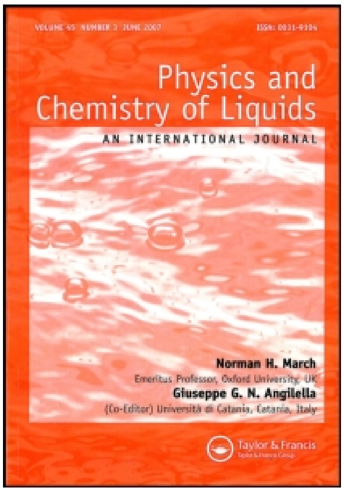

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High-frequency dielectric response of the binary mixture formamide-butylene glycol

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High-frequency dielectric response of the binary mixture formamide–butylene glycol

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Dielectric relaxation study of formamide (FMD) has been carried out with butylene glycol (BLG) at different temperatures. Time domain reflectometry in reflection mode has been used to measure the reflection coefficient in the frequency range of 10 MHz–20 GHz. The dielectric parameters, that is, static dielectric permittivity ($\in_0$) and relaxation time (τ) have been obtained by Fourier, transform and least square fit methods. The experimental results show non-linear variation in dielectric permittivity and relaxation time with volume fraction of BLG, confirm the structural formation due to the intermolecular interaction between FMD and glycol. The variation in excess permittivity (ε^E), excess inverse relaxation times $(1/\tau)^E$, Kirkwood correlation factors (g^{eff}, g^f), activation enthalpy (ΔH) and entropy (ΔS) for the binary mixtures have also been reported in this article.

Keywords: dielectric study; formamide; butylene glycol and TDR technique

1. Introduction

The dielectric relaxation study of solute–solvent mixture at microwave frequency gives information about formation of monomers and multimers. It gives understanding of solute–solvent interaction and liquid structure. In this experimental study, formamide (FMD) is considered as liquid A and butylene glycol (BLG) as liquid B of the binary mixture. The time domain reflectometry (TDR) [1] in reflection mode has been used to obtain the dielectric parameters. The objective of this article is to report the dielectric parameter study of FMD–BLG binary mixture by using TDR technique in the temperature range 20°C–40°C. Amides and glycols have attracted the attention of a number of researchers [2–7] in different fields because of high dielectric permittivity and biological applications. The amide represents an important class of organic solvent due to high polarity, strong solventing power and large liquid state range.

2. Experimental

2.1. *Material*

The chemicals used in the present investigation are of spectroscopic grade and used without further purification. The solutions were prepared by mixing FMD with BLG at 11 different volume percentages of glycol 0–100% in steps of 10%.

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2.2. *Apparatus*

Apparatus used in this study was the Tektronix 7854 sampling oscilloscope with a 7512 TDR unit. In this apparatus, a fast rising step voltage pulse of 200 mV amplitude and 25 ps rise time with reflection frequency of 1 KHz is generated and propagated through a coaxial transmission line. The sample is placed at the end of the coaxial transmission line in a standard military application (SMA) coaxial cell. The SMA cell used for this work had a 3.5 mm outer diameter and a 1.35 mm effective pin length. The step pulse generated by a tunnel diode and the pulse, which is reflected from the sample cell, were sampled by a sampling oscilloscope in the time window of 5 ns. The reflected pulse without sample R_1 (t) and with sample Rx (t) were digitised with 1024 points in the oscilloscope memory and then transferred to a PC through a general purpose interface bus (GPIB) card.

The temperature controller system with water bath and a thermostat has been used to maintain the constant temperature within the accuracy limit of $\pm 1^\circ$C. The sample cell is surrounded by a heat-insulating container through which the water of constant temperature is circulated.

3. Data analysis

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 [8,9] as

$$\rho^*(\omega) = \frac{c}{(j\omega d)} \cdot [p(\omega)/q(\omega)], \tag{1}$$

where $p(\omega)$ and $q(\omega)$ are Fourier transforms of $R_1(t) - Rx(t)$ and $R_1(t) + Rx(t)$, respectively, c is velocity of light, ω is angular frequency, d is 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 [10]. The example of $\varepsilon^*(\omega)$ spectra for pure FMD and its Cole–Cole plot for three temperatures are shown in Figure 1(a) and (b), respectively. The experimental values of ε^* are fitted with Debye equation [11–13]

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{[1 + (j\omega\tau)]}, \tag{2}$$

where ε_0, ε_∞ and τ as fitting parameters. In Equation (2) ε_0 is the static permittivity, τ is the relaxation time and ε_∞ is the permittivity at high frequency. A non-linear least-squares fit method [14] was used to determine the values of dielectric parameters.

