

161. Factors modifying the Polarisation of Liquids.

By FRANK R. GOSS.

IN a discussion (Goss, this vol., p. 502) of the effects of association and the anisotropy of the field on the dielectric polarisation of liquids and certain liquid mixtures, the formulæ developed, when applied to the data for mixtures of nitrobenzene with other liquids, showed that the polarisation coefficients of the solvents were in some cases increased by a term (K) which was considered to arise from the orientation, in the electric field, of the co-ordinate links to which association is attributed. This view was supported by evidence that the abnormal polarisation is most marked in those liquids for which a large measure of association is deduced from their other physical properties.

Association of this nature cannot arise in the vapour state, and in order to test the conclusion that a non-polar liquid may possess a "false" orientation polarisation in the liquid state due to association, although in the vapour state it is undoubtedly non-polar, a careful comparison has been made between benzene and carbon tetrachloride. In the vapour state both these substances have been shown, by McAlpine and Smyth (*J. Amer. Chem. Soc.*, 1933, **55**, 453) and by Sanger (*Physikal. Z.*, 1926, **27**, 556) respectively, to have an electrical polarisation which does not vary with temperature, and hence a dipole moment and orientation polarisation of zero. In the liquid state the electrical polarisation of both these substances is depressed by the anisotropy of the field in accordance with the Raman-Krishnan theory, but it is to be expected that the association effect in benzene would result in the observed depression being less than that required by this theory.

The anisotropy factor for benzene has been given by Krishnan (*Proc. Roy. Soc.*, 1929, *A*, **126**, 155), who calculated that at 20° the observed polarisation of the liquid should be 3.6% lower than the true polarisation P_E as observed for the vapour. This diminution is given by the product of the volume polarisation p_E and the molecular anisotropy factor * A_E , previously defined (Goss, *loc. cit.*), so that

$$[R_L]_\infty = P_E - p_E A_E \quad \dots \quad (1)$$

where $[R_L]_\infty$ is the molecular refractivity corrected for dispersion, and $P_E = (n_\infty^2 - 1)/(n_\infty^2 + 2)$; n_∞ is the refractive index calculated from known values of the refractive index n corresponding to wave-lengths λ by an expression similar to that of Sellmeier, *viz.*, $n^2 = n_\infty^2 + k_E/(\lambda^2 - \lambda_E^2)$ (cf. Goss, *J.*, 1933, 1341).

From the experimental data given in Table VI, values of $[R_L]_\infty$ and p_E over the temperature range 10–50° are given for benzene (Table III), and the values of P_E and A_E can be readily calculated by employing expression (1) combined with Krishnan's data for the effect of anisotropy ($p_E A_E/P_E = 0.036$ at 20°); P_E is found to be 26.244 c.c. and is, of course, a constant, but A_E decreases rapidly with temperature, having the value $3.3 - 0.007t + 0.00003t^2$. The molecular refractivity of benzene at infinite wave-length is thus

$$[R_L]_\infty = 26.244 - (3.3 - 0.007t + 0.00003t^2)(n_\infty^2 - 1)/(n_\infty^2 + 2).$$

Numerous attempts have been made to modify the Lorentz-Lorenz expression for molecular refraction in order to obtain a function of the refractive index independent of temperature, one of the most successful being Eykman's empirical expression $(n^2 - 1)M/(n + 0.4)D$ (*Rec. trav. chim.*, 1895, **14**, 185). The only function which can theoretically be independent of temperature is the electron polarisation, $P_E = (n_\infty^2 - 1)(A_E + M/D)/(n_\infty^2 + 2)$, where allowance is made both for the anisotropy of the local field and for dispersion, as the variations of these two factors with temperature are not inter-related. Nevertheless, if the Lorentz-Lorenz formula is corrected by the anisotropy factor A_E alone, it becomes $(n^2 - 1)(A_E + M/D)/(n^2 + 2)$, which, as is shown in the penultimate line of Table I, is nearly independent of temperature and should equal the molecular refraction

* It has been suggested that the use of the term "anisotropy factor" in this sense might lead to confusion owing to the use of the same expression by Kukn and Braun (*Z. physikal. Chem.*, 1930, *B*, **8**, 445) for the Cotton effect. Its use here, in defining the modification of the polarisation field, would appear, however, to be the more logical and is a reasoned development of the work of Krishnan (*loc. cit.*).

