

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

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Received 12 January 2006; received in revised form 31 January 2006; accepted 31 January 2006

Available online 7 March 2006

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.

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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 as 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 invalidate 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 m² 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 were 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].

Table 1
Values of surface tension [19], viscosity [33] and density (as given by suppliers) of the *n*-alkanes

	γ (10^3 J m $^{-2}$)	η (10^3 Pa s)	ρ (kg m $^{-3}$)
<i>n</i> -Octane	21.6	0.546	700
<i>n</i> -Decane	23.8	0.907	730
<i>n</i> -Dodecane	25.35	1.492	748
<i>n</i> -Tetradecane	26.6	2.322	762
<i>n</i> -Hexadecane	27.5	3.451	773

The imbibition experiments have consisted of the measurement of the increase in the weight of the porous columns caused by the imbibition. This weight increase was measured with the aid of an automatic measurement device previously described [32,34–38], similar to those used by other authors [2,17,22,39]. Basically, it was a digital balance (Mettler AE240) with the porous columns hung in the below-the-balance weighing facility. The glass receptacle with the liquid used in the experiment was placed on a mobile stage. This platform was lifted up at very low speed by means of a computer controlled Oriol motor just until the free surface of the liquid contacted with the bottom of the glass tube. Weight–time data acquisition by the computer started before contact between the liquid and the porous column was achieved in order to avoid the loss of information at the very beginning of the experiment. It finished when the porous column was saturated with liquid, indicated by a constant weight value. Finally, the liquid mass inside the porous media was determined as the weight after breaking the contact between the column and the free surface of the liquid. The imbibition experiments were carried out at 20 ± 0.5 °C, and they were repeated done at least by quadruplicate for each one of the liquids.

3. Analysis of results and discussion

To illustrate the experimental measurements, the curves associated to one of the experiments carried out with each liquid have been plotted in Fig. 1. These results are shown as the experimental weight increase, w_{exp} , versus the penetration time, t . As seen, the highest penetration rate was obtained for *n*-octane and the lowest for *n*-hexadecane. This is the consequence of a larger increase in viscosity than in surface tension of the *n*-alkanes (Table 1) [19,20,40]. On the other hand, the maximum weight registered by the digital balance increases with the chain length of these liquids, effect that is caused by the increment in their densities.

As we proved in previous works [34–38], the experimental increase in the weight is a combination of the contributions caused by the two simultaneous processes that happen during the experiments: the filling of the interstices of the porous column by the liquid, $w_{\text{imb}}(t)$, and the formation and subsequently evolution of a meniscus at the bottom of the glass tube when it is put in contact with the free surface of the liquid, $w_{\text{cont}}(t)$. Therefore, w_{exp} can be written as:

$$w_{\text{exp}}(t) = w_{\text{imb}}(t) + w_{\text{cont}}(t) \quad (1)$$

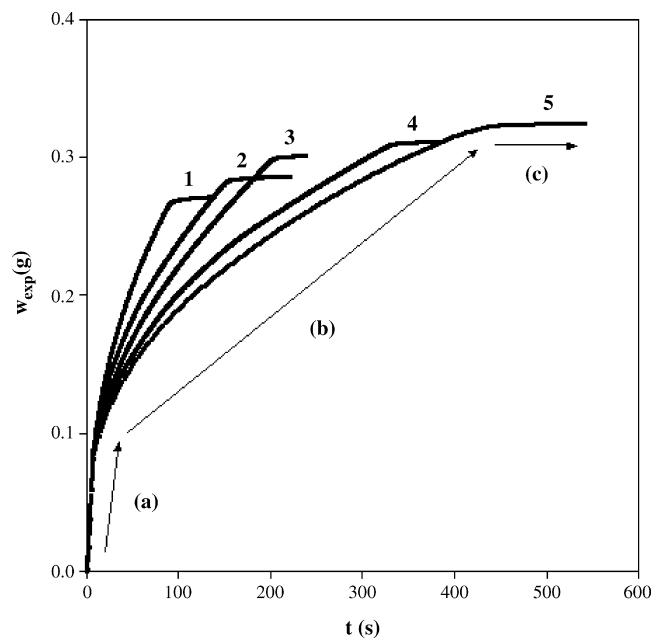


Fig. 1. Experimental weight vs. time for one experiment carried out with each *n*-alkane: (1) *n*-octane, (2) *n*-decane, (3) *n*-dodecane, (4) *n*-tetradecane and (5) *n*-hexadecane.