The information regarding the interaction of the binary mixture may be obtained by excess properties [15–18] related to the permittivity and relaxation time in the mixture. The excess permittivity ε^{E} is defined as

$$\varepsilon^{\mathrm{E}} = (\varepsilon_0 - \varepsilon_\infty)_m - \left[(\varepsilon_0 - \varepsilon_\infty)_{\mathrm{A}} \cdot X_{\mathrm{A}} + (\varepsilon_0 - \varepsilon_\infty)_{\mathrm{B}} \cdot X_{\mathrm{B}}\right], \tag{3}$$

where X is mole fraction, and suffices m, A, B, represents mixture, liquid A (FMD) and liquid B (BLG), respectively. The excess permittivity may provide qualitative information about multimer formation in the mixture as follows:

(i) $\varepsilon^{\mathrm{E}} = 0$: Indicates the solute and solvent do not interact.

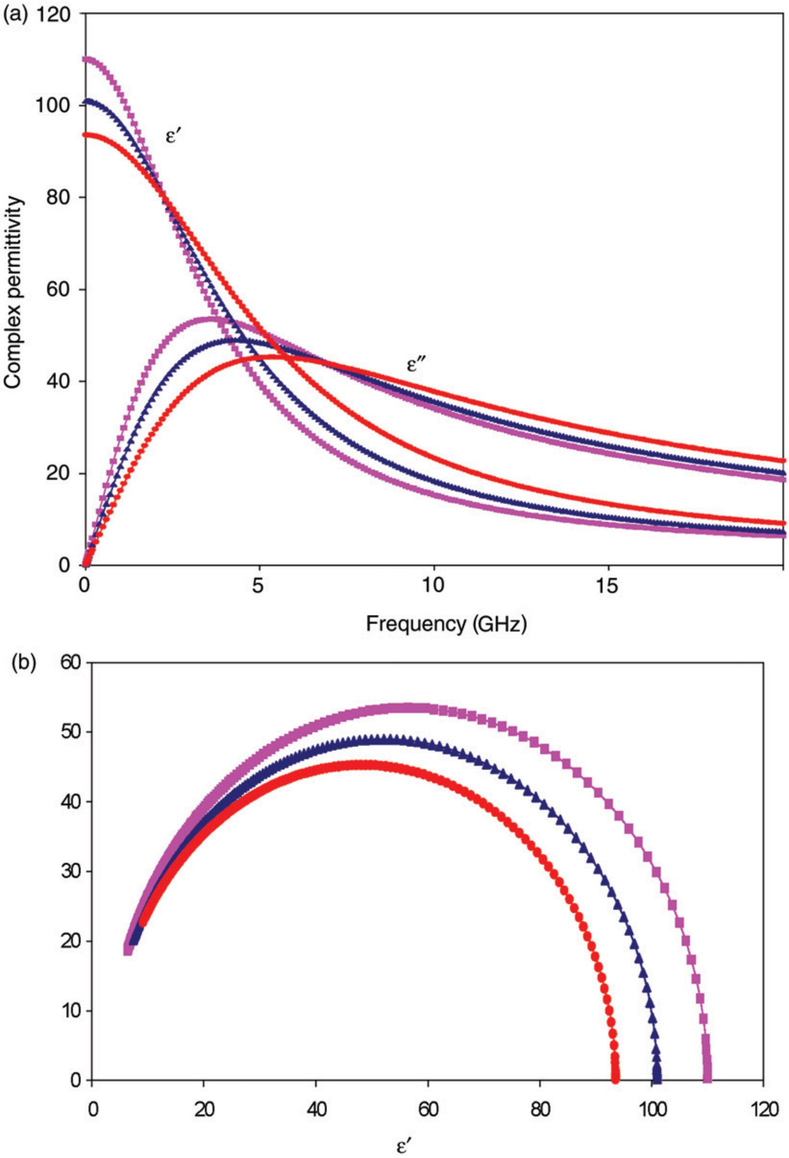

Figure 1. (a) Dielectric spectrum of pure FMD for three temperatures. (b) Cole–Cole plot of pure FMD for three temperatures.

