185. *Studies in Solvent Action. Part III. Rotatory Powers of* l-*Menthyl Methyl Naphthalate in Mixtures of Alcohols with Benzene or Hexane.*

By HAROLD GORDON RULE and ANDREW McLEAN.

IN a previous communication (J., 1931, 674) it was shown that the rotatory power of *l*-menthyl methyl naphthalate in solvents derived from the same parent hydrocarbon is dependent upon the polarity and disposition of the substituent groups in the solvent molecule. For monosubstituted derivatives the rotatory power varies with the

dipole moment, and in general, the higher the polarity of the medium the lower is the observed rotation.

Further confirmation of a definite relationship between rotatory power and the polar properties of the solvent was gained by utilising the polarisation–dissociation diagrams deduced by Debye (" Polare Molekeln," p. 48) for an associated polar liquid on dilution with benzene or hexane. By a simple calculation, Debye eliminates the contribution due to the non-polar liquid present and is able to follow diagrammatically the change in the polarisation of the polar compound as it becomes progressively dissociated. In a similar manner the rotatory powers of *l*-menthyl methyl naphthalate as determined in mixtures of polar and non-polar liquids were corrected for the rotation contributed by the non-polar component. For mixtures containing nitrobenzene or ether, it was found that the rotation-dissociation diagrams thus deduced (representing the change in rotation as the polar solvent became progressively dissociated) closely resembled those quoted by Debye for the corresponding variation in polarisation. Here also an increase in polarisation was accompanied by a fall in rotatory power, and the form of the polarisation curve proved to be the inverse of that obtained for the optical rotation.

With ethyl alcoholic mixtures the agreement was less exact. The polarisation diagram for alcohol is irregular and for benzene solutions rises to a maximum at a point representing about 0·3 mol.-fraction of alcohol. The deduced rotation curve appeared to give a corresponding minimum somewhat below 0·1 mol.-fraction, but, owing to the errors involved in the calculation at such low concentrations, the result was regarded as inconclusive.

For different alcohols, however, the polarisation–dissociation curves vary within wide limits, and it was considered of interest to extend the comparison to some of the higher homologues, the polar irregularities of which are so characteristic as to offer exceptional facilities for comparison with the optical changes.

The experimental figures obtained for ethyl alcohol, *n*-propyl, *n*- and *iso*-butyl alcohols, and *iso*- and *tert.*-amyl alcohols are summarised in Figs. 1—7. Polarisation curves indicated by broken lines are taken from Debye (*op. cit.*) (1) or from Lange (*Z. Physik*, 1925, **33**, 174) (2—6). Rotatory powers are represented by continuous lines, the values being calculated by a simple modification of Debye's method, as described in Part I of this series (J., 1931, 682). In Fig. 1 the concentration of alcohol in the solvent mixture is expressed in mol.-fractions, but in the remaining figures it is given in normalities, since the data in Lange's paper are insufficient to allow of conversion into mol. fractions.

Correlation of Rotatory Power with the Polarisation of the Hydroxylic Component.—An examination of the polarisation (broken) curves illustrates the manner in which these vary with the molecular structure of the alcohol. Ethyl, propyl, and the *n*- and *iso*-butyl alcohols on dilution with benzene give diagrams each containing a single well-defined maximum, the position of which is displaced towards a higher concentration with rise in molecular weight. In *iso*amyl alcohol the original maximum undergoes a further displacement, whilst a second one appears at a low concentration. *tert.*-Amyl alcohol, on the other hand, gives a polarisation diagram which approximates to a straight line.

