

Research Article

Effect of Solvents on the Ultrasonic Velocity and Acoustic Parameters of Polyvinylidene Fluoride Solutions

S. S. Kulkarni¹ and U. V. Khadke²

¹Department of Physics, KLS Gogte Institute of Technology, Belgaum 590008, India

²Department of Physics, Bheemanna Khandre Institute of Technology, Bhalki 585328, India

Correspondence should be addressed to U. V. Khadke; khadke@email.com

Received 12 March 2016; Accepted 10 April 2016

Academic Editor: Ramki Kalyanaraman

Copyright © 2016 S. S. Kulkarni and U. V. Khadke. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Ultrasonic studies provide a wealth of information in understanding the molecular behavior and intermolecular interaction of polymer solvent mixtures. Attempts were made to measure ultrasonic velocity, density, and viscosity for the mixture of polyvinylidene fluoride (PVDF) in acetone and dimethylformamide (DMF) of various stoichiometric ratios at 300 K using crystal controlled ultrasonic interferometer (Mittal make), pycnometer (specific gravity bottle), and Ostwald viscometer, respectively. The acoustic parameters adiabatic compressibility (β), intermolecular free path length (L_f), acoustic impedance (Z), relative association (RA), ultrasonic attenuation (α/f^2), and relaxation time (τ) have been estimated using experimental data with well-known techniques. The variation of these acoustic parameters is explained in terms of solute-solvent molecular interaction in a polymer solution.

1. Introduction

Ultrasonic studies in polymeric solutions have drawn the attention of many researchers in the recent years [1–4]. The extensive use of polymeric materials in technology has necessitated investigations of the molecular interactions of polymers and solvents [5–9]. The ultrasonic technique is a powerful and effective tool for investigation of polymer solutions and behavior of polymer chain in an ultrasonic field.

Polyvinylidene fluoride (PVDF) is a semicrystalline polymer that has a simple chemical structure $[-(\text{CH}_2-\text{CF}_2)-]_n$. It is the first ferroelectric polymer and unique among many inorganic and organic ferroelectric substances [10, 11]. The PVDF exists in four crystalline forms, namely, α , β , γ , and δ , depending upon preparation conditions. It has attracted researchers due to its piezo-, pyro-, and ferroelectric characteristics [12]. These properties are useful for device application such as ultrasound transducers, nonvolatile memory, sensors, actuators, sonar instruments, and solar cells. The scarcity of knowledge regarding the ultrasonic studies of solutions of PVDF in the literature has promoted us to understand the effect of concentration and nature of solvents

on the molecular interactions in the polymer solution. The physical properties of this ferroelectric polymer can be understood better by the study of molecular interaction.

In our experimental investigation, we used the ultrasonic technique to find the acoustic parameters such as adiabatic compressibility (β), intermolecular free path length (L_f), acoustic impedance (Z), relative association (RA), ultrasonic attenuation, and relaxation time to correlate with the physical properties.

2. Materials and Methods

AR grade (99.8% pure) ferroelectric polymer PVDF in powder form is procured from Sigma Aldrich, Bangalore, India. Figure 1 shows the X-ray diffraction pattern of the procured PVDF. The diffraction peak observed at $2\theta = 18.09^\circ$, 19.58° confirms the β -phase of the powder sample. This PVDF powder is mixed with different concentrations of acetone (AR grade 99.5%) and DMF (AR grade 99.5%), both the solvents procured from High-Media Laboratories Pvt. Ltd., Mumbai, India. The solution was magnetically stirred for 2 hours, so

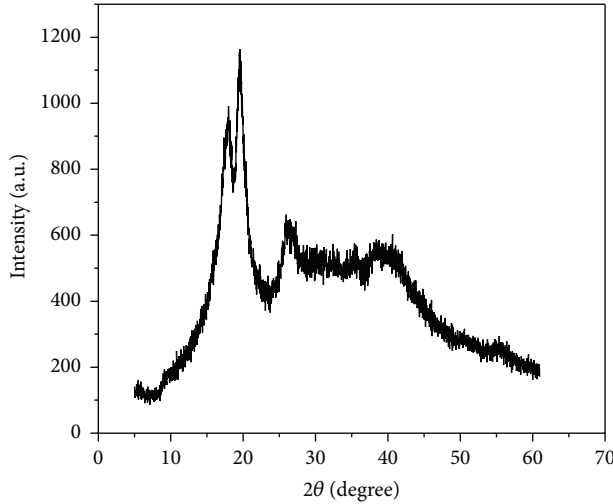


FIGURE 1: XRD pattern of virgin PVDF powder confirming the phase formation.

that the powder dissolves completely. The acoustic properties are studied in this prepared solution.

