MOLECULAR INTERACTION STUDY OF POLYVINYL CHLORIDE IN DIMETHYLFORMAMIDE

Abstract

In present investigation values of density, viscosity and ultrasonic velocity are experimentally measured of polyvinylchloride in dimethylformamide at different concentration and temperatures at frequency of 1MHz. Using these measured values various acoustical parameters of solute- solvent have been calculated to understand molecular interactions between solute and solvent.

This study is helpful to understand the interaction between polymer and solvent. The change of temperature and concentration on various parameters has been studied.

Keywords: ultrasound sound velocity, adiabatic compressibility, Ultrasonic absorption.

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I. INTRODUCTION

In last few years the ultrasonic studies of solution of polymers and in solid polymers have been the become the area of interest for research [1-5]. A literature review on volumetric studies on liquid solution reveals that measurement studies of ultrasonic velocity are helpful to understand the kind of molecular interactions in solute and solvent [6-9].As compared to other plastics, the third most widely used plastic of synthetic polymer is Polyvinylchloride (PVC). Polyvinyl Chloride has many advantages and is generally known to be used to have advantages of least ingredient cost, wide processing adaptability, high ornamental potential and is used to produce different types of products having different range from extremely flexible to highly rapid. Using ultrasonic techniques, a revolutionary work has been done by many researchers [10-11] on polymer and polymer compatibility. As PVC is a major polymer for industry therefore it is chosen to investigate the behavior of interactions of polyvinylchloride in dimethylformamide.

Takeda and Endo [12] observed the viscosity study of solution of polyvinylchloride in dilute form. B. Thapa ET. Al. studied the volumetric studies of polyvinylchloride with solution of cyclohexanone and 1,4-Dioxane. During Polyvinyl chloride plastisol's gelation and fusion with light scattering at small angle, Xiang et. al. [13] survey an effective means for the characterization of structural changes in Polyvinyl chloride particles. From the density, viscosity and viscometric measurement, the compatibility study of blend system of PVC and starch acetate in 1, 4 dioxane studied by Thakore ET. al.[14].Molecular interaction study in organic liquid with CCl_4at different temperature has been carried by C Duraivathi et. al and results are interpreted in terms of thermoacoustic parameters [15]. In interest of observing the outcome of temperature and concentration, experiment was carried out at different concentration and temperature. Very limited literature is available on polyvinylchloride so it is interesting to study molecular interaction in polyvinylchloride. In present investigation various interaction parameters at different range of concentration and temperature of polyvinylchloride in dimethylformamide have been measured and the analysis is described in terms of molecular interaction between solute and solvent. Ultrasonic parameters are very important to understand the physio-chemical behavior of PVC and dimethyl formamide and for production, their applications in different field.

II. EXPERIMENTAL DETAILS

In present study Polyvinyl chloride (of molecular weight ≈ 134.5 Da) in form of liquid is used with dimethylformamide. By mixing the fixed volume of polyvinyl chloride to known volume of dimethylformamide, solutions were prepared and it was stirred spontaneously till a clear solution was obtained. The studied range of concentration in solution is 1%, 0.8%, 0.6%, 0.5%,0.4% and 0.3% in the temperature range 30°C, 35°C, 40° C, 45° C, 50°C, 55°C, 60°C, 65°C at 1 MHz frequency. Ultrasound velocity is measured by using Ultrasonic interferometer having a reliability of ± 4 m/s at 30^{0}C. Specific gravity bottle of 10 ml capacity and single pan micro balance is used for density measurements with the reliability of $0.5 kg/m^3$. Ostwald's viscometer is used for measuring the viscosity of the solution that was kept inside a double walled jacket, in which water was flowed from thermostat water bath. Water of required temperature was used to fill the inner cylinder of this double wall glass jacket so as to initiate and keep up the thermal equilibrium. In uncertainty in each measurement was measured to be 0.01MPa.s.By the use of standard formulae [16-18] the different acoustical parameters is calculated.

III. RESULTS AND DISCUSSION

In the present study, the mixtures property parameters, namely, ultrasonic velocity, viscosity, density and its related parameters like adiabatic compressibility, acoustic impedance, intermolecular free length, relaxation time and ultrasonic absorption for polyvinyl chloride with dimethylformamide in different temperature range 30° C, 35°C, 40° C, 45° C, 50°C, 55°C, 60°C, 65°C and concentration range 1.0%, 0.8%, 0.6%, 0.5%,0.4% and 0.3% have been presented in Table 1 to Table 8 respectively.

