

ZIEGLER–NATTA CATALYTIC SYSTEMS Calorimetric and DFT study on TiCl_4 -Lewis base interactions

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A calorimetric investigation on the reactions of TiCl_4 with phthalates in 1,1,2,2-tetrachloroethane (TCE) is presented in order to better understand the complex interactions present in Ziegler-Natta catalytic systems. The Lewis bases diethyl isophthalate (**L1**), diethyl terephthalate (**L2**) and the *ortho*-isomer diethylphthalate (**L3**), have been chosen to study how the substituent positions could influence the energy and the stoichiometry of the complexation reactions.

FTIR spectroscopy was used to obtain information on the coordination mode of the ligands and diffusion measurements by NMR was carried out to verify the presence of oligo- or polymeric species. Experimental results were compared with theoretical calculations based on Density Functional Theory (DFT).

Keywords: calorimetry, DFT, diffusion-ordered NMR, titanium tetrachloride, Ziegler–Natta catalysts

Introduction

Modern supported Ziegler–Natta catalysts allow to control the polyolefins morphology in the process of polymerization ensuring an easy control of polymer properties: these multi-site catalysts are a mixture of Lewis acids (MgCl_2 , TiCl_4 , AlR_3) and Lewis bases and therefore their design is extremely complicated. Although their discovery can be traced back to the early 1950's [1], some important aspects concerning their nature are not clear yet [2]. One is the specific role played by the Lewis bases, used both as internal and external donors: exchanging these pairs, it is possible to modulate the performance of the catalyst (activity and stereoselectivity) and the characteristics of the resulting polymer (molecular mass, molecular mass distribution, microtacticity intra and inter comonomer distribution).

The role of these bases has been supposed to range from 'simple' poisoning of aspecific sites [3], to a direct chemical and sterical modification of the surroundings of isospecific sites with a direct control on monomer insertion [4–6]: ethylbenzoate [7] and phthalic esters [8], always combined with external donor, are the most widely internal bases studied in literature [9, 10]. In recent years, novel 2,3 disubstituted succinates have been also successfully proposed [11].

Recently, a calorimetric investigation has been performed to obtain the specific interaction energies

between TiCl_4 and a number of donors [12]. Despite the real nature of the catalyst active center is mainly a mixed MgCl_2 – TiCl_4 system, the study of the energetic of the reactions of TiCl_4 reported represents an important attempt to rationalize the whole catalytic system and the results show that some correlation seem to exist between catalyst efficiency and enthalpy terms.

In this paper, we extend the investigation to the interaction of TiCl_4 with other two Lewis bases, diethyl isophthalate (**L1**), and diethyl terephthalate (**L2**) to understand how different isomerism influences the nature of the species formed and the energies of the interaction with titanium. Comparisons are made with available data for TiCl_4 complexation with the *ortho*-diethylphthalate (**L3**) [12].

Furthermore, thermochemical data on new TiCl_4 -Lewis base systems could provide additional information on correlation found between reaction enthalpies and catalyst efficiency [12]. The enthalpy functions have been obtained by calorimetric titration in solutions of 1,1,2,2-tetrachloroethane (TCE), chosen for its low donating properties [13] to better focus our attention on the metal-donor interaction. Also the stability constants for the complex formation have been obtained from the fit of calorimetric data. The bonding mode of the ligands was probed by means of FTIR spectroscopy. NMR diffusion measurements were used to provide information on the possible for-

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mation of oligo- or polymeric species in solution in the case of **L1** and **L2**. The previously tested computational approach [12], based on Density Functional Theory (DFT), was employed to obtain the binding energies of the phthalates to TiCl_4 .

Experimental

General remarks

Titanium tetrachloride is easily hydrolyzed by water, so extreme care was taken to work with the lowest content of water in the systems, by working under an inert atmosphere in a MB Braun 150 glovebox (containing less than 1 ppm of water).