As indicated by the continuous-line graphs, these changes are reflected in the variations in the rotatory power of *l*-menthyl methyl naphthalate when dissolved in the corresponding benzene–alcohol
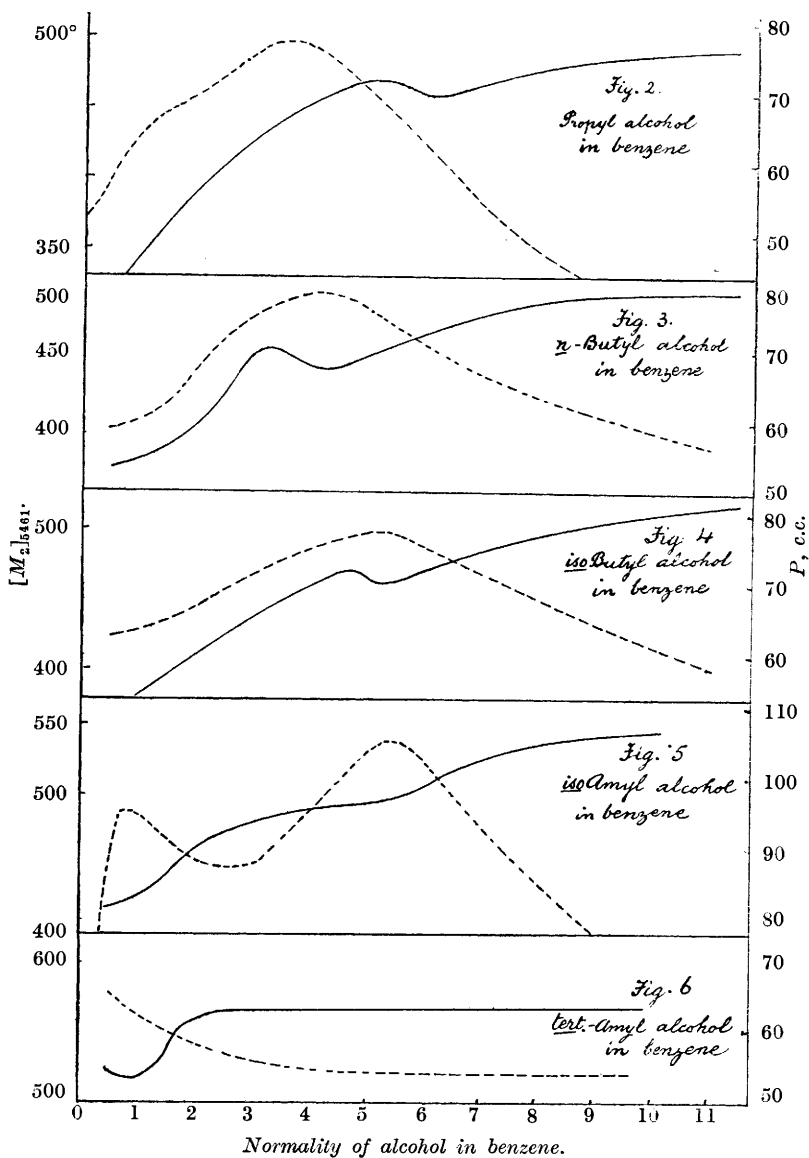
FIG. 1.

Ethyl alcohol in benzene.
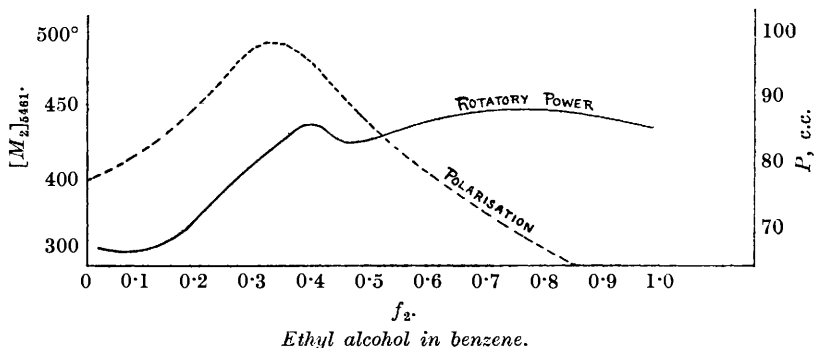
mixtures and corrected for the rotation due to the benzene present: a maximum in the polarisation of the alcohol corresponds to a minimum in rotatory power. This agrees with the relationship already established in connexion with mono-substituted hydrocarbon solvents, where an increase in polarity leads to a diminished rotation.

