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Hydrocarbons imbibition for geometrical characterization of porous media through the effective radius approach

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Abstract

Surface energetic characterization of porous solids usually requires the determination of the contact angle. This quantity is deduced by imbibition experiments carried out in such media with high surface tension liquids. Now then, this methodology needs the geometrical characterization of the porous medium by means of the deduction of its effective radius. Normally, this is made by imbibition experiments with *n*-alkanes, liquids whose surface tension is low enough as to suppose their contact angles with the solid surface are null. However, this last procedure is not free from some criticisms. Among them, the possible influence of the imbibition velocity on the contact angle, the effect of the precursor liquid film ahead the advancing liquid front on the driving force that gives rise to the movement, or the dependence of the effective radius on the length of the hydrocarbon chain of the *n*-alkanes. In an attempt of going deeply in these questions, imbibition experiments with *n*-alkanes have been carried out in porous columns of powdered calcium fluoride. These experiments have consisted of the measurement of the increase in the weight of the columns caused by the migration of the liquids through their interstices. The analysis of their results has been carried out by means of a new procedure based on the study of the velocity profile associated to the weight increase. This analysis has permitted us to conclude that, at least in the calcium fluoride columns, the contact angle of the *n*-alkane is not influenced by the capillary rise velocity, it taking in fact a null value during the process. On the other hand, it has been also proved that the driving force of the movement is caused by the replacement of the solid–vapour interface by the solid–liquid interface that happens during the imbibition, which means that only the Laplace's pressure, and not the precursor liquid film, contributes to the development of the phenomenon. Finally, it has been compared the values of the effective radius associated to each *n*-alkane, similar values being found independently from the particular liquid employed in the experiments, fact that indicates that the porous solid can be considered as a bunch of cylindrical and parallel capillaries of the same radius.

Keywords: Imbibition; Porous media; Effective radius; Contact angle; Precursor film

1. Introduction

The imbibition consists of the spontaneous flux of liquids inside capillaries or in porous media as a result of capillary forces. This phenomenon is present in lots of processes, as the movement of water in porous soils and rocks [1], the wetting and drying of textiles [2,3], the recovery of oil from fractured reservoirs [4–8], or the filtration of water in building materials [9]. On the other hand, the imbibition is usually employed in industrial procedures developed in industries such us ceramics, pictures, textiles and pharmaceuticals. This fact gives an idea of the interest this phenomenon arouses in the present society.

The physical bases of the capillary movement were established by Washburn in an early paper published in the first years of the twentieth century [10]. There, the temporary dependence of the length the liquid goes through the capillary system was deduced. Washburn's work reveals that both the surface tension of the liquid and the contact angle with the solid are the driving quantities of the movement. Washburn's equation has been the starting point for the most of the theoretical and experimental, basic or applied, studies carried out about the imbibition. Among them, it is worth to enhance those ones that reveal the weakness of this equation at microscopic level because it neglects the viscous drag of the liquid due to dissipation near the contact line and the inertial effects [11,12], which can be especially important during the

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initial stages of the penetration processes. However, these same studies ratify its validity at macroscopic scale for describing the phenomenon of the imbibition [11,13]. With regard to the applied research, it has been made experiments, and nowadays they are being carried out, that try to determine the wetting properties of diverse systems, such as fabrics [2], sands [14], pharmaceutical substances [15,16], membranes [17] or foods [18]. Nevertheless, the major number of studies is related to the thermodynamic characterization of the surface of porous or powdered solids, the deduction of their surface free energy being the main aim of all of them [19–23].

In order to carry out the surface thermodynamic characterization of porous media, these are considered as an assembly of cylindrical and parallel capillaries of the same radius [19–22,24]. Therefore, the effective radius of its interstices must be evaluated before the deduction of the surface free energy of the solid. The determination of this parameter is normally made through imbibition experiments with low surface tension liquids, *n*-alkanes being the most common [19–22,24]. Now then, this procedure does not lack controversy, since some researches reveal diverse unsolved problems.

