22. *Dielectric Relaxation Times for Normal Alcohols at Infinite Dilution in Carbon Tetrachloride or Benzene.*

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Relaxation times are reported, ranging from *ca.* 2×10^{-12} sec. for methyl alcohol to *ca.* 8×10^{-12} sec. for hexadecyl alcohol. Such values are much smaller than others known for the pure liquids but are of the orders forecast in 1957 by an equation of Chau, Le Fèvre, and Tardif. The loss tangents of the solutions if plotted against concentrations show discontinuities, attributable to the onset of association, at roughly the same points as do graphs of the apparent partial dielectric polarisation *versus* weight fractions.

This paper reports measurements of the apparent dielectric relaxation times (τ) of a number of normal alcohols at infinite dilution in carbon tetrachloride or benzene. The literature [1-5] shows that previously attention has been given often to the pure alcohols and seldom to their solutions, although sufficient evidence exists to suggest that τ determined for a given alcohol in the liquid or the dissolved state may, one from the other, be very different. Examples will be quoted later when discussing the new observations listed in Tables 1 and 2.

[1] Whiffen, *Quart. Rev.*, 1950, **4**, 131.
[2] Böttcher, "Theory of Electric Polarisation," Elsevier, Amsterdam, Houston, London, New York, 1952, Chap. X.
[3] Davies, *Quart. Rev.*, 1954, **8**, 250.
[4] Smythe, "Dielectric Behaviour and Structure," McGraw-Hill, New York, Toronto, London, 1955, Chap. IV.
[5] Dryden and Meakins, *Rev. Pure Appl. Chem.*, 1957, **7**, 1.

TABLE 1. *Dependence of ψ on w_2.*

A. *Solutions in carbon tetrachloride.*

Solute: Methyl alcohol

10^5w_2	205	215	268	297	467	527	548	915	1182	1222	1298
$10^2\psi$	28	33	32	29	44	53	52	73	91	91	101

Solute: Ethyl alcohol

10^5w_2	170	280	316	379	404	450	468	480	522	532
$10^2\psi$	27	33	29	28	32	25	25	27	36	30
10^5w_2	551	615	690	783	796	820	911	973	979	980
$10^2\psi$	30	25	32	36	31	33	36	35	40	43
10^5w_2	1004	1136	1150	1155	1190	1621	1721	1874	1944	2518
$10^2\psi$	34	39	38	41	44	55	55	58	58	60

Solute: Propyl alcohol

10^5w_2	502	689	834	838	1140	1167	1204
$10^2\psi$	23	21	24	24	26	29	27
10^5w_2	1328	1608	1637	2244	2572	2697	3457
$10^2\psi$	29	33	34	38	42	42	47

Solute: Butyl alcohol

10^5w_2	343	567	610	630	715	825	869	1360	1384	1389
$10^2\psi$	23	21	20	20	19	21	23	23	26	23
10^5w_2	1452	1487	1677	1818	1943	2055	2143	2323	2514	
$10^2\psi$	24	23	24	25	29	30	28	30	31	

Solute: Pentyl alcohol

10^5w_2	278	493	578	682	944	952	1286
$10^2\psi$	25	22	22	22	22	23	23
10^5w_2	1405	1462	1787	2407	2433	3575	4489
$10^2\psi$	23	22	25	28	27	31	21

Solute: Hexyl alcohol

10^5w_2	366	884	957	1144	1482	1627
$10^2\psi$	20	20	21	21	23	22
10^5w_2	1800	2388	2831	3443	4513	
$10^2\psi$	23	24	26	27	28	

Solute: Heptyl alcohol

10^5w_2	607	886	1194	1809	1853	2175	3357	4644
$10^2\psi$	22	21	21	23	23	24	23	25

Solute: Octyl alcohol

10^5w_2	565	868	1079	1689	1817	1869	2449
$10^2\psi$	18	18	18	19	19	20	20
10^5w_2	2502	2992	3091	3273	3599	6342	
$10^2\psi$	20	21	21	21	21	24·5	

Solute: Nonyl alcohol

10^5w_2	623	1430	1611	2244	2999	3124	4024	5860	6266
$10^2\psi$	17	17	17	17	19	18	19·4	20	21·3

Solute: Decyl alcohol

10^5w_2	241	587	623	970	1058	1439	1480	1484	1646	1844
$10^2\psi$	15	14	15	16	15	17	17	16	16	18
10^5w_2	1964	2101	2108	2515	2793	2987	4088	5523	5747	9145
$10^2\psi$	16	17	18	17	15	18	19	20	19	21

Solute: Dodecyl alcohol

10^5w_2	243	510	869	1168	1644	1701	2133	2754	2959	3951	4907
$10^2\psi$	16	14	12	13	14	14	14	13	15	14	15

