Solvatación de dibenzotiofeno 5,5-dióxido en mezclas binarias de solventes

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Resumen

En este trabajo es presentado el estudio de la solvatación de Dibenzotiofeno 5,5-dióxido (DBTO2) en mezclas binarias de solventes conteniendo acetonitrilo como el componente polar. Esta molécula presenta un desplazamiento modesto de la banda electrónica $\pi-\pi*$ con la composición de la mezcla de disolventes. Se observó una dependencia no lineal para esta banda de absorción electrónica con la fracción molar de acetonitrilo. El desplazamiento inducido por el disolvente fue analizado usando diversas formulaciones para el campo de reacción de los solventes mezclados. El dieléctrico continuo fue especificado en términos de la constante dieléctrica ε y el índice de refracción h, y cálculos teóricos con AMSOL 6,8 con el modelo de carga clase IV fueron realizados. Únicamente en las mezclas de acetonitrilo/benceno, fue observada la solvatación preferencial por el componente polar. Los resultados experimentales y teóricos obtenidos sugieren que efectos de saturación dieléctrica de la polarización orientacional y auto-asociación del disolvente acetonitrilo fueron los factores dominantes en este sistema, por tanto, el desplazamiento solvatocrómico de **DBTO**2 puede ser explicado adecuadamente mediante la función de dipolaridad de Block-Walker.

Palabras clave: Dibenzotiofeno 5,5-dióxido, solvatocromismo, campo de reacción, solvatación preferencial.

Solvation of Dibenzothiophene 5,5-dioxide in Binary Solvent Mixtures

Abstract

In this paper the study of the solvation of Dibenzothiophene 5,5-dioxide (DBTO2) in binary mixtures of solvents containing acetonitrile as the polar component is presented. This molecule shows a modest shift of the electronic band $\pi-\pi*$ with solvent composition. Nonlinear dependence is observed for its electronic band with the molar fraction of acetonitrilo. The solvent-induced shift was analyzed using several model formulations for the reaction field of the solvent mixtures. The dielectric continuum is specified in terms of dielectric constant ε and refraction index η, and theoretical calculations with AMSOL 6.8 with charge class IV model. Only in the acetonitrile/benzene mixtures, preferential solvation by the polar component was observed. The experimental and theoretical results obtained suggest that dielectric saturation and self association of acetonitrile were the dominant effects in this system and the solvatochromic shift of DBTO2 can be adequately explained through Block-Walker function of polarity.

Key words: Dibenzothiophene 5,5-dioxide, solvatochromism, reaction field, preferential solvation.

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1. Introduction

Dibenzothiophenes are present in light oils which are removed by hydrodesulfurization process [1-4]. However, these compounds are little reactive under this process. In spite of this, in recent years, an oxidative desulfurization biphasic system (no polar solvent/acetonitrile) has received more attention because hindered dibenzothiophenes can be oxidized selectively to their corresponding sulphones as the major product. The oxidation proceeds in the acetonitrile phase while sulphones do not migrate into the n-octane phase [5, 6]. This behavior is controlled by various interactions of the solute with the two different solvent components. Therefore, the study of solvation of dibenzothiophene 5,5-dioxide (**DBTO2**) should be very important for the physico-chemical understanding of this reaction. In fact, in miscible binary system and aqueous/alkane interface, experimental evidence suggests that a dipolar solute may induce a change of composition in the solvation shell of solute molecules with respect to the bulk [7, 8, 9].

This phenomenon, termed preferential solvation, has long been used qualitatively to rationalize spectral measured shifts of probe molecules in mixed media. It affects the linear dependence on the solvent composition [10-14]. Preferential solvation commonly results from specific (e.g., Hydrogen-bonding) and nonspecific (dielectric enrichment) solute-solvent interactions [10-12, 15-20]. In the latter case, dielectric enrichment is derived by an increase of the concentration of the polar solvent component throughout the solvation sphere [10, 11, 13, 16]. The effect of this local polarity of solvent mixture on the electronic properties of solute in binary mixture are correlated with expressions obtained from continuum theories approximating the solute as a dipole immersed in a continuum dielectric and it is expressed in terms of Onsager-like functions [9, 10, 21, 22].

