**Molecular interaction study of Polyvinyl chloride in dimethylformamide**

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**Abstract**

In present investigation experimental values of density, viscosity and ultrasonic velocity of polyvinylchloride in dimethylformamide is measured at different concentration and temperatures at 1 MHz frequency. Using these data different acoustical parameters have been calculated to understand molecular interactions between solute and solvent. This study is helpful to understand the polymer and solvent interaction. The effect of concentration and temperature on various parameters have been discussed.

**Keywords:** Ultrasonic velocity, adiabatic compressibility, Ultrasonic absorption

**I Introduction**

Acoustical studies in polymer solution and in solid polymers have been the subject of research in recent years [1-5]. A review of literature on acoustical studies on polymer solution reveals that ultrasonic velocity measurement studies are helpful to understand the nature of molecular interactions in solute and solvent [6-9]. Polyvinylchloride (PVC) is a well-known versatile thermoplastic commodity, whose production and consumption is second as worldwide compared to other plastics. Polyvinyl Chloride is generally used known to have the advantages of low ingredient cost, wide processing versatility, high decorative potential and is used to manufacture various types of products ranging from highly rapid to very flexible. Many researchers [10-11] have carried out pioneering work on polymer/polymer compatibility using ultrasonic techniques. As polyvinyl chloride is an industrially important polymer therefore it is decided to study the molecular interactions of polyvinylchloride in dimethylformamide.

Takeda and Endo [12] observed the viscosity of dilute polyvinylchloride solution. B. Thapa et. al. studied the ultrasonic studies of polyvinylchloride in cyclohexanone and 1, 4-Dioxane. Xiang et. al. [13] explored an effective means of characterizing structural changes of PVC particles during gelation and fusion of PVC plastisol’s with small angle light scattering. Thakore et. al. [14] studied the compatibility of blend system of PVC and starch acetate in 1, 4 dioxane from viscometric, ultrasonic and density measurements. In order to observe the influence of heat 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 acoustical parameters at different temperature and concentration of polyvinylchloride in dimethylformamide have been calculated and the results are discussed in terms of molecular interaction of solute and solvent. Acoustical parameters are useful to understand the physio-chemical behavior of PVC and dimethyl formamide and for production, their applications in different field.

1. **Experimental Details**

## In present investigation polyvinyl chloride (molecular weight ≈ 134.5 Da) in liquid form is used with dimethylformamide. The solutions were prepared by adding known volume of polyvinyl chloride to fixed volume of dimethylformamide and stirring under reflex until a clear solution was obtained. The concentration range studied 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. Ultrasonic velocity is measured by using variable path Ultrasonic interferometer with reproducibility of ± 4 m/s at 30⁰C. The temperature of the solution has been kept constant by circulating water from the electronically operated digital constant temperature bath (Mittal Enterprises, New Delhi) with an accuracy of ± 0.1⁰ C) through the outer jacket of the double walled measuring cell containing experimental liquid. The densities at different temperatures were measured using 10 ml specific gravity bottle and single pan micro balance. The uncertainty in density measurements was found to be 0.5 kg/m3. The viscosity of the mixtures was determined by using Ostwald’s viscometer, which was kept inside a double walled jacket, in which water from thermostat water bath was circulated. Inner cylinder of this double wall glass jacket was filled with water of desired temperature so as to establish and maintain the thermal equilibrium. In each measurement the uncertainty was measured to be 0.01MPa.s. The acoustical parameters are calculated by using standard formulae[15-17].

