Concentration dependent wetting by aniline-ethanol binary system

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Abstract: Wetting of five substrates namely glass, indium tin oxide, aluminum oxide, hylam and teflon by aniline-ethanol binary system over the entire concentration range is studied using contact angle measurements. Rapid wetting of the substrates, especially hylam in the aniline rich region is understood in terms of the surface energies of the substrates and the intermolecular interactions between the two moieties. FTIR, dielectric and conformational analysis are used to study the molecular interactions in the binary system.

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

Introduction:

Wetting of a surface by a binary liquid is different from that by pure liquids. Surface studies of polymeric blends indicate that the more hydrophilic component tends to attach itself to the substrate while the less hydrophilic component forms a layer towards air[1]. Wetting of substrates by binary liquids have been studied for long with most studies concentrating on the wetting behavior of substrates by thin liquid films[2-7], and of binary liquids confined to pores[8-14]. Wetting phenomenon near the critical point of a binary liquid is well understood[15] while this behavior far from the critical point is not known, except for some phenomenological studies.

Wetting of a substrate by a sessile drop is the equilibrium between three phases (solid (s), liquid (l) and gas (g)) that are present. Complete wetting of a substrate by a liquid is said to occur if the contact angle (θ) is zero. Wetting by diphasic liquid drops, where one drop is completely enclosed by another, shows encapsulation of the inner drop by water and glycerol and no encapsulation by other liquids such as alcohols[16].

In this study the wetting of five different substrates namely glass, indium tin oxide (ITO), aluminum oxide, hylam and teflon by aniline-ethanol binary system over the entire concentration range using a sessile drop to measure the contact angle is presented. Glass and ITO and aluminum oxide coated glass are well known for their applications as electronic device substrates; hylam is a phenolic resin bonded fiber laminate known for its industrial strength and hence applications as substrates while Teflon is chosen for its hydrophobic property. Since the wetting behavior is dependent on the intermolecular interactions between the two liquids, these interactions actions are studied through a combination of infrared spectroscopy, static dielectric measurements and conformational analysis using ab inito

Hartree-Fock method. Contact angle measurements are used to determine the surface tension of liquid (the liquid surface energy) and the surface energy of solid. Surface energies roughly represent the magnitude of possible interactions that the particular material is capable of, due to either chemical properties (number of unsatisfied bonds) or physical properties (roughness in case of solids). While infrared and dielectric spectroscopic studies are useful in the determination of molecular bonding, the dynamics of a binary liquid system adds to the difficulty in interpretation of the results. Hence computational conformational analysis is taken up in order to determine the most probably sites of interactions between the two molecular species that form the binary liquid.

The presence of an inhomogeneous distribution of aniline in the aniline-ethanol binary liquid was previously determined by laser photonionization studies[17]. Aniline and ethanol form an associated liquid and the thermodynamics of this binary liquid were analyzed using the Universal Quasi Chemical (UNIQUAC) model[18] wherein activity coefficients are used to describe phase equilibria. Literature is sparse about the wetting behavior of binary liquids, in general, and aniline-ethanol in particular. What is known is that the surface properties of substrates, including the surface energies, cannot be determined accurately from the wetting data of binary liquids[19].

Results and Discussion:

Computational conformal analyses at different basis sets were performed to determine the interaction between aniline and ethanol. The results are presented in Table 1. The conformer for aniline-ethanol is shown in Figure 1, among which Figure 1(c) is that with lowest energy at STO-3G and also for higher basis sets. STO-3G is the minimal basis set for Hartree-Fock computations in which three primitive Gaussian type orbitals are fitted to a Single slater type orbital. Since this conformer gives the lowest energy, it is taken to be the most probable conformation of aniline-ethanol. This shows no interaction between the phenyl ring of aniline and the ethyl group of alcohol. A complete explanation of the various basis sets used can be found in any text book on quantum chemistry such as that by Atkins[20].
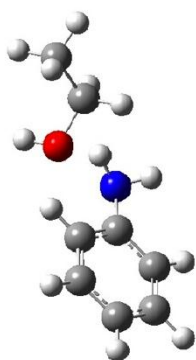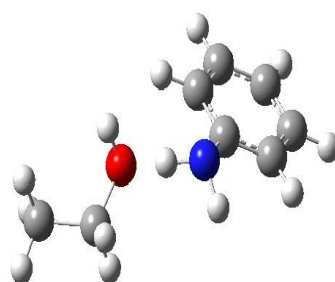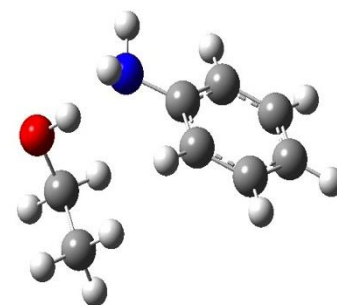

Figure (a).   Figure 1 (b)   Figure 1(c).

