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Dielectric Behavior and Intermolecular Association for Octanol Isomers. Existence and Transformation of a Nonpolar Cyclic Polymer

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The equilibrium dielectric constants of ten isomeric $C_8H_{17}OH$ and binary mixtures of 1-butanol in four isomeric $C_8H_{17}OH$ have been measured at temperatures from 135 to −55 °C. These isomeric $C_8H_{17}OH$ can be grouped roughly into three types, namely, more polar, intermediate, and more sterically hindered alcohols. The dielectric behavior of each of the three types can be explained by equilibrium among a linear hydrogen-bonded chain polymer (**CHAIN**), a free monomer inclusive of a chain dimer and trimer (**MONOMER**), and a nonpolar cyclic polymer (**RING**). As the temperature decreases, **MONOMER** transforms into **CHAIN** for more polar alcohols. Two transformations, **MONOMER** into **RING** at high temperatures and **RING** into **CHAIN** at low temperatures, occur for intermediate alcohols. **MONOMER** transforms into **RING** and **CHAIN** can not be observed for more hindered alcohols. However, a transformation of **RING** into **CHAIN** can be observed by adding 1-butanol to the more hindered alcohols. **CHAIN** is most stable. When formation of **CHAIN** becomes difficult, **RING** can be formed. The transformation is dependent on temperature, molecular geometry, and the amount of 1-butanol in the mixture.

In general, the equilibrium dielectric constants for many compounds increase monotonically with decreasing temperature. However, it is well-known that the dielectric constant for a carboxylic acid decreases conversely with decreasing temperature because of the formation of a nonpolar cyclic dimer. For liquid alcohols, temperature dependence of the dielectric constant indicates a complex and interesting behavior. Dielectric studies have indicated the formation of various hydrogen-bonded species by intermolecular association in pure alcohols and dilute solutions of alcohols. Smyth and Stoops[1] measured the equilibrium dielectric constants for various isomeric $C_8H_{17}OH$ and explained the dielectric complex behavior by molecular orientation. Dannhauser[2] measured the interesting dielectric behavior for 8 isomeric $C_8H_{17}OH$. He analyzed the behavior by the Kirkwood–Fröhlich equation[3,4] and introduced a molecular model which consists of monomers in equilibrium with nonpolar ring dimers and with chain polymers. For various secondary and tertiary alcohols at 15, 25, and 35 °C, we obtained four concentrations, **CHAIN** (C_1), a chain dimer and trimer (C_2), a free monomer (C_3), and **RING** (C_R), by means of a modified Kirkwood–Fröhlich equation.[5,6] An extrapolation of these concentrations to the high- and low-temperature portions was used to explain the complex dielectric behavior for the temperature dependence of the dielectric constant.

The existence of **RING** has been postulated for more sterically hindered alcohols. It is evident that the variable and complex dielectric behavior is attributed to the existence of **RING**. However, there has been little experimental evidence for the existence of **RING** in order not to contribute to the dielectric constant. Therefore, we measured binary mixtures of 1-butanol in some isomeric $C_8H_{17}OH$ to investigate the existence of **RING** and the transformation of **RING** into **CHAIN**.

Experimental

Purification of Materials. Commercial alcohols were fractionally distilled twice, as described in a previous paper.[6]

Apparatus. The equilibrium dielectric constants were measured by making use of a ratio-arm transformer bridge (Ando Electric Co. Type TR-10) at the frequency range of 3—1000 kHz. The cell is a three terminal guarded electrode arrangement of gold-plated brass with Teflon insulation. The cell was made by reference to those reported by Hassion and Cole[7] and Dannhauser and Bahe.[8] The capacitance of the cell is 5.05 pF. The temperature control was maintained within ±0.5 °C.

Results and Discussion

Temperature Dependence of Equilibrium Dielectric Constants (ε_0). Our data shown in Fig. 1 are qualitatively similar to those of eight isomeric $C_8H_{17}OH$ measured by Dannhauser.[2] These isomers have approximately the same dipole moment and the same molecular volume, though the relative positions of the hydroxyl and methyl groups are different. Figure 1, however, shows a variety and complexity of dielectric behavior for these isomeric $C_8H_{17}OH$. This variety and complexity can be attributed to a difference of the hydrogen-bonded species formed by intermolecular association. If it is assumed that all alcohol molecules exist as free monomers, the ε_0 can be calculated from the Kirkwood–Fröhlich equation.[3,4] The behavior of the ε_0 is shown in Fig. 1 as a dotted

