Consequences of cavity size and chemical environment on the adsorption properties of isoreticular metal-organic frameworks: an IGC Inverse Gas Chromatography study

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Abstract

The role of the structure of three isoreticular metal-organic frameworks (IRMOFs) on their adsorption behavior has been studied in this work, selecting different kinds of volatile organic compounds (VOCs) as adsorbates (alkanes, alkenes, cycloalkanes, aromatics and chlorinated).

For this purpose, three samples (IRMOF-1, IRMOF-8 and IRMOF-10) with cubic structure and without functionalities on the organic linkers were synthesized. Adsorption capacities at infinite dilution were derived from the adsorption isotherms, whereas thermodynamic properties have been determined from chromatographic retention data. A great influence of the molecule size on both the capacity and the strength of adsorption was strongly influenced by the adsorbate size. This effect is especially relevant for n-alkanes adsorption, indicating the relevance of the cavity size on this phenomenon, and hence the importance of the IRMOF structural properties. A different behavior has been observed for the polar compounds, where an enhancement on the specificity of the adsorption with the π-electron rich regions being observed. This fact suggests the specific interaction of these molecules with the organic linkers of the IRMOFs.

Keywords:
Isoreticular metal-organic frameworks; Inverse gas chromatography; Adsorption properties; Surface properties; VOCs adsorption
1. Introduction

Isoreticular metal-organic frameworks (IRMOFs) are coordination polymers constituting an important family of porous crystalline materials [1,2]. These materials are constituted by two major components: a metal ion or metal oxide and an organic linker. The metal ions are situated in vertices joined by the organic linker molecules to form the IRMOF structure [3,4]. The structures formed by these materials are diverse, since many different combinations of metal-containing ions and the organic linkers can be made. The main features of these materials are the high surface area (500 to 4 500 m$^2$/g) [5], and high pore volume [6,7], as well as the easiness for tuning their structure [3,8] by selecting the two IRMOF constituents [3,8].

Due to these properties, these materials are attractive candidates for a variety of applications such as: storage and separation of gases (N$_2$, Ar, CO$_2$, CH$_4$, and H$_2$) [2,9-13], catalysis [13-16], sensors for different molecules [13,14], and semiconductors [17]. In this way, there are many published works dealing with the synthesis, characterization and gas storage applications for MOFs. However, the research on the adsorption of organic molecules on this type of materials is relatively scarce, in spite of their potential for this application (similar to zeolites), as well as its possibility to tune both the structure and the organic linkers in order to enhance the interactions between the adsorbates and the pore wall. In this way, there are just few works dealing with experimental [18-21] and simulated [20,22] studies related to the adsorption of organic molecules on MOFs. Furthermore, the scope of these works makes difficult to compare the different results among them, since there are works focused on the vapor-phase separation processes of several compounds [23], the understanding of organic compounds adsorption on a selected MOF [21,24], or the adsorption of selected compounds on different MOFs, with different structures and metal ions [20]. Taking into account the large number of applications of adsorption processes for the separation and removal of the harmful vapors of these compounds, a systematic study on the adsorption behavior of organic molecules on this type of structures is of high scientific interest.

In this work, we report the adsorption of several compounds representative of volatile organic compounds (VOCs) on three different IRMOFs: IRMOF-1, IRMOF-8 and IRMOF-10. The IRMOF structure is made of Zn$_4$O tetranuclear clusters connected by rigid dicarboxylic linkers to create a cubic framework, with square channels which are connected in the three
dimensions [6]. These structures are very open and the crystal density is very low [25]. The linkers, terephthalic acid (IRMOF-1), 2,6-napthalene dicarboxylic acid (IRMOF-8) and 4,4’-diphenyl dicarboxylic acid (IRMOF-10) confer the structured materials different open windows. The IRMOFs here chosen have no functional groups in the linkers, thus the resulting materials only differ on the sizes of the created cages. The inverse gas chromatography (IGC) was chosen as technique to study the interaction of organic compounds of selected families (n-alkanes, alkenes, cyclic, aromatic and chlorinated compounds) on these three IRMOFs. This technique provides thermodynamic information about the adsorption, which can be used to estimate and compare the relative strengths of intermolecular forces between the adsorbent and different adsorbates, and to study the interactions between the adsorbate and the adsorbent [26,27,28]. IGC is a chromatographic technique that differs from the gas-solid chromatography in its goal: the characterization of the stationary phase, instead of the separation of solutes in the mobile phase. Furthermore, IGC offers an alternative to the conventional gravimetric or volumetric methods for determining adsorption equilibrium isotherms, due to its simplicity, the shorter measurement time and a wider range of experimental possibilities. IGC measurements can provide information on thermodynamic, surface energy, reaction kinetics, and textural parameters (such as surface area and porosity).

