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# Influence of the interfacial adsorptions on the imbibition of aqueous solutions of low concentration of the non-ionic surfactant Triton X-100 into calcium fluoride porous medium

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## Abstract

The imbibition of aqueous solution of Triton X-100 in porous columns of calcium fluoride has been carried out in order to investigate the surfactant influence on the capillary rise. Experiments have consisted of the measurement of the increase in the weight of the porous columns caused by the imbibition of the solutions. From their analysis, it has been found that the capillary rise velocity does not depend on the surfactant concentration, and that imbibition of these solutions behaves as in the case of water. This unexpected finding can not be attributed to depletion of the surfactant molecules from the advancing meniscus, since this effect can not be caused by the adsorption at the solid. This lack of surfactant adsorption on the solid is precisely the reason that justifies the observed behaviour. So, it has been proved that the driving force for the capillary rise movement will remain unaltered despite the surfactant addition whenever the free energies of the solid interfaces are not modified by the adsorption on the solid. Therefore, it is concluded from this study that only if adsorption on the solid happened, the imbibition could be influenced by the surfactant concentration.

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## 1. Introduction

The imbibition of aqueous surfactant solutions in capillary media arises a considerable interest due to the expected ability of surfactant molecules to modify the features of the pure solvent capillary rise. In order to understand the process, different kinds of works have been carried out. One of the main groups deals with the imbibition in hydrophilic media, where water spontaneously penetrates [1–5]. When surfactant solutions are imbibed, the surfactant adsorption on the moving meniscus would cause a decreasing in the surface tension and the contact angle in relation to their values corresponding to water. This would lead to a higher capillary pressure that should increase the imbibition velocity. On the other hand, as the moving contact line advances on dry solid surface, the adsorption on it could befall simultaneously to the imbibition in the behind

closeness of the moving meniscus [1,5], which could deplete its surfactant concentration [1–3,5]. If it is considered that the adsorption strength is inversely proportional to the radius of the capillaries of the porous medium, and if it is taken into account that the imbibition is lower as smaller the radius is, it would be expected that a competitive process would be established between them [5]. Thus, if the capillary radius was small enough, the adsorption would proceed faster than imbibition, so that all the surfactant molecules would be adsorbed on the solid [2,5]. As a result, the surfactant concentration in the advancing meniscus could be considered negligible, and hence, the imbibition rate must not depend on surfactant concentration, taking a value equal to the observed for water [2,5].

According to these arguments, and as it has been suggested elsewhere [6], if adsorption of the surfactant molecules were carried out on the solid substrate before the capillary movement, the surfactant concentration in the meniscus would remain unaltered due to the absence of the adsorption on the solid surface during the imbibition. Therefore, the imbibition rate

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should acquire the maximum value compatible with the concentration of the solution. This situation could be also achieved if the imbibition were carried out with an aqueous solution of a surfactant that was not able to be adsorbed on the solid surface. Under this assumption, the surfactant molecules would not be displaced from the moving meniscus during the imbibition, and then the capillary rise should always depend on the surfactant concentration.

However, this type of experiments has not been carried out yet. The analysis of this kind of systems is precisely the end of this work: we try to state precisely how surfactant influences on the imbibition if its concentration in the moving meniscus is not modified as a result of its adsorption on the solid. With this aim, calcium fluoride has been selected as substrate, since it has been proved elsewhere that it is not able to adsorb the non-ionic surfactant Triton X-100 [7].

