solubility range of the respective salts. The results confirm our earlier conclusions that there is a definite Hofmeister series of anions (I > Br > Cl) in their effects on the optical rotation of gelatin. There is also a definite Hofmeister series for cations (Li > Cs > Rb > Na) but the effects of cations are much less in magnitude than those of the anions.

In the absence of added salts, the optical rotation of the gelatinates of the alkali metals increases slightly with atomic number to a maximum rotation with potassium, after which the rotation slightly decreases.

GENEVA, N. Y. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Influence of Neutral Salts on the Optical Rotation of Gelatin. IV. Rotatory Dispersion of Gelatin in Sodium Iodide Solutions[1]

BY D. C. CARPENTER AND F. E. LOVELACE

Despite the large amount of work on the rotatory dispersion of optically active substances there has been comparatively little done on the proteins. Hafner[2] discussed briefly the measurements he made at four different wave lengths in the visible on serum albumin and serum globulin. Hewitt[3] studied several proteins, making measurements at four wave lengths in the visible. Hewitt confined himself to graphing the reciprocal of the specific rotation against the square of the wave lengths and obtained straight lines which showed only that the dispersion may be expressed by a single term of Drude's equation $[\alpha]_\lambda = \sum \frac{k_n}{\lambda^2 - \lambda_0^2}$. From Hewitt's work one would conclude that absorption bands somewhere below 2700 Å. governed the rotatory dispersion of proteins.

Hansen[4] investigated the rotatory dispersion of egg albumin as influenced by protein concentration, concentration of ammonium sulfate added, *p*H and temperature. Hansen was the first investigator to calculate dispersion constants from his data. He concluded that λ_0 was largely independent of *p*H, temperature and concentration of added salt and protein, while *k* varied under most experimental conditions.

The rotatory dispersion of gliadin has been studied by Haugaard and Johnson[5] at three different wave lengths and by Wiles and Gortner[6] at six wave lengths. In the former paper the workers recognized that the presence of lithium chloride, as well as changes in *p*H, greatly influenced the rotations. They pointed out that the effect of lithium chloride might be due to complex salt formation or to changed conditions of dissociation of the protein or to a combination of these effects. However, their data were more or less fragmentary and evaluation of the dispersion constants was not attempted. Other alkali halides, potassium iodide, potassium bromide and sodium chloride were used by Wiles and Gortner, who confined themselves to showing that a linear relation existed between the reciprocal of the observed rotations and the square of the wave lengths used.

The purpose of the present investigation was to study the rotatory dispersion of gelatin in sodium iodide solutions, primarily to ascertain the cause of the rapid decrease in rotation experienced with iodide salts at low temperatures.

Experimental

In the present work the specific rotations of gelatin solutions at 0.5 and 40° were measured at five different wave lengths in the visible spectrum, *viz.*: red lithium line, λ = 6707.86 Å.; sodium D line, λ = 5892.617 Å. (optical mean); yellow mercury line, λ = 5780.13 Å. (optical mean); green mercury line, λ = 5460.73 Å.; and the deep blue mercury line, λ = 4358.34 Å. A quartz mercury arc lamp was used as the source for all mercury lines and an electric arc between carbons the cores of which were filled with powdered sodium glass or lithium carbonate was the source of the sodium and lithium lines, respec-

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 97. Abstracted from a thesis presented to the Graduate School of Cornell University by F. E. Lovelace in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hafner, *Biochem. Z.*, **166**, 424 (1925).

[3] Hewitt, *Biochem. J.*, **21**, 216 (1927).

[4] Hansen, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 10 (1927).

[5] Haugaard and Johnson, *ibid.*, **18**, No. 2 (1930).

[6] Wiles and Gortner, *Cereal Chem.*, **11**, 36 (1934).

