

# Kinetics of adsorption and isobaric desorption of styrene on activated coal Supersorbon\*

\*P. FARKA, <sup>b</sup>M. MANSFELD, <sup>a</sup>M. NOVOTNÝ, and <sup>b</sup>Z. SEDLÁČEK

<sup>a</sup>Research Institute of Synthetic Rubber,  
CS-278 52 Kralupy n/Vltavou

<sup>b</sup>Department of Physical Chemistry, Institute of Chemical Technology,  
CS-166 28 Prague

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The kinetics of adsorption of styrene on activated coal Supersorbon was investigated at different temperatures and pressures. This problem is interesting from the theoretical as well as practical view-point because the intensification of production and protection of environment require, in the first approximation, to describe the experiment and on its basis to choose the conditions convenient for achieving the optimum solution of a given problem.

Изучена кинетика адсорбции стирола при различных температурах и давлениях на активированном угле Суперсорбон. Данная проблема представляет интерес с теоретической и практической точки зрения, поскольку для целей интенсификации производства и охраны окружающей среды необходимо в первом приближении описать эксперимент и на его базе выбрать подходящие условия для достижения оптимального решения данной проблемы.

The solution of this problem is complicated by the fact that a violation of the optimum conditions may bring about polymerization of styrene in the pores of activated coal and thus block the access of adsorbate into the fine pores. The structure of activated coal consists of carbon crystallites the arrangement of which forms a very varied and diversely interlinked network of pores of different dimensions.

## Theoretical

For description of adsorption kinetics we used the method which enabled us to calculate the half-life from the whole course of the relationship between the

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amount of the adsorbed substance and time at a given pressure and temperature, and to compare the results with the experimental value of the half-life. On the basis of the obtained constants expressing the initial rate, the adsorbed amounts were calculated as a function of time and compared with the experimental values.

The linear regression equation (1)  $y = b_1x$  (a straight line going through the origin) and eqn (2)  $y = a_2 + b_2x$  (a general straight line) were applied to the kinetic curves obtained at a given pressure and temperature (Fig. 1). Thus it was possible to estimate the parameters  $b_1$ ,  $a_2$ , and  $b_2$  and standard deviations by the use of the method of least squares.

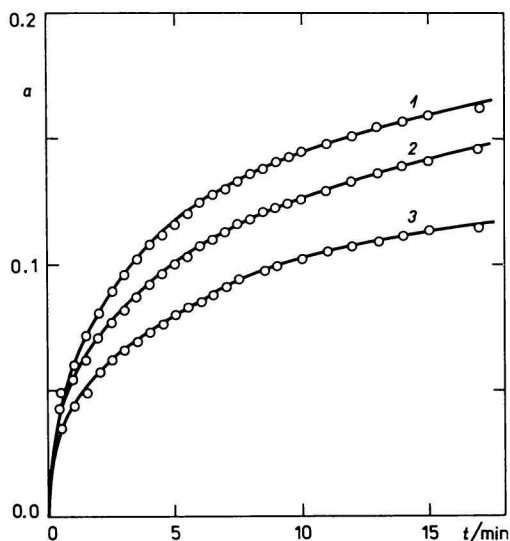


Fig. 1. Kinetic isotherms of styrene on activated coal Supersorbon at pressure  $p = 173$  Pa and different temperatures:  
1. 30 °C; 2. 50 °C; 3. 70 °C.

$a$  — Adsorbed amount at a given time;  
 $a = m/m_s$ ;  $m$  — mass of adsorbed substance,  $m_s$  — mass of sorbent;  $t$  — time (min).

The algorithm of calculation was so chosen that, first of all, adsorption data containing  $N$  pairs of the values of adsorbed amount and time might be used. Then the point with the greatest percentage error was eliminated, the calculation of parameters was repeated, and the point with the greatest percentage error was eliminated again. For each cycle the maximum and mean deviations of the adsorbed quantity were determined (Table 1).

Eqn (2)  $y = a_2 + b_2x$  (Fig. 2) is an equation the physical interpretation of which has been presented in paper [1] and eqn (1)  $y = b_1x$  is an integral equation for the first order, i.e. an equation analogous to the Langmuir equation if the rate of desorption is neglected where  $y = \ln(1/(1 - \varphi))$ ,  $x = t$ , and  $\varphi = a/a_s$  is the relative adsorption at a given time at temperature  $T$  and pressure  $p$ .

