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Effect of Iodide on Absorption Spectra for Dyes Adsorbed to Silver Halide Substrates

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EFFECT OF IODIDE ON ABSORPTION SPECTRA FOR DYES
ADSORBED TO SILVER HALIDE SUBSTRATES

by

Mark E. Hinz

A thesis submitted in partial fulfillment
of the requirements for the degree of
Bachelor of Science in the School of
Photographic Arts and Sciences in the
College of Graphic Arts and Photography
of the Rochester Institute of Technology

April, 1980

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ABSTRACT

The effects due to iodide in a silver bromide octahedral crystal on the absorption spectra of adsorbed 3,3'-Diethyl-9-Methylthiacarbocyanine and 5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine were investigated. It was found that iodide encouraged J_a -band aggregation for 5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine but not for 3,3'-Diethyl-9-Methylthiacarbocyanine. The suggestion is made that iodide is acting as nucleation centers for 5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

List of Figures.....	iv
Introduction.....	1
Objectives.....	5
Hypothesis.....	6
Experimental.....	7
Data.....	15
Analysis of Data.....	26
Discussion.....	29
Conclusions.....	31
Recommendations for Further Work.....	32
List of References.....	33
a. General References.....	36
Appendix A Emulsion Formulas.....	37
Appendix B Calculation of Substrate Surface Area.....	40
Appendix C Calculation of Surface Area Covered by One Dye Molecule.....	42

LIST OF FIGURES

Figure 1	Structures of dyes used in experiment.....	9
Figure 2	Coating platen and knife.....	12
Figure 3	Schematic of film dryers.....	14
Figure 4	Absorption spectra of cyanine 1 in silver bromide emulsion.....	16
Figure 5	Absorption spectra of cyanine 1 in silver iodobromide emulsion.....	17
Figure 6	Surface area extrapolation curve for silver bromide emulsion.....	18
Figure 7	Surface area extrapolation curve for silver iodobromide emulsion.....	19
Figure 8	Absorption spectra of cyanine 2 in silver bromide emulsion.....	20
Figure 9	Absorption spectra of cyanine 2 in silver iodobromide emulsion.....	21
Figure 10	Absorption spectra of cyanine 3 in silver bromide emulsion.....	22
Figure 11	Absorption spectra of cyanine 3 in silver iodobromide emulsion.....	23
Figure 12	Grain size distribution for the silver bromide emulsion.....	24
Figure 13	Grain size distribution for the silver iodobromide emulsion.....	25

INTRODUCTION

The spectral sensitivity of pure silver halide extends only into the blue region of the spectrum. The use of dyes has allowed the silver halide photographic emulsions to show sensitivity from the ultraviolet to the infrared region of the electromagnetic spectrum.

The sensitizing is the result of a photo-chemical reaction between the sensitizing dye and the silver halide crystal. It has been shown that the absorption spectrum for the dye adsorbed to the substrate will have a maximum value corresponding to the maximum for the sensitivity spectrum. It is of interest to determine to what extents the composition and habit of the crystal habit affect the absorption spectra of dyes while adsorbed to the silver halide.

In general the following have been shown to be factors which affect the dye adsorption to silver halide crystals:

1. Gelatin
2. pAg
3. pH
4. Electrolytes

Gelatin depresses the rate of adsorption.¹ Gelatin does not however affect the saturation coverage maximum.² A high pAg favors adsorption of cyanines but discourages adsorption of merocyanines.³ It has been demonstrated that strongly bound

cyanines are not affected by simple organic electrolytes.⁴ Cyanines can be desorbed by emulsion anti-foggants and stabilizers made of sulfur and nitrogen acids. The above influences on dye adsorption show the need for emulsion formulas which contain the same levels of gelatin, pAg, pH and electrolytes.

This thesis is concerned with one variable affecting dye absorption spectra. The variable under consideration is the effect due to iodide in the silver bromide crystals of a photographic emulsion.

The absorption maxima of adsorbed dyes depends on the crystal habit and the composition of the silver halide substrate.⁵ The popular view today concerning dye adsorbed in aqueous silver halide dispersions is that for low surface dye concentrations the dye molecules are isolated and lie flat on the substrate. Increasing the surface coverage causes the interacting dye molecules to form a tight array with each molecule oriented on its long edge to the surface. The change in molecule orientation results in the appearance of B, H_a or J_a-bands.⁶

Work by Philippaerts et al⁷ concluded that changes of the absorption spectra of dyes when iodide is incorporated into the silver bromide crystal is due to a change in crystal habit to (111) octahedral surfaces and not directly because of the influence of the iodide in the adsorption of the dye. Scrutton⁸ has determined with results more conclusive than

Philippaerts et al that iodide in an octahedral silver bromide crystal will affect the absorption spectra by enhancing J_a -band aggregation. Both studies support the idea that J_a -band aggregation occurs more readily on octahedral silver bromide than on cubic silver bromide for a majority of dyes. Markocki and Kazmierczak⁹ found that a J_a -band was formed on cubic crystals of pure silver bromide for 3,3'-Dihydroxyethyl-5,5'-Dimethoxy-9-Ethylthiacarbocyanine but not on octahedral crystal habits which contrasts the work of Philippaerts et al and Scrutton.

Markocki and Kazmierczak contend that differences as to J_a -band aggregation on octahedral surfaces arise due to differences in dye structures, in particular differences in the epitaxial groups. According to Markocki and Kazmierczak cyanine dyes with methoxy or phenyl groups in the 5,5' positions or one methoxy group in the 5 position and a carboxymethyl group in the 3' position will prefer to form J_a -band aggregates on (100) cubic faces of silver bromide. Cyanine dyes with no substituents in the 5,5' positions or with chlorine or methyl groups in these positions will tend to form J_a -band aggregates on (111) octahedral faces.

The works of Scrutton, Philippaerts et al and Markocki & Kazmierczak as cited above indicate that iodide and dye structure strongly influence the J_a -band effect. The work of Walworth et al¹⁰ indicated that iodide produced a slight shift to longer wavelengths for the J_a -band of 3,3'-Sulfopropyl

Benzothiacarbocyanine on an octahedral surface of silver iodobromide as compared to silver bromide.

None of the above works specifically investigates the relationships that might exist between crystal habit of the silver halide substrate and incorporation of iodide into the crystal on the basis of equal percent surface coverages of the substrate by the dye and the effect that these relationships might have on the absorption spectra of the adsorbed dye. Also of interest is to determine if iodide will affect the absorption spectra of dyes differing in structure, specifically the 5,5' substituents, differently. Valid comparisons to determine if J_a -band aggregation is encouraged can be made by using the spectra of each emulsion and comparing the results at each percent surface coverage.

OBJECTIVES

To determine the effect of iodide incorporated into octahedral silver bromide crystals on the absorption spectra for the adsorbed dyes 3,3'-Diethyl-9-Methylthiacarbocyanine and 5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine.

To determine the effect of varying the percent surface coverage of the substrate by the above dyes on the absorption spectra for the adsorbed dyes.

HYPOTHESIS

The work of Kazmierczak and Markocki¹² would indicate that 3,3'-Diethyl-9-Methylthiacarbocyanine and 5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine will form J_a -band aggregates on octahedral silver bromide grains. The work of Scrutton¹³ indicates iodide will encourage J_a -band aggregation by acting as nucleation centers, thus leading to the formation of longer aggregates and a shift to longer wavelengths by 5 to 10 nm for the J_a -band maximum. Since the epitaxial substituents play a major role in the formation of J_a -band aggregates according to Kazmierczak and Markocki, and iodide will promote J_a -banding on octahedral surfaces of silver bromide then the two together should produce stronger J_a -banding aggregation than either does alone. Along with the formation of longer J_a -band aggregates a shift of the bands maximum to longer wavelengths should occur.

EXPERIMENTAL

The data of primary interest are the spectrograms for each dye-emulsion combination. These spectrograms will show any changes of the spectrum by comparison to each other. Certain assumptions are made when reading these spectrograms. The dye concentration of interest is the amount of dye on the surface of the silver halide substrate. The concentration was measured as a function of percent surface area coverage. This then meant that the surface area of the substrate needed to be determined. To verify that the spectrograms represented data depicting effects due to iodide, dye structure and dye concentration only and not effects due to crystal habit, pH, pAg, gelatin or grain size distribution it was necessary to have electron micrographs made, to measure pH and pAg, carefully control the gelatin levels and measure the grain size distribution.

The emulsion formulas were constructed to give 0.10 gram moles of silver in 400 ml of emulsion. The halide excess needed to produce the octahedral habits was kept at 0.01 N throughout the precipitation. The same amount of gelatin was used in each emulsion to control any effects due to the gelatin when the surface was not saturated by dye molecules. The addition of NaOH ensured that low pH which can inhibit

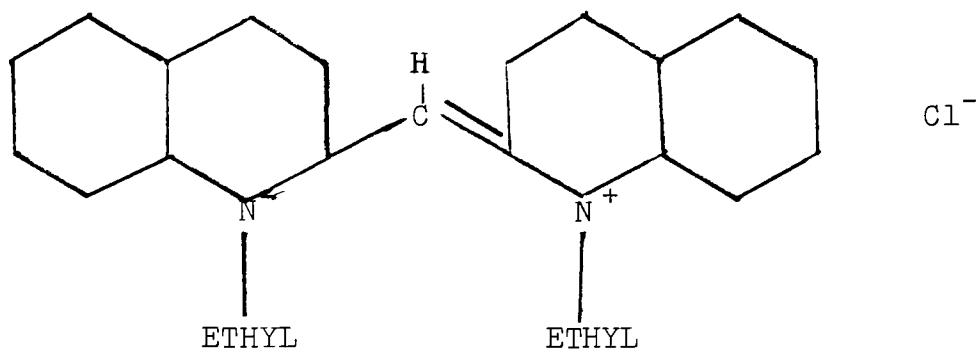
adsorption of cyanines would not occur. The amount of NaOH in each emulsion was the same. No other additives such as anti-foggants or stabilizers were used. The emulsions were kept in a refrigerator when not used, thus a stabilizer was not needed to prevent ripening. The formulas appear in Appendix A.