Thus, the scope of this work is to evaluate the interaction of selected organic compounds –representative of different families of VOCs– on three IRMOFs without functionalization of the organic linkers (IRMOF-1, IRMOF-8 and IRMOF-10) in order to evaluate adsorption behavior and correlate it to the morphologic structure of the network. IGC adsorption studies have been used for evaluating different thermodynamic parameters (adsorption capacity, adsorption enthalpy, entropy and free energy; as well as dispersive and specific contributions to these terms), useful for gaining further understanding on the adsorption features of these materials. To the best of our knowledge, there is only one work [24] dealing with the determination of thermodynamic properties (enthalpies of adsorption, free energies of adsorption and the dispersive and specific components of the surface free energy) systematically for different adsorbates on IRMOFs by IGC, specifically this work was devoted to the influence of synthesis procedure of IRMOF-1 on the adsorption of several organic compounds.
2. Experimental

2.1. Synthesis of IRMOFs

IRMOFs were synthesized at room temperature according to the method described in the literature [26, 29], the main features of the procedures being summarised below.

For the synthesis of the IRMOF-1, 120 mmol of zinc acetate, Zn(OAc)$_2$·2H$_2$O (>98%, Sigma-Aldrich), were dissolved in 774 mL of N,N'-dimethylformamide, DMF (99.8%, Panreac). Likewise, 47.2 mmol of terephthalic acid (98%, Sigma-Aldrich) and 13 mL of triethylamine (99%, Sigma Aldrich) were dissolved in 619 mL of DMF, where the molar ratio between terephthalic acid and zinc acetate was 0.4. The zinc salt solution was added to the organic solution with stirring during 15 min, and then the solution was stirred at 325 rpm for 2.5 h. The precipitate was centrifuged at 6 500 rpm for 15 min to 293 K and immersed in 387 mL of DMF overnight. Afterwards, it was centrifuged again and immersed in 542 mL of trichloromethane, CHCl$_3$ (99%, Panreac). The solvent was exchanged 3 times over 7 days. The solution was centrifuged and the white solid was dried in oven at 373 K for 48 h. The resulting solid was activated at different temperatures (393, 473, 523 and 573 K) for 6 h at a heating rate of 1 K/min under a helium atmosphere at a flow rate of 0.6 L/min. The IRMOF-1 was kept in a desiccator to avoid its further contact with moisture and air.

IRMOF-8 and IRMOF-10 were synthesized following the same method and molar ratio as the IRMOF-1, using 2,6-napthalene dicarboxylic acid (95%, Sigma-Aldrich) and 4,4'-diphenil dicarboxylic acid (97%, Sigma-Aldrich) as organic compounds, respectively. The activation temperature of materials was optimize following the BET surface area, in this way, 573 K was chosen for IRMOF-1 and 8, whereas 523 K for IRMOF-10.

2.2. Apparatus and procedure

The crystallographic structures of the IRMOFs were determined by XRD using a Philips X'Pert Pro powder diffractometer, working with the Cu-K$_\alpha$ line ($\lambda = 0.154$ nm) in the range 2θ between 5° and 20° at a scanning rate of 0.02°/s. The X-ray tube voltage and current were set at 45 kV and 40 mA, respectively.
Specific surface area, pore diameter and volume were estimated by nitrogen adsorption at 77 K in a Micromeritics ASAP 2020 surface area and porosity analyzer. The surface area ($S_{BET}$) was calculated according to the Brunauer-Emmett-Teller (BET) method, whereas the micropore volume ($V_{\text{micro}}$) was obtained using the Harkins and Jura $t$ method. The average pore diameter ($D_p$) and mesopore volume ($V_{\text{meso}}$) were determined from the desorption branch using the Barrett-Joyner-Halenda (BJH) method.

The thermal decomposition of IRMOFs were characterised by thermogravimetric analysis in a TG-DSC (Setaram, Sensys). A sample of material (20 mg) - and α-alumina as inert reference material- was treated in Pt crucibles at a heating rate of 5 K/min from 298 to 973 K in N$_2$ atmosphere at a flow rate of 20 mL/min.