Figure 1: Conformation of the aniline-ethanol 1:1 binary system.

Basis	Parameter	Aniline	Ethanol	Structure 1	Structure 2	Structure 3
	HF Energy	-282.206100704	-152.032674708	-434.353122003	-434.353142317	-434.353542285
STO-3G	Dipole Moment	1.3267	1.4364	3.4779	3.3711	3.0316
	HF Energy	-285.633042967	-154.013229094	-439.655520179	-439.655520166	-439.653146044
6-31G	Dipole Moment	1.456	2.1048	4.1503	4.1519	2.5209
	HF Energy	-285.728226746	-154.075744647	-439.813111028	-439.814045772	-439.814696840
6-31G(d)	Dipole Moment	1.6087	1.7376	3.3514	1.6635	2.8082
	HF Energy	-285.745539086	-154.090161446	-439.844336054	-439.844336551	-439.845556635
6-31G(d,p)	Dipole Moment	1.6037	1.7030	3.3878	3.4548	2.7168

Table 1: Computational modeling data of aniline-ethanol system.

Solvation modelling data of aniline-ethanol binary system is shown in Table 2 and their corresponding hydrogen bond energies, calculated by using eqn. (1) are shown in Table 3. Onsager's solvation model is used to model the interactions between the two molecular species in the regions that are rich in either one of the components. The region rich in ethanol, with small concentrations of aniline is treated as solvation of a molecule of aniline by ethnol solvent.

$$H_{total}=H_A+H_B-H_{AB} \tag{1}$$

Table 2: Solvation modeling data

Basis	Parameter	Aniline rich region	Ethanol rich region
	HF Energy	-282.206506083	-152.133126111
STO-3G	Dipole Moment	1.5584	1.4869
	HF Energy	-285.631669179	-154.009355460
6-31G	Dipole Moment	1.6443	2.4135
	HF Energy	-285.726944066	-154.072616060
6-31G(d)	Dipole Moment	1.8246	2.0196
	HF Energy	-285.744068735	-154.086547127
6-31G(d,p)	Dipole Moment	1.7923	1.9930

Table 3: Hydrogen bond energy of the three aniline-ethanol conformer

Basis set	Structure1 (kcal/mol)	Structure2 (kcal/mol)	Structure3 (kcal/mol)
STO-3G	-9.002637	-9.015384	-9.266479
6-31G	-5.803262	-5.803253	-4.313468
6-31G(d)	-5.735271	-6.321877	-6.730383
6-31G(d,p)	-5.418896	-5.419208	-6.184823

The values of μ were compared with the experimentally determined value μ_e. Dipole moment of the 1:1 binary system was determined from Guggenheim's method[21]. The experimental results shown in figures 2 yield an experimental dipole moments of μ= 1.75D.

Figure 2: δ vs. concentration (mol/cc) of the aniline-ethanol binary system used to determine the experimental dipole moment.

The IR spectra show a blue-shift in the O-H peak of alcohol rich region and a red shift in the aniline rich region. As seen from computational solvation data, the polar nature of alcohol destroys the symmetry of the hydrogen bonded cluster in the ethanol rich region. At lower concentration of aniline (approximately at 20%) there is a significant change in the O-H peak position, which indicates the breaking of the hydrogen bond cluster of alcohols by aniline. On increasing aniline concentration, the O-H peak position does not show significant shift. NH_2 scissor frequency also does not shift with addition of alcohols. A dramatic change in the O-H peak is observed at lower concentration of aniline approximately from 20% as shown in Figure 3.

Figure 3: IR Spectra of O-H stretching aniline- ethanol mixture (Concentration in mole fraction).