Solute: Hexadecyl alcohol

10^5w_2	338	683	1067	1436	1742	1983	2812
$10^2\psi$	17	11	12	11	11	10	11

Solute: Cyclohexyl alcohol

10^5w_2	454	663	1120	1147	1168	1688	1867	1969	2020	2560
$10^2\psi$	20	21	24	24	24	27	27	28	29	29

TABLE 1. (*Continued.*)

Solute: Cyclopentyl alcohol

10^5w_2	444	716	857	942	1417	1490	1571	1829	2151	2557	3106	5643
$10^2\psi$	18	18	20	20	16	20	22	21	22	22	23	28

B. *Solutions in Benzene.*

Solute: Methyl alcohol

10^5w_2	233	464	477	529	620	627	738	775
$10^2\psi$	17	20	22	20	22	21	23	23
10^5w_2	875	890	1047	1256	1277	1356	1689	
$10^2\psi$	24	24	29	33	33	37	46	

Solute: Ethyl alcohol

10^5w_2	371	487	578	647	734	754	838	862
$10^2\psi$	13	12	12	13	13	12	12	14
10^5w_2	1241	1241	1278	1787	2051	2606	2626	
$10^2\psi$	18	18	20·6	24	28	33	34	

Solute: Propyl alcohol

10^5w_2 ...	414	564	596	903	1125	1372	1414	1519	1888	2060	2375	3145	3343
$10^2\psi$ ...	14	14	13	14·5	14	15	16	18	17·5	19	23	25·5	26

Solute: Butyl alcohol

10^5w_2	438	882	975	1254	1371	1671	1703	1778	2294	2372	2834	3638
$10^2\psi$ ...	12	12	12·7	13	13	13·5	13	13	16·5	17	19	22

Solute: Pentyl alcohol

10^5w_2	723	1036	1201	1375	1558	1706	1766	2158	2490	2963	3415	3563
$10^2\psi$ ...	12	11	12	12·5	12	12	13	15	15	16	18	18

Solute: Hexyl alcohol

10^5w_2	585	870	1281	2082	2237	2254	2385	2909	3376	3931
$10^2\psi$	11	11	12	12	11	12	12	14·5	15	16·7

Solute: Nonyl alcohol

10^5w_2	870	1261	1824	2586	2727	3168	3653	5159
$10^2\psi$	9·7	9·5	10·5	11	10	11	11	13

TABLE 2. *Relaxation times of n-alcohols at infinite dilution in carbon tetrachloride or benzene.*

Solute alcohol	$(\psi)_{w_2}=0$	Temp. (°K)	μ (D)	$10^{12}\tau$ (sec.)	Solute alcohol	$(\psi)_{w_2}=0$	Temp. (°K)	μ (D)	$10^{12}\tau$ (sec.)
A. *In carbon tetrachloride.*									
Methyl	0·30 *	301—303	$1\cdot7_8$	1·8	Octyl	0·18	295—296	$1\cdot7_9$	4·6
Ethyl	0·29 †	300—303	$1\cdot8_0$	2·5	Nonyl	0·17	295	$1\cdot7_9$	4·3
Propyl	0·22	301—304	$1\cdot7_5$	2·6	Decyl	0·16	300—303	$1\cdot8_2$	4·7
Butyl	0·20	301—303	$1\cdot7_7$	2·9	Dodecyl ...	0·14	294	$1\cdot7_9$	4·8
Pentyl	0·22	298	$1\cdot7_4$	3·6	Hexadecyl	0·11	288	$1\cdot7_3$	7·9
Hexyl	0·20	296	$1\cdot7_9$	3·8	Cyclopentyl	0·18	288	$1\cdot7_4$	2·9
Heptyl	0·21	295	$1\cdot8_0$	4·4	Cyclohexyl	0·17	290	$1\cdot8_8$	3·0
B. *In benzene.*									
Methyl	0·20	296—297	$1\cdot7_6$	2·2	Butyl	0·13	295—297	$1\cdot7_5$	3·2
Ethyl	0·12	,,	$1\cdot7_5$	1·9	Pentyl	0·12	296—297	$1\cdot6_6$	4·1
Propyl	0·14	,,	$1\cdot7_5$	2·9	Hexyl	0·11	298	$1\cdot6_8$	4·3
					Nonyl	0·10	297—298	(1·7—1·8) ‡	*ca.* 5

* Mean for first four solutions. † Mean for first twelve solutions. ‡ Assumed in benzene.

EXPERIMENTAL

Solutes and solvents were those used for the work of the preceding paper. Apparatus, methods, and calculation procedures were as described by Le Fèvre and Sullivan [6] and Chau,

[6] Le Fèvre and Sullivan, *J.*, 1954, 2873.

