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Dielectric Relaxation and Molecular Structure. XIII. The Dielectric Behavior of Mixtures of 1-Propanol with Hydrogen-bonding and Non-hydrogen-bonding Solvents

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The dielectric constants and losses of 1-propanol and its mixtures with benzene, chlorobenzene, 1,4-dioxane, and pyridine have been measured in the frequency range of 1—0.35 GHz in the temperature range of 10—40 °C. The concentrations of the mixture lie between 1—0.6 mol fractions of the alcohol. The dielectric relaxations of the observed systems in the above frequency range are all of the Debye type. The measured data were used to calculate the activation enthalpy, ΔH^*, and the entropy, ΔS^*. The dependence of ΔH^* and ΔS^* upon the concentration differs with the nature of the solvent. Both ΔH^* and ΔS^* decrease upon the addition of a hydrogen-bonding solvent, while they increase slightly upon the addition of a non-hydrogen-bonding solvent. The mechanism of the principal relaxation of 1-propanol is discussed on the basis of these observations.

Since Mizushima[1] made his classic study of alcohols, the dielectric properties of mono-alcohols have been extensively investigated by a number of workers using a wide range of both frequencies and temperatures. The dielectric dispersions of primary aliphatic alcohols in the liquid state are now known to have three different absorptions.[2] The most important of these absorptions is the principal Debye-type dispersion on the low-frequency side; it is regrettable, however, that we have still no reliable explanation for the true mechanism of this principal dispersion.

The activation enthalpy, ΔH^*, and the entropy, ΔS^*, have been well studied for liquid alcohols,[3,4] but seldom for solutions except for those in non-polar solvents.[5,6]

In the preceding papers,[7,8] dielectric measurements at 25 °C were described. In this report, we shall deal with the dielectric measurements of 1-propanol in the same set of solvents (benzene, chlorobenzene, 1,4-dioxane, and pyridine) and in the same frequency range at four or three temperatures; we shall also discuss the ΔH^* and ΔS^* derived therefrom. Emphasis will be placed upon the solvent interactions of the alcohol with hydrogen-bonding solvents.

Experimental

The experimental materials were purified as described previously.[7] The dielectric constants and losses were measured by the use of a UHF apparatus of the coaxial-slotted-line type, the details of which were given in a preceding report.[7] The relaxation time, τ, and the limiting low- and high-frequency dielectric constants, ε_0 and ε_∞ respectively, were calculated from the Debye equation (1):

$$\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \tag{1}$$

by an iterative method using an electronic computer. In order to determine the activation enthalpy, ΔH^*, and the entropy, ΔS^*, from the temperature dependence of the relaxation time, τ, $\log_{10}(\tau T)$ was plotted against $1/T$ using Eq. (2)[9]:

$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H^* - T\Delta S^*}{RT}\right) \tag{2}$$

where h, k, and R are the Planck, the Boltzmann, and the gas constants respectively, and where T is the absolute temperature. A straight line fitting best with the points was obtained by the use of the least-square method. ΔH^* was obtained from the slope of this line, and ΔS^*, from its intercepts with the $\log_{10}(\tau T)$ axis.

Results

The Cole-Cole plots[10] for 1-propanol mixtures with benzene and pyridine are shown in Fig. 1. It may be seen that almost all the measured points lie exactly on the Debye semicircles; hence, they can be considered to be associated with the principal dispersions of the alcohols.[7]

The low- and the high-frequency intercepts of the Debye semicircle with the ε' axis, ε_0 and ε_∞, are compared with the static dielectric constants, ε_0, and the square of refractive indices, n^2 (for the H_α-line) in the literature respectively, in Tables 1 and 2. The low-frequency intercepts, ε_0, obtained in this work are in fair agreement with the real static dielectric constants, ε_0 (Table 1), while the high-frequency intercepts, ε_∞, are much larger than the squares of the refractive indices, n^2 (Table 2). The appreciable differences, $\varepsilon_\infty - n^2$, are due to the existence of minor dispersions of alcohols in the higher-frequency range.[2] In Fig. 1(a), we find that the limiting high-frequency dielectric constants, ε_∞, remain almost constant with an increase in

Table 1. Limiting low frequency dielectric constants ε_0 of liquid 1-propanol

Temp. (°C)	ε_0 (This work)	ε_0 (Literatures)			
10.0	21.0±0.2	(22.2)[11]	(22.6)[12]	(22.8)[13]	
20.0	20.9±0.5	20.8[11]	21.1[12]	(21.2)[13]	21.3[3]
30.0	19.6±0.2	19.4[11]	(19.8)[12]	19.7[13]	
40.0	18.9±0.3	18.2[11]	18.5[12]	18.4[13]	

The values in parentheses were obtained from the literature by inter- or extrapolation of values given at different temperatures.