(ii) $\varepsilon^{\mathrm{E}} < 0$: Indicates the solute and solvent interaction is in such a way that the effective dipole moment gets reduced. The solute and solvent may form multimers leading to the less effective dipoles.

(iii) $\varepsilon^{\mathrm{E}} > 0$: Indicates the solute and solvent interact in such a way that the effective dipole moment increases.

Similarly, the excess inverse relaxation time is defined as

$$(1/\tau)^{\mathrm{E}} = (1/\tau)_{\mathrm{m}} - \left[(1/\tau)_{\mathrm{A}} \cdot X_{\mathrm{A}} + (1/\tau)_{\mathrm{B}} \cdot X_{\mathrm{B}}\right], \tag{4}$$

where $(1/\tau)^{\mathrm{E}}$ is the excess inverse relaxation time which represents the average broadening of dielectric spectra in the resonance spectroscopy [19,20].

The information regarding the dynamics of binary mixture interaction is as follows:

(i) $(1/\tau)^{\mathrm{E}} = 0$: There is no change in solute–solvent interaction.
(ii) $(1/\tau)^{\mathrm{E}} < 0$: The solute–solvent interaction produces a field such that the effective dipoles rotate slowly.
(iii) $(1/\tau)^{\mathrm{E}} > 0$: The solute–solvent interaction produces a field such that the effective dipoles rotate faster i.e. the field will co-operate in rotation of dipoles.

The experimental values of both the excess parameters were fitted to the Redlich–Kister equation [21].

$$Y^{\mathrm{E}} = (X_{\mathrm{A}} \cdot X_{\mathrm{B}}) \sum_{K} B_K (X_{\mathrm{A}} - X_{\mathrm{B}})^K, \tag{5}$$

where Y^{E} is either ε^{E} or $(1/\tau)^{\mathrm{E}}$. The coefficient B_K was then calculated and used as a guideline to draw the smooth curves.

3.1. *The Kirkwood model*

The structural information about the liquids from the dielectric relaxation parameters may be obtained using the Kirkwood correlation parameter g [22]. This parameter is also used to obtain the information regarding orientation of electric dipoles in polar liquids.

The thermodynamic parameters e.g. molar energy of activation ΔH and molar entropy of activation ΔS were determined from the Ayring's rate equation [23] by a least-square fit.

The Kirkwood correlation parameter g and thermodynamic energy parameters has been reported by many workers for different binary mixtures [1,2,15–18,24,25].

4. Results and discussion

The estimated values of static dielectric permittivity (ε_0) and relaxation time (τ) of FMD with increasing volume percent of BLG are listed in Tables 1 and 2, respectively. It has been observed that the dielectric permittivity decreases with an increase in temperature as well as with an increase in volume fraction of BLG. The relaxation time for FMD–BLG system increases with the increase in concentration of glycol, and decreases with an increase in temperature.

The variation in dielectric permittivity and relaxation time with increasing concentration of BLG with different temperatures are shown in Figures 2 and 3.

In an ideal mixture of polar liquids, if the molecules are interacting, a non-linear variation in dielectric permittivity and relaxation time with concentration is expected, and the same is inferred from these figures. This confirms that the intermolecular association is taking place in the system [26].

The excess property related to permittivity and relaxation time provides significant information regarding interaction between the polar–polar liquid mixtures. The excess dielectric permittivity of the mixtures was calculated by using Equation (3) and its variation with mole fraction of glycol for the three temperatures is shown in Figure 4. From the figure it is observed that ε^{E} is negative up to a 0.4 mole fraction of BLG and

Table 1. Estimated values of static dielectric constant (ε_0) for FMD–BLG binary mixture at different temperatures.

Volume percent of BLG	$T = 20°C$	$T = 30°C$	$T = 40°C$
00	110.87	101.95	95.64
10	101.40	98.23	86.15
20	94.62	87.72	75.65
30	85.38	76.36	61.61
40	76.17	62.71	56.64
50	64.40	55.71	43.59
60	40.59	36.76	33.22
70	32.77	27.15	24.69
80	28.82	23.01	21.88
90	26.38	21.93	19.28
100	22.84	20.14	17.54

Table 2. Estimated values of relaxation time (τ in ps) for FMD–BLG binary mixture at different temperatures.

