View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

59. *The Magnitude of the Solvent Effect in Dipole-moment Measurements. Part V. The Solvent-effect Constant and the Moments of Alkyl Iodides.*

By Arnold Audsley and Frank R. Goss.

The dielectric polarisation of binary mixtures of eighteen alkyl iodides with carbon tetrachloride has been shown to obey the solvent-effect equation introduced in Part I (J., 1937, 1915). The dipole moments of these iodides have been calculated from the coefficients in this equation by means of the intercept ratio (Part II, J., 1940, 752) and by making use of the additive character of the atom polarisation postulated in Part IV (J., 1941, 864), for which further evidence is now given. The solvent-effect constant [K] is defined, and its relationship to molecular structure summarised. The function of the solvent-effect equation and constant is shown to be that of adapting dipole formulæ based on the Lorenz field to the more correct model proposed by Onsager. The moments and the solvent-effect constants of the alkyl iodides fall into regular series, primary, secondary, and tertiary, the primary being modified by an alternation of the odd and even members. The moments in each series exhibit a decrement of 0·01 D. for each member of the series, this being modified by systematic differences attributable in the case of the lowest members to induced moments. It is deduced that alkyl chains in the liquid phase are curled, whereas in the vapour phase they are free to rotate. In the series Me, Et, Pr^{β}, Bu^{γ} the induced moments can be calculated from a group dipole moment of 0·64 for the methyl group. The calculated atom polarisations increase very slightly with increasing chain length, being, as explained in Part IV, mainly dependent on the nature of the polar atom.

Dipole Moments of the Alkyl Iodides.—In Part IV (*loc. cit.*) it has been shown that by combining polarisation data in both the liquid and the vapour state, the dipole moments of an entire homologous series may be derived reasonably free from any uncertainty due to the difficulties in the way of direct

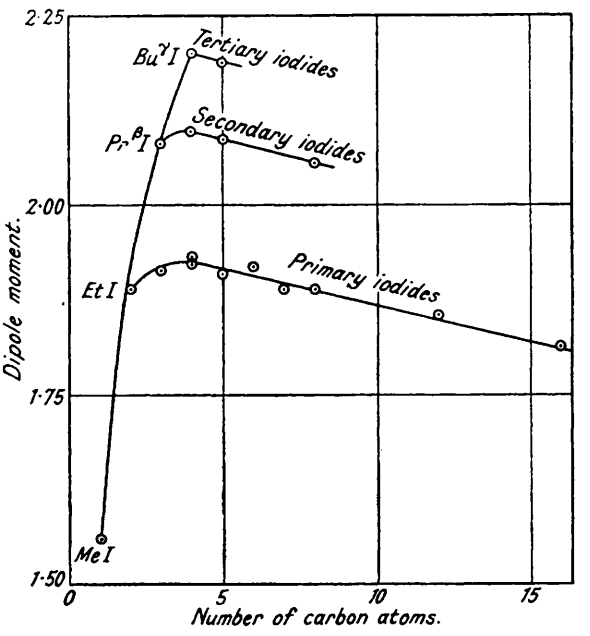
View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

measurement of P_{E+A}. This procedure can be applied with special confidence to the alkyl iodides, since both methyl and ethyl iodide have been found (*loc. cit.*) to give the same contributory value of P_{E+A} for the iodine atom. A number of the higher alkyl iodides have now been examined in the liquid state, and the results are summarised in Fig. 1 and Table I. Solvent-effect corrections have been applied in a uniform manner throughout the series in accordance with principles elaborated in earlier papers. Additive values of P_{E+A} (see below) have been calculated from the contributory values given in Table II of Part IV with addition of the appropriate enhancements for the branched-chain members, corresponding to experimental measurements for the molecular refractivity.

FIG. 1.

Dipole moments of alkyl iodides.



The moments vary from a minimum value for methyl iodide to a maximum at *tert.*-butyl iodide. Increasing complexity of the hydrocarbon residue involves reinforcement of the primary moment of the C–I bond by vectorial components of the induced moments in the adjacent C–C bonds up to the butyl compounds. The increases in these moments due to the successive replacement of the three hydrogens of methyl iodide by methyl groups for Et, Pr$^{\beta}$, and Bu$^{\gamma}$ are seen to be 0·33, 0·52, and 0·64, respectively. The magnitude of these increases can be accounted for by the assumption that the induced moment in each bond is 0·64, and the angle between them tetrahedral.

Evidence concerning the increase in moment with lengthening of the alkyl chain, and the possibility that a constant value might be reached at some point in the series, has been summarised by Cowley and Partington (J., 1938, 977). Measurements have now been extended as far as cetyl iodide. Up to the butyl members there is a small series induced moment, but beyond this point there is a regular decrement

TABLE I.

Polarisation constants of carbon tetrachloride solutions at 20°.

	Calc. values.*			Exptl. values,	Derived poln. coefficients.			Solvent-effect constant,	Corrected dipole moment,
	P_{E+A}.	P_E.	P_A.	P_∞.	Z.	Y.	P_0.	$[K]$.	μ, D.
Methyl iodide	21·9	18·5	3·4	63·3	34·3	92·1	51·2	1·72	1·56
Ethyl iodide	26·7	23·3	3·4	89·9	47·3	140·5	75·1	1·62	1·89
n-Propyl iodide	31·3	27·9	3·4	98·7	61·7	149·9	77·3	1·53	1·92
*iso*Propyl iodide	31·7	28·3	3·4	113·0	67·1	180·8	91·0	1·47	2·08
n-Butyl iodide	35·8	32·4	3·4	105·6	74·6	154·9	78·4	1·49	1·93
*iso*Butyl iodide	35·8	32·4	3·4	107·0	80·0	157·7	78·0	1·43	1·92
sec.-Butyl iodide	36·2	32·8	3·4	121·9	84·5	190·2	92·6	1·39	2·10
tert.-Butyl iodide	36·9	33·5	3·4	132·0	88·8	211·1	101·7	1·36	2·20
n-Amyl iodide	40·3	36·9	3·4	111·2	92·9	157·0	76·8	1·40	1·91
β-Iodopentane	40·6	37·2	3·4	128·4	104·0	194·5	91·7	1·30	2·09
γ-Iodopentane	40·5	37·1	3·4	128·3	104·5	194·8	91·6	1·30	2·09
tert.-Amyl iodide	41·0	37·6	3·4	137·7	106·5	214·5	100·6	1·29	2·19
n-Hexyl iodide	44·9	41·4	3·5	117·0	105·7	159·6	77·5	1·38	1·92
n-Heptyl iodide	49·4	46·9	3·5	120·0	119·6	156·1	75·1	1·36	1·89
n-Octyl iodide	53·9	51·4	3·5	124·7	131·1	156·4	75·1	1·35	1·89
β-Iodo-octane	54·1	51·6	3·5	144·0	160·0	198·3	88·9	1·16	2·06
Lauryl iodide	72·0	69·5	3·5	142·7	182·7	152·9	72·3	1·31	1·85
Cetyl iodide	90·2	87·6	3·6	158·5	240·5	148·9	69·2	1·26	1·81

