# DISPERSION OF DEPOLARISATION OF LIGHT-SCATTERING IN COLLOIDS.

## Part V. Colloidal Dye-Stuffs.

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## 1. Introduction.

MANY dye-stuffs are salts of more or less basic or acidic properties and possess a colloidal nature. They are often hydrolysed and have colloidal tendencies because of this. However, in cases where hydrolysis plays no important part the colloidal character is often quite pronounced, for instance in the alkali salts of the sulpho-acids. In general, those with high molecular weights tend to go into the colloidal state (W. Biltz, 1910). Perhaps the most convincing evidence of the colloidal nature of dye-stuffs is given by the ultra-microscopic observations of Raehlmann, Michaelis and others.

Although most of the work done on dye-stuffs has been concerned with the practical application in textile industry, it has often been attempted from various sides to investigate and characterise the dye solutions. The results are often contradictory, because, in the first place, dyes are not well defined as chemical individuals and one does not know whether the different workers are really dealing with the same substance. Further, the methods of investigation differ in value.

In spite of the fact that much work has been done on ultra-microscopy, diffusion, dialysis, osmotic pressure, conductivity, etc., very little work has been done on the optical properties of colloidal dye-stuffs, especially the study of the absorption of light and Tyndall scattering. The absorption coefficient of a large number of colloidal dye-stuffs were measured by Pihlblad (1918) in the spectral region $\lambda = 2500–7000$ A.U. The dispersed phase of the investigated systems consisted of aniline blue, indophenol, azobenzene, bordeaux, fast red and butter yellow. He studied the light absorption in relation to the degree of dispersion of the particles. No fundamental difference was noticed in the form of the absorption curve when the degree of dispersion was altered except a lateral shift of the absorption maximum in some of the colloids. It was also found that as the size of the colloidal particles increased the absorption curve became flatter and flatter, in accordance with Mie's theory. Very recently, Kortüm (1936) has studied the absorption of light by aqueous solutions of some organic dye-stuffs in

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relation to the dispersivity of the ions. Measurements of the validity range of the Beer law in aqueous solutions of dye-stuffs have revealed relationships between the degree of dispersivity on the one hand and ionic magnitude, the number and distribution of hydrophillic groups and stearic influences on the other. Although the study of the absorption of light in colloidal dye-stuffs has been useful to some extent for the determination of the state of dispersivity of ions in solutions, more accurate methods based on the study of the Tyndall effect are particularly suitable for establishing the commencement of micelle formation and therewith the transition from ionic dispersion to colloid-like solutions. The recent investigations of the author (1937) on the dispersion of depolarisation in a large number of colloidal elements have advanced notably our knowledge of the structure of colloidal particles. It is, however, felt desirable to extend these investigations to the case of colloidal dye-stuffs also. In the present paper the results obtained from a study of the absorption and the scattering of light in aqueous solutions of some ten dye-stuffs are given. This investigation should be taken as only preliminary since no attempt has been made to vary the state of dispersion of the dye-stuff ions by the addition of suitable electrolytes. The study of the optical properties of colloidal dye-stuffs which can be obtained in suspension with the particles graded down from those of microscopic to those of molecular dimensions is of great importance to understand the connection between the degree of dispersivity and the kinetics of the dyeing processes.

## 2. *Preparation of the Sols.*

In the present investigation some ten typical dye-stuffs have been selected for study. The list comprises of colloidal dye-stuff solutions, *i.e.*, those which are completely resolvable under the ultra-microscope, semi-colloids, *i.e.*, those which are partially resolvable and molecular dye solutions, *i.e.*, those which are not resolvable.

*Aniline blue.*—The hydrosol of this dye-stuff was prepared by adding to 100 c.c. of double distilled water at 90–95°C. 1 c.c. of an alcoholic solution of aniline blue. The concentration of aniline blue in the alcoholic solution was 0·2 g. in 5 c.c. of alcohol.

The other dye-stuff solutions were prepared by dissolving 0·01 g. of the substance in 100 c.c. of water. Since congo rubin is insoluble in water, the sol of this dye was prepared by pouring a solution of the dye in ethyl alcohol into water.

## 3. *Absorption and Depolarisation Measurements.*

The methods of measuring the extinction coefficients and the depolarisation factors $\rho_u$, $\rho_v$ and $\rho_h$ from $\lambda$ 2500–7000 A.U. have already been

described in detail in the earlier parts of this series. The scattering power of the solutions of the dye-stuffs is comparatively weaker than that of the inorganic colloids. Moreover, even in very dilute solutions certain regions of the spectrum are completely absorbed. Consequently the depolarisation measurements could not be pushed through the entire region of the spectrum from 2967–7000 A.U. In such cases the depolarisation curves are discontinuous. In most of these dye-stuffs the depolarisation factors $\rho_v$ and $\rho_h$ were measured only for a single wave-length far away from the region of characteristic absorption. The extinction coefficients for the ten dyes are given in Tables I, III and VI. The values $\rho_u$, $\rho_v$ and $\rho_h$ after applying the necessary corrections for the finite angle of convergence of the incident beam, are given in Tables II, IV, V, VII and VIII. The curves of absorption and the depolarisation factor $\rho_u$ are reproduced in Figs. 1 to 10.

