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An investigation of anomalous time-fractional diffusion of isopropyl alcohol in mesoporous silica

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ABSTRACT

Anomalous behavior of Isopropyl alcohol transport in mesoporous silica is experimentally and theoretically investigated. Fitting of the experimental data by the solutions of the second Fick's law with various pore geometries shows no coincidence between the experimental data and theoretical curves. We demonstrate that experimental data are in an excellent correspondence with the solution of the time-fractional diffusion equation with fractional order value ranging from 1.07 to 1.3, obtained for boundary conditions that correspond to the experimental conditions. These findings reveal that isopropyl alcohol in mesoporous silica may exhibit anomalous mass transfer behavior because of geometrical restrictions of silica pores.

1. Introduction

Mass transfer processes with memory effects are described by the time-fractional diffusion equation [1]. Memory effects concerning temporal non linearity may be explained as time-scaled inequalities between particles jumps' time so that in case of time-fractional movement the current position of a moving particle is unknown at a particular moment of time. However, for standard diffusion the mean square displacement (MSD) of the diffusing species is linear with respect to time and may be defined as a product of time and diffusion coefficient [2].

If mass transfer process exhibits memory effects, Brownian motion no more holds for this process and the second Fick's law is useless for describing the diffusing species' motion [3]. Therefore, the time-fractional diffusion equation is introduced for describing this unusual phenomenon. Depending on the order of the fractional derivative, different types of anomalous transport are reported. For fractional order $0 < \alpha < 1$ holds sub-diffusive regime of transport, which is slower comparing to normal diffusion, and for $1 < \alpha < 2$ holds super-diffusive regime of transport, which is faster in comparison with Fickian transport [4,5]. These types of transport typically occur in the media with fractal or porous structure [6]. Contrary to standard diffusion, based on Brownian motion model, for which the MSD is proportional to time, anomalous diffusion is characterized by the MSD proportional to the non-integer order power of time [7]. Continuous time random walk model is most often used for describing the statistical probability of particle position, based on fractional diffusion equation concerning the Levy diffusion process [8–10]. The order of fractional derivative and diffusion constant may be easily determined from the time-fractional diffusion equation solution, fitted to the experimental data. However, the physical meaning of the measured parameters is not always clear, because of phenomenological merits of the corresponding approach.

The physical origins of the anomalous diffusion itself and its regime differ for each particular case and may be explained by different reasons concerning the nature of the system investigated [11]. This differs from traditional Fickian and Knudsen diffusion, which are of clear physical reasons and are governed by Wiener Brownian motion of Markovian nature and pores of smaller size than the mean free path of the species respectively. For instance, in viscoelastic media the anomalous sub-diffusive regime is driven by the additional degrees of freedom, the presence of traps in chaotic systems is also the reason of the anomalous diffusion [11], fractal structure of solid media leads to non-usual diffusion [6]. Inertial effects of diffusive transport, concerning the case of dominating the particle's inertia before friction forces between the particles, sometimes causes the deviation from standard Fickian transport [12]. For the gaseous transport in the restricted porous media the kinetics of mass transfer is defined by the retention time of the diffusing species in the pores of the solid media. The retention time may be associated with geometrical confinements inside the pores and the adsorption process of the diffusing species on the internal

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surface of the pores. The adsorption process leads to different time intervals that the diffusing molecules spend at one site. The latter may be associated with the energetic disorder of the surface of solid porous media. These time delays govern the nonlinearity and the memory effects of random particles movements, which results into Brownian motion of non-Markov nature, described by the continuous time random walk model, and replacing the integer order temporal derivative in the corresponding transport equation by the fractional derivative [13].

The aforementioned considerations are in agreement with the following findings. Skaug et al. [14] demonstrated that the generation of the random process in terms of the restricted transport models strongly depends on the configuration of the obstacles in the free space of the media, where the mass transfer process occurs. The distance of the single molecule movement affected by the geometrical confinements defines the fractional exponent. Moreover, Nicolau et al. [15] showed that the anomalous diffusion origin is affected by different types of the interactions between the diffusing molecules and the obstacles of the media, e.g. the interactions of the protein molecules with fixed confinements, lipid obstructions, and cytoskeletal blocks. The overall effect of the interactions of different types is roughly additive. However, notwithstanding that these experimental results concern the investigation of the anomalous diffusion of proteins in the membrane cells of the living organisms we believe that the physical origin of the anomalous transport provided is also applicable for the system studied in the current paper.