Materials

Ligand solutions were supplied by Basell, Centro Ricerche G. Natta, Ferrara Italy. Their purity (>99%) was checked by GC mass spectrometry and ^1H NMR measurements. TiCl_4 solutions were prepared from the Aldrich ReagentPlus™ 99.9% using anhydrous TCE (Fluka, purum >98%) stored over 4 Å molecular sieves. All standard solutions were prepared and stored in glovebox. The water content in the solutions, typically 5–7 ppm, was determined by a Metrohm 684 KF Coulometer.

Methods

Titration calorimetry

A Tronac model 87–558 precision calorimeter equipped with a 25 mL titration vessel, was used to measure the heats of reactions. The cover of the titration vessel and its connection to the calorimeter were modified in order to ensure the reactions proceed in an inert atmosphere. Both the vessel and the piston burette were filled and joined together inside the glove-box, taken out and connected to the calorimeter for measurements. The experimental value of the heat of neutralization of tris(hydroxymethyl)methylamine (THAM) with 0.1 mol dm^{-3} HCl was found to be $\Delta H^0 = -47.59 \text{ kJ mol}^{-1}$, in good agreement with the accepted value of $-47.53 \pm 0.13 \text{ kJ mol}^{-1}$ [14]. The calorimetric titrations were performed at $298.00 \pm 0.02 \text{ K}$ by adding at constant rate known volumes of ligand solutions ($200 < C_{\text{L}}^0 < 400 \text{ mmol dm}^{-3}$) to 20 mL of TiCl_4 solution ($2.0 < C_{\text{TiCl}_4}^0 < 20.0 \text{ mmol dm}^{-3}$). As far as ligand **L2** was concerned, the maximum $C_{\text{TiCl}_4}^0$ investigated was about 10 mmol dm^{-3} due to the formation of a white precipitate beyond this concentration, once that **L2** was added. For each system, usually 3–4 titration runs

with different $C_{\text{TiCl}_4}^0$ were performed to achieve better statistics in the calculation of formation constants and reaction enthalpies. The heat of dilution of titrate was found to be negligible in the metal concentration range used. The stability constants and enthalpy changes of the identified complexes, were calculated by using the computer program Letagrop Kalle [15].

FTIR spectroscopy

The FTIR spectra were recorded covering the wavenumbers range of $800/4000 \text{ cm}^{-1}$ under dry-air purge at $25 \pm 1^\circ\text{C}$ on a Bruker Vector 22 FTIR spectrometer with a 2 cm^{-1} resolution and 256 scans. Cell with barium fluoride windows (thickness of $25 \mu\text{m}$) was filled with the sample solutions in the glovebox, tightly closed, and quickly transferred to the spectrometer. The spectrum of TCE was kept as background.

NMR spectroscopy

The ^1H -NMR spectra were collected on a Bruker Avance spectrometer at 500.13 MHz. Diffusion coefficients of TiCl_4 -L1 and TiCl_4 -L2 systems in 1,1,2,2-tetrachloroethane- d_2 (TCDE) were determined at $T=298 \text{ K}$ on solutions containing 20 mmol dm^{-3} of TiCl_4 and 10 mmol dm^{-3} of the ligand concerned, **L1** and **L2** respectively. The TiCl_4 -L3 system (10 mmol dm^{-3} both in TiCl_4 and in **L3**) was used as reference as it was shown to form only a mononuclear 1:1 complex.

Diffusion coefficient

Translational diffusion coefficient D is approximately related to the hydrodynamic radius of the molecule (r_s) by the Stokes–Einstein equation:

$$D = \frac{kT}{6\pi\eta r_s}$$

where k the Boltzmann constant, η the viscosity of the solvent. The formation of slowly-moving entities would give a significant decrease of D .

The currently used pulse sequences for D determination are an evolution of the original pulsed field gradient spin-echo (PFG-SE) experiment developed by Stejskal and Tanner [16] and utilize pulsed field gradient stimulated echo (PFG-STE). The advantage over the classic PFG-SE is the minimization of transverse relaxation and of J-modulation effects.

In order to control the interference of convection currents induced by temperature gradients, the Bruker defined pulse program `dstepg3s` was utilized [17, 18]; the double stimulated echo makes the sequence insensitive to variations of diffusion velocities due to temperature gradients.