Adsorption measurements were carried out in a conventional gas chromatograph (Varian model 3800) with a thermal conductivity detector (TCD). About 0.25 g of each IRMOF was placed into a 25 cm length of Supelco Premium grade 304 stainless steel column (about 4 cm of IRMOF packed), with passivated inner walls and inside diameter of 5.3 mm. Pyrex glass, between 250-355 µm, was used as inert material to fill the column and at the ends of itself was used silanized glass wool to prevent any loss of the adsorbent. The columns were stabilized in the GC system at 573 K (IRMOF-1 and IRMOF-8) and at 523 K (IRMOF-10) overnight under a helium flow rate of 30 mL/min.

Measurements were performed in the temperature range of 393 – 423 K. Helium (99.999%, Praxair) was used as carrier gas, for all experiments, at a flow rate of 30 mL/min, which was measured using a calibrated soap bubble flowmeter. Samples injected consists of 0.1 µL of adsorbate, in order to satisfy the requirement of adsorption at infinite dilution, corresponding to zero coverage and GC-linearity, the samples injected were and 0.1 µL of adsorbate and the same amount of air, to meet the time-out in order to estimate the dead time of the column. The validity of this the zero coverage hypothesis was confirmed by the symmetry of the elution peaks and by the constancy of the retention times measured over the range of the sample sizes studied. The specific retention volume, $V_g$, in cm$^3$/g, was calculated using the equation:

$$V_g = P_j \frac{t_R - t_M}{m} \left(\frac{p_0 - p_w}{p_w}\right) \left(\frac{T}{T_{\text{meter}}}\right)$$  \hspace{1cm} (1)
where $F$ is the volumetric flow rate of carrier gas, $j$ the James-Martin compressibility factor, $t_R$ the retention time, $t_M$ the retention time of a non-adsorbing marker (air), $m$ the mass of the adsorbent, $p_0$, the outlet column pressure, $p_w$ the vapour pressure of water at the flowmeter temperature, $T_{meter}$ the ambient temperature and $p_i$ the inlet column pressure. The meaning of the symbols is indicated in the list of symbols. For each measurement, the adsorbent was injected three times, obtaining reproducible results ($\pm5\%$ retention volume).

Chromatographic measurements of a given compound (n-hexane) were randomly repeated during the use of each column in order to ensure the stability of the material. The procedures used for the calculation of adsorption parameters (capacities, Henry constants, enthalpies, free energies, entropies and the surface free energy, both the specific and the dispersive components) from IGC experiments are described in detail in a previous work [2730].

The selected adsorbates, representative of different families of volatile organic compounds are: n-pentane (99%, Panreac), n-hexane (99%, Sigma-Aldrich), n-heptane (99%, Sigma-Aldrich), n-octane (99.5%, Sigma-Aldrich), 1-hexene (97%, Sigma-Aldrich), cyclohexane (98%, Panreac), methylcyclohexane (99%, Fluka), benzene (99%, Panreac), toluene (99.5%, Panreac), chlorocyclohexane (98%, Fluka), trichloroethylene and tetrachloroethylene (99%, Panreac).

3. Results and discussions

3.1. Textural and morphologic characterization of adsorbents

XRD patterns of synthesized IRMOFs samples are shown in Fig. 1. For IRMOF-1, it is observed that the main peaks at $2\theta = 6.5$ and $9.5^\circ$ are dismissed in comparison to simulated diffractograms [24]. The decrease in the size of the main peaks is related to the influence of guest molecules in the structure [2831]. Likewise, a dominating peak at $2\theta = 8.7^\circ$ is observed, being attributed this peak to the presence of a nonporous phase resulting from water induced structural degradation [2932]. The IRMOF-8 shows two main peaks at $2\theta = 6.0$ and $8.5^\circ$, consistent with data observed in the literature [3033]. However, three small peaks at $2\theta = 11.8$-13.3$^\circ$ are also observed, that could indicate the presence of lattice defects such as
metal cluster in the pores or lattice interpenetration [3434]. For IRMOF-10, these peaks are observed: the main one at 2θ = 6.4°, and two minor ones at 2θ = 5.2 and 10.4°, although the relative order of the intensities do not follow the trend reported for simulated diffractograms [3235]. This fact is also related, as in the case of IRMOF-1, to the presence of guest molecules in the structure.