The experimental values of density, viscosity and ultrasonic velocity have been presented in Table 1, 2 and 3 and their variation with temperature and concentration is presented in Figure 1 to 6 respectively. Table 1, Fig. 1 and Fig.2 indicates the variation of density with different temperature and concentration respectively. It is reported that density decreases with increase in the value of temperature and increases with increase in concentration of polyvinylchloride in the solution. Increase in the value of density is because of the reason that number of polymer chains increases in addition in the solution with increase in concentration of the PVC. As compared to solvent, polymer has large molecular weight that also contributes in the increase in density. The result reported in the present investigation is in good agreement with the results reported by earlier researchers [19, 20]. Viscosity is an important property and it depends on the molecular size, shape and intermolecular attraction. The measurement of viscosity provides useful information for study of solute- solvent interaction and for interaction of solute-solute. Table 2 and Fig.3 and Fig.4 reports the variation of viscosity with temperature and concentration respectively. It is observed that viscosity measurements decrease with temperature increase and increases with increment in concentration of polyvinylchloride in the solution. The solution becomes more and more viscous as the solute is added`, less fluidity thus led to increase in the viscosity. With the increase in the concentration, the fractional resistance between the medium layers increases and that led to increase in the viscosity. A similar behavior was made by previous authors [21]. Ultrasonic velocity decreases with increase in temperature due to weakening of intermolecular force and increases with increase in concentration of polyvinyl chloride as presented in Table 3, Fig. 5 and Fig.6 respectively. This may be due to increase in mobility of the molecules which may further increase the cohesion between molecules and thus filling all the available free spaces between it. This behavior in the ultrasonic velocity may be because of changes in the structure in the mixture may be because of increasing intermolecular forces. Similar trend is observed by earlier authors [22].A V Narasimham et al. have concluded the similar results for polyvinyl chloride solutions [23]. Table 4 and Fig. 7 shows that intermolecular free length increases with increase in range of temperature and decreases with increase in the concentration of Polyvinylchloride as presented in Table 4 and Fig.8. The variation of ultrasonic velocity in solution depends on intermolecular free length. According to Eyring and Kincaidmodel [24], intermolecular compressibility is purely kinetic in origin, attractive intermolecular forces give rise to internal pressure that is independent of volume and ultrasonic velocity is inversely proportional to intermolecular free length, ultrasonic velocity should decrease with the increase of intermolecular free length and inverse is also true. The results reported in present study are in similar trends with proposed model. Variation of adiabatic compressibility with temperature and concentration are shown in Table 5 and Fig. 9 and 10 respectively. It is reported that adiabatic compressibility increases with increase in temperature and decreases with increase in concentration of polyvinyl chloride in solution. This decrease in value suggests the weakening of molecular interactions in the liquid mixtures. This can be explained in terms of the electrostatic effects of the polymer on the solvent molecules surrounding. The results also indicate that the medium become more compressible. The adiabatic compressibility is inversely proportional to ultrasonic velocity square value; therefore the trend in the adiabatic compressibility is reverse of the trend of ultrasonic velocity with temperature and concentration. With the increase in the velocity with concentration and the density also increases, the compressibility must decrease with increase in concentration of PVC. Some earlier workers have also reported similar behavior of adiabatic compressibility [25]. Acoustic impedance is an important property as it is related to elastic properties of the medium. Therefore, its variation with temperature and concentration is studied. Table 6 and Fig.11 and Fig. 12 shows the variation of acoustic impedance with temperature and concentration. It is found that acoustic impedance decreases with increase in temperature of solution and increases as concentration of polyvinylchloride in solution increases. This is the resistance of the medium to the longitudinal wave motion. Due to the prominent interaction among the molecules, there is more resistance that results in increase in the value. This may be also due to increase in density and viscosity in solution and also because increase in elasticity of the medium. Table 7, Fig. 13and Fig. 14 represents the variation of relaxation time with different temperature and concentration range respectively. It is observed from Table 7 and Fig.13 that relaxation time decreases with increase in the value of temperature and increases with increase in polyvinylchloride concentration in the solution (Table 7 and Fig.14).The relaxation time take place due to structural relaxation process and it is presumed that because of the cooperative process, the molecules get rearranged. Variation of ultrasonic absorption with temperature and concentration is presented in Table 8 and Fig. 15 and Fig.16 respectively. It is clear that ultrasonic absorption decreases with increase in temperature and increases with increase in concentration of polyvinyl chloride in solution. The increase in the value of relaxation time and ultrasonic absorption with increase in concentration can be understand in terms of macromolecular interchain forces motion, which are influenced by density, viscosity and ultrasonic velocity.

IV. CONCLUSION

Density, viscosity and velocity of ultrasound have been measured for PVC in dimethylformamide at different concentration and temperature. Using these values different acoustical parameters like adiabatic compressibility, acoustic impedance, intermolecular free length, relaxation time and ultrasonic absorption have been calculated. Effect of temperature and concentration have been studied on these parameters can lead to structural investigation of the medium. The results show that there is strong molecular interaction between polymer and the solvent with the increase in concentration. This study is helpful in understanding the nature of polymer, their production and uses.

Table 1: Density($x10^3 kg/m^3$) of PVC at Different Temperature and Concentration

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	1.053	1.036	1.031	0.989	0.979	0.964	0.948	0.942
0.8%	1.042	1.034	1.028	0.981	0.967	0.951	0.944	0.941
0.6%	0.964	0.937	0.918	0.867	0.840	0.831	0.827	0.825
0.5%	0.917	0.904	0.893	0.843	0.832	0.818	0.811	0.81
0.4%	0.891	0.868	0.855	0.808	0.796	0.783	0.777	0.776
0.3%	0.854	0.803	0.789	0.745	0.735	0.722	0.722	0.716

Table -2: Viscosity($x10^{-2}$MPas) of PVC at Different Temperature and Concentration –

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	0.0029	0.0024	0.0022	0.0021	0.00195	0.0018	0.0017	0.0016
0.8%	0.0027	0.0024	0.0022	0.0021	0.0019	0.0018	0.0017	0.0016
0.6%	0.0027	0.0023	0.0020	0.0019	0.0017	0.00169	0.0016	0.0015
0.5%	0.0023	0.0021	0.0019	0.0018	0.0016	0.0015	0.0015	0.0014
0.4%	0.0023	0.0020	0.0019	0.0017	0.0016	0.0015	0.0015	0.0014
0.3%	0.0022	0.0019	0.0018	0.0017	0.0016	0.0015	0.0014	0.0013

