UDC 541.183+543.08

INVESTIGATION OF ADSORPTION DYNAMICS OF VOLATILE COMPOUNDS ON FINE-DISPERSED ADSORBENTS WITH A PULSING MODE BY QUARTZ CRYSTAL MICROBALANCE METHOD

A.P. Filippov*, P.E. Strizhak, N.V. Vlasenko, Yu.N. Kochkin, T.G. Serebrii

L.V. Pisarzhevsky Institute of Physical Chemistry of National Academy of Sciences of Ukraine
31 Nauki Pr., Kiev, 03039, Ukraine

It is shown that the quartz crystal microbalance method can be utilized to study adsorption-desorption processes proceeding for several seconds and more. The pulse of sorbate vapor with half-width of a few seconds can be obtained by the injection of a dose of liquid sorbate at appropriate evaporator temperature and flow rate of carrier gas with the use of a device combined with the flow-through cell of the type of electronic nose. The use of piezoquartz resonator with a chemical coating based on a metal stearate, thiolate or cross-linked polymer is proposed as a simple, relatively quick-response sensor to control the current adsorbate concentration in gas phase. The method has been applied for determination of effective diffusion coefficients in the process of ethanol adsorption-desorption on fine dispersed macroporous sulfonic acid resin Amberlyst 15.

INTRODUCTION

The use of the quartz crystal microbalance method (QCM) for adsorption studies is attractive because of its high sensitivity: a few micrograms of sorbent required for its study, and a few nanograms of adsorbed compound can be detected. The study of variety of solid adsorbents became possible with the development of methods of attaching of fine-dispersed sorbents (with a particle diameter smaller than several microns) onto the piezoquartz resonator (PQR) electrodes [1–3]. As a result, the time required to reach adsorption equilibrium can be reduced to several minutes or even seconds. In the study of adsorption-desorption dynamics of volatile compounds by QCM the use of small weighed sample enables to eliminate or significantly reduce the contribution of diffusion between grains of the adsorbent to the overall speed of the process. So, this method can be used to study the dynamics of adsorption-desorption which is determined mainly by diffusion of sorbate interior of the grains of the sorbent (catalyst).

In the study of adsorption in stationary mode the velocity of sorbate vapor inlet in electronic nose (EN) cell does not matter. Only the stationary vapor concentration and the adsorption values are important. But for the study of an adsorption dynamics the change of sorbate concentration in the gas phase of the working cell should be significantly faster than the rate of adsorption-desorption process. Otherwise, the shape of response of the PQR covered with studied adsorbent will reflect the dynamics of change in the adsorptive concentration in the cell, rather than the dynamics of its adsorption or desorption.

This problem is solved by use of pulsing mode, i.e. by introducing a small dose of liquid sorbate into the evaporator, as is done in flow system of gas chromatograph (GC) or of GC coupled with EN for the analysis of mixtures of volatile compounds [4]. The injection of the sample in this way takes a fraction of a second but the time and the character of distribution of the adsorbate vapor in the cell strongly depends on the flow rate of carrier gas, the nature of the sorbate, the evaporator temperature. The shape and volume of the cell EN are also important for the vapor distribution.

In our setup at a pulsing mode, the transient concentration wave of sorbate vapor through the cell takes a time ranging from seconds to tens of seconds varying both in time and space. At sufficiently high carrier gas flow velocity the PQR coated with porous adsorbent can give a response, which in duration and shape may differ significantly from the duration and shape of the sorbate concentration wave flowing around the PQR. This difference can

be used to study the dynamics of adsorption-desorption of a volatile substance on a given adsorbent. In this way a qualitative difference was detected between the sulfonic acid resins KU-2-8 and Amberlyst 15 (A-15) in the rate of adsorption-desorption of reactants and products of the catalytic synthesis of ethyl *tert*-butyl ether [5].

For a quantitative description of the adsorption-desorption process in the pulsing mode the problem is to determine the sorbate current concentration in the position where the PQR covered with an adsorbent under investigation is placed, and it is desirable that the adsorbtive concentration being measured by an inertial-less transducer placed in the same position.

With the present method the simplest way to control the sorbate vapor current concentration is also to use a PQR with nonporous chemical covering as a relatively low inertia transducer.

EXPERIMENTAL

The setup analogues described in [4] was used, but for the study of adsorption of individual substances there was no need for the chromatographic column (Fig. 1).
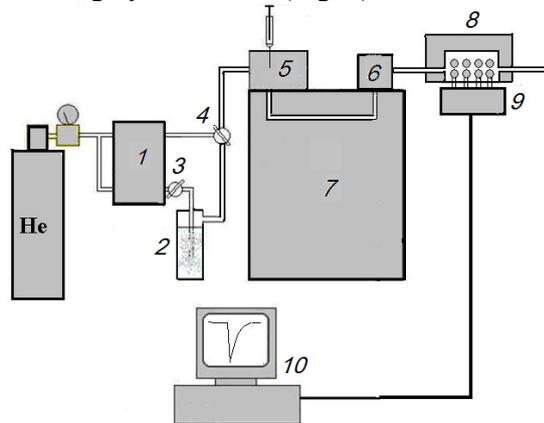

Fig. 1. Block scheme of the setup:
1 – mass flow controller; *2* – bubbler-saturator; *3, 4* – stop-cocks; *5* – evaporator; *6* – katharometer; *7* – thermostat for chromatograph; *8* – thermostat for EN; *9* – EN cell with generators and frequency counter; *10* – PC

The setup can be used for both research of equilibrium adsorption (in the steady flow mode) and of adsorption-desorption dynamics (in the pulsing mode).

