

Acoustical Studies of Some Derivatives of Azomethines in Methanol and N, N-Dimethylformamide at 303.15 K

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Abstract The acoustical parameters of some synthesized azomethines have been studied from ultrasonic velocity and density measurement at different concentration in methanol and dimethyl formamide at 303.15 K. The apparent adiabatic molar compressibilities and apparent molar volume were also evaluated. The results provide useful information about solute-solute and solute-solvent interactions and are of significant help in understanding the behavior of synthesized compounds in solutions.

Keywords: azomethines, ultrasonic velocities, apparent adiabatic molar compressibility, apparent molar volume, methanol, dimethyl-formamide

1. Introduction

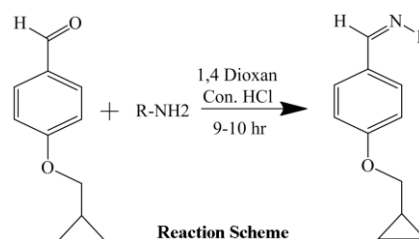
Azomethines are an important class of compounds, which is becoming increasingly important due to their broad spectrum of biological activities [1,2,3,4]. Literature survey shows that many azomethines are known to exhibit antibacterial [5,6], antifungal [7] and cytotoxic [8] and anticonvulsant [9] activities.

In continuation of our ongoing program of research [10,11,12,13], this paper reports the systematic measurement of thermodynamic properties of synthesized biologically active azomethines in polar aprotic and protic solvents. The present study is undertaken to determine experimentally density and sound velocity of solutions of different substituted azomethines in N, N-dimethylformamide and methanol at 303.15 K. With this data, the apparent adiabatic molar compressibility and apparent adiabatic molar volumes are computed.

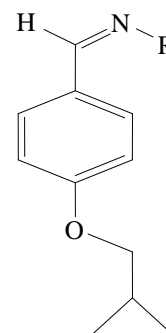
2. Experimental

A mixture of 4-(oxiran-2-ylmethoxy) benzaldehyde (0.01M) and different aromatic amines (0.01M) in 1, 4-Dioxan was refluxed for 9-10 hours in presence of few drops of concentrated HCl as catalyst. After the completion of reaction, the reaction mass was poured into crushed ice and crude product was isolated. The purity of compounds was checked by thin layer chromatography and the characterization was done by IR, ¹H NMR and Mass spectral data.

The synthesized azomethines derivatives were recrystallized in methanol and characterized by IR, NMR and Mass spectra. Figure 1 shows the general structure of azomethines.



The solvents, methanol and Dimethylformamide (DMF) used in this study were of LR grade and were purified by the procedure described in the literature [14].



Where, R =
BKC-1: 4-CH₃C₆H₄; BKC-2: 4-OCH₃C₆H₄; BKC-3: 4-ClC₆H₄; BKC-4: 4-NO₂C₆H₄

Figure 1. General Structure of Azomethines derivatives

The solutions of azomethines were prepared in methanol/ DMF over a wide range of concentrations. The densities of pure solvents and their solutions were measured by using a single capillary Pyknometer, made of borosil glass having a bulb capacity of 10ml. The ultrasonic velocity of pure solvents and their solutions were measured by using Single Crystal Variable Path Ultrasonic Interferometer operating at 2MHz. The accuracy of density and velocity are $\pm 0.0001 \text{ g/cm}^3$ and $\pm 0.1\% \text{ cm/sec}$ respectively. All the measurements were

carried out at 303.15K. The uncertainty of temperature is $\pm 0.1\text{K}$ and that of concentration is $0.0001\text{ moles / dm}^3$.

3. Results and Discussion

According to Newton-Laplace equation [15,16] the isentropic compressibility of solution κ_s , is a function of density (ρ) and sound velocity (U).

$$\kappa_s = 1 / (U^2 \rho)$$

which provides the link between thermodynamics and acoustics.

