Acoustical Studies of Some Derivatives of 4-Amino Benzoic Acid in 1, 4-Dioxane and Dimethyl Formamide at 308.15 K

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ABSTRACT: *The ultrasonic velocity, density and viscosity of some Schiff bases of 4-amino benzoic acid were measured in 1,4-dioxane and dimethylformamide at 308.15 K. Various acoustical properties such as isentropic compressibility (κ_s), Rao's molar sound function (R_m), the Van der Waals constant (b), molar compressibility (W), inter molecular free length (L_f), relaxation strength (r), internal pressure (π), solvation number (S_n) etc., were calculated. The results are interpreted in terms of molecular interaction occurring in the solutions.*

KEY WORDS: *Acoustical studies, 4-amino benzoic acid, Schiff bases, 1,4-dioxane, Dimethyl-formamide, Molecular interactions.*

INTRODUCTION

Ultrasound can be viable technology because it is readily available and can be used for wide range of application in different fields like consumer industries, pharmaceuticals, medical field process industries, chemical industries, physics etc. [1-3]. In chemistry, ultrasound velocity along with related thermo acoustic parameters have been extensively used in the recent past to study molecular interactions in binary and ternary liquid mixtures by a number of researchers [4-7].

Literature survey on ultrasound velocity measurement shows that very little work has been done for solid organic compounds [8-10]. Thus, in present paper we have used this technique for the better understanding of the molecular interactions in some solutions. Thus, in continuation of previous work [11-13], the density, viscosity and ultrasonic velocity of some schiff bases

of 4-amino benzoic acid are measured in 1, 4-dioxane (DO) and dimethylformamide (DMF) at 308.15 K over a wide concentration range.

The experimental data is used for the evaluation of various thermodynamic and acoustical parameters by which molecular interactions in solutions are interpreted.

EXPERIMENTAL

For the present study, 1, 4-dioxane and dimethyl-formamide were selected. The selection of solvent was limited because of solubility problem. Both the solvents were purified [14]. The estimated purity was better than 99.5 %, checked by GLC and moisture detection. All the Schiff bases are recrystallized before use. The structures of all these Schiff bases are given in Fig. 1.