The dyes chosen for use in the experiment were 1,1'-Diethyl-2,2'-Cyanine (to be referred to as cyanine 1), 3,3'-Diethyl-9-Methylthiacarbocyanine (to be referred to a cyanine 2) and 5,5'-Dichloro-3,3',9-Triethyl thiacarbocyanine (to be referred to as cyanine 3). Cyanine 1 was chosen to be used according to the in situ method of Herz and Helling^{14,15} for determining surface area of the silver halide substrate. Cyanine 2 was chosen to represent a weakly aggregating dye.¹⁶ This dye also represents a dye without 5,5' substituents and thus is in the category given by Markocki and Kazmierczak¹⁷ as a dye which prefers to J_a -band aggregate on octahedral silver bromide habits. Cyanine 3 should also prefer to J_a -band aggregate in the octahedral silver bromide faces as it falls in the same class as cyanine 2 because of the 5,5' chloride atoms. The dye structures appear in Figure 1.

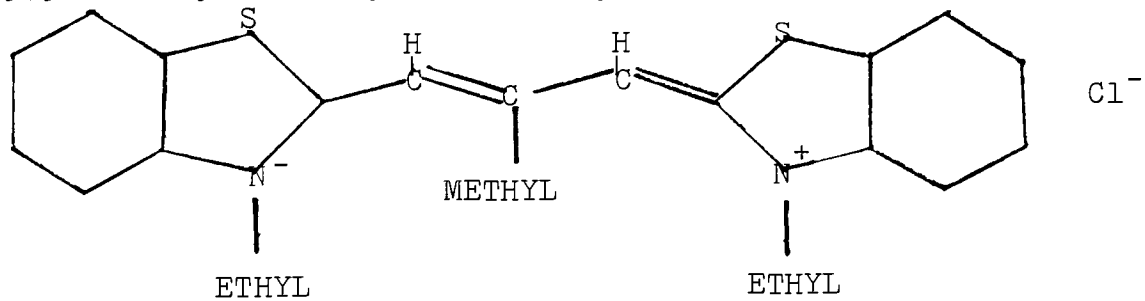
The emulsions were precipitated by means of a double jet technique. This allowed for a narrow grain size distribution along with insuring that the grains would have the same composition throughout the crystal. The run times and temperature were adjusted so as to attempt to produce crystals of

Figure 1

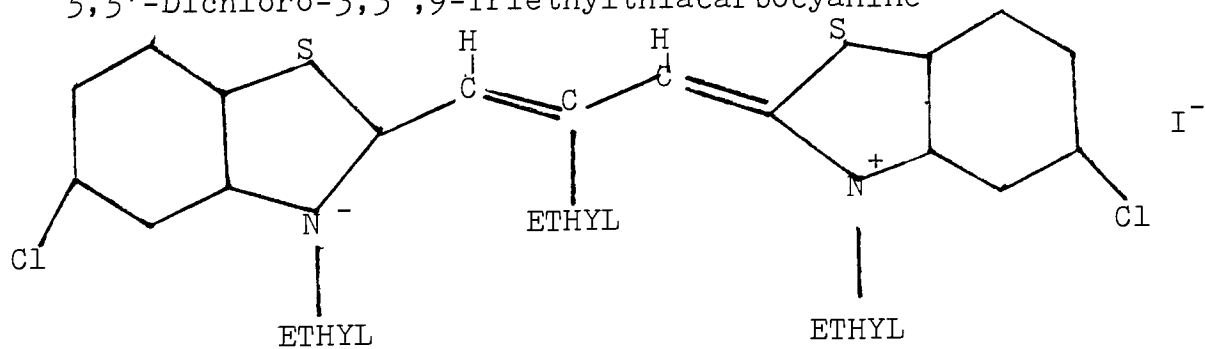
Structures of dyes used in experiment
1,1'-Diethyl-2,2'-Cyanine



3,3'-Diethyl-9-Methylthiacarbocyanine



5,5'-Dichloro-3,3',9-Triethylthiacarbocyanine



approximately the same size between the two emulsions. The use of iodide will cause smaller grains, thus a temperature of 65 degrees Celsius to give more grain growth for the iodobromide emulsion was used.¹⁸ The pure bromide emulsion was precipitated at 45 degrees Celsius. As the temperature variation was used to control grain size the precipitation times were to be kept constant (the actual times for the AgBr and AgI₂Br runs were 21 minutes and 25 minutes respectively). When the precipitation was finished 50 ml of 0.200 N H₂SO₄ was added to coagulate the phthalated gelatin. This was then left in the refrigerator overnight. Redispersion was done the next day. The liquid was drained from the coagulum. The coagulum was rinsed with distilled water. Solution D was then poured over the coagulum and the solution stirred until the coagulum had been dispersed. This produced the final volume of 400 ml for each emulsion.

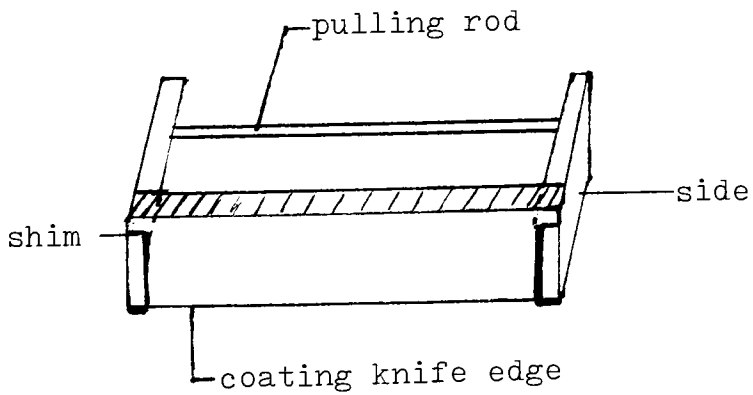
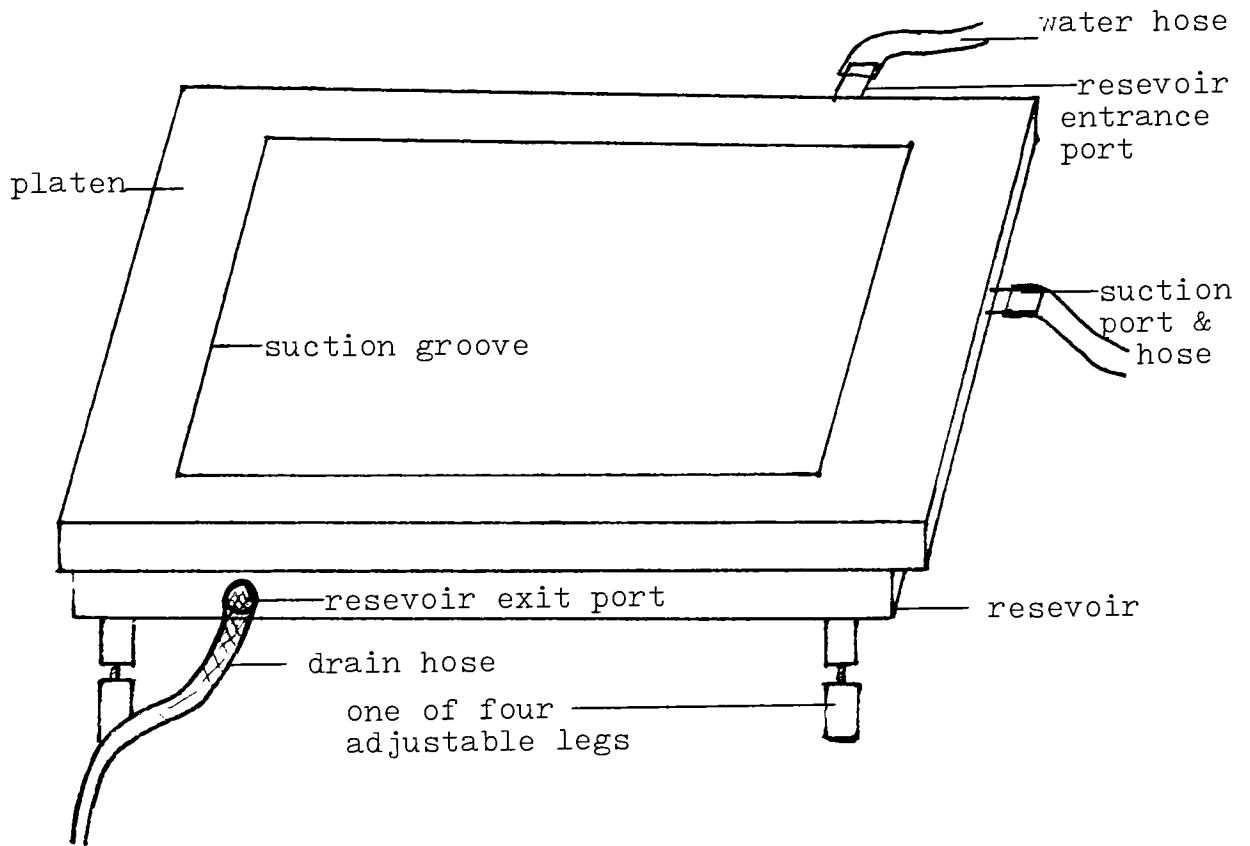
The surface area of the silver halide crystals was determined using the Herz method.¹⁹ This involved the use of the dye cyanine 1 at the concentrations of 0.01, 0.03, 0.10, 0.20, 0.50, 1.00, 1.80 and 2.00 grams of dye per mole of silver. The reflectance spectra were then used to differentiate between the growth of M-band absorption and J_a-band absorption. The linear portions for the plot of J_a-band peak $-\log_{10}$ reflectance versus the amount of dye used produced the extrapolated surface area of the substrate. The use of this method is based on the assumption that all of cyanine 1

adsorbs to the surface until saturation of the surface occurs, then the bands occurring as a result of adsorption reach a limiting maximum value while bands due to solution spectra will continue to increase. Plotting the J_a and M density ratios against the amount of dye used results in a similar extrapolation using the linear portions of the curve. Knowing the surface area available on each substrate then made possible the calculations to determine the specific dye concentrations for the percent surface coverages of 10, 25, 50 and 80%. An example of the calculations used is found in Appendix B.

