Published in Carbon 42 issues 8-9, 1619-1624, 2004
which should be used for any reference to this work

Specific and non-specific interactions between ammonia and activated carbons

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Abstract

It is shown that the adsorption of NH_3 by activated carbons at different temperatures follows Dubinin's theory and, as in the case of water, for carbons with high oxygen contents one observes an upward deviation in the initial section of the DR plot. This indicates a strong primary adsorption, due to specific interactions. At higher relative pressures, this adsorption is followed by a classical micropore filling mechanism, where NH_3 conforms to the pattern of non-specific adsorption. The affinity coefficient $\beta_1(NH_3)$ associated with primary adsorption varies between 0.4 and 1.2. It depends on the characteristic energy E_0 and on the ratio between the amount of oxygen present on the surface and the limiting amount of ammonia adsorbed in the micropores. This behaviour had been reported earlier for the adsorption of short alcohols, but with a single DR plot, due to the fact that specific and non-specific interactions were similar. For carbons with little oxygen on the surface, NH_3 adsorption leads to a single DR plot, irrespective of the average pore-size.

Keywords: A. Activated carbon; B. Oxidation; C. Adsorption; D. Adsorption properties

1. Introduction

The adsorption of ammonia vapours by activated carbons has been studied by different authors, using either adsorption [1–10] or calorimetric techniques [11,12]. However, this adsorptive has not received as much attention as, for example, organic vapours and water. It also appears that the adsorption mechanism of ammonia, in relation to the surface chemistry, has not been considered in great detail. This was probably due to the fact that the adsorption isotherms are of type I or II, as observed for most organic and inorganic vapours. However, a finer analysis by Kaneko et al. [2] indicated that, with respect to benzene, ammonia displays deviations from the classical Dubinin–Radushkevich plot. This behaviour is also revealed by the analysis of the work of Tamon and Okazaki [5] and the recent data of Helminen et al. [9]. A closer study of NH_3 adsorption is therefore worthwhile, in particular within the framework of Dubinin's theory for the volume filling of micropores [13–17].

For the majority of organic and inorganic vapours adsorbed by activated carbons, the interactions are non-specific and the adsorption equilibrium can be predicted on the basis of simple physico-chemical parameters. In this context, Dubinin's theory provides a useful basis. However, due to the presence of variable amounts of oxygen-containing groups, or other chemical entities, specific interactions may also be present and lead to a more differentiated adsorption process. This is the well-known case of water [18–20], which has a low affinity for carbon, but interacts strongly with surface oxygen and with basic centres.

In recent years, it has been shown that, beside ammonia, the adsorption of molecules such as short alcohols [21,22], sulfur dioxide [3,5,22] and hydrogen chloride [23], can be enhanced by surface groups. In the case of water, it appears that adsorption follows two distinct mechanisms [20]: Firstly, a primary coating of the oxygen-containing centres, corresponding to a type I Dubinin isotherm. Secondly, the filling of the

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micropores under the influence of much weaker dispersive interactions, which leads to a type V isotherm. The latter isotherm is also described by the Dubinin–Astakhov equation, since it follows the principle of temperature invariance.

In the case of short alcohols [21], the specific interactions of the –OH group with the surface oxygen are of the same order as for the non-specific filling of the micropores. As a result, one observes an overall type I (or II) isotherm and a quasi-linear Dubinin–Radushkevich plot, but with different slopes, due to variable affinity coefficients β (alcohol).

The present study deals with the specific and non-specific interactions of ammonia with activated carbons and examines, along similar lines, the effect of surface oxygen on the adsorption process. Unfortunately, in the case of NH_3 no independent correlation can be established by immersion calorimetry, but it is shown that this adsorptive follows a pattern similar to that of water and of alcohols. The overall NH_3 isotherms are of type I (or II if an important external surface is present), which means that the overall interactions are strong. However, the break in the Dubinin–Radushkevich plots (upward deviation in the original section) suggests that the specific interactions are significantly stronger than the non-specific interactions, as opposed to the case of short alcohols, where they are close.

