DFT theoretical studies of UV–Vis spectra and solvent effects in olefin polymerization catalysts

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Abstract

DFT theoretical studies of UV–Vis spectra and solvent effects on Cp_2ZrCl_2/MAO metallocenic system were performed. The excitation energies have been predicted using the time-dependent density functional theory. Calculations of solvation energies, in the dissociative reaction of metallocenic ion-pair, were performed using two approaches of the self-consistent reaction field theory. One is the Onsager model, with a simple spherical cavity, and the other is a polarized continuum solvation model with overlapping spheres. Results are consistent with experiments previously reported.
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1. Introduction

Metallocene-based catalysts of IV group are particularly used to produce a wide variety of polymers with narrow molecular weight distribution, which can be useful for different applications. This new catalyst generation is constituted by a metallocene L_2MtX_2 (L = π-ligand; Mt = Ti, Zr Hf; X = halogen or alkylic group) and a co-catalyst with Lewis acid nature (as MAO-methylaluminoxane) [1]. The acidity of co-catalyst is the most important factor of the cationic active site formation. It is widely accepted that the resulting cationic L_2MtR^+ (R = alkylic group) species plays a fundamental role on the polymerization mechanism, but the chemical structure of the active sites is still a subject of controversy. The different proposed models for the catalytically active species comprise contact ion-pairs as well as isolated cationic species [2,3].

Recently, it was possible to study within the density functional theory (DFT) formalism both the atomic and the electronic structure of these active sites, particularly including the presence of a MAO co-catalyst [4]. Moreover, the influence of an additive modifying the Lewis acidic properties of co-catalyst has been considered [5].

Several investigations using Ultraviolet–Visible (UV–Vis) spectroscopy have been carried out in the past to study the metallocene/MAO interaction at different molar ratios $[Al_{MAO}]$:[Zr] [6,7]. This interaction was evaluated through the changes of the ligand-to-metal charge transfer (LMCT) band, which is related to the transport of an electron from the HOMO of cyclopentadienyl ligand to the metal LUMO. Some results of metallocene/MAO systems showed significant changes in the LMCT bands with the addition of a catalyst modifier ($AlCl_3$) [8,9]. The theoretical analysis and predictions related to the LMCT band position was firstly performed using EHMO methods. More recently the DFT methods have been successful to determine with reasonably accuracy the properties of the fundamental

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and first excited electronic states of these systems. The obtained DFT results have been used as prediction and interpretation tools of UV–Vis spectra for different systems [10]. However, the implementation of these theoretical methods on metallocenic systems is very recent. In such calculations the active sites were modeled merely as isolated cations [11,12].

On the other hand, the polymerization reactions with homogeneous metallocenic catalysts need a solvent medium to take place. For this reason, the presence of solvent is a fundamental component for the active sites formation. Indeed, previous experimental results indicated that the catalytic system performance could be modified by changing the solvent medium [13,14]. Kinetics and thermodynamic studies performed on the $(1,2\text{-}Me_2C_5H_3)_2\ MtCH_3^+CH_3B(C_6F_5)^-$ (Mt = Zr, Hf) catalytic system showed significant variations of both the association and dissociation reaction rate constants of the ion-pair when the transition metal and solvent were changed [15,16]. With more polar solvents as chlorobenzene and dichloromethane the dissociation/association constant ratio increases, suggesting the solvent assistance to attain a higher ion-pair separation.

The properties of molecules and transition states can differ considerably between the gas-phase and solution. At the present the DFT methods are able to treat the quantum chemical problem of complex molecular systems. Nevertheless, it is still hard to carry out these kinds of calculations including at least a limited number of solvent molecules. In the last years some computational formalisms, which simulate the solvent effect, have been developed. One kind of them is that named as self-consistent reaction field (SCRF), which are useful to describe the macroscopic effect of the solvent. It is well known that the theoretical results in the absence of solvent molecules conclude that the ion-pair dissociation in gas-phase is a highly endothermic process (~100 kcal/mol) [4,17]. An important question to answer is the influence of solvent on this result.