In the case of *n*- and *iso*-butyl alcohols the maxima and minima respectively occur at the same concentrations. For propyl alcohol, however, the minimum in rotatory power apparently corresponds to a somewhat higher concentration of alcohol ($N = 6$) than the polarisation maximum ($N = 3.7$). This displacement, coupled with the fact that the deduced optical deviations are small and unexpectedly localised, led to the determination of a number of new points on the original ethyl alcohol diagram (*loc. cit.*, p. 684), which revealed the existence of a previously undetected minimum rotatory power in a mixture containing 0·46 mol.-fraction of alcohol (Fig. 1). Here also the rotation minimum is slightly displaced as compared

with the polarisation maximum, and in the same direction as for propyl alcohol.

Fig. 2. Propyl alcohol in benzene

Fig. 3. n-Butyl alcohol in benzene

Fig. 4. isoButyl alcohol in benzene

Fig. 5. isoAmyl alcohol in benzene

Fig. 6 tert.-Amyl alcohol in benzene

Normality of alcohol in benzene.

Among the alcohols under examination, perhaps the greatest interest attaches to the *iso-* and *tert.*-amyl compounds, which

differ strongly from the lower homologues in the variations undergone by the polarisation with change of concentration. It will be seen (Fig. 5) that the twin maxima in the polarisation diagram of the *iso*-alcohol are reflected in the corresponding depressions in the rotation diagram. As has already been indicated, the course of the latter at low concentrations is somewhat uncertain, not only owing to the errors involved in the calculation, but also because in this region the concentration of the optically active solute may become a factor of importance. The calculations are based on the assumption that the alcohol is at all times evenly distributed throughout the mixture, but at low concentrations it may be assumed that a greatly increased proportion of the total number of alcohol molecules will tend to cluster around the molecules of ester, the latter component being present in every case in a uniform concentration of $c = 2$. The resulting increased dipole association between ester and alcohol would still further reduce the internal molecular field of the ester, and thus lead to a greater depression in rotatory power. Probably this is the cause of the gradual fall in all the rotation curves on approaching the left-hand axis, and prevents the realisation of a complete correlation with the polarisation diagram which would have been attained in examples 1—5 had the rotation risen in solutions having a low concentration of alcohol.

The agreement is equally good with mixtures of benzene and *tert.*-amyl alcohol, for which both polarisation and rotation curves flatten out into an approximation to horizontal lines, with no sign of maxima or minima (Fig. 6). In this case the polarisation is exceptional in tending towards a higher value at low concentrations, thus emphasising the normal downward trend of the rotation diagram and leading to a sudden fall in the latter at about $N = 2$.

The polarisation maxima under consideration are explained by Debye on the assumption that, as the concentration increases, the individual alcohol molecules undergo dipole association to form in the first instance agglomerates having a higher polarisation. At still higher concentrations these rearrange themselves to give more complex agglomerates of a lower polarisation value. On this basis, the progressive flattening of the characteristic minima obtained for the normal alcohols with rise in molecular weight and their displacement towards higher concentrations are readily understood, since an increase in the length of the alkyl chain will tend to screen the hydroxyl dipole and so diminish and delay the process of association. The progressive changes in the rotatory power of the ester when dissolved in alcohol–benzene mixtures are illustrated in Figs. 1—6, and appear still more clearly in Fig. 7, which shows the deduced

rotation-dissociation curves for the ester in mixtures of alcohol and hexane. With hexane as diluent the curves are steeper and the maxima sharper than when benzene is employed.

