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Microwave Absorption and Molecular Structure in Liquids. LXXVI. Relaxation Behavior of Several Primary Alcohols in Dilute Benzene and *p*-Dioxane Solutions¹

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Abstract: Dielectric constants and losses of methanol, 1-butanol, and 1-decanol have been measured at concentrations of 0.02–0.05 mole fraction in benzene and *p*-dioxane solutions at wavelengths of 0.20, 1.25, 3.22, 9.8, 24.8, 49.8, and 3×10^6 cm at 25°. Measurements have also been made on 1-butanol in *p*-dioxane and its mixtures with benzene and *n*-heptane at 20, 40, and 60° at the same wavelengths. In benzene solutions the arc plots show contributions from two relaxation processes corresponding to relaxation times 2×10^{-12} – 5×10^{-12} and 13×10^{-12} – 36×10^{-12} sec. These are attributed to –OH group and molecular reorientation, respectively. In dioxane solutions a symmetrical distribution of relaxation times is found with $\tau_0 = 3 \times 10^{-12}$ – 9×10^{-12} sec. In mixtures of benzene and *n*-heptane with dioxane, 1-butanol also shows a distribution of relaxation times with the distribution parameter, α , decreasing with increasing temperature. Reorientation of alcohol–dioxane complexes of varying sizes seems a plausible explanation for the distribution of relaxation times. Fluctuations of local environment around a reorienting dipole, caused by H-bond forming and breaking, may also account for this behavior.

The dielectric absorption region in pure aliphatic alcohols is characterized by three discrete relaxation processes.² The lowest frequency process, which dominates the dispersion region, is generally agreed to originate from hydrogen-bonded clusters and to involve the breaking of the hydrogen bond. In dilute solutions of alcohol in a nonpolar solvent, where the internal field and the viscosity effects are very small, extensive intermolecular association through hydrogen bonding would be practically negligible. Therefore, one would then expect alcohols to show a dielectric absorption similar to that exhibited by most aliphatic compounds in dilute solutions.

Two nonpolar solvents, namely, benzene and *p*-dioxane, were chosen for this study, *p*-dioxane appearing to be a particularly attractive solvent. Addition of *p*-dioxane should break the H-bonded structure in liquids,

while the dioxane molecule, being an electron donor, would attach itself to proton donor molecules by forming a hydrogen bond and thus giving rise to a different H-bonded structure. Dielectric studies of water–dioxane mixtures in this laboratory^{3,4} showed that strong dioxane–water interactions give rise to two relaxation processes in these mixtures. Since alcohols, on the basis of extensive intermolecular association, are often regarded as somewhat similar in structure to water, it seemed desirable to study several alcohols in *p*-dioxane. In this paper we report on a study of methanol and two other primary alcohols in dilute benzene and *p*-dioxane solutions.

Experimental Methods

Apparatus. The dielectric apparatus and various methods of measurement have been described in previous papers.^{5–9} The refractive indices were measured with a Pulfrich refractometer.

(1) This research was supported by the U. S. Army Research Office (Durham). Reproduction in whole or in part by or for the U. S. Government is permitted.

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Table I. Dielectric Constants and Losses of Alcohols in Benzene and *p*-Dioxane as a Function of Concentration at 25°