Table 3: Ultrasonic Velocity (M/S) Of PVC At Different Temperature and Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	1264.1	1258.3	1210.8	1197.5	1189.8	1160.8	1153.9	1143.6
0.8%	1242.8	1238.6	1207.3	1190.6	1187.6	1154	1143	1138.5
0.6%	1240.6	1210.4	1204.6	1188.3	1177.3	1150.6	1142.6	1136
0.5%	1224.2	1206	1181.6	1178	1150.7	1148.4	1142	1132.2
0.4%	1187	1181.8	1172.5	1165.2	1150.4	1146.7	1142	1131.6
0.3%	1177.6	1168.1	1156.8	1152	1146	1136.6	1131.2	1130.6

Table 4: Intermolecular Free Length ($X10^{-13}$m) of PVC at Different Temperature and Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	3.3	3.341	3.481	3.596	3.637	3.756	3.809	3.855
0.8%	3.374	3.396	3.496	3.629	3.665	3.803	3.855	3.875
0.6%	3.514	3.653	3.708	3.868	3.967	4.056	4.123	4.24
0.5%	3.65	3.795	3.834	3.957	4.087	4.122	4.148	4.2
0.4%	3.819	3.887	3.948	4.087	4.17	4.218	4.252	4.266
0.3%	3.933	4.164	4.164	4.305	4.344	4.431	4.452	4.475

Table 5: Adiabatic Compressibility($X10^{-10}kg^{-1}m^4s^2$) of PVC at Different Temperature and Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	5.95	6.09	6.62	7.06	7.22	7.7	7.92	8.11
0.8%	6.21	6.30	6.67	7.19	7.33	7.89	8.11	8.20
0.6%	6.74	7.28	7.51	8.17	8.59	8.98	9.28	9.58
0.5%	7.27	7.86	8.02	8.55	9.08	9.28	9.39	9.63
0.4%	7.96	8.25	8.51	9.12	9.49	9.71	9.87	9.94
0.3%	8.44	9.13	9.47	9.51	9.53	9.77	9.88	9.96

Table 6: Acoustic Impedance ($X10^3kgm^2s^{-1}$) of PVC at Different Temperature And Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	1330.6	1304.1	1248.2	1183.1	1164.2	1118.9	1094.0	1077.6
0.8%	1294.9	1282.2	1241.6	1168.2	1148.5	1097.7	1078.7	1071.7
0.6%	1195.8	1134.4	1105.9	1030.5	988.6	962.0	944.1	920.1
0.5%	1123.1	1072.4	1054.9	993.3	957.2	938.8	928.8	917.2
0.4%	1057.9	1026.0	1002.3	941.4	915.6	897.9	887.2	883.6
0.3%	1005.7	937.5	913.2	903.2	858.0	821.0	817.0	809.2

Table 7: Relaxation Time ($x10^{-12}$s) of PVC at Different Temperature and Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	2.720	2.520	2.460	2.455	1.970	1.920	1.838	1.764
0.8%	2.680	2.498	2.420	2.394	1.950	1.876	1.860	1.700
0.6%	2.640	2.420	2.391	2.351	1.868	1.830	1.82	1.976
0.5%	2.610	2.380	2.330	2.251	1.780	1.942	1.726	1.605
0.4%	2.560	2.332	2.290	2.227	1.750	1.730	1.690	1.62
0.3%	2.454	2.310	2.234	2.180	1.72	1.690	1.620	1.600

Table 8: Ultrasonic Absorption ($X10^{-15}s^2m^{-1}$) of PVC at Different Temperature and Concentration-

Temperature → Concentration ↓	30°C	35°C	40°C	45°C	50°C	55°C	60°C	65°C
1.0%	3.56	3.52	3.47	3.44	3.40	3.34	3.31	3.20
0.8%	3.55	3.50	3.45	3.41	3.38	3.28	3.22	3.16
0.6%	3.51	3.47	3.42	3.38	3.35	3.25	3.20	3.05
0.5%	3.48	3.45	3.38	3.35	3.33	3.21	3.18	3.03
0.4%	3.45	3.41	3.35	3.32	3.29	3.18	3.15	3.01
0.3%	3.42	3.39	3.32	3.30	3.25	3.21	3.14	3.01

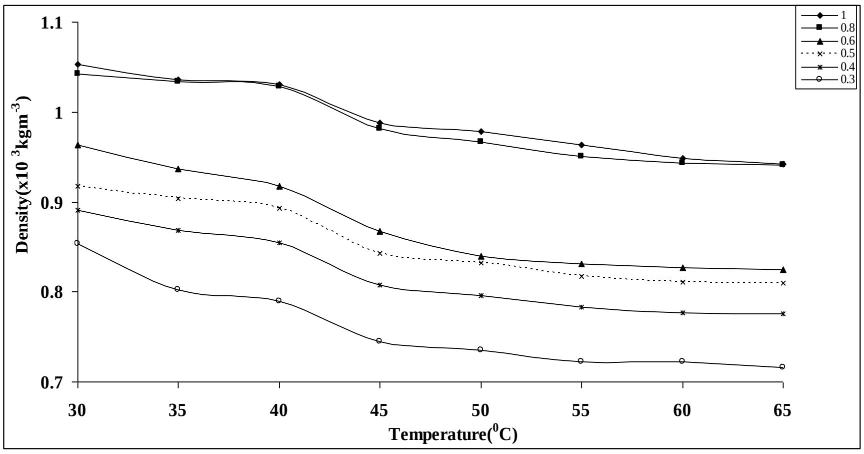

Figure 1: Variation of Density with Temperature at Different Concentration of PVC

