Dielectric Relaxation and Molecular Structure. X. Dielectric Behavior of 2-Propanol, 2-Methylpropanol, and 2-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 2-propanol and its mixtures with benzene, chlorobenzene, 1,4-dioxane or pyridine and 2-methylpropanol or 2-butanol and their 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 fractions of the mixtures. The principal relaxation times and the Kirkwood correlation factor g were evaluated. Variation of the principal relaxation times against the concentrations of these branched alcohol mixtures is not much different from that of normal alcohol mixtures. The g factor decreases almost monotonously with increasing amount of solvent exception being found in case for propanol–benzene mixtures.

Smyth *et al.*[1] have made dielectric measurements on several isomeric octanols in non-polar solvent (*n*-heptane). For those isomers in which a methyl group is attached to the same carbon atom as the hydroxyl group or to the adjacent carbon, the dielectric absorption is characterized by two relaxation times and the principal relaxation does not appear at the concentrations employed. However, the isomers containing a relatively less shielded hydroxyl group exhibit an additional low-frequency relaxation at the higher alcohol concentrations. Crossley *et al.*[2] have made dielectric investigation on several isomeric butanols with various solvents in a wide concentration range. He found that the basicity of the solvent plays an important role in determining the extent of self association of alcohol, that is, cyclohexane was regarded as an inert solvent and the other three solvents had a disassociating effect which increases in the order of *p*-xylene$\leq$mesitylene$<$1,4-dioxane.

We have made dielectric measurements on branched-alcohol mixtures with solvents having various properties such as different dipole moments, dielectric constants or hydrogen-bonding capacities. The side chain of those alcohols is expected to have an effect on the relaxation mechanism. The relaxation time observed in our frequency range was the principal (long) relaxation time and its variation with the concentration of solvents was examined.

Experimental

The purification of the samples has been given in the previous paper[3]. The observed refractive indices: 2-propanol n_D=1.3750, 2-methylpropanol n_D=1.3932, 2-butanol n_D=1.3945 at 25.0 °C are in agreement with the literature values[4]. The dielectric constants and losses were measured by use of the method previously described[3]. Viscosities were measured with an Ostwald type viscometer.

The Kirkwood correlation factor g is represented in the following equation[5].

$$g = \frac{9kT(\varepsilon_0-\varepsilon_\infty)(2\varepsilon_0+\varepsilon_\infty)}{4\pi N\varepsilon_0(\varepsilon_\infty+2)^2\mu_0^2} \quad (1)$$

where μ_0 is the dipole moment of the molecule, N the number of molecules per unit of volume, k the Boltzmann constant and T the absolute temperature. ε_0 and ε_∞ are the static and the high frequency dielectric constants, respectively. We used the values of ε_0 and ε_∞ obtained from the low and the high frequency intercepts of the Debye-type semicircle, respectively and μ_0 from the values in the gaseous state.[6] The values of ε_0 obtained above are compared with those measured at the frequency of 10 kHz; both are generally in good agreement.

Results and Discussion

The measurements in dielectric constants and losses are recorded in Table 1. The dispersion and absorption curves of branched-alcohol mixtures are similar to those observed in normal-alcohol mixtures. (See Fig. 1 of Ref. 3).

The principal relaxation times were calculated by the method previously employed[3] and are plotted against the concentration in Fig. 1. The trend similar to normal-alcohol mixtures is observed, that is, the plots can be grouped into two groups (curves A and B). The relaxation times of 2-propanol depend very little upon the polarity of the solvent; the dipole moments of pyridine, chlorobenzene, 1,4-dioxane, and benzene are 2.25, 1.70, 0.4, and 0.0 D in gaseous state, respectively. They are also independent of the dielectric constant (ε for pyridine, chlorobenzene, 1,4-dioxane, and benzene are 12.3, 5.62, 2.21, and 2.27 at 25 °C, respectively) and depend only upon the hydrogen-bonding capacity. These facts strongly suggest that the principal relaxation times of the alcohol may be mainly dominated by hydrogen bonding of alcohol molecules.