2.1. Experimental Technique. Ultrasonic interferometer, specific gravity bottle, and Ostwald viscometer are used to measure ultrasonic velocity, density, and viscosity, respectively.

Ultrasonic velocity was measured using a single-crystal interferometer (Mittal Enterprises, New Delhi) operating at 1 MHz with an accuracy of ± 1.0 m/s. The experimental procedures are standard and described elsewhere [13]. Densities of the solutions were measured using a 25 mL specific gravity bottle and the weight of the liquid was measured using an electronic balance (Model Shimadzu AX200). The measurement was repeated thrice for the same solution to obtain better accuracy. Accuracy in the measurement of densities of the solutions is ± 0.1 kg/m³. The viscosity was measured with Ostwald's viscometer and the flow time with a digital stopwatch. The measurements were repeated thrice to confirm the accuracy of results. The time flow is measured using digital stopwatch capable of registering time accurate to ± 0.1 s.

The acoustic parameters were computed as follows.

The ultrasonic velocity is calculated as

$$v = f\lambda, \quad (1)$$

where " f " is the frequency of the ultrasonic waves and " λ " is the measured wavelength value of ultrasonic waves in a given solution.

The viscosity of the solution is calculated using

$$\eta = \frac{d_l t_l}{d_w t_w} \eta_w, \quad (2)$$

where d_l and t_l are density and time flow of liquid, whereas d_w and t_w are density and time flow of water. The density of the solution is taken as mass per unit volume.

The following equations are used to compute the acoustic parameters: adiabatic compressibility (β), intermolecular free

path length (L_f), acoustic impedance (Z), relative association (RA), ultrasonic attenuation (α/f^2), and relaxation time (τ).

2.2. Theoretical Calculations

- (1) Adiabatic compressibility (β) has been calculated from the ultrasonic velocity " v " and the density " ρ " of the solution using the Newton-Laplace equation [14]:

$$\beta = \frac{1}{\rho v^2}. \quad (3)$$

- (2) Intermolecular free path length (L_f) has been determined as follows [15]:

$$L_f = K\beta^{1/2}, \quad (4)$$

where K is the temperature dependent Jacobson's constant ($K = 205.35 \times 10^{-8}$ at 300 K) and β is the adiabatic compressibility.

- (3) Acoustic impedance (Z) is given as follows:

$$Z = \rho v, \quad (5)$$

where ρ and v are the density and velocity of the solution, respectively.

- (4) Relative association (RA) is as follows:

$$RA = \left(\frac{\rho}{\rho_o} \right) \left(\frac{v_o}{v} \right), \quad (6)$$

where ρ_o and v_o are the density and velocity of the solvent.

- (5) Ultrasonic attenuation (α/f^2) and relaxation time (τ) were calculated using the following [16]:

$$\begin{aligned} \frac{\alpha}{f^2} &= \frac{8\pi^2\eta}{\rho v^3}, \\ \tau &= \frac{4\eta}{3\rho v^2}, \end{aligned} \quad (7)$$

where η is the viscosity of the solution.

3. Results and Discussion

The experimentally obtained values of density, viscosity, and ultrasonic velocity of PVDF with different concentrations of acetone and DMF are reported in Tables 1 and 2, respectively. Due to specific molecular interactions such as association, expansion, and unfolding the variation of η and v with c is considerably more than that of ρ . Molecular interactions depend on the strength of the repulsive forces acting among solvent and solute molecules and hence intermolecular motion is affected accordingly. Attractive forces result into molecular association (solvation), that is, modification of the PVDF molecule. Molecular association

TABLE 1: Variation of density, viscosity, and ultrasonic velocity of PVDF with different concentrations of acetone at 300 K.

