

INFLUENCE OF THE NATURE OF THE VOLATILE ORGANIC COMPOUND ON INTERACTIONS ENERGIES DURING ADSORPTION ONTO ACTIVATED CARBON

P. Pré, F. Delage and P. Le Cloirec

*Ecole des Mines de Nantes, Département Systèmes Energétiques et Environnement,
4 rue Alfred Kastler, BP 20722, 44307 NANTES Cedex 03, France*

Introduction

Adsorption onto activated carbon beds is one of the most effective technologies to capture organic vapors. However, the exothermal nature of the adsorption induces a warming of the bed which could be significant for high volatile organic compounds (V.O.C) concentrations [1]. High temperature increases might result in performance degradation. Moreover ignition of the bed can occur, especially when a flammable material like activated carbon is employed [2]. Thus, the temperature evolution during the operation should be controlled to insure the efficiency and the safety of the process.

For that purpose, a dynamic modeling tool was elaborated in order to predict the variations of the temperature and pollutant concentrations within the bed [3]. The model was validated with experimental tests. A very good agreement was observed between experimental and simulation results. But a correct simulation needs the knowledge of the adsorption energies of the VOCs involved.

The adsorption energies are usually obtained by experimental means. However, VOCs are so numerous that it seems unrealistic to constitute a representative data base from measurements only.

For that reason, it would be interesting to develop relationships between the adsorption energies of a great number of compounds and their structural characteristics in order to predict that of new compounds without experimentation. This approach would be also useful to understand the interactions between the organic molecule and the adsorbent surface.

The quantitative structure-properties relationships (QSPR) were first developed in the pharmaceutical area to predict the toxicity of chemicals or to study drug properties. More recently, the QSPR approach was extended to other areas such as environmental chemistry. Some studies were reported for the prediction of the adsorption rates of organic pollutants in water onto activated carbon [4].

The aim of this work was thus to set up quantitative relationships between the adsorption energies of 40 VOCs onto an activated carbon material and their structural and physical properties. The statistical method used was multiple linear regressions. The component characteristics were described either

with their physico-chemical data or with the topological index of Randic [5, 6].

Theory

Molecular connectivity indexes (MCI), originally proposed by Randic [5] are commonly involved in QSPR methods. These parameters, fundamental in nature, give structural information about the molecule. They are computed only from its bonding and atomic content and may be related to several physico-chemical properties [6].

The MCI were computed using MolconnZ software. These indexes are calculated from the hydrogen suppressed skeleton of the molecule. Each atom is assigned two descriptors δ and δ_v , based upon the count of sigma or valence electrons, other than those bonded to hydrogen atoms. δ and δ_v enable the simple and valence MCI to be computed, which are symbolized by ${}^m\chi_t$, where m is the index order and number of edges and t the fragment configuration (p for path, c for cluster, pc for path-cluster, ch for chain) :

$${}^m\chi_t = \sum_{i=1}^M \left(\prod_{k=1}^{m+1} \frac{1}{\delta_k} \right)_i \quad (1)$$

where M is the number of m -bond fragments in the molecule.

Each MCI encoded some specific information relative to the topological, geometrical and spatial characteristics of the molecule. The valence indexes contain the electronic information not included in the simple indexes.

Materials and Methods

Adsorption heat measurements.

Differential scanning calorimetry coupled to a thermogravimetric analysis (Setaram TG-DSC 111) was used to determine the heat of adsorption for a wide range of VOCs : 40 compounds among the principal chemical families. The measures were performed onto granular activated carbon material (Picactif NC60), whose main characteristics are given in Table 1.

A sample of the adsorbent material was first placed in a cell and heated until 120°C under inert atmosphere. This preliminary step allowed to remove the residual water content of the material. After cooling, the adsorption energies were determined at a constant temperature of 20°C. A gaseous mixture composed of VOC at a concentration of 50 g.m⁻³ diluted in helium was continuously flowing through the sample until saturation of the adsorbent. The mass variations and heat released were simultaneously collected.

VOCs physico-chemical data.

Physical adsorption is strongly dependent on the electronic properties of the molecule. So, the nature of the pollutant may be expected to have an effect on the energetic interactions with the adsorbent. Terzyk and Rychlicki [7] reported that the adsorption energies might be related to the polarisability, the ionization potential and the dielectric constant of the molecule. That's why a first attempt to correlate parameters representative of the electronic properties of the molecule with its adsorption energy was made.