* Calculated from the contributory values recorded in J., 1941, 864, Table II.

of 0·01 D., not only in the primary, but also in the secondary and tertiary series. This must be due to a reversal in direction of the component of the induced moment, owing to the flexible nature of the chain. This reversed induced moment is more pronounced in alkyl chlorides and bromides and is recognisable right from the *n*-propyl derivatives, and it has been noted by Stuart (*Physikal. Z.*, 1930, **31**, 80) in the case of *n*-propyl chloride. He showed that the induced moment may fall outside that space within which the primary moment should be reinforced by the induced moments. Likewise, Cowley and Partington

View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

(*loc. cit.*, p. 979) deduced that, although the bulk of the polarisable matter added by lengthening the hydrocarbon chain of compounds with a negative solvent effect (solvent-effect constant, $[K]>1$, see below) augments the primary moment, yet parts of the molecule may occupy positions leading to a diminution of the moment. This prediction has thus been realised for the higher alkyl iodides. However, as the above authors and also Frank (*Proc. Roy. Soc.*, 1935, *A*, **152**, 171) point out, the approximations made in the theoretical derivation of the sign and magnitude of the induced moments to not permit of rigid and exact calculation.

In the primary series of iodides there is an alternation, the even members having higher and the odd ones lower moments than the average. After allowance for an experimental error of ±0·01 D., this deviation of the odd and even members has the value of 0·01 D. The moment for *iso*butyl iodide falls on the curve of the odd members, and is nearly identical with that for *n*-propyl iodide which has the same chain length. The moments of the two secondary amyl iodides lie on the secondary curve and are identical. These moments, recorded in Table I, depend on the use of the additive values of P_{E+A} given in Part IV, and do not differ by more than 0·03 D. from those calculated from the empirical relationship $P_{E+A} = 1{\cdot}05\ [R_L]_D$. Hence, our conclusions regarding the influence of the alkyl radicals on the moments are independent of any assumption concerning the magnitude of P_{E+A}. However, we provide further evidence (see p. 363) in favour of the additive method of assessing P_{E+A}.

Definition of the Solvent-effect Constant.—The solvent-effect constant, $[K]$, expresses the effect of the field anistropy on the polarisation. The method of deriving $[K]$ has been described in Part II (J., 1940, 754) where the symbol K was used. The scale of $[K]$ was devised in such a way that it has a natural *fixed point* of unity for symmetrical molecules, but has an arbitrary *unit* chosen to give values for the reference compounds (see Table II) most nearly corresponding with those of the ratio of their respective optical polarisation axes $2b_1/(b_2 + b_3)$ as calculated by Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 284). It follows from its derivation from the coefficients Y and Z of the solvent-effect equation (see below), by the expressions given below, that for a very long molecule, for which Z might conceivably approach very closely to zero and hence have Y equal to P_O, $[K]$ would have the value 2·73. This value appears therefore to form an upper limit to the scale of solvent-effect constants. As the ratio of the molecular axes could, at least in theory, extend to infinity, the equivalence between $[K]$ and $2b_1/(b_2 + b_3)$ is seen to be only a *first approximation*, as was stated in Part II.

It was explained in Part I that the solvent effect can be expressed by the equation for the partial polarisation of either component of a binary liquid mixture, $P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon$, where the Y/ε term expresses the change in the orientation polarisation (P_O) due to the induced moments

TABLE II.

Equivalence of certain solvent-effect constants with the corresponding ratios of the optical polarisation axes.

	$[K]$.	$2b_1/(b_2 + b_3)$.		$[K]$.	$2b_1/(b_2 + b_3)$.
Nitrobenzene	1·68	1·69	Acetone	1·15	1·19
Chlorobenzene	1·61	1·53	Chloroform	0·70	0·74

arising from the neighbouring dipoles (this may be a diminution or augmentation according to the shape of the molecules), whilst $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ is the enhancement by these dipoles of the distortion polarisation (P_{E+A}). These induced moments depend in magnitude and direction on modifications of the local field due to interaction of molecules in the liquid state, the Y and Z components of the solvent effect being dependent on the field anisotropy caused by the dissymmetry of the polar molecules. *The solvent-effect constant* $[K]$ is, as argued in Part II, *a measure of the shape of the molecule*, since *it expresses the proportion of the polarisable matter which is disposed along the dipole axis*; it consequently bears a constant relation to both the Y and the Z component of the solvent effect, so that if $[K]$ is known, the solvent effect for the carbon tetrachloride mixture can be immediately calculated. The relationship between $[K]$, Y, and Z is defined in the manner already described, in such a way that for symmetrical molecules $[K]$ is unity. As deduced in Part II, $[K] = 4 - 2{\cdot}85Y/\varepsilon_1 P_O = 6{\cdot}55 - 3{\cdot}82\sqrt[4]{(Z + P_{E+A})/P_{E+A}}$ (where ε_1 is the dielectric constant of the solvent). Hence we may derive the intercept ratio $(Y/P_O - 1)/[\sqrt[4]{(Z + P_{E+A})/P_{E+A}} - 1] = 3$*, which has been extensively employed in this work to calculate P_O from the intercepts Y and Z. The ratio $Y/\varepsilon_1 P_O$ is usually less or greater than unity (see Part I) according as the partial polarisation of the infinitely dilute solution (P_∞) is less than or greater than the polarisation of the vapour, or again, according as the moment lies along the major or one of the minor axes of the molecule, or as the Kerr constant is positive or negative, in accordance with the generalisation of Higasi (*loc. cit.*; cf. *Bull. Inst. Phys. Chem. Res. Tokyo*, 1934, **13**, 1167; 1935, **14**, 146); *i.e.*, as $[K]$ is greater or less than unity.