A similar study on the relaxation times for 2-butanol dioxane mixture was reported by Sakellaridis and Hinopoulos.[7] Their relaxation times are, however, much lower than those of our experiment: possibly it may come from their measurement at the single frequency of 9.3 GHz.

The separation between curves A and B is not the same for all the alcohols. This separation is more pronounced in 1-propanol** than in 2-propanol, while

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

** Data for 1-propanol and 1-butanol are given in Ref. 3.

Table 1(a). Dielectric constant and loss of pure alcohols at 25.0 °C

Substance f(GHz)	2-Propanol		2-Methylpropanol		2-Butanol	
	ε'	ε''	ε'	ε''	ε'	ε''
0.356	13.77	7.58	8.10	6.74	9.23	6.44
0.515	10.28	7.81	6.31	5.80	7.20	5.90
0.697	8.44	7.31	5.06	4.71	5.77	4.98
1.00	6.18	5.76	4.24	3.47	4.67	3.83
1.50	4.57	4.23	3.60	2.52	3.97	2.88
2.11	4.07	3.36	3.43	1.92	3.62	2.21

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''
	2-Propanol in benzene							
	mf=0.900		mf=0.827		mf=0.742		mf=0.618	
0.356	12.56	6.01	11.96	5.01	10.58	3.76	8.75	2.34
0.515	10.36	6.44	10.05	5.51	9.19	4.40	7.80	2.83
0.697	8.46	6.36	8.25	5.60	7.76	4.66	6.99	3.24
1.00	6.85	5.49	6.39	4.87	6.25	4.22	5.72	3.21
1.50	4.75	4.16	5.01	3.90	4.85	3.47	4.74	2.70
2.11	4.25	3.39	4.10	2.95	4.23	2.93	4.19	2.35
	2-Propanol in chlorobenzene							
	mf=0.937		mf=0.894		mf=0.814		mf=0.625	
0.356	12.86	6.46	13.11	5.79	12.21	4.48	9.97	2.16
0.515	10.91	6.90	10.85	6.27	10.43	5.10	9.18	2.76
0.697	8.30	6.53	8.94	6.24	8.73	5.18	8.44	2.97
1.00	6.72	5.57	6.58	5.26	7.27	4.73	7.45	2.97
1.50	5.18	4.26	5.43	4.27	5.88	3.85	6.40	2.75
2.11	4.51	3.36	4.69	3.35	5.16	3.29	5.90	2.48
	2-Propanol in 1,4-dioxane							
	mf=0.919		mf=0.856		mf=0.769		mf=0.601	
0.356	13.38	5.44	12.73	3.80	11.15	2.39	7.85	0.91
0.515	11.50	6.05	11.47	4.67	10.43	3.08	7.59	1.15
0.697	9.66	6.32	9.85	5.24	9.62	3.72	7.33	1.43
1.00	7.18	5.56	8.13	5.08	8.18	3.83	6.90	1.76
1.50	5.54	4.64	6.24	4.52	6.60	3.77	6.04	2.03
2.11	4.70	3.76	5.23	3.83	5.66	3.54	5.50	2.21
	2-Propanol in pyridine							
	mf=0.912		mf=0.822		mf=0.752		mf=0.550	
0.356	15.08	5.86	16.00	4.09	16.07	3.09	15.49	1.44
0.515	13.11	6.59	14.64	5.13	15.14	4.04	15.19	2.26
0.697	10.44	6.71	13.13	5.87	14.27	4.58	14.85	2.62
1.00	8.62	6.28	10.94	6.01	12.24	5.46	14.03	3.40
1.50	6.60	5.23	8.59	5.75	10.18	5.46	12.65	4.19
2.11	5.44	4.55	7.39	5.24	8.55	5.39	11.50	4.98
	2-Methylpropanol in benzene							
	mf=0.888		mf=0.799		mf=0.664		mf=0.609	
0.356	8.36	6.06	8.43	5.14	7.86	3.65	7.42	2.96
0.515	6.69	5.35	6.67	4.83	6.51	3.71	6.33	3.10
0.697	5.47	4.55	5.39	4.21	5.44	3.31	5.30	2.97
1.00	4.42	3.47	4.46	3.26	4.49	2.78	4.52	2.46
1.50	3.71	2.56	3.81	2.51	3.89	2.19	3.85	2.01
2.11	3.44	1.96	3.45	1.96	3.53	1.74	3.52	1.62
	2-Methylpropanol in pyridine							
	mf=0.904		mf=0.801		mf=0.701		mf=0.619	
0.356	11.49	6.03	13.54	3.98	14.12	2.98	14.21	2.12
0.515	9.38	6.09	12.08	5.03	13.11	3.76	13.64	2.98
0.697	7.74	5.56	10.62	5.46	12.31	4.44	12.90	3.68
1.00	6.36	4.72	8.73	5.14	10.54	4.78	11.76	4.13
1.50	5.07	3.72	6.99	4.50	8.11	4.84	10.10	4.52
2.11	4.53	3.11	5.90	4.11	7.68	4.59	8.88	4.56

