
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 57

DECEMBER 27, 1935

NUMBER 12

[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. III. Effect of the Halides of Lithium, Sodium, Rubidium and Cesium¹

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

Previous communications² from this Laboratory have shown that in the case of the halides of potassium, the customary Hofmeister series for anions is observed in their effect on the optical rotation of gelatin held at a constant *pH* on the alkaline side of the isoelectric point. When other uni-univalent salts of potassium³ are examined, the effect on the rotation is represented by a typical Hofmeister series arranged as follows— $\text{KCNS} > \text{KI} > \text{KClO}_3 > \text{KNO}_3 > \text{KBr} > \text{KCl}$, CH_3COOK , $\text{C}_2\text{H}_5\text{COOK}$ and HCOOK . For uni-bivalent salts we have the series $\text{K}_2\text{SO}_4 > (\text{COOK})_2 > \text{K}_2\text{CrO}_4$.

In the work herein reported we have examined the effect of the halides of the other alkali metals to find whether the effect of the halides is a general one and to ascertain the magnitude of the effect of the alkali metal.

Materials and Method

The halide salts used in the experiments to be described were recrystallized several times from water and were either oven dried at 104° for several days or in the case of salts crystallizing as hydrates, dried *in vacuo* over anhydrous phosphorus pentoxide for several days.

The gelatin was the same sample of calfskin gelatin that

had been used in previous work. It was de-ashed by electro-dialysis and further purified and dehydrated by the method described by Sheppard.⁴ A 1.4% stock solution of this purified calfskin gelatin was prepared by swelling 14 g. (dry weight) in water for several hours, warming to 50° for "solution" to take place and cooling to 30°. Before making the volume up to 1000 cc. a measured quantity of 0.1 *N* lithium, sodium, rubidium or cesium hydroxide was added to adjust the *pH* of the gelatin solution to approximately 6.3. The gelatin content of this stock solution was determined by drying a known volume of solution to constant weight at 104° and correcting for the weight of alkali metal contained therein.

In preparing the various solutions for observation of the rotation, varying amounts of the pure anhydrous salts were weighed into a series of small weighed flasks and 25-cc. portions of the stock gelatin solution (*pH* 6.3) added. The total weight of solution in each flask was then brought to 50 g. by adding carbon dioxide-free distilled water. As some of the salts were extremely hygroscopic, precautions were taken in weighing and transferring and in many cases the salt concentration was determined by titrating portions of the prepared solutions with 0.1 *N* silver nitrate solution.⁵ To obviate any deleterious effects on the gelatin due to the heat evolved when certain of the anhydrous salts dissolved in water, the flasks were cooled at 0° during this operation. The salt concentration was calculated to a molal basis. From each flask of a series for a given salt, a 200-mm. polarizing tube was filled. It was found advantageous to coat each end of the polarizing tube with vaseline before adjusting the cover glass and to permit a small

(1) Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 96. Abstracted from a thesis presented to the Graduate School of Cornell University by F. E. Lovelace in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927).

(3) Carpenter and Kucera, *ibid.*, **35**, 2619 (1931).

(4) Sheppard, Sweet and Benedict, *This Journal*, **44**, 1857 (1922).

(5) The writers wish to acknowledge their indebtedness to the General Electric Company of Schenectady, N. Y., for placing at their disposal a quantity of rubidium and cesium compounds from which the salts used herein were prepared.

air bubble to remain in the tube to obviate strains within the gels, which otherwise would lead to erratic polariscope readings. The polarizing tubes were then placed in the constant-temperature bath at $0.5 \pm 0.02^\circ$ to come to equilibrium. A constant rotation was usually reached after five days, but the readings recorded in the tables for 0.5° were obtained after seven days so as to insure the attainment of equilibrium in all cases.

After a series of readings was completed at 0.5° the tubes were allowed to warm to room temperature and were then placed in the constant-temperature bath at 40° for half an hour for equilibrium to be established before polarizing at this higher temperature. Equilibrium is practically reached after fifteen minutes at 40° .

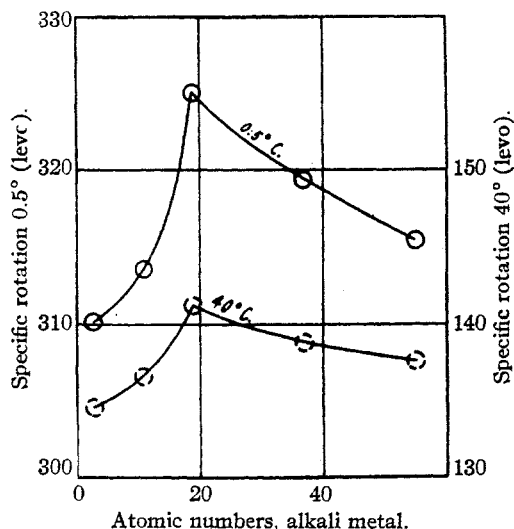


Fig. 1.—Specific rotation of alkali gelatinates.