The amount of surface coverage by a single dye molecule was taken to be a result of length and width of the dye molecule inclined at an angle to the substrate surface as proposed by Carroll and West¹⁹ with an adjustment for any 5,5' substituents. For the iodobromide crystals the same values are used as an approximation on the assumption that the iodide does not distort the crystal because of the small percentage present of the iodide. The covering area for cyanine 1 was then taken to be 57 \AA^2 , for cyanine 2 to be 76 \AA^2 and for cyanine 3 to be 81 \AA^2 .¹¹ The calculations appear in Appendix C.

Emulsion coating was done by hand using a platen and coating knife as depicted in Figure 2. The platen was kept level by the use of adjustable legs. Suction held the film base to the platen. A 7% saponin solution was added to the

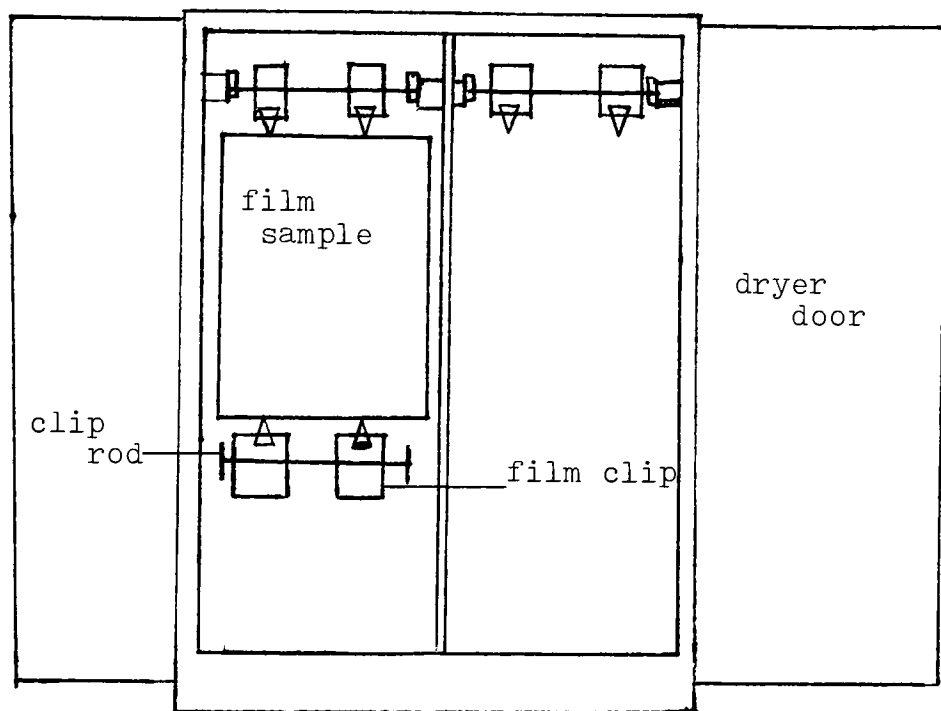
Figure 2
Platen and coating knife



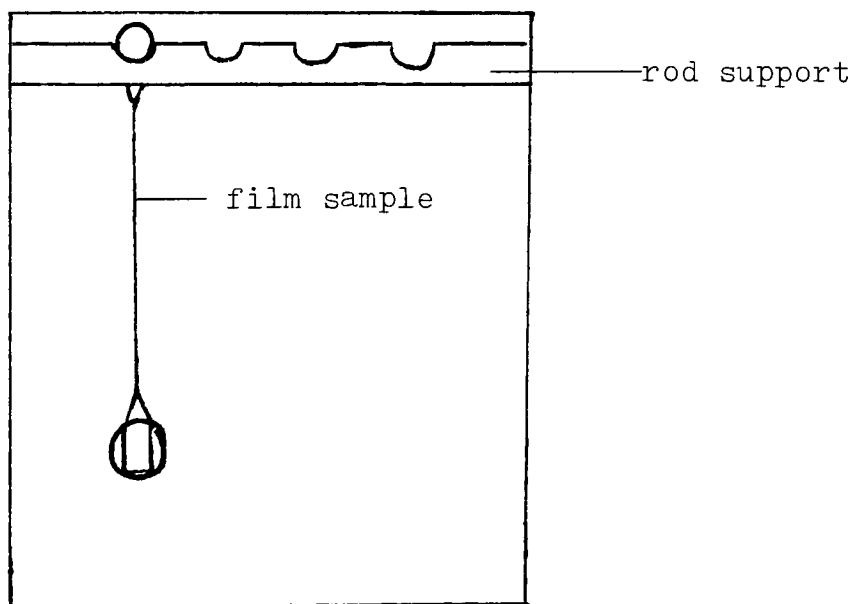
emulsion for coating to improve uniform emulsion flow. Hot water was run through the resevoir during coating and for 90 seconds afterward to allow the emulsion to flow and even out the thickness across the film base. Then cold water was run through the resevoir to chill the emulsion and set it. The emulsion when set was then dried in the film dryers which are shown schematically in Figure 3.

Electron micrograms of undyed emulsion samples gave visual observations of the silver halide crystal habits. The reflectance spectra were determined using total reflectance on a Beckman Dk-2 spectrophotometer. The grain size distributions were determined by a grain size counter.²¹ The size of the grains indicated that inter-particle light scatter could be neglected and that the use of reflectance as a parameter of the optical properties of the dye valid.²² Beckman pH meters were used to determine the pH and pAg of each emulsion.

Figure 3
Schematic of film dryers



front view



side view

DATA

Most of the data obtained in this experiment was taken in graphical form. This data is found in Figures 4 to 13 on the following pages. The pH and pAg measurements for each emulsion were: for the silver bromide emulsion, pH= 7.6, pAg= 9.8; for the silver iodobromide emulsion, pH= 7.7 pAg= 9.8.

