

## STUDIES OF LIQUIDS DIFFUSION IN THE CHOSEN MATERIAL SAMPLES Thermogravimetric and Q-TG method

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The new method of diffusion coefficient calculations from thermogravimetry Q-TG data has been presented. Programmed thermodesorption of polar and apolar liquids from aluminium oxide and montmorillonite-Na and -La samples in quasi-isothermal conditions has been made. The result from above method was compared with literature data and good correlation were obtained.

**Keywords:** aluminium oxide, diffusion coefficient, Fick's laws, montmorillonite-La, montmorillonite-Na, thermogravimetry Q-TG

### Introduction

Adsorption and desorption processes of molecules on the surface of adsorbents on the samples of aluminum oxide and other materials are significantly affected by diffusion of adsorbate molecules towards the surface in the adsorbent pores. The difference of concentration at the gas/solid interface is the direct cause of diffusion. The fractality of the surface has an influence on the diffusion of molecules through porous materials [1, 2].

Thermal motion of the molecules possessing the kinetic energy of translation is responsible for spontaneous, mutual penetration of various gases and liquids. This phenomenon called diffusion leads to formation of homogeneous mixture of gases or liquids. Its direct cause is the existence of concentration gradient at the contact boundary of two substances. The larger the concentration gradient is, the quicker the diffusion process proceeds. The amount of the substance,  $dm$ , diffusing in the time,  $dt$ , from one to another layer distant by  $dx$  is directly proportional to the surface size  $S$  through which transfer takes place and to the concentration gradient  $dc/dx$ . This dependence is expressed by the first law of Fick formulated in 1855 [3, 4]:

$$\frac{dm}{dt} = -DS \left( \frac{dc}{dx} \right) \quad (1)$$

where  $D$  is the diffusion coefficient.

The analytical solution of Fick's law of diffusion in solids where internal diffusion plays a dominant role is developed for the Henry's region of adsorption isotherm [5]. Its solution for the adsorption in solids possessing the spherical-shaped granules is given by Eqs [3, 4]:

$$1 - \frac{a_t}{a_{\max}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{10^{-0.4343n^2 K}}{n^2} \quad (2)$$

where  $a_t$  and  $a_{\max}$  – the adsorption at the time  $t$  and adsorption capacity (maximal adsorption),  $K=(\pi^2 D/r)t$  and  $1 \leq n < \infty$  ( $\neq$  constants).

For the adsorption process proceeding in solids possessing cylindrical-shaped granules (with length of cylinder equal to  $L$ ) it can be written as [5–7]:

$$1 - \frac{a_t}{a_{\max}} = \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\alpha_n^2 (2m-1)^2} \cdot 10^{-0.4343[\alpha_n^2 / \pi^2 + (2m-1)^2 r^2 / L^2] K} \quad (3)$$

where  $r$  – the radius of the intersection of a cylinder,  $\alpha_n$  – the roots of the equation  $I_0(x)=0$ , and  $I_0(x)$  is the Bessel function of the first kind 0 order and  $1 \leq m < \infty$ .

Equations (2) and (3) based on the analytical solution of Fick's law of diffusion were used for the description of physisorption kinetics. The migration of species into the spherical adsorbent can be described by the following form of Fick's second law of diffusion as the first approximation [8]:

$$\frac{dc}{dt} = D \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc}{dr} \right) \right] \quad (4)$$

where  $r$  – the distance from the center of the particle,  $c$  – the solute concentration in the adsorbent.

The migration of species into the cylindrical adsorbent particle can be described by Fick's second law of diffusion in the cylindrical form for  $D$ =constant (from Eq. (4) follows Eq. (5)) [3, 5]:

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$$\frac{dc}{dt} = D \left( \frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} \right) \quad (5)$$

The solution of Eq. (5) is given in paper [9]. The diffusion coefficient in the adsorbent particle is smaller than the diffusion coefficient in the free solution. The solution of Eq. (4) was made by Ruthven [10]:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r_0^2}\right) \quad (6)$$

where  $m_t$  – the amount of species adsorbed by the adsorbent particle at time  $t$ ,  $m_\infty$  – the amount of species adsorbed by the adsorbent particle at equilibrium,  $r_0$  – initial adsorbent radius.