Volume percent of BLG	$T = 20°C$	$T = 30°C$	$T = 40°C$
00	44.31	37.00	29.68
10	59.14	49.23	36.39
20	66.31	61.30	55.87
30	89.05	82.38	69.25
40	98.06	93.41	83.29
50	123.61	109.04	90.28
60	257.65	210.38	140.39
70	368.90	288.37	208.26
80	488.10	357.37	306.68
90	525.37	498.88	388.40
100	608.81	588.76	520.85

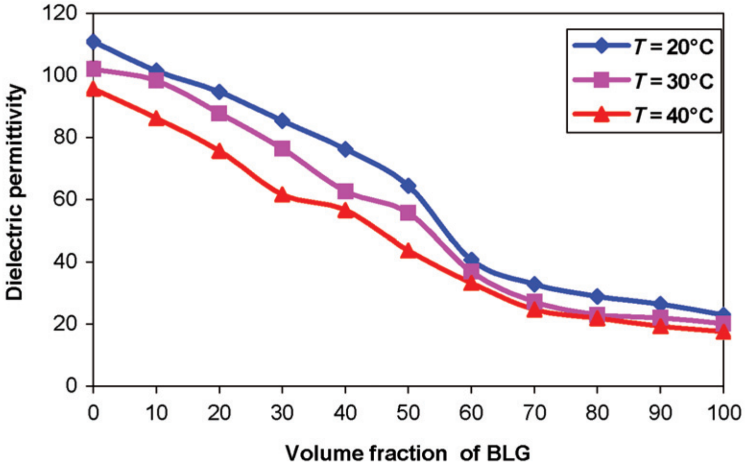

Figure 2. Variation of estimated values of static dielectric constant *vs*. volume fraction of BLG at different temperatures.

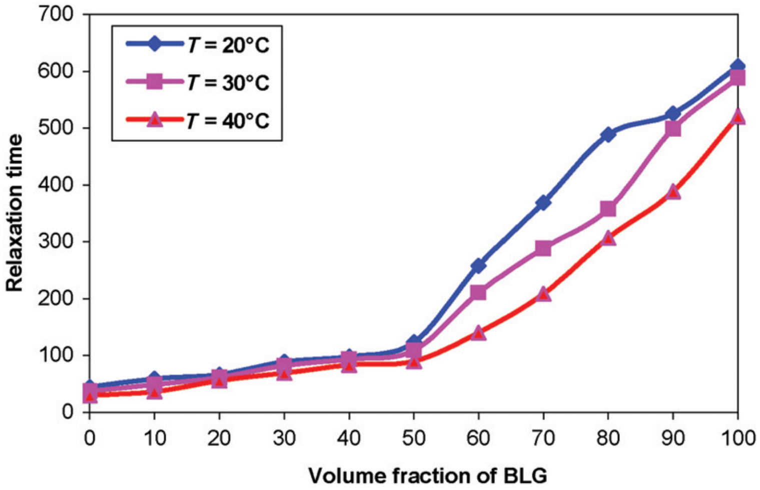

Figure 3. Variation of estimated relaxation time *vs.* volume fraction of BLG at different temperatures.

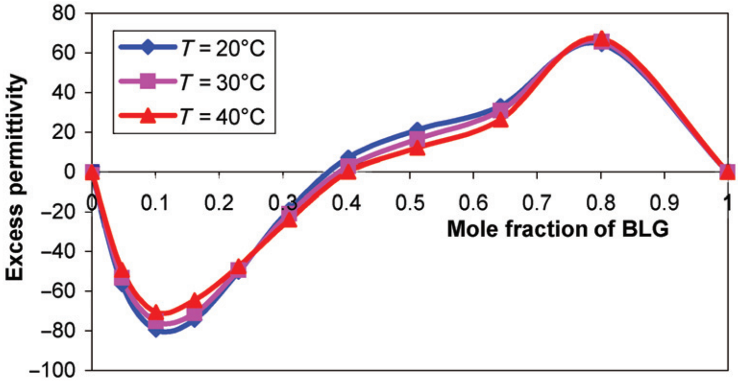

Figure 4. Variation of estimated excess permittivity (ε^E) as a function of mole fraction of BLG in FND at different temperatures.

