



Comparitive study of ultrasound and electrolytes on polyaniline base and salt form

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ABSTRACT

Polyaniline (PAni), shows a unique feature, that it can be modified in a controlled manner by adding electrolyte. The effect of electrolytes like LiCl, NaCl and KCl on the doping behaviour of Polyaniline emeraldine base (EB) has been investigated. The study of the effect of ultrasonic waves on electrolyte - Polyaniline picrate (PAPI) mixture and their interactions were compared.

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Introduction

Among conducting polymers, PAni is unique due to its electrical and electrochemical properties, high environmental stabilities, easy preparation and low cost of the monomer with a variety of applications in the fields of sensors, optoelectronics, corrosion etc.,^[1-5] This paper initiates the application of sonochemical principles to polymer chemistry where the effects of ultrasound on the polyanilines have been studied in the presence of various alkali halides such as LiCl, NaCl and KCl throwing an essence on the doping mechanism and sonochromic behaviour.

Experimental

EB and PAPI solutions in DMF were mixed with electrolytes such as LiCl, NaCl and KCl in DMF of varying concentrations (Table I). The solutions were placed in an ultrasonic variable path interferometer (3 MHz) for about 30 minutes. The UV-Visible spectra of the all the solutions were recorded before and after passing ultrasound using Lambda 25 Perkin Elmer spectrophotometer. The densities were determined using specific gravity bottles (10ml) and viscosities were measured using a Cannon Fenske viscometer. The conductivities were measured using Elico Digital conductivity meter CM180.

Results and Discussion

The ultrasonic velocities increase with the increasing size of the electrolytes (Table I). After mixing with EB this trend in size increase is retained. On mixing PAPI with electrolytes there is an increase in ultrasonic velocities similar to EB (Table II) but the trend among different electrolytes is LiCl > NaCl > KCl indicating strong interaction for LiCl-PAPI mixtures.

A plot of adiabatic compressibility (β) vs electrolyte concentrations for EB revealed random behaviour with increasing electrolyte concentrations (Fig 1). There is a decrease in β for LiCl (Fig 2) initially, followed by a almost linear trend at high concentrations. NaCl exhibited a sudden decrease in the $1.50\text{-}2.25 \times 10^{-5}$ g/ml after which almost constant

value is observed. With KCl, a dip is observed in the region $1.5\text{-}3.0 \times 10^{-5}$ g/ml with a wedge pattern. These changes indicate ion association between NaCl and KCl with EB i.e. EB is doped by these ions (Fig 3,4) to a great extent.

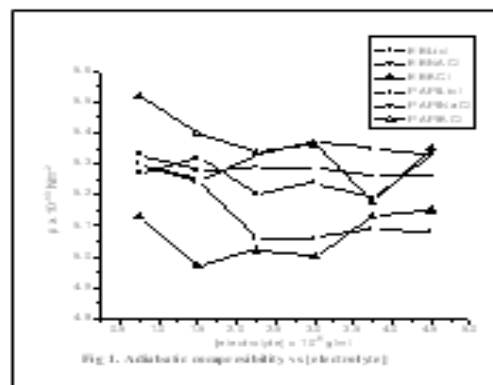


Fig 1. Adiabatic compressibility vs [electrolyte]

When PAPI and electrolytes are mixed together an opposite pattern is observed in these regions (Fig 1). There is an increase in β initially followed by a steep decrease for LiCl besides a wedge like pattern indicating strong association between LiCl and PAPI (Fig 2).

