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NOTE

Study of Molecular Complex Formation between Components, Chloroform and Arylamine in Methanol with Dye Indicator Part-I

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Molecular complex formation is possible in binary organic liquids due to different types of interactions as concluded by several workers by studying different physical properties. Hence it was thought interesting to study the interaction between two organic components, chloroform and arylamine, in polar solvent methanol spectrophotometrically by monovariation method using dye indicator crystal violet and found that two types of molecular complexes were formed in the stoichiometric ratios 1 : 1 and 1 : 2.

Scatchard and Raymond[1] studied vapour-liquid equilibrium and observed large attraction between two unlike organic liquids such as ethanol and chloroform. When the dipoles are parallel and collinear with hydroxyl group of alcohol near the chloroform hydrogen and when the hydroxyl hydrogen is between its oxygen and chlorine atoms on the line of carbon-chlorine bond, then one to three molecules of alcohol might cluster about one chloroform molecule.

Excess Gibb's energy of activation ΔG^E and excess viscosity has been studied and it has been observed that there exists a strong hydrogen bond N—H- - -N in aniline molecules, hence found in dimeric or polymeric form.[2] But when it is mixed with solvents such as benzene, toluene, xylene and chlorobenzene, rupture of N—H- - -N bond takes place and orientation starts with solvent molecule; hence ΔG^E value is found negative when it is mixed with methanol and butanol and ΔG^E values found high positive due to hydrogen bonding with aniline molecules.[3]

While excess volume measurements are positive indicating randomly distributed aniline molecules with solvent molecules, small negative excess volume indicates N-π interaction, but with methanol large negative excess volume is due to smaller size of methanol.[3]

Oswal and Patel[4] studied molecular interaction in binary mixture of ethylacetate and chloroalkanes and derived the conclusion that when interaction takes

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place molecular complexes are formed, hence negative excess volume is observed.

Gupta and co-wokers[5] studied dielectric constants of alcohol mixtures with aromatic hydrocarbons and cyclohexane, and observed that due to interaction molecular complexes are formed; hence the dielectric constant of the system increases and hydroxyl hydrogen interacts with π-electron of benzene nucleus. Due to this complex formation takes place and the factors which increase the π-electron density interaction become strong.

Oswal[6] studied dielectric constants of binary mixture of ethyl acetate with $CHCl_3$ and CCl_4 and showed that ε is small positive for EA + CCl_4 and large positive for EA + $CHCl_3$ which indicates specific interaction between unlike components, leading to formation of molecular complex. The EA acts as an electron donor atom through free electrons of carboxyl group and $CHCl_3$/CCl_4 act as σ-type sacrificial electron acceptors.

Thus it has been seen that several workers studied different physical properties of binary liquid mixtures such as vapour-liquid equilibrium, excess volume, viscosity, dielectric constant and dipole moment and came to the conclusion that molecular complex formation is possible due to different types of interaction such as:

1. breakdown of self-associated structure,
2. intermolecular hydrogen bond formation,
3. donor-acceptor interaction,
4. closer molecular arrangement,
5. dipole-dipole interaction,
6. breaking of dipole association,
7. H-π and N-π interaction.

In this communication it was therefore thought interesting to study complex formation between organic components chloroform with aryl amine in polar solvent methanol spectrophotometrically by monovariatioin method using dye indicator.[7]

A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements. Organic components chloroform, aniline, *p*-chloroaniline, *p*-toluidine and *p*-nitroaniline M/10 concentration and dye crystal violet (C.V.) 5×10^{-5} M concentration solution were prepared in methanol. All compounds used in the study are AR grade.

Using monovariation method, eight sets of solutions of chloroform with aryl amine (aniline, *p*-chloroaniline, *p*-toluidine and *p*-nitroaniline) were prepared increasing the concentration of chloroform/aryl amine solution and aryl amine/chloroform solution and dye crystal violet solution concentration being kept constant. Absorbance of pure dye solution at λ_{max} was taken as standard and absorbance at λ_{max} in each set of solutions was measured and plotted against increasing chloroform/aryl amine solutions concentration, the graphs indicate peaks corresponding to the ratio of concentration of the two components chloroform and aryl amine in stoichiometric proportions 1 : 1 and 1 : 2.

When two organic components are mixed in liquid phase, specific interaction

takes place, hence dipole moment and dielectric constant of the system increase and result into molecular complex formation.

In chloroform solution in methanol, hydrogen of chloroform forms bond with oxyen of methanol and chlorine of chloroform forms bond with hydroxyl group of methanol forming cluster and in one cluster one molecule of chloroform associates with one or more molecules of methanol.[1] Similarly in aryl amine solution in methanol, due to H-π interaction, molecular complex is formed, hence dielectric constant of the solution increases.[2]

It was found by spectrophotometric study of a set of solutions of chloroform with aryl amine in methanol, using dye indicator crystal violet, that molecular complexes are formed in stoichiometric proportions 1 : 1 and 1 : 2. This can only be possible if the dielectric constant of the system might have been increased. Chloroform and aryl amine molecules are surrounded by polar solvent molecules forming molecular complex. But when both solutions are mixed, the methanol molecules of the complexes will be replaced by the interaction between the two molecules chloroform and aryl amine. The chloroform hydrogen interacts with π-electron of benzene nucleus, hence H-π interaction takes place. Moreover, aryl amine amino group hydrogen also forms hydrogen bond with chloroform chlorine. Due to release of methanol molecules and interaction between the two molecules, dielectric constant of the system increases, hence molecular complex of the two components is formed and solvated by solvent methanol molecules. Any factor which increases the π-electron density of benzene nucleus and basicity of aryl amine amino group facilitates the molecular complex formation.[5]

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