

A comparative dielectric relaxation study between hydrogen- and non-hydrogen-bonded liquids: Nitriles vs alcohols

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Abstract. Dielectric properties of nitriles have been studied using time domain reflectometry in the frequency range of 10 MHz to 10 GHz over the temperature range of 0°C to 45°C. The calculated dielectric relaxation parameters are compared with values for the corresponding n-alcohols. The dielectric behaviour in n-nitrile systems is quite different from the corresponding behaviour in n-alcohols. The dipoles in n-nitrile systems show a tendency to remain antiparallel, unlike in alcohol systems. The activation energy decreases with the increase of molecular size, whereas in hydrogen bonded liquid it increases.

Keywords. N-nitriles; dipoles; relaxation times-microwaves; dielectrics.

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1. Introduction

Structural information about n-alcohols in the liquid state has been extensively studied through dielectric relaxation measurements [1–3]. Three features with respect to the number of carbon atoms N_C , in n-alcohols have been observed.

- (1) An increase in the Kirkwood correlation factor with N_C : this indicates that the n-alcohols with larger N_C become more ordered in the liquid phase.
- (2) Increase of the relaxation time with N_C : this indicates a slower rotation for the heavier molecules, and
- (3) Increase of the activation energy with N_C : this indicates that the hydrogen bonded energy strengthens with increase in N_C .

The above features have been associated with hydrogen bonding. This study on the nitriles was undertaken to determine the role of dipole moment in the above mentioned features. Nitriles were studied because (1) many nitriles exist in the liquid state at room temperature, (2) these are not hydrogen bonded and (3) they have large dipole moments. The dielectric constant results are available only for acetonitrile [4] and butanenitrile [5]. The dielectric properties on seven n-nitriles with $N_C = 1$ to 5, 7, 9 and 10 are determined in this work.

In § 2, the experiment is described. The results and conclusions are given in § 3.

2. Experimental

All the nitriles was obtained from BDH spectrograde with 99% purity and are used without further purification.

The dielectric spectra were obtained by the time domain reflectometry (TDR) technique [6, 7]. In the TDR technique a fast rising step pulse of about 25 ps generated by S-52 pulse generator and was transmitted through 3.5 mm coaxial line with characteristic impedance 50 ohms. The sample cell has been placed at the end of the transmission line after the sampling head. The SMA (Standard Military Application) type cell was used for the work. The cell had outer and inner dimensions of 3.5 mm and 1.52 mm, respectively. The effective pin length of inner conductor was 1.35 mm. The Tektronix 7854 sampling oscilloscope was used to sample the reflected pulse. The time window used for the experiment was kept 5 ns. The reflected pulse was digitized with 1024 points in the selected time window and transferred to personal computer (PC/XT) through IEEE-488 card. The complex reflection function ρ^* of the sample liquids were determined through Fourier transforming the measured reflected pulse [7-10]. The spectra show the single Debye relaxation type as expected [11]. The complex dielectric spectra obtained are fitted to the Debye equation

$$\varepsilon^* = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (1)$$

with ε_0 and τ as fitting parameters. In the fitting procedure, ε_∞ is not fitted and assumed to be 3.5. This is done because the data are not sensitive to ε_∞ in the frequency range under consideration. The details are given in an earlier paper [12].

3. Results and discussion

The values of static dielectric constant (ε_0) and relaxation time (τ) at different temperatures are given in tables 1 and 2 respectively. The static dielectric constants of acetonitrile [4] ($\varepsilon_0 = 35.9$) and butanenitrile [5] ($\varepsilon_0 = 20.2$) as reported earlier are in good agreement with the values reported here.

In general, ε_0 decreases with increase in the number of carbon atoms. This decrease can be ascribed to decrease of dipoles per unit volume with an increase in the size of the

Table 1. Static dielectric constant ε_0 for n-nitrile at different temperature.

Nitrile	ε_0				
	$t = 0^\circ\text{C}$	$t = 10^\circ\text{C}$	$t = 25^\circ\text{C}$	$t = 35^\circ\text{C}$	$t = 45^\circ\text{C}$
Acetonitrile	40.0 (1)	38.2 (1)	36.9 (1)	36.1 (1)	33.7 (3)
Butanenitrile	26.2 (1)	24.3 (4)	22.0 (2)	21.1 (1)	20.3 (1)
Pentanenitrile	23.0 (1)	21.5 (1)	21.0 (2)	19.1 (1)	11.3 (1)
Hexanenitrile	18.1 (1)	18.0 (1)	16.3 (1)	16.0 (1)	14.2 (1)
Octanenitrile	14.7 (1)	13.2 (1)	13.0 (1)	12.2 (1)	10.8 (2)
Decanenitrile	11.4 (1)	11.0 (1)	10.6 (1)	10.4 (1)	10.2 (1)
Undecanenitrile	*	11.0 (1)	10.3 (1)	9.1 (1)	9.1 (5)

* not studied.

