

Adsorption of Methylamines on Carbon Materials at Zero Surface Coverage

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This paper deals with the adsorption of mono-, di- and trimethylamine (MMA, DMA and TMA) on carbon materials at zero surface coverage studied by inverse gas–solid chromatography (IGSC). The adsorbents have different textural characteristics and chemical surface groups, as revealed by N₂ and CO₂ adsorption, mercury porosimetry, FTIR spectroscopy and selective titrations. These properties are related to the type of interactions of the adsorbates. MMA is adsorbed almost totally by specific interactions, and this type of force is weaker in DMA and TMA, following the same trend as the dipolar moment of the adsorbates. There is evidence to support a dipole–dipole type adsorbate–adsorbent interaction instead of an acid–base one.

Introduction

Methylamines are important intermediates in the chemical industry for the synthesis of nitrogen containing organic compounds. They are produced in large amounts by amination of methanol with ammonia over acid catalysts.¹ In this synthesis the interaction between the reaction products and the surface catalyst is a very important factor because this can be determinant in the products' selectivity.^{2,3} Increasing interest is being paid to the use of carbon materials as catalysts for this and other organic chemical syntheses.^{4–6} Another important aspect in relation to methylamines is the adsorption process, since this can be a way to eliminate them from pollutant atmospheres. At high airborne concentrations methylamines display an asphyxiating character, at lower concentrations they induce damage to the eyes and respiratory tract, and even the slightest leak produces an unpleasant fishy odor, which is detectable above 0.1 ppm.⁷ The elimination of these substances by adsorption on activated carbons will depend on the textural and chemical surface characteristics of the adsorbent.

As already mentioned, carbon materials are used as either catalysts or adsorbents and their efficiency is determined by the nature of the interaction with the adsorbate. For this reason, it would be of interest to study the type of interaction between methylamines and carbon materials. As methylamines are polar molecules, they can interact with the chemical surface groups of the carbon materials through dipole–dipole, acid–base or hydrogen bond interactions, producing, so-called, specific interactions. They can also interact through London dispersion forces, or nonspecific interactions.

Carbon materials have a great versatility of textural and chemical surface characteristics. Among the former, the surface area and porosity vary in relation to the raw material and the preparation conditions. Porosity can often be tailored by using organic polymers or copolymers as precursors, by chemical treatments or by carbon deposition.^{8–12} Among the chemical characteristics, it is necessary to take into account the chemical surface functionalities, mainly oxygen surface groups, which appear as acidic, basic, or neutral.¹³ The amount and type of chemical surface groups can be changed by several treatments such as aqueous acid treatments (HNO₃, HCl, H₂SO₄, ...), gas phase (O₂, CO₂, ...) or plasma.¹⁴ The textural characteristics (surface area and porosity) determine the nonspecific interactions, whereas the oxygen surface groups condition the specific interactions.

The aim of this paper is to study the adsorption of mono-, di- and trimethylamine (MMA, DMA and TMA) at very low vapor concentration (zero surface coverage) on several carbon materials. Inverse gas–solid chromatography (IGSC) has been used in this study. The process under study was carried out on several carbon materials with different textural characteristics with varying amounts of oxygen surface functionalities produced by several treatments.

Experimental Section

The adsorbents used were several carbon materials of different origins and methods of preparation. A char, C0, was obtained by pyrolysis of almond shells in N₂ flow at 1223 K. C20 is an activated carbon obtained by treatment of C0 in CO₂ flow at 1223 K for 1 h, producing 20% of burnoff. GAe is a commercial activated carbon manufactured by CECA. This was demineralized by

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treatments with HF and HCl solutions. GAe-ox1 is a carbon material obtained by treatment of GAe in aqueous solution of ammonium persulfate,¹⁵ (NH₄)₂S₂O₈. For this, the carbon material was put in contact with a saturated solution of (NH₄)₂S₂O₈ in 1 M H₂SO₄ (1 g of carbon/10 mL of solution) for 2 days. GAe-ox2 was also obtained by treatment of GAe in aqueous solution, but of H₂O₂ in this case.¹⁶ The sample was kept in a concentrated H₂O₂ solution (9.8 M) (1 g of carbon/50 mL of solution) for 2 days. After the treatments of GAe with both solutions the samples were heat treated in N₂ flow up to 773 K. GAe-1%O₂P is a sample obtained from GAe by oxygen plasma treatment. The percentage (1%) appended to the name GAe refers to the percentage of weight loss produced during the treatment. Further details of this preparation method are given elsewhere.¹⁷

The samples were characterized by N₂ and CO₂ adsorption and mercury porosimetry. From the adsorption measurements at 77 and 273 K for N₂ and CO₂ respectively, the surface areas accessible to these molecules were determined. Moreover, the micropore size distributions were deduced by applying the Dubinin–Stoeckli equation to the CO₂ adsorption data.¹⁸ Mercury porosimetry up to 4200 kg/cm² was used to determine the volume of pores, V_2 , between 3.6 and 50 nm in width (mesopores), and V_3 , the volume of pores larger than 50 nm in width (macropores).