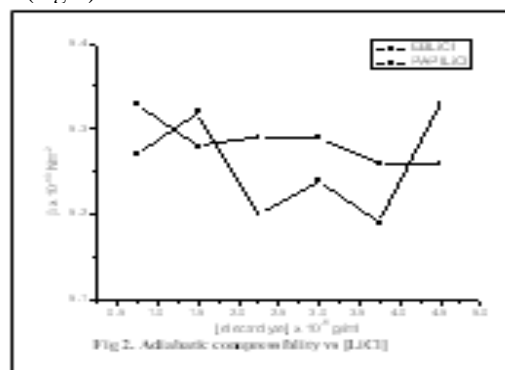
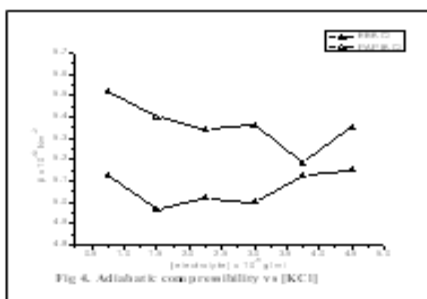
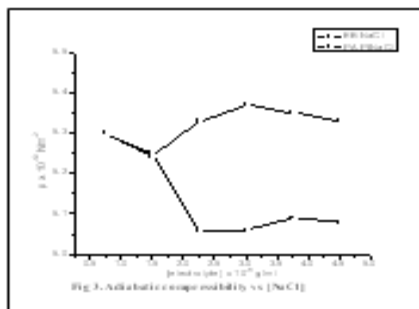


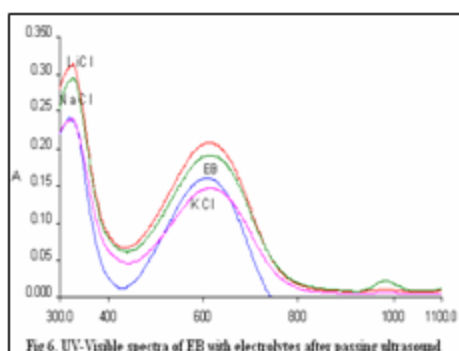
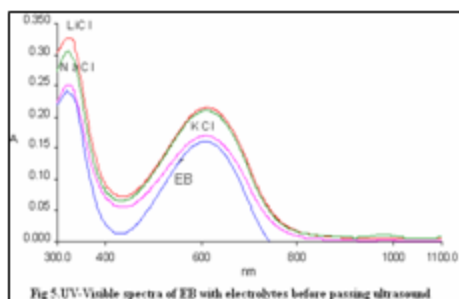
Fig 2. Adiabatic compressibility vs [LiCl]

With NaCl (Fig 3) an increase is observed after an initial dip at 1.5×10^{-5} g/ml indicating association while at higher concentrations almost a constant value is found. With KCl (Fig 4), a strong association is observed at 4×10^{-5} g/ml. Thus LiCl brings about maximum changes among the electrolytes in the order $\text{LiCl} < \text{NaCl} < \text{KCl}$.



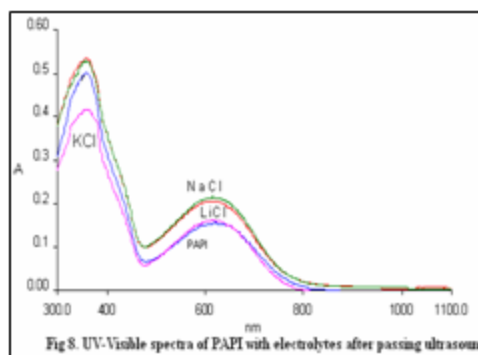
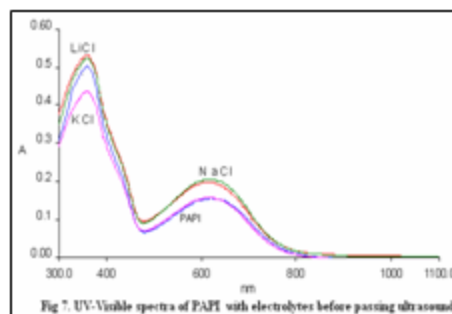
UV-Visible Spectra:

The UV-Visible spectrum of EB in DMF (Fig 5) exhibited a benzenoid peak at 320 nm and the broad absorption in the region 500-620 nm has been attributed to transitions in the quinoid rings. The addition of electrolytes (Table III) to the solutions of EB in DMF causes a bathochromic shift by a value of ~ 8 nm for the benzenoid peaks and the quinoid peaks are also shifted bathochromically by ~ 4 nm for LiCl and NaCl whereas no shifts are observed for KCl additions. However passage of ultrasound for 30 minutes produces the following changes in the UV-Visible spectra (Fig 6).

