

LXXXVIII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XII. Ethyl Tartrate in Aromatic Halogen Derivatives.*

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IN continuation of this investigation, the last part of which (Trans., 1908, **93**, 355) dealt with the behaviour of certain aliphatic halogen derivatives, we have examined the solvent influence of a number of aromatic halogen substitution products on the rotation of ethyl tartrate, the procedure being exactly the same as formerly described.

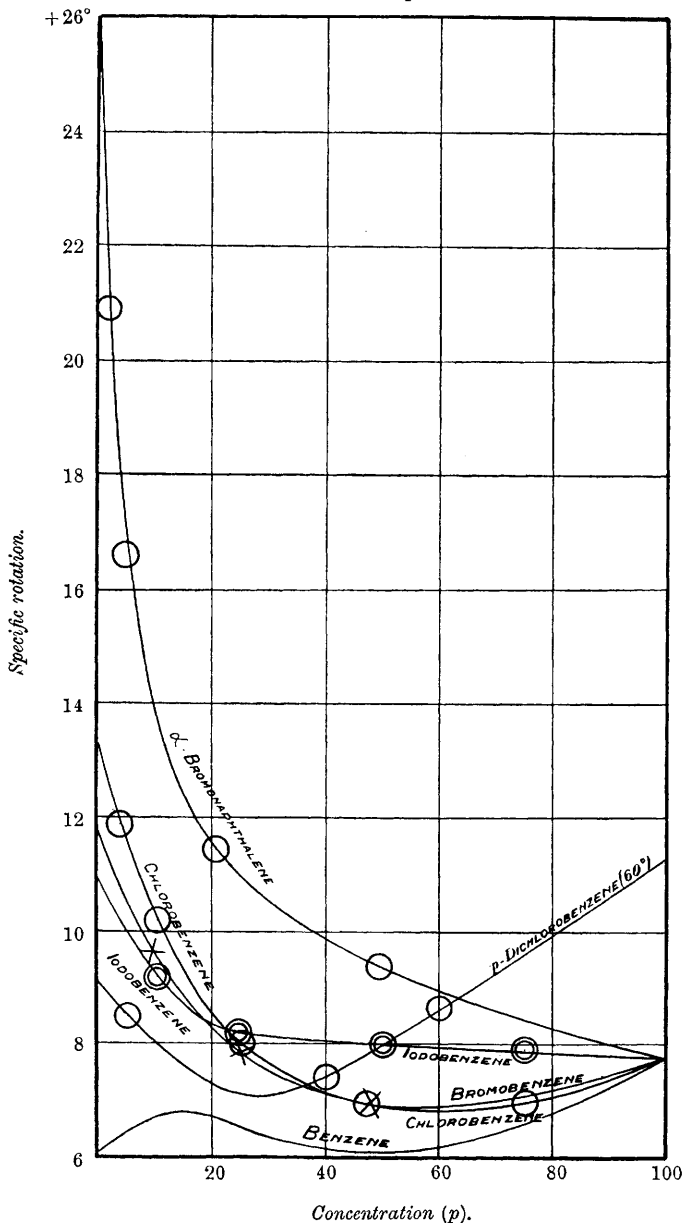
The numerical data are collected together at the end of the paper, but the main points of interest are brought out by the diagram, in which are shown curves representing the variation of the specific rotation of ethyl tartrate with change of concentration in the various solvents used.

We may consider first the curves of chloro-, bromo-, and iodo-benzene. It will be observed that they are of a similar character and that, as might have been expected, they show a progressive variation.

Addition of chlorobenzene at 20° to ethyl tartrate gradually lowers the specific rotation of the ester from +7.76° until a distinct minimum of +6.8° is reached at, or near,  $p=58$ . With further dilution, the specific rotation rises again, reaching the original value at about  $p=27$ , and continuing to rise at an increasing rate as the solution becomes more dilute, attaining, finally, to a value of +13.3° at infinite dilution.

The solvent effect of bromobenzene is of a very similar character, but the initial lowering of the rotation is not so great. A minimum rotation of about +6.93° occurs at practically the same concentration as in chlorobenzene, but the subsequent rise in rotation is not so rapid, so that the two curves intersect at about  $p=30$ . The rotation in bromobenzene at infinite dilution would be +11.8°.

*Ethyl tartrate in benzene, chlorobenzene, bromobenzene, iodobenzene, and  $\alpha$ -bromonaphthalene at 20° and in p-dichlorobenzene at 60°.*



The chlorobenzene curve is marked by circles, that for bromobenzene by crosses, and that for iodobenzene by concentric circles.

