Ultraviolet Spectroscopical Studies on the Antagonistic Action of Salts in Organic colloidal Solution.

By

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Spectroscopical studies of colloidal solutions have been discussed by several investigators in the last ten years, but their experimental data were not enough to show the real value of the application of the spectroscope in this field. ZSIGMONDY and OSTWALD[1] state that the absorption band of any colloidal solution moves to the shorter wave lengths with increasing dispersion. The optical character of the colloidal solution depends not only upon the material and the degree of dispersion but also on the form and surface of the particles.

SVEDBERG[2] studied the relation of colloidal and molecular solutions i.e. gold, selenium, indigo, anilin blue, indophenol and azobenzene and he stated that if the absorption of light by a very disperse colloidal solution is quite similar to that of the molecular solution of the same substance, it is conceivable that the descrete particles of the colloidal solution are molecules.

K. VOIGT[3] studied the color and the degree of dispersion of colloidal suspensions and emulsions and stated that the color depends on the degree of dispersion in colloidal solutions of suspensoid character but that the color is independent of the degree of dispersion in emulsoid solutions.

J. LIFSCHITZ[4] stated that the light absorption of colloidal solutions

1) ZSIGMONDY:—Zur Erkentniss d. Kolloide, Jens, 112, 1905.
OSTWALD:—Grundriss der Kolloid Chemie, Dresden, 222, 1909.
„ Kolloid Chemie Beih., 2, 409, 1910.

2) SVEDBERG:—Die Existenz der Moleküle, 1912.

3) VOIGT:—Kolloid Zeits., Bd. XV, 84, 1914.

4) LIFSCHITZ:—Kolloid Zeits., XXII, 53, 1918.

depends upon following five factors:—1, The chemical nature of the dispersion phase; 2, its concentration; 3, the degree of dispersion; 4, the form of the particles; 5, the inner structure and the character of the surface of particles.

Thus the light absorption of colloidal solution is governed by many physico-chemical factors and it is almost impossible to determine the effect of single physico-chemical factors on light absorption. But in the comparative study of two colloidal solutions of the same nature and the same concentration it is not difficult to determine changes in the degree of dispersion and in the inner and outer structure of particles. Changes in the colloidal state, which are governed by many physico-chemical factors, may occur in a great many different ways, because the colloidal state may be changed in all cases by qualitative and quantitative combinations of these factors. In account of the great differences between all organic colloidal solutions of different origin, it is possible to identify the natural organic colloidal solutions of the same origin by changes in the colloidal state.

If we compare the results of ultraviolet spectroscopic investigations of colloidal solutions with the results obtained by using the ultramicroscope, which investigates only the qualitative characteristics of the particles of the colloidal solutions, the former have greater significance than the latter. Last year we[1] studied the antagonistic action of salt in organic colloidal solutions i.e.—eggwhite, milk, plant juice and blood serum—and observed that the diffusion of an ion of one salt through the colloidal solution was antagonised by the presence of an another salt of a different ion. On the present investigation we intended to show the change of the colloidal state of organic colloidal solutions i.e.—gelatine, eggwhite, blood serum, plant juice and Takadiastase solution —by using a quartz ultraviolet spectroscope (1 D. 15. made by ADAM HILGARD in London) during the antagonistic action of the salt.

EXPERIMENTAL.

In the following experiments we used as a source of light a hydrogen tube with a capillary 5 cm. long which filled with hydrogen at 8 mm. pressure. For the operation of this hydrogen lamp we used an

1) TADOKORO:—Journ. Tokyo chem. soc, July, 1918,
„ —Journ. Coll. Agr, Hokkaido Imp. Univ., Sapporo, Japan, Vol, VIII., p. 5, 1919.

alternating high voltage current obtained from a transformer. The primary circuit was supplied with alternating current at 220 volts, and a rheostat in series was used to maintain the primary current at 4 amperes, giving a voltage above 2000 in the secondary. A quartz cell 12 mm. thick was filled with a mixture of the organic colloidal solution and salt solution and was interposed between the hydrogen lamp and the quartz-prismed spectrograph. All photographs were taken with seven minutes exposure, using panchromatic Wratten and Wainright dry plates. The method of obtaining a uniform ultra-violet spectrum by the use of the hydrogen tube was discribed by Prof. H. B. LEMON[1] and we used it as a light source.

1. *The antagonistic action between $ZnSO_4$ and $CaCl_2$ solution in eggwhite.*

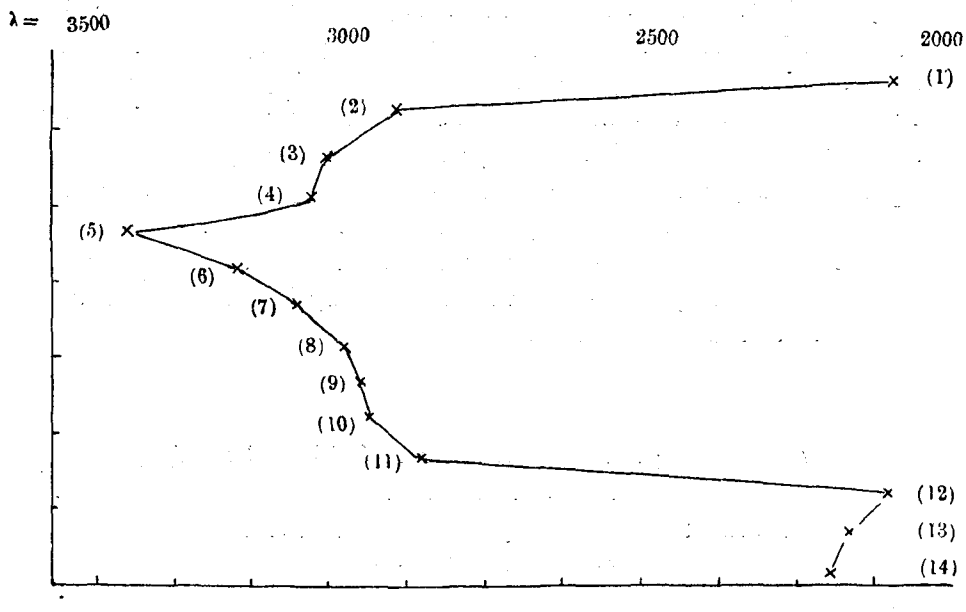
(The diluted eggwhite was prepared mixing with six volumes of water: See Fig. 1 and Phot. A.)

TABLE 1.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2100
2.	10 cc. diluted eggwhite + 1 cc. H_2O	2991
3.	10 cc. „ „ + 0,1 cc. N/50$ZnSO_4$ + 0,9 cc. H_2O	3050
4.	10 cc. „ „ + 0,25 cc. N/50$ZnSO_4$ + 0,75 cc. H_2O...	3085
5.	10 cc. „ „ + 0,5 cc. „ + 0,5 cc H_2O ...	3415
6.	10 cc. „ „ „ + 0,1 cc. N/2$CaCL_2$ + 0,4 cc. H_2O	3225
7.	10 cc. „ „ „ + 0,25 cc. N/$CaCL_2$ + 0,25 cc. H_2O	3120
8.	10 cc. „ „ „ + 0,5 cc. „ ——	3035
9.	10 cc. „ „ „ + 0,75 cc. „ ——	3021
10.	10 cc. „ „ „ + 1,0 cc. „ ——	3000
11.	10 cc. „ „ „ + 1,1 cc. „ ——	2950
12.	10 cc. H_2O + hydrogen lamp	2150
13.	5 cc. N/50$ZnSO_4$ + 5 cc. N/2$CaCL_2$.....	2190

1) H. B. LEMON:—Astrophysical Journal, Vol. XXXV, pp. 109–124, 1912.

Fig. 1.



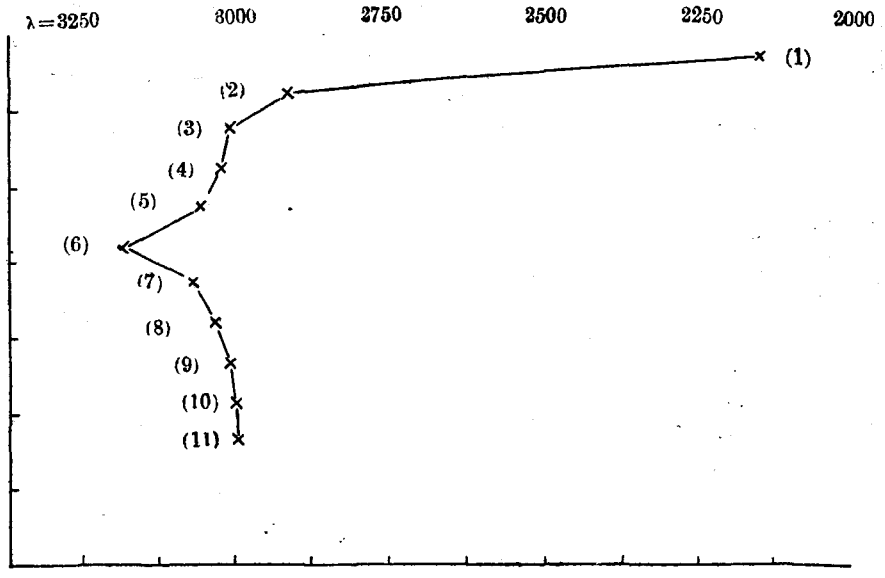
2. *The antagonistic action between $ZnSO_4$ and KCL solution in eggwhite.*

(See Fig. 2 and Phot. B.)

TABLE 2.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2140
2.	10 cc. diluted eggwhite + 2 cc. H_2O	2995
3.	10 cc. ,, + 0,25 cc. N/50 $ZnSO_4$ + 1,75 cc. H_2O...	3005
4.	10 cc. ,, + 0,4 cc. ,, + 1,6 cc. H_2O ...	3015
5.	10 cc. ,, + 0,6 cc. ,, + 1,4 cc. H_2O ...	3055
6.	10 cc. ,, + 0,8 cc. ,, + 1,2 cc. H_2O ...	3225
7.	10 cc. ,, ,, ,, + 0,5 cc. N/KCL + 0,7 cc. H_2O	3060
8.	10 cc. ,, ,, ,, + 1,0 cc. N/KCL + 0,2 cc. H_2O	3030
9.	10 cc. ,, ,, ,, + 1,5 cc. ,, ——	3015
10.	10 cc. ,, ,, ,, + 2,0 cc. ,, ——	3001
11.	10 cc. ,, ,, ,, + 2,5 cc. ,, ——	3000

Fig. 2.