HPI - 5 : 4-{[-3-phenylprop-2-en-1-ylidene] amino} benzoic acid

HPI - 7: 4-{[(4-hydroxy-3-methoxyphenyl) methylene] amino} benzoic acid

HPI - 6 : 4-{[(2-hydroxyphenyl)methylene]amino} benzoic acid

HPI - 8: 4-{[-(3-nitrophenyl)methylene]amino} benzoic acid
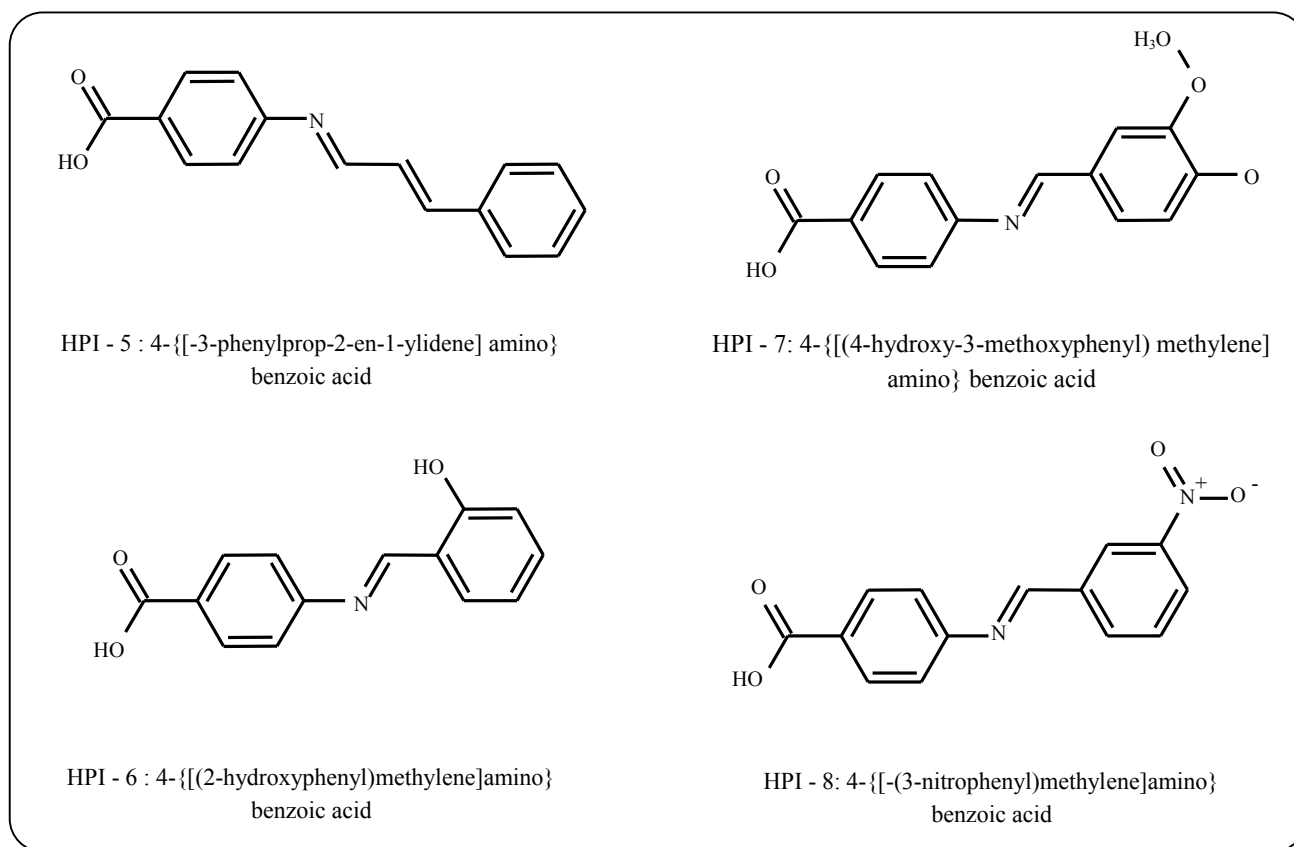
Fig. 1: Structures of Schiff bases.

The density, viscosity and ultrasonic velocity of solvents and solutions of different concentrations of Schiff bases of 4-amino benzoic acid were measured at 308.15 K by using specific gravity bottle, Ubbelhode viscometer and ultrasonic interferometer operating at 2 MHz with the uncertainties of 0.0001 g/ml, ± 0.06 % and ± 0.01 % respectively. The uncertainty of temperature is ± 0.1 K and that of concentration is 0.0001 mol/dm^3.

RESULTS AND DISCUSSION

The experimental data of ultrasonic velocity (U), viscosity (η) and density (ρ) of all the Schiff bases in dimethylformamide and 1, 4-dioxane solutions at 308.15 K are reported in table 1. For all the solutions, velocity (U), viscosity (η) and density (ρ) increased linearly with concentration (correlation coefficient: 0.9840-0.9999).

Various acoustical parameters were evaluated from experimental data of density, viscosity and ultrasound sound velocity, using the following standard equations:

Adiabatic compressibility (k$_s$): $k_s = 1/(U^2\rho)$

Rao's molar sound function (R$_m$): $R_m = (M/\rho)U^{1/3}$

where M is the molecular weight of solution.

Vander Waals Constant (b): $b = (M/\rho)(1-RT/MU^2(\sqrt{(1+MU^2/3RT)}-1))$

where R is gas constant and T is absolute temperature.

Molar compressibility (W): $W = (M/\rho)k_s^{-1/7}$

Intermolecular length (L$_f$): $L_f = K.k_s^{1/2}$

where K is Jacobson constant ($= 6.0816 \times 10^4$).

Relaxation strength (r): $r = 1-(U/U_\infty)^2$ where $U_\infty = 1.6 \times 10^5$ cm/s.

Internal pressure (π): $\pi = bRT(K\eta/U)^{1/2} \rho^{2/3}/M^{7/6}$

where b is the packing fraction (=2) and other symbols have their usual significance.