2. Theoretical

Non-specific adsorption of vapours by activated carbons is described by Dubinin's theory, as discussed in detail elsewhere [13–17]. It is based on the thermodynamic potential $A = RT\ln(p_s/p)$, and the fundamental expression is the Dubinin–Astakhov (DA) equation,

$$N_a = N_{ao}\exp[-(A/E)^n] \qquad (1)$$

N_a is the amount adsorbed at relative pressure p/p_s and temperature T; N_{ao} is the limiting amount filling the micropore volume $W_0 = N_{ao}V_m$, assuming that V_m is close to the molar volume in the liquid state, and E is the so-called characteristic energy of the system. The latter can be written as $E = \beta E_0$, where β is the affinity coefficient of the adsorptive, benzene being the reference ($\beta(C_6H_6) = 1$). These coefficients have recently been compiled and analysed by Wood [24]. In the case of non-specific interactions, β does not depend on the chemistry of the carbon surface and it can be predicted on the basis of simple relations. (For example, the ratio of the parachors, as suggested by Dubinin many years ago.) For typical organic and inorganic molecules adsorbed by standard activated carbons, the isotherm is of type I (or II) and often the exponent $n = 2$. This corresponds to the original Dubinin–Radushkevich (DR) equation used in the present study.

In the case of water adsorbed by microporous carbons containing little or no oxygen, the characteristic energy E is much smaller than for a typical organic vapour such as benzene (respectively 1–2 $\mathrm{kJ\,mol^{-1}}$ and 15–30 $\mathrm{kJ\,mol^{-1}}$). Consequently, Eq. (1) leads to a type V isotherm for water [15–21].

A basic requirement of Dubinin's theory, often overlooked, is the temperature invariance of parameters E and n. This is reflected by a unique characteristic curve a plot of the relative amount adsorbed at different temperatures and pressure N_a/N_{ao} versus A, or a single straight line for the plot of $\ln(N_a/N_{ao})$ versus A^n (for $n = 2$, the classical DR plot). As shown elsewhere [15,16], Eq. (1) leads to an exact expression for the enthalpy of immersion of the carbon into the corresponding liquid (e.g. benzene) [15,16],

$$\Delta_i H\ (\mathrm{J/g})_{mi} = -N_{ao}E(1 + \alpha T)\Gamma(1 + 1/n) \qquad (2)$$

α is the expansion coefficient of the liquid filling the micropores and Γ is the tabulated 'Gamma' function (for $1.5 < n < 5$, it varies between 0.88 and 0.92). The experimental enthalpy of immersion contains a supplementary term h_iS_e for the wetting of the external (non-microporous) surface area S_e of the solid. Typically, $h_i(C_6H_6) = -0.114\ \mathrm{J\,m^{-2}}$ [16]. Eq. (2) has been verified for a large number of systems [15,16,18,19,21], a procedure which may be regarded as a test of self-consistency for Dubinin's theory.

3. Experimental

For the present study we selected a series of well-characterized activated carbons (CARBO-S, DCG-5 [20]) and two activated carbon fibers, in their original state (KF-1500 [25], SWA5) and after oxidation (KF-1500-ox, SWA5-ox). Ammonia adsorption was carried out with the help of a high pressure equipment described in detail elsewhere [6] and a classical MacBain spring balance for measurements below atmospheric pressure. All samples were characterized with the help of benzene adsorbed at 293 K and/or 308 K and the results were cross-checked with the help of the enthalpies of immersion into benzene at 293 K. For each carbon, this procedure provides a verification of the data obtained with the non-specific adsorbates and the subsequent comparison with NH_3. Furthermore, we considered the adsorption of NH_3 and CO_2 by fiber KF-1500 over a wide range of temperature (253–363 K), in order to confirm that the principle of temperature-invariance is fulfilled.

The main properties of the carbons, including their surface oxygen content determined by TPD between 300 and 1000 K [18,21], are given in Table 1.

The high pressure experiments with NH_3 on the untreated fiber KF-1500 were carried out at 253, 273, 298,