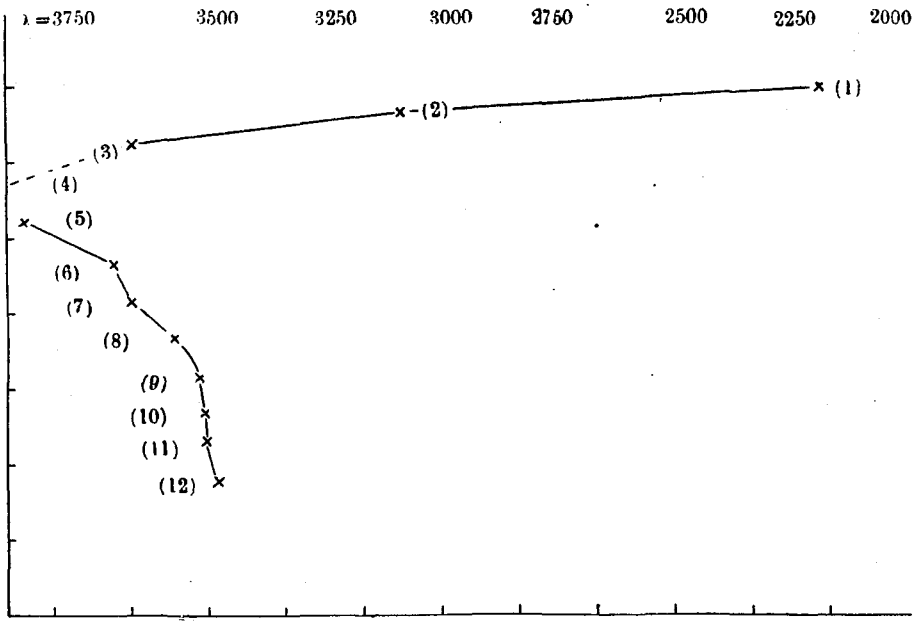
3. *The antagonistic action between $CaCL_2$ and KCL in Takadiastase solution.*

(1 gr. Takadiastase was dissolved in 100 cc. H_2O: See fig. 3 and Phot. C.)

TABLE 3.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2140
2.	10 cc. Takadiastase sol. + 2,0 cc. H_2O.....	3115
3.	10 cc. ,, + 0,25 cc. N/10$CaCL_2$ + 1,75 cc. H_2O	3670
4.	10 cc. ,, + 1,0 cc. N/10$CaCL_2$ + 1,0 cc. H_2O	dark
5.	10 cc. ,, ,, + 0,25 cc. N/KCL + 0,75 cc. H_2O	3790
6.	10 cc. ,, ,, + 0,50 cc. ,, + 0,50 cc. ,,	3725
7.	10 cc. ,, ,, + 0,75 cc. ,, + 0,25 cc. ,,	3670
8.	10 cc. ,, ,, + 1,0 cc. ,, —— ...	3630
7.	10 cc. ,, ,, + 1,25 cc. ,, —— ...	3545
8.	10 cc. ,, ,, + 1,50 cc. ,, —— ...	3535
9.	10 cc. ,, ,, + 1,75 cc. ,, —— ...	3525
10.	10 cc. ,, ,, + 2,0 cc. ,, —— ...	3490

Fig. 3.



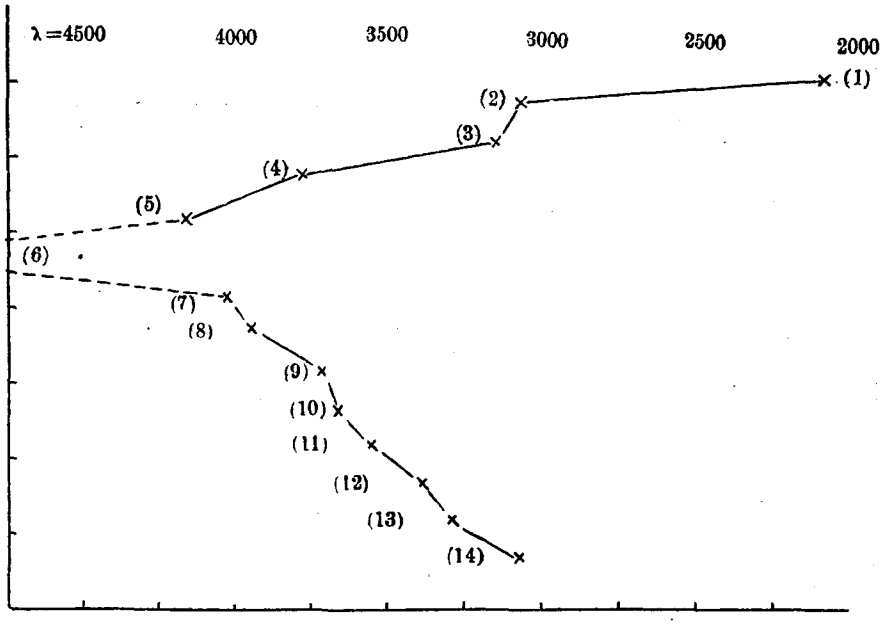
4. The antagonistic action between $CaCL_2$ and $MgCL_2$ in Takadiastase solution.

(See Fig. 4 and Phot. D.)

TABLE 4.

	Concentration of the solution.			Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	.....		2140
2.	10 cc. Takadiastase sol. + 2 cc. H_2O	.....		3085
3.	10 cc. ,,	+ 0,25 cc. N/2$CaCL_2$ + 1,75 cc. H_2O	.....	3150
4.	10 cc. ,,	+ 0,5 cc. ,,	+ 1,5 cc. ,, ...	3761
5.	10 cc. ,,	+ 0,75 cc. ,,	+ 1,25 cc. ,, ...	4175
6.	10 cc. ,,	+ 1,0 cc. ,,	+ 1,0 cc. ,, ...	darke
7.	10 cc. ,,	,,	+ 0,1 cc. N/$MgCL_2$ + 0,9 cc. H_2O	4020
8.	10 cc. ,,	,,	+ 0,2 cc. ,,	+ 0,8 cc. ,, 3955
9.	10 cc. ,,	,,	+ 0,3 cc. ,,	+ 0,7 cc. ,, 3733
10.	10 cc. ,,	,,	+ 0,4 cc. ,,	+ 0,6 cc. ,, 3675
11.	10 cc. ,,	,,	+ 0,5 cc. ,,	+ 0,5 cc. ,, 3555
12.	10 cc. ,,	,,	+ 0,75 cc. ,,	+ 0,3 cc. ,, 3385
13.	10 cc. ,,	,,	+ 1,0 cc. ,,	—— 3265
14.	10 cc. ,,	,,	+ 1,25 cc. ,,	—— 3085

Fig. 4.



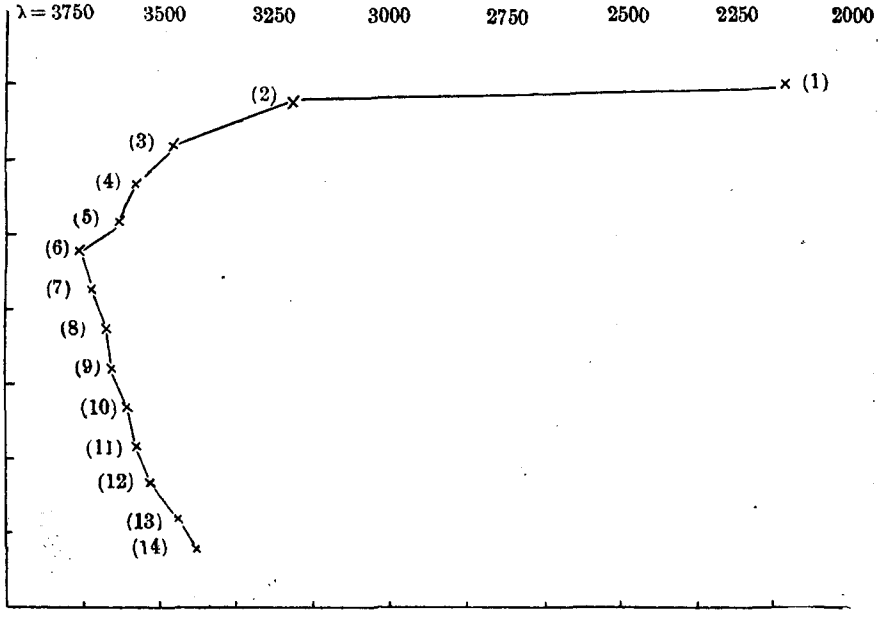
5. *The antagonistic action between $CaCL_2$ and $NaCL_2$ in Takadiastase solution.*

(See Fig. 5 and Phot. E.)

TABLE 5.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2140
2.	10 cc. Takadiastase sol. + 2 cc. H_2O	3225
3.	10 cc. ,, + 0,1 cc. N/2$CaCL_2$ + 1,9 cc. H_2O	3475
4.	10 cc. ,, + 0,25 cc. ,, + 1,75 cc. ,, ...	3555
5.	10 cc. ,, + 0,50 cc. ,, + 1,5 cc. ,, ...	3595
6.	10 cc. ,, + 0,75 cc. ,, + 1,25 cc. ,, ...	3685
7.	10 cc. ,, ,, + 0,1 cc. NaCL + 1,15 cc. H_2O...	3665
8.	10 cc. ,, ,, + 0,25 cc. ,, + 1,0 cc. ,, ...	3635
9.	10 cc. ,, ,, + 0,50 cc. ,, + 0,75 cc. ,, ...	3622
10.	10 cc. ,, ,, + 0,75 cc. ,, + 0,5 cc. ,, ...	3585
11.	10 cc. ,, ,, + 1,0 cc. ,, —— ...	3565
12.	10 cc. ,, ,, + 1,25 cc. ,, —— ...	3540
13.	10 cc. ,, ,, + 1,5 cc. ,, —— ...	3520
14.	10 cc. ,, ,, + 1,75 cc. ,, —— ...	3482

Fig. 5.