In a similar manner the depression in the rotatory power of l-menthyl methyl naphthalate when dissolved in alkyl or aryl derivatives containing a given polar substituent becomes less pronounced as the molecular weight of the hydrocarbon radical rises (see Part I, p. 678).

tert.-Amyl alcohol presents a case of special interest in which the molecular structure is such that the hydroxyl group is largely enveloped and screened by the three alkyl groups united to the

FIG. 7.
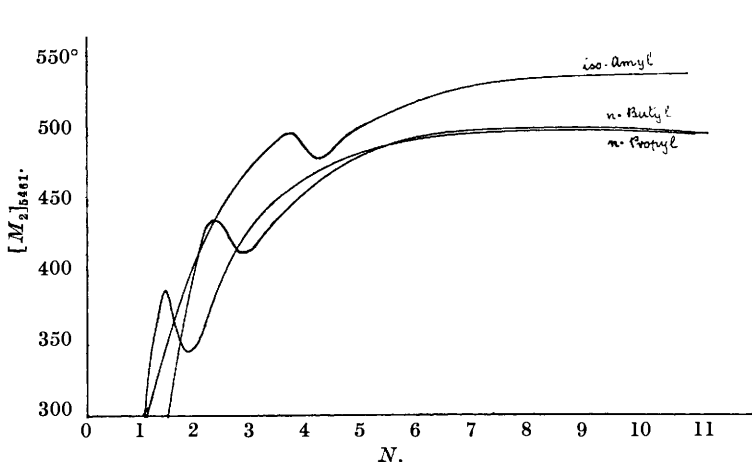
Rotatory power in mixtures of alcohols with hexane.

tertiary carbon atom. Although this does not appreciably affect the value of the dipole moment, it will diminish molecular association by hindering the approach of neighbouring hydroxyls, thus accounting for the regular nature of the polarisation changes. Similarly the steric hindrance offered to association between alcohol and ester results in this alcohol behaving more like a pure hydrocarbon, yielding a solution of high rotation.

Influences of the same nature are revealed in the molecular rotations of the ester when dissolved in the homogeneous alcohols, as summarised in the following table. Among the isomeric butyl and amyl alcohols, the rotatory powers are lowest for the normal and highest for the tertiary compounds, the values in the latter case lying between those found for benzene ($-543°$) and hexane ($-651°$)

z z 2

respectively. Here also the differences may be supposed to arise from the greater capacity of the normal alcohols to become associated with the ester, leading to a diminished internal field in the latter and a reduction in rotatory power.

Rotatory Powers of l-*Menthyl Methyl Naphthalate in Homogeneous Alcohols* (t = 20°, c = 4).

Solvent.	$[M]_{5461}.$	Solvent.	$[M]_{5461}.$
MeOH	−383°	*tert.*-BuOH*	−546°
EtOH	439	*n*-AmOH	536
n-PrOH	499	*iso*-AmOH	542
n·BuOH	502	*tert.*-AmOH	568
iso-BuOH	517		

* In this case *c* = 1·5 and *t* = 30°. *tert.*·Butyl alcohol is a solid at the ordinary temperature.

EXPERIMENTAL.

Purification of Solvents.—Propyl alcohol. The purest available alcohol (B.D.H.) was found to boil over a considerable range. It was refluxed over calcium filings, and a main fraction collected at 96·5—96·7°/750 mm. *l*-Menthyl methyl naphthalate gave the same rotation in this as in another sample which had been dried over sodium sulphate.

The following alcohols, after preliminary drying and fractionation, were dried for an extended period over sodium sulphate and again fractionated :

n-Butyl, b. p. 117·6—117·8°; *iso*butyl, b. p. 107·8—108·2°; *tert.*-butyl, b. p. 82·6°, m. p. 24·8°; *n*-amyl, b. p. 137—137·2°; *iso*amyl, b. p. 130·8—131°; *tert.*-amyl, b. p. 102·5—102·6°.

For other solvents and the preparation of *l*-menthyl methyl naphthalate, see Part I (*loc. cit.*).