Number in bracket denotes uncertainties in the last significant digits obtained by the least squares fit method. For ex. 40.1 (1) means 40.1 ± 0.1 . The realistic errors in the values is about 2% considering other experimental aspects.

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Table 2. Relaxation time τ for n-nitrile at different temperature.

Nitrile	τ (ps)				
	$t = 0^\circ\text{C}$	$t = 10^\circ\text{C}$	$t = 25^\circ\text{C}$	$t = 35^\circ\text{C}$	$t = 45^\circ\text{C}$
Acetonitrile	6.4 (7)	3.6 (1)	3.4 (1)	2.7 (1)	1.3 (8)
Butanenitrile	10.2 (3)	9.9 (5)	8.9 (7)	8.0 (4)	6.7 (5)
Pentanenitrile	16.8 (4)	14.4 (2)	13.0 (2)	11.3 (1)	10.9 (1)
Hexanenitrile	28.2 (3)	22.0 (3)	17.4 (4)	16.3 (2)	14.2 (3)
Octanenitrile	45.0 (4)	36.6 (3)	31.4 (3)	25.6 (2)	22.0 (3)
Decanenitrile	84.8 (13)	73.7 (3)	67.5 (8)	53.6 (2)	49.2 (4)
Undecanenitrile	*	76.8 (5)	64.6 (1)	62.6 (1)	58.7 (5)

* not studied

Table 3. Kirkwood correlation factor g at different temperatures.

Nitrile	g				
	$t = 0^\circ\text{C}$	$t = 10^\circ\text{C}$	$t = 25^\circ\text{C}$	$t = 35^\circ\text{C}$	$t = 45^\circ\text{C}$
Acetonitrile	0.87 (5)	0.86 (5)	0.88 (5)	0.89 (5)	0.85 (5)
Butanenitrile	0.80 (4)	0.76 (4)	0.73 (4)	0.72 (4)	0.71(4)
Pentanenitrile	0.74 (4)	0.71 (4)	0.73 (4)	0.68 (4)	0.66 (4)
Hexanenitrile	0.72 (4)	0.74 (4)	0.70 (4)	0.71 (4)	0.64 (4)
Octanenitrile	0.72 (4)	0.66 (4)	0.68 (4)	0.66 (4)	0.59 (3)
Decanenitrile	0.65 (4)	0.65 (4)	0.65 (4)	0.66 (4)	0.66 (4)
Undecanenitrile	*	0.69 (4)	0.67 (4)	0.62 (3)	0.61 (3)

Number in brackets denote errors in least significant digits by assuming 2% error in the values of ϵ_0 and ϵ_∞ .

molecules. Structural information can be obtained from the Kirkwood correlation factor [13], g , as

$$g = \frac{4\pi N\mu^2}{9kTV} = \frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)(\epsilon_\infty + 2)} \quad (3)$$

where μ is the dipole moment, N/V is number density and ϵ_∞ is the square of the refractive index. The values of ρ and ϵ_∞ have been taken at 25°C , from the Aldrich Catalog handbook of Chemical [14]. The values of g obtained by the Kirkwood Frohlich [13] equation is given in table 3. The values of g are less than one, indicating that the dipoles are oriented in antiparallel direction. As the size of the molecule increases, the values of g further decreases. The tendency to remain antiparallel increases with increase of chain size in the molecule. This tendency is due to dipole-dipole interactions between two molecules.

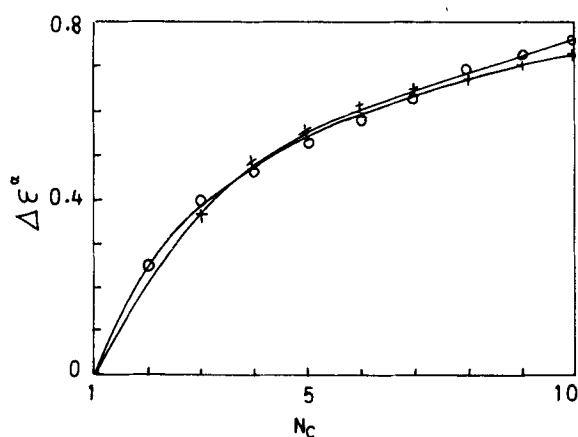


Figure 1. Plot of relative change in ϵ_0 , $\Delta\epsilon_0$ with number of carbon atoms in n-nitriles and n-alcohols at 25°C. (O), OH; (+), CN

