21. *The Dielectric Polarisations and Apparent Dipole Moments of Alcohols as Solutes.*

By R. J. W. Le Fèvre and A. J. Williams.

Fourteen normal alcohols from methyl to octadecyl, together with cyclopentyl and cyclohexyl, have been studied as solutes in carbon tetrachloride at 25°, and their apparent partial polarisations calculated by mixture formulæ. The first six normal alcohols have also been similarly treated in benzene. Concentrations at which P_2 *versus* w_2 curves exhibit their initial minima are noted, and extrapolations to infinite dilution carried out only with solutions having lower values of w_2. The ${}_{\infty}P_2$ values so obtained correspond to dipole moments which, in nearly all cases, are slightly higher than those given in earlier literature. The factors $(\alpha\varepsilon_1)_{w_2=0}$ and $(\beta d_1)_{w_2=0}$ are found to be related by quadratic or cubic expressions to the number of carbon atoms in the alkyl chain, and various empirical equations connecting these quantities are quoted; as would be expected, therefore, ${}_{\infty}P_2$ also shows a smooth dependence on the carbon-atom content.

In connection with work [1] on the molar Kerr constants of alcohols as solutes in carbon tetrachloride, information was needed on the concentration-dependence of the dielectric constants and densities of such solutions. In particular, values were required of the factors $\alpha\varepsilon_1$ and β for each alcohol at infinite dilution. (These relate to dielectric constants and densities respectively, cf. ref. 2, p. 4045; ref. 3, pp. 55—58; ref. 4, p. 283. Definitions of other symbols used in this paper are also given in refs 2—4. Concentrations are expressed as weight fractions w_2 of solutes in solutions.)

The literature proved unhelpful. Refs. 5—17, it is true, included data obtained with carbon tetrachloride as solvent, but, first, they dealt most frequently with methyl and ethyl alcohols and only occasionally with higher normal alcohols, and secondly, they reported apparent polarisations over different concentration regions. It is well established [18-20] that the polarisation–concentration graphs for several alcohols exhibit

---

[1] Le Fèvre, Le Fèvre, and Williams, *J.*, 1960, 123.
[2] Le Fèvre and Le Fèvre, *J.*, 1953, 4041.
[3] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. II.
[4] Le Fèvre and Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.
[5] Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2408.
[6] Peterson and Rodebush, *J. Phys. Chem.*, 1928, **32**, 709.
[7] Stranathan, *Phys. Rev.*, 1928, **31**, 156, 653.
[8] Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312, 3330.
[9] Errera and Sherrill, *J. Amer. Chem. Soc.*, 1930, **52**, 1993.
[10] Mortier, *Bull. Acad. roy. Belg.*, 1935, **21**, 594.
[11] Mortier and Müller, *Physikal. Z.*, 1935, **36**, 371.
[12] Hoecker, *J. Chem. Phys.*, 1936, **4**, 431; 1937, **5**, 372.
[13] Goss, *J.*, 1940, 888.
[14] Rodebush, Eddy, and Eubank, *J. Chem. Phys.*, 1940, **8**, 889.
[15] Dunken, Judenberg, and Wolf, *Z. phys. Chem.*, 1941, *B*, **49**, 43.
[16] Maryott, *J. Amer. Chem. Soc.*, 1941, **63**, 3079.
[17] Schupp, *Z. Elektrochem.*, 1949, **53**, 12.
[18] Davies, *Ann. Reports*, 1946, **43**, 26.
[19] Smyth, " Dielectric Behaviour and Structure," McGraw-Hill, New York, Toronto, London, 1955, p. 80.
[20] Smith, " Electric Dipole Moments," Butterworths, London, 1955, p. 303.

TABLE 1. *Weight fractions, dielectric constants, densities, and apparent polarisations of n-alcohols in carbon tetrachloride at 25°.*