Another type of transport, which is sometimes called anomalous comparing to standard Fickian diffusion, is Knudsen diffusion. The latter phenomenon occurs in the porous media in case if the mean free path of the diffusing species is equal or larger than the pore diameter. As it was demonstrated by Gopalakrishnan [16] for aerosol collision rate the transition regime between Fickian and Knudsen transport may be easily determined only by simple comparison of the Smoluchowski radius and orientationally averaged projected area of the particle. The influence of the surface roughness of the porous media on the diffusion in Knudsen regime was demonstrated by Malek and Coppens [17]. Transport diffusion has weak dependence on the roughness because of the independence of the fluxes on the detailed residence time distribution. Gaseous self-diffusion in Knudsen regime is strongly affected by surface roughness, including roughness of the fractal pores. However, the same considerations are not absolutely true for microscopic self-diffusion in the Knudsen regime [18]. The self-diffusivity decreases with the increasing of the roughness of the pores surface. Molecular-scaled fractal surface roughness in case of Knudsen diffusion regime may significantly increase the selectivity and the conversion of the porous catalysts in heterogeneous catalytic processes [19]. However, the influence of the pores roughness on the diffusion kinetics is not highlighted in the discussed works, because they focus only on transport diffusion, concerning fluxes. The fluxes correspond to the stationary case of the transport and, therefore, are useless for investigating the dynamical systems, e.g. mass transfer kinetics.

Theoretical modeling of the fractional behavior of different physical processes and biological objects is widely used [20,21]. Attempts of description of the natural and social phenomena in the frame of fractional calculus are also reported. For instance, molecules and organelles transport in cells of the living organisms demonstrates anomalous behavior, which is approved by the experimental observations [22]. Diffusion–reaction kinetics in chemical systems with non-Fickian dynamics was revisited recently [23]. However, experimental verification of the time-fractional diffusion still remains scarce and needs to be investigated in depth.

Non-usual transport through porous media, including silica, plays important role for industrial engineering, because speeding up chemical agents' mass transfer may significantly increase the efficiency of different chemical processes, concerning sorption, catalysis and distillation. Silica is widely used in sorption technologies and catalytic processes due to its unique properties like high surface area and pore distribution, which are easily controlled during its synthesis. Silica has fractal structure because of the singularities of its formation during sol–gel synthesis [24]. For instance, silica is obtained by inorganic polymerization reaction which leads to cluster formation with further aggregation to large inorganic polymer particles [25]. Self-similar relaxations of density fluctuations with fractional dynamics are typical for silica clusters [26]. The anomalous transport in silica structure and the correspondence between fractal structure and mass transfer regime in silica still are not studied in a proper way.

The goal of the present paper is to verify unusual non-Fickian diffusion regime of isopropyl alcohol in the mesoporous silica, which is associated with time-fractional diffusion. We demonstrate that the standard diffusion approach fails to describe the experimental data in a proper way. Contrary, experimental data coincide in a good manner with theoretical tests, established in accordance with the time-fractional diffusion equation.

2. Preliminaries

2.1. Fick's law and time-fractional diffusion

In non-stationary case diffusion process occurs in accordance with the second Fick's law, which for the sake of simplicity we consider in one-dimensional form:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \tag{1}$$

Here C denotes linear concentration of diffusate, mole/cm; D – diffusion coefficient, cm^2/sec; t – time, sec; x – space coordinate, cm.

If left-side derivative in Eq. (1) is replaced by the non-integer order derivative of α in the range from 0 to 2, the time-fractional diffusion equation is arisen:

$$I^{\alpha} C = K \cdot \frac{\partial^2 C}{\partial x^2} \tag{2}$$

where K is fractional diffusion coefficient, cm^2/sec$^{\alpha}$. I^{α} is a fractional operator. In terms of Caputo fractional integral I^{α} is given by [27]:

$$I^{\alpha} C(x,t) = \frac{\partial^{\alpha} C}{\partial t^{\alpha}} = \frac{1}{\Gamma(m-\alpha)} \cdot \int_0^t (t-\tau)^{m-\alpha-1} \cdot \frac{\partial^m C}{\partial \tau^m} d\tau \tag{3}$$

Here and afterwards m is 1 for $0 < \alpha < 1$, and m is 2 for $1 < \alpha < 2$, $\Gamma(z)$ is Euler gamma function.

The diffusion equation is commonly solved via application of Green's function. For standard diffusion equation Green's function is defined as normal Gauss distribution [28]:

$$G(x,t) = \frac{1}{\sqrt{4 \cdot \pi \cdot D \cdot t}} \cdot \exp\left[-\frac{x^2}{4 \cdot D \cdot t}\right] \tag{4}$$

Spatial Fourier and temporal Laplace transform of Eq. (2) leads to the time-fractional diffusion equation in terms of complex variables [29,30]:

$$C(k,s) = \frac{s^{\alpha-1}}{s^{\alpha} + K \cdot (-i \cdot k)^2} \tag{5}$$

Here k and s are the complex number frequency.