## 2. Experimental

Imbibition experiments have been carried out using glass tubes of the same diameter ( $4.95 \pm 0.05$  mm) and length ( $73.30 \pm 0.05$  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 ( $1.0005 \pm 0.0005$  g) of powdered sintered calcium fluoride (Merck, purity 99.5%) previously dried into an oven at  $150^\circ\text{C}$  overnight. The BET surface area ( $\text{N}_2$ , 77 K) of the stored sample was  $4.64 \pm 0.03$   $\text{m}^2\text{g}^{-1}$  and its solubility in water at 298 K was  $3.3 \times 10^{-4}$   $\text{mol dm}^{-3}$  [7]. The mean particle size, calculated from the BET surface area and the density of the material ( $3.18$   $\text{g cm}^{-3}$ ), was  $2$   $\mu\text{m}$ . To obtain a good experimental reproducibility, the filled glass tubes were mechanically tapped by an automatic controlled-frequency device 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 ( $35.3 \pm 0.3$  mm). The increase in the weight of the porous columns caused by the imbibition was measured with the aid of an automatic measurement device previously described [8–13], similar to those used by other authors [14–17]. The measurements were carried out at  $20 \pm 0.5^\circ\text{C}$ . The liquids were water, distilled and deionised from a Milli-Q system, and aqueous solutions of the non-ionic surfactant Triton X-100 (Fluka, purity 99.0%). Its critical micelle concentration (cmc) in water at  $20^\circ\text{C}$  is  $3.0 \times 10^{-4}$  M [18]. The concentration of the surfactant solutions was comprised between  $10^{-4}$  and  $10^{-9}$  M. Viscosities have been considered, as elsewhere [3], equal as for water due to the low surfactant concentration. For each surfactant concentration, imbibition experiments were repeated done at least by quadruplicate.

## 3. Results and discussion

Imbibition experiments consisted of the measurement of the increase in the weight,  $w_{\text{exp}}$ , as a function of the time,  $t$ . As an

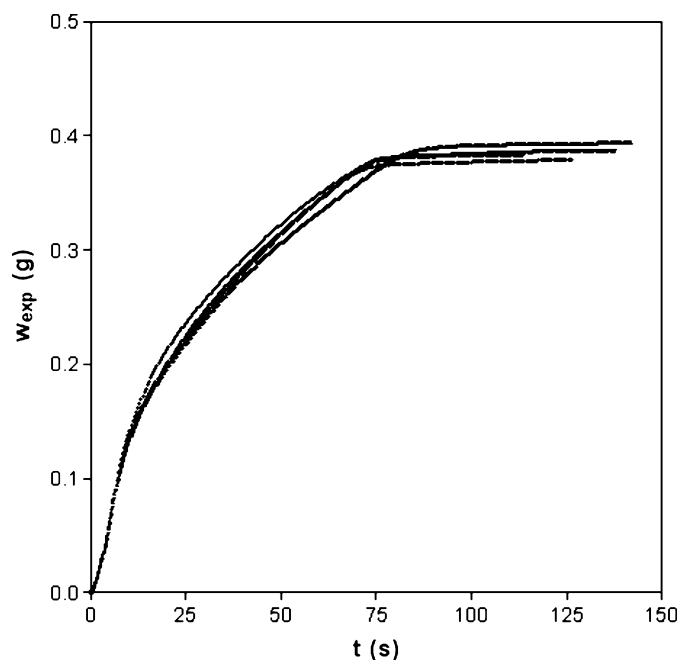


Fig. 1. Experimental weight vs time corresponding to the imbibition carried out with the aqueous solutions whose Triton X-100 concentration is  $5.9 \times 10^{-5}$  M.

