Adsorption of Water Vapor on Modified Activated Carbons

R. Dobrowolski[1], M. Jaroniec[2, *], and A. Swiatkowski[3]

[1] Central Laboratory, M. Curie-Sklodowska University, PL-20031 Lublin, Poland
[2] Faculty of Chemistry, M. Curie-Sklodowska University, PL-20031 Lublin, Poland
[3] Institute of Chemistry, Military Technical Academy, PL-00908 Warsaw, Poland

Summary. The adsorption isotherms of water vapor on modified activated carbons are measured in order to study the role of various surface groups in the primary adsorption of water molecules on these adsorbents. These adsorption isotherms are analysed by means of the Dubinin-Serpinsky and Jovanovic equations, which take into account the special features of water vapor adsorption on microporous activated carbons. Numerical analysis of the measured adsorption isotherms by means of the above mentioned equations showed their limited applicability for interpreting adsorption mechanism of water molecules on activated carbons.

Keywords. Activated carbons; Adsorption isotherms; Adsorption of water vapor; Pore filling mechanism.

Adsorption von Wasserdampf auf modifizierter Aktivkohle

Zusammenfassung. Die Adsorptionsisothermen von Wasserdampf auf modifizierter Aktivkohle wurden gemessen, um die Rolle verschiedener Oberflächentypen auf die Primäradsorption von Wassermolekülen auf diesen Adsorbenzien zu untersuchen. Die Adsorptionsisothermen wurden mittels der Dubinin-Serpinsky- und Jovanovic-Gleichungen analysiert, welche die speziellen Eigenheiten von Wasser auf mikroporöser Aktivkohle berücksichtigen. Die numerische Analyse der gemessenen Adsorptionsisothermen mittels der genannten Gleichungen zeigte ihre limitierte Anwendbarkeit zur Interpretation von Adsorptionsmechanismen von Wassermolekülen auf modifizierter Aktivkohle.

Introduction

Adsorption of water vapor on activated carbons depends strongly on the concentration of surface oxide groups and on the specific adsorption of water molecules in the micropores. Extensive studies [1–5] were carried out in order to recognize the role of surface groups in this phenomenon. Puri et al. [6] reported that adsorption of water vapor increases when the amount of oxygen bonded to the surface as the CO_2- desorbing species increases. Barton et al. [7] showed that the adsorption sites initiating adsorption of water molecules on activated carbons are the CO-desorbing surface groups; however, Stoeckli et al. [8] suggested that the carbonyl-

type groups are adsorption centers for primary adsorption of water molecules on various types of charcoals. Recently, Barton and Koresh [5] proposed a reasonable mechanism of water vapor adsorption on activated carbons. According to this mechanism, it is possible that at low relative pressures the pore filling of very small pores (micropores) is promoted by the presence of hydrophilic surface oxides. On the other hand, the same oxides can reduce the pore volume available for filling at higher relative pressures. The above mechanism can explain the changes in both the adsorbed amount and the isotherm type, which are observed in experiments. Nevertheless, the existence of pores of definite sizes and shapes, and/or surface functional groups that initiate primary adsorption of water molecules in the micropores of activated carbons is not finally confirmed and further studies in this direction are desirable.

The present studies have been undertaken to recognize adsorption sites responsible for primarily adsorption of water vapor on microporous activated carbons. In contrast to the former studies [1–8], this work presents the equilibrium adsorption isotherms of water vapor on 14 modified activated carbons. The aim of this modification was to prepare carbon adsorbents with different surface functional groups and different porous structures. The measured adsorption isotherms were analysed on the basis of the Dubinin-Serpinsky (DS) [9, 10] and the Jovanovic-type [11] equation. Although the DS equations were derived for water vapor adsorption, this study showed their limited applicability for interpreting the adsorption isotherms of water vapor on activated carbons.