* The value 3·25 assigned to this ratio in Part I was corrected to 3 in Part II.

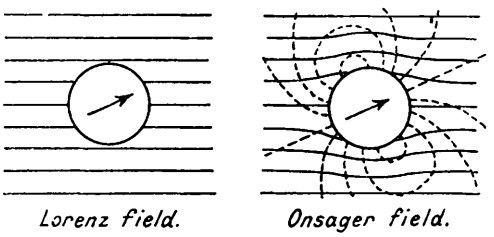
View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

If Higasi's generalisation were strictly true, $Y/\varepsilon_1 P_0$ should be *exactly* unity for any symmetrical molecule, because $P_\infty - P_{E+A}$, which approximates to Y/ε_1 would equal P_0; $[K]$, being unity, would then have the values $4 - 3Y/\varepsilon_1 P_0$ or $4 + 6/\varepsilon_1 - 9\sqrt[4]{(Z + P_{E+A})/P_{E+A}}/\varepsilon_1$. However, Frank has pointed out (*loc. cit.*, p. 180) that in the theoretical treatment of the solvent effect "the field distribution is considered to be always the same as it is in a uniform medium." In the binary liquid mixtures now under consideration the distribution necessarily varies, and consequently "the chief result of this error is that the molecules considered to have zero solvent effect according to the simple deduction, will actually show a positive effect." This error is compensated for in our derivation of the solvent-effect constant by the addition of an empirical term $0{\cdot}15Y/\varepsilon_1 P_0$, which, together with the value $4 - 3Y/\varepsilon_1 P_0$ obtained by applying the Higasi generalisation, gives finally the above correct expression for $[K]$, *viz.*, $4 - 2{\cdot}85Y/\varepsilon_1 P_0$ as first obtained in Part II of this series.

Interpretation of the Solvent Effects in Terms of the Solvent-effect Constant and the Onsager Field.—The use of the solvent-effect constant enables us to adapt the Debye theory to the liquid state even when the molecular shapes are far from spherical. Onsager (*J. Amer. Chem. Soc.*, 1936, **58**, 1486; see also Cole, *J. Chem. Physics*, 1938, **6**, 385, and Kirkwood, *ibid.*, 1939, **7**, 911), on the contrary, has rejected the Debye formula as applied to liquids and has proposed an expression for the dipole moment of liquid molecules which, as he admits, is open to the objections that the molecules are assumed to be spherical, and also to fill the whole volume of the liquid. His formula is somewhat complex for actual application to the measurement of dipole moments and, as he says, requires "some arbitrary exercise of judgement." Onsager's equation, as it applies to homogeneous liquids, has been employed by Böttcher (*Physica*, 1939, **6**, 59), who found quite good agreement in certain cases. An examination of his figures shows, however, that the discrepancies are most marked where the molecules are farthest removed from the spherical shape assumed by Onsager. Those having $[K]>1$ have low values of the moment in Böttcher's tabulation and *vice versa*, just as in the Debye theory. The Onsager formula for binary mixtures is more complicated, but it has been applied by Rodebush and Eddy (*J. Chem. Physics*, 1940, **8**, 424; see also Hobbs, *ibid.*, 1939, **7**, 849, and Piekara, *Proc. Roy. Soc.*, 1939, *A*, **172**, 360), who obtain values which are in general also too low or too high according as $[K]$ is $>$ or <1. Van Vleck (*J. Chem. Physics*, 1937, **5**, 556) discussed the Lorenz and the Onsager model of the local field, which have been depicted by Falkenhagen (*Physikal. Z.*, 1938, **39**, 806; cf. van Vleck, *J. Chem. Physics*, 1937, **5**, 320) (see Fig. 2). Van Vleck pointed out that "there is apparently no easy way to decide by simple physical considerations" which "is really the better." From work in this series, it has been concluded (see Part II) that the Onsager field model is the more correct, but that, since the shape of the molecule also affects the field distribution, the empirical solvent-effect equation gives a truer expression for the polarisation than Onsager's complex dipole formula, for which he assumes a spherical molecule. In the solvent-effect equation, $P_S = P_{E+A} + Z(\varepsilon - 1)^4/(\varepsilon + 2)^4 + Y/\varepsilon$, the Onsager reaction field R, shown in Fig. 2 by broken lines, corresponds to the $Z(\varepsilon - 1)^4/(\varepsilon + 2)^4$ term, which is an enhancement of the polarisation, and is independent of the moment because the field R is parallel to the dipole. The cavity field G (continuous lines) similarly corresponds to $P_{E+A} + Y/\varepsilon$, which expresses the difference between the classical polarisation $P_{E+A} + P_0$, arising from the internal field, and the opposing effect of the induced moments due to G. Onsager has criticised the Debye formula because highly polar compounds do not exhibit a Curie point or a permanent electric polarisation, involving an apparent volume polarisation greater than unity. However, the Lorenz field being assumed, the local polarisation of a single liquid molecule will be given by $(\varepsilon - 1)/(\varepsilon + 2) = P^{vap}{\cdot}d/M$, which in the case of nitrobenzene has a value of 4·3, thus fulfilling Onsager's requirement. In the Onsager field this value is reduced by the effects of the surrounding molecules to the average volume polarisation of 0·9 actually observed.

FIG. 2.



