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Internal Pressure, Free Volume, Thermochemical and FTIR Spectral Study on Polyaniline Monochloro Acetate Solution

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ABSTRACT

The study of liquids using thermodynamic, thermochemical properties and spectroscopy constitutes mining fields for scientists. Ultrasonic studies of solutions yield valuable information about the ionic interactions, the nature and the strength of the interactions. The thermodynamic property such as internal pressure, free volume and thermochemical properties such as apparent molal volume, apparent molal compressibility plays an important role in elucidation of the nature of molecular interactions. In the present investigation an analysis of polyaniline solution are studied for different concentrations from low temperature to high temperature. This analysis reveals that the weak solute-solvent interaction takes place in the solution. These results are compared with FTIR spectroscopic study. They are in good agreement with each other in elucidating their structural changes occurring in the solution. The study of acoustic and FTIR spectra confirms the structure breaking property of the polymer solution.

Key words - Polyaniline Solutions, Formamide, Internal Pressure.

INTRODUTION

It is well known that ultrasonic technique has wide range of applications in industry, medical scanning equipment testing etc., Ultrasonic study of the aqueous solutions also reveal some important information regarding internal pressure of liquid and solution which is a single factor appears to vary due to all the internal cohesive forces due to ion-solvent interaction, quantum mechanical forces of dispersion, dielectric

constant effect, etc. Thermodynamic and thermochemical properties are the important parameters which elucidates the structural influence of the solute in the solvent i.e., in liquid medium. So, in the present investigation an attempt is made primarily to analyse the various interactions occurring in the PANI solutions, based on acoustic measurements at different molalities with different temperatures.

EXPERIMENTAL TECHNIQUE

The solution of Polyanilinemonochloroacetate (PMCA) salt in formamide is prepared with five different molalities. The density of the solution is measured with an accuracy of 0.0001gm/cc using 25 ml specific gravity bottle. Viscosity measurements are carried out within 1% error using Canon-Fenske viscometer. The ultrasonic velocities of the solutions at different temperatures are measured using the ultrasonic interferometer of 2 MHz with an accuracy of ±0.5m/s.

COMPUTATION

Internal pressure (π_i) and free volume (V_f) are computed using the following formulae.

$$\pi_i = bRT \left[\frac{k\eta}{U}\right]^{1/2} \frac{\rho^{2/3}}{M_{eff}^{7/6}} \text{ atms}$$

$$V_f = \left[\frac{MU}{k\eta}\right]^{3/2} \text{ cc}$$

Where

K → constant equal to 4.28×10^9

η → viscosity of the solution in poise

M_{eff}→ effective molecular weight of the solution in gm

U → Ultrasonic velocity of the solution in cm/sec

Apparent molal volume

$\varphi_v = 1000\ (\rho_0 - \rho)/n_2\rho_0 + M_2/\rho_0$ ml/mole

Apparent molal compressibility

$\varphi_k = (1000/\ n_2)[\ \rho_0\beta - \rho\beta_0] + \beta_0\ M_2/\rho_0$ ml mol^{-1} cm^2 $dyne^{-1}$

Where

n_2 is the molal concentration,

M_2 is the molecular weight of the solute,

ρ is the density of the solution and

ρ_0 is the density of the solvent.

RESULTS & DISCUSSION

Thermodynamic Parameters

Internal pressure (π_i) and Free volume (V_f)

The variation of internal pressure is shown in Table (1&2) & Figure (1&2).Internal pressure is found to be minimum at 0.01m from 15°c - 55°c. This decrease in internal pressure indicates the weak solute – solvent interaction. The decreasing trend reveals the tendency of breaking the structure of the solvent. This behaviour emphasizes that the solute behaves as a structure breaker. The structure breaking effect is also confirmed by increasing values of free volume at low molalities at different temperatures. These results are in good agreement with the FTIR spectroscopic study [1,2].