The aim of this Letter is to extend previously DFT calculations for the Cp_2ZrCl_2/MAO y $Cp_2ZrCl_2/MAO*AlCl_3$ systems in order to predict UV–Vis spectra, specially the influence of MAO and MAO*AlCl_3 on LMCT zirconocene bands. Furthermore, the energetic changes in the ion-pair dissociation when the solvent is included in the theoretical model were considered. In particular, the solvation energies of the active catalytic species were obtained using two different solvents.

2. Computational details

Using the time-dependent DFT method (TD-DFT) it is possible to evaluated vertical electronic excitation spectra. The capability of TD-DFT approach with hybrid functionals (B3LYP) has been successfully used

in the past to calculate the electronic spectra of several systems [18,19]. This method provides excitation energy values of reasonably accuracy, allowing to assign its changes due to molecular geometry or moderated chemical modifications.

The theoretical calculations of solvation energies for the species involved in the dissociative ion-pair reaction have been performed using two different techniques, both in the framework of the self-consistent reaction field theory (SCRF) [20]. These methods consider the solvent as a continuum of uniform dielectric constant ϵ. The first, named the Onsager model (ONS) [21,22] places the molecule within a fixed spherical cavity. The second one, named as the polarized continuum solvation model (PCM), defines the cavity as the union of overlapping spheres [23,24].

The solvation effect on the dissociative reaction of the ion-pair was evaluated for two different solvents: toluene and dichloromethane, which were represented by their dielectric constants, with $\epsilon = 2.379$ and 8.930 values, respectively. The following equations express the equilibrium between the ionic isolated species and the active sites, and its total energy balance ΔE:

$$cation + anion \leftrightarrow ion\text{-}pair,$$
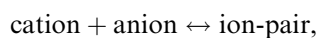
$$\Delta E = E_T(ion\text{-}pair) - E_T(cation) - E_T(anion),$$

where: cation = $Cp_2ZrCH_3^+$, anion = $MAO\text{–}CH_3Cl^-$, ion-pair = $Cp_2ZrCH_3^+ \cdots MAO\text{–}CH_3Cl^-$.

Theoretical studies of excited electronic states and the solvent effect in the ion-pair dissociation were performed using the active sites models previously studied [4]. Two types of active sites were studied with different geometrical configurations: *Site* 1, where the Zr atom has its nearest interaction with the central O* atom of the counterion, and *Site* 2, where the interaction is established through a chlorine bridge (Fig. 1). In case of sites modified with AlCl_3, the additive resides over a lateral oxygen atom of counterion for *Site* 1 and over the central O* atom for *Site* 2 [5].