The pH of the solutions was determined by the quinhydrone electrode, being set up as half cells against a standardized 0.1 N calomel electrode at 25° with a saturated potassium chloride solution as junction. The pH was calculated from the relation $pH = (0.3614 - E)/0.0591$ disregarding corrections for junction potential and for any effect the high salt concentrations may have had upon the quinone-hydroquinone equilibrium within the cell. The pH measurements were made primarily to show that the pH was fairly constant. We have shown before⁶ that between pH 6 and 7 the change in rotation at 0.5° caused by increase in pH is not greater than 2%, and as all of our measurements fall well within this limit, pH can have no great effect on our results.

Density determinations were made of all solutions at 25° in a carefully calibrated pycnometer. For the purpose of calculation in this and subsequent articles it is assumed that the density at 0.5 and 40° is the same as that at 25° . The actual error will not be large if this assumption is made and in many cases the density at 0.5° is not experimentally attainable by pycnometer as the solutions are gels.

Specific rotation was calculated from the equation $[\alpha] = (a \times 100)/(l \times d \times p)$ where a is the angle measured, l

the length of tube in decimeters, p the grams of gelatin in 100 g. of solution and d the density of the solution. A Schmidt and Haensch triple field polarimeter was used throughout.

Discussion and Conclusions

In Table I are given the data for the specific rotation of the gelatinates of the various alkali metals without added halide salts, and in Fig. 1 these data are shown graphically. It will be seen that the effect of the alkali metal ion on the rotation of gelatin is of minor importance but that the rotation increases with increase in atomic number to a maximum value (potassium) and thereafter decreases. This decrease appears to be connected with the appearance of the shell of eighteen electrons in rubidium and the decrease becomes further augmented with cesium where an additional shell of eighteen electrons is present. Inasmuch as the ratio $[\alpha]^{0.5D}/[\alpha]^{40D}$ is practically constant for all of the alkali gelatinates, it is concluded that the effect of temperature on configuration of the gelatin molecule as shown by the rotation, is alike for all of the alkali gelatinates at pH 6-7 and that they are of analogous structure.

TABLE I
SPECIFIC ROTATION OF ALKALI GELATINATES

Alkali metal	Atomic no.	pH	Levo degrees		$\frac{[\alpha]^{0.5D}}{[\alpha]^{40D}}$
			$[\alpha]^{0.5D}$	$[\alpha]^{40D}$	
Li	3	6.31	310.2	134.6	2.304
Na	11	6.30	313.6	136.6	2.295
K	19	6.36	325.0	141.2	2.301
Rb	37	6.24	319.4	138.8	2.301
Cs	55	6.38	315.1	137.6	2.290

Razukin⁷ found that the specific rotation of lithium, sodium and potassium proteinates increased in magnitude with the atomic weight of the metal ion, the order of magnitude of the effect being $K > Na > Li$. Darmois⁸ has found a similar effect on the rotation of tartrates. In the case of the alkali gelatinates we find the magnitude of the rotation to be given by the order $K > Rb > Cs > Na > Li$ at 0.5 and 40° .

As to the effect of neutral salts on the specific rotation of gelatin, our data are recorded in Table II. To present our results clearly and at the same time with economy of space we have shown the results with the lithium halides in Fig. 2. Similar curves are obtained for the halides of each of the alkali metals. In Fig. 3 are collected to-

(7) Razukin and Logunova, *J. Russ. Phys.-Chem. Soc.*, **47**, 1059 (1915); Razukin and Brando, *ibid.*, **48**, 269 (1916); Razukin, *ibid.*, **48**, 265 (1916).

(8) Darmois, *Trans. Faraday Soc.*, **26**, 384 (1930).

(6) Carpenter, Dahlberg and Hening, *Ind. Eng. Chem.*, **20**, 397 (1928).

