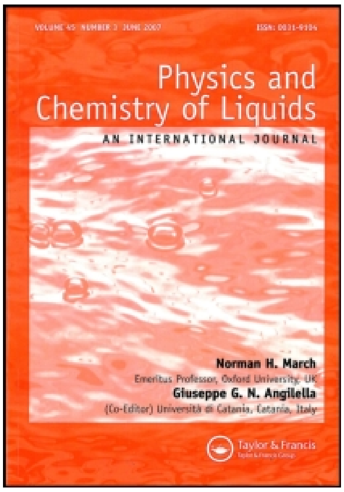

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Dielectric relaxation study of *N*-methyl formamide with glycols using time domain reflectometry technique

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Dielectric relaxation study of *N*-methyl formamide with glycols using time domain reflectometry technique

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The dielectric relaxation study that is static dielectric permittivity ($\in_0$) and relaxation time (τ) of amide of *N*-methyl formamide (NMF) with increasing volume percent propylene glycol (PLG) and BLG has been carried out at different temperatures. The time domain reflectometry (TDR) technique has been used to measure reflection coefficient in frequency range of 10 MHz to 20 GHz. The dielectric parameters have been obtained by fitting experimental data with the Havriliak–Negami equation. The experimental observation shows that the static dielectric permittivity and relaxation time decreases with increasing temperature. The experimental observation also shows that the static dielectric permittivity decreases and relaxation time increases with increasing percentage volume of Propylene glycol (PLG) and Butylene glycol (BLG) in NMF. The nature of (ε_0) and (τ) is same for the temperature ranges (20, 30, and 40°C). The thermodynamic parameters enthalpy (ΔH) and entropy (ΔS) of the binary mixture are also reported in this work.

Keywords: dielectric properties; *N*-Methyl formamide; propylene glycol; butylene glycol; TDR technique

1. Introduction

Dielectric techniques have been used to observe the well-known α or structural relaxation process over a broad frequency and temperature range. Recently, special interest in the dynamic at high frequencies, in the microwaves and sub-millimeter range has arisen due to the prediction of some theoretical and scaling approaches elaborated in the past [1,2]. The static permitivity of bipolar liquid is closely related to its molecular structure. In former theories [3,4] this relation finds an obvious expression in the orientation correlation factor [5] which has been related to the fact that, under certain conditions, the dipole orientation, an ensemble of neighbored molecules, are not randomly distributed but may be object to molecular order [6].

Amide and glycol have attracted the attention of number of researchers [7–10], in different fields because of high dielectric permittivity and biological applications. FA and PLG are important aqueous solvents. The amide represents an important class of organic solvent due to high polarity, strong solvating power and large liquid state range [11,12].

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Dielectric relaxation of liquid mixture gives information about molecular interaction. In this article, we reported the dielectric study of binary mixture of NMF with increasing percentage volume of PLG and BLG. The *N*-methyl formamide is an associative liquid with C=O group. *N*-Methyl formamide represent an important characteristic of amides of organic solvents due to high polarity, strong solvating power [13]. Substitution at the *N*-methyl formamide nitrogen atom allows us to control the extent of intermolecular hydrogen bonding, which is the dominating factor for the physical properties exhibited by the liquid. *N*-Methyl formamide is the excellent proton donors as well as proton acceptor [14] and hence is strongly associated through intermolecular H-bonds.

The association pattern and level of hydrogen bonding in liquids like monoalcohols, water and mixture of these has been a subject of intense research. These studies have been extended to dialcohols (diols), which have the possibility to form both intra and intermolecular hydrogen bonds. The interest in diols is further emphasised by the fact that these molecules play an important role in many chemical and biological processes. For the study of interaction between *N*-methyl formamide with propylene glycol and butelen glycol, we reported the dielectric relaxation parameters of these binary mixtures by using time domain reflectometry (TDR) technique over the frequency range 10 MHz–20 GHz and at three different temperatures 20, 30 and 40°C.

2. Experimental

Measurement were carried out on a TDR spectrometer, which allows one to study the change in shape of a fast rising voltage step propagated through a coaxial line section filled with the material under study. Transmission line system under test was placed at the end of coaxial line in the standard military applications (SMA) coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. All measurements were carried out under open load conditions. The sampling oscilloscope monitored the change in the pulse after reflection from the sample placed in the cell. In the experiment the time window of 5 ns was used. The reflected pulse without sample $R_1(t)$ and with sample $R_x(t)$ were digitised in 1024 points in the memory of the oscilloscope and transferred to a PC through a 1.44 MB floppy diskette drive.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of ±1°C. The sample cell is surrounded by a heat insulating container through which the water of constant temperature using a temperature controller system is circulated. The temperature at the cell is checked using the electronic thermometer.