## TABLE I.

### *Extinction Coefficient.*

| Wave-length | Aniline blue | Congo red |
|:---:|:---:|:---:|
| 2250 | >1·8 | 0·7 |
| 2500 | >1·8 | 0·55 |
| 2750 | >1·8 | 0·3 |
| 3000 | >1·8 | 0·4 |
| 3250 | >1·8 | 0·63 |
| 3500 | 0·73 | 0·69 |
| 3750 | 0·43 | 0·5 |
| 4000 | 0·3 | 0·39 |
| 4500 | 0·22 | 0·65 |
| 5000 | 0·5 | 1·05 |
| 5500 | 0·91 | 0·6 |
| 6000 | 0·73 | 0·21 |
| 6500 | 0·47 | 0·14 |
| 7000 | 0·2 | 0·09 |

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TABLE II.

*Dispersion of Depolarisation $\rho_u$.*

| Wave-length | Aniline blue | | | Congo red | | |
|---|---|---|---|---|---|---|
| | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % |
| 3650 | 4·5 | 0·28 | .. | .. | .. | .. |
| 4046 | 2·5 | 0·2 | 11 | .. | .. | .. |
| 4358 | 2 | 0·15 | 8·9 | .. | .. | .. |
| 4750 | 2·3 | 0·5 | 23 | .. | .. | .. |
| 5000 | 2·9 | 0·88 | 49 | 18 | 10 | 100 |
| 5500 | 4·2 | 1·2 | 67 | 20 | 13 | 100 |
| 6000 | 3·6 | 1·05 | 49 | 18 | 11 | 100 |
| 6500 | 3·3 | 0·88 | .. | 17 | .. | .. |
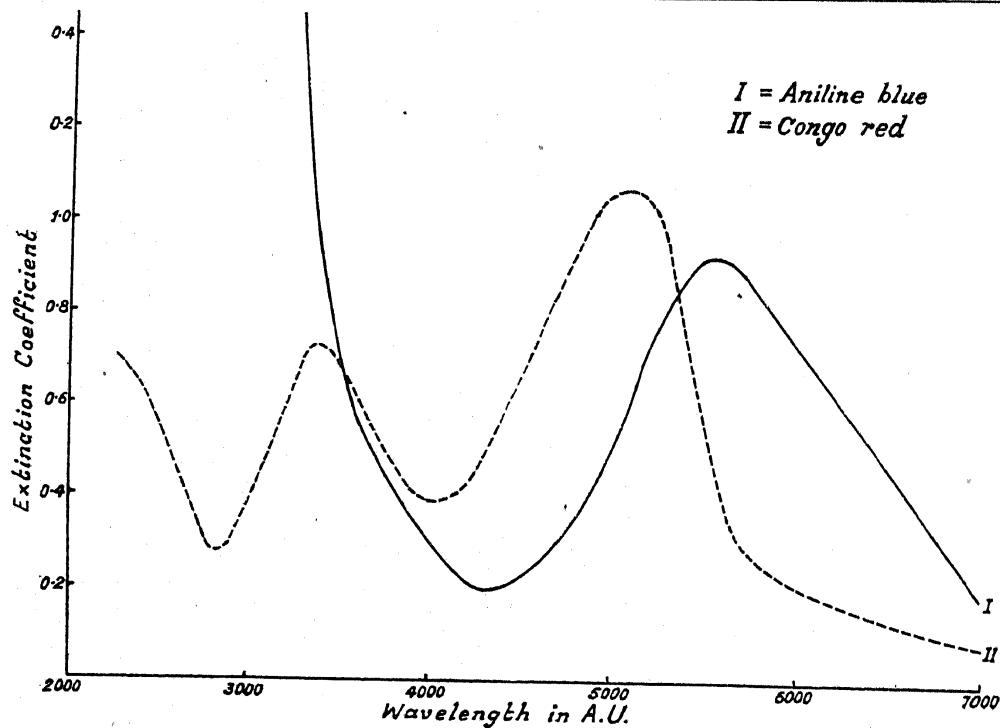


FIG. 1.