Le Fèvre, and Tardif.[7] Essential measurements are recorded in Table 1; these lead to the relaxation times τ in Table 2. Headings and other symbols are as in ref. 7, concentrations being expressed as weight fractions, w_2. The frequency f_r is 3109 Mc/sec. The quantity ψ for a given solution is the quotient (incremental loss tangent) $\div w_2$; it is concentration-dependent. To save space, only ψ and w_2 values are listed in Table 1. When, as for weak solutions, both $\Delta \tan \delta$ and w_2 are small, the individual quotients ψ exaggerate the errors in the incremental loss tangents, which for all solutes have been determined at different times and with different batches of solvent, 3—6 solutions being compared with the solvent on each occasion. In Table 1, however, the ψ's are reassembled in order of increase of w_2. For the calculations of r in Table 2, magnitudes of ψ at infinite dilution were either extrapolated from graphs of ψ *versus* w_2 or averaged (see notes below Table 2).

Discussion

Variation of ψ with w_2.—Graphs showing the quotient ψ *versus* concentration exhibit forms as follow: for methyl alcohol, a very steep rise in ψ starts from w_2 *ca.* 0·005; for the alcohols ethyl to nonyl, analogous but less sudden breaks occur, which, as the carbon chain is lengthened, appear at higher concentrations and become progressively less pronounced; for the alcohols beyond decyl, the plots are rectilinear and parallel to the w_2 axis; for cyclopentyl alcohol and cyclohexyl alcohol, the graphs are straight lines inclined to the w_2 axis.

These discontinuities may be attributed to onsets of association: they correspond approximately (in their w_2 values) to the changes of curvature when the P_2's listed in the preceding paper, are similarly plotted against concentrations.

Relaxation Times at Infinite Dilution.—The smallness of τ (Table 2) is of interest. Fairly numerous studies[1-5] have already shown that the apparent relaxation times of pure alcohols are many times greater than those now obtained at infinite dilution, *e.g.*, $10^{12}\tau$ for the five alcohols $CH_3{\cdot}OH$, $C_2H_5{\cdot}OH$, n-$C_3H_7{\cdot}OH$, n-$C_4H_9{\cdot}OH$, and n-$C_8H_{17}{\cdot}OH$ are given as 69, 144, 532, 665, and 1760 respectively from measurements on the 100% phase (cf. pp. 383, 384 of ref. 2) against 2, 2—3, 2—3, 2—3, and 4—5 now recorded for $w_2 = 0$ in carbon tetrachloride. Certain estimates by Fischer,[8] made on dilute solutions of alcohols in benzene at 23°, although not extrapolated to infinite dilution, are obviously comparable with those by us:

Alcohol	Methyl	Ethyl	Propyl	Hexyl	Octyl	Hexadecyl
$10^{12}\tau$ (Fischer)	1·3	1·6	2·0	3·0	4·5	10·3
$10^{12}\tau$ (Le F. and W.) ...	1·8	2·5	2·6	3·8	4·6	7·9

Such small relaxation times can reasonably be assigned to the separated single molecules. Since τ's between 1 and 3 $\times$ 10^{-12} sec. would correspond to wavelengths between 0·19 and 0·57 cm., the detection by Saxton[9] of resonance absorption at 0·25 cm. with methyl alcohol and at 0·5 cm. with ethyl alcohol is harmonious with present results and with the existence, in the undiluted alcohols, of equilibria involving the monomeric species.

Finally, we note that if r^3 is estimated from the molar volume of a pure liquid alcohol as 0·296 $\times$ $10^{-24}V$, and inserted in the simple equation $\tau = 4\pi\eta r^3/kT$, values of τ are predicted which are some 20 times those observed at infinite dilution; if, however, eqn. (2) of Chau, Le Fèvre, and Tardif[7] be used, the forecasts achieved are much nearer the correct magnitudes:

Alcohol *	$10^{26}\alpha_{mean}$	$10^{12}\tau_{calc.}$ (sec.)	$10^{12}\tau_{obs.}$ (sec.)	Alcohol *	$10^{26}\alpha_{mean}$	$10^{12}\tau_{calc.}$ (sec.)	$10^{12}\tau_{obs.}$ (sec.)
Methyl ...	319	2·3	1·8	Butyl ...	859	6·3	2·9
Ethyl ...	500	3·7	2·5	Pentyl ...	1041	7·7	3·6
Propyl ...	680	5·0	2·6	Hexyl ...	1218	9·0	3·8

* exp h^2 taken as unity; for carbon tetrachloride η = 0·97 $\times$ 10^{-2} poise, ε = 2·238, Δ_1 = 0·0346.

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[7] Chau, Le Fèvre, and Tardif, *J.*, 1957, 2293.
[8] Fischer, *Physikal. Z.*, 1939, **40**, 645; *Z. Naturforsch.*, 1949, **4**, *a*, 707.
[9] Saxton, *Proc. Roy. Soc.*, 1952, **213**, *A*, 473.