

DETERMINATION OF DEPENDENCIES BETWEEN THE SPECIFIC RETENTION VOLUMES AND THE PARAMETERS CHARACTERISING THE ADSORBENTS PROPERTIES

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Introduction

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

The Dubinin-Radushkevich (DR) equation has been widely employed for the analysis of vapour adsorption on homogeneous adsorbents. Its 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, $\frac{P}{P_s}$, goes to 0. Hobson and Armstrong [5] were the first to show that

the DR equation was able to describe low pressure gas adsorption data well, although it lacked the fundamental Henry law. This work inspired us to apply IGC to describe the adsorption pore space on the basis of the DR equation parameters (e.g. W_o is the limiting volume of the adsorption space of micropores, and E_o is the characteristic adsorption energy). 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 mesopores.

Experimental

In this work, attempts have been made to apply IGC to the evaluation of the adsorption pore space in active carbons loaded with the known amounts of *tert*-butylacetate (*tert*B) and *n*-butylacetate (*n*B) and regenerated involving supercritical method with employing CO₂.

Commercial active carbon type NP5 (Gryf-Skand, Poland) was used in the study. The sample after deashing was denoted as P5O. The total amount of mineral impurities in the P5O sample was lower than 0.1 %.

The sample of the P5O active carbon was subjected to adsorption/desorption experiments employing nitrogen gas at 77 K as the adsorbate. The specific surface area calculated on the basis of the obtained isotherm for this sample was $1330 \text{ m}^2/\text{g}$, while its micropore volume was $0.55 \text{ cm}^3/\text{g}$.

The P5O adsorbent was separated in two parts and loaded with *tert*B, and *n*B. They were then subjected to supercritical fluid extraction in an apparatus employing a 10 cm^3 extraction cell at 325 K and 15 MPa pressure by a dynamic method using CO_2 [6].

The samples loaded with butylacetates and extracted were subjected to chromatographic measurements of retention times of propane, employing helium at a flow rate $17.5 \pm 0.05 \text{ cm}^3/\text{min}$.

The chromatographic peaks obtained were asymmetrical in shape, the retention times connected with their peak maxima and the centres of gravity depended on the size of the sample injected, and with superposition of their diffusive sides – see Figure 1.

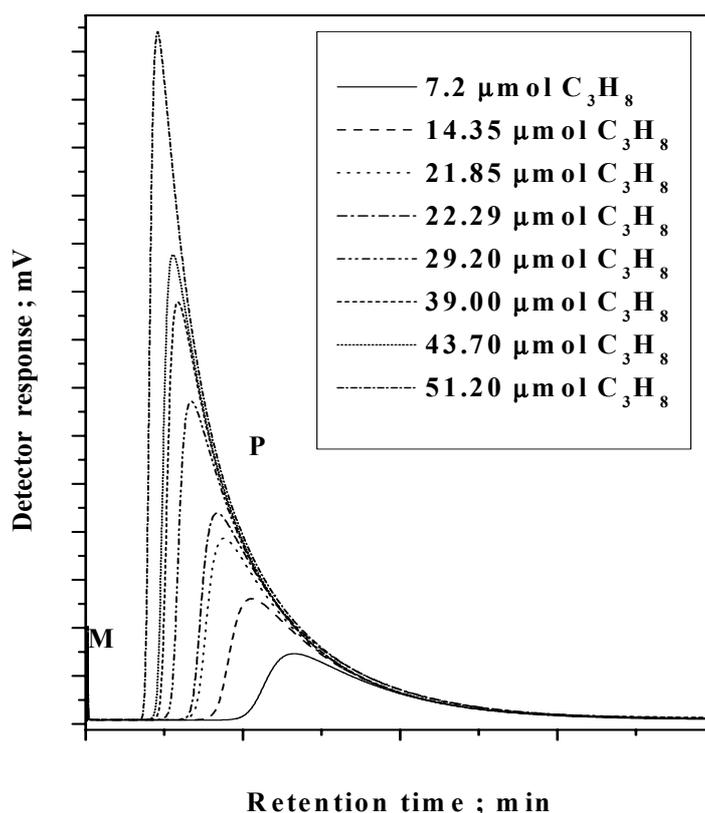


Figure 1. Chromatographic peaks for methane (M) and propane (P) at 318 K for different amounts of propane injected onto the column.

Results and Discussion

The dependency between the pore volume filled with propane, W , and molar differential work of adsorption, A , was determined on the basis of the propane adsorption isotherms [7]. The $W = f(A)$ expressions obtained were then differentiated with respect to the molar differential work of adsorption. The corresponding distribution functions were asymmetric in shape with coordinates for their extremities which depended on the amount of adsorbate; it is presented in Figure 2.