The chemical surface functionalities of the samples were determined by selective neutralization and Fourier transformed infrared spectroscopy (FTIR). Selective neutralizations were carried out using the selective method proposed by Boehm.¹⁹ This uses NaHCO₃ to titrate carboxyl groups; lactones are determined by the difference between the groups titrated by Na₂CO₃ and by NaHCO₃; the difference between these groups titrated by NaOH and by Na₂CO₃ are phenols; basic groups are titrated by HCl. Transmission FTIR spectra were recorded between 4000 and 400 cm⁻¹ using a Nicolet 20 SXB spectrophotometer. Wafers of KBr containing about 0.5% of carbon material were prepared and were dried overnight at 393 K before the spectra were recorded.

The adsorption of methylamines (MMA, DMA and TMA) was studied with a gas–solid chromatograph equipped with a flame ionization detector. A 3 mm i.d. glass column was used and nitrogen was the carrier gas. Before the adsorption runs the column with the adsorbent was conditioned at 613 K in nitrogen flow overnight. The adsorption experiments were carried out within 473 and 593 K. The adsorbates, as vapor, were withdrawn with a syringe from a bulb at constant temperature and injected into the column. At least three different amounts (between 0.1 and 5 μ L) of sample were injected at each temperature in order to check that the retention time did not depend on the amount injected. This means that the adsorption process is produced in the region of Henry's law (zero surface coverage) where the amount adsorbed and the adsorbate vapor pressure fit to a linear relationship. In addition to these measurements, the adsorption of linear hydrocarbons (from *n*-C₄ to *n*-C₇) was also studied in the same experimental conditions. This was carried out because adsorption of *n*-alkanes is considered as a reference to evaluate the specific contributions to the adsorption free energy of molecules capable of these interactions. This aspect will be considered in detail latter on.

Results and Discussion

The surface areas and pore volumes are recorded in Table 1. C0 has relatively small surface areas and pore volumes. Moreover, the difference between SCO₂ and SN₂ means that there are constrictions in the micropore network that hinder the access of N₂ molecule at 77 K.²⁰

Table 1. Textural Characteristics

sample	SN ₂ (m ² •g ⁻¹)	SCO ₂ (m ² •g ⁻¹)	V ₃ (cm ³ •g ⁻¹)	V ₂ (cm ³ •g ⁻¹)	W ₀ (cm ³ •g ⁻¹)
C0	412	575	0.053	0.079	0.218
C20	771	977	0.115	0.027	0.371
GAe	1026	1185	0.146	0.171	0.449
GAe-ox1	1129	1403	0.165	0.283	0.532
GAe-ox2	1196	1304	0.204	0.433	0.495
GAe-1%O ₂ P	1017	1167	0.136	0.179	0.443

The activation of C0 produces C20 by developing the surface areas and pore volumes, but there are still constrictions in the micropore network hindering the access of N₂ (SCO₂ > SN₂). Samples of the GAe series have larger surface areas and pore volumes with a well developed microporosity. Moreover, sample GAe-ox2 (obtained by treatment with H₂O₂) has a very well developed mesoporosity (V₂).

The micropore distribution can be obtained if a Gaussian distribution of half-width Δ is accepted. Taking L as the pore width, L_0 the pore width at the maximum of the distribution, W the micropore volume of pores of L in width, and W_0 the total micropore volume, the equation for the micropore distribution is^{21,22}

$$\frac{dW}{dL} = \frac{W_0 ML}{2\Delta \sqrt{2\pi}} \exp\left[-\frac{M^2(L_0^2 - L^2)}{32\Delta}\right] \quad (1)$$

