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Analysis of Rotatory Dispersions of Configurationally Related Halides

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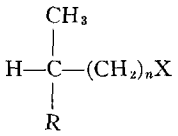
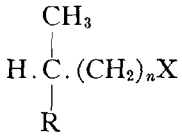
The rotatory dispersion curves of halides of the type



(where X = halogen atom, R = alkyl group) have been analyzed in the visible and the ultraviolet regions. The three halogen atoms function similarly with respect to the character of the rotatory dispersion curve in substances of identical structure. A periodicity is observed in the sign of some of the partial contributions of the halogen atom with the progressive increase in the value of n. The course of the rotatory dispersion of the halides with $n=1$ is anomalous. An attempt was made to apply the results of the observations obtained on substances having $n>0$ to elucidate the sign of rotation of the configurationally related substances having $n=0$.

THE present communication deals with the analysis of rotatory dispersion curves of halides of the general type (I)



where R is an alkyl group, X a halogen atom, and n has the value 0, 1, 2, or 3.

Recent studies have shown that the absorption spectra of organic iodides, bromides and chlorides are analogous.[1, 2] With decreasing wave-lengths there is found first, a broad region of continuous absorption with a maximum located at λ2600 for the iodides, λ1900 for the bromides, and λ1720 for the chlorides. For smaller wave-lengths, the absorption may be resolved into lines which fit two series of Rydberg. They converge towards two limits corresponding to the respective ionization potentials.

Although experimental proof is lacking so far, it might be assumed that all the rotatory contributions of the terms belonging to the same Rydberg series are of the same sign. In this case, their sum should be expressed with a fair degree of accuracy for the near ultraviolet and the visible regions, by a one-term Drude formula with a dispersion constant located between the first term and the limit of the series. Three dispersion terms might then be required to take care of the rotatory contribution of the halogen atom in the halides, one corresponding to the continuum, and the other two to the two Rydberg series.

In Table I are given the rotations for the sodium D line of the members of several homologous series of bromides of the general formula I having $n>0$. It can be seen from this table that with the change of the value of n from 1 to 2 there is observed an increase in the rotation (in the case given in Table I a shift of the rotation to the right). On further increase of the value of n to 3 the value of the molecular rotation drops (shift of the rotation to the left). Thus a periodicity is observed in the direction of the shift of rotation on progressive increase in the value of n.

It was desired (by means of analysis of the rotatory dispersion curves of these substances) to answer the question as to the part the halogen atom plays in the rotatory events associated with the progressive increase in the value of n. On the assumption that the corresponding absorption bands in the iodides, bromides, and chlorides function similarly with respect to their rotatory powers, it was deemed advantageous to extend the analysis of the rotatory dispersions to the iodides and chlorides. The iodides offer an advantage by virtue of the relative proximity of their first continuum and second absorption region, and the chlorides by virtue of their greater transparency.

Table II contains the composite results of the direction and of the relative magnitude of the

* The part of Mr. Marker consisted in the preparation of the substances marked by an asterisk.

[1] W. C. Price, Phys. Rev. **47**, 419 (1935).

[2] W. C. Price, Phys. Rev. **47**, 510 (1935).

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TABLE I. *Configurationally related bromides* $[M]_D^{25}$ Max. (homogeneous).

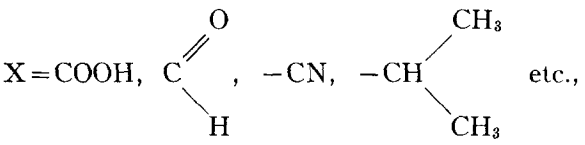
$H.C(CH_3)(C_2H_5).CH_2Br$	$H.C(CH_3)(C_2H_5).(CH_2)_2Br$	$H.C(CH_3)(C_2H_5).(CH_2)_3Br$	$H.C(CH_3)(C_2H_5).(CH_2)_4Br$	$H.C(CH_3)(C_2H_5).(CH_2)_5Br$
+7.9	+38.8	+21.9	+14.9	+14.0
$H.C(CH_3)(C_3H_7).CH_2Br$	$H.C(CH_3)(C_3H_7).(CH_2)_2Br$	$H.C(CH_3)(C_3H_7).(CH_2)_3Br$	$H.C(CH_3)(C_3H_7).(CH_2)_4Br$	
low dextro	+21.0	+14.5	+7.8	
$H.C(CH_3)(C_4H_9).CH_2Br$	$H.C(CH_3)(C_4H_9).(CH_2)_2Br$	$H.C(CH_3)(C_4H_9).(CH_3)_3Br$	$H.C(CH_3)(C_4H_9).(CH_3)_4Br$	
low dextro	+16.8	+8.3	+5.3	
$H.C(CH_3)(C_5H_{11}).CH_2Br$	$H.C(CH_3)(C_5H_{11}).(CH_2)_2Br$	$H.C(CH_3)(C_5H_{11}).(CH_2)_3Br$	$H.C(CH_3)(C_5H_{11}).(CH_2)_4Br$	
low dextro	+14.7	+6.2	+4.0	

rotation of each absorption region of the halogen atom.

