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Relaxation of Non-Wetting Liquid Dispersed in Nanoporous Medium with Partial Filling

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Abstract. In the present work the results of experimental studies of relaxation of non-wetting liquid captured by the system of nanopores of Fluka 100 C8+C1 medium are presented. New data on dependence of filling degree on time in the process of outflow at partial initial filling have been obtained. In all the experiments carried out, fluid outflow was carried out in two stages: in the first stage of fast relaxation the characteristic time of outflow is a few seconds, in the second stage of slow relaxation the characteristic time can reach 10^4 seconds. It was found that "fast" states exist at any initial filling, and the degree of these states increases both with increasing temperature and with increasing initial filling of nanoporous medium with non-wetting liquid.

1. Introduction

Theoretical and experimental study of systems consisting of nanoporous medium immersed in non-wetting liquid has recently attracted increased attention [1-8]. These studies are stimulated by the practical use of systems: from absorption and accumulation of mechanical energy of shock, explosion and vibration [9] to objects for drug delivery [10]. These possibilities are associated with a number of unusual effects. In [11, 12] it has been established that when a certain critical degree of filling is reached and the excess pressure decreases to zero, the dispersion transition occurs and a part of the non-wetting liquid may remain in the disordered porous medium. This means that the captured non-wetting liquid is effectively in the wetting state as an ensemble of liquid nanoclusters in the disordered confinement of the porous medium, despite the action of surface forces ejecting the non-wetting liquid. Moreover, by changing the pre-filling of the pore system, it is possible to change the pore ensembles in the volume of a random medium in which the liquid is captured [11, 13]. According to [11, 13], the capture of the non-wetting liquid is caused by the effect of "interaction of attraction" of liquid clusters in neighboring filled pores. The energy of this interaction is positive, because the meniscus and the liquid-gas interface in the throats connecting the neighboring pores disappears. If the force of this attraction is greater than the force of expulsion of the non-wetting liquid, then non-outflow is possible.

Capturing of the non-wetting liquid is observed as non-outflow during the experience of a part of the liquid from the porous medium after its filling. The time elapsed after the overpressure had decreased to zero up to the moment the fraction of liquid was measured, the remaining porous medium in these works [11, 13, 14] was only a few seconds.

For the porous medium Libersorb23 and distilled water it was found [2,15], that depending on the fraction of the liquid remaining in the pores from time two sections can be distinguished. The first section corresponding to fall of a fraction of the remained liquid on times $t_{exp} \sim 1\,\mathrm{s}$

is connected with outflow of a liquid in the course of reduction of excess pressure to zero. Time of such reduction of excess pressure in these experiments made $\sim 1\,\mathrm{s}$, that is much more hydrodynamic time ($\sim 0.1\,\mathrm{s}$) outflow of a liquid from pores of granules in the size of 10 microns [16]. In this connection, such states of liquid clusters in pores, the decay time of which is the order of time of hydrodynamic outflow of liquid were called "fast" states. The decay of these states forms a new initial state of the system, which at times $> 1\,\mathrm{s}$ is decayed by the steppe law, $\theta \sim t^{-\alpha}$, where $\alpha \sim 0.1 \div 0.3$ [2,15]. The decaying states according to the steppe law correspond to "slow" states. The relaxation of "slow" states has been investigated experimentally and theoretically for an completely filled porous medium [2,15]. The behavior of "fast" states has not been previously investigated. It should be noted that in practical application of systems "non-wetting liquid - nanoporous medium" for multiple absorption of shock effects it is necessary that the system has only "fast" states and the liquid does not remain in the pores of the porous medium after removing the load. This underlines the urgency and necessity to study the behavior of "fast" states, including partial fillings. In this regard, this paper is devoted to an experimental study of the decay of "fast" states, both for the initially fully filled medium and partially filled. Fluka medium was chosen as a porous medium. This medium is characterized by a wide distribution of pores in size, so we can assume that it should be observed at partial filling of both "fast" and "slow" states at high temperatures [16].