Extinction coefficients.
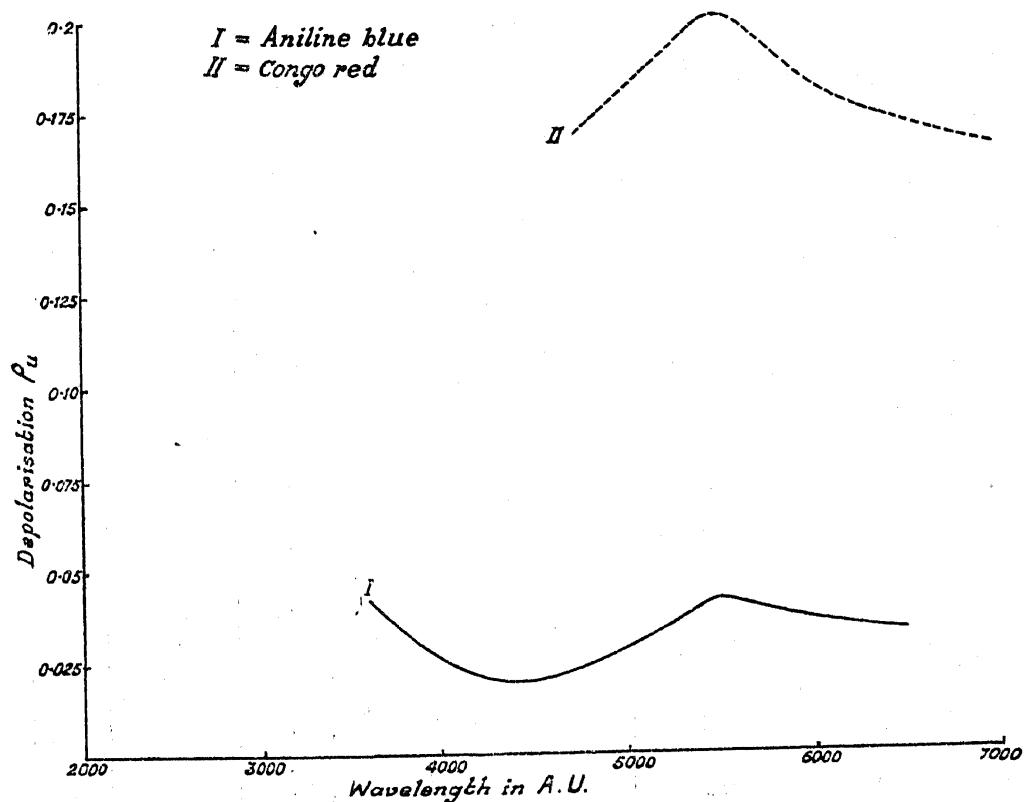
FIG. 2.

Dispersion of depolarisation factor $\rho_u$.


## TABLE III.

### *Extinction Coefficients.*

| Wave-length | Iodine green | Nigrosin | Congo rubin | Indigotin |
|---|---|---|---|---|
| 2250 | >1·8 | 1·7 | >3 | 1·2 |
| 2500 | >1·8 | 1·7 | 2·8 | 1·65 |
| 2750 | 0·95 | 1·68 | 1·2 | 2·45 |
| 3000 | 0·48 | 1·66 | 1·36 | >3 |
| 3250 | 0·21 | 1·47 | 1·86 | 1·85 |
| 3500 | 0·07 | 0·78 | 1·6 | 1·15 |
| 3750 | 0·02 | 0·48 | 1·06 | 0·38 |
| 4000 | 0·01 | 0·37 | 0·96 | 0·15 |
| 4500 | 0·06 | 0·54 | 1·6 | 0·25 |
| 5000 | 0·18 | 0·67 | >3 | 0·4 |
| 5500 | 0·44 | 1·0 | >3 | 1·0 |
| 6000 | 0·85 | 1·05 | 0·96 | 2·75 |
| 6500 | 0·27 | 0·85 | 0·27 | 2·0 |
| 7000 | 0·15 | 0·7 | 0·2 | 0·7 |

TABLE IV.

*Dispersion of Depolarisation* $\rho_u$.

| Wave-length | Iodine green | | | Nigrosin | | |
|:---:|:---:|:---:|:---:|:---:|:---:|:---:|
| | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % |
| 2967 | 3·0 | .. | .. | 46·8 | .. | .. |
| 3650 | 3·7 | .. | .. | 8·4 | .. | .. |
| 4046 | 5·0 | .. | .. | 6·3 | .. | .. |
| 4358 | 7·0 | .. | .. | 7·3 | .. | .. |
| 4750 | 10·8 | 4·2 | .. | 14·5 | .. | .. |
| 5000 | 18·3 | 5·6 | 50 | 19·6 | .. | .. |
| 5500 | 73 | . 45 | 65 | 30·5 | .. | .. |
| 6000 | 73 | 65 | 100 | 31·8 | .. | .. |
| 6500 | 28·5 | 13 | .. | 21·5 | .. | .. |
| 7000 | 11·7 | 5·3 | .. | 13·9 | 4·4 | 52·7· |

TABLE V.

*Dispersion of Depolarisation* $\rho_u$.