In spite of this, it was measured the electronic absorption spectra of dibenzothiophene 5,5 dioxide (**DBTO2**) in mixtures containing acetonitrile (**ACN**) paired with a cosolvent having a lower dielectric constant, namely tetrahydrofurane-**ACN**, dioxane-**ACN** and benzene-**ACN**. These results have been analyzed in terms of continuum functions changing solvent composition. In addition, theoretical calculations of standard-state free energy of solvation with the quantum mechanical self-consistent reaction field method (SM5.4P) included in version 6.8 of AMSOL package [23] were carried out.

2. Theory

Polarity of neat solvent and binary mixtures

The polarity of solvent is a measure of the electric field induced inside a solute cavity. In terms of reaction field theories is defined as a function *f* of the bulk dielectric constant e and refractive index h. Several continuum functions $f(\varepsilon, \eta)^{2}$ have been stated in terms of the Born, Onsager, McRae, Brady-Carr, London, Bekarek-Kolling electrostatic models and unhomogeneous function of Block-Walker (Table 1) [24]. Fundamental of this, is the connection between the energy of solvation and reaction field and the permanent dipole moment for the rigid dipolar molecule (solute) as the general statement in equation 1.

$$E_{SOLV} = -\frac{\mu}{2} E_R \qquad (1)$$

and by following Kolling´s procedure; a generalized expression for reaction field function can be stated in the expression of the solute-solvent interaction energy as [24, 25]:

$$E_R = \left(\frac{\mu}{a^3}\right)\int\left(\varepsilon, \eta^2\right) \qquad (2)$$

Here, a is the molecular radius of solute. In the case of a binary mixture of polar χ_p and nonpolar χ_n solvents, is expected to hold a linear function of the molar fraction of the polar component χ_p,

$$\int\left(\varepsilon, \eta^2\right) = \int\left(\varepsilon_{n,} \eta_n^2\right)\chi_n + \int\left(\varepsilon_p, \eta_p^{2\,2}\right)\chi_p \qquad (3)$$

But, in general, binary mixtures are not ideal and $f(\varepsilon, \eta^{2})$ should be calculated from experimental values and for solvent mixtures [20, 26-30].

The molecular dielectric theory predicts that solvatochromic shifts of the absorption spectra for a dipolar molecule in homogeneous mixture of solvents with different polarity should be proportional to $f(\varepsilon, \eta^{2})$ [10, 11, 13,16, 31-33]. Therefore, Suppan used the Onsager and Debye functions in dielectric constant for descriptors of polarity and Kolling considered other functions in both, index of refraction and static dielectric constant [10, 18] However, nonlinear relationships between the solvatochromic shifts of absorption spectra of organic solutes and the Onsager and Debye functions of solvent polarity was observed experimentally [16, 33-35]. But in contrast, a linear relation has been found between solvent-induced shift of the electronic band of solute and Onsager function in liquid-liquid interfaces [9]. However, the deviation observed in absence of specific interaction is generally attributed to the immediate group of dipolar solute. The polarity differs from the bulk mixture. Then, for dielectric mixtures the total solute-solvent energy in the single shell approximation is

$$E_{r} = \frac{\mu^{2}}{2a^{3}} \int(\varepsilon, \eta^{2})_{\mathrm{eff}}, \quad (4)$$

$$\int(\varepsilon, \eta^{2})_{\mathit{eff}} = \int\left(\varepsilon_{n}, \eta_{n}^{2}\right) + \left(1 + \frac{\chi_{p}}{\chi_{n}} e^{-2}\right)^{-1} \Delta\int(\varepsilon, \eta^{2})n, p, \quad (5)$$

where $f(\varepsilon, \eta^{2})_{\mathit{eff}}$ is the effective local polarity of solvent mixture in the near vicinity of the dipolar solute, $\mathrm{D}f(\varepsilon, \eta^{2})_{n,p}$ is the difference of the polarity function of pure polar $(\chi_{p} = 1)$ and pure nonpolar solvents $(\chi_{p} = 0)$ and, Z is a preferential solvation index.

Recently, Kauffman et al. have compared different methods of approximation of the index of preferential solvation based on experimental data and its equation [17]. The effective local polarity is a microscopic electrostatic property whereas $f(\varepsilon, \eta^{2})$ represents the polarity in the bulk solution and can be analyzed in terms of the dipolarity-polarizability of the solvent (Table 1).