Table 1
Main characteristics of the carbons and their sorptive properties

Carbon	W_0 ($cm^3 g^{-1}$)	E_0 ($kJ\,mol^{-1}$)	E_1 (NH_3) ($kJ\,mol^{-1}$)	E_2 (NH_3) ($kJ\,mol^{-1}$)	$\beta_1(NH_3)$	$\beta_2(NH_3)$	N_{ao1} ($mmol\,g^{-1}$)	N_{ao2} ($mmol\,g^{-1}$)	$N_{ao\,tot}$ ($mmol\,g^{-1}$)	[O] ($mmol\,g^{-1}$)	[O]/ $N_{ao\,tot}$
KF-1500	0.52	20.0	12.2	6.0	0.61	0.28	3.17	16.53	19.7	2.2	0.111
KF-1500-ox	0.52	20.0	17.4	5.6	0.87	0.28	4.91	14.79	19.7	5.0	0.253
SWA5-init	0.74	15.0	–	8.9	–	[0.59]	–	29.3	29.3	0.5	0.017
SWA5-ox	0.74	15.0	18.0	6.9	1.2	0.46	5.0	23.5	28.5	9.0	0.316
DCG-5-1	0.54	21.2	11.3	7.4	0.53	0.35	4.1	15.1	19.2	2.2	0.115
DCG-5-2	0.54	21.2	13.9	6.0	0.66	0.28	3.4	14.7	18.1	3.1	0.171
CARBO-S	0.43	24.7	–	9.9	–	0.40	–	17.1	17.1	0.5	0.029

323, 343 and 363 K and in the pressure range of 0–0.9 MPa. The low pressure experiments, with all carbons, took place at 293 and 308 K and in the pressure range of 0.1 Pa to 0.1 MPa. In the case of the untreated fiber KF-1500, these measurements allowed an overlap of the domains of $A = RT\ln(ps/p)$, respectively of $RT\ln(f_s/f)$. (It should be pointed out that for pressures above 0.5 MPa one must use fugacities f in the DR equation).

The densities and consequently the molar volumes of adsorbed ammonia and carbon dioxide, at different temperatures, were calculated with the help of Ozawa's equation [26]

$$\rho(T) = \rho_e \exp[\alpha(T - T_e)] \qquad (3)$$

where $\rho(T)$ and ρ_e are respectively the densities at temperature T and at the ebullition point T_e. Eq. (3) gives good correlations with other determinations of the micropore volume W_0, but deviations are not excluded.

In parallel with vapour adsorption, enthalpies of immersion of the carbons into water and benzene were determined with a calorimeter of the Tian–Calvet type [15,16], using 0.050–0.150 g and 5 ml of liquid.

Prior to adsorption and immersion experiments, the samples were outgassed for approximately 12 h in a vacuum of at least 0.1 Pa and at a temperature not exceeding 120–150 °C, in order to prevent the possible destruction of carboxylic surface groups.

4. Results and discussion

Figs. 1 and 2 show respectively the characteristic curve and the DR plot obtained for the adsorption, by KF-1500, of NH_3 and CO_2 over a wide range of pressures and temperatures. It appears, beyond doubt, that the principle of temperature invariance is fulfilled for the different vapours, including NH_3. However, for the latter adsorptive one observes a clear deviation in the common characteristic curve.

In the classical DR plot (Fig. 2), this deviation corresponds to an initial section with a characteristic energy $E_{NH_3} = 6$ kJ/mol and consequently the affinity coefficient $\beta_1(NH_3)$ is equal to 0.61. On the other hand, the upper section can be superimposed on the DR plot of non-specific adsorbates (benzene or CO_2) with an affinity coefficient $\beta_2(NH_3) = 0.28$. It is in good agreement with the value of 0.31 derived from the parachors (63.8/206.1). On the other hand, the experimental values given in Wood's compilation [24] vary between 0.31 and 0.39. It may be assumed that the upper section of the plot corresponds to a classical, and essentially non-specific filling of the micropore volume, as described by Dubinin's theory.

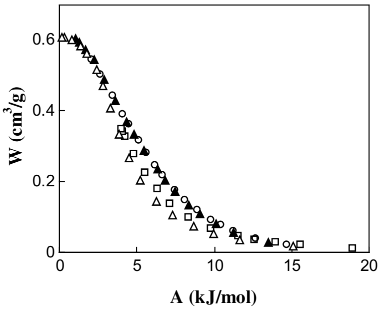

Fig. 1. Characteristic curves for the adsorption of NH_3 on fiber KF-1500 at 298 K (△), 353 K (□) and CO_2 adsorption at 258 K (▲), 273 K (○); $\beta(NH_3) = 0.28$, $\beta(CO_2) = 0.35$. For the sake of clarity, only part of the data is shown.

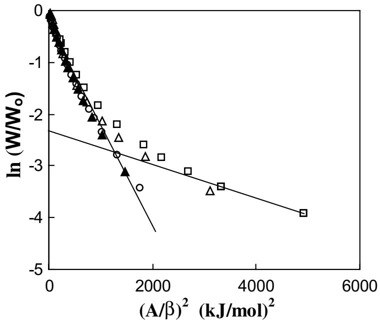

Fig. 2. DR plot corresponding to the characteristic curve of Fig. 1 and showing the initial deviation for NH_3, for which $\beta_1(NH_3) = 0.61$.

