

latter, the theory predicts that a difference should always exist. For nitrobenzene this difference is predicted to be 11 cc. but only 1 cc. has been found experimentally. The theory also indicates the presence of considerable divergences in the behavior of substituted diphenyl and naphthalene derivatives from that of the corresponding benzene compounds. That this is unlikely is demonstrated by the fact that the polarization of 4-chlorodiphenyl in benzene is close to that of chlorobenzene; further experimental work will be undertaken shortly to test this point.

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Summary

Theoretical objections to the Raman-Krishnan theory of anisotropic dielectrics are raised.¹⁵ Empirical tests further indicate that the application of the above theory to dielectric constant measurements of dilute solutions of polar solutes in non-polar media would enable one to predict the difference between the moments as determined by the dilute solution method and those derived from gas measurements only as to order of magnitude.

(15) Subsequent to the submittal of this manuscript to the Editor a paper by Hans Mueller appeared [*Phys. Rev.*, **50**, 547 (1936)] in which essentially similar conclusions were reached through the use of arguments quite unlike those presented here.

PASADENA, CALIF.

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

The Influence of Neutral Salts on the Optical Rotation of Gelatin. V. Rotatory Dispersion of Gelatin in Sodium Bromide Solutions¹

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Previous work from this Laboratory² has shown that a single term Drude equation $[a]_{\lambda} = k/(\lambda^2 - \lambda_0^2)$ expressed the rotatory dispersion of gelatin dissolved in sodium iodide solutions and that the dispersion was governed by an absorption band at 2200 Å. At 40° the rotatory dispersion constant k was linearly related to sodium iodide concentration and at 0.5° was found to be expressed by the sum of two equations, $C_{\text{NaI}} = k \log [a/(1-a)] - \log (1/K)$ and the linear equation $K_{0.5^\circ} = K - k_0 C_{\text{NaI}}$. It was concluded that the tremendous effect of sodium iodide on the rotation of gelatin at 0.5° was due to an association or dissociation of the gelatin molecule.

The purpose of the present investigation was to continue the rotatory dispersion studies using sodium bromide solutions as solvent and ascertain if the above equations were applicable to other alkali metal halide systems.

Experimental

The procedure for preparing the solutions and for the measurement of rotations, density, pH, etc., was the same as has been described before.³

(1) Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 153.

(2) Carpenter and Lovelace, *THIS JOURNAL*, **57**, 2342 (1935).

(3) Carpenter, *J. Phys. Chem.*, **31**, 1873 (1927); Carpenter and Kucera, *ibid.*, **35**, 2619 (1931); Carpenter and Lovelace, *THIS JOURNAL*, **57**, 2337 (1935).

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, $\lambda = 6707.86$ Å.; sodium D line, $\lambda = 5892.617$ Å. (optical mean); yellow mercury line, $\lambda = 5780.13$ Å. (optical mean); green mercury line, $\lambda = 5460.73$ Å.; and the deep blue mercury line, $\lambda = 4358.34$ Å. The various light filters employed have been described. The gelatin concentration of the solutions was 0.7824 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 wave lengths employed. In Figs. 1 and 2 these data are graphed, plotting the reciprocal of specific rotation against the squares of the wave lengths at which the rotations were obtained. The relationship is linear, which means that a single-term Drude equation adequately expresses the results.

As with sodium iodide solutions of gelatin, the straight lines cut the x -axis at the same point, corresponding to $\lambda_0 = 2200$ Å., the location of the absorption band of gelatin. The same value for λ_0 was obtained by solving our data mathematically by the method used before. The values of k , numerator in the Drude equation, were calculated for each concentration of sodium bromide and appear in Table III and are graphed in Fig. 3. At 40° the k values bear a linear relation to