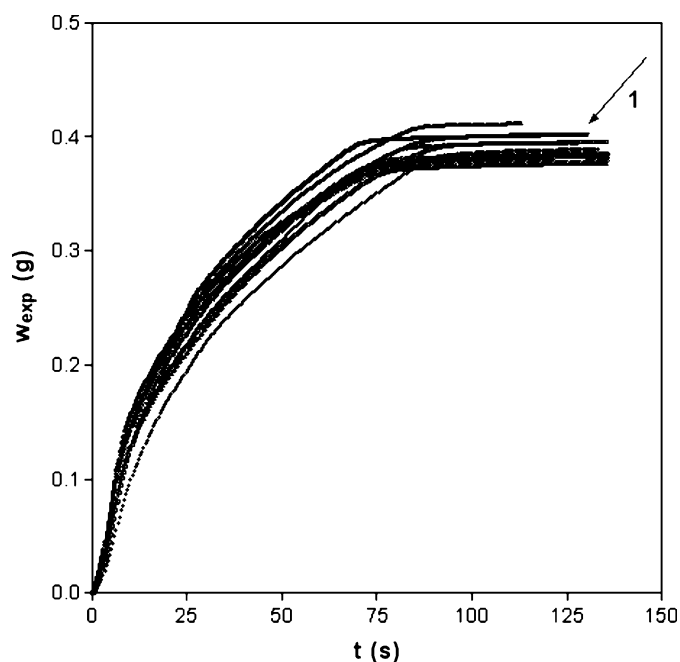


Fig. 2. Experimental weight vs time for one experiment carried out with each Triton X-100 solution of different concentration and with water (marked as 1).

example, the curves obtained in four different experiments done with the same surfactant concentration ( $5.9 \times 10^{-5}$  M) have been plotted in Fig. 1. This figure proves the good reproducibility of the studied systems and the techniques employed. On the other hand, Fig. 2 shows one of the experimental curves obtained from each one of the twelve different surfactant solution used (comprised between 0, pure water, and  $1.5 \times 10^{-4}$  M, just below the surfactant cmc). Taking into account the experimental reproducibility shown in Fig. 1, we can state that the imbibition behaviour is the same for all the concentration studied.

We proved in our previous works that the experimental increase in the weight,  $w_{\text{exp}}$ , is due to two contributions caused by the simultaneous processes that happen during the imbibition experiments [8,10]: the filling of the pores of the solid by the liquid,  $w_{\text{imb}}(t)$ , and the formation of a meniscus at the bottom of the glass column,  $w_{\text{cont}}(t)$ . Thus,  $w_{\text{exp}}$  can be split as

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

The contribution due to the external meniscus reaches a constant value,  $w_{\text{cont}}$ , after some unknown instant  $t'$  from the starting of the experiments [8,10], and then  $w_{\text{imb}}(t)$  is deduced as

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

where the parameter  $w_{\text{cont}}$  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.

Once the weight differences of the right-hand side of Eq. (2) have been deduced from the beginning of the experiments, the velocity profile has been derived by applying a computer routine based on Savitzky–Golay algorithm to every pair of data ( $w_{\text{exp}}(t) - w_{\text{cont}}, t$ ) [19,20]. As an example, the rate profile associated with one of the experiments carried out with the solution of concentration  $5.9 \times 10^{-5}$  M is shown in Fig. 3 as a function of the inverse of the differences  $w_{\text{exp}}(t) - w_{\text{cont}}$ .

In a recent paper we explained in detail the physical meaning of the rate profile shown in Fig. 3 [13]. As laid down in that paper, the negative values of the weight differences  $w_{\text{exp}}(t) - w_{\text{cont}}$  correspond to the first instants of the experiments when the experimental weight is lower than the contribution due to the meniscus,  $w_{\text{exp}}(t) < w_{\text{cont}}$ . Section 1a reflects the sudden acceleration caused by the initial contact between the 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