The introduction of aniline at lower concentration of ethanol does not have adverse effect on smaller cluster of ethanol where as the larger clusters are broken by aniline leading to a significant red shift in the IR peak position in Figure 4.
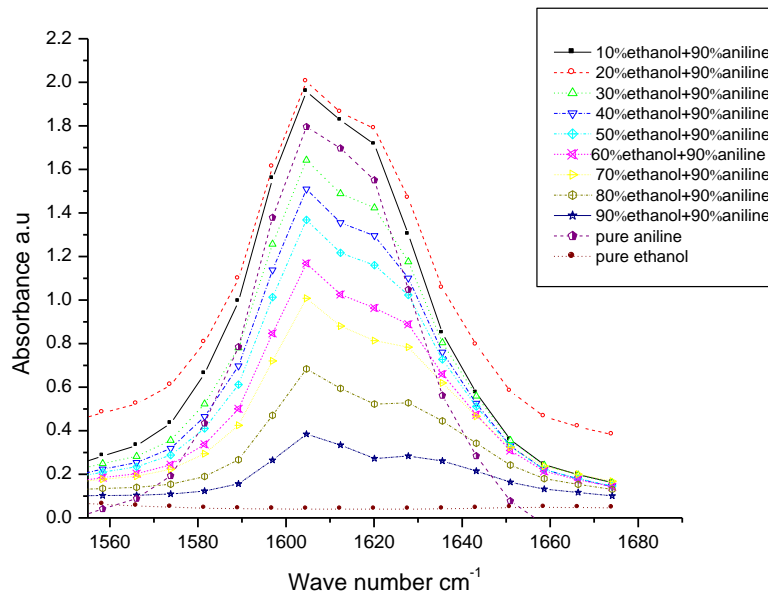

Figure 4: IR Spectra of NH_2 Scissor frequency of aniline-ethanol mixture (Concentration in mole fraction).

Surface energies of the chosen substrates are shown in Table 4.

Table 4: Surface energies of various substrates.

Substrates	Surface energy (mj/m^2)		
	Polar	Dispersive	Total
Glass	29.22	26.52	55.74
ITO	00.46	30.60	31.06
AlO	05.07	30.39	35.46
Hylam	05.32	20.57	25.89
Teflon	01.31	21.93	23.24

Alcohol rich region shows a better wetting than the aniline rich region.Test liquids used for the characterization of the substrates in the present studies are water, glycerol and diiodomethane. When the drop of the liquids contact with the substrates, the angle between them are measured from goniometer and subsequently the surface energies are calculated using advance drop image programmed of the goniometer.

The contact angle made by aniline-alcohols binary system over the entire concentration region on the same substrates was measured and is reported in figure 5. A dramatic wetting (decrease in contact angle by ~ 10°)is observed at about 20% aniline for this system over

hylam. This is because the surface tension of the binary liquid at this concentration approximately equals the surface energy of the hylam substrate and hence wetting is seen.
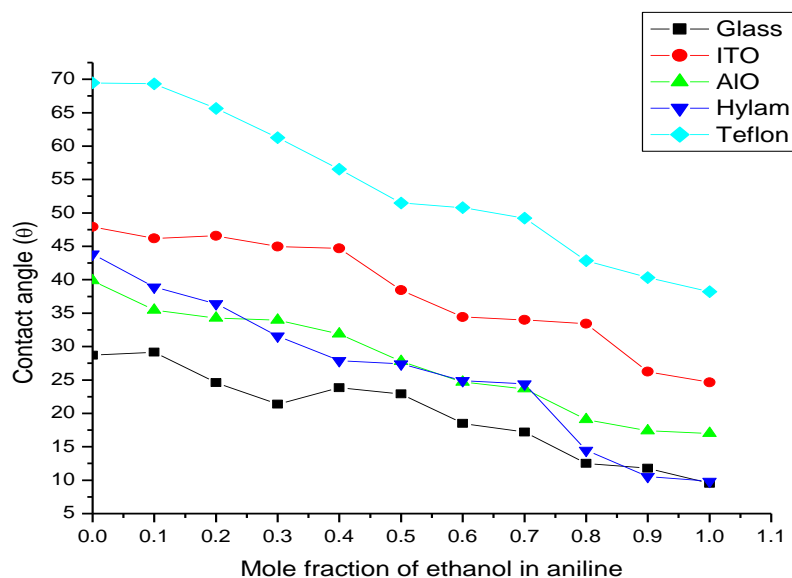

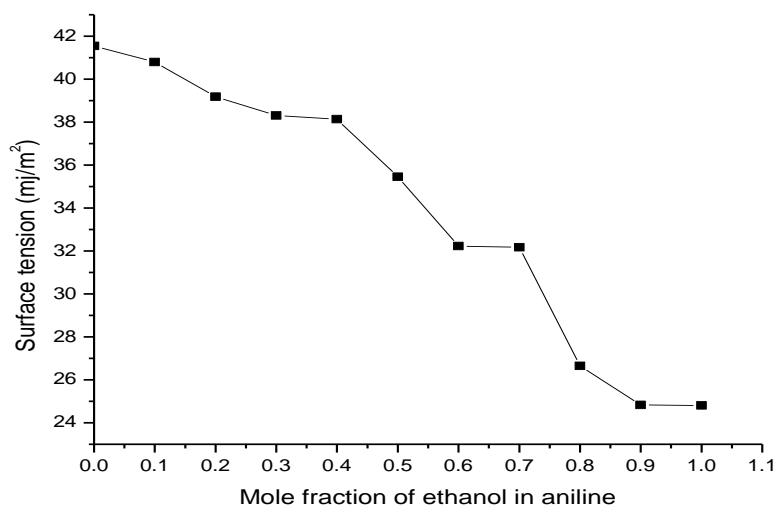**Figure 5**: Variation of contact angle with mole fraction of ethanol in aniline over different substrates.