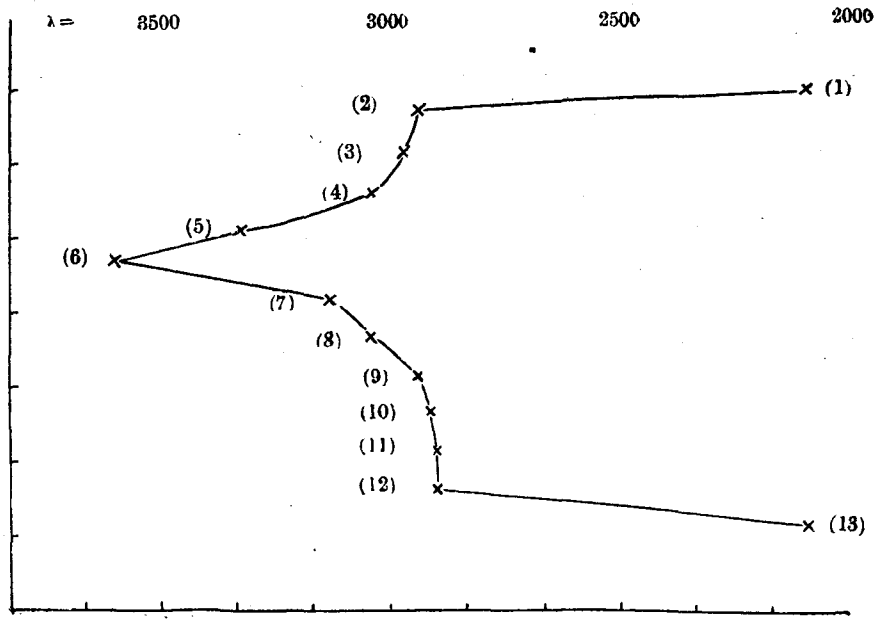
6. *The antagonistic action between $ZnSO_4$ and $CaCL_2$ in blood serum.*

($\frac{1}{8}$ dilution of rabbit serum was prepared: See Fig. 6 and Phot. F.)

TABLE 6.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2130
2.	10 cc. rabbit serum + 2 cc. H_2O	2941
3.	10 cc. ,, + 0,1 cc. N/50$ZnSO_4$ + 1,9 cc. H_2O	2950
4.	10 cc. ,, + 0,2 cc. ,, + 1,8 cc. H_2O	3050
5.	10 cc. ,, + 0,25 cc. ,, + 1,75 cc. ,,	3345
6.	10 cc. ,, + 0,50 cc. ,, + 1,5 cc. ,,	3805
7.	10 cc. ,, + 0,50 cc. ,, + 0,5 cc. N/2$CaCL_2$ + 1,0 cc. H_2O	3125
8.	10 cc. ,, ,, ,, + 1,0 cc. ,, + 0,5 cc. ,,	3045
9.	10 cc. ,, ,, ,, + 1,5 cc. ,, ——	2985
10.	10 cc. ,, ,, ,, + 2,0 cc. ,, ——	2945
11.	10 cc. ,, ,, ,, + 2,5 cc. ,, ——	2940
12.	10 cc. ,, ,, ,, + 3,0 cc. ,, ——	2940
13.	5 cc. N/5$ZnSO_4$ + 5 cc. N/2$CaCL_2$	2135

Fig. 6.



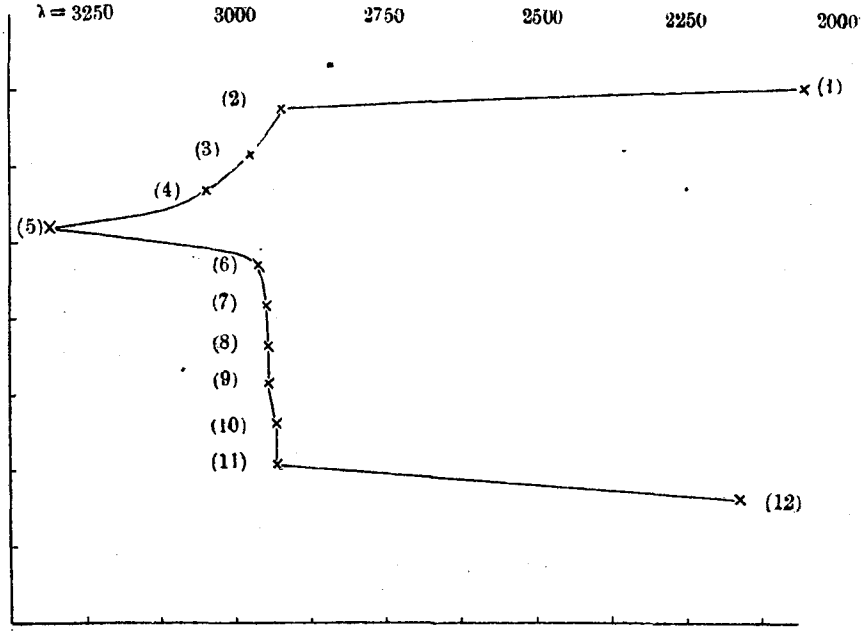
7. *The antagonistic action between $ZnSO_4$ and NaCL in blood serum.*

(See Fig. 7 and Phot. G.)

TABLE 7.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2100
2.	10 cc. serum + 2 cc. H_2O	2910
3.	10 cc. ,, + 0,1 cc. N/50$ZnSO_4$ + 1,9 cc. H_2O.....	2995
4.	10 cc. ,, + 0,15 cc. ,, + 1,85 cc. H_2O.....	3050
5.	10 cc. ,, + 0,20 cc. ,, + 1,8 cc. ,, ...	3310
6.	10 cc. ,, + 0,20 cc. ,, + 0,5 cc. N/NaCL + 1,3 cc. H_2O	2985
7.	10 cc. ,, ,, ,, + 0,75 cc. ,, + 1,15 cc. ,,	2960
8.	10 cc. ,, ,, ,, + 1,0 cc. ,, + 0,8 cc. ,,	2960
9.	10 cc. ,, ,, ,, + 1,25 cc. ,, + 0,55 cc. ,,	2951
10.	10 cc. ,, ,, ,, + 1,5 cc. ,, + 0,30 cc. ,,	2950
11.	10 cc. ,, ,, ,, + 2,0 cc. ,, —— ...	2940
12.	5 cc. N/50$ZnSO_4$ + 5 cc. N/NaCL	2190

Fig. 7.



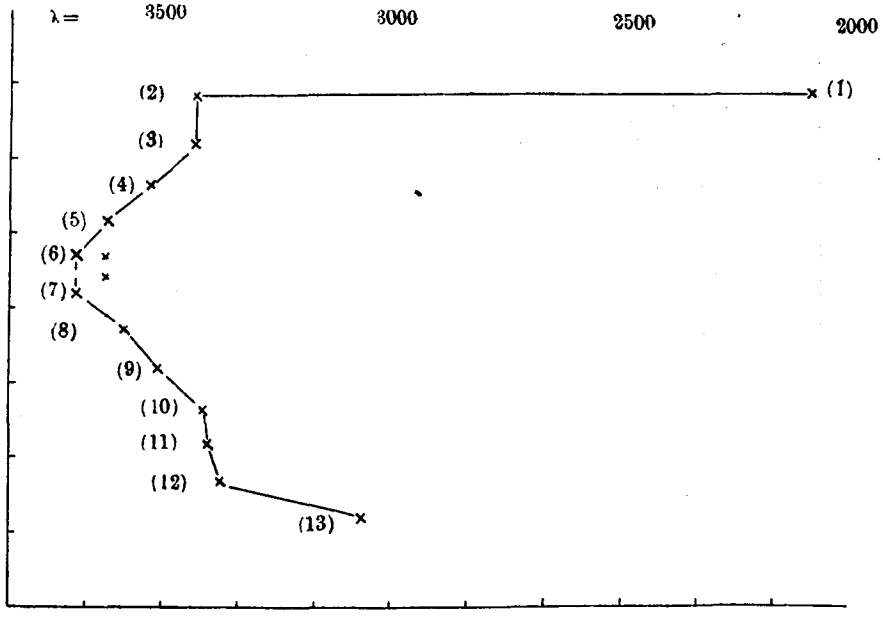
8. The antagonistic action between $Ca(NO_3)_2$ and KCL in lettuce juice.

(The lettuce juice was prepared, grinding, filtered and diluted with three volumes of water: See Fig. 8 and Phot. H.)

TABLE 8.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2100
2.	10 cc. juice + 2 cc. H_2O	3495
3.	10 cc. „ + 0,1 cc. N/2$Ca(NO_3)_2$ + 1,9 cc. H_2O	3495
4.	10 cc. „ + 0,25 cc. „ + 1,75 cc. H_2O	3545
5.	10 cc. „ + 0,50 cc. „ + 1,50 cc. „	3595
6.	10 cc. „ + 1,0 cc. „ + 1,0 cc. „	3635
7.	10 cc. „ „ „ + 0,25 cc. N/KCL + 0,75 cc. H_2O	3635
8.	10 cc. „ „ „ + 0,50 cc. „ + 0,50 cc. „	3575
9.	10 cc. „ „ „ + 0,75 cc. „ + 0,25 cc. „	3520
10.	10 cc. „ „ „ + 1,00 cc. „ —— ...	3475
11.	10 cc. „ „ „ + 1,25 cc. „ —— ...	3445
12.	10 cc. „ „ „ + 1,50 cc. „ —— ...	3385
13.	10 cc. „ „ „ + 1,75 cc. „ —— ...	3160

Fig. 8.