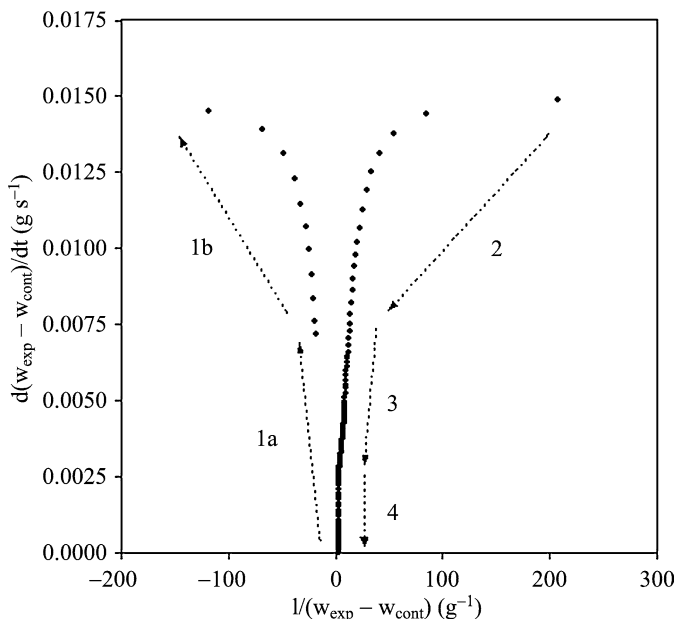


Fig. 3. Velocity profile associated with the weight differences  $w_{\text{exp}}(t) - w_{\text{cont}}$ .

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. 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,  $w_{\text{cont}}$ , so 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 linear relationship in section 3 is in accordance with the behaviour predicted by Washburn's equation in terms of weight increase [11]:

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

where the slope  $B$  is a parameter that takes into account the liquid viscosity,  $\eta$ , the effective radius  $R$  of the interstices in the solid and the free energy reduction per surface unit accompanying the imbibition process  $\Delta g$ :

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

On the other hand,  $w_{\text{imb-max}}$  represents the maximum weight increase caused by the imbibition and  $h_{\text{max}}$  is the maximum height that liquid reaches in the porous columns, which is equal to the length of the solid inside it. From these parameters, both experimentally measured, a coefficient  $A$  is deduced from the slope  $B$ :

$$A = \frac{R \Delta g}{4\eta}. \quad (5)$$

The average values of these two parameters  $B$  and  $A$  are in Table 1 as a function of the Triton X-100 concentration. This set of data shows that the values of the coefficients  $A$  and  $B$  for the solutions are equal to the corresponding to the water. This result indicates, in accordance with Fig. 2, that the velocity associated with the imbibition is independent of the surfactant concentration. This fact is revealed as different to the expected behaviour.

Table 1  
Average values of parameters  $B$  and  $A$  of Eqs. (4) and (5) vs surfactant concentration  $C$  of the aqueous solutions

$C$ (M)	$B$ ( $10^{10} \text{ kg}^2 \text{ s}^{-1}$ )	$A$ ( $10^6 \text{ cm}^2 \text{ s}^{-1}$ )
0 (water)	$7.60 \pm 1.10$	$9.00 \pm 1.40$
$5.9 \times 10^{-9}$	$8.00 \pm 1.60$	$9.20 \pm 1.80$
$6.5 \times 10^{-7}$	$7.65 \pm 1.30$	$8.40 \pm 1.30$
$1.3 \times 10^{-6}$	$7.05 \pm 0.70$	$8.20 \pm 0.90$
$1.9 \times 10^{-6}$	$6.67 \pm 1.00$	$8.10 \pm 1.30$
$1.8 \times 10^{-5}$	$7.07 \pm 0.60$	$8.30 \pm 0.80$
$2.9 \times 10^{-5}$	$7.24 \pm 0.70$	$8.90 \pm 0.70$
$3.2 \times 10^{-5}$	$7.10 \pm 1.20$	$8.50 \pm 1.40$
$5.9 \times 10^{-5}$	$7.56 \pm 0.90$	$9.00 \pm 1.30$
$6.5 \times 10^{-5}$	$8.40 \pm 1.10$	$9.70 \pm 0.90$
$1.2 \times 10^{-4}$	$7.40 \pm 0.90$	$9.00 \pm 1.40$
$1.5 \times 10^{-4}$	$7.70 \pm 1.60$	$9.10 \pm 1.90$