The results given in Table 1 show that the proposed eqn (2)  $y = a_2 + b_2x$  ( $y = t/a$ ,  $x = t$ , and  $a$  is the adsorbed quantity at the temperature  $T$  and pressure  $p$ ) is more convenient for describing the kinetic curves.

Table 1

Percentage deviation of experimental and calculated amounts of adsorbed substance by using eqn (1) and eqn (2): deviation/% =  $100(a_{exp} - a_{calc})/a_{exp}$

Number of experimental points	Eqn (1) deviation/%		Eqn (2) deviation/%	
	maximum	mean	maximum	mean
$\theta = 30\text{ }^{\circ}\text{C}$				
$p = 173\text{ Pa}$				
<i>N</i>	66.5	10.9	41.1	4.0
<i>N</i> -1	47.9	8.9	19.1	2.5
<i>N</i> -2	38.5	7.4	12.5	1.8
$\theta = 50\text{ }^{\circ}\text{C}$				
$p = 173\text{ Pa}$				
<i>N</i>	74.5	16.9	45.8	4.8
<i>N</i> -1	60.9	15.0	26.3	3.3
<i>N</i> -2	51.0	13.3	15.7	2.3
$\theta = 70\text{ }^{\circ}\text{C}$				
$p = 173\text{ Pa}$				
<i>N</i>	75.6	19.0	46.4	5.0
<i>N</i> -1	62.9	16.9	28.1	3.3
<i>N</i> -2	52.0	15.1	15.2	2.2

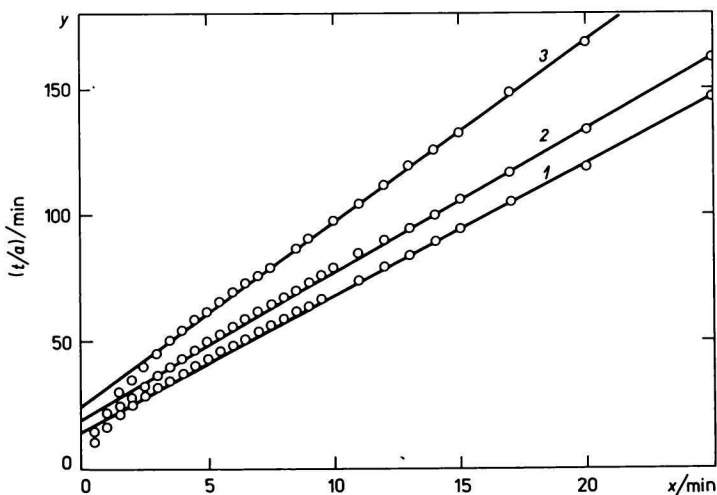


Fig. 2. Kinetic isotherms of styrene on activated coal Supersorbon obtained from eqn (2) (Fig. 1).  $y = t/a$  (min);  $x = t$  (min).

## Experimental

The measurement of kinetic isotherms has been described in paper [2] and, for this reason, we are going to present only the procedure of isobaric desorption of styrene. The terminal point of each isotherm is a point for the characteristic curve (white circles) (Fig. 4). After establishment of equilibrium the temperature in the thermostat was raised to the final temperature of 90 °C. The temperature as well as the grain of adsorbent changed with the increasing temperature in the thermostat, owing to which a gradual desorption of styrene took place. The kinetic isotherms, the terminal points of which are denoted in Fig. 3 by the

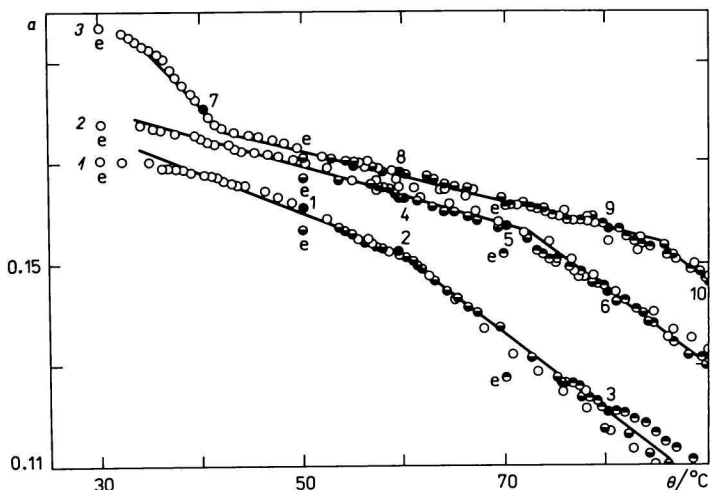


Fig. 3. Isobaric dependence of the adsorbed amount on temperature at different pressures: 1. 173 Pa; 2. 547 Pa; 3. 1053 Pa.