In the present work the results of experimental studies of relaxation of non-wetting liquid captured in porous medium are presented. Experimentally new data on dependence of filling degree on time in the process of outflow are obtained. It has been found that in all the experiments carried out the outflow of the liquid passed in two stages: in the first stage of fast relaxation the characteristic time of outflow is a few seconds, in the second stage of slow relaxation the characteristic time is about $10^2 \div 10^4$ seconds. In addition, one would expect that by choosing such partial filling, when the fraction of the filled volume is smaller than the fraction that remains in the porous medium at full filling, "fast" states should not be observed. However, it was found that "fast" states are observed at any initial filling, and the fraction of these states increases both with increasing temperature and with increasing initial degree of filling of nanoporous medium with non-wetting liquid.

2. Experiment, methodology and porous medium

The previously untested Fluka 100 C_8+C_1 nanoporous medium was selected for the experiments. This medium was obtained by additional chemical modification with alkylsilane C_1 of surface of commercially available industrial design Fluka 100 C_8 (60759-50G, SigmaAldrich, USA). This allowed improving hydrophobicity of Fluka 100 C_8+C_1 surface. Chemical modification of the surface was performed in laboratory G.V. Lisichkin according to the method described in [17]. The characteristics of the nanoporous medium were obtained by low-temperature sorption of nitrogen. Specific pore volume and specific surface area are given in Table 1 for the Fluka 100 C_8+C_1 sample before and after chemical surface modification. From the table it is visible, that modification leads to insignificant change ($\sim 5\%$) of specific surface area and specific volume of pores. Additional modification of C_1 has led to a significant reduction in the fraction of unleaked liquid to 0.83 at 293 K (see Fig. 2 and [18]). The Fluka 100 C_8+C_1 is characterized by a wide pore size distribution (see Fig. 1) in comparison with the previously studied medium Libersorb 23.

The experimental work was carried out on the stand described in [19]. The research was carried out at a constant temperature, which was maintained by a thermostat. Fluka 100 C_8+C_1 nanoporous medium weighing $3.3\,\mathrm{g}$ was placed in a high pressure chamber. The high pressure chamber consists of a cylindrical body, a bushing with rubber seals, a cover and a rod. The chamber was filled with distilled water ($30\ \mathrm{cm}^3$) and a sample of Fluka 100 C_8+C_1 powder.

By moving the rod, overpressure was created in the chamber. Figure 2 shows the volume

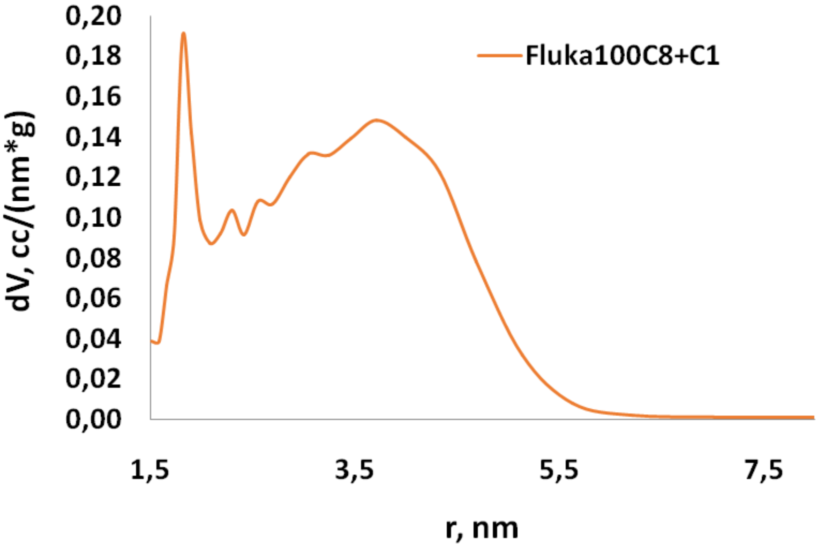

Figure 1. The pore size distribution function for Fluka100C8+C1 (nitrogen desorption, technique BJH)