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
Methyl alcohol			
96	2·2456	1·58277	77·3
115	2·2477	1·58241	73·9
183	2·2583	1·58138	70·4
207	2·2620	1·58095	69·4
267	2·2714	1·57994	68·2
375	2·2889	1·57852	67·3
404	2·2895	1·57775	64·1
453	2·2971	1·57713	63·9
674	2·3256	1·57325	61·1
830	2·3502	1·57107	61·3
974	2·3685	1·56868	60·2
984	2·3704	1·56852	60·4
1143	2·3949	1·56608	60·5
1434	2·4456	1·56144	61·9
1658	2·4859	1·55780	62·6
2191	2·5958	1·54984	65·7
2524	2·6770	1·54425	68·1
3017	2·8047	1·53670	70·9
3877	3·0603	1·52399	75·3
4270	3·1957	1·51793	77·4
Ethyl alcohol			
45	2·2329	1·58379	81·3
72	2·2353	1·58320	79·7
95	2·2378	1·58275	78·6
101	2·2393	1·58266	77·6
180	2·2486	1·58126	76·6
194	2·2501	1·58135	75·2
214	2·2510	1·58083	73·6
286	2·2608	1·57935	75·7
386	2·2692	1·57793	70·7
390	2·2705	1·57785	72·4
420	2·2747	1·57752	72·5
574	2·2902	1·57485	70·8
660	2·2959	1·57356	67·8
789	2·3077	1·57142	66·8
1088	2·3355	1·56649	65·4
1479	2·3720	1·56039	64·3
1614	2·3859	1·55816	64·4
2339	2·4624	1·54674	64·9
2883	2·5276	1·53841	66·2
3449	2·6137	1·52890	69·3
5090	2·8539	1·50545	72·3
Propyl alcohol			
87	2·2353	1·58302	84·4
113	2·2370	1·58269	79·3
146	2·2404	1·58204	81·0
214	2·2459	1·58092	79·0
323	2·2550	1·57922	77·6
355	2·2576	1·57865	77·3
532	2·2711	1·57583	75·0
735	2·2860	1·57256	73·2
773	2·2880	1·57191	72·4
1106	2·3101	1·56665	69·9
1195	2·3153	1·56532	68·9
1518	2·3327	1·56046	66·1
1773	2·3513	1·55654	66·2
2223	2·3816	1·54977	65·8
2865	2·4261	1·54024	65·5
3395	2·4505	1·53227	63·3
3899	2·5075	1·52483	66·7
4948	2·6004	1·50980	68·4
Butyl alcohol			
52	2·2310	1·58360	90·1
60	2·2318	1·58351	91·5
111	2·2351	1·58264	85·5
113	2·2358	1·58258	90·5
172	2·2398	1·58160	87·1
223	2·2429	1·58072	85·0
251	2·2451	1·58047	84·3
390	2·2548	1·57838	83·0
453	2·2590	1·57738	82·6
471	2·2601	1·57700	82·3
631	2·2700	1·57458	80·4
954	2·2881	1·56952	77·3
1197	2·3009	1·56576	75·4
1539	2·3181	1·56064	73·2
2203	2·3512	1·55060	71·1
3124	2·4017	1·53709	69·5
3640	2·4309	1·52914	69·6
5142	2·5209	1·50844	70·0
Pentyl alcohol			
339	2·2470	1·57937	86·9
398	2·2506	1·57839	87·5
476	2·2548	1·57716	86·6
734	2·2683	1·57326	84·4
957	2·2794	1·56981	82·9
1269	2·2935	1·56517	80·7
1811	2·3162	1·55721	77·6
1917	2·3204	1·55554	77·2
2179	2·3307	1·55183	76·1
2268	2·3344	1·55042	75·9
2789	2·3551	1·54285	74·6
3474	2·3832	1·53280	73·7
4316	2·4164	1·52149	72·5
5625	2·4721	1·50346	72·2
6429	2·5085	1·49264	72·3
Hexyl alcohol			
227	2·2391	1·58107	94·2
385	2·2476	1·57865	94·5
586	2·2575	1·57570	93·1
907	2·2722	1·57078	90·7
1236	2·2857	1·56592	88·0
1741	2·3053	1·55840	85·3
1782	2·3055	1·55782	84·4
2814	2·3417	1·54297	80·8
3209	2·3566	1·53733	80·4
4048	2·3877	1·52347	80·3
4577	2·4023	1·51749	78·4
Heptyl alcohol			
180	2·2355	1·58179	101·3
270	2·2398	1·58015	101·2
353	2·2438	1·57907	100·7
440	2·2479	1·57779	100·2
469	2·2492	1·57728	100·3
470	2·2495	1·57675	99·4
477	2·2495	1·57737	99·6
706	2·2599	1·57376	99·4
766	2·2624	1·57306	98·6
950	2·2699	1·56998	97·7
1229	2·2807	1·56597	95·7
1429	2·2881	1·56272	94·7
1694	2·2963	1·55926	92·1
2225	2·3140	1·55150	89·9
2633	2·3270	1·54556	88·5
Octyl alcohol			
162	2·2334	1·58195	102·6
330	2·2402	1·57961	101·7
336	2·2409	1·57937	104·0
589	2·2509	1·57565	102·7
625	2·2524	1·57502	103·1
669	2·2539	1·57451	102·1
734	2·2561	1·57340	101·6
737	2·2567	1·57438	102·5
882	2·2625	1·57135	102·2
1086	2·2682	1·56830	98·9
1256	2·2746	1·56571	99·5
1627	2·2856	1·56041	96·3
1764	2·2898	1·55826	95·9
1977	2·2958	1·55543	94·6
Nonyl alcohol			
176	2·2338	1·58186	111·8
379	2·2410	1·57882	108·3
392	2·2415	1·57864	108·2
558	2·2478	1·57611	108·9
694	2·2525	1·57412	107·9
862	2·2583	1·57171	107·1
896	2·2595	1·57108	107·3
1015	2·2637	1·56935	106·9
1287	2·2718	1·56536	104·7
1499	2·2778	1·56232	103·4
1617	2·2812	1·56053	103·0
1996	2·2911	1·55525	100·6
2447	2·3027	1·54889	98·8
2590	2·3063	1·54664	98·5
2972	2·3143	1·54151	96·5
3198	2·3193	1·53809	95·8
3859	2·3346	1·52924	94·3
4186	2·3440	1·52474	94·4
Decyl alcohol			
82	2·2303	1·58332	123·5
87	2·2300	1·58307	119·9
100	2·2309	1·58312	124·9
132	2·2319	1·58256	118·7
166	2·2334	1·58213	120·6
201	2·2344	1·58157	118·2
225	2·2352	1·58107	119·2
307	2·2380	1·57999	117·3
377	2·2402	1·57870	116·4
433	2·2424	1·57804	116·4
530	2·2452	1·57669	115·6
692	2·2511	1·57419	115·2
1199	2·2659	1·56621	112·2
1484	2·2736	1·56251	109·4
2630	2·3017	1·54596	104·5
2774	2·3058	1·54391	104·6
4188	2·3354	1·52427	100·4
4872	2·3476	1·51525	98·5
5968	2·3710	1·50047	97·5
Dodecyl alcohol			
125	2·2307	1·58277	123·5
243	2·2340	1·58098	124·8
662	2·2446	1·57482	118·5
869	2·2511	1·57186	120·8
964	2·2525	1·57048	118·2
1168	2·2588	1·56750	119·7
1288	2·2602	1·56575	117·0
1644	2·2698	1·56067	117·6
1701	2·2726	1·55969	119·4

