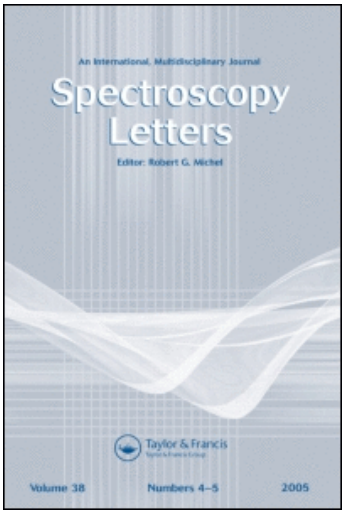

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A Spectroscopic Model for the Study of Preferential in the Ground and Excited Electronic States.

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A Spectroscopic Model for the Study of Preferential in the Ground and Excited Electronic States.

Key words: Triphenylene, solvatochromism, solvent mixtures, solvation

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Abstract

The preferential solvation of a solute molecule in mixed solvents is analysed in terms of the spectral solvent shifts. A spectroscopic model is developed in order to know the preferential solvation degree in the ground electronic state as well as in the first excited electronic state by measuring the absorption and fluorescence spectra respectively.

Triphenylene was found to be a good model probe molecule in n-butanol/carbon tetrachloride mixtures for both electronic states. Furthermore Tryphenylene in its ground electronic state was studied in chloroform/methanol mixtures.

Introduction

A few years ago, Frankel et al.[1] developed two methods for investigating the preferential solvation degree in mixed solvents from nuclear magnetic resonance (NMR) techniques. Both methods[1,2], the effect of the solvent on the NMR chemical shift of the solute and the effect of a paramagnetic solute on the transverse relaxation time of the solvent nuclei, were applied to tris-(acetylacetone)-Cobalt(III) and tris(acetylacetone)-Chromium(III) in mixtures of $CHCl_3/CCl_4$, $CHCL_3$/acetone,

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$CHCl_3$/p-dioxane, and others, and were well interpreted in terms of a thermodynamical treatment for preferential solvation developed in a similar way to preferential adsorption from a liquid mixture onto a surface. active solid.

Thus, they considered the solvent to be distributed between two phases, the bulk solvent and the solvation shell of the solute, and for simplicity the solvation number was taken to be the same for both solvents (A and B), with a one-to-one replacement of solvent molecules.

After the solvation sphere has been formed from n_A moles of A and n_B moles of B, and remembering that the configuration entropy can be calculated on the assumption that both the bulk solvent and the solvation shell obey the laws of regular solutions, the change in free energy for the process leads to a simple relationship between the composition of the bulk solvent and the solvation shell along an isotherm (Eq./1/) [1].

$$\frac{y_A}{y_B} = K \frac{Y_A}{Y_B} \qquad /1/$$

Here y_A and y_B represent the mole fractions of A and B in the solvation shell, respectively, Y_A and Y_B refer to the bulk solvent, and K is the equilibrium constant for the process, where $\Delta G^\circ = -RT \ln K$. For experimental purposes, the Y_A and Y_B values can be determined directly if the solution is highly diluted and K can be obtained from the slope of a plot of (y_A/y_B) versus (Y_A/Y_B).

Based on this thermodynamic approach for binary mixed solvents [1], we have developed in the present work an electronic spectroscopic model in order to determine the preferential solvation degree in the ground electronic state or in the first excited electronic state from the absorption or fluorescence spectral shifts of a probe solute-chromophore-molecule in solution.

The Model

The following properties are required in order to stablish the main characteristics of the present model.

a. The binary solvent of molecules A and B in the solute molecule solvation shell, i.e., solvation phase, contribute in a additive

way to the total solvation energy. Therefore, they are assumed to be independent in the solvation shell localization, and it is assumed that the solvation energy can be considered as the contribution arising from each molar fraction (y_A and y_B) that constitues the solvation phase.

b. For simplicity it has been assumed that the solvation number (N) is the same for both solvents, i.e., similar molecular volume. Thus, if the solution is diluted, the molar fractions of A and B in the bulk solvent (Y_A and Y_B respectively) will be present in the solvation phase according to the following probability distribution:

$$P(r) = \frac{N!}{r!\,(N-r)!}\; Y_A^{\,r} \cdot Y_B^{\,N-r} \quad , \; 0 \leq r \leq N \qquad /2/$$

where P(r) is the solvent configuration number for the total of solvation boxes in the solvation shell of solute[3].

c. The most probable configuration in the solvation phase should be dependent on the molar fractions of A and B in the bulk solvent (Eq./2/). However, since electronic spectroscopy give us information for each configuration in the solution through the spectral band, the molar extinction coefficient of the solute molecule in the binary mixture of solvents A and B should not change in a significant way. The frequency of the absorption maxima can also be considered a representative value of the mixture in the solvation phase (ν_M).

