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Adsorption of Acetone, Methyl Ethyl Ketone, 1,1,1-Trichloroethane, and Trichloroethylene in Granular Activated Carbons

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The adsorption isotherms of two oxygenated and two chlorinated volatile organic compounds, namely acetone, methyl ethyl ketone, 1,1,1-trichloroethane, and trichloroethylene, were determined at 298 K, by the gravimetric technique, in four granular activated carbons. The textural properties of the adsorbents were evaluated from low-temperature nitrogen adsorpion. The Dubinin−Astakhov equation was used to fit the data, and a discussion of the results was made on the basis of relevant physical properties of the adorbate molecules.

Introduction

In recent years a particular class of substances, known as volatile organic compounds (VOCs), has attracted the attention of the authorities, the scientific community, and the industries, due to the recognition that a large proportion of these compounds, which are used in a variety of processes, can cause severe health effects. Considering only the present 15 E.C. countries, and admitting that recent regulations will be met, an amount higher than 6.5×10^6 tons of volatile organic compounds will be released to the atmosphere by the year 2010. In the U.S. it is estimated that about 0.5×10^6 tons of VOCs are emitted annually.[1,2]

The use of activated carbons in gas separation by adsorption is a fact known for a long time and does not need to be justified.[3,4] The potentialities of using such materials in the abatement of VOCs in the vapor phase are, obviously, high, particularly due to their high adsorption capacity and their hydrophobicity.[5,6] The limitations of these solids, in relation to their use as adsorbents of volatile organic compounds, are mainly related with temperature constraints,[7] since these materials are flammable. This is an important fact that has to be taken into account, since the regeneration of adsorbents is frequently made by increasing the temperature.

One important group of studies concerning the adsorption of VOC molecules in activated carbons was related with the development of suitable adsorbents for sampling and, therefore, for increasing the accuracy of the analytical methods currently used when monitoring the level of a particular volatile organic compound in the atmosphere.[8,9]

The adsorption isotherms can be regarded as the primary source of information on a particular adsorbent/adsorbate system whose data can be used to evaluate the suitability of a particular adsorbent, or as a starting point for modeling the adsorption process, that can include the recollection of VOCs or even their selective separation.[10] A number of studies of adsorption of volatile organic compounds in activated carbons, with different insights, can be found in the literature.[10−25] However, the understanding of such adsorbent/adsorbate systems at a physical−chemistry level, in the majority of cases, is far from clear. This work aims to contribute to the understanding of the role of the main factors, from the adsorbent and from the adsorbate, which influence the adsorption isotherm, a question that has several practical implications. To this effect, four commercial activated carbons and four VOC molecules were selected. The activated carbons had a granular form, since this work is part of a project related with the development of filters, by supporting the adsorbent materials in polymeric matrixes, and in this way, granular activated carbons are advantageous over, for instance, powder activated carbons. The selected VOCs are representative examples of oxygenated and halogenated solvents, which have wide use in the industry, namely acetone, methyl ethyl ketone (MEK), 1,1,1-trichloroethane (TCA), and trichloroethylene (TCE).

Experimental Section

Materials. Four commercial activated carbons, labeled as RB1, RB3, RB4, and CarbTech, were used. The former three are indicated for the removal of contaminants from gas flow, and the latter is used in some incinerators of urban residues. The micropore size distributions of the four samples, evaluated from the Horvath−Kawazoe method,[26] are narrow and present a maximum for a width of 0.65 nm, the differences between the samples being within the precision of the method. The surface chemistry of these samples was characterized by the method of Boehm titration, as described in detail elsewhere.[26] Briefly, this method consists of equilibrating a given amount of solid (1 g during 24 h), with different basic or acid solutions (each solution in a given vessel) of NaOH, $NaCO_3$, $NaHCO_3$, and HCl. After equilibration the excess of acid or base, which did not react with the activated carbon, was titrated with NaOH or HCl, respectively. The concentration of each aqueous solution was 0.05 N. The results, expressed as type of site, total acidity, and total basicity,[26] are summarized in Table 1.