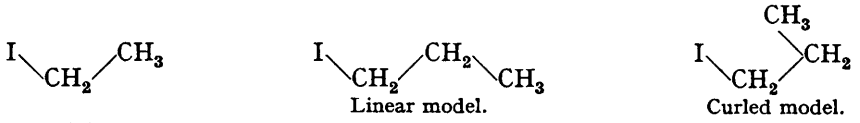
Rodebush and Eddy (*loc. cit.*) regard the polarisation of benzene–ethyl ether mixtures as providing special evidence against the Debye theory. They assume with Debye ("Polar Molecules," 1929, p. 46) that, for this mixture, the partial polarisation of the ether is independent of concentration. There is, however, nothing remarkable about this particular mixture and any difference from the usual curves is a difference of degree and not of kind. It just happens that $[K]$ for diethyl ether has the small value of 0·22, and consequently the polarisation of the pure liquid ether is only slightly less than that of the molecules in dilute solution. For carbon tetrachloride–ethyl ether mixtures, the difference is a little greater (see Part I), and indeed, there is nothing unusual about these mixtures to provide any evidence for or against any particular theory. Rodebush and Eddy have a further criticism of the Debye method

View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

of extrapolating polarisation data in dilute solutions to obtain P_∞; this criticism is met in our work by the employment of the tangent method of obtaining the partial polarisations. The same value of P_∞ is obtained in either case, and in practice we use both methods to ensure the greatest possible accuracy.

Solvent-effect Constants and Structure of the Alkyl Iodides.—All the alkyl iodides dealt with in this paper have a solvent-effect constant greater than unity (see Fig. 3 and Table I). In the series Me, Et, Pr^β, Bu^γ there is a regular fall for each member. This is accompanied by alternation of the odd and even members. The constant decreases at first rapidly, but beyond the fifth member more slowly with increasing chain length. This is in agreement with our interpretation of the series decrement of the dipole moments (see above). It appears that in the liquid state the alkyl chains must be curled in the manner proposed by Stuart (*loc. cit.*). A propyl iodide molecule of linear structure (II) has, by comparison with

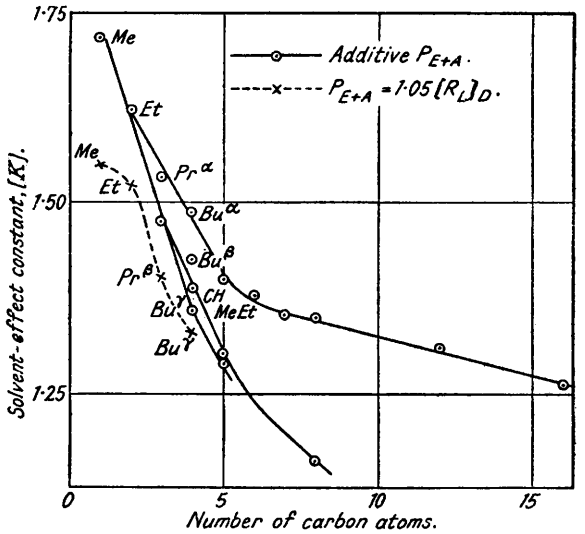


(I.) (II.) (III.)

ethyl iodide (I), had its length extended in line with the dipole, and should have a larger $[K]$ than its lower homologue. The experimentally observed lowering of $[K]$ is in agreement with Stuart's curled structure (III). Therefore the experimental evidence of both dipole moments and solvent-effect constants is in favour of this curled form for the liquid molecules, although the amount of curl is not sufficient to affect the moment until beyond butyl iodide. The effect of this curling on the shape of the molecule should be most marked for the first five members of a series, after which a pseudo-ring will have been formed. This will be seen from Fig. 3 to be in agreement with the ascertained facts. After the fifth member, although $[K]$ continues to fall, with presumably further curling of the chain, the effect on the shape of the molecule is greatly diminished. The value of $[K]$ shows a marked alternation in the primary series, which, owing to the known relationships between the solvent-effect constant on the one hand and melting points on the other with molecular symmetry, may be compared with the alternation of the melting points of the primary series of alkyl halides (Baker and Smyth, *J. Amer. Chem. Soc.*, 1939, **61**, 1695).

FIG. 3.

Solvent-effect constants of alkyl iodides.



The change in solvent effect with increasing length of the alkyl chains is in a direction contrary to that expected by Frank (*loc. cit.*, p. 187). Consequently, the relative differences of the change of radical and solvent effect do not explain, as was supposed by Cowley and Partington (*loc. cit.*, p. 981), the fact that the moments of *n*-propyl and *n*-butyl iodides have higher values in the vapour than in the liquid state. This difference appears to persist even after correction for solvent effect and for atom polarisation, and is recorded in Table III, where the moments obtained in the present work from measurements in the liquid

TABLE III.

Comparison of dipole moments measured in the liquid and the vapour phase.

		Dipole moments.		
		Liquid phase, corrected	Vapour phase.	
	P_{E+A}.	for solvent effect.	Smyth and McAlpine.	Groves and Sugden.
Methyl iodide	21·9	1·56	1·56	1·62
Ethyl iodide	26·7	1·89	1·89	1·86
n-Propyl iodide	31·3	1·92	—	2·00
n-Butyl iodide	35·8	1·93	—	2·07

phase are compared with vapour values. The latter have been recalculated, the additive values of P_{E+A} given in Table I being used. Agreement of the present values for methyl and ethyl iodides with those of Smyth and McAlpine (*J. Chem. Physics*, 1934, **2**, 499) is a necessary consequence of the use of their

View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

measurements (which were corrected by them for ideal-gas deviations) to calculate the value of P_{E+A} for the iodine atom (see Part IV). In considering this divergence between the vapour values of Groves and Sugden (J., 1937, 158) and our corrected values for the liquid phase, which is restricted to those iodides with chains of two or more carbon atoms, it is evident that, although we have shown that in the liquid state these molecules have a curled structure (III), yet the alkyl chains in the vapour molecules may well have greater freedom of rotation, with the consequence that the statistical average may be somewhere between the curled and the linear forms (II and III). This would result in a higher moment, so that our hypothesis affords a complete explanation of the available data.

