LIV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXIV.* Menthyl Benzenesulphonate, Menthyl Naphthalene-α-sulphonate, and Menthyl Naphthalene-β-sulphonate in Various Solvents.*

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We have examined the rotations of the esters described in the foregoing paper for three different colours of light, mercury yellow ($\lambda = 5790$), mercury green ($\lambda = 5461$), mercury violet ($\lambda = 4358$),

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and in several solvents which, for convenience of reference, are indicated by letters of the alphabet, namely, (*a*) ethyl alcohol; (*b*) benzene; (*c*) pyridine; (*d*) nitrobenzene; (*e*) ethylene dibromide; (*f*) quinoline. Since the object of our investigation was, in the first place, to obtain a general oversight, we examined only one solution in each case at a concentration between 4·45 and 1. The data are given in the tables of specific rotations.

TABLE I.

Specific Rotations of Menthyl Sulphonates in Various Solvents.

t = approximately 17·5° throughout.

Menthyl benzenesulphonate.

Solvent	a	b	c	d	e	f
Concentration	4·0	4·5	4·0	4·0	4·0	3·0
y	− 74·7°	− 65·5°	− 67·9°	− 67·4°	− 72·7°	− 64·4°
g	− 84·6	− 74·0	− 76·3	− 75·9	− 82·6	− 72·8
v	−142·2	−123·2	−127·4	−127·9	−137·6	−122·8

Menthyl naphthalene-α-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	1·0	1·0	1·0	3·0	1·0	3·0
y	−101·8°	− 81·4°	− 87·3°	− 92·2°	−145·2°	− 84·8°
g	−114·8	− 93·2	− 98·4	−104·6	−163·5	− 97·2
v	−194·3	−158·1	−166·0	−178·1	−276·2	−167·1

Menthyl naphthalene-β-sulphonate.

Solvent	a	b	c	d	e	f
Concentration	1·0	1·0	1·0	3·0	1·0	3·0
y	− 56·1°	− 51·9°	− 47·7°	− 43·9°	− 49·3°	− 31·2°
g	− 64·0	− 59·3	− 55·0	− 48·7	− 56·3	− 35·1
v	−108·0	−101·9	− 92·2	− 82·6	− 95·7	− 59·1

Although the rotations vary considerably in each case with change of solvent, the change is not sufficient to cause any overlapping, so that the solutions of each substance form a separate group, the rotations of menthyl naphthalene-β-sulphonate being lowest, and those for menthyl naphthalene-α-sulphonate being highest. The rotations for the benzenesulphonate solutions lie wholly between the others. It may also be noticed that the different solvents do not influence the rotations in the same way, although there is some similarity. Quinoline, which usually has a powerful influence either towards exaltation or depression, produces the lowest rotation in menthyl naphthalene-α-sulphonate and in menthyl benzenesulphonate, and the second lowest in menthyl naphthalene-β-sulphonate. Ethylene dibromide, on the other hand, which usually has a powerful influence of the opposite character to quinoline, produces the highest rotation in menthyl naphthalene-α-sulphonate, the second highest in menthyl benzenesulphonate, and the third highest in menthyl naphthalene-β-sulphonate. On the whole, therefore, this general tendency is recognisable.

These values were then plotted on a characteristic diagram and lay with good agreement along lines intersecting one another very close to the point of origin of the diagram, and in such a way, as far as can be judged when extrapolation has to be carried out through some 35° of rotation, as to indicate little or no region of anomalous rotation dispersion. The data thus present a behaviour which we think is rare and it follows that the dispersion coefficients for all these compounds calculated by the ordinary method ought to be almost the same throughout. (For a general discussion of this subject, see J., 1916, **109**, 413.) That this is the case is shown by the following table of dispersion ratios.

TABLE II.

	Menthyl benzene-sulphonate. Dispersion.		Menthyl naphthalene-α-sulphonate. Dispersion.		Menthyl naphthalene-β-sulphonate. Dispersion.	
Solvent.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.	Hg_v/Hg_g.	Hg_y/Hg_g.
Alcohol	1·680	0·883	1·692	0·887	1·687	0·878
Benzene	1·664	0·884	1·695	0·873	1·716	0·875
Pyridine	1·669	0·890	1·686	0·887	1·676	0·859
Nitrobenzene ...	1·685	0·888	1·703	0·881	1·698	0·902
Ethylene dibromide	1·665	0·879	1·689	0·888	1·700	0·876
Quinoline	1·685	0·885	1·709	0·872	1·683	0·889

These data, we think, form an almost unique example of constancy of ordinary dispersion ratios for a series of related substances, the rotation of which, for mercury green, varies over so wide a range as −35·1° for menthyl naphthalene-β-sulphonate in pyridine, up to −163·5° for menthyl naphthalene-α-sulphonate in ethylene dibromide.

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