Considering the first condition (a) and ν_A and ν_B, the frequencies of the absorption maxima in the solvents A and B respectively,

$$\nu_M = \nu_A Y_A + \nu_B Y_B \qquad /3/$$

and rewriting this eq./3/ in terms of Y_A,

$$\Delta\nu_M = \Delta\nu Y_A \qquad /4/$$

where $\Delta\nu_M = \nu_M - \nu_B$, $\Delta\nu = \nu_A - \nu_B$ and $Y_B = 1 - Y_A$.

Thus, any other funcionality observed between both $\Delta\nu_M$ and Y_A parameters can be considered as a preferential solvation case.

d. The last condition in our model is expressed in terms of the Franck-Condon principle. The absorption electronic spectra permits one to obtain information about the solvation shell composition of the chromophore solute molecule in the ground state, and the fluorescence electronic spectrum permits one to obtain information about the solvation shell in the first excited electronic state (in this last situation can be found changes in the intensity of fluorescence due to the mixed solvent composition). However, from the absorption spectra the same information must be obtained for different π-π^* electronic transitions.

In according with the above postulate, triphenylene[4] has been studied as a model solute molecule because of its high molecular symetry, and the mixtures butanol/CCl_4 and methanol/$CHCl_3$ have been chossen because of their interesting structural properties[5,6,7].

EXPERIMENTAL SECTION

The absorption spectra were obtained with a Cary 17 recording spectrophotometer operated at room temperature (about 20°C).

The instrumental calibration is known to be accurate to better than $\pm$ 2Å and the reproductibility of the measurements reported was better than $\pm$ 0.5Å. The fluorescence spectra were carried out on a modular equipment consisting of a 1000 W Hanovia Xe-Hg lamp, a Hilger Monospek 1000 excitation monochromator, a Perkin-Elmer E-1 emission monochromator, an EMI 9559 QB photomultiplier tube, and the amplifier, recorder, wavelenght drive and detector power supply from a Perkin-Elmer E-11 spectrophotometer.

Excitation of dilute ($<10^{-4}$M) solutions of triphenylene, with light of wavelength 2747 Å, leads to a UV fluorescence.

Triphenylene from Aldrich Chem. Co., was fractionally sublimated. The solvents, spectroscopic grade, Uvasol Merck, were used without further purification.

Results and Discussions

Triphenylene presents a high electronic symetry which would favour little preferential solvation from a molecular structure

point of view. The spectral solvent shifts of triphenylene have been studied in our Laboratory lately[4,8]. However, we have extended this last study to n-butanol and we have found that the spectral shift observed in solution of carbon tetrachloride respect to the n-butanol is large enough to measure the energy difference from the maximum absorption bands with good accuracy.

From the search model system point of view both solvent n-butanol and carbon tetrachloride are two interesting molecules due to their similar molecular volume; n-butanol and carbon tetrachloride under the sphericity assumption present a molecular radii of 3.32Å and 3.38Å respectively[9]. Furthermore the n-butanol/carbon tetrachloride mixtures had been largely studied in the past[5,6]. The solution volumes change have been found to be relatively small at 25°C never exceeding 0.14 cm^3/mole. Therefore, this mixture has been assumed to be an appropriate experimental model system.

In Table I the ^1A-^1B_b and ^1A-^1L_a electronic transition frequencies of n-butanol/carbon tetrachloride mixtures are presented. From Figure 1 a linear functionality between $\Delta\nu_M$ and Y is observed in agreement with the additive solvation energy scheme in the solvation shell of triphenylene.

On the other hand it is interesting to observe that the same effect is present in both (π,π^*) electronic transitions, in accordance with the assumed model characteristics.

