176. *A Simple Relation between Molecular Polarisation in Solution and the Dielectric Constant of the Solvent.*

By Raymond J. W. Le Fèvre.

The expression ${}_0P_1/{}_0P_2 = K(\varepsilon_2 + 2)/(\varepsilon_1 + 2)$, in which ${}_0P_1$ and ${}_0P_2$ are the orientation polarisations of a solute molecule in two media of dielectric constants ε_1 and ε_2 respectively, appears to be valid over a wide range of ε values. Three groups of examples of its applicability are given in the following tables : (*a*) for pairs of solutions, (*b*) for solutions, and the corresponding solutes in the vapour states, and (*c*) for solutions, and the (liquid) solutes in bulk.

(a) *Pairs of Solutions.*—The solvents are indicated under S_1 and S_2 ; except where otherwise stated by the authors to whom reference is made, ${}_0P_1$ and ${}_0P_2$ are in each case taken as the differences between the total polarisations extrapolated to infinite dilution and the molecular refractions for the Na_D line ; T is the temperature at which both measurements were made ; the appropriate references are listed on p. 775. The value of the constant K is seen to be about unity.

T.	S_1.	${}_0P_1$.	ϵ_1.	S_2.	${}_0P_2$.	ϵ_2.	K.
			Nitrobenzene.				
25°	C_6H_6[1]	321·2	2·273	CCl_4	320·5	2·227	1·01
	$CHCl_3$[1]	208·6	4·724	C_6H_6	321·2	2·273	1·02
25	*cyclo*-C_6H_{12}[1]	327·4	2·016	*n*-C_6H_{14}[1]	339·9	1·887	1·00
	CCl_4[1]	320·5	2·228	$C_{10}H_{18}$[1]	320·3	2·162	1·02
	CS_2[1]	277·4	2·633	C_6H_6	321·2	2·273	0·94
	$CHCl_3$[1]	208·6	4·724	CS_2	277·4	2·633	1·09
	,,	,,	,,	*n*-C_6H_{14}	339·9	1·887	1·06
	,,	,,	,,	*cyclo*-C_6H_{12}	327·4	2·016	1·07
20	CCl_4[2]	340·2	2·236	*n*-C_6H_{14}	344·8	1·912	1·07
	C_6H_6[2]	329	2·282	$C_{10}H_{18}$	350	2·16	0·97
	CS_2[2]	294·5	2·640	*n*-C_6H_{14}	344·8	1·92	1·01
18·5	C_6H_5Cl[3]	169·6	5·82	C_6H_6	335	2·241	0·93

T.	S$_1$.	$_0P_1$.	ϵ_1.	S$_2$.	$_0P_2$.	ϵ_2.	*K.*
				Chlorobenzene.			
20°	C_6H_6 [2]	50	2·28	CCl_4	50	2·23	1·01
	CS_2 [2]	44·5	2·64	C_2Cl_4	49	2·30	0·98
	CCl_4 [2]	50	2·23	$C_{10}H_{18}$	52	2·16	0·98
	$C_{10}H_{18}$ [2]	52	2·16	*cyclo*-C_6H_{12}	53	2·02	1·02
	cyclo-C_6H_{12} [2]	53	2·02	C_6H_{14}	55	1·91	0·99
18	C_6H_5Me [3]	55	2·347	C_6H_6	51·5	2·241	1·09
25	Dioxan [12]	50·1	2·306	*cyclo*-C_6H_{12}	53	2·02	1·01
				o-*Dichlorobenzene.*			
20	CS_2 [2]	95	2·64	C_6H_6	111·5	2·28	0·92
	C_6H_6 [2]	111·5	2·28	$C_{10}H_{18}$	106·5	2·16	1·08
	$C_{10}H_{18}$ [2]	106·5	2·16	*n*-C_6H_{14}	111	1·91	1·02
				Acetone.			
20	$C_{10}H_{18}$ [2]	158	2·16	*n*-C_6H_{14}	169	1·91	0·99
	C_6C_6 [2]	160	2·28	CCl_4	176	2·23	0·92
	CS_2 [2]	154	2·64	C_6H_6	160	2·28	1·04
18·5	$C_6H_5{\cdot}NH_2$ [3]	118·4	7·23	$CHCl_3$	149·7	5·04	1·04
				Benzophenone.			
20	CS_2 [2]	174	2·64	C_6H_6	184	2·28	1·03
	C_6H_6 [2]	184	2·28	CCl_4	186	2·23	1·00
	CCl_4 [2]	186	2·23	$C_{10}H_{18}$	181	2·16	1·04
	$C_{10}H_{18}$ [2]	181	2·16	*n*-C_6H_{14}	185	1·91	1·04

It is to be noted that the relation now proposed satisfactorily includes the data for the polar solvents, chloroform, aniline, and chlorobenzene; the rule previously given by Jenkins [1] (*viz.*, total polarisation ∝ 1/dielectric constant of solvent) fails in this respect, as is seen from the following data :

Total polarisation of nitrobenzene in various solvents at 25°.