Figure 4

Absorption spectra of cyanine 1
in silver bromide emulsion

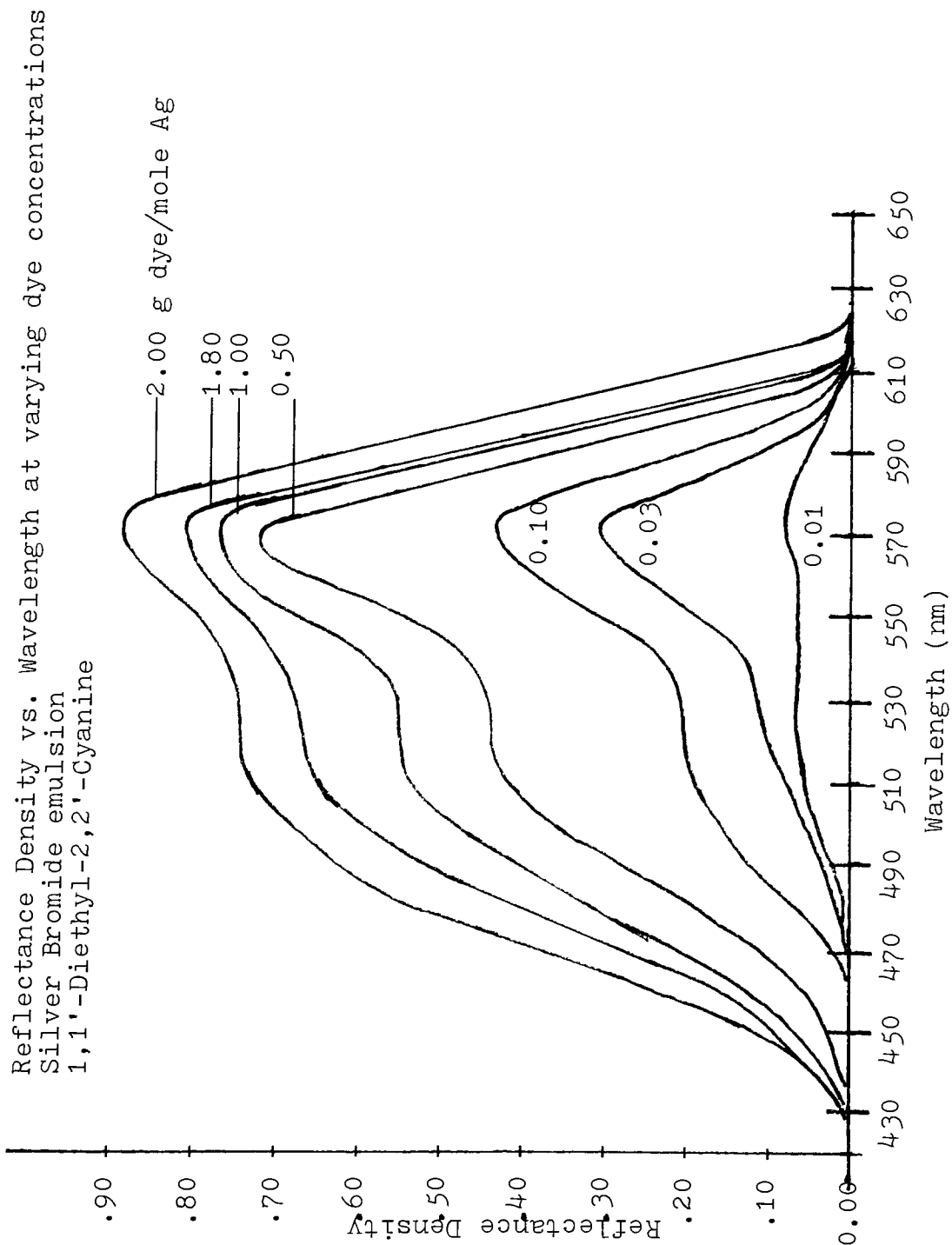


Figure 5

Absorption spectra of cyanine 1 in
silver iodobromide emulsion

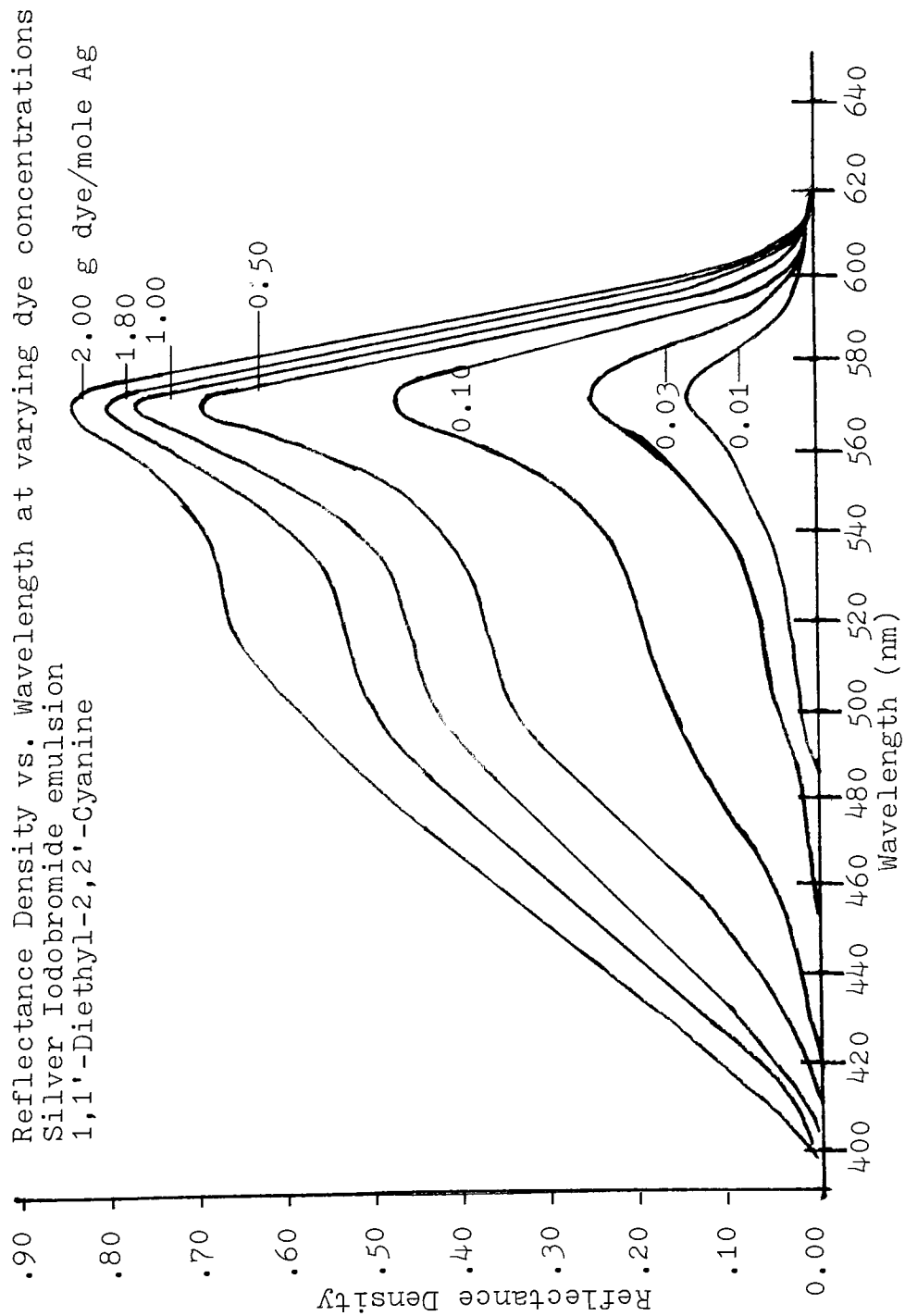


Figure 6
Surface area extrapolation curve
for silver bromide emulsion

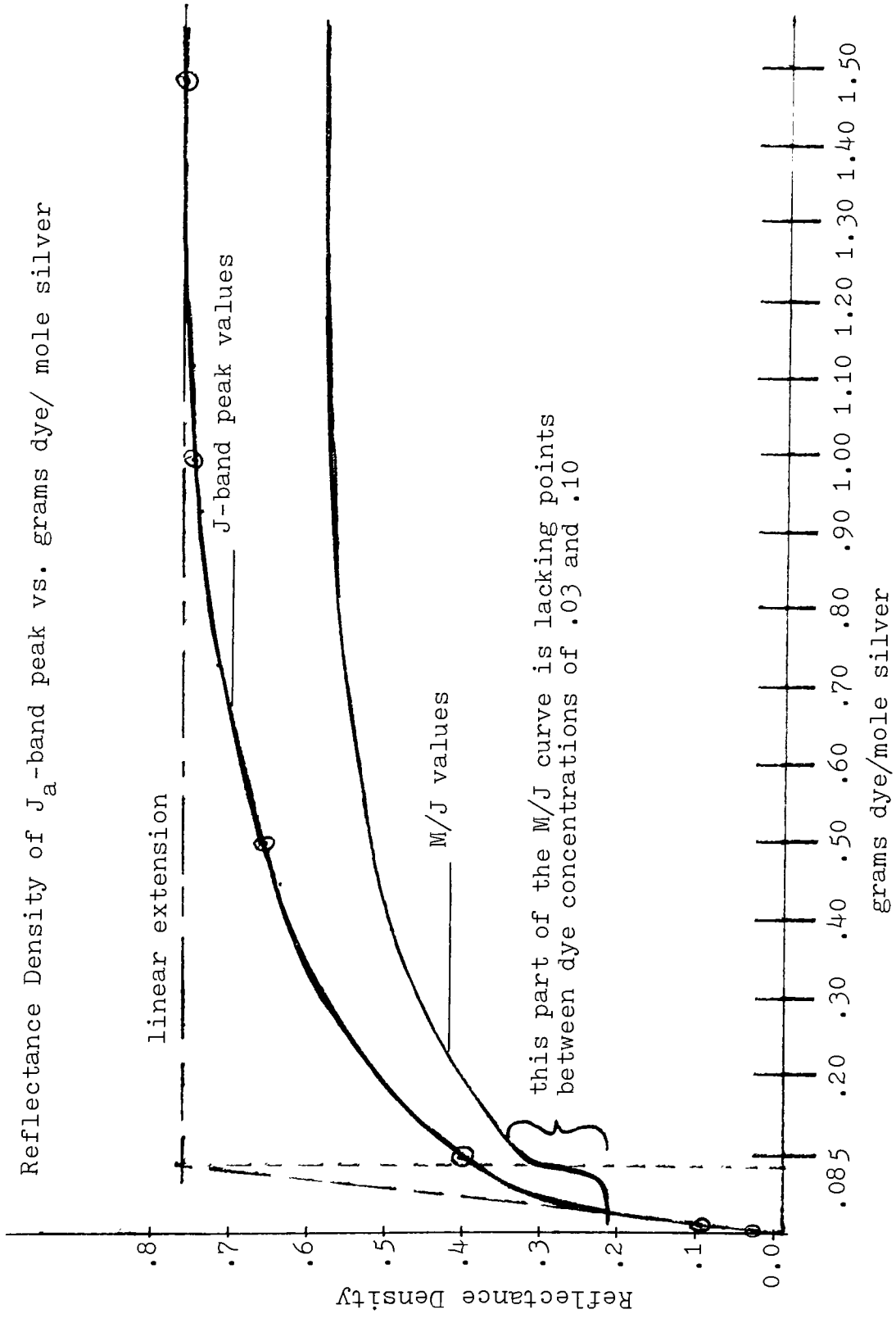


Figure 7
 Surface area extrapolation curve for
 silver iodobromide emulsion

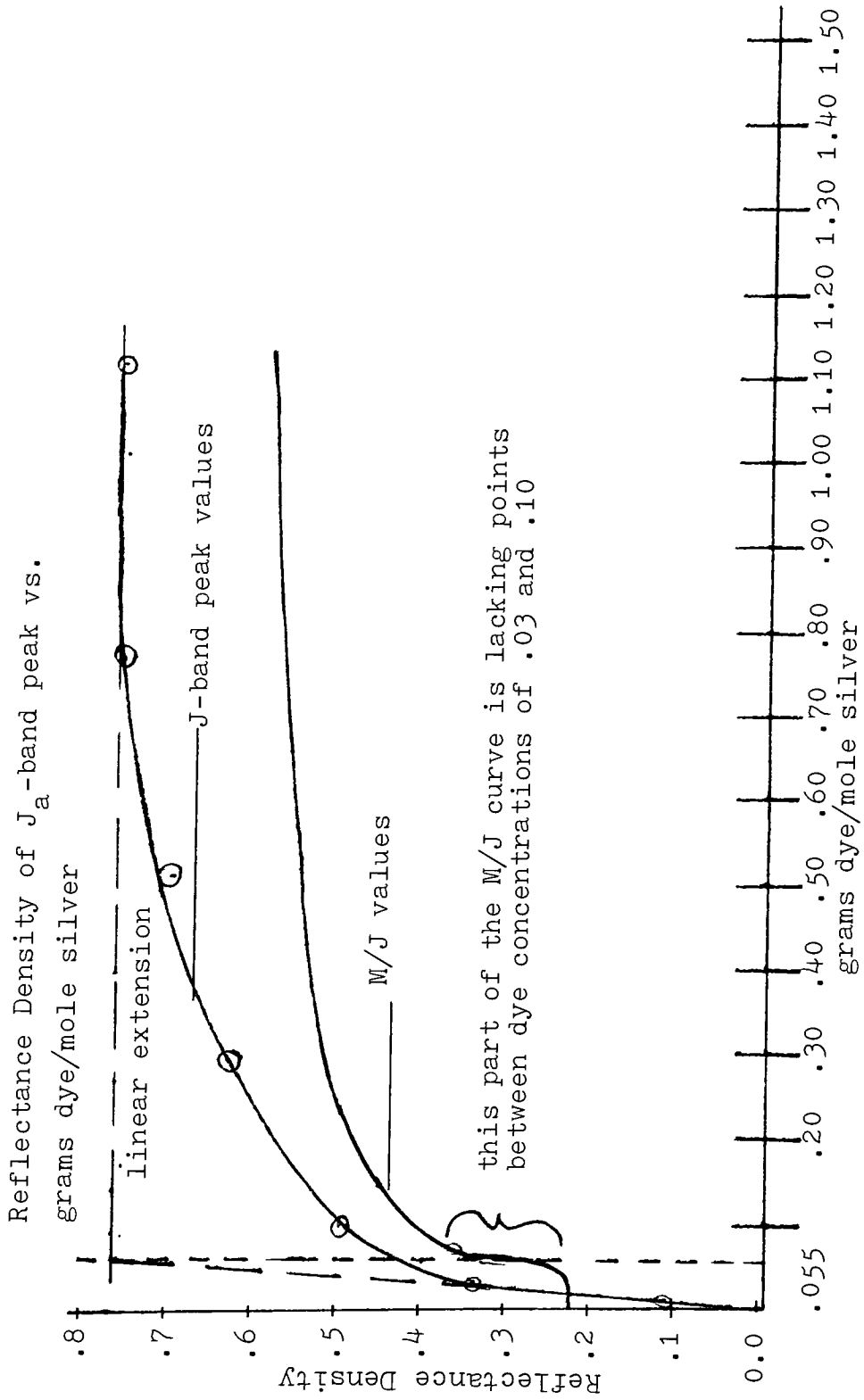


Figure 8

Absorption spectra of cyanine 2
in silver bromide emulsion

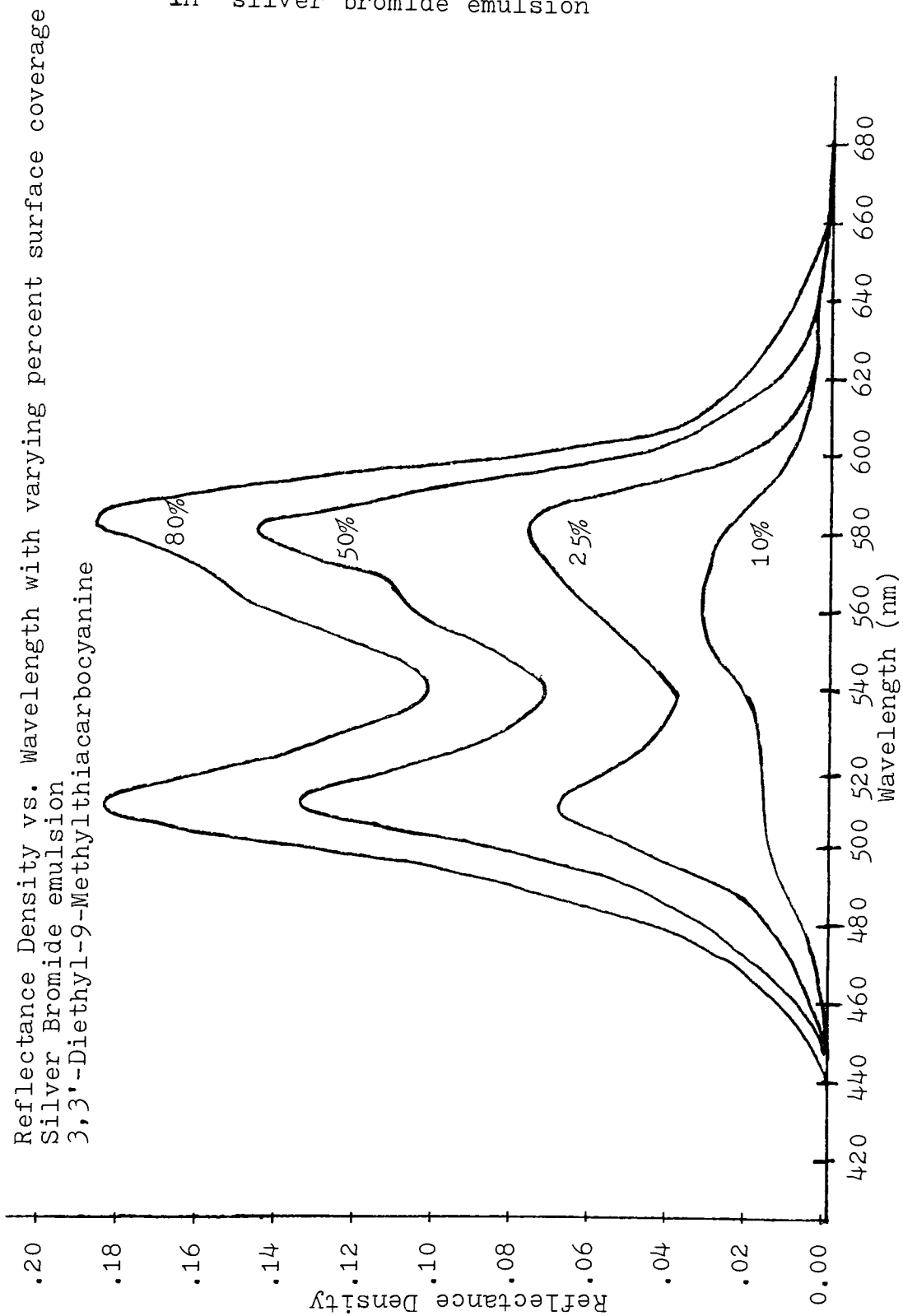


Figure 9

Absorption spectra of cyanine 2 in
silver iodobromide emulsion

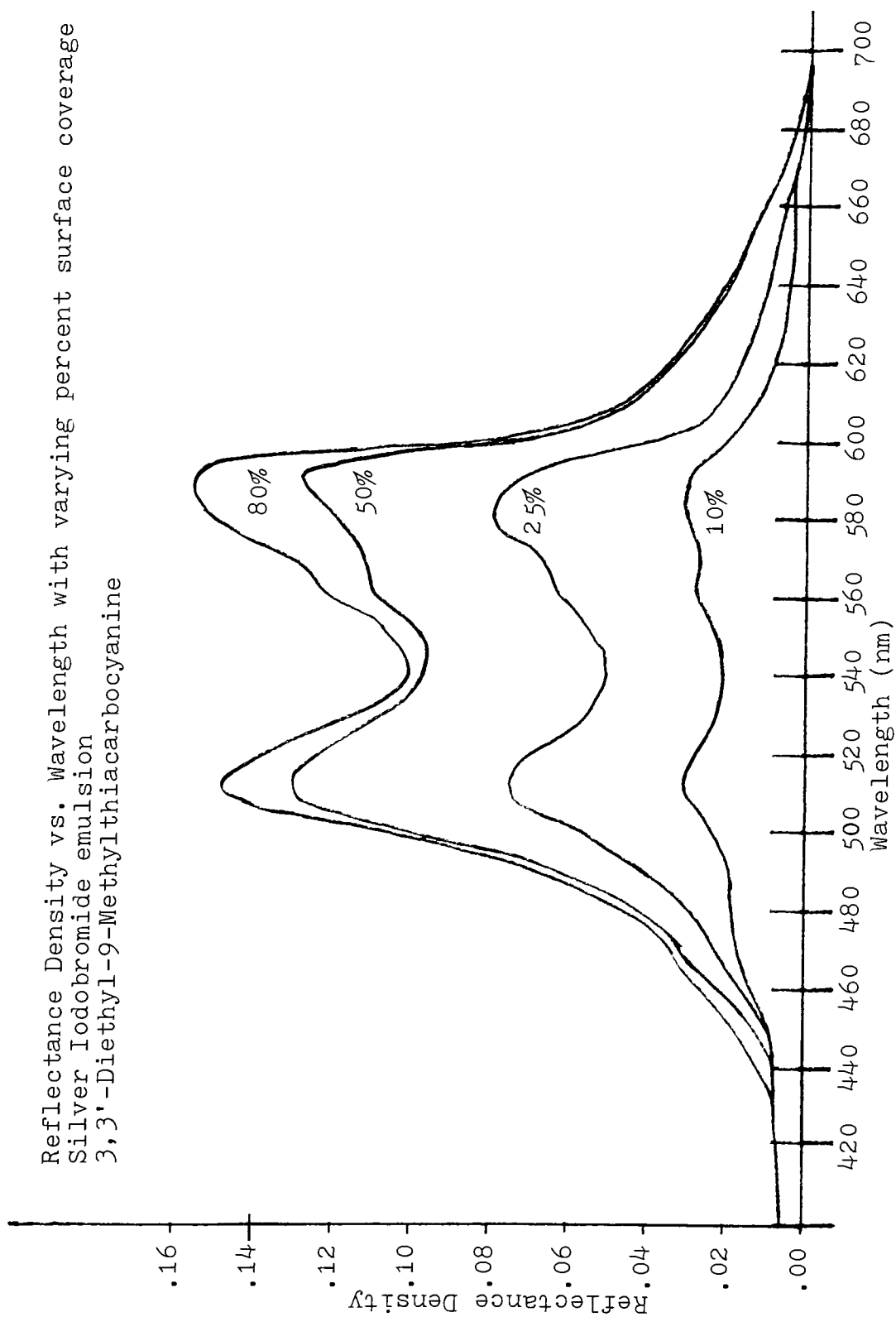


