BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 618—622 (1974)

Dielectric Relaxation and Molecular Structure. IX. Dielectric Behavior of 1-Propanol and 1-Butanol in a Variety of Solvents

Taro Koshii, Eiji Arie,* Masahiko Nakamura, Hiroaki Takahashi,
and Keniti Higasi
Department of Chemistry, Waseda University, Shinjuku, Tokyo 160

(Received November 22, 1973)

The dielectric constants and losses of 1-propanol and its mixtures with benzene, chlorobenzene, 1,4-dioxane or pyridine, and 1-butanol and its mixtures with benzene or pyridine have been measured in the frequency range of 0.35—2.1 GHz at 25.0 °C. Concentrations of alcohols are 1—0.6 mol fraction of the mixtures. Densities and refractive indices have also been determined. The dielectric data were used to calculate the relaxation times of the alcohols. The Cole-Cole plots for these systems showed Debye-type semicircles in lower frequencies where the principal relaxation of alcohols dominates. Deviations from the semicircle, however, have been observed in the region of upper frequencies, where the second dispersion of alcohol, the dispersion of solvent itself and of hydrogen-bonded species between alcohol and solvent may occur. The principal relaxation times of alcohols calculated from the data of lower frequencies change with concentration in two different manners by solvents, and this difference is due to whether the solvent has hydrogen-bonding capacity or not, and does not depend upon the dielectric constant and/or the polarity of the solvent.

Since Mizushima published his measurements on a number of liquid alcohols in 1926,[1] the monoalcohols have been considered to provide an example with which the Debye dispersion of polar molecules occurs in the liquid state. Later, Smyth *et al.*[2] studied ten normal alcohols from propyl through dodecyl in a wide frequency range up to 150 GHz, and established that the dielectric dispersion of primary aliphatic alcohols in the liquid state is characterized by three relaxation regions the most important (the principal relaxation) being at the lower frequency region, and that the principal relaxation cannot be accounted for as arising from rotation of single alcohol molecules. Although a number of dielectric investigations have been made on alcohols since, the precise mechanism of the principal relaxation is still unknown.

In this report the dielectric behavior of normal alcohols has been investigated in the frequency range in which the principal relaxation occurs. Several solvents having different properties in the dielectric constant, the dipole moment and the hydrogen-bonding capacity were added to alcohols and the effect of this addition on the principal relaxation was examined.

Experimental

Materials. All the samples were of the best grade available from commercial sources. They were dehydrated by the usual methods and fractionally distilled prior to their use. The observed refractive indices at 25.0 °C: 1-propanol $n_D=1.3830$, 1-butanol $n_D=1.3968$ are in agreement with the literature values[3].

Apparatus. The apparatus (UHF Material Characteristics Test Assembly) is a coaxial-slotted line type, manufactured by Rohde and Schwarz Co. Ltd., (München, Germany). The principle of the measurement is the standing-wave method, that is, if there is any attenuation in the dielectrics there will be a reduction in the voltage standing-wave ratio (E_{max}/E_{min}), since all the incident wave intensity would not be reflected. A water-jacket surrounding the cell allows for the temperature control of samples within 0.05 °C during a run.

Densities were determined with a Lipkin type pycnometer calibrated with pure water. Refractive indices for sodium D line were measured with a Pulfrich type refractometer.

Evaluation of data. Dielectric constants and losses were calculated as follows. The measured value of the standing-wave ratio E_{max}/E_{min} is mathematically related to the propagation constant γ of the wave along the coaxial line within the sample in the following equation.

$$\frac{\tanh \gamma d}{\gamma d} = -j\left(\frac{\lambda}{2\pi d}\right)\frac{\dfrac{E_{min}}{E_{max}}-j\tan\left(\dfrac{2\pi x}{\lambda}\right)}{1-j\dfrac{E_{min}}{E_{max}}\tan\left(\dfrac{2\pi x}{\lambda}\right)} \tag{1}$$

where x is the distance from the first electric field strength minimum of the standing-wave to the surface of the sample, d the specimen length and λ the wavelength along the coaxial line outside the sample. A graphical solution of Eq. (1) has been given by von Hippel[4] in the charts of the following equation.