With the substitution of an iodine atom in the molecule, the rotation of the dissolved ester constantly rises, slowly at first, and much more rapidly in dilute solution, reaching a final value at infinite dilution of  $+11^\circ$ . There is in this solvent at  $20^\circ$  no concentration of minimum rotation.\*

A number of interesting comparisons can be instituted between these solvents and others previously examined. For this purpose, the curve for benzene (Trans., 1902, 81, 1098) is shown in the diagram, and it will be observed that in fairly concentrated solutions, down to about  $p=30$ , the behaviour of benzene is similar to that of its monochloro- and monobromo-derivative. Dilution of ethyl tartrate with any of these three substances causes initial diminution of the rotation of the ester. A minimum rotation occurs at practically the same concentration in each case. This resemblance in behaviour ceases, however, in more dilute solutions, since in benzene a maximum rotation is reached at  $p=12$ , and in solutions less concentrated than this the rotation diminishes instead of increasing with further dilution.

Between the curves for chloro-, bromo-, and iodo-benzene and those for the aliphatic halogen derivatives there is, on the whole, a striking contrast. The latter solvents in all cases examined and at all concentrations depressed the rotation of ethyl tartrate considerably below that of the homogeneous ester, and, at least in a number of important instances, this diminution becomes more rapid with increasing dilution, so that in such cases the action of the two classes of solvents is exactly of an opposite character. Concentrations of minimum rotation occur in the aliphatic halides, but these are by no means so pronounced as in chlorobenzene and bromobenzene. In any case, concentrations of minimum rotation cannot be regarded as characteristic of any one series of solvents, as they appear to occur in all classes, particularly at low temperatures.

In the figure is also shown a curve for *p*-dichlorobenzene, but in this case, since the solvent easily crystallises out even from solutions containing a considerable proportion of tartrate, the polarimetric observations could only be extended down to a temperature of about  $50^\circ$ . The concentration curve shown is for  $60^\circ$ . It is obvious, of course, that the concentration-rotation curve for *p*-dichlorobenzene at  $20^\circ$  would lie much below that for benzene. A rough idea of what its appearance would be may be obtained by imagining the curve for  $60^\circ$  lowered on the diagram so that the point on it for  $p=100$  coincides with the point common to all the other curves. It will be observed that dilution of ethyl tartrate with *p*-dichlorobenzene also diminishes

\* Separation of iodine seemed to take place somewhat more rapidly from the solutions than from the pure solvent. After the solutions had stood overnight, their rotation had always diminished slightly.

the rotation of the ester from  $11.3^\circ$  ( $p=100$ ) until a concentration of about  $p=25$  is reached, at which a minimum rotation ( $+7.1^\circ$ ) occurs. Further dilution brings about a slight rise in rotation. Thus, comparing benzene, chlorobenzene, and *p*-dichlorobenzene, it appears that, whereas the introduction of one chlorine atom in the molecule of the solvent causes increase in the rotation of the dissolved ester, a second chlorine atom in the para-position produces a solvent having a greater depressing effect than the mother substance.

In all three cases, a concentration of minimum rotation is distinctly marked.

We have also determined the molecular solution-volume of ethyl tartrate in the monohalogen substitution derivatives \* for comparison with the corresponding rotations, since, from previous work, it might be expected that these variables should show an inverse relationship. In the solvents mentioned, for concentrations below about  $p=20$ , both rotation and molecular solution-volume increase rapidly, which is apparently in opposition to the regularity referred to. It is, however, only on the limiting value of the solution-volume that any valid arguments can be based (Trans., 1901, 79, 192), but, unfortunately, in the instances under consideration the increase of molecular solution-volume is so rapid in dilute solution that it is very difficult by extrapolation to arrive at any satisfactory estimate for the value at infinite dilution. Therefore, in the table below, the figures for solution-volume are given for  $p=5$ , whilst those for rotation are for  $p=0$ :

Ethyl tartrate in	M.S.V. <sup>20°</sup> $p=5$ .	$[\alpha]_D^{20^\circ}$ infinite dilution.
Chlorobenzene .....	173.71 c.c.	+13.3°
Bromobenzene.....	174.91 „	11.7
Iodobenzene .....	175.38 „	11.0

It will be seen that the inverse relationship does appear to hold for the solvents in question, but it must be admitted that the data for molecular solution-volume are somewhat unsatisfactory, since, on account of the rapid increase of volume in dilute solution and on account of the fact that any small error in the density determination of dilute solutions is greatly magnified in the process of calculation, it is difficult definitely to decide whether or no at low concentrations the solution-volume curves intersect like those for rotation.