With the progressive increase in the value of n it can be seen from this table that in the members having $n \geq 1$, the direction of the partial rotation of the second and third absorption regions displays a periodic change which is associated in the visible region with a periodic change in the direction of the shift of rotation. From the dispersion formulae given in the last paragraph it may be seen that the partial rotations of the halogen atoms constitute the major contributions to the rotation of the halides in the visible region.

The members having $n=0$ cannot be correlated by the methods of classical organic chemistry to those having $n \geq 1$ and therefore the direction of their partial rotation is not given in Table II.

It was desired to attempt this correlation on the basis of observations on substances of the same general formula (I) but with



in which all members can be correlated by methods of classical organic chemistry.

The rotatory events in the latter substances are illustrated best in the case of the aldehydes,[3] in which there is observed: first, a change of sign in the partial rotation of the functional group on passing from $n=0$ to $n=1$, and second, a periodicity in the direction of the shift of this partial rotation with progressive increase of the value of n (from 0 to 3).

It is now proposed to assign alternately the signs plus and minus to the first three absorption regions of the halogen atom of the members having $n=0$ and then to compare the course of events in the series thus formed with respect to n with that in the series represented by the aldehydes.

By assigning levorotation to the members having $n=0$, a series emerges which resembles that of the aldehydes in that the change of n

TABLE II. *Directions and relative values of the partial contributions of the halogen atom in halides of the general formula (I).*

n	0	1	2	3
First band	moderate	0	($\lesssim$0)	0
Second region	strong	−	++	0
Third region	weak	++	−	++
Fourth (in the main in rest of the molecule)	of opposite sign	?	?	−

[3] P. A. Levene and A. Rothen, J. Chem. Phys. **4**, 48 (1936).

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from 0 to 1 brings about a change in the direction of the partial rotation of X; it differs from the aldehyde series in that the periodicity in the direction of the shift of rotation with the progressive increase in the value of n begins not with the member having $n=0$, but with that having $n=1$.

By assigning dextrorotation to the members having $n=0$, a series is obtained which resembles that of the aldehydes in that there is a periodicity in the direction of the shift of rotation beginning with the member having $n=0$; it differs from the aldehyde series in that the change of $n=0$ to $n=1$ is not associated with a change in the direction of rotation of the two members.

Hence, whatever sign is attributed to the members having $n=0$, no complete analogy exists between the series where X is a halogen atom with those in which X equals one of the above-mentioned groups.

Thus the problem of the correlation of the configurations of the halides having $n=0$ to those having $n=1$ must await for its solution the development of a physical theory of optical rotation more satisfactory than those now in existence and capable of explaining on a rational basis the events in the series in which the members having $n=0$ have been correlated to those having $n>0$ by methods of classical organic chemistry. The theoretical models suggested, and the mathematical formulae developed to date fail to do this.

Recently Kuhn[4] suggested a model on the basis of which he formulated the absolute configuration of secondary carbinols. His model is inadequate to explain the difference in the sign of rotation of two configurationally related carbinols, 2-methylpentanol-1 and 2-ethylpentanol-1. Hence it is at best not sufficiently comprehensive. In fact, his formulation of the absolute configuration of secondary carbinols is doubtful. However, if a satisfactory model could be constructed based on Kuhn's theory that the direction of polarizibility and of the electric moment of a group may determine the sign of its rotatory contribution, then in such a model a change of direction of 90° of the vibration should produce a reversal of sign of rotation. The periodicity observed in some of the partial rotations of a functional group could very well be produced by this phenomenon, since the angle made by the bond joining the functional group to the rest of the molecule and the line joining two of the three other groups attached to the asymmetric carbon atom, varies periodically with n if one considers a restricted free rotation.

[4] W. Kuhn, Zeits. f. physik. Chemie **B31**, 23 (1935).

Absorption Spectra

The absorption curves of the continuum of the iodides may be seen in Fig. 1. They remain practically unchanged in magnitude and position with the variation of n. There is a difference of about 60A in the position of the maximum in the secondary iodides as compared with the primary. The uniformity met within the absorption curves contrasts sharply with the state of affairs found in the rotatory dispersions of the same compounds.

