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Determination of dependencies between the specific retention volumes and the parameters characterising adsorbent properties

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Abstract

Propane adsorption isotherms have been chromatographically determined on active carbon for different amounts of the injected adsorbate on column. The dependencies between the specific retention volume corrected to the standard temperature (273.15 K), $V_{g(273)}$, and the molar differential work of adsorption, A , have been calculated on the basis of the propane isotherms and using the retention times of the peak maxima. The obtained equations: $\ln V_{g(273)} = f_1(A)$ and $(dW/dA)_{T,FC} = f_2(\ln V_{g(273)})$ have been used to explain the dependency between the chromatographic peak profile and the distribution function of pore volumes filled with propane with respect to the molar differential work of adsorption at different column temperatures (303–318 K).

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1. Introduction

Gas chromatography is widely used, mainly as an analytical method. Applying chemical compounds with well defined physical properties as chromatographed substances (adsorbates), also enables this technique to be used for investigating the properties of carbon and noncarbon adsorbents [1] and polymers [2]. When used in this context, the technique is known as inverse gas chromatography. In terms of the conditions employed for the chromatographic process, most studies have employed nonideal, linear chromatography [3] and, more rarely, ideal, nonlinear chromatography [4,5]. Only in a few papers have adsorbent investigations been described where

the results obtained have involved conditions typical of nonideal, nonlinear chromatography process [6,7].

Unlike the situation in static tests, an equilibrium state is not always attained during chromatographic measurements of adsorption processes proceeding under dynamic conditions. Hence, there is still some doubt as to whether the results obtained on the basis of chromatographic measurements are plausible. The observed differences in the adsorption values have been linked to the similarity between the dimensions of the adsorbate molecules and the entrances to the micropores as being connected to their not being filled with the adsorbate in the chromatographic process. This leads to the question as to whether the adsorption chromatographic tests can replace the static ones.

The Dubinin–Radushkevich (DR) equation has been widely used for over 50 years for the analysis of vapour adsorption on micropore adsorbents. Its

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derivation is based on an arbitrary assumption that there is a Gaussian distribution of adsorption space with respect to the molar differential work of adsorption. Further, the DR equation does not reduce to Henry's law as the relative pressure, p/p_s , goes to 0. Hobson and Armstrong [8] were the first to show that the DR equation was able to describe low pressure pure gas adsorption data well, although it lacked the fundamental Henry law. This work inspired us to apply inverse gas chromatography to describe the adsorption pore space on the basis of the DR equation parameters (e.g. W_0 is the limiting volume of the adsorption space of micropores, and E_0 is the characteristic adsorption energy). The DR parameters were calculated on the basis of the first derivatives parameters $(dW/dA)_{T,F_C} = f_2(\ln V_{g(273)})$, for the corresponding retention volumes, $V_{g(273)}$. However, when the DR equation is applied to the description of chromatographic data, some plausible reservations arise regarding the impossibility of calculating the correction for adsorption in micropores.

2. Experimental

2.1. Adsorbents

Commercial active carbon type NP5 (Gryf-Skand, Poland) was used in this study. The grains of the adsorbent have an irregular flat shape and the 0.30–1.25 mm fraction was separated for investigation. The mineral matter was removed from the NP5 adsorbent by Korver's method using concentrated HF and HCl [9]. The carbon was denoted as NP5O. The total amount of mineral impurities in the NP5O carbon was 0.1%.

The amounts of some metal cations in the mineral matter were determined. The metal cations were separated from the test adsorbent as follows. A 2-g sample of dried active carbon was mineralised in a muffle oven for 4 h. The residuum obtained was treated with 3 ml of perchloric acid and heated until the evolution of white vapour had ceased. It was then dissolved in 1 ml of chloric acid (1:1) and 5 ml of distilled water added to the resulting solution. The

