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Comparitive study on ultrasonic property on polyaniline salts

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ABSTRACT

Polyaniline salts were synthesized via chemical polymerization and are subjected to ultrasonic waves of 3 MHz. The physicochemical parameters like density, viscosity and compressibility parameters were measured and their effect on ultrasound has been extensively studied. Solvent properties and the spectroscopic properties such as λ_{max}, frequency shifts have been correlated. A study of effect of ultrasonic waves on the organic acid doped PAni has also been attempted.

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Introduction

Ultrasound has been widely used in various fields such as medicine, under water signaling and detecting the flaws in the materials.[1-4] The physical properties of the electrolyte solutions have been affected by the propagation of ultrasound. The present work has been initiated with a view to analyse the effect of ultrasound on polyaniline (PAni) emeraldine base (EB) and its salts such as Polyaniline picrate (PAPI) and Polyaniline chloride (PACl) in Dimethyl formamide (DMF) and N-Methyl-2-pyrrolidone (NMP). The polymer solvent interactions in these solvents and the effect of ultrasound on their spectral shifts may throw light on solute solvent interactions.

Experimental

PAni was synthesized by Chemical oxidative polymersiation.[5] The HCl doped PACl was converted to the base form (EB) by treating with Sodium hydroxide for 24 hours. EB was doped with picric acid.[6,7] Effect of ultrasound on these three polymers EB, PaniCl and PAniPI in NMP and DMF were probed in the present study.

Solutions of different molalities were prepared by dilution methods. The densities were determined using specific gravity bottles (10 ml) and viscosities were measured using a Cannon Fenske viscometer. For the propagation of ultrasound of 3MHz variable path Interferrometer was used. The UV-Visible spectra of the all the solutions were recorded before and after passing ultrasound for 30 minutes in Lamda 25 Perkin Elmer spectrophotometer.

Results and Discussion

NMP is a polar basic solvent with dielectric constant 32 and DMF is a dipolar protic solvent with a dielectric constant of 38.3. For EB/DMF solutions, the viscosities are found to decrease to about 0.7 cp while in EB/NMP the values are found to be 1.6-1.3 cp. The lower values of viscosities show that the solutions are less viscous than the solvent. This may be due to the decrease in the cohesive energy of solvent.

The observed changes may be explained qualitatively by postulating 3 opposing sets of contributions.

i. Expansion due to breaking up of PAni by the addition of NMP.

ii. Contraction due to specific interaction between PAni and NMP and size differences.

iii Expansion due to steric repulsion in PAni.

The ultrasonic velocities were higher for NMP compared to that of DMF due to solute-solvent interaction (Fig 1,Table 1). The irregular behaviour of adiabatic compressibility 'β' (Table 1, Fig 2) indicates that there is a weak solute solvent interaction or dissociation taking place in the solution.

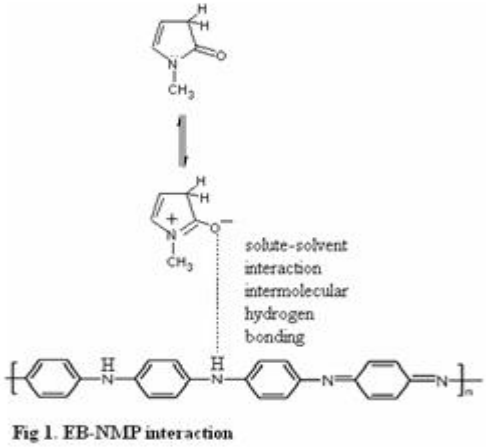

Fig 1. EB-NMP interaction

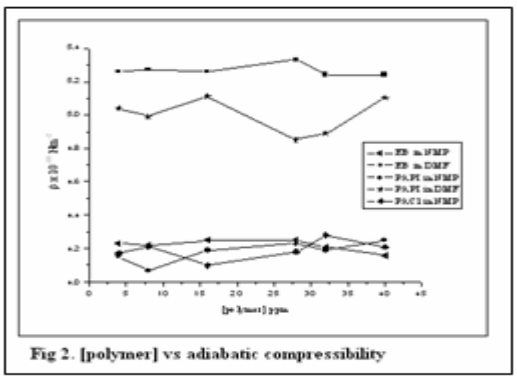

Fig 2. [polymer] vs adiabatic compressibility

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Table 1. Ultrasonic parameters of NMP and DMF

ppm	[EB]				[PAPI]				[PACl]	
	NMP		DMF		NMP		DMF		NMP	
	υ ms^{-1}	$\beta \times 10^{10}$ Nm^{-2}	υ ms^{-1}	$\beta \times 10^{10}$ Nm^{-2}	υ ms^{-1}	$\beta \times 10^{10}$ Nm^{-2}	υ ms^{-1}	$\beta \times 10^{10}$ Nm^{-2}	υ ms^{-1}	$\beta \times 10^{10}$ Nm^{-2}
40	1524	4.16	1446	5.24	1518	4.25	1446	5.10	1524	4.21
32	1518	4.21	1428	5.24	1530	4.19	1470	4.89	1512	4.28
28	1518	4.25	1428	5.33	1512	4.23	1464	4.85	1536	4.18
16	1518	4.25	1422	5.26	1530	4.19	1434	5.11	1536	4.10
8	1518	4.22	1434	5.27	1536	4.07	1452	4.99	1524	4.21
4	1518	4.23	1434	5.26	1530	4.15	1452	5.04	1530	4.17
0	1518	4.14	1428	5.20	1518	4.14	1428	5.20	1518	4.14

When ultrasound is passed over EB/NMP solutions for 30 minutes a hypsochromic shift of ≈ 40 nm (≈ 620 nm to 580 nm) is observed for quinoid moieties while the benzenoid peak at 320 nm was slightly shifted by 5-7 nm (Fig 3); besides these a hypochromic effect is also observed by 4 units for benzenoid band and 0.2 units for quinoid band (Table 2).