Now then, three different sections can be observed in the experimental curves shown in Fig. 1, depending on the relative importance of these two contributions. The first of them, marked as (a) in the corresponding to the experiment carried out with *n*-hexadecane, is characterized by a fast and strong weight increase during a short temporary interval. This fact gives an idea of the effect of the meniscus placed at the bottom of the glass tubes. As the force that causes this weight depends exclusively on the external radius of the glass tubes, which is identical for all the columns, and on the surface tension of the liquids, which takes similar values (Table 1), the section (1) associated to each *n*-alkane appear overlapped, they being practically indistinguishable [41]. In the section (b), a smooth increase in the weight is observed. This behaviour is caused by the decelerated movement of the liquids through the pores of the columns. As seen in Fig. 1, the section (b) of each *n*-alkane is distinguished perfectly from the rest, which reflects the influence of the surface tension and the viscosity of these liquids on the imbibition. Finally, the section (c), where the increase in the weight is practically zero, reveals the saturation state that the porous solid reaches at the end of the imbibition.

It has to be noticed that, despite the fact that the meniscus evolution depends on the imbibition as a result of the decreasing in the level of the liquid contained in the receptacle [36], its corresponding weight increase, $w_{\text{cont}}(t)$, reaches a constant value, w_{cont} , after some unknown instant t' from the starting of the experiments [2,34,36,42]. The value of this parameter is calculated as the difference of the maximum weight registered at the end of the experiments and the weight value found when the contact between the porous columns and the free surface of the liquid is broken. This fact is the key that allows to isolate the increase in the weight caused by the

capillary rise, and so to carry out its analysis on the basis of the study of its velocity profile. Taking this into account, $w_{imb}(t)$ can be deduced as

$$(t \geq t') \quad w_{imb}(t) = w_{exp}(t) - w_{cont} \quad (2)$$

Nevertheless, as t' is a priori unknown, the weight differences of the right-hand side of Eq. (2) have been calculated from the beginning of the experiments. Once it has been done, the velocity profile can be derived by differentiating every pair of data ($w_{exp}(t) - w_{cont}, t$) through computer routine based on Savitzky-Golay algorithm [43]. As an example, the rate profile so obtained for one of the imbibition experiments carried out with *n*-octane is shown in Fig. 2 as a function of the inverse of these differences.

In a recent paper we explained in detail the physical meaning of the rate profile shown in Fig. 2 [32]. As laid down in that paper, the negative values of the weight differences ($w_{exp}(t) - w_{cont}$) correspond to the first instants of the experiment when the experimental weight is lower than the contribution due to the meniscus, $w_{exp}(t) < w_{cont}$. Section (1a) reflects the sudden acceleration caused by the initial contact between the porous column and the free liquid surface in the container. This acceleration is associated both with the force of the meniscus on the bottom of the glass tube and the initial impulse occasioning the migration of the liquid through the pores of the solid. Nevertheless, this initial impulse is counteracted immediately by the imbibition and the evolution of the meniscus shape. Despite this fact, acceleration continues being positive in section (1b), but it reaches negative values starting from section (2). This fact means that the initial impulse that originates the movement has been completely neutralized. Once the imbibition is slow enough, changes in the meniscus shape gets negligible and its contribution to the experimental weight increase acquires a constant value, w_{cont} . Thus, the behaviour

shown by the velocity profile in section (3) is caused exclusively by the imbibition. Finally, section (4) reports the end of the capillary movement when the porous medium reaches the saturation state.

The section (3) shows a linear relationship between the velocity and the inverse of the weight increase caused by the imbibition. Therefore, the next equation can be established between these two quantities [32]:

$$\frac{dw_{imb}(t)}{dt} = \frac{B}{w_{imb}(t)} \quad (3)$$

where the slope B takes into account the liquid viscosity, η , the effective radius R of the interstices in the solid on the assumption that its pores are considered as an assembly of identical parallel cylindrical capillaries, and the free energy reduction per surface unit accompanying the imbibition process Δg :

$$B = \left(\frac{w_{imb-max}}{h_{max}} \right)^2 \frac{R\Delta g}{4\eta} \quad (4)$$

In this equation, $w_{imb-max}$ represents the maximum weight increase caused by the imbibition and h_{max} is the maximum height that liquid reaches in the porous columns, which is equal to the length of the solid inside it.