positive for the rest of the mole fraction of the glycol in the liquid mixtures. Negative ε^E indicates that the molecules of the mixtures may form multimer structure via hydrogen bonding in such a way that the effective dipole gets reduced. This means that there is an association of FMD–BLG hydrogen bonding with the formation of multimer like structure. Positive ε^E indicates that the molecules of the mixture may form monomers or dimer structures in such a way that the number of effective dipoles increases. It is also observed that the excess permittivity is minimum around $X = 0.15$ and maximum around $X = 0.8$ mole fraction.

The variation in excess inverse relaxation time $(1/\tau)^E$ with mole fraction of BLG was calculated by using Equation (4) at 20, 30 and 40°C which is shown in Figure 5. As seen from the figure, $(1/\tau)^E$ is negative up to 0.5 mole fraction and positive for the rest of the mole fraction of the glycol at all temperatures studied. The negative values indicate that the addition of glycol to FMD has created a hindering field such that the effective dipole

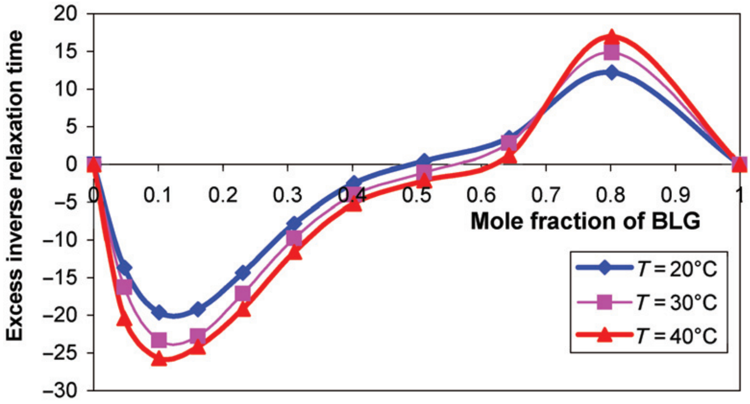

Figure 5. Variation of estimated excess inverse relaxation time $(1/\tau)^E$ as a function of mole fraction of BLG in FMD at different temperatures.

Table 3. Estimated values of Kirkwood angular correlation factors (g^{eff}) for FMD–BLG binary mixture at different temperatures.

Mole fraction of BLG	$T = 20°C$	$T = 30°C$	$T = 40°C$
0.0	4.2546	3.9091	3.332
0.1	3.4143	3.273	2.9563
0.2	2.8381	2.5817	2.1523
0.3	2.3073	2.0109	1.9052
0.4	1.872	1.4918	1.2245
0.5	1.4494	1.2089	1.0231
0.6	0.8359	0.7271	0.6235
0.7	0.6232	0.4921	0.2236
0.8	0.5095	0.3855	0.1526
0.9	0.436	0.343	0.212
1.0	0.353	0.2946	0.223

rotates slowly. The positive values indicate that the glycol–FMD interaction produces a field such that the effective dipoles rotate faster i.e. the field will co-operate in rotation of dipoles.

The Kirkwood angular correlation factor (g^{eff}) is calculated and is given in Table 3 for the three temperatures. The $g^{eff} > 1$, in FMD-rich region which show that in the mixture the dipole pairs have been formed in such a way that their orientation is parallel up to 0.5 mole fraction of glycol. The $g^{eff} < 1$ shows that in the mixture the dipole pairs have been formed in such a way that their orientation is antiparallel in the glycol-rich region. The Kirkwood correlation factor (g^{f}) is also calculated and is given in Table 4. The g^{f} values are greater than one for all mole fraction of glycol in the binary system, which indicates that the system will be oriented in such a way that the effective dipole will be greater than the corresponding values of pure liquids.

The energy parameters ΔH and ΔS have been also calculated and reported in Table 5. From this table it is clear that the enthalpy of activation energy ΔH, has got a low value in FMD-rich regions. This indicates that less energy is required to achieve group dipole reorientation in this region. This means that more energy is needed for group dipole

Table 4. Estimated values of Kirkwood correlation factors (g^f) for FMD–BLG binary mixture at different temperatures.

