768. *The Polarisations and Apparent Dipole Moments of Fourteen n-Alkyl Bromides between Methyl and Octadecyl in Carbon Tetrachloride*

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Dielectric polarisations and apparent dipole moments in carbon tetrachloride are recorded for the n-alkyl bromides, $C_nH_{2n+1}Br$, in which $n = 1$—10, 12, 14, 16, and 18. From ethyl to octadecyl bromide the μ's appear nearly constant, lying between $1{\cdot}9_0$ and $1{\cdot}9_7$D (mean, $1{\cdot}9_5$D). Empirical equations, connecting the density and dielectric-constant factors of the solutions with the numbers of carbon atoms in the solute molecules, can be devised; these, in conjunction with the Le Fèvre–Vine extrapolation formula, lead to polarisations and moments close to those observed.

Carbon tetrachloride, because of its small Kerr constant, is preferable to benzene as a medium in which to measure the electric birefringence of solutes. Unfortunately, however,

Table 1

Dipole moments, μ(D), listed by Wesson [1] for n-alkyl bromides as vapours and as solutes in benzene or carbon tetrachloride *

	μ_{vap}	μ_B	μ_{CT}		μ_{vap}	μ_B	μ_{CT}
CH_3Br	1·75—1·79	1·82	1·82	C_2H_5Br ...	1·779—2·01	1·77—2·12	1·89, 1·99
C_3H_7Br ...	1·789—2·15	1·93—2·00	1·99	C_4H_9Br ...	2·15	1·88—1·98	1·95, 1·98
$C_5H_{11}Br$ ...	—	1·95, 2·02	—	$C_6H_{13}Br$ ...	—	1·97	—
$C_7H_{15}Br$ ...	2·15	1·8, 1·85	—	$C_8H_{17}Br$ ...	—	1·96	—
$C_9H_{19}Br$ ...	—	1·89	—	$C_{10}H_{21}Br$...	—	1·90	—

* Where more than two values are given in ref. 1 their range is indicated.

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[1] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948.

TABLE 2

Weight fractions, dielectric constants, densities, and apparent polarisations of n-alkyl bromides in carbon tetrachloride at 25°

