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PHYSICS

EVALUATION OF THERMODYNAMIC PARAMETERS OF CONDUCTION POLYMER IN SOLUTIONS USING ULTRASONIC INTERFERROMETRIC TECHNIQUE

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Abstract
The electrical conduction polymer Polyaniline (PANI) base is soluble in selected organic (polar) solvents. The PANI becomes conductive upon partial oxidation or reduction by a process commonly known as doping. The PANI base was doped by chemical method using perchloric acid ($HClO_4$) 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 ultrasonic velocity values were measured for the polymer in solutions using fixed frequency (3MHz) continuous wave ultrasonic interferometer technique at three different temperatures. The related thermodynamic parameters were calculated and their variations with concentration have been discussed with a view to understand the molecular interactions of the conduction polymers in solutions. Hence the acoustic properties of doped PANI in solutions will provide possibly a new product ideas and benefits over the traditional polymers owing to its properties in solutions.

Key Words: Polyaniline (PANI); Conduction polymer; Ultrasonic velocity; Thermodynamic; Parameters.

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 [1, 2]. Further the ultrasonic velocity is also useful for evaluating the some important acoustic parameters Adiabatic compressibility (β), Intermolecular free-length (L_f), Relaxation Time (τ) 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 of acoustic parameters and their variations with temperature [3].

In the recent past a large number of research and review articles have been published on conduction polymers [4-8]. 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 [9].

The present paper discusses the synthesis of polyaniline in base form and its behaviour in solutions of different organic solvents. Since the solublization of PANI is important for the development of many technologies involving PANI as a class of new electronic material. The PANI is available in various forms as leuco emeraldine, emeraldine base and pernigraniline [10].

Materials and Methods

Polyaniline is synthesized through chemical polymerization method from its monomer aniline following the procedure reported in the literatures [11, 12]. It was also doped with perchloric acid of strength 1.0 N as the dopant.

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 given in Table 1 and are in agreement with the reported values [13, 14]. The accuracy of the measurement of the ultrasonic

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velocity, density and viscosity was within ±0.02, ±0.2 and ±0.2 % respectively.

Table 1. Thermodynamic Properties of Solvents

Solvent	Density Kgm^{-3}	Viscosity Nsm^{-2}	Velocity ms^{-1}
2-chlorophenol (2CPL)	1.241	3.054	1377.6
p-cresol (PCL)	1.016	5.537	1441.1
Dimethyl sulphoxide (DMSO)	1.0955	1.989	1487.2

The molecular weight of the doped PANI was determined using MALDI-TOF-MS technique at Indian Institute of Science, Bangalore, India. Nitrogen laser of wavelength 337 nm of accuracy 0.001nm was used as ionizing source. The molecular weight value so determined was 5830.246. The ultrasonic velocity values were measured for the conduction polymer Polyaniline in solutions, using ultrasonic interferometer (MITTEL) type using PCL, 2CPL and DMSO were used as the solvents. The ultrasonic velocity along with the density and velocity values were measured at three different temperatures respectively. The acoustic parameters of interest were also calculated from the standard relations I-IV.

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

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

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

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

In equation (II), K_T is the temperature dependent constant = [(93.875+0.345T) X 10^{-8}] where the suffix T stands for the absolute temperature [15].

Results and Discussion

The ultrasonic applied to scientific investigations on the behaviour of molecules in the liquids and solutions have become a powerful tool in this last two decades. The characteristic physical and chemical behaviour of the medium can be understood from the ultrasonic sound velocity data. The structure and properties of various liquids and effect of mixing on binary and ternary solutions may also be explained by the study of molecular interaction. The study of the elastic properties, structure aspects, molecular relaxation process and molecular interaction by ultrasonic studies provides valuable information about the polymers, copolymers and about mixtures.

The values velocity, density, viscosity, adiabatic compressibility, intermolecular free length, relaxation time and specific acoustic impedance of the solvated part of the PANI doped with $HClO_4$ (1.0N) are computed for all concentrations in molality at three different temperatures were given in Tables 2.1,2.2 and 2.3.

Table 2. Acoustic parameters of HClO4 (1N) doped PANI in solutions

Table 2.1 Acoustic parameters of Polyaniline doped with HClO4 (1.0 N) in 2CPL

Temp K	Molality m	Viscosity Nsm-2	Density Kg/m3	Velocity m/s	β X 10^{10} N-1m2	L_f X 10^{11} m	τ X 10^{12} Sec	Z X 10^{6} $Kgm^{-2}s^{-1}$
303	0.001	5.0967	1257.72	1402.1	4.0444	4.0141	2.7484	1.7634
	0.002	5.1836	1258.93	1403.5	4.0325	4.0082	2.7870	1.7669
	0.003	5.3276	1260.54	1404.8	4.0199	4.0019	2.8555	1.7708
	0.004	5.4471	1261.85	1406.2	4.0077	3.9959	2.9107	1.7744
	0.005	5.6070	1263.46	1408.1	3.9918	3.9879	2.9843	1.7791
313	0.001	4.2000	1247.10	1367.2	4.2898	4.2049	2.4023	1.7050
	0.002	4.3149	1248.57	1368.8	4.2747	4.1975	2.4593	1.7090
	0.003	4.4128	1249.99	1370.3	4.2605	4.1905	2.5068	1.7129
	0.004	4.5682	1251.52	1371.9	4.2454	4.1831	2.5858	1.7170
	0.005	4.6614	1253.01	1373.5	4.2305	4.1757	2.6293	1.7210
323	0.001	3.2739	1237.12	1327.5	4.5869	4.4119	2.0023	1.6423
	0.002	3.3718	1238.82	1328.8	4.5716	4.4046	2.0553	1.6461
	0.003	3.5200	1240.02	1330.3	4.5569	4.3975	2.1387	1.6496
	0.004	3.5912	1241.76	1331.9	4.5396	4.3891	2.1737	1.6539
	0.005	3.7172	1242.98	1333.2	4.5263	4.3827	2.2434	1.6571