Figure 10
Absorption spectra of cyanine 3
in silver bromide emulsion

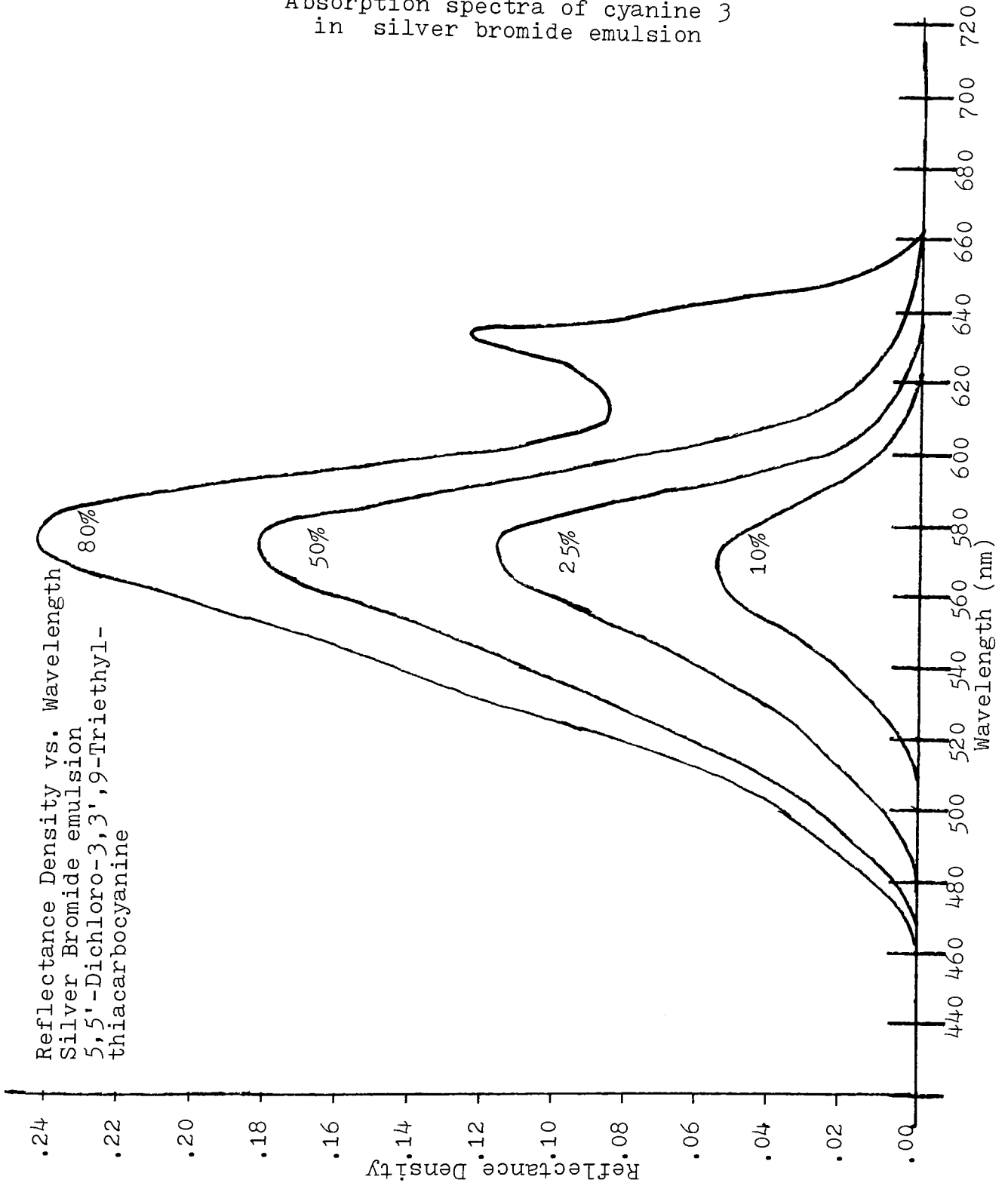


Figure 11
Absorption spectra of cyanine 3 in
silver iodobromide emulsion

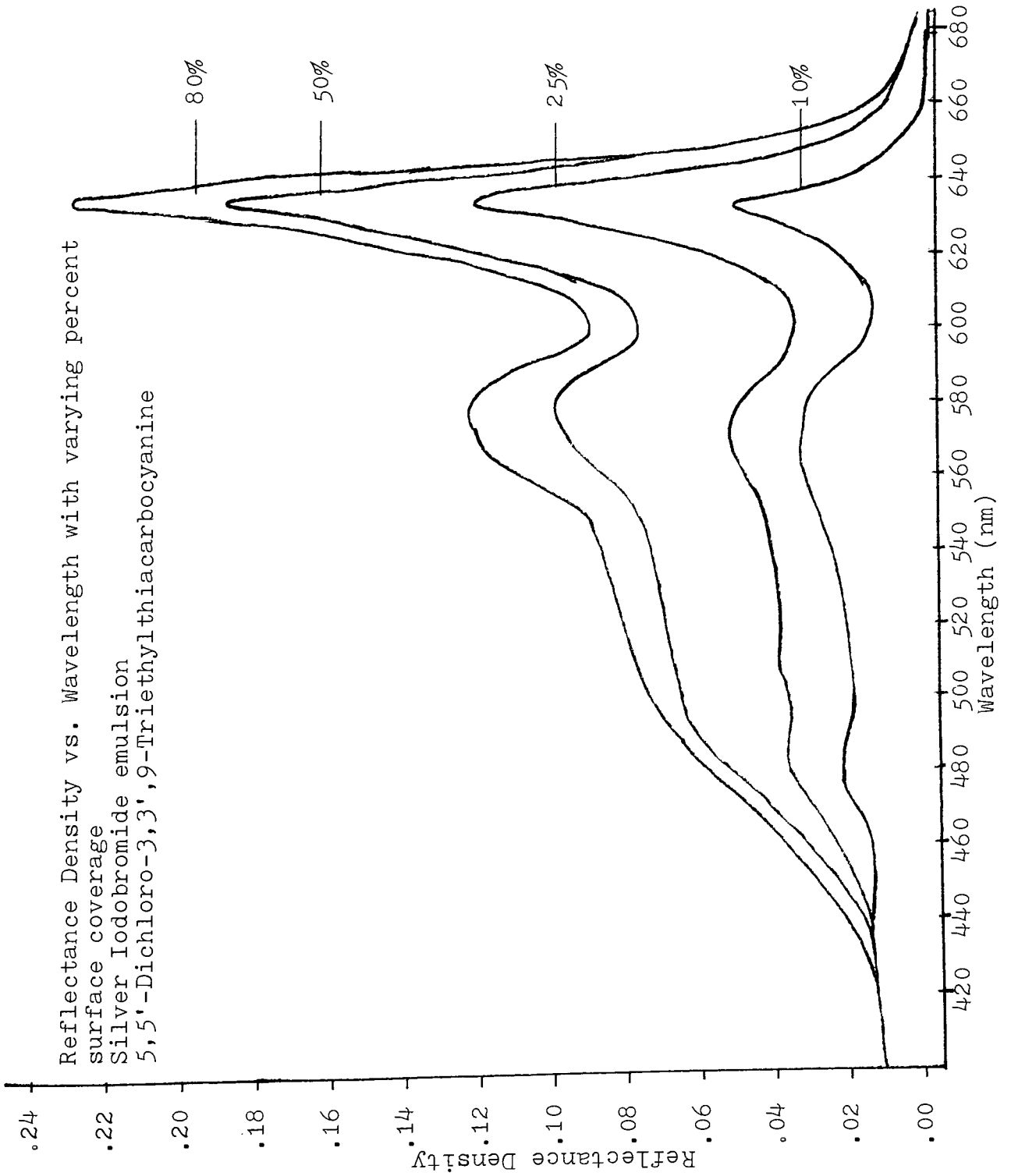


Figure 12
Grain size distribution for the
silver bromide emulsion

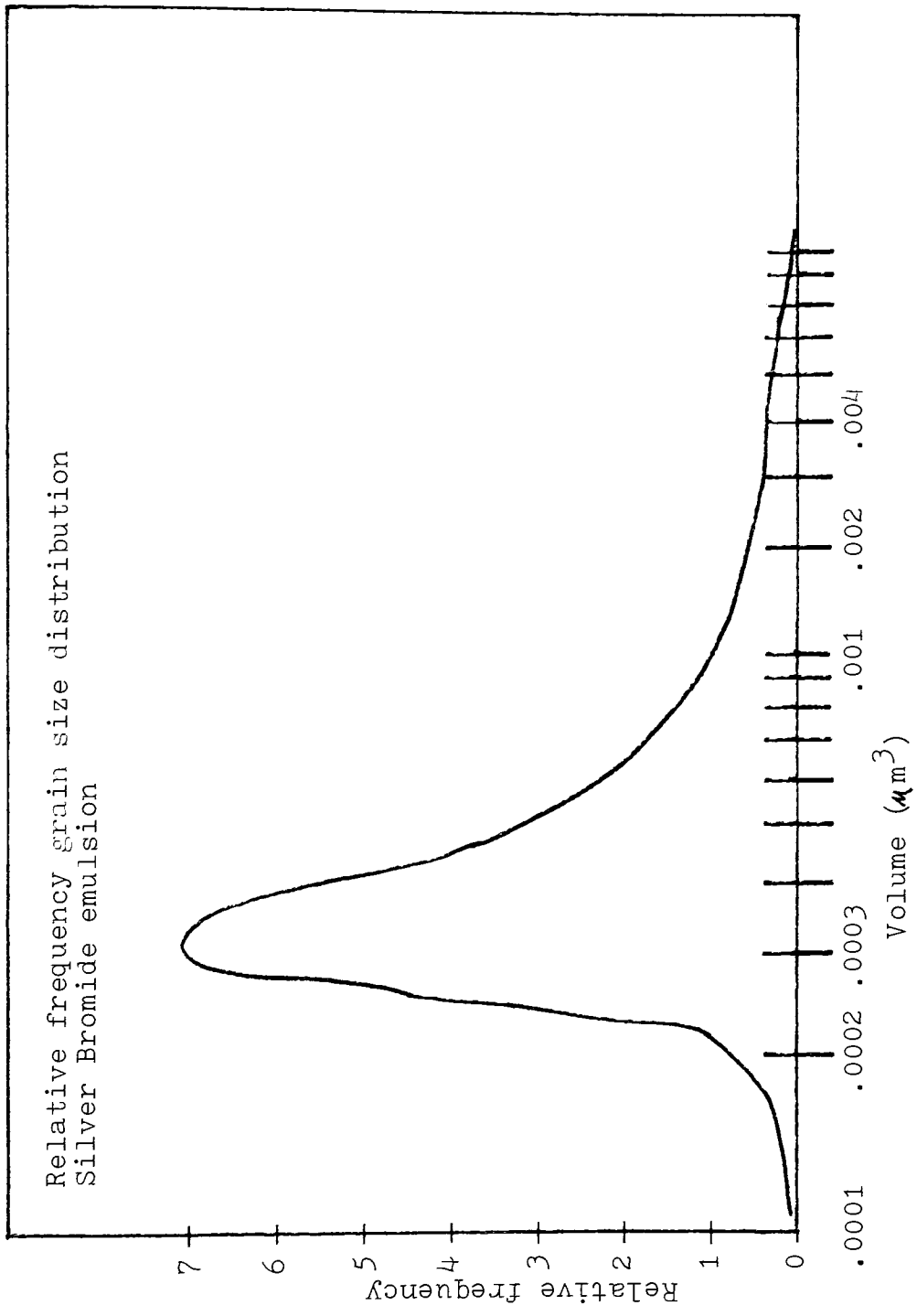
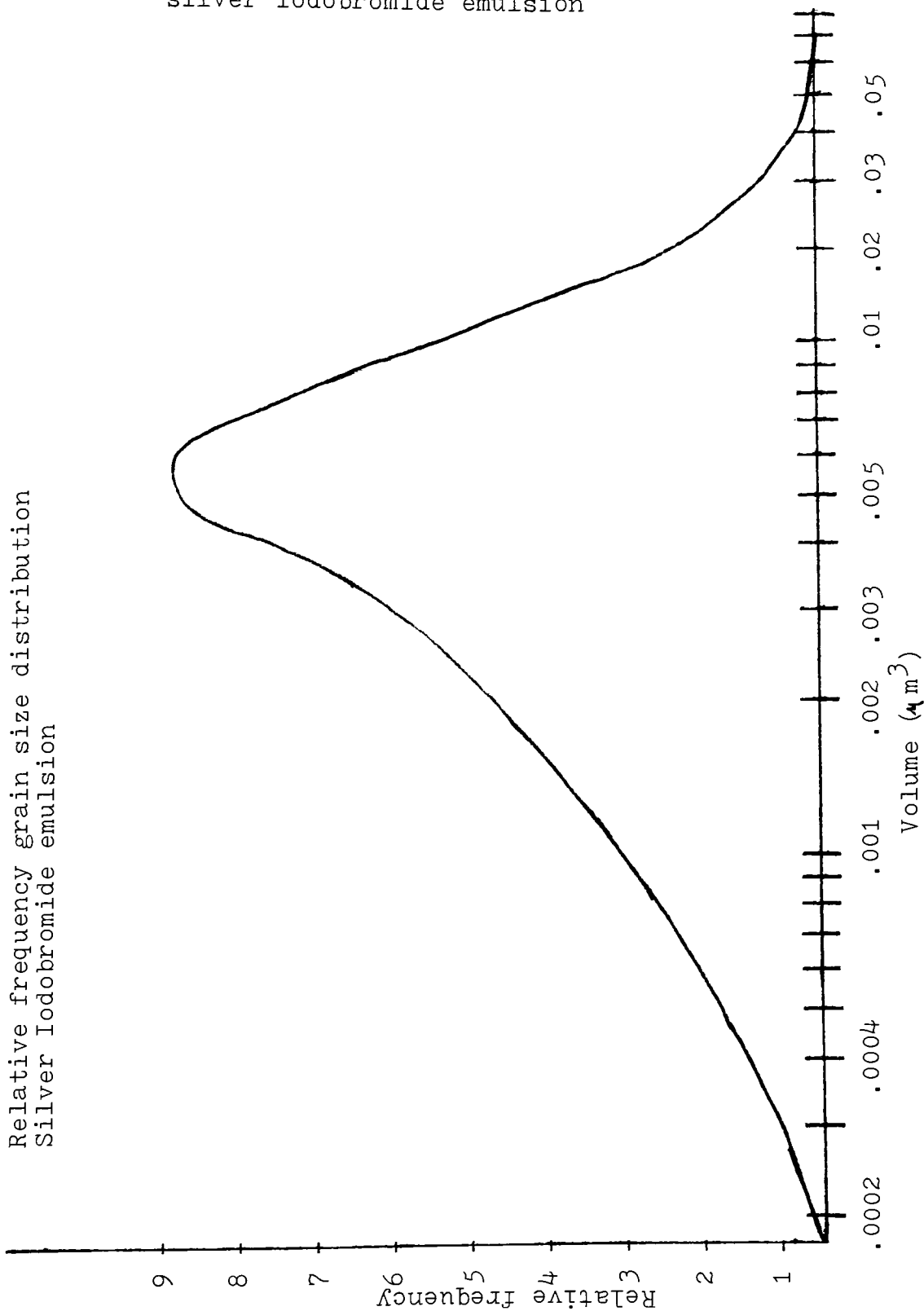


Figure 13
Grain size distribution for the
silver iodobromide emulsion



ANALYSIS OF DATA

To determine the available surface area of substrate for each emulsion the in situ Herz²³ technique was applied. The dye 1,1'-Diethyl-2,2'-Cyanine was used in each emulsion at various levels of concentration as indicated in Figures 4 and 5. Figures 4 and 5 show the tendency that this dye has for forming J_a -band aggregates on octahedral silver bromide and silver iodobromide crystals. The absorption maximum from the J_a -band is at 568 nm for the pure silver bromide grain emulsion, and at 569 nm for the silver iodobromide emulsion. In each dye concentration series the formation of an M-band is quite evident at .1 grams of dye per mole of silver and higher concentrations.

Plotting of the reflectance density at each dye concentration J_a -band peak versus dye concentration resulted with two linear portions as needed for the Herz technique. Extending the linear portions gave the extrapolated dye concentration at the saturation level of the surface. For the pure silver bromide emulsion the dye concentration was .85 grams of dye per mole of silver. For the silver iodobromide emulsion the dye concentration at saturation was .55 grams of dye per mole of silver. Figures 6 and 7 show the extrapolations. Plots of the M-band density divided by the J_a -band density

did not give easily interpreted results. The M-band density divided by J_a -band density versus dye concentration was lacking the points between .03 and .10 grams of dye per mole of silver needed to provide linear sections which could give an extrapolated value for saturation of the surface.