λ_0 , cm	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
Methanol in Benzene								
	$f_2 = 0.0142$		$f_2 = 0.0260$		$f_2 = 0.0333$		$f_2 = 0.0430$	
3×10^6	2.331		2.383		2.420		2.463	
49.82	2.331		2.382	0.001	2.420	0.003	2.463	0.006
24.75	2.330	0.001	2.382	0.002	2.417	0.005	2.459	0.009
9.856	2.330	0.002	2.380	0.007	2.414	0.012	2.454	0.019
3.226	2.322	0.006	2.366	0.014	2.393	0.023	2.421	0.034
1.199	2.316	0.010	2.345	0.026	2.374	0.038	2.397	0.054
0.201	2.289	0.011	2.299	0.021	2.314	0.036	2.315	0.037
1-Butanol in Benzene								
	$f_2 = 0.0152$		$f_2 = 0.0235$		$f_2 = 0.0353$		$f_2 = 0.0524$	
3×10^6	2.341		2.367		2.417		2.487	
49.82	2.341	0.001	2.367	0.002	2.417	0.004	2.485	0.008
24.25	2.340	0.003	2.366	0.004	2.416	0.007	2.483	0.009
9.856	2.337	0.005	2.361	0.008	2.409	0.016	2.466	0.031
3.226	2.334	0.011	2.351	0.018	2.389	0.030	2.428	0.050
1.196	2.321	0.023	2.340	0.032	2.373	0.043	2.406	0.065
0.203	2.287	0.018	2.308	0.025	2.306	0.036	2.309	0.051
1-Decanol in Benzene								
	$f_2 = 0.0254$		$f_2 = 0.0296$		$f_2 = 0.0349$		$f_2 = 0.0423$	
3×10^6	2.371		2.387		2.409		2.427	
49.82	2.371	0.004	2.387	0.003	2.409	0.008	2.425	0.008
24.75	2.369	0.008	2.383	0.009	2.405	0.011	2.423	0.016
9.856	2.362	0.015	2.374	0.018	2.393	0.022	2.406	0.030
3.226	2.345	0.025	2.362	0.030	2.361	0.034	2.370	0.042
1.197	2.330	0.032	2.333	0.038	2.341	0.041	2.353	0.048
0.200	2.294	0.011	2.296	0.014	2.308	0.012	2.302	0.020
Methanol in Dioxane								
	$f_2 = 0.0194$		$f_2 = 0.0276$		$f_2 = 0.0405$		$f_2 = 0.0528$	
3×10^6	2.303		2.345		2.408		2.474	
49.82	2.303		2.344	0.003	2.406	0.004	2.471	0.006
24.75	2.302	0.003	2.342	0.004	2.406	0.008	2.470	0.009
9.856	2.299	0.007	2.340	0.011	2.401	0.016	2.462	0.030
3.226	2.293	0.016	2.332	0.023	2.388	0.035	2.440	0.048
1.196	2.275	0.028	2.309	0.041	2.354	0.057	2.403	0.073
0.204	2.235	0.025	2.240	0.033	2.259	0.050	2.280	0.065
1-Butanol in Dioxane								
	$f_2 = 0.0177$		$f_2 = 0.0290$		$f_2 = 0.0464$			
3×10^6	2.305		2.354		2.421			
49.82	2.304	0.002	2.353	0.004	2.419	0.006		
24.75	2.304	0.005	2.352	0.006	2.418	0.011		
9.856	2.302	0.011	2.348	0.017	2.411	0.024		
3.226	2.290	0.024	2.322	0.034	2.383	0.050		
1.196	2.271	0.034	2.295	0.051	2.333	0.074		
0.203	2.228	0.020	2.236	0.031	2.245	0.042		
1-Decanol in Dioxane								
	$f_2 = 0.0287$		$f_2 = 0.0323$		$f_2 = 0.0400$		$f_2 = 0.0455$	
3×10^6	2.337		2.350		2.380		2.386	
49.82	2.325	0.001	2.346	0.006	2.376	0.007	2.382	0.008
24.75	2.332	0.009	2.345	0.010	2.376	0.013	2.381	0.013
9.856	2.324	0.020	2.334	0.021	2.363	0.027	2.366	0.027
3.226	2.291	0.037	2.301	0.043	2.314	0.050	2.321	0.055
1.196	2.249	0.036	2.253	0.042	2.260	0.048	2.268	0.054
0.202	2.217	0.0215	2.219	0.022	2.222	0.027	2.226	0.029

Purification of Materials. Methanol (Reagent grade) obtained from Matheson Coleman and Bell was refluxed over calcium hydride and fractionally distilled. 1-Butanol and 1-decanol from Aldrich Chemical Co. were refluxed over calcium hydride and fractionally distilled. The boiling points of the samples were in excellent agreement with literature values.

Benzene from Allied Chemical Corp. was stored over sodium wire and used as such.

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Extra care was taken to remove water impurity from dioxane. *p*-Dioxane obtained from Matheson Coleman and Bell was refluxed over sodium for several days. Fresh pieces of sodium were added until corrosion of sodium ceased to occur. The liquid was then fractionally distilled through a 4-ft glass helix-packed column.

