SOLVATOCHROMIC EFFECTS IN BINARY MIXTURES OF BIFUNCTIONAL ETHYLENE DERIVATIVES WITH DIMETHYL SULFOXIDE

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Among bifunctional solvents ethylene glycol (EG), ethanolamine (ETA) and ethylene diamine (ETDA) are commonly used. Those solvents form 3d hydrogen bond network that is similar to water. The only difference is in the fact that groups forming H-bond is separated with ethylene fragment in EG, ETA, ETDA. Thus, the size of organic solvents compared to water is higher as well [1-3].

Because of the feature described above EG, ETA and ETDA cause a quite interest to investigate as components of binary mixtures.

In order to research individual solvents and its mixture are widely used solvatochromic probes among which Reichardt dye [4] is the most approachable. However, Nandi dye [5] (fig. 1) found its application in the recent decade. Nandy dye's specialty is related to the availability of two solvatochromic centers – phenolate Oxygen atom in the ground state and nitrofragment in the excited state.

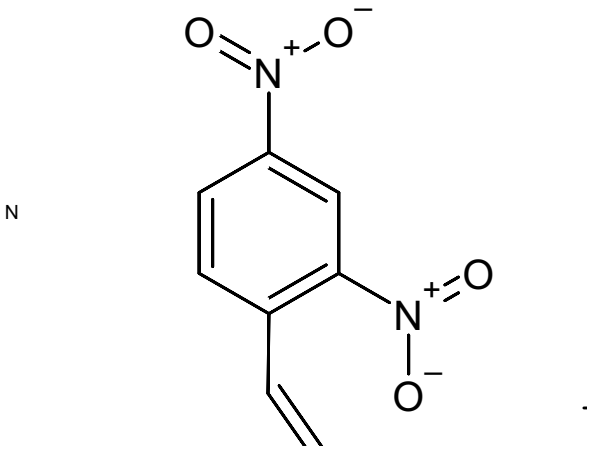

Figure 1. Ground (I) and excited (II) states of Nandi dye

The presence of two solvatochromic centers allows us to employ Nandi dye for binary mixture investigation.

Water/organic mixtures show an unusual behavior on the $E_T(X)$ curves with the change of X (fig. 2), where X is mole fraction of water, E_T is an empirical parameter of polarity obtained from solvatochromic properties of corresponding probes in the solvent mixtures. An unusual behavior appears in preferential solvation in water-rich region by water: by adding water to DMSO E_T mildly grow up to certain concentration, and then sharp decrease of E_T up to the pure water value is observed [6].

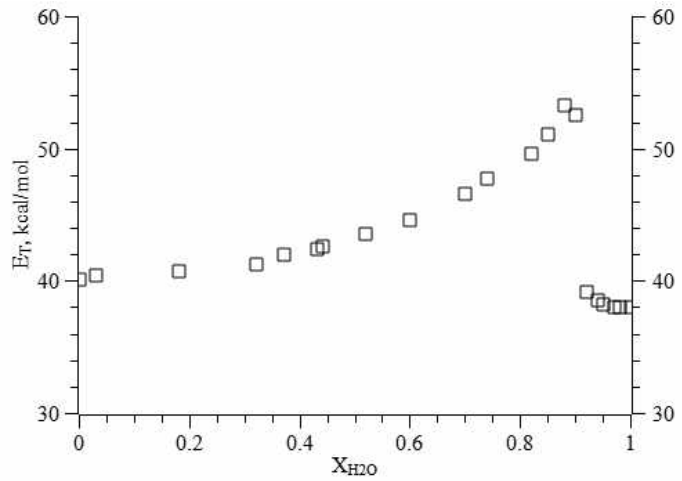

Figure 2. Plot of E_T against mole fraction (x=0 for DMSO, x=1 for water)

That occurs because water solvate Nandi dye in nitrofragment in the excited state, while Reichardt dye is solvated in phenolate Oxygen atom in the ground state.

In present work binary mixtures of EG, ETA and ETDA with dimethylsulfoxide have been investigated using Reichardt and Nandi dye. Plots E_T against mole fraction are shown in the fig. 3(A-C).

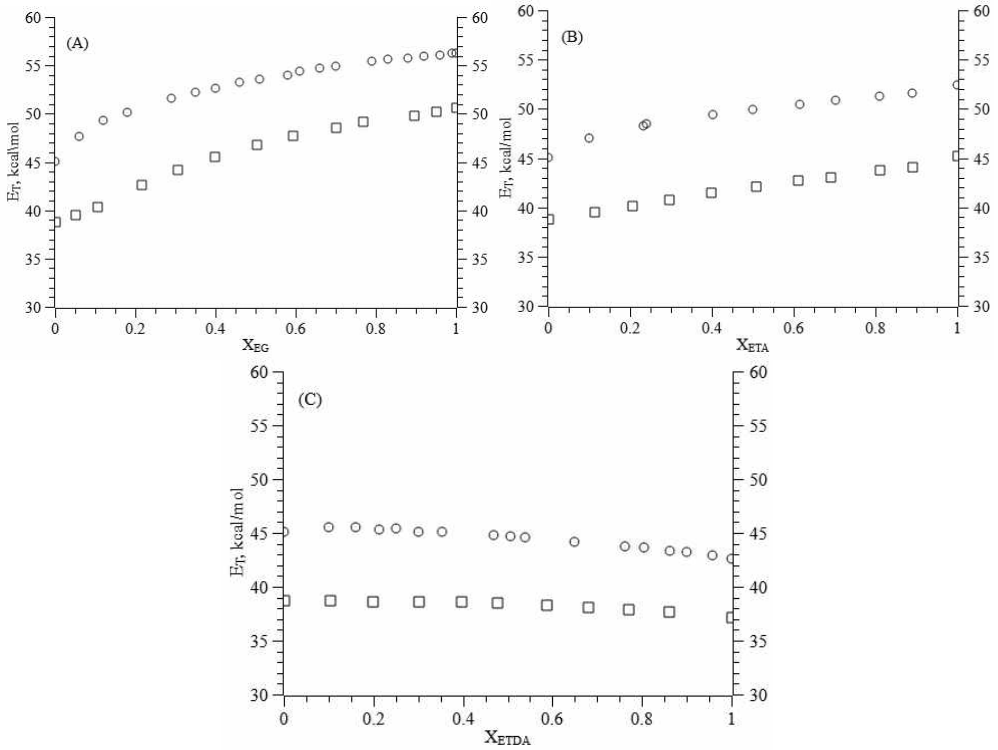

Fig. 3. Plots E_T against mole fraction of (A) EG, (B) ETA, (C) ETDA
(○ – E_T(30) obtained using Reichardt dye, □ – E_T obtained using Nandi dye)

Despite the similarity of water and bifunctional organic solvents, the size of molecules makes huge difference of them that appears in the solvation ability. If extreme behavior of E_T-value is observed in the water/organic mixture, there is no such phenomenon discovered for binary mixture of bifunctional ethylene solvents. Both E_T and E_T(30) curves are plain with no extreme points. Nevertheless, slight preferential solvation by EG in presence of both probes is discovered for EG/DMSO-system. The deviation from linearity for ETA/DMSO and EDTA/DMSO-systems iscommensurate with the experimental error.

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