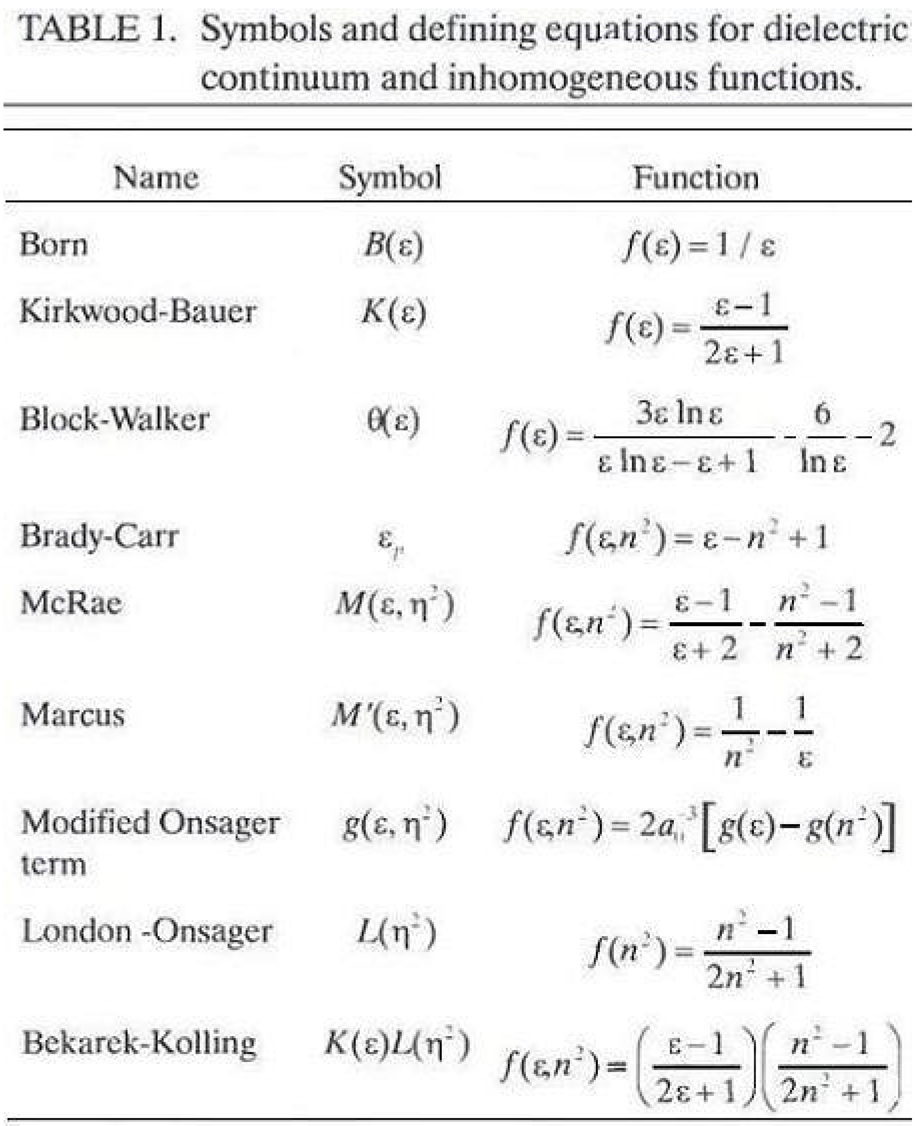

TABLE 1. Symbols and defining equations for dielectric continuum and inhomogeneous functions.

Name	Symbol	Function
Born	$B(\varepsilon)$	$f(\varepsilon) = 1/\varepsilon$
Kirkwood-Bauer	$K(\varepsilon)$	$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1}$
Block-Walker	$\theta(\varepsilon)$	$f(\varepsilon) = \frac{3\varepsilon \ln \varepsilon}{\varepsilon \ln \varepsilon - \varepsilon + 1} - \frac{6}{\ln \varepsilon} - 2$
Brady-Carr	ε_p	$f(\varepsilon, n^2) = \varepsilon - n^2 + 1$
McRae	$M(\varepsilon, \eta^2)$	$f(\varepsilon, n^2) = \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}$
Marcus	$M'(\varepsilon, \eta^2)$	$f(\varepsilon, n^2) = \frac{1}{n^2} - \frac{1}{\varepsilon}$
Modified Onsager term	$g(\varepsilon, \eta^2)$	$f(\varepsilon, n^2) = 2a_0^{-3}\left[g(\varepsilon) - g(n^2)\right]$
London -Onsager	$L(\eta^2)$	$f(n^2) = \frac{n^2 - 1}{2n^2 + 1}$
Bekarek-Kolling	$K(\varepsilon)L(\eta^2)$	$f(\varepsilon, n^2) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right)\left(\frac{n^2 - 1}{2n^2 + 1}\right)$