In the steady flow mode a certain concentration of adsorbate vapor was produced by mixing of helium saturated with the adsorbate

vapor and pure helium in certain proportion by means of mass flow controller. The obtained vapor comes immediately through a short tube, located in thermostat of the chromatograph, to katharometer and then into temperature-controlled EN cell.

In the pulsing mode a doze of liquid sorbate from 0.2 to 1 µl was injected into the chromatograph evaporator using microsyringe. The impulse of adsorbate vapor, obtained after the evaporator, came by the same way into the EN cell.

The internal cavity of the cell had dimensions of $15 \times 17 \times 56$ mm. Along the long axis of the cell there are 4 pairs of PQR's, so that both PQR's in each pair were in the equivalent position relative to the gas flow (total of 4 positions). Each successive PQR pair of downstream was at the time in an earlier phase of the adsorptive concentration wave compared to the previous pair. Also, the concentration wave was somewhat reduced in height and broadened when passing through the cell from the entrance to the exit. Therefore, to study the dynamics of adsorption-desorption on adsorbent covered PQR, it is necessary to have a fast-response sensor for measuring the adsorptive current concentration in the same position.

In this work the PQR's with chemical coatings based on metal stearates and thiolates or with fine dispersed nonporous styrene divinylbenzene copolymer (StDVB) were studied as potential sensors. The metal stearates or thiolates based coverings were prepared as described in [6, 7] using compounds of general formula MSt_2 or ML_n, where M^{n+} – a metal cation, n was 2, St^- – anion of stearic acid and L^- – octadecylthiolate anion $C_{18}S^-$. The sensor covering based on fine dispersed cross-linked styrene divinyl benzene copolymer ("AZOT", Cherkassy, Ukraine) was made by attaching of the copolymer (ground and fractionated to particles with diameter < 0.1 µm) to the PQR electrodes by using a polymer composition. The composition consisted of saponated copolymer of vinyl chloride with vinyl acetate and polyurethane rubber in the ratio 3:2 dissolved in methyl ethyl ketone. Prior to depositing the hardening agent and hardening catalyst (amine GM-3 and dodecyl benzene sulfonic acid) were added to the composition, and the mixture was diluted with methyl ethyl ketone to 0.2 % solution. Then the solution was applied to the PQR electrodes by means of airbrush taking into account that after the solvent evaporation the covering loading being about 0.1–0.3 kHz. After the applying the PQR was dried at room temperature during 2–3 min and whereupon a dispersion of fine StDVB in acetone

was applied over the polymer composition sublayer taking into account that after the solvent evaporation the StDVB covering loading being about 7–10 kHz. Afterwards the PQR was exposed at 70 °C during 30 min and then at 120 °C during 30 min.

The macroporous sulfonic resin Amberlyst 15 (Rohm and Haas, USA) was used as an adsorbent covering. It was ground and fractionated to particles with diameter < 0.1 μm and attached to PQR electrodes by the same way as aforesaid for StDVB.

The PQR's with fundamental frequency of 10 MHz on the basis of quartz plates with AT-cut nickel-silver electrodes, produced by AOA "Ukrpiezo" (Cherkassy, Ukraine) were used to prepare the sensors and the adsorbent coverings.

The response of the sensors was studied both at the steady flow mode and at the flow-impulse mode at the cell temperature $t_{EN} = 25$ °C or 40 °C. Evaporator temperature t_{Evap} was from 50 ° to 100 °C. The rate of carrier gas – helium was from 5 to 100 cm^3/min.

The aliphatic hydrocarbons from pentane to nonane and methyl alcohol qualification "chemically pure for chromatography" were studied as adsorbates.

RESULTS AND DISCUSSION

Definitions and relations. If noninertial sensor has a linear dependence of the height response (Δf, Hz) on the adsorbate vapor concentration (C, mg/l), the area bounded by the peak response (S_{peak}) corresponds approximately to the area of a triangle equals to:

$$S_{peak} = \Delta f_{max} \times \tau_{hw}, \tag{1}$$

where Δf_{max} is the maximum response (Hz) and τ_{hw} is the half-width of the peak, s. This area is proportional to the dose (mass) of liquid adsorbate introduced into the evaporator, mg.

It can be shown that the concentration of the adsorbate at the time of attaining the peak maximum (C_{max}, mg/l) is equal to:

$$C_{max} = \frac{m}{\tau_{hw} \cdot v_{He}}, \tag{2}$$

where v_{He} is the carrier gas flow velocity, l/s. The coefficient of sensitivity of the sensor does not matter for the calculation. It is only necessary to know a dose (m) of liquid adsorptive administered and values τ_{hw} and v_{He}. However, it is crucial that the half-width of the sensor

response peak coincides with the true half-width of the adsorbate concentration wave, i.e. senor is not inertial. Assessing the value of C_{max}, the value C_{τ} (mg/l), the concentration of the adsorbate vapor at each time τ, for this pulse can be calculated:

$$C_{\tau} = C_{max} \frac{\Delta f_{\tau}}{\Delta f_{max}}. \tag{3}$$

Here Δf_{max} and Δf_{τ} represent magnitude of the response inertialess transducer at the time of attaining of the maximum and at the time τ, correspondingly.

The magnitude of adsorption was calculated from the following relations:

$$A_{stat} = \frac{\Delta f_{stat}}{\Delta F_{Cov}} \text{ (for stationary regime)} \tag{4}$$

and $$A_{max} = \frac{\Delta f_{max}}{\Delta F_{Cov}} \text{ (for pulsing mode)}. \tag{4a}$$

Henry's law constant – from the following formulas:

$$K_H^{stat} = \frac{A_{stat}}{C_{stat}} \text{ (for stationary regime)} \tag{5}$$

and $$K_H^{max} = \frac{A_{max}}{C_{max}} \text{ (for pulsing mode)}, \tag{5a}$$

where A_{stat} (or A_{max}) – adsorption, mg/g, Δf_{stat} (Δf_{max}) – the height of response in the stationary regime (or maximum peak response in the pulsing mode), Hz, and ΔF_{Cov} is a chemical covering (or adsorbent) loading, i.e.change in frequency of PQR due to the covering, kHz. The quantity of K_H has the dimension *l/g* with the above indicated dimension values.

