Phenomenon of non-outflow of a non-wetting liquid dispersed in nanoporous medium. The influence of modification and size of granules.

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Abstract. In this paper was studied the non-outflow phenomenon of a non-wetting liquid dispersed in nanoporous medium and the influence of porous medium surface modification and size of porous medium granules. The study of this phenomenon is important for development of mechanical energy dampers and for extraction of medicinal substances under certain conditions devices. The presented results for four commercial hydrophobized porous media Fluka 100 C18 (60756), Fluka 100 C18 (60758), Fluka 100 C8 (60755) and Fluka 100 C8 (60759) with the different thickness of the modifying layer and the size of the granules are show that the less of granules size and more narrow pore size distribution lead to decreasing of non-outflow phenomenon. The study of non-outflow phenomenon of non-wetting liquid from the pores of a nanoporous medium was carried out by time relaxation method and dispersed non-wetting liquid distribution recovery method at different temperatures.

1. Introduction

When the excess pressure is applied in a porous medium - nonwetting liquid system, the pores of the medium are filled with a liquid that passes into a dispersed state. When the excess pressure is reduced in the intrusion-extrusion cycle, the hysteresis is observed, and the filling pressure is greater than the outflow pressure [1]. Depending on various parameters of the system, both energy and geometric, different scenarios of this fluid behavior are possible with decreasing pressure. At the certain critical degree of filling and temperature, a dispersion transition occurs and part of the liquid can remain in a disordered porous medium [2]. It was assumed that the phenomenon of non-outflow of non-wetting liquid and the dispersion transition are determined by the filled pores arrangement, and the temperature dependence is related to the temperature dependence of the specific surface energy of the liquid-gas and the liquid-solid interfaces ([1,3]).

Parameters of the nanoporous media - non-wetting liquid system can significantly affect the amount of liquid remaining in the pores. Thus, it was shown that the volume of entrapment liquid depends, in addition to the observation time, on the temperature and size of the granules of the porous medium under investigation [4]. It was shown in [5, 6] that due to the increase in the length of the grafted alkylsilane, the contact angle of wetting of the modified surface also increases, while another group of researchers observed its insignificant decrease [7]. At the same time, it was shown in [9] that
the effect of the pore geometry on the coating density is significantly manifested when the alkyl chain extends independently of the structure of the sample.

It was also described in [9, 10] that the non-outflow of liquid is observed when small pores surrounded by pores larger in size. The existence of such pore arrangements can also explain the dependence of the volume of entrapment liquid on the size of the silica gel granules. In [4], the link between the length of the modifier and the presence of large and small pores was noted using the example of the study of Fluka 100 C8 and Fluka 100 C18 silica gels, and the same was also obtained in [11]. Due to fluctuations in the pore size of the porous medium, which are determined from the pore size distribution function, at different times the liquid can flow out of pores of different sizes and the number of these pores also depends on the observation time.

The practical interest of observing the relaxation of the metastable state of a non-wetting liquid dispersed in a nanoporous medium is associated with the possible use of devices for the accumulation and dissipation of mechanical energy. Also, the results of these observations can be used in the study of time-dependent and temperature-dependent processes, such as extraction of drugs from porous structures.

2. Methods and materials
The investigated porous media were silica gel Fluka 100 C8 (catalog number 60755 and 60759) and silica gel Fluka 100 C18 (catalog number 60756 and 60758), the industrial samples of hydrophobized silica gel from Sigma-Aldrich, and carriers of these samples after removal of the modifying layer. For the original samples and then for their carriers after removal of the modifying layer, the specific surface area (BET) [12], specific pore volume, density and pore size distribution function (BJH) [12] were determined. The measurements were carried out using a helium pycnometer ULTRAPYC 1200e and a gas sorption analyzer Autosorb IQ (Quantachrome Instruments). The results for modified samples are shown in Tables 1 and compare of pore size distribution (BJH) for modified and non-modified samples in Figure 1. Samples Fluka 100C8 (60755) and Fluka 100C8 (60759) have the same length of the modifier, but different granule size, while in Fluka 100C8 (60755) and Fluka 100C18 (60756) the granules have the same size.

| Sample          | $V_{\text{por}}$, cm$^3$ g$^{-1}$ | $S_{\text{por}}$, m$^2$ g$^{-1}$ | $<R>$, nm | $\rho$, g cm$^{-3}$ | Granule size$^1$, μm |
|-----------------|---------------------------------|---------------------------------|------------|---------------------|----------------------|
| Fluka 100C8 (60755) | 0.61                            | 326                             | 3.8        | 1.73                | 15-35                |
| Fluka 100C8 (60759) | 0.44                            | 222                             | 4.0        | 1.75                | 40-63                |
| Fluka 100C18 (60756) | 0.37                            | 142                             | 3.8        | 1.62                | 15-25                |
| Fluka 100C18 (60758) | 0.47                            | 195                             | 4.5        | 1.90                | 40-63                |

As can be seen from the presented table, the samples are similar in pore radius, but have different specific pore volume and surface area. At the same time, these values are the smallest for the C18 samples, which is connected with the longer length of the modifier molecule and, correspondingly, its volume in the pores of the medium.

$^1$Material safety data sheet
From the obtained pore size distribution functions for carriers (Fig.1), it can be seen that they are similar in samples with the same granule size. This means that only the grafted layer of the modifier can affect the differences in the characteristics of these samples. The greatest difference in the characteristics of the modified sample and carrier are observed for Fluka 100 C18 (60756), which are natural given the greater length of its modifier.