TABLE I
SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM BROMIDE AT 0.5° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaBr, molal	Density at 25°	pH	λ 6707.86 Å.		λ 5892.62 Å.		Levo degrees λ 5780.13 Å.		λ 5460.73 Å.		λ 4358.34 Å.	
				(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.00	1.0023	6.50	3.83	248.01	5.14	332.84	5.38	348.38	6.15	398.24	10.86	703.23
2	.50	1.0414	6.28	3.94	241.80	5.30	325.27	5.54	339.99	6.33	388.47	11.18	686.11
3	1.01	1.0869	6.18	3.91	229.89	5.25	308.68	5.49	322.79	6.28	369.24	11.09	652.05
4	1.34	1.1186	6.21	3.78	215.98	5.08	290.25	5.31	303.39	6.08	347.39	10.72	512.60
5	1.65	1.1490	6.14	3.49	194.13	4.70	261.43	4.91	273.11	5.62	312.61	9.91	551.22
6	1.95	1.1790	6.09	3.02	163.17	4.06	220.10	4.24	229.85	4.85	262.92	8.57	464.58
7	2.20	1.2048	5.90	2.54	134.74	3.41	180.89	3.57	189.38	4.08	216.43	7.19	381.42
8	2.45	1.2321	6.02	2.18	113.07	2.93	151.97	3.06	158.71	3.50	181.53	6.18	320.53
9	2.68	1.2608	5.88	1.94	98.33	2.61	132.29	2.73	138.37	3.12	158.14	5.50	278.77
10	3.05	1.3050	5.93	1.71	83.74	2.29	112.15	2.40	117.54	2.74	134.19	4.84	237.04
11	3.40	1.3518	6.04	1.61	76.11	2.17	102.59	2.26	106.85	2.59	122.45	4.57	216.19
12	4.20	1.4626	5.67	1.48	64.67	1.99	86.95	2.08	90.88	2.38	104.00	4.20	183.52

TABLE II
SPECIFIC ROTATION OF GELATIN SOLUTIONS CONTAINING SODIUM BROMIDE AT 40° FOR DIFFERENT WAVE LENGTHS OF LIGHT

Soln.	Concn. of NaBr, molal	Density at 25°	pH	λ 6707.86 Å.		λ 5892.62 Å.		Levo degrees λ 5780.13 Å.		λ 5460.73 Å.		λ 4358.34 Å.	
				(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]	(a)	[α]
1	0.00	1.0023	6.50	1.71	110.73	2.30	148.94	2.41	156.06	2.75	178.07	4.86	314.71
2	.50	1.0414	6.28	1.72	105.56	2.31	141.76	2.42	148.52	2.77	170.00	4.88	299.48
3	1.01	1.0869	6.18	1.70	99.95	2.28	134.05	2.39	140.52	2.73	160.51	4.82	283.40
4	1.34	1.1186	6.21	1.68	95.98	2.26	129.13	2.36	134.84	2.70	154.27	4.77	272.54
5	1.65	1.1490	6.14	1.66	92.33	2.23	124.04	2.34	130.16	2.67	148.51	4.71	261.99
6	1.95	1.1790	6.09	1.64	88.90	2.21	119.80	2.31	125.22	2.64	143.11	4.66	252.62
7	2.20	1.2048	5.90	1.62	85.93	2.18	115.64	2.28	120.95	2.61	138.49	4.60	244.02
8	2.45	1.2321	6.02	1.59	82.46	2.14	110.99	2.24	116.18	2.56	132.78	4.52	234.43
9	2.68	1.2608	5.88	1.59	80.59	2.14	108.47	2.24	113.54	2.56	129.76	4.52	229.10
10	3.05	1.3050	5.93	1.57	76.89	2.11	103.33	2.20	107.74	2.52	123.41	4.45	217.93
11	3.40	1.3518	6.04	1.54	72.80	2.07	97.86	2.17	102.59	2.48	117.25	4.38	207.07
12	4.20	1.4626	5.67	1.48	64.67	1.99	86.95	2.08	90.88	2.38	104.00	4.20	183.52

concentration of sodium bromide as given by the equation

$$k_{40^\circ} = 44.517 - 4.415C_{\text{NaBr}} \quad (1)$$

At 0.5° the curve for the k values is made up of two simultaneously occurring effects, the one a linear relationship to concentration of sodium bromide

$$k_{0.5^\circ} = 46.330 - 4.8476C_{\text{NaBr}} \quad (2)$$

similar to the one above except for the fact that the constants are slightly different in magnitude from those at 40°, and a second relationship

$$C_{\text{NaBr}} = \frac{1}{1.33} \log \left(\frac{a}{1-a} \right) - \log (1/K) \quad (3)$$

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 2.002. The factor $1/1.33$ preceding the dissociation term regulates how rapidly the dissociation or association takes place.