TABLE 1. (*Continued.*)

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
	Dodecyl alcohol		
1720	2·2703	1·55964	115·8
2133	2·2813	1·55346	116·8
2754	2·2913	1·54484	112·6
2959	2·2938	1·54227	110·8
3951	2·3127	1·52789	109·7
4907	2·3276	1·51517	107·3
	Tetradecyl alcohol		
255	2·2330	1·58078	130·3
370	2·2355	1·57913	130·0
470	2·2378	1·57762	128·2
551	2·2397	1·57646	128·4
728	2·2441	1·57383	129·7
752	2·2444	1·57348	129·0
779	2·2446	1·57322	127·6
863	2·2472	1·57188	129·9
1054	2·2511	1·56916	128·0
1092	2·2524	1·56866	128·8
1164	2·2534	1·56758	127·5
1232	2·2552	1·56663	128·0
1391	2·2589	1·56444	127·9
1938	2·2695	1·55672	125·7
2142	2·2734	1·55314	126·0
	Hexadecyl alcohol		
438	2·2358	1·57838	137·5
825	2·2440	1·57286	137·9
957	2·2467	1·57105	137·4
	Hexadecyl alcohol		
1208	2·2517	1·56760	137·4
1492	2·2577	1·56369	137·2
1762	2·2630	1·55989	137·2
1806	2·2632	1·55908	136·5
2030	2·2680	1·55607	136·9
2580	2·2774	1·54812	135·7
2846	2·2825	1·54519	134·9
	Octadecyl alcohol		
411	2·2349	1·57857	150·3
476	2·2366	1·57766	153·1
760	2·2418	1·57362	151·0
871	2·2438	1·57193	150·8
1086	2·2477	1·56878	150·5
1110	2·2485	1·56846	151·1
1459	2·2546	1·56369	149·5
1521	2·2556	1·56265	149·5
1612	2·2571	1·56145	148·9
1849	2·2615	1·55809	149·0
2692	2·2742	1·54630	146·0
	Cyclopentyl alcohol		
88	2·2325	1·58333	88·0
90	2·2330	1·58347	88·2
202	2·2400	1·58223	86·4
221	2·2406	1·58204	87·4
309	2·2466	1·58100	85·3
466	2·2564	1·57928	84·4
	Cyclopentyl alcohol		
704	2·2699	1·57654	82·5
768	2·2734	1·57594	81·9
1032	2·2863	1·57302	79·1
1216	2·2947	1·57107	77·4
1337	2·3000	1·56965	76·5
2069	2·3318	1·56187	72·6
2336	2·3433	1·55915	71·7
3379	2·3825	1·54839	68·1
3668	2·3965	1·54514	68·3
	Cyclohexyl alcohol		
72	2·2317	1·58374	100·5
187	2·2389	1·58241	98·8
316	2·2468	1·58104	97·7
435	2·2543	1·57973	97·8
531	2·2600	1·57859	97·2
713	2·2714	1·57694	96·5
831	2·2769	1·57534	94·5
1092	2·2907	1·57247	92·7
1177	2·2961	1·57150	93·1
1805	2·3267	1·56469	89·3
1968	2·3328	1·56316	87·6
2418	2·3555	1·55887	86·5
2746	2·3688	1·55543	84·9
3054	2·3832	1·55244	84·2
4662	2·4557	1·53587	81·8

maxima or minima through the development of complexes of greater or less polarity as the concentration is progressively increased. Since the molar Kerr constants desired in ref. 1 were to be those of unassociated single molecules, it was essential that observations, used for the calculations of values of $_\infty({}_\mathrm{m}K_2)$ should only be made *between* $w_2 = 0$ and those w_2's at which the first marked curvature changes occur in the polarisation–concentration plots. The initial motive for the present work was therefore to ascertain by experiment suitable w_2 ranges for each of sixteen alcohols named in the Tables below.

EXPERIMENTAL

Materials.—Carbon tetrachloride of the best commercial grade was dried ($CaCl_2$), fractionated, stored over calcium chloride, and filtered immediately before use. Thiophen-free benzene was partially frozen, and the remelted solid dried and kept with sodium wire. The solutes were redistilled or recrystallised as necessary and had the b. p.s or m. p.s recorded for pure samples in Beilstein's " Handbuch." Gifts of n-octyl and n-tetradecyl alcohols were received from Dr. R. J. Meakins (National Standards Laboratories, C.S.I.R.O.) and are gratefully acknowledged.

Methods and Apparatus.—Measurements and calculations followed the directions given by Le Fèvre,[3] except that the circuit used for dielectric-capacity comparison was that described in ref. 21. All work was at 25°.

Observations.—Table 1 lists dielectric constants ε^{25}, densities d_4^{25}, and apparent total polarisations P_2 of solutions containing weight fractions w_2 of alcohols in carbon tetrachloride. Table 2 gives parallel data secured for a few alcohols with benzene as solvent. The P_2 values also shown have been calculated by Sugden's mixture rule,[22] by use of specific polarisations p_{12} and p_1 of solutions and solvent, in conjunction with the molecular weights M_2 of the *monomers* concerned in each case:

$$P_2 = M_2p_2 = M_2[p_1 + (p_{12} - p_1)/w_2]$$

---

[21] Buckingham, Chau, Freeman, Le Fèvre, Narayana, Rao, and Tardif, *J.*, 1956, 1405.