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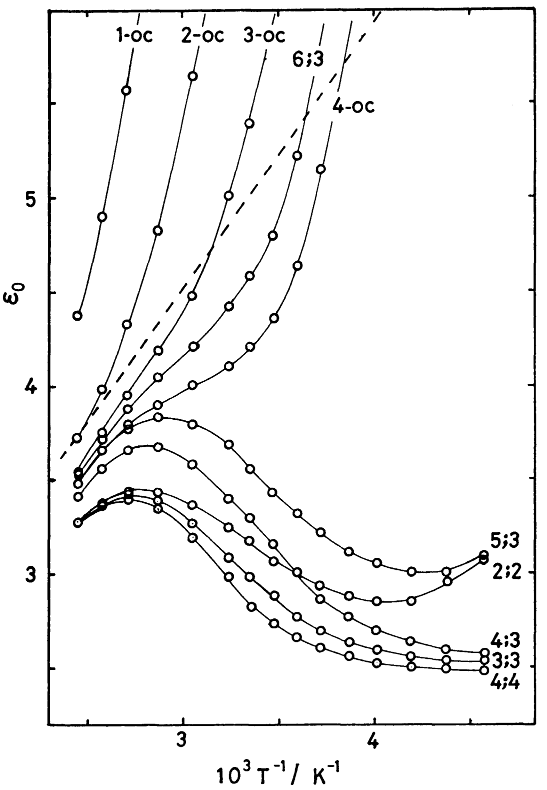

Fig. 1. Equilibrium dielectric constants as a function of reciprocal absolute temperature for ten isomeric $C_8H_{17}OH$. Octanol, 6-methyl-3-heptanol, and 4-methyl-4-heptanol are abbreviated to oc, 6;3, and 4;4, respectively. Dotted line shows a calculated dielectric constant, when all molecules exist as free monomers.

line. In this equation, the limiting high-frequency dielectric constant ($\varepsilon_\infty = \varepsilon_3$) for the third region was evaluated by using $(\varepsilon_\infty - 1)/(\varepsilon_\infty + 2) = (n_D^2 - 1)(1 + 0.19)/(n_D^2 + 2)$, as described before.[9]

For the isomeric $C_8H_{17}OH$, the behavior of ε_0 can be grouped roughly into three types and explained by estimation of the relative concentrations of the C_{1-R}. A chain dimer and trimer could not be distinguished from a free monomer by the temperature dependence of ε_0. Therefore, **MONOMER** described hereunder includes the existence of a chain dimer and trimer.

The dielectric behavior of the first type is typical of more polar alcohols, such as 1-octanol shown in Fig. 1. The ε_0 is larger than that of the dotted line even at high temperatures and increases linearly with decreasing temperature. This observation indicates that **CHAIN** can be formed at the high temperatures. We established that for 1-octanol at 25 °C the percentages of the C_1, C_3, and C_R are 69, 26, and 5% of the gross concentration, respectively. The C_1 increases and the C_3 decreases because of the transformation of **MONOMER** into **CHAIN**, as the temperature decreases. The ε_0–$1/T$ curve can be explained by an equilibrium between **MONOMER** and **CHAIN**.

The second type consists of intermediate alcohols, such as 4-octanol and 5-methyl-3-heptanol. The ε_0 is smaller than that of the dotted line at high temperatures. Therefore, **RING** can be formed at the high temperatures. For 5-methyl-3-heptanol at 15 °C, the percentages of the C_1, C_3, and C_R are 8, 16, and 76%, respectively. The C_3 decreases and the C_R increases, as the temperature decreases. The C_1 could not be obtained at 25 and 35 °C, since they are small values. The ε_0–$1/T$ curve for 5-methyl-3-heptanol indicates a complex and interesting curve. The ε_0 at first increases with decreasing temperature and becomes a maximum at about 75 °C ($1/T = 2.87 \times 10^{-3}\,K^{-1}$) and then decreases conversely with decreasing temperature. Additionally, the ε_0 becomes a minimum at about −40 °C ($1/T = 4.29 \times 10^{-3} K^{-1}$), and increases again with decreases temperature. Therefore, it is necessary to consider the coexistence of **MONOMER**, **RING**, and **CHAIN**, especially, inclusive of two transformations of **MONOMER** into **RING** at high temperatures and of **RING** into **CHAIN** at low temperatures.

