47. *The Apparent Dielectric Polarisations of (+)- or (−)- and (±)-α-Pinene, -Camphor, -Piperitone, and -Menthol, of Limonene and Dipentene, and of Diethyl Tartrate or Racemate.*

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The measurements indicated by the title were recorded, with benzene as solvent. As the concentrations of the more polar substances were increased a tendency was noted for the polarisations of (±)-forms to be less than those of the respective (+)- or (−)-optical isomers alone. Some intermolecular interaction dependent upon an antipodal relationship seems therefore to be evident.

THE measurements now reported bear upon the possible existence of racemates in the dissolved state; they were made on an assumption that if combination of the (+)- and the (−)-form of a substance were to occur in solution then the apparent polarisation, at a given concentration, of the (±)-mixture would be different from that of either form alone.

By the investigation of the common physical properties, as well as others such as the rate of change of molecular surface energy with temperature (Smith and Mitchell, *J.*, 1913, **103**, 489), magnetic rotatory power (Perkin, *J.*, 1887, **51**, 363; 1902, **81**, 315; 1906, **89**, 849), viscosity (Dunstan, *J.*, 1908, **93**, 1815; 1910, **97**, 1249), or electric double refraction (De Mallemann, *Ann. Physique*, 1924, **2**, 1), earlier investigators seem to have inclined to the belief that the antipodes were not combined in a liquid or molten " racemate " (cf. Findlay, "The Phase Rule," Longmans, Green and Co., 5th edn., 1923, p. 175), although in a number of cases, *e.g.*, molecular refraction (Brühl, *J.*, 1907, **91**, 115), dielectric constant (Stewart, *J.*, 1908, **93**, 1059), and with (+)- and (±)-camphor in De Mallemann's study (*loc. cit.*), there were signs that such a conclusion was not wholly correct, while Fajans's experiments (*Z. physikal. Chem.*, 1910, **73**, 25) on the decomposition rates of (+)- or (±)-camphorcarboxylic acid in acetophenone, like the colour changes described by Cotton (*Ann. Chim. Phys.*, 1896, **8**, 347) on mixing equimolecular solutions of copper (+)- and (−)-tartrates, gave strong indications of mutual interaction or an equilibrium : $(\pm) \rightleftharpoons (+) + (-)$.

The general question has been considered more recently by Campbell (*J.*, 1929, 1111) and Cotton (*Trans. Faraday Soc.*, 1930, **26**, 377). The latter quotes facts to show that, in water, salts of racemic acid are different from equivalent mixtures of the corresponding two tartrates, while the former comments on the " very conflicting nature of the evidence and of opinions " in the literature, and presents evidence that the viscosities of ethyl, propyl, butyl, and amyl tartrates as pure liquids exceed those of the related racemates by amounts well beyond observational errors. For the ethyl esters, included in the present work, the ratio $\eta_{\text{tartrate}}/\eta_{\text{racemate}}$ was 1·51 at 18°.

The first relevant dipole-moment studies on benzene solutions were made by Weissberger and Sängewald (*Z. physikal. Chem.*, 1931, *B*, **13**, 383) who examined the methyl esters of mandelic, tartaric, and racemic acids; within the accuracy of their published measurements the moments of the (+)- and the (±)-forms appeared not to differ by more than 0·2 D. Coppock and Goss (*J.*, 1939, 1789) later found the partial polarisations of (+)-, (−)-, or (±)-octan-2-ols in benzene to be identical to the nearest c.c. over a composition range from 0 to 1 molar fraction. They concluded therefore that the inactive alcohol is simply a racemic mixture.

After this work was started, we found that Sahney, Barucha, and Sarna (*J. Indian Chem. Soc.*, 1948, **25**, 285) had made similar measurements on, *inter alia*, the camphors. We refer to their results later.