f(GHz)	ε'	ε''	ε'	ε''	ε'	ε''	ε'	ε''
	2-Butanol in benzene							
	mf=0.897		mf=0.809		mf=0.675		mf=0.533	
0.356	9.23	5.34	8.95	4.25	7.86	2.52	6.04	1.31
0.515	7.38	5.36	7.42	4.41	6.87	2.74	5.78	1.51
0.697	5.85	4.47	5.96	4.02	5.93	2.96	5.21	1.62
1.00	4.64	3.64	5.01	3.42	4.99	2.57	4.80	1.60
1.50	3.92	2.80	4.10	2.71	3.98	2.06	4.09	1.53
2.11	3.52	2.20	3.68	2.10	3.73	1.83	3.77	1.35
	2-Butano lin pyridine							
	mf=0.900		mf=0.809		mf=0.699		mf=0.616	
0.356	11.56	5.31	12.99	3.76	13.52	2.51	13.49	1.72
0.515	9.60	5.55	11.71	4.51	12.80	3.10	13.03	2.42
0.697	8.06	5.37	10.28	4.92	11.86	3.80	12.59	3.14
1.00	6.56	4.54	8.57	4.70	10.10	4.25	11.54	3.63
1.50	5.25	3.71	6.89	4.33	8.79	4.38	9.44	4.43
2.11	4.59	3.15	5.89	3.93	7.72	4.32	8.85	4.48

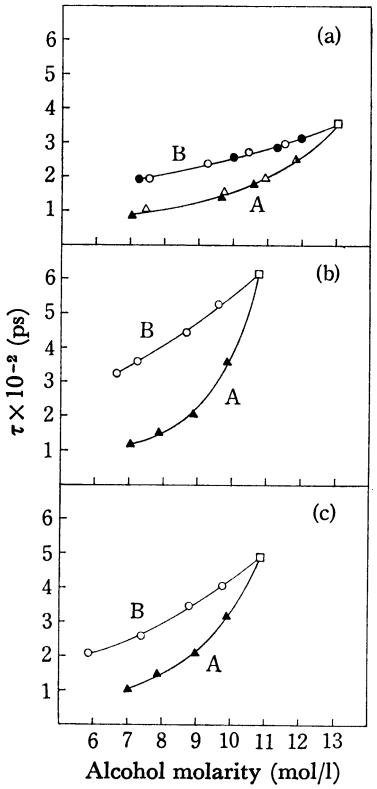

Fig. 1. Relaxation time τ *vs.* concentration for (a) 2-propanol, (b) 2-methylpropanol and (c) 2-butanol mixtures with solvent.
Solvent:
○: Benzene, ●: Chlorobenzene, △: *p*-Dioxane,
▲: Pyridine, □: Pure alcohol