| Wave-length | Congo rubin | | | Indigotin |
|:---:|:---:|:---:|:---:|:---:|
| | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % | $\rho_u$ % |
| 3650 | 37·5 | .. | .. | 6·3 |
| 4046 | 22·8 | .. | .. | 5·0 |
| 4358 | 29·8 | .. | .. | 4·5 |
| 4750 | .. | .. | .. | 8·0 |
| 5000 | .. | .. | .. | 13·3 |
| 5500 | 30·5 | .. | .. | 23·8 |
| 6000 | 14 | .. | .. | 34·7 |
| 6500 | 11 | .. | .. | .. |
| 7000 | 8 | 2·8 | 55 | 16·3 |
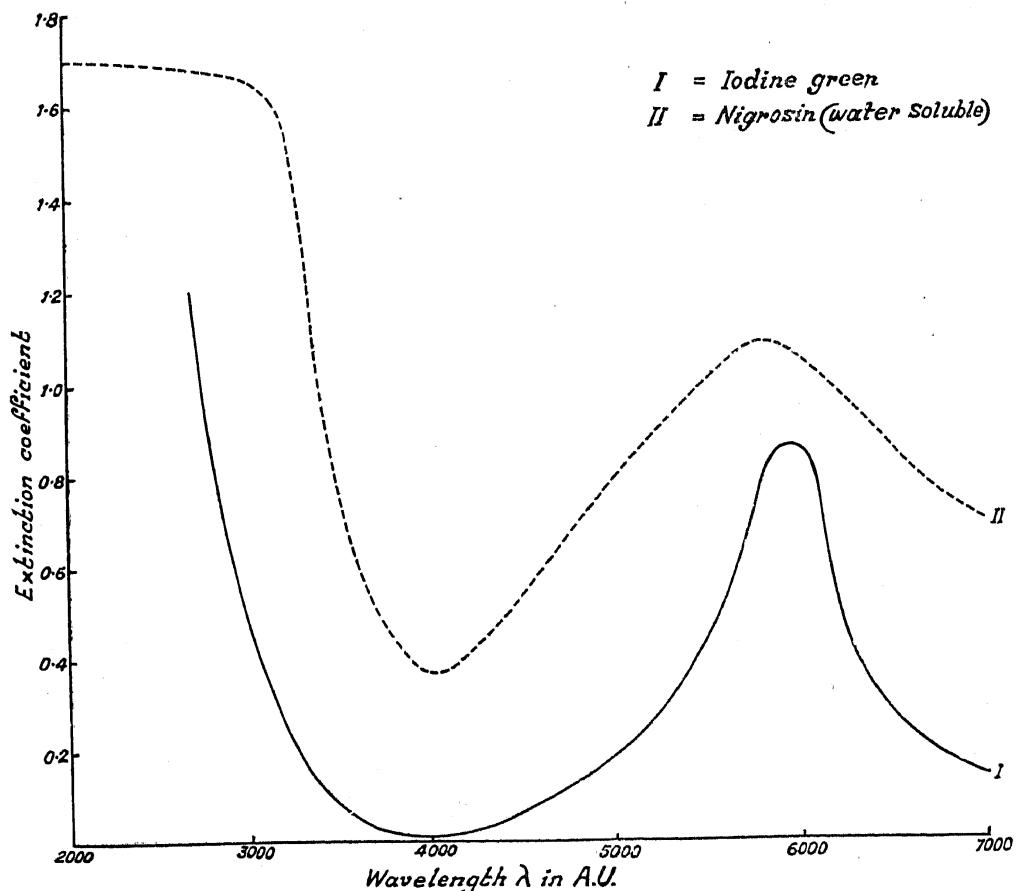
FIG. 3.

Extinction coefficients.
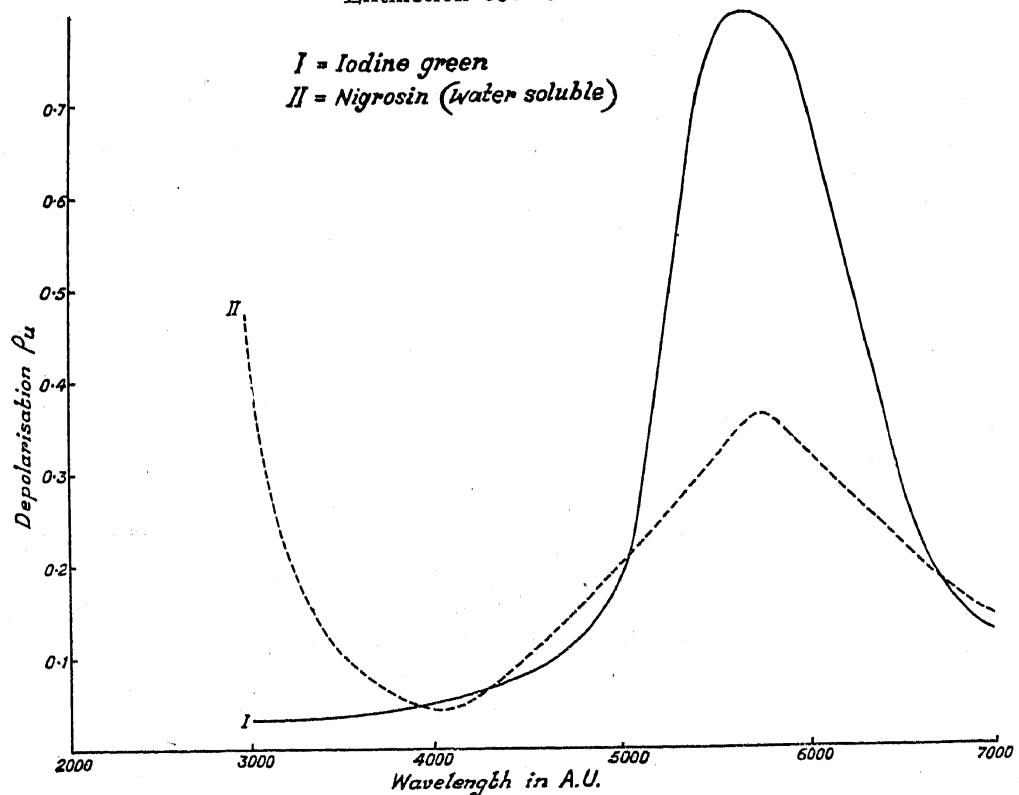


FIG. 4.

Dispersion of depolarisation factor $\rho u$.