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

TABLE 2. *Weight fractions, dielectric constants, densities, and apparent polarisations of n-alcohols in benzene at* 25°.

Methyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
166	2·2904	0·87359	77·0
244	2·2982	0·87350	75·4
397	2·3144	0·87329	75·7
509	2·3264	0·87318	75·4
685	2·3444	0·87309	74·4
855	2·3628	0·87284	74·7
903	2·3683	0·87281	74·9
1228	2·4030	0·87250	74·5
1372	2·4216	0·87229	75·7
1512	2·4374	0·87224	75·6
1527	2·4383	0·87224	75·3
1608	2·4477	0·87215	75·2
1640	2·4518	0·87214	75·6
2161	2·5149	0·87164	76·3
2324	2·5376	0·87143	77·1
3167	2·6445	0·87091	77·4
3636	2·7140	0·87055	78·6
4986	2·9223	0·86912	80·6

Ethyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
158	2·2835	0·87361	77·1
206	2·2861	0·87359	74·2
224	2·2889	0·87352	80·0
271	2·2906	0·87349	75·0
308	2·2934	0·87347	76·0
428	2·3016	0·87335	76·1
530	2·3078	0·87316	75·1
542	2·3091	0·87313	75·8
586	2·3121	0·87308	75·8
736	2·3231	0·87311	76·1
739	2·3225	0·87291	75·8
766	2·3250	0·87290	76·5
787	2·3263	0·87287	76·3
1047	2·3447	0·87257	76·6
1102	2·3494	0·87267	76·8
1131	2·3510	0·87246	77·0
1138	2·3518	0·87255	77·6
1166	2·3544	0·87246	77·5
1389	2·3706	0·87219	77·6
1626	2·3868	0·87191	77·2
2027	2·4177	0·87149	77·9
2190	2·4270	0·87137	76·8
3117	2·5019	0·87041	78·4
4101	2·5831	0·86945	79·1
5416	2·7010	0·86813	80·3

Propyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
156	2·2804	0·87368	78·9
331	2·2892	0·87347	79·5
401	2·2922	0·87345	77·8
474	2·2959	0·87333	78·3
574	2·3014	0·87311	79·8
675	2·3060	0·87308	78·7
793	2·3124	0·87297	79·3
1006	2·3243	0·87272	80·5
1053	2·3258	0·87270	79·8
1111	2·3300	0·87263	80·8
1221	2·3344	0·87254	80·2
1558	2·3543	0·87217	81·3
1701	2·3587	0·87205	79·2
1767	2·3656	0·87197	81·3
2411	2·4013	0·87134	81·7
2896	2·4241	0·87102	80·1
3090	2·4361	0·87075	80·7
3932	2·4829	0·86998	80·7
4021	2·4888	0·86993	80·9
4239	2·5007	0·86974	80·8

Butyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
289	2·2842	0·87357	82·4
353	2·2863	0·87349	81·8
627	2·2979	0·87327	83·7
635	2·2980	0·87316	83·8
762	2·3028	0·87307	83·0
899	2·3095	0·87293	84·9
914	2·3094	0·87293	83·8
987	2·3123	0·87285	83·8
1293	2·3252	0·87260	84·1
1306	2·3262	0·87255	84·7
1467	2·3350	0·87249	86·4
1523	2·3354	0·87260	84·1
1794	2·3474	0·87208	85·3
1800	2·3475	0·87214	85·1
2066	2·3593	0·87194	85·4
2221	2·3644	0·87169	84·6
2837	2·3920	0·87121	85·2
3251	2·4089	0·87082	84·8
3339	2·4144	0·87088	85·3
3802	2·4334	0·87037	84·9

Pentyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
297	2·2820	0·87359	84·9
467	2·2875	0·87346	85·0
722	2·2951	0·87327	84·1
836	2·2994	0·87316	85·5
1335	2·3155	0·87272	85·7
1752	2·3293	0·87240	85·8
2057	2·3403	0·87212	86·7
2283	2·3477	0·87197	86·5
2856	2·3685	0·87144	87·6
3581	2·3951	0·87093	88·1

Hexyl alcohol

10^5w_2	ε^{25}	d_4^{25}	P_2 (c.c.)
309	2·2804	0·87358	86·3
525	2·2869	0·87344	89·9
722	2·2919	0·87323	89·2
931	2·2980	0·87309	88·3
990	2·3001	0·87308	90·9
1176	2·3048	0·87283	90·4
1359	2·3111	0·87272	92·0
1755	2·3211	0·87240	90·6
2028	2·3301	0·87218	91·9
2139	2·3349	0·87206	93·4
2434	2·3425	0·87180	92·6
2468	2·3452	0·87177	93·8
2707	2·3509	0·87166	92·8
3079	2·3620	0·87136	92·8

TABLE 3. *Weight-fraction range used for computation of* $\Delta\varepsilon$ *and* Δd *increments for normal alcohols in carbon tetrachloride at* 25°.