Nanoporous Medium	V_{por}, cc/g	S_{por}, m^2/g	$\langle r \rangle$, nm
Fluka 100 C_8 (60759–50G)(before modification)	0.44	222	4
Fluka 100 C_8+C_1 (60759–50G*)(after modification)	0.42	211	3.8

Table 1. Characteristics of the studied porous media, measured by the method of low-temperature sorption of nitrogen. V_{por} — specific pore volume, S_{por} — specific pore surface area, $\langle r \rangle$ — average pore radius

dependence of the Fluka100 $_8$+C_1 system - water $\Delta V(P)$ on the pressure for several cycles of consecutive filling. The dependencies are given after deduction of volume change due to elastic compression of the system. The dependencies $\Delta V(P)$ with characteristic points 1-2-4 correspond to the filling of an empty pore system. The limit fill at point 4 corresponds to a full pore filling of 3.3 g of powder particles.

The value of the total volume of pores is determined by the difference in volume (V_4-V_1). In the first cycle of partial filling of the empty porous medium the pressure increase (points 0-1-2 in Fig. 2) and filling up to point 2 are made. Then the overpressure was reduced to 0 (2-2*). The re-filling is carried out after a waiting time to point 2. In this case, the dependence of $\Delta V(P)$ with characteristic points 3-2 was obtained. Then the pressure was again reduced to zero (2-2*). Such cycle was repeated for different waiting times from 1 to 10^4 with fixed partial filling. As a result of a series of experiments at a constant temperature and a fixed fraction of partial filling of a porous medium, a set of points of dependence of the fraction of the unleaked liquid on the waiting time at different partial fillings was obtained. The fraction of filled volume of pores was calculated as (V_2-V_1)/(V_4-V_1) and the fraction of unleaked liquid is (V_3-V_1)/(V_4-V_1). This set shows the effect of filling level on fast and slow relaxation of non-wetting liquid dispersed in pore space. Researches are carried out for 3 temperatures that allows to define influence of temperature on fast and slow states of system at a fixed fraction of filling of space of porous medium. In additional experiments with a chamber filled only with liquid it was shown that the change of the system volume at primary and repeated pressure change is equal to zero within the measurement error.

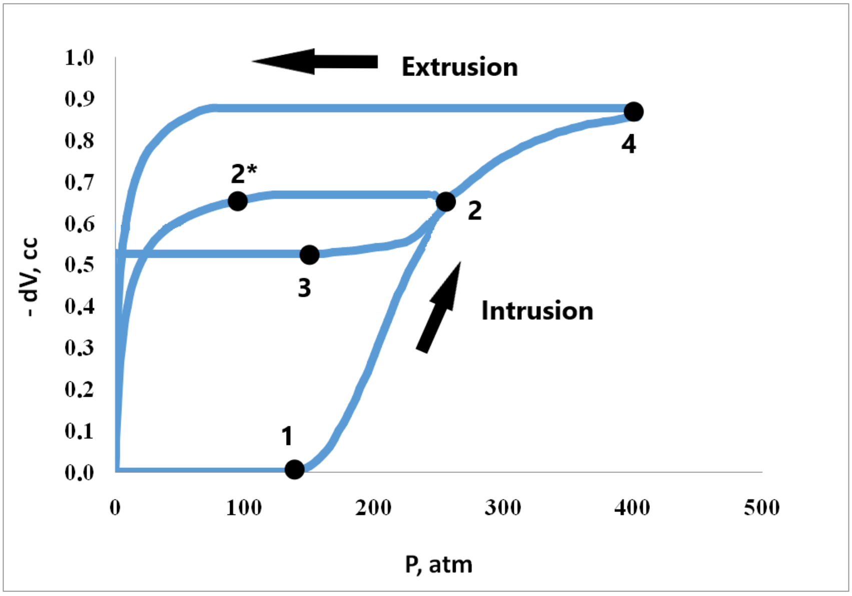

Figure 2. Volume change of the Fluka 100 C_8+C_1 system – water at a constant temperature of 293 K.