Solvation number (S$_n$): $S_n = M_2/M_1 [1-.k_s/.k_{s1}] [(100-X)/X]$

where, X is the number of grams of solute in 100 gm of the solution, M$_1$, M$_2$, k$_S$ and k$_{s1}$ are the molecular weights and adiabatic compressibility of solvent and solute respectively. Table 2 reports some of the acoustical parameters.

The variation of ultrasonic velocity with concentration is given in Fig. 2. The ultrasonic velocity (U) depends on intermolecular free length (L$_f$). The ultrasonic velocity U

Table 1: The density (ρ), ultrasonic velocity (U) and viscosity (η) of Schiff bases in 1, 4-Dioxane and DMF solutions at 308.15 K.

Conc. (M)	Density ρ. (gm/cm^3)	Velocity $U \times 10^{-5}$ (cm/s)	Viscosity $\eta \times 10^3$ (poise)	Density ρ. (gm/cm^3)	Velocity $U \times 10^{-5}$ (cm/s)	Viscosity $\eta \times 10^3$ (poise)
		DO			DMF	
		HPI-5			HPI-5	
0.00	1.0201	1.3296	10.7600	0.9356	1.4344	8.9695
0.01	1.0203	1.3236	10.9289	0.9369	1.4171	9.2350
0.02	1.0208	1.3261	11.1452	0.9377	1.4196	9.2929
0.04	1.0215	1.3300	11.3609	0.9383	1.4208	9.4056
0.06	1.0224	1.3339	11.5823	0.9387	1.4241	9.4802
0.08	1.0229	1.3365	11.7933	0.9394	1.4280	9.6396
0.10	1.0245	1.3422	12.0215	0.9398	1.4301	9.7459
		HPI-6			HPI-6	
0.01	1.0208	1.3317	11.1311	0.9383	1.4193	9.4974
0.02	1.0219	1.3353	11.2583	0.9389	1.4213	9.6112
0.04	1.0230	1.3381	11.4298	0.9395	1.4247	9.7428
0.06	1.0239	1.3432	11.7257	0.9399	1.4313	9.8167
0.08	1.0249	1.3481	11.9715	0.9406	1.4381	9.9114
0.10	1.0261	1.3549	11.2300	0.9412	1.4476	10.0386
		HPI-7			HPI-7	
0.01	1.0209	1.3273	11.2250	0.9373	1.4181	9.5494
0.02	1.0217	1.3286	11.4794	0.9381	1.4205	9.6773
0.04	1.0222	1.3312	11.7377	0.9390	1.4237	9.7766
0.06	1.0238	1.3327	12.0001	0.9399	1.4261	9.8817
0.08	1.0248	1.3373	12.2591	0.9408	1.4285	9.9749
0.10	1.0257	1.3405	12.5184	0.9416	1.4317	10.0663
		HPI-8			HPI-8	
0.01	1.0215	1.3326	11.3832	0.9387	1.4187	9.5721
0.02	1.0225	1.3348	11.6451	0.9401	1.4207	9.7035
0.04	1.0237	1.3373	12.0020	0.9415	1.4239	9.7961
0.06	1.0246	1.3397	12.3732	0.9429	1.4280	9.9692
0.08	1.0256	1.3421	12.6997	0.9443	1.4293	10.1241
0.10	1.0266	1.3448	13.0340	0.9458	1.4325	10.1982

Table 2: Variation of some acoustical parameters with concentration of Schiff bases in 1,4-dioxane and DMF Solutions at 308.15 K.