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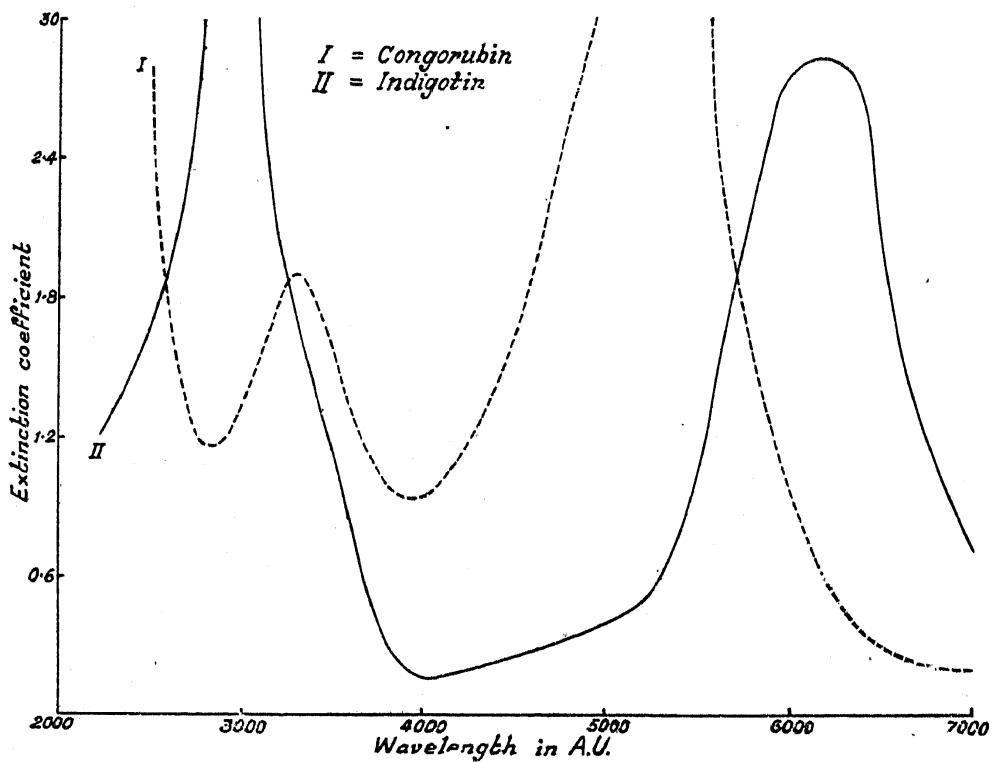


FIG. 5.

Extinction coefficients.
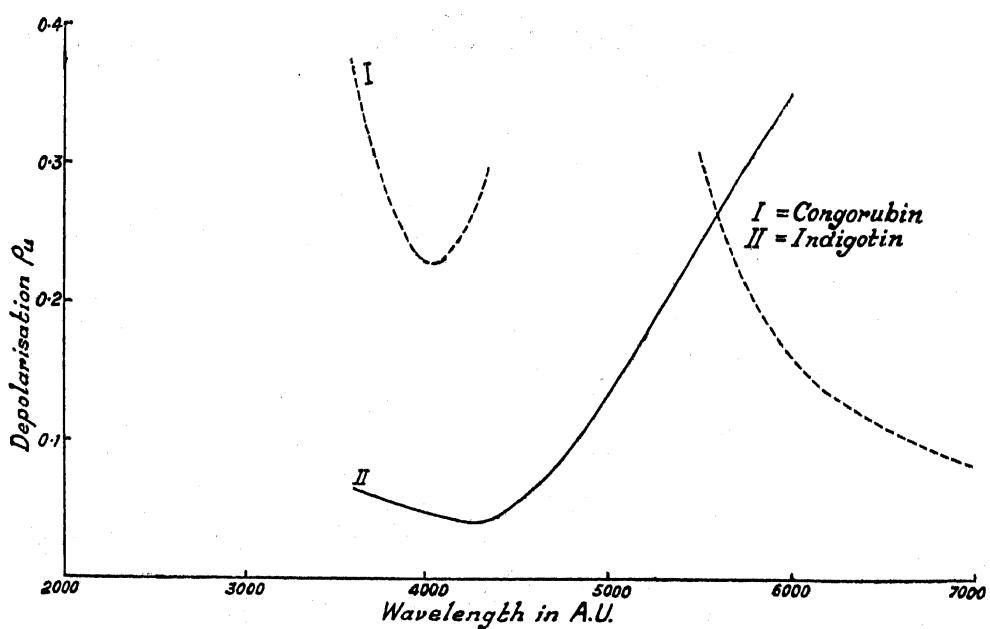


FIG. 6.

Dispersion of depolarisation factor $\rho_u$.

