BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1317—1318 (1975)

Dielectric Relaxation and Molecular Structure. XIV. The Dielectric Behavior of Six Isomeric Pentyl Alcohols

Hiroshi Sato, Taro Koshii, Hiroaki Takahashi, and Keniti Higasi
Department of Chemistry, Waseda University, Shinjuku, Tokyo 160

(Received October 17, 1974)

Synopsis. The dielectric constants and losses of six isomeric pentyl alcohols have been measured in the frequency range of 1—0.35 GHz at 25 °C. The relaxation times of these alcohols decrease with an increase in the steric hindrance of the hydroxyl group.

Low-frequency measurements at room temperature showed that both the dielectric constants, ε_0, and the Kirkwood correlation factors, g, decrease with an increase in the steric hindrance of the hydroxyl groups of butanol,[1,2] heptanol,[3,4] and octanol.[5] Few repotrs are available, however, regarding the dependence of the relaxation times upon the isomeric configuration, especially in the liquid state at room temperature.[5-7] Emphasis will be placed in this report on the dielectric relaxation of six isomeric pentyl alcohols at 25 °C.

Experimental

Commercial chemicals were dehydrated by the usual methods and were fractionally distilled prior to their use. In order to check the purity of the samples, the refractive indices for the Na D line were measured with a Pulfrich refractometer. Both the boiling points and the refractive indices of the purified samples were in good agreement with the literature values[8,9]; 1-pentanol, bp=138.2—140.0 °C, $n_D=1.408$; 3-methyl-1-butanol, bp=131.0—131.2 °C, $n_D=1.406$; 2-pentanol, bp=118.8—119.2 °C, $n_D=1.405$; 3-pentanol, bp=113.6—115.0 °C, $n_D=1.408$; 3-methyl-2-butanol, bp=112.2 °C, $n_D=1.407$; and 2-methyl-2-butanol, bp=102.8—103.2 °C, $n_D=1.403$.

The dielectric constants and losses were measured at the frequencies of 0.356, 0.515, 0.601, 0.697, 0.807, and 1.00 GHz by the use of an UHF apparatus of the coaxial-slotted-line type.[10] The relaxation time, τ, and the limiting low- and high-frequency dielectric constants, ε_0 and ε_∞ respectively, were calculated on the basis of the Debye equation.[11] This is because the Debye equation has been found to be valid for the principal, low-frequency dispersion of any mono-alcohol[5,10,12,13] ever studied in the liquid state. The Kirkwood correlation factor, g,[14] was calculated by the use of ε_0 and ε_∞ in the following equation:

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

The g values thus obtained are denoted by $g(\varepsilon_0,\varepsilon_\infty)$, which are also compared with the $g(\varepsilon_0,n_D{}^2)$ values obtained by substituting $n_D{}^2$ for ε_∞. Since the exact value of the dipole moment, μ_0, in the liquid state is still unknown, we tentatively assumed the value of $\mu_0=1.66$ D obtained by the dilute-solution method.[15]

Results and Discussion

Debye semicircles are plotted from the dielectric data obtained for six isomers of pentyl alcohols (Fig. 1). The relaxation time, τ, and the limiting low- and high-frequency dielectric constants, ε_0 and ε_∞ respectively, in the Debye equation are listed in Table 1, together with the Kirkwood correlation factor, g. The static dielectric constants, ε_0, from the literature for 1-pentanol are 13.9[16] and 14.6,[13]* for 3-methyl-1-butanol, 14.7,[16] and for 2-methyl-2-butanol, 5.82.[16] It should be noted that these values compare fairly well with the observed limiting values, which are not entirely free from error because of the large extrapolation. The relaxation time, τ, for 1-pentanol is also in fair agreement with the literature values, 7.5×10^2 ps[13]* and 7.6×10^2 ps.[17]* The differences between ε_∞ and $n_D{}^2$ are 1.1—1.3 for all the isomeric alcohols, which seems to reveal that there exists no essential difference in the high-frequency absorption.

1-Pentanol, which has the least sterically hindered OH group, has the largest ε_0, while the smallest ε_0 is found for 2-methyl-2-butanol, with the most sterically hindered OH group. The static dielectric constants decrease with an increase in the degree of steric hindrance. Of the two g values, $g(\varepsilon_0,n_D{}^2)$ is larger than $g(\varepsilon_0,\varepsilon_\infty)$; both $g(\varepsilon_0,n_D{}^2)$ and ε_0 decrease with an increase in the amount of steric hindrance of the hydroxyl group; similar trends have been observed by other workers[1-4] for other mono-alcohols.

The dielectric relaxation time, τ, decreases in the

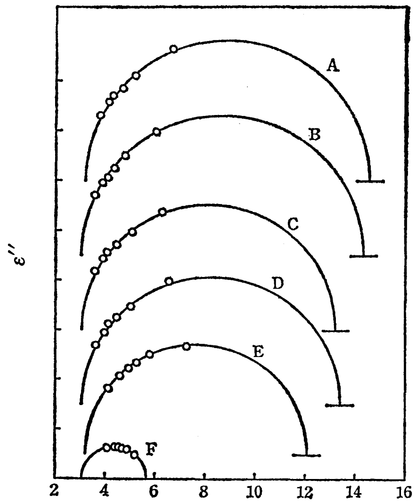
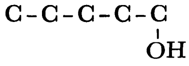
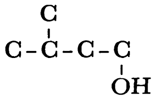
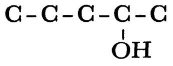
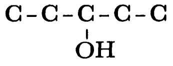
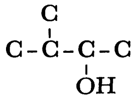
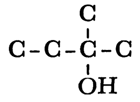


Fig. 1. Semi-circle plots for liquid isomeric pentanols at 25 °C.
A: 1-pentanol, B: 3-methyl-1-butanol, C: 2-pentanol, D: 3-pentanol, E: 3-methyl-2-butanol, F: 2-methyl-2-butanol.