TABLE I

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM IODIDE AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaI, molal	Density at 25°	pH	Levo degrees									
				λ6707.86 Å.		λ5892.617 Å.		λ5780.13 Å.		λ5460.73 Å.		λ4358.34 Å.	
				(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.000	1.0023	5.95	3.83	248.01	5.14	332.84	5.38	348.38	6.15	398.24	10.86	703.23
2	.350	1.0436	6.02	3.89	241.95	5.23	325.30	5.47	340.23	6.26	389.36	11.04	686.67
3	.851	1.1011	5.88	3.31	195.09	4.45	262.29	4.65	274.07	5.32	313.56	9.39	553.46
4	1.001	1.1316	5.99	2.89	165.78	3.89	223.13	4.07	233.46	4.65	266.73	8.20	470.36
5	1.121	1.1484	5.96	2.48	140.15	3.33	188.18	3.48	196.66	3.98	224.91	7.02	396.72
6	1.251	1.1676	5.87	2.10	116.74	2.84	157.88	2.96	164.55	3.38	187.89	5.97	331.87
7	2.001	1.2940	5.85	1.63	81.76	2.19	109.85	2.29	114.87	2.62	131.42	4.62	231.74
8	2.578	1.4097	5.64	1.58	72.74	2.12	97.60	2.22	102.21	2.54	116.19	4.48	206.25
9	3.295	1.5824	5.63	1.46	59.89	1.96	80.40	2.05	84.09	2.35	96.39	4.15	170.23

TABLE II

SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM IODIDE AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaI, molal	Density at 25°	pH	Levo degrees									
				λ6707.86 Å.		λ5892.617 Å.		λ5780.13 Å.		λ5460.73 Å.		λ4358.34 Å.	
				(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.000	1.0023	5.95	1.71	110.73	2.30	148.94	2.41	156.06	2.75	178.07	4.86	314.71
2	.350	1.0436	6.02	1.69	105.12	2.27	141.19	2.38	148.03	2.72	169.18	4.80	298.55
3	.851	1.1011	5.88	1.66	97.84	2.23	131.44	2.33	137.33	2.67	157.37	4.71	277.61
4	1.001	1.1316	5.99	1.66	95.22	2.23	127.92	2.34	134.23	2.67	153.15	4.72	270.74
5	1.121	1.1484	5.96	1.65	93.24	2.22	125.46	2.32	131.11	2.66	150.32	4.69	265.04
6	1.251	1.1676	5.87	1.64	91.16	2.20	122.30	2.31	128.41	2.64	146.76	4.65	258.49
7	2.001	1.2940	5.85	1.59	79.75	2.14	107.34	2.24	112.36	2.56	128.41	4.52	226.73
8	2.578	1.4097	5.64	1.55	71.36	2.09	96.22	2.18	100.37	2.50	115.10	4.40	202.57
9	3.295	1.5824	5.63	1.45	59.48	1.95	79.98	2.04	83.68	2.34	95.98	4.13	169.41

tively. To eliminate all lines but the desired wave length the light was passed through either appropriate Corning glass filters or through a glass absorption cell 1 cm. thick containing an appropriate dye solution or through both of these as required to give monochromatic light before entering the polariscope. The filters employed were as follows: Li red line, Corning Red G5 + alkaline solution containing brom thymol blue in cell; Na D line, Corning Green G701C1 + saturated alcoholic solution of Sudan IV in cell; Hg yellow line, Corning Yellow G34-O through which green and blue Hg lines do not pass; Hg green line, aqueous solution of "Light Green SF" dye, 0.1575 gm. per liter, in cell; Hg blue line, Corning Blue G585 through which yellow and green lines do not pass. To ascertain the wave lengths actually transmitted in each case, the light which reached the eyepiece of the polariscope was checked with a spectroscope.

The procedure for preparation of solutions and for measurement of rotations, density, pH, etc., was the same as has been described before.[7] The gelatin concentration of these solutions was 0.7704 g. per 100 g. of solution.