Concentration c mass%	Density ρ kg/m ³	Viscosity η 10 ⁻³ Nsm ⁻²	Ultrasonic velocity v m/s
0.00	783.00	0.3635	1165.00
0.10	783.56	0.3665	1165.90
0.20	784.10	0.3672	1166.50
0.30	784.68	0.3747	1168.00
0.40	787.76	0.3836	1169.00
0.50	790.36	0.3893	1170.80

Compounded uncertainty in measurement of density ($U\rho$) = ± 0.52 , viscosity ($U\eta$) = ± 0.0188 , and ultrasonic velocity (Uv) = ± 0.20 with level of confidence is 95%.

TABLE 2: Variation of density, viscosity, and ultrasonic velocity of PVDF with different concentrations of dimethylformamide at 300 K.

Concentration c mass%	Density ρ kg/m ³	Viscosity η 10 ⁻³ Nsm ⁻²	Ultrasonic velocity v m/s
0.00	934.20	0.7921	1454.00
0.10	934.92	0.9084	1474.00
0.20	937.04	0.9156	1478.00
0.30	938.16	1.0505	1482.50
0.40	939.04	1.0818	1485.00
0.50	940.88	1.3422	1486.60

Compounded uncertainty in measurement of density ($U\rho$) = ± 0.52 , viscosity ($U\eta$) = ± 0.0188 , and ultrasonic velocity (Uv) = ± 0.20 with level of confidence is 95%.

leads to change in apparent molecular volume as well as mass and hence density changes accordingly. Under a set of experimental conditions the values of ρ , η , and v are affected by molecular interaction. Vander Waals, H-bonding, dipolar, and London types forces between solvent and solute molecules result in the aggregation of solvent molecules around solute molecules. It shows that the density, viscosity, and ultrasonic velocity of the solution increase with increase in concentration. This linear increase of ρ , η , and v with concentration confirms an increase of cohesive forces because of strong molecular interactions [17]. The values of density, viscosity, and ultrasonic velocity of the solution increased by $\sim 1\%$, $\sim 7.1\%$, and 0.5% and 0.7% , 69% , and 2% , respectively, for the 50% concentration of PVDF in acetone and DMF. The least square equations along with regression coefficients are reported in Table 3. A fairly good to excellent correlation between given parameters and concentration was observed in acetone and DMF solvents. The observed correlation between ρ , η , and v with concentration is $R^2 = 0.929$ – 0.992 , 0.949 – 0.961 , and 0.90 – 0.987 , respectively. The obtained values of R^2 support linear dependence of ρ , η , and v with concentration.

In order to understand the effect of concentration and nature of solvent on PVDF polymeric solution, the acoustic parameters such as adiabatic compressibility (β), intermolecular free pathlength (L_f), acoustic impedance (Z), relative

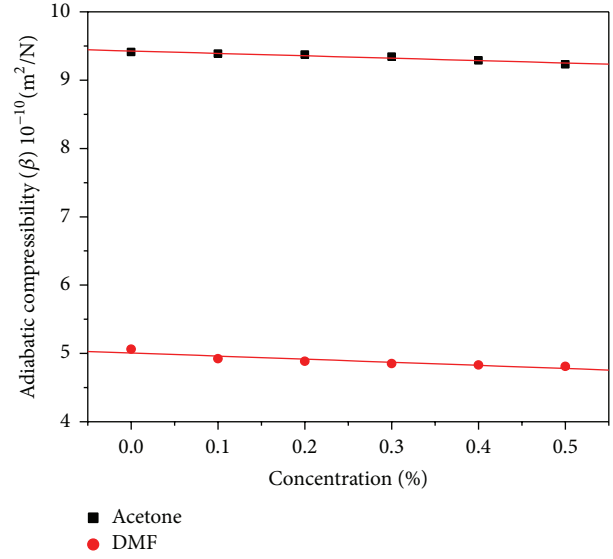


FIGURE 2: Variation of adiabatic compressibility with concentration of PVDF in acetone and DMF at 300 K.