Conc. (M)	1,4-dioxane			DMF		
	$R_m . 10^{-3}$	b	$W . 10^{-3}$	$R_m . 10^{-3}$	b	$W . 10^{-3}$
	HPI-5			HPI-5		
0.00	4.4089	81.2520	2.5209	4.0893	73.4171	2.3012
0.01	4.4210	81.5896	2.5286	4.0938	73.7618	2.3055
0.02	4.4417	81.9362	2.5403	4.1192	74.1954	2.3199
0.04	4.4831	82.6491	2.5639	4.1705	75.1651	2.3492
0.06	4.5235	83.3431	2.5870	4.2252	76.0850	2.3797
0.08	4.5643	84.0654	2.6103	4.2789	77.0146	2.4098
0.1	4.6034	84.7005	2.6327	4.3321	77.9631	2.4391
	HPI-6			HPI-6		
0.01	4.4259	81.5365	2.5308	4.0877	73.6187	2.3024
0.02	4.4432	81.8003	2.5407	4.1106	74.0118	2.3154
0.04	4.4775	82.4007	2.5605	4.1592	74.8582	2.3427
0.06	4.5153	83.0222	2.5820	4.2118	75.7278	2.3719
0.08	4.5523	83.6324	2.6031	4.2632	76.5712	2.4006
0.1	4.5905	84.2291	2.6247	4.3184	77.4370	2.4311
	HPI-7			HPI-7		
0.01	4.4268	81.6330	2.5317	4.0983	73.8314	2.3082
0.02	4.4491	82.0314	2.5446	4.1289	74.3623	2.3255
0.04	4.4983	82.9157	2.5728	4.1917	75.4730	2.3609
0.06	4.5412	83.6151	2.5977	4.2535	76.5775	2.3958
0.08	4.5902	84.5444	2.6257	4.3151	77.6783	2.4307
0.1	4.6380	85.3881	2.6531	4.3779	78.7863	2.4661
	HPI-8			HPI-8		
0.01	4.4298	81.5964	2.5332	4.0920	73.7165	2.3053
0.02	4.4520	81.9767	2.5460	4.1197	74.1916	2.3210
0.04	4.4974	82.7927	2.5722	4.1793	75.2460	2.3548
0.06	4.5441	83.6300	2.5990	4.2396	76.2965	2.3890
0.08	4.5902	84.4561	2.6255	4.2967	77.3335	2.4216
0.1	4.6365	85.2799	2.6521	4.3550	78.3606	2.4547
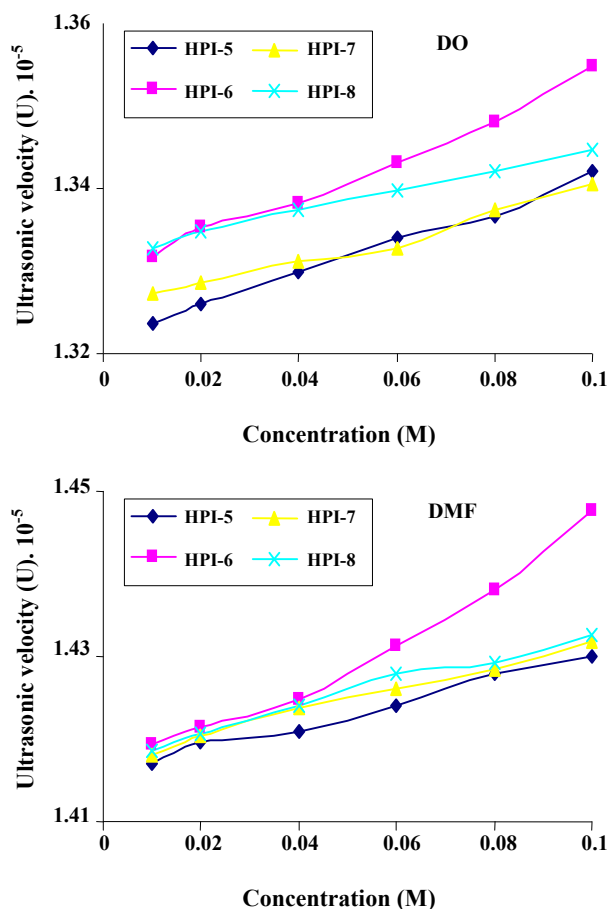
Fig. 2: Variation of ultrasonic velocity (U) with concentration in 1,4-dioxane (DO) and DMF solutions.
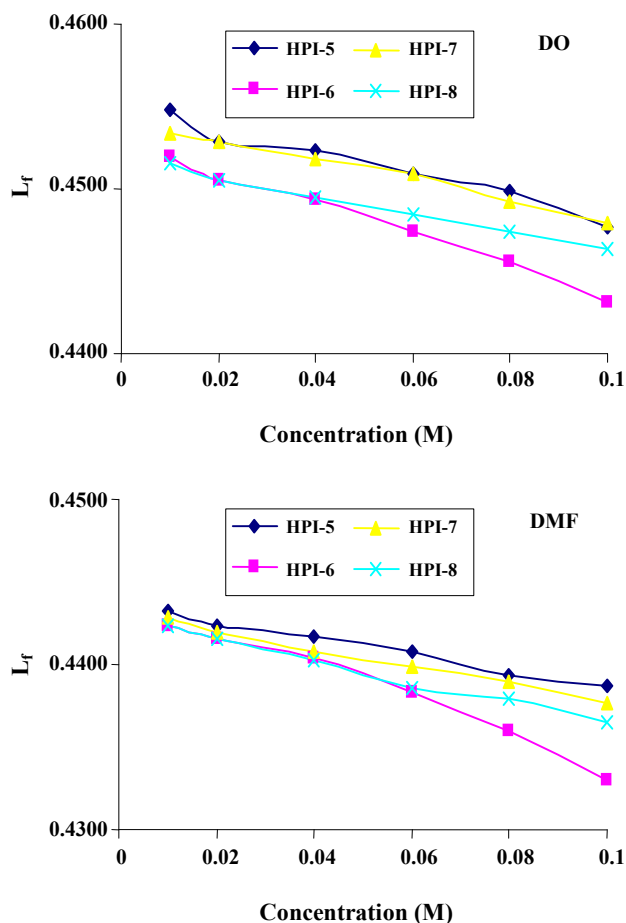

