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Molecular Insights into Aniline–Methanol Interactions at Bulk and Interface Levels

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ABSTRACT

Interactions between aniline and methanol over the entire concentration region are studied using dielectric, FTIR, conformational analysis and contact angle studies over various substrates. The present studies indicate maximum interaction between the moieties in the aniline-rich region at about 20% Methanol and this is in agreement with previous report. However we see no indication of a weak interaction between the phenyl and the methyl groups, as reported previously.

Keywords: *Contact angle, hydrogen bond, FTIR, wettability, dipole moment*

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1. INTRODUCTION

Aniline-methanol binary system is important in the understanding of the biologically important N--O-H hydrogen bond [1] and its properties dependent on the concentration of the moities. Pure methanol shows microscopic inhomogenities with rich chain-like micro-heterostructure [2]. The structure of methanol has been previously studied by neutron scattering [3,4] and monte carlo simulations [5] among others. The three-methanol molecular cluster simulation was seen to give a good approximation of infra-red spectrum of methanol [6]. Pure aniline does not show any dipole-dipole interaction [1]. The structure of aniline (C6H5NH2) has been previously determined and the non-planarity of amino group in aniline is well documented [7]. A pyramidal distortion at the NH2 group is seen for the S0 state and in the S1 state it is quasi-planar and in computational analysis, B3LYP has been found to be better for the determination of vibrational frequencies of aromatic molecules [8].

Methanol is dominated by hydrogen bonding and aniline lacks such strong intermolecular interactions leading to interactions of different natures at different concentrations in the aniline-methanol binary system. Inhomogenities in the solvent structure are the reason why the solvent cannot be treated as a continuous medium with a uniform dielectric permittivity [1]. A few studies have been reported for this binary system. Adsorption of aniline-methanol system on zeolite was studied using in situ MAS NMR spectroscopy [9]. Aniline was adsorbed strongly on the zeolite while three species of adsorbed methanol were seen. The first is mobile methanol that is attached to the bridging hydroxyl group, the second is the methanol with limited mobility due to its hydrogen bonded interaction with aniline and the third was the small fraction of methanol bound to the zeolite.

Molecular dynamics study of the methanol-rich region in methanol-water system shows a structure similar to pure methanol [10]. Monte Carlo simulations of the water-methanol system show an enhancement in the number of hydrogen bonded complexes at a concentration of 25% of methanol 11. The study of aniline-water and aniline-methanol complexes in the S1 state indicate a weaker interaction between the two molecules in the excited state with a large difference in the geometry of the ground state and the electronically excited first state12. Dielectric relaxation studies of the aniline-methanol using ps TDR measurements indicate the formation of hydrogen bonded aniline-methanol species in the aniline rich region. The methanol rich region is dominated by clusters of methanol of various sizes (monomers, dimers, trimers etc.) 13. In a study of the same system, based on the Kirkwood g factor from dielectric data, the interaction between the two moieties is seen to be pronounced at 20% methanol concentration14.

The primary aim of this work is to study the intermolecular interaction between aniline and methanol over the entire concentration region and understand the interaction of the binary system at various concentrations with solid substrates. FTIR, dielectric data and computational conformational analysis using SCF-HF methods are used for this purpose.
All chemicals were of AR grade, procured commercially and were used after distillation. The substrates were sonicated for

30 minutes in a 50 W ultrasound sonicator filled with distilled water, dried in a hot-air dryer and cooled to room temperature before use. FTIR spectra were recorded using ABB BOMEM model MB 3000 FTIR spectrometer using the ATR technique15. Dielectric measurements were made using a Fluke LCR meter working at 1 KHz. The dipole moments of the binary liquids were determined using Guggenheim method16by varying the concentration of a polar solute (the binary liquid) in a non-polar solvent (benzene). Conformational analysis was done using Gaussian-03 software17. Contact angle measurements were made using Rame-Hart contact angle goniometer at ambient temperature and the surface energy of the substrate was determined using the multi-liquid tool of the goniometer.