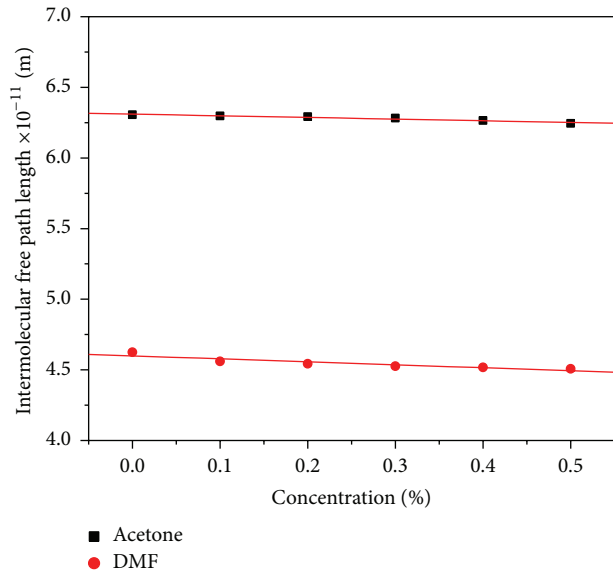


FIGURE 3: Variation of intermolecular free path length with concentration of PVDF in acetone and DMF at 300 K.

association (RA), ultrasonic attenuation (α/f^2), and relaxation time (τ) were determined using standard equations and are correlated with concentration as shown in Figures 2, 3, 4, 5, 6, and 7. The least square and regression coefficients of these acoustic parameters are shown in Table 3.

Ultrasonic speed in the solutions depends on intermolecular free path length. When ultrasonic waves are present in the solution, the molecules get perturbed. Due to some elasticity of the medium, perturbed molecules regain their equilibrium positions. When a solute is added to a solvent, its molecules attract certain solvent molecules towards them. The phenomenon is known as compression and also as limiting compressibility. The aggregation of solvent molecules

TABLE 3: The least square equations and regression coefficients for PVDF solution in acetone and DMF.

Parameters	Regression coefficients (R^2)	
	Acetone	DMF
$\rho \text{ kg/m}^3$	$14.28c + 782.00$ (0.929)	$13.394c + 934.024$ (0.992)
$\eta 10^{-3} \text{ Nsm}^{-2}$	$5.257 \times 10^{-5}c + 3.611 \times 10^{-4}$ (0.961)	$9.685 \times 10^{-4}c + 7.7219 \times 10^{-4}$ (0.949)
$\nu \text{ m/s}$	$11.37c + 1164.69$ (0.987)	$57.285c + 1462.36$ (0.890)
$\beta 10^{-10} \text{ m}^2/\text{N}$	$-0.35097c + 9.42638$ (-0.968)	$-0.45354c + 5.0065$ (-0.916)
$Z 10^6 \text{ kgm}^2\text{s}^{-1}$	$0.02309c + 0.91106$ (0.971)	$0.07346c + 1.36582$ (0.940)
$L_f 10^{-11} \text{ m}$	$-0.11817c + 6.31044$ (-0.968)	$-0.21003c + 4.59886$ (-0.917)
RA	$2.2614 \times 10^{-5}c + 2.3064 \times 10^{-14}$ (0.957)	$2.207 \times 10^{-14}c + 2.095 \times 10^{-14}$ (0.931)
$\tau 10^{-13} \text{ s}$	$4.913 \times 10^{-14}c + 4.534 \times 10^{-13}$ (0.962)	$5.1685 \times 10^{-13} + 5.7522 \times 10^{-13}$ (0.938)
$\alpha/f^2 10^{-14} \text{ s}^2\text{m}^{-1}$	$0.96994c + 8.95398$ (0.962)	$2.207 \times 10^{-14}c + 2.0959 \times 10^{-14}$ (0.931)

