

THE APPLICATION OF THE TÓTH AND UNILAN EQUATIONS FOR TESTING THE ADSORPTION PROPERTIES OF ACTIVE CARBONS EMPLOYED IN SAMPLE PREPARATION

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Introduction

Active carbon is generally considered to consist of rigid clusters of microcrystallites, with each microcrystallite made up of a stack of graphene planes (2D-, the sp^2 -type of hybridisation of carbon valence orbitals). Free spaces between the planes create a pore network (i.e. pores of different sizes). Strongly activated carbons have a wider distribution of the adsorption space of the micropores as a function of their dimensions which may be accurately described by the superposition of two distributions. A means of mutual access of these types of pore is one of the factors of particular relevance to the kinetics of adsorption/desorption and adsorbate elution. There are a number of different even totally divergent hypotheses on this subject. For example, according to one of them (developed on the basis of a tree-like porous structure), micropores represent branching from mesopores, while another hypothesis views the three types of pores as having direct connection to the surface of the carbon grains [1]. Hence, the investigations of gas-active carbon equilibria, i.e. the adsorption properties are very difficult. The specific physical and chemical properties of activated carbons render these materials to be difficult for testing by chromatographic method, because the process of chromatographing the test substance takes place at the conditions rather difficult for an exact description:

- on the two-dimensional surface of pore walls,
- in the three-dimensional space of their pore structure.

According to Erickson active carbon has to characterise a very specific adsorption properties to be employed for sample preparation [2]. For example, it is an adsorbent which is employed to separate those polychlorinated biphenyls for which a planar conformation can be employed [2]. In this case a commonly employed characteristics of adsorbents on the base of specific surface area is even irresponsible because some important adsorbents features are completely omitted, e.g. structural and surface heterogeneity, concentration of surface species, and so on.

The inverse gas chromatography (IGC) seems to be a suitable and highly sensitive technique for studying the adsorption of very small concentrations of gases or vapours on different adsorbents employed in sample preparation.

Therefore, the general equation for the net retention volume, V_N , can be written after Rudziński in the following form [3]:

$$V_N = j \left(\frac{\partial a}{\partial \rho_o} \right)_{T, F_c} \quad (1)$$

Neglecting the non-ideality effects in the bulk gas phase [3], i.e. assuming that $\rho_o = \frac{p}{RT}$, the equation (1), after simple transformations may be given by:

$$\left(\frac{da}{dp}\right)_{T,F_c} = \frac{V_N}{jmRT} = \frac{V_{g(T)}}{jRT} \quad (2)$$

According to The Jaroniecs and Gawdzik the methods for determining the monolayer capacity by using inverse gas chromatography fall in two groups [4]:

- indirect methods – the monolayer capacity is calculated from adsorption isotherms obtained from chromatographic data;
- direct ones – the retention data are used directly for calculating the monolayer capacity.

Jaroniec *et al.* suggested that the most useful methods would be those employing retention data directly [5]. Tremaine and Gray employed the BET equation for calculation of the monolayer capacity on the basis of retention volume data [6].

Experimental

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 [7,8]. The propane peaks, as signals creating the frequency functions, $f(t)$, were acquired over 480 minutes at the digital acquisition rate of 10 Hz and stored. In the acquisition time employed the propane elution peaks reached the base line. A mixture of the known amounts of methane, and propane was used in the chromatographic tests (BOC gases, p.a., U.K.). 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 cm^3/min .

The micropores were modelled as two parallel graphite planes separated by the distance, $x_o = \frac{(13.028 - 1.5310^{-5} E_o^{3.5})}{E_o}$, which in this case was measured between

the planes of carbon atom centres on opposite walls. This distance is also referred to as the “physical” width of the pore. In such a case the external potential $U_{pore}(z, x_o)$ experienced by an adsorbate molecule at z (the intermolecular separation of the colliding molecules) is then given by:

$$U_{pore}(z, x_o) = U_{ij}(z) + U_{ij}(x_o - z) \quad (3)$$

The fact that active carbons can contain high energy sites such as heteroatoms (see page 3) and edge sites may be crucial in determining the properties of an intermolecular interactions model. Obviously a model that fails to account for such features may be misleading.

Some adsorption potential energy profiles for different x_o values are depicted in Figure 1.

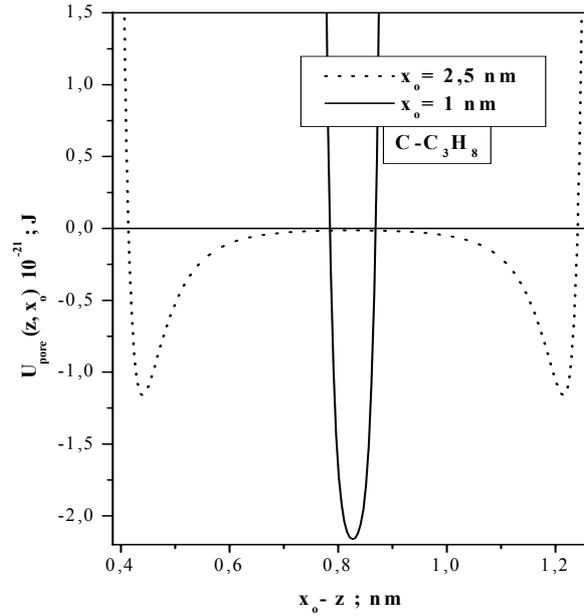


Figure 1. The adsorption potential energy profiles for two physical pore widths.