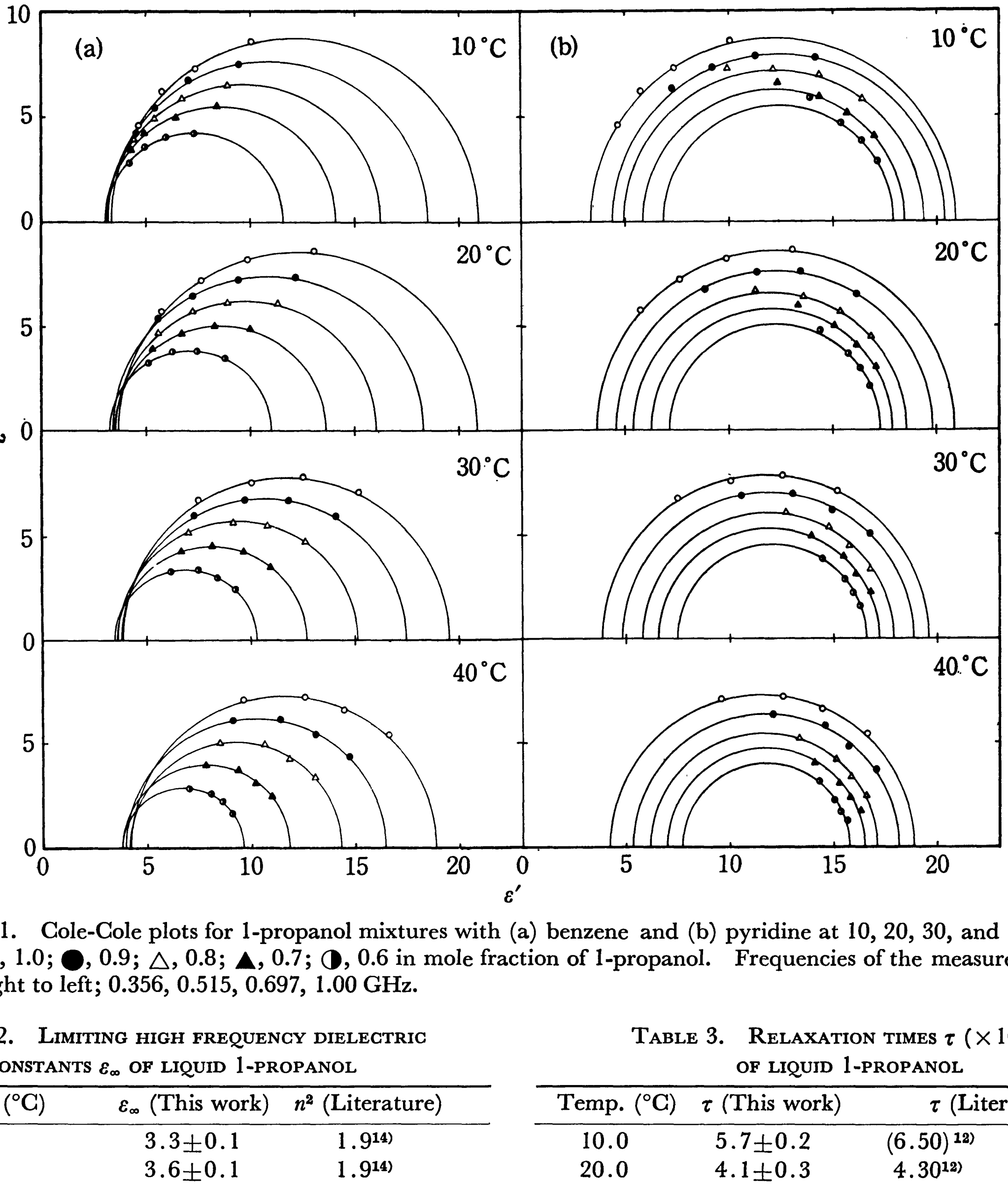

Fig. 1. Cole-Cole plots for 1-propanol mixtures with (a) benzene and (b) pyridine at 10, 20, 30, and 40 °C. ○, 1.0; ●, 0.9; △, 0.8; ▲, 0.7; ◑, 0.6 in mole fraction of 1-propanol. Frequencies of the measurement, right to left; 0.356, 0.515, 0.697, 1.00 GHz.