Alcohol	w_2 range	Alcohol	w_2 range	Alcohol	w_2 range
Methyl	0—0·00674	Heptyl	0—0·02633	Tetradecyl	0—0·02142
Ethyl	0—0·00789	Octyl	0—0·01977	Hexadecyl	0—0·02846
Propyl	0—0·01518	Nonyl	0—0·02972	Octadecyl	0—0·02692
Butyl	0—0·01539	Decyl	0—0·02630	Cyclopentyl	0—0·02069
Pentyl	0—0·02789	Dodecyl	0—0·02959	Cyclohexyl.........	0—0·01968
Hexyl	0—0·01782				

Dielectric constants and densities for the pure solvents, *i.e.*, when $w_2 = 0$, are: for carbon tetrachloride, $\varepsilon_1^{25} = 2{\cdot}2270$, $d_4^{25} = 1{\cdot}58454$; for benzene, $\varepsilon_1^{25} = 2{\cdot}2725$, $d_4^{25} = 0{\cdot}87378$.

Tables 3, 4, and 5 deal with the calculation of P_2 at infinite dilution in carbon tetrachloride. Table 4 gives equations, fitted by least-squares, of the type recommended by Harris, Le Fèvre, and Sullivan [23] for $\Delta\varepsilon$ (or Δd) in terms of w_2; Table 3 reports the limits of concentration beyond which, in individual instances, these fits have not been carried. In Table 5 μ_R and μ_D are the moments found by using R_D or $1{\cdot}05R_D$ respectively as distortion polarisations.

DISCUSSION

Variation of Polarisation of Solute with Concentration.—The Figure shows the P_2 values from Table 1 plotted against their appropriate weight fractions. Only for the first four

---

[23] Harris, Le Fèvre, and Sullivan, *J.*, 1953, 1622.

TABLE 4. *Equations for dielectric constant and density increments in carbon tetrachloride at 25°.*

Alcohol *	$\Delta\varepsilon$	Δd	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta d_1)_{w_2=0}$
Methyl	$17\cdot842w_2 - 491w_2^2$	$1\cdot737w_2 - 11\cdot1w_2^2$	$17\cdot8_4 \pm 0\cdot2_3$	$1\cdot74 \pm 0\cdot02$
Ethyl	$12\cdot541w_2 - 297w_2^2$	$1\cdot822w_2 - 20\cdot5w_2^2$	$12\cdot54 \pm 0\cdot08$	$1\cdot82 \pm 0\cdot02$
Propyl	$8\cdot998w_2 - 134w_2^2$	$1\cdot681w_2 - 6\cdot3w_2^2$	$9\cdot00 \pm 0\cdot02$	$1\cdot681 \pm 0\cdot003$
Butyl	$7\cdot464w_2 - 103w_2^2$	$1\cdot625w_2 - 4\cdot8w_2^2$	$7\cdot46 \pm 0\cdot04$	$1\cdot625 \pm 0\cdot007$
Pentyl	$6\cdot098w_2 - 64\cdot6w_2^2$	$1\cdot557w_2 - 2\cdot4w_2^2$	$6\cdot10 \pm 0\cdot02$	$1\cdot557 \pm 0\cdot003$
Hexyl	$5\cdot547w_2 - 62\cdot5w_2^2$	$1\cdot527w_2 - 1\cdot5w_2^2$	$5\cdot55 \pm 0\cdot03$	$1\cdot527 \pm 0\cdot002$
Heptyl	$4\cdot898w_2 - 43\cdot1w_2^2$	$1\cdot554w_2 - 2\cdot7w_2^2$	$4\cdot90 \pm 0\cdot02$	$1\cdot554 \pm 0\cdot003$
Octyl	$4\cdot279w_2 - 40\cdot7w_2^2$	$1\cdot527w_2 - 2\cdot4w_2^2$	$4\cdot28 \pm 0\cdot02$	$1\cdot527 \pm 0\cdot005$
Nonyl	$3\cdot885w_2 - 32\cdot1w_2^2$	$1\cdot520w_2 - 2\cdot4w_2^2$	$3\cdot885 \pm 0\cdot008$	$1\cdot520 \pm 0\cdot001$
Decyl	$3\cdot638w_2 - 30\cdot6w_2^2$	$1\cdot521w_2 - 3\cdot4w_2^2$	$3\cdot638 \pm 0\cdot008$	$1\cdot521 \pm 0\cdot004$
Dodecyl	$2\cdot966w_2 - 22\cdot9w_2^2$	$1\cdot481w_2 - 1\cdot8w_2^2$	$2\cdot97 \pm 0\cdot01$	$1\cdot481 \pm 0\cdot004$
Tetradecyl	$2\cdot415w_2 - 11\cdot3w_2^2$	$1\cdot464w_2 - 0\cdot6w_2^2$	$2\cdot42 \pm 0\cdot02$	$1\cdot464 \pm 0\cdot007$
Hexadecyl	$2\cdot136w_2 - 6\cdot6w_2^2$	$1\cdot420w_2 - 0\cdot9w_2^2$	$2\cdot14 \pm 0\cdot02$	$1\cdot42 \pm 0\cdot01$
Octadecyl	$2\cdot033w_2 - 10\cdot2w_2^2$	$1\cdot457w_2 - 1\cdot4w_2^2$	$2\cdot03 \pm 0\cdot02$	$1\cdot457 \pm 0\cdot003$
Cyclopentyl	$6\cdot482w_2 - 69\cdot8w_2^2$	$1\cdot143w_2 - 2\cdot3w_2^2$	$6\cdot48 \pm 0\cdot03$	$1\cdot143 \pm 0\cdot003$
Cyclohexyl	$6\cdot556w_2 - 58\cdot9w_2^2$	$1\cdot113w_2 - 1\cdot1w_2^2$	$6\cdot56 \pm 0\cdot04_5$	$1\cdot113 \pm 0\cdot006$

* Normal isomers, except the last two.