Rotatory Powers of the Ester in Mixtures of Solvents (1 = 2, t = 20°).—In the following tables, f_2 = mol.-fraction of polar component in solvent mixture, *c* = g. of ester in 100 c.c. of solution; $[M_{1, 2}]$ = molecular rotation in mixture (experimental) for λ_{5461}; $[M_2]$ = molecular rotation in alcoholic component (calculated) for λ_{5461}; N = concentration of polar solvent (mols./l.).

I. *Benzene and Ethyl Alcohol.*

$f_2.$	$c.$	$\alpha_{5461}.$	$[M_{1, 2}].$	$[M_2].$	$f_2.$	$c.$	$\alpha_{5461}.$	$[M_{1, 2}].$	$[M_2].$
1	1·514	−3·59°	−437°	−437°	0·506	2·004	−5·29°	−486°	−430°
0·866	2·004	4·96	456	446	0·454	2·000	5·33	490	427
0·701	2·008	5·14	471	449	0·427	1·998	5·37	495	433
0·609	2·008	5·26	482	443	0·397	2·006	5·46	501	443

For other values see J., 1931, 689.

II. *Benzene and* n-*Propyl Alcohol.*

f_2.	c.	$\alpha_{5461}^{20°}$.	$[M_{1, 2}]$.	$[M_2]$.	N.
1·000	2·004	−5·43°	−499°	−499°	13·40
0·830	2·000	5·44	500	491	10·57
0·644	2·010	5·47	501	476	7·96
0·546	2·000	5·45	501	464	6·62
0·495	2·000	5·47	503	459	5·96
0·472	2·006	5·54	508	466	5·64
0·444	2·002	5·57	512	469	5·29
0·391	2·000	5·58	513	466	4·61
0·339	2·000	5·58	513	449	3·98
0·285	2·000	5·60	515	439	3·31
0·230	2·000	5·63	518	420	2·65
0·178	2·000	5·63	518	393	2·03
0·119	1·998	5·71	526	365	1·34
0·062	2·004	5·77	530	331	0·69
0·000	2·018	5·96	543	—	0·00

III. *Hexane and* n-*Propyl Alcohol.*

1·000	2·004	−5·43°	−499°	−499°	13·40
0·875	1·498	4·24	521	502	10·58
0·801	1·496	4·31	530	503	9·26
0·723	1·504	4·45	544	505	7·95
0·633	1·508	4·53	553	501	6·60
0·532	1·506	4·58	560	491	5·28
0·426	1·500	4·67	573	473	3·98
0·302	1·494	4·71	580	424	2·66
0·235	1·494	4·71	580	359	2·01
0·199	1·496	4·79	589	347	1·68
0·164	1·500	4·94	606	390	1·36
0·127	1·506	4·95	605	299	1·03
0·086	1·498	4·95	608	233	0·69
0·047	1·500	5·08	623	150	0·37
0·000	1·950	6·89	651	—	0·00

IV. *Benzene and* n-*Butyl Alcohol.*

1·000	2·004	−5·47°	−502°	−502°	(10·95)
0·791	2·004	5·50	505	493	8·30
0·685	2·000	5·50	506	486	7·44
0·587	2·004	5·48	503	477	6·39
0·495	2·000	5·50	506	465	5·39
0·440	2·008	5·50	504	455	4·79
0·391	2·004	5·50	505	445	4·28
0·342	2·000	5·58	513	453	3·74
0·290	2·000	5·66	521	466	3·19
0·244	2·006	5·66	519	443	2·68
0·195	2·000	5·63	518	413	2·17
0·100	2·000	5·75	529	385	1·10
0·000	2·018	5·96	543	—	0·00

V. *Hexane and* n-*Butyl Alcohol.*

1·000	2·004	−5·47°	−502°	−502°	10·95
0·851	1·502	4·35	533	506	8·65
0·765	1·502	4·40	539	504	7·57
0·681	1·502	4·45	545	502	6·53
0·585	1·496	4·53	557	491	5·43
0·483	1·498	4·59	564	476	4·32
0·375	1·504	4·66	570	435	3·24
0·317	1·504	4·74	580	426	2·69
0·264	1·508	4·86	593	439	2·20
0·202	1·498	4·78	587	347	1·65
0·139	1·506	4·90	599	269	1·11
0·071	1·502	5·04	618	200	0·56
0·000	1·950	6·89	651	—	0·00

