



Microwave Dielectric Study of Binary Mixture of Ethyl Acetate with Propylene Glycol using Time Domain Reflectometry Technique

S.B. KOLHE^{1,*} and S.G. BADHE²

¹Department of Physics, Shivaji Arts, Commerce and Science College, Kannad-431103, India

²Department of Physics, R.B. Attal Arts, Science and Commerce College, Georai-431127, India

*Corresponding author: E-mail: kolhe_sb71@yahoo.com

Received: 1 September 2024;

Accepted: 19 October 2024;

Published online: 30 October 2024;

AJC-21801

Microwave dielectric study for the binary mixtures of ethyl acetate with propylene glycol was performed over the frequency range of 10 MHz –20 GHz and in the temperature range of 288 K to 318 K using time domain reflectometry technique. Dielectric parameters such as static dielectric constant (ϵ_s), relaxation time (τ), excess dielectric constant (ϵ_s)^E, excess inverse relaxation time ($1/\tau$)^E, Kirkwood correlation factor (g^{eff}), Bruggeman factor (f_B) and thermodynamic parameters *viz.* molar enthalpy of activation, molar entropy of activation were also determined. Variation of measured dielectric and thermodynamic parameters have been used to explain the intermolecular interactions between the ethyl acetate and propylene glycol.

Keywords: Time domain reflectometry technique, Dielectric constant, Relaxation time, Bruggeman factor, Thermodynamics.

INTRODUCTION

Exploring the dielectric properties of binary polar liquids is crucial for obtaining the information regarding the interaction between the solute and the solvent. Several researchers have used various methods to study the dielectric characteristics of liquids [1-8]. The dielectric constant of mixed solvents is necessary in the analytical and pharmaceutical sciences to predict the drug's solubility and chemical stability [9]. One of the chemicals used for this study is ethyl acetate which is mostly employed as a solvent and diluent due to its affordability, low toxicity and pleasing smell. Solutions containing ethyl acetate are often used in laboratories for extractions and column chromatography. Propylene glycol, which is utilized in the food sector, cosmetics, plastic, paint and pharmaceuticals, is the second most used chemicals. Propylene glycol and ethyl acetate have a wide variety of uses, so it is important to understand their structural and dynamical characteristics. Therefore, from this view, the dielectric relaxation behavior of the binary mixture of ethyl acetate and propylene glycol has been investigated using time domain reflectometry technique.

EXPERIMENTAL

The ethyl acetate and propylene glycol were procured from Qualigens, India with purity 99% and 98%, respectively and used without further purification. Using 1 mL micropipette, the concentrations were accurately prepared for a 5 mL solution with a 99.5% accuracy.

Characterization: Complex permittivity spectra were studied using time domain reflectometry. The Hewlett Packard HP54750A sampling oscilloscope with HP54754A TDR plug in module was used. A fast-rising step voltage pulse of about 39 ps rise time generated by a pulse generator was propagated through a flexible coaxial cable with characteristics impedance of 50 Ω . The sample was placed at the end of the coaxial line in the standard military application (SMA) coaxial cell coaxial connector with 3.5 mm outer diameter and 1.35 mm effective pin length. At four different temperatures (288 K, 298 K, 308 K and 318 K), data was collected for 15 different concentrations. All measurements were performed under open load conditions and the time window was kept to 5 ns. The time dependent response waveform without sample $R_1(t)$ and with sample $R_x(t)$

were digitized in 1024 points in the memory of the oscilloscope. The temperature dependent dielectric measurements were done using temperature bath. The temperature of sample was maintained at desired value, within accuracy limit of $\pm 1^\circ\text{C}$, by circulating constant water through heat insulating jacket surrounding sample cell.

