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On the constancy of the free energy reduction caused by imbibition in porous media

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Abstract

The presents study brings to light that the free energy reduction per surface unit, Δg, which is considered as the driven force that leads the imbibition of liquids into porous media, does not show any dynamic behaviour during the rise of the liquids. Therefore, this quantity is a constant parameter that characterized the capillary rise processes. As a consequence, it has been also proved that, because of this fact, the liquid flow verifies the hypotheses that are needed in order to the results of the imbibition experiments can be analysed by Washburn's equation. This study has been carried out by means of a new methodology based on the analysis of the velocity profile associated to the increase in the weight of the porous medium caused by the rise of the liquid.

Keywords: Imbibition; Capillary rise; Free energy; Porous media; Washburn's equation

1. Introduction

Capillary rise of liquids into porous media is the base of some experimental techniques employed to carry out the thermodynamic characterization of these solids. In these methods, their solid surface free energy can be deduced from the free energy change of the system caused by the replacement of the solid–vapour interface by the solid–liquid interface along the imbibition. Two experimental methods have been broadly employed: the first one, related to the study of the length advanced by the liquid inside the interstices of the porous medium [1–14]; the other one, consisting of the evaluation of the weight increase caused as a consequence of the filling of the pores [7,10,11,14–21]. This last experimental technique was proposed in order to avoid the difficulties of measurements that arise when the liquid front was not visible or did not reflect the whole progression of the fluid into the porous solid.

In both cases, the experimental results have been described by means of Washburn's equation [22] expressed in terms of adequate measurable parameters—distance and time or weight and time. As it is well known, this equation can be written as [2–5,12]

$$h^2 = \frac{R\Delta g}{2\eta} t \tag{1}$$

if the length the liquid front, h, goes through the porous medium is measured against the time, t, or, as [7,8,10,11,14]

$$w_{\mathrm{imb}}^2 = \left(\varepsilon\rho\pi R'^{\,2}\right)^2 \frac{R\Delta g}{2\eta} t \tag{2}$$

if the interest of the study is focused on the measurements of the imbibition increase in the weight, w_{imb}, versus the time. In these equations, η and ρ are the viscosity and the density of the liquid, respectively, R being the effective radius of the porous solid considered as a bunch of identical, parallel and cylindrical capillaries. On the other hand, in Eq. (2), $\pi R'^2$ represents the transversal section of the porous solid. As it is seen from Eqs. (1) and (2), Washburn's equation relates the decrease of the free energy per surface unit accompanying the capillary rise process, Δg, to the proper quantities of the experiments, the imbibition length or the weight increase. This parameter, considered as the driven force responsible

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for the movement and that takes into account the interfacial interactions, is given in terms of the solid–vapour, γ_{SV}, and solid–liquid, γ_{SL}, interfacial free energies as

$$\Delta g = (\gamma_{SV} - \gamma_{SL}) \quad (3)$$

if it is considered that it is caused by the continuous disappearance of the solid–vapour interface and substituted by a solid–liquid interface [23]. However, if Young's equation [24] is introduced into Eq. (3), it comes as

$$\Delta g = \gamma_{LV}\cos\theta \quad (4)$$

where θ is the solid–liquid contact angle, which allows to understand the movement of the liquid as caused by the pressure difference—Laplace's pressure—established across the meniscus that the liquid shapes on the capillaries of the solid [1,7,11]. However, some researches [2–5] assume that the precursor film that precedes the liquid front during its advance also may contribute to the flow movement [25]. In this situation, the free energy reduction per surface unit, Δg, can be written as [2–5]

$$\Delta g = \gamma_{SV} - \gamma_{SL} + \Pi_e \quad (5)$$

where Π_e, called the surface pressure, is the additional decrease in the surface free energy of the solid because of the precursor film. If Young's equation [24] is considered again, and it is taken into account that the surface pressure is given by the difference between the adhesion work, W_A, and the cohesion work, W_C, Eq. (5) is transformed as

$$\Delta g = \gamma_{LV}\cos\theta + (W_A - W_C) \quad (6)$$

which constitutes an alternative expression for the driven force that produces the imbibition [2–5].