The behavior of the third type is typical of more sterically hindered alcohols, such as 3-methyl-3-heptanol and 4-methyl-4-heptanol. The ε_0's for these tertiary alcohols are nearly equal at 135 °C ($1/T = 2.45 \times 10^{-3}\,K^{-1}$) and are smaller than that of the dotted line at high temperatures. The ε_0–$1/T$ curve has a maximum at about 80 °C ($1/T = 2.83 \times 10^{-3}\,K^{-1}$). The maximum for the tertiary alcohols appears at higher temperature than that for the secondary alcohols, because of the ease of the transformation of **MONOMER** into **RING**. For 3-methyl-3-heptanol at 25 °C, the percentages of the C_1, C_3, and C_R are 0, 22, and 78%, respectively. **CHAIN** can not exist at temperatures between 135 and −55 °C. The C_3 decreases and the C_R increases, as the temperature decreases. The third type shows the equilibrium between **MONOMER** and **RING**.

Binary Mixtures of 1-Butanol in Some Isomeric $C_8H_{17}OH$. When 1-butanol is added to the three types of isomeric $C_8H_{17}OH$, the ε_0–$1/T$ curve for the mixtures differs from that of the pure octanol.

The ε_0–$1/T$ curves for mixtures of 1-butanol in 1-octanol are shown in Fig. 2, together with the dotted line. The ε_0 of pure 1-octanol increases linearly with decreasing temperature, since **CHAIN** can be formed even at high temperatures. The ε_0–$1/T$ curve for the mixture increases in parallel over the temperatures from 135 °C to a freezing point or −55 °C, as 1-butanol is added to 1-octanol. It can be considered that the **CHAIN** formed is composed of both 1-butanol and 1-octanol molecules because the ε_0 increases approximately in proportion to the 1-butanol concentration. Therefore, the first dispersion can be explained by a single relaxation process for binary mixtures of normal alcohols.[10,11]

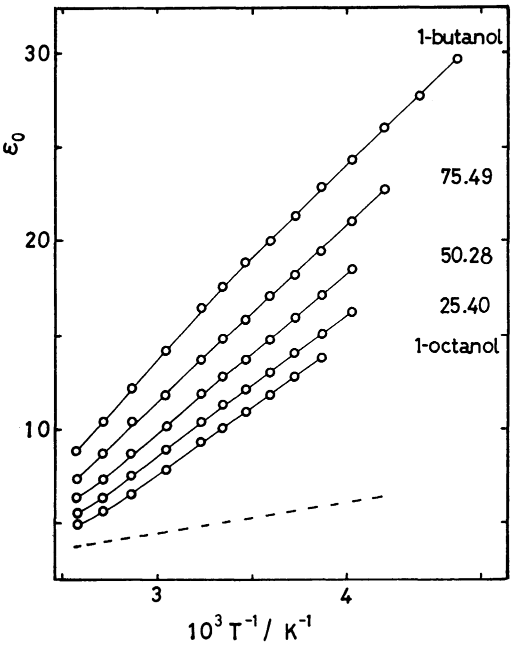

Fig. 2. Equilibrium dielectric constants as a function of reciprocal absolute temperature for the mixtures of 1-butanol in 1-octanol. Number is mol% of 1-butanol.

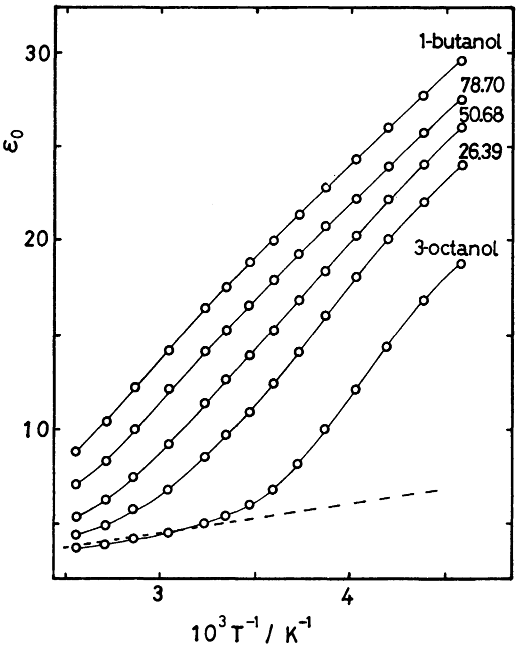

Fig. 3. Equilibrium dielectric constants as a function of reciprocal absolute temperature for the mixtures of 1-butanol in 3-octanol. Number is mol% of 1-butanol.