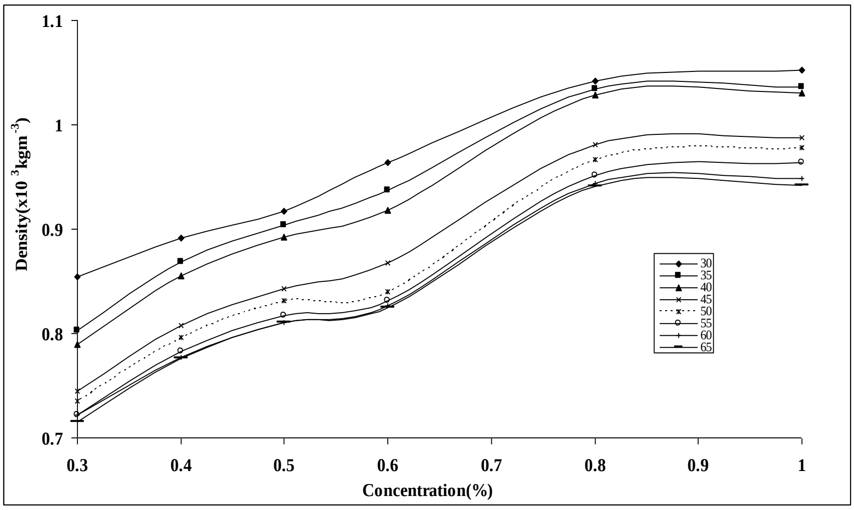

Figure 2: Variation of Density with Concentration at Different Temperature of PVC

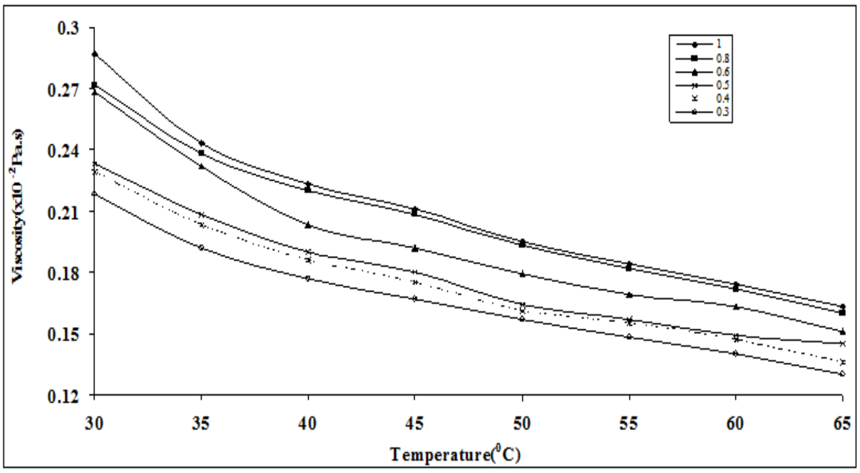

Figure 3: Variation of Viscosity with temperature at different concentration of PVC

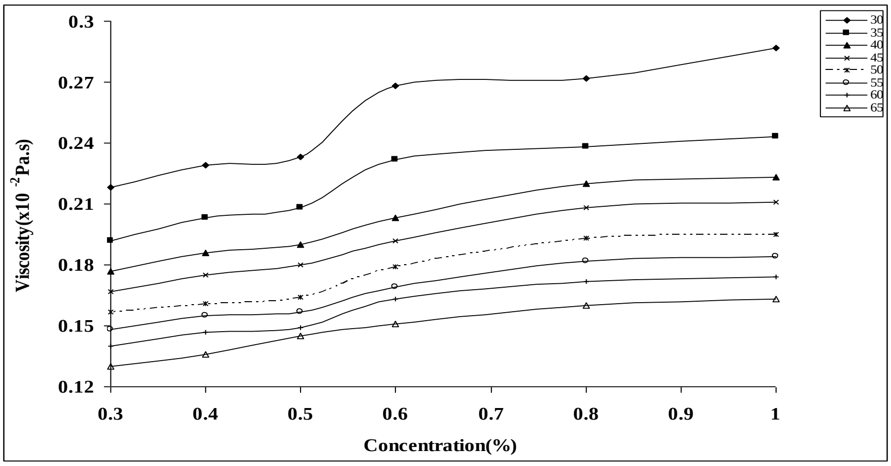

Figure 4: Variation of Viscosity with Concentration at Different Temperature of PVC

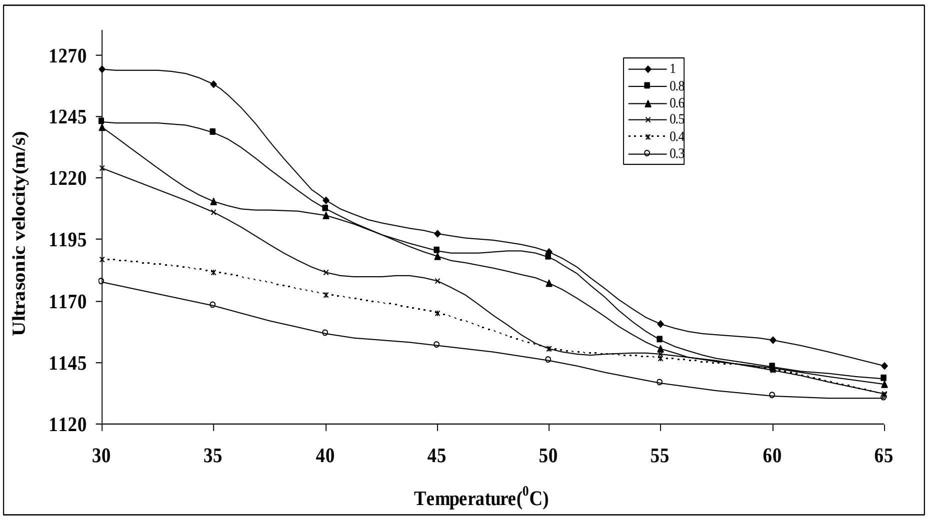

Figure 5: Variation of Ultrasonic Velocity with Temperature at Different Concentration of PVC