In this paper we record density and dielectric-constant observations at 25° for mixtures with benzene of the substances named in the title. Instead of directly estimating the solute polarisations by mixture formulæ, we have proceeded as set out by Le Fèvre (*Trans.*

Faraday Soc., 1950, **46**, 1) and fitted experimental values of $(\varepsilon_{12} - \varepsilon_2)/w_1$ and $(d_{12} - d_2)/w_1$ —written as $(\alpha\varepsilon_2)_{w_1}$ and $(\beta d_2)_{w_1}$ respectively in what follows—to equations of the type $(\alpha\varepsilon_2)_{w_1} = A + Bw_1$ (cf. Mellor, " Higher Mathematics," Longmans, Green and Co., 1931, p. 326).

EXPERIMENTAL.

Materials and Measurements.—Commercial specimens (from B.D.H., London) of the two active pinenes were steam-distilled, separated from water, and roughly fractionated without drying. The portions boiling at 155·5—156·5° were partially frozen (as described for *p*-cymene in *J.*, 1933, 980), the solid obtained after draining being then melted, dried (Na_2SO_4), and redistilled. The main bulk, boiling at 156°/760 mm. in each case, was stored over sodium for use in this work. The inactive material was made by mixing the (+)- with a slight excess of the (—)-form until the polarimetric reading was *ca.* 0°. Rotations, densities, and dielectric constants recorded were :

	$[\alpha]_D^{19}$	d_4^{2}	ε^{25}	n_D^{15}
(+)-α-Pinene	+ 44·2°	0·8540	2·3684	1·4652
(—)- ,, ...	— 39·4	0·8546	2·3701	1·4655
(±)- ,, ...	*ca.* 0	0·8547	2·3695	1·4645

Stewart (*loc. cit.*) gives ε^{20} of (+)-, (—)-, and (±)-pinene as 2·60, 2·70, and 2·75, Müller (*Physikal. Z.*, 1937, **38**, 283) those of (—)- and (±)-pinene as 2·762 and 2·42, respectively, and Svirbely, Ablard, and Warner (*J. Amer. Chem. Soc.*) give ε^{25} of (+)-pinene as 2·6428. Our measurements are lower than these; they correspond to a total polarisation (50·0 c.c.) which is about 1·5 c.c. less than that at infinite dilution in benzene (see below). However, part of the above (±)-pinene stock, after it had been in an ordinary stoppered bottle (*i.e.*, in partial contact with atmospheric moisture, air, and light) for about two months, was found to have ε^{25} *ca.* 2·6. The higher figures reported by earlier authors may therefore have been due to the unsuspected presence of polar moloxides of pinene. A note by Walker (*J.*, 1925, **127**, 1491) suggests that some such addition products with oxygen are formed very readily.

Limonene was purchased (B.D.H., London), the dipentene prepared from α-terpineol (Wall, *Annalen*, 1893, **275**, 104). Both were purified as described for the pinenes, and finally collected at 177—178°/760 mm. Properties recorded were :

	$[\alpha]_D^{18}$	d_4^{25}	ε^{25}	n_D^{25}
(+)-Limonene........................	+ 98°	0·8423	2·446	1·4759
(±)-Dipentene	0	0·8445	2·452	1·4785

Stewart (*loc. cit.*) found ε^{20} to be 2·36 and 2·30, respectively. On our figures the total polarisations are 52·3 and 52·6 c.c.

A sample of natural " refined camphor," obtained from the Taiwan Camphor Bureau, Taipeh, Taiwan, China, and purified by sublimation, had $[\alpha]_D^{20}$ +44·7° (10% alcoholic solution). Inactive camphor was synthetic material from the Eastman Kodak Co. It was also purified by sublimation.

Kannonikow (*J. pr. Chem.*, 1885, **32**, 504) reported the $[R_L]_\alpha$ for camphor as 44·4 c.c. Using sodium light, we found an 8·722% solution in benzene (d_D^{25} 0·87378, n_D^{25} 1·4972) to have d_D^{25} 0·88033 and n_D^{25} 1·4942, whence the molecular refraction of the solute is 43·7 c.c. Since only an Abbé refractometer was available, in the following tables we have used the value (44·0 c.c.) calculated from Vogel's constants (*J.*, 1948, 1842).