S$_1$.	Total P_1.	ϵ_1.	S$_2$.	Total P_2.	ϵ_2.	$P_1\epsilon_1/P_2\epsilon_2$.
cyclo-C_6H_{12}	360	2·016	*n*-C_6H_{14}	372·5	1·887	1·03
CCl_4	353·1	2·228	$C_{10}H_{18}$	352·9	2·162	1·03
CS_2	310·0	2·633	C_6H_6	353·8	2·273	1·01
$CHCl_3$	341·2	4·722	CS_2	310	2·633	1·97
,,	,,	,,	C_6H_6	353·8	2·273	2·00
,,	,,	,,	*n*-C_6H_{14}	372·5	1·887	2·29

(b) *Solutions, and Solutes as Vapours.*—If ε_2 is put $= 1$, and $_0P_1$ has the significance defined in section (a), then $_0P_1/_0P_2$ gives the ratio between the orientation polarisations in the dissolved (infinitely dilute) and in the gaseous state; *K* in this case is higher than unity :

T.	S$_1$.	$_0P_1$.	ϵ_1.	S$_2$.	$_0P_2$.	*K.*
			Chlorobenzene.			
20°	C_6H_6 [2]	50	2·28	Vac.[5]	58·1	1·23
			n-*Propyl chloride.*			
20	*n*-C_6H_{14} [2]	84	1·91	Vac.[7]	87·8	1·25
	$C_{10}H_{18}$ [2]	82	2·16	,,	,,	1·29
	CCl_4 [2]	80	2·23	,,	,,	1·28
	C_6H_6 [2]	77·5	2·28	,,	,,	1·26
	C_2Cl_4 [2]	77	2·30	,,	,,	1·26
	CS_2 [2]	68	2·64	,,	,,	1·20

T.	S$_1$.	$_0P_1$.	ϵ_1.	S$_2$.	$_0P_2$.	*K.*
			Nitrobenzene.			
18·5°	C_6H_5Cl [1]	169·6	5·82	Vac.[4]	377·3	1·17
25	C_6H_6 [1]	321·2	2·273	,,	373	1·22
25	$CHCl_3$ [3]	208·6	4·724	,,	,,	1·25
			Acetone.			
20	*n*-C_6H_{14} [2]	169	1·91	Vac.[6]	175	1·26
	$C_{10}H_{18}$ [2]	169	2·16	,,	,,	1·34
	C_6H_6 [2]	160	2·28	,,	,,	1·30
	CS_2 [2]	154	2·64	,,	,,	1·36

Müller's rule [10] [that $_0P_{\text{soln.}}/_0P_{\text{gas}} = 1 - k(\varepsilon - 1)^2$], when applied to the above data, is found to hold only for solvents of low dielectric constant (for which $k = 0{\cdot}075 \pm 0{\cdot}005$); it breaks down for chloroform ($k = 0{\cdot}032$) and chlorobenzene ($k = 0{\cdot}035$).

(c) *Solutions, and Solutes in Bulk.*—For a given substance, the expression relates measurements made on dilute solutions with those on the undissolved material; thus a liquid in bulk can be regarded as a solution of itself in itself, *i.e.*, in a solvent S$_1$ of dielectric constant ε_1. For most of the cases worked out, *K* lies between 1 and 2, an observation which suggests a simple method for the approximate determination of the dipole moment of a liquid substance of known type: from the dielectric constant, density, molecular weight, and refractive index of the substance *in bulk*, the atomic plus orientation polarisation in, say, benzene can be calculated by the general equation as ${}_0P_1(\varepsilon_1 + 2)/4{\cdot}273K$; then at 25° μ will equal $0{\cdot}22[{}_0P_1(\varepsilon_1 + 2)/4{\cdot}273K]^{\frac{1}{2}}$ Debye units.

In the following table ${}_0P_1$ is the difference between the value of $[(\varepsilon_1 - 1)/(\varepsilon_1 + 2)]M/d$, and the molecular refraction for sodium light; ${}_0P_2$ has the meaning used in Section (a).