Experimental

Activated carbons prepared from polymers (SCN) polyfurfuryl alcohol (PFA), and hardwood (CWN, CWZ) were used to study adsorption of water vapor. In this work we also included the activated carbon from Merck (FRG). These carbons were used also in the previous adsorption studies [12–16]. The activated carbons prepared from hardwood (charcoals) underwent ash discharging [17]. All above mentioned activated carbons were modified by using different methods (cf., Table 1). Before adsorption measurements, activated carbons were outgassed at room temperature to a pressure of 10^{-5} mmHg. Next, 1 g of each sample was used to measure the water vapor adsorption isotherm at 298 K. The adsorption measurements were carried out by using a volumetric conventional apparatus equipped with a mercury manometer. The establishment of the adsorption equilibrium was checked according to recommendations proposed by Everett [18]. For each dose of water vapor the adsorption equilibrium was checked separately; the time required to attain adsorption equilibrium depended on the carbon sample and on the relative pressure of water vapor.

The amount of acidic surface oxides, which influenced partially adsorption of water vapor on activated carbons, was determined by the reaction with four kinds of bases: $NaHCO_3$, Na_2CO_3, NaOH, and $NaOC_2H_5$ [19]. Five grams of each carbon sample was stirred in 50 cm^3 of the base solution in especially designed vessels at nitrogen atmosphere. After twelve hours, the supernatant solution was separated by centrifuging, and then the solution was titrated potentiometrically by using an automatic titrator set from the Radiometer Copenhagen Ltd., Denmark. A digital pH-meter PHM-64 with the glass electrode G202C and the Calomel reference electrode K4018 was used. The titrations were carried out in nitrogen atmosphere by using a 0.05 M HCl solution. In order to compare the amount of oxygen contained in the acidic surface groups of a carbon sample with the total oxygen content, the coulometric measurements were performed for five modified activated carbons by using a conventional automatic apparatus [20].

Results and Discussion

Because the adsorption isotherms of water vapor measured on 14 activated carbons listed in Table 1 have analogous shapes, Fig. 1 illustrates only three isotherm curves for the SCN activated carbons: unmodified (SCN-u), oxidized by nitric acid (SCN-o), and heated at 1 400 K in argon atmosphere (SCN-h). Modification of the SCN activated carbon by nitric acid increases the amount of the acidic groups on the carbon surface, and therefore the amount of water adsorbed on the SCN-o carbon is higher in comparison to that on the unmodified carbon (SCN-u). Also the isotherm shape for the SCN-o carbon differs significantly from that observed for the unmodified SCN carbon. On the other hand, the thermal treatment of the SCN carbon at 1 400 K in argon atmosphere removes almost completely the acidic groups from its surface without a significant change in its microporous structure; therefore, for SCN-h carbon we observe a smaller adsorption of water vapor in comparison to that on the SCN-o and SCN-u carbons. It is seen in Fig. 1 that for relative