Fig. 3: Variation of intermolecular free path length (L_f) with concentration in 1,4-dioxane (DO) and DMF solutions.

increases with decrease in L_f or vise versa. Fig. 3 shows that for both the solvents, L_f decreases linearly with concentration, which suggests the presence of solute-solvent interactions. This is further confirmed by viscosity values, which increases with increasing concentration, suggesting more association between solute and solvent molecules.

The isentropic compressibility (κ_s) and relaxation strength (r) as shown in Figs. 4 and 5 are also observed to decrease with increasing concentration for all the bases in both the solvents, which further confirms the presence of solute-solvent interactions. Further, R_m, W and b increase (correlation coefficient: 0.9892-0.9999) continuously for all the systems suggesting the absence of complex formation in these systems.

The internal pressure (π) is the resultant of the forces of attraction and repulsion between the entities present in

the solutions. The variation of internal pressure with concentration is given in Fig. 6. It is observed that π values decrease with increase in concentration in all the bases in DMF indicating thereby the decrease of these forces in all the solutions. However, in 1, 4-dioxane solutions, for HPI-5 and HPI-7 π values decrease, for HPI-6 π values are almost constant whereas for HPI-8, slight increase is observed which indicates that both solute-solute and solute-solvent interactions exist in the solutions. The different behavior of different Schiff bases is due to the different substituent groups present in these compounds (as shown in Fig. 1), which interact differently with different solvents.

DMF is polar solvent whereas 1,4-dioxane is a non polar solvent. There are lone pairs of electrons on both oxygen atoms of 1,4-dioxane whereas in DMF, lone pairs of electrons are present on both oxygen and
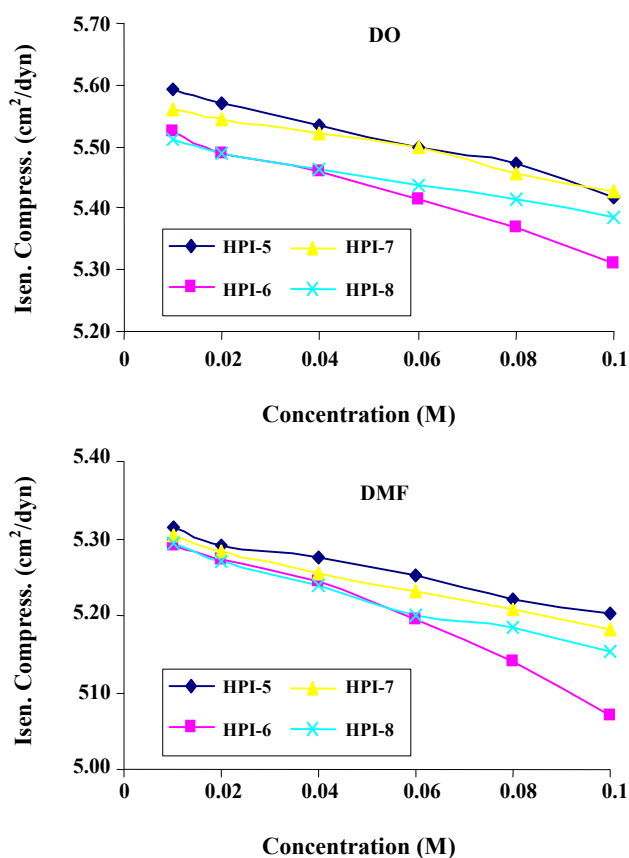
Fig. 4: Variation of isentropic compressibility (κ_s) with concentration in 1,4-dioxane (DO) and DMF solutions.