TABLE 5. *Polarisations at infinite dilution in carbon tetrachloride at 25°, and apparent dipole moments.*

Solute alcohol	${}_\infty P_2$ (c.c.)	R_D (c.c.) *	μ_R (D)	μ_D (D)
Methyl	$72\cdot8_7$	8·22	$1\cdot7_8$	$1\cdot7_7$
Ethyl	$79\cdot3_6$	12·90	$1\cdot8_0$	$1\cdot7_9$
Propyl	$79\cdot9_9$	17·54	$1\cdot7_5$	$1\cdot7_{35}$
Butyl	$86\cdot0_9$	22·14	$1\cdot7_7$	$1\cdot7_5$
Pentyl	$89\cdot0_2$	26·84	$1\cdot7_4$	$1\cdot7_{25}$
Hexyl	$96\cdot8_8$	31·39	$1\cdot7_9$	$1\cdot7_7$
Heptyl	102·5	36·04	$1\cdot8_0$	$1\cdot7_8$
Octyl	105·9	(40·73)	$1\cdot7_{85}$	$1\cdot7_6$
Nonyl	111·2	45·34	$1\cdot7_9$	$1\cdot7_6$
Decyl	117·9	50·00	$1\cdot8_2$	$1\cdot7_9$
Dodecyl	124·6	(59·32)	$1\cdot7_9$	$1\cdot7_3$
Tetradecyl	130·6	(68·61)	$1\cdot7_4$	$1\cdot6_9$
Hexadecyl	139·2	(77·90)	$1\cdot7_3$	$1\cdot6_{75}$
Octadecyl	153·3	(87·20)	$1\cdot8_0$	$1\cdot7_4$
*Cyclo*pentyl	86·29	24·57 [a]	$1\cdot7_4$	$1\cdot7_2$
Cyclohexyl	101·3	29·16 [a]	$1\cdot8_8$	$1\cdot8_6$

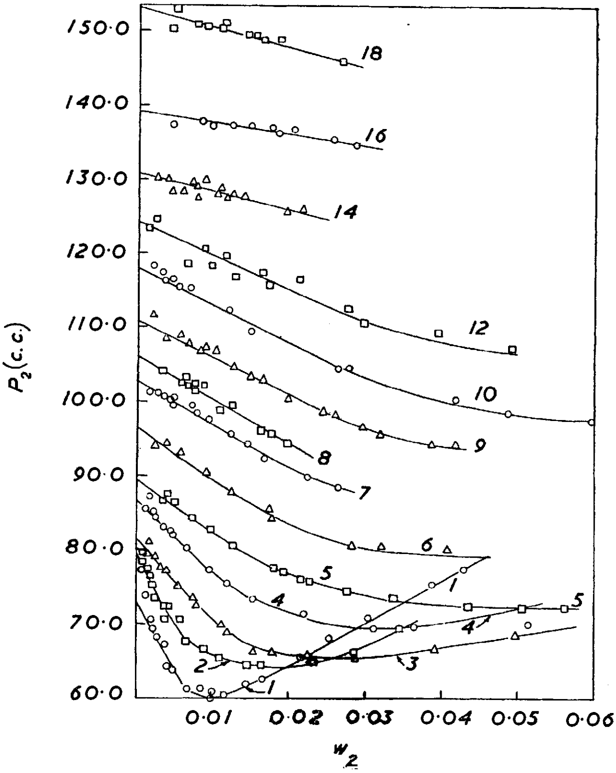
* From Vogel, *J.*, 1948, 1814, except values in parentheses which are calculated from group refractivities listed by Vogel in *J.*, 1948, 1833.

[a] From Vogel, *J.*, 1938, 1323.

TABLE 6. *Equations for dielectric constant and density increments for the n-alcohols in benzene at 25°, together with polarisations at infinite dilution and apparent dipole moments.*

Solute alcohol	$\Delta\varepsilon$	Δd	$(\alpha\varepsilon_1)_{w_2=0}$	$-(\beta d_1)_{w_2=0}$	${}_\infty P_2$ (c.c.)	μ_R (D)
Methyl	$9\cdot910w_2 + 62\cdot0w_2^2$	$0\cdot1083w_2 - 0\cdot28w_2^2$	$9\cdot91 \pm 0\cdot01$	$0\cdot108 \pm 0\cdot008$	71·99	1·76
Ethyl	$6\cdot708w_2 + 20\cdot9w_2^2$	$0\cdot1176w_2 - 0\cdot28w_2^2$	$6\cdot71 \pm 0\cdot02$	$0\cdot118 \pm 0\cdot001$	75·95	1·75
Propyl	$5\cdot034w_2 + 8\cdot3w_2^2$	$0\cdot1068w_2 - 0\cdot26w_2^2$	$5\cdot03 \pm 0\cdot02$	$0\cdot1068 \pm 0\cdot0007$	79·93	1·75
Butyl	$4\cdot060w_2 + 4\cdot9w_2^2$	$0\cdot0967w_2 - 0\cdot19w_2^2$	$4\cdot06 \pm 0\cdot02$	$0\cdot097 \pm 0\cdot001$	84·66	1·75
Pentyl	$3\cdot064w_2 + 9\cdot4w_2^2$	$0\cdot0817w_2 - 0\cdot05w_2^2$	$3\cdot06 \pm 0\cdot02$	$0\cdot0817 \pm 0\cdot0009$	83·66	1·66
Hexyl	$2\cdot678w_2 + 8\cdot6w_2^2$	$0\cdot0785w_2 + 0\cdot07w_2^2$	$2\cdot68 \pm 0\cdot03$	$0\cdot079 \pm 0\cdot001$	89·41	1·68