The value Δf_{max} may vary from several Hz to hundreds and can be defined with a relative error up to 1–3 %, depending on sorbate dose, carrier gas flow rate and the evaporator temperature, as well as on the sorbate nature (boiling point) and manner (reproducibility) of injection of the sorbate dose by an operator. But all these factors can give proper weight with the *in situ* measurement of sensor response half-width τ_{hw} when calculating the current concentration of the

adsorptive by the proposed method. With the setup presented in this work, the half-width of the concentration wave of lower hydrocarbons (up to C_{10}) vapor at flow rates from 5 to 100 cm^3/min can range from 2 seconds to tens of seconds and can be measured to within 0.1 s. The adsorptive dosing error at a dose of 1 µl is no more than 5 %. The flow rate of carrier gas 10–100 cm^3/min can be settled to within 1 %. Thus, the error in the estimate of C_{max} caused only by the parameters of the setup can reach 10–15 %. Therefore, the possible error of value τ_{hw}, caused by the inertia of PQR sensor must be no more than the same amount.

The responses of the potential sensors. The criterion for inertance of a transducer can be determined by comparison of the magnitude of its response in a pulsing mode with its steady state response for the same adsorptive vapor at the same concentration. A sensor, whose response in a pulsing mode within the error does not differ from its steady-state response at the same concentration of the adsorptive hereinafter, will be named as inertialess.

Preliminary experiments showed that PQR's with coatings based on metal stearates or thiolates or fine StDVB have a relatively low inertia.

Following to above mentioned criterion we have compared responses of such potential sensors in a stationary and a pulsing mode with the same concentration of some hydrocarbons as adsorbates.
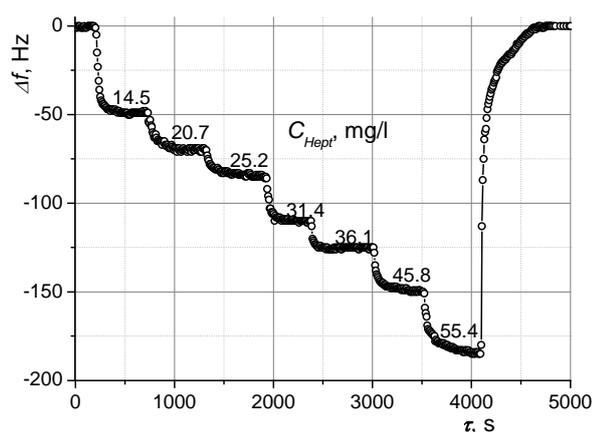

Fig. 2. The responses of the PQR sensor with chemical covering based on CoL$_2$ (loading 7.6 kHz) to step-wise change of heptane vapor concentration in a stationary regime at $t_{EN} = 25$ °C

As can be seen from the Fig. 2, the stationary response is achieved only 3–4 min after switching the system to a new level of concentration. However, this is not due to adsorption process but to the delivery dynamics in the system. The results of experiments carried out with the same PQR sensor in the pulsing mode with various doses of heptane (Fig. 3) prove that the adsorption process in these conditions is not limiting.
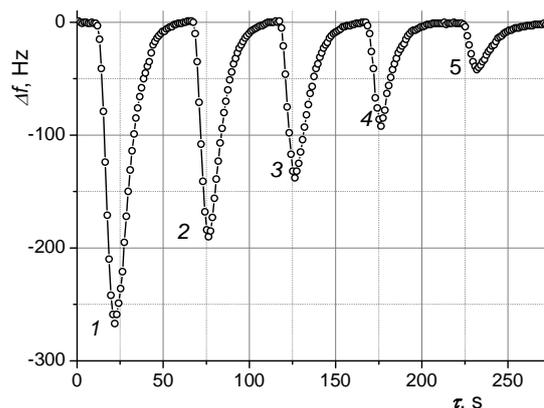

Fig. 3. The responses of the PQR sensor with chemical covering based on CoL$_2$ (loading 7.6 kHz, position 2) in a pulsing mode to different doses of heptane (µl): 1.0 *(1)*, 0.8 *(2)*, 0.6 *(3)*, 0.4 *(4)*, 0.2 *(5)*; $t_{EN} = 25$ °C, $t_{evap} = 50$ °C and $v_{He} = 44$ cm^3/min

In Fig. 4 two dependencies are compared for the same PQR sensor: dependence of its response magnitude on heptane concentration C_{stat} in the steady state and that of the response magnitude in the pulsing mode, C_{max} being calculated by the Eq.(2).
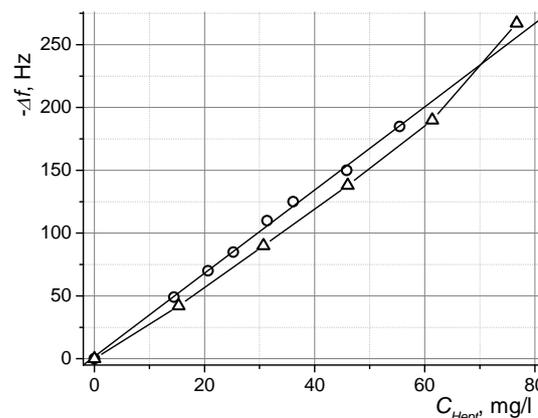

