
CHAPTER 1: INTRODUCTION

By an IUPAC definition, solvation is an interaction of a solute with the solvent, which leads to stabilization of the solute species in the solution [1]. Solvation is an ubiquitous phenomenon in chemistry because much of chemistry is carried out in solution. It has been noticed that a solvent not only acts as a medium for reaction, it also modifies the free energy of the substrate (solute) which is reflected in the *solvent effect* on kinetic, equilibrium and spectroscopic processes involving the solute. In the primitive model a solvent is represented by a continuum characterized by bulk dielectric constant and refractive index. In the molecular picture a molecule of solute in a solution interacts with the solvent molecules in its immediate neighbourhood. Thus the distribution of solvent molecules in the vicinity of the solute molecule (local or cybotactic region) is different from that in the bulk. The term solvation denotes the net effect of all interaction in the cybotactic zone. Solvation of a solute and its source in terms of solute-solvent and solvent-solvent interaction are important areas in physical chemistry [2-4]. It has been established that a pure solvent is characterized by several modes of interaction with a solute and the change of free energy due to solvation shows a linear dependence on the parameters representing the different modes [5-8]. The vast literature of solvent effect on equilibrium, kinetic and spectroscopic properties indicate that only a few modes of solute-solvent interaction need to be considered. One is nonspecific long range interaction due to collective influence of solvent as a dielectric medium. In contrast, specific modes of interaction involving electron pair donation and acceptance ability of the solvent molecules may also be distinguished. In the multi parametric approach the three basic modes of interaction, namely, dipolarity–polarisability, hydrogen bond donation (HBD) and acceptance (HBA) ability have been characterized for homogeneous media [5-8]. Besides these modes, solvent-solvent interaction as represented by the energy required for a cavity formation in the medium also determines the solvation phenomenon [9-11]. While this interaction is constant in pure solvent, the use of mixed solvents provides a means for its modification by varying the composition of the solvent mixture. As such, chemical physics of solvation in solvent mixtures is a subject of current interest [12-19]. Moreover, experimental evidence suggests that a solute may induce a change in the

composition of the solvation sphere compared to that in the bulk. The phenomenon, known as preferential solvation, has been studied extensively in recent years for binary solvent mixtures in terms of solute-solvent and solvent-solvent interactions [20-28]. Besides the homogeneous media, aqueous micelles provide important media for solubilising hydrophobic solute molecules. Enhanced solubility of organic molecules in the micellar phase points to the existence of significant interaction of the molecules with the micellar environment. The concept of the solvation interaction can also be applied to a heterogeneous medium. The multiparameter approach has recently been extended to binary solvent mixtures and heterogeneous media and the parameters representing dipolarity–polarisability, HBD and HBA ability of micellar media have been determined [29-34]. Study of solvation interaction is done experimentally by monitoring thermodynamic or kinetic, parameters of a *model process* [35, 36]. A thermodynamic or a kinetic process showing large solvent sensitivity can serve as a model process. Parameters related to Gibbs free energy change ($\log K$ in the case of an equilibrium process, $\log k$ in the case of a kinetic process) is usually studied. Spectroscopic transition leading to absorption or emission of a photon also serves as a model process. If one assumes that entropy does not change due to a spectral transition [37], the maximum energy of transition can be looked upon as a free energy term. It may be pointed out in this context that sensitivity of maximum energy of transition towards a variation of environment depends on the nature of transition. Thus optical response of molecules showing charge transfer transition has been found to depend significantly on solvation interaction.

1.1 Scope and objective of the thesis

In this thesis solvation characteristics of solutes have been studied in homogeneous and heterogeneous media. Homogeneous media include pure and mixed (binary, ternary) solvents. Aqueous micellar systems formed by surfactants (single / binary) have been used as heterogeneous media. Most often, electronic spectroscopic parameters have been extensively utilised for obtaining information on solvation in pure and mixed solvents [36]. But a spectroscopic process, in general, involves an equilibrated initial state and a non-equilibrium Frank-Condon final state. It is instructive to investigate whether a thermodynamic parameter involving only the equilibrium ground state of the solute gives

similar information. Solubility of indicator solutes and the electronic absorption maximum have been studied respectively as thermodynamic and spectroscopic property in the present work.