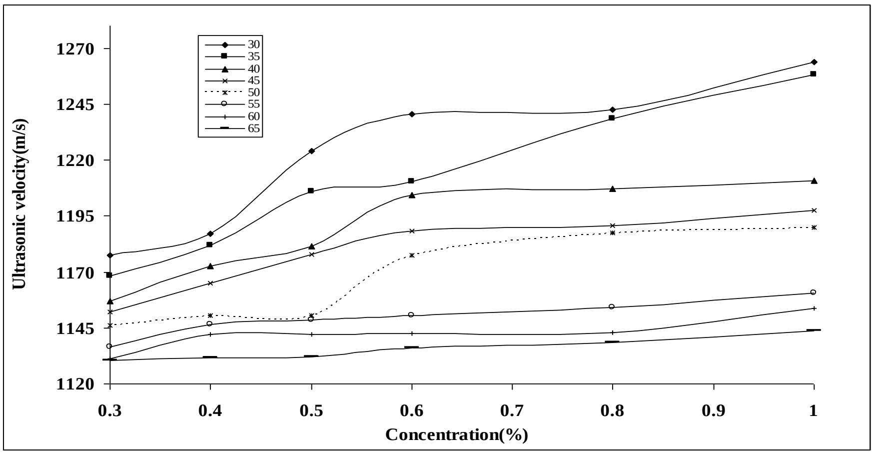

Figure 6: Variation of Ultrasonic Velocity with Concentration at Different Temperature of PVC

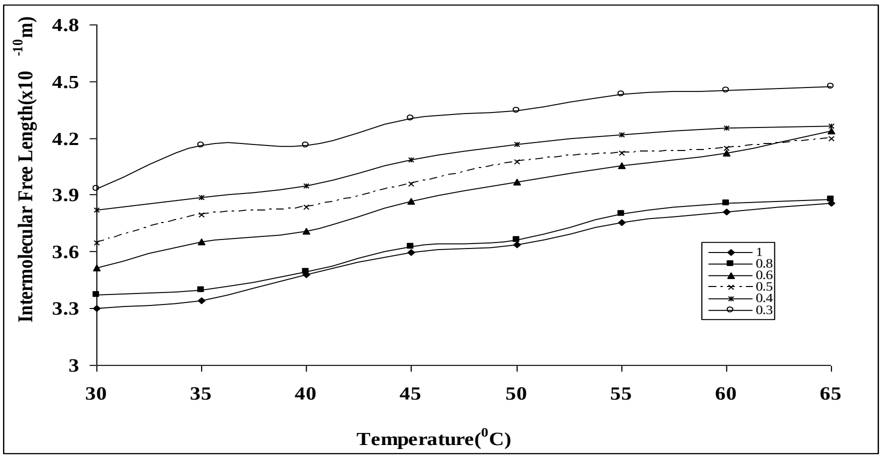

Figure 7: Variation of Intermolecular Free Length with Temperature at Different Concentration of PVC

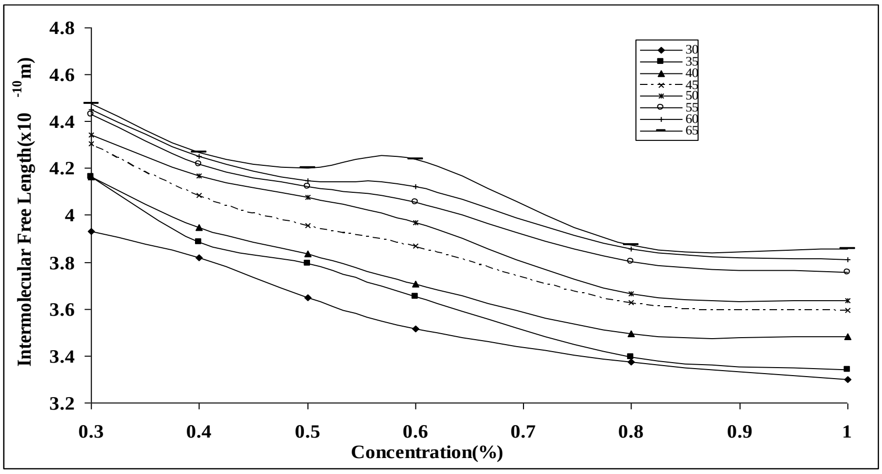

Figure 8: Variation of Intermolecular Free Length with Concentration at Different Temperature Of PVC

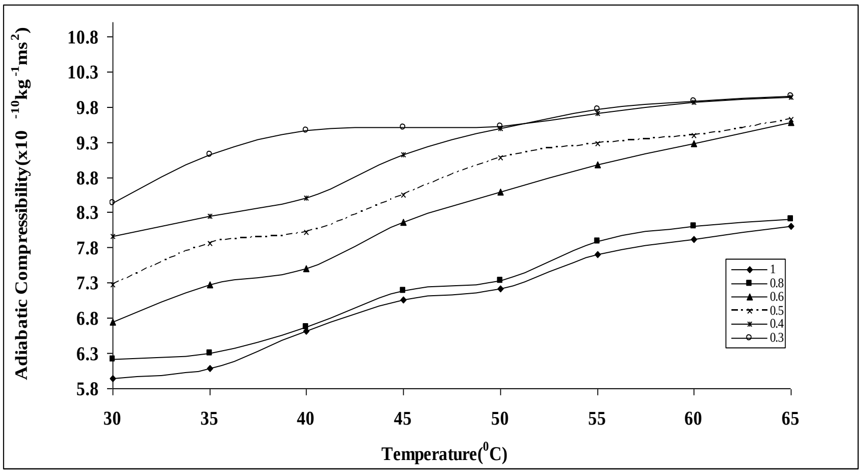

Figure 9: Variation of Adiabatic Compressibility with Temperature at Different Concentration of PVC