This behaviour has also been reported some years ago by Kaneko et al. [2] for the adsorption of NH_3 at 303 K by a series of pitch-based activated carbon fibers P-10, P-15 and P-20. In all cases, the DR plots for benzene at 303 K are linear, but for samples P-15 and P-20, one observes deviations for NH_3. Our analysis of Kaneko's data suggests values of $\beta_1(NH_3)$ between 0.81 and 0.87.

The upper sections of the DR plots lead to $\beta_2(NH_3)$ values of 0.39 and 0.43, against 0.43 for the initial fiber, P-10, which shows no deviation. The analysis of data recently provided by Helminen et al. [9] (NH_3 at 298 K, on carbons *Merck* and *Sigma*) reveals a similar behaviour, but no quantitative assessment can be made, in view of the fact that no data is given for a non-specific adsorbate (for example C_6H_6).

Our results, discussed below, confirm the general pattern and suggest that the adsorption of NH_3 can be treated, to a first approximation, as a sum of two DR equation (1). The DR plots obtained for the other carbons of the present study are shown in Figs. 3–5 and the corresponding values of $\beta_1(NH_3)$ and $\beta_2(NH_3)$ are given in Table 1.

The data for our carbons and the carbons reported by Kaneko [2,3] give an average value $\beta_2(NH_3) = 0.39 \pm 0.07$. (The untreated carbon fiber SWA5 was not taken into account, in view of its exceptionally high value of 0.59.) This average suggests that the upper section of the DR plots reflects essentially the non-specific filling of the micropores. This behaviour is confirmed by carbons CARBO-S and the original fiber SWA5, which contain relatively small amounts of oxygen (ratios $[O]/N_{ao\,tot}(NH_3)$ of 0.029 and 0.017) and show no deviation in the DR plots. The corresponding characteristic energies E_0 (24.7 and 15.0 kJ/mol), indicate that the absence of an initial break in the DR plots for NH_3 is independent of the pore-size. (As shown elsewhere [16], E_0 is an inverse function of the average micropore size.)

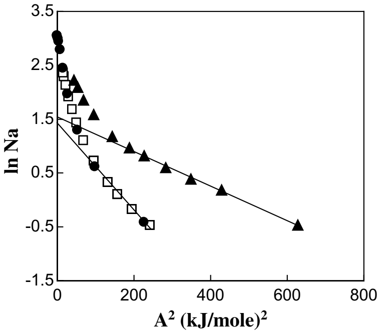

Fig. 3. DR plot for NH_3 adsorption on the oxidized fiber KF-1500 at 308 K (▲). For comparison purposes, NH_3 on the original fiber KF-1500 at 353 K (□) and 293 K (●).

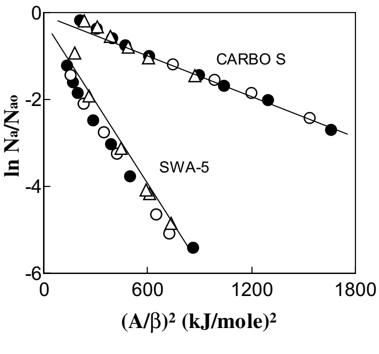

Fig. 4. DR plot for NH_3 adsorption and desorption at 308 K (● ○) by carbon CARBO-S and fiber SWA5-init. For comparison purposes, the adsorption of C_6H_6 at 293 K (△) is shown.

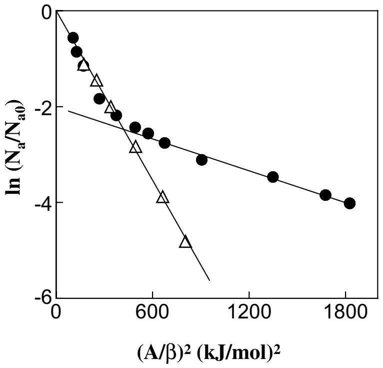

Fig. 5. DR plot for NH_3 adsorption at 308 K (●) by the oxidized carbon fiber SWA5-ox. For comparison purposes, the adsorption of C_6H_6 at 308 K (△).