The study of the non-outflow phenomenon of a non-wetting liquid dispersed in nanoporous medium was carried out in accordance with [4] and [13].

3. Results

Figure 2 shows the intrusion-extrusion curves (with account of the compressibility of the system). As it can be seen from Fig. 2, investigated samples have the same intrusion pressure: $P_{\text{in}} \approx (145 \pm 5)$ atm. The pore size distribution functions of the samples were obtained according to the procedure described in [13]. Sample Fluka 100 C18 (60758) was excluded from the investigation because of modification layer destruction during experiments.

The smoothed function $dV(p)$ is differentiated. The resulting function is approximated by the analytic function with high accuracy ($R^2 \geq 0.998$). The analytical form of the derivative $dV(p)/dp$ allows us to obtain a function of the pore size distribution, assuming pores are cylindrical and the contact angle $\theta = 115^\circ$ (Fig. 3). It can be seen from the presented distributions that for an equal average pore radius, determined from the maximum value of the distribution functions, their half-width at half-height is different.
To observe the relaxation of the liquid in the space of media, they were filled at different time delay [4]. The fraction of the volume filled with liquid was defined as the ratio of the volume of liquid entering the pores to the total pore volume. The fraction of entrapment liquid was defined as the ratio of the volume of liquid remaining in the pores after removal of the excess pressure to the total pore volume. First, one full intrusion-extrusion cycle was done by loading and subsequent unloading of the system (t = 0 s). Further the cycle was repeated after t = 1 s. Then, the cycle was repeated with various time delays.

The results of observing the relaxation of the liquid under study for three different temperatures (20, 40, 60 °C) are presented in Figures 4.1-4.3. It can be seen that the fractions of entrapment liquid remaining in the pores θ\text{ent} for the sample C8 (60755) remains approximately constant, but for samples with a smaller granule size C8 (60755) and C18 (60756) this fraction decreases significantly with temperature, especially for sample C18.

![Figure 4.1](image1.png)

![Figure 4.2](image2.png)

![Figure 4.3](image3.png)

**Figure 4.** The time dependence for fraction of entrapment liquid for C8 (60755) (4.1), C8 (60759) (4.2), C18 (60756) (4.3) (logarithmic scale)

There may be a number of reasons for the observed differences. First, most of the liquid naturally flow from samples with a large granule size. Further, since the energy barrier of intrusion of fluid changes following the change in the surface tension of the liquid-porous interface, as the temperature increases to 60°C, it becomes negative and the liquid leave the porous medium. In turn, the interaction energy of the surface of silica gel and water depends on the modification of the surface, i.e. perhaps the thickness of the layer also has an effect. In addition, the reason can be the difference in the distribution functions of the investigated samples, and, consequently, the difference in the local configurations of empty and filled pores.

To study the size and number of pores that remain filled at different times, for a pair of samples with significant increase in temperature - Fluka 100 C8 (60755) and Fluka 100 C18 (60756) - pore size distribution functions were constructed (Fig. 6) for each intrusion cycle. The calculation method described in [13] was used. The results are presented for relaxation at 60 °C.
As can be seen from Figs. 5.1-5.2, the amount of liquid remaining in pores decreases with increasing observation time. In this case, the sizes of the pores remaining filled are different for the samples. In sample Fluka 100 C8 (60755), the liquid flows out only from small pores each time, in contrast to Fluka 100 C18 (60756), for which in each cycle of intrusion the number of filled pores decreases among pores of different sizes. Perhaps this is a consequence of the difference in the width of the pore size distribution function of the samples.

4. Conclusion
The study of non-outflow phenomenon of non-wetting liquid from the pores of a nanoporous medium was carried out by time relaxation method and dispersed non-wetting liquid distribution recovery method at different temperatures. The presented results for four commercial hydrophobized porous media Fluka 100 C18 (60756), Fluka 100 C18 (60758), Fluka 100 C8 (60755) and Fluka 100 C8 (60759) with the different thickness of the modifying layer and the size of the granules are show that the less of granules size and more narrow pore size distribution lead to decreasing of non-outflow phenomenon.

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References
[1] Borman V D, Belogorlov A A, Grekhov A M, et al., 2005 JETP 139 446.
[2] Borman V D, Belogorlov A A, Byrkin V A, et al., 2012 JETP Lett 95 579.
[3] Jaromec C P, Kruk M, Jaroniec M, 1998 J. Phys. Chem. 102 5503.
[4] Borman V D, Belogorlov A A, Tronin V N, 2015 Coll. Surf. A: Phys. Eng. Asp. 496 63.
[5] Turowski M, Morimoto T, Kimata K, Monde H, 2001 Chrom. J. 91 177.
[6] Horii J, Ralston J, Smart R, 1995 Coll. Surf. A: Phys. Eng. Asp. 97.
[7] Korosi G, Kovats E, 1981 Colloid Surf. 2 315.
[8] Chabert J B, Chapel J P, Jerard J F, et al., 1997 Langmuir 13 2271.
[9] Borman V D, Belogorlov A A, Byrkin V A, et al., 2013 JETP Lett. 114 1139.
[10] Rigby S P, Edler K J, 2002 J. Colloid Interface Sci. 250 175.
[11] Suciu C V, Iwatsubo T, Yaguchi K, et al., 2005 J. Colloid Interface Sci. 283 196.
[12] Lowell S, Shields J E, Thomas M A, et al., 2006 Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, (Springer, New York).
[13] Belogorlov A A, Borman V D, Bortnikova S A, et al., 2016 J. Phys.: Conf. S. 751.