$(n^2 - 1)M/3D$ of the vapour for the same wave-length. A comparison of the values given by the various formulæ which have been proposed, including those of Gladstone and Dale and of Parker and Thompson (J., 1922, **121**, 1341), is given in Table I, calculated from the values of n_D and D for benzene given in Table VI.

TABLE I.
Molecular refraction of liquid benzene.

t	10°.	20°	30°.	40°.	50°.
$(n_D^2 - 1)M/(n_D^2 + 2) D$	26·16	26·19	26·23	26·26	26·29
Lorentz-Lorenz					
$(n_D - 1)M/D$	44·58	44·55	44·51	44·49	44·44
Gladstone-Dale					
$(n_D^2 - 1)M/(n_D + 0·4) D$	58·59	58·61	58·61	58·61	58·61
Eyckman					
$(n_D^2 - 1·15)M/(n_D^2 + 1) D$	30·13	30·14	30·16	30·18	30·18
Parker-Thompson					
$(n_D^2 - 1)(A_E + M/D)/(n_D^2 + 2)$	27·12	27·13	27·13	27·14	27·15
$(n_\infty^2 - 1)(A_E + M/D)/(n_\infty^2 + 2)$	26·24	26·24	26·24	26·24	26·24

Now, corresponding to expression (1), there is the equation (2) which expresses the electrical polarisation P_2 of a non-polar, non-associating liquid such as carbon tetrachloride, in terms of the true polarisation P_{E+A} as obtained by measurements on the vapour :

$$P_2 = P_{E+A} - pA_{E+A} \quad \dots \quad (2)$$

where p is the volume polarisation of the liquid [$p = (\epsilon - 1)/(\epsilon + 2)$] and A_{E+A} is the anisotropy factor. The probability that the anisotropy factors for the optical and the electrical field in a non-polar liquid are equal has already been discussed on the basis of existing data (Goss, J., 1933, 1341). The physical constants of carbon tetrachloride have now been redetermined to ensure that the data employed refer to a single sample, and are suitable for substitution in the differentials of equations (1) and (2). Krishnan (*loc. cit.*) has made use of this differentiation, and it is found that

$$-(n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt) = (1 + DA_E/M)/[(dA_E/dt)D/M - (dD/dt)/D] \quad (3)$$

$$\text{and } -(\epsilon - 1)(\epsilon + 2)/3(d\epsilon/dt) = (1 + DA_{E+A}/M)/[(dA_{E+A}/dt)D/M - (dD/dt)/D] \quad (4)$$

These equations provide a very sensitive test of the relationship between the anisotropy factors A_E and A_{E+A} ; within the limits of the experimental accuracy attained, the results of the present investigation show (Table II) that for carbon tetrachloride the left-hand sides of (3) and (4) are equal over a range of temperature, and therefore, the right-hand sides being equal, it follows that $A_E = A_{E+A}$, so (2) and (4) may be rewritten

$$P_2 = P_{E+A} - pA_E \quad \dots \quad (5)$$

$$-(\epsilon - 1)(\epsilon + 2)/3(d\epsilon/dt) = (1 + DA_E/M)/[(dA_E/dt)D/M - (dD/dt)/D] \quad (6)$$

TABLE II.
Carbon tetrachloride. Benzene.

t	Carbon tetrachloride.					Benzene.				
	10°.	20°.	30°.	40°.	50°.	10°.	20°.	30°.	40°.	50°.
$-(n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt)$	904	881	859	837	815	919	901	883	865	847
$-(\epsilon - 1)(\epsilon + 2)/3(d\epsilon/dt)$	903	880	857	835	813	943	925	906	888	870

For benzene, the left-hand sides of equations (3) and (6) are definitely unequal, and consequently it is possible to calculate from the relationship $(n_\infty^2 - 1)(n_\infty^2 + 2)/3(dn_\infty^2/dt) = (\epsilon' - 1)(\epsilon' + 2)/3(d\epsilon'/dt)$ the dielectric constant ϵ' which benzene would have if the electrical polarisation were modified solely by the anisotropy of the local field as represented in equation (2). It is found that $\epsilon' = 2·2960 - 0·00198t$, and the corresponding polarisations P' will give the true value of P_{E+A} since

$$P_{E+A} = P' + pA_E \quad \dots \quad (7)$$

The observed polarisation of liquid benzene in an electrical field is greater than P' , so $P_2 = P_{E+A} - pA_E + K$, the term K representing the "false" orientation polarisation previously observed and referred to on p. 727. The values calculated for the polarisation coefficients of benzene are in Table III.