The morphology of these structures was determined by nitrogen sorption analysis at 77 K, Fig. 2 showing the adsorption-desorption isotherms. All of materials characterized clearly corresponded to type I (microporous solids), according to the IUPAC classification. The textural properties of the samples are summarized in Table 1. The BET surface areas of IRMOFs studied decrease from 1 to 10. For IRMOF-1, the BET area is similar to that reported in the literature for these materials: 2900 m²/g by Eddaoudi et al. [3336] and 3362 m²/g by Rowell et al. [10]. Also similar values have been found for IRMOF-8, Wang et al. [4437] reporting an area of 1343 m²/g. It should be pointed out that in all cases the IRMOFs were synthesised by the solvothermal method, and there are not evidences about the decomposition of the material during the chromatographic experiments. At this point, samples prepared through microwave-assisted methods exhibit higher surface areas, but these structures are not stable at the operation conditions. However, in good agreement with the XRD findings, the greatest differences are observed for IRMOF-10: the surface area (265 m²/g) of this material is one order of magnitude lower than the BET area reported by Bae et al. [3538], although in this case the surface area was not experimental but calculated using simple geometrical techniques. Pore volume, both microporous and mesoporous, and pore diameter are consistent with the surface area data.

The thermal evolution of the IRMOFs is a key point because these materials will be used as adsorbents and desorption will be carried out by increasing temperatures. The typical thermogravimetric-differential thermogravimetric (TG-DTG) profile of the IRMOFs treatment is shown in Fig. 3. Thermal behavior is nearly the same in all cases. A first region, associated to a DTG peak around 350 K, is observed, attributed to N,N’-dimethylformamide loss [3639]. A sharp weight loss occurs from 650 K, indicating the collapse of the structure. This phenomenon was reported to occur between 573 and 773 K [3639, 3740]. According to these results, IRMOFs structures seem to be an interesting alternative to more conventional adsorbents, since thermal treatment produces the selective decomposition of the oxygenated groups of activated carbons, even at lower temperatures [3841], and in the case of zeolites, the thermolysis of the template could begin at 573 K [3942].
3.2. Adsorption parameters

According to the procedure outlined in the previous papers [2730,4043], adsorption isotherms were determined in the region of infinite dilution, the so-called Henry’s law region, using the elution by characteristic point (ECP) method, neglecting the 10 % lower part of the elution peaks, and correcting them by the Betchold method. Henry’s constant values, at 423 K (<1% of variation between successive measurements), for an n-alkane compound (n-hexane), an alkene (1-hexene), cyclic (cyclohexane and methylcyclohexane), aromatic (benzene and toluene) and chlorinated compounds (trichloroethylene and tetrachloroethylene), are shown in Fig. 4. These constants are measured at the linear portion of the isotherm, where the interactions between adsorbed molecules can be neglected. For all the compounds, the Henry’s constant increases in the order: IRMOF-1 < IRMOF-8 < IRMOF-10. Luebbers et al. [24], in a study about the adsorption of VOCs on three different IRMOF-1 by IGC, reported also higher values of the Henry’s constant for materials with the lowest surface area, attributing this result to the structural degradation of the sample, due to changes in pore geometry, increasing the surface area accessible for nitrogen molecules but not the available for the adsorption of larger VOCs. However, these authors are comparing the same IRMOF, prepared under different conditions. The same explanation could be plausible here, and consistent with XRD data. Furthermore, the aromatic compounds, as well as trichloroethylene and tetrachloroethylene are, in general terms, the compounds with the highest adsorption capacity, whereas the linear and cyclic compounds exhibit markedly lower values for the Henry’s constant. These data suggest that the π-bonds are determinant in the capacity of adsorption, and more important than the molecular sizes or the dipolar moment reported for carbon materials as it was already shown for the adsorption of hydrocarbons on ZIF-8 [4144].

A positive linear relationship between the Henry’s constant for the n-alkanes and their molecular cross-sectional area (i.e. the area of the projection of a molecule where a spherical molecular shape in a hexagonal close-packed configuration is accepted [452]) was observed, Fig. 5. This phenomenon, which is not observed for the other compounds, implies that the interaction between the surface of IRMOFs and the adsorbates increases with the size of the molecule. Furthermore, it is notorious that whereas differences are scarce for IRMOF-8 and IRMOF-10 for n-pentane to n-heptane, larger differences are observed for n-octane, and also lower slope is observed for IRMOF-1. This behavior can be understood taking into account that
whereas two of the three dimensions of n-alkanes are very similar (molecular x-axis of them is equal the same) for all n-alkanes and the variation of the other one between n-pentane and n-octane is about just 0.015 Å between n-pentane and n-octane for y-axis was measured), whereas the third one axis presents variations from the 9.1 Å for n-pentane to 12.8 Å for n-octane [436]. Taking into account the pore openings of Table 1, n-pentane is the only n-alkane which is not limited by the diameter of the entrance cavity in any IRMOF, thus this justifies the lowest slope for IRMOF-1. Concerning the different behavior of n-octane for IRMOF-8 and IRMOF-10, it is remarked that it could still cross freely the IRMOF-10 pores but not the IRMOF-8.