## TABLE VI.

*Extinction Coefficients.*

| Wave-length | Chryosidine | Hoffman's blue | Methyl violet | Orange II |
|---|---|---|---|---|
| 2250 | >3 | 1·8 | 1·0 | >3 |
| 2500 | 1·75 | 1·5 | 1·8 | >3 |
| 2750 | 1·05 | 1·0 | 0·9 | >3 |
| 3000 | 0·7 | 2·6 | 2·2 | 2·6 |
| 3250 | 0·45 | 0·7 | 0·55 | >3 |
| 3500 | 0·4 | 0·2 | 0·13 | >3 |
| 3750 | 0·9 | 0·10 | 0·02 | >3 |
| 4000 | 1·8 | 0·05 | 0·01 | >3 |
| 4500 | >3 | 0·6 | 0·38 | >3 |
| 5000 | >3 | 3 | 2·2 | >3 |
| 5500 | 0·5 | >3 | >3 | 2·4 |
| 6000 | 0·2 | >3 | >3 | 0·4 |
| 6500 | 0·075 | 1·1 | 3·0 | 0·32 |
| 7000 | 0·0 | 0·2 | 0·25 | 0·3 |

## TABLE VII.

*Dispersion of Depolarisation $\rho_u$.*

| Wave-length | Chryosidine | | | Hoffman's blue |
|---|---|---|---|---|
| | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % | $\rho_u$ % |
| 2967 | .. | .. | .. | 8·3 |
| 3650 | 3·1 | .. | .. | 5·4 |
| 4046 | 6·9 | .. | .. | 5·4 |
| 4358 | 9·5 | .. | .. | 7·3 |
| 5500 | .. | .. | .. | .. |
| 6000 | 25·4 | 13 | 100 | .. |
| 6500 | 18 | 8·5 | 87 | 11·1 |
| 7000 | 4 | 1·5 | 70 | 7·1 |

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TABLE VIII.

*Dispersion of Depolarisation $\rho_u$.*

| Wave-length | Methyl violet | | | Orange II | | |
|---|---|---|---|---|---|---|
| | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % | $\rho_u$ % | $\rho_v$ % | $\rho_h$ % |
| 3650 | 8·4 | .. | .. | .. | .. | .. |
| 4046 | 12·8 | .. | .. | .. | .. | .. |
| 4358 | 15·9 | .. | .. | .. | .. | .. |
| 4750 | 18·6 | .. | .. | .. | .. | .. |
| 5000 | 23·8 | .. | .. | .. | .. | .. |
| 5500 | 45·4 | .. | .. | 4·0 | .. | .. |
| 6000 | 82·0 | .. | .. | 2·9 | .. | .. |
| 6500 | 57·6 | .. | .. | 2·3 | .. | .. |
| 7000 | 11·8 | 3·1 | 45·5 | 1·7 | 0·3 | 50 |
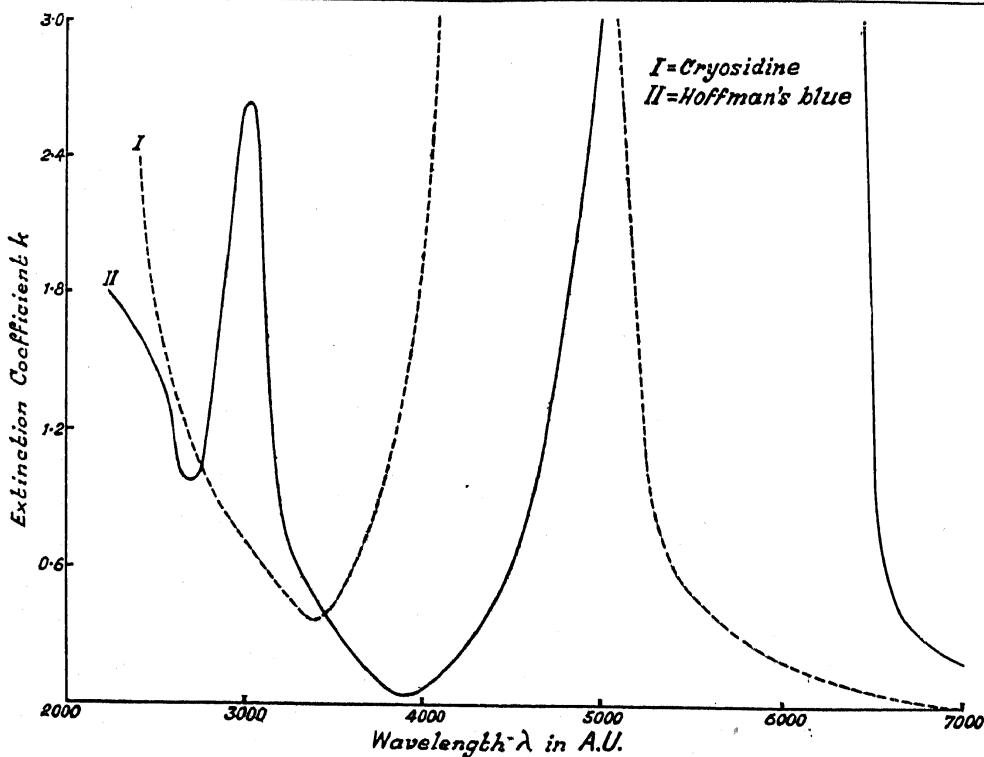


Fig. 7.
Extinction coefficients.

I = *Cryosidine*
II = *Hoffman's blue*

FIG. 8.

Dispersion of depolarisation factor $\rho_u$.