Results and Discussion

It was found, for the adsorption system studied, that the chromatographic peaks were asymmetrical in shape (i.e. non-Gaussian with a sharp front and diffuse rear boundary), the retention times of their maxima and centres of gravity depended on the amount of the propane injected and with very good superposition of the diffusive rear boundaries of the peaks. The peak-shapes obtained indicate that axial dispersion was negligibly small with the kinetic rate of mass transfer being infinite (i.e. the column efficiency was infinite under the chromatographic conditions employed). The concentration of propane on the active carbon surface under equilibrium conditions is no longer proportional to its concentration in helium.

The Tóth and Unilan equations were chosen for the description of chromatographic adsorption data because they contain only three parameters including heterogeneity parameter and give analytical expressions for the amount adsorbed. Hence, they seem to be the best all-round equations for describing adsorption on microporous adsorbents.

After differentiating the afore-mentioned equations with respect to equilibrium pressure, p , we have:

- for the Tóth:

$$\left(\frac{da}{dp}\right)_{T,F_c} = -a_m p^t (b + p^t)^{-1-\frac{1}{t}} + a_m (b + p^t)^{-\frac{1}{t}} \quad , \quad (4)$$

- and for the Unilan equation:

$$\left(\frac{da}{dp}\right)_{T,F_c} = \frac{a_m}{2s} \left\{ \frac{\exp(s)}{[c + p \exp(-s)]} - \frac{[c + p \exp(s)]}{\exp(s)[c + p \exp(-s)]^2} \right\} \left\{ \frac{[c + p \exp(-s)]}{[c + p \exp(s)]} \right\} \quad , \quad (5)$$

The hiperbolic dependencies (4) and (5) were equalled by sides with the equation (2) to obtain the following mathematical links: $V_{g(T)} = f(a_m, t, b)$ and $V_{g(T)} = f_1(a_m, s, c)$.

The suggested method can be only applied in those cases where the temperature retention dependence (calculated taking the retention times of the peak maxima and the centres of gravity of peaks into account) is a continuous function over the column-temperature interval in which chromatographic measurements were undertaken. The theoretical treatment of monolayer adsorption, a_m , is mainly concerned with two-dimensional arrays of interacting molecules (e.g. analytes).

The experimental verification of the links demonstrated their utility for describing retention values on heterogeneous adsorbents in IGC. The variation of the equation (5) is presented in Figure 2.

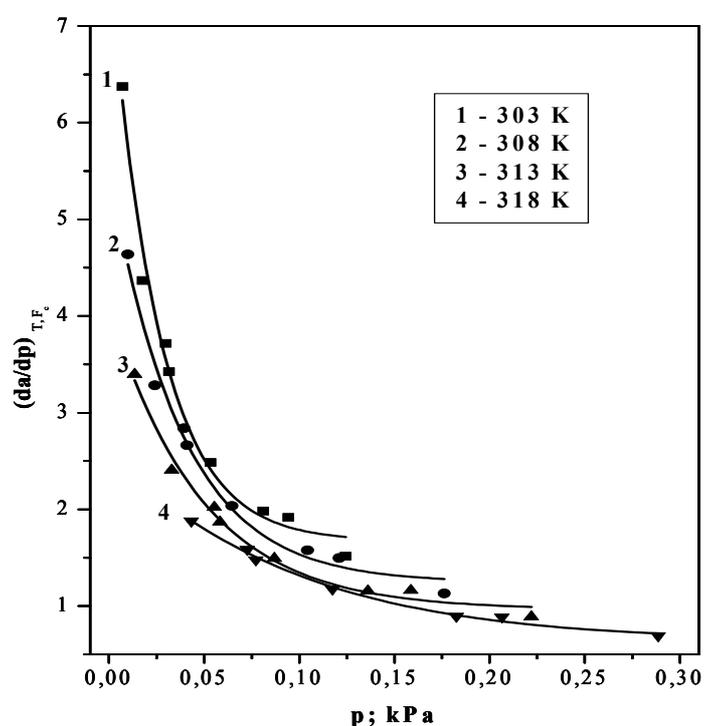


Figure 2. The variation of the equation (5) versus column temperature for the P5O active carbon.

A new method for calculating the parameters of the Tóth and Unilan equations and the differential isosteric adsorption enthalpies and entropies based on the adsorption second virial coefficients, B_{2S} is presented in the Table.