The strength of the interaction of each compound with the surface of the adsorbent is represented by the enthalpy of adsorption, $\Delta H_{ads}$, given by Eq. (3):

$$\Delta H_{ads} = -R \frac{\partial (\ln V_g)}{\partial \left(\frac{1}{T}\right)}$$

Adsorption enthalpies were achieved from the slope of plots of $\ln V_g$ vs. $1/T$, where this linear dependence implies a constant value of the enthalpy of adsorption in the range of studied temperatures (393 - 423 K). Results of adsorption enthalpies are showed in Table 2, whereas the parent plots, recorded at four different temperatures are provided as Supplementary Information. The heats of liquefaction ($\Delta H_{liq}$) [474] are also reported in this table, observing that the differential heats of adsorption over the three IRMOFs are higher than the heats of liquefaction, thus adsorbate-adsorbent interactions are stronger than adsorbate-adsorbate ones. In general, the strength of the adsorption increases with the size of the cage of IRMOF, in agreement with Henry’s constants. This fact could seem contradictory, since usually at a given loading, the adsorbate-framework strength of interaction increases with the lower pore diameter as the molecules are forced to be closer together in the small pores. At this point, it is necessary to point out that the surface area of the IRMOFs under study decreases with the increasing cavity size (Table 1), due to the presence of a nonporous phase. This hypothesis is confirmed by comparison of the measured enthalpies of adsorption for IRMOF-1 with the equivalents reported by Luebbers et al. [24] over three different samples of IRMOFs-1. For all common adsorbates analysed, Luebbers et al. [24] reported values of enthalpy of adsorption higher than the reported in this work, which is justified attending to the lower $S_{BET}$ reported: 1161, 781 and 208 m$^2$/g. Likewise, since the adsorption of organic molecules is considered, they would have higher affinity for organic compounds, thus this also
justifies that the strength to adsorption increases with the number of carbon atoms in the linker molecule: $-\Delta H_{\text{ads,IRMOF-1}} < -\Delta H_{\text{ads,IRMOF-8}} < -\Delta H_{\text{ads,IRMOF-10}}$. This appreciation is in good agreement with molecular simulations of $n$-butane adsorption on IRMOFs [25], where it was observed that $n$-butane isosteric heat of adsorption was higher for IRMOF-14 than for IRMOF-8. Comparing the enthalpies of adsorption of IRMOFs with more conventional adsorbents such as alumina, zeolites or activated carbons [4043], it is observed that differences among different materials are even lower than between the three IRMOFs here studied; and, in all cases higher than for non microporous carbons such as carbon nanotubes, carbon nanofibers or high-surface-area graphites [4048].

From chromatographic data, the standard free energy of adsorption at infinite dilution, $-\Delta G_{\text{ads}}$(kJ/mol), and the entropy of adsorption, $-\Delta S_{\text{ads}}$(J/mol K), were also calculated according to the procedure outlined in a previous work [485]. Briefly, the standard free energy of adsorption at infinite dilution, $-\Delta G_{\text{ads}}$(kJ/mol), can be expressed by Eq. (4):

$$\Delta G_{\text{ads}} = -RT \ln \left( \frac{P_0 V_f}{\pi_0 A} \right)$$

(4)

Where $A$ is the specific surface area of the adsorbent, and $\pi_0$ is the spreading pressure of the adsorbed gas in the De Boer standard state, which was taken as 338 μN/m. The other symbols were already indicated in the text. The meaning of the symbols is indicated in the list of symbols. Subsequently, the entropy of adsorption is calculated straightforwardly according to Eq. (5):

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

(5)

Results obtained are summarized in Table 2. The trend observed for all the IRMOFs was consistent over the whole temperature interval studied, although being only shown the data obtained at 423 K for simplicity. Fig.6 shows the existence of a so-called “thermodynamic compensation effect”, i.e., a linear dependence of $\Delta S$ on $\Delta H$. This effect for $n$-alkanes indicates that the stronger adsorption of longer $n$-alkanes is accompanied by a greater loss of mobility of the molecules (this means stronger interaction between the molecule and the surface). This type of plot allows highlighting differences in adsorbate–adsorbent interactions. A good fit of the compensation effect data to a straight line indicates the non specific nature of the adsorbate–adsorbent interactions. In the case of Fig. 6, just one straight line is depicted. Thus,
the lattice defects or the differences on the organic linkers do not affect the interaction of \( n \)-alkanes on these IRMOFs, suggesting that the surface of the studied materials is chemically analogous. In fact, as the organic linkers of the studied IRMOFs have not any functionality, the nature of the interaction does not vary with the size of the cage.