---

* These values were obtained by the interpolation or extrpolation of the literature values given at different temperatures.

Table 1. The relaxation times, τ, the limiting low- and high-frequency dielectric constants, ε_0 and ε_∞ respectively, the differences, $\varepsilon_\infty - n_D^2$, and two Kirkwood correlation factors, g, for six isomeric pentyl alcohols at 25 °C

	1-Pentanol	3-Methyl-1-butanol	2-Pentanol	3-Pentanol	3-Methyl-2-butanol	2-Methyl-2-butanol
	 $\mathrm{C{-}C{-}C{-}C{-}}\underset{\mathrm{OH}}{\mathrm{C}}$	 $\mathrm{C{-}}\overset{\mathrm{C}}{\mathrm{C}}\mathrm{{-}C{-}}\underset{\mathrm{OH}}{\mathrm{C}}$	 $\mathrm{C{-}C{-}C{-}}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}C}$	 $\mathrm{C{-}C{-}}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}C{-}C}$	 $\mathrm{C{-}}\overset{\mathrm{C}}{\mathrm{C}}\mathrm{{-}}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}C}$	 $\mathrm{C{-}C{-}}\overset{\mathrm{C}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{{-}C}$
$\tau(\times 10^{-2}$ ps)	6.7	7.4	6.5	6.5	4.8	2.0
ε_0	14.6	14.3	13.2	13.4	12.1	5.7
ε_∞	3.2	3.0	3.0	3.1	3.3	3.1
$\varepsilon_\infty - n_D^2$	1.2	1.1	1.1	1.1	1.3	1.1
$g(\varepsilon_0, \varepsilon_\infty)$	1.8	1.9	1.7	1.7	1.4	0.5
$g(\varepsilon_0, n_D^2)$	3.3	3.2	3.0	3.0	2.7	1.1

order of: the primary pentyl alcohols (1-pentanol $\tau=6.7\times10^2$ ps, 3-methyl-1-butanol $\tau=7.4\times10^2$ ps)> secondary pentyl alcohols (2-pentanol $\tau=6.5\times10^2$ ps, 3-pentanol $\tau=6.5\times10^2$ ps, 3-methyl-2-butanol $\tau=4.8\times10^2$ ps)> tertiary pentyl alcohol (2-methyl-2-butanol $\tau=2.0\times10^2$ ps). In a preceding paper[18] we found, in contrast to this, that the relaxation time for tertiary butyl alcohol ($\tau=5.3\times10^2$ ps) is longer than that for normal butyl alcohol ($\tau=5.1\times10^2$ ps) at 25 °C. The longer relaxation time of the former than that of the latter may be associated with the considerable viscosity of the former. If we take the reduced relaxation time, τ/η, instead of τ, it will be found that τ/η decreases in the order of: primary butyl alcohols (1-butanol $\tau/\eta=2.0\times10^2$ ps/cP,** 2-methyl-1-propanol $\tau/\eta=1.9\times10^2$ ps/cP**)>secondary butyl alcohol (2-butanol $\tau/\eta=1.4\times10^2$ ps/cP***)> tertiary butyl alcohol (2-methyl-2-propanol $\tau/\eta=1.1\times10^2$ ps/cP**). For isomeric pentyl alcohols, a similar trend exists in the reduced relaxation time; *e.g.*, primary pentyl alcohol (3-methyl-1-butanol $\tau/\eta=2.0\times10^2$ ps/cP**)>secondary pentyl alcohol (3-methyl-2-butanol $\tau/\eta=1.4\times10^2$ ps/cP**)>tertiary pentyl alcohol (2-methyl-2-butanol $\tau/\eta=0.6\times10^2$ ps/cp**).

References

1) W. Dannhauser and R. H. Cole, *J. Chem. Phys.*, **23**, 1762 (1955).

2) W. Dannhauser and L. W. Bohe, *ibid.*, **40**, 3058 (1964).

3) J. Middelhoek and C. J. F. Böttcher, "Molecular Relaxation Processes," Chem. Soc., Spec. Publ., 20, p. 69 (1966).

4) P. Bordewijk, F. Gransch, and C. J. F. Böttcher, *Trans. Faraday Soc.*, **66**, 293 (1970).

5) W. Dannhauser and A. F. Flueckinger, *Phys. Chem. Liquids*, **2**, 37 (1970).

6) W. Dannhauser, *J. Chem. Phys.*, **48**, 1918 (1968).

7) J. Crossley, L. Glasser, and C. P. Smyth, *ibid.*, **55**, 2197 (1971).

8) Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik," 2 Band, 8 Teil, Optische Konstanten (1962).

9) E. W. Washburn, "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," NRC McGraw-Hill Book Co., Inc., New York and London (1926).

10) T. Koshii, E. Arie, M. Nakamura, H. Takahashi, and K. Higasi, This Bulletin, **47**, 618 (1974).

11) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, Toronto, and London (1955), p. 56.

12) *ibid.*, p. 105.

13) S. K. Garg and C. P. Smyth, *J. Phys. Chem.*, **69**, 1294 (1965).

14) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

15) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco and London (1963).

16) A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular 514 (1951).

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

18) H. Sato, T. Koshii, H. Takahashi, and K. Higasi, *Chem. Lett.*, **1974**, 579.

19) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Pub. Co., Inc. (1950).

** η from the Critical Table.[9]

*** η from Timmermans.[19]