Its worth to notice that Eqs (2) and (5) follow from solution of Eq. (6). The desorption rate can be determined from the kinetic-molecular theory. Most liquid molecules getting to the interface due to thermal movements do not possess enough energy to overcome the attraction force and can not pass into the gas phase. The desorption rate depends on temperature, i.e. on the minimal molar kinetic energy of the molecules necessary for their transition from the liquid to gas phase which should equal to the molar enthalpy of evaporation,  $\Delta H$ . The formed vapor must do volumetric work but its pressure,  $p$ , depends on temperature,  $T$ , according to the equation given in the book [4]:

$$p = NRT e^{-\frac{\Delta H}{RT}} \quad (7)$$

where  $N$  – the number of molecules in the unit of volume.

Our previous papers present the application of thermogravimetry Q-TG for calculation of fractal coefficients [11, 12] as well as studies of adsorption layer properties [13, 14], adsorbate-adsorbent interactions [15] and total heterogeneity of solid surfaces [16]. The studies include the process reverse to adsorption, i.e. programmed thermodesorption of liquids from solids under the quasi-isothermal conditions.

The paper presents a simple method for calculation of liquid diffusion coefficient during thermodesorption in quasi-isothermal conditions of liquid molecules from the aluminium oxide and montmorillonite-Na and -La surfaces based on the Q-TG and Q-DTG data.

## Experimental

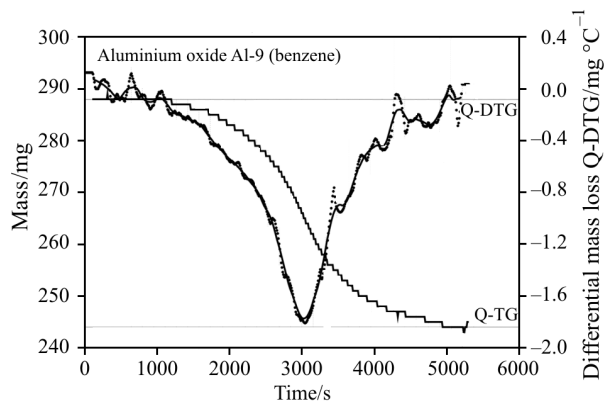
Studies of polar and apolar thermodesorption of liquids from the samples of commercial aluminium oxide (type Al-9, Aluminium Co., Al-COA Center, USA) and pure montmorillonite-Na and -La were carried out using a derivathograph Q-1500D (MOM Hungary) [17]. The montmorillonite employed came from Lago

Pellegrini (Rio Negro, Argentine) with an average percent composition of  $\text{SiO}_2$  – 68.83,  $\text{Al}_2\text{O}_3$  – 22.86,  $\text{Fe}_2\text{O}_3$  – 4.41,  $\text{MgO}$  – 3.09,  $\text{CaO}$  – 0.24,  $\text{Na}_2\text{O}$  – 0.49 and  $\text{K}_2\text{O}$  – 0.16. A size fraction  $<2$  mm was prepared by dispersion in water. After left standing for 24 h in order to allow impurities like quartz and feldspar to settle down the upper 3/4 of the suspension was taken. The substituted samples were obtained by saturation of the cation exchange capacities of the water-suspended clay samples with sodium and/or lanthanum chloride (0.5 M). This was followed by repeated washing with distilled water and centrifugation until complete removal of chloride ions in solution was achieved. At this stage the solution has a pH of about 6.5. Finally, the samples were air dried [18]. The Q-TG mass loss curve and Q-DTG differential mass loss curve in relation to temperature and time were measured under quasi-isothermal conditions over a 20–300°C temperature range. The curves were measured over a constant heating rate of 6 K  $\text{min}^{-1}$ . The sample was thermally treated in air in 300°C already located in the vacuum desiccator, where the relative vapor pressure of benzene was  $p/p_0=1$ . About 0.5 g of the wetted samples were placed in the special platinum crucible of the thermogravimetric analyzer.