Fig.4. The dependence of responses of the PQR sensor with covering based on CoL$_2$ on heptane vapor concentration in stationary (○) and in pulsing (Δ) modes. Conditions see Fig. 2 and 3

As can be seen, both dependences have a linear character for the studied range of heptane concentrations. The values of Henry's law constants for corresponding dependence calculated from the slope are: in the stationary mode $K_H^{stat} = 0.43 \pm 0.01$ l/g, in the pulsing mode $K_H^{max} = 0.40 \pm 0.02$ l/g. Similar results were obtained with heptane adsorption on sensor coverings based on thiolates CuL_2 and NiL_2 (Figs. 5 and 6).
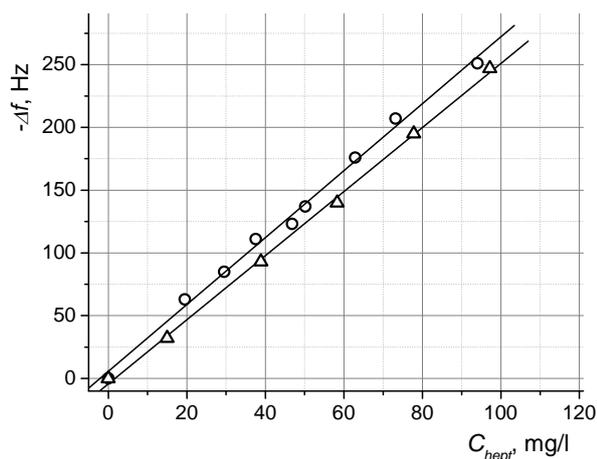

Fig. 5. The dependence of response of the PQR sensor coated with CuL_2 (loading 7.4 kHz) on heptane vapor concentration in stationary (○) and pulsing (Δ) mode at $t_{EN} = 25\ °C$. $v_{He} = 6$ cm³/min, position 3, $t_{evap} = 50\ °C$
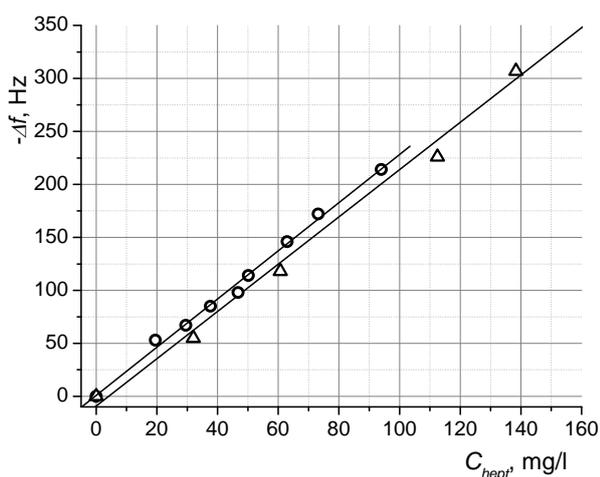

Fig. 6. The dependence of response of PQR sensor coated with NiL_2 (loading 8.0 kHz) on heptane vapor concentration in stationary (○) and pulsing (Δ) mode at $t_{EN} = 25\ °C$. $v_{He} = 5$ cm³/min, position 1, $t_{evap} = 50\ °C$

For the first covering the Henry constant was $K_H^{stat} = 0.34 \pm 0.02$ l/g in the stationary regime, and $K_H^{max} = 0.37 \pm 0.01$ l/g in the pulsing mode (at $v_{He} = 5$ cm³/min). For the latter: $K_H^{stat} = 0.28 \pm 0.02$ l/g in the stationary regime and $K_H^{max} = 0.29 \pm 0.02$ l/g in the pulsing mode. Thus, PQR with these coatings can be also used in pulsed mode for estimating the heptane vapor concentration in the cell EN (at least within indicated conditions). The applicability of CoL_2 coated PQR as a sensor for estimating some of the vapors concentration in the pulsing mode could be inferred from Table 1, where the values K_H^{stat} and K_H^{max} (obtained at $t_{EN} = 25\ °C$, $t_{evap} = 50\ °C$ and $v_{He} = 20$ cm³/min) are compared for corresponding adsorptive.

Table 1. The K_{Henry} values (in 1/g) obtained in stationary (K_H^{stat}) and pulsing (K_H^{max}) modes for adsorption of hydrocarbons and other substances vapors on the covering CoL_2 at $t_{EN} = 25\ °C$

Adsorbate	K_H^{stat}	K_H^{max}
pentane	0.138	0.14
hexane	0.249	0.23
cyclohexane	0.304	0.29
heptane	0.432	0.40
isooctane	0.415	0.39
3-methylheptane	0.619	0.60
octane	0.691	0.65
nonane	1.139	1.13
decane	1.751	1.68
undecane	2.435	2.48
methanol	0.283	0.27
water	0.523	0.49

In the pulsing mode the shape and height of adsorptive concentration wave depends on the rate of carrier gas, the evaporator temperature, as well as the location of PQR in EN. The influence of these factors on the response height Δf_{max} and half-width τ_{hw} to octane vapor for a PQR based on $CuSt_2$ coating (loading 6.5 kHz) can be seen in Table 2.

In all cases the dose of liquid octane was 1 μl which corresponds to octane mass m = 0.7 mg. Table 2 shows the values C_{max} of octane vapor calculated by the Eq.(2) for the corresponding gas rate v_{He}. In addition, it shows the values A_{max} of octane adsorption calculated by the Eq. 4a at the peak maximum, as well as corresponding Henry's law constant K_H^{max} (Eq. 5a).