$$Ce^{j\zeta} = \frac{\tanh Te^{j\delta}}{Te^{j\delta}} \tag{2}$$

where $T\exp(j\delta)$ is the polar form of γd and $C\exp(j\zeta)$ is the polar form of the right hand side of Eq. (1). The charts given in Ref. 4 are limited in range. A computer solution of Eq. (2) was used in order to extend the range. Then the dielectric constant and loss factor are calculated by the following equation.

$$\varepsilon' - j\varepsilon'' = -\left(\frac{\lambda}{2\pi d}\right)^2(\gamma d)^2 \tag{3}$$

When the value of E_{min}/E_{max} is large enough (more than 0.7), it can be measured directly. If the value is small, the distance between the points of twice minimum power Δl is measurable and it connects with E_{max}/E_{min} as follows.

$$\frac{E_{max}}{E_{min}} = \frac{\sqrt{2-\cos^2\left(\dfrac{\pi\Delta l}{\lambda}\right)}}{\sin\left(\dfrac{\pi\Delta l}{\lambda}\right)} \tag{4}$$

If the dielectric constant of the sample is approximately

---

* Present address: Mitsubishi Monsanto Chemical Company, Iwatsuka, Nakamura, Nagoya 453.

known, the optimum length d is given by the condition that d should be at least a quarter wavelength in the material[5], that is,

$$d = \frac{\lambda}{4\sqrt{\varepsilon'}} \tag{5}$$

To determine the relaxation time τ, the distribution parameter α and the high-frequency dielectric constant ε_∞, the Cole-Cole equation[6]

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1+(j\omega\tau)^{1-\alpha}} \tag{6}$$

was fitted to the data by an iterative method using an electronic computer.

Results and Discussion

The dielectric constants and losses of alcohols and their mixtures obtained in this experiments are recorded in Table 1. Dielectric spectra for 1-propanol–benzene and 1-butanol–pyridine mixtures are shown in Fig. 1. (See also Fig. 1 of the preceding letter[7] regarding those for 1-propanol–pyridine mixtures.) It is found for all the mixtures that with increasing amount of solvent the intensity of the maximum absorption decreases and the critical frequency shifts to the higher frequency side. The shift of the frequency is more pronounced in the 1,4-dioxane and in the pyridine mixtures than those in the benzene and in the chlorobenzene mixtures.

The high frequency intercepts of the Cole-Cole plots (ε_∞) for pure alcohols are always much larger than the square of refractive indices for sodium D line (Table 2). It suggests that the second and the third dispersions of alcohols exist in higher frequency range. Values of ε_∞ for the pyridine and chlorobenzene mixtures increase with increasing concentration of solvent, (see *e.g.* Fig. 2-a), while those of ε_∞ for the 1,4-dioxane and benzene mixtures do not change with an increase in the concentration, (see *e.g.* Fig. 2-b). The above difference is due to whether the dispersion of polar solvent contributes to this effect or not. Deviation from the Debye-type semicircle was observed in the frequency range higher than 1 GHz for pure alcohols. For pyridine mixtures the deviation in higher frequency range increases with increasing amount of solvent, while such is not observed for benzene mixtures as in Fig. 2-a and 2-b. The above trend is an indication for the existence of the dispersions of polar solvent, of interaction species between solute and solvent, of second dispersion of the alcohol, *etc.*

Using Eq. (6) the distribution parameter α of the Cole-Cole plot and the relaxation time τ were evaluated

TABLE 1 (a). DIELECTRIC CONSTANT AND LOSS OF PURE ALCOHOLS AT 25.0 °C

Substance	1-Propanol		1-Butanol	
f(GHz)	ε'	ε''	ε'	ε''
0.356	14.41	7.97	9.44	6.84
0.515	11.64	8.43	7.35	6.17
0.697	8.92	7.71	5.85	5.24
1.00	7.06	6.39	4.79	3.99
1.50	5.55	4.93	4.01	2.95
2.11	4.67	3.92	3.70	2.11