Table 2. Limiting high frequency dielectric constants ε_∞ of liquid 1-propanol

Temp. (°C)	ε_∞ (This work)	n^2 (Literature)
10.0	3.3±0.1	1.9[14]
20.0	3.6±0.1	1.9[14]
30.0	3.8±0.1	1.9[14]
40.0	4.2±0.1	1.9[14]

Table 3. Relaxation times τ ($\times 10^{-2}$ ps) of liquid 1-propanol

Temp. (°C)	τ (This work)	τ (Literatures)	
10.0	5.7±0.2	(6.50)[12]	
20.0	4.1±0.3	4.30[12]	5.31[3]
30.0	2.8±0.2	(3.34)[12]	
40.0	2.0±0.2	2.86[12]	

Regarding the values in parentheses see the note below Table 1.

the amount of non-polar solvent (benzene), while in Fig. 1(b) they increase considerably with an increase in the polar solvent (pyridine). The difference in the latter parallels the amount of pyridine added and must be due largely to the main dispersion of pyridine* in the high-frequency region.[11]

The dependence of the dielectric relaxation time, τ, upon the concentration is examined in Fig. 2. The relaxation times, τ, decrease gradually and linearly in mixtures with benzene (a), while they decrease sharply in mixtures with pyridine (b), the curves becoming concave in the latter mixtures. The dependence of the relaxation time upon the concentration in mixtures with chlorobenzene (●) seems to coincide with that in mixtures with benzene (○), while the points for mixtures with 1,4-dioxane (▲) lie on the curves for mixtures with pyridine (△).

The principal relaxation times, τ, of liquid 1-propanol are recorded in Table 3, together with those obtained by other workers. The disagreement with the literature[12] values might be due to the difference in the frequency ranges; the frequency range of this study is higher than in most of the works concerned.

Some representative plots of $\log_{10}(\tau T)$ against $1/T$ are shown in Fig. 3. The ΔH^* and ΔS^* values obtained are plotted against the concentration of the alcohol in Fig. 4. For liquid 1-propanol, ΔH^* is obtained as 5.5 kcal/mol, which compares well with the literature values of 5.0,[12] 5.3,[3] 5.4,[5] 5.5[4] kcal/mol, while the ΔS^* of the present work, 1.7 e.u., lies between the values of 1.2[12] and 2.1[3]—3.0[5] e.u. of the other workers.

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* See also the first footnote on errors on page 621 in a preceding report.[7]

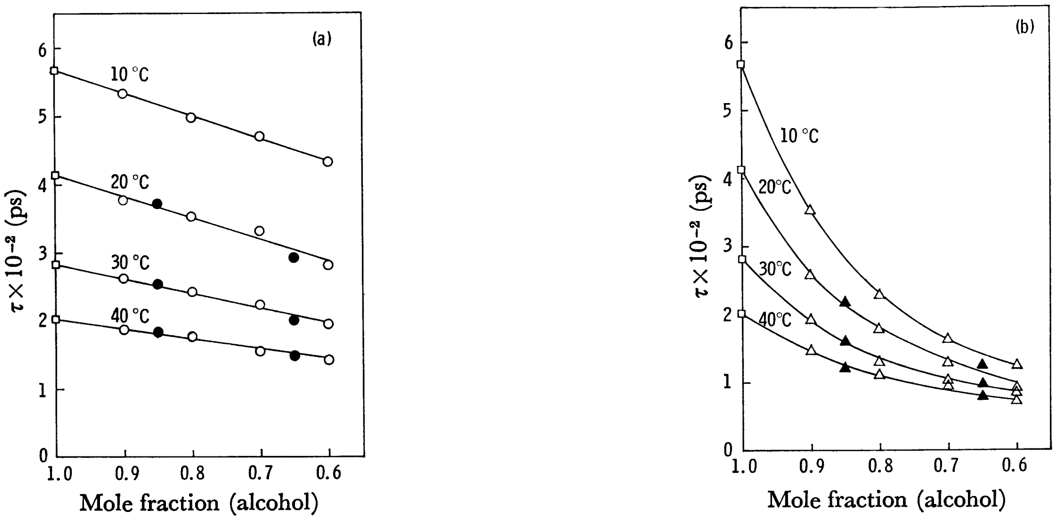

Fig. 2. Variation of relaxation time τ with concentration (for 1-propanol mixtures with solvents). (a) Non-hydrogen-bonding: ○, benzene; ●, chlorobenzene; (b) hydrogen-bonding: ▲, 1,4-dioxane; △, pyridine. □, Pure alcohol.