Results

The dielectric constants and losses measured at various wavelengths for solutions of methanol, 1-butanol, and 1-decanol in benzene and in dioxane are given in Table I, in which each set of data is headed by the mole fraction, f_2 , of the alcohol. Typical Cole-Cole plots obtained in benzene and dioxane solutions are presented in Figures 1 and 2, respectively. In Table II

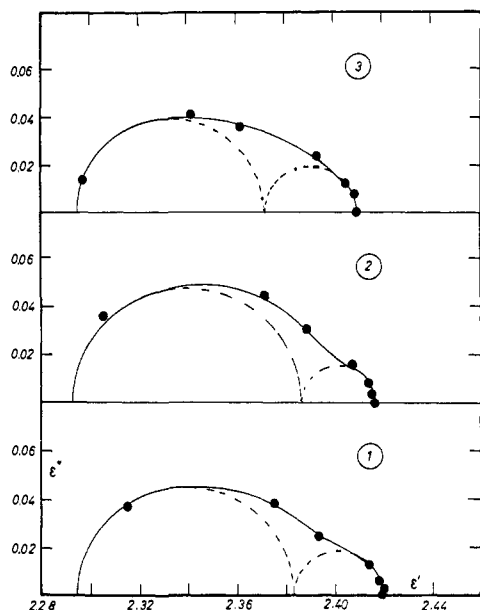


Figure 1. Cole-Cole plots for alcohols in benzene solutions at 25°. Broken lines show the resolved dispersion region: (1) methanol ($f_2 = 0.0333$); (2) 1-butanol ($f_2 = 0.0353$); and (3) 1-decanol ($f_2 = 0.0393$).

the dielectric constants and losses are given as a function of temperature.

Table II. Dielectric Constants and Losses of 1-Butanol in Dioxane and Mixed Solvents as a Function of Temperature

λ_0 , cm	20°		40°		60°	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
1-Butanol ($f_2 = 0.0331$) in Dioxane						
3×10^6	2.375		2.324		2.274	
49.82	2.374	0.004	2.323	0.004	2.273	0.001
24.75	2.372	0.009	2.321	0.007	2.273	0.004
9.856	2.365	0.019	2.318	0.013	2.270	0.008
3.226	2.343	0.033	2.301	0.030	2.257	0.021
1.206	2.309	0.045	2.284	0.037	2.243	0.028
0.202	2.267	0.026	2.236	0.030	2.215	0.027
1-Butanol ($f_2 = 0.0418$) + Dioxane ($f_3 = 0.1521$) in Benzene						
3×10^6	2.476		2.402		2.342	
49.82	2.474	0.009	2.400	0.005	2.342	
24.75	2.468	0.014	2.405	0.008	2.341	0.001
9.856	2.452	0.029	2.398	0.017	2.340	0.010
3.226	2.415	0.049	2.376	0.032	2.324	0.024
1.206	2.390	0.058	2.350	0.046	2.321	0.037
0.203	2.295	0.040	2.289	0.040	2.246	0.041
1-Butanol ($f_2 = 0.0549$) + Dioxane ($f_3 = 0.4218$) in <i>n</i> -Heptane						
3×10^6	2.192		2.143		2.084	
49.82	2.190	0.002	2.142	0.001	2.085	
24.75	2.187	0.008	2.140	0.006	2.082	0.001
9.856	2.174	0.023	2.134	0.015	2.080	0.008
3.226	2.150	0.032	2.124	0.026	2.068	0.014
1.203	2.130	0.041	2.111	0.032	2.056	0.027
0.203	2.065	0.026	2.047	0.026	2.018	0.024

The shape of the plot in benzene solution in Figure 1 for each of the three alcohols at each concentration is such as to indicate the presence of more than one dispersion region. The dielectric constant and loss data were, therefore, analyzed for two Debye-type relaxation processes by a computer-based method, similar to one described before,¹⁰ using an IBM 360 computer. The

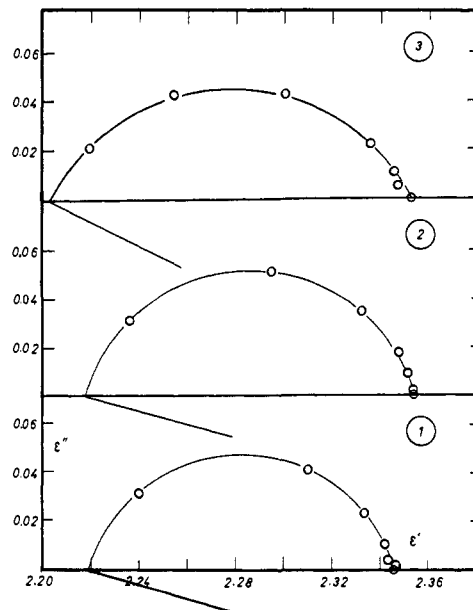


Figure 2. Cole-Cole plots for alcohols in *p*-dioxane solutions at 25°: (1) methanol ($f_2 = 0.0276$); (2) 1-butanol ($f_2 = 0.0290$); and (3) 1-decanol ($f_2 = 0.0323$).