The DFT calculations were performed by using the hybrid functional which mixes the Lee et al. [25] functional for the correlation part and Becke's three-parameter functional for the exchange (B3LYP), as its implemented in the GAUSSIAN 98 program [26]. Different basis sets were employed, according to the type of result we are interested. In the study of solvent effect the 3-21G(d,p) basis set was used for C, H, O, Al and Cl atoms, a 3-21G basis for the valence orbitals of the Zr atom and an effective core potential basis set LanL2DZ for the inner orbitals of this atom. For comparison purposes additional calculations with 3-21G(d,p) basis set for all the atoms were included. In this case the results were obtained from single-point computations using the optimized geometries corresponding to the smaller basis of the Zr atom. Comple-
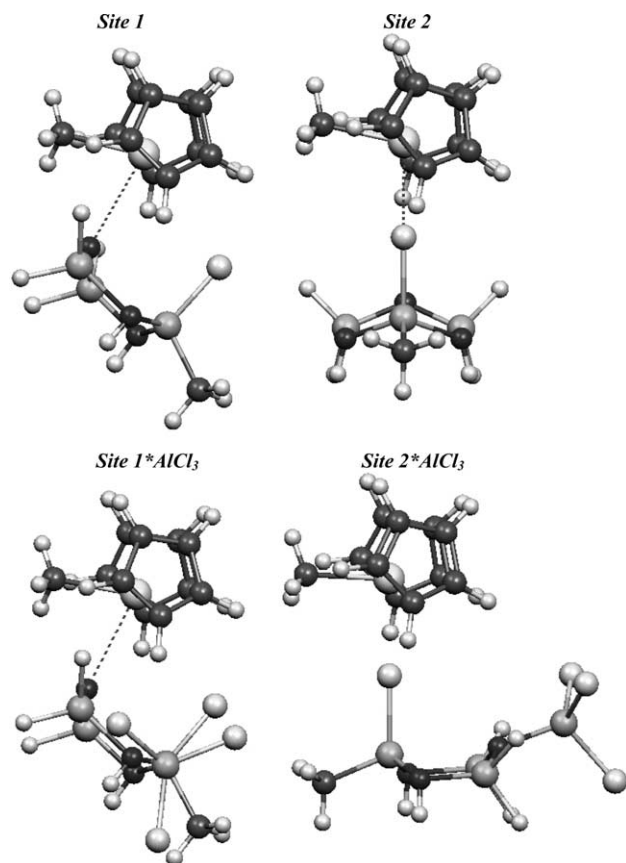
Fig. 1. Optimized model of *Site* 1 and *Site* 2 and AlCl$_3$, respectively, counterparts.

rate diffuse and polarization functions for all the atoms excepting the Zr atom. This type of basis set includes diffuse functions, essentially to obtain a reasonably accuracy for the excited state properties [20]. For the Zr atom the LanL2DZ and 3-21G basis sets were used. In all these cases, the TD-DFT single-point studies were performed using the optimized geometries obtained with the 3-21G(d,p) basis set.

3. Results and discussion

3.1. The UV–Vis spectrum

The excited electron states of Cp$_2$ZrCl$_2$/MAO system, with and without the additive AlCl$_3$, were studied by means of the TD-DFT method. The excitation energies from the ground state, their values expressed as optical maximum wavelengths λ_{max} and the corresponding oscillator strengths f are summarized in Table 1. The theoretical UV–Vis spectra were simulated with gaussian functions centered on λ_{max}, being the area proportional to f (Fig. 2). The calculated oscillator strengths should be proportional to the intensities of absorption

mentary calculations where the cation–anion distance was optimized were performed in order to show the influence of the solvent on this distance and on the stability of the system.

In case of TD-DFT calculations the gaussian basis sets were extended to the 6-31++G(d,p), which incorpo-

Table 1
Excitation energies of ligand to metal charge transfer for Cp$_2$ZrCl$_2$, *Site* 1 and *Site* 2 with and without AlCl$_3$

Species	$\lambda_{max.}$ (nm)	Energy (eV)	f	q[Zr] (e)
Cp$_2$ZrCl$_2$	316.34	3.92	0.0451	1.56
Site 1	332.08	3.73	0.0245	1.79
Site 1*AlCl$_3$	336.71	3.68	0.0208	1.81
Site 2	329.20	3.77	0.0221	1.71
Site 2*AlCl$_3$	331.13	3.74	0.0198	1.74

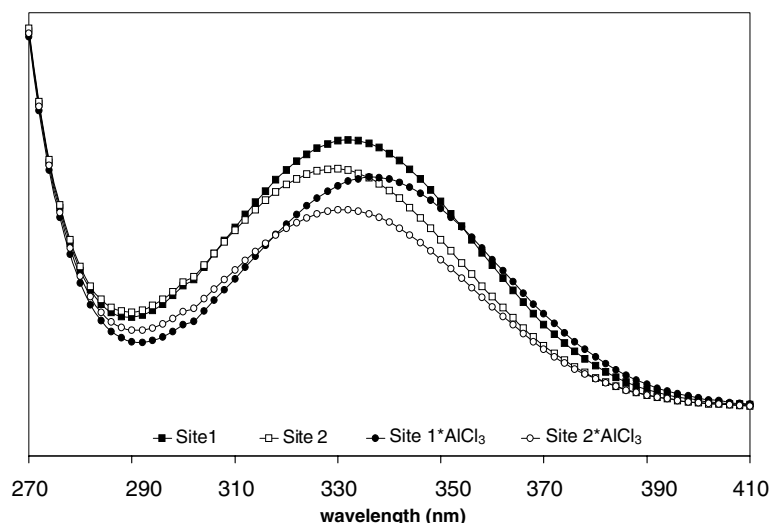The NBO charge of zirconium atom q[Zr] is also reported.