The first conclusion that can be derived from the analysis of the rate profile shown in Fig. 2 is related to the value that takes the free energy reduction per surface unit, Δg , during the imbibition experiments. This parameter is normally understood as the driving force that causes the rise of the liquid through the pores of the solid. As it is directly proportional to the slope B of the straight-line section (3), it can be concluded that the free energy reduction per surface unit, Δg , takes a constant value during the time the capillary rise lasts. This means that the movement state of the liquid through the pores of the solid does not depend on the velocity of the imbibition. Now then, if we take into account the expression that assumes the Laplace's pressure is the cause of the rise of the liquid [15,19,22,24,44–46],

$$\Delta g = \gamma_L \cos \theta \quad (5)$$

where γ_L is the surface tension of the liquid and θ is the contact angle on the solid surface, or the equation that considers the movement is also favoured by the energetic reduction caused by the liquid film ahead the advancing liquid front [20,21,47],

$$\Delta g = \gamma_L \cos \theta + W_A - W_C \quad (6)$$

where W_A and W_C represent the adhesion work of the liquid to the solid surface and the cohesion work of the liquid, respectively, we can conclude that, at least for the imbibition of *n*-alkanes in porous columns of calcium fluoride, the contact angle is not a quantity that changes with the rate of the imbibition, since it is only a function of quantities ($\Delta g, \gamma_L, W_A$ and W_C) that remain constant during the capillary movement.

With regard to the second and third problems raised in the introduction section, the choice of the physical model that

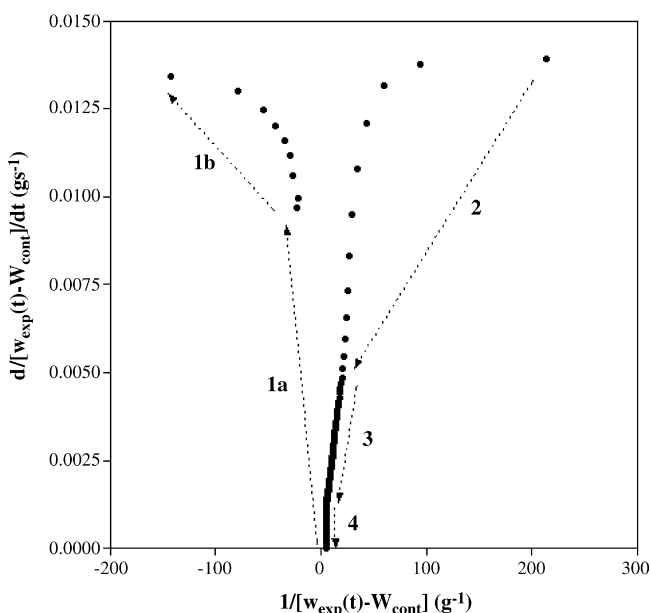


Fig. 2. Velocity profile associated with the weight differences, $w_{exp}(t) - w_{cont}$, for one experiment with *n*-octane.

Table 2

Average values of the parameters B and A of Eqs. (3) and (8), respectively, as well as values of the effective radius, R , together with their average, deduced from the analysis of the imbibition experiments with n -alkanes

	B ($10^{10} \text{ kg}^2 \text{ s}^{-1}$)	A ($10^6 \text{ m}^2 \text{ s}^{-1}$)	R (10^6 m)
n -Octane	2.52 ± 0.37	6.33 ± 0.88	0.64 ± 0.09
n -Decane	1.88 ± 0.04	4.37 ± 0.10	0.67 ± 0.02
n -Dodecane	1.30 ± 0.29	2.96 ± 0.73	0.70 ± 0.17
n -Tetradecane	1.00 ± 0.20	2.08 ± 0.39	0.73 ± 0.14
n -Hexadecane	0.62 ± 0.16	1.24 ± 0.28	0.62 ± 0.14

Average value of the effective radius: $0.67 \pm 0.04 \times 10^{-6} \text{ m}$.

describes adequately the capillary rise of the n -alkanes and the possible dependence of the average radius of the porous solid on the length of the hydrocarbon chain of the n -alkanes, in order to approach them, let us calculate the free energy reduction per surface unit, Δg , associated to the imbibition experiments. As deduced, this parameter is a constant, related to the slope B of Eq. (3), which characterizes the imbibition. Therefore, such slope has to be deduced before. This can be done by fitting the linear section (3) of the velocity profile shown in Fig. 2 to the equation that describes its behaviour (Eq. (3)). The average values of this parameter so obtained, which gives information about the geometrical features of the porous medium as well as about the solid–liquid interactions that causes the imbibition, are in Table 2.