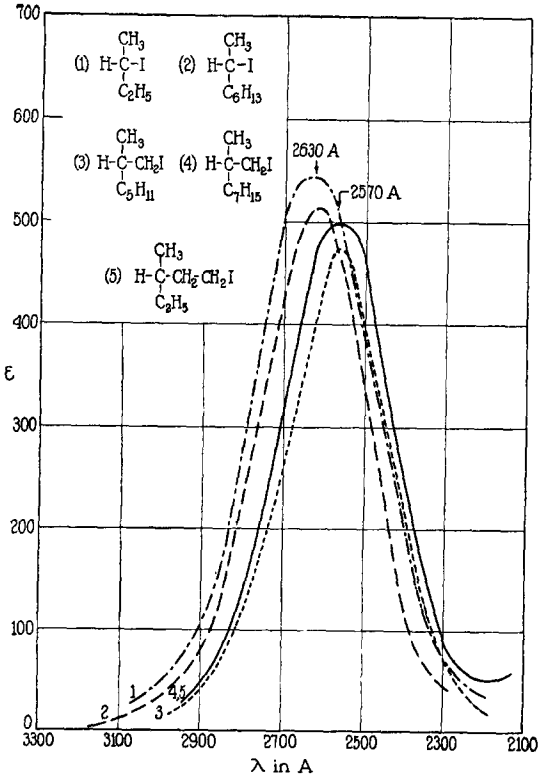

FIG. 1. Absorption spectra of iodides (ϵ = molecular extinction coefficient).

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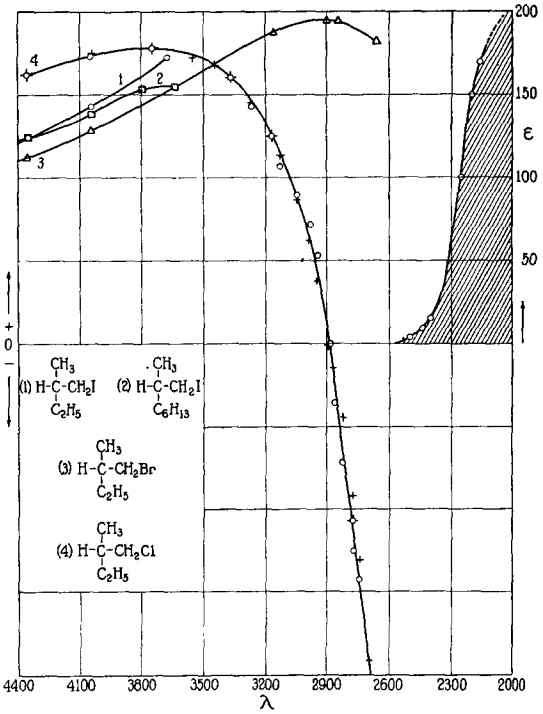

FIG. 2. Rotatory dispersion curves of primary halides. The ordinate represents the rotations in arbitrary units. The absorption curve of the bromide may be seen to the right (shaded surface).

ROTATORY DISPERSION CURVES

Experimental data concerning the rotatory dispersions are summarized in Tables IV to VI and in Fig. 2. In order to save space, only the observed rotations have been given for the iodides. A two-term formula has been calculated for each compound, which reproduces the observed dispersion curve within experimental errors (0.05 percent in the visible, and about 1 percent in the ultraviolet region). The numerators of the terms have been so adjusted that the formulae express the maximum rotations. The maximum values are, of course, very approximate, but their order of magnitude is correct.

TABLE III. *Configurationally related halides.*

COMPOUNDS	$[M]_D^{25}$ max	n_D^{25}	d_4^{25} (in vacuum)
Levo 2-iodobutane*	−58 8	1.4975	1.589
Levo 2-iodooctane	−97.4	1 4863	1 3158
Dextro 1-iodo-2-methylbutane*	11.2	1 4950	1.5138
Dextro 1-iodo-2-methylheptane	5.0	1.4875	1.3331
Dextro 1-iodo-2-methylnonane	5.0	1.4850	1.2536
Dextro 1-iodo-3-methylpentane	47.0	1.4884	1 4187
Dextro 1-iodo-4-methylhexane	26.7	1.4893	1.3480
Levo 2-bromobutane*	−30.0	—	1.2536
Levo 2-bromooctane	−62.5	1.4484	1.0983
Dextro 1-bromo-2-methylbutane	7.9	1.4426	1 2144
Dextro 1-bromo-3-methylpentane*	38.8	1.4468	—
Levo 2-chlorooctane	−39.5	1.4247	0.8613
Dextro 1-chloro-2-methylbutane	1.7	1.4101	0.8810
Dextro 1-chloro-3-methylheptane	7.9	1.4289	—
Dextro 1-chloro-4-methylhexane	21 0	1.4228	0.8702
Dextro 1-chloro-5-methylnonane	2.3	1 4364	0.8690