The set of physical and chemical variables retained with their descriptive statistics are reported in table 2. The physical data were taken from [8], except the molar refraction R_m and the parachor Pa which result from a combination of other variables, according to the following equations :

$$R_m = \frac{(n^2 - 1)M}{(n^2 + 2)\rho_l} \quad (2)$$

$$Pa = \frac{M \sigma^{1/4}}{\rho_l - \rho_g} \quad (3)$$

where

- M molar mass (g.mol⁻¹)
- n refraction index
- σ_{LV} surface tension (mN.m⁻¹)
- ρ_g, ρ_l gas and liquid density (g.cm⁻³).

Because of its low standard deviation, the refraction index was finally removed from the selected parameters.

The MCI database.

For each compound, the χ path indexes up to the 5th order and the ${}^3\chi_c$ ${}^4\chi_c$ ${}^3\chi_{pc}$ ${}^4\chi_{pc}$ were computed using the MolconnZ software. Table 3 presents the descriptive statistics of the different χ indexes which were set up for the 40 compounds. The high standard deviation values show that each index encoded distinctive molecular characteristics, and have to be taken into account.

Results

Adsorption energies.

For the panel composed of 40 VOCs, adsorption energies measured ranged from 40 to 82 kJ.mol⁻¹ (Table 4).

The values reported are generally 1,5 to 2 times higher than condensation heats. These results show also that the length of the carbon chain has a significant effect on the adsorption heat. Figure 1 enlightens this influence by showing the adsorption heat increases with the number of carbon atoms constitutive of alkanes, alcohols, aldehydes and ketones molecules. Furthermore, a substitution scheme with halide or amino groups leads to greater energetic interactions. For example, the molar adsorption enthalpy of trichloroethylene (65.6 kJ.mol⁻¹) is lower than that of tetrachloroethylene (70.2 kJ.mol⁻¹). At last, it appears that double bonds may enhance electronic interactions with the solid, thus compared to alkanes, adsorption energies measured for alkenes are higher.

Prediction of adsorption energies from physico-chemical data.

A quantitative relationship between the physico-chemical data base and the adsorption energies measured was investigated. A multiple linear regression was carried out using a stepwise procedure (Minitab software). The best result obtained is given by equation (4) :

$$-\Delta H_{ads} = 91,3 (\pm 8,62) - 5,64 (\pm 0,71) IP + 0,071 (\pm 0,027) M + 0,083 (\pm 0,015) Pa \quad (4)$$

$$r^2 = 0.897 \quad s = 3.419 \quad N = 40$$

where r^2 is the determination coefficient, s the standard deviation and N the sample size.

The predictive ability of the above equation is illustrated on figure 2. The statistic quality of this regression seems to be correct, as the precision obtained is about 10%.

From this result, an increase of the adsorption energy value with the Parachor is observed. This parameter is therefore a function of the molar volume and the surface tension (equation 3). The molar volume is connected to the molecular overcrowding. The surface contact between bulky molecules and carbon is larger, and electronic interactions are then supposed to be favoured.

On the other hand, according to the model of Young [9], the interfacial tension liquid-vapor σ_{LV} involved in the parachor expression may be related with the interfacial tensions solid/liquid σ_{SL} and solid/vapor σ_{SV} (figure 3). Consequently, as σ_{SL} and σ_{SV} are representative of the interactions with the solid, the energies are influenced by σ_{LV} .

The adsorption energy varies conversely with the ionization potential. The ionization potential is indeed representative of the intensity of the electronic bonds with the atomic nucleus. Its influence on the potential energy of the London forces is expressed by [10]:

$$E_{London} = -\frac{3}{2} \frac{IP_1 IP_2}{IP_1 + IP_2} \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2 d^6} \quad (5)$$

where :

E_{London} London potential energy (J.mol⁻¹)

ϵ_0 vacuum permittivity (C².N⁻¹.m⁻²)

d distance between molecules 1 and 2 (m).

So it can be concluded that high ionization potentials reduce the contribution of the dispersive interactions. Although Debye's, Keesom's and London's energies are directly proportional to the polarisability of the molecule [10], this parameter doesn't appear in the predictive correlation. Actually, the linear correlation matrix between the physical variables shows that the polarisability α is strongly connected to the ionization potential IP.

Prediction of adsorption energies from connectivity indexes.

Most studies focused on the prediction of adsorption energies from physico-chemical data [7,10]. The approach based on the use of the MCI is therefore more innovative.