RESULTS AND DISCUSSION

Methanol-aniline interactions were determined from computational conformal analysis at different basis sets. The results of the same are presented in table 1. The molecular structure of methanol-aniline predicted from microwave rotational spectra18 indicated a hydrogen-bonded interaction between the NH2 of aniline and OH of methanol with a second weak interaction of the methyl group of alcohol with the phenyl ring of aniline. However conformational analysis of the same system based on density functional theory19 indicate a linear bond with a single hydrogen-bonding site between the two molecules. In the present studies the conformer shown in figure 1 is that with lowest energy at STO-3G. For higher basis sets structure 3 shown in figure 3 possesses the lowest energy. Hydrogen bonded structures are best described by non-directional basis sets. Structure 1in figure 1 is taken to be the possible conformation of the 1:1 aniline-methanol system. No interaction between the phenyl ring and the methyl group is seen.

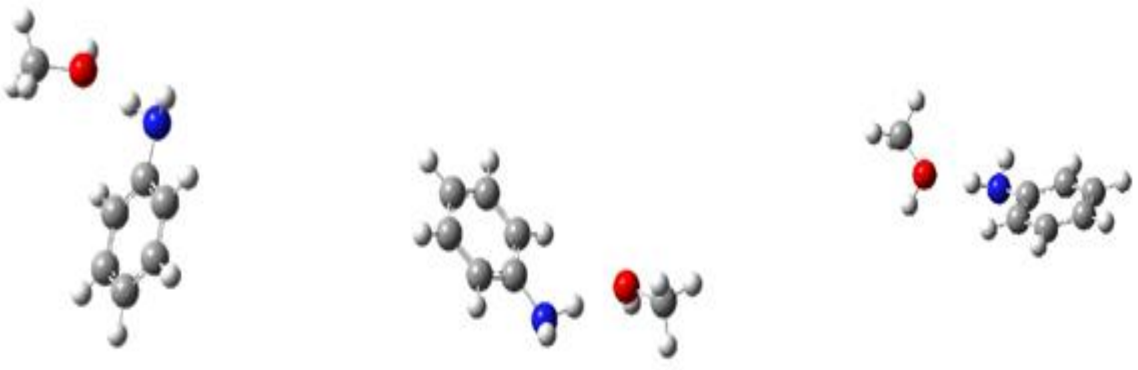

Figure 1 . Figure 2 . Figure 3 .

Figure 1. Conformation analysis of aniline-methanol binary mixture

Table 1: Computational modelling data of aniline-methanol system.

Basis	Parameter	Aniline	Methanol	Structure 1	Structure 2	Structure 3
STO-3G	HF Energy	-282.206100704	-113.549193204	-395.768990954	-395.768618282	-395.767582707
	Dipole Moment	1.3267	1.5094	3.1958	3.3431	3.6310
6-31G	HF Energy	-285.633042967	-114.988165278	-400.630823535	-400.630823536	-400.630823537
	Dipole Moment	1.456	2.2875	4.1539	4.8001	4.1527
6-31G(d)	HF Energy	-285.728226746	-115.035418040	-400.772841972	-400.772841908	-400.773012233
	Dipole Moment	1.6087	1.8656	3.3547	3.4274	3.1823
6-31G(d,p)	HF Energy	-285.745539086	-115.046709859	-400.800935132	-400.800936558	-400.801119791
	Dipole Moment	1.6037	1.8405	3.3414	3.4245	3.1554

In order to study the binary system in the aniline rich and alcohol rich regions, Onsager’s solvation model was applied to methanol molecule with aniline as solvent and vice versa. The results are presented in table 2. On solvation by aniline, the dipole moment (□) of methanol is more or less constant where as there is an increase in the □ of aniline on solvation by methanol. This is consistent with the results of IR and contact angle studies discussed below.