A crude sample of (—)-piperitone extracted from the oil of *Eucalyptus dives* was fractionated and a portion having b. p. 93·0°/5 mm., $[\alpha]_D^{20}$ —38·5°, n_D^{20} 1·4848, selected for the present work. An impure specimen of the above piperitone was well shaken with a saturated solution of sodium hydrogen sulphite. The resulting complex was washed with alcohol and with ether, then dissolved in hot water, filtered, and made alkaline, and the regenerated ketone separated. After being dried (Na_2SO_4), a fraction of b. p. 117°/18·5 mm., n_D^{20} 1·4845, was collected. On a second occasion these operations were repeated with a new supply of piperitone; the product, however, although showing the same b. p. and n_D^{20}, seemed to be slightly more polar than the first. Six solutions of this sample are reported in the following tables—they may be distinguished by $\alpha\varepsilon_2$ values of 10·0 or higher.

The menthols used were commercial samples; recrystallisation of the synthetic (±)-material from light petroleum gave needles, m. p. 34·5°, which were not quite optically inactive ($[\alpha]_D^{16}$

−1·85°); the natural (−)-menthol was redistilled, b. p. 104—105°/10 mm., and used without further purification (cf. Pickard and Littlebury, *J.*, 1912, **101**, 109).

Ethyl tartrate (from B.D.H., London) was refractionated before use, b. p. 142°/8 mm., $[\alpha]_D^{16}$ 7·9°. Ethyl racemate proved somewhat difficult to prepare. The acid (15 g.; cf. *Org. Synth.*, **6**, 88) was dehydrated at 110° for 6 hours, then finely powdered, and absolute alcohol (18 c.c.) added. The mixture was saturated with dry hydrogen chloride, first on the water-

10^5w_1	ε^{25}	$\alpha\varepsilon_2$	d_4^{25}	βd_2	10^5w_1	ε^{25}	$\alpha\varepsilon_2$	d_4^{25}	βd_2
0	2·2725	—	0·87378	—	—	—	—	—	—

α-Pinenes.

590·2	2·2733	0·136	0·87366	−0·020	(+) *
609·1	2·2735	0·164	0·87365	−0·021	(−)
1050·8	2·2743	0·171	0·87358	−0·019	(−)
1657·0	2·2757	0·193	0·87350	−0·017	(+)
5237·0	2·2830	0·200	0·87283	−0·018	(−)
5584·0	2·2834	0·195	0·87276	−0·018	(+)

whence $(\alpha\varepsilon_2)_{w_1} = 0{\cdot}157 + 0{\cdot}8w_1$, and mean $\beta d_2 = -0{\cdot}018_8$.

703·1	2·2736	0·156	0·87365	−0·018	(±)
1015·8	2·2743	0·177	0·87358	−0·020	(±)
1179·1	2·2746	0·178	0·87358	−0·017	(±)
4099·0	2·2803	0·188	0·87299	−0·019	(±)
5011·8	2·2825	0·200	0·87284	−0·019	(±)

whence $(\alpha\varepsilon_2)_{w_1} = 0{\cdot}163 + 0{\cdot}7w_1$, and mean $\beta d_2 = -0{\cdot}018_6$.

Limonene.

905·1	2·2745	0·221	0·87348	−0·033	(+)
1099·5	2·2751	0·236	0·87344	−0·031	(+)
2173·1	2·2774	0·225	0:87308	−0·032	(+)
2211·6	2·2775	0·226	0·87308	−0·032	(+)

whence mean $\alpha\varepsilon_2 = 0{\cdot}227$, and mean $\beta d_2 = -0{\cdot}032$.

Dipentene.

793·8	2·2743	0·227	0·87354	−0·030	(±)
995·2	2·2748	0·231	0·87346	−0·032	(±)
1867·1	2·2768	0·230	0·87322	−0·030	(±)
2089·6	2·2772	0·225	0·87316	−0·030	(±)

whence mean $\alpha\varepsilon_2 = 0{\cdot}228$, and mean $\beta d_2 = -0{\cdot}030_5$.