It may further be noticed that in these solvents, as in the aliphatic halogen derivatives (Trans., 1908, 93, 355), ethyl tartrate has in general the greatest volume in iodides and the least in chlorides. This is shown by the preceding table and by the one on p. 940.

\* In a solvent like *p*-dichlorobenzene, trustworthy values for molecular solution-volume could hardly be obtained.

Ethyl tartrate in	Infinite dilution.		Ethyl tartrate in	Infinite dilution.	
	M.S.V. <sup>20°</sup> .	$[\alpha]_D^{20°}$ .		M.S.V. <sup>20°</sup> .	$[\alpha]_D^{20°}$ .
	in c.c.			in c.c.	
Ethyl iodide .....	178.3	-2.2°	Methylene iodide .....	177.7	-0.8°
Ethyl bromide .....	172.6	-0.95			
Ethylene bromide .....	176.8	-20.0	( $p=1.4$ ).		
Ethylene chloride .....	176.0	-4.1	Methylene chloride .....	174.1	-1.6
Acetylene tetrabromide	176.6	-18.8	Bromoform .....	177.1	+0.2
Acetylene tetrachloride	173.6	-16.6	Chloroform .....	175.0*	-3.0

In all these cases, the volume of the ethyl tartrate is greater in iodides than in bromides, and greater in bromides than in chlorides. In the three instances on the left of the table, the greater volume is associated with the lower rotation, whilst in the other two cases the opposite obtains.

In an earlier paper (Trans., 1902, 81, 1134), it was shown by one of us that naphthalene as a solvent has a very marked influence on the rotation of ethyl tartrate, an influence distinctly different from that of benzene. It was of interest to ascertain whether a similar difference exists between the monohalogen derivatives of benzene and naphthalene respectively, and therefore we have investigated the solvent effect on ethyl tartrate of  $\alpha$ -bromonaphthalene, the concentration-rotation curve being reproduced in the diagram. It will be noticed that the curve for  $\alpha$ -bromonaphthalene is similar both to those for bromobenzene (although there is no concentration of minimum rotation at 20°) and for naphthalene in what is, perhaps, the most important particular, namely, rapid increase of specific rotation with diminishing concentration, especially in dilute solution. In  $\alpha$ -bromonaphthalene this is very striking indeed, the rotation increasing from 16.5° for  $p=5$  to 20.9° for  $p=2$ . It is not possible to give an accurate estimate for the value of the specific rotation at infinite dilution, but it probably is nearly +26°. It is difficult to say whether the value for the solution-volume of ethyl tartrate is in agreement with that for the rotation or not. For  $p=5$  the molecular solution-volume is 174.2 c.c., which is a little greater than in a chlorobenzene solution of the same strength, but is less than in bromo- and

\* In the last part of this research (Trans., 1908, 93, 357, note), the opinion was expressed that the value formerly estimated (Trans., 1905, 87, 320) for the M.S.V. of ethyl tartrate in chloroform might be too high, this idea being formed from a comparison of the M.S.V. curve for chloroform with the curves for other solvents. We have, therefore, re-examined the matter and have obtained the following data:

$p$ .	$d$ .	$\delta$ .	M.S.V. <sup>20°</sup> .
3.00068	1.47773	1.48864	172.43 c.c.
4.00196	1.47425	1.48864	172.13 „
5.92138	1.46783	1.48881	171.90 „

Taking the new data along with those formerly found, a mean value of about 175 c.c. is obtained for M.S.V.<sup>20°</sup> at infinite dilution.

iodo-benzene. The form of the solution-volume curve is such, however, as makes it highly probable that at infinite dilution the volume of the ester in  $\alpha$ -bromonaphthalene is distinctly less than in the other three solvents, which is, so far, in agreement with the suggested inverse relationship of rotation and volume.