amounts of cations in mineral impurities in the samples were determined by the inductively-coupled plasma atomic emission spectroscopy (ICP-AES) method using Jobin-Yvon 38+ atomic emission spectroscope employing inductively coupled plasma. The potassium and sodium cations contents were determined by flame atomic emission spectrometry (FAES) using a Perkin-Elmer 3030B instrument. The lead cation content was determined by flame atomic adsorption spectrometry (FAAS). Determination of sulphur content was carried out by means of a Leco analyser (Leco, Poland). Concentrations of cations (in ppm) in mineral impurities of the NP5O active carbon are: Ca 33.2, Mg 22.1, Pb 0.7, Ni 2.4, Mn 0.5, Fe 19.9, Cr 0.5, Al 10.4, Cu 51.7, Na 2.3, K 62.6 and S 2805. Approximate estimations of the concentrations of the cations in the mineral impurities were also obtained via an analytical set-up involving a Philips XL-40 scanning electron microscope associated with an EDAX 4i/DX GSR energy dispersive X-ray spectrometer; they are depicted in Fig. 1.

2.2. Static measurements

The sample of the active carbon was subjected to adsorption–desorption experiments employing nitrogen gas at 77 K as the adsorbate. Measurements of the extent of adsorption–desorption observed were made using a Carlo Erba Sorptomatic 1900 automatic adsorption apparatus. The adsorption characteristics were calculated on the basis of such an isotherm at 77 K. The specific surface area calcu-

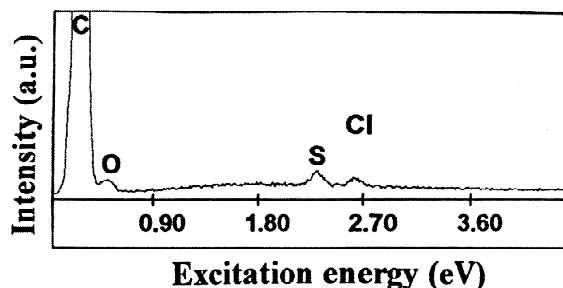


Fig. 1. Energy-dispersive X-ray spectrum of the NP5O surface.

lated for this sample was $1330 \text{ m}^2/\text{g}$, while its micropore volume was $0.55 \text{ cm}^3/\text{g}$.

2.3. Chromatographic measurements

The chromatographic measurements were undertaken using a Unicam type 610 gas chromatograph fitted with an on-line Unicam 4880 chromatography data handling system which was switched on when a sample was injected. The instrument was equipped with flame ionisation and thermal conductivity detection. The active carbon was placed in $65 \times 0.2 \text{ cm}$ I.D. glass columns, the length of the adsorbent bed in each column being 6–7 cm. The part of the column which was unoccupied by the adsorbent was filled with glass beads of 80 mesh size. The filled column was mounted in the chromatograph thermostat and heated at 603 K for 10 h in a helium stream at a flow-rate of 40 ml/min. A mixture of known amounts of methane and propane was used in the chromatographic tests (BOC gases, UK; analytical reagent grade). Measurements of retention times of propane were carried out at 303–318 K using helium at a flow-rate $F_c = 17.5 \pm 0.05$ of ml/min.

The interaction energy of simple nonpolar molecules adsorbed on the de-ashed active carbon can be attributed to dispersion forces. The Kirkwood–Müller potential function was used to calculate the dispersion force for the interaction energy between the adsorbent surface and the adsorbed simple nonpolar gas molecules: Ar, Kr, Ne and Xe. The values of the potential functions were applied to determine the hold-up time, t_M , from the following dependence [10]:

$$\ln [(t_{Ri} - t_M)\sqrt{M_i}] = a + bU(r) \quad (1)$$

where t_{Ri} and M_i are the retention time and molecular masses of the inert gases i (Ar, Kr, Ne and Xe), a and b are constants and $U(r)$ is the value of the Kirkwood–Müller potential function [11]. The temperature of the flame ionisation detector was 388 K and that of the thermal conductivity detector was 513 K.