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)	10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
	Ethyl bromide				*n-Propyl bromide*		
968	2·2898	1·58324	95·7	605	2·2623	1·58290	102·5
1388	2·3164	1·58266	94·6	776	2·2723	1·58219	102·3
1427	2·3194	1·58259	95·0	1074	2·2902	1·58149	102·5
1972	2·3547	1·58192	94·4	1086	2·2904	1·58122	102·1
2063	2·3577	1·58187	92·7	1519	2·3164	1·58020	101·9
2715	2·4012	1·58092	93·0	1928	2·3398	1·57929	100·9
2804	2·4042	1·58081	91·9	2002	2·3445	1·57887	101·3
2983	2·4157	1·58063	91·7	2916	2·3979	1·57652	100·2
3453	2·4490	1·57994	92·4	3701	2·4440	1·57447	99·6
4715	2·5304	1·57831	91·3	4832	2·5117	1·57159	98·9
	n-Butyl bromide				*n-Pentyl bromide*		
172	2·2360	1·58377	109·0	375	2·2449	1·58277	112·4
344	2·2449	1·58322	106·8	753	2·2630	1·58100	111·9
777	2·2676	1·58139	107·7	1088	2·2788	1·57939	111·5
1205	2·2898	1·57976	106·2	1306	2·2892	1·57849	111·2
1281	2·2939	1·57957	106·2	1640	2·3051	1·57675	111·2
1803	2·3208	1·57676	106·3	1805	2·3130	1·57599	111·2
2319	2·3481	1·57554	105·4	2363	2·3392	1·57332	110·6
3173	2·3931	1·57231	105·0	2858	2·3632	1·57116	110·1
3764	2·4249	1·56986	105·0				
	n-Hexyl bromide				*n-Heptyl bromide*		
540	2·2511	1·58142	119·1	793	2·2586	1·57956	121·2
550	2·2516	1·58141	119·0	836	2·2605	1·57926	121·5
932	2·2680	1·57926	117·6	1113	2·2716	1·57752	121·5
1255	2·2821	1·57759	117·1	1285	2·2779	1·57650	120·5
1930	2·3115	1·57383	116·5	2087	2·3106	1·57146	121·1
1983	2·3136	1·57359	116·3	2161	2·3129	1·57103	120·4
2172	2·3220	1·57251	116·4	2953	2·3450	1·56614	120·5
3175	2·3653	1·56705	115·5	4327	2·3995	1·55773	119·8
3254	2·3684	1·56659	115·3				
	n-Octyl bromide				*n-Nonyl bromide*		
812	2·2568	1·57932	124·6	510	2·2439	1·58085	128·1
1609	2·2862	1·57405	124·8	727	2·2511	1·57937	127·7
3665	2·3623	1·56034	124·8	1112	2·2638	1·57658	127·6
3857	2·3693	1·55912	124·6	1865	2·2889	1·57130	127·6
6977	2·4834	1·53928	123·3	2085	2·2961	1·56979	127·3
				3407	2·3401	1·56065	127·1
	n-Decyl bromide				*n-Dodecyl bromide*		
211	2·2334	1·58307	129·5	217	2·2333	1·58272	148·0
736	2·2495	1·57881	132·2	487	2·2408	1·58034	145·5
751	2·2500	1·57873	132·1	595	2·2437	1·57947	144·6
889	2·2545	1·57761	133·0	783	2·2496	1·57782	146·5
1188	2·2638	1·57525	133·0	936	2·2532	1·57658	144·2
1486	2·2730	1·57293	132·9	1086	2·2575	1·57578	143·2
1627	2·2768	1·57186	132·1	1492	2·2690	1·57190	144·5
1992	2·2884	1·56886	132·8	1895	2·2802	1·56847	144·4
2442	2·3020	1·56557	132·3	2203	2·2889	1·56596	144·3
3595	2·3370	1·55678	131·8				
4315	2·3595	1·55125	131·9				
	n-Tetradecyl bromide				*n-Hexadecyl bromide*		
250	2·2330	1·58248	148·5	175	2·2311	1·58297	164·4
353	2·2355	1·58149	149·7	312	2·2341	1·58159	162·8
769	2·2455	1·57764	150·3	353	2·2349	1·58115	162·4
876	2·2477	1·57717	147·4	673	2·2422	1·57818	162·6
1278	2·2577	1·57349	149·3	729	2·2430	1·57753	161·1
1329	2·2586	1·57337	147·8	918	2·2479	1·57577	163·4
	n-Octadecyl bromide			958	2·2489	1·57526	164·3
811	2·2438	1·57670	172·1	1225	2·2549	1·57280	163·8
1012	2·2479	1·57483	171·1	1600	2·2632	1·56920	163·4
1128	2·2504	1·57379	171·4	1632	2·2632	1·56925	161·3
1665	2·2619	1·56857	172·6	3940	2·3152	1·54747	162·6
1737	2·2632	1·56788	172·1	4964	2·3389	1·53804	163·3
2443	2·2776	1·56120	171·9				
2539	2·2797	1·56040	171·8				
3450	2·2979	1·55207	171·1				

the majority of the dielectic polarisation data in the literature have been obtained with benzene as solvent. This is true of the n-alkyl bromides, as Table 1 shows, for which no determinations in carbon tetrachloride are available above n-butyl bromide. As a preliminary to the work of the following Paper, therefore, the observations and other details, summarised in Tables 2 and 3, are placed on record.