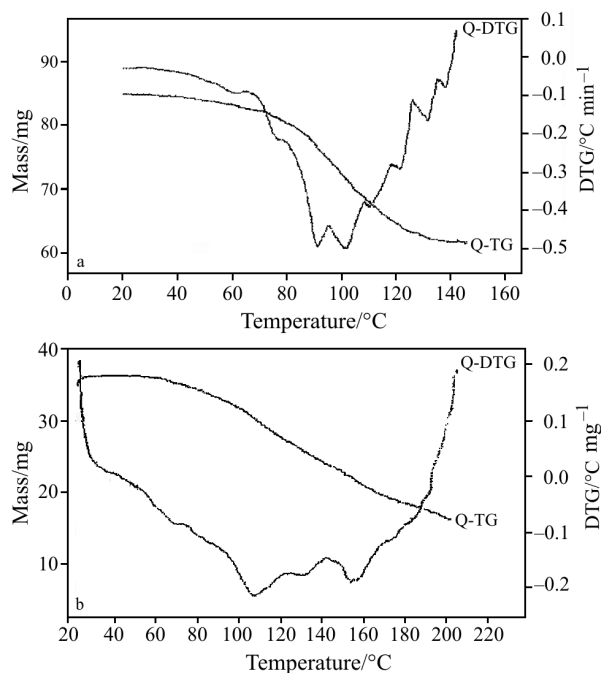
## Results and discussion

Figure 1 presents the curves Q-TG and Q-DTG depending on the time of benzene thermodesorption from the aluminium oxide surface. The Q-DTG curve shows one peak and a few inflections corresponding to evaporation of benzene molecules from pores and active centers of sample surface.

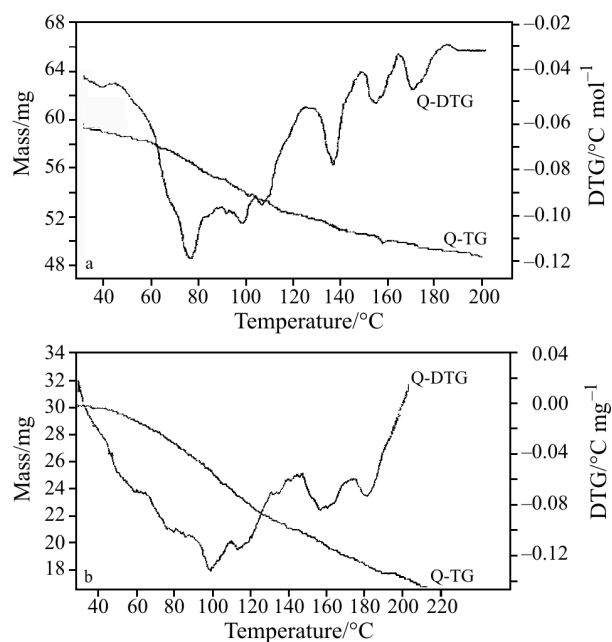
The experimental Q-TG mass loss and Q-DTG differential mass loss curves in relation to temperature for the desorption of water from Na-(left side) and La-montmorillonite (right side) samples wetted with



**Fig. 1** The Q-TG and Q-DTG thermodesorption curves of benzene from the aluminium oxide sample made using the programmed quasi-isothermal method



**Fig. 2** The mass loss Q-TG and differential Q-DTG curves of water thermodesorption from a – montmorillonite-Na and b – montmorillonite-La samples



**Fig. 3** The mass loss Q-TG and differential Q-DTG curves of *n*-butanol thermodesorption from a – montmorillonite-Na and b – montmorillonite-La samples

vapour in vacuum desiccator are presented in Fig. 2. It can be seen that two parts appear in this spectrum: the first peaks with minimum located near 100–120°C and the second parts with inflexion at 120–200°C. In the case of *n*-butanol thermodesorption (Fig. 3) it appears that there are similar peaks and inflections with its minimum located at 100–200°C.