Data analysis: The time domain data is converted into frequency domain data in frequency range of 10 MHz to 20 GHz. The frequency domain data obtained from Fourier Transform is further used to calculate frequency dependent complex reflection coefficient $\rho^*(\omega)$ given by eqn. 1:

$$\rho^*(\omega) = \frac{C}{i\omega d} \frac{p(\omega)}{q(\omega)} \quad (1)$$

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 velocity of light; ω is angular frequency; d is the effective pin length and $i = \sqrt{-1}$. The complex permittivity spectra $\epsilon^*(\omega)$ [10] were obtained from reflection coefficient spectra $\rho^*(\omega)$ by applying a bilinear calibration method [11]. Using the complex permittivity spectrum, static dielectric permittivity constant (ϵ_s), dielectric constants at infinite frequency (ϵ_∞) and relaxation time (τ) can be calculated by using Havriliak-Negami expression [12].

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau)^{1-\alpha}]^\beta} \quad (2)$$

where $\epsilon^*(\omega)$ is the complex permittivity at an angular frequency ω ; ϵ_∞ is the permittivity at high frequency, ϵ_s 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. The value of ϵ_∞ was taken to be 3.2, for the frequency range considered here, ϵ^* is not sensitive to ϵ_∞ . Eqn. 2 includes Cole-Cole [13] ($\beta = 1$), Davidson-Cole [14] ($\alpha = 0$) and Debye [15] ($\alpha = 0, \beta = 1$) relaxation models. The dielectric model for fitting dielectric parameters suitable for present system is Davidson-Cole model.

Excess dielectric constant and excess inverse relaxation time: The structural formation, their rotation and to understand the role of hydrogen bonding, the excess dielectric properties such as excess dielectric permittivity (ϵ^E) and excess inverse relaxation time $(1/\tau)^E$ are obtained. The excess permittivity is given as follows:

$$\epsilon^E = \epsilon_m - (\epsilon_A X_A + \epsilon_B X_B) \quad (3)$$

where X is the mole fraction and suffices m, A, B represents mixtures, liquid A (EA) and liquid B (PG), respectively. Since, the permittivity includes static dielectric permittivity and permittivity at infinite frequency above equation can be written as:

$$\epsilon^E = (\epsilon_s - \epsilon_\infty)_m - [(\epsilon_s - \epsilon_\infty)_A X_A + (\epsilon_s - \epsilon_\infty)_B X_B]$$

where $\epsilon_s, \epsilon_\infty$ are static permittivity and permittivity at infinite frequency. The excess permittivity values provide the quantitative information regarding the solute-solvent interaction as follows:

(i) $\epsilon^E = 0$: This means the liquid A and liquid B do not interact at all.

(ii) $\epsilon^E < 0$: This means the solute and solvent interact in such a way that the effective dipole moment gets reduced. Solute and solvent interactions lead to the less effective dipoles.

(iii) $\epsilon^E > 0$: It indicates that the solute and solvent interact in such a way that the effective dipole moment increases.

Similarly, the excess inverse relaxation time is given by:

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

where $(1/\tau)^E$ is the excess inverse relaxation time.

The quantitative information regarding the dynamics of solute-solvent interaction obtained from excess inverse relaxation time is as follows:

(i) $(1/\tau)^E = 0$: This indicates that there is negligible change in the dynamics of the solute-solvent interaction.

(ii) $(1/\tau)^E < 0$: This indicates that the solute-solvent interaction produces a field such that the effective dipoles rotate slowly.

(iii) $(1/\tau)^E > 0$: This indicates that the solute-solvent interaction produces a field such that the effective dipoles rotate faster *i.e.*, the field will cooperate in rotation of dipoles. The experimental values of both the excess parameters were fitted to the Redlich-Kister [16] equation:

$$P^E = x_A \cdot x_B \cdot \sum_{j=0}^n B_j \cdot (x_A - x_B)^j \quad (5)$$

where P^E is either ϵ^E or $(1/\tau)^E$, x_A and x_B are the mole fractions of ethyl acetate and propylene glycol, respectively, using these B_j values excess parameters at various concentration were calculated and used to draw the smooth curves.