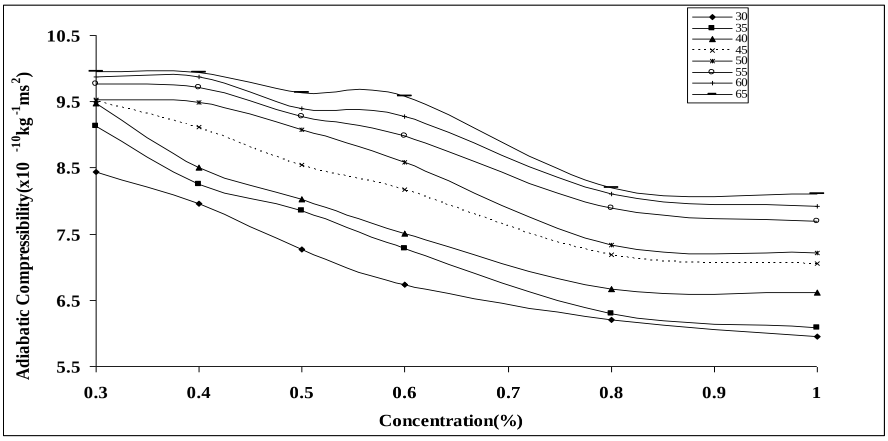

Figure 10: Variation of Adiabatic Compressibility with Concentration at Different Temperature of PVC

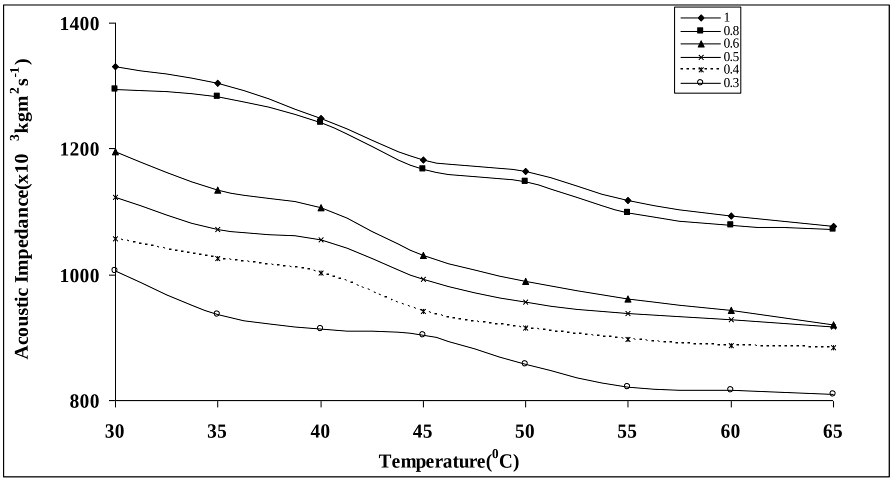

Figure 11: Variation of Acoustic Impedance with Temperature at Different Concentration of PVC

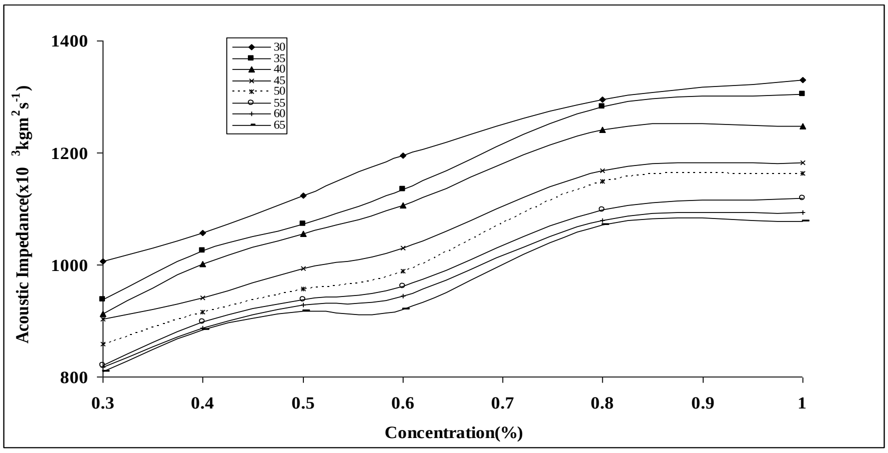

Figure 12: Variation of Acoustic Impedance with Concentration at Different Temperature of PVC

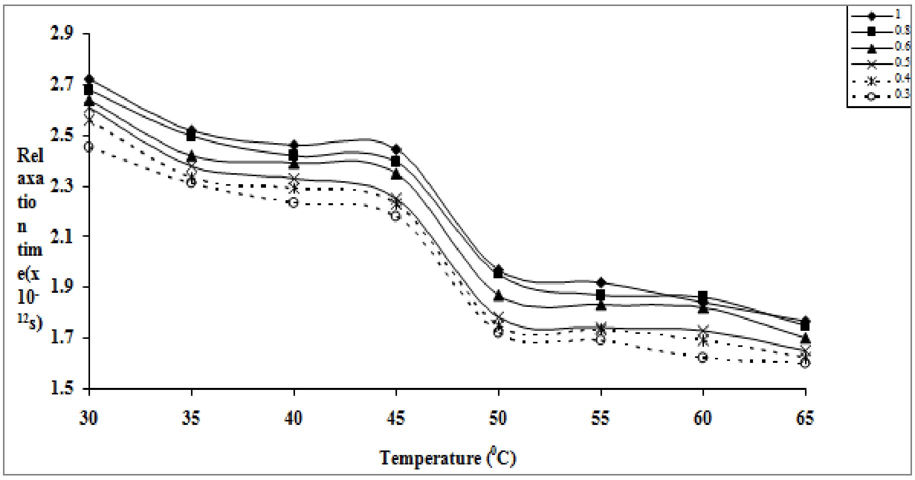

Figure 13: Variation of Relaxation Time with Temperature at Different Concentration of PVC

