

Dynamics of adsorption of industrial vapour on carbon sorbent*

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The dynamics of adsorption on active carbon HS 43 was investigated for the following adsorptives: ethyl acetate, butyl alcohol, toluene, and vapour of industrial solvents S 6001, S 6712, and C 6000. Nitrogen was used as carrier gas. On the basis of the calculated degree of sorbent saturation and height of zone of mass transfer, it has been found that active carbon HS 43 is suited to trapping the vapour of solvents S 6001 and S 6712. It has been revealed from the course of temperature curves that the layer need not be cooled before adsorption because all released heat is removed by the carrier gas.

Динамика адсорбции на активированном угле HS 43 была исследована для следующих адсорбируемых веществ: этилацетат, бутиловый спирт, толуол, а также для паров промышленных растворителей S 6001, S 6712 и C 6000. В качестве газа-носителя использовался азот. На основании вычисленной степени насыщения адсорбента и высоты зоны переноса масс было найдено, что активированный уголь HS 43 пригоден для улавливания паров растворителей S 6001 и S 6712. Из хода температурных кривых было видно, что слой адсорбента не обязательно охлаждать перед адсорбцией, поскольку все выделяющееся тепло уносится газом-носителем.

The greatest amount of exhalations in furniture industry arises during surface treatment of wood. First of all, the application and drying of coating compositions, staining, and polishing give rise to releasing of volatile components the quantity and quality of which depend on technology and kind of coating system. In most cases, these components are toxic organic substances, mainly benzene and its homologues (toluene, xylene), acetates, alcohols, formaldehyde, etc.

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On the basis of analysis of average mass flow and mass concentrations of vapour of organic solvents in waste gases, it is recommended to remove these substances by adsorption on active carbon [1].

The possibility of separation the vapour of some solvents used in furniture and wood industry on active carbon, *i.e.* currently produced industrial adsorbent is analyzed in this paper.

Theoretical

In laboratory conditions, the dynamics of adsorption is investigated in an integral adsorber where the adsorptive passes through a fixed-bed adsorber in the stream of carrier gas and the change in concentration of adsorptive in effluent gas is measured at the outlet from column. As a matter of fact, it is analogy to an industrial adsorber.

The breakthrough curves expressing the dependence of concentration of adsorptive in effluent gas on time $q = f(t)$ were represented in transformed coordinates $Q = f(z)$.

The coordinate of time was transformed according to the equation

$$z = t - t^* \quad (1)$$

where t is time and t^* stands for the time necessary for adsorbent saturation to equilibrium concentration.

The dimensionless concentration Q is defined as

$$Q = \frac{q}{q_0} \quad (2)$$

where q and q_0 are concentration of adsorptive in gas and concentration of adsorptive in the gas at the column inlet. The merit of this transformation consists in the fact that the shapes of breakthrough curves in layers of different heights at certain concentrations and flow rates may be compared.

The time t^* is to be calculated by integration of breakthrough curve as follows

$$t^* = \int_0^{\infty} (1 - Q) dt \quad (3)$$

In calculating the adsorber, we have been adhering to the idea put forward by Michaels which involves the assumption that the adsorptive moves in counter-current gas with the rate corresponding to progression of the zone of mass transfer through the layer of fixed-bed sorbent. The Michaels procedure is usable if the following conditions are fulfilled:

1. Concentration of adsorptive is small, *i.e.* gases are dilute.
2. Equilibrium curve has favourable form, *i.e.* it is convex with respect to the axis of abscissa.
3. Constant pattern conditions of mass transfer zone are established. This zone does not change its shape and proceeds along the layer with constant rate.
4. Height of the layer of sorbent is much greater than the height of the zone of mass transfer.

The following relationships are valid for the Michaels model [2]

$$f_a = \frac{\int_{m_B}^{m_E} (Y_0 - Y) dm}{Y_0 m_a} = \int_0^1 \left(1 - \frac{Q}{Q_0}\right) d\left(\frac{m - m_B}{m_a}\right) \quad (4)$$

where f_a , m , m_B , m_E , Y , and Y_0 are measure of adsorption ability of sorbent in the zone of mass transfer, amount of inert gas which passes through adsorber in a certain time interval, amount of inert gas which passed through adsorber in the time interval necessary for reaching the state characterized by the lower break in breakthrough curve, amount of inert gas which passed through adsorber before the concentration of adsorptive in effluent gas reached the value characterized by the upper break in breakthrough curve, relative concentration of adsorptive in gas, and relative concentration of adsorptive in gas coming into adsorber, respectively.

