

Effect of Hydrogen Bonding and Solvation of 5-Substituted Indole Carboxaldehydes in Methanol-Benzene

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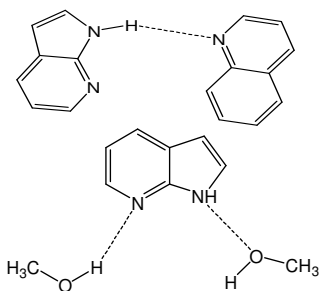
Abstract

Effect of hydrogen bonding of 5-substituted indole carboxaldehyde has been investigated by viscometric measurement. The viscosity of the system increases with the increase in concentration. The Trend Change Point (TCP) values have been determined by intersection of two straight lines, which are found to be dependent on the composition of solvent mixtures. The study confirms that the nature of synthesized compounds forms clusters in methanol-benzene mixture. The viscometric data have been analyzed in terms of Einstein, Vand, Moulik and Jones-Dole equations. These well known equations have been successfully applied to explain the results of viscosity measurements and the viscometric parameters show that the behavior of compound changes in alcohol-benzene. These results show that the formation of cluster depends on the methanol concentration. This indicates that the observed methanol concentration effect on the formation of clusters interferences in formation of hydrogen bonding of methanol with molecule.

Keywords: Hydrogen bonding, viscosity, molar volume, indole

Introduction

The increasing knowledge of the structures of aggregates in organic solvents are stimulating research into the role that the different possible aggregates play in defining the reaction mechanism in solution¹. Molecular self-assembly is of much interest, and recently it has been found to occur readily in solution since non covalent interactions, such as hydrogen bonding, dipole-dipole, hydrophobic interactions etc, lead to the formation of molecular clusters².



It has been observed that indole interacts with alcohols and aromatic hydrocarbons like benzene. In order to know the nature and extent of solute-solute and solute solvent interactions^{3,4}. Viscosity behavior in dilute solutions is very sensitive to predict solute-solute and solute solvent interactions⁵.

Never the less several papers have focused on the fluorescent behaviour of indolic compounds in non aqueous

environments, in particular, the effect of small amounts of alcohols in non polar solvent produce dramatic changes in the emission spectra of indole and its derivatives^{6,7,8}.

The presence of polar co solvents has been explained through the formation of exiplexes between one indole molecule and one or several molecules of the polar additive. It was observed that non polar aromatics such as benzene also have dramatic effect on the emission of indole and some of its derivatives. This was attributed to the formation of an excited state complex in benzene solution and it was found that an N-H bond in indole ring is essential for this to happen⁹.

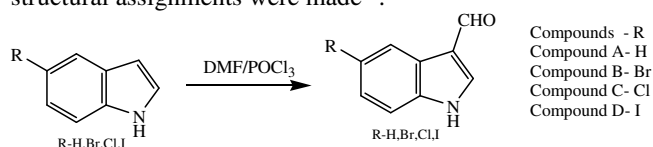
Hydrogen bonded complexes of indole in methanol, ethanol aromatics benzene, toluene, and p- xylene. In this case they are forming π hydrogen bonds^{10,11}. Indole forms this type of hydrogen bond in the ground state has been shown by several authors using IR spectroscopy and constitutes the mechanism of indole auto association. At higher benzene concentration the presence of multiple benzene molecules in the complex have been reported¹²⁻¹³. N-substituted indole does not show this types of complex formation, where there is no N-H moiety is available¹⁴.

In the view of the potential applications of these compounds, present work has been undertaken to explain colloid chemical behavior in mixed solvents. Benzene and methanol has been chosen as the co solvents in this study. The mixed solvents have a tendency to interact with compounds, which affect the aggregation of molecules. The viscosity data based on various equations have been extensively used to furnish

information concerning the structural changes in solution trend change point (TCP) and nature of molecule-solvent interaction. This vital information plays an important role in their selection for various industrial and biological applications.

Material and Methods

The compounds are synthesized using known protocol. The synthesis begins from the commercially available indole, we were able to synthesis of 5-substituted indoles in three steps¹⁵. The further formylation with DMF/POCl₃ by Wilsmeier-Hack method to obtain indole -3-carboxaldehydes in good yield¹⁶. Correlating melting point, ¹H NMR and IR data for corresponding compounds the structural assignments were made¹⁷.



Compounds - R
Compound A- H
Compound B- Br
Compound C- Cl
Compound D- I

Solubility of compounds in methanol and benzene was determined. The calculated amount of the compound was weighed in standard flask and the solution was made by adding the required amount of benzene and methanol. In this way, a number of solutions were prepared containing different concentration of compound and varying compositions of benzene and methanol. Ostwald's type viscometer was used to measure the viscosity of the solutions. The accuracy of the results was checked by determining the viscosity of known solutions and the agreement was found to be good and the difference was below 0.5%. All measurements were made at a constant temperature $30 \pm 0.1^\circ\text{C}$ in thermostat. The viscosity results are expressed in centipoises.