Thermodesorption process of liquids from Na- and La-montmorillonite samples and course of Q-TG and Q-DTG curves depend on the amount of the water and *n*-butanol deposited on their surfaces. As follows from the studies carried out so far, the presence of a great number of liquid molecules on the sample surface diminishes resolving power distribution and selectivity of thermodesorption process. It results from the lateral interactions of liquid molecules which diminish the bonding energy of the molecules adsorbed with the surface active centers. The thickness of adsorbed liquid layers on the surfaces can be controlled by the immersion mode of solid samples. The immersing of surface samples with water and *n*-butanol vapors in a vacuum desiccator, where  $p/p_0=1$  blocks all adsorption active centers, the surface and capillary forces of the sample studied, only. Under this condition the surface and capillary forces are compensated as in the static McBain balance adsorption method. The samples prepared in this way did not include the excess of bulk liquid whose presence influenced the thermodesorption kinetics and mechanism (screening of the surface).

From the data of mass loss of the studied sample in relation to time there were calculated the values  $m_i/m_0$ , where  $m_i$  is the sample mass after the time of thermodesorption  $t_i$ ,  $m_0$  is the initial mass of the sample. Then the diagram of the dependences  $\ln(m_i/m_0)=f(t)$  was prepared and is presented for example of benzene/aluminium oxide system in Fig. 4. As follows from the analysis of the data presented in this figure the process of thermodesorption can be divided into two times intervals [19]:

- $t < 2500$  s in which desorption from the sample surface takes place (2500 s is the time corresponding to benzene evaporation at its boiling temperature), and
- $t > 2500$  s which is characteristic of benzene diffusion in the aluminium oxide pores

The second stage of thermodesorption is described by the following kinetic equation [3]:

$$\frac{m_t}{m_0} = \sum_{n=1}^{\infty} B_n \exp(-\mu_n^2 F_0) \quad (8)$$

where  $F_0 = Dt/h^2$ ,  $h$  – plate thickness and  $\mu_n$  – the constant taken from [3].

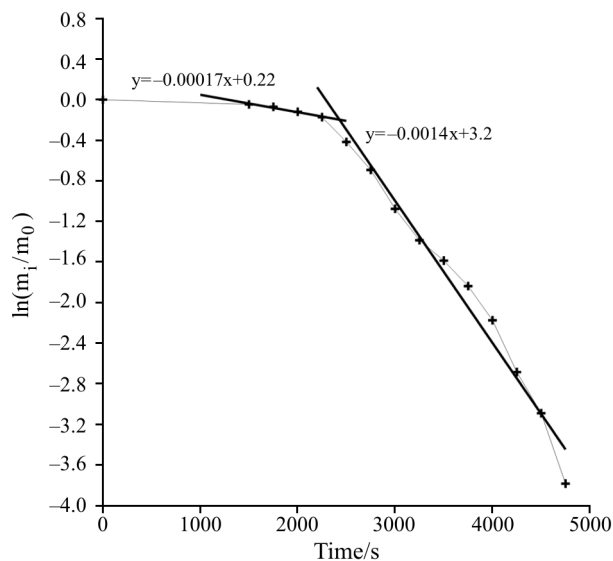
Using data presented in Fig. 1 the dependence:

$$\ln \frac{m_t}{m_0} = f(t) \quad (9)$$

have been prepared and given in Fig. 4.