The values of the parameters W_0 and Δ , required to apply eq 1 can be determined from two equations: the Dubinin–Astakhov (eq 2) and the empirical eq 3.¹⁸ Further details of this method to determine the micropore size distribution are given elsewhere.^{18,22–24}

$$W = W_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \quad [2] \quad (2)$$

$$n = 2.00 - 1.78 \times 10^6 \Delta \quad (3)$$

The plots obtained using eq 1 are compiled in Figure 1. The curve for sample C0 is not depicted because the n value (eq 3) is larger than 2, and, therefore, the empirical eq 3 cannot be used. Figure 1 shows that samples from GAe series have a more opened microporosity than the C series. Moreover, as shown by the shifts of curves for GAe-ox1 and GAe-ox2, the treatments of GAe in solutions of (NH₄)₂S₂O₈ and H₂O₂ produce a further opening of the microporosity. Moreover, it has been reported²⁴ that both treatments in solution also produce opening of the very small micropores (between 0.43 and 0.60 nm). The treatment with oxygen plasma, sample GAe-1%O₂P, does not change the micropore network determined by CO₂ adsorption (Figure 1) because the micropore distribution curve is coincident with that of GAe. This is in agreement with reported data that show plasma treatments only affect the external surface of carbon materials,^{17,25} creating new porosity and/or opening the preexistent small micropores on the external surface. This latter effect is particularly important at low degrees of burnoff.

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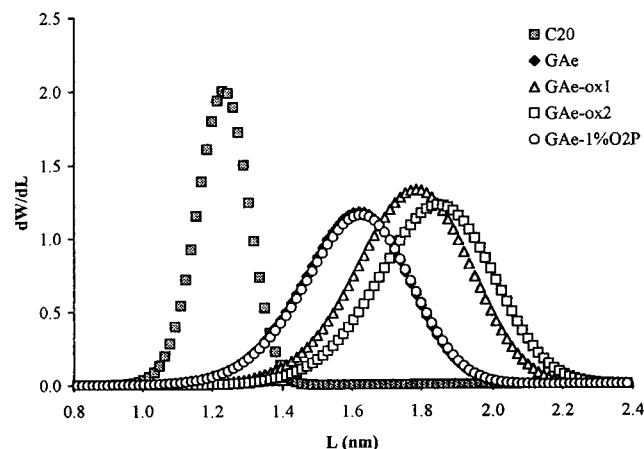


Figure 1. Micropore size distribution obtained with eq 1.

The results of the chemical surface groups analyses consisting of selective titrations are compiled in Table 2. C-series samples (C0 and C20) have an important number of basic groups whereas the amount of acid groups (carboxyls, lactones and phenols) is very small. However, GAe-series samples have important amounts of acid groups. This amount is increased, in comparison to GAe, in samples obtained by the treatments in solution (GAe-ox1 and GAe-ox2) and by plasma treatment, GAe-1%O₂P. Moreover, in this last sample the number of basic groups has also been increased. To sum up (i) samples C0 and C20 mainly have basic groups, (ii) the chemical surface groups in GAe, GAe-ox1 and GAe-ox2 are mainly acid, (iii) GAe-1%O₂P has the largest number of acid surface groups.

The presence of these chemical surface groups can be seen by FTIR. The spectra of the samples of C0 and C20 are shown in Figure 2a and those of GAe-series in Figure 2b. The assignment is based in the literature.^{17,26–28} C0 and C20 show two low intensity bands at 2920 and 2850 cm⁻¹ assigned to aliphatic structures. In relation to the oxygen containing surface groups, these samples have a broad band in the range between 1100 and 1200 cm⁻¹ and at 1380 cm⁻¹, which are related to the C–O vibration of different oxygen functionalities. The lower intensity of these two bands in C0 and C20 compared to those in GAe series is noticeable. This is in agreement with the data compiled in Table 2, which show a smaller amount of acid groups in samples C0 and C20. Also, in these samples the lack of the band at 1720 cm⁻¹, related to lactones, carbonyl and carboxyl groups is also evident. In general, the intensity of the bands assigned to the different oxygen functionalities in the spectra of GAe series is clearly increased in samples obtained by the treatments in solution and plasma (GAe-ox1, GAe-ox2 and GAe-1%O₂P). Moreover, sample GAe-1%O₂P shows a band at 3420 cm⁻¹, which is not evident in the other samples and which is assigned to O–H groups of phenols or carboxylic functionalities.

From the data of textural and chemical surface characterization one can deduce the following: (i) C0 has medium values of surface areas and microporosity with constrictions that are partially opened after activation to obtain C20. Moreover, these samples are mainly basic, as revealed by selective titrations. (ii) GAe, GAe-ox1 and GAe-