TABLE III.
Polarisation of benzene.

t		10°.	20°.	30°.	40°.	50°.
Optical poln., corr. for distortion	$[R_L]_\infty$	25·311	25·339	25·365	25·389	25·411
Electrical poln., obs.	P_2	26·567	26·604	26·639	26·672	26·703
Electrical poln., corr. for association ...	P^2	26·193	26·222	26·249	26·273	26·295
Anisotropy factor	A_E	3·233	3·172	3·117	3·068	3·025
Electron poln.	P_E	26·244	26·244	26·244	26·244	26·244
Electron and atom poln.	P_{E+A}	27·172	27·172	27·172	27·172	27·172
Atom poln.	P_A	0·928	0·928	0·928	0·928	0·928
Association term	K	0·374	0·382	0·390	0·399	0·408
Optical anisotropy term	pA_E	0·932	0·905	0·879	0·855	0·834
Electrical anisotropy term	pA_E	0·979	0·950	0·923	0·899	0·876
Electl. poln., corr. for anisotropy only	P''	27·546	27·554	27·562	27·571	27·579
Optical volume poln.	p_E	0·2884	0·2852	0·2821	0·2788	0·2756
Electrical volume poln.	p	0·3027	0·2995	0·2962	0·2929	0·2896

The value of P_{E+A} given by expression (7) is seen to be independent of temperature and is in good agreement with the value of 27·0 c.c. found by McAlpine and Smyth (*loc. cit.*) for the vapour. A value of 26·2 c.c. for the vapour has been recorded by Groves and Sugden (J., 1934, 1094), but this, contrary to theory, is lower than the polarisation of the liquid. If the observed electrical polarisation of liquid benzene is corrected for anisotropy but not for association, the resulting coefficient P'' increases with temperature, and the value (Table III) is considerably higher than that of the vapour.

It is now possible to obtain more accurate values for the atom polarisation than hitherto, since it is evident that a true value is only obtained if allowance is made for association, and if, in addition, the optical and the electrical polarisation are compared under the same physical conditions of state and temperature, *i.e.*, $P_A = P_2 - [R_L]_\infty - K$, where P_2 and $[R_L]_\infty$ are at the same temperature, or, more accurately, $P_A = P_{E+A} - P_E$. The atom polarisation of carbon tetrachloride has been calculated by the former relation, and the data are in Table IV.

TABLE IV.
Polarisation of carbon tetrachloride.

t		10°.	20°.	30°.	40°.	50°.
Optical poln., corr. for distortion	$[R_L]_\infty$	25·986	26·016	26·040	26·058	26·069
Electrical poln., obs.	P_2	28·100	28·131	28·157	28·176	28·187
Atom poln.	P_A	2·1	2·1	2·1	2·1	2·1

EXPERIMENTAL.

Purification of Materials.—The measurements were made with the samples of benzene and carbon tetrachloride previously described (Goss, *loc. cit.*).

Variation of Physical Properties with Temperature.—The variation of physical properties recorded in Table VI can be reduced in every case to an expression of the form $X = a - bt \pm ct^2$ for $t = 10-60^\circ$. The physical properties of liquid benzene at temperatures lower than 10° do not, however, as Piekara (*Bull. Acad. Polonaise*, 1933, A, 305) has shown, conform to an expression of this type. No evidence was obtained in support of the allotropy of liquid benzene reported by Menzies and Lacoss (*Proc. Nat. Acad. Sci.*, 1932, 18, 144; cf. Deinum, *Rec. trav. chim.*, 1934, 53, 1061). In some cases more exact data than those here recorded are already available, but in order to obtain values suitable for the calculation of the polarisation coefficients, it is essential that all the necessary measurements should be carried out under standardised conditions on one sample of material. Special care has been taken to obtain accurate values for the *temperature coefficients* of the refractive indices and dielectric constants, since these quantities are involved in the above formulæ. The dielectric constant of benzene has been taken as $2\cdot3221 - 0\cdot00198t$ (Hartshorn and Oliver, *Proc. Roy. Soc.*, 1929, A, 123, 685; Meyer,

Z. physikal. Chem., 1930, B, 8, 27; Piekara, *loc. cit.*); this value is assumed to be the dielectric constant of the above sample of benzene which was used in calibrating the condenser (see below).

Measurement of Temperature.—Temperatures were measured by thermometers which were from time to time compared with an N.P.L. standard; they were kept constant to the nearest 0.05°, which corresponds with a change of one unit in the fourth place of decimals for the various properties examined.

