130. *The Influence of Solvents and of other Factors on the Rotation of Optically Active Compounds. Part XXXIV.* The Influence of Water and of Deuterium Oxide.*

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WHEN these experiments were started, the only relevant publication was Pascu's observation (*J. Amer. Chem. Soc.*, 1934, **56**, 745) that the rotation at equilibrium of α-*d*-glucose in deuterium oxide was $[\alpha]_D^{20°}$ + 52·14° as against +52·06° in water. Erlenmeyer and Schenkel (*Helv. Chim. Acta*, 1936, **19**, 1381) have since shown that phenylbenzylmethyl*iso*propylammonium nitrate gives a small difference in rotation in water and in heavy water. From Pascu's observation it appeared that any effect would probably be small, so methyl *d*-tartrate was first chosen for examination, since the rotation of the alkyl tartrates is very sensitive to changes of solvent; also, since the methyl ester is solid, it could be more readily recovered from solution if necessary. It was recognised that any rotation difference with this compound might be due either to hydrogen interchange or to solvent effect, or both, but it was thought that some idea of the magnitude of the rotation changes to be expected with heavy water might be obtained.

The rotation of methyl *d*-tartrate in deuterium oxide (99%) is less than in water for the same concentration in g. per 100 g. of solution. The rotations were examined at different temperatures, and from the temperature-rotation curves by interpolation, we find:

In deuterium oxide, $p = 24·84$: $[\alpha]_D^{20°} = +18·10°$; $[\alpha]_{5461}^{20°} = +20·35°$.
In water, $p = 24·89$: $[\alpha]_D^{20°} = +18·65°$; $[\alpha]_{5461}^{20°} = +21·10°$.

The differences, for $[\alpha]_D$ 0·55°, and for $[\alpha]_{5461}$ 0·75°, are greater than the probable experimental error. If, however, the rotations for the same concentration in g. per 100 c.c. had been compared, the difference would be much less, and probably not more than the experimental error. A better comparison would be between solutions containing the same molecular proportion of solvent to methyl tartrate; for such solutions, $p = 24·84$ in deuterium oxide would correspond to $p = 26·87$ in water, and for the latter solution it can be calculated from Patterson's data (J., 1904, **85**, 1149) that $[\alpha]_D^{20°} = +18·30°$. The difference would thus be 0·20°, which is about the probable experimental error. There is no appreciable difference in the shape of the temperature-rotation curves, each of which shows a maximum at about 25°.

An attempt was made to find if methyl *d*-tartrate, which had been dissolved in deuterium

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* Part XXXIII, J., 1936, 1007.

oxide, and presumably had exchanged two hydrogens for deuterium, would show any difference in rotation when recovered from the solvent and examined in an indifferent solvent, as has been observed by Erlenmeyer and Schenkel (*Helv. Chim. Acta*, **1936**, **19**, 1199) for *l*-mandelic and *l*-atrolactinic acids. No such difference in rotation could be detected.

Methyl *d*-dimethoxysuccinate was next examined, since it contains no replaceable hydrogen atoms. No difference was observed in the rotation of this substance for solutions having $p = 20$ in water and in deuterium oxide.

Nicotine was also examined, as its rotation is considerably influenced by solution in water. For solutions having $p = 10$, nicotine has a somewhat higher rotation in deuterium oxide, $[\alpha]^{20^\circ}_{5461}$ −96·28°, than in water, $[\alpha]^{20^\circ}_{5461}$ −95·05°. As the specific rotation of nicotine at this concentration is practically unaltered by small changes in concentration (cf. Landolt, *Annalen*, 1877, **189**, 322; Tate and Warren, *J. Soc. Chem. Ind.*, 1937, **56**, 39), the same difference would be obtained by comparing solutions of the same concentration in g. per 100 c.c. Here, again, there is no appreciable difference in the shape of the temperature–rotation curves.

It was observed, incidentally, that there is a distinct difference in the solubility of nicotine in deuterium oxide and in water: a solution of nicotine in deuterium oxide, $p = 10·09$, on heating becomes turbid at 60·5°; nicotine in water, $p = 10·22$, becomes turbid at 73·5°.

EXPERIMENTAL.

The water and the deuterium oxide (99%) were boiled gently for a short time, to expel the bulk of the dissolved air, before being used for the solutions. The rotations were examined in a 40 mm. tube.

Methyl d-*Tartrate*.—(i) *In water*, $p = 24·89$. Densities determined :

t	11°	26°	36°	49·5°	69°	86°	97·5°
d	1·0809	1·0746	1·0693	1·0617	1·0489	1·0361	1·0272

t.	d.	α_D.	α_{5461}.	$[\alpha]_D$.	$[\alpha]_{5461}$.
0°	1·0848	+2·00°	+2·24°	+18·52°	+20·74°
17	1·0780	1·99	2·27	18·54	21·15
33·5	1·0706	1·955	2·26	18·33	21·20
50	1·0616	1·915	2·15	18·12	20·34
64·5	1·0523	1·85	2·09	17·66	19·95
80·5	1·0407	1·74	2·00	16·79	19·30
94	1·0299	1·67	1·87	16·29	18·24
17	after cooling	2·01	2·27	18·72	21·15

The above values for $[\alpha]_D$ and the corresponding values given by Patterson (*loc. cit.*) lie on the same curve.