The chromatographic peaks obtained were asymmetrical in shape, the retention times depended on the size of the sample injected and with superposition of the diffusive sides of the peaks. Therefore

for calculating the propane adsorption isotherms the peak profile method was used. Account was taken of the effect of the adsorbate diffusion in the active carbon on adsorption according to the suggestion of Dollimore et al. in calculating the adsorption isotherms [12]. This is based on the assumption that the diffusion in front of a peak is equal to the diffusion to the rear of a peak at each adsorbate concentration level.

3. Results and discussion

The isotherms are depicted in Fig. 2. Electron micrographs, taken at an accelerating voltage of 25 kV and with a magnification of $3000\times$, depicting the surface of the NP50 carbon are shown in Fig. 3. It exhibited distinct edges of carbon crystallite shapes at the same magnification of their surface segment.

The dependency between the pore volume filled with propane during chromatographic process, W , and molar differential work of adsorption, A , was determined on the basis of the propane adsorption isotherms. The $W = f(A)$ expressions obtained were then differentiated with respect to the molar differential work of adsorption, the corresponding distribution functions obtained being asymmetric in shape with coordinates for their extremities which depended on the amount of adsorbate injected onto the chromatographic column. For each adsorption system studied, the pore volume distribution functions obtained extended to higher values of the molar differential work of adsorption. This suggests that the functions obtained were approximate to the real distribution of propane adsorption energy on the active carbon surface and to the asymmetrical chromatographic peak from which the adsorption isotherm for propane was previously calculated.

Analyzing the results shows that superposition of the rear profiles of the distribution function occurred for the test adsorbents, which corresponds to the case of ideal, nonlinear chromatography.

In view of these results, a check was made as to whether a correlation between the extremum of dependency:

$$\left(\frac{dW}{dA}\right)_{T, F_c} = g(A) \quad (2)$$

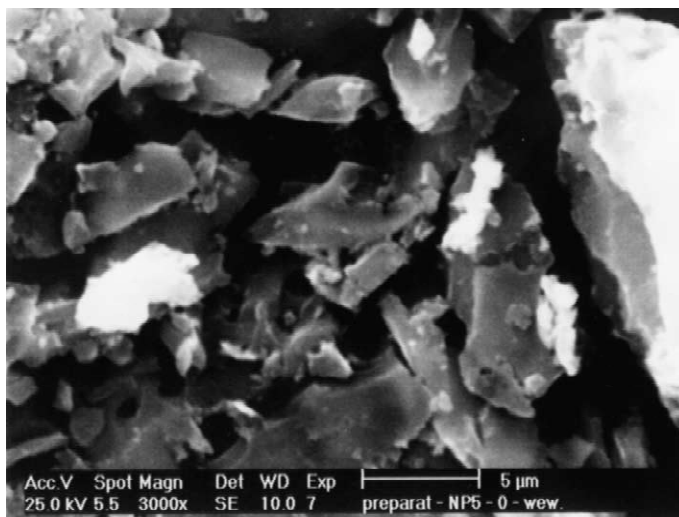


Fig. 2. Micrograph (3000 \times magnification) depicting the NP50 surface (Photo H. Grajek).

existed for a constant column temperature, T , and a constant volumetric flow-rate, F_C , of the carrier gas–adsorbate mixture through the adsorbent bed in the chromatographic column and the specific retention volume, $V_{g(273)}$. The dependence obtained connecting

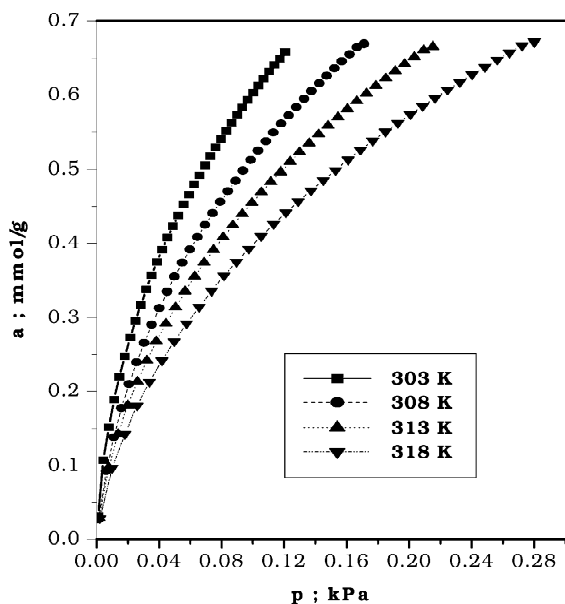


Fig. 3. Chromatographically determined adsorption isotherms of propane at 303–318 K on the P50 active carbon.

