

Microwave dielectric characterization of binary mixture of formamide with *N, N*-dimethylaminoethanol

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Abstract. Dielectric relaxation measurements of formamide (FMD)–*N, N*-dimethylaminoethanol (DMAE) solvent mixtures have been carried out over the entire concentration range using time domain reflectometry technique at 25, 35 and 45°C in the frequency range of 10 MHz to 20 GHz. The mixtures exhibit a principle dispersion of the Davidson–Cole relaxation type at microwave frequencies. Bilinear calibration method is used to obtain complex permittivity $\varepsilon^*(\omega)$ from complex reflection coefficient $\rho^*(\omega)$ over the frequency range of 10 MHz to 10 GHz. The excess permittivity (ε^E), excess inverse relaxation time $(1/\tau)^E$, Kirkwood correlation factor (g^{eff}), activation energy and Bruggeman factor (f_B) are also calculated to study the solute–solvent interaction.

Keywords. Time domain reflectometry; formamide; dimethylaminoethanol; excess parameters; Kirkwood correlation factor; Bruggeman factor; activation energy.

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1. Introduction

The knowledge of frequency-dependent dielectric properties of binary liquid mixtures is important both in fundamental studies of solvent structure determination and its dynamics as well as in the practical application of microwave heating process [1,2]. At a fundamental level, the frequency-dependent dielectric behavior of liquid mixtures provides information on molecular interactions and mechanism of molecular process. The dielectric relaxation behavior of mixtures of polar molecules under varying conditions of compositions is very important as it helps in obtaining

information about relaxation process in mixtures. There have been several investigations on the dielectric behavior of solvent mixtures in which dielectric relaxation spectra were used to examine molecular orientations, hydrogen bonded networks and microdynamics of these systems [3–20].

In this paper, we report a systematic investigation of dielectric relaxation in binary mixture of FMD with DMAE at various concentrations and temperatures employing time domain reflectometry [21–23]. The dielectric relaxation spectra have been obtained for solutions of various compositions in the frequency range of 10 MHz to 20 GHz, at temperatures 25, 35 and 45°C. The experimental data are fitted to the three different relaxation models [24–27] by the non-linear least squares fit method. It is observed that the Davidson–Cole model is adequate to describe major dispersion of the various solute and solvent mixtures over this frequency range. Static dielectric constant and dielectric relaxation time could be obtained by fitting the spectra to the Davidson–Cole model. The static dielectric constant and relaxation time have been used to determine the excess permittivity, excess inverse relaxation time, Kirkwood correlation factor and Bruggeman factor. Kirkwood correlation factor characterizes the dipole alignment within the solutions. The excess permittivity, excess inverse relaxation time and Bruggeman factor provide information related to molecular interaction. These parameters will provide useful description of the structure and dynamics of the binary mixtures.

Both FMD and DMAE are polar liquids with dipole moments 3.73 and 2.6 Debye respectively. FMD is a common dipolar aprotic (without –OH group) solvent and DMAE is a protic (with –OH group) solvent. The dielectric study of the binary system of these two liquids will give information about the interaction between –OH and –N(CH₃)₂ groups.

2. Experimental set-up

2.1 Chemicals and sample preparation

FMD and DMAE were obtained commercially with 99.9% purity and were used without further purification. The solutions were prepared at different volume percentage of FMD in DMAE in the step of 10% at room temperature. The concentrations were prepared for 5 ml solution at room temperature assuming ideal mixing behavior, within 0.02% error limit.

Using these volume per cents, the weight fraction is calculated as

$$X_A = \frac{(V_A \times \rho_A)}{(V_A \times \rho_A) + (V_B \times \rho_B)}, \quad (1)$$

where V_A and V_B are the volume and ρ_A and ρ_B are the density of liquid A and B respectively.

2.2 TDR set-up and data acquisition

The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug-in module has been used. After observing TDR response for the sample under study, the time window was kept to 5 ns. Also by observing TDR response for the sample under study, the SMA sample cell with 1.35 mm effective pin length has been used. To reduce noise, time-dependent response curve was averaged for 64 times and then stored in the memory of the oscilloscope with 1024 points per wave-form. First, the reflected pulse from the empty cell is acquired and stored in the memory and then, the reflected pulse from the cell with sample is acquired and stored in the memory. The empty cell wave-form is used as the reference wave-form. Both response wave-forms are the reflected wave-forms from the sample cell with open termination of transmission line.