T.	S_1.	${}_0P_1$.	ϵ_1.	S_2.	${}_0P_2$.	ϵ_2.	K.
20°	$Me\cdot NO_2$ [15]	37·25	39·4	C_6H_6 [17]	192·5	2·280	1·85
25	$Ph\cdot NO_2$ [8]	62·27	35·22	C_6H_6 [1]	321·2	2·273	1·69
,,	,,	,,	,,	CCl_4 [1]	320·5	2·227	1·71
,,	,,	,,	,,	$CHCl_3$ [1]	208·6	4·724	1·65
,,	,,	,,	,,	C_6H_5Cl [3]	169·6	5·82	1·74
25	o-$C_6H_4Me\cdot NO_2$ [15]	68·7	20·07	C_6H_6 [12]	293	2·273	1·54
20	C_6H_5Cl [3]	31·99	5·82	C_6H_6 [2, 9]	51·1	2·28	1·14
,,	,,	,,	,,	CCl_4 [2, 9]	51·1	2·23	1·16
,,	,,	,,	,,	CS_2 [2, 9]	45·6	2·64	1·18
,,	,,	,,	,,	n-C_6H_{14} [2, 9]	56·1	1·91	1·14
,,	,,	,,	,,	C_2Cl_4 [2, 9]	49·1	2·30	1·18
	$COCl_2$ [13]	21·34	4·724	CCl_4 [14]	27·4	2·275	1·23
25	$COMe_2$ [8]	48·1	20·87	CCl_4	154	2·227	1·69
18	$COPhMe$ [15]	63·1	18·31	C_6H_6 [3]	187·5	2·241	1·61
25	$CHCl_3$ [8]	24·3	4·80	C_6H_6	26·5	2·273	1·46
	,,	,,	,,	CCl_4	28·8	2·227	1·36
20	$C_6H_5\cdot CO_2Me$ [11]	43	6·633	C_6H_6 [11]	67·9	2·280	1·28
20	$MeCN$ [15]	37·16	36·2	C_6H_6 [16]	251	2·280	1·32
25	$C_6H_5\cdot NH_2$ [19]	28·81	6·677	C_6H_6 [11]	50·8	2·273	1·15
25	$C_6H_5\cdot NHMe$ [19]	31·96	5·903	C_6H_6 [12]	57	2·273	1·04
25	$C_6H_5\cdot NMe_2$ [19]	30·24	4·811	C_6H_6 [12]	53	2·273	0·91
25	C_5H_5N [19]	39·39	12·013	C_6H_6 [18]	109·4	2·273	1·18
25	C_9H_7N [19]	42·58	8·704	C_6H_6 [18]	99	2·273	1·08
25	*iso*-C_9H_7N [19]	48·2	10·711	C_6H_6 [18]	132·2	2·273	1·08

Certain liquids, *e.g.*, water and alcohols, stand alone and yield constants which are considerably higher than the foregoing. Accurate dielectric-constant data are lacking, and we hope to make an experimental study of this group in the near future. The data for water and ethyl alcohol are given as examples:

25°	H_2O [8]	13·59	79·45	C_6H_6	60·2	2·273	4·30
	,,	,,	,,	Dioxan	78·2	2·306	3·29
				,,	75·3	,,	3·41
25	$EtOH$ [8]	40·5	24·69	CCl_4	61	2·227	4·19

Treatment in the same way of bulk-vapour state figures leads to similar results in the few cases where the available measurements permit a test to be made.

References used in the tables.

[1] Jenkins, *Nature*, 1934, **133**, 106. [2] Müller, *Physikal. Z.*, 1933, **34**, 689. [3] Hassel and Uhl, *Z. physikal. Chem.*, 1930, *B*, **8**, 187. [4] Calc. from results of Sugden and Groves, J., 1934, 1091. [5] Calc. from Smyth and McAlpine, *J. Chem. Physics*, 1935, **3**, 55. [6] Zahn, *Physikal. Z.*, 1932, **33**, 686. [7] Sänger, *ibid.*, 1931, **32**, 20; *Helv. Phys. Acta*, 1930, **3**, 161. [8] Graffunder and Heymann, *Z. Physik*, 1931, **72**, 744. [9] Müller, *Physikal. Z.*, 1932, **33**, 731. [10] Müller, *Trans. Faraday Soc.*, 1934, **30**, 729. [11] Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 134. [12] Williams, *Physikal. Z.*, 1931, **32**, 27. [13] Schlundt and German, *J. Physical Chem.*, 1925, **29**, 353. [14] Le Fèvre, forthcoming paper. [15] Walden, *Z. physikal. Chem.*, 1910, **70**, 569. [16] Partington and Cowley, *Nature*, 1935, **135**, 474. [17] Partington and Hunter, J., 1933, 312. [18] Le Fèvre and Smith, J., 1932, 2810. [19] Present paper.