Camphors.

545	2·3101	6·90	0·87443	0·119	(+)
955	2·3379	6·85	0·87488	0·115	(+)
1484	2·3734	6·80	0·87513	0·091	(+)
1850	2·3952	6·63	0·87527	0·081	(+)
5283	2·6258	6·69	0·87812	0·083	(+)
8685	2·8587	6·75	0·88101	0·083	(+)

whence $(\alpha\varepsilon_2)_{w_1} = 6{\cdot}81 - 1{\cdot}3w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}106 = 0{\cdot}34w_1$.

509	2·3081	7·00	0·87436	0·114	(±)
1077	2·3456	6·79	0·87493	0·107	(±)
1443	2·3688	6·68	0·87510	0·092	(±)
4546	2·5636	6·70	0·87776	0·092	(±)
9306	2·8929	6·67	0·88150	0·083	(±)

whence $(\alpha\varepsilon_2)_{w_1} = 6{\cdot}84 - 2{\cdot}2w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}107 - 0{\cdot}28w_1$.

Piperitones.

143·1	2·2867	9·92	0·87385	0·049	(−)
393·3	2·3112	9·84	0·87392	0·036	(−)
649·4	2·3350	9·63	0·87401	0·035	(−)
892·4	2·3586	9·65	0·87409	0·035	(−)
1035·5	2·3725	9·66	0·87417	0·038	(−)
3169·7	2·5709	9·41	0·87519	0·044	(−)

whence $(\alpha\varepsilon_2)_{w_1} = 9{\cdot}84 - 14{\cdot}7w_1$, and mean $\beta d_2 = 0{\cdot}039_5$.

362·8	2·3088	10·00	0·87394	0·044	(±)
391·7	2·3109	9·80	—	—	(±)
428·4	2·3150	9·92	0·87396	0·042	(±)
545·9	2·3289	10·33	—	—	(±)
896·0	2·3640	10·21	0·87411	0·037	(±)
1311·4	2·4081	10·34	—	—	(±)
1555·8	2·4277	9·97	0·87455	0·043	(±)
2030·4	2·4823	10·33	—	—	(±)
2677·4	2·5503	10·37	0·87494	0·043	(±)

whence mean $\alpha\varepsilon_2 = 10{\cdot}14$, and mean $\beta d_2 = 0{\cdot}042$.

Menthols.

119·1	2·2750	2·10	0·87381	0·025	(−)
404·7	2·2804	1·95	0·87387	0·032	(−)
536·6	2·2837	2·09	0·87395	0·032	(−)
898·2	2·2896	1·90	0·87398	0·022	(−)
1757·5	2·3048	1·84	0·87468	0·051	(−)
7568·7	2·4113	1·83	0·87500	0·016	(−)

whence $(\alpha\varepsilon_2)_{w_1} = 2{\cdot}00 - 2{\cdot}61w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}033 - 0{\cdot}18w_1$.

153·4	2·2758	2·15	0·87385	0·046	(±)
353·0	2·2796	2·01	0·87394	0·045	(±)
859·1	2·2882	1·83	0·87433	0·064	(±)
989·0	2·2930	2·07	0·87418	0·040	(±)
1717·0	2·3048	1·88	0·87536	0·092	(±)
3873·8	2·3453	1·88	0·87448	0·028	(±)

whence $(\alpha\varepsilon_2)_{w_1} = 2{\cdot}04 - 5{\cdot}2w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}057 - 0{\cdot}36w_1$.

Ethyl tartrate.

220·8	2·2863	6·25	0·87430	0·236	(+)
603·1	2·3088	6·02	0·87522	0·239	(+)
972·1	2·3318	6·10	0·87629	0·258	(+)
1121·3	2·3388	5·91	0·87679	0·268	(+)
1669·1	2·3705	5·87	0·87827	0·269	(+)
4743·9	2·5304	5·44	0·88761	0·296	(+)

whence $(\alpha\varepsilon_2)_{w_1} = 6{\cdot}18 - 16{\cdot}2w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}242 + 1{\cdot}23w_1$.