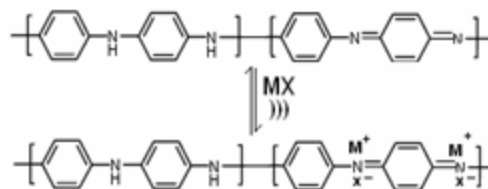


i. A small decrease in the intensity of 324nm band and a bathochromic shift of ~ 4 -8 nm.

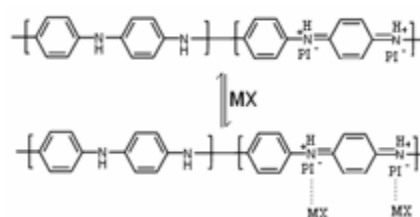
- ii. The band around 609 nm decrease in intensity and a bathochromic shift of ~ 7 nm.
- iii. Emergence of a new peak at ~ 982 nm of very low intensity specifically for NaCl.
- iv. Isosbestic points are observed at 400, 750 and 900 nm.



All these changes indicate that electronic transitions in the ring structure are enhanced by the addition of electrolytes. This remarkably different behaviour of EB towards halide ions and ultrasound may be due to the doping of EB. The changes can be represented as $\text{EB} \rightleftharpoons \text{ES}$ (Scheme I). Similar changes have been observed for Poly (2-methoxyaniline-5-sulphonic acid) in the presence of alkali and alkaline earth metal salts.^[6] These ionochromic effects are rare in Polyaniline chemistry. The sonochromism observed in this study is also indicative of the role of ultrasonic waves in increasing the electron delocalization. The behaviour of electrolytes on PAPI in DMF is entirely different (Fig 7). When PAPI is mixed with the electrolytes a shift of 359 – 364 nm and 620-615 nm is observed.



Scheme-I Effect of ultrasound and electrolyte in EB



Scheme II Effect of ultrasound and electrolyte in PAPI

The hypsochromic shift of the quinoid band indicates distortion of the benzenoid and the quinoid ring which decreases the conjugation in the ring.^[7] This indicates ionochromism in PAPI. However, on passing ultrasound a little shift is observed (Table IV).

Table I Effect of ultrasound on EB in the presence of different electrolytes

[electrolyte] x 10 ⁻⁵ g/ml	[EB] = 1x 10 ⁻⁵ g/ml					
	LiCl		NaCl		KCl	
	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²
6*	1428	5.41	1428	5.31	1434	5.26
0.75	1428	5.33	1440	5.30	1476	5.13
1.50	1434	5.28	1446	5.25	1476	4.97
2.25	1434	5.29	1458	5.06	1476	5.02
3.00	1428	5.29	1458	5.06	1470	5.00
3.75	1434	5.26	1458	5.09	1458	5.13
4.50	1434	5.26	1458	5.08	1470	5.15

*-Absence of EB

Table II PAPI – Electrolyte interactions

[electrolyte] x 10 ⁻⁵ g/ml	[PAPI] = 1 x 10 ⁻⁵ g/ml					
	LiCl		NaCl		KCl	
	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²	v ms ⁻¹	β x 10 ¹⁰ Nm ⁻²
6*	1428	5.41	1428	5.31	1434	5.26
0.75	1434	5.27	1428	5.30	1428	5.52
1.50	1428	5.32	1434	5.24	1416	5.40
2.25	1440	5.20	1434	5.33	1434	5.34
3.00	1434	5.24	1428	5.37	1422	5.36
3.75	1446	5.19	1428	5.35	1446	5.18
4.50	1422	5.33	1434	5.33	1428	5.35