EXPERIMENTAL

Solutes and Solvent.—The alkyl bromides were prepared from their corresponding alcohols, constant-boiling hydrobromic acid being used for the lower members, and phosphorus with bromine for those above n-hexanol, as described by Vogel.[2] Carbon tetrachloride, as solvent, was a sulphur-free commercial product, dried and purified as in earlier work.[3]

Apparatus, Methods, Observations, and Calculations.—Dielectric constants, ε, were measured in the circuit noted in ref. 4; otherwise procedures followed those outlined by Le Fèvre.[5] Table 2 lists dielectric constants and densities d_4^{25}, for solutions containing weight fractions w_2 of the bromides in carbon tetrachloride. The apparent total polarisation P_2 of the solute at each particular w_2 value has been calculated by the mixture rule of Sugden,[6] which involves the specific polarisations p_{12} and p_1 of solution and solvent: $P_2 = M_2p_2 = M_2[p_1 + (p_{12} - p_1)/w_2]$. Extrapolations to infinite dilution have been effected using the equation of Le Fèvre and Vine:[7] ${}_{\infty}P_2 = M_2[p_1(1 - \beta) + C\alpha\varepsilon_1]$, where $\alpha\varepsilon_1 = \Sigma(\varepsilon_{12} - \varepsilon_1)/\Sigma w_2$ and $\beta = (1/d_1)/\Sigma(d_{12} - d_1)/\Sigma w_2$, and suffixes 12, 1, and 2 indicate, respectively, solution, solvent, and solute. Values of β and $\alpha\varepsilon_1$, drawn from the observations in Table 2, are given in Table 3 together with their corresponding ${}_{\infty}P_2$'s. Apparent moments, μ, of the bromides are calculated in D units at 25° as $0{\cdot}2211\,({}_{\infty}P_2 - R_{\text{D}})^{\frac{1}{2}}$, *i.e.*, the distortion polarisations are taken as equal to the molecular refractions R_{D}. The following constants are adopted for carbon tetrachloride: $\varepsilon_{25} = 2{\cdot}2270$; $p_1 = 0{\cdot}18319$; $d_4^{25} = 1{\cdot}58454$; $C = 0{\cdot}10596$.

TABLE 3

Dielectric constant and density coefficients, polarisations, and apparent dipole moments calculated from observations in Table 2

Solute	$\alpha\varepsilon_1$	$-\beta$	${}_{\infty}P_2$ (c.c.)	R_{D} (c.c.)	μ (D)
CH_3Br	5·72 [a]	−0·051 [a]	75·83	14·42 [b]	1·73
C_2H_5Br	6·44	0·084	95·60	19·07 [c]	1·93
n-C_3H_7Br	5·87	0·175	102·98	23·72 [c]	1·97
n-C_4H_9Br	5·23	0·249	107·30	28·26 [c]	1·96
n-$C_5H_{11}Br$	4·76	0·297	112·11	32·89 [c]	1·96
n-$C_6H_{13}Br$	4·37	0·351	117·29	37·68 [c]	1·97
n-$C_7H_{15}Br$	3·99	0·394	121·47	42·26 [c]	1·97
n-$C_8H_{17}Br$	3·68	0·413	125·92	46·90 [c]	1·96
n-$C_9H_{19}Br$	3·33	0·448	128·05	51·49 [c]	1·94
n-$C_{10}H_{21}Br$	3·07	0·489	132·35	56·34 [c]	1·93
n-$C_{12}H_{25}Br$	2·82	0·533	143·57	65·52 [c]	1·95
n-$C_{14}H_{29}Br$	2·39	0·541	148·46	74·71 [d]	1·90
n-$C_{16}H_{33}Br$	2·26	0·597	162·43	83·97 [d]	1·96
n-$C_{18}H_{37}Br$	2·07	0·601	171·01	93·41 [b]	1·95

[a] From Le Fèvre and Le Fèvre.[8] Calc. from bond refractivities (cf. ref. 9). [c] Cf. Vogel.[10]
[d] Cf. Vogel.[11]

DISCUSSION

Dipole Moments of n-Bromides.—The increase of 0·2D between μCH_3Br and μC_2H_5Br is almost identical with that between the corresponding values for μ_{gas} reported by Groves

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[2] A. I. Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1956, pp. 277—283.

