LIV.—*Existence of Racemic Compounds in the Liquid State.*

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DURING the past twenty years various physical properties of liquids have been utilised in an attack on the problem of the existence of racemic compounds in the liquid state, but the change of the molecular surface energy with temperature appears not to have been applied until Gróh a few months ago (*Ber.*, 1912, **45**, 1441) recorded the result of two experiments on dimethyl tartrate and dimethyl racemate.

A survey of the results obtained by different investigators, a summary of which can be found in recent papers on this subject by Dunstan and Thole (*T.*, 1908, **93**, 1815; 1910, **97**, 1249; this vol., p. 19) leaves on the mind the impression that the existence in the liquid state of a racemic compound of two enantio-stereoisomerides has not been definitely and satisfactorily established. Several investigators assert that liquid racemates do exist, but the weight such statements carry is a matter of opinion, in view of the uncertain quantitative value of most of the methods by which the problem has been treated. Methods based on the determination of the density or of the refractive index (Traube, *Ber.*, 1896, **29**, 1394; Pope and Peachey, *T.*, 1899, **75**, 1111), by which therefore the greatest accuracy can be attained, definitely deny the existence of racemic compounds in unassociated liquids.

Ramsay and Shields have shown (*Phil. Trans.*, 1893, **184**, 647) how the molecular weight of a pure unassociated liquid can be determined from the rate of change of the molecular surface energy with temperature; for such liquids the relation between the change and the temperature is linear, except in the neighbourhood of the critical point, and the rate of change is a constant, k , the average value of which, determined by six "normal" liquids, is 2.1209. Before the application of this method to the problem of the existence of liquid racemates is described, some discussion of the significance of the constant k is necessary. The average value, 2.1209, is the mean of six lying between 2.2256 for ethyl acetate and 2.0419 for methyl formate. Values even greater than the former have been recorded in recent years by Hewitt and Winmill (*T.*, 1907, **91**, 441), Turner and Merry (*ibid.*, 1910, **97**, 2069), Walden and Swinne (*Zeitsch. physikal. Chem.*, 1912, **79**, 700), and others. The criterion of the unaltered molecular complexity of a liquid with change of temperature is not so much the absolute value of k , as its constancy. When the liquid is unassociated, k remains the same over a wide range of temperature, but in the case of an associated liquid the dissociation which accompanies rise of temperature is manifested by a rapid increase in the value of k . Thus, for ethyl alcohol and for glacial acetic acid, k has the values 1.070 and 0.8815 respectively at 20° and 1.569 and 1.198 respectively at 150°.

The application of this method to the problem under examination is as follows. The surface tensions and the densities of each of the optically active modifications of a substance are determined over as wide a range of temperature as is practically convenient, and thereby, assuming a normal molecular weight for the substance, several values of k are obtained by the equation

$$k = \frac{\delta[\gamma(Mv)^{\frac{2}{3}}]}{\delta t},$$

and the mean is calculated.

The same measurements are made with the inactive modification, and the mean value of k' is determined, again assuming a normal molecular weight for the substance. If this assumption is correct, that is, if the inactive modification is a liquid mixture of the two active forms, the mean values of k and k' will be identical or nearly so. On the other hand, if the inactive substance is a liquid racemic compound, and therefore has twice the molecular weight of the active modifications, k' will be smaller than k , the two quantities being related by the equation $k = 2k'$. Finally, the inactive liquid may be a mixture of the two active forms in equilibrium with the racemic compound. In this case k will the more exceed k' the greater the amount of the racemic compound present, a change of

0.01 in the value of k' corresponding roughly with a change of about 0.7 per cent. in the molecular weight. (Strictly speaking, the name "molecular weight" is inapplicable to such a liquid; its meaning, however, is obvious, and the name will be retained to avoid circumlocution.)

There remains to be considered the question of the association, other than the chemical combination, of the liquid molecules. This complication has been avoided by selecting for examination substances which the experience of previous workers has shown are little prone to association, namely, hydrocarbons and esters. The active and the inactive modifications of pinene and of limonene, and dimethyl *d*-tartrate and dimethyl racemate have been examined. The concordant values of k for the active and the inactive modifications of each substance and its constancy over a wide range of temperature prove that the substances selected fulfilled expectation, and that the results are not complicated by changes due to ordinary association.

EXPERIMENTAL.