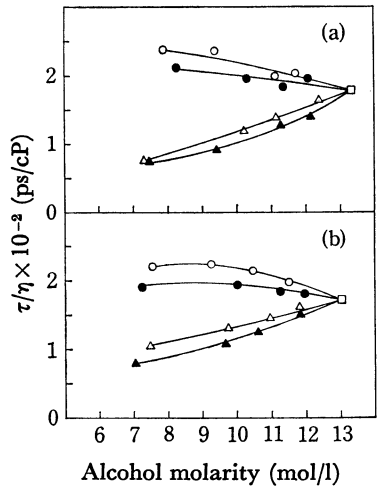

Fig. 2. Reduced relaxation time τ/η *vs.* concentration for (a) 1-propanol and (b) 2-propanol mixtures with solvent. Same notations as in Fig. 1.

for 1-butanol** and 2-methyl propanol it is similar to each other, being much diminished in 2-Butanol Thus, the relaxation process of normal alcohols is more strongly effected by hydrogen-bonding capacity of solvents than that of *iso* and *secondary* alcohols in which hydrogen bonding of the hydroxyl group is hindered by the screening effect of side chains.

The reduced relaxation time τ/η in which τ is the relaxation time and η is the viscosity of the mixture is considered. Plots of τ/η against the molarity are shown in Fig. 2. We find four curves in Fig. 2 instead of two curves A and B in Fig. 1. Again in the pyridine and 1,4-dioxane mixtures the decrease in τ/η, which represents the volume of rotating units in the Stokes assumption, is sharper with increasing amount of solvent than that in the benzene and chlorobenzene mixtures.

Figure 3 shows the Kirkwood correlation factor g against the concentration of mixture. The values of g were calculated by means of Eq. (1). A large value of g, a parameter for the self association, is found in the pure liquid alcohols, and the value of g decreases with increasing amount of solvent (see Fig. 3). At infinite dilution, or, for free molecules g is equal to unity.[2] Small g values less than the unity found *e.g.*, in pyridine mixtures, might reveal the formation of multimers having smaller dipole moments than the free monomer. Further, if the g factor represents the short-range interaction of molecules, the observed decrease in g would suggest that the degree of this interaction decreases in dilution. It will be seen that the decrease is sharpest in case of the mixture with hydrogen-bonding pyridine (ε=12.3, μ=2.25 D) and followed by

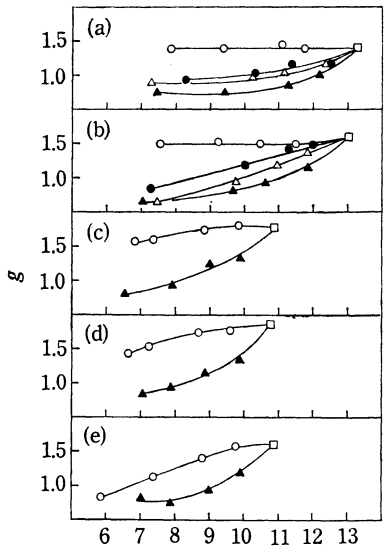

Fig. 3. Kirkwood correlation factor g *vs.* concentration for (a) 1-propanol, (b) 2-propanol, (c) 1-butanol, (d) 2-methylpropanol and (e) 2-butanol mixtures with solvent. Same notations as in Fig. 1.

another hydrogen-bonding 1,4-dioxane (ε=2.21, μ=0.4 D), non-hydrogen-bonding chlorobenzene (ε=5.62, μ=1.7 D) and benzene (ε=2.27, μ=0.0 D). This order of decrease in g agrees with that in reduced relaxation time in Fig. 2. This would suggest that the multimer is associated with the volume of rotating unit. The fact that g is almost independent of the concentration in propanol–mixtures with benzene would indicate that the interaction between alcohol and solvent molecule does not change with dilution.

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

References

1) J. Crossley, L. Glasser, and C. P. Smyth, *J. Chem. Phys.*, **55**, 2197 (1971).
2) G. E. Rajala and J. Crossley, *Can. J. Chem.*, **49**, 3617 (1971).
3) T. Koshii, E. Arie, M. Nakamura, H. Takahashi and K. Higasi, This Bulletin **47**, 618 (1974).
4) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 2 Band, 8 Teil, Optische Konstanten.
5) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).
6) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company (1963).
7) P. Sakellaridis and B. Hinopoulos, *J. Appl. Chem. Biotechnol.*, **22**, 1077 (1972).