A comparative study between these alternative functions for the reaction field [36, 37] and the E_r values obtained from the maximum of the spectrum at each solvent composition, should be useful to set up the electrostatic effect as dominant upon electronic spectra of solute in binary mixtures.

Theoretical Solvation Model of Solvation

The free energy of solvation in SM5.4 model is written as [38, 39]

$$DG^{0} = DG_{ENP} + DG_{CDS} \quad (6)$$

where DG_{ENP} is the contribution of the electronic-nuclear-polarization of solute and it includes the change in the electronic and nuclear internal energy of solute and the electric polarization free energy of the solute-solvent system upon insertion of the solute in the solvent. DG_{CDS} is the contribution of first-solvation-shell effects to the standard-state free energy of transfer (cavitation-dispersion solvent-structure) [38-40]. The first contribution is called the electrostatic term and is written as

$$DG_{ENP} = DE_{EN} + G_p \ , \qquad (7)$$

where the first contribution is the electronic and nuclear energy of the solute in going from the gas phase to solution, and the second term is the polarization free energy and has the form [41].

$$G_p = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{k,k} \mathrm{q}k\mathrm{q}k\left(r_{kk}^2 + \alpha_k\alpha_k, \exp\left[-\frac{r_{kk}^2}{d_{kk,}\alpha_k\alpha_k}\right]\right)^{-\frac{1}{2}} \qquad (8)$$

where $r_{kk'}$ is the interatomic distance between atoms k and k', α_κ is an effective atomic radius for atom k in the electrostatic part of the calculation and will be called a coulomb radius and $d_{kk'}$ is an empirically optimized constant [39].

The Standard-state free energy in solution is approximated as

$$G\frac{0}{s} = E_{(g)} + \Delta G\frac{0}{s} \qquad (9)$$

where $E_{(g)}$ is the Born-Oppenheimer solute energy in the gas phase, the quantum mechanical self-consistent reaction field treatment used for this step and all parameters for the polarization free energy in the SM5.4 model is based on several previous references [38-41]. The hamiltonian solute is modeled using NNDO molecular orbital theory (AM1 and PM3) with class IV atomic charges from the CM1A and CM1P charge models [39]. The contribution of first-solvation-shell term is written as

$$\mathrm{G}_{CDS} = \sum_k \alpha_k A_k\left(R_s^{CD}\right) + \bar{\sigma}^{CS}\sum_k A_k\left(R_s^{CS}\right) \qquad (10)$$

where k denotes an atom, $A_k(R)$ is the solvent-accessible surface area of atom k calculated with solvent radius R, R_S^{CD} is the short-range effective solvent radius, σ_k is the microscopic surface tension of atom k, σ^{CS} is the intermediate-range molecular surface tension, and R_S^{CD} is the intermediate-range effective solvent radius [39].

The functional forms used for the solute-geometry dependence and solvent-property dependence of σ_k and σ respectively, were previously described by Truhlar and Cramers's group [42]. The atomic surface tensions σ_k depend on the solute geometry, the hydrogen-bonding acidity (α), the hydrogen-bonding basicity (b), and the index of refraction (h) of the solvent [23].

3. Methodology

Dibenzotiophene 5,5-dioxide (**DBTO2**) (97%) was purchased from Aldrich and was dissolved in acetonitrile (**ACN**) and activated carbon was added to the mix, the suspension was heated and stirred for 2h. Then, the product was quickly filtrated and collected by crystallization from this solution. The solvents were rigorously dried and fractionally distilled by standard methods and storage over molecular sieve. The spectra were recorded on a Shimadzu UV-1201 spectrophotometer. The concentrations of **DBTO2** varied within $2.78 \cdot 10^{-4} - 3.1 \cdot 10^{-4}$ M and the pathlength used was 1 cm. The UV cutt-off point of the solvents in a UVcell of 10 mm against air was used as purity criterium. ν_{max} was measured by taking the middle point between the two positions of the band where the absorbance was equal to 0.90 [43]. The details of the experimental technique for measurement of refractive index of the mixtures have been described in previous works [44-46].

