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# Molecular interaction on conducting polymer (Polypyrrole) in different solutions by ultrasonic interferometer technique

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**ABSTRACT**

The conduction polymer Polypyrrole base is soluble in selected organic solvents. The Polypyrrole becomes conductive upon partial oxidation or reduction by a process commonly known as doping. The Polypyrrole base was doped by chemical method using Hydrochloric acid (HCl) as a dopant. The doped conducting polymer was dissolved in three selective organic solvents namely p-Cresol (PCL), Dimethyl sulphoxide (DMSO) and 2-Chlorophenol (2CPL). The variation in the ultrasonic velocity values measured using fixed frequency (3MHz) continuous wave ultrasonic interferometer technique with temperature and their related thermodynamic parameters have been discussed with a view to understand the molecular interactions of the conduction polymers in solutions. Hence the acoustic properties of Polypyrrole base and its doped polymer in solutions will pave the way to obtain possibly a new product ideas and benefits over the traditional polymers.



## Introduction

In recent years the measurement of ultrasonic velocity has been adequately employed in understanding the nature of the molecular interactions of polymers in solutions. It is also noted that the ultrasonic investigations find extensive applications in identifying the characteristic aspects of molecular interactions existing in binary systems (Anwar Ali et al, 2004; Moore and Uddin, 1969). Further the ultrasonic velocity is also useful for evaluating the some important acoustic parameters Adiabatic compressibility (β), Intermolecular freelength ($L_f$), Relaxation time($\tau$) and Specific acoustic impedance (Z). The physical nature and strength of the intermolecular interactions in solutions are also being obtained qualitatively from the ultrasonic velocity values and their variations with temperature (Palandhi and Singh, 1990).

In the recent past a large number of research and review articles have been published on conductivity of polymers (Pethric, 1973; Desai and Prasania, 1996). The unique stability of polymers has become so important on the development of conducting polymers as a class of synthetic metals with promising applications. Compared to solid polymers, solutions of synthetic polymers find widespread technological applications. In solutions, it is possible to gain the details of information about the dimensions of the solute polymer molecules. Such information cannot be ascertained with so ease from the solid polymers (Kamani and Parsania, 1996).

The present paper discusses the synthesis of Polypyrrole in base form and its behavior in solutions of different organic solvents. Since the solublization of Polypyrrole is important for the development of many technologies involving Polypyrrole as a class of new electronic material.

## Materials and Methods

Polypyrrole is synthesized through chemical polymerization method from its monomer pyrrole following the procedure reported in the literature (Bell and Pethrick, 1982; Kalyanasundaram, 1995)

The purity of the solvents selected was maintained by repeated distillation. The measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) for the solvents(PCL, 2CPL and DMSO) are found as $U_{2CPL}$=1377.6 $ms^{-1}$, $\rho_{2CPL}$ =1.241 $Kg/m^3$ and $\eta_{2CPL}$ =3.054 $Nsm^{-2}$ ; $U_{PCL}$ =1441.1 $ms^{-1}$, $\rho_{PCL}$ =1.016 $Kg/m^3$ and $\eta_{PCL}$ =5.537 $Nsm^{-2}$ and $U_{DMSO}$=1487 $ms^{-1}$, $\rho_{DMSO}$ =1.0955 $Kg/m^3$ and $\eta_{DMSO}$ =1.989 $Nsm^{-2}$ and are in agreement with the reported value (Manwar et al, 2004). The accuracy of the measurement of the ultrasonic velocity, density and viscosity was within ±0.02, ±0.2 and ±0.2 % respectively.

The molecular weight of the doped Polypyrrole was determined using MALDI-TOF-MS technique at Indian Institute of Science, Bangalore, India with laser radiation of wavelength 300 nm of accuracy 0.001nm as ionizing source. The molecular weight value so determined was 3846.542. The ultrasonic velocity values were measured for the conduction polymer Polypyrrole, using ultrasonic interferometer. The sample Polypyrrole is doped with Hydrocholori acid (0.01N) as the dopant. The Mittel ultrasonic interferometer was used for the polymer in solutions with PCL, 2CPL and DMSO as the solvents to measure the ultrasonic velocity values at three different fixed temperatures along with the density and velocity values respectively. The other related acoustic parameters were also calculated by applying the following relations I-IV.

$$\beta = \frac{1}{c^2 \rho} \qquad \text{--------- I}$$

$$L_f = K_T \beta^{\frac{1}{2}} \qquad \text{--------- II}$$

$$\tau = \frac{4}{3}\eta\beta \qquad \text{-------- III}$$

$$Z = \rho c \qquad \text{--------- IV}$$

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In equation (II), $K_T$ is the temperature dependent constant = [(93.875+0.345T) X $10^{-8}$] where T stands for the absolute temperature.( Kannappan and Hemalatha, 2005)