difference in this program from the previous one was that percentage error in measurements at each wavelength rather than a lumped value for errors was used, and that deviation for ϵ' and ϵ'' at each wavelength rather than a sum of the squares of deviations was used to decide the best fit to data points. The calculated values for τ_1 , τ_2 , the fractional contribution, c_2 , the static dielectric constant, ϵ_0 , and the very high frequency or optical dielectric constant, ϵ_∞ , are given in Table III.

Table III. Resolved Relaxation Times, τ_1 , τ_2 , Static and Optical Dielectric Constants, Weight Contribution, C_2 , and Squares of Refractive Index for Alcohols in Benzene Solutions as a Function of Mole Fraction, f_2 , at 25°

f_2	ϵ_0	ϵ_∞	n^2D	τ_1 (10^{-12} sec)	τ_2 (10^{-12} sec)	C_2
Methanol						
0.0142	2.331	2.285	2.2401	12.3	1.8	0.64
0.0260	2.383	2.292	2.2395	11.9	2.3	0.67
0.0333	2.420	2.298	2.2361	11.1	1.9	0.70
0.0430	2.463	2.300	2.2369	18.7	2.2	0.67
1-Butanol						
0.0152	2.340	2.286	2.2369	18.2	2.6	0.77
0.0235	2.367	2.296	2.2348	18.6	2.9	0.77
0.0353	2.417	2.296	2.2301	22.9	2.9	0.77
0.0524	2.487	2.295	2.2267	22.2	2.9	0.75
1-Decanol						
0.0254	2.371	2.292	2.2306	34.5	5.0	0.71
0.0296	2.389	2.295	2.2289	31.2	4.9	0.75
0.0349	2.409	2.298	2.2269	34.7	4.9	0.69
0.0423	2.427	2.299	2.2250	32.6	5.2	0.65

The Cole-Cole plots for the three alcohols in dioxane solution (Figure 2) are smooth depressed-center arcs. The data were fitted to the Cole-Cole equation¹¹ for distribution of relaxation times on an IBM 360 com-

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puter to obtain the values for the static dielectric constant, ϵ_0 , the optical dielectric constant, ϵ_∞ , the most probable relaxation time, τ_0 , and the distribution parameter, α , given in Table IV.

Table IV. Most Probable Relaxation Times, τ_0 , Distribution Parameters, α , Calculated Static and Optical Dielectric Constants, and Squares of Refractive Index for Alcohols in *p*-Dioxane Solutions as a Function of Mole Fractions, f_2 , at 25°

f_2	ϵ_0	ϵ_∞	n^2D	τ_0 (10^{-12} sec)	α
Methanol					
0.0194	2.303	2.214	2.0143	3.1	0.20
0.0276	2.345	2.218	2.0134	3.1	0.20
0.0405	2.408	2.222	2.0126	3.1	0.19
0.0528	2.474	2.228	2.0120	3.0	0.21
1-Butanol					
0.0177	2.305	2.216	2.0146	4.6	0.17
0.0290	2.354	2.217	2.0137	4.5	0.18
0.0464	2.421	2.220	2.0126	5.0	0.18
1-Decanol					
0.0287	2.337	2.200	2.0169	8.6	0.29
0.0323	2.350	2.201	2.0168	8.8	0.29
0.0400	2.380	2.203	2.0166	8.7	0.29
0.0455	2.386	2.205	2.0164	8.7	0.28

The values of the optical dielectric constant, ϵ_∞ , obtained from this analysis are slightly higher than those of the square of the refractive index, n^2D , of the benzene solutions in Table III, as would be expected, but are considerably higher in the case of the *p*-dioxane solutions in Table IV. As found in this study and from the literature,¹² the difference between ϵ_0 and n^2D is about 1.5% for pure benzene (ϵ_0 2.2741, n^2D 2.2443) and about 10% for pure *p*-dioxane (ϵ_0 2.2092, n^2D 2.0171), about the same as the difference between the ϵ_∞ and n^2D for the solutions of the alcohols in the two solvents. The differences between ϵ_∞ and n^2D for the solutions evidently reflect primarily the properties of the solvents.