Ethyl racemate.

255·5	2·2888	6·38	0·87435	0·262	(±)
598·3	2·3089	6·08	0·87506	0·214	(±)
668·3	2·3102	5·79	0·87508	0·195	(±)
1102·2	2·3348	5·65	0·87679	0·273	(±)
2389·4	2·4041	5·51	0·88092	0·304	(±)
3586·8	2·4893	5·53	0·88164	0·219	(±)

whence $(\alpha\varepsilon_2)_{w_1} = 6{\cdot}12 - 20{\cdot}6w_1$, and $(\beta d_2)_{w_1} = 0{\cdot}238 + 0{\cdot}419w_1$.

* This column shows the optical form of the solute.

bath and finally under ice-cooling. After 24 hours the whole was roughly distilled under reduced pressure. Such ester as had formed was then returned, plus more absolute alcohol, to the reaction flask, and the hydrogen chloride saturation repeated until all the racemic acid had disappeared. Finally, distillation, extraction with ether, neutralisation with aqueous sodium carbonate, drying (Na_2SO_4), etc., afforded a preparation with b. p. 138°/5 mm. (Beilstein, " Handbuch," III, 527, quotes b. p. 157°/11·5 mm.).

The measurements tabulated above have been obtained by means of the apparatus and methods described before (cf. *J.*, 1948, 1949; 1949, 333; " Dipole Moments," Methuen, 1948, Chapter II). The symbol convention follows that used in *Trans. Faraday Soc.*, 1950, **46**, 1, wherein extrapolation procedures are also discussed. The solvent has been benzene throughout and all d and ε determinations have been fixed relatively to the d_2 and ε_2 values shown for $w_1 = 0$.

From the above and other data the apparent dipole moments of the solutes are as shown in the last column of the following table :

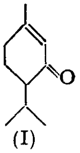
	M_1	$(\alpha\varepsilon_2)_{w_1=0}$	$(\beta_{w_1})_{=0}$	$_\infty P_1$ (c.c.).	$[R_L]_D$, c.c.	μ, D
(+)- or (−)-α-Pinene...	136·2	0·157	$-0{\cdot}021_5$	51·4	44·1	$0{\cdot}6_0$
(±)-α-Pinene	,,	0·163	$-0{\cdot}021_3$	51·6	44·0	$0{\cdot}6_1$
(+)-Limonene	,,	0·227	$-0{\cdot}036_6$	53·9	45·6	$0{\cdot}6_4$
(±)-Dipentene	,,	0·228	$-0{\cdot}034_9$	53·9	45·7	$0{\cdot}6_3$
(+)-Camphor	152·2	6·81	0·121	240·6	44·0	$3{\cdot}1_0$
(±)-Camphor	,,	6·84	0·122	241·4	44·0	$3{\cdot}1_0$
(−)-Piperitone	,,	9·84	0·045	331·2	46·8 [1]	$3{\cdot}7_3$
(±)-Piperitone	,,	10·14	0·048	339·7	46·7 [1]	$3{\cdot}7_8$
(−)-Menthol	156·2	2·00	0·038	110·0	47·6 [2]	$1{\cdot}7_5$
(±)-Menthol	,,	2·04	0·065	109·7	47·7 [3]	$1{\cdot}7_4$
Ethyl tartrate	206·2	6·18	0·227	290·5	45·6 [4]	$3{\cdot}4_6$
Ethyl racemate	,,	6·12	0·272	288·5	45·5 [5]	$3{\cdot}4_5$

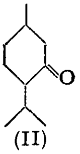
[1] Read and Smith, *J.*, 1923, **123**, 2268. [2] Quoted by Guenther, " The Essential Oils," Van Nostrand Co., 1949, Vol. II, p. 255. [3] Zeitschel and Schmidt, *Ber.*, 1926, **59**, 2298. [4] Peacock, *J.*, 1915, **107**, 1553. [5] Kuhn and Wagner-Jauregg, *Ber.*, 1928, **61**, 491.