TABLE IV.

Criteria of purity.

	Observed values.		Previously recorded.			Observed values.		Previously recorded.	
Iodide.	$d_4^{20°}$.	$n_D^{20°}$.	$d_4^{20°}$.	$n_D^{20°}$.	Iodide.	$d_4^{20°}$.	$n_D^{20°}$.	$d_4^{20°}$.	$n_D^{20°}$.
n-Propyl	1·7458	1·5050	1·7471 [2]	1·5051 [1]	γ-Iodopentane	1·5128	1·4979	1·5176 [4]	1·4968 [4]
*iso*Propyl	1·7043	1·4991	1·7042 [3]	1·4997 [1]	*tert.*-Amyl	1·4937	1·4981	—	—
n-Butyl	1·6137	1·5000	1·6123 [2]	1·5001 [1]	*n*-Hexyl	1·4329	1·4930	1·4387 [2]	1·4929 [2]
*iso*Butyl	1·6038	1·4961	1·6035 [3]	1·4960 [1]	*n*-Heptyl	1·3792	1·4909	1·3790 [5]	1·4905 [5]
sec.-Butyl	1·5984	1·5000	1·5975 [3]	1·5001 [3]	*n*-Octyl	1·3295	1·4890	1·3299 [5]	1·4886 [5]
tert.-Butyl	1·5445	1·4918	—	—	β-Iodo-octane...	1·3251	1·4896	—	—
n-Amyl	1·5108	1·4965	1·5095 [2]	1·4955 [2]	Lauryl	1·2015	1·4844	—	—
β-Iodopentane...	1·5020	1·4960	—	—	Cetyl	1·1207 [7]	1·4817 [7]	1·1264 [6]	1·4826 [6]

[1] Brühl, *Annalen*, 1880, **203**, 1. [2] Karvonen, *Ann. Acad. Sci. Fennicæ*, 1914, *A*, **5**, 1. [3] Timmermans and Delcourt, *J. Chim. physique*, 1934, **31**, 85. [4] Rosanoff, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 180. [5] Deffet, *Bull. Soc. chim. Belg.*, 1931, **40**, 385. [6] Delcourt, *ibid.*, p. 284 (extrapolated values). [7] Supercooled liquid.

The experimental polarisation data for methyl and ethyl iodide have been recorded in Part IV. The coefficients for the higher iodides have been calculated from the data in Table V, use being made of the additive character of P_{E+A} postulated in Part IV, of the solvent-effect equation, and of the intercept ratio. These general empirical equations, previously developed for the solvent effect, are now further confirmed. The number of polar compounds already examined has been doubled, and it is found that amongst all 36 compounds of widely differing chemical type, the partial-polarisation data fit the solvent-effect equations as shown in Fig. 4, and the constants Y, Z, $[K]$, and μ are independent of the concentration of the binary mixtures. Similarly, the partial polarisations of the carbon tetrachloride in all the mixtures depend on the dielectric constants of the mixtures and are largely independent of the other component of the mixture. As explained in earlier papers, the partial polarisations only become to some extent dependent on the nature of the polar components when, owing to anisotropy effects, the polar compounds have low values of the solvent-effect constant. This consideration does not apply to the alkyl iodides here investigated.

The solvent-effect constants of these alkyl iodides appear to provide further support for our view (Part IV) that a correct evaluation of P_{E+A} is given by additive values based on solvent-effect data and obtained by the elimination method. In Fig. 3 we have plotted, in addition to the values of $[K]$ from Table I, some of the corresponding figures which would be given on a basis of $P_{E+A} = 1{\cdot}05\,[R_L]_D$. The values do not show the regular fall for the series Me, Et, Pr^{β}, Bu^{γ} which is to be expected from the regular increase in symmetry. It will be seen that the value of P_{E+A} has a considerable influence on $[K]$, unlike its negligible effect on the moment, and it is for this reason that it is necessary to decide on the best way of determining P_{E+A}.

The extensive confirmation of the solvent-effect theory given in this paper is illustrated in Fig. 4, where the partial polarisations of some of the iodides and of carbon tetrachloride are plotted against $1/\varepsilon$, and the characteristic shape of the curves for both polar and non-polar compounds may be compared with others to be found in Parts I, II, and III of this series (*locc. cit.* and J., 1940, 888).

EXPERIMENTAL.

Density, dielectric constant, and temperature were measured as previously described (Goss, J., 1933, 1343; 1935, 730; 1940, 893).

Preparation and Purification of Materials.—(A) n- *and* iso-*Propyl and* n-*octyl iodides.* B.D.H. Samples were washed with sodium carbonate and thiosulphate solutions and with water, dried with calcium chloride, and distilled, the middle fraction being collected.

(B) *Cetyl iodide.* A B.D.H. sample was liquefied then washed and dried as in section (A). The middle fraction had b. p. 156°/0·5 mm., m. p. 225°. (The physical constants at 20° recorded in Tables III and IV for this substance apply to the supercooled liquid.)

(C) n- *and* iso-*Butyl,* n-*amyl, and lauryl iodides.* These were obtained from the middle fractions distilled

View Article Online

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

TABLE V.