Bruggeman factor: The static permittivity of two component mixtures must lie somewhere between two extremes corresponding to static permittivity of two liquids. Many mixture formulae have been proposed to explain the dipole interaction in the mixture of two liquids [14,15].

Bruggeman factor [17] can be used as first evidence of molecular interactions in binary mixture. This formula states that static permittivity of binary mixture (ϵ_{sm}), solute A (ϵ_{sA}) and solvent B (ϵ_{sB}) can be related to volume fraction of solvent (V), ethyl acetate in mixture as:

$$f_B = \left(\frac{\epsilon_{sm} - \epsilon_{sB}}{\epsilon_{sA} - \epsilon_{sB}}\right) \left(\frac{\epsilon_{sA}}{\epsilon_{sm}}\right)^{1/3} = 1 - V \quad (6)$$

Kirkwood correlation factor: The Kirkwood correlation factor 'g' is another measure that defines the electric dipole orientation in polar liquids [18]. The factor 'g' for pure liquid is given by the following expression:

$$\frac{4\pi N \mu^2 \rho}{9KTM} g = \frac{(\epsilon_s - \epsilon_\infty)(2\epsilon_s - \epsilon_\infty)}{\epsilon_s(\epsilon_\infty + 2)^2} \quad (7)$$

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 and N is the Avogadro's number. The corresponding equation for binary mixtures is not available in literature. However, for mixture of two polar liquids say A (EA) and B (PG), above equation can be modified using some assumptions.

Assume that (g) for mixture is expressed by an effective averaged correlation factor (g^{eff}) such that Kirkwood equation for the mixture can be expressed as:

$$\frac{4\pi}{9KT} \left(\frac{\mu_A^2 \rho_A}{M_A} X_A + \frac{\mu_B^2 \rho_B}{M_B} X_B \right) g^{\text{eff}} = \frac{(\epsilon_{\text{sm}} - \epsilon_{\infty\text{m}})(2\epsilon_{\text{sm}} - \epsilon_{\infty\text{m}})}{\epsilon_{\text{sm}}(\epsilon_{\infty\text{m}} + 2)^2} \quad (8)$$

where X_A and X_B the volume fractions of liquids A (EA) and B (PG) respectively.

Thermodynamic parameters: The relationship between activation enthalpy, entropy, and relaxation time is given by the Eyring rate equation [19]:

$$\tau = \left(\frac{h}{KT} \right) \exp \left(\frac{(\Delta H - T\Delta S)}{RT} \right) \quad (9)$$

where ΔH is the molar enthalpy of activation and ΔS is the molar entropy of activation for the dipole reorientation process and h is Planck's constant. ΔH is obtained from the slope of $\ln(\tau T)$ versus T^{-1} . It follows from this equation that if ΔH and ΔS are independent of temperature, the plot of $\ln(\tau T)$ versus T^{-1} is linear.

$$\Delta H - T\Delta S = RT(\ln \tau) - RT \left[\ln \left(\frac{h}{KT} \right) \right] \quad (10)$$

The order of magnitude of the enthalpy of activation and entropy of activation can give some clue to the molecular energy and order of molecules engaged in the relaxation process.

RESULTS AND DISCUSSION

The values of the static dielectric constant and relaxation time for binary mixture of ethyl acetate + propylene glycol is reported in Table-1, which indicate that static permittivity values decrease with increase in volume fraction of ethyl acetate in the mixture also with increase in temperature. This trend may be attributed to decrease in the degree of polarization of the dipoles [20]. Moreover, the relaxation time also decreases with increase in volume fraction of ethyl acetate in the mixture with increase in temperature. This trend may be attributed to greater size of ethyl acetate molecules than propylene glycol mole-

cules. The decrease of relaxation time values with temperature rise may be due breakage of a greater number of hydrogen bonds in the liquid mixtures due to the thermal vibrations [21].