2.1. Results and discussion

The relaxation of the non-wetting liquid was investigated at three different temperatures: 293, 313 and 333 K. The initial states of the system were also different - the fractions of the initially filled volume were: 0.24, 0.54, 0.83 and 1. Figure 3 presents experimental data on the dependence on the waiting time of the fraction of the non-outflow liquid for the Fluka 100 C_8+C_1 system - water. Initial time $t = 0.1$ s is given in accordance with [16] as the time of hydrodynamic outflow in the condition of pressure decrease at elastic stress removal in the system.

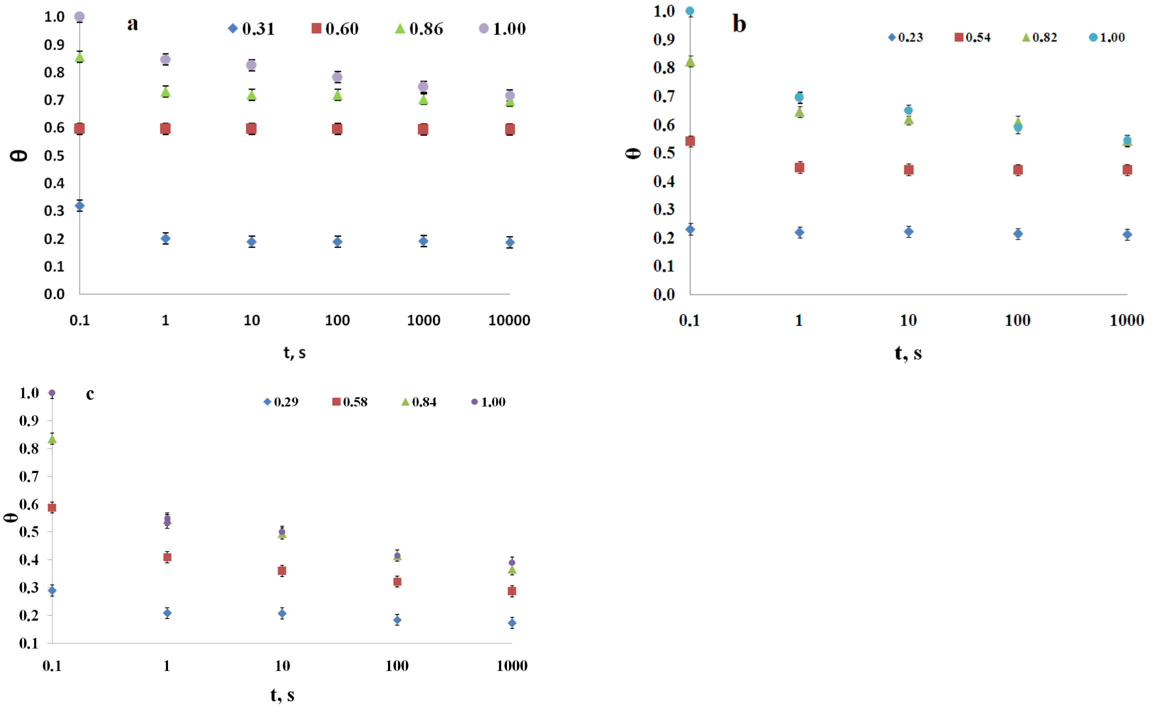

Figure 3. Dependence of the fraction of the non-outflow liquid on the time elapsed after removal of the overpressure at various initial filling levels and temperatures: 293K (a), 313K (b), 333K (c) for a porous medium Fluka 100 C_8+C_1 ($m = 3.3\,\mathrm{g}$) and water (30 cm^3)

From Fig. 3 it follows that the dependence of the fraction of the filled volume of porous medium on time can be characterized by the initial fall of the fraction of the filled volume on time $t = 0.1 - 10$ seconds with the subsequent slow fall of the fraction of the remaining liquid on time $t = 10 - 10^4$ seconds. It can be seen that the fraction of unleaked liquid depends both on temperature and initial filling. The exception is the dependence of $\theta(t)$ at initial filling 0.2–0.3 and temperatures 313–333 K and at initial filling 0.6 and temperature 293K.