TABLE 1(b). DIELECTRIC CONSTANT AND LOSS FOR ALCOHOL MIXTURES (mole fraction of alcohol, mf) at 25.0 °C

f(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
	1-Propanol in benzene							
	mf=0.899		mf=0.857		mf=0.741		mf=0.633	
0.356	13.33	6.79	12.75	6.10	11.30	4.83	9.61	3.35
0.515	11.11	7.22	10.76	6.72	9.56	5.33	8.43	3.82
0.697	8.48	6.54	8.98	6.59	8.08	5.25	7.47	4.09
1.00	6.79	5.70	6.75	5.42	6.45	4.63	6.07	3.67
1.50	5.36	4.48	5.55	4.37	5.16	3.77	4.87	3.07
2.11	4.41	3.55	4.52	3.42	4.45	3.07	4.24	2.47
	1-Propanol in chlorobenzene							
	mf=0.929		mf=0.887		mf=0.822		mf=0.690	
0.356	13.92	6.95	14.17	6.31	13.63	5.42	11.76	3.91
0.515	11.23	7.36	11.67	6.96	10.87	5.92	10.43	4.47
0.697	8.53	6.48	9.64	6.66	9.45	5.90	8.96	4.45
1.00	7.30	5.81	7.36	5.67	7.82	5.27	7.59	4.07
1.50	5.90	4.75	5.41	4.38	6.12	4.13	6.32	3.33
2.11	5.00	3.53	5.27	3.55	5.25	3.26	5.71	2.82
	1-Propanol in 1,4-dioxane							
	mf=0.940		mf=0.856		mf=0.790		mf=0.581	
0.356	14.90	6.12	13.83	4.02	12.63	2.79	8.19	0.85
0.515	12.63	6.94	12.63	4.98	11.89	3.67	8.20	1.13
0.697	9.79	6.85	10.54	5.64	10.96	4.28	7.94	1.51
1.00	8.23	6.36	9.15	5.53	9.20	4.63	7.51	1.93
1.50	6.21	5.21	7.19	5.03	7.47	4.43	6.81	2.21
2.11	5.52	4.43	6.05	4.38	6.57	4.17	6.22	2.32

f(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
	1-Propanol in pyridine							
	mf=0.980		*mf*=0.960		*mf*=0.947		*mf*=0.917	
0.356	15.37	7.63	15.81	7.14	16.07	6.82	16.86	6.06
0.515	12.37	8.14	13.12	7.82	13.38	7.56	14.51	7.12
0.697	9.71	7.72	10.62	7.85	10.93	7.76	12.66	7.60
1.00	7.57	6.55	9.35	7.16	8.55	6.78	9.58	6.82
1.50	5.97	5.15	6.19	5.30	6.64	5.57	7.94	5.96
2.11	4.97	4.12	5.34	4.41	5.48	4.55	6.05	4.86
	mf=0.905		*mf*=0.855		*mf*=0.719		*mf*=0.577	
0.356	16.52	6.06	17.48	4.78	17.44	2.83	16.75	1.76
0.515	14.75	6.84	15.51	6.08	16.95	3.77	16.27	2.29
0.697	12.69	7.25	13.58	6.77	15.99	4.72	15.93	3.10
1.00	9.94	6.85	11.30	6.76	14.24	5.69	14.84	4.14
1.50	7.93	5.93	8.73	6.16	12.32	6.10	13.18	4.69
2.11	6.38	4.99	7.23	5.49	10.27	5.87	12.01	5.22
	1-Butanol in benzene							
	mf=0.899		*mf*=0.806		*mf*=0.670		*mf*=0.620	
0.356	9.40	6.09	9.02	5.27			7.77	3.15
0.515	6.78	5.61	7.20	5.04	6.79	3.89	6.57	3.34
0.697	5.86	4.88	5.78	4.47	5.62	3.39	5.67	3.20
1.00	4.82	3.81	4.80	3.46	4.73	3.00	4.68	2.71
1.50	3.99	2.78	4.01	2.64	3.99	2.28	3.98	2.14
2.11	3.67	2.22	3.64	2.10	3.64	1.85	3.65	1.70
	1-Butanol in pyridine							
	mf=0.894		*mf*=0.807		*mf*=0.699		*mf*=0.568	
0.356	12.62	5.69	13.96	4.18	14.52	2.90	14.59	1.77
0.515	10.35	5.91	12.56	5.00	13.67	3.74	14.10	2.44
0.697	8.88	5.93	11.14	5.43	12.70	4.40	13.51	3.10
1.00	7.17	5.11	9.15	5.51	10.87	4.84	12.53	3.79
1.50	5.67	4.20	7.18	4.69	9.00	4.89	10.91	4.33
2.11	5.00	3.48	6.20	4.26	8.08	4.67	9.90	4.64