On the other hand, a new coefficient can be defined like:

$$A = \frac{R\Delta g}{4\eta} \quad (7)$$

which can be determined from the slope B as

$$A = \left(\frac{h_{\max}}{w_{\text{imb-max}}} \right)^2 B \quad (8)$$

where h_{\max} and $w_{\text{imb-max}}$ have the meaning previously established. Again, the average values of the parameter A for the experiments carried out with the different n -alkanes are in Table 2. As might have been expected, a decreasing behaviour in these two set of values, A and B , is observed as the length of the hydrocarbon chain increases, which is in agreement with the experimental results shown in Fig. 1.

Next, let us assume that the n -alkanes are liquids that totally wet the surface of the calcium fluoride. This hypothesis is based on the fact that they are liquids with low surface tension. In this case, the contact angle should be equal to zero. On the other hand, let us consider Eq. (5), which proposes the imbibition is driven by the pressure difference established between the sides of the meniscus the liquid shapes on the capillaries of the solid. If imbibition experiments verified these two conditions, the quotient between the values of the coefficient A defined by Eq. (7) for two particular n -alkanes should be equal to the

Table 3

Values of the quotients given by the left and right hand side of Eq. (9) for each pair of n -alkanes

	$\frac{A_i}{A_j}$	$\frac{\gamma_L \eta_j}{\gamma_j \eta_i}$
n -Octane/ n -decane	1.45 ± 0.23	1.51
n -Octane/ n -dodecane	2.14 ± 0.82	2.33
n -Octane/ n -tetradecane	3.04 ± 0.99	3.45
n -Octane/ n -hexadecane	5.10 ± 1.86	4.96
n -Decane/ n -dodecane	1.48 ± 0.40	1.54
n -Decane/ n -tetradecane	2.10 ± 0.44	2.29
n -Decane/ n -hexadecane	3.52 ± 0.88	3.29
n -Dodecane/ n -tetradecane	1.42 ± 0.62	1.48
n -Dodecane/ n -hexadecane	2.39 ± 1.13	2.13
n -Tetradecane/ n -hexadecane	1.68 ± 0.69	1.44

quotient between the surface tension and the viscosities of these liquids:

$$\frac{A_i}{A_j} = \frac{\gamma_{L_i} \eta_j}{\gamma_{L_j} \eta_i} \quad (9)$$

the subscripts i and j denoting the n -alkanes of shorter and larger length, respectively. Table 3 contains the ratios of the left and right hand side of Eq. (9) for each possible pair of n -alkanes. As it is seen, the two set of values are agree each other, which leads to conclude that, on the one hand, the porous columns can be considered a bunch of identical capillaries, and, on the other hand, the adequate description of the flow of the n -alkanes through the interstices of the solid is achieved by assuming that the free energy reduction caused exclusively by the replacement of the solid–vapour interface by the solid–liquid interface is the driving force of the movement. This fact means that the change of the free energy of the system due to the precursor film ahead the advancing liquid front does not favour the movement but it is entirely burned in the film region, it being able to be transformed directly into heat [26].

Anyway, let us take up again the problem related to the determination of the effective radius of the porous solid. As just proved above, the n -alkanes rise through the porous columns of calcium fluoride in such a way that their contact angles take null values. So, the numerical value of the radius can be determined by joining together Eqs. (5) and (7):

$$R = \frac{4\eta A}{\gamma_L} \quad (10)$$

In order to check if Eq. (10) permits to deduce a unique value of the effective radius independently from the n -alkane, the numerical value of such radius for each one of them has been deduced from the coefficient A shown in Table 2. This set is also in Table 2 as well as its average. As it is seen, they are similar in spite of the fact that they come from experiments carried out with different n -alkanes. On the other hand, Eq. (10) predicts a rectilinear relationship between the parameter $4\eta A$ and the surface tension of the liquid, γ_L , its slope being precisely the value of the effective radius of the porous solid. In order to see if the imbibition experiments verify this behaviour, we have drawn in Fig. 3 the values of this parameter, deduced from Tables 1 and 2, as a function of the surface tension of the n -