Fig. 4 shows the results of the relaxation study at a fixed initial state (the fraction of the initially filled volume is given) and different temperatures: 293, 313, 333 K.

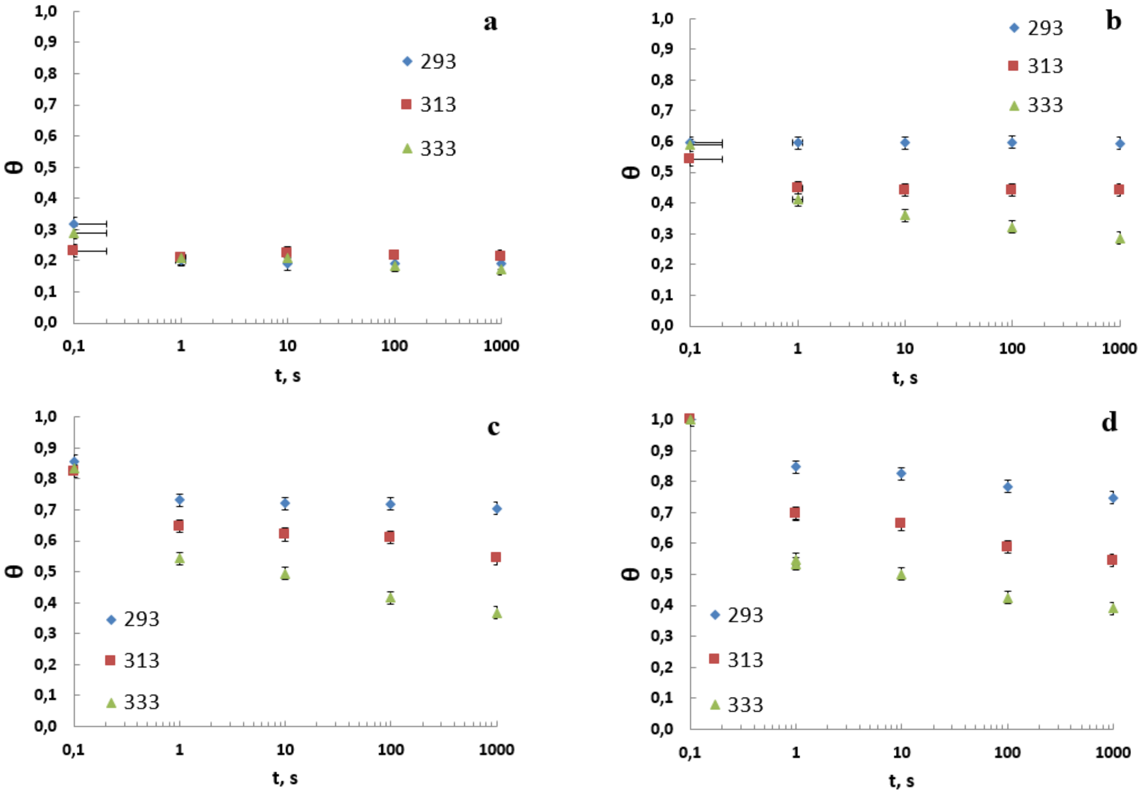

Figure 4. Dependence of the fraction of the non-outflow liquid on time at different temperatures and the fixed initial fraction of the filled volume of porous medium

Figure 4a shows that at a low degree of initial filling $\theta = 0.2 \div 0.3$ near the possible percolation threshold for the three-dimensional system θ_c $(0.16 \div 0.3)$ [20] within the measurement error of dependence at temperatures T=(313-333) coincide. At these temperatures and times (1-1000 s) neither fast nor slow outflow is observed. Liquid outflow from the porous medium is not observed even at long times (1000 s) (index $\alpha = 0.01 \pm 0.001$ in the degree law of slow relaxation, $\theta \sim t^{-\alpha}$).