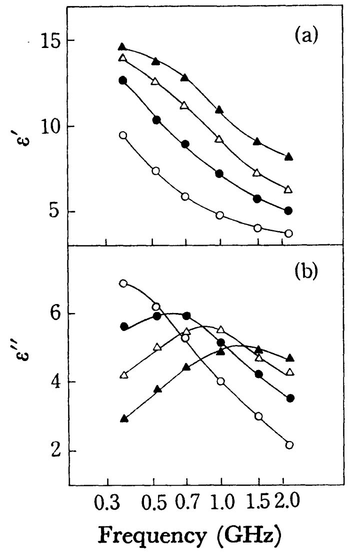

Fig. 1-1. (a) Dielectric dispersion and (b) absorption curves for 1-butanol mixtures with pyridine.
Mole fraction of alcohol
○: 1.00, ●: 0.894, △: 0.807, ▲: 0.699

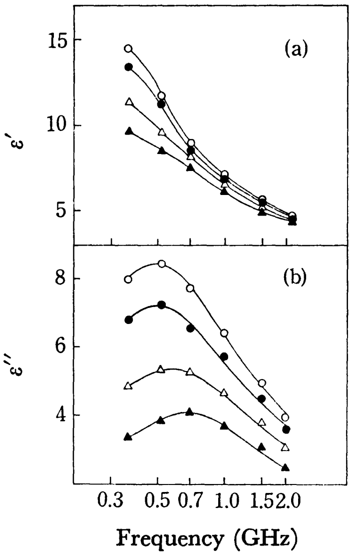

Fig. 1-2. (a) Dielectric dispersion and (b) absorption curves for 1-propanol mixtures with benzene.
Mole fraction of alcohol
○: 1.00, ●: 0.899, △: 0.741, ▲: 0.633

in two ways, that is, (1) the higher frequency data over 1 GHz are neglected and (2) all the data are taken into equal consideration. The values of α calculated from (1) are nearly equal to zero in all the mixtures, *viz.* α=0.00—0.03, while those of calculated from (2) are larger, *viz.* α=0.04—0.07. Presumably

Table 2. Values of ε_∞, $n_D{}^2$ and τ

Substance	ε_∞	$n_D{}^2$	τ ps (25.0 °C)		
			This work	Lit.[2)a)]	Lit.[8)]
1-Propanol	3.93	1.91	340	350	330
1-Butanol	3.50	1.95	505	540	480

a) Recalculated from low-frequency data and corrected to 25.0 °C.

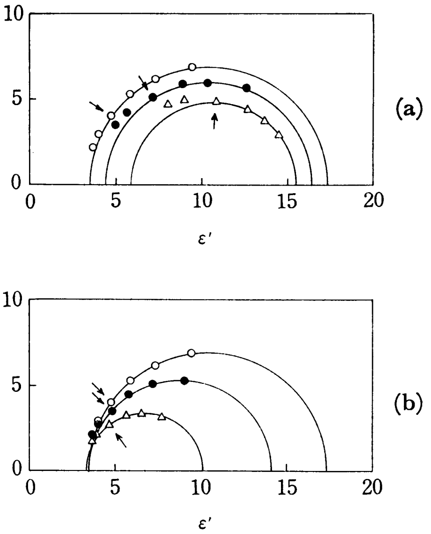

Fig. 2. Cole-Cole plots for 1-butanol mixtures with (a) pyridine and (b) benzene.
Mole fraction of alcohol
(a) ○: 1.00, ●: 0.894, △: 0.699
(b) ○: 1.00, ●: 0.806, △: 0.620
Arrows indicate the points measured at the frequency of 1.00 GHz.

the Debye dispersions observed in the frequency range lower than 1 GHz are of the principal relaxation.** The values of principal relaxation times of normal alcohols are thus determined from (1) and compared with those of the literature in Table 2.