From Fig. 1, it is observed that excess permittivity (ϵ^E) values for ethyl acetate + propylene glycol binary system are positive upto 0.71 and 0.74 mole fraction of ethyl acetate in the mixture at temperatures 288 K and 298 K, respectively. Beyond 0.71 and 0.74 mole fraction of ethyl acetate in the mixture, these values are negative for 288 K and 298 K temperatures, respectively. Also, it is seen from Fig. 1 that ϵ^E values for this binary system are positive upto 0.30 and 0.37 mole fraction of ethyl acetate in the mixture at temperatures 308 K and 318 K, respectively. Beyond 0.30 and 0.37 mole fraction of ethyl acetate in the mixture, these values are negative for temperatures 308 K and 318 K respectively. Positive ϵ^E values show a rise in the total number of dipoles in the binary mixture under study, which is initiated by parallel alignment of dipoles of the interacting molecules. The negative ϵ^E values indicate that the total number of dipoles in the mixture decreases which is due to opposite alignments of the dipoles of interacting molecules in the mixture [22].

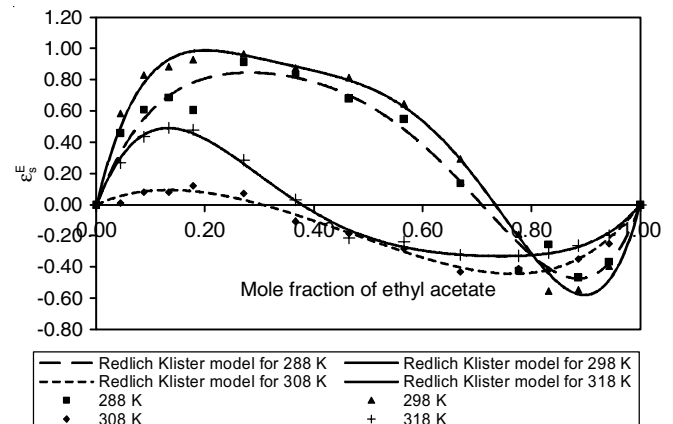


Fig. 1. Excess permittivity (ϵ^E) for ethyl acetate + propylene glycol binary system

TABLE-1
STATIC DIELECTRIC CONSTANT (ϵ_s) AND RELAXATION TIME (τ) VALUES
FOR BINARY MIXTURE OF ETHYL ACETATE + PROPYLENE GLYCOL

Volume fraction of ethyl acetate	288 K		298 K		308 K		318 K	
	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)	ϵ_s	τ (ps)
0.00	29.00	309.64	28.00	258.87	27.49	200.76	27.01	185.95
0.05	28.31	297.56	27.48	229.63	26.41	186.18	26.20	166.52
0.10	27.31	283.28	26.62	207.36	25.39	165.76	25.29	150.25
0.15	26.24	262.63	25.57	187.74	24.3	147.09	24.27	137.23
0.20	25.01	240.27	24.51	165.87	23.25	135.83	23.18	126.54
0.30	23.02	194.83	22.34	134.62	21.02	111.03	20.83	104.11
0.40	20.64	156.21	20.04	107.53	18.66	90.10	18.42	85.84
0.50	18.19	124.82	17.77	84.79	16.4	71.72	16.02	69.38
0.60	15.76	103.66	15.39	65.83	14.12	55.85	13.84	54.59
0.70	13.05	73.44	12.83	50.35	11.79	42.09	11.60	40.74
0.80	10.19	47.11	10.14	32.58	9.63	28.58	9.44	26.76
0.85	9.21	35.60	8.67	23.48	8.53	22.84	8.38	22.23
0.90	7.85	21.00	7.57	19.50	7.51	14.21	7.35	14.04
0.95	6.80	16.10	6.62	11.43	6.52	11.35	6.34	11.25
1.00	6.02	6.37	5.91	6.06	5.68	5.79	5.46	5.07

Fig. 2 shows excess inverse relaxation time values $(1/\tau)^E$ for ethyl acetate + propylene glycol binary system. The values of excess inverse relaxation time are negative for all concentrations and temperatures under study, which shows newly formed effective dipoles rotate slowly under the impact of an external varying field. At all temperatures these values become more negative at around 0.8 mole fraction of ethyl acetate. This shows that the addition of ethyl acetate to propylene glycol triggered the newly formed dipoles to rotate slowly [23].