The calculations of free energy of solvation of **DBTO2** in tetrahydrofuran (THF), acetonitrile (ACN), p-dioxane (Diox), and Benzene (BZ) were performed with version 6.8 AMSOL code program package [47]. The optimization of **DBTO2** molecular geometry was carried out following of procedure into the SM5.4P method using PM3 halmitonian.

4. Results and discussion

In spite of **DBTO2** is a molecule with high ground state dipole moment of 5.03D [48] their electronic spectra do not show solvatochromic shifts. However, the frequencies of the second UV absorption band $(\pi - \pi^*$ band) are modestly solvent sensitive and show blue shifts in polar solvents. In the binary mixture case, this absorption band shifts to the blue is observed with increasing concentration of a polar component in solvent mixtures. The blue shifts can be observed already at very small concentrations of acetonitrile (Figure 1). The absorbance of **DBTO2** in *p*-dioxane is at 99.34 Kcal/mol, while in THF, benzene and acetonitrile is at 99.30, 99.06 and 99.81 Kcal/mol, respectively. In fact, the spectras showed that the blue shifts of the absorption band of DBTO2 in all mixtures were not a linear function of the concentration χ_p of acetonitrile solvent (Figure 1). When binary mixture comprises ACN + THF and ACN + Diox, preferential solvation by THF and Diox was observed in each case. This reflects the fact that the self-association of ACN is dominating even through the regions rich of Diox and THF, allowing to free molecules of solvent of low polarity (Diox and THF) to solvate the DBTO2 molecules (Figure 1b).

Furthermore, the theoretical values obtained in this work with SM5.4P model for the free energy of solvation of ACN in Diox and THF were 23.08 and 19.76 Kcal respectively; these results reveal that the process is not spontaneous, and that clustering process of ACN is energetically favored. This permits that the THF and Diox molecules to be near to the **DBTO2** molecule [27, 49, 50]. On the other hand, the values of the free energy of solvation of **DBTO2** in each solvent demonstrate that it is a very favorable process and this has relation with the blue shifts of the electronic band in this pure solvent (Figure 1).

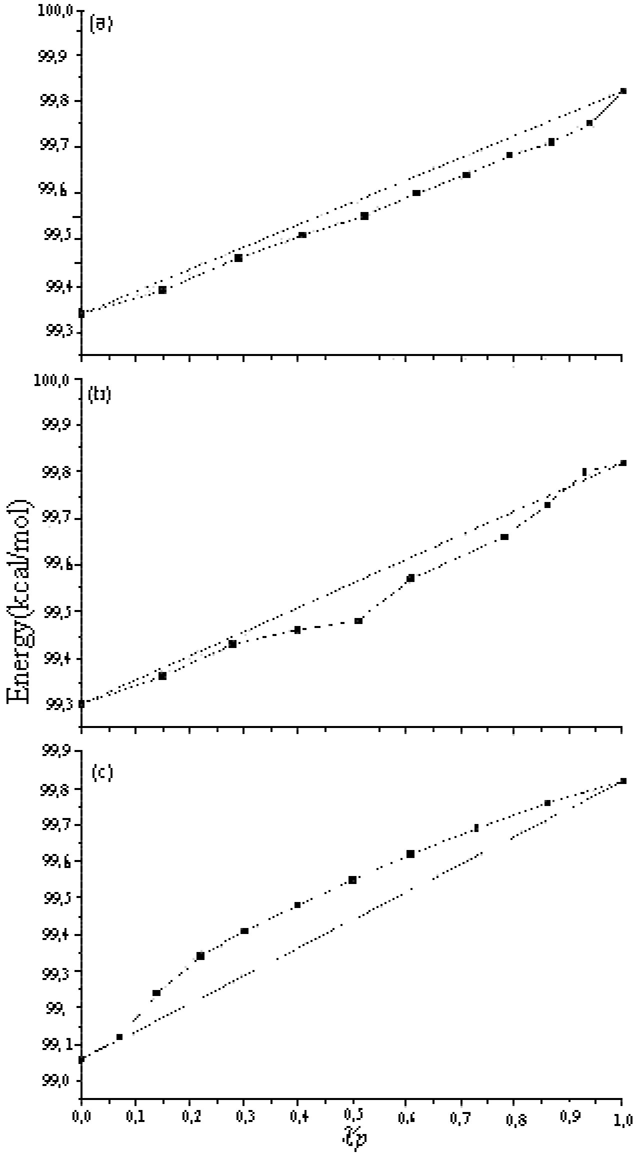

Figure 1. Plot of the bot **DBTO2** electronic absorption band energy of as a function of acetonitrile mole fraction (χ_n)in (a)

