

STUDY OF THE SURFACE HETEROGENEITY ON POROUS ACTIVATED CARBONS USING SCHAY'S KINETIC MODEL

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Introduction

Using a simple kinetic model, G. SCHAY [1] has established a relationship for the concentration dependence from binary liquid mixtures. Interactions both among the molecules and between the molecules and the sorbent in case of monomolecular coverage, planar surface and identical specific molecular surface areas are expressed as:

$$\alpha = \frac{\tau_1^{\circ}}{\tau_2^{\circ}} \exp \left\{ \frac{1}{kT} [(\varepsilon_1 - \varepsilon_2) + (z + 1)(\beta_2 \varepsilon_{22} - \beta_1 \varepsilon_{12}) - (z + 1) \right. \\ \left. (\beta_1 \varepsilon_{11} - \beta_1 \varepsilon_{12} - \beta_2 \varepsilon_{12} + \beta_2 \varepsilon_{22}) x_1] \right\} \quad (1)$$

where α is the distribution coefficient, i. e. the enrichment factor:

τ_1° and τ_2° are extrapolated mean times;

ε_1 and ε_2 are fundamental values of the respective desorption energies of the two kinds of molecules, corresponding to the direct interaction with the solid surface;

ε_{iq} are energies necessary for severing the respective contacts between two molecules of the liquid;

β_1 and β_2 are respective proportionality factors;

z is the number of the neighbours of a molecule in a complete layer and

x_1 is the equilibrium mole fraction of the species in question.

The relationship is about linear if the surface of sorbent is about homogeneous hence the differences in the desorption energies are constant:

$$\lg \alpha = A - Bx_1. \quad (2)$$

The validity of Eq.2 can be proven by some examples beside the given parameters [1]. But in the case of adsorption on the surface of porous activated carbons

the relationship is not linear, namely surface points with different degrees of heterogeneity have various desorption energies.

Porous activated carbons of different surface properties have been studied with an attempt to describe and quantitatively determine these differences using Schay's method.

Selection of the systems studied

According to our experimental results the surface heterogeneity of activated carbons is mainly due to the sorption fields varying in the pores of different sizes, hence pore size distribution and heterogeneity are closely related [2]. Therefore the carbons used as model materials were classified according to their pore size distribution. Determination of the exact size distribution of pores belonging to the order of the average molecule diameter ($d = 5$ to 30 \AA) of the sorbates is problematic because of the curvature of the liquid surfaces developing in the capillar condensation process and therefore the detailed analysis of pore statistics was given up by the time. Carbons were classified according to pore size distribution, and distinction was made between pore size distribution curves decreasing continuously with increasing pore size in the micropore range (up to 30 \AA) and those with maxima in the $10 \text{ \AA} < d < 30 \text{ \AA}$ range; the respective carbons being denoted by S (steam activated) and by C (chemically activated).

Data in Fig. 1. refer to ethanol—benzene mixtures on activated carbons of S- and C-type. These two different curves are difficult to discuss because of the changes of both the co-ordination numbers and of the desorption energies related to the curvature of surfaces studied. Information supplied by differences

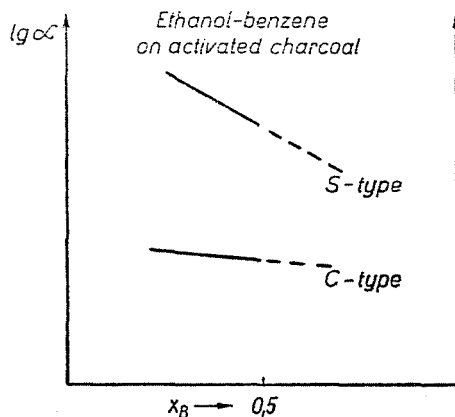


Fig. 1

in the slopes of linear sections about the curvature of surface is of no use because of the complex relationship.

For convenience the preferential sorption from dilute solutions of partially mixing liquid systems was investigated. In this case the last term of Eq.1 could be omitted. The practical importance of similar systems also influenced our choice. At the same time unidentity of the specific molecular surface areas in the chosen systems, i. e. in the phenol-water had to be taken into consideration. All these were kept in mind in studying the application possibility of the Schay equation for sorbents of curved surface and sorbates of different specific molecular areas.

Theoretical

Though the convex surface elements must not be ignored, their quantity is negligible compared to the size of the adsorbing molecules on porous activated carbons. Hence the co-ordination number of the desorption energy is expected to be greater than unity owing to the curved surface, and on the liquid side of the interface there are less molecules than on a plane surface. The effect of the average surface curvature can be corrected by interdependent factors.