The fluorescence spectral data presented in Table I corresponding to the ^1L_b-^1A transition show the same linear functionality as the absorption (Figure 2). Notwithstanding the fact that the ^1L_b excited electronic state is less sensitive to the solvent, the observed spectral shift permits us to show that preferential solvation in the excited state is similar to the ground electronic state.

From molecular interactions point of view this phenomenon is indicative of a dynamic molecular exchange between the solvent bulk and the solvation shell of triphenylene. However, in spite of the different interaction energy of the two solvent molecules, it can not be forgotten that the physical interaction is due to London interaction forces, and that the polarizability value of carbon tetrachloride is approximately 15% greater than n-butanol[10].

It is not easy to think that triphenylene generate any kind of specific interaction in solution. Some authors have postulated that

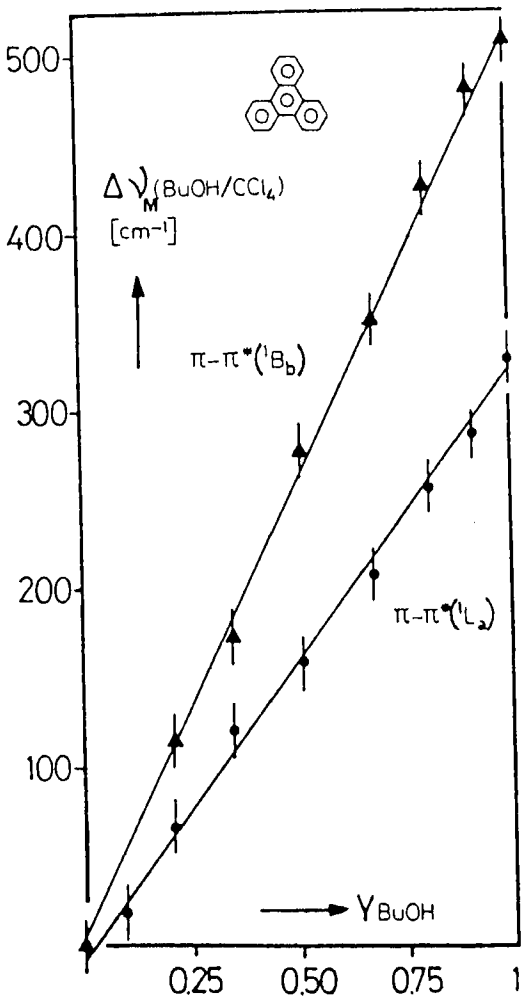

Figure 1.

The spectral shift of the absorption band maxima frequency of triphenylene in n-butanol (BuOH)/carbon tetrachloride mixtures ($\Delta\nu_M$) is plotted with respect to the molar fraction of n-butanol (Y_{BuOH}) in the bulk solvent.

Table I.

Frequencies of absorption and emission band maxima (cm^{-1}) of triphenylene in n-butanol (BuOH)/carbon tetrachloride mixtures (ν_M).

Y_{BuOH}	absorption		emission
	$\nu_M(^1L_a - ^1A)$	$\nu_M(^1B_b - ^1A)$	$\nu_M(^1A - ^1L_b)$
0	34796 ± 15	38275 ± 15	28159 ± 10
0.096	34812		28168
0.175			28180
0.209	34863	38389	28176
0.260			28190
0.346	34917	38448	
0.413			28208
0.514	34954	38552	28215
0.679	35003	38626	28224
0.808	35052	38701	28244
0.914	35083	38731	
1	35126	38784	28272

aromatic hydrocarbons could present a solvent hydrogen bond-π aromatic system interaction[10]. Whenever it is a weak molecular interaction and some mixture solvents could present this phenomenon.

Chloroform/methanol mixtures are very irregular solutions as can be seen from thermodynamical studies in solution[7]. The presence of the hydroxyl group in methanol give rise to the conventionally accepted view of a highly structurated solvent. Furthermore the large negative excess entropies of mixing over the greater part of the composition range are due to clustering of like molecules in a polymeric way, held together in chainfashion by transient hydrogen bonding.

The incorporation of a new phase to the mixture solvent, the solvation shell of triphenylene, should be a competitive way for methanol clustering formation. Hence, a kind of preferential solvation must occur which can be observed through triphenylene spectral shifts in methanol/chloroform mixtures.