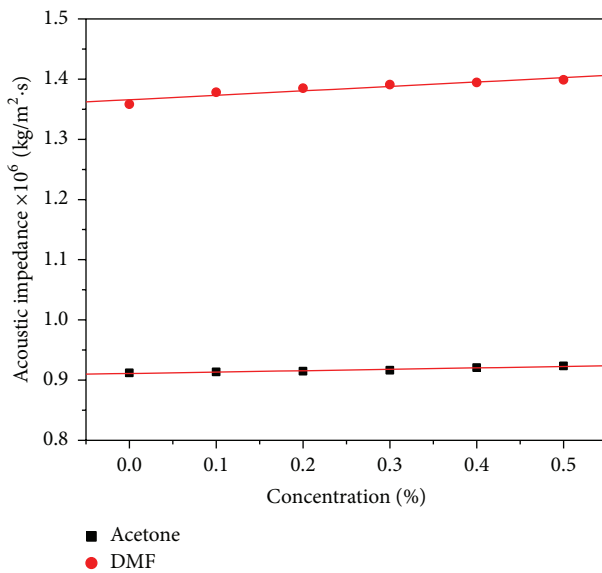


FIGURE 4: Variation of acoustic impedance with concentration of PVDF in acetone and DMF at 300 K.

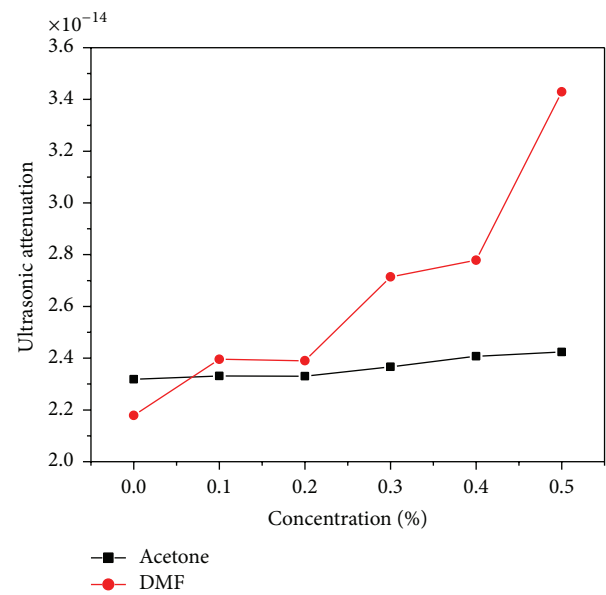


FIGURE 5: Variation of ultrasonic attenuation with concentration of PVDF in acetone and DMF at 300 K.

around solute molecules supports powerful solvent-solute interactions. Because of solvent-solute interactions, the structure of the solute is modified to the considerable extent. The adiabatic compressibility and intermolecular free path length decrease from those of pure solution by ~2% and 1% and 5% and 2.5%, respectively, in acetone and DMF. Decrease of L_f with concentration supports solvent-solute interactions. However, acoustic impedance, relative association, ultrasonic attenuation, and relaxation time increase by 1.2%, 0.7%, 4.5%, and 5.05% and 3%, 0.027%, 57%, and 61% with respect to those in pure solution of acetone and DMF, respectively. This indicates a strong intermolecular interaction between solute and solvent molecules in the system at higher concentration of PVDF and suggests more association between solute and solvent molecules in the system.

The variation of ultrasonic velocity in a solution depends on the intermolecular free length on mixing. On the basis of a model for sound propagation proposed by Kincaid and Eyring [18] ultrasonic velocity increases with decrease of free path length and vice versa.

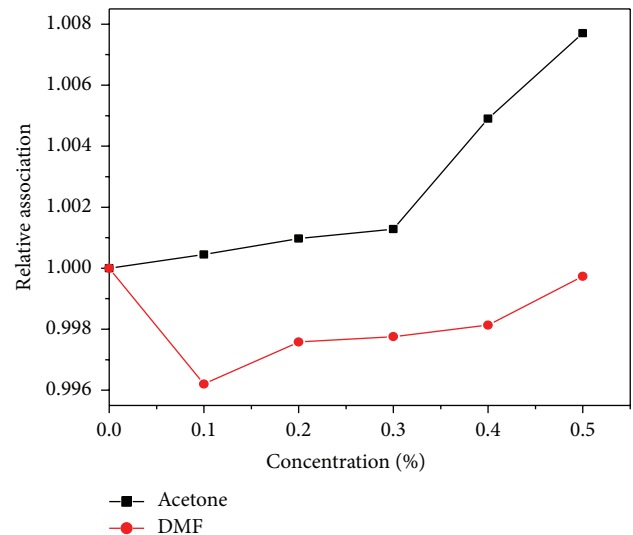


FIGURE 6: Variation of relative association with concentration of PVDF in acetone and DMF at 300 K.