the magnitudes calculated directly from the chromatographic measurements and the values characterizing the dynamic adsorption process occurring in a chromatographic column were calculated by the Levenberg–Marquardt method [13]. The Levenberg–Marquardt method of minimisation uses the partial derivatives with respect to the calculated parameters. The parameters were iteratively adjusted to minimise a goodness of fit merit function. If the procedure was fully successful, a true global minimum was achieved. The analytical function thus obtained describes the changes of $V_{g(273)}$ as the function of A :

$$\ln V_{g(273)} = \exp \left(a + \frac{b}{A} + c \ln A \right) \quad (3)$$

The second dependency is the distribution function for pore volume filling with adsorbate with respect to A which depended on the specific retention volume:

$$\left(\frac{dW}{dA} \right)_{T, F_C} = a + b (\ln V_{g(273)}) + \frac{c}{[\ln V_{g(273)}]^2} \quad (4)$$

The magnitudes of the coefficients in Eqs. (3) and (4), the values of nonlinear regression coefficients and the residual variance values are listed in Table 1. Taking into account the data listed in Table 1 it may be stated that the dependencies given in the Eqs. (3) and (4) describe the values calculated directly from

Table 1
Parameters of Eqs. (3)

$$\left[\ln V_{g(273)} = \exp\left(a + \frac{b}{A} + c \ln A\right) \right]$$

and (4)

$$\left\{ \left(\frac{dW}{dA} \right)_{T,FC} = a + b(\ln V_{g(273)}) + \frac{c}{[\ln V_{g(273)}]^2} \right\},$$

the values of the nonlinear regression coefficients, r , and the residual variance values, S_x^2 , for the NP50 active carbon tested

Column temperature (K)	Parameter	Equation	
		(3)	(4)
303	a	7.490	-0.074
	b	-48.241	0.0074
	c	-1.078	0.153
	r	0.9974	0.9885
	$S_x^2 \cdot 10^3$	1.67	$10^3 \cdot 0.37$
308	a	7.934	-0.094
	b	-51.066	0.0094
	c	-1.191	0.475
	r	0.9983	0.9936
	$S_x^2 \cdot 10^3$	1.05	$10^3 \cdot 0.24$
313	a	6.426	-0.030
	b	-41.700	0.0045
	c	-0.850	-0.958
	r	0.9963	0.9894
	$S_x^2 \cdot 10^3$	2.00	$10^3 \cdot 0.39$
318	a	8.452	-0.099
	b	-55.060	0.0105
	c	-1.323	0.4903
	r	0.9969	0.9872
	$S_x^2 \cdot 10^3$	1.22	$10^3 \cdot 0.36$

the chromatographic measurements and the distribution functions accurately.

Eq. (4) is the missing link, connecting the parameters of the DR equation [14], and the specific retention volumes calculated in the case of ideal, nonlinear and nonideal, nonlinear chromatography.

In general, the first derivative of the DR equation with respect to the molar differential work of adsorption is expressed in the following equation:

$$\left(\frac{dW}{dA} \right)_{T,FC} = 2W_o \cdot \left[\frac{-A}{(\beta E_o)^2} \right] \exp \left[- \frac{A^2}{(\beta E_o)^2} \right] \quad (5)$$

where β is the affinity coefficient.

Comparison of Eqs. (4) and (5) enables us to calculate the DR parameters on the basis of the specific retention volumes. The results of such calculations are listed in Table 2. Taking into account the W_o and E_o values the distribution functions of the pore volume filled with propane relative to A were calculated; for 303 and 318 K they are depicted in Fig. 4.