Previous studies about the imbibition of surfactant solutions in hydrophilic media assume that the velocity depends on the surfactant concentration in the advancing meniscus [1–3,5]. The physical model proposed for describing this phenomenon predicts that the imbibition of the solutions will be identical to the capillary rise of the solvent only if the adsorption on the solid surface is powerful enough to remove entirely the surfactant from the liquid–vapour interface [5]. However, Triton X-100 does not adsorb on calcium fluoride surface [7]. Then, the depletion of the surfactant molecules in the advancing meniscus would never happen in these imbibition processes. This indicates that the physical mechanism causing the observed behaviour has to be different from the proposed elsewhere [1–3,5].

In order to understand why the imbibition velocity does not depend on the surfactant concentration, let us consider Eq. (5). The parameter  $\Delta g$  is interpreted as the driving force that causes the imbibition [21,22]. It can be written as

$$\Delta g = \gamma_{LV} \cos \theta, \quad (6)$$

where  $\gamma_{LV}$  and  $\theta$  are the surface tension of the solution and the contact angle at the advancing meniscus, respectively. From Table 1 and Eq. (5), the value of  $\gamma_{LV} \cos \theta$  can be deduced. Obviously, it stays constant despite the surfactant concentration. On the other hand,  $\gamma_{LV} \cos \theta$  is related to the free energies of the solid–vapour,  $\gamma_{SV}$ , and solid–liquid interfaces,  $\gamma_{SL}$ , by Young's equation:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}. \quad (7)$$

This equation states that  $\gamma_{LV} \cos \theta$ , and hence the imbibition rate, will be independent of the surfactant concentration if the difference of the interfacial free energies remains unaltered despite the surfactant addition. If this equation is differentiated with respect to the logarithm of the concentration,  $C$ , of surfactant, and if Gibbs's equations, which relate the adsorption of the surfactant with the free energies of the solid–vapour and the solid–liquid interfaces, are considered [23], the next relationship is obtained:

$$\frac{d(\gamma_{LV} \cos \theta)}{d(\ln C)} = -RT[\Gamma_{SV} - \Gamma_{SL}], \quad (8)$$

where  $R$  is the ideal gas constant and  $T$  is the absolute temperature;  $\Gamma_{SL}$  and  $\Gamma_{SV}$  represent the surface excess of the surfactant molecules at both solid interfaces. As it is deduced from this equation,  $\gamma_{LV} \cos \theta$  will be independent of the surfactant concentration if both adsorptions are equal. If it is taken into account that  $\Gamma_{SV}$  can be always considered negligible because of the spontaneous imbibition of the solvent in the porous solid [1,5], and that, as was proved elsewhere [7], the adsorption of Triton X-100 on the aqueous solution–calcium fluoride interface does not happen, Eq. (8) justifies the results found on analysing the experiments (Table 1): the independence of the imbibition velocity with regard to the surfactant concentration. Therefore, it can be concluded from this study that the imbibition of the solutions will depend on the surfactant concentration only if the adsorption of the surfactant molecules at the solid interfaces gives rise to the depletion of the surfactant molecules from the advancing meniscus.

#### 4. Conclusions

The imbibition of aqueous solution of Triton X-100 in porous columns of calcium fluoride has been investigated. This solid–solution system has been chosen because the surfactant can not be adsorbed on the surface of this solid. The results of these experiments show that the capillary rise velocity does not depend on the surfactant concentration. The imbibition of the solutions happens in the same way as in the case of the water. This finding indicates that the depletion of the surfactant molecules from the advancing meniscus because of the adsorption on the solid can not justify these experimental results. In order to find the reasons for supporting them, a discussion about the driving force that directs the movement has been carried out. From it, it is found that the lack of the adsorption on the solid is precisely the cause of the observed behaviour. Finally, it is concluded that only if the free energies of the solid–vapour and solid–liquid interfaces were modified by the adsorption of the surfactant molecules, the imbibition would be affected by the surfactant concentration.

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