The data acquisition is carried out for 11 concentrations at 25, 35 and 45°C with an accuracy of $\pm 1^\circ\text{C}$. At each time the response wave-forms without sample and with sample were recorded. The time-dependent response wave-form without sample is referred as $R_1(t)$ and with sample is referred as $R_x(t)$.

2.3 Data analysis

As explained earlier, the $R_1(t)$ and $R_x(t)$ wave-forms are analyzed further to obtain reflection coefficient spectra. In this process, the time-dependent wave-form is converted to frequency-dependent wave-form using Fourier transformation in the frequency range of 10 MHz to 10 GHz. The reflection coefficient is related to dielectric response of the sample under study for the range of frequency from 10 MHz to 10 GHz in terms of complex permittivity spectra [21–23,29]. The value of ϵ_∞ is not sensitive to $\epsilon^*(\omega)$ [24] and taken to be fixed as 3.2. A sample complex permittivity spectra with ϵ' and ϵ'' are shown in figure 1.

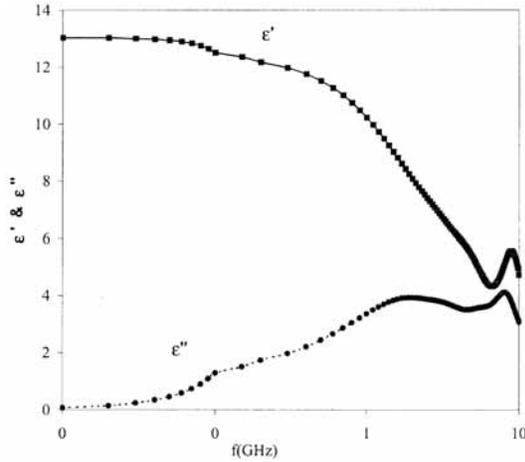


Figure 1. Complex permittivity spectra for pure dimethylaminoethanol.

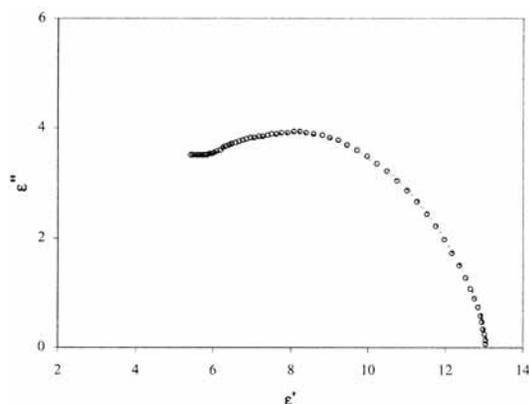


Figure 2. Cole–Cole plot.

Table 1. Physical properties of formamide and dimethylaminoethanol.

Name of solvent	Molecular weight	Density	Dipole moment	Liter. value of (ε_0)	Liter. value of τ
FMD	45.04	1.134	3.73	111	51
DMAE	89.14	0.8866	2.6	–	–

3. Results and discussion

The physical constants of these two liquids used along with literature values are given in table 1.

The complex permittivity spectra determined using TDR are fitted by the non-linear least squares fit method to the Havriliak–Negami expression [25] to obtain various dielectric parameters.

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

where $\varepsilon^*(\omega)$ is the complex permittivity at an angular frequency ω , ε_∞ is the permittivity at high frequency, ε_0 is the static permittivity, τ is the relaxation time of the system, α is the shape parameter representing symmetrical distribution of relaxation time and β is the shape parameter of an asymmetric relaxation curve.

Equation (2) includes Cole–Cole ($\beta = 1$) [26], Davidson–Cole ($\alpha = 0$) [27] and Debye ($\alpha = 0, \beta = 1$) [28] relaxation models. From the Cole–Cole plot shown in figure 2, the dielectric model for the fitting dielectric parameters suitable for the present system is Davidson–Cole model. Therefore, the complex permittivity spectra have been fitted in Davidson–Cole model with $\alpha = 0$ and β ($0 < \beta \leq 1$) as one of the fitting parameters along with ε_0 and τ . The value of the fitting parameter β in Havriliak–Negami equation obtained is in the range of 0.91 to 1 for different concentrations. The value of ε_∞ was kept fixed as 3.2 while fitting this data.