alcohols are minima seen, respectively at $w_2 = 0{\cdot}01$, 0·02, 0·025, and 0·035 for methyl, ethyl, propyl, and butyl alcohols. The last three points cannot be fixed precisely, owing to the flatness of the curves. The values of w_2 quoted correspond, in turn, to molar fractions $f_2 = 0{\cdot}05$, 0·06, 0·06, and 0·07; these agree roughly with other estimates [8,11,13] in different solvents. No such marked features appear with the six alcohols examined in benzene (Table 2); methyl and ethyl seem to exhibit slight signs of an initial dropping off of P_2 at concentrations between zero and 0·5—0·6%, but these may arise from small errors in ε_{12} or d_{12} which, as w_2 diminishes, affect the calculation of P_2 by mixture formulæ more and more strongly; the values of P_2 for propyl, butyl, pentyl, and hexyl alcohols rise slowly as w_2 is increased. Table 7 gives the total polarisations as pure liquids of those alcohols for which a dielectric constant at room temperature is recorded.[24] It is noteworthy (see Tables 5 and 6) that alcohols above pentyl have $_TP_{\text{liquid}}$ values which exceed those at infinite dilution. To meet the objection that $_TP$ has here been calculated by using the molecular weight of the monomer, the last column of Table 7 shows ratios of the *specific* orientation polarisations of the liquids to those of their respective monomers.



Apparent polarisations of alcohols dissolved in carbon tetrachloride versus *concentrations as weight fractions. (Numerals are number of carbon atoms in the normal alcohol.)*

TABLE 7. *Total polarisations of liquid alcohols.*

Alcohol	Temp.	ε	d_4^t	$_TP$ (c.c.)	$_Op_{\text{liquid}}/_Op_{\text{monomer}}$
Methyl	25°	32·63	0·7866	37·2	0·45
Ethyl	25	24·30	0·7851	52·0	0·59
Propyl.....................	25	20·1	0·7998	65·0	0·76
Butyl	25	17·1	0·8057	77·5	0·87
Pentyl	25	13·9	0·8110	88·2	0·99
Hexyl	25	13·3	0·8153	101	1·06
Heptyl	22	12·10	0·8187	112	1·14
Octyl	20	10·34	0·8270	119	1·20
Decyl	20	8·1	0·8287	134	1·24
Dodecyl	25	6·5	0·8309	145	1·31

The ratios pass through unity as the carbon content changes from 5 to 6. Despite the undoubted complexity of these liquid phases (cf. refs. 19, 20, 26—30), it is relevant that

[24] Maryott and Smith, " Table of Dielectric Constants of Pure Liquids," Nat. Bur. Stand. Circular 514, issued Aug. 1951.

[25] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, 1948.

[26] Stuart, " Die Struktur des Freien Moleküls," Springer, Berlin, 1952, p. 270.

[27] Jacobsen, *Acta Chem. Scand.*, 1955, **9**, 997.

[28] Oster and Kirkwood, *J. Chem. Phys.*, 1943, **11**, 175.

[29] Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3793.

[30] Pierce and MacMillan, *J. Amer. Chem. Soc.*, 1938, **60**, 779.

if in a polymer the moments of the monomers were additive (so that $\mu_{\text{polymer}} = n \times \mu_{\text{monomer}}$) the orientation polarisation would be $(4\pi/9\boldsymbol{k}t)(\boldsymbol{N}/n)(n^2\mu^2)$ while that of the monomer is $(4\pi/9\boldsymbol{k}t)(\boldsymbol{N}\mu^2)$; division by the molecular weights (nM and M respectively) shows the specific orientation polarisations to be the same, so that ${}_{\text{O}}p_{\text{liquid}}/{}_{\text{O}}p_{\text{monomer}} = 1$. Evidently the aggregates from the alcohols up to pentyl alcohol are not uniformly constructed on the pattern described; they must include cyclic or helical forms, with $\mu_{\text{resultant}}$ less than $n\mu_{\text{monomer}}$.

Simple considerations suggest that the size of R in ROH has an important influence on the configuration of the polymer $(\text{ROH})_n$: the length [26] of the O····H–O unit is *ca.* 2·8 Å, $r_{\text{C–O}}$ is 1·43 Å, and the C–O–H angle is 108°; even if we allow that in the complex the oxygen atoms may have valency angles as large as 120°, the inter-centre distances between adjacent methyl groups in a cyclic $(\text{MeOH})_n$ would be around 4 Å, not much more than twice the " Wirkungsradius " of the CH_3 group. With alkyl groups having a greater volume demand than methyl, this steric obstacle to a *cis*-arrangement will be more pronounced: it can be avoided by rotations about the O····H–O axes, thus inducing (in terms of the O····H–O bonds) zig-zag configurations, which may be twisted into loose helices; in such forms the moments of the individual alcohols [acting (cf. Smyth,[19] p. 302) at *ca.* 60° to the C–O link in a separate molecule] are seen to contribute co-operatively to the resultant moment of the polymer more and more as the alkyl groups achieve all-*trans*-dispositions. Of course, in such extended arrangements, with the component monomer moments roughly one behind the other, there will be mutual augmentation by induction, thus making μ_{polymer} numerically greater than $n\mu_{\text{monomer}}$; Table 7 indicates that this is the situation for those alcohols above hexyl, for which ${}_{\text{O}}p_{\text{liquid}}/{}_{\text{O}}p_{\text{monomer}}$ ratios exceed unity.