Table 1. Information about activated carbons studied

| Carbon	Raw material	Source of carbon	Modification
SCN-u	Polymer	Inst. of General and	Unmodified
SCN-o		Inorganic Chemistry, Ukrainian Acad. of	Oxidized with concentrated nitric acid
SCN-h		Sci., Kiev, USSR	Heat at 1 400 K in Ar atmosphere
PFA-o	Polyfurfuryl alcohol	Inst. of Chemistry Copernicus Univ.	Oxidized with concentrated nitric acid
PFA-h		Torun, Poland [13]	Heated at 1150 K in H_2 atmosphere
CWN-u	Hardwood	Carbon Electrodes	Ash removed
CWN-o		Comp., Raciborz Poland	Oxidized 6 h with air at 673 K
CWN-h			Outgassed 24 h at 773 K to a pressure 10^{-5} mmHg
CWZ-u	Hardwood	Wood Dry-Distillation	Ash removed
CWZ-o		Plant, Hajnowka Poland	Oxidized with concentrated nitric acid
CWZ-h			Heated at 1 400 K in Ar atmosphere
Merck-u	Hardwood	Merck, FRG	Ash removed
Merck-o			Hume acids removed; oxidized with 13% H_2O_2
Merck-h			Heated at 1 400 K in Ar atmosphere
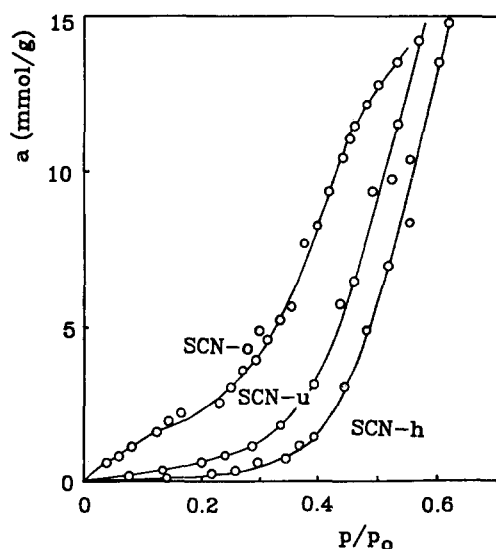
Fig. 1. Adsorption isotherms of water vapor on the SCN activated carbons at 298 K

pressures below 0.3 the surface functional groups play a dominant role in the adsorption process of water molecules on activated carbons. At higher relative pressures this process is controlled additionally by the micropore-size distribution. Another interesting feature of the isotherms shown in Fig. 1 appears in the relative pressure region from 0.4 to 0.6. In this region the isotherm curves for the unmodified and thermally treated SCN carbons are parallel and show almost linear increase with increasing p/p_0; however, in the same pressure region the adsorption ability of the SCN-o carbon, which possesses many acidic surface groups, is much smaller than that observed for the SCN-u and SCN-h carbons.

To study adsorption of water vapor on the primary adsorption sites of activated carbons, the low-pressure parts of the measured equilibrium isotherms were analysed. The adsorption isotherms of water vapor measured on 14 activated carbons listed in Table 1 have shapes, which are characteristic for this type of adsorption systems [21]. To describe these isotherms we employed the Dubinin-Serpinsky (DS) equations, which were derived especially for adsorption of water vapor on microporous solids [9, 10, 22]. These equations may be written as follows,

$$p/p_0 = a/[C(a_0 + a)] \qquad \text{(equation DS-I)} \qquad (1)$$

and

$$p/p_0 = a/[C(1 - ka)(a_0 + a)] \qquad \text{(equation DS-II)} . \qquad (2)$$

Here a is the amount of water adsorbed at the relative pressure p/p_0 and the absolute temperature T, a_0 characterizes the primary adsorption sites through the amount of water adsorbed on them, C is the constant associated with the adsorption and desorption rates, and k is the parameter associated with the micropore filling; the expression $(1 - ka)$ takes into account the decreasing role of the acting adsorption sites in the process of micropore filling at higher relative pressures.

Table 2 contains the values of a_0 calculated according to the DS Eqs. (1) and (2). To evaluate a_0 according to the DS-I equation the following linear form of Eq. (1) was employed [9, 10],

$$(p/p_0)/a = (Ca_0)^{-1} - (a_0)^{-1} (p/p_0) . \qquad (3)$$

Table 2. Amounts of the primary adsorption sites evaluated by means of the DS Eqs. (1) and (2) and Jovanovic-type Eq. (5) in comparison with those obtained by the potentiometric titration with 0.05 M NaOH

Activated carbon	a_0 Eq. (1) mmol/g	a_0 Eq. (2) mmol/g	a^* Eq. (5) mmol/g	Potentiometric method (mmol/g)
SCN-u	0.98	1.30	0.11	0.29
SCN-o	4.80	6.50	0.86	1.27
SCN-h	0.35	0.41	0.03	0.02
PFA-o	1.77	3.23	0.54	1.58
PFA-h	0.26	0.35	0.08	0.10
CWN-u	1.34	2.70	0.18	0.18
CWN-o	4.41	6.50	0.75	1.97
CWN-h	0.50	1.03	0.05	0.06
CWZ-u	1.99	3.30	0.23	0.22
CWZ-o	5.60	6.70	0.95	1.08
CWZ-h	0.53	0.90	0.04	0.05
Merck-u	2.60	3.60	0.22	0.76
Merck-o	4.50	6.20	0.49	1.80
Merck-h	0.50	0.70	0.09	0.06