Provided assumption 1 is fulfilled and temperature and pressure are constant we may write

$$\frac{Y}{Y_0} \approx \frac{Q}{Q_0} \quad \text{and} \quad m_a = m_E - m_B$$

The degree of saturation of adsorbent after reaching the lower break in breakthrough curve (φ) is defined by the relationship

$$\varphi = \frac{h_k - (1 - f_a) h_z}{h_k} \quad (5)$$

where h_z is height of adsorption zone and h_k is height of the layer of sorbent. The value of h_z may be calculated from the following equation [3]

$$h_z = h_k \frac{\Delta t}{t_m - (1 - P) \Delta t} \quad (6)$$

where Δt , t_m , and P are difference in time between reaching the maximum and minimum concentration of adsorptive at the outlet from the layer of adsorbent, time necessary for reaching the maximum concentration of adsorptive at the outlet from the layer of adsorbent, and factor of symmetry of breakthrough curves, respectively. The factor P is equal to the ratio of the area over breakthrough curve to area of the oblong which is restricted by breakthrough curve. For symmetrical breakthrough curves the value of P is equal to 0.5.

The liberation of adsorption heat is, however, of considerable importance for higher concentrations of adsorptive which are accompanied by increased amounts of the exhaled component. There are two waves that proceed in the layer during nonisothermal adsorption, *i.e.* concentration wave and temperature wave. The above-mentioned constant pattern conditions of mass transfer zone appear in the course of adiabatic adsorption if the temperature wave overtakes the adsorption wave. In this case, all released adsorption heat is delivered to the gas stream and the adsorption takes place on the cooled adsorbent. Thus the heat effect cannot have any influence on the sorption process. A very important circumstance was observed and verified for this regime. It consists in the fact that it is not necessary to cool the layer after its thermal regeneration in systems working in this regime because the layer is rapidly cooled by the stream of passing gas and preserves its sorptive ability.

Experimental

The dynamics of sorption was investigated in an apparatus designed at the Department of Chemical Technology of Inorganic Substances. The adsorption column consisted of glass column with ground joints equipped with an electrical heating which comprised internal asbestos isolation, kanthal winding, and external asbestos isolation. The adsorbent was activated by heating the column over 400–420 °C and simultaneously blowing pure nitrogen through it. The column of 0.195 m diameter was so adjusted that one bed of glass ball was under the layer of adsorbent and the other bed of glass balls was over the layer of adsorbent (ball diameter was equal to 4 mm). Thus a stabilization of hydrodynamic parameters in the layer of adsorbent was achieved. The column was vertically positioned and the gas inlet was on the top. The outlet concentration of adsorptive was controlled with an interferometer, type LI 3 (Zeiss, Jena). The temperature of gaseous mixture at the column inlet was held constant ($(20.0 \pm 0.1)^\circ\text{C}$). The constant temperature in a saturator where the gas was saturated with the vapour of adsorptive was achieved by means of an ultrathermostat U-10. The thermostating of the laboratory at the temperature of $(20.0 \pm 0.1)^\circ\text{C}$ was performed by means of an air condition installation KT-2. The temperature in the layer of sorbent was observed by means of three thermocouples (Cu-constantan) placed immediately in the layer of sorbent in the distances of 0.20 m, 0.10 m, and 0.17 m from the bottom of column. The fourth thermocouple (Fe-constantan) was laid 0.065 m under the lower border of layer. Every temperature change was recorded with a six-point recorder.

Active carbon HS 43 (Moravian Chemical Works, Ostrava-Hrušov), mesh fraction 4–5 mm, was used as adsorbent. It is an active carbon activated with zinc chloride. Its physical properties are as follows: real density 1700 kg m^{-3} , apparent density 730 kg m^{-3} , gravimetric density 440 kg m^{-3} , porosity of grains 0.569, voidness of layer 0.397. The following adsorptives were investigated with this sorbent: ethyl acetate, butyl alcohol, toluene, vapour of industrial solvents S 6001, S 6712, and C 6000. Nitrogen was used as carrier gas. The measurements were carried with the superficial velocity of gas equal to