The $-\Delta H_{ads}$ and $-\Delta S_{ads}$ values were calculated with the confidence limits of the arithmetic mean of them for a probability level of 95 %. A comprehensive analysis of the values of the regression coefficients, r , and the residual variances, S_x^2 , shows that employing the equations which outperform the Langmuir model it is possible to obtain magnitudes of the r^2 higher than 0.998 and the S_x^2 values lower than $6.0 \cdot 10^{-6}$.

The values of the afore-mentioned quantities (e.g. the $-\Delta H_{ads}$ and $-\Delta S_{ads}$ values, except for the P5O+OtBr employing the Unilan equation) calculated for the centres of gravity are higher in comparison with the peak maxima ones. However, the

differences between the thermodynamic values calculated for the retention times of peak maxima and their centres of gravity are not significant.

Table. The comparison of the values of the isosteric enthalpies of adsorption and entropies of adsorption calculated [employing Eq.; $\ln \frac{B_{2S}^o}{T} = \frac{-\Delta H_{ads}^o}{R} \frac{1}{T} + \frac{\Delta S_{ads}^o}{R} + \ln(RSm)$] on the basis of the Tóth and Unilan equation parameters by different methods (i.e. calculated on the basis of the peak maxima – *pm* and the centres of gravity – *cg*), the values of the linear regression coefficients, *r*, and the residual variance values, S_x^2 , for the active carbon samples tested.

Equation	Parameter	P50	P50+OnBr	P50+OtBr
Tóth	$-\Delta H^{pm}$; kJ/mol	52.5±0.2	39.0±0.3	43.5±0.2
	$-\Delta S^{pm}$; J/mol·K	181.6±3.4	161.5±3.9	172.6±3.6
	$r^2_{(pm)}$	0.995-0.996	0.995-0.998	0.991-0.993
	$S_x^2 \cdot 10^4$	0.55	4.71	0.76
	$-\Delta H^{cg}$; kJ/mol	53.9±0.2	39.4±0.2	44.8±0.1
	$-\Delta S^{cg}$; J/mol·K	193.4±3.3	158.9±3.1	176.0±3.6
	$r^2_{(cg)}$	0.994-0.996	0.995-0.997	0.993-0.994
	$S_x^2 \cdot 10^4$	4.90	1.04	0.06
Unilan	$-\Delta H^{pm}$; kJ/mol	51.0±0.3	44.0±0.2	42.9±0.3
	$-\Delta S^{pm}$; J/mol·K	176.0±3.3	172.4±2.9	166.7±3.9
	$r^2_{(pm)}$	0.992-0.996	0.993-0.996	0.993-0.996
	$S_x^2 \cdot 10^4$	3.39	0.67	4.91
	$-\Delta H^{cg}$; kJ/mol	54.7±0.2	44.7±0.1	41.2±0.1
	$-\Delta S^{cg}$; J/mol·K	193.3±2.2	179.6±3.1	162.3±3.0
	$r^2_{(cg)}$	0.993-0.997	0.994-0.995	0.992-0.994
	$S_x^2 \cdot 10^4$	0.98	3.64	0.22

The results presented in the Table show, as expected, that c.a. 9.2 % of *tert*-butylacetate and c.a. 8.4 % of *n*-butylacetate remaining in the P50 micropore structure have a tremendous influence on the thermodynamic properties of the active carbon. The change in the differential entropy of propane is just a measure of the loss of freedom or randomness that a molecule has when migrating in tree-like porous structure of an active carbon. The larger the entropy change is the greater is the restriction of motion of the adsorbate molecules being eluted [8].

Conclusions

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

- i) the first derivatives of the Tóth and Unilan equation can be successfully employed for the characterisation of changes in the monolayer capacity of

- active carbons brought about through their demineralization and supercritical extraction of sparingly desorbing substances;
- ii) in inverse gas chromatography the mechanism for transporting molecules in an adsorbent appears to be composed of the following processes: penetration of the propane molecules inside an adsorbent particle; diffusion inside the particle; physical adsorption; surface diffusion along the adsorbed phase; desorption, and diffusion out of the particle. All the aforementioned processes have a significant influence on the resulting quantitative characteristics particularly for microporous adsorbents. Hence, the determined quantities of the monolayer capacity can only represent effective values, however useful for analysts employing active carbon in sampling of environmental impurities;
 - iii) despite the fundamental influence of the above successive steps in establishing the rate of dynamic adsorption equilibrium in adsorbent beds, through the use of active carbon samples with developed micropore structure, it was possible to determine reproducible net retention volume data for propane;
 - iv) finding the dependency between the net and/or specific retention volumes and the monolayer capacity enables a phenomenological description of the adsorption behaviour while completing a monolayer;
 - v) the greater the forces between propane molecules and the outermost layer of active carbon atoms, the greater the isosteric enthalpy of adsorption contribution and the greater the retention. Conversely, any reduction in the random nature of the adsorbate molecules or any increase in the amount of order in the chromatographic system attenuates the adsorbate retention. In IGC, the differential isosteric enthalpy and differential entropy oppose each other in their influences on adsorbate retention.

Acknowledgments

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