TABLE II
INFLUENCE OF SALTS ON OPTICAL ROTATION OF GELATIN
AT pH 6-7

Soln. no.	Molality of salt soln.	pH 25°	Wt. gelatin per 100 g. solvent, g.	Density, 25°	$[\alpha]_D^{20}$, Levo degrees	$[\alpha]_D^{40}$, Levo degrees
Lithium Chloride						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.62	6.32	.7673	1.0187	307.1	130.3
3	.93	6.48	.7673	1.0255	296.7	128.4
4	1.29	6.47	.6343	1.0361	287.6	123.3
5	1.87	6.52	.7673	1.0480	268.0	121.9
6	2.10	6.01	.7673	1.0577	252.6	119.5
7	2.49	6.61	.7674	1.0634	228.5	117.0
8 ^a	2.76	6.53	.7673	1.0752	201.8	115.8
9 ^a	2.89	5.99	.7673	1.0777	183.8	113.7
10 ^a	3.11	6.59	.7673	1.0843	149.0	113.6
11 ^a	3.49	6.80	.7673	1.0941	123.9	116.1
12 ^a	3.89	6.79	.7673	1.0995	112.0	108.5
Lithium Bromide						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.59	6.63	.7673	1.0405	297.5	127.1
3	.90	6.53	.7673	1.0608	288.1	125.3
4	1.13	6.33	.7674	1.0770	272.8	124.6
5	1.22	6.50	.7678	1.0825	265.4	123.8
6	1.41	6.25	.7673	1.0953	244.7	120.0
7	1.55	6.53	.7678	1.0973	229.4	120.1
8 ^a	1.69	6.33	.7673	1.1179	189.2	116.0
9 ^a	1.73	6.49	.7673	1.1196	181.0	116.4
10 ^a	1.92	6.57	.7673	1.1343	141.3	115.5
11 ^a	2.23	6.28	.7674	1.1602	121.3	110.1
12 ^a	2.84	6.30	.7673	1.2091	109.4	104.0
13 ^a	3.38	5.81	.7673	1.2564	102.2	97.5
Lithium Iodide						
1	0.00	6.31	0.7674	1.0021	310.2	134.6
2	.58	6.29	.7673	1.0619	278.0	125.2
3	.61	6.62	.7673	1.0654	275.2	122.3
4 ^a	.90	6.38	.7673	1.0962	225.3	119.5
5 ^a	.91	6.21	.7673	1.0979	220.1	118.7
6 ^a	1.21	6.37	.7673	1.1321	134.7	112.2
7 ^a	1.52	6.23	.7673	1.1715	115.1	107.9
8 ^a	1.76	6.26	.7673	1.2093	109.4	105.1
9 ^a	2.40	6.15	.7674	1.2950	102.1	94.1
Sodium Chloride						
1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	0.67	6.30	.7730	1.0303	308.9	128.0
3	1.01	6.32	.7730	1.0441	306.1	125.8
4	1.34	6.26	.7731	1.0582	303.1	119.2
5	1.68	6.13	.7730	1.0734	297.7	119.3
6	2.02	6.27	.7730	1.0875	286.1	115.4
7	2.69	6.23	.7731	1.1174	276.1	108.8
8 ^a	3.35	6.17	.7697	1.1482	246.1	110.9
9 ^a	4.21	6.23	.7731	1.1883	204.7	94.2
Sodium Bromide						
1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	0.65	6.33	.7744	1.0558	305.2	130.5
3	1.00	6.17	.7730	1.0842	293.5	123.6
4	1.34	6.17	.7730	1.1182	279.4	120.1

5	1.68	6.25	0.7745	1.1516	245.6	116.0
6 ^a	2.10	6.22	.7745	1.1937	182.8	111.4
7 ^a	2.41	6.47	.7132	1.2274	145.1	106.5
8 ^a	2.69	6.07	.7730	1.2601	114.5	102.4
9 ^a	3.34	6.00	.7698	1.3410	95.4	91.1
10 ^a	4.20	6.02	.7744	1.4638	82.9	82.5

Sodium Iodide

1	0.00	6.30	0.7730	1.0023	313.6	136.6
2	.35	6.31	.7730	1.0437	300.7	129.9
3	.67	6.27	.7745	1.0847	277.3	124.5
4	.85	6.36	.7730	1.1095	253.0	120.2
5 ^a	1.03	6.16	.7730	1.1308	208.2	115.3
6 ^a	1.10	6.11	.7745	1.1445	191.2	118.5
7 ^a	1.18	5.93	.7731	1.1526	161.6	111.7
8 ^a	1.25	6.19	.7730	1.1672	141.9	110.3
9 ^a	1.34	6.14	.7744	1.1813	129.0	109.3
10 ^a	1.68	5.94	.7745	1.2370	105.9	99.9
11 ^a	2.01	5.90	.7731	1.2942	98.4	95.7
12 ^a	2.58	5.68	.7731	1.4065	86.0	84.1
13 ^a	3.02	5.58	.7744	1.5132	76.8	74.7
14 ^a	3.30	5.68	.7745	1.5862	70.4	68.8