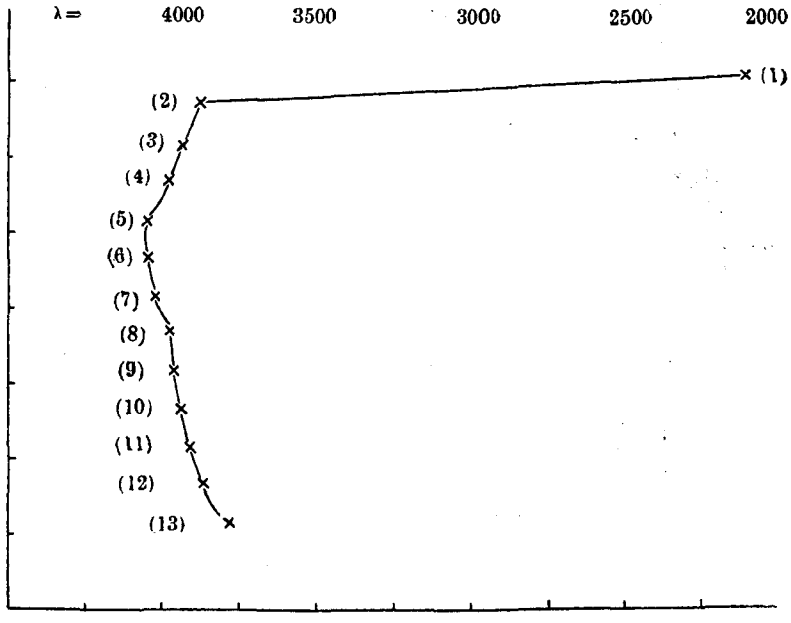
9. *The antagonistic action between $AlCL_3$ and $MgCL_2$ in lettuce juice.*

(The juice is the $\frac{1}{4}$ dilution: See Fig. 9 and Phot. I)

TABLE 9.

	Concentration of the solution.	Wave length (λ) of a boundary line of the absorbed ray.
1.	10 cc. H_2O + hydrogen lamp	2100
2.	10 cc. juice + 2 cc. H_2O	3870
3.	10 cc. ,, + 0,1 cc. N/10 $AlCL_3$ + 1,9 cc. H_2O	3905
4.	10 cc. ,, + 0,25 cc. ,, + 1,75 cc. H_2O	3975
5.	10 cc. ,, + 0,50 cc. ,, + 1,50 cc. ,, ...	4045
6.	10 cc. ,, ,, ,, + 0,1 cc. N/$MgCL_2$ + 1,4 cc. H_2O	4045
7.	10 cc. ,, ,, ,, + 0,25 cc. ,, + 1,25 cc. ,,	4020
8.	10 cc. ,, ,, ,, + 0,50 cc. ,, + 1,0 cc. ,,	3995
9.	10 cc. ,, ,, ,, + 0,75 cc. ,, + 0,75 cc. ,,	3975
10.	10 cc. ,, ,, ,, + 1,0 cc. ,, + 0,50 cc. ,,	3940
11.	10 cc. ,, ,, ,, + 1,25 cc. ,, + 0,25 cc. ,,	3920
12.	10 cc. ,, ,, ,, + 1,50 cc. ,, —— ...	3865
13.	10 cc. ,, ,, ,, + 1,75 cc. ,, —— ...	3755

Fig. 9.

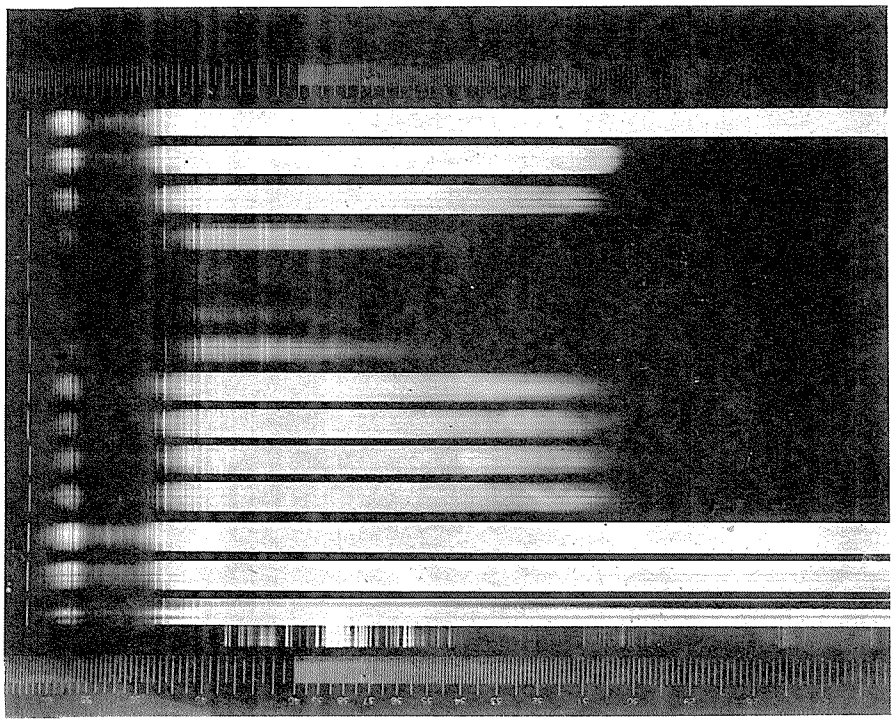


RESULTS.

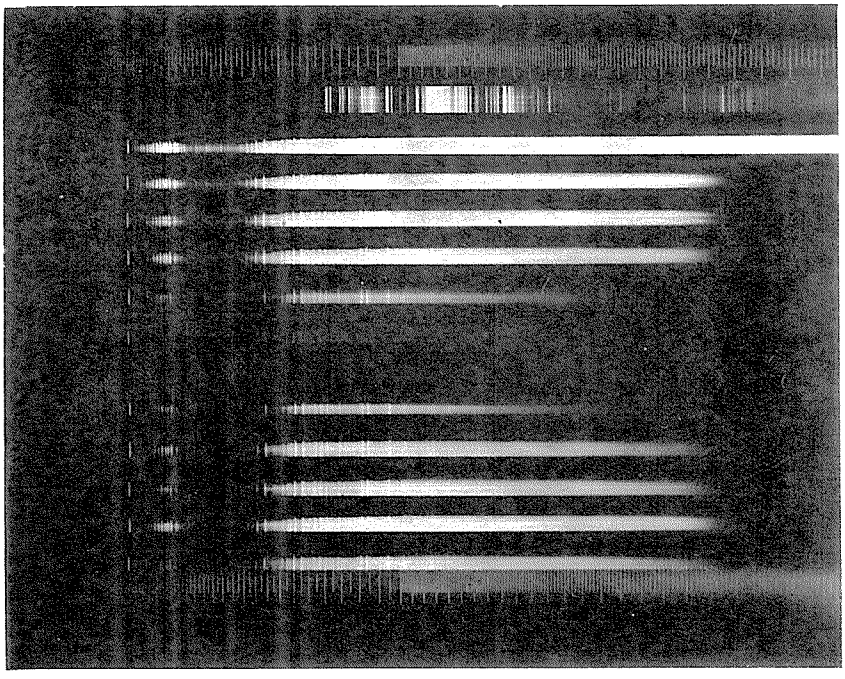
From these nine experiments it was observed that the following pairs of salts acted as antagonistic toward each other:

1. Zinc sulphate and calcium chloride solution in eggwhite,
2. Zinc sulphate and potassinm chloride solution in eggwhite,
3. Calcium chloride and potassium chloride in takadiastase,
4. Calcium chloride and magnesium chloride in takadiastase,
5. Calcium chloride and sodium chloride in takadiastase,
6. Zinc sulphate and calcium chloride in blood serum,
7. Zinc sulphate and sodium chloride in blood serum,
8. Calcium nitrate and potassium chloride in lettuce juice,
9. Alminium chloride and magnesium chloride in lettuce juice,

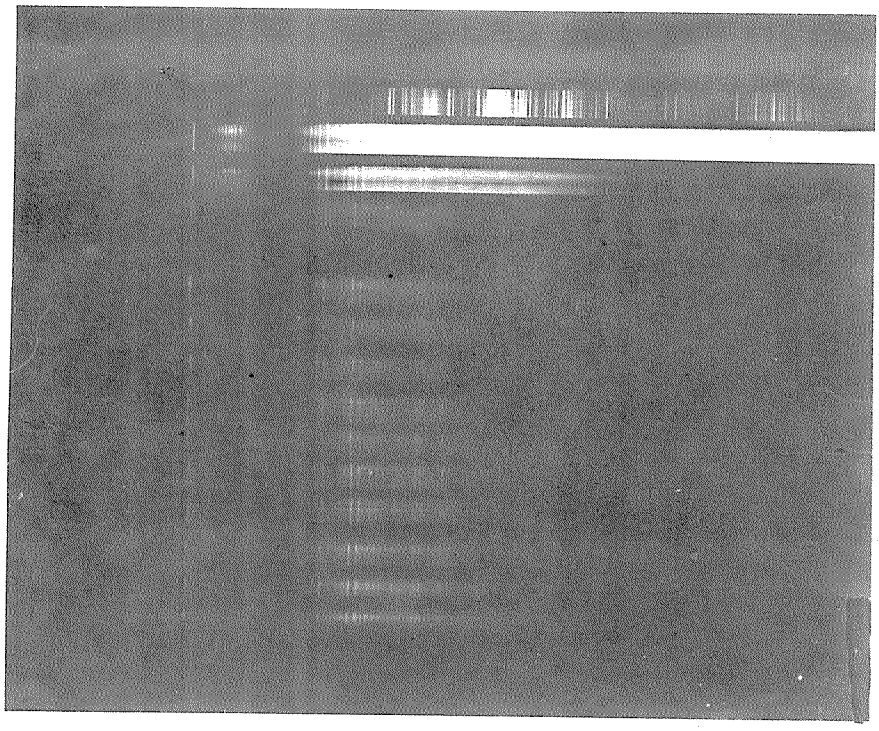
accordingly change in the state of a colloidal solution produced by one salt was reversed by another salt. This change must depend upon the dispersion, the form or the structure of the particles, because in our experiments we used the same organic colloidal solution of the same concentration.