At the initial filling above the percolation threshold, $\theta > 0.5$, an increase in temperature at $T > 293\,\mathrm{K}$ leads both to an increase in the fraction of fast outflow and to an acceleration of slow relaxation.

At increase of a fraction of initial filling increase in volume of fast flowing liquid (on 0.1-1 s) for three investigated temperatures (fig.4b-4d) is observed.

On the basis of the experimental data obtained, the dependence of the fraction of rapidly relaxing states on the initial degree of filling and temperature was constructed. The fraction of fast states was determined as the difference between the fraction of the initially filled volume and the fraction of the unleaked volume at the time of 1 s divided by the fraction of the initially filled volume. This dependence is shown in Fig. 5.

It can be seen from Fig. 5 that the increase in temperature and the increase in the initially filled fraction of the volume of nanoporous medium leads to the growth of the fraction of fast states, with the characteristic time of outflow of about a few seconds. At initially completely filled porous medium, the fraction of the volume of liquid that has flowed out at 293K in seconds is 0.15. It would seem that if now the initial filling of the porous medium is less than 0.85, there should be no fast states. But from Fig. 5 it is visible, that the fraction of fast states remains non-zero and at degrees of filling close to threshold value $\theta_0 \approx \theta_c$. At any initial filling level above 0.2, relaxation of the fast states is observed, the fraction of which decreases with temperature.

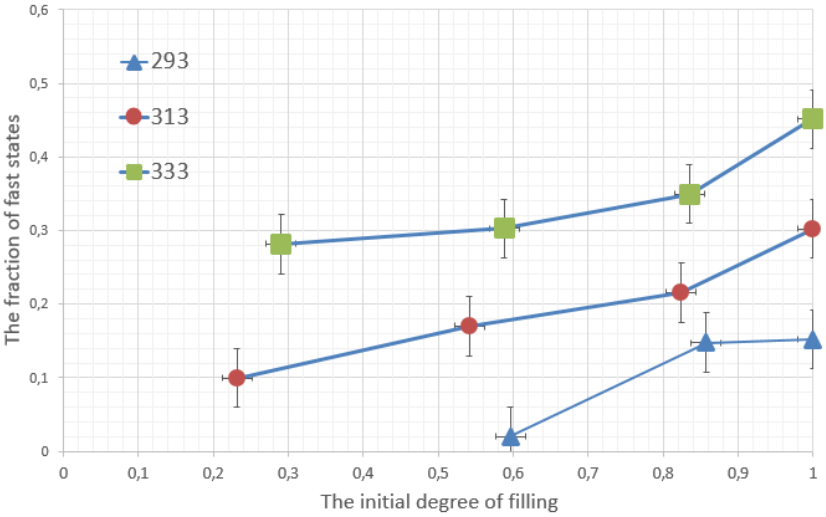

Figure 5. Dependence of the fraction of fast states on the initial degree of filling at different temperatures

So at temperature 333 K in a range of investigated degrees of filling the fraction of fast states changes a mouth 0.28 to 0.45, and at temperature 293 K from 0.2 to 0.15.

3. Conclusions

For system Fluka 100 C_8+C_1 – water "fast" states are experimentally investigated, i.e. such states of clusters of a liquid in pores from which the liquid has outflow in the course of reduction to zero of excess pressure for time 1 s. It is established that "fast" states exist at the initial filling with a large percolation threshold, and the fraction of these states increases with increasing temperature and the initial filling degree. For the system under study, the index α in the degree law $t^{-\alpha}$ of relaxation of "slow" states of non-wetting liquid captured in a porous medium increases with increasing initial degree of filling and temperature.

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