$v = (0.400 \pm 0.001) \text{ m s}^{-1}$, 2.0 g m^{-3} , 5.0 g m^{-3} , 10.0 g m^{-3} , and 20.0 g m^{-3} inlet concentration of toluene, 2.0 g m^{-3} , 5.0 g m^{-3} , 10.0 g m^{-3} , and 15.0 g m^{-3} concentration of ethyl acetate, 2.0 g m^{-3} and 5.0 g m^{-3} concentration of butyl alcohol, 2.0 g m^{-3} , 5.0 g m^{-3} , and 10.0 g m^{-3} concentration of solvent S 6001, 2.0 g m^{-3} , 3.0 g m^{-3} , 5.0 g m^{-3} , 10.0 g m^{-3} , and 15.0 g m^{-3} concentration of solvent S 6712, and 2.0 g m^{-3} , 5.0 g m^{-3} , 10.0 g m^{-3} , and 20.0 g m^{-3} concentration of solvent C 6000. The precision of concentration adjusting was $\pm 0.1 \text{ g m}^{-3}$.

As the adjusted inlet concentration could not be attained after finishing individual measurements with solvents S 6001, S 6712, and C 6000, the chromatographic analyses of these solvents were performed between individual measurements. The changes in composition of the vapour of adsorptive at the inlet into adsorption column are given in Tables 1—3.

The height of layer of activated carbon HS 43 was equal to 0.1 m, 0.15 m, and 0.2 m. Because of possibilities of this apparatus, we could not perform measurements at greater heights of layer of the adsorbent. The composition of solvents S 6001, S 6712, and C 6000 was determined by chromatographic analysis. The analyses were carried out with a chromatograph C. Erba under these conditions: stationary phase — squalane, carrier gas — nitrogen, temperature 70°C , gauge pressure 0.2 MPa, feed 0.2 mm^3 , column $150 \text{ mm} \times 0.25 \text{ mm}$. The results of analysis of individual solvents before measurement are given in Tables 1—3.

Results and discussion

The breakthrough curves obtained for individual investigated systems have been confronted in Q — z coordinates where Q and z are relative concentration and transformed time, respectively.

It was found that constant pattern conditions of mass transfer zone appeared in the system solvent S 6001—activated carbon HS 43 even at low concentrations. The breakthrough curves of parallel measurements were identical which indicated the existence of the well desorbed layer of sorbent and good reproducibility of the conditions of measurements. The investigation of the composition of adsorptive before entrance into adsorption column by means of a chromatograph (C. Erba, Milan) showed that toluene preferentially evaporated from the solvent at 20°C (Table 1). This fact is to be confirmed by comparing the breakthrough curves of solvent S 6001 and toluene (Fig. 1).

Constant pattern conditions of mass transfer zone were also observed in the system solvent S 6712—activated carbon HS 43 in the whole investigated concentration range. The results of chromatographic analysis of solvent S 6712 (Table 2) disclose that ethyl acetate preferentially evaporates from the solvent at 20°C , which also results from the comparison of the course of breakthrough curves of solvent S 6712 and ethyl acetate (Fig. 2).

Table 1

Chromatographic analysis of solvent S 6001 in the course of measurement

Component	1. sample w/%	2. sample w/%	3. sample w/%
Toluene	56.68	52.25	37.51
n-Octane	1.72	0.27	1.77
n-Nonane	5.39	6.21	6.38
n-Decane	4.32	6.66	6.36
o-Xylene	0.72	0.43	0.86
Ethylcyclohexane	1.22	0.90	1.38
2-Methyloctane	1.03	0.54	0.88
4-Methyloctane	0.82	0.85	1.05
3-Methyloctane	1.36	0.97	1.95
1,2,4-Trimethylbenzene	0.86	1.84	1.59

1. Sampling at the start of measurements.
2. Sampling after two measurements.
3. Sampling after finishing the whole series of measurements.

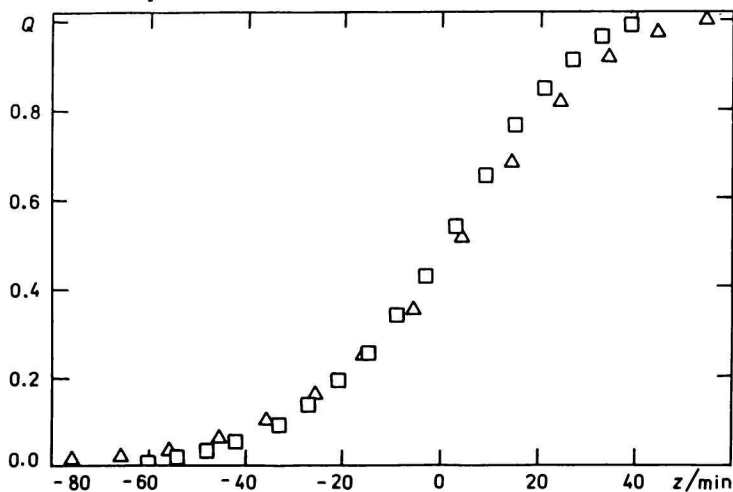


Fig. 1. Comparative breakthrough curves of solvent S 6001 and toluene. $h_k = 0.15$ m, $v = 0.4$ m s⁻¹, $\rho_0 = 5.0$ g m⁻³.