As it is seen from Eqs. (3), (4), (5) and (6), these two physical models basically differ in their considerations about the contributions leading to the free energy reduction that causes imbibition. So far this difference, they utilize the Washburn's equation to describe the experimental imbibition results. Its deduction is carried out by assuming a quasi-steady process, a Newtonian liquid with laminar flow and neglecting inertia effects. Thus, from Poiseuille's law [26], the differential equation that governs the movement of a liquid into a capillary can be deduced, in terms of the capillary rise length, as [7,22]

$$\frac{dh}{dt} = \frac{R\Delta g}{4\eta}\frac{1}{h} \quad (7)$$

or as

$$\frac{dw_{imb}}{dt} = \left(\varepsilon\rho\pi R'^{2}\right)^2 \frac{R\Delta g}{4\eta}\frac{1}{w_{imb}} \quad (8)$$

if the increase in the weight of the porous solid is the measurable quantity [7].

The integration of Eqs. (7) and (8), which leads to the well-known Washburn's Eqs. (1) and (2), is possible by accepting that the free energy reduction per surface unit, Δg, is a constant parameter characteristic of the imbibition process. However, this hypothesis has not been proved experimentally yet. This one is precisely the aim of this paper. For this purpose, imbibition experiments with n-alkanes have been carried out in columns made from powdered calcium fluoride, and analyzed through the rate profile associated to the weight increase during the capillary rise experiments, employing Eq. (8) that describes the velocity of the capillary rise.

2. Experimental

Imbibition experiments were carried out with porous columns made from calcium fluoride powder (Merck, purity 99.5%) introduced inside cylindrical glass capillaries. The imbibition liquids 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%), n-hexadecane (Sigma, purity >99.0%), water (doubly distilled and deionized from a Q-Millipore system), formamide (Fluka, purity >98.0%), diiodomethane (Fluka, purity >98.0%) and α-bromonaphthalene (Panreac, purity >97%). All the measurements were carried out at 20±0.5 °C.

The glass capillaries, selected with identical inner diameter (4.95±0.05 mm) and length (73.30±0.05 mm), were acid-cleaned and washed several times with water before their use. Once they were completely dried, one of their ends was sealed by means of a filter paper disc in order to prevent the wastage of the powdered solid and to allow the imbibition.

For the elaboration of the porous columns, identical amounts of powdered calcium fluoride (1.0005±0.0005 g), previously dried overnight in an oven at 150 °C, were introduced with a funnel into the glass capillaries. Packing procedure consisted of mechanical tapping of the lower end of the glass tubes by means of an automatic controlled-frequency device. During the packing, a massive metallic rod was introduced into the glass capillaries' top to assure a uniform powder compacting of the porous columns. This process was performed continuously until a constant length (35.34±0.30 mm) was reached for all the calcium fluoride columns.

The weight-time imbibition experiments were carried out with an automatic measuring device, which was used by us in previous works [10,11,14,20,21]. Basically, it consists of a digital balance (Mettler AE240) where the porous columns are hung in the below-balance weighing facility, a glass receptacle containing the liquid, situated on top of a horizontal mobile stage, and a computer that controls the apparatus and collects the experimental weight-time data. The stage was lifted up at a very low speed just up to the point where the free surface of the liquid came into contact with the base of the porous column. The acquisition of weight-time data started before contact between the liquid surface and the column was established to prevent the loss of information from the very beginning of the capillary rise, and it finished when porous solid was saturated by the liquid, the weight indicating a constant value. Finally, once this state was got, the weight marked by the balance on breaking the contact between the column and the liquid free surface was considered, since this value was the total mass of liquid introduce inside the porous tube because of the imbibition.

3. Analysis of results and discussion

The results obtained from the imbibition experiments are shown in Fig. 1 as the increase in the weight registered by the balance during the capillary rise, w_{exp}, against the time, t. As it was shown elsewhere [10,11,14,15,20,21], these experimental weight increases are a consequence of two simultaneous processes: the capillary rise of the liquid and the formation of a meniscus at the bottom of the glass walls due to their contact with the free surface of the liquid. Therefore, the experimentally obtained weight increase, w_{exp}, can be split as [10,11,14,20,21]

$$w_{exp}(t) = w_{imb}(t) + w_{cont}(t) \tag{9}$$

where $w_{imb}(t)$ represents the increase in the weight associated to the capillary rise, and $w_{cont}(t)$ is the contribution due to the initial contact between the liquid and the glass column. It has to be noted that this last contribution depends on the former as a consequence of the modification meniscus shape of the because of the liquid level fall inside the container when imbibition progresses [21]. Now then, this effect seems to end at the initial instants of the experiments [10,11,14,20,21]. Therefore, the weight increase caused by the meniscus could be considered constant during almost all the duration of the experiments. If this hypothesis is true, let t_1 be the instant when w_{cont} reaches a constant value:

$$(t \geq t_1) w_{cont}(t) \equiv w_{cont,\ total} \tag{10}$$

This parameter is obtained as the difference between the maximum weight registered in the experiment and the total mass of the liquid introduced by capillary rise inside the porous column. Thus, the weight increase associated to the capillary rise, $w_{imb}(t)$, can be deduced from Eq. (9) by subtracting $w_{cont,\ total}$ from the experimental results:

$$(t \geq t_1) w_{imb}(t) = w_{exp}(t) - w_{cont,\ total} \tag{11}$$

The velocity at which the liquid is imbibed in the porous solid can be calculated by applying a computer routine based on Savitzky–Golay algorithm [27,28] to every pair of data ($w_{exp}(t) - w_{cont,\ total}$, t) from the beginning of the experiments. According to the analytical procedure described in Introduction, these rates are shown in Fig. 2 as a function of the inverse of the weight increase given by Eq. (11), and they can be gathered in different sections. In that named as (1), an increment of the velocity is observed (1a), which gives idea of a sudden acceleration in the system due to the establishment of the contact between the solid and the liquid free surface. This effect is associated both with the initial force the meniscus exerts on the glass column and the initial impulse leading to the migration of the liquid through the pores of the solid. The description of this last one is given by the inertial terms that are neglected from Navier–Stokes equations on deducting Washburn's equation [29–32]. Immediately after, this increase in the rate is less pronounced (1b), indicating that the acceleration, nonetheless positive, is continuously decreasing as a consequence of the two decelerated phenomena that take part in the experiments; the capillary rise of the liquid and the evolution of the geometrical shape of the meniscus. With regard to the rest of the sections, all of them show a decrease in the weight

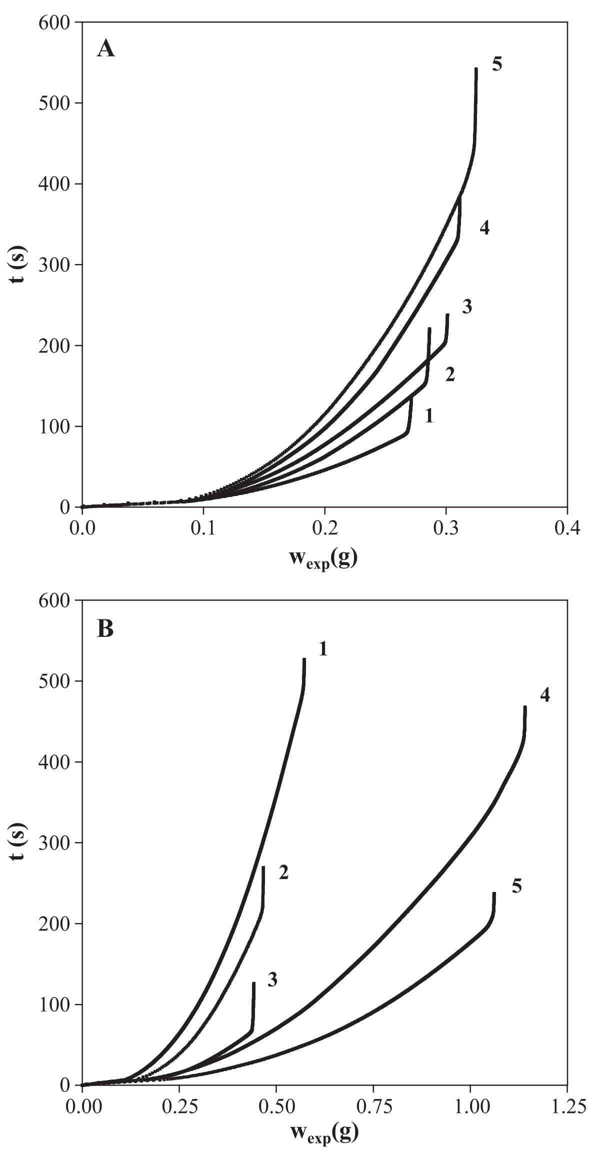

Fig. 1. Experimental weight increase, $w_{exp}(t)$, vs. time, t, on porous columns of calcium fluoride: A—(1) n-octane, (2) n-decane, (3) n-dodecane, (4) n-tetradecane and (5) n-hexadecane; B—(1) α-bromonaphtalene, (2) formamide, (3) water, (4) diiodometane and (5) bromoform.