Table 2.UV-VIS spectral data in NMP and DMF

[EB] ppm	NMP				DMF			
	Before		After		Before		After	
	λ_{max}	O.D	λ_{max}	O.D	λ_{max}	O.D	λ_{max}	O.D
40	621	1.756	617	1.464	607	0.516	615	0.500
32	621	1.417	580	1.202	607	0.400	614	0.375
28	621	1.010	587	0.833	608	0.263	611	0.252
16	623	0.750	587	0.534	608	0.160	612	0.071
8	623	0.428	589	0.286	607	0.069	624	0.071
4	620	0.196	560	0.145	609	0.037	617	0.022

After passing ultrasound an isosbestic point is also observed between the benzenoid and quinoid peaks indicating an interconversion between the two forms (Fig 2). PAni has a switching property between various redox states (Fig 4). It also exhibits thermochromism.[8,9] In the present work sonochromism of PAni is investigated. On aging, the EB/NMP solutions degrade and intensity gets reduced (Fig 3). In EB/DMF solutions the benzenoid and quinoid peaks were observed at (Fig 5). The polymer is highly stable in this solvent.

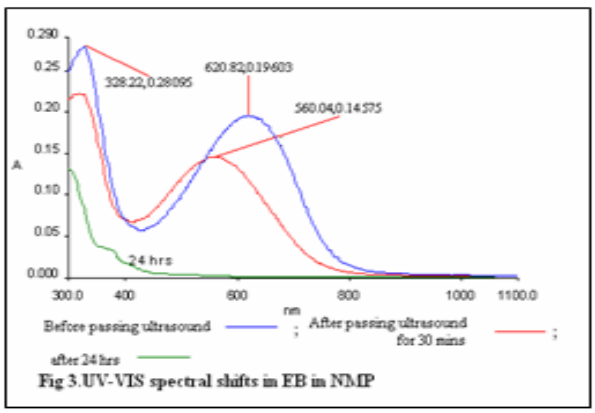

Fig 3.UV-VIS spectral shifts in EB in NMP

PACl in NMP shows dedoping behaviour[10] and the λ_{max} was observed to be similar to EB. It also exhibited hypochromism. The properties are similar to emeraldine base thus indicating that the hydrochloride ion dissociates out of the polymer matrix.

PAPI in NMP exhibited little shift in the visible spectra after passing ultrasound (Fig 6) for 30 mins which indicates compact coil conformation in the picrate salt.

Conclusion:

Polyaniline synthesized via chemical polymerization shows sonochromic effect in EB /NMP solutions. Degradation of PAni is enhanced by sonochromic effect which is evidenced from the spectral shifts and the appearance of the isosbestic points in the UV – Visible spectra. Polyaniline salts doped with organic acids shows no effect after passing ultrasound.

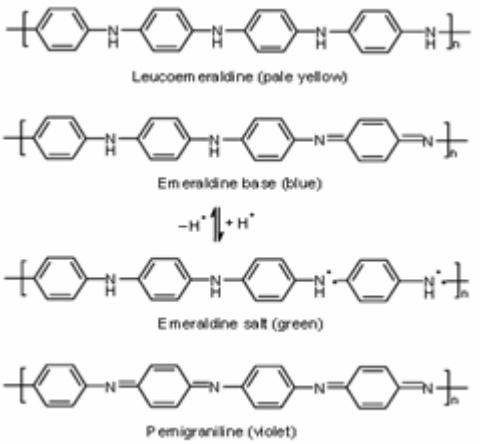

Fig 4. Switching property of polyaniline

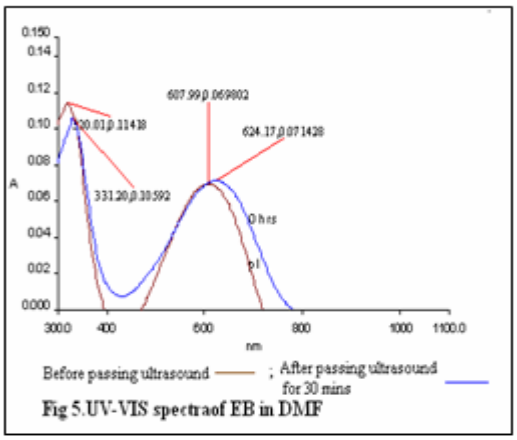

Fig 5.UV-VIS spectraof EB in DMF

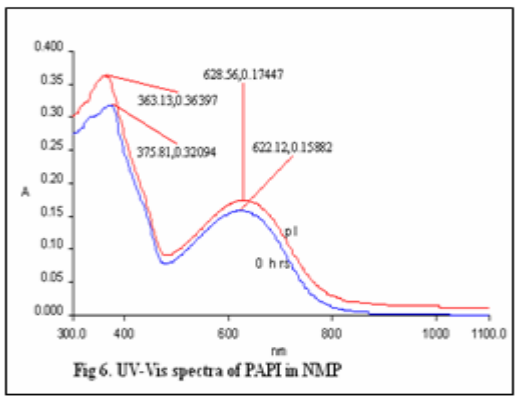

Fig 6. UV-Vis spectra of PAPI in NMP

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