Diffusion coefficients were obtained by fitting the experimental signal intensities with the following equation:

$$I = I_0 e^{\left[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \right]}$$

where γ is the gyromagnetic ratio of proton, Δ the diffusion time, g the gradient strength, δ the pulse duration. Gradient strength was calibrated and checked by measuring the diffusion coefficient of water in D_2O . The values of diffusion coefficients of TCDE in the different experiments were obtained with accuracy of $\pm 2\%$.



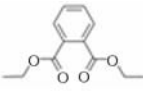
Computational details

The calculations were performed with the TURBOMOLE 5.8 package [19]. The GGA PBE functional was applied [20, 21]. A triple- ζ basis set augmented with two polarization shells on each atom and augmented with a s-function on C and O and a d-function on Ti, referred as def2-TZVPP in TURBOMOLE, was used [22]. Solvation in TCE was modeled using the COSMO solvation model [23] with a dielectric constant of 8.42 and a solvent radius of 2.79 Å. The cavity was defined using Klamt's optimized radii for H, C, O and Cl and a value of 2.223 for Ti. As TCE is a low polarity solvent, non-electrostatic cavitation, dispersion and repulsion terms are expected to play a non-negligible role. To evaluate these terms the Gaussian03 program was run. All the binding energies were corrected of the Basis Set Superposition Error (BSSE) using Boys and Bernardi's counterpoise method [24].

Results and discussion

The thermodynamic parameters of complexation for **L1** and **L2** are summarized in Table 1 where the

Table 1 The overall stability constants and corresponding thermodynamic parameters for the formation of $TiCl_4$ -ligand complexes; $T=298$ K, the error limits represent 3σ

	Ligand	Complex	$\log\beta_j$	$-\Delta G_{\beta_j}^0/kJ mol^{-1}$	$-\Delta H_{\beta_j}^0/kJ mol^{-1}$	$-T\Delta S_{\beta_j}^0/kJ mol^{-1}$
L1		ML	2.8±0.1	16.0±0.5	31.0±0.4	15.0
		ML ₂	4.0±0.1	22.8±0.6	71.0±7.4	48.2
L2		ML	2.7±0.1	15.4±0.5	28.8±1.0	13.4
		ML ₂	3.9±0.1	22.3±0.7	70.0±8.0	47.7
L3^a		ML	4.5±0.1	25.6±0.7	85.8±0.7	60.2

^aRef. [12] Cavallo 2007

values previously found for **L3** have also been entered. Various combinations of mono- and poly-nuclear species were considered to model these systems: the best results from the data refinement were obtained when two mononuclear complexes 1:1 and 1:2, were taken into account. The analysis of the thermogram reported in Fig. 1 as Δh_v vs. R_c , the ligand to metal ratio ($R_c = C_L/C_{TiCl_4}$), shows that for both $TiCl_4$ -**L1** and -**L2** systems, the plots have different curvatures at different $TiCl_4$ concentrations thus indicating presence of weak complexes, consequently both the formation constants and the enthalpy of complexation can be simultaneously evaluated [25]. The fit between the experimental and calculated data is good for all the systems considered.

In Fig. 2 the FTIR spectra relative to the free ligands **L1**, **L2** and **L3** and to their $TiCl_4$ -L complex are reported. Table 2 lists the diffusion coefficients D_{comp} ,