p-dioxane-ACN (b) THF-ACN and (c) benzene-ACN mixtures

In fact, the values of free energy of solvation of **DBTO2** in ACN, THF and benzene (-21.51, -20.30 and 16.97 Kcal, respectively), are expected; however, the magnitude of the free energy of solvation of solute in Diox solvent (-15.80 Kcal) and transition energy of electronic band have an anomalous behavior. Theses results can be explained in terms of the model of conformation polarization of the solvent. The effective polarity of Diox in cybotatic region of DBTO2 was greater than expected, when it was considered only its low dielectric constant [10]. It is clear, from this results, that the scarce contribution of solvent-solvent thermodynamic interactions is a crucial factor in theses mixtures because the preferential solvation of **DBTO2** occurs for low polarity solvents.

For benzene-ACN mixtures, a preferential dielectric solvation of **ACN** was observed when solvatochromic shifts were analyzed in function of the molar fraction, as mixture polarity parameter, and in this case, only, the Suppan model can be applied. However, this parameter is not known as a good measure of bulk solvent polarity [16]. Because of this, solvatochromic shifts of the absorption band of **DBTO2** in this mixture was analyzed as a function of $f(\varepsilon)$ or $f(\varepsilon, h^2)$ instead of molar fraction χ_p of **ACN** solvent.

The values of η were measured for each Bz/ACN mixture and the data of dielectric constant were taken from the literature [27]. The single variable functions in dielectric permittivity ε or refractive index η such as Born $B(\varepsilon)$, Kirkwood-Bauer KB and London L (h^2) used in this work can be seen in Table 1. These dielectric continuum models assume that the nonpolarizable dipolar solute is located in a solvent cavity a and the energy of the dipolar solute-dipolar solvent interaction is determined under the condition of an electrostatic equilibrium [37]. In Figure 2a, the transition energy E_r values of DBTO2 are plotted against the reciprocity of the dielectric constant (Born model) of Bz/ACN mixtures, showing a nonlinear decreasing of E_r with increasing ACN, this result indicated that this electrostatic model is inadequate to explain the variation of E_r values in this dielectric medium.

This result was tested by applying the function of Kirkwood-Bauer $KB(\varepsilon)$, reaction field parameter (Figure 2b), Nonlinear behavior has also been observed earlier [34, 35, 51]. However, for London function a linear dependence was observed, although this disappears completely up to the $L(\eta^2)$= 0.213, which corresponded to a composition higher than 78% in ACN. It evidences the influence of the polarizability-hiperpolarizability of the solvent species upon the solvation energy of DBTO2, consequently, it become necessary to explore other function that incorporate this factor.