The best fit between the experimental and calculated values was obtained using the following correlation :

$$\begin{aligned} -\Delta H_{ads} &= 25,5 (\pm 2,6) + 5,77 (\pm 0,95) {}^0\chi \\ &+ 2,32 (\pm 0,90) {}^0\chi^v - 7,16 (\pm 2,12) {}^3\chi_c \\ &+ 11,9 (\pm 4,59) {}^4\chi_{pc}^v \end{aligned} \quad (6)$$

$$r^2 = 0.884 \quad s = 3.61 \quad N = 39$$

Figure 4 compares the measured adsorption heats with those computed from equation 6. For all the compounds except one (butylamine), a correct agreement is observed, with deviations less than 10%.

From the matrix correlation between the molecular connectivity indexes and the physical parameters (table 5), we have to notice that the ${}^0\chi$, ${}^0\chi^v$ indexes are strongly related to the parachor Pa, the molar volume V_m and the polarisability α . This confirms the major influence of these parameters on the energetic interactions. The ${}^0\chi^v$ index encodes molecular size whereas the ${}^4\chi_{pc}^v$ index is related to the substituents location and their orientation. The ${}^3\chi_c$ index which is indicative of very ramified molecules, has a negative effect on the adsorption heat. Assuming that the interactions with the carbon surface are mainly induced with the peripheral atoms, very ramified molecules will have a lower adsorption heat than flat molecules.

The statistic quality of the multiple linear regression set up from the MCI is a bit lower than

that stemmed from the physico-chemical data. However, the use of MCI brought some additional information, especially about the influence of the molecular structure. Thus, in case of isomers, the adsorption of the most ramified molecules should be less energetic.

Conclusion

The adsorption enthalpies of 40 VOCs onto a porous carbon material type (Pica NC60) were accurately determined using a calorimetric method (ATG-DSC). The measured values range from 40 to 80 kJ.mol⁻¹. The effect of the chemical's nature was first underscored from a qualitative point of view.

Quantitative structure properties relationships (QSPR) between the adsorption energies and the molecular properties were afterwards investigated. Two kinds of parameters were taken into account : physico-chemical data and molecular connectivity indexes. Multiple linear regressions were applied to set up the QSPR. Whatever the database used, a correct agreement was observed between the experimental and predicted values. Furthermore, these different approaches brought some substantial and complementary information about the mechanisms which have an effect on the intensity of the energetic interactions.

The method based on the physical parameters showed the major influence of the ionization potential and of the parachor. An high ionization potential inhibits the dispersion forces, leading to a diminution of the adsorption energy. Moreover, the parachor allows to account for the large surface contact available with great molar volume.

Except for one compound, the use of the connectivity indexes provided a similar statistics quality regression. The indexes involved in the final equation encodes specific informations about the molecular substitution scheme.

In this study, only one type of activated carbon was used and the characteristics of the adsorbent were not taken into account. In our future work, the database should be extended to elaborate QSPR representative of the influence of the material.

To improve the statistic quality of the predictive equations, the use of a more sophisticated tool like neural networks could be considered.

Acknowledgments

The financial support provided by ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie, France) is gratefull acknowledged. The authors wish also to thank Pica Co. And G. Dagois, the managing director, for the supply of activated carbon.

References

1. Delage F., Pré P., Le Cloirec P. Effects of moisture on the warming of an activated carbon bed. *J. Environ. Eng.* 1999; 125(12) :1160-1167.
2. EPA, Chemical Emergency Preparedness and Prevention Office. Fire hazard from carbon adsorption deodorizing systems. EPA 550-F-97-002-e, May 1998.
3. Delage F., Pré P., Le Cloirec P. Mass transfer and warming during adsorption of high concentrations of VOCs on an activated carbon bed : experimental and theoretical analysis. *Environ. Sci. Technol.* 2000; 34(22): 4816-4821.
4. Brasquet C., Bourges B., Le Cloirec P. Quantitative Structure-property relationships (QSPR) for the adsorption of organic compounds onto activated carbon cloth: comparison between multiple linear regression and neural network. *Environ. Sci. Technol.* 1999; 33: 4226-4231.
5. Randic M. On characterization of molecular branching. *J. A. Chem. Soc.* 1975; 97(23) : 6609-6615.
6. Kier L.B, Hall L.H. Molecular connectivity in structure-activity analysis 1986; John Wiley and Sons, Ed. Reas. Studies Press : Letchworth, England.
7. Terzyk A.P, Rychlicki G. Empirical relationship describing energetics of adsorption at low coverages of microporous carbons. *J. Thermal. Anal.* 1999; 55:1011-1020.
8. Lide D.R. Handbook of Chemistry and Physics. 77th Ed .1996.
9. Perry R.H, Green D.W. Perry's Chemical Engineering Handbook. 7th Ed. 1997; McGraw Hill, New York, USA.
10. Ruthven D.M. Principles of adsorption and adsorption processes. 1984; Wiley Interscience, USA.