Discussion and Conclusions

In Tables I and II are given our data for 0.5 and 40°, respectively, for the various wave lengths employed. In Figs. 1 and 2 these data are shown graphically, plotting the reciprocal of specific rotation against the squares of the wave lengths at which these rotations were obtained. It is seen that the relationship is linear, which means that a single-term Drude equation will adequately express our results. Each straight line on these graphs represents the rotatory dispersion of a gelatin solution containing a definite quantity of sodium iodide.

It will be seen in both graphs that each straight line cuts the x-axis at the same point. This point represents λ^2_0 and graphically locates the absorption band of gelatin at 2200 Å. The same numerical value for λ_0 was obtained by solving our data by the method employed by Lowry and Owen.[8] So far as can be found in the visible spectrum the rotatory dispersion of gelatin dissolved in sodium iodide solutions obeys a single term of Drude's law.

That gelatin has a tremendous absorption in the neighborhood of 2200 Å. was observed in this Laboratory several years ago (D.C.C.). Although the head of the absorption band for gelatin could not be definitely determined, the graph of the extinction coefficient for gelatin (curve 2) is

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(7) Carpenter and Lovelace, THIS JOURNAL, **57**, 2337 (1935).

(8) Lowry and Owen, *Trans. Faraday Soc.*, **26**, 371 (1930).

shown in Fig. 3. In this figure we have also plotted the absorption spectrum of sodium iodide (curve 1) recalculated from the data of Fromherz and Menschick.[9] The head of the absorption band for aqueous sodium iodide is located at 2225 Å. from these data. While the head of the absorption band for gelatin was not definitely determined it seems safe to say that the absorption is very great in the neighborhood of 2200 Å., which agrees with the position of the band calculated from our dispersion data.

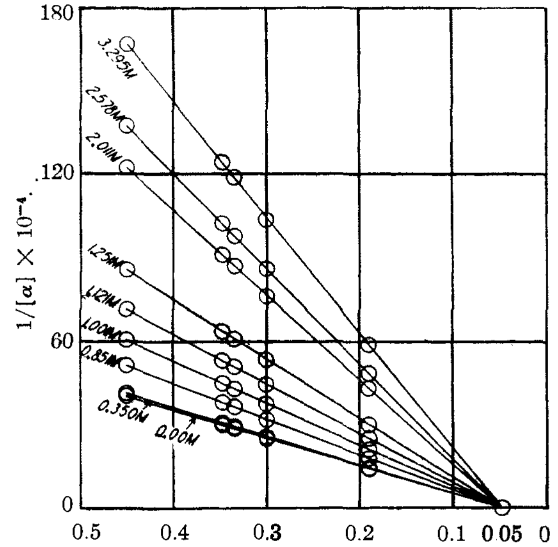

Fig. 1.—Graph of reciprocal of specific rotation *versus* wave length squared at (0.5°).

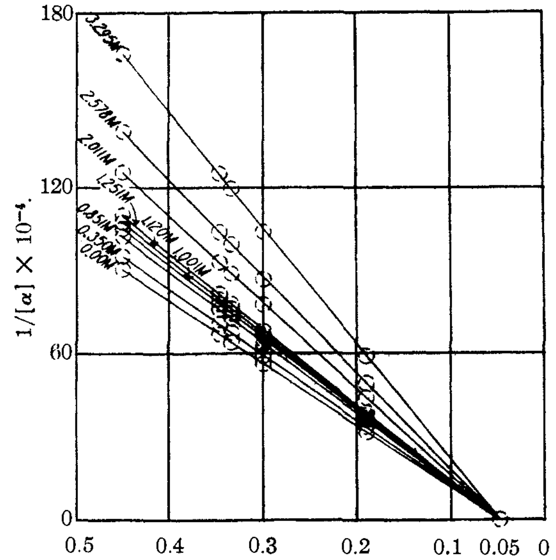

Fig. 2.—Graph of reciprocal of specific rotation *versus* wave length squared at (40°).