In regard to the effect of temperature change, the rotation of solutions of ethyl tartrate in  $\alpha$ -bromonaphthalene are of some special interest. It has been noticed already in the course of this investigation that when the effect of a large excess of a given solvent is to raise considerably the rotation of ethyl tartrate or similar substance, the influence of rise of temperature is to diminish the rotation of such a solution. This is the case, for instance, with dilute solutions of ethyl tartrate in water (Trans., 1901, 79, 172; 1904, 85, 1129) and in naphthalene\* (Trans., 1902, 81, 1139), and the same behaviour is shown by methyl tartrate and *n*-propyl tartrate in water (Trans., 1904, 85, 1127, 1131). A somewhat similar behaviour is shown by dilute aqueous solutions of methyl-, ethyl-, and *n*-propyl-potassium tartrate, in which cases the specific rotation on heating at first increases to reach a maximum value and then diminishes again (Trans., 1904, 85, 1121, 1123, 1125). We therefore suspected that, since the rotation of dilute solutions of ethyl tartrate in  $\alpha$ -bromonaphthalene is so high, a maximum should occur in the temperature-rotation curve at a comparatively low temperature. The  $p=2$  solution was therefore examined throughout a greater range of temperature than the others. Its rotation increased rapidly at first, but gradually more slowly, and passed through a maximum value of  $+29.6^\circ$  at a temperature of  $94^\circ$ . The occurrence of such temperatures of maximum rotation is of very considerable interest, and further examples will be discussed in a future paper.

## EXPERIMENTAL.

### *Ethyl Tartrate in Chlorobenzene.*

The chlorobenzene boiled at  $44.8^\circ$  under a pressure of 30 mm. (oil-bath,  $112^\circ$ ):

I.  $p=3.8059$ .

$t^\circ$ .....	$13.8^\circ$	$17.4^\circ$	$33.6^\circ$	$40.0^\circ$	$43.7^\circ$
$\alpha_D^{20}$ (400 mm.).....	$+1.872$	$1.955$	$2.275$	$2.391$	$2.450$
$[\alpha]_D^{20}$ .....	$+11.02$	$11.55$	$13.65$	$14.45$	$14.86$

\* In this case, diminution of the observed rotation was detected in a  $p=10$  solution, but the specific solution showed a slight increase between  $70^\circ$  and  $100^\circ$ . At a higher temperature, the specific rotation also would doubtless have commenced to decrease.

*Ethyl Tartrate in Chlorobenzene (continued).*II.  $p = 10.0073$ .

$t^\circ$ .....	11.3°	21.7°	32.0°	40.1°	47.8°	56.0°	100.0°
$\alpha_D^{25}$ (249.6 mm.)	+2.453	2.893	3.292	3.537	3.742	3.93	4.408
$[\alpha]_D^{25}$ .....	+8.74	10.41	11.97	12.96	13.82	14.63	17.19

III.  $p = 24.9956$ .

$t^\circ$ .....	13.0°	24.8°	38.8°	44.6°	59.3°	68.7°	100.0°
$\alpha_D^{25}$ (249.6 mm.)	+4.783	6.098	7.378	7.782	8.728	9.192	10.167
$[\alpha]_D^{25}$ .....	+6.75	8.78	10.68	11.52	12.87	13.71	15.66

IV.  $p = 47.469$ .

$t^\circ$ .....	9.1°	13.1°	21.9°	37.9°	46.5°	57.3°	67.2°	100.0°
$\alpha_D^{25}$ (100 mm.)	+2.969	3.252	3.93	5.029	5.534	6.054	6.415	7.815
$[\alpha]_D^{25}$ .....	+5.39	5.92	7.22	9.37	10.40	11.49	12.29	14.49

V.  $p = 75.345$ .

$t^\circ$ .....	13.0°	22.0°	38.6°	55.5°	66.6°
$\alpha_D^{25}$ (100 mm.)	+5.463	6.476	8.067	9.26	9.9
$[\alpha]_D^{25}$ .....	+6.11	7.31	9.24	10.77	11.64

*Densities determined:*

Solvent.		I.		II.		III.	
$t^\circ$ .	$d.$	$t^\circ$ .	$d.$	$t^\circ$ .	$d.$	$t^\circ$ .	$d.$
17.05°	1.10974	18.5°	1.11071	15.0°	1.12025	14.7°	1.13432
24.12	1.10215	24.25	1.10451	39.3	1.09382	36.0	1.11108
38.53	1.08650	31.87	1.09622	68.1	1.0622	63.2	1.0812
				99.0	1.0278	99.0	1.0415

IV.		V.	
$t^\circ$ .	$d.$	$t^\circ$ .	$d.$
17.9°	1.15180	18.8°	1.1797
36.3	1.13223	24.91	1.1732
65.5	1.1013	49.5	1.1472
101.3	1.0619		

*Ethyl Tartrate in Bromobenzene.*

The bromobenzene boiled at 43° under a pressure of 18 mm.:

I.  $p = 9.93184$ .

$t^\circ$ .....	11.0°	14.8°	24.0°	39.6°	47.0°	52.0°	100.0°
$\alpha_D^{25}$ (249.6 mm.)	+2.91	3.127	3.705	4.402	4.66	4.84	5.725
$[\alpha]_D^{25}$ .....	+7.99	8.62	10.29	12.41	13.22	13.8	17.09

II.  $p = 24.94$ .

$t^\circ$ .....	9.6°	13.2°	18.0°	24.0°	37.7°	45.5°	55.3°	62.5°	100.4°
$\alpha_D^{25}$ (249.6 mm.)	+5.439	5.97	6.655	7.354	8.859	9.574	10.32	10.838	12.584
$[\alpha]_D^{25}$ .....	+6.17	6.79	7.6	8.44	10.30	11.21	12.19	12.89	15.51

*Ethyl Tartrate in Bromobenzene (continued).*III.  $p = 47.967$ .

$t^{\circ}$ .....	10.4°	13.0°	23.1°	41.2°	48.3°	56.2°	62.0°	100.3°
$\alpha_D^{25}$ (100 mm.) .....	+3.686	3.895	4.778	6.095	6.523	6.915	7.176	8.51
$[\alpha]_D^{25}$ .....	+5.70	6.04	7.48	9.69	10.44	11.15	11.63	14.31

*Densities determined :*

Solvent.		I.		II.		III.	
$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$
14.3	1.50188	18.6	1.45914	19.4	1.4048	19.1	1.33699
42.8	1.46425	36.1	1.43590	38.0	1.3820	38.5	1.31434
58.6	1.44313	59.0	1.4059	61.6	1.352	61.0	1.2875
100.6	1.3862	100.6	1.3508	100.8	1.302	101.0	1.2392

*Ethyl Tartrate in Iodobenzene.*

The iodobenzene boiled at 69° under a pressure of 15 mm. (oil-bath, 110°):

I.  $p = 10.6375$ .

$t^{\circ}$ .....	24.2°	40.1°	51.1°
$\alpha_D^{25}$ (170 mm.) .....	+3.05	3.62	4.04
$[\alpha]_D^{25}$ .....	+9.78	11.77	13.26

II.  $p = 24.9011$ .

$t^{\circ}$ .....	16.8°	21.1°	36.4°	52.4°
$\alpha_D^{25}$ (70 mm.) .....	+2.21	2.35	2.88	3.36
$[\alpha]_D^{25}$ .....	+7.83	8.36	10.38	12.29

III.  $p = 49.8182$ .

$t^{\circ}$ .....	13.6°	26.4°	40.4°	51.5°	59.9°
$\alpha_D^{25}$ (70 mm.) .....	+3.65	4.45	5.12	5.61	5.94
$[\alpha]_D^{25}$ .....	+7.18	8.86	10.33	11.43	12.18

IV.  $p = 75.2983$ .

$t^{\circ}$ .....	15.6°	21.6°	33.5°	45.5°
$\alpha_D^{25}$ (70 mm.) .....	+5.19	5.55	6.37	7.12
$[\alpha]_D^{25}$ .....	+7.48	8.03	9.32	10.53

*Densities determined :*

Solvent.		I.		II.		III.		IV.	
$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$
19.5°	1.83257	18.85°	1.73208	19.5°	1.61552	18.3°	1.45079	19.25°	1.31392
24.8	1.82363	24.1	1.72429	24.5	1.60846	24.15	1.44344	25.05	1.30724
31.25	1.8138	34.3	1.7090	29.6	1.6011	35.75	1.4288	36.2	1.2948
38.5	1.8027	51.6	1.6832	38.9	1.5881	53.2	1.4069	53.7	1.2749
				50.6	1.5716				



*Ethyl Tartrate in p-Dichlorobenzene:\** $p = 5.002.$ 

$t^{\circ}$ .....	50.8°	55.6°	60.0°†	63.6°	72°	79.3°	97.0°
$[\alpha]_D^{25}$ .....	+6.78	7.44	8.05	8.53	9.44	10.23	11.85

 $p = 40.01.$ 

$t^{\circ}$ .....	53.7°	60.0°†	63.4°	72.4°	99.0°
$[\alpha]_D^{25}$ .....	+6.62	7.4	7.8	8.82	11.18

 $p = 60.01.$ 

$t^{\circ}$ .....	52.7°	57.0°	60.0°†	66.0°	75.0°	89.7°
$[\alpha]_D^{25}$ .....	+7.77	8.35	8.7	9.37	10.25	11.5