The interaction of \( n \)-alkanes with the surface has been also studied attending to the dispersive component of the surface free energy of the adsorbent. The dispersive component, \( \gamma_S^D \), is attributed to London forces and it is unspecific for all molecules. Comparing to the enthalpy of adsorption, \( H \), this parameter is slightly more sensitive to surface changes. The formula of Dorris and Gray has been used to calculate the values of this parameter [4496]:

\[
\gamma_S^D = \frac{1}{4} \frac{\Delta G_{CH_2}^2}{\gamma_{CH_2}^2 N^2 a_{CH_2}^2}
\]

where \( \Delta G_{CH_2} \) is the difference between the free energy of adsorption of two \( n \)-alkanes with succeeding values of carbon atoms, \( N \) is the Avogadro number, \( a_{CH_2} \) is the area occupied by a \( CH_2 \) group (0.06 nm\(^2\)), and \( \gamma_{CH_2} \) (mJ/m\(^2\)) is the surface tension of a surface consisting of \( CH_2 \) groups, which is a function of temperature in °C:

The meaning of the symbols is indicated in the list of symbols. The surface tension of a surface consisting of \( CH_2 \) groups, \( \gamma_{CH_2} \) (mJ/m\(^2\)), is a function of temperature in °C:

\[
\gamma_{CH_2} = 35.6 + 0.058 (20 - T)
\]

Values of the dispersive component for the range of temperature studied are shown in Fig. 7. The values of the dispersive component are very similar for the three tested adsorbents, indicating that the nature of the interaction is very similar as it was previously deduced from the thermodynamic compensation effect. In any case, it may be noteworthy that IRMOF-1 exhibits values of \( \gamma_S^D \) slightly higher than the others IRMOFs. This difference was attributed to the increase in the interaction potential in the smallest pores. In fact, according to the textural characterization, due to the structural damage, IRMOF-1 has the lowest pore diameter and the highest surface area. In all cases, the dispersive component of the surface free energy decreases with the temperature, due to the entropic contribution to the surface energy. This difference is slightly more marked for IRMOF-10, in agreement with the highest values of the
entropy. Comparing the values of the $\gamma_s^D$ here reported with those of the literature, they are very similar to those obtained by Luebbers et al. [24] for IRMOF-1, and much lower than those obtained, also by IGC, for microporous materials such as zeolites or activated carbons [4043].

Adsorption of $n$-alkanes takes place through dispersive interactions, yielding information related to carbon structure, polar probes are needed to determine the acid–base character of the surfaces. The adsorption of these molecules on the stationary phase involves, in addition to the dispersive interactions, specific contributions. One of the most useful methods is the “parameter of specific interaction”, $I^{sp}$, which is determined from the difference in free energy of adsorption between a polar solute and the real or hypothetical $n$-alkane with the same surface area [4507]:

$$I^{sp} = \frac{\Delta (\Delta G)}{N_a} = \frac{\Delta G_{ads}^S}{N_a}$$

Where $a$ is the probe surface area. Although this parameter has several sources of errors, it is satisfactory for those adsorbents without functional groups, and with values of $\gamma_s^D$ lower than 100 mJ/m² [5148]. The specific interaction parameters for the IRMOFs as well as the area of the projection of the molecule probe (nm²), the dipolar moment (D) and the polarizability deformation (Cm² V⁻¹) of the molecules are summarized in Fig. 8. It is worth noting that cyclohexane and methylcyclohexane show the lowest values of the $I^{sp}$. Contrary, aromatic compounds and trichloroethylene as well as tetrachloroethylene exhibit the largest specific interaction. As can be seen from Fig. 8, this behavior cannot be exclusively explained attending to the surface area of the molecules, thus, add to the structure effects detected by the $n$-alkanes adsorption dependence on the cavity size, other effects are also present. It is also remarkable, that the dipolar moment (a parameter that could be expected to be relevant in the specific interaction) is especially relevant for chlorocyclohexane, compound with a quite moderate specific interaction. Finally, the molecular polarizability of the different polar adsorbates could be, with some exceptions, an indicative of the specificity of this interaction. Thus, in order to assess the degree of importance of each of these parameters on the specificity of the interaction of these compounds, all of them have been adjusted according to the following expression:

$$I^{sp} = \alpha \cdot \text{surface area of molecule } + \beta \cdot \text{dipolar moment } + \chi \cdot \text{polarizability}$$
The fitting parameters \((\alpha, \beta, \gamma)\) were obtained for three different families of compounds, for the three IRMOFs under study. The goodness of the fit is shown in Fig. 9. It was found that for cyclohexane and methylcyclohexane, the most important parameters were the dipolar moment of the adsorbates \((\beta=14.3)\), and in lower extent, their polarizability \((\gamma=1.6)\). However, for the aromatic and the chlorinated compounds, the polarizability \((\gamma=4.1\text{ and } 3.2, \text{ respectively})\) of the molecules seems to be the most important parameter \((\alpha \approx \beta \approx 0)\). Furthermore, it is remarkable that the compounds with \(\pi-\pi\) bonds (trichloroethylene, tetrachloroethylene and aromatic compounds) are those with the largest values of \(I^0\), thus the specific interactions between the \(\pi\)-electron rich regions of the organic linkers and the double bonds of the molecules enhanced the adsorption. This observation is in agreement with molecular simulations of methane and butane on IRMOFs, showing that interaction energy was stronger as the number of carbon atoms in the linker molecule increases and the cavity size decreases [25].

4. Conclusions

Inverse gas chromatography has been used as technique to determine the adsorption properties of several organic compounds on three different IRMOFs, with cubic structure and without functionalities on the organic linkers: IRMOF-1, IRMOF-8 and IRMOF-10. It is shown that the capacity of adsorption at infinite dilution and the enthalpy of adsorption increase with the cavity diameter of the structures. For \(n\)-alkanes it is deduced a size dependence related to the pore opening of the IRMOFs. As general trend, it is observed that the strength of the interaction increases in the order IRMOF-1 < IRMOF-8 < IRMOF-10 because of two complementary effects: the presence of the lattice defects and the increase in the number of carbon atoms of the organic linkers. Likewise, from the thermodynamic compensation effect and the dispersive component of the surface free energy is deduced that the \(n\)-alkanes present the same centres of adsorption on the three IRMOFs. Concerning the specific interaction component, it was observed that the presence of \(\pi\)-electron rich zones (aromatic rings or double bonds) enhanced the specificity of the interaction by the favoured interaction with the aromatic rings of the organic linker molecules. Therefore, the specificity of the interactions is more related to the chemistry of the organic linkers than the structure of the IRMOFs.
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Nomenclature

Latin symbols

\( a \) —— probe surface area
\( A \) —— surface area of the adsorbent
\( \alpha_{\text{CH}_2} \) —— area occupied by a \( \text{CH}_2 \) group (0.06 nm\(^2\))
\( F \) —— volumetric flow rate of carrier gas
\( I^{sp} \) —— specific interaction parameter
\( j \) —— James-Martin compressibility factor
\( m \) —— mass of the adsorbent
\( N \) —— is the Avogadro number
\( p_i \) —— inlet column pressure.
\( \rho \) —— inlet column pressure.
\( p_0 \) —— outlet column pressure
\( p_w \) —— vapour pressure of water at the flowmeter temperature
\( t_{M} \) —— the retention time of a non-adsorbing marker (air)
\( t_R \) —— retention time
\( R \) —— ideal gas constant
\( T \) —— operation temperature
\( T_{\text{ambient}} \) —— ambient temperature
\( V_s \) —— specific retention volume

Greek symbols

\( \Delta G_{ads} \) —— free energy of adsorption
\( \Delta G_{\text{CH}_2} \) —— difference between the free energy of adsorption of two \( n \)-alkanes with succeeding values of carbon atoms
\( \Delta H_{ads} \) —— enthalpy of adsorption
\( \Delta H_{\text{liq}} \) —— heat of liquefaction
\( \Delta S_{ads} \) —— entropy of adsorption
\( \gamma_{\text{CH}_2} \) —— surface tension of a surface consisting of \( \text{CH}_2 \) groups
\( \gamma^D \) —— dispersive component of the surface free energy of the adsorbent
\( \pi_0 \) —— spreading pressure of the adsorbed gas in the De-Boer standard state, 338 \( \mu \text{N/m} \)
References


Table 1. Textural properties of IRMOFs studied in this work.

<table>
<thead>
<tr>
<th>IRMOF</th>
<th>$S_{BET}$</th>
<th>$V_{\text{micropores}}$</th>
<th>$V_{\text{mesopores}}$</th>
<th>$D_p$</th>
<th>Pore opening</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m^2/g$</td>
<td>$cm^3/g$</td>
<td>$cm^3/g$</td>
<td>Å</td>
<td>Å [25]</td>
</tr>
<tr>
<td>IRMOF-1</td>
<td>3046</td>
<td>1.103</td>
<td>0.115</td>
<td>24.9</td>
<td>10.9</td>
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<tr>
<td>IRMOF-8</td>
<td>1362</td>
<td>0.545</td>
<td>0.041</td>
<td>41.8</td>
<td>12.5</td>
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<tr>
<td>IRMOF-10</td>
<td>265</td>
<td>0.106</td>
<td>0.023</td>
<td>132.6</td>
<td>16.7</td>
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</tbody>
</table>
Table 2. Enthalpies of adsorption, standard free energies, entropies of adsorption and enthalpies of liquefaction of all adsorbates over the studied IRMOFs (free energies and entropies at 423 K).