Polarisations of carbon tetrachloride mixtures at 20°.

c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	P_{S_2}.	P_{S_1}.	c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	P_{S_2}.	P_{S_1}.
		n-*Propyl iodide.*						iso*Propyl iodide.*			
0·00000	2·2376	1·5937	28·19	99	28·2	0·00000	2·2353	1·5939	28·15	113	28·2
0·00559	2·2631	1·5946	28·60	98	28·2	0·00559	2·2662	1·5944	28·65	112	28·2
0·01185	2·2898	1·5956	29·02	97	28·2	0·01137	2·2976	1·5951	29·15	111	28·2
0·02384	2·3379	1·5980	29·76	96	28·3	0·02142	2·3494	1·5963	29·96	109	28·2
0·03347	2·3834	1·5989	30·47	95	28·3	0·04354	2·4644	1·5990	31·70	105	28·3
0·04504	2·4350	1·6008	31·24	93	28·3	0·06717	2·5804	1·6018	33·37	102	28·5
0·05154	2·4577	1·6023	31·56	93	28·3	0·09591	2·7318	1·6054	35·42	99	28·7
0·07652	2·5703	1·6067	33·16	90	28·5	0·23752	3·538	1·6224	44·54	86	32
0·12662	2·7999	1·6141	36·21	86	29	0·39262	4·464	1·6406	52·32	78	36
0·17142	3·0045	1·6210	38·70	83	30	0·65918	6·101	1·6702	62·01	72	43
0·24475	3·364	1·6327	42·59	78	31	0·85118	7·280	1·6898	67·12	71	46
0·48505	4·568	1·6703	52·58	70	36	1·00000	8·194	1·7043	70·39	70·4	49
0·74250	5·789	1·7088	59·67	66	41						
1·00000	7·004	1·7458	64·93	64·9	45						
		n-*Butyl iodide.*						iso*Butyl iodide.*			
0·00000	2·2365	1·5938	28·17	106	28·2	0·00000	2·2350	1·5934	28·15	107	28·2
0·00457	2·2571	1·5939	28·52	105	28·2	0·00677	2·2673	1·5935	28·71	106	28·2
0·00966	2·2792	1·5941	28·90	105	28·2	0·01236	2·2917	1·5936	29·12	105	28·2
0·01817	2·3178	1·5943	29·55	104	28·2	0·02562	2·3508	1·5937	30·12	103	28·3
0·03376	2·3881	1·5946	30·72	102	28·3	0·05858	2·5002	1·5943	32·54	99	28·4
0·06361	2·5251	1·5954	32·90	99	28·4	0·08669	2·6395	1·5946	34·67	96	28·6
0·12099	2·7804	1·5969	36·73	94	29	0·12355	2·7943	1·5952	36·96	92	29·0
0·23061	3·286	1·5996	43·47	86	30	0·28691	3·537	1·5976	46·60	83	32
0·44686	4·273	1·6043	54·42	77	35	0·63659	5·037	1·6016	61·99	75	38
0·73421	5·453	1·6088	65·36	73	40	1·00000	6·466	1·6038	74·08	74·1	44
1·00000	6·288	1·6137	72·76	72·8	43						
		sec.-*Butyl iodide.*						tert.-*Butyl iodide.*			
0·00000	2·2359	1·5937	28·16	122	28·2	0·00000	2·2351	1·5939	28·14	132	28·2
0·00923	2·2362	1·5938	29·02	120	28·2	0·00775	2·2846	1·5935	28·99	130	28·2
0·01321	2·3089	1·5939	29·39	119	28·2	0·01478	2·3241	1·5932	29·65	129	28·2
0·02777	2·3872	1·5940	30·68	117	28·3	0·02843	2·4051	1·5925	30·98	126	28·3
0·05126	2·5195	1·5943	32·77	113	28·4	0·05531	2·5736	1·5912	33·62	121	28·5
0·11572	2·8934	1·5952	38·16	106	29·2	0·10813	2·8983	1·5877	38·34	114	29
0·21257	3·448	1·5964	45·11	98	31	0·21238	3·582	1·5838	46·80	104	31
0·45961	4·904	1·5986	59·33	85	38	0·23846	3·756	1·5820	48·74	102	32
0·73044	6·439	1·5993	70·88	81	44	0·42229	4·935	1·5721	60·12	92	37
1·00000	7·874	1·5984	80·15	80·2	48	0·52197	5·619	1·5687	65·54	89	39
						0·67022	6·506	1·5613	72·17	86	43
						1·00000	8·416	1·5445	84·83	84·8	50
		n-*Amyl iodide.*						*β-Iodopentane.*			
0·00000	2·2374	1·5942	28·18	111	28·2	0·00000	2·2350	1·5940	28·14	144	28·1
0·00912	2·2774	1·5930	28·91	110	28·2	0·00488	2·2621	1·5916	28·70	143	28·2
0·01437	2·3015	1·5924	29·35	109	28·2	0·00888	2·2865	1·5896	29·19	142	28·2
0·02597	2·3533	1·5913	30·28	108	28·2	0·01775	2·3327	1·5853	30·14	140	28·2
0·04734	2·4514	1·5890	32·00	105	28·3	0·03742	2·4405	1·5759	32·33	137	28·3
0·10562	2·6948	1·5832	36·14	99	28·7	0·07249	2·6277	1·5599	36·10	132	28·5
0·24796	3·294	1·5695	45·50	90	31	0·16219	3·080	1·5227	45·13	126	30
0·64658	4·788	1·5364	66·26	82	37	0·34834	3·915	1·4601	62·07	118	32
1·00000	5·811	1·5108	80·74	80·7	42	0·67275	5·009	1·3811	87·75	112	37
						1·00000	5·770	1·3251	111·24	111·2	41
		γ-Iodopentane.						tert.-*Amyl iodide.*			
0·00000	2·2390	1·5943	28·20	128	28·2	0·00000	2·2350	1·5940	28·14	138	28·1
0·00597	2·2732	1·5936	28·81	127	28·2	0·00698	2·2781	1·5932	28·90	136	28·2
0·01137	2·3009	1·5931	29·30	126	28·2	0·01174	2·3070	1·5925	29·41	135	28·2
0·02078	2·3541	1·5922	30·23	125	28·3	0·02106	2·3644	1·5913	30·40	133	28·2
0·03821	2·4538	1·5903	31·92	122	28·3	0·03837	2·4722	1·5892	32·22	131	28·3
0·08002	2·6917	1·5862	35·77	117	28·7	0·07715	2·7174	1·5844	36·13	125	28·7
0·13920	3·032	1·5803	40·88	111	30	0·22309	3·668	1·5674	49·16	111	32
0·28936	3·915	1·5666	52·42	100	33	0·65807	6·386	1·5231	77·14	95	42
0·69252	6·055	1·5342	75·45	90	42	1·00000	8·192	1·4937	93·56	93·6	49
1·00000	7·432	1·5128	89·27	89·3	47						
		n-*Hexyl iodide.*						n-*Heptyl iodide.*			
0·00000	2·2351	1·5943	28·14	117	28·1	0·00000	2·2377	1·5937	28·19	120	28·2
0·00643	2·2639	1·5929	28·70	116	28·2	0·00845	2·2739	1·5909	28·94	119	28·2
0·00807	2·2720	1·5921	28·86	116	28·2	0·01618	2·3111	1·5880	29·68	118	28·2
0·01724	2·3140	1·5899	29·66	115	28·2	0·02963	2·3661	1·5834	30·82	117	28·3
0·03278	2·3876	1·5863	31·05	113	28·2	0·06890	2·5313	1·5700	34·18	113	28·4
0·08108	2·6095	1·5755	35·14	108	28·5	0·17458	2·9512	1·5376	42·66	105	29
0·12688	2·8062	1·5653	38·71	104	29	0·44749	3·834	1 4704	61·50	97	33
0·49194	4·227	1·4949	63·26	91	35	0·81408	4·659	1·4050	83·17	94	37
0·58308	4·509	1·4854	68·15	90	36	1·00000	4·969	1·3792	93·36	93·4	38
0·00000	5·366	1·4329	87·73	87·7	40						

