

Solvatochromic and Kinetic Response Models in (Ethyl Acetate + Chloroform or Methanol) Solvent Mixtures

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Abstract: The present work analyzes the solvent effects upon the solvatochromic response models for a set of chemical probes and the kinetic response models for an aromatic nucleophilic substitution reaction, in binary mixtures in which both pure components are able to form intersolvent complexes by hydrogen bonding.

Introduction

Recently, we analyzed the preferential solvation of a set of solvatochromic solutes 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (I), *N,N*-diethyl-4-nitroaniline (II), 4-nitroanisole (III), 4-nitroaniline (IV), 4-nitrophenol (V), and β -carotene (VI) (corresponding to the parameters $E_T(30)$, π^* , α , β y π_2^*) by the application of preferential solvation models [1] (PSM), in mixtures of the following type: aprotic strong hydrogen-bond acceptor solvent and an aprotic cosolvent with hydrogen-bond donor capability [ethyl acetate (EAc) + chloroform] [2a,b].

On the other hand, we extended the preceding analysis to the kinetic data of an aromatic nucleophilic substitution (S_NAr) reaction between 1-fluoro-2,4-dinitrobenzene and morpholine carried out in the explored mixtures, relating the solvatochromic response model with the kinetic one.

Now, it is of interest to apply the preceding analysis to binary mixtures of EAc with a strong hydrogen-bond donor cosolvent (EAc + methanol), with the object to establish the influence of the acidity of the cosolvent.

Experimental

The experimental data were obtained by the methods reported previously [1]. The parameters of solvation were calculated by the application of the MATLAB 4.2 Program (The Mathworks, 0.1 inc.).

Results and Discussion

The preferential solvation models were applied to the solvatochromic data. The parameters of sol-

vation $f_{2/1}$ and $f_{12/1}$, which measure the tendency of the solutes to be solvated by an individual component of the mixture or by the mixed solvent, indicate similar solvatochromic response model for (EAc + CHCl_3) [2a] and (EAc + MeOH) mixtures. The observed general trends are: (i) the solutes are preferentially solvated by the mixed solvent (donor acceptor complexes) and by the cosolvent, in preference to the EAc ($f_{2/1}$ and $f_{12/1} > 1$); (ii) the preferential solvation order is complex > CoS > EAc ($f_{12/1} > f_{2/1}$); (iii) the solute of reference β -carotene shows a tendency to ideality ($f_{12/1}$ and $f_{2/1} \approx 1$).

We extended the application of the PSM to the kinetic data. The analysis was performed at constant amine concentration and as a function of the solvent composition. The obtained results show a similar general tendency: preferential solvation by the cosolvent CHCl_3 or MeOH in preference to the complex and EAc.

Both mixtures, which are capable to form complexes by hydrogen bonding between the EAc and the cosolvent, and also with self-association in the case of MeOH, reveal similar solvatochromic and kinetic response models.

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References and Notes

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