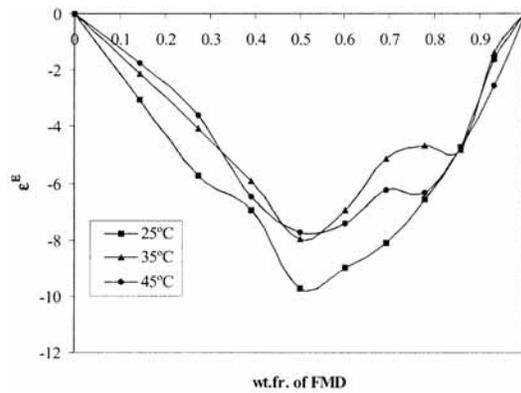


Figure 3. Variation of the estimated excess dielectric constant ϵ^E as a function of weight fraction of formamide in dimethylaminoethanol at 25, 35 and 45°C.

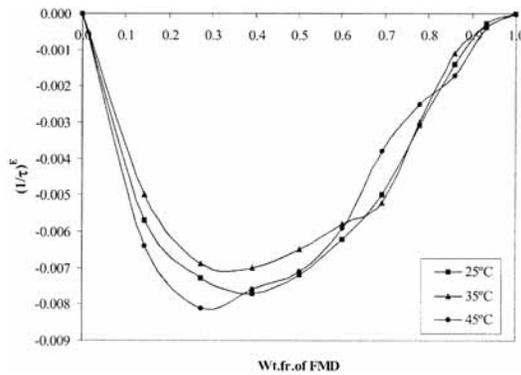


Figure 4. Variation of the estimated excess inverse relaxation time $(1/\tau)^E$ as a function of weight fraction of formamide in dimethylaminoethanol at 25, 35 and 45°C.

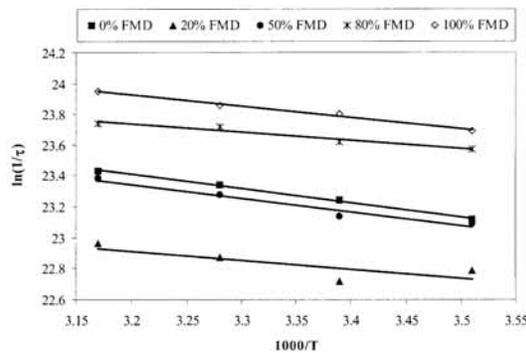


Figure 5. The Arrhenius plots of $\ln(1/\tau)$ vs. $(1000/T)$ formamide–dimethylaminoethanol binary system.

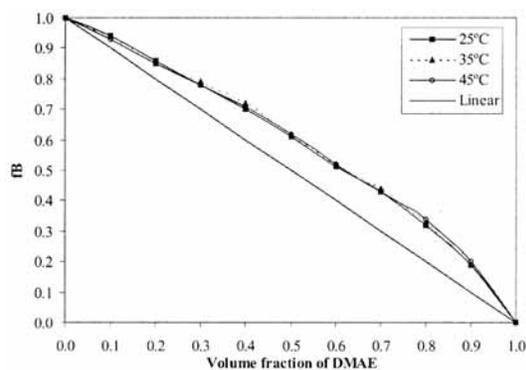


Figure 6. Plot of Bruggeman factor (f_B) vs. volume fraction of dimethylaminoethanol.

Table 2. Estimated static dielectric constant for formamide at different temperatures.

Volume percentage of formamide	25°C		35°C		45°C	
	ϵ_0	τ	ϵ_0	τ	ϵ_0	τ
00	13.59	80.50	12.80	73.21	12.15	66.50
10	23.70	127.78	22.82	109.24	22.70	99.54
20	33.50	136.24	32.13	116.99	32.00	106.56
30	43.60	126.01	40.50	104.41	39.30	92.01
40	51.20	107.13	47.89	89.32	47.30	82.14
50	61.50	89.44	57.55	77.70	56.20	70.27
60	71.10	76.18	67.30	69.97	65.20	58.60
70	80.80	63.61	75.11	57.59	72.40	52.74
80	90.20	55.41	81.82	49.97	80.70	48.98
90	100.00	49.46	91.58	45.67	89.20	44.90
100	110.21	46.30	105.16	43.50	97.77	39.50

Table 2 reports the values of dielectric parameters obtained from fitting eq. (2). It can be seen that by increasing the concentration of FMD in DMAE, the static permittivity values increase whereas relaxation time values increase only up to 20%. On increasing the volume percentage of formamide in the solution, the relaxation time values decrease towards the value corresponding to formamide. With increase in temperature, both static dielectric constant values and relaxation time values decrease maintaining the same type of change with the corresponding change in the concentration. In the system the values of average relaxation time of the molecules of the system has a maxima when static dielectric constant of the system is near 30. This indicates that the intermediate structures formed at this stage rotate slowly thereby giving higher values of τ in the solution.