Fig. 2. Simulated UV–Vis absorption spectra of *Site* 1 and *Site* 2 with and without AlCl$_3$ additive.

bands and can be related to ligand-to-metal charge transfers.

Experimental shifts of λ_{max} were reported for several L_2MtX_2 (X = alkyl group, halogen) metallocenes when the type of σ-ligand is modified. The analysis of these results indicated that the electron-withdrawing effect of the σ-ligands was the reason of the λ_{max} increase [11]. In case of the Cp_2ZrCl_2 zirconocene a LMCT absorption band at 316 nm was obtained. This value is in satisfactory agreement with experimental results reported by other authors for Cp_2ZrCl_2 in different solvents (332 nm) [27,28]. An important bathochromic change (by 5%) occurs when the LMCT band for dichloride zirconocene is compared with that for the active sites formed as ion-pairs $Cp_2ZrCH_3^+ \cdots MAO–CH_3Cl^-$ (Table 1). The LMCT band for the latter species shifts to higher wavelengths. This result corresponds to a less energetic electron transition due to the counterion acting as electron-withdrawing ligand in the active sites. Notice that in this case the methylated zirconocene has a net positive charge with a higher positive value in the metal atom. On the other hand, the oscillator strengths for both active sites show a large decrease. This is in qualitative agreement with the experimental results obtained when the molar ratio [Al]:[Zr] is high [8,9,29].

Once the ion-pairs are formed, the $AlCl_3$ addition generates in comparison with the sites without additive slightly shifts in wavelengths and significant decreases in the intensities of the bands (Table 1). The theoretical results of the LMCT intensities with the addition of $AlCl_3$ are shown in Fig. 2. The reduction of LMCT intensities is associated with a lower charge transfer from π-ligand to Zr atom due to the localization of π-electrons on the cyclopentadienyl rings [29]. The same behavior was observed experimentally in zirconocene catalysts with different [Al]:[Zr] molar ratios [8,29]. Notice that the addition of $AlCl_3$ acts in the same way as the presence of higher MAO concentrations. Obviously the [Al]:[Zr] molar ratios (values of 2000 and higher) present in experiments are very difficult to be modeled. Nevertheless, our calculations show the same trend than those for large [Al]:[Zr] molar ratios.

3.2. The solvent effect

Usually the theoretical studies of metallocenic systems are performed in gas-phase. Recently several systems have been evaluated using appropriated models to describe the solvent effect. The solvent normally modifies the energy or the conformational barriers of a particular reaction. Thus, a greater reaction rate can be achieved by lowering the energy of the transition state, or alternatively, by increasing the energy of the reactants. In this work the effect of two solvents with different dielectric constant values, toluene and dichloromethane, was evaluated. On the other hand, two different approaches have been considered to represent the solvent and, in each case, the influence of the basis set was also studied.

The values of total energies for both active sites calculated with different models and basis sets are summarized in Table 2. The results obtained for the ion-pair dissociation in gas-phase showed the endothermicity of the process. Next, we considered the influence of solvent when it is included in the single-point calculations for the optimized geometries of active sites. In almost all the situations the application of solvent model makes the reaction less endothermic. In case of ONS approach, *Site* 1 and *Site* 2 have very similar dissociation energy values for both solvents with respect to the gas phase results. On the other hand, the PCM formalism gives the same tend for the two active sites when solvent and basis set are modified. In all the cases, the solvent favors the ion-pair dissociation, being the isolated species formation privileged when the solvent has the higher dielectric constant value (i.e., dichloromethane). A completely different situation is predicted for the *Site* 2, where for this solvent the dissociation reaction is exothermic.