**Results and Discussion**

The values of ultrasonic velocity, density and viscosity of all the three systems increase with increasing of concentration and decrease with increasing of temperatures. In the present investigation also the adiabatic compressibility of polymer solutions is less than that of the three solvents employed in accordance with the data found in the literatures (Moore and Uddin, 1969; Paladhi and Singh, 1990)

In the process of solvation, highly polar forces result in a localized field and an incompressible region was formed by the solvating molecules which result in lesser value of adiabatic compressibility for the polymer in solutions than solvents (Kalyanasundaram et al, 2000). Increase of ultrasonic velocity with concentration and decrease of adiabatic compressibility with concentration indicate that the molecules are forming a more tightly bound system (Ali and Nain, 1997)

The increase in velocity with concentration suggests that increase in cohesive forces due to powerful polymer-solvent interactions, i.e., intermolecular interactions. The decrease of density and viscosity with temperature supports decrease in cohesive forces and hence decrease of intermolecular freelength. Increasing thermal energy of the system causes volume expansion and hence decreases in density and viscosity while an increasing in $L_f$ is observed.

Relaxation time ($\tau$) for doped Polypyrrole has been reported in solutions at different temperatures by varying the concentration form 0.001M to 0.005M. It is found the relaxation time in all the three solvents decrease non-linearly with temperature and increase with concentration as exhibited by viscosity values as a result of the change in the thermodynamic parameters. The non-linear increase the relaxation time over a range of increase in polymer concentration suggests the existence of interaction between the polymer and solvent molecules.

The acoustic impedance of the polymer is also increases with increase of concentration in all the three system and decreases with increase of temperature. The nonlinear variation of impedance both with concentration and temperature is the indication that there is a strong interaction between solute and solvent molecules. The specific acoustic impedance is a significant factor affecting reflection and transmission of sound waves in the medium and solvent molecules.

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**Table1 Acoustic parameters of polypyrrole in solutions**