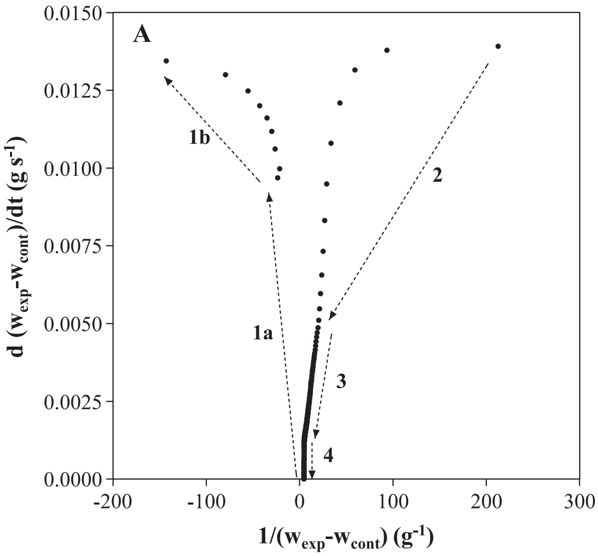

Fig. 2. Velocity profile, corresponding to the experiments carried out with n-octane, as given by left-hand side of Eq. (12) vs. the inverse of the weight differences given by right-hand side Eq. (11).

velocity, revealing that these processes have succeeded in counteracting the initial impulse at the start of the experiment. In Section (2), this trend is more pronounced as the experiment is elapsed. However, Section (3) is considerably different, since a straight-line relationship is established between the rate values and the inverse of the weight differences, which could be related to the behaviour predicted by Eq. (8). Finally, in Section (4) the velocity falls down quickly, reflecting the end of the capillary rise due to the saturation of the interstices of the porous solid.

In order to understand the meaning of the linear section (3), let us subtract the total increase in the weight associated to the meniscus, $w_{\mathrm{cont,\ total}}$, from the experimental increase in the weight, $w_{\mathrm{exp}}(t)$. So, if Eq. (10) is taken into account, it is deduced that the velocity associated to this difference is the rate of the experimental weight increase:

$$\frac{\mathrm{d}\left(w_{\mathrm{exp}}(t)-w_{\mathrm{cont,\ total}}\right)}{\mathrm{d}t}=\frac{\mathrm{d}w_{\mathrm{exp}}(t)}{\mathrm{d}t}=\frac{\mathrm{d}w_{\mathrm{imb}}(t)}{\mathrm{d}t}+\frac{\mathrm{d}w_{\mathrm{cont}}(t)}{\mathrm{d}t} \quad (12)$$

On the other hand, if Eq. (8), which described the rate of the increase in the weight associated to the liquid flow through the porous medium, is introduced into Eq. (12), it is obtained that

$$\frac{\mathrm{d}\left(w_{\mathrm{exp}}(t)-w_{\mathrm{cont,\ total}}\right)}{\mathrm{d}t}=\left(\varepsilon\rho\pi R'^{\,2}\right)^{2}\frac{R\Delta g}{4\eta}\frac{1}{w_{\mathrm{imb}}(t)}+\frac{\mathrm{d}w_{\mathrm{cont}}(t)}{\mathrm{d}t} \quad (13)$$

As it is seen, only if there is an instant t_1 from which the increase in the weight caused by the meniscus reaches a constant value, the behaviour this equation proposes would be reduced to a straight-line relationship as the one observed in Section (3). In that case, the second term in the right-hand side of Eq. (13) becomes zero, and as a consequence, it is turned through Eq. (12) into Eq. (8), which describes the velocity associated to the increase in the weight of the porous solid because of the imbibition.

Once the hypothesis about the increase in the weight due to the meniscus has been verified, and that the meaning of the linear section (3) of the curves in Fig. 2 has been found, the question raised in Introduction can be just resolved by taking into account the geometrical character of such section. So, as this one is a straight-line relationship, its slope is a constant. On the other hand, it has been concluded that this graphical behaviour reflects the velocity of the weight increase of the porous column because of the imbibition, which is described by Eq. (8). Therefore, the only way to bring together these two facts can be achieved if the coefficient of this equation is also constant. Finally, if the expression of this parameter is considered, it is seen that it is proportional to the free energy reduction per surface unit, Δg. From all of these, it is deduced that this physical quantity, which characterized the liquid flow inside the solid, does not change during the capillary rise processes, fact that confirms, as it was expected, that the results of the imbibition experiments fulfil the needed conditions as to be analysed by means of Washburn's equation.

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