The time dependent data was processed to obtain a complex reflection coefficient spectra $\rho^*(\omega)$ over the frequency range from 10 MHz to 20 GHz. Using Fourier transformation [15, 16] as

$$\rho * (w) = \left(\frac{c}{jwd}\right)\left[\frac{p(w)}{q(w)}\right], \tag{1}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $R_1(t) - R_x(t)$ and $R_1(t) + R_x(t)$, respectively, C is the speed of light, ω the angular velocity, d the effective pin length and $j = .\sqrt{-1}$.

The complex permittivity spectra $\varepsilon^*(\omega)$ were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying calibration method [17]. The experimental values of ε^* are fitted with Debye equation [18]

$$\varepsilon^*(w) = \varepsilon_\infty + \left(\frac{\varepsilon_0 - \varepsilon_\infty}{1 + jw\tau}\right), \tag{2}$$

where ε_0, ε_∞ and τ as fitting parameters.

A nonlinear least squares fit method [19] was used to determine the values dielectric parameters.

3. Results and discussion

The values of static dielectric permittivity (ε_0) and relaxation time (τ) of *N*-methyl formamide with increasing volume percent of propylene and butelen glycols are given in Tables 1 and 2, respectively. The enthalpy (ΔH) and entropy (ΔS) of the binary mixtures is given in Tables 3 and 4.

From Tables 1 and 2 it is observed that the static dielectric permittivity and relaxation time decreases with increases in temperature. It is also observed that the static dielectric permittivity decreases and relaxation time increases with increasing volume percent of PLG and BLG in *N*-methyl formamide and its nature is the same for all temperature ranges.

The decrease in static dielectric permittivity and relaxation time with increasing temperature is as expected, as temperature increases the relaxation time of the polar liquids falls off very rapidly because the increasing thermal motion reduces the alignment of the permanent dipoles by the applied field that causes to decrease in permittivity and relaxation time of this binary polar liquid.

The dielectric permittivity of these binary solutions decreases with increasing volume percent of PLG and BLG in *N*-methyl formamide. The decrease in dielectric permittivity of this amide group with increasing volume percent of PLG and BLG indicates the formation of hydrogen bonding with oxygen's of neighboring molecules, the molecules are

Table 1. Temperature dependant dielectric permittivity (ε_0) and relaxation time (τ) for NMF + PLG mixture.

Volume percent of PLG	$T = 20°\text{C}$		$T = 30°\text{C}$		$T = 40°\text{C}$	
	(ε_0)	(τ)	(ε_0)	(τ)	(ε_0)	(τ)
00	178.2	134.5	168.3	120.3	160.2	107.3
10	165.2	170.6	154.2	155.5	146.3	130.3
20	152.2	201.3	143.1	187.4	136.8	164.8
30	137.2	231.2	126.3	216.3	118.6	189.9
40	120.4	269.1	111.2	256.0	104.3	221.6
50	110.1	290.4	102.6	274.1	94.1	251.2
60	90.5	301.3	82.6	281.3	71.4	231.1
70	56.0	311.4	48.3	286.6	40.9	260.7
80	40.6	326.7	29.6	291.9	26.4	270.3
90	31.2	332.5	27.5	299.9	24.3	274.2
100	29.8	340.5	25.3	301.2	22.1	278.6

Table 2. Dielectric permittivity (ε_0) and relaxation time (τ) of NMF + BLG binary mixture.

Volume percent of BLG	$T = 20^\circ$C		$T = 30^\circ$C		$T = 40^\circ$C	
	(ε_0)	(τ)	(ε_0)	(τ)	(ε_0)	(τ)
00	175.6	133.1	169.4	121.8	159.7	107.8
10	147.3	151.2	140.2	135.6	131.1	115.9
20	122.2	192.8	116.3	166.1	106.7	130.0
30	103.7	226.2	96.8	206.6	86.6	165.1
40	86.1	252.7	79.1	229.7	66.6	205.1
50	63.70	307.1	57.6	285.5	49.4	254.9
60	50.5	365.6	46.6	326.8	41.0	309.2
70	40.7	419.9	36.5	400.8	36.1	382.2
80	33.0	474.0	29.2	455.2	29.0	427.0
90	26.6	520.0	23.0	501.3	23.1	484.8
100	22.0	611.6	20.4	588.4	17.8	521.8

Table 3. Values of molecular enthalpy and molecular entropy of NMF + PLG.