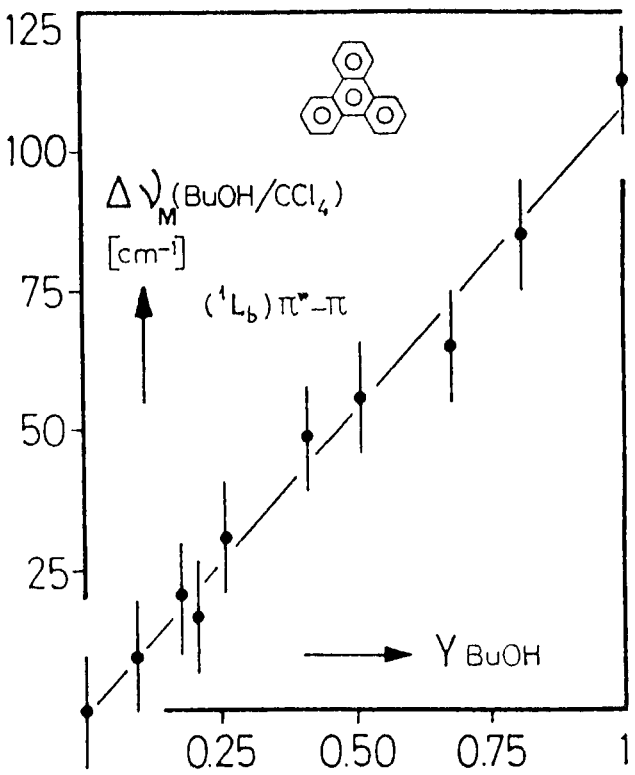

Figure 2.

Spectral shift of the emission (fluorescence) band maxima frequency of triphenylene in n-butanol (BuOH)/carbon tetrachloride mixtures ($\Delta\nu_M$) is plotted with respect to the molar fraction of n-butanol (Y_{BuOH}) in the bulk solvent.

Table II shows the absorption spectral data of triphenylene in this mixture and figure 3 shows a non linear dependence between $\Delta\nu_M$ and Y (methanol) in agreement with a preferential solvation effect. Chloroform would seem to present a better solvation pattern with respect to methanol, however this effect could be interpreted in terms of the methanol preference for remaining in the polymeric bulk solvent state rather than entering into the solvation shell of triphenylene.

The K value according to eq.1 can be estimated from Table II. The appropriate plots for solvent mixtures containing methanol with chloroform is presented in figure 4, where y_{MeOH} has been calculated

Table II.

Frequencies of absorption band maxima (cm^{-1}) of triphenylene in methanol (MeOH)/chloroform mixtures (ν_M) and molar fraction of methanol in the solvation shell (y_{MeOH}), of triphenylene.

y_{MeOH}	ν_M (^1B_b-^1A)	y_{MeOH}
0	38479 ± 15	0
0.050	38485	0.012
0.100	38492	0.026
0.250	38515	0.071
0.300	38530	0.100
0.400	38574	0.187
0.500	38612	0.261
0.600	38656	0.348
0.724	38754	0.540
0.800	38794	0.619
0.850	38847	0.723
0.900	38878	0.784
0.950	38935	0.896
0.975	38959	0.943
1	38988	1

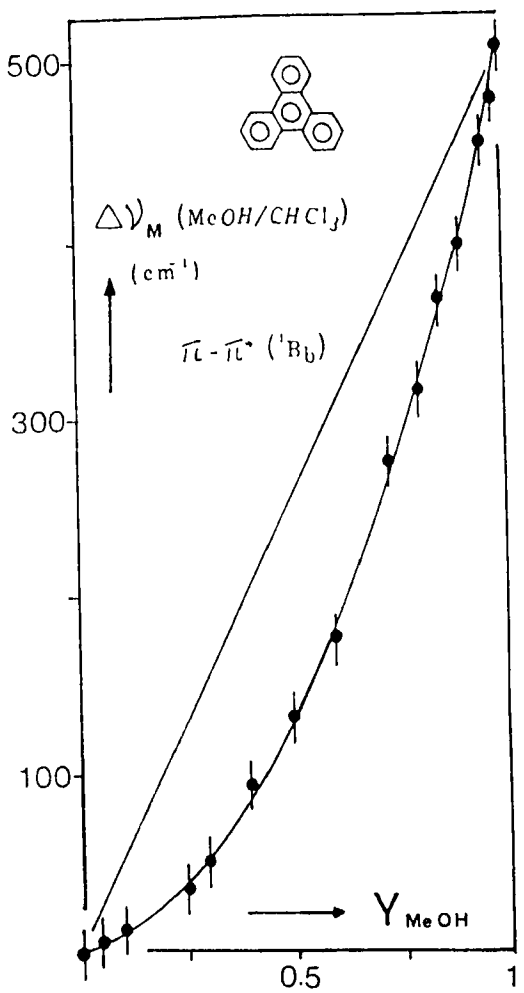

Figure 3.

