0
2.0
3.0
4.0
5.0
CHANGE IN FILM THICKNESS (ANGSTROMS)
○ CLEAN SURFACE
□ AMINE FILM
△ CETANE FILM
0
10
20
30
40
50
60
70
80
90
100
110
TIME (MINUTES)

of withdrawal. The cetane film was rapidly diminished by evaporation for about 45 minutes after which the film thickness remained nearly constant. It is possible that a dynamic equilibrium was established after the initial fast evaporation and further evaporation was offset by adsorption of material from the air. The amine film showed a slight initial loss of material, probably due to the evaporation of cetane occluded in the film, after which the film thickness increased slightly.