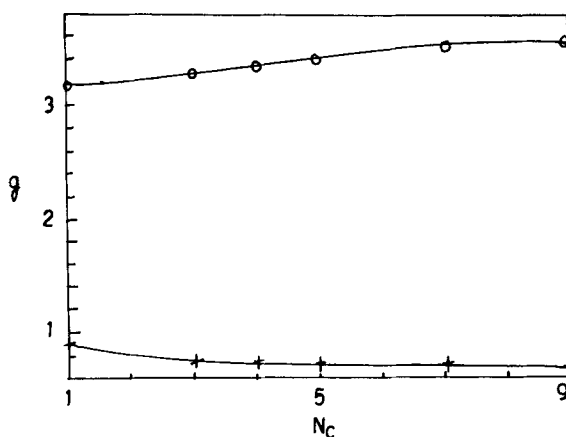


Figure 2. Plot of Kirkwood correlation factor vs number of carbon atoms for n-nitriles and n-alcohols at 25°C. (O), (OH); (+), CN

It will be interesting to compare the results with the corresponding results of hydrogen bonded liquids, like alcohols. The figure 1 shows the plot of change in $\Delta\epsilon^a$ with the number of carbon atoms in n-nitriles and n-alcohols [3, 4].

The value of $\Delta\epsilon^a$ is defined as

$$\Delta\epsilon^a = \frac{(\epsilon_0)_{N_c=0}^a - (\epsilon_0)_{N_c=0}^a}{(\epsilon_0)_{N_c=0}^a} \quad (4)$$

where $(\epsilon_0)_N^a$ is the value of the static permittivity for the system with N carbon atoms. The g values are given in figure 2. It shows that the g values decrease with N_c in nitrile systems. It remains almost constant in alcohol systems.

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The change in relaxation times, $\Delta\tau$, for alcohol and nitrile systems are shown in figure 3.

The value of $\Delta\tau$ is defined as

$$\Delta\tau = (\tau)_{N_{c=0}}^a - (\tau)_{N_{c=0}}^a \quad (5)$$

where $(\tau)_N^a$ is the relaxation time for the system a with N carbon atoms.

In figure 3, the change in relaxation in alcohols is larger than corresponding values in nitriles. This may be because of the $-OH$ group in alcohol which is a hydrogen bonded liquid. As the chain is long and as there is the strong hydrogen bonding with neighbouring molecules, relaxation time tends to increase with number of carbon

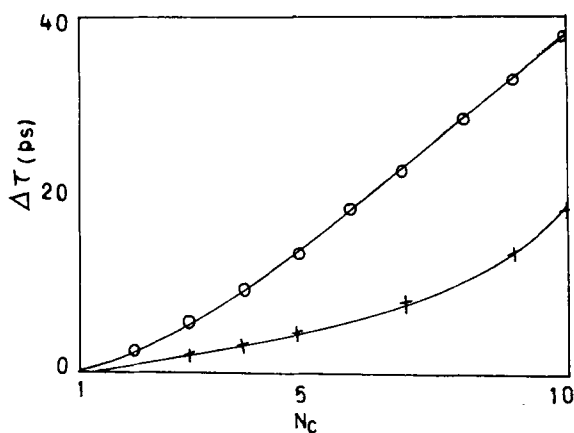


Figure 3. Plot of relative change in τ , $\Delta\tau$ with number of carbon atoms in n-nitriles and n-alcohols at 25°C. (O), (OH); (+), CN

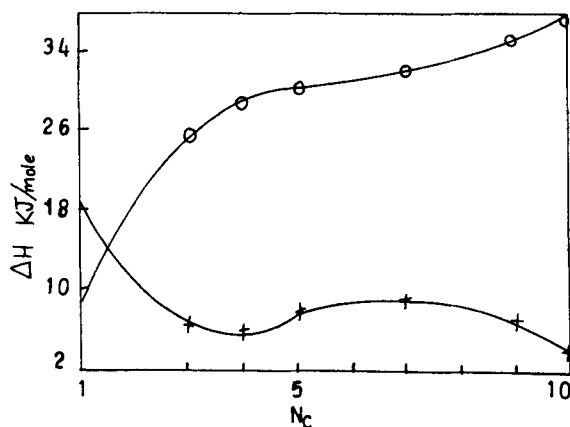


Figure 4. Plot of activation energies (ΔH) KJ/mole vs number of carbon. (O), (OH); (+), CN

atoms. In case of nitriles though chain is long, there is no such strong bonding with neighbouring molecules.

The activation energies were calculated from Eyring equation [15]. The activation energies are associated with dipole-dipole interaction. The results are shown in figure 4 along with the corresponding values for n-alcohol systems [2, 3]. It can be seen that nitrile system behave in a very different manner. This may be because of the fact that the activation energies in nitrile systems are due to the dipole-dipole interactions, whereas, in alcohol systems it may be due to the hydrogen bonding. It is interesting to note that the trend in the activation energy is similar to the trend as observed in the (*g*) factor, related to the cooperative effect. The higher correlation factor leads to the higher value of the activation energy.

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