The solvation number (S_n) can be calculated according to the equation

$$S_n = M_2/M_1 [1 - \kappa_s / \kappa_{s1}] [(100 - X) / X]$$

where X is the number of grams of solute in 100gm of the solution. M_1 and M_2 are the molecular weights and κ_{s1} and κ_s are isentropic compressibility of solvent and solute respectively.

Table 1 shows the experimental density (ρ) and ultrasonic velocity (U) of synthesized compounds in both DMF and methanol solutions. Figure 2 shows the variation of ultrasonic velocity with concentration in both the solvents. It is observed to increase in both DMF and methanol. Figure 3 shows the variation of isentropic compressibility with concentration. Comparison of Figures 2 and 3 shows that in both the solvents, the nature of velocity is reverse of that of isentropic compressibility (κ_s). The decrease of κ_s with increasing concentration might be due to aggregation of solvent molecules around solute molecules thereby indicating the presence of solute-solvent interactions.

Table 1. The experimental density and ultrasonic velocity of azomethines compounds in methanol and DMF solutions at 303.15 K

Conc. (M)	$U \times 10^{-5}$ cm/s	ρ g/cm ³	$U \times 10^{-5}$ cm/s	ρ g/cm ³
Methanol		DMF		
BKC-1		BKC-1		
0.00	1.0924	0.7884	1.4452	0.9456
0.01	1.1004	0.7919	1.4536	0.9486
0.02	1.1032	0.7959	1.4542	0.9498
0.04	1.1040	0.7978	1.4552	0.9508
0.06	1.1044	0.8009	1.4556	0.9527
0.08	1.1078	0.8010	1.4564	0.9534
0.10	1.1092	0.8136	1.4574	0.9551
BKC-2		BKC-2		
0.01	1.1002	0.7921	1.4512	0.9477
0.02	1.1020	0.7962	1.4520	0.9491
0.04	1.1038	0.7969	1.4540	0.9515
0.06	1.1040	0.7995	1.4564	0.9520
0.08	1.1060	0.8018	1.4579	0.9534
0.10	1.1072	0.8032	1.4598	0.9565
BKC-3		BKC-3		
0.01	1.0936	0.7893	1.4488	0.9484
0.02	1.0968	0.7910	1.4495	0.9503
0.04	1.0999	0.7928	1.4504	0.9511
0.06	1.1044	0.7955	1.4519	0.9524
0.08	1.1076	0.7918	1.4526	0.9527
0.10	1.1112	0.7989	1.4540	0.9534
BKC-4		BKC-4		
0.01	1.1016	0.7946	1.4492	0.9488
0.02	1.1040	0.7979	1.4502	0.9493
0.04	1.1058	0.7988	1.4526	0.9503
0.06	1.1072	0.7996	1.4546	0.9527
0.08	1.1084	0.8001	1.4558	0.9543
0.10	1.1096	0.8008	1.4572	0.9551

Table 2. Apparent molar compressibility and Apparent Molar Volume of azomethines in methanol and DMF at 303.15 K

Conc. (M)	$\Delta \kappa \times 10^8$	ΔV	$\Delta \kappa \times 10^8$	ΔV
Methanol		DMF		
BKC-1		BKC-1		
0.00	-	-	-	-
0.01	-20.0281	-428.9776	-8.6911	-238.6298
0.02	-15.2649	-250.5065	-3.7189	-142.9983
0.04	-8.6201	-214.2998	-1.1351	-57.5640
0.06	-6.5338	-148.8556	-1.0255	-44.0670
0.08	-7.2924	-260.9243	-0.7414	-21.0464
0.10	-6.3885	-400.5653	-0.5130	-17.2644
BKC-2		BKC-2		
0.01	-10.0010	-425.5817	-4.9001	-143.8041
0.02	-15.7776	-447.3947	-2.7123	-106.0565
0.04	-13.7853	-222.0285	-1.9187	-75.5782
0.06	-4.7900	-184.7019	-0.9074	-31.3369
0.08	-3.8564	-160.1555	-0.7233	-20.3748
0.10	-2.9090	-133.4117	-0.4933	-31.0501
BKC-3		BKC-3		
0.01	-0.8848	-72.3081	-3.9631	-217.4849
0.02	-3.8717	-121.5544	-2.9147	-169.0181
0.04	-0.0534	-93.7279	-1.8597	-65.0069
0.06	-3.1018	-101.5882	-1.2276	-38.1937
0.08	-0.4143	-3.9223	-0.3726	-11.0263
0.10	-2.4626	-79.9090	-0.3351	-18.6040
BKC-4		BKC-4		
0.01	-30.1759	-738.7395	-4.6073	-259.4895
0.02	-19.6909	-552.7172	-3.1506	-116.3994
0.04	-11.5639	-280.4590	-1.5212	-43.7639
0.06	-3.7609	-185.9912	-1.4911	-43.0590
0.08	-2.7266	-132.8886	-0.6600	-31.4800
0.10	-1.0406	-102.5242	-0.2389	-15.5927