Adsorption Isotherms. To determine the adsorption isotherms of nitrogen at 77 K, the samples (about 50 mg) were outgassed at 573 K, for 2 h after a ramp of 10 K/min, under a dynamic vaccum better than 10^{-2} Pa. Nitrogen was 99.995% (Air Liquide, France) pure, and the results were

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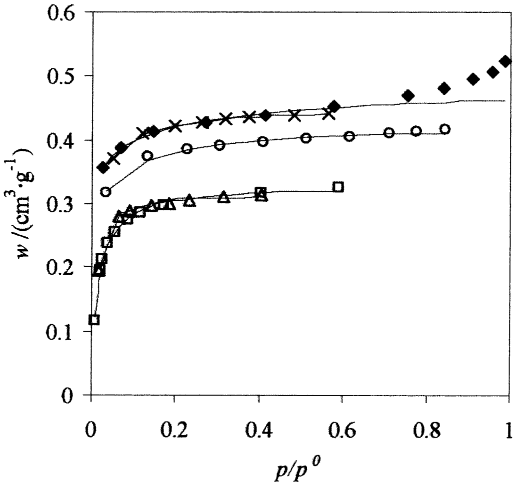

Figure 1. Adsorption isotherms of (◆) nitrogen, (□) acetone, (△) TCA, (×) TCE, and (O) MEK in the RB1 sample (nitrogen at 77 K and others at 298 K).

Table 1. Results of the Boehm Titration (Sites in mmol·g^{-1})

sample	carboxylic	lactonic	phenolic	tot acidity	tot basicity
RB1			0.238	0.238	0.445
RB3			0.150	0.150	0.510
RB4			0.135	0.135	0.475
CarbTech	0.005	0.038	0.143	0.185	0.220

collected, either in a manual Pyrex-made volumetric apparatus where the pressure readings were made with a model 600a (Datametrics, USA) pressure transducer, or in an automated instrument model ASAP 2010 (Micromeritics, USA). The adsorption isotherms of acetone (BDH, 99.5%), methyl ethyl ketone (BDH, 99.5%), 1,1,1-trichloroethane (Aldrich, 99%), and trichloroethylene (Fluka, 99.5%) were determined by the gravimetric method using microbalances from C.I. Electronics (U.K.), which allowed a precision of 10 μg. The pressure readings were made with capacitance transducers from Shaevitz (U.K.). A combination of rotary/oil diffusion pumps and heating the solids, in a similar way as described for the case of the nitrogen adsorption isotherms, accomplished the outgassing of the adsorbents. The adsorption temperature was maintained at (298 ± 0.1) K with a water bath (VWR Scientific, USA). Prior to adsorption, the vapors were purified in situ by freeze−vacuum−thaw cycles. Adsorbed amounts are expressed in cubic centimeters per gram of the outgassed samples, obtained through the respective liquid density at the adsorption temperature.

Results and Discussion

In Figures 1−4, the adsorption isotherms, for nitrogen at 77 K and acetone, TCA, TCE, and MEK at 298 K, in the various adsorbents, are plotted. In the case of the nitrogen adsorption, and for all the adsorbents, the curves presented a slight adsorption hysteresis at high relative pressures (not shown). Thus, the nitrogen adsorption isotherms can be considered of type IV, according to the IUPAC classification,[28] but the highly rectangular character of the curves indicates that these materials are mainly microporous solids. The values of the micropore volumes, estimated from the Dubinin−Astakhov (D−A) equation as indicated below, and the total pore volumes (from the adsorbed amounts at relative pressures of 0.95−0.98) are given in Table 2. For each adsorbent the maximum adsorption capacity is, in general, given by the nitrogen isotherm. This is clearly verified for the RB1, RB3, and RB4 samples. For CarbTech the amounts adsorbed of TCE and

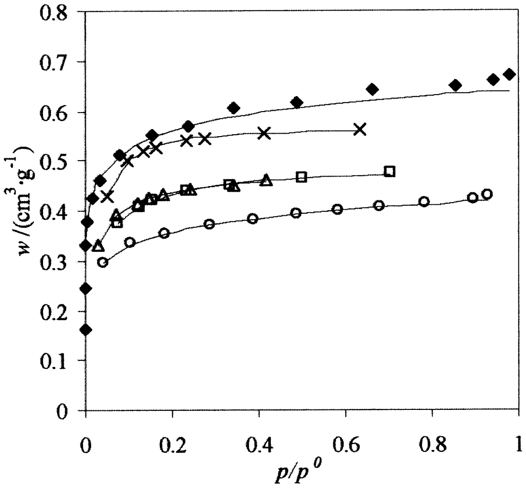

Figure 2. Adsorption isotherms of (◆) nitrogen, (□) acetone, (△) TCA, (×) TCE, and (O) MEK in the RB3 sample (nitrogen at 77 K and others at 298 K).