Table 1. Properties of the activated carbon used

Raw material	coconut
Porosity	microporous
Mesh size	20×50–14×35
Pore volume (cm ³ .g ⁻¹)	0.55
BET surface area (m ² .g ⁻¹)	1240
Heat capacity (J.kg ⁻¹ .K ⁻¹)	880
Bed density (kg.m ⁻³)	425-440
Oxidation temperature (°C)	203

Table 2 . Physico-chemical parameters and their statistic descriptives.

Parameter	Mean m	Standard deviation s	$\frac{m}{s}$ (%)
Ionization potential IP	9.82	0.98	10.0
Molar mass M	85.70	26.71	31.2
Parachor Pa	215.6	54.78	27.7
Molar refraction R _m	23.76	7.40	31.1
Molar volume V _m	99.76	29.18	29.2
Refraction index n	1.397	0.041	2.9
Surface tension σ	22.98	3.88	16.9
Dipolar moment μ	1.40	0.92	65.7
Polarisability α	9.38	2.98	31.8
Dielectrical constant ϵ	9.02	7.93	87.9

Table 3 : Molecular connectivity indexes and their statistic descriptives

Index	Mean m	Standard deviation s	$\frac{m}{s}$ (%)
⁰ χ	4.359	1.190	27.3
¹ χ	2.468	0.756	30.6
² χ	1.818	0.875	48.1
³ χ	0.810	0.600	74.1
⁴ χ	0.476	0.446	93.7
⁰ χ^v	3.946	1.178	29.9
¹ χ^v	2.101	0.708	33.7
² χ^v	1.442	0.834	57.8
³ χ^v	0.552	0.452	81.9
⁴ χ^v	0.305	0.324	106.2
³ χ_c	0.272	0.413	151.8
³ χ_c^v	0.219	0.408	186.3
⁴ χ_{pc}	0.191	0.329	172.2
⁴ χ_{pc}^v	0.108	0.202	187.0

Table 4 . Heats of adsorption of various VOCs onto an activated carbon material (Pica NC60)

Molecule	Adsorption heat (kJ.mol ⁻¹)	Molécule	Adsorption heat (kJ.mol ⁻¹)
ethanal	48.5	Ethyl-formate	51.4
Ethyl acetate	61.2	Heptane	72.9
Iso-propyl acetate	68.5	Hexane	61.4
Acetone	50.6	1-Hexene	63.0
Ethyl acrylate	76.2	1-Hexyne	56.9
2-Bromopropane	54.2	Isobutylvinylether	64.7
Butylamine	74.9	Methyl-alcohol	40.8
Butyraldéhyde	53.2	Methylethylketone	56.2
Chloroform	50.5	Methylethyldioxolane	70.9
2-Chloro-propane	49.4	Methylisobutylketone	67.6
Cyclo-hexane	55.4	2-Methyl-1-propanol	56.6
Cyclo-hexene	63.5	Pentane	57.9
1.2-Dichloroéthane	51.2	Propyl alcohol	50.0
Dichloromethane	48.6	Propionaldehyde	49.4
Diethyléther	56.9	Tetrachloroethylene	70.2
Diisopropylamine	74.4	Tetrahydrofurane	49.1
Diméthoxyméthane	64.2	Toluene	63.1
Ethyl alcohol	48.6	Trichloroethylene	65.6
Isopropyl-ether	62.2	Triethylamine	81.9
Formaldéhyde	42.3	2.2.4-Trimethylpentane	75.3