The ε_0–$1/T$ curves for mixtures of 1-butanol in 3-octanol are shown in Fig. 3. The ε_0 of pure 3-octanol at high temperatures is smaller than that of the dotted line and increases gradually as shown by the dotted line with decreasing temperature. For pure 3-octanol at 25 °C ($1/T=3.35\times10^{-3}\,K^{-1}$), the percentages of the C_R, C_3, and C_1 are 51, 25, and 24%, respectively. The C_R and C_3 decrease and the C_1 increases, as the temperature decreases. Figure 3 shows that **MONOMER** and **RING** coexist at high temperatures and that the transformation of **MONOMER** and **RING** into **CHAIN** occurs, since the ε_0 of pure 3-octanol increases suddenly at about 25 °C. It favors the formation of **CHAIN** at temperatures below about 25 °C. As 1-butanol is added to 3-octanol, the transformation occurs at higher temperatures, namely, at about 25 °C for pure 3-octanol, at about 70 °C ($1/T=2.91\times10^{-3}$ K^{-1}) for 26 mol% mixture of 1-butanol, and at about 110 °C ($1/T=2.61\times10^{-3}\,K^{-1}$) for 50 mol% mixture of 1-butanol.

The ε_0–$1/T$ curves are shown in Fig. 4 for mixtures of 1-butanol in 4-methyl-4-heptanol and in Fig. 5 for solutions of 1-butanol in heptane in order to emphasize the difference of the dielectric behavior between 4-methyl-4-heptanol and heptane. The ε_0–$1/T$ curve for pure 4-methyl-4-heptanol is similar to that for pure heptane which is a nonpolar solvent. The ε_0 is slightly larger than that of heptane because of the existence of **MONOMER** having a dipole moment. As described above, **CHAIN** can not be formed for pure 4-methyl-4-heptanol over the temperatures from 135 to −55 °C. For 26 mol% mixture of 1-butanol in 4-methyl-4-heptanol, however, the ε_0 at high temperatures increases as indicated by the dotted line with decreasing temperature. It becomes smaller than that of the dotted line over the temperature range of 72—−29 °C and then increases suddenly at about −29 °C ($1/T=4.10\times10^{-3}\,K^{-1}$), although ε_0 of the 25 mol% solution of 1-butanol in heptane hardly changes over the temperature range. This observation can be explained by two transformations of **MONOMER** into **RING** at high temperatures and **MONOMER** and **RING** into **CHAIN** at low temperatures. In a 50 mol% mixture of 1-butanol in 4-methyl-4-heptanol, the transformation of **MONOMER** into **CHAIN** occurs at higher temperatures. The ε_0 of 4-methyl-4-heptanol mixtures is larger than that of heptane solution at the same concentration of 1-butanol and at the same temperature. This difference of ε_0 indicates that the transformation of **RING** into **CHAIN** occurs by the addition of 1-butanol.

At a fixed temperature of −55 °C ($1/T=4.58\times10^{-3}$ K^{-1}), the ε_0 of the binary mixtures are plotted in Fig. 6 against mol% of 1-butanol. Since the ε_0 of pure 3-octanol is 18.68 at this temperature, almost every molecule exists as **CHAIN** in both pure 3-octanol and mixtures of 1-butanol in 3-octanol. It is noticeable that the ε_0 of the mixtures is larger than that of pure normal alcohols at the same concentration of the hydroxyl group. Figure 6 also shows that the ε_0 is 2.48 for pure 4-methyl-4-heptanol and 2.00 for pure heptane. The difference, 2.48—2.00, suggests the

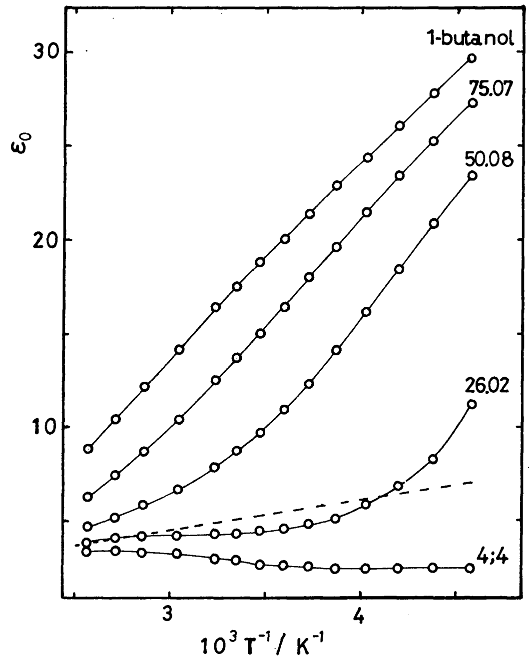

Fig. 4. Equilibrium dielectric constants as a function of reciprocal absolute temperature for the mixtures of 1-butanol in 4-methyl-4-heptanol (4;4). Number is mol% of 1-butanol.