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>$-\Delta H_{\text{liq}}$ (kJ/mol)</th>
<th>$-\Delta H_{\text{ads}}$ (kJ/mol)</th>
<th>$-\Delta G_{\text{ads}}$ (kJ/mol)</th>
<th>$-\Delta S_{\text{ads}}$ (J/mol K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IRMOF-1</td>
<td>IRMOF-8</td>
<td>IRMOF-10</td>
<td>IRMOF-1</td>
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<tr>
<td>$n$-Pentane</td>
<td>26.4</td>
<td>31.5</td>
<td>38.0</td>
<td>46.2</td>
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<tr>
<td>$n$-Hexane</td>
<td>31.6</td>
<td>34.1</td>
<td>49.2</td>
<td>50.8</td>
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<tr>
<td>$n$-Heptane</td>
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<td>41.1</td>
<td>57.0</td>
<td>58.7</td>
</tr>
<tr>
<td>$n$-Octane</td>
<td>41.5</td>
<td>51.9</td>
<td>68.0</td>
<td>66.7</td>
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<tr>
<td>1-Hexene</td>
<td>30.6</td>
<td>32.7</td>
<td>45.7</td>
<td>41.1</td>
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<tr>
<td>Cyclohexane</td>
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<td>34.1</td>
<td>35.9</td>
<td>37.6</td>
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<tr>
<td>Methylcyclohexane</td>
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<td>38.2</td>
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<td>47.5</td>
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<tr>
<td>Benzene</td>
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<td>35.1</td>
<td>43.9</td>
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<tr>
<td>Toluene</td>
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<td>64.3</td>
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<tr>
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<td>56.9</td>
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<tr>
<td>Trichloroethylene</td>
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<td>41.3</td>
<td>52.9</td>
<td>58.0</td>
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<tr>
<td>Tetrachloroethylene</td>
<td>39.7</td>
<td>48.5</td>
<td>57.3</td>
<td>53.0</td>
</tr>
</tbody>
</table>
Figure 1.
Figure 2.
Figure 3.
Henry's constant (µmol/g·mm Hg)
Figure 4.
Figure 5.
Figure 6.
Figure 7.
Figure 8
Figure 9.
Figure captions

Figure 1. XRD patterns for IRMOF-1, IRMOF-8 and IRMOF-10.

Figure 2. N$_2$ adsorption-desorption isotherms at 77 K for IRMOF-1 (●), IRMOF-8 (▲) and IRMOF-10 (■). Filled symbols: adsorption and open symbols: desorption.

Figure 3. TG and DTG curves of: (a) IRMOF-1, (b) IRMOF-8 and (c) IRMOF-10. Solid line: TG and broken line: DTG.

Figure 4. Henry’s constant at 423 K for n-hexane (HEX), 1-hexene (1-HEX), cyclohexane (CHX), methylcyclohexane (MCHX), benzene (BEN), toluene (TOL), trichloroethylene (TCE) and tetrachloroethylene (TTCE) over: IRMOF-1 (rectangle light grey), IRMOF-8 (cone dark grey) and IRMOF-10 (cylinder black).

Figure 5. Relationship between Henry’s constants and the molecular area for the n-alkanes (IRMOF-1 (●), IRMOF-8 (▲) and IRMOF-10 (■)).

Figure 6. The thermodynamic compensation effect for: IRMOF-1 (●), IRMOF-8 (▲) and IRMOF-10 (■).

Figure 7. Dispersive component of the surface free energy of the IRMOFs at several temperatures: 393 K (rectangle white), 403 K (cone light grey), 413 K (cylinder dark grey) and 423 K (pyramid black).

Figure 8. Influence of surface area (SA), dipolar moment (DM) and molecular polarizability (MP) of selected adsorbates on the l'' parameter at 423 K. Follow left axis for l'' and right axis for the other three parameters.

Figure 9. Predicted versus experimental l'' parameter at 423 K for selected compounds, for the three studied adsorbents: IRMOF-1 (●), IRMOF-8 (▲) and IRMOF-10 (■).