Discussion

Alcohols in Benzene. The three normal primary alcohols in benzene solutions, as seen in Figure 1, exhibit the presence of only two relaxation processes: a dominant high-frequency dispersion, having a relaxation time of 2×10^{-12} sec in methanol increasing to one of 5.2×10^{-12} sec in 1-decanol, and a low-frequency dispersion region with a relaxation time 12×10^{-12} sec in methanol increasing to one of 36×10^{-12} sec in 1-decanol (Table III). The very short relaxation time corresponding to the high-frequency dispersion region is very close to values attributed to the orientation of the hydroxyl group by rotation about the C-O bond in solutions of substituted phenols^{13,14} and in pure alcohols.^{2b} The increase in τ_2 with chain length is to be expected in view of the fact that the hydroxyl-group reorientation depends to some extent on the length of the alkyl group, and the viscosity of the liquid.^{2b}

The relaxation time for the low-frequency dispersion region is of the size generally considered to be due to an over-all molecular reorientation. There is no evidence

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for any significant concentration of aggregates formed by molecular association through hydrogen bonding in these solutions. It is, therefore, reasonable to attribute the relaxation process for the low-frequency dispersion to the reorientation of the free alcohol monomer. The relaxation time, τ_1 , and the relative contribution c_2 in Table III remain constant with concentration within the experimental error except at the highest concentration where τ_1 seems to increase. The large τ_1 value for methanol at this concentration may indicate the onset of multimer formation and, therefore, would require consideration of an additional relaxation process for a correct analysis. The relaxation time τ_1 in Table III increases with increasing chain length in agreement with the fact that the relaxation time of a molecule is directly related to its size, and is reasonably consistent with the approximate values obtained for the molecules of 1-butanol and 1-decanol in the pure liquids.^{2b}

Studies from ultrasonic,¹⁵ spectrophotometric,^{16,17} nmr,¹⁸ infrared,^{19,20} and vapor pressure²¹ measurements in the solutions of alcohols in nonpolar solvents have indicated the presence of alcohol monomers in equilibrium with small multimers. Although the dispersion data suggest the presence of only monomers in dilute solutions, the possible existence of linear dimers in addition to the monomers cannot be disregarded. Near-infrared spectra of methanol and 1-butanol in benzene solutions at comparable concentrations²² show two OH stretching frequency peaks at about 3600 and 3500 cm^{-1} . These peaks have been attributed to the presence of monomers and dimers. From a very careful study of the equilibrium dielectric polarization of several alcohols in dilute benzene solutions, Ibbitson and Moore²² have concluded that the positive deviations of the dielectric constant from linear dependence on concentration are due to the formation of linear dimers and trimers. The ROH molecule at each end of such a dimer or trimer may be able to rotate about its hydrogen bond. This would give a relaxation time so close to that of the free molecule as to be indistinguishable from it within our errors of analysis.

Alcohols in *p*-Dioxane. In dioxane solutions the Cole-Cole plots for the three alcohols are smooth depressed-center arcs at each concentration (Figure 2). The most probable relaxation time τ_0 and the distribution coefficient α for each alcohol are independent of concentration in Table IV within the limits of our experimental errors. Because of the large values of α , one is tempted to analyze in terms of two overlapping dispersion regions. The values of the parameters obtained from an attempted analysis do not indicate the presence of two relaxation processes. However, the fact that constant values of τ_0 and α with varying concentration in solution for each alcohol are obtained suggests that a symmetrical distribution of relaxation

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times in dioxane is probably the real behavior. The values for the most probable relaxation time, τ_0 , of 3.1×10^{-12} , 4.6×10^{-12} , and 8.7×10^{-12} sec in the methanol, 1-butanol, and 1-decanol solutions, respectively, are much smaller than those found for free monomer reorientation in benzene solutions (τ_1 in Table III), and are of the order of that found for the hydroxyl group rotation.

