Local Configurations of Pores that Course Non-Wetting Liquid Non Outflow

S A Bortnikov, A A Belogorlov and V D Borman

1 A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 119991, Russia, Moscow, Leninsky prospect, 29
2 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute) Molecular Physics Department, 115409, Russia, Moscow, Kashirskoe highway, 31

E-mail: svetlana.sweta7@yandex.ru, AABelogorlov@ips.ac.ru

Abstract. It is known that for the most nanoporous medium - non-wetting liquid systems are observed non-outflow phenomenon. It is shown that this phenomenon may depend on many factors, one of which is a waiting time. The observed anomalously slow relaxation (non-wetting liquid outflow) caused by formation of strongly interacting states of liquid clusters in pores. Previously was shown that relaxation of such states can occur due to relaxation of metastable local configurations of filled and empty pores. In the present work the relaxation of non-wetting liquid (water) dispersed in disordered nanoporous medium (hydrophobic silica gel Libersorb 23) for 6 and 9ºC is considered. The pore size distribution functions of captured liquid for 9ºC are obtained. Some local configurations for 6 and 9ºC are analyzed and their lifetimes are defined.

1. Introduction

It is now known that nanoporous media can only be filled with a non-wetting liquid if overpressure is applied. After the overpressure has been relieved, there are phenomena such as hysteresis of intrusion and extrusion pressures and total or partial non-wetting liquid non outflow from pores. In works [1, 2] it was found that non-wetting liquid dispersed in the disordered nanoporous medium Libersorb 23 can be in two metastable states. One of these states occurs when clusters of filled pores belonging to the percolation cluster do not become empty due to the energy barrier. In the second case, clusters of filled pores are decay into separate clusters. Such decay causes blow out the passage for non-wetting liquid and non-wetting liquid cannot flow out. The effect of anomalously slow relaxation of non-wetting liquid dispersed in the pores was found in [3, 4]. It has been shown that as waiting times increase, the fracture of non-outflowed liquid decreases. The authors have shown that the reduction of the volume of liquid with time is described by the power law.

The results obtained are of great importance for the study of disordered media of various nature, such as glasses, colloids, polymers and nanoporous media [5-8]. In a number of works devoted to this problem, it has been shown that the state of such systems is no ergodic and characterized by anomalously slow relaxation, which is described either by the law or by the stretched exponent, or the power law [7-10]. Anomalously slow relaxation within the framework of the models is explained by the supposed existence and decay of metastable states of random local structures in the disordered medium.
This work continues the study of local configurations of filled and empty pores on the example of hydrophobic silica gel system Liebersorb 23 - distilled water. Earlier in [11] the results of relaxation of non-wetting liquid dispersed in disordered nanoporous medium at 6º C were obtained and pore size distribution functions of non-wetting liquid captured in pores and their evolution over time were determined in accordance with the proposed methodology. In the present work we investigated the experimental results of relaxation of non-wetting liquid dispersed in disordered nanoporous medium at 9º C and the time evolution of pore size distribution functions of non-wetting liquid captured in pores was determined. A number of possible local configurations of filled and empty pores were analyzed based on previously obtained data at 6º C and new results. On an example of some local configurations it is shown possibility of the description of effect of reduction of a non-outflowed non-wetting liquid volume from pores at temperature increase.

2. Materials and Methods
The object of our study was the system disordered nanoporous medium - hydrophobized silica gel KSK-G L23 and non-wetting liquid - distilled water. The porous medium L23 has the next characteristics: carcass density $\rho = 1.7798\pm0.0016$ g/cm$^3$, unit pore volume $V_p = 0.62\pm0.02$ cm$^3$/g, porosity of the material $\varphi = 0.52$, surface area $S_p = 199\pm7$ m$^2$/g, average pellet size ~ 10 μm, average pore radius $<R> = 5.0\pm0.2$ nm. The design and characteristics of this material described in [12]. Previously for this system was carried out experiments and obtained the experimental data of metastable states relaxation [3].

Results were obtained for the following experimental conditions: weight nanoporous medium – 4g, volume of liquid – 55 cm$^3$, temperature – 9º C and time interval between intrusion – extrusion cycles – 1, 10, 100 minutes.

The used method of obtaining the distribution of non-wetting liquid dispersed in pores for the L23-water system described in the paper [11]. In this method the cylindrical pore approximation and the Laplace equation were used for a qualitative representation of pores distribution remaining in the filled state.

3. Results and Discussion
The resulting pore size distributions for 6º C [11] and 9º C (present work) are shown in Figures 1 and 2, respectively.

![Figure 1](image-url)  
**Figure 1.** Distribution of water dispersed in nanoporous medium L23 at full filling (solid black line) (1) and remaining in pores after waiting 1 (2), 10 (3) and 100 minutes (4) at 6º C. [11]
According to the results presented in Fig. 2, outflow is observed over the entire pore size range. The distribution shows the presence of a peak in the area of small pores (~4 nm) and a pronounced peak in the area of large pores (~5 nm). The volume of the outflowed liquid increases relative to 6º C. The peak is pronounced in the area of large pores (~5 nm), which indicates that there is non-outflow of liquid mainly from large pores. Also the presence of liquid in pores of medium size (~4.5 nm) and in small pores (~4 nm) is observed.