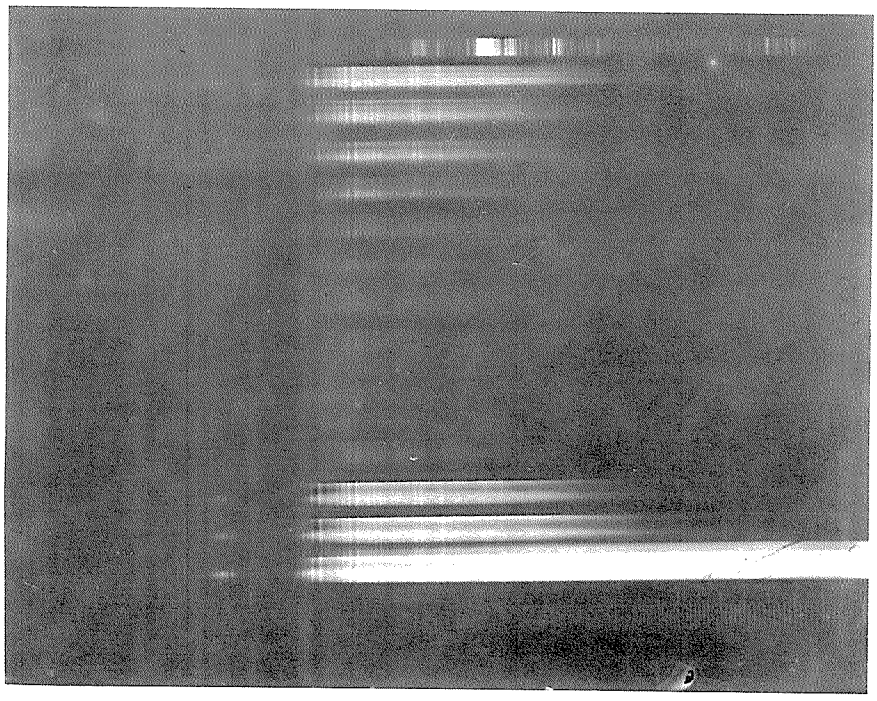
Phot. A.



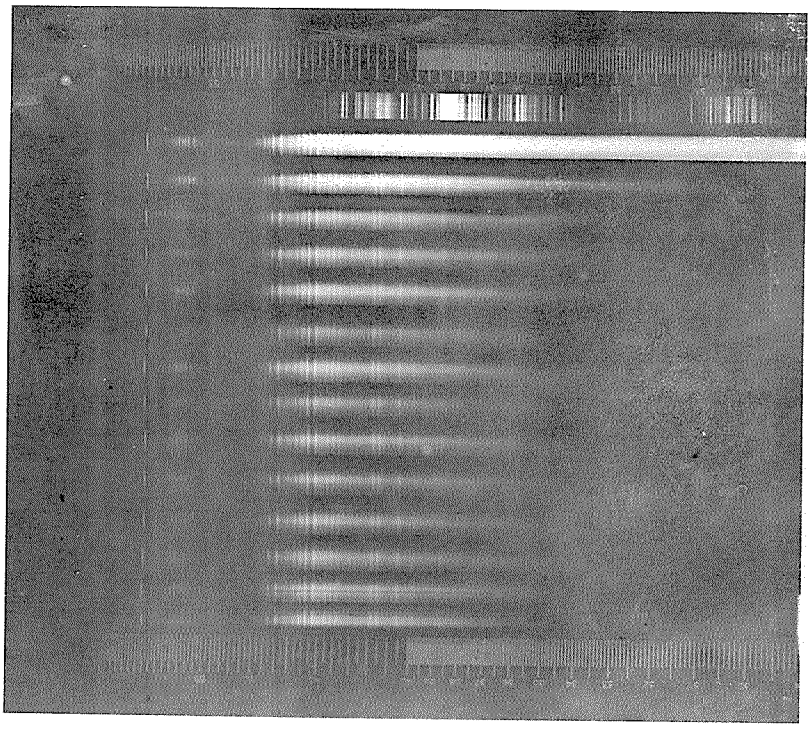
Phot. B.



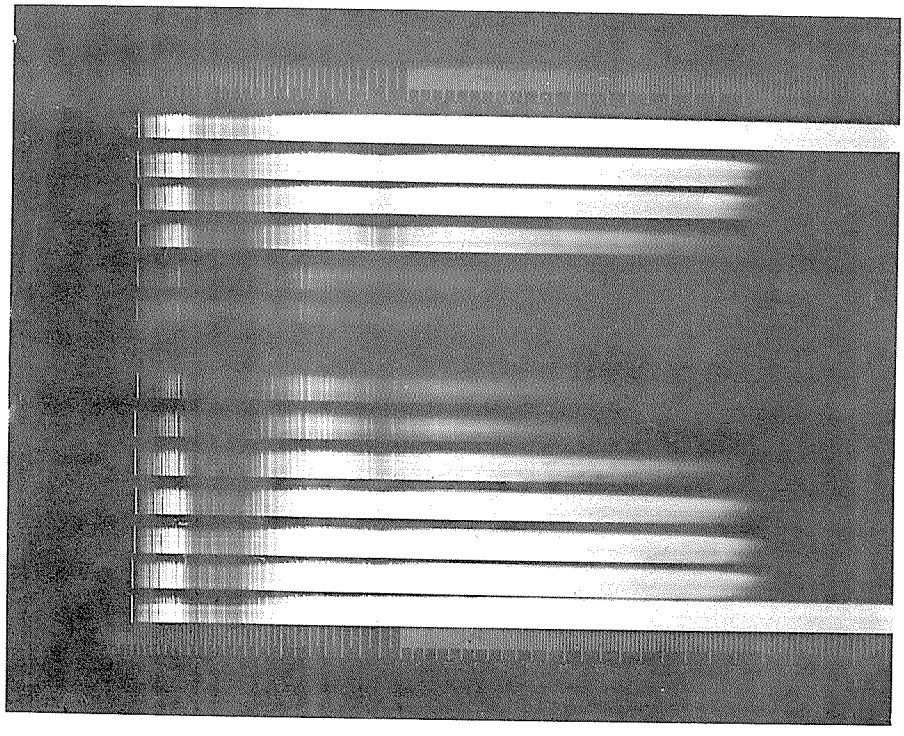
Phot. C.



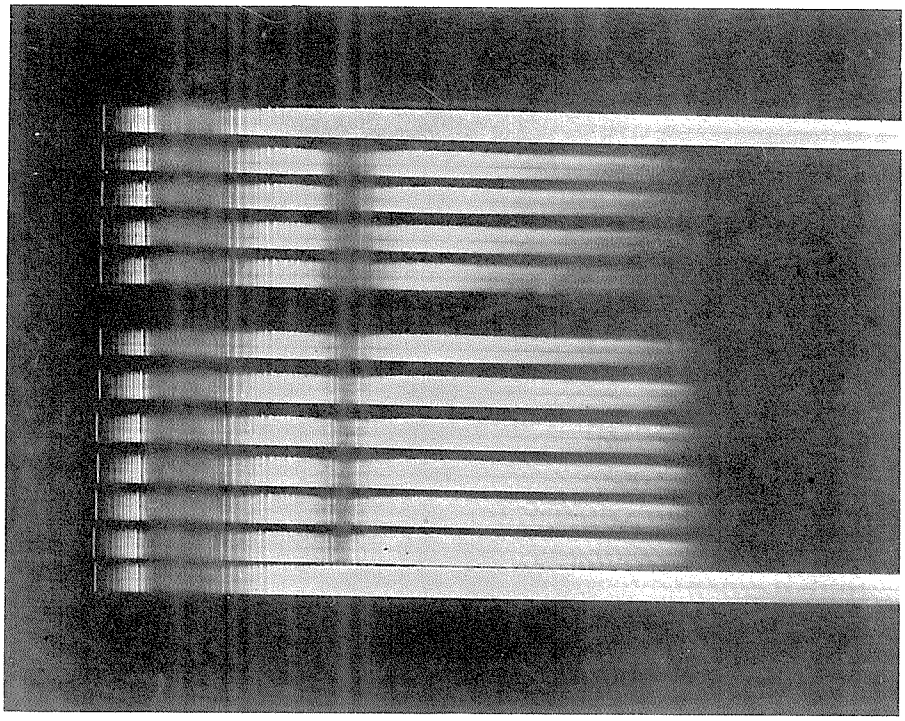
Phot. D.



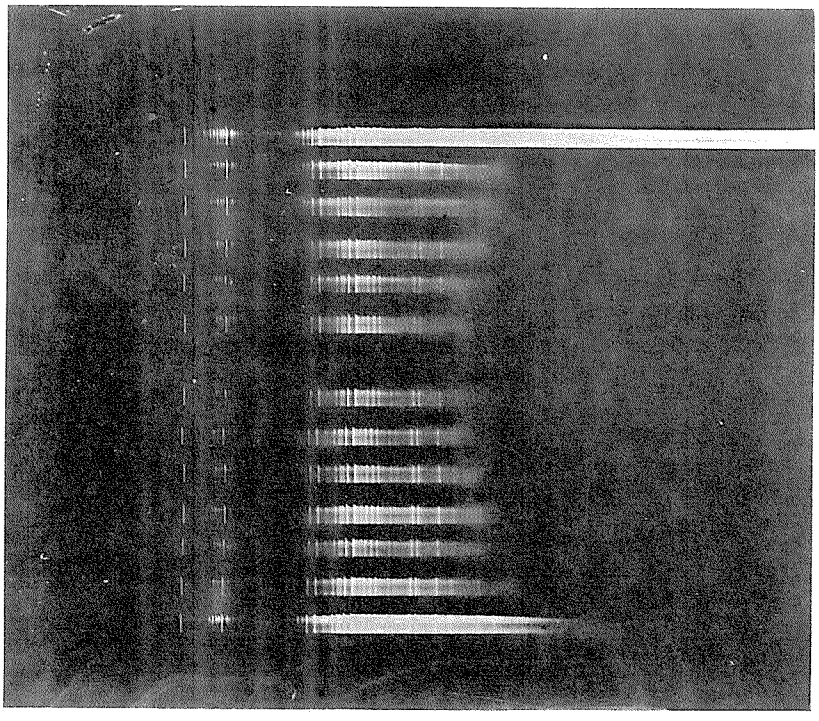
Phot. E.