Rubidium Chloride

1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	0.67	6.18	.7906	1.0647	307.1	126.5
3	1.34	6.18	.7668	1.1318	294.4	117.5
4	1.68	6.06	.7668	1.1748	287.0	114.9
5	2.01	6.04	.7667	1.2101	279.2	113.2
6	2.58	5.98	.7667	1.2687	265.3	105.4
7	3.02	5.87	.7636	1.3428	247.2	99.5

Rubidium Bromide

1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	.48	6.28	.7903	1.0662	307.4	131.1
3	.88	6.39	.7902	1.1252	293.0	125.4
4	1.29	6.14	.7902	1.1926	270.2	121.6
5	1.50	6.24	.7902	1.2295	245.5	114.3
6 ^a	1.69	6.09	.7902	1.2645	224.3	113.6
7 ^a	1.86	6.20	.7903	1.2993	196.7	111.0
8 ^a	2.09	6.01	.7903	1.3466	159.7	111.4
9 ^a	2.22	6.16	.7903	1.3734	137.7	105.5
10 ^a	2.40	6.02	.7904	1.4179	119.6	102.6
11 ^a	2.80	5.77	.7904	1.5244	100.0	96.3

Rubidium Iodide

1	0.00	6.24	0.7902	1.0026	319.4	138.8
2	.48	6.09	.7904	1.0849	297.9	128.9
3 ^a	.88	5.84	.7903	1.1639	236.5	117.4
4 ^a	1.08	5.88	.7648	1.2034	182.5	118.4
5 ^a	1.19	5.95	.7649	1.2289	151.6	117.5
6 ^a	1.29	5.99	.7903	1.2623	125.8	112.8
7 ^a	1.69	5.74	.7903	1.3701	103.9	102.6
8 ^a	2.09	5.58	.7903	1.4948	94.4	94.0
9 ^a	2.36	5.50	.7904	1.5934	88.5	88.1

Cesium Chloride

1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.50	6.42	.7581	1.0706	307.0	130.5
3	1.00	6.27	.7581	1.1467	295.3	126.5
4	1.50	6.09	.7432	1.2303	283.3	120.8
5	2.00	6.12	.7581	1.3400	265.8	114.7
6	2.50	6.12	.7581	1.4582	243.8	109.0

TABLE II (Concluded)

Soln. no.	Molality of salt soln.	pH 25°	Wt. gelatin per 100 g. solvent, g.	Density, 25°	$[\alpha]_D^{0.5}$ Levo degrees	$[\alpha]_D^{40}$ Levo degrees
Cesium Bromide						
1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.47	6.21	.7582	1.0833	305.0	132.1
3	.91	6.24	.7582	1.1771	289.6	123.8
4	1.29	6.16	.7582	1.2678	265.8	118.1
5	1.45	5.88	.7581	1.3095	249.8	117.4
6 ^a	1.68	5.87	.7581	1.3707	218.0	113.0
7 ^a	1.87	5.82	.7566	1.4384	189.3	107.0
8 ^a	2.13	6.00	.7582	1.5286	145.8	106.1
Cesium Iodide						
1	0.00	6.38	0.7582	1.0022	315.1	137.6
2	.33	6.34	.7581	1.0641	304.5	131.0
3	.64	6.31	.7581	1.1283	279.0	125.1
4	.80	6.17	.7581	1.1886	249.7	119.3

^a Solutions did not gel at 0.5°. All others were solid gels at 0.5°.

gether graphs for all of the salts reported in this investigation.