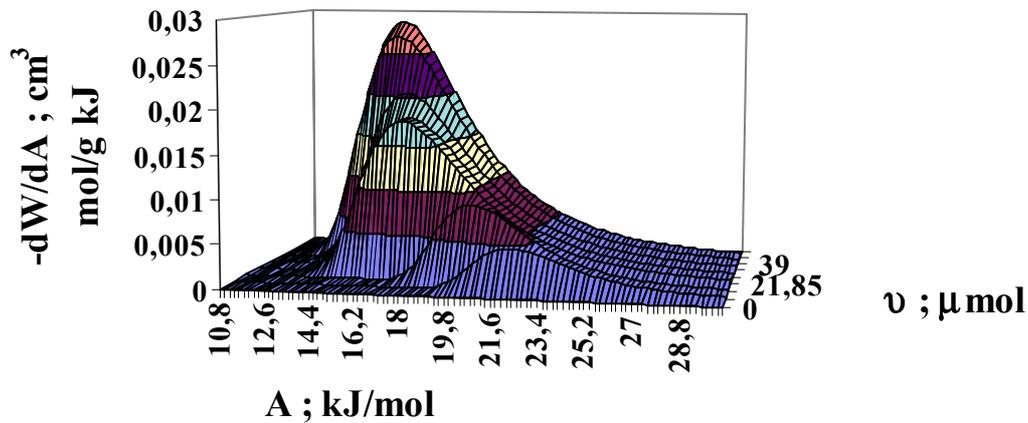


Figure 2. The corresponding distribution functions of the pore volume filled with propane relative to the molar differential work of adsorption for different volumes of adsorbate injected onto the column, as calculated on the basis of the chromatographic peaks depicted in Figure 1 for propane.

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 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 [8].

The results show that superposition of the rear profiles of the distribution function for the tested adsorbents correspond to the case of ideal, non-linear chromatography.

Taking all these observations into account, a check was made as to whether a correlation between the extremum of dependency [9]:

$$\left(\frac{dW}{dA}\right)_{T,v} = g(A) \quad (1)$$

existed for a constant column temperature, T , and a constant volumetric flow rate, v , of the carrier gas-adsorbate, and the specific retention volume, $V_{g(273)}$. The dependencies obtained connecting the magnitudes calculated directly from the chromatographic measurements and the values characterising the dynamic adsorption process occurring in a chromatographic column were calculated by Levenberg-Marquardt method [9]. The analytical functions thus obtained may be divided into two groups. The first of them describes the changes of the specific retention volume, $V_{g(273)}$, as the functions of the molar differential work of adsorption, A :

$$\ln V_{g(273)} = a + b \ln A \quad (2)$$

$$\ln V_{g(273)} = ab^A A^c \quad (3)$$

while the other is composed of the distribution functions for pore volume filling with adsorbate with respect to the molar differential work of adsorption which depended on the specific retention volume:

$$\left(\frac{dW}{dA} \right)_{T,v} = \frac{ab + c(\ln V_{g(273)})^d}{b + (\ln V_{g(273)})^d} \quad (4)$$

The distribution functions of the pore volume filled with propane relative to A for different volumes of adsorbate injected onto column, calculated on the basis of propane adsorption isotherms at 303 and 318 K are depicted in Figure 3.

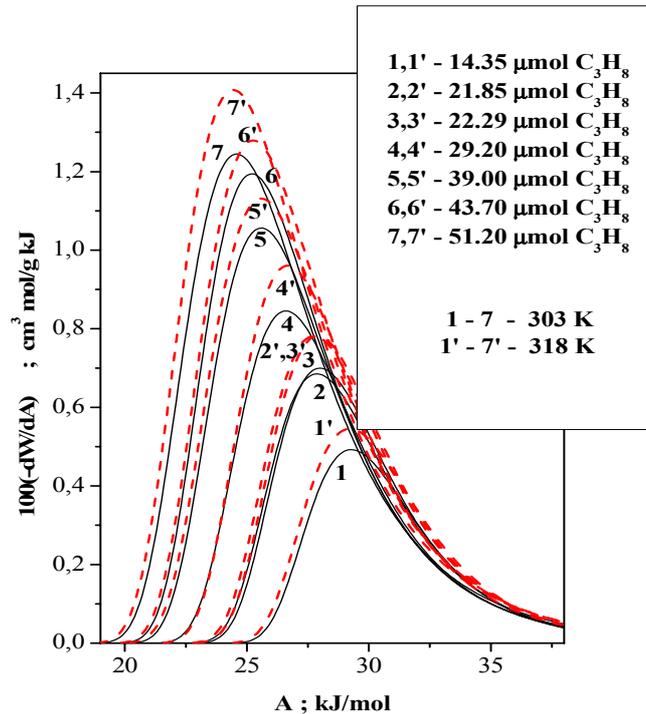


Figure 3. Distribution functions of the pore volume filled with propane relative to the molar differential work of adsorption for different volumes of adsorbate injected onto the chromatographic column, calculated on the basis of propane adsorption isotherms at 303 and 318 K [8,9].

The value of the dependence $\frac{dW}{dA} = f(A)$ 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 58 J/mol for 14.35 $\mu\text{mol C}_3\text{H}_8$. 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. [10]. Obtaining similar results on the basis of chromatographic adsorption data confirms their compatibility with the static ones.

Conclusions

- i) 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;
- ii) for ideal, non-linear chromatography, the profiles of the distribution function with respect to molar differential work of adsorption superimpose in the same manner as the tails of peaks;
- iii) 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, non-linear chromatography;
- iv) the magnitudes of the molar differential work of adsorption for the minimum of the dependency $\left(\frac{dW}{dA}\right)_{T,v} = g(W)$ increase with the increase of temperature.

Acknowledgments

This work was partly supported by the Polish State Committee for Scientific Research, Grant No. 4 T09B 025 24.

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