The apparatus and the general mode of procedure for the determinations of the surface tension at different temperatures were similar to those described by Hewitt and Winmill (*loc. cit.*). All measurements of length were made with a vernier microscope reading directly to 0.01 mm., and by means of a micrometer eye-piece to 0.001 mm. Many capillary tubes were tested until one was found with a uniform bore over a length of 5–6 cm. This was then sealed to the wide tube of the apparatus, so that the surface of the liquid within the capillary was always situated within the uniform portion. The usual precautions were observed of thoroughly wetting the capillary walls and of determining the surface tension of the liquid in contact with its own vapour. The diameter of the uniform part of the capillary tube was determined by direct measurement with the micrometer eye-piece, by calibration with a mercury thread, and by a determination of the surface tension of benzene; the three methods gave practically identical results.

The densities of the liquids at different temperatures were determined by means of a dilatometer consisting of a cylindrical bulb of about 9 c.c. capacity sealed to a capillary tube, in which six or seven small bulbs, of about 0.04 c.c. capacity, were blown at intervals of about 2.5 cm. File marks were made on the capillary stem between the small bulbs. The dilatometer with the bulb completely filled with the liquid under examination was immersed in a large bath of water or other liquid heated by a small flame.

The temperatures to 0.1° were noted at which the liquid surface coincided with the various file marks on the capillary stem. The dilatometer was calibrated by a series of readings with water. This method of determining the densities of a liquid at different temperatures was devised by Mr. T. F. Winmill. It is very convenient and accurate. After the densities of benzene at different temperatures between 15° and 75° had been determined, it was found that the results agreed to 0.0001 with those obtained by Walden (*Zeitsch. physikal. Chem.*, 1909, **65**, 129).

The values of h recorded are obtained from smoothed curves of the experimental values.

Pinene.

d-Pinene.—The liquid, after repeated fractionation under diminished pressure, boiled at $85^\circ/80$ mm., and had $[\alpha]_D^{15} 13.4^\circ$.

l-Pinene.—Purified in a similar manner. Boiling point $70.5^\circ/35$ mm.; $[\alpha]_D^{15} -22.0^\circ$.

i-Pinene.—Sample I. Prepared from pinene nitrosochloride by Wallach's method. Boiling point 156° . Optically inactive. In the experiments, it became slightly yellow after keeping for some time at the higher temperatures, but after cooling, the surface tension was found to be unchanged.

Sample II. Prepared by mixing *d*- and *l*-pinenes to produce an optically inactive liquid.

d-Pinene. $M=136$. $r=0.02790$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{3}}$.	$k_{(12.6-t)}$.
12.6	0.8686	2.292	27.23	790.9	$k_{(12.6-62.0)}=2.38$
23.8	0.8592	2.222	26.11	764.0	—
35.9	0.8491	2.146	24.93	735.4	$k_{(23.8-71.0)}=2.37$
49.8	0.8378	2.058	23.60	702.3	2.38
62.0	0.8277	1.983	22.45	673.4	$k_{(35.9-82.5)}=2.35$
71.0	0.8202	1.927	21.61	652.1	2.38
82.5	0.8106	1.856	20.58	625.9	$k_{(49.8-91.4)}=2.33$
91.4	0.8032	1.801	19.79	605.5	2.35
Mean = 2.36					2.37

l-Pinene. $M=136$. $r=0.02790$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{3}}$.	$k_{(11.4-t)}$.
11.4	0.8709	2.290	27.27	790.8	$k_{(11.4-58.8)}=2.36$
20.9	0.8630	2.229	26.32	767.7	—
34.3	0.8519	2.147	25.03	736.3	$k_{(30.9-69.7)}=2.33$
47.7	0.8410	2.064	23.74	704.6	2.37
58.8	0.8317	1.996	22.71	679.0	$k_{(34.3-79.7)}=2.33$
69.7	0.8226	1.929	21.70	654.0	2.35
79.7	0.8143	1.868	20.81	630.8	$k_{(47.7-93.8)}=2.26$
93.8	0.8025	1.786	19.61	600.3	2.31
Mean = 2.32					2.36

i-Pinene (sample I). $M=136$. $r=0.02790$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(32.6-t)}$.
32.6	0.8513	2.124	24.73	728.1	—
35.6	0.8488	2.105	24.43	720.5	—
49.2	0.8377	2.019	23.13	688.2	$k_{(35.6-88.0)}=2.32$
61.4	0.8275	1.941	21.96	658.9	2.40
63.2	0.8260	1.930	21.80	655.1	2.39
77.8	0.8139	1.837	20.45	620.4	2.38
88.0	0.8054	1.775	19.60	598.9	2.33
93.8	0.8003	1.738	19.00	582.9	2.37
95.0	0.7994	1.731	18.91	580.5	2.37
Mean = 2.35					2.38