In Table III the maximum $[M]_D$ values have been tabulated for all the compounds studied. It may be seen from Table IV and related equations, that the secondary iodides have their first two absorption regions active.[5] The contribution of the first continuum is important, and the fact that both contributions are of the same

[5] In this connection we wish to refer to a recent article of Kuhn, Zeits. f. physik. Chemie **B29**, 256 (1935), criticizing our interpretation of the dispersion of the iodides, already published by us in a short note, P. A. Levene and A. Rothen, Am. Chem. Soc. **55**, 429 (1935). His contention that the rotatory contribution of the continuum of the iodides is negligible seems in accord with his published rotatory dispersion curve. A comparison of our measurements with his curve, however, shows a great discrepancy between his experimental values and our own (it is unfortunate that Kuhn's failure to give figures besides his curves makes a precise comparison difficult). Taking at random a few values brought to coincide at λ5000, ($\alpha=100$) we found, $\alpha_{4000}=230$ (Kuhn), $\alpha_{4000}=185.4$ (Levene and Rothen); $\alpha_{3000}=1000$ (Kuhn), $\alpha_{3000}=613$ (Levene and Rothen); $\alpha_{2300}=1400$ (Kuhn), $\alpha_{2300}=600$ (Levene and Rothen). We are at a loss to explain this difference. We duplicated our measurements (see below) on different samples of 2-iodooctane and determined the dispersion of the lower homolog 2-iodobutane, which has been found analogous. The difference between the dispersion in heptane and in homogeneous state has been found very small. Our measurements were made with two different polariscopes, one for the visible, and one for the ultraviolet regions. The data so obtained were consistent. The measurement made at λ4046.6, the smallest wave-length used in the visible region, already indicates that the curvature of the dispersion curve is that required by two terms of the same sign, the first one corresponding to the continuum. Kuhn criticizes our interpretation, based on extrapolation. We agree that, as a rule, extrapolation methods are treacherous, but when absorption makes it impossible to obtain good experimental values, they have to be resorted to. The results so obtained are correct, provided: First, that extrapolation is not extended too far; second, that the experimental values used for the extrapolation are of a high degree of accuracy. Both conditions were fulfilled in our work. In the case of the secondary iodides, for instance, we predicted that the first continuum was active from extrapolated values; actual measurements made later on on the short wave-length side of the band confirmed our prediction. Furthermore, Kuhn compares his results obtained on secondary iodides with our results on primary iodides ($n=1$), taking for granted that the dispersion of the latter is comparable to that of the former. From that comparison Kuhn concludes that our results ($n=1$) are erroneous. Our present article shows that such comparisons are not legitimate. What is true concerning the partial rotatory contributions of the different bands of the iodine atom, in a compound in which n has a certain value, cannot be applied to those in which n has a different value. The distance of the chromophoric group from the asymmetric carbon atom is of the utmost importance, a factor as essential, in a way, as the order in which the three other groups attached to the asymmetric carbon atom are arranged.

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TABLE IV. *Experimental rotatory values (homogeneous state) of configurationally related iodides.*

	Levo 2-Iodobutane	Levo 2-Iodooctane	Dextro 1-Iodo-2-Methylbutane	Dextro 1-Iodo-2-Methylheptane	Dextro 1-Iodo-2-Methylnonane	Dextro 1-Iodo-3-Methylpentane	Dextro 1-Iodo-4-Methylhexane
$\alpha^{25}_{5875\ 6}$		48.265 (10 cm)	5.439 (10 cm)	5.518 (40 cm)		12.977 (10 cm)	4.987 (10 cm)
$\alpha^{25}_{5780\ 1}$	6.672 (20 cm)	50.186	5.626	5.696	1.242 (10 cm)	13 468	5.172
$\alpha^{25}_{5460\ 7}$	7.670	57.613	6 314	6.325	1.374	15.390	5.873
$\alpha^{25}_{4358\ 3}$	13.988	104 16	9 915	9.225	2.01	27.01	9.94
$\alpha^{25}_{4046\ 6}$	17.51	129.63	11.458	10.16	2.23	33.03	11.96
α^{25}_{3780}	5.40 (5 cm)		6.90 (5 cm) for λ3680	1.40 (5 cm) from λ3800 to λ3640	1.25 (5 cm) from λ3850 to λ3600		
α_{3710}		86 15 (5 cm)				22.8 λ3628 (5 cm)	1.8 λ3500 (1 cm)
α_{3685}		88 15				23.8 λ3580	1.9 λ3450
α_{3568}		19.82 (1 cm)				2.72 λ3445	
α_{2300}		0.07 (0.1 cm) conc. 0.155M in heptane					