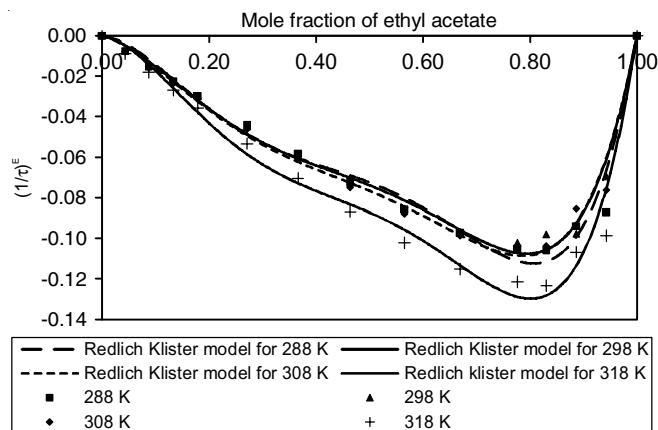


Fig. 2. Excess inverse relaxation time $(1/\tau)^E$ for ethyl acetate + propylene glycol binary system

Fig. 3 gives Bruggeman factor (f_b) plot for ethyl acetate + propylene glycol binary mixture. For all temperature ranges and concentrations, the Bruggeman factor deviates above linear values. Positive shift in Bruggeman factor suggests a decrease in the complex's effective volume. Additionally, it shows a strong intermolecular interaction between the molecules of propylene glycol and ethyl acetate [24].

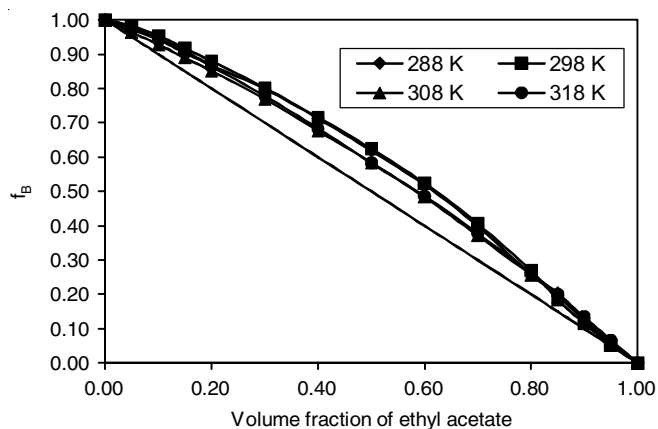


Fig. 3. Bruggeman factor for ethyl acetate + propylene glycol binary system

The value of effective correlation factor (g^{eff}) for ethyl acetate + propylene glycol binary mixture has been reported in Table-2. The values of g^{eff} increase up to 0.5 volume fraction of ethyl acetate in the mixture and then decrease with increase in volume fraction of ethyl acetate in the mixture. This suggests better molecular dipole alignment up to a volume fraction of 0.5 ethyl acetate in the mixture. The g^{eff} values less than unity

TABLE-2
KIRKWOOD CORRELATION FACTOR (g^{eff}) FOR ETHYL ACETATE + PROPYLENE GLYCOL BINARY SYSTEM

Volume fraction of ethyl acetate	288 K	298 K	308 K	318 K
0.00	0.86	0.86	0.87	0.88
0.05	0.88	0.88	0.87	0.89
0.10	0.89	0.89	0.88	0.90
0.15	0.89	0.90	0.88	0.91
0.20	0.89	0.91	0.88	0.91
0.30	0.91	0.92	0.89	0.91
0.40	0.92	0.92	0.88	0.90
0.50	0.92	0.93	0.88	0.89
0.60	0.92	0.93	0.87	0.88
0.70	0.90	0.91	0.85	0.87
0.80	0.84	0.86	0.84	0.85
0.85	0.84	0.81	0.82	0.83
0.90	0.80	0.79	0.81	0.81
0.95	0.79	0.79	0.80	0.79
1.00	0.82	0.82	0.80	0.78

indicates antiparallel alignments of dipoles which reduces dipole rotation [25].