Results and Discussion

The flow of characterization of solutions in terms of viscometric measurements has been employed as a tool to find out the TCP of molecule in benzene - methanol mixtures. The viscosity of solutions of varying composition of benzene- methanol mixtures increases with the increase in the concentration.

The increase in viscosity with the increase in concentration may be due to the increasing tendency of molecules to associate in the form of clustering entity in the solvent system. The numbers of workers have reported the molecular interaction and characterizing aspects of physicochemical behavior of binary liquid mixtures and mixed solvent. The difference in the viscosities of solutions in varying composition of benzene methanol mixtures is mainly due to the difference in the viscosities of the solvent mixtures. The plots of viscosity (η) against concentration (C) are

characterized by an intersection of two straight lines at a definite concentration corresponding to TCP of the molecule (figure1-4) of course this is the maximum concentration of molecular dispersion where balancing of the internal forces causes the formation of aggregates. It is apparent from the data that the values of TCP are dependent on the composition of solvent mixtures. The values of TCP in the solution containing benzene below 50% are lower as compared to those containing higher volume percent of benzene. This may be attributed to the change in the mobility of the molecules due to change in the dielectric constant of the solvent mixture having different composition of benzene-methanol. Further it is suggested that predominance of lipophilic character in the solvent mixture plays a pertinent role in the clustering alignment of the solute molecules. Thus there is delay in the aggregation due to increase in the interaction between lipophilic solvent and solute molecules. The viscosity of solutions as well as those of the solvent mixtures increases as the volume percent of benzene increases which may be attributed to the cumulative effect of the variation of dielectric constant, degree of aggregation and the nature of the agglomerate. The values of specific viscosity (η_{sp}) of solutions in varying compositions of benzene-methanol mixtures also increase with the increase in the concentration. The nature of curves and TCP values are in good agreement with those observed for viscosity data. The fluidity of solutions in benzene methanol mixtures decreases with the increase in the concentration as well as with the increase in volume percent of benzene (figure 3). A perusal of table-2 indicates that TCP values are in good agreement with those derived from viscosity and specific viscosity curves and are dependent on the solvent composition. The viscosity results have been explained in terms of equations proposed by Einstein¹⁸ and Thomas¹⁹.

$$\text{Einstein: } \eta_{sp} = 2.5 \bar{V} C$$

$$\text{Thomas: } (\eta/\eta_0 - 1)/C = 2.5 \bar{V} + (10.05 \bar{V}^2) C$$

Where V, C, Q, η , η_0 and η_{sp} are molar volume, concentration, interaction coefficient, viscosity of the solution, viscosity of solvent and specific viscosity respectively. The plots of specific viscosity (η_{sp}) against concentration (C) are characterized by an intersection of two straight lines at a definite concentration, which corresponds to the TCP. The plots with intercept almost equal to zero are linear below TCP, which shows that the equation proposed by Einstein is applicable to dilute solutions. It is observed that the values of molar volume V obtained from the plots of Einstein equation and Vand equation. It is interesting to note that the values of molar volume enumerated from these equations are almost equal and the trend remains unaltered irrespective of the type of equation applied. The Moulk equation²⁰ also fits well to the solutions, as the plots $(\eta/\eta_0)^2$ vs. C² are almost linear.

$$(\eta/\eta_0)^2 = M + KC^2$$

Where M and K are constants. The values of M and K have been calculated from the intercepts and slopes of the $(\eta/\eta_0)^2$ vs. C^2 plots and are recorded in table-3.