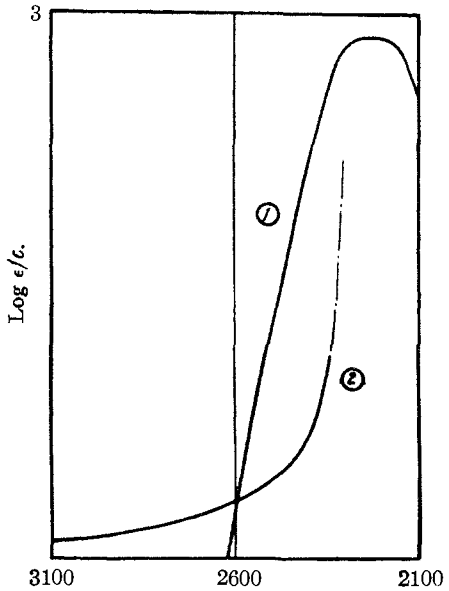

Fig. 3.—Extinction coefficient of aqueous gelatin (2) and sodium iodide solutions (1).

The values of k, numerator in the Drude equation, were calculated for each concentration of sodium iodide and appear in Table III and are graphed in Fig. 4. At 40° the k values bear a linear relation to the concentration of sodium iodide as given by the equation

$$k_{40^\circ} = 44.5170 - 6.220C_{\mathrm{NaI}} \qquad (1)$$

At 0.5° the curve for the k values is made up of two parallel straight lines at the extreme ends as salt concentration is varied, united by a curve which resembles the general type of curve representing a dissociation or association process. In the straight line portion of the curve the k values bear the relation to salt concentration given by the equation

$$k_{0.5^\circ} = 46.3300 - 6.7605C_{\mathrm{NaI}} \qquad (2)$$

and in the rapidly changing part of the curve

$$C_{\mathrm{NaI}} = \frac{1}{2.66}\log\left(\frac{a}{1-a}\right) - \log(1/K) \qquad (3)$$

where a represents the fraction dissociated as shown by the change in magnitude of the dispersion constants $k_{0.5^\circ}$. In Table III are given the a values for the dissociated fraction and the calculated values obtained for log $(1/K)$. The latter agree very well with one another and indicate a mean value of 0.9983.

It is obvious that there will be a log $(1/K)$ value that will be characteristic for iodide and which

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(9) Fromherz and Menschick, *Z. physik. Chem.*, **B7**, 439 (1930).

will be different in magnitude but equally characteristic for bromides, etc. It is seen from the graphs in the previous paper[7] that the log $(1/K)$ values are approximately 1.0 for iodides, 1.8 for bromides and 3.7 for chlorides (LiCl). The factor $^{1}/_{2.66}$ preceding the dissociation term regulates how rapidly the dissociation takes place. The numerical value of this factor increases in going from iodides to chlorides, approaching unity in the latter case.

Inasmuch as the rotatory dispersion constants for gelatin at 0.5° in the presence of salts follow a dissociation equation, it is concluded that the transformation from what we have hitherto designated as the "gel" form of gelatin to the "sol" form, is a process of dissociation or association of the gelatin molecule.

TABLE III

ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. NaI (molal)	$k_{0.5^\circ}$	a	Log $(1/K)$	k_{40°
1	0.000	99.5410	..	...	44.517
2	.350	97.2054	..	...	42.243
3	.851	78.3378	0.291	0.997	39.281
4	1.001	66.6307	.492	.999	38.278
5	1.121	56.2071	.675	1.004	37.495
6	1.251	46.9638	.830	0.993	36.611
7	2.011	32.8214	..	...	32.074
8	2.578	29.1903	..	...	28.702
9	3.295	24.0540	..	...	23.929

$k_{0.5^\circ} = 46.3300 - xC_{\text{NaI}}$ where $x = 6.7605$
$k_{40^\circ} = 44.5170 - xC_{\text{NaI}}$ where $x = 6.220$
mean log $(1/K) = 0.9983$