**Table 1** Diffusion coefficients (in  $\text{cm}^2 \text{s}^{-1}$ ) of polar and apolar liquids during thermodesorption processes from montmorillonites-Na and -La

Sample	Water	Benzene	<i>n</i> -Butanol	<i>n</i> -Octane
Na-montmorillonite	$6.7 \cdot 10^{-14}$ – $5.4 \cdot 10^{-12}$	$1.0 \cdot 10^{-13}$ – $3.1 \cdot 10^{-12}$	$2.1 \cdot 10^{-13}$ – $5.6 \cdot 10^{-12}$	$2.5 \cdot 10^{-13}$ – $3.2 \cdot 10^{-12}$
La-montmorillonite	$7.8 \cdot 10^{-14}$ – $3.9 \cdot 10^{-12}$	$1.2 \cdot 10^{-13}$ – $1.1 \cdot 10^{-11}$	$2.7 \cdot 10^{-13}$ – $3.4 \cdot 10^{-12}$	$3.6 \cdot 10^{-13}$ – $4.8 \cdot 10^{-12}$

**Fig. 4** Dependence  $\ln(m_t/m_0)$  in relation to time

On the basis of the analysis a kinetic curve it is possible to draw a conclusion that process of diffusion is described by the first member of series Eq. (8):

$$\frac{m_t}{m_0} = B_1 \exp(-\mu_n^2 F_0) \quad (10)$$

We shall differentiate the Eq. (10):

$$\frac{1/m_t}{dm_t/dt} = -B_1 \frac{\mu_n^2 D}{h^2} \exp(-\mu_n^2 F_0) \quad (11)$$

Next, we can divide Eq. (11) into Eq. (10):

$$\frac{1/m_t}{dm_t/dt} = -\frac{\mu_n^2 D}{h^2} \quad (12)$$

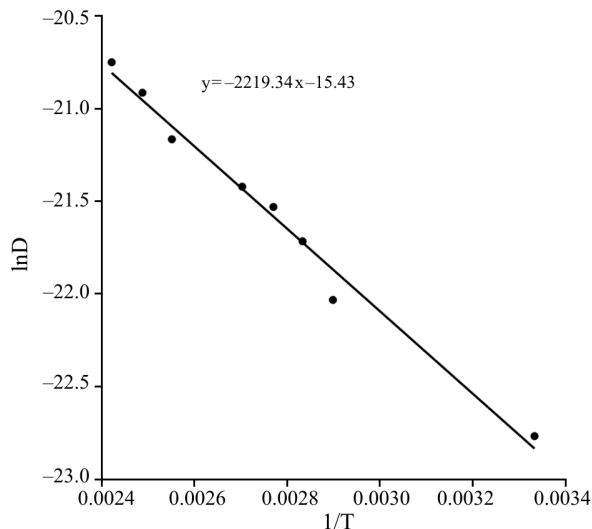
From Eq. (12) we shall receive Eq. (13):

$$D = -\frac{h^2}{\mu_n^2} \frac{1/m_t}{dm_t/dt} \quad (13)$$

From Eq. (13) we shall calculate the diffusion coefficient for  $h=10^{-3}$  m,  $\mu_n^2 = 2.46$  from Eq. (14) presented in Fig. 5 in the dependence:

$$\ln D = f(1/T) \quad (14)$$

The obtained value of benzene diffusion coefficient in the pores of aluminium oxide sample is  $1.16 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in  $T=25^\circ\text{C}$ .

**Fig. 5** The Arrhenius diagram of the diffusion coefficient dependence on  $1/T$ 

Additionally, calculation of the diffusion coefficient  $D$  of adsorbed layers based on the analytical solution of Fick's law of diffusion for desorption process of liquids in temperature range of  $20$ – $200^\circ\text{C}$  were made for liquids/montmorillonite-Na and -La samples [18, 20, 21]. The  $D$  parameters of the tested materials are presented in Table 1 and they are close to the value presented in the literature. Gay-Duchnal *et al.* [22] used quasielastic incoherent neutron scattering (QINS) to study the diffusion of interlayer water in partially oriented montmorillonite-Na samples and diffusion coefficient  $D=1.3 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  was obtained.

## Conclusions

This study discusses the special use of the Q-TG and Q-DTG thermogravimetric data on preadsorbed vapor of polar and apolar liquids for quantitative calculations of the diffusion coefficients. Using presented equations and simple method is possible to study diffusion processes of liquid molecules in different materials. The obtained  $D$  values are in good agreement with those presented in literature.

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