TABLE III
ROTATORY DISPERSION CONSTANTS AT 0.5 AND 40°

Soln.	Concn. NaBr, molal	$k_{0.5^\circ}$	a	$\log (1/K)$	k_{40°
1	0	99.541	44.517
2	0.50	97.117	42.407
3	1.01	92.261	0.045	2.010	40.110
4	1.34	86.723	.116	1.995	38.553
5	1.65	78.023	.254	2.002	37.122
6	1.95	65.723	.458	2.005	35.756
7	2.20	54.064	.654	1.992	34.548
8	2.45	45.375	.795	2.008	33.167
9	2.68	39.502	.884	2.016	32.411
10	3.05	33.558	.962	1.993	30.842
11	3.40	30.568	.987	2.002	29.275
12	4.20	25.971	1.000	...	25.974

$$k_{0.5^\circ} = 99.541 - XC_{\text{NaBr}} \text{ where } X = 4.8476$$

$$k_{40^\circ} = 44.517 - XC_{\text{NaBr}} \text{ where } X = 4.4149$$

$$\text{Mean } \log (1/K) = 2.002.$$

Attention is called to the identity of the ratio, for the salts sodium iodide and sodium bromide, between the respective constants for the linear equation (eq. 1 and 2); $k_{40^\circ}/k_{0.5^\circ} = 0.92$ for sodium iodide and 0.91 for sodium bromide. Attention

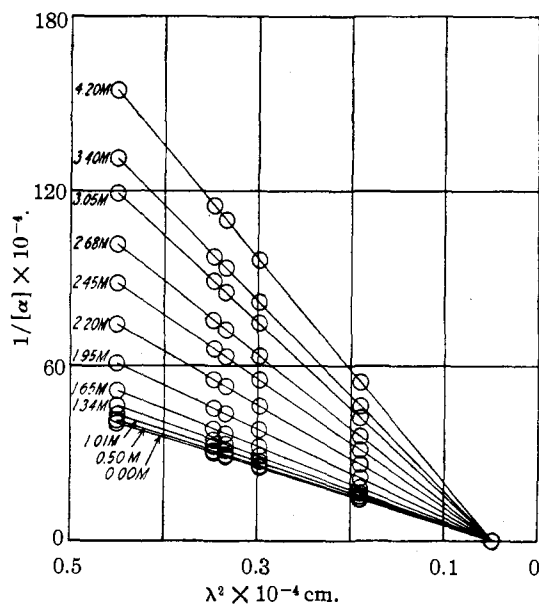


Fig. 1.—Graph of reciprocal of specific rotation versus wave length squared at 0.5° .

is also directed to the change in the value of the constant preceding the logarithmic term, $\log [a/(1-a)]$ (eq. 3), in going from sodium iodide to the bromide. With sodium bromide this constant (1/1.33) is exactly double that found for sodium iodide (1/2.66). Our preliminary experiments with sodium chloride indicate a value of 1/0.67, a further doubling of the value of this constant. The $\log (1/K)$ term meanwhile changes from 0.9983 for sodium iodide to 2.002 for sodium bromide, an almost exact doubling; a preliminary

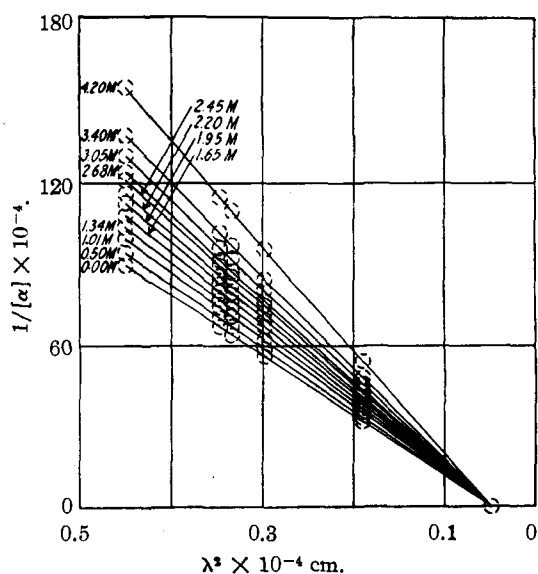


Fig. 2.—Graph of reciprocal of specific rotation versus wave length squared at 40° .

value of 4.0 is indicated for sodium chloride, again a doubling. It is clear that for all the sodium halides the various $\log (1/K)$ terms can be rewritten now as a common constant $k' \log (1/K)$ of value 2.66, k' being the reciprocal of the former k .

It is clear that in our experiments the influence of salts on the optical rotation cannot be explained as the polarization of the optically active molecules in an ionic atmosphere. According to Debye and Hückel, such an effect would require a greater effect for ions with small radii and large charges. If this were the case chlorides would be expected to have a greater effect on the rotation than iodides, which is contrary to fact.