In the above tables ${}_0P$ has been taken, in nearly every case, as the difference between the total polarisation and the molecular refraction for sodium light, *i.e.*, with each example a different and probably inadequate allowance for the atomic polarisation contribution to the total polarisation has been made. The effects of an erroneously large orientation polarisation figure (increase of K, as, *e.g.*, in instance of nitromethane) will obviously be most marked, for arithmetical reasons, with the greater dielectric constant values [*i.e.*, Section (c)]. The indication, however, is that—applied to accurately corrected orientation polarisations—the constant is of the order unity.

The molecular polarisation ($= {}_AP + {}_EP + {}_0P$) values shown by a substance in the liquid, dissolved, or gaseous state are now easily related. Recorded data show that a non-polar solute ($_0P = 0$) has much the same molecular polarisation in all solvents : only polar solutes exhibit appreciable alterations. Therefore, since the distortion polarisation (= atomic and electronic polarisations) of a substance is usually practically independent of its state of aggregation, these differences are wholly referable to the orientation polarisation factor, the variations of which it is now shown can, in turn, be simply associated with the dielectric constant of the medium in which the solute molecules are dispersed.

Form and Physical Meaning of the Relation.—With the rather limited range of experimental data at present available, it is not possible to decide whether some similar relation of the type $_0P_1/_0P_2 - K(\varepsilon_2 + n)/(\varepsilon_1 + n)$ would not describe the facts better than the $\varepsilon + 2$ expression used in this paper; *e.g.*, if $n = 3$, the first eight pairs of nitrobenzene solutions (p. 773) yield constants : 1·01, 0·95, 0·99, 1·01, 0·92, 1·03, 0·97, and 0·98 respectively.

For the time being, however, the $n = 2$ form is to be preferred, since it can be derived *a priori* from the not unreasonable assumption that the orientation polarisation of a solute molecule may, within limits, vary in some approximately direct manner with the space between the solvent molecules; this quantity, in 1 c.c. of a medium of dielectric constant ε, should be $1 - (\varepsilon - 1)/(\varepsilon + 2) = 3/(\varepsilon + 2)$ c.c. (Clausius, " Mechanische Wärmetheorie," **2**, 94), so that, generally, $_0P = 3k/(\varepsilon + 2)$. Application to the case of a gas at low pressure shows, because $\varepsilon_{\text{vac.}} = 1$, that the constant k is numerically the orientation polarisation in the vapour state. Clearly then, the ratio of the orientation polarisations developed by a given solute in two media of dielectric constants ε_1 and ε_2 is

$$_0P_1/_0P_2 = \frac{3k_1/(\varepsilon_1 + 2)}{3k_2/(\varepsilon_2 + 2)} = \frac{k_1}{k_2} \cdot \frac{\varepsilon_2 + 2}{\varepsilon_1 + 2} = K\frac{\varepsilon_2 + 2}{\varepsilon_1 + 2}$$

in which K should be exactly unity.

EXPERIMENTAL.

The dielectric constants and densities at 25° of the following pure liquids have been measured by the resonance and pyknometric methods employed previously (this vol., p. 480), and the total polarisations computed according to the Clausius–Mosotti relation in the usual way; these results, less the appropriate molecular refractions for sodium light, are tabulated in Section (c) above under ε_1 and $_0P_1$.

Aniline.—Purified by redistillation, b. p. 182—183°, and finally by freezing; $d_{4^\circ}^{25^\circ}$ 1·01742, ε_{25° 6·6773.

Methylaniline.—The commercial product was *p*-toluenesulphonated by the standard Schotten–Baumann process, and the derivative crystallised from dilute ethyl alcohol until of constant m. p.; hydrolysis, etc. (Ullmann, *Annalen*, 1903, **327**, 110), afforded pure methylaniline, b. p. 193°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·98409, ε_{25° 5·9032.

Dimethylaniline.—A commercial " pure " specimen was redistilled, b. p. 193°/760 mm., and twice frozen, m. p. 2—3°, $d_{4^\circ}^{25^\circ}$ 0·95309, ε_{25° 4·8114.

Quinoline.—Purified by distillation, b. p. 236—238°/761 mm., over lime, followed by freezing in a calcium chloride–ice mixture, m. p. – 20°, $d_{4^\circ}^{25^\circ}$ 1·08979, ε_{25° 8·7044.

iso*Quinoline.*—Purified by redistillation, b. p. 240°/762 mm., followed by freezing; m. p. 25°, $d_{4^\circ}^{25^\circ}$ 1·09897, ε_{25° 10·7108.

Pyridine.—A commercial " pure " specimen, after standing for two days over sodium hydroxide, was distilled; b. p. 114—115°/758 mm., $d_{4^\circ}^{25^\circ}$ 0·97796, ε_{25° 12·0132.

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[*Received, April 2nd,* 1935.]