sign explains the high rotation observed in the visible region. On the other hand, the first continuum in iodides for which $n=1$ seems but slightly active, and the two rotatory contributions due to the second and third absorption regions are of opposite sign; hence a low value for the maximum rotation in the visible region. The second rotatory component is even greater than the first in the visible and near ultraviolet regions, with the result that the dispersion curve becomes anomalous. In the corresponding chlorides it is possible to observe that, with decreasing wave-lengths, the rotation goes through a maximum, reaches zero and increases in the opposite sense. The maximum could be reached in the bromides, but not in the iodides (see Fig. 2). These facts are easily understood if one considers that the wave-length interval between the inactive continuum and the first lines of the Rydberg series is much greater in the iodides than in the other halides. Similar considerations explain the failure to detect the contribution furnished by the third region (see Table II) in secondary and primary iodides having $n=2$. In this case, the contributions of the continuum and second absorption region predominate and mask the other contribution completely.

The rotatory dispersion of the secondary halides needs special consideration. From the dispersion equations it may be seen that it is only in the case of the iodides that the dispersion

TABLE V. *Rotatory dispersion of configurationally related bromides.*

Levo 2-Bromobutane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 1 cm from λ2827 to λ2745.			Levo 2-Bromooctane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=10$ cm, 5 cm from λ2932 to λ2870, 1 cm from λ2842 to λ2823, 0.1 cm for λ2710 and λ2633.			Dextro 1-Bromo-2-Methylbutane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 0.5 cm for λ2660.			Dextro 1-Bromo-3-Methylpentane in Heptane. Visible region: conc. 0.6037M. $l=40$ cm. U.V. region: conc. 0.9146M $l=10$ cm.		
λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$
5780 1	42.782	31.333	5875.6	51.622	62.927	5875.6	5.024	7.938	6678.1	3.40	30.0
5460.7	48.757	35.709	5780.1	53.525	65.247	5780.1	5.192	8.203	5875 6	4.446	39 24
4358.3	84.01	61.53	5460.7	60.960	74.310	5460.7	5 806	9.173	5780.1	4.578	40.41
4046.6	101.68	74.47	4358.3	104.47	127.35	4358 3	8.965	14.165	5460.7	5.205	45.94
3797	30.1	88.2	4046.6	126.19	153 82	4046.6	10.30	16.27	4358.3	8 765	77.36
3630	34 1	99.9	3378	103.8	253.1	3160	3.75	23.7	3445	6.10	142
3490	38.1	111.6	3274	113.8	277.4	2900	3.90	24.6	3250	7.10	165
3382	42.1	123.3	3190	123.8	301.8	2845	3.90	24 6	3170	7.60	177
3259	47.1	138.0	3113	133.8	326 2	2660	0.37	23	3000	9.10	212
3139	53.1	155 5	3075	138.8	338.4				2845	10.60	247
3040	59.1	173.1	3044	143.8	350.6				2745	11.90	282
2827	15 1	221	3010	148 8	362.8						
2790	16.1	236	2982	153 8	375 0						
2765	16.6	243	2932	81.8	398.8						
2745	17.1	250	2891	85.8	418.4						
			2870	87 8	428.1						
			2842	18.1	441						
			2823	18 6	453						
			2710	2.25	548						
			2633	2.55	622						

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TABLE VI. *Rotatory dispersion of configurationally related chlorides.*