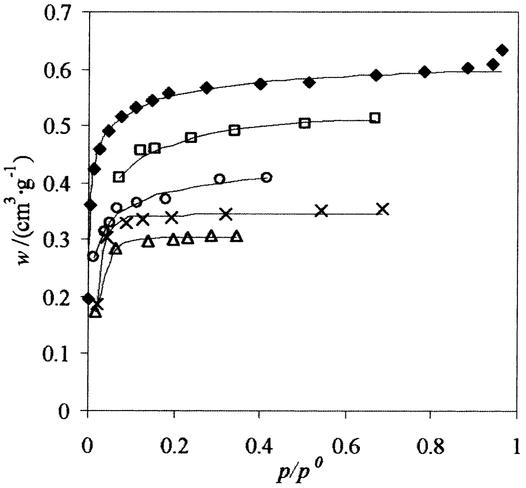

Figure 3. Adsorption isotherms of (◆) nitrogen, (□) acetone, (△) TCA, (×) TCE, and (O) MEK in the RB4 sample (nitrogen at 77 K and others at 298 K).

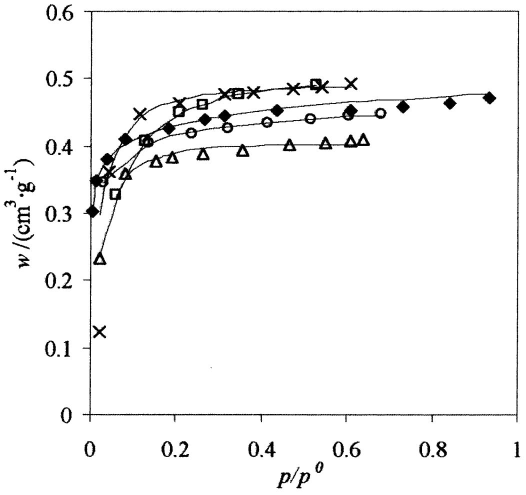

Figure 4. Adsorption isotherms of (◆) nitrogen, (□) acetone, (△) TCA, (×) TCE, and (O) MEK in the CarbTech sample (nitrogen at 77 K and others at 298 K).

Table 2. Textural Characteristics of the Studied Samples, Obtained from the Nitrogen Adsorption at 77 K: Micropore Volume, V_μ (D−A Method), and Micro- + Mesopore Volumes, $V_{\mu+\mathrm{meso}}$

	V_μ/cm^3·g^{-1}	$V_{\mu+\mathrm{meso}}$/cm^3·g^{-1}
RB1	0.46	0.51
RB3	0.64	0.66
RB4	0.59	0.63
CarbTech	0.48	0.49

Table 3. Results of the D−A Equation for the Studied Systems (w_0 in cm^3·g^{-1} and E in kJ·mol^{-1})

		RB1	RB3	RB4	CarbTech
nitrogen	E	6.99	5.89	5.98	7.57
	w_0	0.46	0.64	0.59	0.48
	n	1.22	1.16	1.48	1.16
acetone	E	12.48	13.89	14.66	10.41
	w_0	0.32	0.48	0.52	0.5
	n	2.77	1.9	1.86	2.31
MEK	E	20.51	20.98	18.07	21.64
	w_0	0.41	0.42	0.42	0.45
	n	1.57	1.10	1.64	1.48
TCA	E	12.49	15.17	11.23	11.90
	w_0	0.31	0.47	0.30	0.40
	n	3.70	2.10	5.54	3.18
TCE	E	17.16	11.62	10.06	12.11
	w_0	0.44	0.56	0.34	0.49
	n	2.09	3.15	8.70	2.90

Table 4. Physical Constants of the Studied VOCs

	μ^a/D	α^b/($\times 10^{-40}$ C·m^2·V^{-1})	r^c/nm	A^c/nm^2	$p^{\circ\, d}$/kPa
acetone	2.8	7.14	0.308	0.298	26.66
MEK	3.3	9.12	0.329	0.339	12.82
TCA	1.8	11.5	0.340	0.364	16.06
TCE	0.9	11.2	0.329	0.340	9.51

[a] From ref 35. [b] Estimated from the Lorenz−Lorentz relation. [c] From the liquid density[34] assuming an equivalent spherical shape. [d] At 298 K from ref 35.