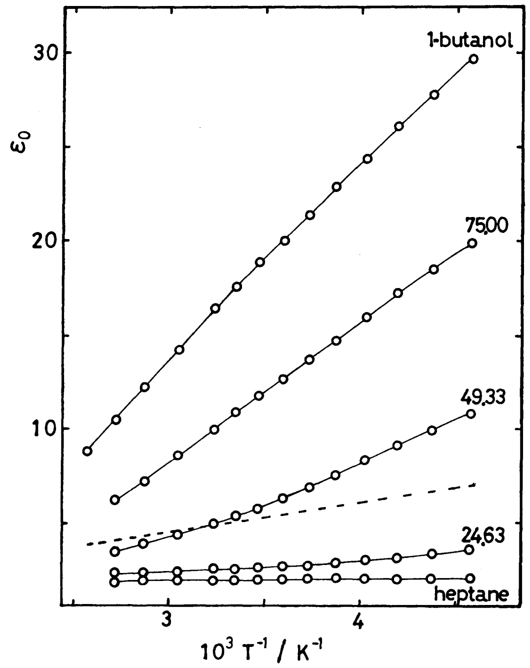

Fig. 5. Equilibrium dielectric constants as a function of reciprocal absolute temperature for the solutions of 1-butanol in heptane. Number is mol% of 1-butanol.

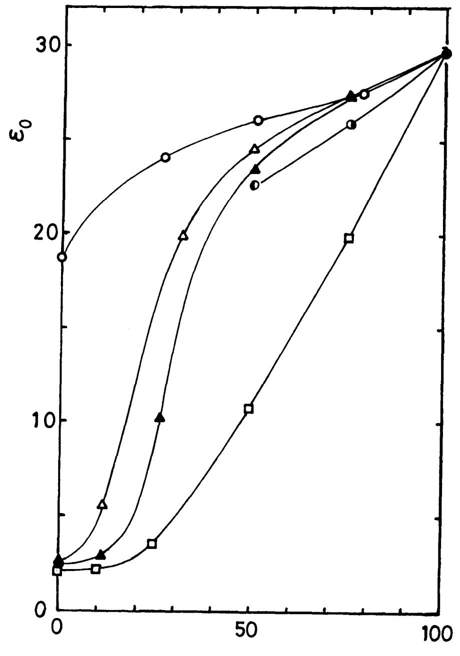

Fig. 6. Equilibrium dielectric constants as a function of mol% of 1-butanol at −55 °C. ○: 1-butanol–3-octanol, △: 1-butanol–4-methyl-3-heptanol, □: 1-butanol–heptane, ▲: 1-butanol–4-methyl-4-heptanol, ◑: pure 1-pentanol, ◐: pure 1-hexanol.

existence of **MONOMER** in pure 4-methyl-4-heptanol. As 1-butanol is added to 4-methyl-4-heptanol, ε_0 increases suddenly at about 30 mol% mixture of 1-butanol. The ε_0 of 50 mol% mixture becomes 23.3 and is larger than 22.5 of pure 1-hexanol having the same concentration of the hydroxyl group, although the ε_0 is 10.9 for 50 mol% solution of 1-butanol in heptane. Therefore, almost every molecule in the 50 mol% mixture is considered to be **CHAIN**, being the same as that in pure normal alcohol. The variation of ε_0, shown in Fig. 6, provides experimental evidence of the existence of **RING**. The mechanism of the transformation of **RING** into **CHAIN** can be envisioned by addition of 1-butanol to some isomeric $C_8H_{17}OH$. For the mixtures of 1-butanol in 4-methyl-4-heptanol at this temperature, for example, **CHAIN** can hardly exist for the 20 mol% mixture which consists of four molecules of 4-methyl-4-heptanol to one of 1-butanol. **CHAIN** can be formed suddenly for 25 and 33 mol% mixtures which are in the molecular ratios of 3:1 and 2:1, respectively. It may be considered that a ring trimer and a ring dimer transform into a chain tetramer and a chain trimer inclusive of one molecule of 1-butanol, respectively. A chain pentamer can not exist because of the repulsion of two alkyl groups of 4-methyl-4-heptanol in both sides of the linear hydrogen-bonded chain. The chain tetramer and chain trimer formed may associate into a chain octamer and chain 3*n*-mer, respectively.

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