It is not at present clear as to why the k constants preceding the dissociation term (1/0.67, 1/1.33 and 1/2.66) bear this mathematical regularity, respectively, for chlorides, bromides and iodides. It is pointed out that the sixth power of

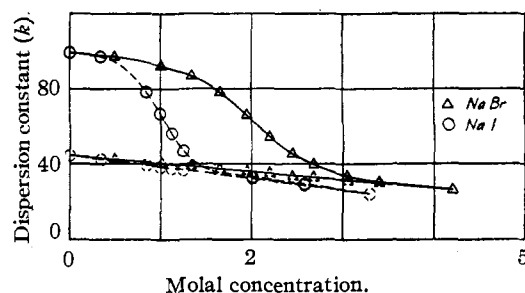


Fig. 3.—Rotatory dispersion constant of gelatin in sodium bromide solutions at 0.5° and 40° .

the ionic radii of the halogens as recorded by Wasastjerna⁴ (Cl = 1.72; Br = 1.92; I = 2.19 Å.) gives a ratio 26:49:109, almost exactly the 1:2:4 ratio given by the respective denominators of the above k constants. While the principal effect of neutral salts on gelatin at 0.5° is no doubt due to the anion of the salt, nevertheless, the cation has a slight influence which is not accounted for in the sixth power relationship mentioned above.

Smith⁵ concluded that the effect of heating gelatin was to cause a bimolecular reaction to take place in which two molecules of the original protein were united together into one molecule at elevated temperatures. We have noted before⁶ that heating to 40° caused a doubling of the molecular weight of the simplest species of casein. Weber and Stover⁷ record osmotic pressure data

(4) Wasastjerna, *Soc. Sci. Fennica Commentationes Phys. Math.*, **38**, 1 (1923).

(5) C. R. Smith, *THIS JOURNAL*, **41**, 135 (1919).

(6) Svedberg, Carpenter and Carpenter, *ibid.*, **62**, 241, 701 (1930)

(7) Weber and Stover, *Biochem. Z.*, **259**, 269 (1933).

giving the molecular weight of muscle protein as 81,000 in water solution and as 300,000 in ammonium thiocyanate solution. We have shown³ that potassium thiocyanate has the same sort of effect on the optical rotation of gelatin at 0.5° and of about the same magnitude as potassium iodide and that the effect of the sodium halides follows the dissociation (association) formulation stated before. The effect of the halide salts on the rotation at 0.5° also appears to be the same effect as that of raising the temperature, recorded by Smith. It seems fairly well established that the influence of the halide salts on gelatin at low temperatures is to cause an association of the protein molecule.

On applying the Lucas formulation⁸ for two optically active components

$$k = \frac{[a]_1 - [a]_2}{[a]_1 - [a]_n} \Big|_{\lambda_a} = \frac{[a]_1 - [a]_2}{[a]_1 - [a]_n} \Big|_{\lambda_b} = \frac{[a]_1 - [a]_2}{[a]_1 - [a]_n} \Big|_{\lambda_c} \text{ etc. (4)}$$

to our data, the constants given in Table IV were

TABLE IV

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

Combination ^a	λ 6708 Å.	λ 5893 Å.	λ 5780 Å.	λ 5461 Å.	λ 4358 Å.
1-2/1-12	0.0338	0.0307	0.0325	0.0332	0.0329
1-3/1-12	.0988	.0982	.0993	.0985	.0984
1-4/1-12	.175	.173	.175	.173	.175
1-5/1-12	.294	.290	.292	.291	.292
1-6/1-12	.463	.459	.460	.460	.459
1-7/1-12	.618	.618	.617	.618	.619
1-8/1-12	.736	.736	.737	.737	.734
1-9/1-12	.816	.816	.816	.816	.817
1-10/1-12	.896	.898	.896	.897	.897
1-11/1-12	.938	.937	.938	.937	.937

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

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

obtained for the various combinations employed. It is obvious that a constant is actually obtained for any combination for a series of different wave lengths, as is required for a mixture of two optically active substances. We conclude therefore that the behavior of gelatin at 0.5° in the presence of sodium bromide is entirely analogous to its behavior with sodium iodide, that two and only two optically active species are present and that one optically active form is converted to the other by the action of the neutral salt and that one active form is the associated form of the other.

Summary

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

As was previously shown with sodium iodide solutions, a single term Drude equation expressed the experimental results. An absorption band at 2200 Å. governed the dispersion.

The rotatory dispersion constants of gelatin at 40° follow the linear equation $k_{40^\circ} = 44.517 - 4.415 C_{\text{NaBr}}$.

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

$$C_{\text{NaBr}} = \frac{1}{1.33} \log \left(\frac{a}{1-a} \right) - \log (1/K)$$

and the linear equation

$$K_{0.5^\circ} = 46.330 - 4.8476 C_{\text{NaBr}}$$

It was concluded that the great change in rotation caused by halides at 0.5° is due to an association of the gelatin molecule.

Based on the Lucas formulation, two and only two optically active species exist in gelatin solutions and gels.

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