Additional studies were considered where the Zr–O* distance in the *Site* 1 and the Zr–Cl distance in the *Site* 2 were optimized (see Table 3). These cation–anion distance optimizations for both active sites were performed with the PCM approach. The reaction energies predicted from these distance optimizations are generally slightly different with respect to the single-point calculations

Table 2
Predicted total energies (ΔE) of the ionic-pairs dissociation for *Site* 1 and *Site* 2

Active site	Solvent	ΔE (kcal/mol)			
Solvent method:		ONS		PCM	
Gaussian basis sets:		All 3-21G(d,p)	3-21G(d,p)/LanL2DZ	All 3-21G(d,p)	3-21G(d,p)/LanL2DZ
Site 1	Gas phase	−117.28	−114.80	−117.28	−114.80
	Toluene	−114.59	−112.85	−74.68	−66.27
	CH_2Cl_2	−112.32	−110.23	−48.65	−39.48
Site 2	Gas phase	−96.50	−95.06	−96.50	−95.06
	Toluene	−97.53	−99.84	−61.01	−31.09
	CH_2Cl_2	−98.58	−96.66	−38.37	+8.27

Results for the two SCRF methods evaluated (ONS and PCM) as a function of solvent and basis sets.

Table 3
Predicted total energies of the ionic-pair dissociation for *Site 1* and *Site 2*, with cation–anion distances optimization for the PCM approach as a function of basis sets

Gaussian basis sets:		All 3-21G(d,p)	3-21G(d,p)/LanL2DZ	All 3-21G(d,p)	3-21G(d,p)/LanL2DZ
Active site	Solvent	Optimized distances (Å)		ΔE (kcal/mol)	
Site 1	Gas phase	2.946		−117.28	−114.80
	Toluene	2.971	2.965	−77.02	−68.33
	CH_2Cl_2	2.996	2.994	−50.01	−44.90
Site 2	Gas phase	2.580		−96.50	−95.06
	Toluene	2.636	2.663	−63.28	−56.33
	CH_2Cl_2	2.648	2.696	−44.91	−39.32

The optimized distances are Zr–O* and Zr–Cl for *Site 1* and *Site 2*, respectively.

(see Table 2). An exception is the case of the *Site 2* analyzed with the basis set 3-21G(d,p) and pseudopotential LanL2DZ, where we observe changes of up to 40 kcal/mol. The endothermicity of the reaction towards the ionic-pair formation increases with the Zr–Cl distance optimization. These results show the relevance of the cation–anion distance optimization in the *Site 2*, because in this way the destabilization of active site due to the presence of solvent is not overestimated. This fact can be related with the elevated dipolar moment of this active site (15.502 and 4.191 Debye for *Site 2* and *Site 1*, respectively). The *Site 2* with an opened geometry distribution is energetically more stabilized when the solvent polarity and the cation–anion distance are increased.

The Zr–O* and Zr–Cl optimized distances for both active sites are longer with respect to the single-point values, giving more isolated ionic-pairs when the solvent polarity is increased (Table 3). In case of *Site 1* the distance stretching was smaller and independent of the basis set used; otherwise the Zr–Cl distance in the *Site 2* increases in the same direction of the solvent polarity and the basis set quality.

Analyzing the dissociation energies of the active sites we can conclude that the model of the solvent is critically to obtain consistent results. The ONS method shows for this system that it is not adequate for describe the experimental results. The similarity of the dissociation energies indicates the poor effect of the solvent when is represented with ONS approach. When the model for the solvent is improved using the PCM method the cation and anion separation is more significant for both active species, especially in the *Site 2* (higher dipolar moment).