By the method of determinants, Lucas[10] has developed a formulation from which the number of optically active species in a system may be determined. Lucas' relation is based on the assumption that the active species have different dispersion constants and, of course, would only apply to systems satisfying this requirement. In the case of two active components the equation takes the form

$$k = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right]_{\lambda_a} = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right] = \left[\frac{[a]_1 - [a]_2}{[a]_1 - [a]_n}\right]_{\lambda_c} \text{etc.} \quad (4)$$

where $[a]_1$, $[a]_2$ and $[a]_n$ represent the specific rotations of the active material in a related series (with a given salt) at wave lengths λ_a, λ_b, λ_c, etc. In applying Lucas' equation a series of any two pairs may be selected for comparison. If a constant is obtained for different wave lengths λ_a, λ_b, λ_c, etc., it is good evidence that two optically active components and only two are present.

TABLE IV

CALCULATION OF THE LUCAS CONSTANT FOR GELATIN-SODIUM IODIDE SYSTEM CONTAINING TWO OPTICALLY ACTIVE COMPONENTS (0.5°)

Combination[a]	λ6708 Å.	λ5892 Å.	λ5780 Å.	λ5461 Å.	λ4358 Å.
1-2/1-9	0.0322	0.0298	0.0308	0.0294	0.0316
1-3/1-9	.286	.278	.281	.280	.280
1-4/1-9	.437	.434	.434	.435	.438
1-5/1-9	.573	.573	.570	.574	.575
1-6/1-9	.697	.693	.695	.696	.696
1-7/1-9	.883	.883	.883	.883	.884
1-8/1-9	.931	.931	.931	.934	.932

[a] The numbers in this column refer to corresponding soln. no. in Table I.

We have applied Lucas' method of analysis to our data for the rotation of gelatin at 0.5° and the results are given in Table IV. In the column headed "Combination" is given the combination of specific rotations employed in the various calculations of k, the numbers 1, 2, 3, 4, etc., referring to the same gelatin solutions as given in Table I. It is obvious from the calculated values of the Lucas constant for the five wave lengths, for the systematic series of combinations employed, that a constant is actually obtained for any combination (within the probable error of polariscope readings) as is required for a mixture of two optically active substances. Any other combination that might be chosen would give a similar constancy for the Lucas constant. We therefore conclude that at 0.5° gelatin is converted from one optically active form to another by the action of neutral salt. There appear to be only two optically active species present. This is entirely in harmony with our foregoing conclusion that the two forms are closely related

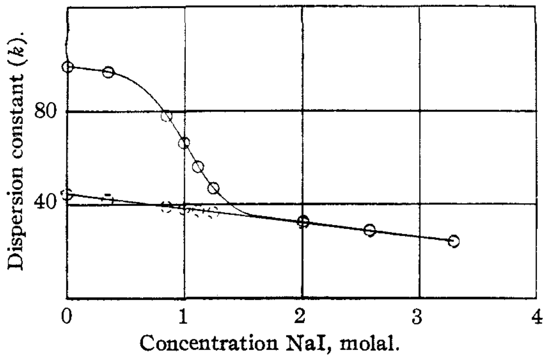

Fig. 4.—Rotatory dispersion constant of gelatin in sodium iodide solutions at 0.5 and 40°.

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(10) Lucas, *Ann. phys.*, [10] **9**, 381 (1928); *Trans. Faraday Soc.*, **26**, 418 (1930).

to each other, one being a dissociated (or associated) form of the other and also that the associated form is likely a polymer of a ring type resulting from the mutual electrostatic neutralization of zwitterion structures.

Summary

The rotatory dispersion of gelatin has been examined in various concentrations of sodium iodide at 0.5 and 40°, at five different wave lengths in the visible spectrum.

A single term Drude equation was shown to express the experimental results. From calculations it was shown that an absorption band at 2200 Å. governed the dispersion. Absorption spectrum data showed that gelatin has a high absorption in this region.