□ Toluene; △ S 6001.

Table 2

Results of chromatographic analysis of solvent S 6712

Component	1. sample w/%	2. sample w/%	3. sample w/%	4. sample w/%
Ethyl alcohol	0.15	0.13	0.15	0.16
Ethyl acetate	26.10	16.72	15.71	16.59
Propyl acetate	71.81	81.11	82.10	87.27
Butyl acetate	1.33	1.42	1.41	1.41

1. Sampling before the start of measurements.
2. Sampling before the seventh measurement $\rho_0 = 10.0 \text{ g m}^{-3}$, $h_k = 0.2 \text{ m}$.
3. Sampling after the seventh measurement.
4. Sampling after finishing the whole series of measurements.

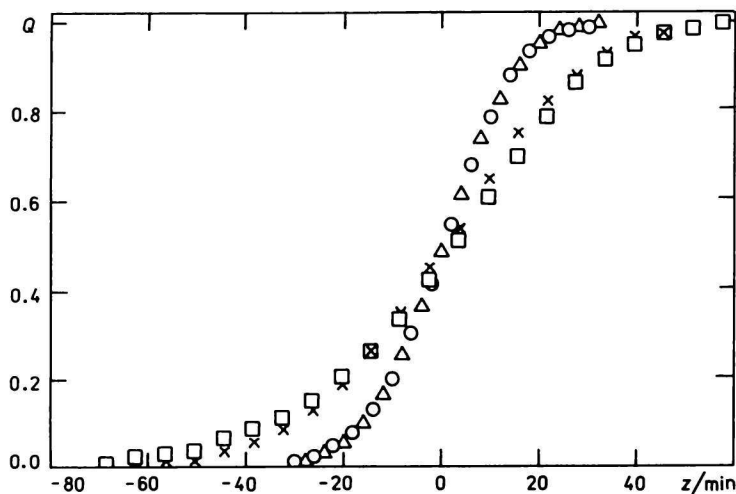


Fig. 2. Comparative breakthrough curves of solvent S 6712 and ethyl acetate. $h_k = 0.15 \text{ m}$,
 $v = 0.4 \text{ m s}^{-1}$, $\rho_0 = 5.0 \text{ g m}^{-3}$.
 \square Ethyl acetate; \times S 6712.
 $h_k = 0.15 \text{ m}$, $v = 0.4 \text{ m s}^{-1}$, $\rho_0 = 15.0 \text{ g m}^{-3}$.
 \circ Ethyl acetate; \triangle S 6712.

A relatively steep course of breakthrough curves for the investigated systems indicates good separation of the vapour of solvents S 6001 and S 6712 on activated carbon HS 43.

The breakthrough curves of the system C 6000—activated carbon HS 43 exhibit smaller slope, which indicates a slower progress of adsorption. A comparison of breakthrough curves at individual heights of the layer of sorbent shows consider-

able difference in the rate of breakthrough. The curves distinguish themselves by dissipation of the values in the whole range of measured concentrations. We may judge from this fact that constant pattern conditions of mass transfer zone are not established in the system. A plateau was observed in the region of positive transformed time. This plateau indicates adsorption of two substances, *i.e.* butyl

Table 3

Results of chromatographic analysis of solvent C 6000

Component	1. sample w/%	2. sample w/%	3. sample w/%	4. sample w/%	5. sample w/%
Ethyl alcohol	3.93	2.71	1.73	1.76	—
i-Propyl alcohol	3.16	1.19	0.77	1.76	—
n-Propyl alcohol	4.03	3.13	2.62	1.94	0.11
Butyl alcohol	68.81	66.49	66.87	63.60	83.35
Butyl acetate	11.27	15.33	16.55	19.44	11.61
Ethyl acetate	7.39	9.72	9.95	11.50	1.71

1. Sampling before the start of measurements.
2. Sampling before the fifth measurement; $\rho_0 = 10.0 \text{ g m}^{-3}$, $h_k = 0.15 \text{ m}$.
3. Sampling after the fifth measurement.
4. Sampling after finishing the whole series of measurements.
5. Results of analysis of the concentrate obtained by desorption.

