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Review

Investigations of absorption and emission spectral data in mixed liquid media. A short review of recent literature

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ABSTRACT

This review presents the principal aspects regarding the absorption and emission spectral behavior of different solutes in binary liquid mixtures mainly from the last seven years. The advantages of using mixed liquid media (heterogeneous media) over other commonly neat solvents (homogeneous media) are provided. The photophysical behavior was described from the point of view of changes of absorption and photoluminescence properties including: spectra patterns, solvatochromic behavior, Stokes shifts, fluorescence lifetimes and emission quantum yields, local microenvironment and preferential solvation. Spectral characteristics of different systems in the mixture of solvents as a function of the solvatochromic parameters of these systems were also reported. The absorption and emission properties of various solutes in binary solvent mixtures are affected strongly by the nature of solvent and composition of the system. This review provides a non-exhaustive compilation of the impact of binary mixtures of solvents on the photophysical behavior of solute molecules.

Contents

1. Introduction

Solvent mixtures play an important role in industry and for research laboratories. They are often used to modify molecular environment in order to tune the chromatographic separation, organic synthesis, reaction kinetic, protein folding [1] and physical properties of the analyzed systems. These systems (mixed) present many benefits and allow the users to control the properties of the system. Thus they can obtain a novel solvent (system, medium) with new, desirable (pre-establishment), appropriate and less hazardous properties, which are absent within a single-solvent system [2–4]. A mixed solvent system differs by the fact that one of the two solvents will have a greater affinity for the solute compared to the other solvent from mixture. This allows to the best elucidation of the nature of the polymer–solvent or solvent–solvent interactions from the system. Also, by working in mixed solvent medium on can choose suitable solvents and proportions so that the new created system (medium) to be more friendly (a positive impact) with the

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ambient medium. The difficulties and the particular aspects of the work in these systems it would be: the choice of the appropriate solvents; the identification and evaluation of the intermolecular interactions within the system (more complexes than in pure solvents) and their correlations with photophysical properties.

Generally, the photophysical properties of various solutes in the mixture of solvents are influenced by the composition (repartitioning of the cosolvent between solvation shell and bulk phase [2], see Fig. 1) of systems and intermolecular interactions (hydrogen bonding, charge transfers, molecular associations, dipole–dipole and dipole–induced dipole interactions) that can be appeared. As consequence of intermolecular interactions, the physicochemical properties of many solvatochromic probes in binary solvent mixtures often show large deviations from the ideal behavior.

Spectroscopic methods have been recently used most to rationalize the nature and the extent of intermolecular interactions from the heterogeneous media (liquid mixtures) [3–8]. Table 1 lists several recent studies about spectroscopic behavior of the different solvatochromic probes in various binary solvent mixtures.

In the last years, a series of the theoretical and experimental studies about photobehavior of different solutes in the various liquid solvent mixtures were published due to specific aspects that occur in these systems. Several examples of the specific mixed liquid systems include:

- the mixtures of polar aprotic solvents — where, both pure solvents are able to form complexes or cross-associated species.
- the systems of water with aliphatic alcohols — where different interactions occurs, such as hydrogen bondings between water (—OH group with role of the donor) and alcohol molecules (which have one acidic H atom on the —OH group with role of the — acceptors). These systems have been studied extensively because of their rich applications in pharmaceutical and chemistry industries.
- the water — DMSO mixtures — has major interest due to remarkable properties of DMSO (applications in diverse fields like, cell biology, pharmacology [25], low toxicity and environmental compatibility [26]).

Over the recent years, a great interest has been shown to the use of a newly generated solvent (medium) — containing ionic liquids (ILs) and different other organic solvents or water. These systems have particular advantages, such as low volatility, high thermal stability [27], moderate polarity [28,29] and are considered green solvents (ease of recycling). The solvation in the systems containing ILs is much more complex to interpret than in classical binary mixed solvent systems. The solute can be preferentially solvated either by organic solvent, anion, cation or by the specie(s) formed after intermolecular interactions between components of the system (ILs and solvent molecules (cation–solvent and/or anion–solvent)).