Table-1
Viscosity of compounds A-D in methanol –benzene

Compound	% methanol	Concentration						
		0.0002	0.0004	0.0006	0.0008	0.0010	0.0012	0.0014
Compound A	40	0.57526	0.58630	0.59600	0.60060	0.60630	0.61171	0.61726
	60	0.55439	0.56310	0.57000	0.57374	0.58130	0.58842	0.59703
	80	0.53592	0.54120	0.54752	0.55280	0.55702	0.56126	0.56654
	100	0.51773	0.52250	0.52880	0.52910	0.53219	0.53530	0.53841
Compound B	40	0.57743	0.58750	0.59810	0.60190	0.60800	0.61396	0.61952
	60	0.55549	0.56310	0.57200	0.57690	0.58440	0.59003	0.59867
	80	0.53803	0.54750	0.55560	0.55810	0.56130	0.56440	0.56885
	100	0.51878	0.52440	0.53130	0.53380	0.53600	0.53753	0.54068
Compound C	40	0.57856	0.58750	0.59750	0.60310	0.61130	0.61736	0.62183
	60	0.55658	0.56500	0.57440	0.58000	0.58630	0.59221	0.60084
	80	0.53810	0.54441	0.55182	0.55600	0.56139	0.56461	0.57000
	100	0.51984	0.52630	0.53250	0.53500	0.53880	0.54167	0.54481
Compound D	40	0.58077	0.58855	0.60060	0.60630	0.61200	0.61970	0.62420
	60	0.55872	0.56630	0.57500	0.57880	0.58691	0.59449	0.60423
	80	0.54123	0.54657	0.55401	0.55728	0.56370	0.56697	0.57339
	100	0.52192	0.52800	0.53440	0.53690	0.54060	0.54285	0.54807

Table-2
Values of molar volume (\bar{V}) in benzene – methanol derived from Einstein and Thomas equations

Compound	% of methanol	Einstein equation		Thomas equation	
		V_1	V_2	V_1	V_2
Compound A	40%	36.4804	19.5932	19.4540	32.8224
	60%	28.4328	28.204	16.9032	19.4420
	80%	21.8092	17.1928	13.9252	21.1656
	100%	21.4760	12.1136	3.8647	13.5812
Compound B	40%	36.3504	20.8092	29.2828	33.9632
	60%	30.0812	26.0012	21.3660	25.2292
	80%	33.0432	13.3672	21.1028	30.8880
	100%	24.2728	8.6484	8.4096	22.4204
Compound C	40%	33.3132	22.0560	31.5936	35.6056
	60%	32.4564	25.0588	25.7984	29.7208
	80%	25.7984	17.1328	20.1124	26.2848
	100%	24.5596	12.6108	13.9388	22.3620
Compound D	40%	34.8696	21.6984	31.9536	39.2628
	60%	29.6584	30.7232	31.1140	29.5628
	80%	24.0532	19.5588	27.6808	26.9688
	100%	24.2028	13.9616	24.2828	24.2188

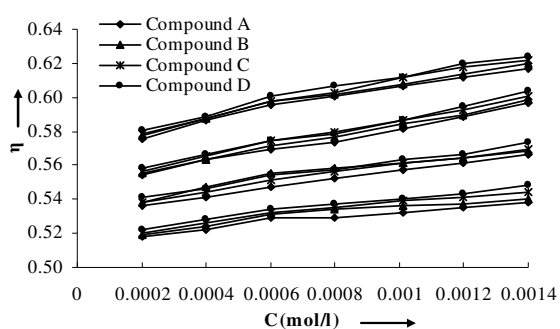


Figure-1

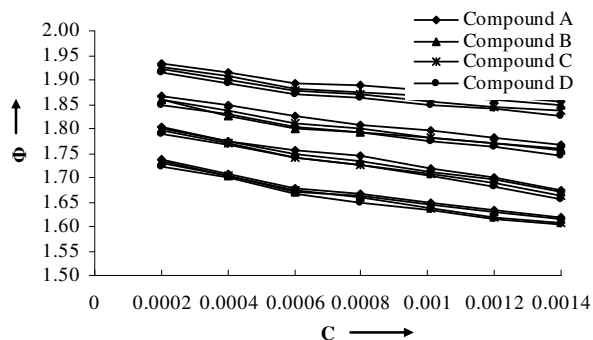


Figure-2

Plot of η v/s C for Compounds A-D in benzene and methanol mixture in benzene – methanol derived from different equations

Compound	% of methanol	Moulik equation				Jones-Dole equation			
		M ₁	M ₂	K ₁	K ₂	A ₁	A ₂	B ₁	B ₂
Compound A	40	1.019	1.087	228952	47433	-0.721	1.049	110.940	32.882
	60	1.017	1.050	176636	68193	-0.477	-0.716	84.701	81.079
	80	1.012	1.055	137129	41102	-0.336	0.315	62.738	37.820
	100	1.004	1.036	135019	28361	-0.755	0.110	72.618	28.532
Compound B	40	1.025	1.090	230701	50468	-0.304	1.041	98.570	36.139
	60	1.018	1.065	190451	63145	-0.501	-0.075	96.608	65.793
	80	1.020	1.081	206845	32244	-0.371	1.711	84.218	5.020
Compound C	40	1.029	1.070	212037	53153	0.080	1.051	80.569	39.897
	60	1.022	1.077	205747	61330	-0.279	0.372	87.912	56.282
	80	1.020	1.064	163046	41028	-0.104	0.721	66.570	31.781
	100	1.013	1.059	153245	29750	-0.458	0.770	73.615	19.890
Compound D	40	1.035	1.105	225902	52922	0.402	1.394	74.168	33.049
	60	1.030	1.064	188667	75141	0.306	-0.462	65.427	83.329
	80	1.031	1.071	153824	47031	0.231	0.578	59.827	40.050
	100	1.021	1.063	152176	33475	0.005	0.822	60.167	21.907