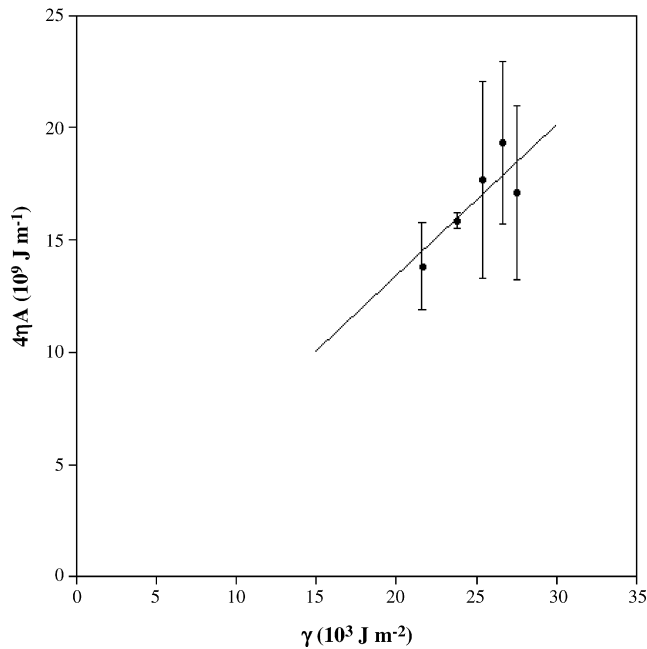


Fig. 3. Effective radius determination through the linear fitting of parameter $4\eta A$ against the surface tension, γ , in agreement with Eq. (10).

alkanes. Besides, this set of data has been fitted to a straight-line relationship. As it is seen, the goodness of such mathematical fitting confirms that the effective radius of the porous medium can be determined through its slope, it giving a numerical value equal to $0.67 \pm 0.02 \mu\text{m}$, the same than that one shown in Table 2. All of this proves that the calculation of the effective radius does not depend on the n -alkane utilized in the experiments, but it is a feature both the size of the solid particles and the packing procedure employed to make the porous columns.

Finally, let us consider Eq. (6) in order to study what happens if it is assumed that the precursor film can also contribute to the movement. In agreement with the physical bases that define this model, this equation can take four different expressions depending on the features of the imbibition experiments and on the liquids employed [20,21,47]:

1. Liquids that form contact angles between 0° and 90° on the solid surface:

(i) If the solid surface is precovered by a duplex liquid film, the adequate equation is:

$$\Delta g = \gamma_L \cos \theta \quad (11)$$

(ii) If the duplex film is not placed on the solid surface previously to the imbibition, then the proper Eq. (6) describe this case.

2. Liquids that totally wet the solid:

(i) If the duplex film covers the solid surface before the imbibition, then

$$\Delta g = \gamma_L \quad (12)$$

(ii) If this duplex film is not formed on the solid surface, Eq. (6) is reduced to:

$$\Delta g = W_A - W_C \quad (13)$$

The last equation, which should be employed to describe the imbibition of the n -alkanes in the porous columns of calcium fluoride if the possible influence of the precursor film was considered, means that the capillary rise is only driven by the difference between the work of adhesion, W_A , and the work of cohesion, W_C . This equation indicates that the contact angle of the n -alkane with the solid takes a value equal to 90° despite the fact these liquids completely wet the solid surface [48]. The reason adduced to justify this hypothesis is that, in a porous medium, if the solid surface has not been covered previously by a duplex film of n -alkane, the kinetics of the capillary rise is such that the precursor film is not formed enough ahead of the advancing front [21]. On the other hand, if is taken into account that the difference given by the right-hand side of Eq. (13) is the work of spreading, W_S , which is written in terms of the surface tension of the liquid, γ_L , the surface free energy of the solid, γ_S , and the free energy of the solid–liquid interface, γ_{SL} , as [49]:

$$W_S = \gamma_S - \gamma_{SL} - \gamma_L \quad (14)$$

and that the n -alkanes are liquids that only interact by means of Lifshitz–van der Waals forces [19], Eq. (13) assumes the more simplified form:

$$\Delta g = 2[(\gamma_S^{LW} \gamma_L^{LW})^{1/2} - \gamma_L^{LW}] \quad (15)$$

where γ_S^{LW} is the Lifshitz–van der Waals component of the surface free energy of the solid and γ_L^{LW} is the surface tension of the liquid. Taking into account all of these considerations, the parameter A defined by Eq. (7) can be written as

$$A = \frac{R}{2\eta} \gamma_L^{LW} \left[\left(\frac{\gamma_S^{LW}}{\gamma_L^{LW}} \right)^{1/2} - 1 \right] \quad (16)$$