Fig. 2 presents the linear dependences plotted according to Eq. (3) for the SCN carbons. It is seen in Fig. 2 that Eq. (3) describes relatively well the adsorption of water vapor at relative pressures between 0.2 and the isotherm inflection point. Eq. (2) gives a good representation of the measured isotherms in the limited pressure region, which is analogous to that mentioned above. A least squares optimization method was employed to evaluate a_0 according to Eq. (2). A comparison of the values of a_0 obtained from the DS-I and DS-II equations shows that the DS-II equation predicts greater values of a_0 than the DS-I equation. This observation illustrates the difficulty of describing the adsorption of water vapor on activated
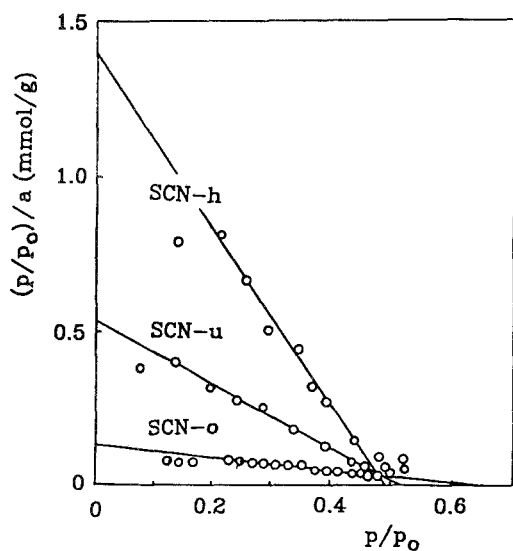
Fig. 2. Linear dependences plotted according to Eq. (3) for the adsorption isotherms shown in Fig. 1

carbons. To provide additional illustration to this problem, we used also the Jovanovic-type equation for describing the measured adsorption isotherms; this equation has the following form [11],

$$a = a^* \exp(\beta p/p_0) [1 - \exp(-\alpha p/p_0)]. \tag{4}$$

In the Jovanovic adsorption model a^* denotes the maximum monomolecular adsorption, α is a constant associated with the adsorption energy, and β is the constant that characterizes multimolecular adsorption (multilayer). The expression $[1 - \exp(-\alpha p/p_0)]$ describes the monomolecular adsorption on a solid surface, whereas the expression $\exp(\beta p/p_0)$ describes the multimolecular adsorption. Because the water molecules adsorb primary on the hydrophilic surface sites, a^* seems to reflect the amount of these sites. The primarily adsorbed water molecules can initiate formation of multimolecular clusters, which stimulate the micropore filling process. At higher relative pressures the adsorption sites responsible for the monomolecular adsorption are occupied, and consequently the expression $[1 - \exp(-\alpha p/p_0)]$ approaches unity; then Eq. (4) may be approximated by the following equation,