*-Absence of EB

Table III UV-Visible Spectral data of EB with electrolyte in DMF

[electrolyte] x 10 ⁻⁵ g/ml	EB 320, 608 nm 0.241 0.126											
	LiCl				NaCl				KCl			
	Before		After		Before		After		Before		After	
	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D
0.75	322	0.324	324	0.316	324	0.294	327	0.294	322	0.251	327	0.240
	609	0.191	611	0.173	609	0.198	609	0.198	608	0.178	577	0.150
1.50	321	0.326	328	0.313	324	0.305	328	0.294	322	0.252	327	0.241
	612	0.215	613	0.208	609	0.210	615	0.191	608	0.169	615	0.146
2.25	322	0.321	328	0.314	325	0.268	330	0.263	328	0.296	328	0.265
	612	0.211	613	0.204	610	0.184	614	0.173	609	0.192	616	0.157
3.00	328	0.313,0.202	328	0.292	324	0.255	330	0.260	325	0.269	329	0.252
	610		612	0.184	614	0.167	614	0.157	608	0.175	615	0.154
3.75	329	0.343,0.22	329	0.332	328	0.258	329	0.262	322	0.204	329	0.195
	610		612	0.203	614	0.171	614	0.158	609	0.136	613	0.118
4.50	321	0.308,0.198	328	0.301	324	0.203	329	0.201	324	0.274	328	0.247
	610		614	0.188	613	0.132	612	0.127	608	0.180	614	0.152
							983	0.014				

Table IV UV-Visible Spectral data of PAPI with electrolyte in DMF

[electrolyte] x 10 ⁻⁵ g/ml	PAPI 359, 620 nm 0.503, 0.155											
	LiCl				NaCl				KCl			
	Before		After		Before		After		Before		After	
	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D	λ _{max} nm	O.D
0.75	357	0.521	360	0.512	364	0.396	363	0.418	361	0.422	357	0.394
	614	0.192	614	0.199	615	0.153	613	0.172	616	0.152	615	0.154
1.50	360	0.532	358	0.534	358	0.528	358	0.528	359	0.436	356	0.416
	614	0.197	614	0.205	617	0.205	616	0.214	616	0.157	616	0.166
2.25	366	0.508	366	0.494	356	0.540	358	0.542	360	0.435	359	0.431
	613	0.202	606	0.218	617	0.210	616	0.220	616	0.156	615	0.170
3.00	361	0.698	363	0.696	363	0.424	359	0.429	360	0.426	359	0.427
	612	0.241	613	0.242	614	0.169	614	0.170	617	0.153	616	0.170
3.75	356	0.623	355	0.631	362	0.417	357	0.428	359	0.419	360	0.425
	614	0.233	615	0.236	616	0.169	614	0.172	616	0.151	616	0.161
4.50	364	0.761	366	0.766	361	0.531	356	0.533	362	0.428	363	0.430
	613	0.315	614	0.313	618	0.213	616	0.214	615	0.156	615	0.165

The absence of isosbestic points and 980 nm peak (Fig 8) indicates that there is no delocalization between benzenoid and quinoid forms. The doped picrate ion being quite big in size prevents the delocalization and hence the visible spectra is unaffected by the passage of ultrasound. This behaviour also is quite unprecedented in polyaniline chemistry (Scheme II).

The very low change in conductivities ($0.01-0.04\text{Scm}^{-1}$) and viscosities (0.71-0.75cp) after adding electrolytes are indicative of electrolyte binding to the polymers.

Conclusion:

Polyaniline synthesized via chemical polymerization shows unique doping and dedoping chemistry in the presence of electrolytes. Ultrasound differentiates dedoped and doped states of polyanilines. The obtained results were confirmed by measuring UV visible spectrum. Ionochromism is observed both in EB and PAPI while sonochromism is observed only for EB.

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