Polarisations at Infinite Dilution, and Apparent Dipole Moments.—Tables 5 and 6 list the values of ${}_{\infty}P_2$ obtained by the equation:

$${}_{\infty}P_2 = M_2[p_1(1 - \beta) + c\,\alpha\varepsilon_1]$$

where M_2 is the molecular weight of the monomeric solute, and other symbols are as in ref. 23 or ref. 3, p. 56. The magnitudes of α and β at infinite dilution are taken from Tables 4 and 6 respectively for solutions in carbon tetrachloride or benzene. Comparisons between Tables 5 or 6 and Table 8 show that in nearly all cases the moments now estimated

TABLE 8. *Moments previously reported * for alcohols dissolved in carbon tetrachloride or benzene, or as vapours.*

Solute alcohol	Solvent	Values reported (D units)
Methyl	C_6H_6	1·66, 1·64, 1·6, 1·664, 1·66, 1·69, 1·62
Ethyl	CCl_4	1·63, 1·674
	C_6H_6	1·74, $1{\cdot}70_7$, 1·74, 1·700, 1·66
Propyl	C_6H_6	1·53, 1·75 [a], $1{\cdot}65_7$, 1·56, 1·71
Butyl	,,	1·65, 1·62, 1·74, 1·660, 1·69 [b]
Pentyl	,,	1·65 [a], 1·65 [c], 1·66, 1·66, 1·65, 1·36, 1·67
Hexyl	,,	1·64, 1·64
Heptyl	,,	1·7, 1·71, 1·66
Octyl	,,	1·62, 1·62, 1·70
Nonyl	,,	1·60, 1·60
Decyl	,,	1·61
Dodecyl	,,	1·62, 1·62
Hexadecyl	,,	1·66, 1·69—1·70
Cyclohexyl	,,	1·9, 1·69
Values as vapour.		
Methyl		1·61, 1·680, 1·69, 1·70 [d], $1{\cdot}70_6$ [e]
Ethyl		$1{\cdot}69_6$, $1{\cdot}68_6$, 1·67
Propyl		1·657, 1·67 [f], 1·64
Butyl		1·659, 1·63, 1·59

* In ref. 25, except for the following :

[a] Stranathan, *Phys. Rev.*, 1928, **31**, 156. [b] Boud, Cleverdon, Collins, and Smith, *J.*, 1955, 3793. Ref. 9. [d] Ramaswamy, *Proc. Ind. Chem. Soc.*, 1936, *A*, **4**, 108. [e] Stranathan, *J. Chem. Phys.*, 1938, **6**, 395. [f] Kubo, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1935, **27**, 65.

are higher than those previously recorded; the cause of this does not lie with the assumption that the distortion polarisation is R_D or $1{\cdot}05R_D$, but with the total polarisations themselves. Since the last-named have been deduced from least-square fits of the observed dielectric constant and density increments to expressions of the forms listed in Tables 4 and 6, and because (as already mentioned) only those values of w_2 on the dilute side of a minimum in the P_2–w_2 curve have been used for calculation, the present data are believed to be more correct than many of those upon which Table 8 is based.

Dependence of Dielectric Constant and Density Factors on Chain Length. -When the values of $(\alpha\varepsilon_1)_{w_2=0}$ and $(\beta d_1)_{w_2=0}$ given in Tables 4 and 6 are plotted against N, the number of carbon atoms in the n-alkyl group concerned, smooth curves result to which various empirical equations may be fitted by the method of least squares. Six examples are given, with standard errors (S.E.):

n-Alcohols–carbon tetrachloride

$(\alpha\varepsilon_1)_{w_2=0} = 17{\cdot}84 - 5{\cdot}4512C + 0{\cdot}610C^2$

(applicable between methyl and hexyl with S.E. $= \pm 0{\cdot}16$; here $C = N - 1$)

$(\alpha\varepsilon_1)_{w_2=0} = 5{\cdot}55 - 0{\cdot}6007C + 0{\cdot}0259C^2$

(applicable between hexyl and octadecyl with S.E. $= \pm 0{\cdot}009$; here $C = N - 6$)

$(\alpha\varepsilon_1)_{w_2=0} = 17{\cdot}84 - 5{\cdot}2897C + 0{\cdot}7016C^2 - 0{\cdot}0315C^3$

(applicable between methyl and dodecyl with S.E. $= \pm 0{\cdot}02$; here $C = N - 1$)

$(\beta d_1)_{w_2=0} = 1{\cdot}74 - 0{\cdot}0392C + 0{\cdot}0012C^2$

(applicable between methyl and octadecyl with S.E. $= \pm 0{\cdot}03$; here $C = N - 1$)

n-Alcohols–benzene

$(\alpha\varepsilon_1)_{w_2=0} = 9{\cdot}96 - 3{\cdot}0428C + 0{\cdot}3257C^2$

(applicable between methyl and hexyl with S.E. $= \pm 0{\cdot}07$; here $C = N - 1$)

$(\beta d_1)_{w_2=0} = 0{\cdot}1083 + 0{\cdot}0025C - 0{\cdot}0019C^2$

(applicable between methyl and hexyl with S.E. $= \pm 0{\cdot}001$; here $C = N - 1$).

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, May* 1*st*, 1959.]