The excess parameters [4,30] related to ϵ_0 and τ provide valuable information regarding interaction between the (solute-solvent) polar-polar liquid mixtures. These properties are also useful for the detection of the cooperative domain in the mixture and may give evidence for the formation of multimers in the mixture due to

Table 3. The Kirkwood correlation factor (g^{eff}) for formamide.

Vol. fraction of formamide	g^{eff}		
	25°C	35°C	45°C
0.0	0.69	0.66	0.64
0.1	0.90	0.89	0.92
0.2	1.01	1.00	1.02
0.3	1.08	1.04	1.03
0.4	1.08	1.04	1.06
0.5	1.12	1.09	1.09
0.6	1.15	1.12	1.12
0.7	1.17	1.12	1.12
0.8	1.18	1.11	1.13
0.9	1.20	1.13	1.14
1.0	1.21	1.20	1.15

intermolecular interaction. The excess permittivity is defined as

$$\varepsilon^{\text{E}} = (\varepsilon_0 - \varepsilon_\infty)_m - [(\varepsilon_0 - \varepsilon_\infty)_A X_A + (\varepsilon_0 - \varepsilon_\infty)_B X_B], \quad (3)$$

where X is the weight fraction and suffixes m, A, B represent mixture, liquid A and liquid B respectively.

The excess permittivity provides qualitative information about structure formation in the mixture as follows:

- (i) $\varepsilon^{\text{E}} = 0$ indicates that the solute and solvent do not interact at all.
- (ii) $\varepsilon^{\text{E}} < 0$ indicates that the solute and solvent interaction act so as to reduce total effective dipoles. This suggests that the solute–solvent mixture may form multimers leading to the less effective dipoles.
- (iii) $\varepsilon^{\text{E}} > 0$ indicates that the solute and solvent interact in such a way that the effective dipole moment increases. There is formation of monomers and dimers.

Figure 3 shows the plot of excess permittivity against weight fraction of FMD for all three temperatures. In this study, the excess permittivity values are found to be negative for all temperatures and concentrations, which indicates that the total number of dipoles decreases in the mixtures. This is due to the opposite alignment of the dipoles of the two interacting solvent molecules. The curves are more deviated from zero about equal concentration region indicates strong intermolecular interaction in this region. The excess inverse relaxation time is defined as

$$\left(\frac{1}{\tau}\right)^{\text{E}} = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_A X_A + \left(\frac{1}{\tau}\right)_B X_B\right], \quad (4)$$

where $(1/\tau)^{\text{E}}$ is the excess inverse relaxation time, which represents average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is the inverse of relaxation time) from the resonant

spectroscopy [17]. The information regarding the dynamics of solute–solvent interaction from this excess property is as follows:

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

The variation of $(1/\tau)^E$ with weight fraction of FMD for all the three temperatures is shown in figure 4. From this figure it can be seen that, for all the three temperatures, the excess inverse relaxation time values are negative which indicate the formation of linear structure, which rotate slowly under the influence of an external varying field. It indicates that addition of FMD to DMAE has created a hindering field such that the effective dipoles rotate slowly.

The structural information about the liquid by dielectric relaxation parameters can be obtained by Kirkwood correlation parameter [31]. The Kirkwood correlation factor g is also a parameter for obtaining information regarding the orientation of electric dipoles in polar liquids. The g for pure liquid can be obtained by the expression

$$\frac{4\pi N\mu^2\rho}{9kTM}g = \frac{(\varepsilon_0 - \varepsilon_\infty)(2\varepsilon_0 + \varepsilon_\infty)}{\varepsilon_0(\varepsilon_\infty + 2)^2}, \quad (5)$$

where μ is the dipole moment in gas phase, ρ is the density at temperature T , M is the molecular weight, k is the Boltzmann constant, N is the Avogadro's number.