Therefore, if the imbibition experiments verified this model and if the solid could be considered as a bunch of identical capillaries, the quotient between the values of the coefficient A defined by Eq. (7) for two particular n -alkanes should be equal to:

$$\frac{A_i}{A_j} = \frac{\eta_j \gamma_{L_i}^{LW} \left[\left(\frac{\gamma_S^{LW}}{\gamma_{L_i}^{LW}} \right)^{1/2} - 1 \right]}{\eta_i \gamma_{L_j}^{LW} \left[\left(\frac{\gamma_S^{LW}}{\gamma_{L_j}^{LW}} \right)^{1/2} - 1 \right]} \quad (17)$$

Finally, if we consider the results given in Table 3, where it was shown that the quotients A_i/A_j take the numerical values predicted by Eq. (9), Eq. (17) yields to

$$\frac{(\gamma_S^{LW})^{1/2} - (\gamma_{L_i}^{LW})^{1/2}}{(\gamma_S^{LW})^{1/2} - (\gamma_{L_j}^{LW})^{1/2}} = 1 \quad (18)$$

condition that could be only verified if the Lifshitz–van der Waals component of the surface tension of the two n -alkanes were equal. However, it is well-known that the surface tensions of the n -alkanes are different each other (see Table 1). This contradictory fact indicates again that, as de Geenes pointed out elsewhere [26], the free energy reduction associated to the liquid film is burned entirely in the film region, it being possibly

transformed directly into heat. Thus, at least for describing the imbibition of the *n*-alkanes in the porous columns of calcium fluoride, the hypothesis assumed before has to be rejected and it must be accepted that the imbibition is exclusively due to the Laplace's pressure.

4. Summary

Geometrical characterization of porous media is normally carried out through the average radius approach. It consists of the determination of the equivalent radius of the pores of the solid, this being considered as a bunch of identical, parallel and cylindrical, capillaries. The experimental procedure is based on the imbibition with low surface tension liquids like the *n*-alkanes. As hypothesis, it is assumed that these liquids totally wet the surface of the solid, which means that their contact angles take null values. However, this approach arouses diverse criticisms. Among them, the possible influence of the imbibition velocity on the contact angle, the effect of the precursor liquid film placed ahead the advancing liquid front on the driving force that causes the movement, or the dependence of the numerical value of the radius with the chain length of the hydrocarbons. If these questions were true, the experimental procedure would have to be modified to take them into account. In order to check them, we have carried out an experimental work where it has been studied the imbibition of five saturated hydrocarbons in porous columns made with powdered calcium fluoride. The experiments have consisted of the measurement of the weight increase caused in the columns due to the migration of the liquids inside their interstices. The analysis of the results has been carried out by a new method based on the study of the velocity profile associated to the weight increase. By the identification of the section of the profile caused only by the imbibition, and the following deduction of the free energy reduction per surface unit from it, it has been concluded that the contact angle is a quantity that remains constant, and equal to zero, during the capillary rise of the *n*-alkanes. Besides, it has been proved that the precursor liquid film ahead the advancing liquid front does not cause any effect on the imbibition, the Laplace's pressure being the only responsible for the movement. This fact means that the free energy change caused by the liquid film is entirely burned in the film region, it being possible transformed directly into heat. Finally, the average radius of the pores of the calcium fluoride columns has been deduced from the experiments carried out with each *n*-alkane. The comparison of these values has allowed establishing that effectively the porous solid can be assumed as a set of capillaries characterized by a same value of the radius.

Acknowledgments

This work has been carried out under "Ministerio de Ciencia y Tecnología: DCI-FEDER" Project No. BFM2002-01738, which is gratefully acknowledged. Also, JAAB thanks the "Valhondo Calaf" foundation for his doctoral fellowship.

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