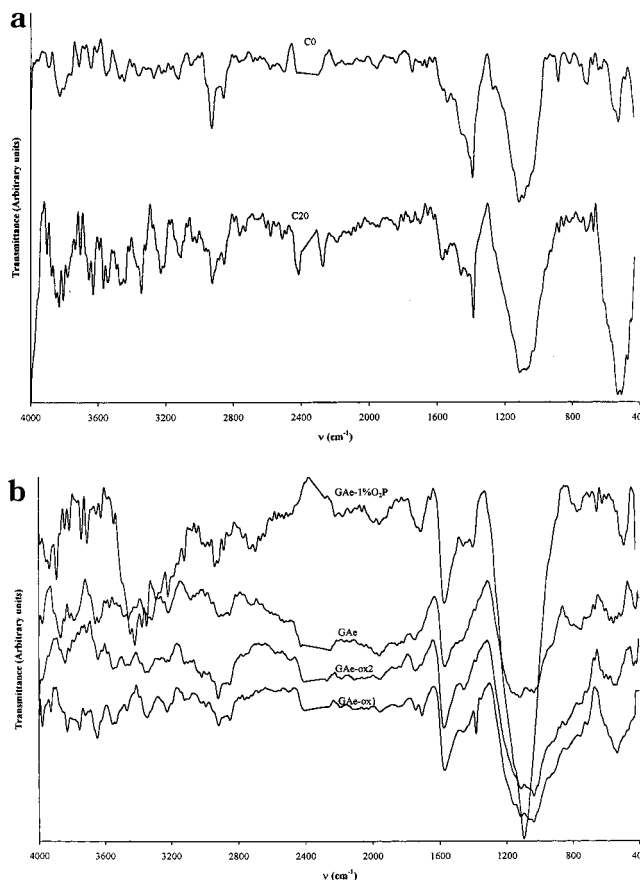


Figure 2. FTIR spectra.

Table 2. Chemical surface groups in (meq·g⁻¹)

sample	carboxyl	lactones	phenols	basic
C0	0.043	0.000	0.039	0.489
C20	0.043	0.000	0.031	0.774
GAe	0.155	0.095	0.395	0.032
GAe-ox1	0.175	0.191	0.503	0.082
GAe-ox2	0.180	0.219	0.499	0.024
GAe-1%O ₂ P	0.338	0.126	0.702	0.377

ox2 have more developed surface areas and more opened microporosity. The chemical character of the oxygen surface groups is mainly acidic. (iii) GAe-1%O₂P has very similar textural characteristics to GAe; it has the highest number of acid groups and also an important number of basic groups. The changes in the textural and chemical characteristics produced by plasma treatment only affect the external surface of the sample.^{17,24} This means that the chemical functionalities are mainly fixed on the external part of the sample and also that only the external porosity is affected.

Under the experimental conditions described above for the adsorption of methylamines the specific retention volume, V_s , is the equilibrium constant.²⁹ This parameter can be obtained from the retention volume, V_R (related to the retention time), and the carrier gas flow rate, which are the direct parameters measured when IGSC is used. When adsorption takes place in the Henry's law region and when the adsorbate concentration is very low the standard enthalpy of adsorption ΔH_A° can be determined from²⁸

$$\ln V_s = -\left(\frac{\Delta H_A^\circ}{RT}\right) + C \quad (4)$$

Moreover, the standard free energy of adsorption, ΔG_A° ,

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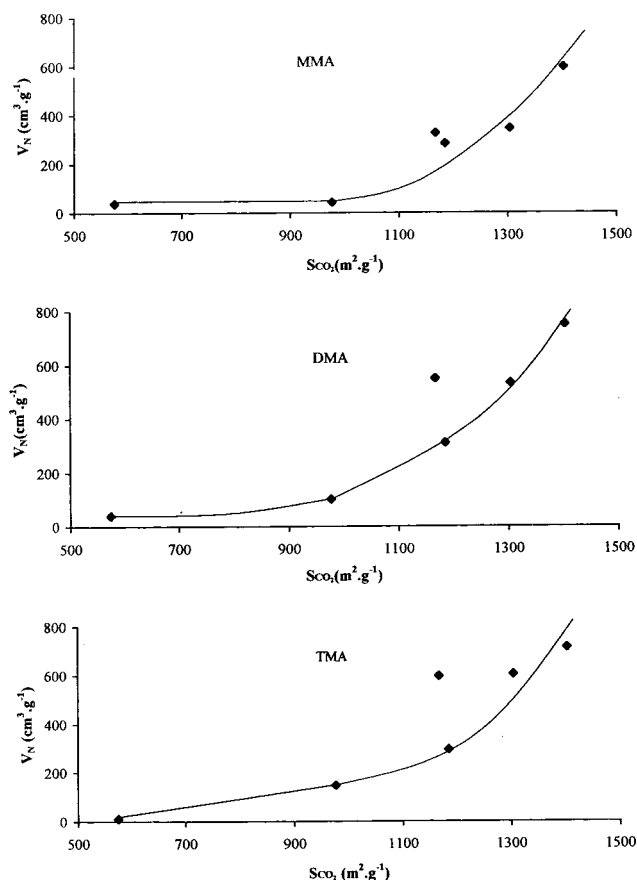