It is obvious from the data and graphs that the principal effect of neutral salts of the uni-univalent

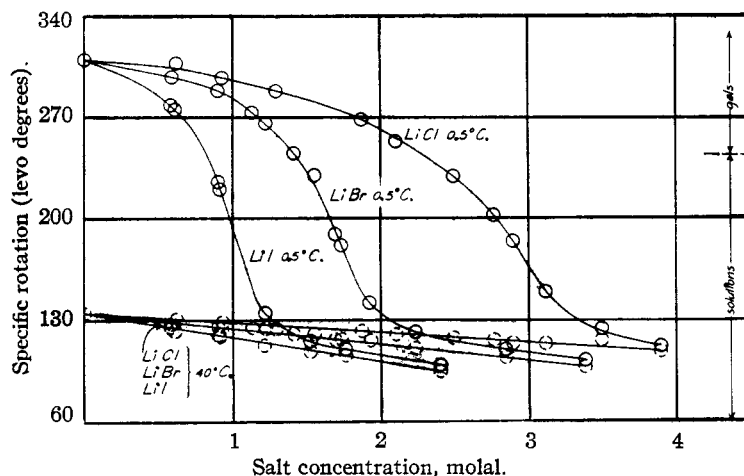


Fig. 2.—Influence of lithium halides on the specific rotation of gelatin.

type is due to the anion of the added salt. The magnitude of the effect produced by iodides is greater than the effect produced by the bromides, which in turn is greater than the effect produced by chlorides. This order is the same at both temperatures for all of the alkali halides, but the effect on the rotation of gelatin is of much greater magnitude at low temperatures. We therefore conclude that, contrary to the views of Loeb,⁹ there is a Hofmeister series for the anions, namely,

(9) Loeb, "Proteins and the Theory of Colloidal Behavior," The Macmillan Co., New York City, 1922.

$I > Br > Cl$, with all the halide salts of the alkali metals.

The data show that there is a very minor effect on the specific rotation of gelatin due to the cation alone, when the alkali metal halides are added. This is more apparent in the case of the chlorides than with the bromides or iodides. The magnitude of this effect can be shown by the following series, $Li > Cs > Rb > Na$ when the concentration of added salt becomes fairly high. The order of this series is practically the same, regardless of the anion in combination with the alkali metal ion, until very high concentrations of bromide and iodide are reached. At this point a slight change in the order occurs.

In experiments which largely concerned the influence of chlorides of various metals on the optical rotation of neutral asparagine, J. Liquier-Milward¹⁰ found that among the alkali metals, the influence was greatest for the metal ion having the smallest radius ($LiCl > NaCl > KCl$). On account of the fact that no changes in rotation were observed on adding neutral salts to acid

solutions of asparagine and none were found with dextrorotatory alanine, (which is largely in the zwitterion form), she ascribed the effect of salts on rotation to a polarization of the asparagine molecule into the zwitterion form. In short she believed the effect of added salt was to produce the zwitterion type of molecule. In acid solutions the NH_2 group is bound to acid and the presence of zwitterion is probably negligible. This fact in any case indicates that the NH_2 group is involved in whatever change in constitution occurs.

Linderstrøm-Lang and Kodama¹¹ found that the solubility of casein in dilute hydrochloric acid decreased with increasing salt concentration, while Sørensen and Sladek¹² found that the solubility of casein in dilute sodium hydroxide solution *increased* with increasing sodium chloride concentration until the salt concentration was about twice normal. A further increase in salt concentration reduced the solubility of the casein.

(10) Liquier-Milward, *Ann. Physik*, **7**, 121 (1927); *Trans. Faraday Soc.*, **26**, 390 (1930).

(11) Linderstrøm-Lang and Kodama, *Compt. rend. trav. lab. Carlsberg*, **16**, No. 1 (1925).

(12) Sørensen and Sladek, *ibid.*, **17**, No. 14 (1929).

These last authors concluded that compound formation had taken place between the casein and salt or one of the latter's ions.

As regards solubility of proteins in salt solutions, we have found with gelatin an effect similar to that noted by Sørensen and Sladek for casein. The gelatin-salt mixtures we have used pass from solid gels to fluids at a point where the specific rotation reaches -250° . This critical rotation value is a measure of "solubility" in our experiments. This indicates that the solubility of gelatin has been increased by the addition of salts and that the increase is largely dependent on the halide part of the salt present. The above view is understood not to exclude possible interaction between the ions and solvent and the idea of salting out coefficients.

Carpenter and Kucera³ called attention to the fact that compounds of the zwitterion type $\text{NH}_3^+-\text{R}-\text{COO}^-$, on account of their electric charges, should suffer a diminution of activity on adding neutral salts and that their solubility should be increased. They suggested that compounds of the type $\text{NH}_3\text{I}-\text{R}-\text{COONa}$ might be formed as the result of the operation of electrostatic forces in which the properties of the zwitterion entirely disappeared and in which the activity coefficient of the salt presumably would be considerably less. It is expected that with a linkage of nitrogen to halogen the $\text{NH}_3\text{I}-\text{R}-\text{COONa}$ type of compound would be ionized completely into I^- and $\text{NH}_3-\text{R}-\text{COONa}^+$ ions, with the protein bound to the metal as a complex.