I = *Methyl violet*
II = *Orange II*
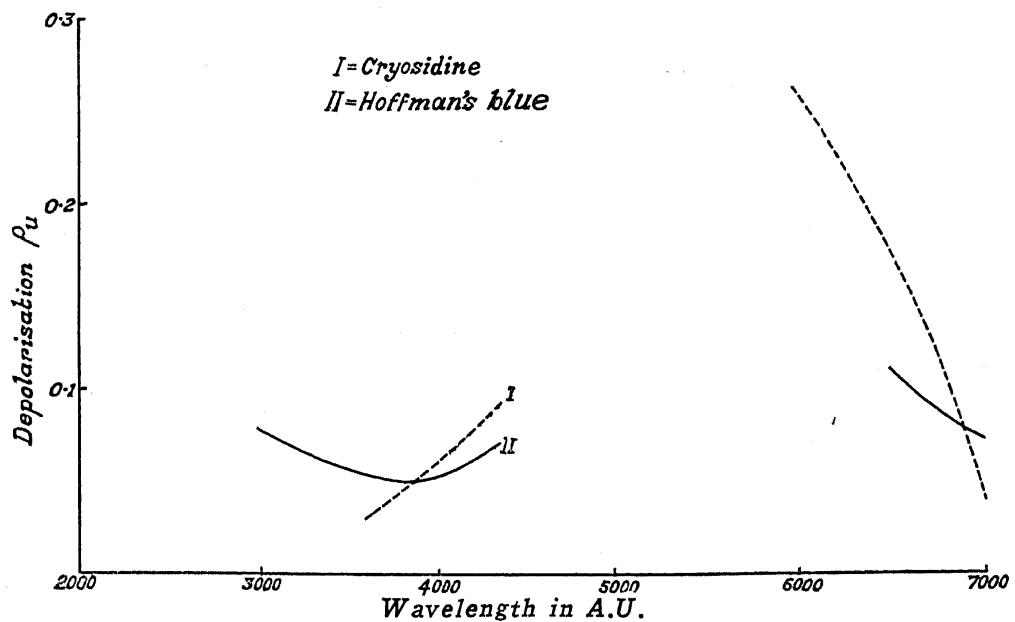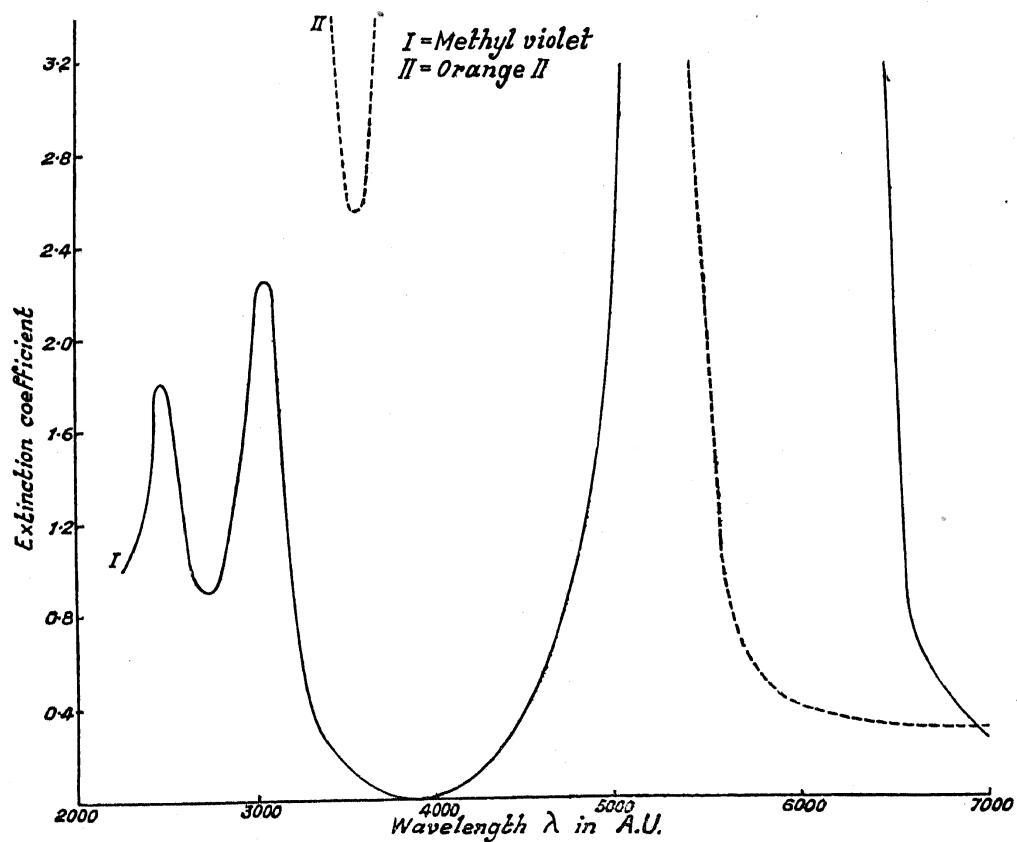
FIG. 9.

Extinction coefficients.