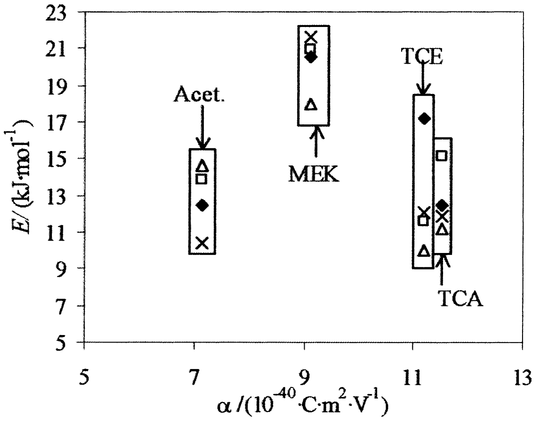

Figure 5. Relation between the E parameter of the D−A equation and the polarizability of the VOC molecules for the various samples: ◆, RB1; □, RB3; △, RB4; ×, CarbTech.

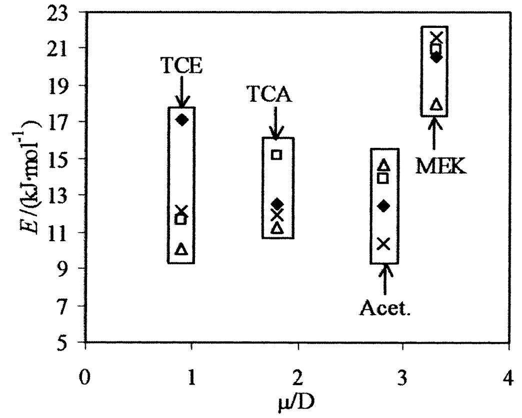

Figure 6. Relation between the E parameter of the D−A equation and the dipole moment of the VOC molecules for the various samples: ◆, RB1; □, RB3; △, RB4; ×, CarbTech.

acetone are slightly higher than those for nitrogen. These differences are within 5%, and although some kind of chemisorption could also explain this fact, those differences are most probably related with the uncertainty that is, to a certain extent, associated with the method used, that is, to the conversion of the adsorbed amounts to liquid volume with the admission that the adsorbed phase behaves as the liquid phase. This hypothesis is, for many systems, a good approximation, but small differences in the subsequent results have to be interpreted with caution. It can also be seen in Figures 1−4 that, except for the CarbTech sample, where the isotherms expressed in liquid volume are all much closer, for the other adsorbents, the curves can be rather dependent on the type of VOC.

The analysis of adsorption isotherms was made using the D−A equation.[5] This equation has been applied to the adsorption of a large variety of organic molecules in different adsorbents.[16,29,30] Briefly, the D−A equation has the form $w = w_0 \exp[-(A/E)^n]$ where the amount adsorbed, w, is related with the value for the limiting adsorbed amount, w_0, and A is the adsorption potential ($A = RT \ln p^\circ/p$). E and n are temperature invariant parameters. E is the characteristic adsorption energy and can be related with the energetics of the adsorbate/adsorbent system.[31−33] The D−A equation was fitted to the experimental data using the nonlinear least-squares method, and therefore, the values of E, w_0, and n were obtained for the adsorption of nitrogen as well as for the adsorption of the VOC molecules. Correlation coefficients were between 0.9910 and 0.9997, and the χ^2 of the fit was between 6.3×10^{-5} and 4.0×10^{-6}, with deviations of less than 3% to the fitted data. The obtained parameters (E, w_0, and n) are recorded in Table 3, and the fittings correspond to the solid lines in Figures 1−4. The observation previously made about the relation between the amounts adsorbed for nitrogen and for the different VOC molecules can now be quantified by the relation of the respective values of w_0. For the majority of the studied systems, a considerable amount of the total micropore volume available to nitrogen is not accessible to the VOCs. Considering the values given in Table 4, in which different physical constants of the adsorbates are recorded, it can be seen that the smaller molecule (acetone) does not correspond necessarily to the larger occupation of the adsorption space but, in contrast, for TCA (the larger molecule) in each adsorbent the lower adsorbed amounts are usually found.