Volume percent of PLG	Enthalpy (ΔH) in kJ mole^{-1}	Entropy (ΔS) in kJ mole^{-1}
00	6.09 (20)	0.47 (1)
10	7.71 (20)	2.02 (6)
20	5.07 (20)	1.38 (4)
30	4.94 (20)	1.52 (5)
40	4.84 (20)	2.18 (7)
50	2.99 (15)	0.72 (2)
60	7.52 (20)	2.97 (9)
70	4.24 (20)	0.36 (1)
80	−0.18 (00)	0.67 (0)
90	4.82 (20)	0.78 (2)
100	5.14 (20)	0.86 (2)

Table 4. Values of molecular enthalpy and molecular entropy of NMF + BLG.

Volume percent of BLG	Enthalpy (ΔH) in kJ mole^{-1}	Entropy (ΔS) in kJ mole^{-1}
00	5.49 (20)	0.87 (2)
10	7.60 (20)	1.22 (4)
20	12.44 (20)	2.36 (7)
30	9.43 (20)	3.15 (1)
40	5.43 (20)	0.52 (1)
50	4.56 (20)	1.00 (3)
60	3.89 (15)	1.15 (3)
70	1.06 (15)	0.07 (0)
80	−0.16 (00)	0.56 (1)
90	1.74 (15)	0.91 (3)
100	3.49 (15)	1.88 (6)

under the influence of ions resulting in lowering of the values of dielectric permittivity of the binary mixture. Also in formamides the rotation of molecules is faster than that of dihydroxyl group. This faster rotation of formamide molecules may be due to dynamics of hydrogen bonds formed between carboxyl oxygen's of an acceptor molecules and formal proton of donor hindered intermolecular rotation around C–N bond. This would be another region for faster relaxation and decrease in static dielectric permittivity in amide with increasing volume of dihydroxyl group.

Another reason in decrease in static dielectric permittivity of this binary mixture may be due to the bigger molecular dimensions of PLG and BLG. Since the molecular dimensions of PLG and BLG are greater than formamide, when these higher dimension glycols are added to formamide the resultant dipole moment of the binary mixture may get increases which will reduce its mobility in the mixture and that may result in decreases in permittivity.

From Tables 1 and 2 it is also observed that the values obtained of static dielectric permittivity of NMF + PLG are greater than that of NMF + BLG mixture over the entire volume range and for three temperature ranges. The reason may be the molecular dimension of BLG. The molecular dimension of BLG is bigger than that of PLG. When BLG is added to *N*-methyl formamide the resultant dipole moment of the mixture may be greater than that of NMF + PLG mixture. This increased molecular dimension may reduce its mobility in the mixture that may reduce the alignment of the dipoles with the applied field and reduces the polarization. This reduced polarization may decrease the static dielectric permittivity more in NMF + BLG mixture than that of NMF + PLG binary mixture.

From Tables 1 and 2 it is also observed that the relaxation time of the binary mixture increases with increasing volume percent of PLG and BLG in NMF. The reason may be due to faster rotation of formamide molecules than that of dihydroxyl group. This faster rotation of formamide molecules may be due to dynamics of hydrogen bonds formed between carboxyl oxygen's of an acceptor molecules and formal proton of donor hindered intermolecular rotation around C–N bond. This may be the reason for fast increases in relaxation time of the binary mixture. This is in agreement with the earlier results of Puranik *et al.* [13].

From Tables 1 and 2 it is also observed that the variation in relaxation time of the binary mixtures is different for NMF + PLG and NMF + BLG in an entire volume range and for three different temperatures. That is, the variation in relaxation time of NMF + PLG mixture is smaller than that of NMF + BLG. The reason may be the molecular dimension of BLG. The molecular dimension of BLG is greater than that of PLG, the greater molecular dimension may reduce its mobility in the mixture or it will take more time to come back to its original position. This may be the reason of higher relaxation time of NMF + BLG than that of NMF + PLG.

The values of molecular enthalpy (ΔH) and molecular entropy (ΔS) for NMF + PLG and NMF + BLG systems are also determined and are given in Tables 3 and 4, respectively.

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Appendix A

Symbols and meanings

C	Speed of light
d	Pin length
NMF	*N*-Methyl formamide
$p(\omega)$ and $q(\omega)$	Fourier spectra
$p(\mathrm{t})$	Subtracted pulse $R_1(t) - R_x(t)$
$p(\omega)$	Fourier transform of $p(t)$
PLG	Propylene glycol
$q(t)$	Added pulse $R_1(t) + R_x(t)$
$q(\omega)$	Fourier transform of $q(t)$
$R_1(t)$	Reflected pulse without sample
$R_x(t)$	Reflected pulse with sample
α and β	Distribution parameters
ε_∞	Dielectric permittivity at high frequency
ε_0	Static dielectric permittivity
$\varepsilon^*(\omega)$	Complex permittivity spectra
$\rho^*(\omega)$	Reflection coefficient spectra
τ	Relaxation time
ω	Angular frequency