| Temp K | Molality M | Velocity m/s (v) | Density $Kg/m^3$ (ρ) | Viscosity $10^{-3}$ $Nsm^{-2}$ (η) | Adiabatic compressibility $10^{-10}$ $m^2N^{-1}$ (β) | Inter molecular Free length $10^{-11}$m ($L_f$) | Relaxation time $10^{12}$ Sec (τ) | Specific Acoustic Impedance $10^6$ $Kgm^{-2}S^{-1}$ (Z) |
|---|---|---|---|---|---|---|---|---|
| Polypyrrole (HCl 0.01N) + P-cresol | | | | | | | | |
| 313 | 0.001 | 1441.2 | 1007.25 | 4.4071 | 4.7798 | 4.3879 | 2.8087 | 1.4516 |
| | 0.002 | 1442.9 | 1008.56 | 4.5049 | 4.7624 | 4.3798 | 2.8605 | 1.4552 |
| | 0.003 | 1444.7 | 1009.31 | 4.5980 | 4.7470 | 4.3727 | 2.9103 | 1.4581 |
| | 0.004 | 1446.1 | 1010.62 | 4.6522 | 4.7317 | 4.3656 | 2.9351 | 1.4614 |
| | 0.005 | 1447.8 | 1011.37 | 4.7446 | 4.7171 | 4.3589 | 2.9841 | 1.4643 |
| 318 | 0.001 | 1427.1 | 1004.05 | 3.3380 | 4.8903 | 4.5085 | 2.1765 | 1.4329 |
| | 0.002 | 1428.5 | 1005.18 | 3.4262 | 4.8752 | 4.5020 | 2.2272 | 1.4359 |
| | 0.003 | 1430.2 | 1005.93 | 3.4804 | 4.8600 | 4.4945 | 2.2553 | 1.4387 |
| | 0.004 | 1431.7 | 1007.24 | 3.5456 | 4.8435 | 4.4873 | 2.2898 | 1.4421 |
| | 0.005 | 1433.6 | 1008.74 | 3.6540 | 4.8235 | 4.4780 | 2.3500 | 1.4461 |
| 323 | 0.001 | 1414.2 | 1001.87 | 2.7129 | 4.9907 | 4.6203 | 1.8053 | 1.3854 |
| | 0.002 | 1415.4 | 1002.63 | 2.7953 | 4.9785 | 4.6138 | 1.8556 | 1.3312 |
| | 0.003 | 1417.4 | 1003.76 | 2.8594 | 4.9589 | 4.6046 | 1.8906 | 1.2941 |
| | 0.004 | 1418.8 | 1005.08 | 2.9141 | 4.9426 | 4.5970 | 1.9205 | 1.2643 |
| | 0.005 | 1420.3 | 1006.21 | 2.9979 | 4.9266 | 4.5896 | 1.9690 | 1.2180 |
| Polypyrrole (HCl 0.01N) + Dimethyl Sulfoxide | | | | | | | | |
| 300 | 0.001 | 1498.6 | 1099.31 | 2.4224 | 4.1010 | 4.0421 | 1.3082 | 1.6474 |
| | 0.002 | 1499.9 | 1100.62 | 2.4788 | 4.0889 | 4.0361 | 1.3348 | 1.6508 |
| | 0.003 | 1501.4 | 1101.74 | 2.5462 | 4.0765 | 4.0300 | 1.3670 | 1.6542 |
| | 0.004 | 1503.6 | 1103.05 | 2.5813 | 4.0597 | 4.0217 | 1.3801 | 1.6585 |
| | 0.005 | 1505.2 | 1104.74 | 2.6534 | 4.0448 | 4.0143 | 1.4135 | 1.6628 |
| 310 | 0.001 | 1467.3 | 1096.25 | 1.9226 | 4.2817 | 4.2009 | 1.0861 | 1.6085 |
| | 0.002 | 1468.5 | 1097.38 | 1.9664 | 4.2703 | 4.1953 | 1.1079 | 1.6115 |
| | 0.003 | 1470.1 | 1098.69 | 2.0247 | 4.2558 | 4.1882 | 1.1369 | 1.6152 |
| | 0.004 | 1471.7 | 1100.19 | 2.0634 | 4.2407 | 4.1807 | 1.1545 | 1.6191 |
| | 0.005 | 1473.2 | 1101.69 | 2.1500 | 4.2262 | 4.1736 | 1.1989 | 1.6230 |
| 320 | 0.001 | 1436.5 | 1091.81 | 1.6201 | 4.4700 | 4.3553 | 0.9588 | 1.5684 |
| | 0.002 | 1438.2 | 1093.13 | 1.6777 | 4.4556 | 4.3483 | 0.9893 | 1.5721 |
| | 0.003 | 1439.9 | 1094.82 | 1.7369 | 4.4405 | 4.3409 | 1.0202 | 1.5764 |
| | 0.004 | 1441.3 | 1096.52 | 1.7735 | 4.4272 | 4.3344 | 1.0381 | 1.5804 |
| | 0.005 | 1442.8 | 1098.03 | 1.8445 | 4.4127 | 4.3273 | 1.0760 | 1.5842 |
| Polypyrrole ( HCl 0.01N) + 2-Chlorophenol | | | | | | | | |
| 303 | 0.001 | 1393.5 | 1234.04 | 4.9505 | 4.1731 | 4.1207 | 2.7545 | 1.7196 |
| | 0.002 | 1395.4 | 1235.16 | 5.0249 | 4.1579 | 4.1132 | 2.7858 | 1.7235 |
| | 0.003 | 1397.1 | 1236.66 | 5.1276 | 4.1428 | 4.1056 | 2.8323 | 1.7277 |
| | 0.004 | 1398.7 | 1237.97 | 5.1606 | 4.1290 | 4.0987 | 2.8411 | 1.7315 |
| | 0.005 | 1400.3 | 1239.28 | 5.2718 | 4.1152 | 4.0918 | 2.8926 | 1.7354 |
| 313 | 0.001 | 1357.7 | 1231.26 | 3.5807 | 4.4060 | 4.3075 | 2.1035 | 1.6717 |
| | 0.002 | 1359.2 | 1232.39 | 3.6605 | 4.3922 | 4.3008 | 2.1437 | 1.6750 |
| | 0.003 | 1360.2 | 1233.51 | 3.7072 | 4.3818 | 4.2956 | 2.1659 | 1.6778 |
| | 0.004 | 1361.8 | 1234.64 | 3.8089 | 4.3675 | 4.2885 | 2.2181 | 1.6813 |
| | 0.005 | 1363.4 | 1235.96 | 3.9099 | 4.3526 | 4.2812 | 2.2691 | 1.6851 |
| 323 | 0.001 | 1324.5 | 1228.30 | 3.0867 | 4.6408 | 4.4836 | 1.9099 | 1.6269 |
| | 0.002 | 1325.6 | 1229.44 | 3.1596 | 4.6288 | 4.4781 | 1.9501 | 1.6297 |
| | 0.003 | 1327.4 | 1230.57 | 3.2066 | 4.6120 | 4.4696 | 1.9719 | 1.6335 |
| | 0.004 | 1329.1 | 1231.89 | 3.2936 | 4.5953 | 4.4610 | 2.0180 | 1.6373 |
| | 0.005 | 1330.8 | 1233.58 | 3.3522 | 4.5773 | 4.4526 | 2.0459 | 1.6416 |