(ii) *In deuterium oxide*, $p = 24·84$. Densities determined :

t	9°	21·5°	31°	44·5°	51·4°	63°	73·5°	94°
d	1·1742	1·1692	1·1639	1·1560	1·1513	1·1427	1·1344	1·1174

t.	d.	α_D.	α_{5461}.	$[\alpha]_D$.	$[\alpha]_{5461}$.
0°	1·1770	+2·115°	+2·37°	+18·09°	+20·27°
25·5	1·1670	2·09	2·36	18·14	20·35
37·8	1·1602		2·33		20·08
47	1·1542	1·99	2·28	17·35	19·88
61°	1·1440	1·95	2·185	17·16	19·22
74·5	1·1336	1·86	2·09	16·16	18·56
25·5	after cooling		2·37		

4 G. of methyl tartrate were dissolved in 4 c.c. of water; 200 c.c. of benzene, dried over freshly heated sodium sulphate, were added, and the mixture shaken. Sodium sulphate in excess was added to take up the water, and, after standing over-night in a desiccator, the solution was filtered, the benzene distilled off, and used to extract the sodium sulphate again. The bulk of the benzene was finally distilled off, freshly dried light petroleum (b. p. 60—80°) (30 c.c.) added, and the solution allowed to crystallise. This was repeated, deuterium oxide being used instead of water, and the rotation of the two samples was examined in freshly distilled nitrobenzene.

Ester from H_2O; $p = 8{\cdot}2174$.

t.	*d.*	α_{5461}.*	$[\alpha]_{5461}$.
0°	1·2307	+3·39°	+21·00°
21	1·2110	3·45	21·72

Ester from D_2O; $p = 8{\cdot}2056$.

t.	*d.*	α_{5461}.*	$[\alpha]_{5461}$.
0°	1·2310	+3·385°	+20·94°
21	1·2116	3·45	21·69

* $l = 160$ mm.

Methyl d-*Dimethoxysuccinate.*—(i) *In water, p* = 19·872. Densities determined :

t	11°	21°	36·8°	50·5°	67°
d	1·0403	1·0365	1·0293	1·0214	1·0108

t.	*d.*	α_D.	α_{5461}.	$[\alpha]_D$.	$[\alpha]_{5461}$.
0°	1·0438	+6·93°	+8·15°	+83·52°	+98·23°
18	1·0375	6·59	7·75	79·91	93·97
38	1·0281	6·22	7·30	76·11	89·32
58	1·0165°	5·87	6·90	72·65	85·39
78·5	1·0027	5·55	6·51	69·63	81·68
18·5			7·745		

This was repeated in order to obtain some idea of the experimental error. *p* = 20·147. Densities determined :

t	11°	33°	49·5°	77·5°
d	1·0413	1·0322	1·0228	1·0040

0	1·0448	+7·07	+8·28	+83·81	+98·15
21	1·0376	6·60	7·78	78·93	93·04
37	1·0300	6·33	7·45	76·26	89·75
61	1·0160	5·91	6·97	72·18	85·13
78·5	1·0040	5·63	6·62	69·58	81·82
18·5	after cooling	—	7·89		

(ii) *In deuterium oxide, p* = 20·013. Densities determined :

t	11·8°	23°	36·5°	50°	66·7°	81·6°
d	1·1321	1·1272	1·1203	1·1123	1·1009	1·0889

0	1·1340	+7·56	+8·90	+83·28	+98·04
20	1·1282	7·16	8·42	79·29	93·23
40	1·1180	6·78	7·96	75·76	88·94
59·5	1·1054	6·43	7·545	72·66	85·26
81·8	1·0888	6·05	7·12	69·41	81·68

After cooling : $\alpha_{5461}^{20^\circ} = 8{\cdot}45^\circ$; after standing over-night : $\alpha_{5461}^{17^\circ} = 8{\cdot}53^\circ$.

Nicotine.—(i) *In water, p* = 10·371. Densities determined :

t	9·5°	22·6°	34·2°	43·2°	53°	65°
d	1·0084	1·0046	1·0005	0·9965	0·9914	0·9845

t.	*d.*	α_D.	α_{5461}.	$[\alpha]_D$.	$[\alpha]_{5461}$.
0°	1·0100	−3·10°	−3·75°	−73·99°	−89·50°
20	1·0053	3·26	3·97	78·17	95·20
39	0·9982	3·48	4·19	84·04	101·20
59·5	0·9878	3·65	4·405	89·07	107·50

In water, p = 10·222. Densities determined :

t	10°	20·1°	29·6°	39·9°	49·5°	60°
d	1·0078	1·0051	1·0020	0·9979	0·9934	0·9875

0	1·0098	−3·05	−3·68	−73·87	−89·12
20·5	1·0050	3·20	3·90	77·87	94·90
39·2	0·9980	3·41	4·13	83·56	101·20
59	0·9878	3·59	4·33	88·88	107·20

(ii) *In deuterium oxide, p* = 10·09. Densities determined :

t	13°	21·5°	30°	41°	52°	59·9°
d	1·1033	1·1012	1·0982	1·0933	1·0876	1·0832

0	1·1056	−3·33	−4·03	−74·62	−90·31
20	1·1014	3·57	4·28	80·31	96·28
39·2	1·0940	3·75	4·52	84·93	102·36
59	1·0836	3·95	4·80	90·32	109·75

SUMMARY.

The optical rotation of solutions in water and in deuterium oxide (99%) of (I) methyl *d*-tartrate, (II) methyl *d*-dimethoxysuccinate, and (III) *l*-nicotine, has been examined for two colours of light and at different temperatures, with the following results:

(I) Concentration, $p = 25$; specific rotation about 3% lower in deuterium oxide. (II) Concentration, $p = 20$; specifical rotations identical. (III) Concentration, $p = 10$; specific rotation about 1% higher in deuterium oxide.

Nicotine was found to be less soluble in deuterium oxide than in water at 60·5°.

The author wishes to thank Professor T. S. Patterson, at whose suggestion this work was undertaken, for advice during its progress.

THE UNIVERSITY, GLASGOW. [*Received, February 25th,* 1937.]