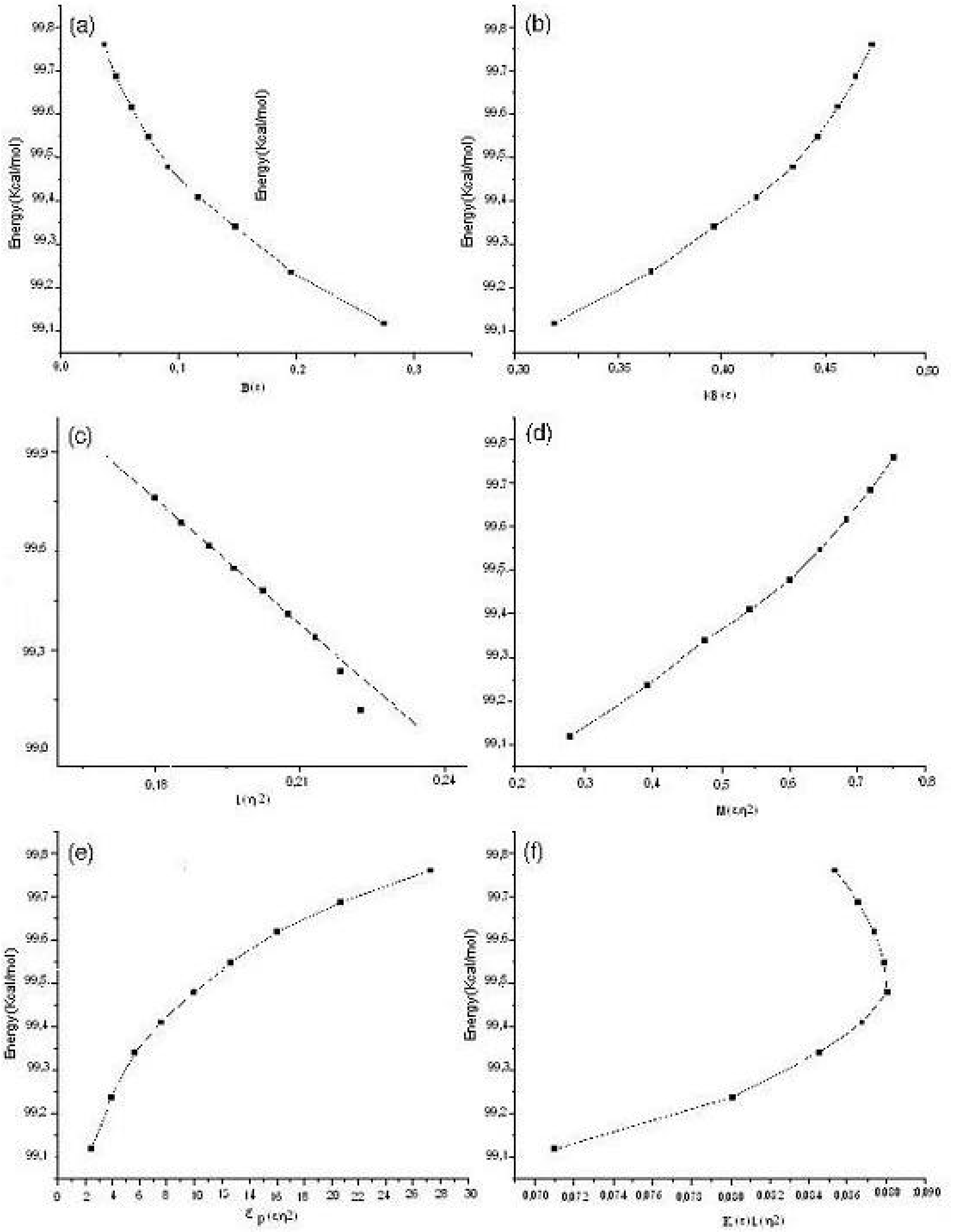

Figure 2. Trends for the **DBTO2** electronic absorption band energy witth especific $f(\varepsilon, \eta^2)$ functions, (a) Born, (b)Kirkwood-Bauer, (c) London, (d)McRae, (e) Brady-Carr and (f) Bekared -Kolling

The two-variable continuum functions shown in Table 1 incorporate separate terms for solvent dipolarity and polarizability with respect to bulk parameters, η and ε, these functions are generally derived from the modified Onsager dipolar term $g(\varepsilon, \eta^2)$ and its simplest form is represented by the McRae function $M(\varepsilon, \eta^2)$ [36], when teste with the data of this work by **DBTO2**, a nonlinear trend was observed (Figure 2d) and equal trends were obtained with the other alternated form by coupling between the contributions from mixture of solvent dipolarity and polarizability ε_p (Figure 2e) and $M(\varepsilon, \eta^2)$ (this figure is not shown by simplicity). In another way, it is also clear that this coupling between these contributions can assume other alternated forms, for example, if the reaction field model function (ε, η^2) is modified to consider the solvent polarity-hyperpolarizability component, this function assumes the form of a cross term correction followed by the Bekarek-Kolling function $K(\varepsilon)\, L(\eta^2$) behavior was observed with this function (Figure 2f).

It is clear from the figure that the contribution of orientational polarization of acetonitrile solvent becomes very much lower than expected by varying the composition of the binary mixture, then, a condition of dielectric saturation is possibly reached. However, all theses functions of polarity show a nonlinear trend with molar fraction (nonideal behavior) and then the relationship 3 is not adequate with function of polarity, which is consistent with microheterogeneity promoted by stronger dipole-dipole association of ACN molecules. The application of the concept of polarity in this binary solvent mixtures is hard to use in this case [52].