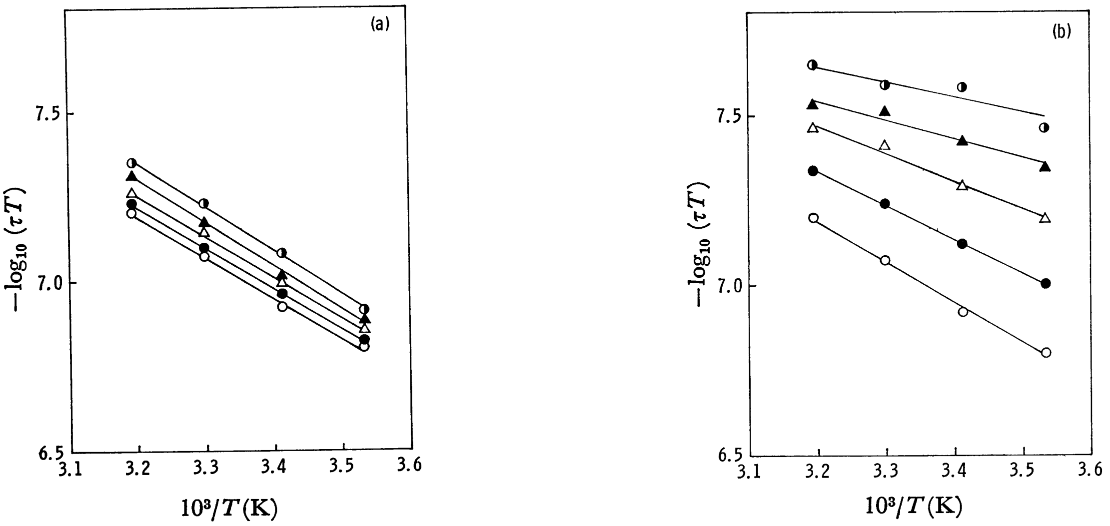

Fig. 3. Plots of $\log_{10}(\tau T)$ against $1/T$ for 1-propanol mixtures with (a) benzene and (b) pyridine. ○, 1.0; ●, 0.9; △, 0.8; ▲, 0.7; ◑, 0.6 in mole fraction of alcohol.

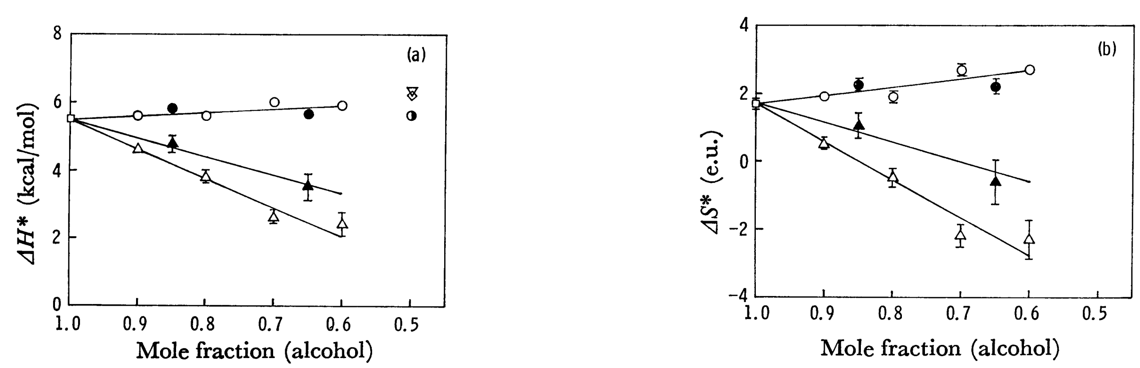

Fig. 4. Variation of (a) ΔH^* and (b) ΔS^* with the concentration (for 1-propanol mixtures with a variety of solvents). This work: ○, benzene; ●, chlorobenzene; △, pyridine; ▲, 1,4-dioxane; □, pure alcohol. From Gemert[5]: ◇, benzene; ◑, hexane; ▽, cyclohexane and carbon tetrachloride. N. B., Φ indicates limits of assessed accuracy of measurement.