Figures 8 and 9 represent dye cyanine 2. The general shape for both series of spectra are not affected by the presence of iodide at the dye concentrations used. The iodobromide emulsion does show a bathochromatic shift for the M-band to around 589 nm as compared to the pure silver bromide at the two highest percent surface coverages of 50 and 80%. The pure silver bromide emulsion for cyanine 2 does not show any discernable shift in M-band peak wavelength between 10 and 80% surface coverage.

The H_a -band does not shift for cyanine 2 with surface coverage variation between 10 and 80% or with the incorporation of iodide into the crystal. The H_a -band peak was always at 510 nm. The peaks for the iodobromide emulsion and cyanine 2 were not as sharp as those for the pure bromide.

The iodobromide emulsion showed bands forming at 10% surface coverage while the pure bromide emulsion showed only a slight shoulder in the region of the M-band for the dye cyanine 2. The reflectance densities for each peak at 25% coverage by cyanine 2 are close between the two emulsions. At 50% surface coverage the pure bromide showed the same reflectance density for the H_a -band as the iodobromide emulsion,

however the M-band has been noticeably lessened in the iodobromide emulsion versus the pure silver bromide emulsion. At 80% surface coverage by cyanine 2 both bands show less density for the iodobromide emulsion than the pure bromide emulsion. Density at wavelengths between the peaks for the pure bromide emulsion is lower relative to the peaks than for the iodobromide emulsion.

For cyanine 3 (Figures 10 and 11) the most obvious change due to iodide is the readily formed J_a -bands at 635 nm in an iodobromide emulsion. The pure bromide emulsion shows a J_a -band only at 80% surface coverage. All other cases showed only an M-band and not the slightest indication of J_a -band aggregation. The M-band for the pure bromide peaked at 570 nm. For the iodobromide emulsion the peak is not sharp for the M-band, thus a specific wavelength could not be assigned. In general the peak is in the 570 to 580 nm region for the M-band of cyanine 3 in the iodobromide and silver substrate. The M-band peak density is much lower for the iodobromide emulsion at each percent coverage than for the silver bromide emulsion. For the iodobromide emulsion and cyanine 3 the J_a -band peak density increases more than the M-band peak density with increased surface coverage until an increase of surface coverage from 50 to 80%.

Figures 12 and 13 represent grain size distributions for each emulsion. Since the grains are well below .2 microns in radius the use of reflectance density could be used as a measure of the dye optical properties with scattering small and insignificant.

Electron micrographs for each emulsion showed that the iodobromide emulsion contained grains on the average larger than the bromide emulsion. The larger grains in each emulsion were clearly of octahedral habit. The smaller grains were not always clearly distinguishable, but those that were distinguished were octahedrals.

DISCUSSION

A look at the data of Figures 8 to 11 shows that the presence of iodide in the crystals will affect the absorption spectra for the dyes cyanine 2 and cyanine 3 in the adsorbed state. The magnitude of the effect is highly dependent on the dye itself.

Both dyes according to Markocki and Kazmierczak²⁴ will prefer to form J_a -band aggregates on octahedral emulsions. However Figures 8 and 10 which have octahedral crystals of silver bromide as the substrate show this to be not true. For cyanine 2 any concentration of dye at or below 80% surface area coverage will not J_a -band aggregate. Figure 9 shows that the addition of iodide has no effect on J_a -band aggregation for cyanine 2.

Figure 10 shows that at or below 50% surface area coverage no J_a -band aggregates form on the substrate surface for cyanine 3 and pure silver bromide crystals. At 80% a J_a -band has formed at 635 nm. The incorporation of iodide into the crystal dramatically increased J_a -band aggregation as seen in Figure 11. J_a -bands formed at all percent coverages used for cyanine 3 and the iodobromide emulsion.

Cyanine 2 did show H_a -band aggregation in both emulsions. The presence of iodide did not result in any significant shift

for the H_a -band peak at any concentration. The M-band peak did show a bathochromic shift of 10nm at 50 and 80% surface area coverage with the addition of the iodide. For cyanine 2 iodide in the crystal gave H_a -band and M-band peaks that were less sharp and a more pronounced shoulder at 565 nm for the M-band. The fact that absorption has increased at wavelengths between the peaks for the iodide as compared to the pure bromide emulsion indicates that aggregates or single molecules are forming with orientations differing from the H_a -band and M-band. Thus the iodide is shown to affect the aggregation of cyanine 2 molecules on the surface. That the general shape for the absorption spectra does not change with the addition of iodide to the crystals suggests that for cyanine 2 iodide does not act as a nucleation center.

For cyanine 3 the incorporation of the iodide did not completely stop M-band aggregation with a peak at 570 nm. No shift for the M-band peaks between emulsions was shown.

Cyanine 3 will J_a -band aggregate with a peak at 635 nm for 80% surface coverage of an octahedral silver bromide crystal or if iodide is present in the crystal. This suggests that iodide is acting as nucleation centers for cyanine 3.

The fact that cyanine 1 J_a -band aggregated readily on both emulsions, that cyanine 2 did not J_a -band aggregate for any of the concentrations used and that cyanine 3 only aggregated readily with the addition of iodide into the crystals supports the idea that iodide is acting as nucleation centers for cyanine 3 molecules.

CONCLUSIONS

Iodide does affect the absorption spectra for dyes cyanine 2 and cyanine 3. Iodide did not produce J_a -band aggregation for cyanine 2. Iodide did encourage J_a -band aggregation for cyanine 3. Percent surface coverage is a factor for the ability of cyanine 3 to J_a -band aggregate when iodide is not present in the substrate (silver bromide).

RECOMMENDATIONS FOR FURTHER WORK

Work that still needs to be done includes investigating the effect on sensitometric properties due to spectral sensitizing and iodide in the crystal. Also of interest is to repeat this experiment using cubic habit crystals. The effects on the absorption spectra for dyes other than those used is needed if any generalizations concerning dye structures and aggregation are to be made.

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20. ibid 10.
21. courtesy of D. Siems, E. I. Dupont de Nemours and Co.
22. ibid 6. p.182.
23. ibid 6.
24. ibid 9.

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APPENDIX A

APPENDIX A

Emulsion formulas:

Silver bromide octahedral crystals

Solution A:

Phthalated gelatin		4.34 grams
KBr (99.6%)		0.60 grams
Distilled H ₂ O	to make	500ml

Solution B:

AgNO ₃		16.99 grams
Distilled H ₂ O	to make	250 ml

Solution C:

KBr (99.6%)		12.29 grams
Distilled H ₂ O	to make	250 ml

Solution D:

Inert gelatin		24.60 grams
KBr solution (2.5x10 ⁻³ N)		80.00 ml
NaOH solution (0.090 N)		8.00 ml
Distilled H ₂ O	to make	400 ml

Silver iodobromide emulsion (5% iodide)

Solution A:

Phthalated gelatin		4.34 grams
KBr (99.6%)		0.57 grams
KI solution (5.00 M)		1.00 ml
Distilled H ₂ O	to make	500 ml

Solution B:

AgNO ₃		16.99 grams
Distilled H ₂ O	to make	250 ml

Appendix A continued:

Solution C:

KBr(99.6%)		11.60 grams
KI		0.83 grams
Distilled H ₂ O	to make	250 ml

Solution D:

Inert gelatin		24.60 grams
KBr solution (2.5×10^{-3} M)		80.00 ml
NaOH solution (0.090 M)		8.00 ml
Distilled H ₂ O	to make	400 ml

APPENDIX B

APPENDIX B

Calculation of substrate surface area:

Area of one molecule of 1,1'-Diethyl-2,2'-Cyanine is 57 \AA^2 .

This dyes molecular weight is 344.65 grams

For a saturation coverage of .85 grams of dye per mole of silver:

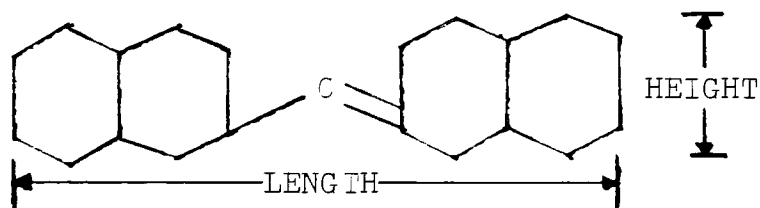
$$\begin{aligned} & \frac{.85 \text{ g/mole Ag}}{344.65 \text{ g/mole dye}} = \frac{2.466 \times 10^{-3} \text{ moles of dye}}{\text{mole of silver}} \\ & \times \frac{6.023 \times 10^{23} \text{ molecules of dye}}{\text{mole of dye}} \quad \times \frac{57 \text{ \AA}^2}{\text{molecule of dye}} \\ & = 8.467 \times 10^{22} \text{ \AA}^2/\text{mole silver} \end{aligned}$$

APPENDIX C

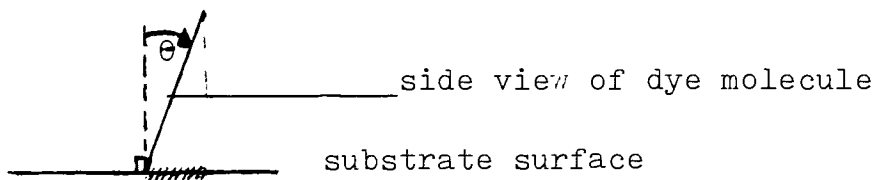
APPENDIX C

Calculation of surface area covered by one dye molecule:

A dye molecule lying flat will cover an area on the substrate approximately equal to the product of the width times the length of the molecule.



When inclined at an angle to the surface the area covered will vary as the sine of the angle from the perpendicular to the surface.



$$\text{Area covered} = \text{length} \times \text{height} \times \sin \theta$$