Molar enthalpy of activation values (ΔH) and molar entropy of activation values (ΔS) for ethyl acetate + propylene glycol binary system are shown in Fig. 4. All concentrations have positive values for the molar enthalpy of activation (ΔH). The positive values of ΔH confirm that heat is absorbed during the molecular reorientation process [26]. For all concentrations, the molar entropy of activation (ΔS) values are negative, which demonstrates that there is highly ordered group dipole reorientation in the mixture [27].

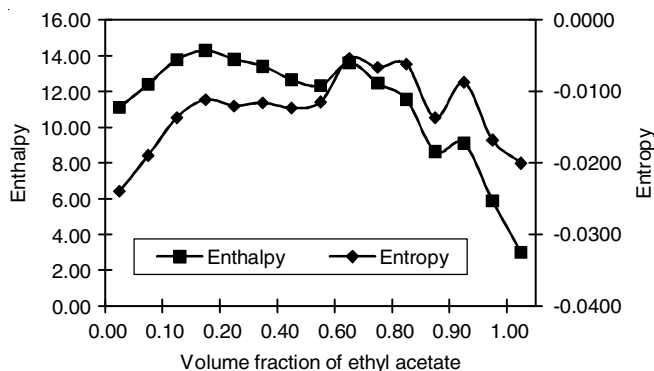


Fig. 4. Variation of enthalpy of activation and entropy of activation for ethyl acetate + propylene glycol binary system

Conclusion

The dielectric constant (ϵ_s), relaxation time (τ) values show a decreasing trend for all concentrations and temperatures. The ϵ^E values are positive and also negative and $(1/\tau)^E$ values are negative for all concentrations and temperatures. The g^{eff} values less than unity indicate effective dipolar ordering due to heterointeraction between ethyl acetate and propylene glycol molecules. Bruggeman factor for this system confirms the decrease in volume during intermolecular interaction. The ΔH values indicates endothermic interaction between ethyl acetate and propylene glycol and ΔS shows more ordered activated state.