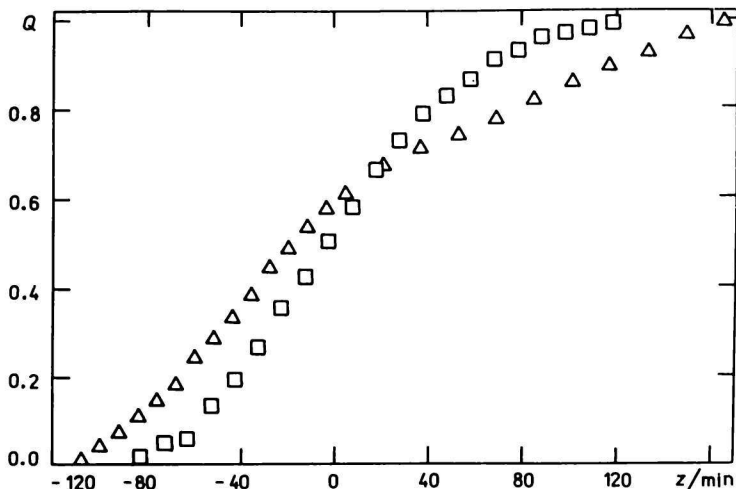


Fig. 3. Comparative breakthrough curves of solvent C 6000 and butyl alcohol. $h_k = 0.10 \text{ m}$, $v = 0.4 \text{ m s}^{-1}$, $\rho_0 = 5.0 \text{ g m}^{-3}$.
 □ Butyl alcohol; △ C 6000.

alcohol and butyl acetate, which is also confirmed by the results of analysis of the condensate obtained by desorption (Table 3) and by the comparison of break-through curves of solvent C 6000 and pure butyl alcohol (Fig. 3).

The height of the zone of mass transfer and the degree of saturation of adsorbent were calculated for all three solvents according to eqns (5) and (6). For calculating f_a according to eqn (4), the adjusted inlet concentration of solvent was substituted for the value of ρ_0 and the change in its composition in the course of measurements was not taken into account. The results of calculations obtained for the systems solvent S 6001—activated carbon HS 43 (Table 4) and solvent S 6712—activated carbon HS 43 (Table 5) confirm that this adsorbent is suited to separate vapour

Table 4

Height of the zone of mass transfer and degree of saturation of adsorbent for solvent S 6001

$\frac{\rho_0}{\text{g m}^{-3}}$	$\frac{h_1}{\text{m}}$	$\frac{h_2}{\text{m}}$	$\frac{\varphi}{\%}$
5.0	0.10	0.089	82.2
10.0	0.10	0.080	76.5
5.0	0.10	0.057	69.7
2.0	0.10	0.064	75.8
10.0	0.15	0.071	78.7
5.0	0.15	0.066	78.5
2.0	0.15	0.091	81.8
10.0	0.20	0.077	81.9
5.0	0.20	0.073	85.1

Table 5

Height of the zone of mass transfer and degree of saturation of adsorbent for solvent S 6712

$\frac{\rho_0}{\text{g m}^{-3}}$	$\frac{h_1}{\text{m}}$	$\frac{h_2}{\text{m}}$	$\frac{\varphi}{\%}$
10.0	0.10	0.082	61.5
5.0	0.10	0.070	66.9
2.0	0.10	0.074	61.4
15.0	0.15	0.075	75.6
10.0	0.15	0.079	75.3
5.0	0.15	0.074	76.9
2.0	0.15	0.061	80.8
10.0	0.20	0.077	81.1
5.0	0.20	0.070	83.7
3.0	0.20	0.069	83.8

containing even higher concentrations of these solvents. Activated carbon HS 43 is not an adsorbent suited for solvent C 6000, which follows from the values of the degree of saturation and height of the zone of mass transfer (Table 6). For the sake of generalization, the symmetry factor $P = 0.5$ was used for calculating the height of the working zone. The minimum and maximum concentrations were calculated for $Q = 0.05$ and $Q = 0.95$, respectively. The time difference Δt in eqn (6) was calculated for these values of minimum and maximum concentration of adsorptive. The breakthrough of the vapours of solvents S 6001, S 6712, and C 6000 are given in Tables 7–9. The time t_p corresponds to the moment of time of the first indicated concentration of adsorptive at the outlet from the layer of adsorbent.