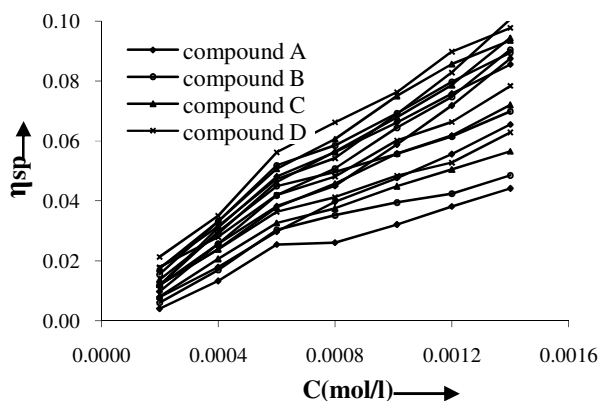


Figure-3

Plot of η_{sp} v/s C for Compounds A-D in benzene and methanol mixture

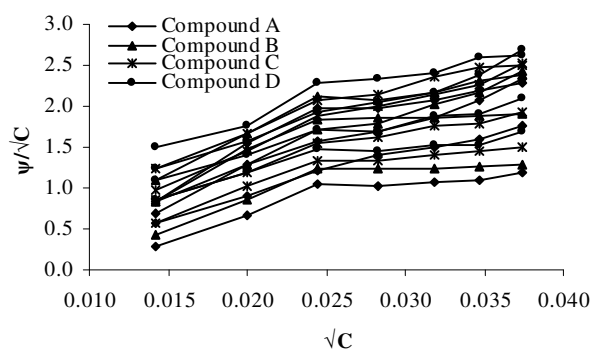


Figure-4

Plot of Ψ/\sqrt{C} v/s \sqrt{C} for compounds A-D in benzene methanol mixture

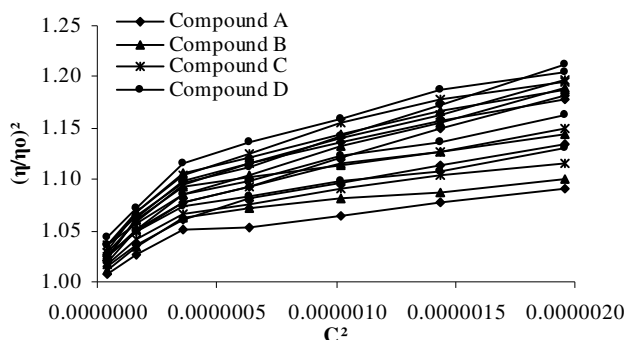


Figure-5
Plot of $(\eta/\eta_0)^2$ v/s C^2 for compounds A-D in benzene methanol mixture

The viscosity data have also been interpreted in the light of Jones-Dole equation²¹.

$$(\eta/\eta_0-1)/\sqrt{C} = A + B\sqrt{C}$$

For convenience, the equation may be expressed as

$$\Psi/\sqrt{C} = A + B\sqrt{C}$$

Where the coefficient A and B refer to solute- solute and solute-solvent interactions respectively. The plots Ψ / \sqrt{C} vs. for the molecules studied here were found to be linear, with least scatter. These plots are characterized by two straight lines intersecting at a point corresponding to the TCP of compounds. The values of TCP are in good agreement with the values derived from the plots of η , η_{sp} and ϕ vs. C.

In view of the two intersecting straight lines for Ψ / \sqrt{C} vs. plots, it is logical to evaluate two values of both the coefficients below and above TCP designated as A1, B1 and A1, B1 respectively. It is observed that the values of these constants depend on the composition of the solvent mixtures.

Conclusion

It has been observed that the viscosity of the system increases with the increase in concentration. The increasing trend of viscosity may be due to combined effect of the variation of dielectric constant of solvent, degree of aggregation and nature of the compound agglomerate. The TCP values obtained from different viscosity data are in good agreement and show maximum concentration of molecular dispersion at which aggregation of molecule initiates. These results show that the formation of cluster depends on the methanol concentration. This indicates that the observed methanol concentration effect on the formation of clusters interferences in formation of hydrogen bonding of methanol with molecule. It is noteworthy to point out on the basis of results obtained that the above treatment gives a phenomenological description of clustering profile and confirms the existence of aggregation in the non-aqueous mixed solvent.

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