ACKNOWLEDGEMENTS

The authors thank Retd. Prof. P.W. Khirade, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University Aurangabad, India for providing the guidance and help.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- S.D. Deshmukh, K.L. Pattebahadur, A.G. Mohod, S.S. Patil and P.W. Khirade, *J. Mol. Liq.*, **297**, 11819 (2020); <https://doi.org/10.1016/j.molliq.2019.111819>
- P.B. Undre, P.W. Khirade, V.S. Rajenimbalkar, S.N. Helambe and S.C. Mehrotra, *Phys. Chem. Liq.*, **50**, 637 (2012); <https://doi.org/10.1080/00319104.2011.646443>
- G. Ravi, P.B. Undre, K. Ramachandran and K. Samuvel, *S. Afr. J. Chem. Eng.*, **24**, 71 (2017); <https://doi.org/10.1016/j.sajce.2017.06.006>.
- P. Senthilkumar, T. Ganesh, K. Vinoth, D.J.S. Anand Karunakaran, M. Mariasylvestre, R. Deshmukh and A.C. Kumbharkhane, *Phys. Chem. Liq.*, **59**, 480 (2021); <https://doi.org/10.1080/00319104.2020.1743701>
- S. Sahoo, K. Dutta, S. Acharyya and S.K. Sit, *Pramana J. Phys.*, **70**, 543 (2008); <https://doi.org/10.1007/s12043-008-0069-1>
- S.B. Sayyad, P.B. Undre, P. Yannewar, S.S. Patil, P.W. Khirade and S.C. Mehrotra, *Lith. J. Phys.*, **51**, 29 (2011); <https://doi.org/10.3952/lithjphys.51103>
- T. Kalaivani, P. Undre, R. Sabesan and S. Krishnan, *Main Group Chem.*, **8**, 125 (2009); <https://doi.org/10.1080/10241220902977646>
- A.P. Maharolkar, A.G. Murugkar, P.W. Khirade and S.C. Mehrotra, *Russ. J. Phys. Chem. A. Focus Chem.*, **96**, 2113 (2022); <https://doi.org/10.1134/S003602442210017X>
- Ch.V.V. Ramana, A.B.V.K. Kumar, M.A. Kumar and M.K. Moodley, *J. Chem.*, **2013**, 687106 (2013); <https://doi.org/10.1155/2013/687106>
- S. Mashimo, S. Kuwabara, S. Yagihara and K. Higasi, *J. Chem. Phys.*, **90**, 3292 (1989); <https://doi.org/10.1063/1.455883>
- R.H. Cole, J.G. Berberian, S. Mashimo, G. Chryssikos, A. Burns and E. Tombari, *J. Appl. Phys.*, **66**, 793 (1989); <https://doi.org/10.1063/1.343499>
- S. Havriliak and S. Negami, *J. Polym. Sci. Part C Polym. Symp.*, **14**, 99 (1966); <https://doi.org/10.1002/polc.5070140111>
- K.S. Cole and R.H. Cole, *J. Chem. Phys.*, **9**, 341 (1941); <https://doi.org/10.1063/1.1750906>
- D.W. Davidson and R.H. Cole, *J. Chem. Phys.*, **19**, 1484 (1951); <https://doi.org/10.1063/1.1748105>
- P. Debye, *Polar Molecules*, Dover Publications: New York (1929).
- O. Redlich and A.T. Kister, *Ind. Eng. Chem.*, **40**, 345 (1948); <https://doi.org/10.1021/ie50458a036>
- D.A.G. Bruggeman, *Ann. Phys.*, **416**, 636 (1935); <https://doi.org/10.1002/andp.19354160705>
- G. Oster and J.G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943); <https://doi.org/10.1063/1.1723823>
- H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); <https://doi.org/10.1063/1.1749836>
- K. Dharmalingam, K. Ramachandran, P. Sivagurunathan, B. Prabhakar Undre, P.W. Khirade and S.C. Mehrotra, *Bull. Korean Chem. Soc.*, **27**, 2040 (2006); <https://doi.org/10.5012/bkcs.2006.27.12.2040>
- T. Vishwam, N.K.S.P.S. Sarma, K. Parvateesam and V.R.K. Murthy, *Int. J. Eng. Res. Technol.*, **4**, 1 (2015).
- P. Undre, S.N. Helambe, S.B. Jagdale, P.W. Khirade and S.C. Mehrotra, *J. Mol. Liq.*, **137**, 147 (2008); <https://doi.org/10.1016/j.molliq.2007.06.004>
- P. Sivagurunathan, K. Dharmalingam, K. Ramachandran, B. Prabhakar Undre, P.W. Khirade and S.C. Mehrotra, *Physica B*, **387**, 203 (2007); <https://doi.org/10.1016/j.physb.2006.04.005>
- P. Aruna Maharolkar, A.G. Murugkar, P.W. Khirade and S.C. Mehrotra, *Bull. Chem. Soc. Ethiop.*, **33**, 349 (2019); <https://doi.org/10.4314/bcse.v33i2.15>
- S. Tabassum and V.P. Pawar, *J. Adv. Dielectr.*, **8**, 1850019 (2018); <https://doi.org/10.1142/S2010135X18500194>
- R.V. Shinde, A.R. Deshmukh, S.A. Ingole and A.C. Kumbharkhane, *J. Adv. Dielectr.*, **9**, 1950018 (2019); <https://doi.org/10.1142/S2010135X19500188>
- A Aathif Basha, F Liakath Ali Khan, P Muzammil and G S Fasiuddin, *Mater. Res. Express*, **9**, 075303 (2022); <https://doi.org/10.1088/2053-1591/ac7ea2>