$$\ln a = \ln a^* + \beta (p/p_0). \tag{5}$$

The linear Eq. (5) was employed to evaluate a^* from the measured adsorption isotherms. For the purpose of illustration Fig. 3 presents the dependence of the natural logarithm of the adsorbed amount on the relative pressure for the SCN activated carbons. The values of a^* evaluated from the linear sections of the $\ln a$ vs. p/p_0 curves are summarized in Table 2. A comparison of the values of a^* with those obtained from the DS-I and DS-II equations shows that the values of a^* are significantly lower than the values of a_0. Also, the values of a^* are often lower than the values of the surface acidity evaluated by the potentiometric tritrations of the activated carbons by means of 0.05 M NaOH (cf., Table 2). In our opinion, this disagreement between the values of a_0 and a^* reflects different activity of the acidic surface groups; it is probable that a^* provides information about the most active acidic surface groups, which initiate monomolecular adsorption of water, whereas a_0 gives some information about the total number of the primary adsorption sites. A confirmation of this suggestion is provided by comparing the values of a^*
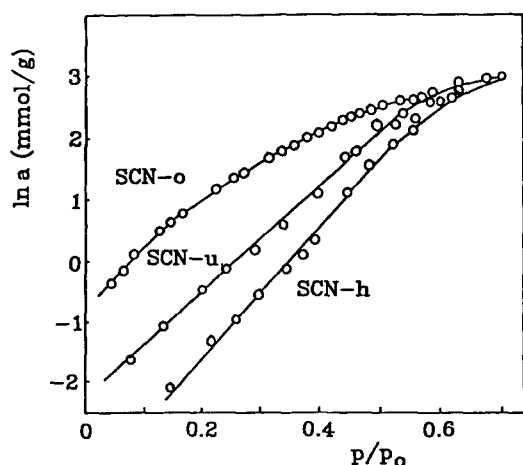

Fig. 3. Dependence of the natural logarithm of the adsorbed amount on the relative pressure plotted according to Eq. (5) for the adsorption isotherms shown in Fig. 1

with those obtained from the potentiometric titration; it is seen in Table 2 that for the thermally treated activated carbons the values of a^* evaluated from the adsorption isotherms of water vapor and from the potentiometric titration are analogous.

A quantitative analysis of acidic surface groups for nine activated carbons from Table 1 is presented in Table 3. This table contains also the total oxygen content for five activated carbons. Because Table 3 provides a quantitative information about acidic surface groups for different modified activated carbons, a comparative analysis of the data contained in Table 3 and the adsorption parameters leads to a better understanding of the role of different acidic surface groups in adsorption of water molecules. The thermal treatment of an activated carbon in neutral gas atmosphere reduces significantly the amount of acidic surface groups, although the carbonyl groups are bonded strongly with the surface and it is more difficult to remove them from this surface. The remaining carbonyl surface groups after the thermal treatment of an activated carbons seem to be the primary sites for adsorption of water molecules. Their small amount on the surface is the main reason of the high hydrophobicity of thermally treated activated carbon, and consequently its small sorption ability at relative pressures below 0.3.

Oxidation of an activated carbon in air atmosphere at 673 K (cf., Table 1 carbon CWN-o) leads to formation of different acidic groups on its surface, mainly carboxyl and phenolic groups. It is seen in Table 2 that this modification does not increase significantly the amount of the primary adsorption sites. Their amount increases significantly when activated carbon is oxidized by nitric acid. On the other hand, the efficiency of the oxidation of an activated carbon depends not only from the oxidation time, but also from the concentration of oxidizer and the type of activated carbon. The type of activated carbon determines to a great degree the total amount of the formed acidic groups, their composition and distribution on the carbon surface; e.g., during the oxidation by nitric acid of the SCN-o and CWZ-o carbons we observed a significant increase in the amount of carboxyl, carbonyl, and phenolic groups, whereas in the case of the PFA-o carbon this oxidation leads to a significant

Table 3. Analysis of the acidic functional groups on the surfaces of activated carbons studied (the amounts are expressed in mmol/g; total oxygen is expressed in mmoles of O_2 per gram of activated carbon)