Figure 3. Variation of the net retention volumes versus the CO_2 surface area.

can be calculated from^{29,30}

$$\Delta G_A^0 = -RT \ln(2.99 \times 10^8 V_N) \quad (5)$$

It is necessary to keep in mind that the adsorption of methylamines is carried out at very low vapor concentration (zero surface coverage) in such a way that the adsorption is produced on the most active sites of the adsorbent.³⁰ These are, in the case of nonspecific interactions, pores of a size close to the molecular dimension, i.e., micropores with a width very similar to the dimensions of the methylamines. In the case of specific interactions, the most active sites are the oxygen surface groups. Indeed, both types of interactions are possible in the case of methylamines' adsorption because of the basic character and the dipolar moment of these molecules.^{31–33} The net retention volumes, V_N , at 553 K, as an example, are plotted versus the CO_2 surface area of the carbon materials in Figure 3. This parameter is a measure of the adsorption capacity of the samples for methylamines. The adsorption capacity clearly increases for surface areas higher than $977 \text{ m}^2/\text{g}$. This could be due to an increase in the accessibility of the adsorbates to the microporosity and to the chemical groups. As mentioned above, on the basis of micropores size distribution in Figure 1 and in reported

data,²⁴ GAe, GAe-ox1 and GAe-ox2 have a relatively open micropore network. However, GAe-1% O_2P has a micropore network coincident with GAe, although the external surface has been changed by the oxygen plasma treatment. There is an experimental value for the three methylamines that does not follow the general trend. This corresponds to the adsorption on the sample obtained by oxygen plasma treatment, GAe-1% O_2P . This can be explained as being due to the existence of more micropores accessible to methylamines, or because the specific interactions increase the amount of methylamines adsorbed. Of these two factors, the second one, i.e., the specific interactions, seems to be least plausible when the different possibilities are analyzed. One of these is that the specific interactions were produced by the basic character of the adsorbates. In this case, the interaction should be favored in the order: $\text{DMA} > \text{MMA} > \text{TMA}$ because this is the trend of K_b .³³ Therefore, the shift of the experimental data for DMA should be the largest. In the case of specific interactions produced by the dipolar moment of the adsorbates the shift of the experimental data in relation to the general trend should be $\text{MMA} > \text{DMA} > \text{TMA}$ because this is how this parameter varies.³³ Since none of these trends are observed, the shift can probably be explained by the existence of more micropores accessible to the adsorbates. As explained above, plasma treatments^{17,24,25} only affect the external surface of the samples. Therefore, besides other effects, the treatment produces the opening of the external preexistent microporosity in such a way that the number of accessible micropores of similar size to the methylamines' molecular dimensions increases. This aspect is addressed later.

The specific retention volumes at 553 K, as examples, are recorded in Table 3. The values of V_N for C0 and C20 are lower than for the other samples because of the reduced accessibility to microporosity in these samples (Figure 1 and Table 1) produced by the constrictions in the micropores that hinder access not only to the pores but also to the chemical groups, although the amount of acid groups in these samples is small. This last factor is important in the (specific) adsorption of these adsorbates because of their basic Lewis character and the dipolar moment. The values of V_N increase in samples GAe-ox1, GAe-ox2 and GAe-1% O_2P in comparison with GAe, because of the rise in the number of acid groups (Table 2). Moreover, the increase in V_N can also be produced by a higher accessibility to the microporosity.

The general trend of the values of ΔH_A^0 (Table 3) is not easily explained at first sight. In fact, the values of ΔH_A^0 for DMA and TMA seem to suggest that these molecules are adsorbed by stronger specific interactions than MMA. If this is produced by specific interactions, the trend expected for the absolute values of ΔH_A^0 should be $\text{DMA} > \text{MMA} > \text{TMA}$ in the case of an acid–base interaction. In the case of dipole–dipole interactions the trend should be $\text{MMA} > \text{DMA} > \text{TMA}$. However, the adsorption process is expected to occur by a mixed mechanism of specific and nonspecific interactions.²⁹ Therefore, it is desirable to obtain the two contributions to the process which is not easy in the case of ΔH_A^0 . However, this can be achieved in the case of the standard free energy of adsorption ΔG_A^0 . For this purpose ΔG_A^0 has been calculated using eq 5. Once ΔG_A^0 is known, the specific component, ΔG_{sp} can be determined using several approaches.^{34–38} Among them,