The rotatory dispersion constants of gelatin at 40° follow the linear equation $k_{40^\circ} = 44.5170 - 6.220C_{\mathrm{NaI}}$.

The rotatory dispersion constants at 0.5° were found to be expressed by the sum of two equations

$$C_{\mathrm{NaI}} = \frac{1}{2.66}\log\left(\frac{a}{1-a}\right) - \log\left(\frac{1}{K}\right)$$

and the linear equation

$$K_{0.5^\circ} = 46.3300 - 6.7605C_{\mathrm{NaI}}$$

It was concluded that the linear effect of salt concentration on the dispersion constant was due probably to a shift in the association of the solvent (hydrol–polyhydrol equilibrium) or an association between solvent and salt, and that the much greater effect of added salt at 0.5° was due to a dissociation or association of the gelatin molecule.

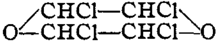
Based on the formulation of Lucas, it was shown that two and only two optically active species exist in gelatin solutions or gels.

GENEVA, N. Y. RECEIVED JULY 5, 1935

[CONTRIBUTION FROM THE DAIRY CHEMISTRY LABORATORY OF THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

The Catalytic Chlorination of Dioxane[1]

BY J. J. KUCERA AND D. C. CARPENTER

According to recent investigations,[2] 1,4-dioxane and 2,3-dichlorodioxane on chlorination without catalysts give poor yields of the tetrachlorodioxanes and particularly of the symmetrical isomers  $O\langle\begin{smallmatrix}CHCl-CHCl\\CHCl-CHCl\end{smallmatrix}\rangle O$, which are valuable because of their quantitative yield of glyoxal on hydrolysis. Since preliminary experiments with copper, iron, manganese, nickel, tin and iodine chlorides showed that the two latter substances catalyzed the chlorination most vigorously, we have carried out carefully chlorinations using them.

Technical dioxane was purified by distillation, crystallization and a final distillation over sodium. The purified dioxane boiled at 101.5–101.7° and melted at 11°. The usual method of chlorination was employed, the amount of chlorine absorbed being calculated from the increase in weight of the reaction vessel.

Starting with 78.5 g. of dioxane and chlorinating at a temperature of 90°, a yield of 96.6% of the 2,3-dichlorodioxane was obtained, both with stannic chloride (added as 1 g. of $SnCl_2$) and with iodine chloride (added as 1 g. of I) catalyst. The amount of decomposition was negligible. This yield is considerably greater than that (69%) previously reported in the absence of a catalyst.[3]

In the chlorination of 47 g. of the 2,3-dichlorodioxane at 145° using stannic chloride as a catalyst (added as 0.5 g. of $SnCl_2$), the following unsymmetrical tetrachlorodioxanes were obtained: 37 g., b. p. 96° at 14 mm., and 1 g., m. p. 57–58°, together with symmetrical tetrachlorodioxanes: 12 g., m. p. 70° and 6 g., m. p. 143°. This corresponds to a total yield of 83% and a 32% yield of the symmetrical tetrachlorodioxanes. In the run with iodine chloride (added as 1 g. of I) as a catalyst at 145°, and starting with 81.8 g. of 2,3-dichlorodioxane, 68 g. of the unsymmetrical tetrachlorodioxane b. p. 96° at 14 mm., and 2 g., 21 g. and 10 g. of the symmetrical isomers melting respectively at 60, 70 and 143° were obtained. This corresponds to a total yield of 85% and a 33% yield of the symmetrical isomers. In

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[1] Approved by the Director of the New York Agricultural Experiment Station for publication as Journal Paper No. 98.

[2] Butler and Cretcher, THIS JOURNAL, **54**, 2987 (1932); Christ and Summerbell, *ibid.*, **55**, 4547 (1933); Baker, *J. Chem. Soc.*, 2666 (1932).

[3] Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).