Discussion

The activation enthalpies, ΔH^*, and the entropies, ΔS^*, obtained in the present experiment are plotted against the concentration of propyl alcohol, in Fig. 4. We find that both ΔH^* and ΔS^* increase slightly upon the addition of benzene or chlorobenzene. On the contrary, though, these two parameters decrease rapidly with the amount of hydrogen-bonding solvent; moreover, the decrease upon dilution with pyridine is more pronounced than that with 1,4-dioxane.

Polar chlorobenzene ($\mu=1.7$ D) has a high dielectric constant ($\varepsilon_0=5.62$), while non-polar benzene has a low dielectric constant ($\varepsilon_0=2.27$). 1,4-Dioxane is similar to benzene in having a low dielectric constant ($\varepsilon_0=2.21$) and a low polarity ($\mu=0$—0.4 D), while pyridine has $\varepsilon_0=12.3$ and $\mu=2.25$ D. It is evident at a glance at Fig. 4 that neither the static dielectric constant nor the polarity of the solvent play any important role in the relaxation processes.

The size of the solvent relative to that of the alcohol will be considered next. Since the molar volumes of benzene (M.V.=89) and chlorobenzene (M.V.=102) are larger than that of 1-propanol (M.V.=75), a larger size of the solvent might be expected to increase these parameters.[5,6] However, this expectation is not supported here; the two hydrogen-bonding solvents also have larger molar volumes than 1-propanol—*i.e.*, 1,4-dioxane has M.V.=85 and pyridine M.V.=81. The size of the solvent relative to that of the alcohol is, thus, not an important factor in the observed relaxation processes.

Changes in the ΔH^* on the addition of non-polar solvents have been well studied. For a number of normal alcohols (methanol, ethanol, 1-propanol, 1-butanol, and 1-heptanol), Gemert *et al.*[5] found that ΔH^* becomes higher on the addition of non-polar, inert solvents (benzene, carbon tetrachloride, cyclohexane, and hexane); their finding on a benzene solution for propyl alcohol is in good agreement with the present observation. A similar increase in the ΔH^* on dilution with cyclohexane was observed,[6] while decreases on dilution with non-polar solvents have also been reported and discussed.[15–17]

Recently, the dielectric properties of solutions of water in straight-chain heptanols were studied by Tjia,[18] who concluded that the relaxation times of these alcohols decrease upon an addition of a small amount of water and that the energy of activation also decreases with an increase in the quantity of water added—the latter statement was definitely proved for both heptanol-2 and heptanol-4. His observation seems to be parallel with our results for propanol mixtures with hydrogen-bonding solvents.

In order to explain why the principal dielectric relaxation of mono-alcohols is of a pure Debye type, Brot,[19,20] and Bauer and Magat[21] introduced a hypothesis that hydrogen-bond breaking is the controlling step in this relaxation and that the activation energy for the principal lower-frequency relaxation must be identical with the energy necessary to break the hydrogen bond.

The so-called switch-over mechanism was introduced by Sagal,[6] who stated: "The hydrogen bond will break when another molecule approaches with its oxygen atom oriented favorably for a switch. It is reasonable to assume that the presence of this third oxygen atom will lower the energy barrier for breaking the hydrogen bond." According to this assumption, the addition of a non-hydrogen-bonding solvent (benzene or chlorobenzene) to alcohols would increase the energy necessary to break the hydrogen bond, because it would decrease the possibility of the approach of a third oxygen atom for a switch over. Contrary to this, the addition of a strongly hydrogen-bonding solvent (1,4-dioxane or pyridine) would provide a new possibility of a switch over to the electronegative atom of the solvent; hence, this would help lower the energy of activation. Sagal's mechanism seems to agree partially with the observations of this work. Furthermore, we note that the variations in ΔH^* and ΔS^* with the two different kinds of solvents are all in the same direction with those of the g factors and the reduced relaxation times, τ/η.[8] However, we shall have to refrain from discussing the possible mechanism in detail since we do not have sufficient evidence at present.

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