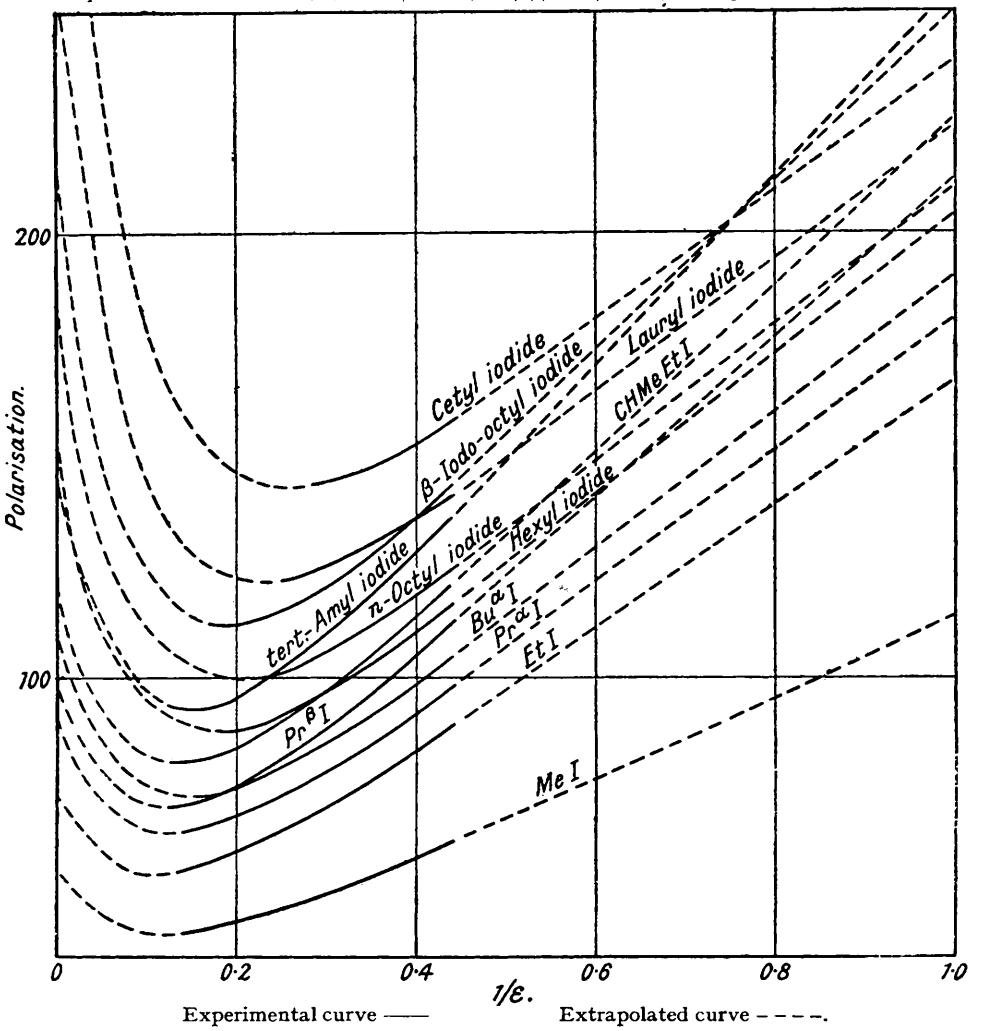
View Article Online

TABLE V.—(*continued*).