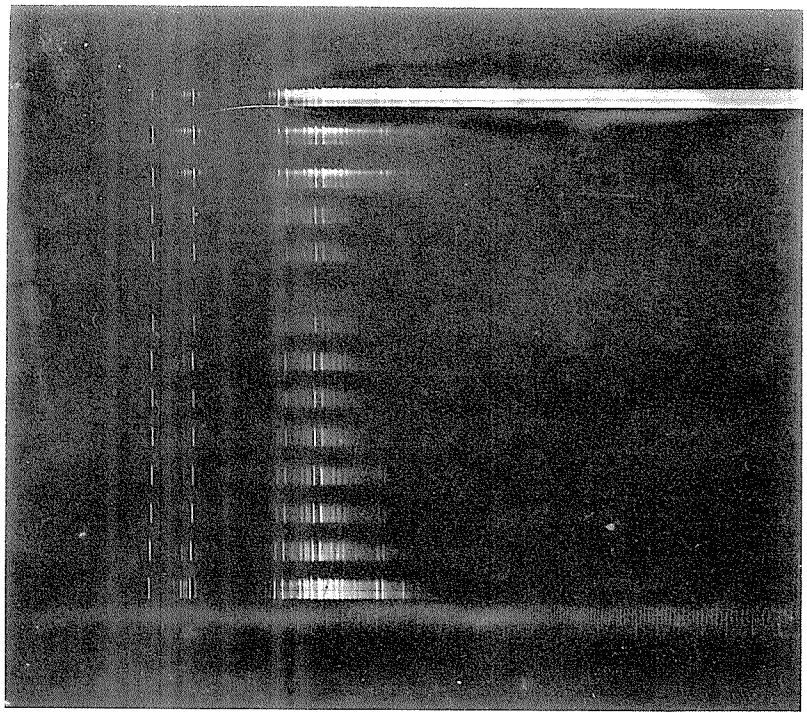
Phot. F.



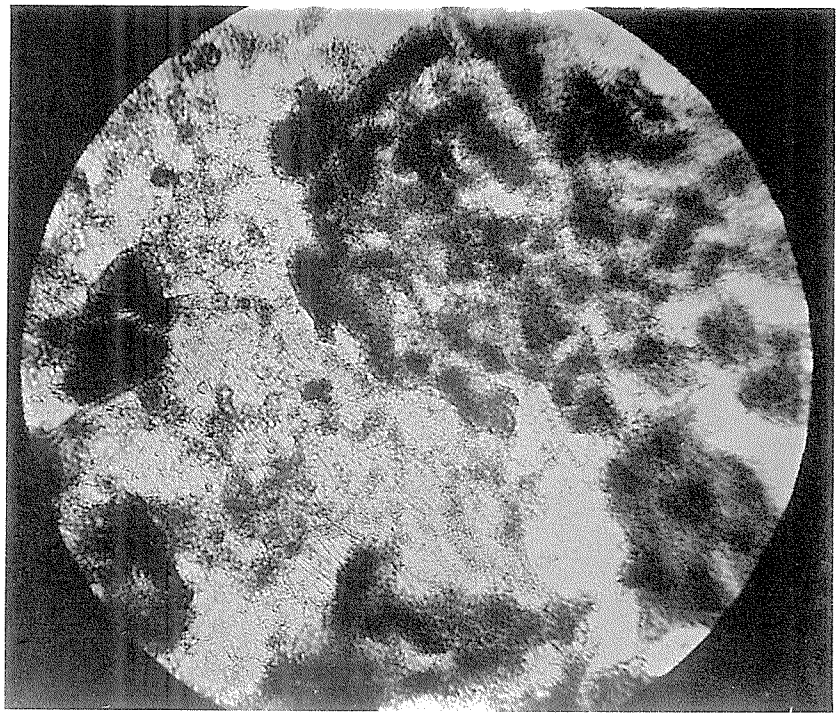
Phot. G.



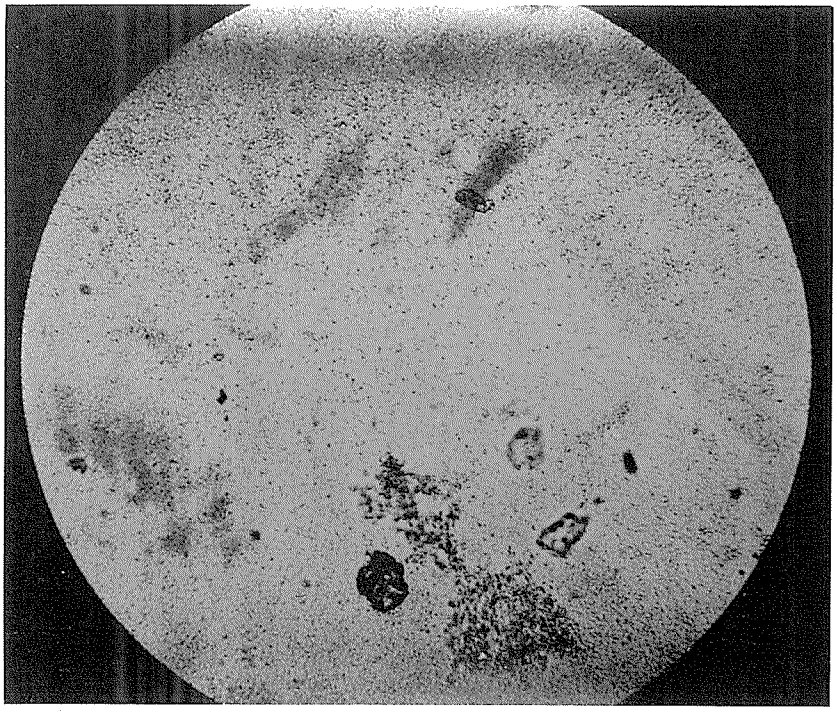
Phot. H.



Phot. I.



Phot. J.



Phot. K.

In order to explain this phenomenon, these changes were observed under an ultramicroscope and the following results obtained (see phot. J and K which are the examples of blood serum).

1. These dilute colloidal solutionss showed one or two submicrones which had Brownian movement in the dark field of the ultramicroscope.

2. If these organic colloidal solution were mixed with zinc sulphate, calcium chloride, calcium nitrate or alminium chloride, their particles formed aggregates of twenty—twenty five submicrones and became heterogeneous and their movement stopped.

3. If these organic colloidal solutions containing zinc sulphate calcium chloride, calcium nitrate or alminium chloride were treated with calcium chloride-, magnesium chloride, potassium chloride or sodium chloride, the aggregated particles became free and homogenous as original colloidal solutions.

From these results we conclude that the antagonistic action between two different salts for these organic colloidal solutions was caused by reversal of the dispersion of these colloidal solution and of the change of the form and structures of particles.

SUMMARY.

From the results of the ultraviolet spectroscopical investigation on organic colloidal solutions, we conclude that the antagonistic action between two salts was caused reversal of the dispersion of these colloidal solutions and the change of the forms and structures of particles.

The author wishes to express his hearty thanks to Prof. STIEGLITZ, Dr. WENDT in the Kent chemical laboratory, university of Chicago and Dr. M. FISCHER in the medical college of Cincinati, for the valuable suggestions they give in carrying out this research.

On the Spectrochemical Reaction of Methylfurfurol and Oxymethyl furfurolphloroglucid.

By

Tetsutaro Tadokoro.

The color reaction of methylfurfurol is always used to detect the presence of methylpentose or methylpentosan in a natural stuff and for this purpose, the most useful method was reported by TOLLENS and OSHIMA[1]. After that time, many investigaters used this method to determine the presence of methylfurfurol in a sample prepared by distillation of natural stuff with 1,06 hydrochloric acid. A few cc. of the distillate was mixed with the same volume of conc. hydrochloric acid and phloroglucin and the solution became a redish yellow color. After standing 5 minutes in a cool place, it was filtered and the filtrate was exermined with a spectroscope. If we could observe a dark absorption band between the green and blue of the spectrum near the "F" line, then the presence of methylfurfurol in the sample was indicated. Recently, YUKAWA[2] reported that this color reaction was similar to that of oxymethylfurfurol which was prepared by hydrochloric distillation of glucose and fructose and condensation products of glucose and of fructose. Afterwards we[3] found out a difference between the color reaction of methyl- and of oxymethylfurfurol-phloroglucid in their absorption bands. Our observation was made by the naked eye with an ordinary spectroscope but it was not determined exactly. Therefore we investigated this problem with an ultraviolet-spectroscope (1. D. 15 made by Adam Hilgard in London) and with the panchromatic dry plate (made in Eastman Kodak Co., Rochester, N.Y.) The detail of this manipulation was described on the former report (p. 38) and as a source of

1) TOLLENS and OSHIMA:—Ber. deuts. Chem. Ges., 34, 1425 (1901).

2) YUKAWA:—Journ. Tokyo chem. soc., 38. p. 429 (1917).

3) OSHIMA and TADOKORO:—Journ. Tokyo chem. soc., 39, p. 23 (1918).

light we used a tungusten lamp and an iron arc. The wave-length of the boundary line of the absorption band of these color reactions was determined not only in the visible portion of the spectrum but in the ultraviolet portion.

1. COMPARISON OF DIFFERENT COLOR REACTIONS OF METHYL- AND OXYMETHYLFURFUROL.

To get a general idea of both color reactions, we will consider briefly several color reactions which have already been reported by many authers and compare them with each other as follows:

A. Methylfurfurol.

1) A green color was observed on treating with alcohol and sulphuric acid by MAQUENNE[1].

