367. *The Polarisations and Related Data of Optically Active and Racemic β-Octanol.*

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Determinations of the density, dielectric constant, molecular polarisation, and partial polarisation in benzene solution of *d*-, *l*-, and *dl*-β-octanol reveal no difference between the active and the racemic forms. These results are in agreement with the view that *dl*-β-octanol is simply a racemic mixture.

It is shown that the hygroscopic nature of the carbinol leads to anomalous results for the moist material, and the need for the careful exclusion of water in the measurements described is emphasised.

The apparent dipole moment of β-octanol in benzene solution is 1·66 D.

ALTHOUGH considerable evidence has accumulated to show that in many cases *dl*-liquids and non-aqueous solutions are liquid mixtures and not compounds there are still conflicting results and conclusions (Stewart, "Stereochemistry," 2nd Edition, 1919, 29; Cotton, *Trans. Faraday Soc.*, 1930, **26**, 377). Evidence in favour of the above view for many substances including β-octanol has been obtained by Thole (J., 1913, **103**, 19) from viscosity measurements and by Smith (J., 1914, **105**, 1703) from density and molecular surface energy determinations.

Dielectric-constant measurements made by Stewart (J., 1908, **93**, 1059) on active ethyl tartrate and the corresponding racemate, and on *d*-, *l*-, and *dl*-camphene showed no difference in ε between the active and inactive forms. Weissberger and Sängewald (*Z. physikal. Chem.*, 1931, *B*, **13**, 383) compared the dielectric polarisations of the *d*- and *dl*-methyl esters of tartaric and mandelic acids in dilute benzene solution with similar results. It was thought advisable therefore to study the polarisations of active and inactive β-octanol over a complete range of concentrations in benzene solution. The pure materials were very kindly placed at our disposal by Dr. J. Kenyon, F.R.S.

Considerable differences were found in the recorded densities of *d*-, *l*-, and *dl*-β-octanol; although these might be due to the difficulty in preparing the pure materials, it was also possible that the hygroscopic nature of such substances (Thole, *loc. cit.*) might be an important factor. Density and dielectric-constant measurements were made under various conditions and the effect of moisture may be judged from the results given in Tables I and II. The effect on the dielectric constant measurements is pronounced, producing an unexpected decrease in ε values. By using carefully distilled materials so that water vapour is excluded, no difference was found in density and dielectric constant between the active and inactive forms. Similarly as *M*, *d*, and ε are all the same, it is clear that the molecular polarisation must be the same in each case. These results are in agreement with the view that inactive β-octanol is a racemic mixture and not a compound. The accuracy of the ε values is about ± 0·01, as is shown by the constancy in the values for the same specimen of *n*-propyl iodide taken at intervals over the period covered by the other readings; *viz.*: Oct. 1938, 7·018; Dec. 1938, 7·017; March 1939, 7·004.

TABLE I.

Values of $d^{20°}_{4°}$ for β-octanol.

Observer.	*d*-.	*l*-.	*dl*-.
Pickard and Kenyon [1]	0·8221	—	—
,, ,, [2]	0·8214	—	—
Brühl [3]	—	—	0·8193
Smith [4]	0·8185	0·8199	0·8199
Dickes [5]	—	0·8201	—
Coppock and Goss [6]	0·8201	0·8208	0·8205
,, ,, [7]	0·8203	0·8208	0·8205
,, ,, [8]	0·8202	0·8201	0·8204
,, ,, [9]	—	—	0·8209

TABLE II.

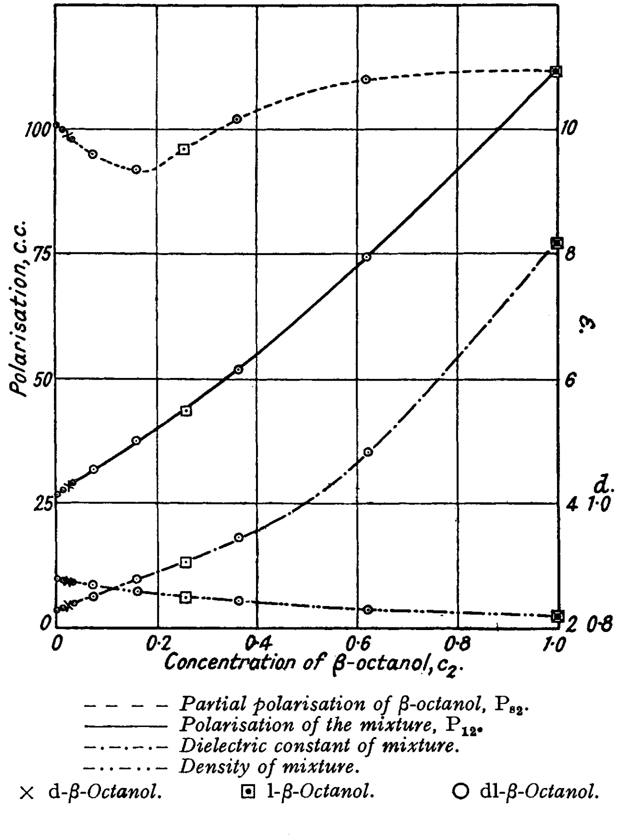
ε values for *d*-, *l*-, and *dl*-β-octanol at 20°.

Condition.	*d*-.	*l*-.	*dl*-.
Within one month of distillation [6]	7·995	7·816	8·120
After *ca.* 6 months' keeping [7]	7·921	7·523	7·786
The same day as distillation with special precautions to exclude moisture [8]	8·157	8·174	8·173
Specimen of (8) with 0·20% water added [9]	—	—	7·982

[1] J., 1907, **91**, 2058. [2] J., 1911, **99**, 45. [3] *Annalen*, 1880, **203**, 28. [4] J., 1914, **105**, 1703. [5] M.Sc. Thesis, London University, 1923. [6, 7, 8, 9] Conditions as described in Table II.