Table 2.2 Acoustic parameters of Polyaniline doped with $HClO_4$ (1.0 N) in PCL

Temp K	Molality m	Viscosity Nsm-2	Density Kg/m3	Velocity m/s	β X 10^{10} N-1m2	L_f X 10^{11} m	τ X 10^{12} Sec	Z X 10^{6} $Kgm^{-2}s^{-1}$
313	0.001	7.6942	1032.46	1454.5	4.5782	4.2708	4.6968	1.5017
	0.002	7.7723	1033.72	1455.9	4.5639	4.2641	4.7296	1.5050
	0.003	7.8814	1035.51	1457.3	4.5472	4.2563	4.7785	1.5091
	0.004	7.9628	1036.74	1458.6	4.5338	4.2500	4.8135	1.5122
	0.005	8.0726	1038.08	1459.8	4.5205	4.2438	4.8656	1.5154
318	0.001	6.9763	1026.70	1441.8	4.6854	4.3945	4.3582	1.4803
	0.002	7.0556	1028.11	1443.2	4.6699	4.3872	4.3932	1.4838
	0.003	7.1782	1029.43	1444.5	4.6555	4.3805	4.4558	1.4870
	0.004	7.2816	1030.98	1445.9	4.6395	4.3729	4.5044	1.4907
	0.005	7.4000	1032.27	1447.5	4.6235	4.3654	4.5618	1.4942
323	0.001	6.0482	1021.31	1426.9	4.8090	4.5175	3.8781	1.4573
	0.002	6.1593	1022.64	1428.3	4.7933	4.5101	3.9365	1.4606
	0.003	6.2731	1024.15	1429.8	4.7762	4.5020	3.9949	1.4643
	0.004	6.3601	1025.33	1431.2	4.7614	4.4951	4.0377	1.4674
	0.005	6.4597	1027.02	1432.4	4.7456	4.4876	4.0874	1.4711

Table 2.3 Acoustic parameters of Polyaniline doped with $HClO_4$ (1.0 N) in DMSO

Temp K	Molality m	Viscosity Nsm-2	Density Kg/m3	Velocity m/s	β X 10^{10} N-1m2	L_f X 10^{11} m	τ X 10^{12} Sec	Z X 10^{6} $Kgm^{-2}s^{-1}$
303	0.001	1.8320	1111.46	1498.0	4.0094	4.0267	0.9794	1.6650
	0.002	1.8681	1112.76	1499.2	3.9983	4.0200	0.9959	1.5063
	0.003	1.9012	1114.25	1501.7	3.9797	4.0137	1.0088	1.5077
	0.004	1.9354	1115.93	1502.8	3.9679	4.0076	1.0239	1.5095
	0.005	1.9776	1117.28	1504.4	3.9547	4.0016	1.0428	1.5113
313	0.001	1.3185	1105.78	1467.2	4.2010	4.1913	0.7385	1.4671
	0.002	1.3542	1106.90	1468.4	4.1899	4.1850	0.7565	1.4687
	0.003	1.3842	1108.31	1469.9	4.1760	4.1779	0.7707	1.4704
	0.004	1.4406	1109.72	1471.2	4.1634	4.1711	0.7997	1.4717
	0.005	1.4710	1111.07	1472.6	4.1504	4.1642	0.8140	1.4737
323	0.001	0.9247	1099.15	1439.8	4.3887	4.3484	0.5411	1.4336
	0.002	0.9564	1100.59	1441.1	4.3751	4.3421	0.5579	1.4351
	0.003	0.9952	1101.86	1442.6	4.3610	4.3352	0.5787	1.4369
	0.004	1.0329	1103.24	1443.8	4.3483	4.3272	0.5988	1.4385
	0.005	1.0712	1104.67	1445.0	4.3354	4.3197	0.6192	1.4401

The value of ultrasonic velocity, density and viscosity of all the three system 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 literature [16, 17]

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 [18]. Increase of ultrasonic velocity with concentration and decrease of adiabatic compressibility with concentration indicate that the molecules are forming a more tightly bound system [19].

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 free length. 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 (τ) for doped polyaniline have been reported in solutions at different temperatures by varying the concentrations from 0.001M to 0.005M. It is found the relaxation time in all the three solvents decrease linearly with temperature and increase with concentrations as exhibited by viscosity values as a result of the change in the thermodynamic parameters. The linear increase of the relaxation time over the selected range of 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 linear 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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