The distributions functions of the pore volume filled with propane relative to A for different volumes of adsorbate injected onto the chromatographic column, calculated on the basis of propane adsorption isotherms at 303 and 318 K are depicted in Fig. 4. The value of the dependence $dW/dA = f(A)$ increased, and their maxima shifted to the decreasing values of A . In the case of 303 and 318 K the shift in the A values was about 144 J/mol for 51.2 μmol C_3H_8 and about 58 J/mol for 14.35 μmol C_3H_8 . The distribution functions evaluated are slightly temperature dependent. Such a slight dependence of distribution functions on temperature has already been observed by Tóth et al. [15]. Obtaining similar results on the basis of chromatographic adsorption measurements confirms their compatibility with the static ones.

Table 2

Values of the Dubinin–Radushkevich equation calculated on the basis of Eq. (5) the values of the nonlinear regression coefficients, r , and the residual variance values, S_x^2 , for the NP50 active carbon tested

Temperature (K)	Parameter DR equation	Value
303	W_o ; cm^3/g	0.84
	E_o ; kJ/mol	20.7
	r	0.9958
	$S \cdot 10^7$	1.13
308	W_o ; cm^3/g	0.88
	E_o ; kJ/mol	20.7
	r	0.9975
	$S \cdot 10^7$	0.80
313	W_o ; cm^3/g	0.93
	E_o ; kJ/mol	20.4
	r	0.9977
	$S \cdot 10^7$	0.73
318	W_o ; cm^3/g	0.86
	E_o ; kJ/mol	21.1
	r	0.9958
	$S \cdot 10^7$	0.94

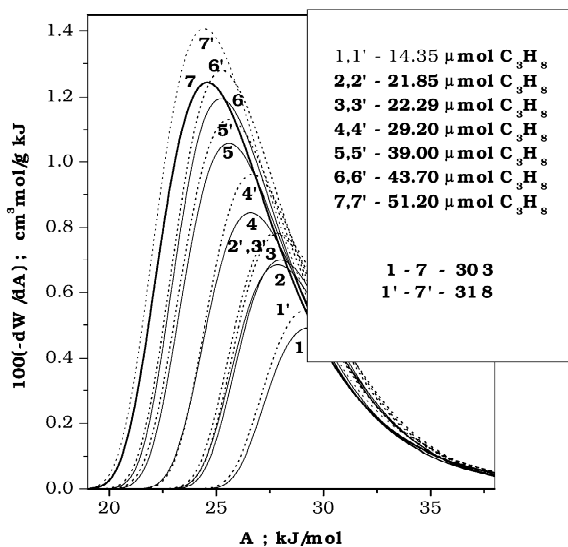


Fig. 4. Distributions functions of the pore volume filled with propane relative to the molar differential work of adsorption for different volumes of adsorbate injected onto the chromatographic column, calculated on the basis of propane adsorption isotherms at 303 and 318 K.

4. Conclusions

The examination of the results for the adsorption systems studied reveals the following:

- (i) it is possible to describe the adsorption pore space of the active carbons (e.g. to calculate the DR parameters) on the base of the $dW/dA_{T,FC} = f_2[\ln V_{g(273)}]$ function;
- (ii) an interdependence does exist between the retention time corresponding to the maxima of propane peaks, the profile of the chromatographic peak and the extremity of the distribution function of pore volume with respect to molar differential work of adsorption;
- (iii) for ideal, nonlinear chromatography, the profiles of the distribution function with respect to A superimposed in the same manner as the tails of asymmetrical peaks from which the adsorption isotherms were previously calculated;
- (iv) the propane adsorption isotherms as calculated

by the peak profile method represent the equilibrium partition isotherm of the adsorbate between solid-phase (adsorbent surface) and mobile phase (carrier gas) in the case of ideal, nonlinear chromatography;

- (v) the magnitudes of A for the minimum of the dependency $(dW/dA)_{T,FC} = g(A)$ change with increasing temperature.

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