In contrast, recently Steel and Walker, reported a correlation of UV excitation maxima of phenols derivatives with Onsager polar function at an nonhomogeneous medium (aqueous/alkane interface). In spite of this, the more adequate definition of polarity is when a measure of the induced electric field inside a solute cavity is considered. It depends on the size of the solute and solvent dipoles, as well as solvent dipolarity-hiperpolarizability properties. Dielectric models mentioned above have been constructed on the assumption that the dielectric properties outside the cavity were homogeneous [9]. However, nonuniformity of dielectric properties can be induced by strong nonlinear electrostatic interactions between the solute and the solvent and saturation of the orientational polarization can become significant (Figure 2f) and reduces the local permittivity. It is favored in this case, because, **DBTO2** has two sites of interaction (aromatic ring and sulfone group) with very different local distribution of charge in from of ACN and Bz molecules [53].

The Block-Walker model differs from all dielectric functions showed in Table 1, because it requires a dielectrically saturated reaction field as an integral part of the permittivity-distance profile for the dipolar field sensed by the polar solute [37]. Plot of the electronic absorption band for DBTO2 as a function of the Block-Walker $\theta(\varepsilon)$ reaction field can be seen in Figure 3. The plot for each solvent composition ACN/Bz did not deviate from the most probable straight line in spite of the experimental error (regression coefficients $\geq$ 0.99) when only the benzene pure data were remove from *this regression,* indicating that dielectric saturation is responsible for the p-p * electronic transition of band shift of **DBTO2** in ACN/Bz mixtures and then the Block-Walker function of polarity is adequate for describing the effective polarity $f(\varepsilon, \eta^2)$ (see equation 4a). Furthermore, the plot of E_r vs $\theta(\varepsilon)$ permits to estimate the ground state dipole moment of **DBTO2** as 5.11D in this medium from the straight line slope and the molecules cavity radius (3.73Å) which were calculated following the method suggested Prabhumirashi, approximating the molecular shape to an ellipsoid [54]. This value is in excellent concordance with the result reported in the literature for DBTO2 in benzene (5.03D) [48].

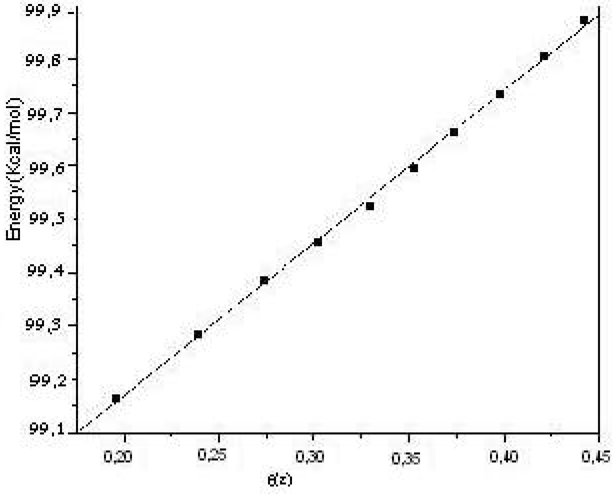

Figure 3. Trend for the energy of electronic absorption band of the DBTO2 with q(e) Block-Walker function.

Conclusions

The solvation of **DBTO2** in binary mixtures can be rationalized in terms of the dielectric perturbation model proposed by Kolling and modest solvatochromic shift of the absorption spectra observed is influenced by solvent dipolarity and polarizability in binary mixtures. For the mixtures studied in this work, solvent polarity function $f(\varepsilon, \eta^2)$ is not a linear function of molar fraction c_p of polar component (acetonitrile). Only in the mixture of acetonitrile/benzene preferential solvation by the more polar component was observed. Therefore, the solvatochromic shifts of solute were analyzed as a function of different kind of $f(\varepsilon, \eta 2)$ instead of χ_p. For all the dielectric continuum functions tested, there is evidence that the preferential solvation phenomenon observed in acetonitrile-benzene mixtures are reasonably well described by the dielectrically saturable Block and Walker reaction field, and then the polarity of the solvent mixture is determined by the DBTO2 molecule in its direct vicinity where the orientation polarization of acetonitrile solvent is subject to stronger saturation effects.

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*Autor para la correspondencia.

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