The principal relaxation times of 1-propanol and 1-butanol against the molarity of the alcohols are plotted in Fig. 3. With increasing alcohol molarity, τ increases; in other words, decrease in τ is accompanied with decrease in the molarity, *i.e.*, with increasing amount of solvent added. It will be seen that this decrease in τ is more pronounced when hydrogen-bonding solvent, pyridine or 1,4-dioxane, is added to 1-propanol. And the plots of τ *vs.* molarity fall into the same curve A for these two solvents inspite of the fact that pyridine has a large dipole moment 2.25 D and high dielectric constant (ε=12.3)*** and 1,4-dioxane is non-polar and has a low dielectric constant (ε=2.21). In sharp contrast to this, the same plots for the addition of two non-hydrogen-bonding solvents, benzene or chlorobenzene, give the identical curve B in which the degree of decrease in τ is much smaller with decreasing molarity. Again the dipole moments μ and the dielectric constants ε differ greatly in benzene (μ=0.0 D, ε=2.27) and in chlorobenzene (μ=1.70 D, ε=5.62).

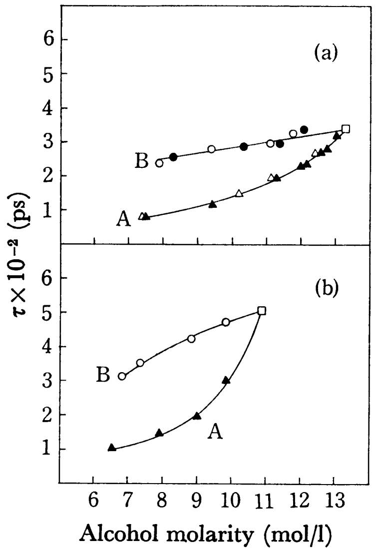

Fig. 3. Relaxation time τ *vs.* concentration for (a) 1-propanol and (b) 1-butanol mixtures with solvent.
Solvent:
○: Benzene, ●: Chlorobenzene, △: 1,4-Dioxane,
▲: Pyridine, □: Pure alcohol

The principal relaxation time of 1-butanol is studied with addition of hydrogen-bonding pyridine and non-hydrogen-bonding benzene. Again the decrease in τ is more pronounced in pyridine mixtures (curve A) than benzene mixtures (curve B).

The dependence of relaxation time upon the concentration in highly concentrated mixture of alcohols has been reported by Sarojini[9)] and Hanna *et al.*[10)] Both of these authors observed that the relaxation time did not change monotonously with the concentration. A minimum in τ was observed in 1-propanol mixture with pyridine,[9)] while a maximum was detected in 1-butanol mixture with carbon tetrachloride and with other viscous non-polar solvents.[10)] These results are inconsistent with ours. Perhaps their choice of the frequency range was inadequate for determining the pure principal relaxation, that is, they failed in eliminating the effects from other dispersions.

We wish to present our sincere thanks to Professor Mansel Davies of University College of Wales for his helpful suggestions and also correcting English in the manuscript. We also thank Toray Science Foundation for the financial aids.

References

1) S. Mizushima, This Bulletin, **1**, 163 (1926).
2) S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, **69**, 1294

** Errors due to the losses of polar solvents, *viz.* pyridine and chlorobenzne, were estimated and the relaxation times with this correction were found to be almost identical with those calculated without the correction. The relaxation times reported in the preceding letter[7)] were those of calculated from the method (2). New relaxation times calculated by use of the Debye equation (α=0) are employed in the present paper.

*** The dielectric constants cited here are those at 25.0 °C.

(1965).

3) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 2 Band, 8 Teil, Optische Konstanten.

4) A. R. von Hippel, "Dielectric Materials and Applications," John Wiley and Sons (1954).

5) R. Payne and I. E. Theodorou, *Rev. Sci. Instr.*, **42**, 218 (1971).

6) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

7) E. Arie, M. Nakamura, H. Takahashi, and K. Higasi, *Chem. Lett.*, **1973**, 533.

8) A. Sugget, P. A. Mackness, M. J. Tait, H. W. Loeb, and G. M. Young, *Nature*, **228**, 456 (1970).

9) V. Sarojini, *Trans. Faraday Soc.*, **58**, 1729 (1962).

10) F. F. Hanna and I. K. Hakim, *Z. Naturforsch.*, **26a**, 1194 (1971).