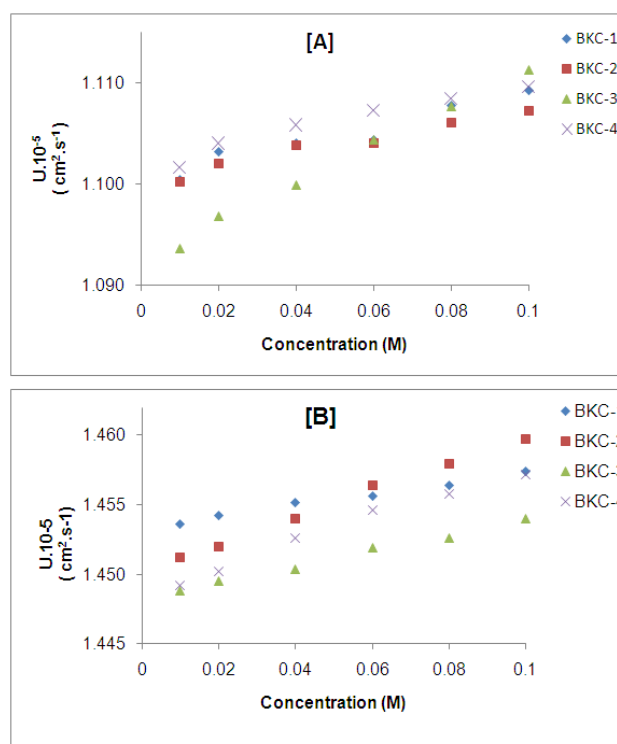


Figure 2. The variation of ultrasonic velocity (U) of azomethines against concentration in [A] methanol and [B] DMF at 303.15 K

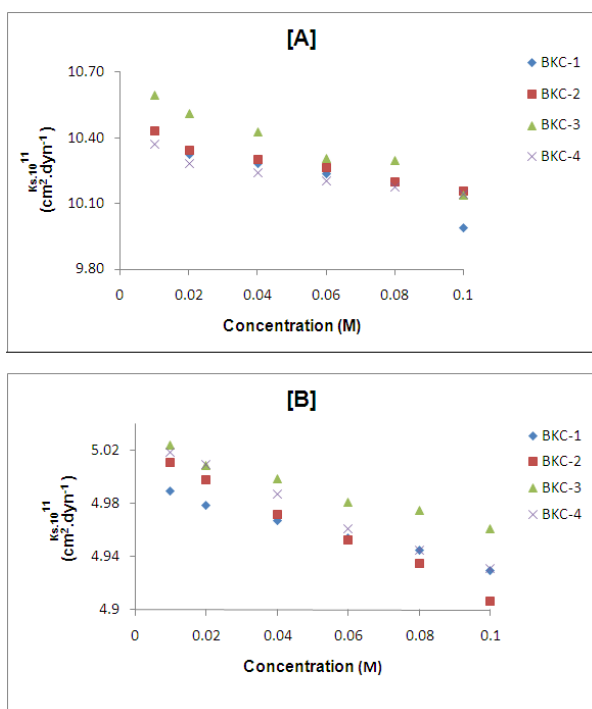


Figure 3. The variation of isentropic compressibility (κ_s) of azomethines against concentration in [A] methanol and [B] DMF in at 303.15K