The affinity coefficients $\beta_1(NH_3)$ associated with the initial deviation can be as high as 1.2, as found for the oxidized fiber SWA5-ox. For this carbon, the ratio $[O]/N_{ao\,tot}(NH_3) = 0.316$, which indicates that the initial deviation is essentially due to this ratio. On the other hand, no deviation is observed for the initial fiber, which contains only a small amount of oxygen.

As reported recently for the adsorption of short alcohols [21] and of water [20] by various carbons, it appears that the affinity coefficient β depends on the amount of oxygen present on the surface. In the case of methanol and ethanol, the DR plot itself showed no deviation from linearity, but, with respect to benzene, the affinity coefficients $\beta(CH_3OH)$ and $\beta(C_2H_5OH)$ were found to increase slightly with the degree of oxidation. The combination of vapour adsorption and of immersion calorimetry led to the general correlation [21]

$$\beta(\text{alcohol}) = \beta_0 + c[O]/\Delta_i H(\text{alcohol}) \qquad (4)$$

where β_0 and c are respectively the limiting value of β and a specific interaction parameter of the given alcohol. With the help of Eq. (2) for the enthalpies of immersion $\Delta_i H(\text{alcohol})$, Eq. (4) becomes

$$\beta(\text{alcohol}) = \beta_0 + c'[O]/E_0 N_{ao}(\text{alcohol}) \times (1 + \alpha T)\Gamma(1 + 1/n) \qquad (5)$$

For methanol and ethanol, c' is equal to 4.7 and 2.7 kJ/mol, respectively.

Eq. (5) clearly identifies the parameters involved in the variation of β and allows an extension of Dubinin's theory to the case of specific interactions, provided that the requirement for temperature-invariance is fulfilled.

More recently, it has been shown by Stoeckli [20] that the adsorption of water by micorporous carbons can be separated in two distinct stages, both described by Dubinin's theory. (The requirement for temperature-invariance of parameter E is fulfilled, as confirmed by immersion calorimetry). For water, the initial stage corresponds to relatively strong specific interactions with the surface oxygen [O] and the basic groups (characterized by their [HCl] equivalents). This mechanism is reflected by a type I Dubinin–Astakhov equation, with an exponent $n \sim 2$–3 and an affinity coefficient $\beta_1(H_2O) = 0.29$. On the other hand, for the subsequent micropore filling, corresponding to a type V isotherm, one observes a *variable* value $\beta_2(H_2O)$, depending on the degree of oxidation of the carbon. By analogy with Eq. (5), it was shown that

$$\beta_2(H_2O) = 0.069(\pm 0.010) + (5.4 \text{ kJ/mol}) \times ([O] + [HCl])/E_0 N_{ao\,tot}(H_2O)(1 + \alpha T)\Gamma(1 + 1/n) \tag{6}$$

(note that for water $(1 + \alpha T)\Gamma(1 + 1/n)$ is close to unity).

This expression reflects the long-range influence of the specific centres (oxygen atoms and basic centres) on the subsequent and energetically weaker micropore filling by water, pure carbon being hydrophobic.

In spite of the fact that in the case of ammonia no independent experimental evidence can be provided by immersion calorimetry, it seems reasonable to assume a similar correlation for the variation of $\beta_1(NH_3)$ with the amount of oxygen present on the surface. However, it is unlikely that NH_3 will interact strongly with the basic centres [HCl] and, in view of their small concentration, these centres can be neglected. As illustrated by Fig. 6, the data of Table 1 leads to the following correlation

$$\beta_1(NH_3) = 0.34(\pm 0.03) + 61 \text{ (kJ/mol)} \times [O]/E_0 N_{ao\,tot}(NH_3)(1 + \alpha T)\Gamma(1 + 1/n) \tag{7}$$

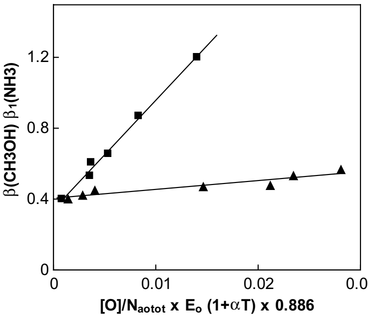

Fig. 6. Correlation between the experimental and calculated values of $\beta_1(NH_3)$ (■), using Equation (7). The earlier data for (CH_3OH) [21] (▲), is also shown on the same scale.

In this expression, $\alpha(NH_3) = 2.4 \times 10^{-3}$ K^{-1} and $\Gamma(1 + 1/2) = 0.886$.