2) A yellow color was observed on treating with con. hydrochloric acid by WIDTSOE and TOLLENS[2].

3) A redish yellow color was observed on treating with conc. hydrochloric acid and phloroglucin by TOLLENS and OSHIMA (l.c.) and it was observed that this color showed a dark absorption band between the green and blue of the spectrum near the "F" line.

B. Oxymethylfurfurol.

1) SELIWANOFF'S reaction:—When the solution is treated with hydrochloric acid and resorcin, it becomes red in color and this color shows a distinct absorption band in the blue of the spectrum near the "F" line[3].

2) A brick red color was observed on treating with aniline acetate by MÜLLER and TOLLENS[4].

3) "Zinnober roth" color was observed on treating with the same volume of conc. hydrochloric acid and phloroglucine by MÜLLER and TOLLENS (l.c.).

2. PREPARATION OF METHYL- AND OXMETHYL-FURFUROL.

A. The preparation of methylfurfurol:—0,1 gr. of rhamnose was distilled with 1,06 hydrochloric acid by TOLLENS and ELLET'S methode

1) Compt. R. Bd., 109, 573, 1889.
2) Ber. deuts. Chem. Ges., 33, 146, 1900.
3) Ber. deuts. Chem. Ges., 20, 181, 1887.
4) Ber. deuts. Chem. Ges., 37, 304, 1904.

until 400 cc. of the distillate was obtained. This distillate was devided into two equal portions and one of them was used to determine the quantity of methylfurfurol-phloroglucid and the other portion was used for the purpose of the spectro-chemical investigation of this color reaction. The quantity of methylfurfurol-phloroglucid which was distilled from 0,05 gr. of rhamnose was 0,01 gr. and the concentration of the original solution of methylfurfurol in our experiment corresponds to 0,01 gr. of methylfurfurol-phloroglucid in 200 cc.

B. The preparation of oxymethylfurfurol:—50 cc. of 30 % cane sugar in 3 % oxalic acid solution was digested three hours in three atmospheric pressure, neutralised with calcium carbonate, clarified with lead acetate and the oxymethylfurfurol was extracted by shaking about 6 times with acetic ester[1]. This purified oxymethylfurfurol was dissolved in 300 cc. of 1,06 hydrochloric acid and divided into two equal portions and one of them was used to determine the quantity of oxymethylfurfurol-phloroglucid. The concentration of the original solution in our experiment was 0,1042 gr. of phloroglucid in 150 cc.

3. THE ABSORPTION BANDS OF METHYL- AND OXYMETHYL-FURFUROL-PHLOROGLUCID,

5 MINUTES AFTER REACTION.

In this experiment, we used a glass-cell 10 mm. thick and a tungsten electric lamp of 100 candle-power and every photograph with thirty seconds exposure in the following different concentration of each solution

A. Methylfurfurol-phloroglucid.

(See Curve I. and Phot. A.)

TABLE 1.

("N" represents original concentration of the solution.)

Numbers.	Concentration of solution.	Wave length of a boundary line of the absorbed ray
1	Water only	3145
2	1 cc. phlorogl. sol.+4 cc. HCL+4 cc. H_2O	3165
3	„ +4 cc. HCL+4 cc. N/8	3270—4525—4665
4	„ „ +4 cc. N/4	3275—4500 4685
5	„ „ +4 cc. N/2	3285—4435 4700
6	„ „ +4 cc. N	3285—4355—4750

1) DÜLL:—Chz., 19, 216. KIERMAYER:—Chz., 19, 1003.

B. Oxymethylfurfurol-phloroglucid.

(See Curve II. and Phot. A.)

TABLE 2.

Numbers.	Concentration of solution.	Wave length of a boundary line of the absorbed ray.
1	1 cc. phlorogl. sol. + 4 cc. HCL + 4 cc. N/40	3410
2	„ „ + 4 cc. N/20	3550
3	„ „ + 4 cc. N/10	3672
4	„ „ + 4 cc. N/5	4520

C. Qxymethylfurfurol-phloroglucid.

(See Curve III. and Phot. B.)

TABLE 3.

1	Water only	3305
2	1 cc. phlorogl. sol. + 5 cc. HCL + 5 cc. H_2O	3395
3	„ „ + 5 cc. N/20	3735
4	„ „ + 5 cc. N/15	3795
5	„ „ + 5 cc. N/10	4235
6	„ „ + 5 cc. N/5	4275
7	„ „ + 5 cc. N/2,5	4425 – 5175 – 5410
8	„ „ + 5 cc. N/2	4975 5500
9	„ „ + 5 cc. N	5875
10	„ „ + 5 cc. 1,5 N	6400
11	„ „ + 5 cc. 2 N	6400 – 6750

From these results we can conclude that there is a clear distinction between the absorption bands of methylfurfurol- and oxymethylfurfurol-phloroglucid in hydrochloric acid solution five minutes after the reaction. The adsorption bands of methylfurfurol-phloroglucid were observed in two parts in the visible portion of spectrum, one is in the part between $\lambda = 3200 - 3300\ \mu\mu$. and another is between $\lambda = 4355 - 4750\ \mu\mu$ but the former varies slightly, while the latter increases from 4525 – 4665 to 4355 – 4750 when the concentration is increased. The absorption band of oxymethylfurfurol-phloroglucid starts from 3550 and grows wider in the direction of longer waves and at last make up a secondary absorption band between $\lambda = 4975 - 5500\ \mu\mu$. But it is not the same position that of methylfurfurol-phloroglucid $\lambda = 4355 - 4750$.

There is a clear distinction between the absorption band of methyl- and oxymethylfurfurol-phloroglucid.

4. THE ABSORPTION BAND OF METHYL- AND OXYMETHYLFURFUROL-PHLOROGLUCID,

HALF AND TWO MINUTES AFTER THE REACTION.

In this experiment we used a quartz-cell 12 mm. thick and an iron arc with 250 volts and 4 amperes of direct current and took photograph with seven seconds exposure of following different concentrations.

D. Methylfurfurol-phloroglucid.

(See Curve IV. and Phot. C.)

TABLE 4.

Numbers.	Concentration of solution.	Wave length of a boundary line of the absorbed ray.
1	Water only	2205
2	1 cc. phlorogl. sol. + 5 cc. HCL + 5 cc. H_2O	2485
3	„ „ + 5 cc. N/2	2635–3190–4500–4775
4	„ „ + 5 cc. N/2 (30 seconds)	2635–3170–4375–4525
5	„ „ + 5 cc. N/2 (1 minutes)	2635–3170–4305–4900
6	„ „ + 5 cc. N/2 (2 minutes)	2635– 4235–5075

E. Oxymethylfurfurol-phloroglucid.

(See Curve V. and Phot. D.)

TABLE 5.

1	1 cc. phlorogl. sol. + 5 cc. HCL + 5 cc. N/40	2445
2	„ „ + 5 cc. N/20	2490
3	„ „ + 5 cc. N/10	2520–4500–4800
4	„ „ + 5 cc. N/5	3000–4160–5075

From these results we could conclude that during five minutes after reaction, methylfurfurol- and oxymethylfurfurol-phloroglucid change their color reactions and in this time they showed the same absorption

band in visible portion of spectrum but that it is not same in ultraviolet portion as shown above.

The color reaction of methylfurfurol-phloroglucid has two absorption bands; one is in the visible portion between $\lambda=4235-5075\ \mu\mu$ and the other is in the ultraviolet portion between $\lambda=2485-3835\ \mu\mu$. The former grows wider during the time of the reaction (during five minutes) but the latter becomes faint after two minutes of the reaction.

In the case oxymethylfurfurol phloroglucid, there is no definite band in the ultraviolet portion i.e. $\lambda=3170-2635\ \mu\mu$ but the boundary line of absorption band increases from $\lambda=2445$ to $\lambda=3000\ \mu\mu$. Therefore we could also distinguish between the reactions even five minutes after reaction in the ultraviolet portion of spectrum.

SUMMARY.

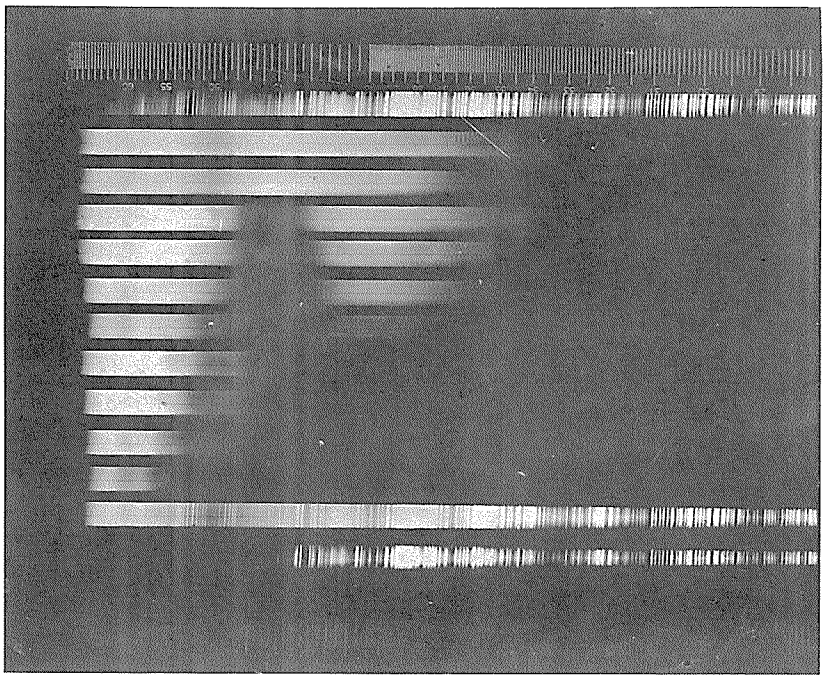
1. There is a clear distinction between the absorption band of methylfurfurol- and oxymethylfurfurol-phloroglucid in hydrochloric acid solution five minutes after reaction began. A concentrated solution of oxymethylfurfurol-phloroglucid makes an absorption band in a position near, but not identical with that of methylfurfurol-phloroglucid in the visible spectrum- i.e. the former is between $\lambda=4355-4750\ \mu\mu$ and the latter is between $\lambda=4955-5500\ \mu\mu$.