It has been shown in [12] that the L23 environment is characterized by the number of nearest neighbors for a given pore of 3-6. On this basis, estimates of the probability of pore neighborhood of different sizes were made in [11]. What was used to analyze possible local configurations of empty and filled pores.

Estimation of metastable state energy $\Delta E$ of the considered local configurations was performed according to the work [12], where the change of liquid energy in time is described as:

$$\Delta E = -\delta\sigma (s - s_m z) + \sigma s_m (2n - z),$$  

(1)

here $\delta\sigma$ - changes in the specific surface energy of a solid body when liquid flows out, $s$ – pore surface area, $s_m$ - the surface area of the meniscus that connects the pores, $z$ the number of pores in the neighborhood, $n$ - the number of filled pores is the neighborhood.

Decomposition of this condition is possible spontaneously if $\Delta E < 0$ or the characteristic time $\tau$, if $\Delta E > 0$. According to [12], the time when the liquid flows out of the pore is determined by the ratio:

$$\tau = \tau_0 \exp(\delta A/T),$$  

(2)

where $\tau_0 \sim 10^{-1}$ c - hydrodynamic time, $\delta A = pV + \Delta E$ – the work that needs to be done to drain the liquid from the pores. If there is no overpressure in the system (p=0), $\delta A = \Delta E$.

Table 1 presents the results of calculations of $\Delta E$ and $\tau$ for a qualitative picture of five local configurations at two temperatures 6 и 9º C. Qualitative pictures of local configurations are presented, where blue spheres are filled with pores, blue - empty pores. The obtained results were correlated with experimental data [3].
Table 1. Local configurations and their characteristics

| Local configuration | T = 6°C | T = 9°C |
|---------------------|---------|---------|
|                     | Δ𝐸, eV | τ, s    | Δ𝑡₁ | Δ𝑡₂ | Δ𝑡₃ | Δ𝐸, eV | τ, s | Δ𝑡₁ | Δ𝑡₂ | Δ𝑡₃ |
| 1                   | 60, 600, 6000, eV | 600, 60, 6000, s |
| 2                   | 0.11  | 10      | yes | yes | yes | < 0  | yes | yes | yes | yes |
| 3                   | 0.2   | 4 * 10² | no  | yes | yes | < 0  | yes | yes | yes | yes |
| 4                   | 0.26  | 5 * 10³ | no  | no  | yes | < 0  | yes | yes | yes | yes |
| 5                   | 0.4   | 2 * 10⁶ | no  | no  | no  | 0.2  | 3 * 10² | no  | yes | yes | yes |
|                     | 0.29  | 1,6     | no  | no  | no  | 0.21 | 8 * 10² | no  | no  | yes | yes |
|                     |       |         |     |     |     |       |       |     |     | (*) yes – outflow, no – non outflow |

4. Conclusion
In the present work we studied experimental results of non-wetting liquid (water) relaxation dispersed in disordered nanoporous medium (Libersorb 23) at 9°C and the time evolution of pore size distribution functions of non-wetting liquid captured in pores. Several possible local configurations of filled and empty pores were analyzed based on previously obtained data for studied system at 6°C and new ones. On an example of some local configurations it is shown possibility of the description of effect of reduction of a non-outflowed non-wetting liquid volume from pores at temperature increase.

5. Acknowledgments
This work is supported by the Russian Science Foundation under grant 18-13-00398.

References
[1] Borman V D, Belogorlov A A, Byrkin V A, Tronin V N and Troyan V I 2012 JETP Lett 95 511
[2] Borman V D, Belogorlov A A, Byrkin V A, Tronin V N and Troyan V I 2013 JETP 144 1290
[3] Borman V D, Belogorlov A A, Tronin V N 2016 Phys. Rev. E 93 022142
[4] Borman V D, Belogorlov A A, Tronin V N 2016 Coll. Surf. A 496 63-68
[5] Borman V D, Belogorlov A A, Grekhov A M and Tronin V N 2014 Eur. Phys. J. B 87 249
[6] Biroli G and Garrahan J P 2013 J. Chem. Phys. 138 12A301
[7] Potuzak M, Welch R C and Mauro J 2011 J. Chem. Phys. 135 214502
[8] Borman V D, Belogorlov A A and Tronin V N 2018 J. Phys.: Conf. Ser. 1099 012026
[9] Langer J S 2012 Phys. Rev. E 85 051507
[10] Phillips J S 1996 Rep. Prog. Phys. 59 1133
[11] Bortnikova S A, Belogorlov A A, Borman V D and Tronin V N 2018 J. Phys.: Conf. Ser. 1099 012023
[12] Borman V D et al 2015 J. Exp. Theor. Phys. 148 1169