One can see that the values K_H^{max} obtained at different rates of carrier gas (11–78 cm^3/min) coincide with an accuracy of 10 %. The change in position of the PQR also has little effect on the calculated value K_H^{max}. This means that at any position at the indicated carrier gas flow rates, the adsorption of octane on the CuSt$_2$ covering is close to equilibrium adsorption, and the measured value reflects correctly the value of τ_{hw} of real concentration wave of the adsorbate. However, when $v_{He} = 100$ cm^3/min the value K_H^{max} is clearly too high. This can be explained by value τ_{hw} being too high and, consequently, the low calculated value of C_{max} and overly high value K_H^{max} obtained. This is not unexpected, because every PQR sensor based on adsorption phenomenon must have its inertia threshold when its response shape no more reflects the veritable shape of real concentration wave of the adsorbate. Thus, with carrier gas flow rate over 100 cm^3/min, the inertia of the sensor becomes an obstacle to a correct assessment of current octane vapor concentration. On the other hand the use of overly low flow rates may be inexpedient, because the concentration wave may become so extended in time and become commensurable with dynamic of an adsorption process. On the whole, the feasibility of using one or another flow rate depends on the rate of adsorption process on the studied adsorbent.

Table 2. The K_H^{max} values for octane vapor adsorption on the covering CuSt$_2$ at $t_{EN} = 25$ ºC calculated from the PQR sensor responses in pulsed mode

v_{He}, cm^3/min	t_{evap}, ºC	Position	Δf_{max}, Hz	τ_{hw}, s	A_{max}, mg/g	C_{max}, mg/l	K_H^{max}, l/g
11	50	1	261	84.3	40.2	45.3	0.89
22	50	1	270	43.0	41.5	44.5	0.93
40	50	1	262	24.5	40.3	42.9	0.94
78	50	1	196	17.0	30.1	31.8	0.95
78	80	1	302	11.3	46.5	47.8	0.97
100	100	1	380	8.5	58.5	49.6	1.18
11	50	4	216	102.0	33.2	37.4	0.89
22	50	4	198	57.0	30.6	33.6	0.91
40	50	4	197	33.0	30.3	31.9	0.95
78	50	4	170	19.0	26.2	28.5	0.92

But the usage of metal stearates or thiolates as covering materials for PQR sensors has some limitations. Their usage is impossible for sensing such adsorbates which can be good solvents for the sensing material. In this case adsorption by the material can proceed not only on its surface but also into its bulk volume making such a sensor too inertial. Another limitation is the use of temperatures above about 90–100 °C, since the sensing material melts and becomes again too inertial. As a more acceptable alternative, a finely dispersed but nonporous cross-linked polymer can be used which can respond to a given vapor only by means of a fast and reversible physical adsorption. The fine dispersed StDVB is an example. The PQR with this covering proved its ability to give fast and reversible responses on different organic and inorganic vapors and operate at temperatures up to 120 °C (Table 3).

Table 3. Henry low constants (in 1/g) for different vapors adsorption on StDVB covering at 80 °C, calculated for stationary and pulse mode ($V_{He} = 60$ cm^3/min)

Adsorbate	Stationary K_H	Pulse K_H
pentane	0.014	0.012
hexane	0.024	0.023
isobutylene	0.0066	0.0061
ethanol	0.071	0.067
ETBE	0.027	0.026
water	0.144	0.142

Adsorption-desorption dynamics of ethanol on fine dispersed Amberlyst 15. For the purpose to demonstrate of foregoing pulse mode approach the results of an experiment using a porous sorbent Amberlyst 15 (the catalyst for ethyl-*tert*-butyl ether synthesis) and ethanol as sorbate are presented below.

The adsorbent in the form of particles about 0.1 μm in diameter was fixed as thin layer on PQR

electrode as it was described above in experimental. A PQR covered with fine dispersed nonporous StDVB (fixed by the same way) was used as a sensor. Both PQRs were placed in position 4 in respects to the gas flow direction. The sensor PQR was used to determine the sorbate (ethanol) current concentration and the Amberlyst 15 covered PQR was used to monitor its current adsorption on the adsorbent. In the course of the experiment 1 µl of liquid ethanol was injected at some point from the start of registration. Some seconds later the both PQR began to respond. But whereas the PQR sensor ("non inertial") gave the response with fast return (graphs C), the PQR with adsorbent Amberlyst 15 gave a protracted one (graphs A).

As it was shown in [8], the process of adsorption on a powdered sorbent at constant sorbate concentration can be described with approximate equation (correct within $\gamma_\tau^{ads} \leq 0.5$):

$$\gamma_\tau^{ads} = \frac{6}{R}\sqrt{\frac{D_e\tau}{\pi}} \, , \tag{6}$$

where $\gamma_\tau^{ads} = \dfrac{A_\tau - A_{ext}}{A_\infty - A_{ext}}$ is the adsorption degree to the current time, τ – the time from the outset of the sorbent contact with sorbate vapor, A_τ is the adsorption at the current time, A_∞ is the equilibrium adsorption at given sorbate vapor concentration, A_{ext} is instantaneous adsorption on the external surface of the sorbent particles (taking into account if it is marked as compared with adsorption in the pores of the sorbent), R is the mean radius of the sorbent particles, D_e is the effective diffusion coefficient.

As it is seen from Fig. 7, we can obtain in the pulse mode a series of sorbate pulses with the same value the sorbate concentration C_{max} but having different pulse duration (i.e. τ_{hw}). Thus the dependence of the A_{max} on the τ_{hw}, obtained at different v_{He} but the same sorbate C_{max}, can be approximately recognized as the dependence of adsorption value on effective contact time of the sorbent with the sorbate at that sorbate concentration.

The dependence of γ_τ^{ads} on $\tau_{hw}^{0,5}$, presented in Fig. 8, was constructed with such approximation.