*Ethyl Tartrate in  $\alpha$ -Bromonaphthalene.*

The  $\alpha$ -bromonaphthalene boiled at 139° under 16 mm. pressure (oil-bath, 166°):

I.  $p = 2.07933.$ 

$t^{\circ}$ .....	16.9°	25.2°	38.5°	52.1°	79.0°	110.5°
$\alpha_D^{25}$ (160 mm.) ...	+1.003	1.07	1.182	1.276	1.38	1.345
$[\alpha]_D^{25}$ .....	+20.36	21.83	24.34	24.51	29.2	29.05

II.  $p = 4.99697.$ 

$t^{\circ}$ .....	15.0°	33.5°	47.2°	59.3°
$\alpha_D^{25}$ (160 mm.).....	+1.806	2.318	2.58	2.76
$[\alpha]_D^{25}$ .....	+15.3	19.9	22.3	24.1

III.  $p = 20.2601.$ 

Only examined for density and solution-volume.

IV.  $p = 20.37.$ 

$t^{\circ}$ .....	19.4°	24.3°
$\alpha_D^{25}$ (100 mm.).....	+3.25	3.51
$[\alpha]_D^{25}$ .....	+11.8	12.22

V.  $p = 49.6882.$ 

$t^{\circ}$ .....	13.5°	20.0°	31.0°	42.5°	52.1°
$\alpha_D^{25}$ (100 mm.) .....	+5.535	6.17	7.216	8.08	8.703
$[\alpha]_D^{25}$ .....	+8.31	9.32	11.04	12.51	13.62

*Densities determined:*

Solvent.		I.		II.		III.	
$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$
18.55°	1.49225	19.8°	1.47853	18.95°	1.47269	18.65°	1.42089
20.75	1.49006	22.8	1.47549	20.95	1.47069	20.75	1.41853
23.0	1.48777	31.3	1.46697	24.3	1.46727	24.25	1.41491
IV.		V.					
$t^{\circ}$ .	$d.$	$t^{\circ}$ .	$d.$				
20.15°	1.414	18.7°	1.33226				
		20.55	1.33026				
		23.6	1.3270				

\* Unfortunately, the manuscript book containing the original data for these solutions has been mislaid, so that the observed rotations and densities cannot be given. As we had a note of the specific rotations at various temperatures, we did not consider it necessary to repeat the experiments in order to obtain values for the missing constants.

† Interpolated.

*Molecular Solution-volume and Specific Rotation at 20° of Ethyl Tartrate in Various Solvents.*

*Molecular Volume of Ethyl Tartrate at 20° = 170.9 c.c. ;  $[\alpha]_D^{20} + 7.76^\circ$ .*

In several cases, two or more different samples of solvent were used. In such instances, the density for  $p=0$  appears more than once. The numbers immediately following each 0 represent solutions made up with that specimen of solvent. We have not attempted to estimate values for M.S.V.<sup>20°</sup> at infinite dilution.

Solvent.	$p$ .	$d\ 20^\circ/4^\circ$ .	M.S.V. <sup>20°</sup> . c.c.	$[\alpha]_D^{20^\circ}$ .
Chlorobenzene .....	0	1.10674	—	+ 13.3°
	5.49034	1.11081	173.71	—
	0	1.10657	—	13.3
	3.8059	1.10909	175.05	11.87
	10.0073	1.11481	172.41	10.14
	24.996	1.12854	171.67	8.00
	47.47	1.14957	171.45	6.98
	75.345	1.1784	171.1	6.99
Bromobenzene .....	0	1.49447	—	11.7
	4.99987	1.47496	174.91	—
	0	1.49434	—	11.7
	9.93184	1.45728	173.15	9.6
	24.94	—	—	7.86
	47.967	1.33594	171.9	7.03
Iodobenzene .....	0	1.83173	—	11.0
	10.6375	1.73038	174.38	9.2
	24.9011	1.61482	173.12	8.2
	49.8182	1.44856	172.17	8.0
	75.2983	1.3131	171.46	7.9
	0	1.83174	—	11.0
	4.96374	1.78225	175.38	—
$\alpha$ -Bromonaphthalene ...	0	1.48651	—	26.0
	2.07933	1.47833	175.46	20.9
	0	1.49081	—	26.0
	4.99697	1.47164	174.2	16.6
	20.2601	1.41937	172.5	—
	20.37	—	—	11.4
	49.6882	1.33085	171.6	9.32

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