The limiting value of 0.35 ± 0.03 corresponds practically to the average value of $\beta_2(NH_3) = 0.34 \pm 0.07$ derived from the upper sections of the DR plots. If one adds the values recalculated from Kaneko's data [2], the average is 0.37 ± 0.07.

The energy factor of 61 kJ/mol for the variation of $\beta_1(NH_3)$ is much higher than obtained for methanol and ethanol (4.7 and 2.71 kJ/mol). For theses short alcohols, the specific and the non-specific interactions are similar, which may explain the absence of two distinct and successive mechanisms (i.e. a break in the DR plot). This is also suggested by the relatively small variation of $\beta(CH_3OH)$ and $\beta(C_2H_5OH)$ with increasing oxidation. As an illustration, the corresponding variation of $\beta(CH_3OH)$ is also shown in Fig. 6, on the same scale.

In the case of water, where the non-specific interactions are much smaller and lead to a type V isotherm, the variation of $\beta_2(H_2O)$ given by Eq. (6) reflects the long-range effect of the primary centres on the micropore filling. This long-range effect, characterized by an energy factor of 5.4 kJ/mol, is still important and it is similar to the primary (specific) interaction of methanol with the surface oxygen.

With respect to the short alcohols and water, the pattern observed for NH_3 reflects yet another situation: specific and non-specific interactions are both strong and correspond to type I isotherms, but they are sufficiently different to lead to separate mechanisms. The primary centres have probably a limited influence on the secondary micropore filling by NH_3, as suggested by the range of values (0.30–0.45) observed for $\beta_2(NH_3)$ in the present study and on the basis of Kaneko's results [2]. However, this variation is not as important as observed for $\beta_2(H_2O)$.

As opposed to the case of water, where $\beta_1(H_2O) = 0.29 \pm 0.02$ [20] is constant, the variation of $\beta_1(NH_3)$ between 0.5 and 1.2 indicates a complex mechanism associated with the specific interactions. This must still be investigated. It is possible, for example, that the type of oxygen-containing complexes and their relative locations play a role. By analogy with the case of water, the data of Table 1 suggests that $N_{ao1}(NH_3)$, the limiting amount of NH_3 adsorbed in the first stage, is close to the amount of surface oxygen (see Table 1). However, no clear correlation can be established yet.

At the present stage, it appears that the adsorption of NH_3 by microporous carbons containing various amounts of oxygen can be described by the sum of two contributions of the DR type,

$$N_a(T; p/p_s) = N_{ao1} \exp\left[-(A/\beta_1(NH_3)E_0)^2\right] + N_{ao2} \exp\left[-(A/\beta_2(NH_3)E_0)^2\right] \tag{8}$$

where $\beta_1(NH_3)$ is given by Eq. (7). To a first an good approximation, one may assume that $\beta_2(NH_3)$ is close to 0.35, and $N_{ao1} \sim [O]$.

5. Conclusions

The present study shows that in the case of NH_3 adsorption by microporous carbons there exist two mechanisms, both corresponding to type I isotherms of the DR type. The first mechanism, related to specific interactions, is characterized by an affinity coefficient $\beta_1(NH_3)$ which depends on the relative amount of surface oxygen $[O]/N_{ao\,tot}(NH_3)$, on the micropore size (an inverse function of E_0) and on the factor $(1 + \alpha T)$ $\Gamma(1 + 1/n)$ introduced earlier on the basis of immersion calorimetry. It appears that the amount of ammonia associated with these interactions is close to the amount of surface oxygen, but a more accurate correlation must be established on a broader experimental basis.

The second mechanism for NH_3 adsorption is a classical process of micropore filling, similar to that observed for non-specific adsorbates (e.g. benzene), with an affinity coefficient $\beta_2(NH_3)$ near 0.35.

Following earlier work with short alcohols [21] and water [18–21], the present study also shows that specific interactions can be described within the framework of Dubinin's theory, since the principle of temperature invariance is fulfilled. The influence of the specific interactions is expressed in the variation of the activity coefficient β and it is likely that this approach can be extended to the case of other molecules (HCl, SO_2, etc.) displaying specific interactions with various surface groups on activated carbons. However, it must be verified, that the requirement for the temperature-invariance of E is fulfilled.

The simplicity of Dubinin's equation and the possibility of predicting adsorption of molecules with both specific and non-specific interactions, over a wide range of pressure and temperature, is of interest in adsorption science and in filtration technology.

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