Spectral shift of the absorption band maxima frequency of triphenylene in methanol/chloroform mixtures ($\Delta\nu_M$) is plotted with respect to the molar fraction of methanol (Y_{MeOH}) in the bulk solvent.

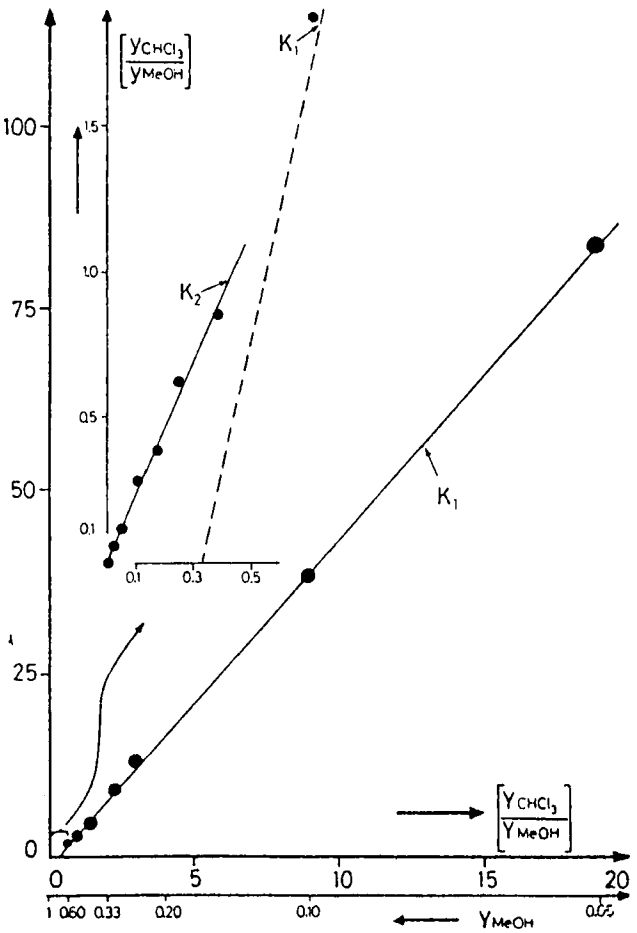

Figure 4.

The molar fraction ratio in the solvation shell of triphenylene (y_{CHCl_3}/y_{MeOH}) is plotted versus the bulk solvent composition (Y_{CHCl_3}/Y_{MeOH}). Two slope are found as a function of the molar fraction of methanol in the bulk solvent. $K_1 = 4.5$ ($Y_{MeOH} < 0.6$) and K_2 ($Y_{MeOH} > 0.6$).

through eq.4 from the $\Delta\nu_M/\Delta\nu$ ratio, and y_{CHCl_3} considering that $y_{CHCl_3} + y_{MeOH} = 1$.

This system shows some curvature near 0.6 molar fraction of methanol and therefore, two slope of lineal shape can be found, $K_1 = 4.5$ ($Y_{MeOH} < 0.6$) and $K_2 = 2.3$ ($Y_{MeOH} > 0.6$). This is probably due to cluster formation with chloroform participation in definite proportions[12] or it could also be due to a break down of the assumption of equal solvation numbers.

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9. $(3M/4\pi d)^{1/3}$, where M is the molecular weight and d is the liquid density at 25°C.
10. a. From London dispersion theory the interaction energy between two particles is given by

$$E = -\frac{\alpha_1\alpha_2}{r^6} \cdot \frac{I_1 \cdot I_2}{I_1+I_2}$$

where the polarizabilities (α) and ionization potentials (I) values for n-butanol and carbon tetrachloride are 8.78$\mathring{A}^3$ and 10.32$\mathring{A}^3$, and 10.09 eV and 11.47 eV, respectively.

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