The effective angular correlation (g^{eff}) between molecules is calculated using the modified form of equation (5) [4,32]. g^{eff} has been used to study the orientation of electric dipoles in binary mixtures. The Kirkwood equation for the mixture may be expressed as [4,32]

$$\frac{4\pi N}{9kT} \left(\frac{\mu_A^2\rho_A}{M_A}\Phi_A + \frac{\mu_B^2\rho_B}{M_B}\Phi_B \right) g^{\text{eff}} = \frac{(\varepsilon_{0m} - \varepsilon_{\infty m})(\varepsilon_{0m} + \varepsilon_{\infty m})}{\varepsilon_{0m}(\varepsilon_{\infty m} + 2)^2}, \quad (6)$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, and Φ_A , Φ_B are volume fraction of liquid A and liquid B, respectively.

The calculated values of g^{eff} are tabulated in table 3. It can be seen from table 3 that, g^{eff} values are less than unity for pure DMAE and 0.2 volume fraction of FMD in DMAE, indicating antiparallel orientation of electric dipoles. It can also be seen that the g^{eff} values are increased with an increasing concentration of FMD in DMAE. These values are greater than unity at all temperatures suggesting parallel orientation of electric dipoles.

The Arrhenius plots of $\ln(1/\tau)$ vs. $(1000/T)$ are plotted in figure 5 for various concentrations. The slope of this plot shows linear nature. The $\ln(1/\tau)$ values decrease up to 20% concentration of FMD and then on further increase in concentration of FMD, not more change in the slope of the plots is observed, which indicates that at all concentrations the activation energy remains almost same.

The modified Bruggeman equation [33] gives another parameter, which may be used as an indicator of solute–solvent interaction. The Bruggeman factor f_B is given by

$$f_B = \left(\frac{\varepsilon_{0m} - \varepsilon_{0B}}{\varepsilon_{0A} - \varepsilon_{0B}} \right) \left(\frac{\varepsilon_{0A}}{\varepsilon_{0m}} \right)^{1/3} = (1 - \Phi_B). \quad (7)$$

According to eq. (7), a linear relationship is expected which will give a straight line when f_B is plotted against Φ_B . However, here the experimental values of f_B were found to deviate from the linear relationship.

To fit the experimental data, the above equation has been modified [34] as follows:

$$f_B = 1 - [a - (a - 1)\Phi_B]\Phi_B, \quad (8)$$

where a is the numerical fitting parameter.

The parameters a were determined for all temperatures. The value $a = 1$ corresponds to the ideal Bruggeman mixture formula. The deviation from 1 relates to the corresponding solute–solvent interaction. Small values of a indicate significant rise in effective volume of solvent as well as weak interaction between solute and solvent. The Bruggeman factor, which is the ratio of theoretical values of static dielectric constant computed from Bruggeman mixture formula and practically obtained values, has been obtained from eq. (8). The values of Bruggeman factor for all three temperatures are plotted in figure 6.

The Bruggeman factor deviates above the ideal values at all the concentrations of FMD in the solution. The deviation is more in DMAE-rich region. Same types of changes in these values have been observed at all temperatures.

4. Conclusion

The dielectric relaxation parameters, the Kirkwood correlation factor, the excess properties and Bruggeman factor have been reported for formamide-*N,N*-dimethylaminoethanol mixtures for different concentrations and temperatures. The static dielectric constant of DMAE is found to be in the range of 12 to 13. In the mixture of FMD and DMAE, the static dielectric constant increases linearly with increase in concentration of formamide in the solution.

The relaxation time of DMAE is found to be ~ 80 ps at 25°C. The higher relaxation time may be due to more association through hydrogen bonding of –OH group in DMAE. The relaxation time of the molecules of the solution increases as concentration of FMD is increased up to 20%. On further increase in concentration of FMD in the solution, the relaxation time values decrease exponentially towards formamide value. This indicates bulky structure formation near 20% concentration of FMD in the solution, i.e. in DMAE-rich region bulky complexes may be formed which gives higher relaxation time in this region.

The Arrhenius plots are linear. The slopes of the plots are almost same indicating no change in activation energy of the system at various concentrations. There is

deviation in Bruggeman factor from linearity in the mixture. This indicates that the static permittivity values at different concentrations are not following Bruggeman mixture formula.