Table 2: Solvation modeling data of the three aniline-methanol 1:1 binary structure

Basis	Parameter	Aniline rich region	Methanol rich region
STO-3G	HF Energy	-282.198621251	-113.549738472
	Dipole Moment	1.4652	1.5439
6-31G	HF Energy	-285.620191636	-114.985889555
	Dipole Moment	1.6065	2.5613
6-31G(d)	HF Energy	-285.716061909	-115.033385747
	Dipole Moment	1.7377	2.1397
6-31G(d,p)	HF Energy	-285.733090795	-115.044212334
	Dipole Moment	1.7336	2.1139

Table 3: Hydrogen bond energies of the three aniline-methanol 1:1 binary

Basis set	Structure1 (kcal/mol)	Structure2 (kcal/mol)	Structure3 (kcal/mol)
STO-3G	-8.595033	-8.361177	-7.711344
6-31G	-6.033687	-6.033691	-6.033691
6-31G(d)	-5.771326	-5.771286	-5.878166
6-31G(d,p)	-5.464774	-5.465669	-5.580649

Hydrogen bond energies are calculated for the 1:1 binary system at various basis levels using the equation ΔE_{HB} = (EA+EB -EAB), where EA and EB are the energy of the individual component and EAB is the energy of the binary system. The results are given in table 3. It is seen from HB energy that the

bond is of intermediate strength (~ -6kcal/mol). Hydrogen bond distance between oxygen of methanol and hydrogen of aniline are 1.80509 for structure (1), 1.82321 for structure (2) and 1.82023 for structure (3). Computational studies are performed to obtain a structure for the interacting moieties that can be used as a framework to interpret the experimental result.

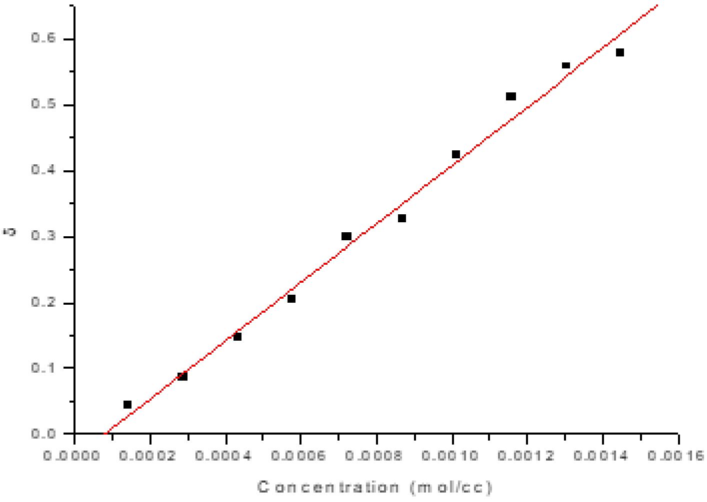

Figure 2: δvs. concentration of the binary system used to determine the experimental dipole moment. The values of μ were compared with the experimentally determined value μe. Dipole moment of the 1:1 binary system was determined from Guggenheim's method21 . The experimental results shown in figures 2 yield an experimental dipole moments of □= 2.04D. while the corresponding value from thecomputation is about 3D, and are in good agreement. A difference of 1D is within the experimental and computational error range (Sathyan et al., 1995).

FTIR spectra of aniline-methanol over the entire concentration range show the following general features. Hydrogen bonds usually cause a red-shift (and occasionally a blue-shift) in the vibrational frequency with respect to the isolated molecule's frequency. In the methanol rich region the spectra shows a blue-shift in the OH peak and a red shift in the aniline rich region, while at the lower concentrations the peak position remains the same. In the methanol rich region the polar nature of alcohol destroys the symmetry of the hydrogen bonded cluster, as seen from computational solvation data. Change on the OH peak position is greatest on the addition of 20% aniline to the methanol indicative of the breaking of the hydrogen bond cluster of methanol by aniline. On further addition of aniline, there is no significant change in the OH peak position. NH2 scissor frequency also does not shift with addition of methanol. Previous studies using cavity ring-down infrared spectroscopy [22] at higher methanol concentrations larger clusters with properties similar to disordered solid phase are formed. In the present case a dramatic change in the OH peak position is seen on the introduction of about 20% aniline shown in figure 3. The smaller clusters of methanol formed at lower concentrations are seemingly unaffected by the introduction of aniline where as the larger clusters are broken by aniline leading to a significant red shift in the IR peak position in figure 4.