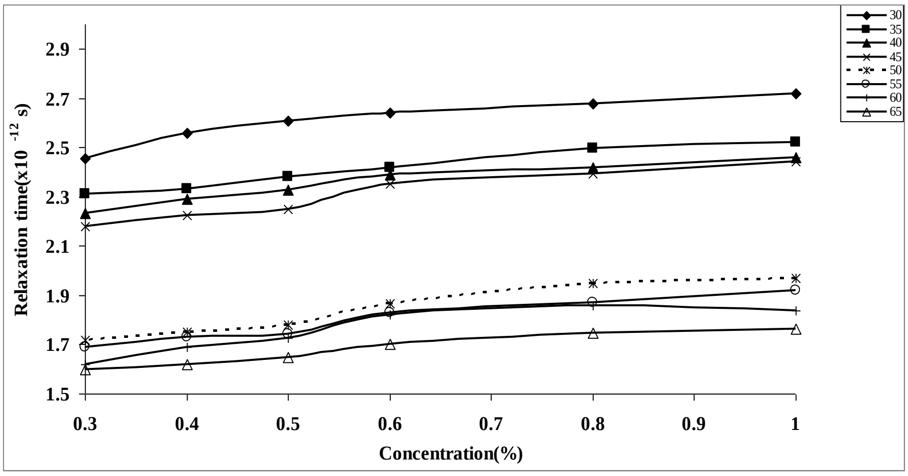

Figure 14: Variation of Relaxation Time with Concentration at Different Temperature of PVC

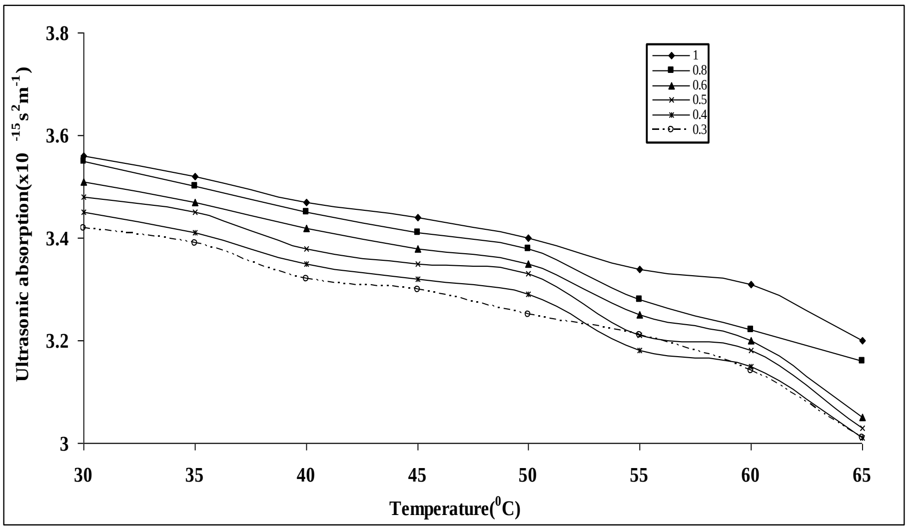

Figure 15: Variation of Ultrasonic Absorption with Temperature at Different Concentration of PVC

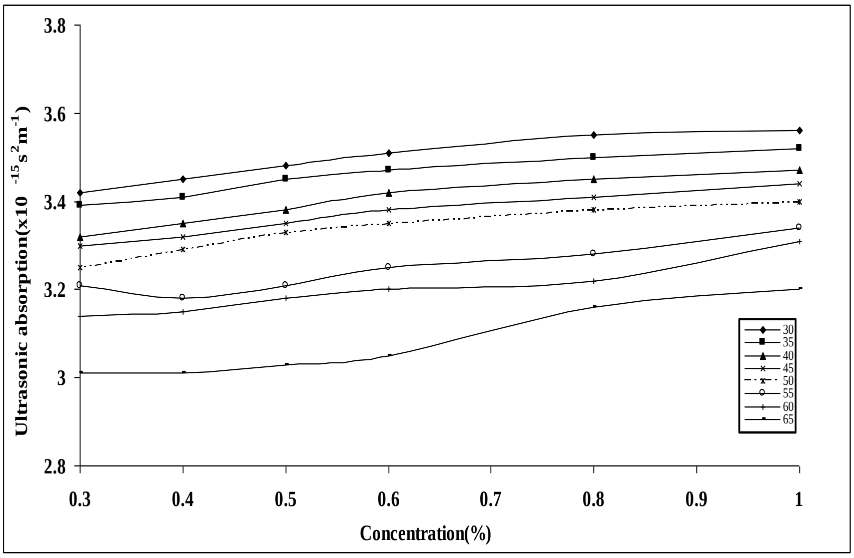

Figure 16: Variation of Ultrasonic Absorption with Concentration at Different Temperature of PVC

REFERENCES

[1] S. K. Hassun, S. H. F. Al-Madfai and M. M. F. Al Jarrah, "Ultrasonic study of molecular association of poly(vinyl chloride) solution in tetrahydrofuran,"*British Polym. J*, 17(4), pp.330-333,1985.
[2] S. Bagchi, S. K. Nema and R. P. Singh, "Ultrasonic and viscometric investigation of ISRO polyol in various solvents and its compatibility with polypropylene glycol," *European Polymer J*, 22, pp.851-857, 1986.
[3] R. A. Pethrick and B. T. Poh, "Ultrasonic attenuation and adiabatic compressibility of polyethyleneoxide-water mixtures," *The BritishPolymerJ*, 15, pp.149-153, 1983.
[4] B. Saraf and K. Samal, "Ultrasonic velocity and absorption in polystyrene solutions," *Acustica*, 55, pp.60-63, 1984.
[5] R. P. Singh, G. V. Reddy, *Acustica*, 46, pp.342, 1980.