1. **Results and discussion**

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

Density, viscosity and ultrasonic velocity are 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 shows the variation of density with temperature and concentration respectively. It is reported that density decreases with increase in temperature and increases with increase in concentration of polyvinylchloride in the solution. Increase in the density is due to the fact that number of polymer chains added to solution increases with increase in concentration of the PVC. As compared to solvent, polymer have large molecular weight that also contributes in the increase in density. The result reported in the present investigation are in good agreement with the results reported by earlier researchers [18, 19]. Viscosity is an important property and it depends on the molecular size, shape and intermolecular attraction. The measurement of viscosity provides useful information about solute- solvent and solute-solute interaction. Table 2 and Fig.3 and Fig.4 reports the variation of viscosity with temperature and concentration respectively. It is observed that viscosity decreases with increase in temperature and increases with increase 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 layers of the medium increases and that increases viscosity. A similar behavior was made by previous authors [20]. 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 trends in the ultrasonic velocity may be due to structural changes taking place in the mixture because of increasing intermolecular forces. Similar trend is observed by earlier authors [21]. A V Narasimham et al. have concluded the similar results for polyvinyl chloride solutions [22]. Table 4 and Fig. 7 shows that intermolecular free length increases with increase in temperature and decreases with increase in 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 model proposed by Eyring and Kincaid [23], ultrasonic velocity is inversely proportional to intermolecular free length, ultrasonic velocity should decrease if the intermolecular free length increases and vice- versa. The results reported in present study are in agreement 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 suggest the weakening of molecular interactions in the liquid mixtures. This may be explained in terms of the electrostatic effects of the polymer on the surrounding solvent molecules. The results also indicates that the medium become more compressible. The adiabatic compressibility is inversely proportional to square of velocity therefore the trend in the adiabatic compressibility is reverse of the trend of ultrasonic velocity with temperature and concentration. As the velocity increases with concentration and the density does so, the compressibility must decrease with increase in concentration of PVC. Some earlier workers have also reported similar behavior of adiabatic compressibility [24]. 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 and increases with increase in concentration of polyvinylchloride in solution. This is the opposition of the medium to the longitudinal wave motion. Due to the greater interaction among the molecules there is more opposition 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. 13 and Fig. 14 represents the variation of relaxation time with temperature and concentration respectively. It is observed from Table 7 and Fig.13 that relaxation time decreases with increase in temperature and increase with increase in concentration of polyvinylchloride in the solution (Table 7 and Fig.14). The relaxation time occurs due to the structural relaxation process and it is presumed that the molecules get rearranged because of the cooperative process. 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 of relaxation time and ultrasonic absorption with concentration can be explained in terms of motion of macromolecular interchain forces which are influenced by density, viscosity and ultrasonic velocity.

1. **Conclusion**

Density, viscosity and ultrasonic velocity have been measured for polyvinylchloride 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 indicate that there is strong interaction between polymer and the solvent at higher concentration. This study is helpful in understanding the behavior of polymer, their production and uses.

**A. Data Availability**

The data used to support finding are included within the article.

**B. Conflicts of interest**

The authors declare that they have no conflicts of interest.

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**Table -1: Density(x103kg/m3) of polyvinyl chloride (PVC) at different temperature and concentration at 1 MHz frequency-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 polyvinyl chloride (PVC) at different temperature and concentration at 1 MHz frequency-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 polyvinyl chloride (PVC) at different temperature and concentration at 1 MHz frequency**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (x10-13m) at different temperature and concentration at 1MHz for polyvinyl chloride (PVC)-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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(x10-10kg-1m4s2) at different temperature and**

**concentration at 1MHz for polyethylene glycol (PEG)-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (x103kgm2s-1) at different temperature and concentration at 1MHz for polyvinyl chloride (PVC)-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (x10-12s) at different temperature and concentration at 1MHz for polyvinyl chloride (PVC)-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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 (x10-15s2m-1) at different temperature and concentration at 1MHz for polyvinyl chloride (PVC)-**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **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** |

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**Fig.-1: Variation of density with temperature at different concentration of PVC**

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**Fig.-2: Variation of density with concentration at different temperature of PVC**

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**Fig.-3: Variation of Viscosity with temperature at different concentration of PVC**

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**Fig.-4: Variation of Viscosity with concentration at different temperature of PVC **

**Fig.-5: Variation of ultrasonic velocity with temperature at different concentration of PVC**

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**Fig.-6: Variation of ultrasonic velocity with concentration at different temperature of PVC**

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**Fig. -7: Variation of intermolecular free length with temperature at different concentration of PVC**

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**Fig.- 8: Variation of intermolecular free length with concentration at different temperature of PVC**

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**Fig. -9: Variation of adiabatic compressibility with temperature at different concentration of PVC**

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**Fig.-10: Variation of adiabatic compressibility with concentration at different temperature of PVC**

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**Fig. -11: Variation of acoustic impedance with temperature at different concentration of PVC**

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**Fig. -12: Variation of acoustic impedance with concentration at different temperature of PVC**

**1.5**

**1.7**

**1.9**

**2.1**

**2.3**

**2.5**

**2.7**

**2.9**

**30**

**35**

**40**

**45**

**50**

**55**

**60**

**65**

**Temperature (**

**0**

**C)**

**Relaxation time(x10-12s)**

1

0.8

0.6

0.5

0.4

0.3

**Fig.-13: Variation of relaxation time with temperature at different concentration of PVC**

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**Fig.-14: Variation of relaxation time with concentration at different temperature of PVC**

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**Fig.-15: Variation of ultrasonic absorption with temperature at different concentration of PVC**



**Fig.-16: Variation of ultrasonic absorption with concentration at different temperature of PVC**