Comparable results were obtained by Ziegler and co-workers [30] when three different methyl precursors in the activation reaction by borane co-catalyst were evaluated. These authors also studied the influence of toluene solvation on the ion-pair formation for the $Cp_2TiCl_2/B(C_6F_5)_3$ system. The dissociation of μ-CH_3 contact ion-pair into the separated cationic complex and anionic counterion both with or without solvent resulted to be endothermic. The presence of this dielectric medium decreases the ion-pair dissociation energy. Indeed, its value changes from 79.5 kcal/mol in gas-phase to 40.3 kcal/mol within toluene.

A comparison between the dissociation energies of both active sites, including different solvents and basis sets is shown in Figs. 3 and 4. Evaluating the solvent effect with the ONS model, the results do not differ significantly if the basis set is modified. The importance of the basis set becomes relevant when the calculation approach of the solvent is improved. Indeed, with the PCM formalism the dependence of the dissociation energy on the dielectric constant of the solvent is remarkable and it becomes more appreciably when the relativistic effect in the transition metal atom (LanL2DZ basis) is included. This fact was found for both active sites.

From the total energies for each species, the solvation energy, i.e., the difference between the values with and without solvent can be calculated. In Table 4 the solvation energies obtained with and without cation–anion distance optimization are summarized. Notice that the PCM approach gives for almost all the species an energetic stabilization due to the solvent. This effect is more significant than that with the ONS model. Looking at the stabilization energies without distance optimization, the *Site 2* with the presence of dichloromethane solvent is the only case where the polarization of solvent produces a destabilization of the ion-pair, indicating that the separation of ions is favored. Here, the stabilization of the ionic species together with a slightly destabilization of the ion-pair are the explanation for a thermodynamic favoring of the isolated ionic species. However, the stabilization energy becomes higher when the cation–anion distance is optimized. Dichloromethane gives the more significant changes for the ionic-pair dissociation owing to its higher dielectric constant.

The results exposed in this Letter showed that the model used to represent the effect of environmental solvent is fundamental to obtain defined tendencies which are in agreement with experimental results. In olefin polymerization reactions, the polar solvent increases the performance of the system because its higher polarity favors the ion-pair separation, giving an active site with lower sterical hindrance for the incoming step of olefin coordination and insertion.
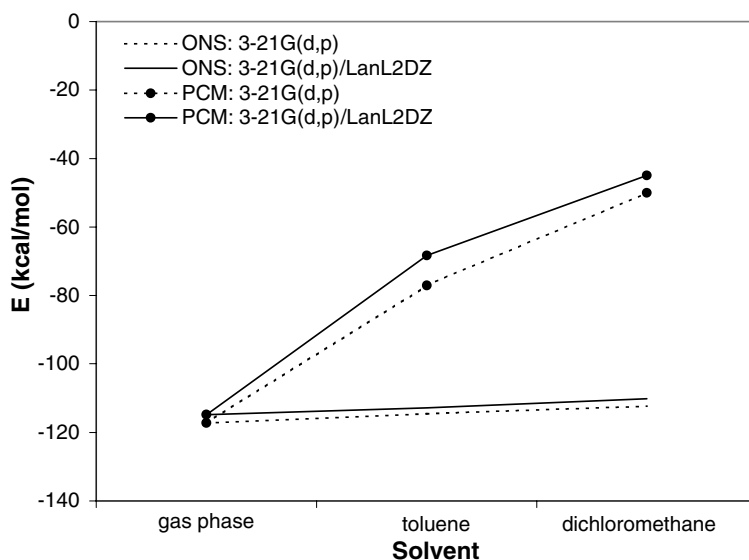
Fig. 3. Energy differences in the dissociative reaction of *Site* 1 when the medium changes from gas phase to solvent phase.
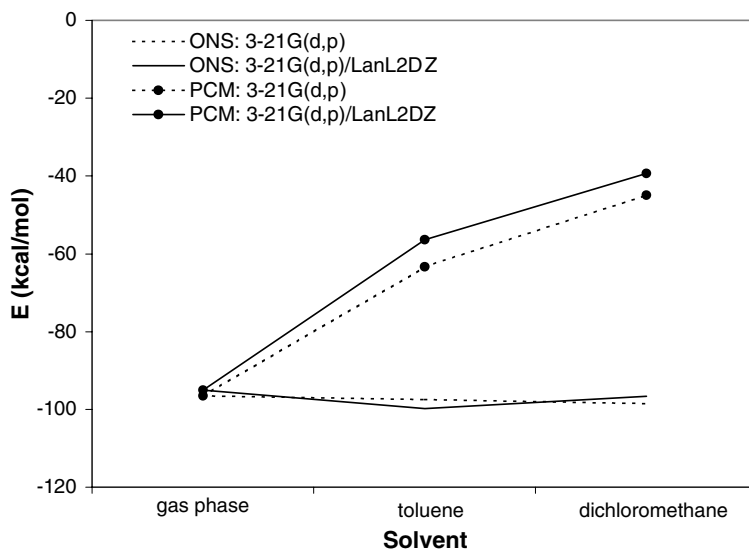