Screening of the surface field and the surface curvature can be taken into consideration by the correction factor B .

Since there are only solvent molecules on the liquid side of interface and the last term of Eq.1 is negligible, the total change in the desorption energy of the preferential sorbing component is as follows:

$$B\varepsilon_1 - \left[(z + 1) - (B - 1) \frac{\theta_1}{\theta_2} \right] \varepsilon_{12} \quad (3)$$

where θ_1 is the specific molecular surface area; B is the surface curvature and screening factor; and for the other component:

$$B \frac{\theta_1}{\theta_2} \varepsilon_2 - \left[(z + 1) - (B - 1) \frac{\theta_1}{\theta_1} \right] \varepsilon_{22}. \quad (4)$$

For the case of identical specific molecular areas, G. SCHAY established

$$\alpha = \frac{\tau_1}{\tau_2} \quad (5)$$

or in case of different specific molecular surface areas:

$$\alpha = \frac{\tau_1 \theta_2}{\tau_2 \theta_1} \quad (6)$$

and following Schay's deduction, the enrichment factor and the energies of interaction in case of strong preferential adsorption from dilute solutions are related as:

$$\alpha = \frac{\tau_1^{\circ}\Theta_2}{\tau_2^{\circ}\Theta_1} \exp \left\{ \frac{1}{kT} \left[B \left(\varepsilon_1 - \frac{\Theta_1}{\Theta_2} \varepsilon_2 \right) + (z+1)(\beta_2\varepsilon_{22} - \beta_1\varepsilon_{12}) - (B-1) \frac{\Theta_1}{\Theta_2} (\beta_2\varepsilon_{22} - \beta_1\varepsilon_{12}) \right] \right\}. \quad (7)$$

The concentration dependence on the difference in sorption energies expressed by Polányi's relationship for the adsorption from partially mixable systems (3):

$$\varepsilon_1 - \frac{\Theta_1}{\Theta_2} \varepsilon_2 = kT \ln \frac{x_{1,\text{sat}}}{x_1} \quad (8)$$

Limiting the prime factors for the strong preferential sorption from partially mixing systems, Eq. 7 becomes by means of Eq. 8:

$$\alpha = \frac{\tau_1^{\circ}\Theta_2}{\tau_2^{\circ}\Theta_1} \exp \left\{ B \ln \frac{x_{1,\text{sat}}}{x_1} + \frac{1}{kT} \left[z+1 - (B-1) \frac{\Theta_1}{\Theta_2} \right] (\beta_2\varepsilon_{22} - \beta_1\varepsilon_{12}) \right\} \quad (9)$$

or, reducing the constants:

$$\lg \alpha = \lg \alpha_{\text{sat}} - B \lg \frac{x_1}{x_{1,\text{sat}}} \quad (10)$$

α_{sat} characterizing the concentration at saturation is an extrapolated value, as the adsorption is not monomolecular near saturation.

Conclusions drawn from Eq. 9 agree with the experimentally proved fact, that the temperature dependence of adsorption is ascribable to the change in concentration at saturation.

Accordingly, constant B in Eq. 10 yields explicit information about the average curvature of the surface in a given system. It has to be emphasized that the validity of this relationship is not supported by the linearity of the function $\lg \alpha = f(\lg x_1)$ in itself, on account of the variability of the co-ordination number on curved surfaces. This problem will also be discussed later.

Experimental

The activated carbons were heated at 110 °C for 12 hours in a vacuum drier to remove the sorbed humidity.

The basic materials of sorbates were bidistilled water and the chemicals of REANAL in p. a. quality.

The change in concentration was measured by a tempered double prisms sinking refractometer in the case of concentrated solutions and by a UV-spectrophotometer for dilute phenol solutions.

The B. E. T. surface area values were not perfectly reliable because of the microporosity of the activated carbons in question. Therefore it seemed to be necessary to control these values by the adsorption from liquid mixtures. The data obtained for benzene-ethanol mixtures were appreciated by the SCHAY—NAGY method [4]. (Table 1).

Table 1

Adsorbent		Surface area	
Denomination	Type	by B. E. T. method (m ² /g)	by the adsorption of binary mixtures (m ² /g)
NORIT WS 55	S	910	780
NORIT CARBO extra	S	1270	1160
CARBORAFFIN P	C	2400	1800
DECOLOR AC	C	1360	1180

The surface values controlled in this way were applied for calculating the enrichment factors. The specific surface areas of molecules considered as spherical were estimated from the molar values, by the method known from references yielding 60 m²/mmol water and 196 m²/mmol for phenol.