The value of effective diffusion coefficient can be derived from tg α of the linear section of this graph. For the present example we have obtained $D_{ef} = 5.58 \cdot 10^{-14}$ cm^2/s. The kinetics of

sorbate desorption from the powdered sorbent in He flow (without of the sorbate vapors) can be represented with the equation analogues to Eq. 6:

$$\gamma_\tau^{des} = \frac{6}{R}\sqrt{\frac{D_e\tau}{\pi}} \, , \tag{7}$$

where $\gamma_\tau^{des} = \dfrac{A_0 - A_\tau}{A_0}$ is the desorption degree to the current time τ, the time from the discontinuance of the sorbent contact with sorbate vapor or any arbitrary point on desorption curve durante absentia sorbate vapor accepted as onset of desorption, A_τ is the total adsorption towards the current time from the onset of desorption, A_0 is the adsorption at the onset of desorption (A_{ext} is implying to be equal zero in such conditions), R is the mean radius of the sorbent particles. D_e is the effective diffusion coefficient. This time it is possible to use of all experimental points, where $C_\tau = 0$ in each separate response.

For instance, as can be seen in Fig. 9, the ethanol desorption proceeds after 50 minutes of the response in absence of the sorbate in gas phase (with indicated conditions).

Thus, the graph can be presented in terms of the Eq. 7 for desorption section of the graph A with 50 seconds being accepted as onset of desorption (i.e. desorption time $\tau = 0$). In this point $A(A_0) = 2$ mg/g.

The value of can be derived from tgα of the linear section of the graph in Fig. 10. For the present example we have obtained $D_{ef} = 1.26 \cdot 10^{-14}$ cm^2/s.

It is easy to see that this D_{ef} value distinctly differs from the D_{ef} value indicated above ($5.58 \cdot 10^{-14}$ sm^2/s). This difference can be explained by the fact that the effective diffusion coefficient is not constant, it actually decreases with adsorption degree increase. The D_{ef} value obtained with <u>adsorption</u> kinetics data processing attitudes to initial adsorption when the sorbent grain is free of the sorbate. However, the D_{ef} value obtained with <u>desorption</u> kinetics data when the grain loaded in some extent with the sorbate. So, for the example presented in Figs. 9 and 10 the initial point was $A_0 = 2$ mg/g. Thus, the obtained difference between the D_{ef} values reflects actually the dependence of the D_{ef} on the adsorption degree.
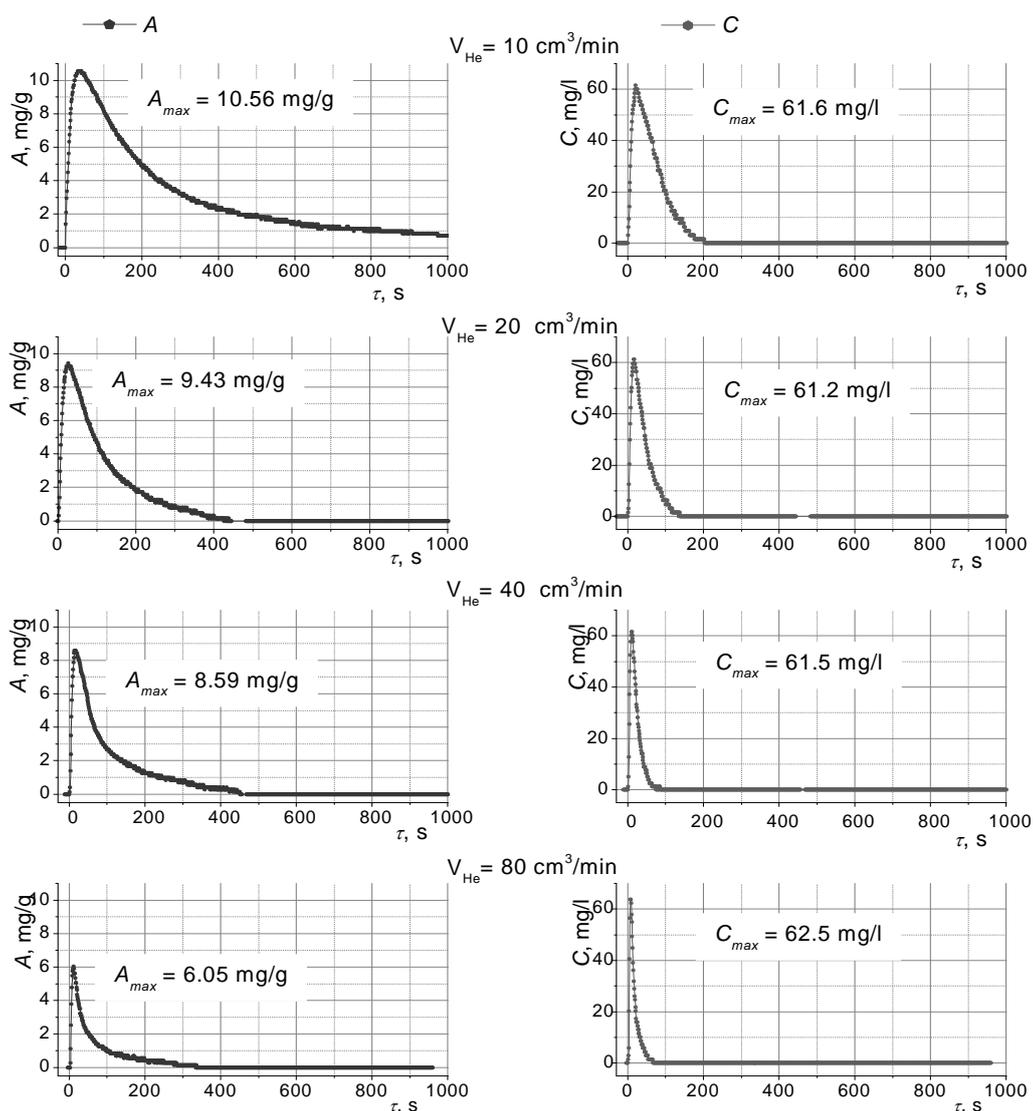
Fig. 7. EtOH adsorption on A-15 in a pulse mode at 80 °C at different He flow rates. EtOH dose is 1 μl. The adsorption A (left) is calculated from responses of the PQR covered with A-15 and EtOH vapour concentration C_τ (right) is calculated from SDVB covering responses
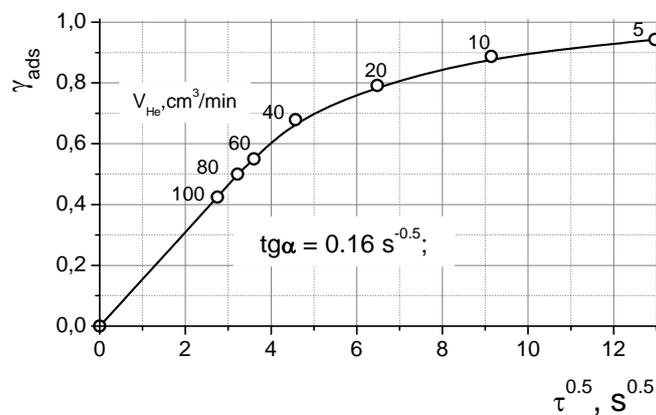