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Table 3. V_s at 553 K

sample	MMA		DMA		TMA	
	V_s (cm ³ •m ⁻² •g ⁻¹)	$-\Delta H_A^p$ (kJ•mol ⁻¹)	V_s (cm ³ •m ⁻² •g ⁻¹)	$-\Delta H_A^p$ (kJ•mol ⁻¹)	V_s (cm ³ •m ⁻² •g ⁻¹)	$-\Delta H_A^p$ (kJ•mol ⁻¹)
C0	0.037	35.6	0.039	19.2	0.020	9.7
C20	0.045	34.7	0.104	50.6	0.150	67.4
GAe	0.238	44.2	0.262	67.8	0.248	51.5
GAe-ox1	0.425	63.2	0.536	77.5	0.507	70.3
GAe-ox2	0.264	60.2	0.409	63.9	0.462	59.1
GAe-1%O ₂ P	0.279	47.5	0.471	79.8	0.509	58.5

Table 4. Specific component of the standard free energy (percentage, %) and standard free energy of adsorption

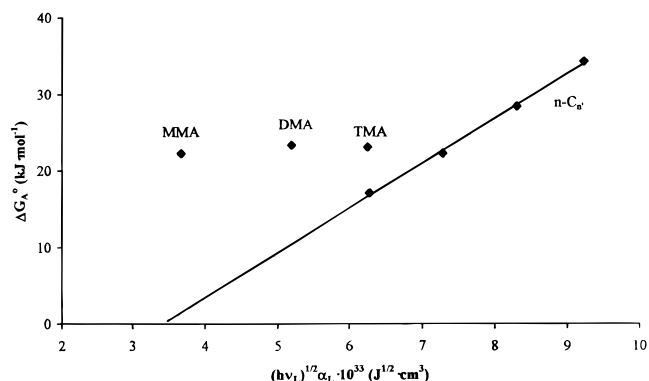
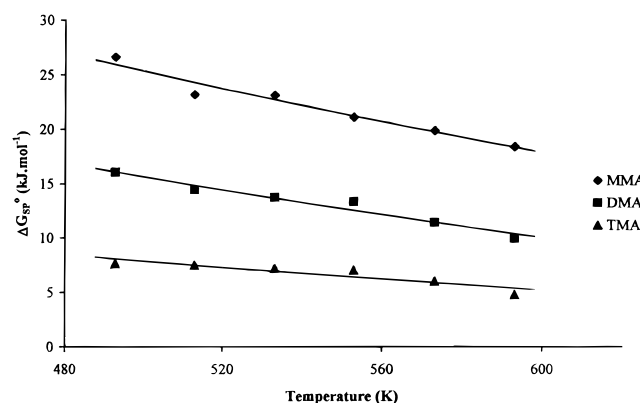
sample	MMA		DMA		TMA	
	%	$-\Delta G_A^o$ (kJ•mol ⁻¹)	%	$-\Delta G_A^o$ (kJ•mol ⁻¹)	%	$-\Delta G_A^o$ (kJ•mol ⁻¹)
C0	86	11.0	44	11.3	4	8.2
C20	94	11.9	24	15.8	-	17.5
GAe	98	19.6	46	20.0	9	19.8
GAe-ox1	93	22.3	55	23.3	28	23.1
GAe-ox2	100	20.1	62	22.1	33	22.7
GAe-1%O ₂ P	88	20.3	48	22.7	20	23.1

the procedure proposed by Donnet et al.³⁶ has been used. This method compares the standard free energy of adsorption of a probe with that of the *n*-alkanes. For this reason the adsorption of linear hydrocarbons (from *n*-C₄ to *n*-C₇) has been measured using IGSC in the same experimental conditions in which the adsorption of methylamines has been carried out. To compare the standard free energy of adsorption of molecules (*n*-alkanes) interacting through dispersion forces (nonspecific) to that of molecules capable of specific interactions (methylamines, in this case) the following equation is used:

$$\Delta G_A^o = K (h\nu_s)^{1/2} \alpha_s (h\nu_L)^{1/2} \alpha_L \quad (6)$$

where K is a constant, h is the Planck's constant, ν_s and ν_L are the characteristic vibration energies of the adsorbent and the adsorbate, and α_s and α_L are the deformation polarizabilities. The plot of ΔG_A^o versus $(h\nu_L)^{1/2} \alpha_L$ for *n*-alkanes is a straight line, which corresponds to the reference line. The values of ΔG_A^o of molecules capable of specific interactions are located above this reference line. The difference between the ordinate value (ΔG_A^o) for each probe and the corresponding value of the *n*-alkane at the same $(h\nu_L)^{1/2} \alpha_L$ value render the specific component of the standard free energy of adsorption, ΔG_{sp} , for a particular probe. Plots similar to that depicted in Figure 4 for sample GAe-ox1 are obtained for all the carbon materials. The values of the specific component obtained by this method, expressed as a percentage, are compiled in Table 4. Also, the values of the standard free energy of adsorption are recorded in Table 4. Some interesting features can be deduced from these data.