2. During five minutes after the reaction began, there is also clear distinction between both color reactions. In the ultraviolet portion of spectrum, the methylfurfurol-phloroglucid shows clearly a wide absorption band between $\lambda=2495-2635\ \mu\mu$ during two minutes after the reaction began. But oxymethylfurfurol-phloroglucid has no definite absorption band in this portion, instead the boundary line of the absorption increases gradually from $\lambda=2445$ to $3000\ \mu\mu$.

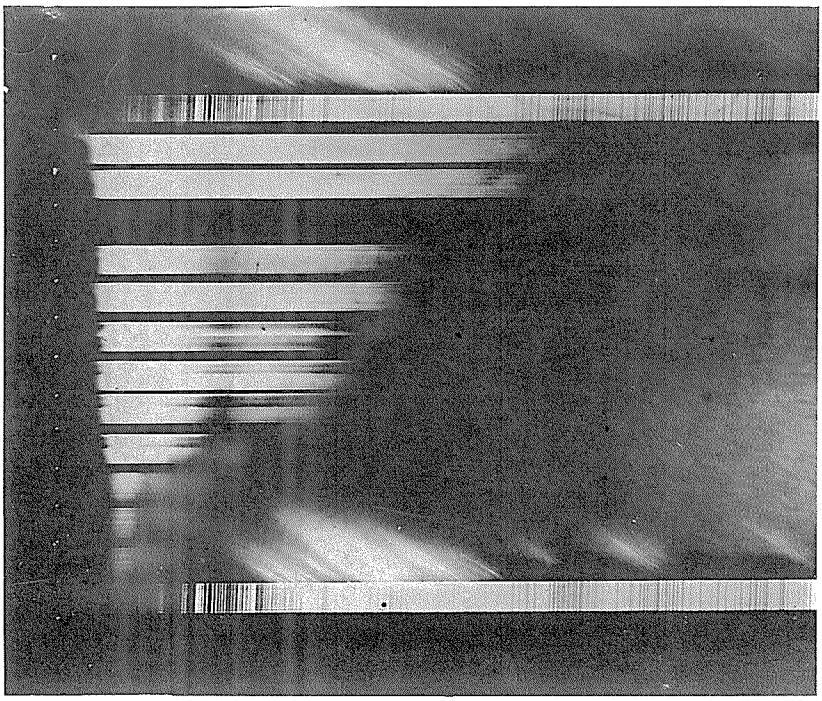
3. Here we summarise the above results on the following table.

	5 minutes after reaction (visible)	½–2 minutes after reaction (invisible)	½–2 minutes after reaction (visible)	Change of the position of absorption band (visible)	Ratio of concentration appeared the band
Methylfurfurol-phloroglucid	4300–4800	2400–3800	4200–5000	no change	1
Oxymethylfurfurol-phloroglucid	5000–5500	——	4100–5000	from 4100–5000 to 5000–5500	ca. 4

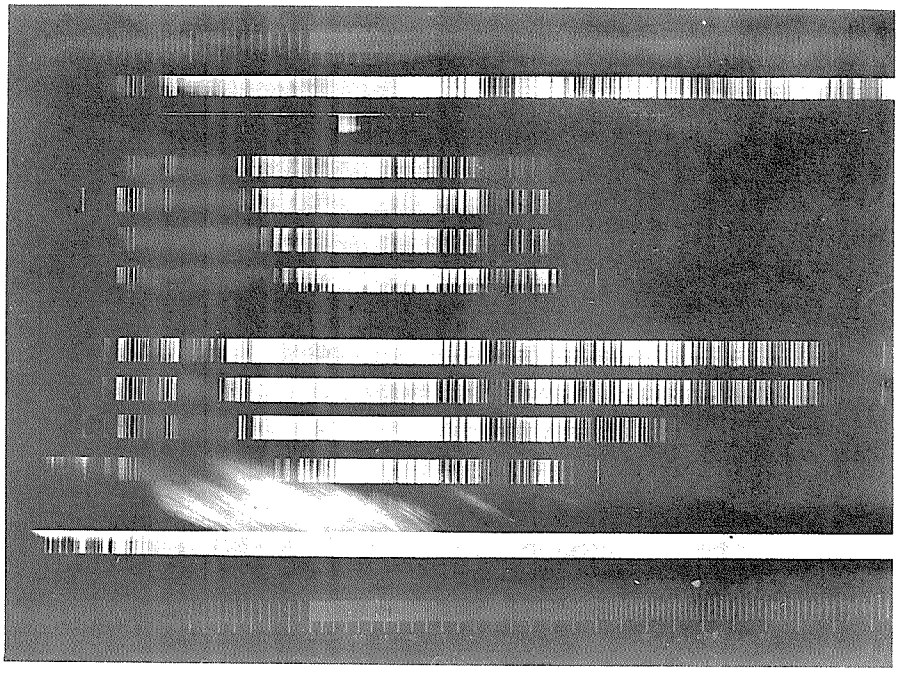
The author wishes to express his hearty thanks to Prof. STIEGLITZ and Dr. WENDT in the Kent chemical laboratory, university of Chicago for the valuable suggestions they give in carrying out this research.



Phot. A.



Phot. B.



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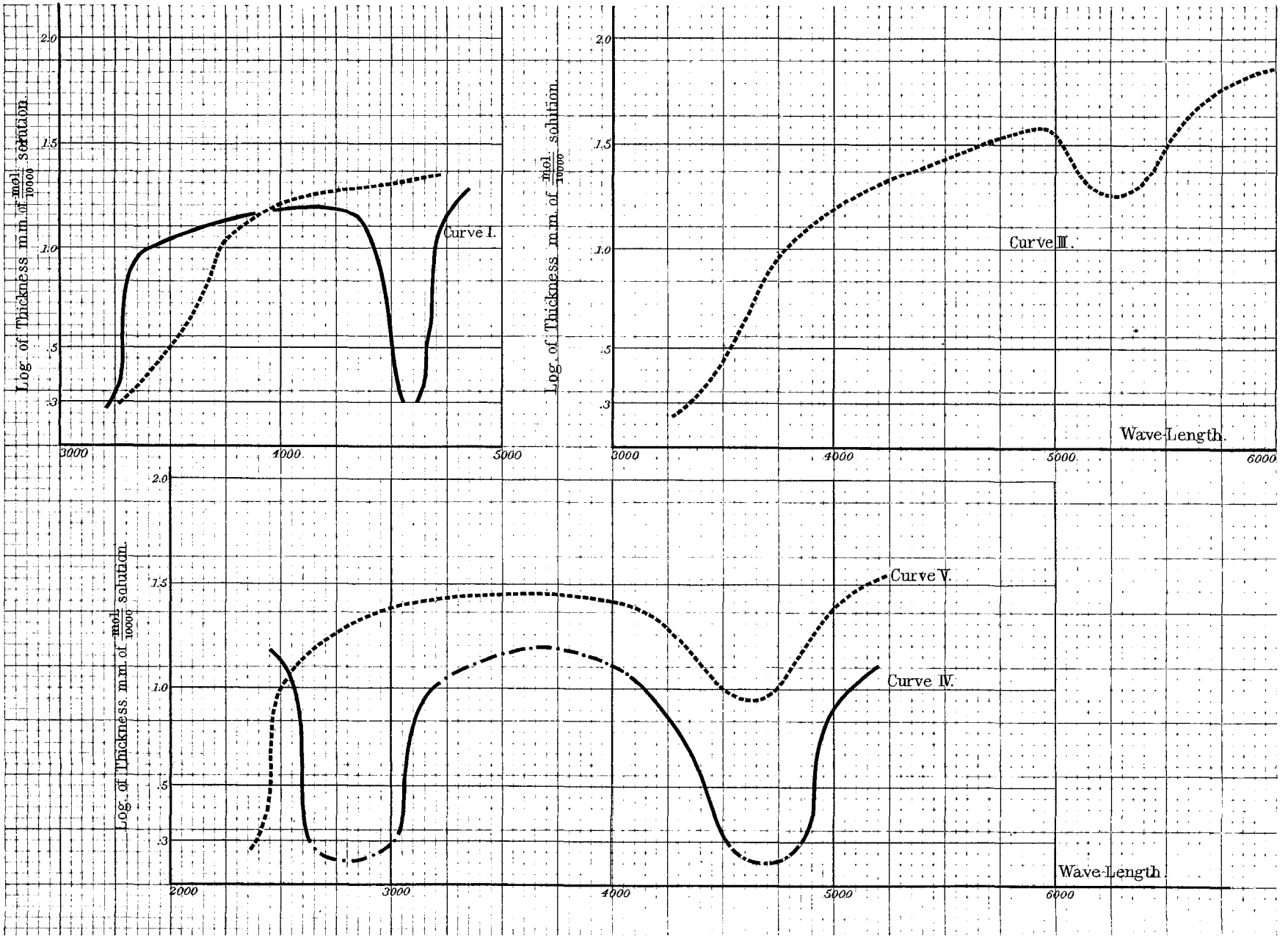
Log. of Thickness m.m. of mol/10000 solution.
2.0
1.5
1.0
.5
.3
3000
4000
5000
Curve I.
Log. of Thickness m.m. of mol/10000 solution.
2.0
1.5
1.0
.5
.3
3000
4000
5000
6000
Curve III.
Wave-Length.
Log. of Thickness m.m. of mol/10000 solution.
2.0
1.5
1.0
.5
.3
2000
3000
4000
5000
6000
Curve V.
Curve IV.
Wave-Length.

ERRATA.

Page.	Line.				
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38	7	„	factor*s*	„	factor
43	1	„	$NaCL_2$	„	NaCL
48	4	„	Potassi*n*m	„	Potassium
49	4	„	solutions*s*	„	solutions
51	1	„	tung*u*sten	„	tungsten