Levo 2-Chlorooctane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=10$ cm, 5 cm for λ2460 to λ2396, 1 cm for λ2348, 0.1 cm for λ2240.			Dextro 1-Chloro-2-Methylbutane Without Solvent. Visible region: $l=10$ cm, U.V. region: $l=5$ cm and 1 cm for λ2495 to λ2360.			Dextro 1-Chloro-3-Methylheptane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm and 1 cm for λ2750.			Dextro 1-Chloro-4-Methylhexane Without Solvent. Visible region: 20 cm, U.V. region: 5 cm and 1 cm for λ2596 to λ2415.			Dextro 1-Chloro-5-Methylnonane Without Solvent. Visible region: $l=20$ cm, U.V. region: $l=5$ cm.		
λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$	λ	α^{25}	$[M]^{25}_{max.}$
5875 6	42.402	39.758	5875.6	0.596	1.751	5892.6	5.013	7.892	5875 6	7.856	21.140	5875.6	1.528	2.303
5780.1	43.965	41.224	5780.1	0.612	1.798	5780.1	5.242	8.252	5780 1	8.142	21 910	5780.1	1.578	2.378
5460.7	49.883	46 773	5460.7	0.666	1.959	5460.7	5 958	9.380	5460 7	9.219	24.808	5460.7	1.800_5	2.714
4358.3	83.775	78 552	4358.3	0.91	2.67	4358.3	10.135	15.955	4358 3	15.375	41.374	4358.3	3.075	4.635
4046 6	100.17	93.92	4046.6	0 97	2.84	4046 6	12.16	19.14	4040 6	18 27	49 16	4046.6	3.68	5 55
3868	56.1	105 2	3750	0.50	2.94	3630	4.1	25.8	3180	8.38	90.2	3540	1.35	8 14
3736	61 1	114 6	3550	0.50	2.94	3340	5.1	32.1	3115	8.88	95 6	3300	1.60	9 65
3622	66.1	124.0	3370	0.45	2.64	3050	6.6	41.6	2990	9.88	106 3	3135	1.85	11.1
3521	71.1	133 3	3270	0.40	2.36	2860	8.1	51.0	2900	10.88	117.1			
3352	81.1	153.4	3170	0.35	2.06	2750	1 85	58.2	2845	11.38	122.5			
3218	91.1	170.8	3050	0 25	1.46				2803	11.88	127.9			
3100	101.1	189.6	2990	0.20	1 17				2765	12.38	133.2			
3000	111.4	208.9	2980	0.15	0.87				2690	13.38	144.0			
2915	121.1	227.1	2885	0.00	0.00				2595	3.00	161			
2838	131.1	245.8	2870	−0.10	−0.58				2460	3 50	188			
2460	105.1	394.2	2830	−0.20	−1.18				2415	3.65	196			
2412	113.1	424.2	2785	−0.30	−1.76									
2396	116.1	435.4	2750	−0.40	−2.35									
2348	25 1	471	2495	−0.40	−11 8									
2240	3.1	580	2440	−0.50	−14.7									
			2400	−0.60	−17.6									
			2360	−0 70	−20.5									

curve may be expressed by two terms of the same sign, corresponding to the first two absorption regions. If one term is tried to reproduce the experimental curve, the dispersion constant falls between these two absorption regions and with the progressive decrease in wave-lengths, the rotations increase more rapidly than is to be expected from a single-term Drude formula. At first sight, the corresponding bromides and chlorides seem to behave differently. If the $1/[M]$ values are plotted against λ^2, the slight curvature observed is opposite to that found in the iodides. There is no doubt that the two main rotatory terms are of opposite sign. The transparency of 2-chlorooctane permitted rotatory measurements very far into the ultraviolet region. A careful analysis showed that when a two-term formula was tried, the dispersion constant of the first and more important term was located between the first two absorption regions. This fact indicates that this term represents the contributions of the first two absorption regions and that they are of the same sign as in the case of the iodides. The dispersion constant of the second term was negative, thus showing definitely that the term was anomalous, i.e., the third contribution was smaller than the the fourth, and of opposite sign. A three-term formula has been calculated, the first term taking care of the rotatory contributions of the first and second absorption regions, the second and third terms representing the third and fourth rotatory contributions, respectively. It is probably true that for the most part the fourth contribution originates in the rest of the molecule (alkyl groups) and cannot be detected in the iodides owing to the great proximity of the first continuum. The dispersion constants of the second and third dispersion terms (corresponding to the third and fourth absorption regions) cannot be considered as significant since they can be changed slightly and still express the experimental values with a reasonable degree of accuracy.

The same state of affairs is found in the secondary bromides. The analysis of their rotatory dispersion curves proved more difficult, on account of the following facts:

1. The departure of the function $1/[M]=f(\lambda^2)$ from a linear relation was very small, only one percent over the whole wave-length interval studied.