Raczy studied 3-ethylpentanol-3 in dioxane and carbon tetrachloride solutions,^{23,24} finding²⁴ a $\tau_0 = 6.4 \times 10^{-12}$ sec and $\alpha = 0.076$ at $f_2 = 0.1078$ in CCl_4 . For a dioxane solution ($f_2 = 0.124$) they reported²⁴ $\tau_0 = 8.8 \times 10^{-12}$ sec and suggested that an increase in τ_0 and in the amplitude of dispersion in dioxane solution is due to the formation of an alcohol-dioxane complex. From their data we have calculated $\alpha = 0.15$. *p*-Dioxane undoubtedly is a strong hydrogen-bonding base. Evidence for the existence of a hydrogen-bonded alcohol-dioxane complex is obtained from measurements of many physical properties. In dilute alcohol-dioxane solutions, the near-infrared spectra show only a single, fairly broad peak at $\sim 3500 \text{ cm}^{-1}$, which is attributed to the OH stretching of the alcohol-dioxane complex.²² This is identical with the peaks observed in the infrared spectra of various alcohol-acceptor complexes, e.g., alcohol-acetone,²⁵ alcohol-ether,²⁶ etc. Ibbitson and Moore²² from measurements of the static dielectric constants of several alcohols in dioxane solutions concluded that the polarization is due to a complex of alcohol with dioxane. Malecki²⁷ interpreted his measurements of dielectric polarization in strong electric fields in terms of the presence of a 1:1 1-hexanol-dioxane complex in addition to higher complexes at mole fractions of alcohol less than 0.1.

In order to ascertain whether the broad dispersion in dioxane is mainly associated in some way with the formation of a hydrogen bond between the alcohol and the dioxane molecule, the relaxation behavior of 1-butanol in benzene and in *n*-heptane, to which a small quantity of dioxane was added, was studied. The dielectric constant and loss data are given in Table II and the values at 20° are plotted in Figure 3, which shows a depressed center arc for both solutions. The calculated values of τ_0 , α , ϵ_0 , and ϵ_∞ are given in Table V. These computerized values of ϵ_0 are in satisfactory agreement with the values measured at the lowest frequency in Table II. There is only a slight change in τ_0 in solution in benzene and *n*-heptane with dioxane from that in pure dioxane, but the distribution parameter, α , changes considerably. Evidently, addition of a small quantity of dioxane to 1-butanol in benzene or *n*-heptane changes the absorption region from a superposition of two discrete processes to a symmetrical distribution of relaxation times, possibly by attachment of the dioxane to the alcohol molecule through a hydrogen bond to form a complex or by provision of a different environment for reorientation of an alcohol monomer.

We now inquire into the origin of the distribution of relaxation times in alcohol-dioxane solutions. The *p*-dioxane molecule is conceivably capable of attaching

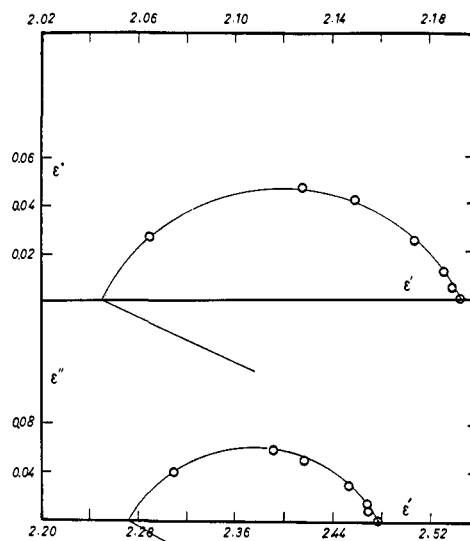


Figure 3. Cole-Cole plots for 1-butanol with *p*-dioxane in benzene (bottom curve) and in *n*-heptane (top curve) at 20° at concentration given in Table II.

four free alcohol molecules or terminal molecules in an intermolecularly hydrogen-bonded chain by forming a hydrogen bond to each of the two pairs of unshared electrons in each of the two oxygen atoms. Owing to strong inductive forces, the oxygen in dioxane is more basic than in alcohol and consequently the alcohol-dioxane hydrogen bond is stronger than the intermolecular H bond in the pure alcohol. Since the number of dioxane molecules is nearly in the ratio of 18:1 to that of the alcohol molecules at the highest concentration, it