i-Pinene (sample II). $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(8.6-t)}$.
8.6	0.8725	1.318	27.22	788.0	—
9.3	0.8719	1.317	27.17	787.2	[1.14]
11.7	0.8699	1.307	26.86	780.5	$k_{(9.3-59.5)}=2.36$
23.9	0.8598	1.264	25.64	752.1	2.35
42.2	0.8446	1.199	23.96	709.3	$k_{(11.7-73.0)}=2.33$
59.5	0.8305	1.137	22.34	668.6	2.35
73.0	0.8192	1.089	21.15	637.7	2.33
88.3	0.8073	1.037	19.82	604.1	2.31
Mean = 2.33					2.35

Limonene.

d-Limonene.—Purified by repeated distillation under diminished pressure. Boiling point $135^{\circ}/240$ mm.; $[\alpha]_D^{15} 122.6^{\circ}$.

l-Limonene.—Purified in a similar manner. Boiling point $100^{\circ}/73$ mm.; $[\alpha]_D^{15} -105.4^{\circ}$.

i-Limonene.—(Dipentene). Sample I. Repeatedly distilled. Boiling point $176^{\circ}/760$ mm.

Sample II. By mixing *d*- and *l*-limonenes to produce an inactive liquid.

d-Limonene. $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(10.9-t)}$.
10.9	0.8511	1.417	28.53	840.0	—
23.1	0.8413	1.372	27.31	810.1	2.45
34.2	0.8329	1.334	26.41	788.9	$k_{(23.1-70.7)}=2.31$
44.4	0.8247	1.297	25.31	761.0	2.36
58.4	0.8138	1.247	24.00	728.4	$k_{(34.2-85.6)}=2.39$
70.7	0.8044	1.203	22.90	700.2	2.34
85.6	0.7927	1.150	21.57	665.9	$k_{(44.4-90.3)}=2.30$
90.3	0.7892	1.133	21.16	655.2	2.33
Mean = 2.34					2.385

l-Limonene. $M=136$. $r=0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.	$k_{(6.2-t)}$.
6.2	0.8600	1.400	28.48	832.7	—
23.2	0.8464	1.342	26.87	794.1	2.27
35.4	0.8368	1.300	25.73	766.2	$k_{(23.2-71.2)}=2.23$
45.1	0.8291	1.267	24.85	744.6	2.26
57.1	0.8197	1.226	23.78	718.0	$k_{(35.4-82.1)}=2.23$
71.2	0.8085	1.179	22.55	687.3	2.24
82.1	0.7999	1.140	21.56	662.0	$k_{(45.1-95.5)}=2.20$
95.5	0.7895	1.096	20.48	633.9	2.23
Mean = 2.23					2.25

i-Limonene (sample I). $M = 136$. $r = 0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.		$k_{(10.5-t)}$.
10.5	0.8668	1.366	28.00	814.7	$k_{(10.5-57.1)} = 2.30$	—
22.8	0.8570	1.322	26.80	785.5		2.38
34.6	0.8475	1.282	25.12	759.1	$k_{(22.8-69.9)} = 2.26$	2.31
45.1	0.8393	1.245	24.72	734.6		2.32
57.1	0.8296	1.204	23.63	707.8	$k_{(34.6-81.7)} = 2.25$	2.30
69.9	0.8195	1.160	22.50	679.1		2.29
81.7	0.8100	1.120	21.46	653.1	$k_{(45.1-93.8)} = 2.24$	2.27
93.8	0.8004	1.077	20.40	625.7		2.27
					Mean = 2.26	2.29

i-Limonene (sample II). $M = 136$. $r = 0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.		$k_{(10.8-t)}$.
10.8	0.8538	1.397	28.22	829.1	$k_{(10.8-57.2)} = 2.33$	—
24.2	0.8432	1.349	26.90	797.1		2.39
35.0	0.8348	1.311	25.89	772.3	$k_{(24.2-69.6)} = 2.29$	2.35
46.6	0.8247	1.270	24.78	745.0		2.35
57.2	0.8174	1.233	23.84	721.1	$k_{(35.0-81.7)} = 2.29$	2.33
69.6	0.8076	1.190	22.73	693.3		2.31
81.7	0.7981	1.147	21.65	665.6	$k_{(46.6-96.2)} = 2.26$	2.31
96.2	0.7868	1.096	20.40	633.1		2.30
					Mean = 2.29	2.33

Dimethyl d-Tartrate.—Repeatedly fractionated under low pressure. The sample employed boiled at $158^{\circ}/13$ mm., melted at 42.4° , and had $[\alpha]_D^{15} = 9.2^{\circ}$ (5 per cent. solution in chloroform).