DISCUSSION

(a) *The Apparent Dipole Moments.*—Svirbely, Ablard, and Warner (*J. Amer. Chem. Soc.*, 1935, **57**, 652) reported moments for (+)-pinene and (+)-limonene, in benzene, of 2·67 and 1·56 D, respectively. Otto (*ibid.*, p. 1147), by recalculations from the experimental data, amended the final results to the—still high—figures 2·60 and 1·57 D. Müller (*Physikal. Z.*, 1937, **38**, 283), however, found for (±)- and (−)-pinene polarities, 0·6 and 0·8 D, more in line with other olefinic hydrocarbons. Later work by Davis, Bridge, and Svirbely (*J. Amer. Chem. Soc.*, 1943, **65**, 857) afforded for pinene in benzene a total polarisation at infinite dilution at 30·1° of 49·0 c.c.; we now find 51—52 c.c. at 25°. For limonene or dipentene we can find no other measurements in the literature since the 1935 reference above. As comparisons the following moments may be cited :

	μ, D	
$Me_2C{:}CH_2$	0·37	Smyth and Zahn (*J. Amer. Chem. Soc.*, 1925, **47**, 2501).
$MeCH{:}CH_2$	0·35	McAlpine and Smyth (*ibid.*, 1933, **55**, 453).
Various methyl- and dimethyl-butadienes	Up to 0·59	Farmer and Warren (*J.*, 1933, 1297, 1302).
*cyclo*Hexene	0·61	Kubo (*Sci. Papers, Inst. Phys. Chem. Res. Tokyo*, 1937, **31**, 296).


(I)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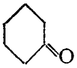
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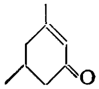
(IV)

The present appear to be the first determinations on piperitone (I), whose moment, 3·7—3·8 D, is in accordance with expectations for a molecule containing the conjugated unit $C{=}\overset{\curvearrowright}{C{-}C}{=}\overset{\curvearrowright}{O}$ Thus we note that the difference between (I) and its dihydro-derivative, menthone (II; μ = *ca.* 2·8 D, cf. M.I.T. Tables), is equal to that between *cyclo*hexanone (III; μ = 3·0 D) and 3 : 5-dimethyl*cyclo*hex-2-enone (IV; μ = 4·0 D; Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957).

With the camphors, menthols, and ethyl racemate, the moments derived from our observations are somewhat higher than those given by previous workers :

Camphor : $\mu = 2{\cdot}95$ D (Donle and Volkert, *Z. physikal. Chem.*, 1930, *B*, **8**, 60) ; 2·94 (Wolf, *Physikal. Z.*, 1930, **31**, 227) ; 3·05 (Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, **11**, 729) ; 2·90—2·91 (Sahney, Barucha, and Sarna, *loc. cit.*) ; 3·10 (present work).

Menthol : $\mu = 1{\cdot}58$ D (Donle and Wolf, *Z. physikal. Chem.*, 1930, *B*, **8**, 55) ; 1·62 (Harms, *ibid.*, 1934, *B*, **30**, 440) ; 1·54—1·55 (Sahney *et al.*, *loc. cit.*) ; 1·74—1·75 (present work).

Ethyl racemate : $\mu = 3{\cdot}1$—$3{\cdot}2$ D (Wolf, *Trans. Faraday Soc.*, 1930, **26**, 315; Wolf and Bodenheimer, *Z. physikal. Chem.*, Bodenstein Festschr., 1931, p. 620); 3·45 (present work).

Inspection of the actual concentration, dielectric constant, and density figures (when given) presented in the above papers, suggests that the disagreements have an experimental origin, and are neither due to the mathematical extrapolative procedure used by us—although this can sometimes lead to higher estimates of $_\infty P_1$ than would the older graphical method (cf. Le Fèvre and Russell, *J.*, 1936, 491, for examples)—nor to different allowances for the distortion polarisations.