Fig. 5: Variation of relaxation strength (r) with concentration in 1,4-dioxane (DO) and DMF solutions.

nitrogen atoms. However, due to different electro negativity of oxygen and nitrogen, in DMF oxygen acquires $\delta-$ charge whereas nitrogen acquires $\delta+$ charge. In Schiff bases also nitrogen as well as oxygen atoms are present. So, in DMF solutions, oxygen of DMF may form hydrogen bond with H (of -OH group) of Schiff base but the nitrogen of Schiff base may also acquire $\delta+$ charge, which may causes repulsion between Schiff base and DMF molecule. Further, as within DMF molecule, $\delta+$ and $\delta-$ charges exist, there may be interaction between different solvent molecules. So, in DMF, both solute-solvent and solvent-solvent (or solute-solute) interactions exist. This is evident by internal pressure, which is found to decrease. The different behavior of internal pressure of different Schiff bases in 1,4-dioxane solutions is also due to different orientation of solute molecules in 1, 4-dioxane solutions which is due to dipole-dipole interactions or repulsion. However, the predominance of solute-solvent interactions in all these bases in both DMF
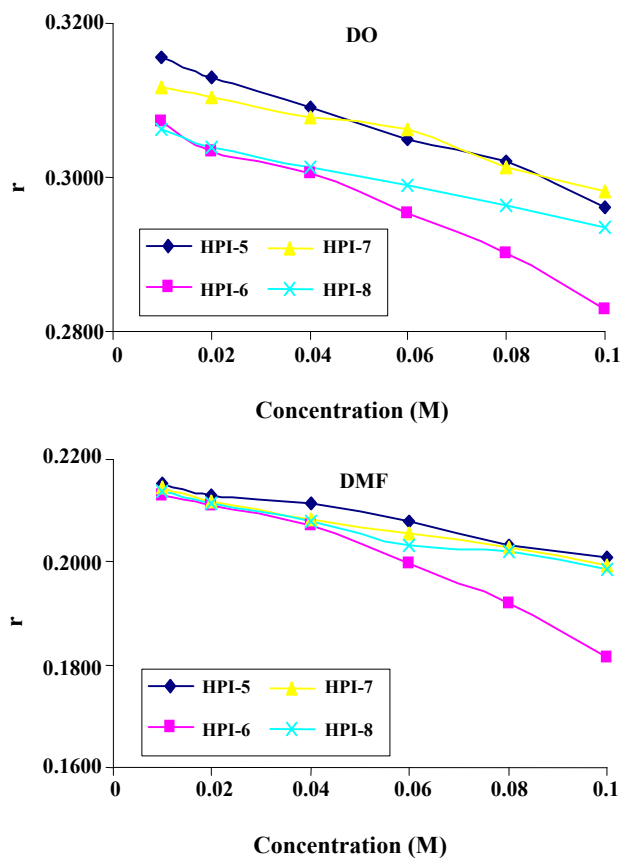
and 1,4-dioxane solutions is confirmed by solvation number (S_n), which is measure of structure forming or structure breaking tendency of solute in solution. Fig. 7 shows that for all bases, S_n increases with concentration, suggesting thereby structure forming tendency of these bases.