$a$  — Adsorbed amount at a given temperature and pressure;  $a = m/m_s$ ,  $\theta/^\circ\text{C}$ .

Black circles denote points obtained at a given temperature and pressure and their denotation agrees with the figures in Fig. 4.

letter e (equilibrium) were measured at three pressures and temperatures of 30 °C, 50 °C, 70 °C, and 90 °C. In certain time intervals the temperature in the thermostated tube containing the sorption cell was registered and simultaneously the elongation of the quartz coil was read. This elongation was used for calculating the adsorbed amount. As obvious from Fig. 3, the isobaric dependence of the adsorbed amount on temperature was to be expressed for individual pressures of 173 Pa, 547 Pa, and 1053 Pa by three plots. In order to ascertain the agreement of the temperature in the thermostated tube with the temperature in the grain of adsorbent, we chose ten points on the isobaric curves in the temperature interval of 40 °C—90 °C (Fig. 3). We assumed that the temperature read in the thermostated tube (the thermometer was placed on the wall of the sorption cell) was practically equal to the temperature of the grain. The distance between the grain and the wall of the sorption cell was 1 cm. Provided this assumption is fulfilled, the chosen points drawn on the characteristic

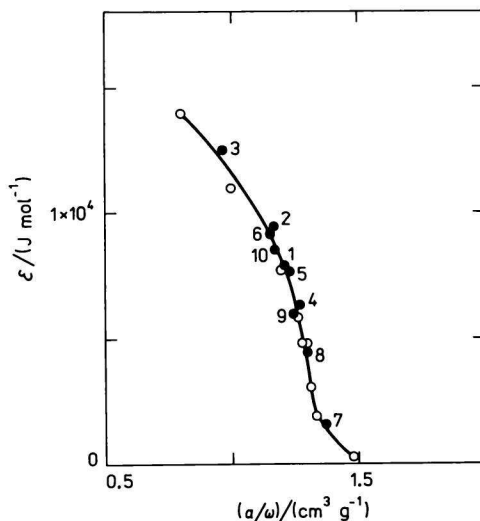


Fig. 4. Characteristic curve for styrene on activated coal Supersorbon expressed by means of expansion factor.  $\epsilon = RT \ln (p_0/p)$  (adsorption potential).

$p_0$  — Saturated tension of adsorbate at temperature  $T$ ;  $a$  — equilibrium adsorbed amount at a given temperature and pressure;  $\omega$  — expansion factor; figures at black circles correspond to figures in Fig. 3.

plot must correspond to the terminal (equilibrium) points of the kinetic isotherms (white circles in Fig. 4).

## Discussion

As obvious from Table 1, the mean deviations of the adsorbed amount calculated from eqn (2) are by one order smaller than the deviations obtained from eqn (1), in which we do not take into consideration the pressure difference inside and outside the grain. A gradual rise in temperature at isobaric desorption satisfies the assumption that the temperature in the thermostated tube and the temperature of the grain of adsorbent are practically equal and that the points on the corresponding curves together with the terminal points of the kinetic isotherms form a single characteristic curve, as required by the theory. For the lack of data concerning the densities at the individual temperatures, the density was replaced by the expansion factor in the sense of the theorem of the corresponding states. The values of constants  $n = 0.64$  and  $\log \{k\} = 1.83$  calculated for styrene on the basis of the relationships given in papers [3, 4] are near the values given in paper [3] for n-pentane and n-hexane, and those in paper [5] for n-heptane. These relationships give the dependence of the half-life on pressure. We may deduce on the basis of the values of constants  $n$  and  $k$  that the transport of adsorbate in the course of the adsorption of styrene is also accompanied by surface diffusion.

## References

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