Fig. 4. Energy differences in the dissociative reaction of *Site* 2 when the medium changes from gas phase to solvent phase.

Table 4
Computed stabilization energies of the different species on passing from gas phase to solvent phase

Active site	Solvent	ΔE (kcal/mol)			
Solvent method:		ONS		PCM	
Gaussian basis sets:		All 3-21G(d,p)	3-21G(d,p)/LanL2DZ	All3-21G(d,p)	3-21G(d,p)/LanL2DZ
Site 1	Toluene	0.33	0.78	10.53 (12.87)[a]	11.50 (13.57)[a]
	CH_2Cl_2	0.59	0.65	22.19 (18.45)[a]	21.50 (26.92)[a]
Site 2	Toluene	4.06	7.51	17.65 (19.91)[a]	−3.94 (21.30)[a]
	CH_2Cl_2	7.63	6.81	32.70 (39.24)[a]	−6.51 (41.08)[a]
$Cp_2ZrCH_3^+$	Toluene	−0.13	0.13	20.38	22.74
	CH_2Cl_2	0.17	0.45	36.87	39.75
$MAO–CH_3Cl^-$	Toluene	2.93	2.60	32.75	37.29
	CH_2Cl_2	5.38	4.76	53.96	57.07

Results for the two SCRF methods evaluated (ONS and PCM) as a function of basis sets.
  [a] Stabilization energies of the both active sites when the cation–anion distances were optimized.

4. Conclusions

In this Letter two important and valuable aspects associated to the metallocenic systems were studied, both related to available experimental data. In a first approach the maximum wavelength of the zirconocene absorption band was evaluated including a Lewis acid addition. The predicted LMCT bands are satisfactory when they are compared with other metallocenic systems such as the *rac* -EtInd$_2$ZrCl$_2$/MAO∗AlCl$_3$. A lower bathochromic shift and an intensity decrease are found when the AlCl$_3$ was incorporated in the ion-pair models. The TD-DFT approach with a high quality basis set is essential to predict satisfactory $\lambda_{max.}$ values.

In addition, the solvent effect on the ion-pair dissociation was investigated. The results depend strongly on the theoretical formalism used. The ONS method is not sensitive to the polarity of the solvent for this system. This conclusion was previously reported by other authors for a different system [31]. However, the PCM method simulates the solvent effect with higher precision, providing a correct description of the molecular system as it was previously demonstrated with the complexly zwitterionic amino acids [32,33]. For this method the quality of the basis set used and the optimization of relevant geometrical parameters become important. We can conclude that, for systems where the catalytic site works in liquid phase, the evaluation of solvent effect is highly important to predict stability of specific chemical components of the active catalytic site.

Acknowledgements

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