Table V. Most Probable Relaxation Times, τ_0 , Distribution Parameters, α , and Calculated Static and Optical Dielectric Constants of 1-Butanol-1 in Pure Dioxane and in Mixtures with Benzene and *n*-Heptane

t , °C	ϵ_0	ϵ_∞	τ_0 (10^{-12} sec)	α
1-Butanol in <i>p</i> -Dioxane ($f_2 = 0.0331$)				
20	2.374	2.249	5.9	0.22
40	2.323	2.213	3.7	0.19
60	2.274	2.190	2.6	0.17
1-Butanol ($f_2 = 0.0418$) and <i>p</i> -Dioxane ($f_3 = 0.1521$) in Benzene				
20	2.476	2.272	5.2	0.29
40	2.402	2.249	3.5	0.26
60	2.344	2.207	2.5	0.24
1-Butanol ($f_2 = 0.0549$) and <i>p</i> -Dioxane ($f_3 = 0.4218$) in <i>n</i> -Heptane				
20	2.192	1.996	4.8	0.27
40	2.143	2.030	3.1	0.23
60	2.084	2.046	2.3	0.18

is unlikely that an appreciable amount of free alcohol monomer or multimer would exist in solution. One can envision small aggregates formed by one, two, or several molecules attached to dioxane through hydrogen bonds with the OR part of the alcohol molecule capable of rotation. Orientation of the alcohol dipole about the H bond inside this complex, however, cannot account for the very short τ_0 found in this study.

The addition of dioxane to alcohol may not give rise to the same effect as in water, since the interactions in

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alcohols are largely determined by the OH group and the steric hindrance introduced by the size and shape of the R group about it, while water consists only of OH groups. Also in dioxane-rich solutions, one alcohol molecule (since it acts as a donor of only one H bond) can hydrogen-bond to only one dioxane molecule, thereby reducing the size of the aggregate, whereas a water molecule can hydrogen-bond to two dioxane molecules.

It appears that alcohol-dioxane complexes of various sizes may exist in dioxane solutions. At these temperatures, the life of a hydrogen bond (which effectively is the low-frequency relaxation time in pure alcohols) is longer than the time required for these small complexes to reorient as a whole. The distribution of relaxation times would, therefore, arise from reorientation of these complexes of various sizes. Thermal motions would tend to disrupt these complexes, and thus one would expect the distribution parameter, α , to decrease with increasing temperature. As seen in Table V, α for the solutions of 1-butanol in pure dioxane, and in benzene and *n*-heptane with dioxane, decreases with increasing temperature. A calculation for a distribution between two limiting relaxation times by a method previously described²⁸ leads to an upper limit of about 76×10^{-12} for 1-decanol, consistent with that expected for the reorientation of the largest possible complex of alcohol with dioxane, but the lower limit obtained is only about 1×10^{-12} sec.

An alternative and equally plausible explanation for a broad distribution of relaxation times comes from Kauzmann's suggestion²⁹ of the consideration of the molecular reorientation in relation to, and consequently affected by, the fluctuation in the environment of a reorienting molecule, the fluctuation in this particular case being the formation and breaking of the hydrogen bond between alcohol and dioxane. By a mathematical treatment based on Kauzmann's model, Anderson and Ullman³⁰ have shown that, if the rate of environmental fluctuations (caused by H-bond breaking in this case) is much slower than the various rates of molecular re-

orientation, the resulting equation predicts a symmetrical distribution of relaxation times. The rate of H-bond breaking is certainly slower than the rate of reorientation of an alcohol monomer or that of small complexes of alcohol with dioxane in these solutions. A broad dispersion found in dioxane solutions may also result if the region consists of several discrete processes consisting of group rotation and molecular rotation in the free alcohol molecule, and the reorientation of alcohol-dioxane complexes as a whole.

Previous studies of several alcohols in nonpolar solvents have shown that the relaxation time of an alcohol decreases with dilution.^{24,25,31,32} The previously reported values³² for methanol and 1-butanol in benzene and dioxane above $f_2 = 0.05$ are considerably higher than those found in this study. In most of the previous studies, however, measurements have been made at $f_2 > 0.05$, in which region our results indicate the onset of extensive molecular association. At relatively higher concentrations there may be a small contribution due to the process associated with H-bond breaking in alcohol "clusters." With dilution this contribution would decrease and finally disappear, and the relaxation time would reach a value characteristic of the relaxation processes associated with an alcohol monomer in very dilute solution.

Conclusion

We conclude that, in their dielectric absorption behavior, alcohols in dilute benzene solutions ($f_2 < 0.05$) exhibit contributions from an intramolecular and a molecular relaxation process, the intramolecular process dominating. In dioxane solutions, alcohols form a complex with dioxane and, consequently, show a distribution of relaxation times. Orientation of complexes of different sizes as a whole is considered as the origin of the distribution of relaxation times. It is also possible that a fluctuating environment caused by H-bond forming and breaking around a reorienting alcohol monomer or an alcohol-dioxane complex may give rise to distribution of relaxation times.

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