(i) The interaction of MMA is produced almost exclusively by specific interactions even on these materials with very low number of acid groups, i.e., C0 and C20 (Table 2). However, in these samples the degree of adsorption is very low, as they have constrictions hindering the access of the molecules to the chemical groups. Otherwise, no large differences in the amount adsorbed in samples C0 and C20 would be expected in comparison to the other samples since the adsorption is produced at zero surface

**Figure 4.** Variation of the standard free energy of adsorption versus $(h\nu_L)^{1/2} \alpha_L$ for sample GAe-ox1.**Figure 5.** Variation of the specific contribution of the standard free energy of adsorption with the temperature.

coverage and, therefore, the number of acid groups, although very low in C0 and C20, would be enough to adsorb MMA mainly through specific interactions.

(ii) The specific contribution to the standard free energy decreases from MMA to TMA following the same trend as the dipolar moment of the adsorbates. This trend can be seen in Figure 5 in which ΔG_{sp} vs T (absolute temperature) is plotted. The larger contribution of ΔG_{sp} at each temperature for MMA is apparent. This means that the specific contribution is caused by dipole–dipole instead of acid–base interactions.

(iii) Although MMA is specifically adsorbed, the adsorption of DMA and TMA is more exothermic (Table 3) in almost all cases (except for TMA in GAe-ox2 which is very close to MMA). This means that a specific interaction is not always more exothermic than a nonspecific one. In fact, high absolute values of ΔH_A^p are produced when molecular size and pore dimension are very similar such that the closer both parameters the higher the ΔH_A^p .^{29–31,39,40} In this respect, it is important to emphasize

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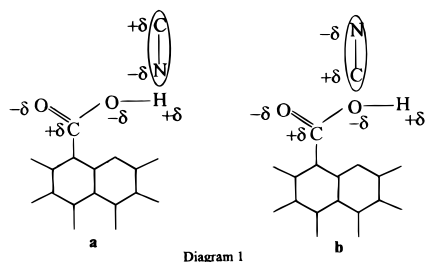
(40) Derouanne, E. G. *J. Mol. Catal. A: Chem.* **1998**, 134, 29.

that the adsorption of methylamines is carried out at very low vapor concentration (zero surface coverage). Therefore, the molecules are adsorbed on the most active sites, which could be the pores of a size similar to the molecular dimension. The result of this is that, although the differences are very small, the adsorption of DMA and TMA is thermodynamically more favored than of MMA although the latter is almost completely adsorbed by specific interactions.

After reaching the conclusion that MMA is adsorbed almost completely by specific interactions, it is interesting to consider again the plots in Figure 3. Now it is plausible to accept that the dispersion observed for sample GAe-1%O₂P, already mentioned, occurs because plasma treatment has produced more external micropores accessible to the methylamines. Therefore, as MMA is adsorbed through specific interactions, the V_N values for GAe and GAe-1%O₂P are very similar. However, DMA and TMA are largely shifted (for sample GAe-1%O₂P in relation to GAe) because the nonspecific interactions (and therefore the external microporosity of the adsorbent) are very important in the adsorption of these molecules.

The percentage of the specific contribution can be used to estimate the contribution of this kind of interaction to V_s , (V_s)_{sp}. The plots of this parameter vs the amount of total acid surface groups (carboxy + lactones + phenols in Table 2) are recorded in Figure 6 for three methylamines. The trend found is similar for the three adsorbates and (V_s)_{sp} increases with rising the amount of acid surface groups. From the slopes of the three plots it can be concluded that (V_s)_{sp} is more affected by the acid groups in MMA adsorption. This means that MMA presents a stronger interaction with these groups than DMA and TMA, following the same trend (MMA > DMA > TMA) as the dipolar moment. This suggests again a dipole-dipole interaction with the acid groups instead of an acid-base one. Moreover, this conclusion is the same as that reached from the above relationship between ΔG_{sp} and the dipolar moment of the adsorbates.

The dipole-dipole interactions can be produced as shown in the following diagrams. Methylamines have a dipolar moment produced by the lone electron pair and by the difference in electronegativity between nitrogen, carbon and hydrogen atoms. The negative charge is close to nitrogen whereas the positive one is near carbon/hydrogen atoms. Therefore, the interaction can take place between the negative charge on the nitrogen atom and the positive charge on the hydrogen of carboxyl groups (a, in diagram 1). They also can be adsorbed by the positive



charge on the carbon interacting with the negative charge on the oxygen atoms (b, in the diagram 1). The interaction with the carbon atom of the carboxylic group would be less favored for steric reasons.