The aim of this review is to show and highlight the main aspects investigated from spectral data of different solvatochromic probes in various binary solvent mixtures, by using the literature expanded over the last years. Also, we consider the specific aspects that occur in these systems in comparison to with behavior of different solutes in neat solvents. This review summarizes the most recent investigations on the photochemical behavior of different solutes in mixed binary solvents.

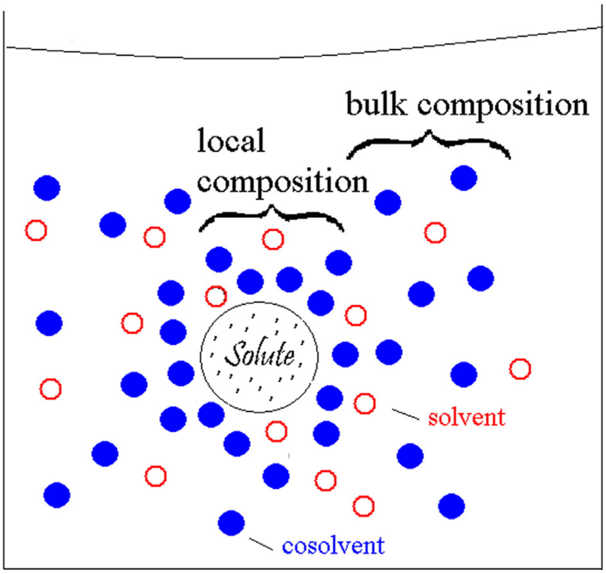

Fig. 1. A visual illustration of the solvation process of a solute in a binary solvent mixture. From Ref. [2].

2. Absorption and emission spectral patterns in mixed solvent solutions

The shape, intensity and maximum wavelengths of the absorption and emission bands of different solutes in mixed solvents depend strongly on the nature of solvents, the ratio between the two solvents, the solute–solvent and solvent–solvent interactions. In mixed polar and non-polar solvents the spectral characteristics of a polar solute are influenced by, the spatial distribution of polar solvent molecules in the system. Thus, a small addition of a polar component changes the permittivity and can determine a red shift of solute absorption and fluorescence bands [30]. The absorption and fluorescence spectral patterns of the perylene end-capped poly(dimethylsiloxane) in mixtures of hexane and chlorinated solvents (dichloromethane, chloroform, dichlorobenzene and carbon tetrachloride) was influenced by, the ratios of hexane within the systems [31]. With increasing content of hexane the absorption peaks become sharper, the doublets became well resolved and the observed peaks were shifted to lower wavelengths. Fluorescence spectra have a similar pattern with UV absorption spectra and the same behavior (depends on the solvent used).

A. Jouyban and coauthors [12] report a mathematical model for representing the effects of binary solvent mixture composition and temperature on the fluorescence intensity of two beta-blocker drugs in aqueous mixtures of methanol, ethanol and 1-propanol at 15, 20, 25, 30 and 35 °C. The proposed models are able to correlate/predict the data with reasonable error.

3. Solvatochromism in mixed solvents

3.1. Stokes shifts in binary solvent mixtures

The solvatochromism exhibits the changes in UV visible absorption bands as a consequence of a modification in polarity of the medium. Although, the solute–solvent and solvent–solvent interactions in the mixed solvent systems are more complex than in pure solvents and due to preferential solvation, the physical parameters of mixed solvent systems are evaluated by the same techniques as those applied for pure solvents.

The dielectric constant, ε_{S_1/S_2} and refractive index, $n^2{}_{S_1/S_2}$ for the binary solvent systems by some authors [2,32], was calculated using a linear additive model, defined by the following equations:

$$\varepsilon_{S_1/S_2} = f_{S_1}\varepsilon_{S_1} + f_{S_2}\varepsilon_{S_2} \qquad (1)$$

$$n^2{}_{S_1/S_2} = f_{S_1}n^2_{S1} + f_{S_2}n^2_{S2} \qquad (2)$$

where, the subscripts S_1 and S_2 represent solvent 1 and 2, respectively, and f is their volume fractions. Other authors [33], established some empirical exponential equations (function of the molar fraction of the polar component, x_p) in order to evaluate the dielectric constant and