VI. *Benzene and* iso*Butyl Alcohol.*

f_2.	c.	$\alpha_{5461}^{20°}$.	$[M_{1,2}]$.	$[M_2]$.	N.
1·000	2·000	−5·62°	−517°	−517°	10·97
0·796	2·000	5·49	505	495	8·53
0·594	2·004	5·50	505	476	6·42
0·542	2·006	5·51	505	472	5·89
0·493	2·004	5·50	505	463	5·37
0·468	2·006	5·52	506	462	5·10
0·443	2·000	5·56	512	473	4·84
0·391	2·012	5·58	510	465	4·28
0·291	1·998	5·61	517	445	3·20
0·196	2·004	5·65	519	416	2·16
0·100	2·000	5·72	526	390	1·11
0·058	2·000	5·74	528	293	0·64
0·051	2·008	5·74	526	235	0·57
0·000	2·018	5·96	543	—	0·00

VII. *Benzene and* iso*Amyl Alcohol.*

f_2.	c.	$\alpha_{5461}^{20°}$.	$[M_{1,2}]$.	$[M_2]$.	N.
1·000	1·500	−4·42°	−542°	−542°	9·25
0·772	2·006	5·78	530	527	7·29
0·665	2·008	5·71	523	514	6·38
0·589	2·000	5·63	518	499	5·75
0·524	2·010	5·65	517	494	5·19
0·453	2·000	5·65	520	491	4·54
0·355	2·000	5·70	524	487	3·63
0·260	2·000	5·70	524	475	2·72
0·173	1·994	5·71	527	457	1·84
0·087	1·996	5·79	534	425	0·94
0·043	1·998	5·83	537	419	0·48
0·000	2·018	5·96	543	—	0·00

VIII. *Hexane and* iso*Amyl Alcohol.*

f_2.	c.	$\alpha_{5461}^{20°}$.	$[M_{1,2}]$.	$[M_2]$.	N.
1·000	1·500	−4·42°	−542°	−542°	9·25
0·827	1·504	4·52	553	536	7·29
0·734	1·494	4·57	563	529	6·37
0·641	1·500	4·60	564	517	5·47
0·543	1·498	4·64	570	499	4·57
0·492	1·500	4·65	570	482	4·10
0·441	1·500	4·78	586	501	3·64
0·388	1·504	4·79	586	489	3·17
0·337	1·496	4·82	593	469	2·73
0·283	1·502	4·84	593	440	2·28
0·230	1·500	4·84	594	404	1·84
0·119	1·500	4·96	608	277	0·94
0·042	1·498	5·09	626	71	0·32
0·000	1·950	6·89	651	—	0·00

IX. *Benzene and* tert.-*Amyl Alcohol.*

f_2.	c.	$\alpha_{5461}^{20°}$.	$[M_{1,2}]$.	$[M_2]$.	N.
1·000	1·496	−4·62°	−568°	−568°	9·19
0·772	2·006	6·14	563	567	7·24
0·561	2·004	6·06	556	567	5·49
0·455	2·010	6·04	553	566	4·56
0·356	2·004	6·00	551	567	3·64
0·266	2·008	5·98	548	566	2·77
0·173	2·000	5·94	547	561	1·84
0·151	2·000	5·92	544	549	1·61
0·129	2·008	5·88	539	528	1·38
0·086	2·004	5·89	541	517	0·94
0·044	2·000	5·88	541	523	0·49
0·000	2·018	5·96	543	—	0·00

One of the authors (A. M.) desires to acknowledge his indebtedness to the Carnegie Trust for a scholarship which has enabled him to take part in this investigation.