Study of solvation using solubility

Use of solubility as a parameter for studying solvation has been made by Marcus [38]. In recent past Bagchi et. al. have studied the solubility of Reichardt $E_T(30)$ betaine dye and a ketocyanine dye and obtained information on solvation interaction [39, 40]. But more systematic studies involving other solute-solvent systems are required to establish a general conclusion. Solute-solvent and solvent-solvent interactions in a solution have been studied in the present work by using solubility of a solute in different media. To this end the values of solubility of indicator solutes have studied in different pure solvents and aqueous binary mixtures. The dye is structurally similar to a ketocyanine dye and its solvation characteristics have been studied in various media using electronic spectral properties [41-44]. It is known that the solubility of a solute is enhanced dramatically in micellar media. The possibility of having information regarding aggregation and micro environmental properties of surfactants by monitoring solubility of a suitable indicator solute in an aqueous solution of surfactant as a function of the surfactant concentration has been studied in this work. Thus, solubility of indicator solutes have been studied in presence of cationic, anionic and neutral surfactants, viz., cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulphate (SDS) and triton X 100 (TX 100) in aqueous solution. Aggregation properties of binary mixtures of SDS and TX 100 have also been studied. At this point it is important to note that according to the two-phase model of micellisation a solute distributes itself between the aqueous phase and the micellar phase. The solubility in an aqueous solution of surfactant beyond the critical micelle concentration (cmc) is always an average of the solubility in the two phases. Below the cmc the experimentally determined solubility, however relates to that in a homogeneous solution of surfactant in water. An estimate of solubility in the micellar phase (s_m) can only be obtained from the observed solubility and knowledge of the distribution coefficient. The method of determination of the value of a spectroscopic parameter in the two phases of micellar medium has been discussed in recent publications [32, 34]. It is worthwhile to study whether a similar analysis is applicable for solubility studies. A novel method has been proposed for determining the cmc , solubility in

micellar phase (s_m) and the distribution coefficient (K). Unlike the spectral parameter, viz. the maximum energy of transition, solubility of a solute depends on the cavity formation energy [39, 40]. Thus knowledge of solubility of an indicator dye in a micellar environment can provide information regarding the cavity formation energy in the medium. The Hildebrand parameter, δ_H^2 , representing cavity formation energy [3] has been determined for the micelle – water interface.

Study of solvation using solvatochromic indicators

Electronic spectroscopy provides a suitable method for studying solvation. It has been observed that maximum energy of electronic transition of various solutes depends to a great extent on the local environment around the solute. While solvation in binary solvent mixture has been studied extensively, systemic study of solvation in ternary mixture is scanty. In the case of binary solvation it has been indicated that, besides solute-solvent interaction, solvation characteristics depend on solvent non-ideality. It is thus instructive to investigate the role of solvent-solvent interaction in ternary solvent mixture. Ternary mixtures in which one of the pairs is only partially miscible are of special interest. Addition of a third component, which is miscible with both the partners, brings about a modification of solvent-solvent interaction and after a critical composition the mixture exists as one phase. The objective of the present work is to study the solvation behavior in a ternary solvent mixture in terms of solute-solvent and solvent-solvent interaction.

Measurements of equilibrium properties of ternary solvent mixtures reveal that the observed solvent property deviates from the mole fraction average in most of the cases [45, 46] indicating the existence of solvent-solvent interaction in a ternary solvent system. In the event of ideal solvation an observed property (P) of an indicator solute is given by the average of the property of the component solvents weighted by the mole fraction of the solvents [3, 47]. Thus,

$$P = \sum x_i P_i \quad (1.1)$$

where x_i denotes the mole fraction of i -th solvent. Any deviation from equation (1.1) would indicate the existence of solute-solvent and solvent-solvent interactions. Recently, Bagchi et. al. have studied the solvation characteristics of Reichardt's $E_T(30)$ betaine dye in ternary mixtures by monitoring the solvatochromic charge-transfer absorption band of the solute [48]. A systematic study using other indicator solutes is required to draw a general

conclusion. In the present work the solvation of ketocyanine dyes have been studied. The longest wavelength absorption band of the dye originates due to an intra molecular charge transfer (ICT) [41, 49, 50]. Absorption and the corresponding fluorescence band show significant solvent sensitivity. Electronic spectral properties of the dye have been studied in mixed binary solvents [49, 50]. The objective of the present work is to study the role of solute-solvent and solvent-solvent interactions on the solvation characteristics of the dyes in mixed ternary solvents by monitoring the longest wavelength absorption band of the solute as a function of solvent composition. Besides ternary solvent mixtures, which are completely miscible at all compositions, studies have been done using mixtures where one of the pairs is partially miscible. In the latter case solvent compositions in the miscible range and also on the binodal curve have been studied. The solvation characteristics in the corresponding binary solvent mixtures have also been studied. Information about the knowledge of binary solvation has been utilized to analyze the results on ternary solvation using a two-phase model of solvation.

1.2 Plan of the thesis

The thesis contains *seven* chapters. A brief introduction to the subject and scope of the thesis has been described in the *first* chapter. The preliminary background for the present study has been described in the *second* chapter. This includes discussion on certain aspects of solvation in various media and representation of ternary solvent composition by triangular graph. The *third* chapter contains description about the materials and methods. Results on solvation in pure and mixed binary solvents using the thermodynamic parameters, viz., solubility have been discussed in the *fourth* chapter. The *fifth* chapter contains study of solubility of indicator dyes in aqueous solution of pure and binary mixed surfactants. Results on solvation in ternary solvent mixtures using UV-VIS absorption probes have been discussed in the *sixth* and *seventh* chapters. The *sixth* chapter contains studies of solvation in completely miscible ternary solvent mixtures. Studies on solvation in ternary mixtures where one of the pairs is partially miscible has been presented in the chapter *seven*.

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