Thus, it is concluded that in the studied concentration range, in both these solvents, solute-solute and solute-solvent interactions exist. However, most of the acoustical parameters suggest predominance of solute-solvent interactions in the studied systems.
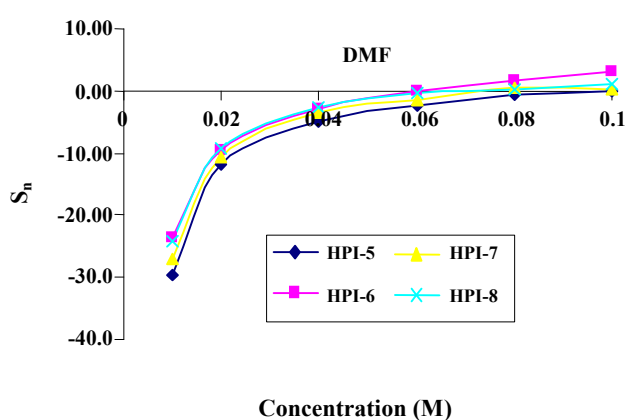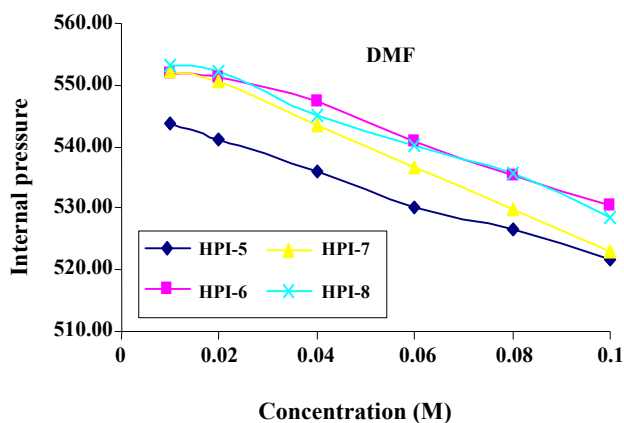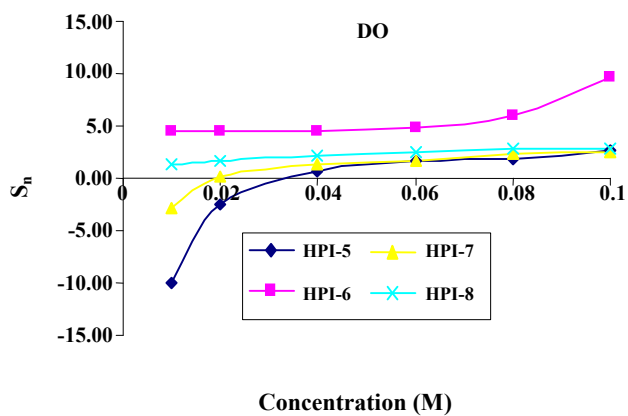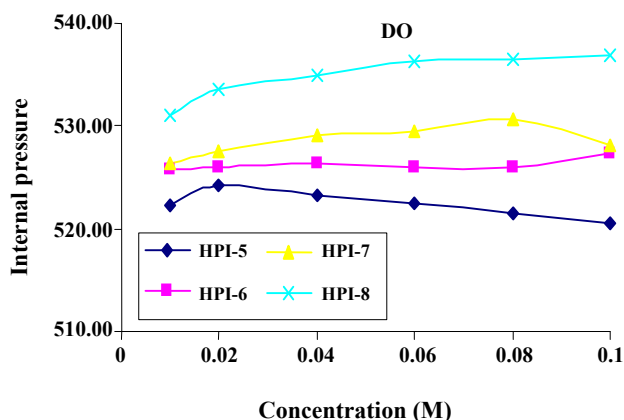
Fig. 6: Variation of internal pressure (π) with concentration in 1,4-dioxane (DO) and DMF solutions.

Fig. 7: Variation of solvation number (S_n) with concentration in 1,4-dioxane (DO) and DMF solutions.

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