To ascertain the influence of aspects related with the adsorbate−adsorbent interactions on the adsorption isotherm, the E parameter of the D−A equation was plotted in Figures 5−7 against different physical properties of the adsorbates: respectively, the molecular radius, the dipole moment, and the polarizability. The polarizabilities were estimated, from the refractive indexes, using the Lorenz−Lorentz relation, with the goodness of the estimate being confirmed in the cases where the polarizabilities were known from other sources.[34]

Considering first the assemblage of the results expressed in Figure 5, it is clear that the characteristic energy, E, is not in line with the polarizability, α, of the molecules. This

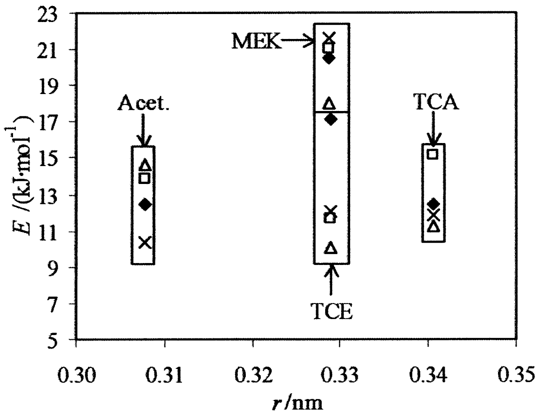

Figure 7. Relation between the E parameter of the D−A equation and the estimated radius of the VOC molecules for the various samples: ◆, RB1; □, RB3; △, RB4; ×, CarbTech.

means that besides the dispersion forces (London forces), which are always present in gas/solid adsorption and increase with α, there are other forces which, at least in some systems, are also relevant.

In the case of the oxygenated VOCs, the increase in the characteristic energy from acetone to MEK is, in general terms, related with the magnitude of the polarizability (Figure 5), the dipole moment (Figure 6), or the molecular radius (Figure 7). The fact that the energetic parameter is related positively to both the polarizability and the dipole moment does indicate that, in this case, besides the dispersion forces, also specific interactions with the dipoles could be significant. Nevertheless, in this phase of the discussion, it is not possible to evaluate the relative importance of these latter interactions, as the E parameter is expected to increase with the polarizability and the polarity of the molecules. In the case of the studied chlorinated molecules, the dependence of the E parameter on the physical properties of the adsorbates is less accentuated and the dipole moment (Figure 6) does not seem to play a marked role, suggesting that, in this case, the dispersion forces are dominant.

In fact, the values of E for TCE and TCA, molecules with different dipolar moments, are, on average, comparable, a situation that can be related with the proximity of the values of the polarizabilities (Figure 5). The relevance of these forces, compared to other more specific interactions, for the studied systems, can be to a certain extent appraised in terms of the small number of specific adsorption sites in the active carbons. In fact, according, for instance, to the values of the acid and basic sites (Table 1), which are a measure of the potential sites for specific adsorption, these are in the range 0.5 mmol·g^{-1} or less. Considering an average value of 0.3 cm^3·g (3.35 mmol·g^{-1}) for the adsorption of the molecule with the higher dipole moment (MEK), it can be concluded that less than 15% of the adsorbed molecules could interact specifically with the surface. So, and admitting now, as said above, that in the studied systems other specific interactions are not significant, and physical adsorption is, indeed, the predominant and almost exclusive process, more information can be obtained considering again, globally, the results, and the average of the values obtained on the different adsorbents, for each adsorbate. The fact that the E parameter does not always increase with the polarizability (Figure 5) discloses the importance of the interaction with the dipoles of the adsorbates, which are greater for the oxygenated VOCs than for the chlorinated molecules. With the latter molecules, the effect of the dipoles in the adsorption energetics is not evident. On the contrary, with the oxygenated VOCs, with lower values of α and higher values of μ, the conditions are more favorable to enlighten the relevance of the polarity on the adsorption and explain the maximum values of E obtained for the adsorbate MEK.

Conclusion

In general, the adsorption data on granular activated carbons presented in this work, as far as the adsorption of volatile organic compounds is concerned and admitting that the studied molecules are representative of two important families of VOCs, pointed out that the nature of the surface and the specific interactions that can be developed in this context, as far as noncompetitive adsorption is concerned, do not seem to be a major factor of importance. These considerations have several implications either in the development of new carbonaceous adsorbent materials or in the selection of this type of adsorbents for the abatement of VOCs, with the textural features, such as high surface areas and high micropore volumes, being more important parameters in this context.

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