Activated carbon	Carboxyl groups	Lactone groups	Phenolic groups	Carbonyl groups	Total oxygen
SCN-u	0.04	0.12	0.14	0.18	
SCN-o	0.38	0.39	0.50	0.40	
SCN-h	< 0.001	0.01	< 0.01	0.09	
PFA-o	0.56	0.76	0.25	1.25	
CWN-u	0.04	0.03	0.11	0.03	0.80
CWN-o	0.90	0.29	0.78	0.03	1.94
CWZ-u	0.02	0.06	0.15	0.17	0.64
CWZ-o	0.34	0.26	0.48	0.38	1.90
CWZ-h	< 0.001	0.01	0.04	0.11	0.11

increase in the amount of lactone and carbonyl groups. On the other hand, for activated carbons oxidized by nitric acid it is difficult to determine what kind of the acidic surface groups is most active in initiating the primary adsorption of water molecules. A comparative analysis of the values of a_0 and a^* given in Table 2 and the results presented in Table 3 (obtained from the potentiometric titration by means of the bases of different values of pK) indicates that for the oxidized activated carbons the most active surface groups in the primary adsorption of water molecules are the carboxyl, lactone and phenolic groups; however, for the deoxidized carbons (i.e., thermally treated in neutral atmosphere) the carbonyl surface groups seem to be the primary adsorption sites.

Table 3 shows that the total content of oxygen on a carbon surface is higher than that obtained by summing the amounts for different acidic surface groups. This is due to the fact that the part of oxygen is contained in other types of surface groups, e.g., the $\equiv C - O - C \equiv$ groups, which are not expected to be the primary adsorption sites.

The extensive measurements of adsorption of water vapor on many modified activated carbons presented here, and the results of analysis of the acidic surface groups provide new arguments to our understanding of the role of acidic surface groups in the primary adsorption of water molecules. Nevertheless, several questions concerning the water adsorption on activated carbons remain and further studies in this direction are desirable.

References

[1] McDermot H. L., Arnell J. C. (1952) J. Phys. Chem. **56**: 756
[2] Barton S. S., Evans M. J. B., Holland J., Koresh J. E. (1984) Carbon **22**: 265
[3] Morimoto T., Miura K. (1985) Langmuir **1**: 658
[4] Morimoto T., Miura K. (1986) Langmuir **2**: 43
[5] Barton S. S., Koresh J. E. (1983) J. Chem. Soc. Faraday Trans. I **79**: 1147
[6] Puri B. R., Murari K., Singh D. D. (1961) J. Phys. Chem. **65**: 37
[7] Barton S. S., Evans M. J. B., Harrison B. H. (1973) J. Colloid. Interface Sci. **45**: 542
[8] Stoeckli H. F., Kraehenbuel F., Morel D. (1983) **21**: 589
[9] Dubinin M. M., Serpinsky V. V. (1981) Carbon **19**: 402
[10] Dubinin M. M., Serpinsky V. V. (1981) Dokl. Akad. Nauk SSSR **258**: 1151
[11] Jovanovic D. S. (1969) Colloid. Polymer Sci. **235**: 1203
[12] Szeglowski Z., Swiatkowski A. (1987) In: Extended Abstracts of 38th Meeting of the International Society of Electrochemistry, Vol. 1. Maastricht, The Netherlands, pp. 176–178.
[13] Rychlicki G. (1981) Polish J. Chem. **55**: 1903
[14] Swiatkowski A. (1982) Biuletyn WAT (Warsaw) **31**: 81
[15] Jankowska H., Swiatkowski A., Oscik J., Kusak R. (1983) Carbon **21**: 117
[16] Jankowska H., Swiatkowski A., Goworek J. (1988) Materials Sci. Forum **25–26**: 501
[17] Korver J. A. (1950) Chem. Weekblad **46**: 301
[18] Everett D. H. (1967) In: Flood E. E. (ed.) The Solid-Gas Interface. Marcel Dekker, New York, p. 1057
[19] Boehm H. P. (1966) Advan. Catalysis **16**: 179
[20] Kopycki W., Fraisse D., Binkowski J. (1980) Chem. Anal. (Warsaw) **25**: 829
[21] Gregg S. J., Sing K. S. W. (1982) Adsorption, Surface Area and Porosity, 2nd edn. Academic Press, New York, pp. 262–268
[22] Dubinin M. M., Zaverina E. D., Serpinsky V. V. (1955) J. Chem. Soc. **55**: 1760