The first of them is related to the interpretation of the results of the imbibition experiments. Their analysis is normally carried out by assuming the contact angle of the liquid with the surface of the solid is a constant quantity during the capillary rise process, this acquiring a value similar to that one that would be established under equilibrium conditions. Precisely, the employment of the *n*-alkanes is based on this hypothesis, since it is considered that, as a result of their low surface tension, their contact angles are equal to zero. However, some research studies indicate this parameter could show a dynamic behaviour [25–30], it changing continuously during the experiments. If it was true, Washburn's equation would not be valid, its modification being necessary in order to take this circumstance into account. Now then, this dependence of the contact angle with the velocity of the liquid has been found in experiments where the rise of the liquid was forced in capillaries, or the movement of drops was induced on flat solid surfaces. Whether imbibition is affected by this effect continues being unknown, since one could wonder how the cause of the movement – the contact angle – could be modified by its proper consequence – the imbibition velocity.

The second lack concerns with the driving force that gives rise to the migration of the liquid through the capillaries of the solid. At the present, there are two physical models for describing the flow of the liquid in porous media. One of them assumes the movement is caused by the reduction of the free energy of the system due to the continuous replacement of the solid–vapour by the solid–liquid interface. It means that the imbibition is driven by the pressure difference, given by Laplace's equation, between the sides of the meniscus the liquid shapes in the capillaries of the solid [19,22,24]. The second of the models considers, together with the former contribution, the possible influence of the liquid film that would precede the advancing liquid front [20,21]. The formation of this film could cause an additional reduction of the free energy of the system that could favour the development of the imbibition. Which of these two physical models has to be chosen to describe the capillary processes is not clear enough, since, although the film has been observed in the spreading of liquids on solid surfaces [26], there is not any outstanding reason as to distinguish if it contributes to the movement or if it is only an additional consequence of the global development of the proper phenomenon.

Finally, it has to be noticed that, despite the fact the *n*-alkanes are liquids commonly utilized for the deduction of the effective radius of the porous media, the found value of this parameter could depend on the length of the chain of the hydrocarbons employed in the imbibition experiments [14,20,23,31], which would invalidates the hypothesis that assumes the porous medium is similar to a bunch of identical capillaries.

In the light of these questions, and in an attempt of going deeply in some of the mentioned aspects, imbibition experiments with *n*-alkanes have been carried out in porous columns made with powdered calcium fluoride. These experiments have consisted of the measurement of the increase in the weight of the porous columns caused by the spontaneous migration of the liquids through their pores. The analysis of their results has been done through a new approach based on the study of the velocity profile associated to the weight increase [32], which gives more information than the deduced from the study of the direct variation of the experimental weight increase against the time. We hope it to be useful to deduce some conclusion that throws some light on the subject raised before.

2. Experimental

Imbibition experiments have been carried out using glass tubes of the same diameter (4.95 ± 0.05 mm) and length (73.30 ± 0.05 mm). Prior to use, the tubes were acid-cleaned, washed with water several times and, once dried, one of their ends sealed by a filter paper disc. The glass tubes were filled with identical amounts (1.0005 ± 0.0005 g) of powdered sintered calcium fluoride (Merck, purity 99.5%) introduced inside it by hand. Previously, calcium fluoride had been dried into an oven at 150 °C overnight. The B.E.T surface area (N_2, 77 K) of the stored sample was 4.64 ± 0.03 m^2 g^{-1}. The mean particle size, calculated from the B.E.T surface area and the density of the material (3.18 g cm^{-3}), was 2 μm. To obtain a good experimental reproducibility, the filled glass tubes where mechanically tapped by an automatic controlled-frequency device placed on their bottom base. To assure the uniform packing of the columns, a massive metallic rod was placed on the top of the powdered solid inside the tube. This tapping was performed continuously until the solid reached the same length in every glass column (35.3 ± 0.3 mm). The liquids employed in the capillary rise experiments were *n*-octane (Fluka, purity $>$ 99.5%), *n*-decane (Fluka, purity $>$ 98.0%), *n*-dodecane (Fluka, purity $>$ 98.0%), *n*-tetradecane (Fluka, purity $>$ 99.0%) and *n*-hexadecane (Sigma, purity $>$ 99.0%). Their surface tensions, viscosities and densities at 20 °C are given in Table 1 [19,33].