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NOTE

Spectral Absorbance of Dye Indicator in Relation to Liquid-Liquid Interactions: Aryl Amines, Acetone and Hexane

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Molecular interactions of binary organic liquids have been studied by several authors. In the present work the molecular interactions of binary mixtures of aniline, *p*-toluidine, 2,6-diethyl aniline with acetone or *n*-hexane in polar solvent methanol spectrophotometrically by mono-variation method using dye indicator have been studied.

Scathard and Raymond[1] studied vapour-liquid equilibrium and observed large attractions between two unlike organic liquids such as ethanol-chloroform when dipoles are parallel and collinear with hydroxyl group of alcohol near the chloroform hydrogen and when the hydroxyl hydrogen between its oxygen and chlorine atom on the line of carbon-chlorine bond. Study of excess viscosity indicated that there exists a strong hydrogen bond N—H—N in aniline molecules, in dimeric or polymeric form[2]. But when it is mixed with solvent such as benzene, toluene, xylene or chlorobenzene, rupture of N—H—N bond takes place and orientation starts with solvent molecules; hence ΔG^E value is found negative. When however mixed with methanol or butanol ΔG^E value was found positive due to hydrogen bonding with anilines molecules. Excess volume measurements are positive indicating randomly distributed aniline molecules with solvent molecules. Small negative excess volume indicated N-π interaction, but with methanol large negative excess volume is due to smaller size of methanol[3, 4]. Modi and Desai[5] studied the molecular interaction between chloro-alkanes with hexane or heptane by using dye indicator method. Modi has also studied the specific interactions of diethyl ether with chloroalkanes, benzene, toluene and xylene using the same method[6].

Hexane or acetone of M/10 concentration solutions and dye crystal violet (C.V.) 1.0×10^{-6} M solutions and dye were kept constant. Different sets of solutions were prepared by increasing hexane or acetone and aniline, or *p*-toludine, or 2,6-diethyl aniline and dye crystal violet (C.V.) by adding methanol

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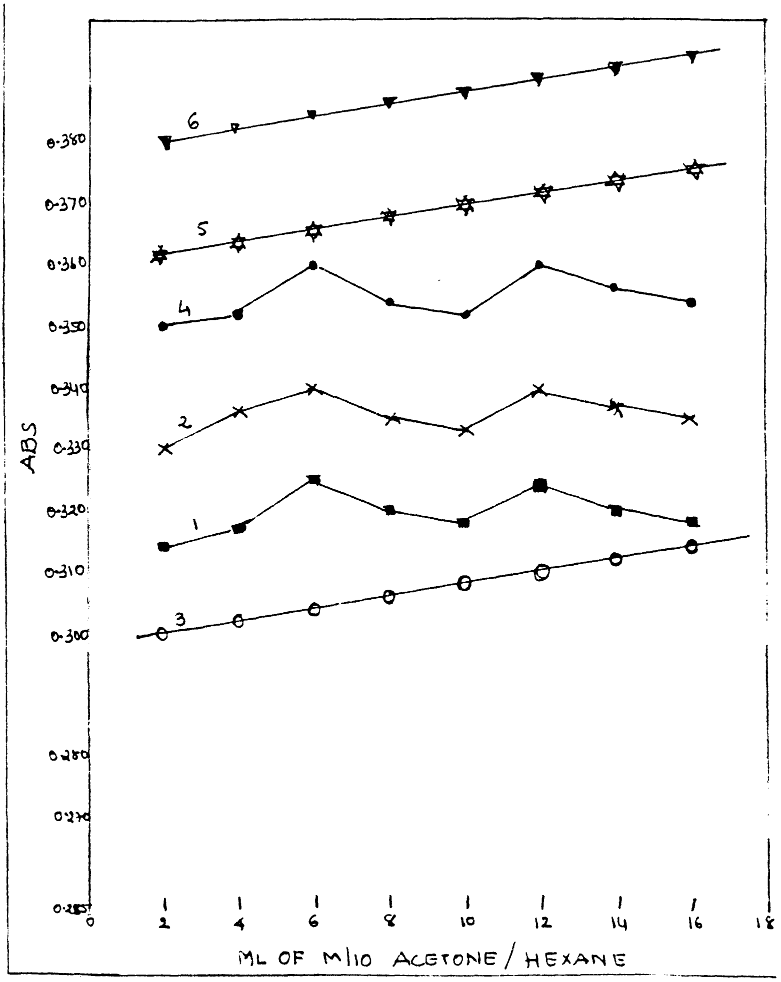
as shown in graph made up to 50 mL. A Shimadzu double beam spectrophotometer UV-160A was used for spectral measurements. Absorbance of pure dye solution at λ_{max} in each set of solutions was measured and plotted against increasing hexane or acetone concentration; The graphs indicates the peaks corresponding to the ratio of two liquids in stoichiometric proportion (Graph-I).



Graph-I

1. mL of acetone + 12 mL aniline + 5 mL (1.0 × 10^{-6} M) C.V. ■
2. mL of acetone + 12 mL *p*-toluidine + 5 mL (1.0 × 10^{-6} M) C.V. ×
3. mL of acetone + 12 mL 2,6-diethyl aniline + 5 mL (1.0 × 10^{-6} M) C.V. ○
4. mL of Hexane + 12 mL aniline + 5 mL (1.0 × 10^{-6} M) C.V. ●
5. mL of hexane + 12 mL *p*-toluidine + 5 mL (1.0 × 10^{-6} M) C.V. ✡
6. mL of Hexane + 12 mL 2,6-diethyl aniline + 5 mL (1.0 × 10^{-6} M) C.V. ▼

The graph 1 and 2 indicate two peaks because of H-bond formation between O of acetone and H of both aryl amines and acetone, forming H-bond monomers and dimers, whereas 2,6-diethyl aniline does not show such interactions due to —$N(C_2H_5)_2$ groups and so no peak is observed in graphh 3.

The graphs 4 shows peaks due to molecular interaction between hexane and aniline, due to π-electrons of aromatic hydrogen of hexane; where as graph 5 does not indicate any peak due to absence of interaction between hexane and *p*-toluidine, possibly due to stabilisation effect of hyperconjugative —CH_3 and mesomeric —NH_2 Graph 6 shows absence of interaction between hexane and 2,6-diethyl aniline.

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