Fig. 8. The kinetics of EtOH adsorption on fine A-15 (R = 50 nm) at 80 °C. v_{He}– from 5 to 100 cm³/min, EtOH pulse doze 1 μl, C_{max} = 58±2 mg/l, $t_{evap} = t_T = t_{det}$ = 100 °C

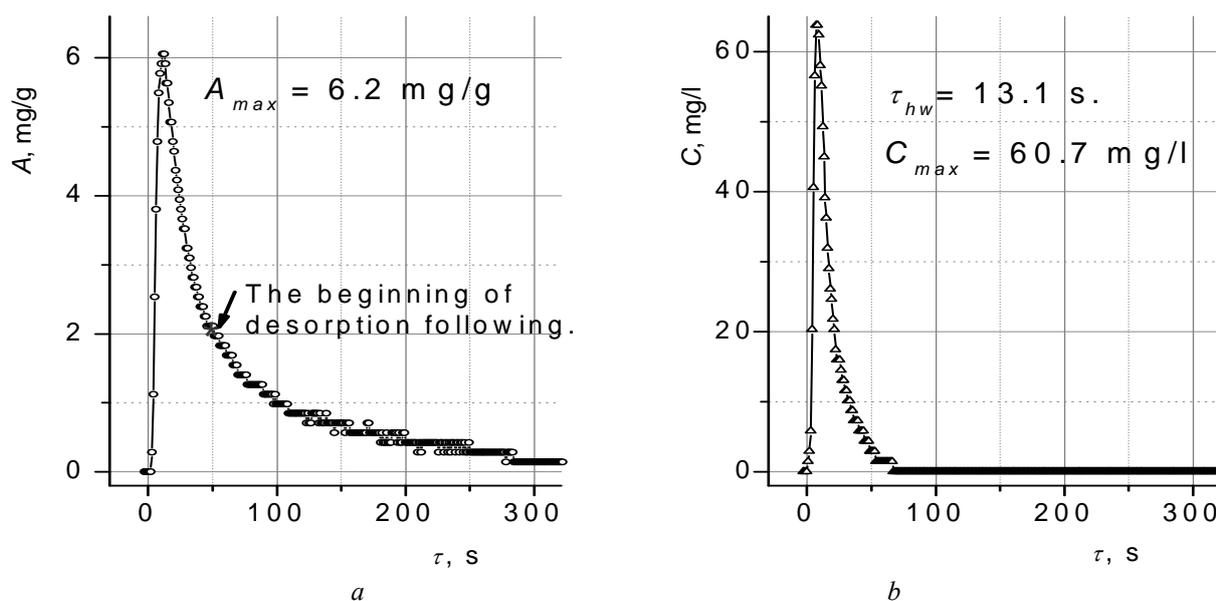**Fig. 9.** Ethanol dsorption-desorption on fine dispersed A-15 at 80 °C – *a* and current EtOH concentration – *b* in pulsed mode; A-15 loading 7.1 kHz, position 4; t_{Evap} = 100 °C, He flow rate 80 cm^3/min, dose of ethanol: 1 µl
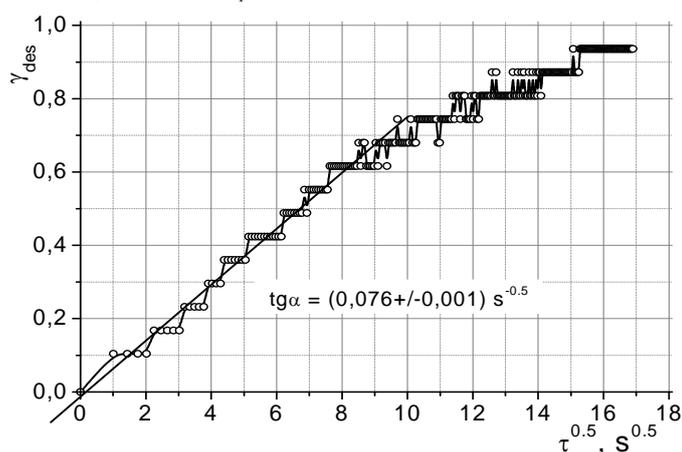

$tg\alpha = (0,076+/-0,001)\ s^{-0.5}$

Fig. 10. The kinetics of EtOH desorption from fine A-15 (R = 50 nm) at 80 °C, He flow rate 80 cm^3/min

CONCLUSIONS

On the basis of the study it is shown that the QCM method with developed setup can be used to study the adsorption-desorption processes continuing for several seconds and more. The pulse of sorbate vapor with half-width of a few seconds can be obtained with appropriate evaporator temperature and flow rate of carrier gas. The use of PQR with a chemical coating based on a metal stearate or thiolate or cross-linked polymer is proposed as a simple, relatively fast response sensor to control the current sorbate concentration in gas phase. The method can be applied for determination of effective diffusion coefficients in adsorption-desorption processes on fine dispersed sorbents.