The interaction between solute and solvent molecules is also measured as solvation number (S_n), which is the number of the solvent molecule attached to the central atom/ion by their translational degree of freedom. In the present case, the positive values of S_n indicate appreciable solvation of solutes. This in turn, confirms the structure forming nature of solute i.e., association with solute and solvent molecule. From Figure 4, it is observed that S_n increases with increase in concentration. This indicates that as solute concentration increases, attraction between solute and solvent increases.

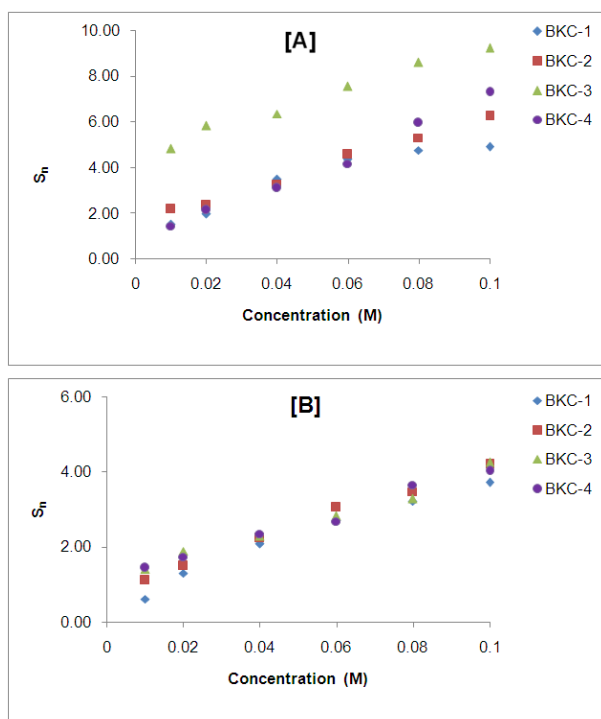


Figure 4. Variation of solvation number (S_n) of azomethines against concentration in [A] methanol and [B] DMF at 303.15 K

The apparent molar compressibility (ϕ_k) of the solution was calculated according to the following equation.

$$\phi_k = [(\rho_{0KS} - \rho_{KS1}) 1000/C\rho_0] + [\kappa_{S1} M_2/\rho_0]$$

where M_2 is the molecular weight of the azomethines derivatives.

The results of adiabatic compressibility have been explained in terms of Bachem's equation [17].

$$\text{Bachem's relation: } \kappa_s = \kappa_s^0 + AC + BC^{3/2}$$

where A and B are constants, C is the molar concentration of azomethines, κ_s and κ_s^0 represent the adiabatic compressibility of the solution and solvent, respectively. Table 3 shows the value of constants A and B, which have been determined from the intercept and slope of the plots of $(\beta - \beta_0)/C$ vs $C^{1/2}$.

Table 3. Bechem's constants A and B and ϕ_v^0 , S_v , ϕ_k^0 and S_k of azomethines in DMF and methanol at 303.15 K