Table 1 Internal Pressure Vs Molality

Molality (m)	Internal pressure (atms)					
	5°c	15°c	25°c	35°c	45°c	55°c
0.001	18461	15894	13228	12735	11451	10662
0.005	18954	15302	12537	12044	11057	10069
0.01	18251	14611	12340	11649	10662	9674
0.015	19251	16289	13525	13031	12241	10760
0.02	19251	17474	13821	12932	12340	10958

Table 2 Free Volume Vs Molality

Molality (m)	Free volume (cc)					
	5°c	15°c	25°c	35°c	45°c	55°c
0.001	0.0098	0.0166	0.0313	0.0384	0.0566	0.0753
0.005	0.0090	0.0169	0.0335	0.0422	0.0589	0.0847
0.01	0.0085	0.0181	0.0329	0.0422	0.0597	0.0862
0.015	0.0085	0.0153	0.0298	0.0362	0.0463	0.0754
0.02	0.0085	0.0124	0.0274	0.0363	0.0459	0.0698

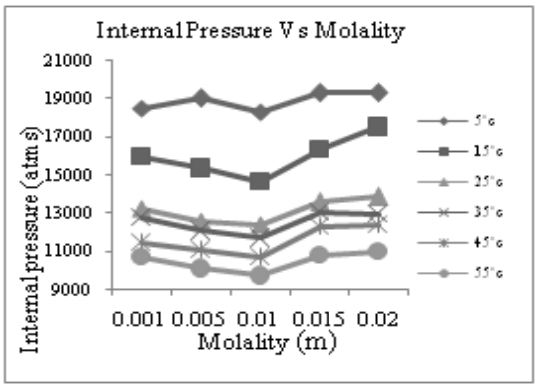


Fig (1)

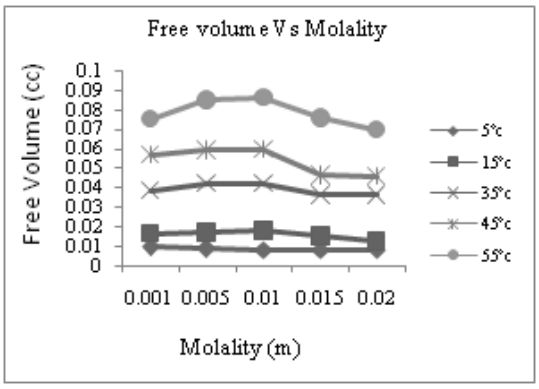


Fig (2)

THERMOCHEMICAL PARAMETERS

Apparent Molal volume (φ_v)

The variation of apparent molal volume is shown in Table(3) & Figure(3). The apparent molal volume is found to be high at low concentrations at all temperatures. At 5˚c the variation of apparent molal volume is found to be parabolic. The concentration dependence on apparent molal volume could be interpreted in terms of cation – cation interaction induced by co-operative ion – solvent interaction. The apparent molal volume is found to be increasing with increasing molality at low temperatures but at higher temperatures the decrease in the apparent molal volume suggests that there is a strong solute – solute interaction prevail in the solution and the increase in apparent molal volume with respect to concentration which supports the weak solute – solvent interactions [3].

Apparent Molal Compressibility (φ_k)

The variation of apparent molal compressibility is shown in Table(4) & Figure(4). The negative values of apparent molal compressibility at higher concentration and at 25˚c are observed in the solutions. At all other molalities the values are found to be positive for all temperatures. The variation in apparent molal compressibility is obvious only at very low concentration at all temperatures. Hence the results obtained from the present investigation suggest that there is a weak solute – solvent interaction in the non- aqueous solution of PMCA in formamide[4].

Table 3 Apparent Molal Volume Vs Molality

Molality (m)	Apparent molal volume $X10^2$ ml/mol					
	5˚c	15˚c	25˚c	35˚c	45˚c	55˚c
0.001	78.16	85.29	100.1	88.93	88.05	92.01
0.005	85.39	87.15	91.95	88.35	86.7	91.95
0.01	87.28	87.64	89.07	89.71	88.05	91.86
0.015	87.08	88.6	88.63	88.1	91.78	91.51
0.02	86.46	88.68	88.12	88.22	88.56	91.36

Table 4 Apparent Molal Compressibility Vs Molality

Molality (m)	Apparent molal compressibility $X10^{-8}$ ml $mol^{-1}cm^2$ $dyne^{-1}$					
	5˚c	15˚c	25˚c	35˚c	45˚c	55˚c
0.001	-171	154.2	-85	292.7	72.23	341.2
0.005	50.42	42.92	-37.3	-0.14	9.191	-13.1
0.01	38.48	24.14	27.46	37.56	25.1	26.17
0.015	29.59	30.59	10.09	30.1	79.97	9.942
0.02	25.64	78.88	36.41	20.58	46.97	34.05