Table 6

Height of the zone of mass transfer and degree of saturation of adsorbent for solvent C 6000

$\frac{q_0}{\text{g m}^{-3}}$	$\frac{h_k}{\text{m}}$	$\frac{h_z}{\text{m}}$	$\frac{\varphi}{\%}$
10.0	0.10	0.226	—
5.0	0.10	0.124	35.8
2.0	0.10	0.177	—
15.0	0.15	0.271	—
10.0	0.15	0.331	—
20.0	0.20	0.281	21.5
15.0	0.20	0.219	41.9
10.0	0.20	0.250	33.8

Table 7

Time of breakthrough of the vapour of solvent S 6001: $v = 0.4 \text{ m s}^{-1}$

h_k/m	0.10			0.15			0.20	
$q_0/(\text{g m}^{-3})$	2.0	5.0	10.0	2.0	5.0	10.0	5.0	10.0
t_p/min	205	70	28	220	110	59	147	84

Table 8

Time of breakthrough of the vapour of solvent S 6712: $v = 0.4 \text{ m s}^{-1}$

h_k/m	0.10			0.15				0.20		
$q_0/(\text{g m}^{-3})$	2.0	5.0	10.0	2.0	5.0	10.0	15.0	3.0	5.0	10.0
t_p/min	120	44	14	201	81	41	21	239	151	83

Table 9

 Time of breakthrough of the vapour of solvent C 6000: $v = 0.4 \text{ m s}^{-1}$

h_k/m	0.10			0.15		0.20		
$\rho_0/(g \text{ m}^{-3})$	2.0	5.0	10.0	10.0	15.0	10.0	15.0	20.0
t_p/min	36	9	5	12	7	18	11	9

The temperatures in the layer of adsorbent were recorded in the course of all measurements. The progress of the temperature wave was observed by means of the thermocouples built into the column. The method of evaluation of temperature curves is described in Ref. [4]. The temperature curves are presented in coordinates $\Delta\theta = f(z)$ where $\Delta\theta$ is the temperature difference between measured temperature θ and the initial temperature $\theta_p = 20^\circ\text{C}$ (Fig. 4). It results from the course of

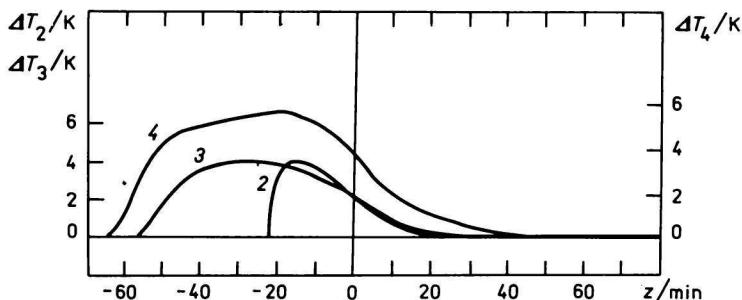


Fig. 4. Temperature curves of solvent S 6712. $h_k = 0.15 \text{ m}$, $v = 0.4 \text{ m s}^{-1}$, $\rho_0 = 15.0 \text{ g m}^{-3}$.
2. 2nd thermocouple; 3. 3rd thermocouple; 4. 4th thermocouple.

temperature waves that the maximum temperature obtained by all thermocouples is attained at negative transformed time. It means that the temperature wave overtakes the concentration wave. This fact has confirmed the assumption that the zone of mass transfer is established provided the temperature wave overtakes the concentration wave.

Conclusion

It has been revealed by studying the dynamics of adsorption of the vapour of industrial solvents S 6001, S 6712, and C 6000 on activated carbon HS 43 in a stream of nitrogen that the constant pattern conditions of mass transfer zone are

established within the measured concentration range. This fact has also been confirmed by the course of temperature curves $\Delta\theta-z$.

The values of the degree of saturation of sorbent and the heights of the zone of substance transition calculated for individual adsorptives as well as the values of breakthrough time suggest that activated carbon HS 43 is as an adsorbent suited for separation the vapour of solvents S 6001 and S 6712. In spite of the fact that nitrogen was used as carrier gas in laboratory measurements, the results may also be applied to air which is used as carrier gas in industrial plants.

The course of temperature curves has confirmed an important fact which may be applied in designing an adsorption cycle. It means that there is no need for cooling the layer before adsorption because all released heat is removed by the carrier gas. However, the purposefulness of rejection of cooling ought to be examined for every particular case from the economical point of view.

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