(b) *The Concentration–Polarisation Relations for Active and Inactive Forms.*—In an optically inactive solvent the total molecular polarisation at infinite dilution of the (+)- and the (−)-form of a solute should be identical. If therefore a (±)-solute were merely a mixture, the constants given by the equations for $(\alpha\varepsilon_2)_{w_1}$ versus w_1—or $(\beta d_2)_{w_1}$ versus w_1—should, when $w_1 = 0$, be the same as for one of the antipodes alone. Among our results this is seen nearly to be realised with limonene and dipentene and with (+)- and (±)-camphor, and to lesser degrees with the other substances. [We except the piperitones since the (±)-form seemed to contain an unknown polar impurity, cf. above.] The differences are not greater than the irregularities among the individual observations for each form shown in the tables. We conclude therefore that our measurements afford no evidence against the view that the (+)- and the (−)-component of a dissolved (±)-preparation exist independently of one another at high dilutions.

The coefficients of w_1 in the equations for $(\alpha\varepsilon_2)_{w_1}$ and $(\beta d_2)_{w_1}$ suggest that in the cases of the pinenes, and of limonene and dipentene, this independence continues throughout the short concentration ranges tabulated (*ca.* 0—5% and 0—2%). For the remaining substances, however, plots of p_1 [evaluated *via* $p_1 = p_2 + (p_{12} - p_2)/w_1$; cf. Sugden, *Trans. Faraday Soc.*, 1934, **30**, 720] versus w_1 are not the same for each optically active and inactive solute pair. The differing effects of concentration can be illustrated by calculating ε_{12} and d_{12} for $w_1 = 0{\cdot}05$ and $0{\cdot}10$, using the equations for $(\alpha\varepsilon_2)_{w_1}$ and $(\beta d_2)_{w_1}$, and therefrom—by the mixture rule—the apparent values of P_1 at these common concentrations :

Camphors.			Menthols.			Ethyl tartrate and racemate.		
(+)	224·7	211·7	(−)	105·5	104·0	(+)	238·9	195·5
(±)	224·0	209·8	(±)	102·0	95·0	(±)	235·4	187·8

It thus seems that in more concentrated solutions the apparent polarisation of a (±)-form becomes relatively less than that of either the (+)- or (−)-form alone : alternatively expressed, our measurements indicate some slight mutual interaction between the dissolved antipodes. Sahney, Barucha, and Sarna (*loc. cit.*) reached a similar conclusion, quoting for 10% weight/volume concentrations in benzene at 20° the following excesses of $(P_1)_{\text{active}}$ over $(P_1)_{\text{inactive}}$: Camphor, 2 ; borneol, 2 ; menthol, 3 ; camphorquinone, 8 c.c.

These results are explicable if association occurs more easily between antipodal molecules than between those of one kind, and if the (±)-complex so produced is more nearly centrosymmetric than is each active component alone. From the mirror-image relationship of the species concerned, the second supposition would seem to be reasonable. As to the forces holding the (+)- and (−)-units together, dipole–dipole and dipole–induced dipole attractions are an obvious guess; we note that solid (+)- or (−)-tartrates have recently been reported to show infra-red spectra different from those of racemates (Duval and Lecomte, *J. Chem. Physics*, 1950, **18**, 1117; cf. Turner and Lonsdale, *ibid.*, p. 156), indicating that in the latter the (+)- and (−)-anions cannot merely be in juxtaposition but must also be influencing one another's link moments, polarisabilities, force constants, etc. Again, whenever, as with camphor and menthol, the inactive form differs from the active in m. p. and other crystal properties (*e.g.*, dielectric relaxation; cf. Kauzmann, *Rev. Mod. Physics*, 1942, **14**, 40) it is obvious that the components undergo some modification in their union. If in such instances we regard the solid phase as the limiting case among progressively more concentrated solutions, then the findings now reported from our experiments are not unexpected.

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