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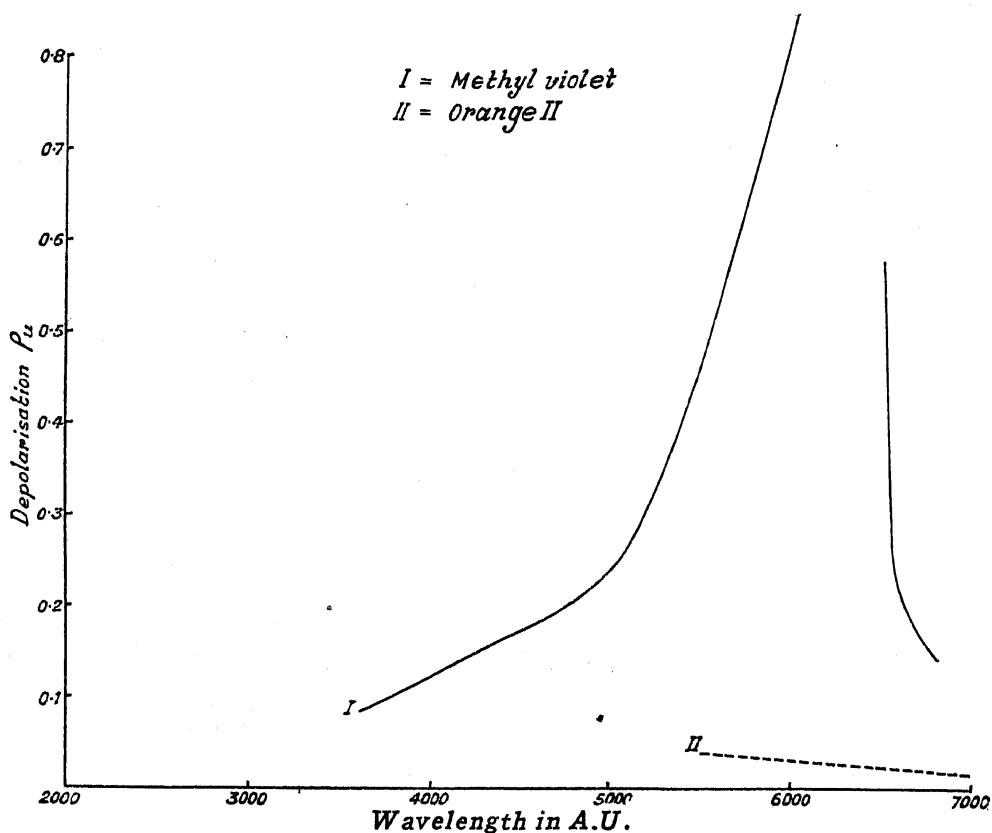


Fig. 10.
Dispersion of depolarisation factor $P_u$.

## 4. Discussion.

A comparative study of the absorption coefficient and the depolarisation factors show that the colloidal organic dye-stuffs behave as do the colloidal metals such as, gold, silver, etc. In the regions of characteristic absorption the depolarisation factors and hence the anisotropy show an enormous increase. In most cases the absorption curves and the depolarisation curves are exactly similar in form. If one side of the maximum in the absorption curve is steeper than the other side, the corresponding side of the maximum of the depolarisation curve is also steeper than the other. Among the ten dye-stuffs investigated, aniline blue, congo red, congo rubin and nigrosin (water-soluble) are typical colloidal electrolytes. Of these aniline blue was obtained very easily in colloidal condition. The scattering power of this sol is considerably greater than that of the other three. The depolarisation measurements show that the solutions of these dye-stuffs contain anisotropic ultra-microscopic micellæ. In congo red solution the anisotropy of the particles is comparatively great, whereas in the case of aniline blue the optical anisotropy is very low.

The solutions of indigotin, Hoffman's blue and iodine green are molecular and not colloidal. The molecules of iodine green are highly anisotropic. In the other two cases because of the low scattering power and intense absorption, the depolarisation factors $\rho_v$ and $\rho_h$ could not be measured accurately with the experimental arrangement employed in the present investigation. The solutions of indigotin and iodine green exhibit a weak fluorescence.

Dyes such as methyl violet, chryosidine and orange II occupy an intermediate position. The solutions of these dyes can be made colloidal by the addition of a suitable electrolyte. In methyl violet solution $\rho_u$ increases enormously as the region of characteristic absorption is reached. The increase is not so much pronounced in chryosidine. Orange II gives the lowest values for $\rho_u$, $\rho_v$ and $\rho_h$.

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### 5. Summary.

The earlier work on the absorption of light by aqueous solutions of organic dye-stuffs has been briefly reviewed. It is pointed out that the study of the optical properties, especially the Tyndall effect, of colloidal dye-stuffs which can be obtained in suspension with the particles graded down from those of microscopic to those of molecular dimensions, is of great importance to understand the connection between the degree of dispersivity and kinetics of the dyeing processes. Measurements of the depolarisation factors $\rho_u$, $\rho_v$ and $\rho_h$ and the extinction coefficients of aqueous solutions of ten typical dye-stuffs are made for different wave-lengths from 2500 to 7000 A.U. As in the case of metallic sols, such as gold and silver, so also in the case of these dye-stuffs the depolarisation values attain their maximum value in the regions of specific absorption. The depolarisation measurements indicate that the sols of aniline blue, congo red, congo rubin and nigrosin contain anisotropic ultra-microscopic micellæ whereas the solutions of indigotin, Hoffman's blue and iodine green are molecular and not colloidal. The solutions of methyl violet, chryosidine and orange II occupy an intermediate position.

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