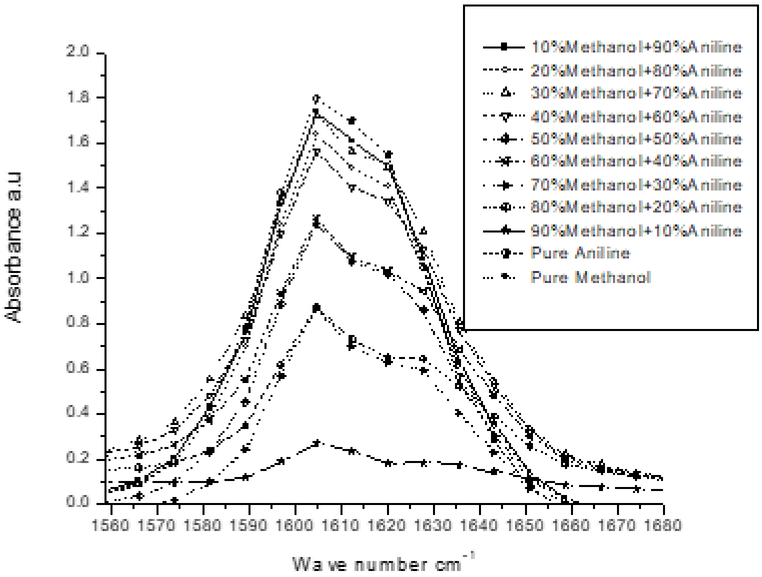

Figure 3: O-H stretching frequency of aniline-methanol mixture.

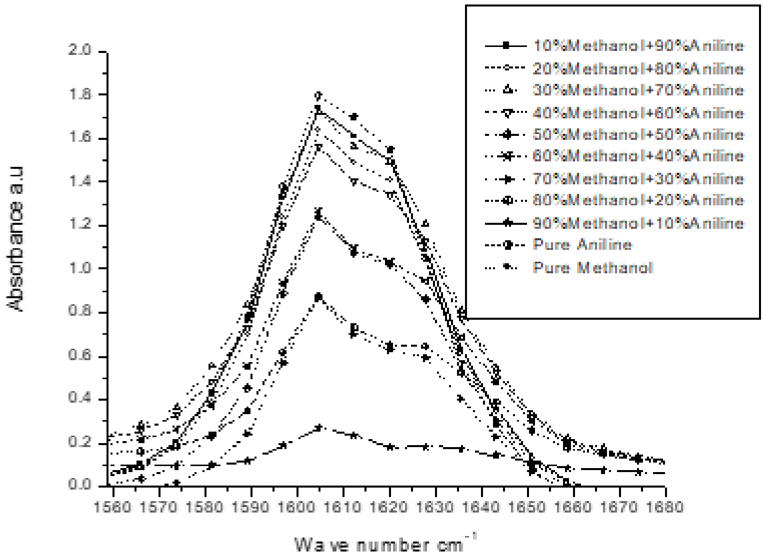

Figure 4: NH2 Scissoring frequency of aniline-methanol mixture.

Surface energies of the chosen substrate are shown in table 4.

Table 4: Surface energies of various substra

Substrates	Surface enerrgy (mj/m^2)		
	Polar	Dispersive	Total
Glass	29.22	26.52	55.74
ITO	0.46	30.60	31.06
Al_2O_3	5.07	30.39	35.46
Hylam	5.32	20.57	25.89
Teflon	1.31	21.93	23.24
Silicon	5.10	36.36	41.46

Methanol rich region shows a greater wetting than the aniline rich region.The contact angle made by a test drop of liquid is measured using a goniometer and subsequently the surface energies are calculated using advance drop image programmed of the goniometer. Test liquids in the present study are water, glycerol and diiodomethane.