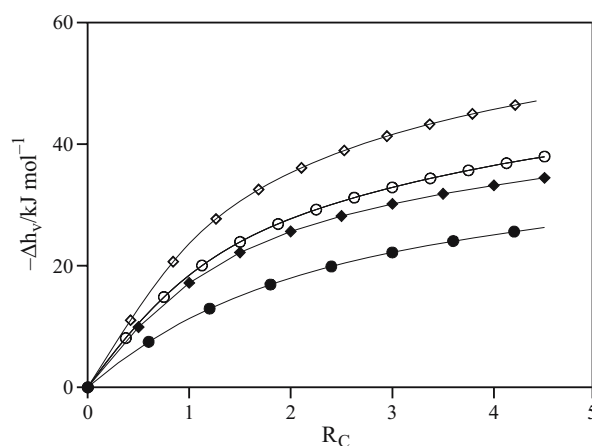


Fig. 1 Total molar enthalpy changes per mole of $TiCl_4$, Δh_v , as a function of the ligand to metal ratio $R_c = C_L/C_{TiCl_4}$ for: $TiCl_4$ -**L1** system: $\diamond - C_{TiCl_4}^0 = 19$ mmol dm^{-3} , $\blacklozenge - C_{TiCl_4}^0 = 8$ mmol dm^{-3} , $TiCl_4$ -**L2** system: $\circ - C_{TiCl_4}^0 = 8$ mmol dm^{-3} , $\bullet - C_{TiCl_4}^0 = 2$ mmol dm^{-3}

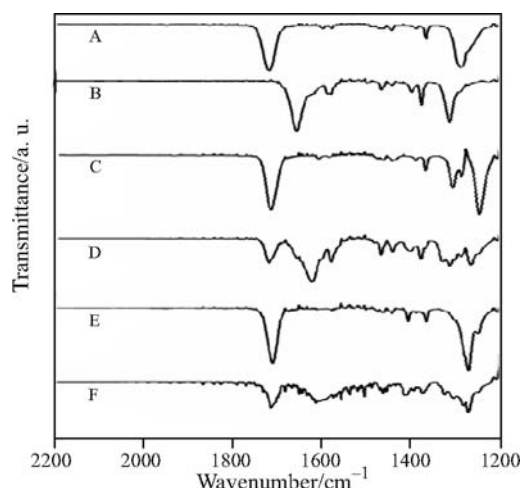
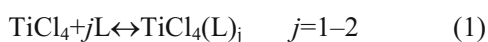


Fig. 2 FTIR spectra of TiCl_4 -phthalate systems in TCE. The spectra show the red shift of C=O vibration frequencies upon complexation with TiCl_4 . A – **L3**; B – **L3**/ $\text{TiCl}_4=0.5$; C – **L1**; D – **L1**/ $\text{TiCl}_4=0.5$; E – **L2**; F – **L2**/ $\text{TiCl}_4=0.5$

compensated as described in the Experimental, for the different TiCl_4 -phthalate systems, as obtained by NMR measurements. The diffusion coefficient of the solvent (Table 2) has been measured in order to check the reproducibility of the experiments.

In Table 3, the $\Delta H_{\beta_j}^0$ experimental values are entered for the TiCl_4 -L (L=**L1**,**L2**,**L3**) systems together with calculated binding energies, ΔE_{PBE} , at the PBE/def2-TZVPP level.

The overall complexation reactions taken into account are represented by equilibrium (1):



The common feature of all these systems is that the complexation of TiCl_4 with the ligands is driven by the highly negative enthalpy (Table 1). Negative enthalpy values found here are typical of reactions involving complexation in aprotic solvents and formation of strong coordinate bonds of marked covalent character [26]. The entropic term, when known, is also negative and therefore opposes to the formation of the $\text{TiCl}_4(\text{L})_j$ adducts. The negative values of $T\Delta S_{\beta_j}^0$ reflect the decrease of internal entropy of the ligand and the loss of translational entropy by the reagents upon complexation. The thermodynamic functions relative to the ML formation for **L3** show that this ligand chelates the titanium *via* the carbonyl groups in octahedral configuration [12]. The much lower stability and exothermicity associated with the complex formation for **L1** and **L2** diesters and the less unfavorable entropy terms, are a clear evidence of monodentation. The values here reported are also in close agreement with those found for TiCl_4 complexation with the

Table 2 Diffusion coefficients of the TiCl_4 -phthalate systems at 298 K

Complex	$D_{\text{comp}}/10^{-10} \text{ m}^2 \text{ s}^{-1}$
TiCl_4 - L1	3.01
TiCl_4 - L2	3.60
TiCl_4 - L3	2.87
Solvent	7.18

Table 3 Experimental enthalpy values, $-\Delta H_{\beta_j}^0$ from Table 1, for formation of TiCl_4 -ligand complexes, and DFT binding energies, $-\Delta E_{\text{PBE}}$. ΔE in parenthesis, obtained by adding the empirical correction term