An explanation of the decrease in dielectric constant produced by slight wetting of the carbinol is that it may be due to water acting as a diluent when present in small amounts. By virtue of its high dielectric constant it has the effect of separating the β-octanol molecules, producing a fall in ε for the moist material; hence on addition of 0·20% of water, the density of the pure *dl*-β-octanol should increase by 0·0004, *i.e.*, from 0·8204 to 0·8208 (found 0·8209), but whereas the ratio of densities for water and β-octanol is approximately unity, that of the dielectric constants is 80/8 and the decrease in ε for the carbinol would be magnified some ten times, *i.e.*, it would be approximately 2% less, as was actually found. That the effect is real is clearly shown by the fact that it is associated with a fall in polarisation of 1·11 c.c., which is much greater than the value 0·19 c.c. calculated on the basis of a linear mixture relationship. Consequently, the polarisation–concentration curve for β-octanol–water mixtures is concave to the concentration axis for low concentrations of water. Such curves for mixtures of non-hydroxylic substances are, as far as data are available, invariably convex to the concentration axis (Goss, J., 1937, 1915). Mixtures containing hydroxylic substances appear to have a concave portion, as exemplified in the β-octanol–benzene curve (see Fig.), and this concave portion passes by inflexion to a convex curve for low concentrations of the carbinol. In consequence, the partial polarisations of β-octanol obtained as previously described (*loc. cit.*) when plotted against molar concentration exhibit an apparent discontinuity at $c_2 = 0{\cdot}18$ corresponding to the inflexion. It is realised that this inflexion may not be discontinuous as we are dealing with a solution property, but in some cases polarisation curves of mixtures appear to exhibit sharp discontinuities (Hrynakowski and Jeske, *Ber.*, 1938, **71**, 1415).

Mixture of β-octanol and benzene at 20°.



– – – – *Partial polarisation of β-octanol,* P_{s2}.
———— *Polarisation of the mixture,* P_{12}.
–·–·–·– *Dielectric constant of mixture.*
–··–··– *Density of mixture.*
× d-*β-Octanol.* ⊡ l-*β-Octanol.* ○ dl-*β-Octanol.*

The partial polarisations of *d*-, *l*-, and *dl*-β-octanol are found to be identical, further emphasising that such solutions are liquid mixtures. They are used to calculate the dipole moment from the values $P_\infty = 101$ (see Table III) and $[R_L]_D = 40{\cdot}71$ (Calc. from Eisenlohr's atomic refractivities : 40·67), whence $P_{E+A} = 42{\cdot}7$ and the apparent dipole moment in benzene solution = 1·66 D. The true moment of alcohols is known to be lower than that given by the benzene solution method, and an attempt will be made to determine the solvent effect in this case.

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730) except that the capacities were measured in condensers of the Sayce–Briscoe type, silvered as described by Sugden (J., 1933, 768).

Preparation of Materials.—*d*- and *l*-β-Octanol had b. p. 86°/20 mm., and the *dl*-isomeride had b. p. 93°/26 mm. The active alcohols had the following specific rotations (not previously recorded) at 20° :

	d-Alcohol.				*l*-Alcohol.			
λ	5893	5780	5461	4358	5893	5780	5461	4358
[α]	+9·91°	+10·38°	+11·64°	+19·2°	−9·72°	−10·09°	−11·48°	−19·2°

Readings were taken after a special distillation, in which the three forms of the carbinol in an all-glass vacuum-distillation apparatus with ungreased joints were kept just below the b. p. until all moisture had been removed, the condenser and receiver being then dried out, warmed, and the distillation then carried out in the usual manner. The *d*-carbinol had $d_{4^\circ}^{20^\circ}$ 0·8202, and the *l*-carbinol $d_{4^\circ}^{20^\circ}$ 0·8201; all three carbinols had $n_D^{20^\circ}$ 1·4264. Dickes (*loc. cit.*) gives $d_{4^\circ}^{20^\circ}$ 0·8201, $n_D^{20^\circ}$ 1·4262 for the *l*-carbinol, and the equation representing the refractive dispersion as $n^2 = 1{\cdot}6931 + 0{\cdot}313\lambda^2/(\lambda^2 - 0{\cdot}0283)$.

Benzene.—A " B.D.H. extra pure " sample was dried over phosphoric oxide and fractionally distilled, the middle fraction being used for the measurements.

Results.—The experimental data and the polarisations (P_{12}) at mol.-fractions c_2 and partial polarisations (P_{S2}) calculated therefrom are recorded in Table III.

TABLE III.

dl-β-Octanol in benzene at 20°.

c_2.	$d_{4^\circ}^{20^\circ}$.	ϵ^{20}.	P_{12}.	P_{S2}.	c_2.	$d_{4^\circ}^{20^\circ}$.	ϵ^{20}.	P_{12}.	P_{S2}.
0	0·8785	2·2813	26·60	101 (P_∞)	0·15966	0·8605	2·790	37·51	92
0·01387	0·8770	2·3308	27·61	100	0·25393 [2]	0·8526	3·068	43·71	96
0·02420 [1]	0·8755	2·3670	28·36	99	0·36130	0·8451	3·455	51·60	102
0·02938	0·8749	2·3867	28·76	99	0·62086	0·8319	4·815	74·30	110
0·03294	0·8739	2·3977	29·02	98	1·0	0·8204	8·173	111·88	112
0·07302	0·8695	2·5305	31·81	95					

The points (1) for *d*-β-octanol and (2) for *l*-β-octanol lie on the same curve as those for the *dl*-octanol (see Fig.).

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[*Received, August 23rd,* 1939.]