Mole fraction of BLG	$T = 20°C$	$T = 30°C$	$T = 40°C$
0.0	1	1	1
0.1	1.2314	1.2469	1.2632
0.2	1.4864	1.5174	1.6521
0.3	1.7491	1.7913	1.813
0.4	1.9931	2.0073	2.0995
0.5	2.1417	2.1759	2.2113
0.6	1.8234	1.8858	2.0321
0.7	1.5812	1.5213	1.4823
0.8	1.3852	1.2729	1.1325
0.9	1.2223	1.1563	1.0603
1.0	1	1	1

Table 5. Estimated values of enthalpy and entropy as a function of volume fraction of BLG.

Volume percent of BLG	Enthalpy (ΔH) in KJ/volume	Entropy (ΔS) in KJ/volume
00	12.7376 (0.2266)	1.1503 (0.0038)
10	15.9392 (0.2350)	2.9422 (0.0097)
20	4.0058 (0.1934)	0.4126 (0.0014)
30	7.0137 (0.0000)	2.2801 (0.0000)
40	3.6766 (0.1890)	1.5485 (0.0051)
50	9.4307 (0.2067)	1.5984 (0.0053)
60	20.5369 (0.2383)	4.8565 (0.0160)
70	19.2378 (0.2311)	2.1329 (0.0070)
80	15.2592 (0.2155)	3.1796 (0.0105)
90	8.9111 (0.1927)	4.5642 (0.0151)
100	3.3924 (0.1728)	2.0488 (0.0068)

reorientation with an increase in volume fraction of BLG in the mixture. This indicates that there is an increase in agitation with an increase in volume fraction of BLG in the mixture, and it is due to hydroxyl group interaction with one another.

The values of entropy of activation ΔS for FMD–glycol interaction are positive, and remain positive for an entire volume fraction range of glycol which shows less order in product than reactant.

5. Conclusion

The dielectric relaxation parameters that are static dielectric permittivity ($\in_0$) and relaxation time (τ), variation in excess permittivity (ε^E), excess inverse relaxation times $(1/\tau)^E$, Kirkwood correlation factors (g^{eff}, g^f), activation enthalpy (ΔH) and entropy (ΔS), have been reported for FMD–BLG mixtures for different temperatures. The static dielectric constant of the mixtures is found to be in the range of 23–111. In the mixtures of FMD–BLG the dielectric constant decreases with the increasing concentration of glycol.

The relaxation time increases with the addition of glycol in FMD, indicates that the intermolecular rotation is the predominant mechanism in the relaxation process, due to the increasing molecular size of BLG.

The excess permittivity is negative in an FMD-rich region which indicates formation of multimers. The ε^{E} values are positive in a glycol-rich region, representing formation of monomers and dimer structures.

The excess inverse relation time $(1/\tau)^{E}$ is negative for a major mole fraction range (up to 60–65%) for the temperatures studied, this confirms that the dipole rotates slowly in the FMD–glycol binary system and it rotates fast in the glycol-rich region.

In the mixture the dipole pairs are formed and orient in parallel directions in FMD-rich regions and in antiparallel directions in glycol-rich regions, which is confirmed from the g^{eff} values.

The thermodynamic parameters of the system have been studied and are reported in Table 5.

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Appendix A

Symbols and meanings

ε_∞ – Dielectric permittivity at high frequency
ε_0 – Static dielectric permittivity
τ – Relaxation time
α and β – Distribution parameters
$\rho^*(\omega)$ – Reflection coefficient spectra
ω – Angular frequency
$\varepsilon^*(\omega)$ – Complex permittivity spectra
$p\ (\omega)$ and $q\ (\omega)$ – Fourier spectra
c – Speed of light
d – Pin length
$R_1(t)$ – Reflected pulse without sample
$Rx(t)$ – Reflected pulse with sample
$p(\omega)$ – Fourier transform of $p(t)$
$q(\omega)$ – Fourier transform of $q(t)$
$p(t)$ – Subtracted pulse $R_1(t) \quad - \quad Rx(t)$
$q(t)$ – Added pulse $R_1(t) + Rx(t)$
DMF – *N*,*N*-dimethyl formamide
PLG – Propylene glycol
BLG – Butylene glycol
FMD – Formamaide