Density.—This was measured in the usual way with an Ostwald–SprengeI pyknometer, and the liquids were freed from dissolved air by boiling just before measurements were made.

Refractive Index.—A Pulfrich refractometer (Messrs. Bellingham and Stanley, Ltd.) was employed, the temperature control being maintained by water flowing, at the rate of about 500 c.c. per min., from a thermostat of 13 l. capacity, through the jackets enclosing the prism and through the tubular heater, the whole of these being enclosed in a specially constructed heat-insulating jacket of asbestos. The temperature of the out-flowing water was determined by a calibrated thermometer in the heater. Lowry (*J. Sci. Inst.*, 1923, 1, 16) has shown that any difference between the temperature so recorded and the real temperature of the liquid under examination is, other conditions being uniform, proportional to the difference between the recorded and the room temperature. Two readings were therefore taken with the circulating water at 30°, and the room temperature successively at 20° and 30°. As the readings were identical, it follows that, under the above conditions, the thermometer in the heater accurately records the temperature of the liquid under examination. Readings were taken for the sodium D line and the hydrogen α and β lines, and the refractive indices at infinite wave-length were calculated from these by the formula given on p. 727.

Dielectric Constant.—The apparatus previously described (Goss, *loc. cit.*) was employed with a few modifications; the temperature of the chlorobenzene bath in which the experimental condenser is immersed was maintained within the desired limits (see above) by water circulated at the rate of 500 c.c. per min. through earthed metal tubes from a thermostat of 13 l. capacity. The experimental condenser, which had an air capacity of 182 $\mu\mu$ F, was recalibrated by Piekara's method (*loc. cit.*), according to which readings are first taken when the condenser contains benzene (E) and dry air (F), the values obtained being given in Table V.

TABLE V.
Calibration of condenser.

t	10°.	20°.	30°.	40°.	50°.	60°.
E	464.535	459.915	454.915	450.335	445.77	441.45
F	228.00	227.065	226.08	225.215	224.435	223.65

$$A = 2.3208 - 0.001975t; B = 1 + 0.159/T; C = 47.9 - 0.074t; D' = 181.9 - 0.013t.$$

TABLE VI.
Experimental data.

t	Benzene.						Carbon tetrachloride.					
	10°.	20°.	30°.	40°.	50°.	60°.	10°.	20°.	30°.	40°.	50°.	60°.
D	—	0.87880	0.86811	0.85744	0.84674	0.83605	—	1.59418	1.57447	1.55492	1.53574	1.51564
ϵ	2.3023	2.2825	2.2627	2.2429	2.2231	2.2033	2.2540	2.2345	2.2146	2.1951	2.1741	2.1544
n_{α}	1.5035	1.4971	1.4907	1.4842	1.4778	—	1.4639	1.4580	1.4520	1.4460	1.4398	—
n_D	1.5079	1.5015	1.4950	1.4885	1.4820	—	1.4661	1.4602	1.4542	1.4482	1.4420	—
n_{β}	1.5204	1.5138	1.5073	1.5006	1.4941	—	1.4737	1.4677	1.4616	1.4555	1.4493	—

Benzene.

$$D = 0.90019 - 0.001069t; \epsilon = 2.3221 - 0.00198t; n^2 = 2.2344 - 0.00186t + (0.0165 - 0.000002t)/(\nu^2 - 0.066).$$

Carbon tetrachloride.

$$D = 163372 - 0.00199t + 0.0000005t^2; \epsilon = 2.2738 - 0.00196t - 0.0000005t^2; n^2 = 2.145 - 0.00170t - 0.0000005t^2 + (0.00603 - 0.000006t)/(\nu^2 - 0.11).$$

The liquid under investigation is then introduced and the new capacity (G) measured; its dielectric constant $\epsilon = (G - C)B/D'$, where B is the dielectric constant of dry air, $C = (E - AF)/(1 - A)$, where A is the dielectric constant of benzene (relative to air), and $D' = F - C$. It will be noted that D' is the true air capacity of the experimental condenser, and C its capacity to earth.

SUMMARY.

1. The molecular anisotropy factors A_E and A_{E+A} , arising respectively from the local asymmetry of the optical and the electrical polarisation field, in liquids, have in earlier work been assumed to be equal. This equality is now proved for carbon tetrachloride.

2. The "false" orientation polarisation of liquid benzene, previously noted and attributed to the presence of co-ordinate links, is measured over a range of temperature.

3. Several expressions for molecular refraction are compared from the point of view of their independence of temperature.

THE UNIVERSITY, LEEDS.

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