[3] R. J. W. Le Fèvre and A. J. Williams, *J.*, 1960, 108.

[4] A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J.*, 1956, 1405.

[5] R. J. W. Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, ch. 2.

[6] S. Sugden, *Trans. Faraday Soc.*, 1933, **30**, 720.

[7] R. J. W. Le Fèvre and H. Vine, *J.*, 1937, 1805.

[8] C. G. Fèvre and R. J. W. Le Fèvre, *J.*, 1954, 1577.

[9] A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

[10] A. I. Vogel, *J.*, 1943, 636.

[11] A. I. Vogel, *J.*, 1948, 645.

and Sugden,[12] although the polarities as gases are slightly higher. Considering the errors of experiment, and uncertainties introduced by the assumption that ${}_{\mathrm{D}}P = R_{\mathrm{D}}$, the moments of members higher than methyl must be viewed as nearly constant, lying between $1{\cdot}9_0$ and $1{\cdot}9_7$D (mean, $1{\cdot}9_5$D). Smyth,[13] while exploring the applicability of the Debye, Onsager, and Kirkwood equations to ε, d, and n data for the pure liquid n-bromides from C_2 to C_{16}, noted a similar situation for the moments obtained, those produced by the Onsager treatment differing from 1·81D by only ±0·03D, and those *via* Kirkwood's equation from $1{\cdot}92_5$D by $\pm 0{\cdot}09_5$D. The lowest (solution) moment shown in Table 3 is that for n-tetradecyl bromide; likewise, among the (liquid) n-alkyl bromides discussed by Smyth,[13] this substance also shows the least polarity.

Empirical Relations.—By plotting the density and dielectric constant factors (βd_1 and $\alpha\varepsilon_1$, derived from the data of Table 2) *versus* the number n of carbon atoms per solute molecule, nearly smooth curves are obtained. Fitting by least squares gives the following empirical equations:

$$-\beta d_1 = 0{\cdot}138 + 0{\cdot}888 \log n \text{ (range } n = 2 \text{ to } 18)$$

$$\alpha\varepsilon_1 = 6{\cdot}44 - 0{\cdot}6052\mathrm{y} + 0{\cdot}0240\mathrm{y}^2 \text{ (range } n = 2 \text{ to } 10,\ \mathrm{y} = n - 2)$$

$$\alpha\varepsilon_1 = 3{\cdot}68 - 0{\cdot}2919\mathrm{z} + 0{\cdot}0135\mathrm{z}^2 \text{ (range } n = 8 \text{ to } 18;\ \mathrm{z} = n - 8).$$

Table 4 compares the moments forecast when $\alpha\varepsilon_1$ and β are calculated by these equations, and the P_2's so produced used instead of the ${}_{\infty}P_2$'s listed in Table 3.

TABLE 4

Comparison of dipole moments from observed data with those from empirical equations for $\alpha\varepsilon_1$ and β

n	μ_{obs} (D)	μ_{calc} (D)	n	μ_{obs} (D)	μ_{calc} (D)	n	μ_{obs} (D)	μ_{calc} (D)
2	1·93	1·94	7	1·97	1·96	12	1·95	1·92
3	1·97	1·96	8	1·96	1·95	14	1·90	1·91
4	1·96	1·97	9	1·94	1·94	16	1·96	1·93
5	1·96	1·98	10	1·93	1·93	18	1·95	1·98
6	1·97	1·97						

Maximum disagreement is seen to be ±0·03D. The moment of n-$C_{14}H_{29}Br$ is still the lowest in the series.

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[12] L. G. Groves and S. Sugden, *J.*, 1937, 158.

[13] C. P. Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, Toronto, London, 1955, pp. 33 and 268.