2. The absorption of the compound prevented measurements over a region of the spectrum as broad as in the case of the chlorides. A three-term

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formula has been calculated for 2-bromooctane (see Table V) in spite of the fact that one term is nearly satisfactory, the dispersion constant of the latter being, of course, greater than that of the first term of the three-term formula. The three-term formula corresponds to that calculated for 2-chlorooctane, the first term, as we have seen, representing the sum of the first two contributions which are of the same sign. It should be expected that as the region of the first continuum is approached, the value of its rotatory contribution should become greater than the calculated one included in the first term. In fact, it is seen that when the $1/[M]$ values are plotted against λ^2, a slight concave curvature is observed in the visible and near ultraviolet regions because the influence of the fourth contribution is greater than that of the first. For low values of λ however, the curvature becomes convex, the effect of the first contribution outbalancing that of the fourth contribution.

In the secondary bromides, the only case where it could be tested—the rule previously enunciated has been verified, namely, that *in a homologous series with respect to R, if the dispersion can be expressed by two terms of opposite sign, then, for any two members, the one with the greater dispersion has the smaller maximum rotation.*

It may be added that on account of the mentioned periodicity observed in the partial rotations of the halogen atom in a series homologous with respect to n, a corresponding periodic effect is observed in the dispersion ratios of the molecule as a whole. The following ratios $R=\alpha_{4046.6}/\alpha_{5780.1}$ for the series of chlorides brings out clearly the phenomenon:

2-chlorooctane $R=2.278$, 1-chloro-2-methylbutane $R=1.58$, 1-chloro-3-methylheptane $R=2.320$, 1-chloro-4-methylhexane $R=2.244$.
1-chloro-5-methylnonane $R=2.332$.

EQUATIONS REPRESENTING THE MAXIMUM MOLECULAR ROTATIONS OF THE IODIDES, BROMIDES AND CHLORIDES, VALID IN THE VISIBLE AND THE NEAR ULTRAVIOLET SPECTRUM

Levo 2-iodobutane:

$$[M]^{25}_{\text{max.}}=-\frac{9.8023}{\lambda^2-0.0685}-\frac{7.2490}{\lambda^2-0.040}$$

(in homogeneous state).

The value $[M]_D^{25}=-58.8$ was taken as maximum.[6] The dispersion of this compound was also taken in heptane. The molecular rotations were 1.49 percent higher than in homogeneous state. The dispersion was practically the same. (If a one-term Drude formula is used to express the dispersion from two given λ, a difference of only 8A is found between the two dispersions constants of the terms corresponding to the measurements in the homogeneous state and in heptane.)

Levo 2-iodooctane:

$$[M]^{25}_{\text{max.}}=-\frac{13.312}{\lambda^2-0.069}-\frac{15.162}{\lambda^2-0.040}$$

(in homogeneous state),

$$[M]^{25}_{\text{max.}}=-\frac{12.226}{\lambda^2-0.069}-\frac{18.175}{\lambda^2-0.040}\ \text{(in heptane).}$$

The dispersion is slightly more susceptible to the effect of the solvent than in the case of the 2-iodobutane. The rotation is about 6.0 percent greater in heptane than in homogeneous state for λ5780.1. The order of magnitude of the rotation on the short wave-length side of the first band is for λ2300, $[M]_{2300}=500°$. The value calculated from the above equation which should hold only approximately for that region is $[M]_{2300}=630°$.

Two samples were prepared, both gave the same dispersion in spite of the fact that one of them had too low a density and index of refraction (some iodine split off, inactive impurity).

Dextro 1-iodo-2-methylbutane:

$$[M]^{25}_{\text{max.}}=-\frac{4.7539}{\lambda^2-0.043}+\frac{8.5535}{\lambda^2-0.028}.$$

Dextro 1-iodo-2-methylheptane:

$$[M]^{25}_{\text{max.}}=-\frac{4.4216}{\lambda^2-0.046}+\frac{6.2033}{\lambda^2-0.032}.$$

Dextro 1-iodo-2-methylnonane:

$$[M]^{25}_{\text{max.}}=-\frac{5.707}{\lambda^2-0.040}+\frac{7.527}{\lambda^2-0.028}.$$

Dextro 1-iodo-3-methylpentane:

$$[M]^{25}_{\text{max.}}=\frac{14.133}{\lambda^2-0.0466}.$$

Dextro 1-iodo-4-methylhexane:

$$[M]^{25}_{\text{max.}}=\frac{8.377}{\lambda^2-0.0336}.$$

Levo 2-bromobutane:

$$[M]^{25}_{\text{max.}}=-\frac{12.6140}{\lambda^2-0.032}-\frac{3.482}{\lambda^2}.$$

Levo 2-bromooctane:

$$[M]^{25}_{\text{max.}}=-\frac{22.159}{\lambda^2-0.034}-\frac{2.540}{\lambda^2-0.025}+\frac{5.434}{\lambda^2-0.010}.$$

Dextro-1-bromo-2-methylbutane:

$$[M]^{25}_{\text{max.}}=-\frac{9.4151}{\lambda^2-0.032}+\frac{12.169}{\lambda^2-0.025}.$$

[6] R. H. Pickard and R. J. Kenyon, J. Chem. Soc. **99**, 45 (1911).