[6] O. P. Chimankar, R. Shriwas, V. A. Tabhane, "Ultrasonic absorption studies in aqueous β-Alanine and L-Glutamic Acid (Monosodium salt),"*Pegalia research library,Advance in Applied Research,*1(3), pp. 78-85, 2010.

[7] O. P. Chimankar, Ranjeeta S. Shriwas, Sangeeta Jajodia, and V. A. Tabhane,"Thermo- acoustic and non-linear properties of milk in NaHCO3 using volume expansion coefficient,"*Advance in Applied Research*, 2(3), pp.500 -508, 2011.

[8] V. D. Bhandakkar, G. R. Bedare, V. D. Muley and B. M. Suryavanshi,"Molecular interactions of Acrylonitrile and Methacrylate in Methanol, Cyclohexane & P- dioxane,"*Advances in Applied Science Research*,2(4) pp.338-347, 2011.

[9] Kant Shashi, Kumar Sunil, Kumar Manish, Bharti Vikas,"Acoustic studies of hydrated Nickel sulphate in aqueous ascorbic acid systems,"*Der Chemica Sinica,* 3(1) , pp.166 -174, 2012.

[10] R. P. Singh, Economical design of sprinkler systems, *Acoust. Soc. India,* 21, pp.159 (1993).

[11] S. Rajgopalan and S J Sharma, "Study of mulberry Silk- Polyacryl amide blend using ultrasonic technique", *J pure and Applied Ultrasonics*, 27, pp.105-109, 2005.

[12] Masatami Takeda and Ryuichi Endo,"Vicosity of dilute polyvinyl chloride solution," The *J. Physical Chem.*,60,pp.1202-1204, 1956.

[13] Guang-ming Xian, Jin-ping Qu and Bi-qing Zeng "An effective on-line Polymer characterization technique by using SALS image processing software and wavelet Analysis,"*J of Automated Methods and Management in Chemistry*,2008, pp. 1-10, 2008.

[14] I. M. Thakore, Sonal Desai,B. D. Sarwade and Surekh Devi, "Evaluation of compatibility of poly(vinyl chloride)/ starch acetate blends using simple techniques,"*J of applied Polymer Science*, 71(11)pp.1851-1861, 1999.

[15] C. Duraivathi, J Jeya Priya, J Poongodi, H Johnson Jeyakumar, "Ultrasonic study of Molecular interactions in organic liquids with CCl^4 at different temperature, *Materials Today: Proceedings*, 49 (5), pp.1968-1972, 2022..

[16] Y. Marcus, *Introduction to liquid state Chemistry,* John Wiley & Sons, London, New York, Sidney, Toronto, 1977.357 Seiten (https://doi.org/10.1002/bbpc.197800140)

[17] Richa Saxena, S. C. Bhatt, "Molecular association studies on polyvinyl alcohol at different concentration,"*Advances in materials Science and Engineering*, 2018, pp.1-5, 2018.

[18] Richa Saxena, S C Bhatt, Manish Uniyal, S C Nautiyal, "Ultrasonic and volumetric studies of aqueous solution of Polyethylene glycol,"*Journal of Mountain research*,17(2), pp.165-171, 2022.

[19] B. Sundaresan and A. Srinivasa Rao, "Molecular interaction studies on poly(vinyl chloride) in chlorobenzene by acoustic method," *Polymer Journal*, 26(10)pp. 1286-1290,1994.

[20] Gennadiy I. Egorov, Dmitriy M. Makarov, volumetric properties (water + 1,3-dimethylurea) mixture over the temperature range from 274.15 to 333.15K at the ambient pressure comparison with other methyl substituted analogues, , *J of Molecular liquids*, 323, pp.114637, 2021

[21] Y. V. Patel, P. H. Parsania, "Ultrasonic velocity study of poly(R,R,4,4-cyclohexylidene diphenylene diphenyl ether-4,4-disulfonate) solutions at 30,35 and 40º C," *European Polymer Journal*, 38(10)pp.1971-1977, 2002.

[22] Akanksha Saini, Aditi Prabhune, A.P. Mishra, Ranjan Dey,"Density,ultrasonic velocity, viscosity, refractive index and surface tension of aqueous choline chloride with electrolyte solutions" Journal of molecular liquids, 323, pp.114593, 2021.

[23] A. V. Narasimham, S. K. J. Al-Ani, S. K. M. Al-Tayyar, "Ultrasonic properties of some polyvinyl chloride solutions,"*Indian J of Pure and applied Physics*, 37, pp.587-590,1999.

[24] H. J. Erything and J. F. Kincaid, "Free volumes and free angles ratios of molecules in liquids," *J Chem. Phys.* (USA) 6,pp.620-629, 1938.

[25] D.S. Wankhede, N.N. Wankhede, M.K. Lande, B.R. Arbad, "Densities and ultrasonic velocities of some oxygen containing compounds," *Journal of Molecular Liquids*, 138, pp. 124–129, 2008.