Dimethyl Racemate.—Purified by distillation under diminished pressure. Boiling point $169^{\circ}/20$ mm.; melting point, 89.5° .

Methyl d-Tartrate. $M = 178$. $r = 0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.		$k_{(62.0-t)}$.
62.0	1.2903	1.278	39.02	1042.0	$k_{(62.0-100.0)} = 2.04$	—
62.6	1.2896	1.276	38.94	1040.0		[3.33]
67.2	1.2850	1.267	38.52	1031.5	$k_{(62.6-124.0)} = 1.98$	2.02
96.3	1.2545	1.204	35.72	972.0		2.04
100.0	1.2506	1.196	35.39	964.6	$k_{(67.2-126.0)} = 1.99$	2.04
124.0	1.2255	1.146	33.23	918.2		2.00
126.0	1.2235	1.142	33.06	914.6	$k_{(96.3-135.1)} = 1.96$	1.99
135.1	1.2140	1.122	32.22	896.0		2.00
					Mean = 1.99	2.015

Methyl Racemate. $M = 178$. $r = 0.04823$.

<i>t</i> .	<i>d</i> .	<i>h</i> .	γ .	$\gamma(Mv)^{\frac{1}{2}}$.		$k_{(89.6-t)}$.
89.6	1.2604	1.181	35.22	955.2	$k_{(89.6-150.6)} = 2.04$	—
92.5	1.2575	1.174	34.93	948.6		[2.28]
103.6	1.2458	1.149	33.86	925.6	$k_{(92.5-157.4)} = 2.03$	2.11
124.8	1.2237	1.103	31.93	883.0		2.05
150.6	1.1968	1.045	29.59	830.5	$k_{(103.6-159.0)} = 2.01$	2.04
157.4	1.1897	1.030	28.99	817.0		2.04
159.0	1.1880	1.027	28.86	814.1	$k_{(124.8-159.2)} = 2.03$	2.03
159.2	1.1878	1.026	28.83	813.3		2.04
					Mean = 2.03	2.05

A comparison of the mean values of k , which are tabulated separately for convenience of reference, obtained with each set of

liquids, shows that the active and the inactive modifications in each case have the same degree of molecular complexity, and, therefore, that the inactive modifications are not racemic compounds.

The last column in each table gives the values of k calculated from the molecular surface energies at the lowest temperature and each succeeding temperature. The mean value in the last column agrees with the mean value obtained at approximately equal intervals of temperature over the whole range. The values in brackets have not been taken into account, being calculated from temperature differences too small to give accurate results. The individual values of k in the last column decrease slightly and fairly uniformly with rise of temperature. This cannot be taken as evidence of racemate formation, because the change occurs both with the active and inactive modifications. Neither can it be due to association, because no evidence has ever been placed on record of association being accompanied by an absorption of heat. It must be attributed to some unknown factor which is operating both in the active and the inactive modifications of the substance.

The case of the methyl esters of active and inactive tartaric acids is interesting. Our values of k are 1.99 and 2.03 respectively, corresponding with association factors (x) of 1.10 and 1.07. In the paper already referred to, Gróh obtains the values 2.37 and 2.26 respectively, corresponding with $x=0.85$ and 0.91. It is, presumably, in view of the latter value that he concludes that the inactive form is unimolecular and not racemic; but by comparison with the value (0.85) for the active ester he would apparently have been justified in indicating slight molecular complexity for the racemate. Our results point to an anomalous state, the tartrate ($x=1.10$) being more associated than the racemate. From these figures it appears that racemates have no existence in the liquid state:

	k .	k' .
<i>d</i> -Pinene.....	2.36	2.37
<i>l</i> -Pinene.....	2.32	2.36
<i>i</i> -Pinene (sample I.).....	2.35	2.38
„ (sample II.)	2.33	2.35
<i>d</i> -Limonene	2.34	3.335
<i>l</i> -Limonene	2.23	2.25
<i>i</i> -Limonene (sample I.)	2.26	2.29
„ (sample II.)	2.29	2.33
Dimethyl- <i>d</i> -tartrate	1.99	2.015
Dimethyl racemate	2.03	2.05

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