	Complex	$-\Delta E_{\text{calc}}/\text{kJ mol}^{-1}$	$-\Delta H_{\text{exp}}^0/\text{kJ mol}^{-1}$
L1	ML	22	30
	ML_2 <i>cis</i>	29 (74)	72
	ML_2 <i>trans</i>	28 (73)	
L2	ML	21	29
	ML_2 <i>cis</i>	29 (74)	70
	ML_2 <i>trans</i>	27 (72)	
L3	ML	40 (85)	86

monodentate ethylbenzoate ($\log\beta_1=2.8$; $\Delta H_{\beta_1}^0 = -31.6$ and $T\Delta S_{\beta_1}^0 = -15.7 \text{ kJ mol}^{-1}$) [12]. The stepwise $\Delta H_{K_2}^0$ values (-40 ± 7 and $-41 \pm 7 \text{ kJ mol}^{-1}$ for **L1** and **L2** respectively) are less accurate than $\Delta H_{K_1}^0$, nevertheless they are quite higher than expected by considering the increased steric repulsions, the reordering of the ligands and the higher electron density on the metal. This trend was experimentally observed [12] also for the coordination of other monodentate ligands like ethylbenzoate ($\Delta H_{K_1}^0 = -31.6 \text{ kJ mol}^{-1}$, $\Delta H_{K_2}^0 = -29 \text{ kJ mol}^{-1}$), ethylacetate ($\Delta H_{K_1}^0 = -45 \text{ kJ mol}^{-1}$, $\Delta H_{K_2}^0 = -57 \text{ kJ mol}^{-1}$), tetrahydrofuran ($\Delta H_{K_1}^0 = -60 \text{ kJ mol}^{-1}$, $\Delta H_{K_2}^0 = -60 \text{ kJ mol}^{-1}$) and can be explained by a better interaction with TCE for the 1:2 complex. This result is reproduced by the corrected binding energies in Table 3 calculated including the implicit solvent (COSMO).

FTIR spectra in Fig. 2 confirm the hypothesis on the coordination mode of **L1** and **L2**: the band at 1720 cm^{-1} (spectrum A), associated to the stretching vibration (ν_s) of the C=O group in **L3**, is red shifted (B) to 1658 cm^{-1} when the ligand is bound to the titanium atom but no band related to the free ligand is present. On the contrary, in the D and F spectra, relative to complexes with **L1** and **L2**, the band typical of the free C=O stretching vibration (1720 and 1717 cm^{-1} respectively, in spectra C and E) is present together with the peaks (1625 (ν_s), 1581 (ν_{as}) cm^{-1} spectrum D and 1617 (ν_s), 1580 (ν_{as}) cm^{-1} spectrum F) associated to the coordinated C=O [27]. The peak intensity of 'free' C=O is more significant than

what expected on the basis of the percentage of the free ligand calculated from the $\log\beta_j$ values: this is indicative of the monodentate behavior of **L1** and **L2**, certainly due to the unsuitable large ring size that chelation should provide. In the ML compounds only one carbonyl group is bound to TiCl_4 producing five coordinated species, as found by NMR solution studies on similar TiCl_4 systems [27].

Given the monodentate behavior of the diesters **L1** and **L2**, some hesitation comes out from the fact that polynuclear species such as $(\text{TiCl}_4)_2\text{L}_2$ are not revealed by the minimization of calorimetric data, despite the presence of the dimeric compound $(\text{TiCl}_4)_2\text{L}_2$ was observed in solid state [27]. Diffusion-ordered NMR experiments were run to clear this point: the different relaxation behavior of the ^1H NMR peaks is a consequence of the mobility of the species carrying the observed nucleus and of molecular environment and therefore slowly-diffusing oligo- or polymeric species can be discriminated on this basis. It is interesting to note that the D values for $\text{TiCl}_4\text{-L1}$ and -L2 are slightly higher than what found for the $\text{TiCl}_4\text{-L3}$ system. This difference is in line with the fact that, due to the relative low β_j values, a small amount of faster diffusing free ligand is present when **L1** and **L2** are concerned. The complex $\text{TiCl}_4\text{-L3}$ was shown to form only the monomer, therefore its diffusion coefficient can be considered as reference for a 1:1 complex and the formation of oligomers should produce D values significantly lower. In our case the results agree with the presence of only monomeric complexes for **L1** and **L2** and consequently confirm the speciation model found by the best-fit of the calorimetric data in the dilute concentration range investigated. Evidently, the energy gain by the formation of additional Ti-carbonyl bonds is not sufficient to balance the energetic cost of the rearrangement of the coordination sphere around the titanium and the very unfavorable entropy associated to oligomerization.