Compound	BKC-1	BKC-2	BKC-3	BKC-4
Methanol				
$A ? 0^{11}$ $\text{dyn}^{-1} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$	-10.20	-8.40	-6.70	-19.50
$B ? 0^{11}$ $\text{dyn}^{-1} \cdot \text{cm}^{1/2} \cdot \text{mol}^{-3/2}$	39.28	36.36	36.58	187.5
$\phi_k^0 ? 0^8$ $\text{dyn}^{-1} \cdot \text{mol}^{-1}$	-5.00	-7.20	-4.10	-7.50
$S_k ? 0^8$ $\text{dyn}^{-1} \cdot \text{cm}^{-3/2} \cdot \text{mol}^{-3/2}$	12.50	45.00	16.98	53.03
ϕ_v^0 $\text{cm}^3 \cdot \text{mol}^{-1}$	-440.0	-285.0	-131.0	-310.0
S_v $\text{cm}^3 \cdot \text{mol}^{-1}$	3676.40	1567.10	519.20	2000.00
DMF				
$A ? 0^{11}$ $\text{dyn}^{-1} \cdot \text{cm}^3 \cdot \text{mol}^{-1}$	-2.10	-3.55	-3.60	-3.25
$B ? 0^{11}$ $\text{dyn}^{-1} \cdot \text{cm}^{1/2} \cdot \text{mol}^{-3/2}$	5.833	22.72	23.75	19.49
$\phi_k^0 ? 0^8$ $\text{dyn}^{-1} \cdot \text{mol}^{-1}$	-2.00	-1.55	-3.70	-3.17
$S_k ? 0^8$ $\text{dyn}^{-1} \cdot \text{cm}^{-3/2} \cdot \text{mol}^{-3/2}$	17.12	10.78	42.50	29.00
ϕ_v^0 $\text{cm}^3 \cdot \text{mol}^{-1}$	-85.00	-132.50	-118.75	-82.50
S_v $\text{cm}^3 \cdot \text{mol}^{-1}$	685.48	1402.40	1339.20	698.65

The apparent molar volume (ϕ_v) can be calculated according to the following equation

$$\phi_v = [M/\rho] - [(1000\{\rho - \rho_0\})/(\rho C)]$$

where ρ and ρ_0 are the densities of solutions and solvent respectively and C is the molar concentration of azomethines solution.

The calculated values of apparent molar volume (ϕ_v) are observed negative in both solvent for azomethines, which suggests that when a small amount of compounds are added to the solvent, there is an initial decrease in the molar volume of the solvents. This again proves that due to solute-solvent interactions, compressibility of solution takes place.

Further, apparent molar compressibility and apparent molar volume of solutions is fitted to Gucker's [18] and Masson's [19] relations

$$\text{Gucker's relation: } \phi_k = \phi_k^0 + S_k C^{1/2}$$

$$\text{Masson's equation: } \phi_v = \phi_v^0 + S_v C^{1/2}$$

where ϕ_k^0 and ϕ_v^0 are limiting apparent molar compressibility and partial molar volume, respectively S_k and S_v are constants. The values of ϕ_k^0 , ϕ_v^0 , and constants S_k and S_v , have been obtained from the intercept and slope of the plots of ϕ_k vs $C^{1/2}$ and ϕ_v vs $C^{1/2}$ respectively and are given in Table 3.

It is evident from Table 3 that in both DMF and methanol solutions, A , ϕ_k^0 and ϕ_v^0 values are negative whereas B , S_k and S_v values are positive. The lower or negative A , B , ϕ_k^0 confirms interaction between solvent and compound molecules. Further, negative values of ϕ_v^0 implies electrostrictive solvation of ions [20,21,22] i.e., more compressibility in solution. Table 3, shows that in comparison to DMF, for methanol solutions, A , ϕ_k^0 and ϕ_v^0 are more negative whereas B , S_k and S_v values are more positive. This suggests that compressibility is higher in methanol than that in DMF solutions. The positive and higher values of interaction parameters S_k and S_v confirms the predominance of solute-solvent interactions in the investigated solutions.

Comparison of different azomethines suggests different extent of solute-solvent interactions in methanol and DMF. All the azomethines have aryl substitution with different functional group at para position as mentioned in Figure 1. Comparison of different parameters reported in Table 3 shows that in methanol, overall solute-solvent interaction is maximum for BKC-4 containing nitro benzyl substitution whereas that in DMF is found to be maximum for BKC-3 containing chloro benzyl substitution.

Thus, it is concluded that in both methanol and DMF solutions of studied azomethines, solute-solvent interactions predominate. The extent of interaction depends upon substitution.

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