Discussion

The excess isotherms in Fig. 2 are almost identical to the individual isotherms of the preferential sorbed component in the range of the very dilute solution. The proportion of the surface area occupied by phenol, calculated from the saturation value of the total surface is greater on *S*-type than on *C*-type carbons.

According to $\lg \alpha$ vs. $\lg x_1$ curve in Fig. 3, sections are invariably linear in the concentration range corresponding to the ascending line of the excess isotherms. The slopes of *S*-carbons are almost identical and considerably greater than those for *C*-carbons. Also the absolute values of the enrichment factor of *S*- and *C*-type carbons may differ. Fig. 3 shows the $\lg \alpha$ values to fit the same line in the case of same (*C* or *S*) type sorbents, calculating $\lg \alpha$ from the B. E. T. surface area. This fact shows the real physical significance of the B. E. T. surface area. Since the saturation values of the enrichment factor α_{sat} , calculat-

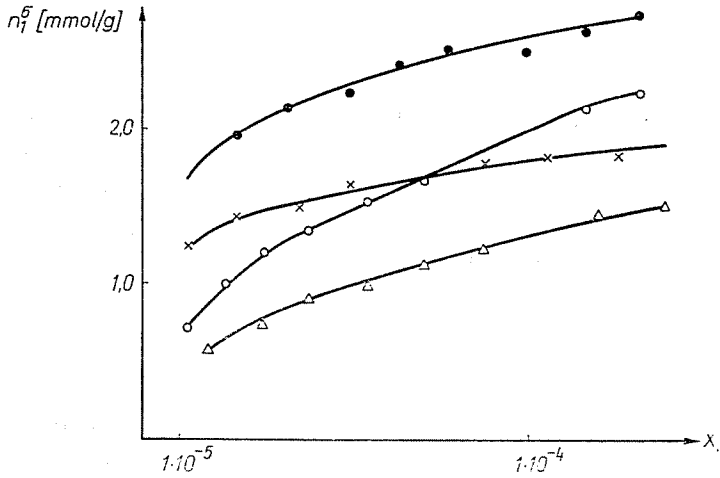
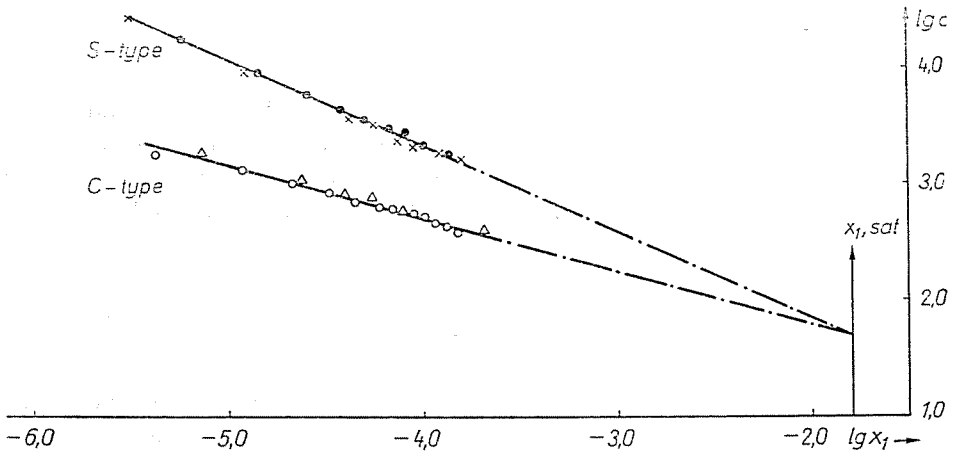


Fig. 2



Figs 2, 3. Adsorption of phenol from water on activated carbon. ● = Norit Carbo C extra; △ = Decolor Ac; × = Norit WS 55; ○ = Carboraffin P

ed from experimental data are the same within the experimental errors, the dependence of α_{sat} on factor B is negligible.

The method seems to be applicable for surface area determinations using an iterative method. Its application is suggested for cases where the type of non-swelling carbon is known or in the case of strong preferential adsorption by swelling and/or disaggregating systems.

Summary

The surface heterogeneity and — first of all — the pore structure of activated carbons have been studied by Schay's tentative kinetic theory for the adsorption of liquid mixtures. Determining the rate of the strong preferential adsorption of very dilute phenol solutions on activated carbon and analyzing the adsorption excess isotherms, the activated carbons in question can be divided in two groups according to the pore distribution data. A possibility is given by this method for investigating the physical reality of the B. E. T. surface area, and for developing a new method of determining the sorption capacity.

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