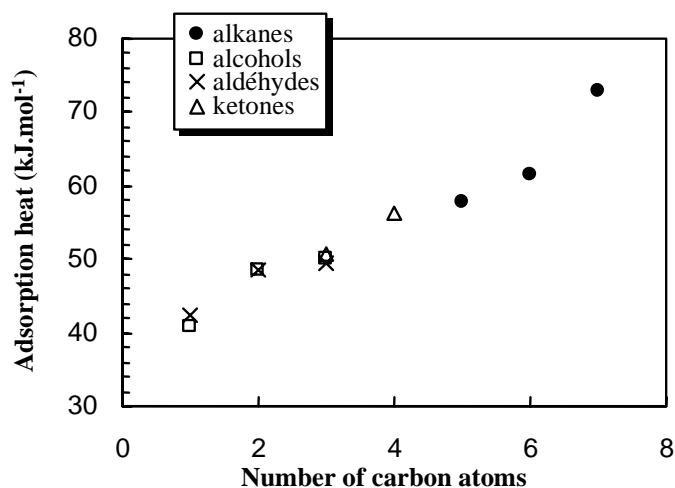


Figure 1. Influence of the carbon chain length on the adsorption heat

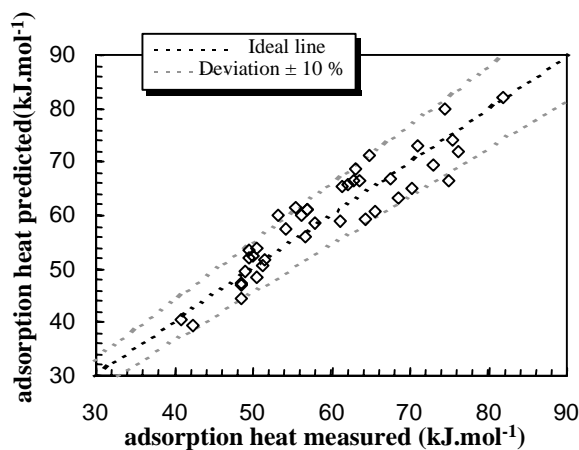


Figure 2. Predictive ability of the correlation from physico-chemical data

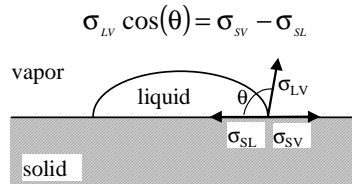


Figure 3. Model of Young (1905)

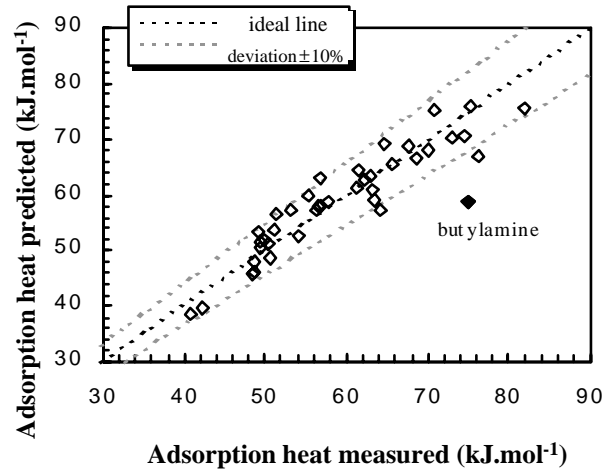


Figure 4. Predictive ability of the correlation from MCI.

Table 5 : Matrix correlation between the physico-chemical data and the MCI

	IP	M	Pa	R _m	V _m	σ	μ	α	ε
⁰ χ	-0.619	0.662	0.899	0.858	0.925	0.001	-0.194	0.865	-0.538
¹ χ	-0.647	0.569	0.868	0.837	0.890	-0.003	-0.258	0.831	-0.618
² χ	-0.490	0.690	0.806	0.831	0.835	0.099	-0.145	0.775	-0.442
³ χ	-0.656	0.466	0.616	0.649	0.643	0.074	-0.302	0.589	-0.473
⁴ χ	-0.549	0.478	0.700	0.695	0.715	0.068	-0.339	0.648	-0.520
⁰ χ ^v	-0.551	0.777	0.889	0.862	0.853	-0.038	-0.391	0.830	-0.578
¹ χ ^v	-0.458	0.689	0.914	0.927	0.922	0.072	-0.516	0.882	-0.617
² χ ^v	-0.241	0.766	0.780	0.826	0.763	0.144	-0.306	0.755	-0.490
³ χ ^v	-0.520	0.519	0.693	0.688	0.681	0.104	-0.492	0.657	-0.526
⁴ χ ^v	-0.443	0.490	0.764	0.719	0.744	0.031	-0.517	0.700	-0.532
³ χ _c	-0.147	0.379	0.474	0.479	0.510	0.008	0.112	0.418	-0.087
³ χ _c ^v	0.007	0.402	0.407	0.432	0.399	-0.012	0.039	0.367	-0.126
⁴ χ _{pc}	-0.486	0.399	0.409	0.456	0.493	0.065	0.013	0.372	-0.099
⁴ χ _{pc} ^v	-0.424	0.431	0.515	0.510	0.555	0.048	-0.141	0.462	-0.140