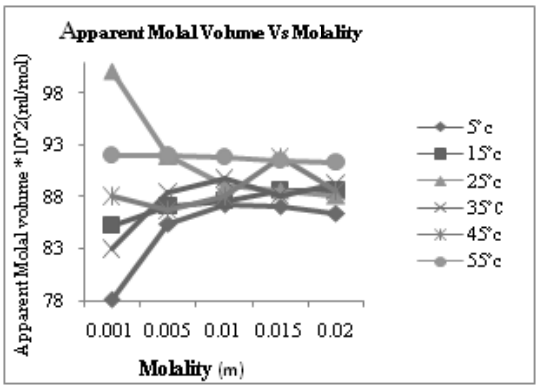


Fig (3)

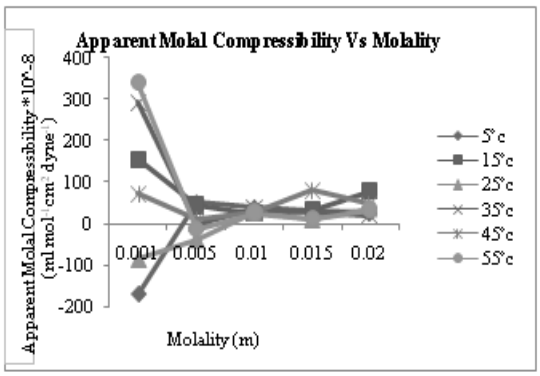


Fig (4)

FTIR ANALYSIS

When PMCA is added to formamide there exists a slight deviation in the absorption peaks (i.e.,) the N-H stretching absorption is observed at 3414.78 cm $^{-1}$. The amide band is noticed at 1686.63cm $^{-1}$. The N-H out of plane bending is found at 605.91cm $^{-1}$. The most important band to be observed is the NH^+ band which is at 2192cm $^{-1}$ (i.e.,) it is shifted to lower frequency side by 4 cm $^{-1}$ [5,6]

From the spectral analysis, it can be inferred that there is a weak solute - solvent interaction in the solution of PMCA (Fig (5&6) & Table (5)).

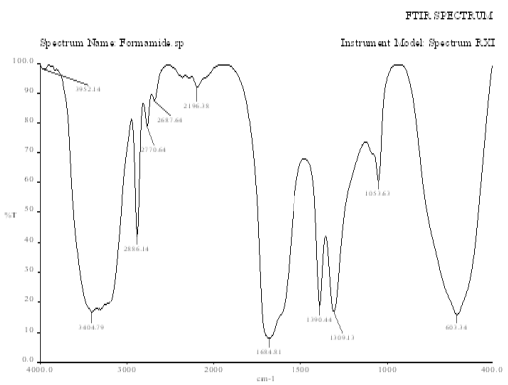


Fig 5 FTIR Spectrum of Formamide

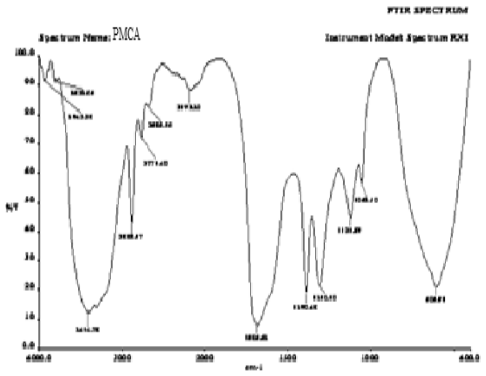
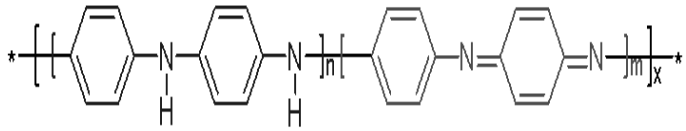


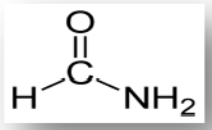
Fig 6 FTIR Spectrum of PMCA with Formamide

Table – 5 FTIR - Spectral Analysis

Name of the sample	N-H (cm^{-1})	C-H (cm^{-1})	NH^+ (cm^{-1})	C=O (cm^{-1})	C=N (cm^{-1})	C-N (cm^{-1})	C-O (cm^{-1})	N-H (cm^{-1})
Formamide	3600-3000	2886, 2771, 2687	2196	1684	1390	1309	1053	603
Polyaniline monochloro acetate with Formamide	3414	2886, 2771, 2685	2192	1686	1390	1310	1053	605



STRUCTURE OF POLYANILINE



STRUCTURE OF SOLVENT

CONCLUSION

In the Present work, the solution of PMCA formamide exhibits weak solute – solvent interaction. This behaviour is also confirmed from the FTIR spectral study.

ACKNOWLEDGEMENT

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