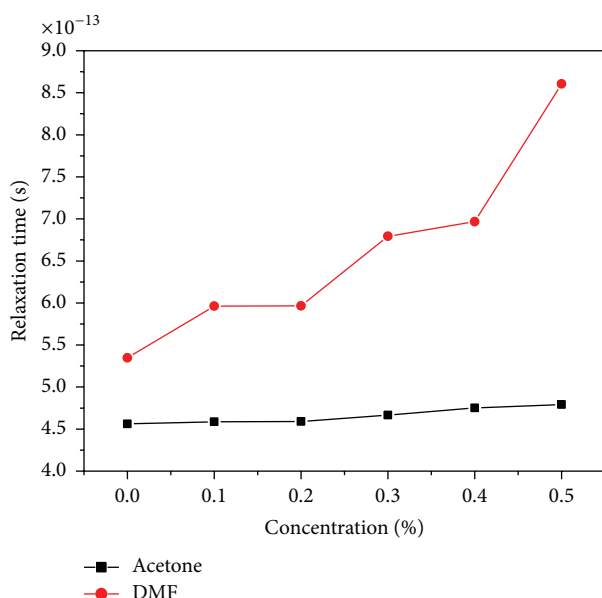


FIGURE 7: Variation of relaxation time with concentration of PVDF in acetone and DMF at 300 K.

The property which can be studied to understand the interaction is relative association (RA). It can be explained by two factors [19]: (1) the breaking up of solvent molecules on addition of solute to it and (2) solvation of the solute molecule. The former leads to decrease and the latter to the increase of relative association. In our study the values of RA increase with increase in the solute concentration due to solvation of the solute molecule.

4. Conclusion

The ultrasonic technique is a powerful and effective tool for the investigation of polymer solutions and behavior of polymer chain in an ultrasonic field. The present study describes the acoustic properties that confirm the molecular interaction of PVDF polymer powder with a acetone and DMF. The acoustic parameters like adiabatic compressibility (β), intermolecular free path length (L_f), acoustic impedance (Z), relative association (RA), ultrasonic attenuation (α/f^2), and relaxation time (τ) have been estimated using experimental data. The variations in the acoustic parameters suggest that there are strong polymer-solvent interactions at higher concentration.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The authors express their deep sense of gratitude to Vision Group of Science and Technology for providing the financial support to carry out this research work. The authors are also

thankful to Dr. M. Revanasiddappa, PESIT, South Campus, Bangalore, for his valuable suggestions.