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Dextro-1-bromo-3-methylpentane:

$$[M]^{25}_{max.} = \frac{12.243}{\lambda^2 - 0.0317}.$$

Levo 2-chlorooctane:

$$[M]^{25}_{max.} = -\frac{15.966}{\lambda^2 - 0.024} - \frac{7.329}{\lambda^2 - 0.020} + \frac{10.820}{\lambda^2 - 0.012}.$$

Dextro 1-chloro-2-methylbutane:

$$[M]^{25}_{max.} = -\frac{3.667}{\lambda^2 - 0.030} + \frac{4.352}{\lambda^2 - 0.020}.$$

Dextro 1-chloro-3-methylheptane:

$$[M]^{25}_{max.} = \frac{4.6373}{\lambda^2 - 0.025} - \frac{2.1879}{\lambda^2 - 0.015}.$$

Dextro 1-chloro-4-methylhexane:

$$[M]^{25}_{max.} = \frac{13.915}{\lambda^2 - 0.015} - \frac{7.249}{\lambda^2}.$$

Dextro 1-chloro-5-methylnonane:

$$[M]^{25}_{max.} = \frac{1.763}{\lambda^2 - 0.025} - \frac{1.059}{\lambda^2 - 0.015}.$$

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Remarks Concerning the Formation and Crystallization of Vitreous Media

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The various characteristics of the liquid-glass transition are examined in an attempt to establish the hypothesis that liquid or vitreous properties depend upon the relation between the thermal relaxation time and the time of measurement, and not upon any discontinuous allotropic change at a fixed temperature. In the course of this survey it is found that the relaxation time involved in the liquid-glass transition for the heat capacity of glucose must be far less than that for the molecules, and is therefore probably that characterizing rotations of groups within the molecules, or certain modes of vibration of atoms or groups. No need is found from any of the measurements examined for the postulation of a "vitreous state of aggregation," since all the properties of glasses appear to be those of undercooled liquids of high viscosity. Since the viscosity of laboratory glass is too high to permit its devitrification within a reasonable time, a mechanism involving surface solution is suggested by means of which observed phenomena may be explained.

INTRODUCTION

IN recent years much interest has been aroused by the vitrification of viscous liquids. From a theoretical standpoint the matter gives a promising attack on some aspects of the liquid state, and it has yielded indispensable information concerning annealing schedules and the like. It is not intended here to give an historical résumé of the subject, since it is not felt that the thesis about to be expounded is either sufficiently complex or fundamental to justify an elaborate introduction. Such references as are made to the literature of the subject will, therefore, be chosen merely for illustrative purposes, without regard to completeness or sequence.

Numerous authors have reported abrupt changes in the temperature derivatives of the heat content, specific volume, and like properties over short temperature ranges for a wide variety of substances in the amorphous state, while the properties themselves appear to undergo no change. The temperature at which the derivatives change is known variously as the glass temperature, the temperature of maximum association, the vitrification point, etc., and is generally designated by T_g. The interpretation of these changes is, however, diverse. One school of thought considers that they indicate an allotropic change to a new state of aggregation. Le Chatelier[1] suggested this some years ago on the basis of viscosity data. Recently Mondain-Monval,[2] who is perhaps the most radical of the group in his views, wrote (p. 22), "We are resolutely partisan to the hypothesis of an allotropic transformation characteristic of the amorphous state" and, concerning T_g (p. 69) "there exists, then, . . . a unique temperature below which the stable crystalline variety cannot appear . . . by crystallization of the body in the vitreous state." Similarly Kobeko and his associates[3–7] consider

[1] H. le Chatelier, Ann. de physique **3**, 5 (1925).
[2] P. Mondain-Monval, Ann. de Chimie **3**, 1 (1935).
[3] P. P. Kobeko, Physik. Zeits. Sowjetunion **4**, 83 (1933).
[4] Kobeko and I. J. Nelidow, ibid. **4**, 516 (1933).
[5] Kobeko and E. Kuwschinsky, ibid. **4**, 680 (1933).
[6] Kobeko and I. J. Nelidow, ibid. **4**, 695 (1933).
[7] Kobeko and I. J. Nelidow, ibid. **4**, 703 (1933).

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