A good correlation was previously observed between enthalpy values and catalyst efficiency, by analyzing some parameters like productivity (P) and xylene-insoluble polymer fraction at 25°C ($X.I.$): the more favorable the TiCl_4 -donor complexation enthalpies, the higher the productivity and stereoregularity were. For **L1** and **L2**, the values of the relevant parameters are $P=10.0$ and 5.0 $\text{kg}_{\text{PP}}/\text{g}_{\text{Cat}}$, and $X.I.=90.0$ and 88.0 mass% respectively, confirming this correlation, at least within the same family of donors (for **L3** $P=36.3$ and $X.I.=98.2$). This result is in line with the suggestion that a higher affinity for TiCl_4 could be taken as a requirement to build a good Ziegler–Natta supported catalyst. This result has been tentatively explained by suggesting that a higher affinity for TiCl_4 (more favorable complexation

enthalpies) could translate in a better interaction with the MgCl_2 surface and, consequently, to a higher stabilization of lateral cuts of MgCl_2 crystallites. This brings about an increase of the number of titanium active sites (i.e. catalyst productivity) and should also improve the selectivity of the interaction with the external donor and hence the catalyst stereoselectivity ($X.I.$) [12].

The DFT binding energies calculated for the formation of the 1:1 complexes (Table 3) are systematically few kilojoules per mole lower than the experimental $\Delta H_{\beta_1}^0$. This underestimation becomes severe when the theoretical result is compared to $\Delta H_{\beta_2}^0$. However, by adding the empirical correction term E_{corr} (-45 kJ mol^{-1}) to the binding energies of the dicoordinated complexes previously proposed and based on calculations for a series of TiCl_4 -ligand complexes with chemically different Lewis bases [12], a remarkable good agreement with the experimental results is obtained. The *cis*- and *trans*- isomers of the $\text{TiCl}_4\text{-L}_2$ complexes have rather similar binding energies for **L1** and **L2**, indicating that they are probably both present in solution. Comparison with the *ortho*-phthalate **L3**, clearly indicates that the calculated ΔE for coordination of two *meta* or two *para*-phthalate molecules to TiCl_4 , is much less favored. Considering that the ΔE of ML_2 for **L1** and **L2** are very similar, the less favored coordination of two donors relative to chelation of the *ortho*-phthalates can be reasonably ascribed to increased congestion at the metal center, which destabilizes complex formation.

The same calculation, extended here also to another *ortho*-substituted ligand, the di-isobutyl phthalate, gives a $\Delta E_{\text{calc}}=-40$ kJ mol^{-1} ($\Delta H_{\text{exp}}^0=-87$ kJ mol^{-1}) [12], providing an additional confirmation of the trend.

Conclusions

Calorimetric investigation allows to quantify the energies of Ti–O coordinative bond in the complexes of titanium tetrachloride with phthalates. The calorimetric and spectroscopic results prove that only mononuclear penta- and hexa-coordinated TiCl_4 complexes are formed and that no polynuclear species are present in the concentration range here investigated. The position of substituents produces significant effects on the complexes formed: chelation is achieved only when the *ortho*-ligand was considered while the *meta*- and *para*- isomers act as monodentate with a behavior similar to ethylbenzoate. Correlation between catalyst efficiency and higher enthalpy terms is confirmed as well as the reliability of the proposed DFT empirical methods in describing the energetic of interaction in these systems.

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