REFERENCES

1. *Belkov V.M.* The piezoelectric method for determination of adsorption isotherms of gases by porous bodies at high pressures in large temperature interval. The theory of the method. // J. Phys. Chem. – 1988. – V. 62, N 12. – P. 3295–3299 (in Russian).
2. *Belkov V.M.* The piezoelectric method for determination of adsorption isotherms of gases by porous bodies at high pressures in large temperature interval. The technology of

adsorbent applying on the resonator. A priori errors of the method // J. Phys. Chem. – 1989. – V. 63, N 4. – P. 984–989 (in Russian).

3. *Yan Y., Bein T.* Molecular recognition acoustic wave devices: Sorption in chemically anchored zeolite monolayers // J. Phys. Chem. – 1992. – V. 96, N 23. – P. 9387–9393.

4. *Pat. 47450 of Ukraine*, G01N 30/00, G01N 29/00, G01R 23/00. The method of analysis of gases and vapors of volatile substances and their mixtures with the help of device for accomplishment of that analysis / *Filippov O.P., Strizhak P.E., Serebry T.G., Snopok B.A.* – No u200903826; Declared 21.04.2009; Publ. 10.02.2010; Bul. N 3 – 11 p. (in Ukrainian).

5. *Vlasenko N.V., Kochkin Yu.N., Filippov A.P. et al.* Effect of adsorption–desorption of reaction mixture components on ethyl-tert-

butyl ether synthesis over commercial sulfonic acid resins // Catal. Commun. – 2011. – V. 12, N 5. – P. 1142–1145.

6. *Filippov A.P., Strizhak P.E., Il'in V.G.* Quartz crystal microbalance modified with Cu(II) stearate and octadecylamine co-ordination chemical compounds for detection of volatile organic compounds // Sensors and actuators B. – 2007. – V. 126, N 1–2. – P. 375–381.

7. *Filippov O.P., Strizhak P.E., Denisiuk D.I., Serebry T.G.* Sensitivity of metal thiolate piezoquartz sensor coatings to hydrocarbons, methanol and water // Theor. Exp. Chem. – 2006. – V. 42, N 6. – P. 378–383.

8. *Timofeyev D.P.* The Kinetics of Adsorption – Moscow: Edit. Acad. Sci. USSR, 1962. – 252 p. (in Russian).

Вивчення динаміки адсорбції летких сполук на тонкодисперсних адсорбентах методом п'єзокварцового мікрозважування в імпульсному режимі

О.П. Філіппов, П.Є. Стрижак, Н.В. Власенко, Ю.М. Кочкін, Т.Г. Серебрій

Інститут фізичної хімії ім. Л.В. Писаржевського Національної академії наук України
пр. Науки, 31, Київ, 03039, Україна, aphylippov_chem@mail.ru

Метод п'єзокварцового мікрозважування застосовано для вивчення процесів адсорбції-десорбції, що перебігають впродовж декількох секунд і більше. Досліджуваний тонкодисперсний адсорбент може бути закріплено на електродах п'єзокварцового резонатора. За допомогою пристрою, що складається з проточної комірки типа електронного носу в комбінації з газовим хроматографом, введенням дози рідкого адсорбату створюється імпульс парів адсорбату з напівшириною до кількох секунд з протяжністю, що визначається температурою випарювача та швидкістю потоку газа-носія. В якості простого, відносно швидкодіючого сенсора для вимірювання поточної концентрації парів адсорбату в газовій фазі запропоновано використовувати п'єзокварцовий резонатор з хімічним покриттям на основі стеаратів або тіолатів металів, або зшитого полімеру. Метод застосовано для визначення ефективного коефіцієнта дифузії в процесі адсорбції-десорбції етанолу на тонкодисперсному макропористому катіоніті Амберліст 15.

Исследование динамики адсорбции летучих соединений на тонкодисперсных адсорбентах методом пьезокварцевого микровзвешивания в импульсном режиме

А.П. Филиппов, П.Е. Стрижак, Н.В. Власенко, Ю.Н. Кочкин, Т.Г. Серебрий

Институт физической химии им. Л.В. Писаржевского Национальной академии наук Украины
пр. Науки, 31, Киев, 03039, Украина, aphylippov_chem@mail.ru

Метод пьезокварцевого микровзвешивания применен для изучения процессов адсорбции-десорбции, протекающих в течение нескольких секунд и дольше. Исследуемый тонкодисперсный адсорбент может быть закреплен на электродах пьезокварцевого резонатора. С помощью установки, состоящей из проточной ячейки типа электронный нос в комбинации с газовым хроматографом, вводом дозы жидкого адсорбата создается импульс паров адсорбата с полушириной до нескольких секунд, длительность которого определяется температурой испарителя и скоростью потока газа-носителя. В качестве простого, относительно быстродействующего сенсора для измерения текущей концентрации паров адсорбата в газовой фазе предложено использовать пьезокварцевый резонатор с химическим покрытием на основе стеаратов или тиолатов металлов, или сшитого полимера. Метод применен для определения эффективного коэффициента диффузии в процессе адсорбции-десорбции этанола на тонкодисперсном катионите Амберлист 15.