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References

- [1] C Gabriel, S Gabriel, E H Grant, B S J Halstead and D M P Mingos, *Chem. Soc. Rev.* **27**, 213 (1998)
- [2] C Kuang and S O Nelson, *J. Microw Pow. And E M Energy* **32**, 114 (1997)
- [3] R H Fattepur, M T Hosamani, D K Deshpande and S C Mehrotra, *J. Chem. Phys.* **101**, 9956 (1994)
- [4] A C Kumbharkhane, S M Puranik and S C Mehrotra, *J. Sol. Chem.* **22**, 219 (1993)
- [5] P Firman, M Marchetti, M Eyrin, E M Xu and S J Petrucci, *Phys. Chem.* **95**, 7055 (1991)
- [6] S P Patil, A S Chaudhari, M P Lokhande, M K Lande, A G Shankarwar, S N Helambe, B R Arbad and S C Mehrotra, *J. Chem. Eng. Data* **44**, 875 (1999)
- [7] J Z Bao, M L Swicord and C C Davies, *J. Chem. Phys.* **104**, 4441 (1996)
- [8] B M Suryavanshi and S C Mehrotra, *Ind. J. Pure Appl. Phys.* **29**, 442 (1991)
- [9] A Choudhari, H Chaudhari and S C Mehrotra *J. Chin. Chem. Soc.* **49**, 489 (2002)
- [10] A Chaudhari, H Chaudhari and S C Mehrotra, *Fluid Phase Equilib.* **201**, 107 (2002)
- [11] V P Pawar and S C Mehrotra, *J. Mol. Liq.* **95**, 63 (2002)
- [12] V P Pawar, G S Raju and S C Mehrotra, *Pramana – J. Phys.* **592**, 693 (2002)
- [13] S Ahire, A Chaudhari, M P Lokhande and S C Mehrotra, *J. Sol. Chem.* **27**, 993 (1998)
- [14] D Bertolini, M Cassettari, C Ferrari and E Tombari, *J. Phys. Chem.* **108**, 6416 (1998)
- [15] S M Puranic, A C Kumbharkhane and S C Mehrotra, *Ind. J. Chem.* **A32**, 613 (1993)
- [16] J Barthel, K Bachhuber and R Z Buchner, *Naturforsch* **50**, 65 (1995)
- [17] A Chaudhari, N M More and S C Mehrotra, *Bull. Korean Chem. Soc.* **22**, 357 (2001)
- [18] A Chaudhari, S Ahire and S C Mehrotra, *J. Mol. Liq.* **94**, 17 (2001)
- [19] J Lou, T A Hatton and P E Laibinis, *J. Phys. Chem.* **A101**, 5262 (1997)
- [20] J Lou, T A Hatton and P E Laibinis, *J. Phys. Chem.* **A101**, 9892 (1997)
- [21] S Mashimo, S Kuwabara, S Yogihara and K Higasi, *J. Chem. Phys.* **90**, 3292 (1989)
- [22] R H Cole, J G Berbarian, S Mashimo, G Chryssikos, A Burns and E Tombari, *J. Appl. Phys.* **66**, 793 (1989)
- [23] S M Puranic, A C Kumbharkhane and S C Mehrotra, *J. Micro. Pow. and EM Energy* **26**, 196 (1991)
- [24] Ajay chaudhari, M K Lande, B R Arbad, D V Jahagirdar and S C Mehrotra, *J. Mol. Liqs.* **100/3**, 207–215 (2002)
- [25] S Havriliak and S Negami, *J. Polym. Sci.* **C14**, 99 (1966)
- [26] K S Cole and R H Cole, *J. Chem. Phys.* **9**, 341 (1941)
- [27] D W Davidson and R H Cole, *J. Chem. Phys.* **18**, 1484 (1950)
- [28] P Debye, *Polar molecules* (Chem. Catalog. Co., New York, 1929)

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- [29] A Chaudhari, A Das, G Raju, H Chaudhari, P Khirade, N Narain and S C Mehrotra, *Natl. Sci. Counc. ROC(A)* **25**, 205 (2001)
- [30] M Tabellout, P Lanceleur and J R Emery, *J. Chem. Soc. Farad. Trans.* **86**, 1493 (1990)
- [31] H Frohlich, *Theory of dielectrics* (Oxford University Press, London, 1949)
- [32] G MouMouzlas, D K Panpoulos and G Ritzoulis, *J. Chem. Eng. Data* **36**, 20 (1991)
- [33] D A G Bruggeman, *Ann. Phys. (Leipzig)* **5**, 636 (1935)
- [34] S M Puranik, A C Kumbharkhane and S C Mehrotra, *J. Mol. Liq.* **59**, 173 (1994)