References

- [1] K. Sreekanth, M. Kondaiah, D. Sravana Kumar, and D. Krishna Rao, "Excess acoustical and volumetric properties and theoretical estimation of ultrasonic velocities in binary liquid mixtures of 2-chloroaniline with acrylic esters at 308.15 K," *Journal of Solution Chemistry*, vol. 41, no. 7, pp. 1088–1102, 2012.
- [2] M. K. Praharaj, A. Satapathy, P. Mishra, and S. Mishra, "Ultrasonic studies of ternary liquid mixtures of N-N-dimethylformamide, nitrobenzene, and cyclohexane at different frequencies at 318 K," *Journal of Theoretical and Applied Physics*, vol. 7, article 23, 6 pages, 2013.
- [3] B. Nagarjun, A. V. Sarma, G. V. Rama Rao, and C. Rambabu, "Thermodynamic and acoustic study on molecular interactions in certain binary liquid systems involving ethyl benzoate," *Journal of Thermodynamics*, vol. 2013, Article ID 285796, 9 pages, 2013.
- [4] D. R. Godhani, P. B. Dobariya, A. M. Sanghani, and J. P. Mehta, "Thermodynamic properties of binary mixtures of 1,3,4-oxadiazole derivative with chloroform, N,N-dimethyl formamide at 303, 308 and 313 K and atmospheric pressure," *Arabian Journal of Chemistry*, 2012.
- [5] F. M. Sannaningannavar, B. S. Navati, and N. H. Ayachit, "Studies on thermo-acoustic parameters in the dilute solutions of poly(ethyleneglycol)," *Polymer Bulletin*, vol. 70, no. 2, pp. 603–618, 2013.
- [6] K. P. Singh and S. C. Bhatt, "Investigation of acoustical parameters of polyvinyl acetate," *Applied Physics Research*, vol. 2, no. 1, 2010.
- [7] P. J. Vasoya, N. M. Mehta, V. A. Patel, and P. H. Parsania, "Effect of temperature on ultrasonic velocity and thermodynamic parameters of cardo aromatic polysulfonate solutions," *Journal of Scientific and Industrial Research*, vol. 66, no. 10, pp. 841–884, 2007.
- [8] S. K. Mehta, R. Jain, S. Sharma, and K. K. Bhasin, "Interaction of poly(ethylene glycol)-400 with tetraethylammonium bromide in aqueous media," *Journal of Molecular Liquids*, vol. 122, no. 1–3, pp. 15–20, 2005.
- [9] V. Kannappan, B. S. Santhi, and D. R. Jonathan, "Ultrasonic investigation on segmental motion of some polymers in solution," *Indian Journal of Chemistry A*, vol. 53, no. 6, pp. 688–694, 2014.
- [10] H. Kawai, "The piezoelectricity of poly (vinylidene fluoride)," *Japanese Journal of Applied Physics*, vol. 8, no. 7, pp. 975–976, 1969.
- [11] R. G. Kepler and R. A. Anderson, "Ferroelectricity in polyvinylidene fluoride," *Journal of Applied Physics*, vol. 49, no. 3, pp. 1232–1235, 1978.
- [12] K. Tashiro and H. S. Nalwa, *Ferroelectric Polymers*, Marcel Dekker, New York, NY, USA, 1995.
- [13] P. S. Nikam, B. S. Jagdale, A. B. Sawant, and M. Hassan, "Ultrasonic study of binary liquid mixtures of benzonitrile with alkanols (C~1C~3) at various temperatures," *Acoustic Letters*, vol. 22, pp. 199–203, 1999.
- [14] D. N. Rao, A. Krishnaiah, and P. R. Naidu, "Excess thermodynamic properties of liquid ethylenediamine+anaromatic hydrocarbon," *Acta Chimica Academiae Scientiarum Hungaricae*, vol. 107, no. 1, pp. 49–55, 1981.

- [15] P. S. Nikam and M. Hasan, "Ultrasonic velocity and apparent molar compressibility of trichloroacetic acid in aqueous ethanol," *Asian Journal of Chemistry*, vol. 5, no. 2, pp. 319–321, 1993.
- [16] J. K. Das, S. K. Dash, N. Swain, and B. B. Swain, "Ultrasonic investigation in a polar-polar system-Methyl isobutyl ketone (MIBK) and aliphatic alcohols," *Journal of Molecular Liquids*, vol. 81, no. 2, pp. 163–179, 1999.
- [17] U. G. Pathak, J. V. Patel, and P. H. Parsania, "Ultrasonic speed and thermodynamic parameters of novel epoxy resin solutions based on cardo symmetric double Schiff bases at 308.15 K," *Journal of Solution Chemistry*, vol. 41, no. 5, pp. 755–765, 2012.
- [18] J. F. Kincaid and H. Eyring, "Free volumes and free angle ratios of molecules in liquids," *The Journal of Chemical Physics*, vol. 6, no. 620, 1938.
- [19] P. B. Agarwal, I. M. Siddiqui, and M. L. Narwade, "Acoustic properties of substituted thiadiazoles and methyl-5-carboxylates in dioxan-water, ethanol-water and acetone-water mixtures at 298.5 ± 0.1 K," *Indian Journal of Chemistry*, vol. 42, no. 5, pp. 1050–1052, 2003.