Figure 6: Variation of surface tension with mole fraction of ethanol in aniline.

Conclusion

Aniline and ethanol interact by means of hydrogen bonds of the kind N-H--O; this is the type of bond that is seen in many biological systems. The interaction between the two moieties over the entire concentration region of the binary liquid shows regions of distinct behavior. Ethanol forms a hydrogen-bonded network, the symmetry of which is broken by

the addition of polar aniline. This causes the breaking of the alcohol clusters into smaller units, as observed from the dipole moment and FTIR data. On further addition of aniline to the ethanol solution, there is no further significant change. Aniline rich region of the binary liquid is characterized by the presence of non-hydrogen bonded associations.

When such a binary liquid is taken as a sessile drop and its wetting characteristics observed over substrates of different surface characteristics, it is seen that the 20%-40% aniline concentration region shows maximum interaction between the moieties. Rapid wetting (time taken for the drop to spread over the surface) 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 gradient.

Acknowledgements

Experimental Section

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 technique[21]. Dielectric measurements were made using a Fluke LCR meter working at 1 KHz. The dipole moments of the binary liquids were determined using Guggenheim method[20] as given in eqn. (2), by varying the concentration of a polar solute (the binary liquid) in a non-polar solvent (benzene).

$$\mu^2 = \left[\frac{27KT}{4\pi N(\varepsilon_1 + 2)(n_1^2 + 2)} \right]\left[\frac{\delta}{C} \right] \tag{2}$$

where,

$$\delta = \left(\varepsilon_{12} - n_{12}^2 \right) - \left(\varepsilon_1 - n_1^2 \right)$$

Subscript 12 indicates solution and subscript 1 indicates solvent. K is the Boltzmann constant; N is the Avogadro number and T the absolutes temperature at which the experiment is conducted.

Contact angle measurements were made using Rame-Hart contact angle goniometer by the Young's equation given in eqn. (3), at ambient temperature and the surface energy of the substrate was determined using the multi-liquid tool of the goniometer given by eqn.(4). The contact angle between substrates and liquids are related by the young equation[22].

$$\cos\theta = \frac{Y_{SV} - Y_{SL}}{Y_{LV}} \tag{3}$$

Where, Y_{SV}=solid-vapor interfacial tension, Y_{SL}=solid-liquid interfacial tension and Y_{LV}=liquid-vapor interfacial tension. Wetting over the entire concentration region of ethanol-aniline mixture over five substrates was studied.

Equation applies for the multiliquid[24] tool can be written as.

$$\frac{(1+\cos\theta)}{2}\frac{Y_{LV}}{\sqrt{Y_L^d}} = \sqrt{Y_S^d} + \sqrt{Y_S^P}\frac{\sqrt{Y_L^P}}{\sqrt{Y_L^d}}$$

(4)

where, Y_L^d = Dispersive component of liquid surface energy, Y_S^d = Dispersive component of solid surface energy, Y_S^P = Polar component of solid surface energy and Y_L^P = Polar component of liquid surface energy.

Conformational analysis was done using Gaussian-03 software[25]. The conformation of molecules has a great contribution in the magnitude of the dipole moment of the polar materials, since experimental dipole moment studied cannot justify the exact conformation. Hartree-fock method has been applied for the computational analysis of these systems, because it involved Born-Oppenhiemer approximation, as it consider only the electronic wave function. semi empirical studies is performed at STO-3G basis set, which act as a starting conformer for the Abinitio calculation using 6-31G(d) basis set, polarization function basis set are further added to the atom. Onsager's solvation model[26] was applied for two cases namely (a) aniline solvated by ethanol and (b) ethanol solvated by aniline. The former represents the ethanol rich region of the binary liquid and the later represents the aniline rich concentrations. Onsager's solvation model uses a spherical cavity for the solvent and approximates the solute to be a dipole. The reaction field as calculated in Gaussian-03 is given by eqn. (5).

$$R = [2m(e-1)/V(e+2)]$$

(5)

where V is the volume of the solvent molecule, μ the dipole moment of the solute and ε the permittivity of the solvent. The cavity size V strongly effects the calculations. In the present study V was determined using an in-built calculation in Gaussian-03 where V is defined as the volume inside a contour of 0.001electrons/bohr^3 density. The molecular volume thus determined is accurate to two significant Figures[22].

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