On calibration of the substrates the contact angle made by aniline-methanol binary system over the entire concentration region on the same substrates was measured and is reported in figure 5. Wetting of aniline-methanol system shows the characteristic change at about 20% aniline. In addition, a rapid wetting over AlO at ~50% concentration is seen and this is because, as seen from table 4 the surface energy of AlO matches with the total energy of the binary system at this concentration reported in figure 6. At higher concentrations, since the total energy of the liquid is greater than that of the substrate, wetting is rapid.

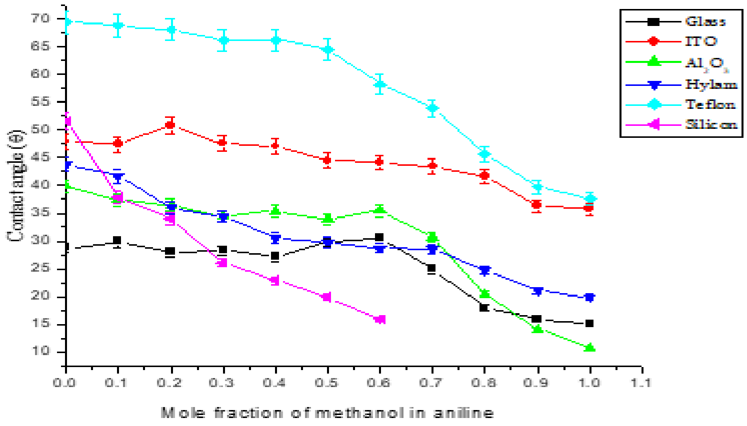

Figure 5: Variation of contact angle with mole fraction of methanol in aniline over different substrates.

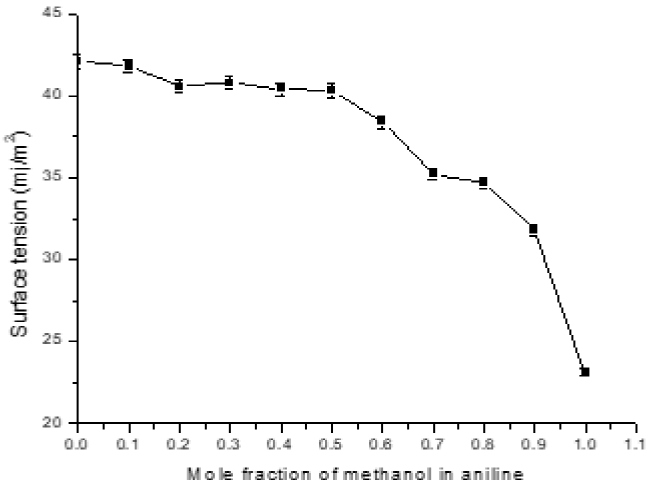

Figure 3.6: Variation of surface tension with mole fraction of methanol in aniline.

2. CONCLUSIONS

Previous studies on aniline- methanol system have indicated. That interaction between the two moieties is maximum at 20% aniline concentration (methanol rich region) and the possibility of a secondary weak interaction between the phenyl group of aniline and the methyl group of methanol. Our studies using FTIR, Contact angle, dielectric and computational analysis that contradict both of these observations. Maximum interaction between the moieties is seen at 20% aniline concentration and is attributed to the destruction of methanol clusters by aniline. Although the possibility of a second weak hydrogen bond between the phenyl ring and the methyl group cannot be fully discarded, we see no major evidence for the existence of the same. Almost all of the present studies indicate 20%-40% aniline concentration region shows maximum interaction between the moieties. Rapid wetting is seen when the surface tension of the binary liquid is of the same magnitude as the surface energy of the substrates. This concept is useful for rheological devices based on concentration variation or gradient

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