c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	P_{S_2}.	P_{S_1}.	c_2.	ϵ.	$d_4^{20°}$.	P_{12}.	P_{S_2}.	P_{S_1}.
		n-*Octyl iodide.*						*β-Iodo-octane.*			
0·00000	2·2384	1·5942	28·19	125	28·2	0·00000	2·2350	1·5940	28·14	144	28·1
0·00548	2·2631	1·5914	28·73	124	28·2	0·00488	2·2621	1·5916	28·70	143	28·2
0·00919	2·2784	1·5896	29·07	124	28·2	0·00888	2·2865	1·5896	29·19	142	28·2
0·01333	2·2964	1·5876	29·45	123	28·2	0·01775	2·3327	1·5853	30·14	140	28·2
0·01555	2·3056	1·5866	29·66	123	28·2	0·03742	2·4405	1·5759	32·33	137	28·3
0·02853	2·3614	1·5804	30·87	122	28·2	0·07249	2·6277	1·5599	36·10	132	28·5
0·03018	2·3697	1·5795	31·04	122	28·2	0·16219	3·080	1·5227	45·13	126	30
0·04645	2·4395	1·5720	32·56	120	28·3	0·34834	3·915	1·4601	62·07	118	32
0·10709	2·6712	1·5458	37·74	114	28·6	0·67275	5·009	1·3811	87·75	112	37
0·11499	2·7123	1·5425	38·57	114	28·8	1·00000	5·770	1·3251	111·24	111·2	41
0·26620	3·218	1·4875	50·53	107	30						
0·47828	3·782	1·4276	65·75	102	33						
1·00000	4·670	1·3295	99·37	99·4	37						
		Lauryl iodide.						*Cetyl iodide.*			
0·00000	2·2367	1·5941	28·17	142	28·2	0·00000	2·2377	1·5938	28·19	159	28·2
0·00608	2·2621	1·5879	28·85	141	28·2	0·00515	2·2574	1·5860	28·84	158	28·2
0·01158	2·2859	1·5825	29·48	140	28·2	0·01051	2·2803	1·5778	29·56	157	28·2
0·02242	2·3310	1·5721	30·70	140	28·2	0·02122	2·3215	1·5621	30·94	156	28·2
0·04340	2·4149	1·5529	33·02	138	28·3	0·05181	2·4344	1·5214	34·89	154	28·3
0·08968	2·5825	1·5145	37·99	135	28·5	0·10118	2·5813	1·4653	40·97	152	28·6
0·17195	2·8368	1·4572	46·47	130	29	0·24559	2·8988	1·3484	58·23	147	29
0·40020	3·311	1·3459	68·15	124	31	0·55900	3·284	1·2139	94·29	144	31
0·75756	3·743	1·2448	100·42	122	32	1·00000	3·504	1·1207	143·01	143·0	32
1·00000	3·930	1·2015	121·81	121·8	33						

FIG. 4.

Partial molar polarisations at 20°. ($P_S = P_{E+A} + Z(\epsilon-1)^4/(\epsilon+2)^4 + Y/\epsilon$ *extrapolated to* $\epsilon = 1$ *and to* $\epsilon = \infty$.)



Experimental curve —— Extrapolated curve – – – –.

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.

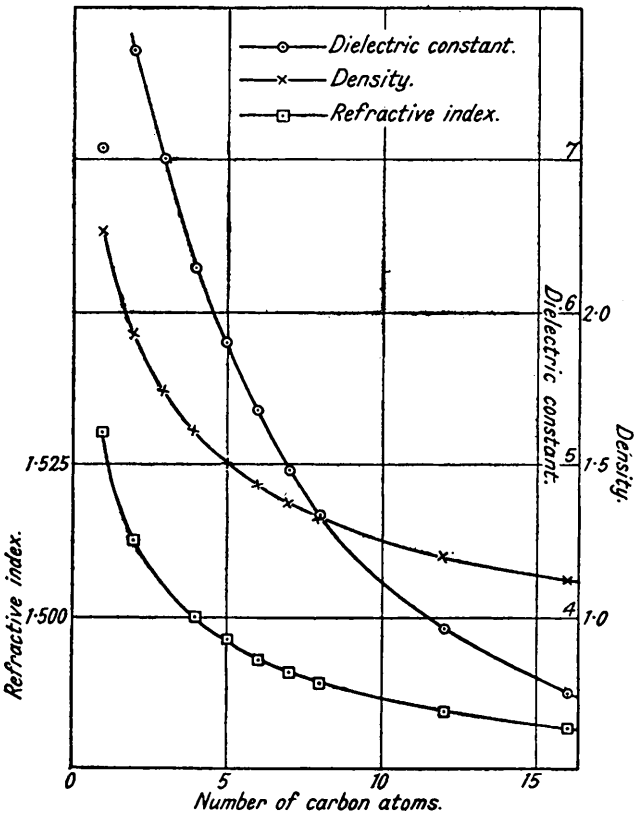
View Article Online

from samples of the appropriate pure alcohols, and prepared by the method of Rieth and Beilstein (*Annalen*, 1863, **126**, 250). Purification was carried out as in section (A).

(D) sec.-*Butyl iodide, γ-iodopentane, and β-iodo-octane.* The procedure was similar to that described in section (C) except that, in the purification of the iodides, sodium carbonate was replaced by bicarbonate and the samples were dried with sodium sulphate.

FIG. 5.

Physical constants of primary alkyl iodides.



(E) tert.-*Butyl and -amyl iodides.* These were prepared as in section (D), except that they were washed only with ice-cold 1% sodium bicarbonate solution. Any residual iodine was removed by distillation at 100—150 mm. The purified tertiary iodides can be kept for a week without appreciable decomposition if stored in Pyrex flasks in the dark.

(F) n-*Hexyl and -heptyl iodides.* The appropriate alcohols, prepared from *n*-butyl alcohol and heptaldehyde respectively, were converted into the iodides and these were purified as in section (C).

(G) β-*Iodopentane.* This was prepared from a Kahlbaum sample of the alcohol. As only a small amount of the latter was available, Norris's method (*Amer. Chem. J.*, 1907, **38**, 639) was modified, the product being distilled with successive amounts of hydriodic acid (*d* 1·7) until the iodide had constant density. It was purified as in section (D).

The criteria of purity of these iodides are listed in Table IV, and compared with values recorded in the available literature. The only compound for which we find a significant difference from the published data is cetyl iodide. In Fig. 5 we have plotted our values for the physical constants of the primary iodides against the number of carbon atoms; from C_2 to C_{16} smooth curves are obtained. Delcourt's values for cetyl iodide, particularly for its refractive index, lie off the curves, and we conclude that our constants are more correct and our standard of purity correspondingly higher.

Results.—The experimental data, the polarisations of the mixtures (P_{12}), and the partial polarisations (P_{82} for the iodides, P_{81} for the carbon tetrachloride), obtained as intercepts of the tangents to the P_{12}–c_2 curves at the axes where c_2 is zero and unity, are recorded in Table V.

The authors' thanks are due to the Chemical Society for a grant.

THE UNIVERSITY, LEEDS, 2. [*Received, February 26th*, 1942.]

Published on 01 January 1942. Downloaded by Michigan State University on 30/01/2016 02:24:26.