It is pointed out that to maintain in solution a structure of the $\text{NH}_3^+-\text{R}-\text{COO}^-$ type it is necessary to assume that a large number of the fields of force associated with the two charged regions mutually form a closed field. Consequently although the zwitterion structure looks as if it were a highly reactive form, capable for instance of forming molecular chains through the operation of electrostatic forces, the fact that this is not the case can only mean that the electrified regions have been largely mutually neutralized. The effect of increase in temperature or the addition of neutral salts might easily be that of opening up the force fields around both electrified regions, so that polymerization of the molecule would be

possible. If the polymer had a chain structure $\text{NH}_3^+-\text{R}-\text{COO}-\text{NH}_3-\text{R}-\text{COO}^-$ it is obvious that this would be only the first step toward the formation of a huge chain. Lewis¹³ in experimenting on the possible polymerization of glycine, found that a dipolymer was formed in a measurable amount and he concluded that higher polymers were unlikely. The fact that the polymerization only goes as far as the double molecule with simple amino acids suggests that the formation of a ring structure is involved which would appear to be a more stable form on account of the relative absence of free force fields. It is assumed that this reaction would be reversible and that while polymerization due to heat or salts would proceed

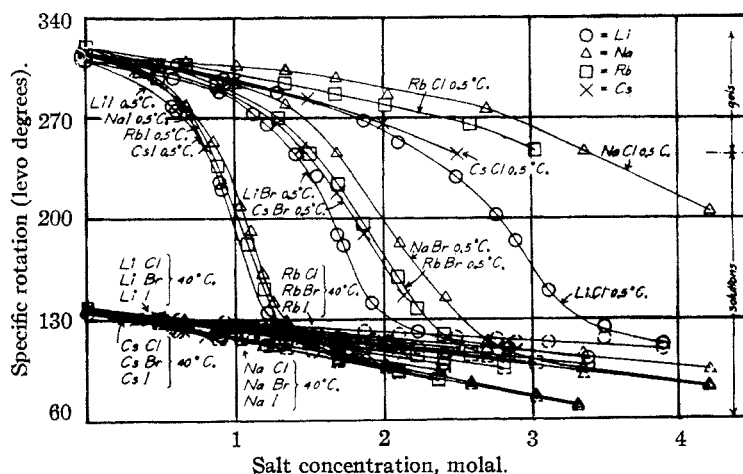


Fig. 3.—Influence of alkali halides on the specific rotation of gelatin.

rapidly, the depolymerization reaction, on the other hand, would proceed much slower due to the greater stability of the ring structure. In the case of the simplest species of casein¹⁴ we have found that heating to 40° while the protein was dissolving in buffer solution changed the molecular weight from around 96,000 to 188,000, an almost exact doubling of the molecular weight. It is possible that gelatin behaves in a similar way in which case, as a choice between the two alternate hypotheses to account for the great change in rotation of gelatin, we would favor that of polymerization to a ring structure.

Summary

The influence of the halides of lithium, sodium, rubidium and cesium on the specific rotation of gelatin at 0.5 and 40° has been examined over the

(13) Lewis, *Chem. Rev.*, **8**, 151 (1931).

(14) Svedberg, Carpenter and Carpenter, *THIS JOURNAL*, **52**, 241 and 701 (1930).

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 magni-

tude 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 Solutions¹

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. Hafner² discussed briefly the measurements he made at four different wave lengths in the visible on serum albumin and serum globulin. Hewitt³ 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.

Hansen⁴ investigated the rotatory dispersion of egg albumin as influenced by protein concentration, concentration of ammonium sulfate added, pH and temperature. Hansen was the first investigator to calculate dispersion constants from his data. He concluded that λ_0 was largely independent of pH, 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 Johnson⁵ at three different wave lengths and by Wiles and Gortner⁶

at six wave lengths. In the former paper the workers recognized that the presence of lithium chloride, as well as changes in pH, 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, $\lambda = 6707.86 \text{ Å.}$; sodium D line, $\lambda = 5892.617 \text{ Å.}$ (optical mean); yellow mercury line, $\lambda = 5780.13 \text{ Å.}$ (optical mean); green mercury line, $\lambda = 5460.73 \text{ Å.}$; and the deep blue mercury line, $\lambda = 4358.34 \text{ Å.}$ 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-

(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 fulfillment 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).