In lactone groups, the interaction is more probable in oxygen atoms with the positive charge on the carbon of methylamines (a). Besides, it also seems possible, although less likely, in the carbon atom with the negative charge on the nitrogen (b). This is depicted in diagram 2.

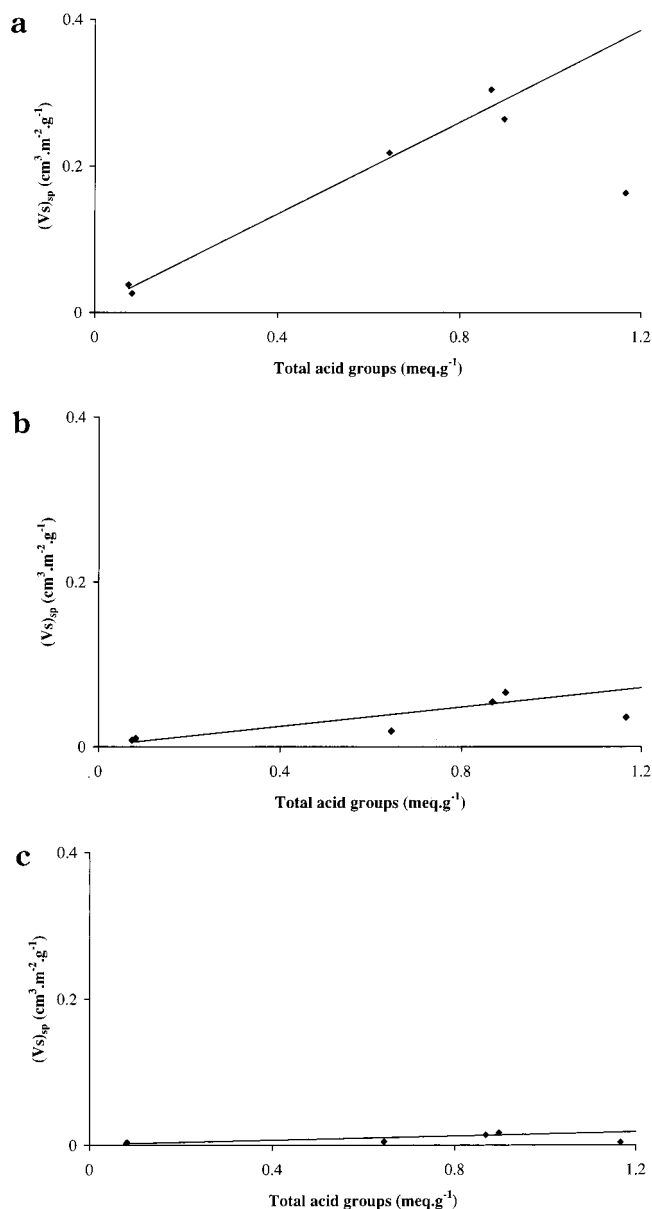
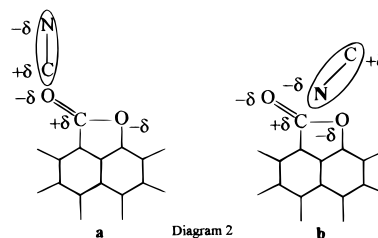


Figure 6. Variation of the specific part of V_s with the amount acid surface groups: (a) MMA, (b) DMA, (c) TMA.



It is likely that phenol groups produce two interactions: with the negative charge from the oxygen of the phenol and the positive charge from the carbon of methylamines (a), or the positive charge from the hydrogen of the phenol with the negative charge of the methylamines (b). These two possibilities are shown in diagram 3.

Conclusions

Adsorption of methylamines on carbon materials is a mixed mechanism composed of nonspecific and specific interactions. The former is almost negligible in MMA and is predominant in TMA. Conversely, the latter is very

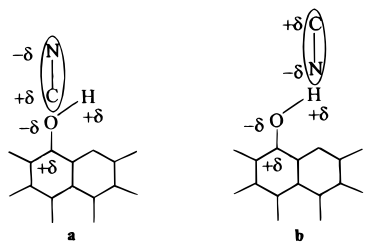


Diagram 3

important in MMA, in such a way that it is dependent on the dipolar moment of the adsorbates: MMA > DMA > TMA. Therefore, although specific interactions could be

produce by acid–base or dipole–dipole forces, there are experimental data supporting the second type. For this reason, none of the acid chemical surface groups is preferred by the adsorbates. In terms of thermodynamic parameters, the standard heat of adsorption alone cannot discriminate between specific and nonspecific interactions in the adsorption of methylamines.

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