

An experimental study about the imbibition of aqueous solutions of low concentration of a non-adsorbable surfactant in a hydrophilic porous medium

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Abstract

The imbibition of aqueous solutions of Triton X-100 in calcium fluoride columns has been studied in order to determine the influence of the interfacial adsorption of the surfactant in the capillary rise of the solutions. This system has been chosen because this surfactant behaves as non-adsorbable at the surface of this solid when it is in aqueous solution. The experiments have consisted of the measurement of the increase in the weight of the porous columns caused by the capillary rise of the solutions. The analysis of the results has been made through a modified expression of Washburn's equation that takes into account that the experimental increase in the weight is caused by the imbibition as well as by the development of a liquid meniscus around the bottom base of the columns. From this analysis, it has been deduced that the surfactant concentration does not influence on the imbibition rate, it being equal to the observed for water. However, it has been also proved that the contact angle depends on the surfactant concentration, taking decreasing values as the surface tension of the solutions decreases. In order to justify these findings, a study about the influence of the interfacial adsorption on the imbibition has been carried out. By means of them, it has been proved that the absence of adsorption at the solid–liquid interface is the reason that explains both the independence of the imbibition rate from the surfactant concentration and the decrease of the contact angle. Moreover, this fact indicates that the depletion of the surfactant molecules from the advancing meniscus, which has been normally adduced as the phenomenon causing the observed behaviour, has to be ruled out as the physical cause that justifies the behaviour found from the analysis of the imbibition experiments. As a corollary, it has been also stated that only if the adsorption at the solid interfaces happened, the imbibition of aqueous solution of surfactant in hydrophilic media could be influenced by the surfactant concentration.

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1. Introduction

Experimental techniques based on capillary rise of pure liquids in porous substrates have been broadly utilised to carry out the thermodynamic characterisation of these solids through the deduction of their surface free energy [1–7]. This is why a considerable group of studies has been developed in order to go deeply in the knowledge of the imbibition phenomenon. From them, the surface tension and the contact angle have been found as the driving quantities for the movement of the liquid inside the pores of the medium [8–10]. However, the researches related to the imbibition of aqueous solutions of surfactant are

rather limited [11–22] despite the well-known fact that these molecules are able to alter the surface tension of the solvent as well as its contact angle on the surface of the solid [23]. As pointed elsewhere [11,13–18,20–22], it would be expected that the possible adsorption of the surfactant at the interfaces that take part in the capillary rise played a decisive role in the imbibition kinetic. On the one hand, it is well known that the adsorption at the liquid–vapour interface decreases the surface tension of the liquids [23]. On the other hand, the probable adsorption at the solid interfaces during the imbibition would cause an additional change of the surface tension with regard to equilibrium value because of the depletion of the surfactant molecules from the liquid–vapour interface [11,13,15,17,18,20–22]. Besides, these adsorptions would give rise to the alteration of the energetic characteristics of the interfaces near the

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three phase contact line, and hence, the contact angle at the advancing meniscus could also change with regard to the value corresponding to the pure solvent [11,13,15,19–22].

All the features just described above seem to indicate that the possible simultaneous adsorption of the surfactant at the mentioned interfaces may change the characteristic quantities of the imbibition of the solvent, surface tension and contact angle, these ones acquiring a value compatible with the surfactant concentration. As a consequence, the higher the concentration of the solution is, the more affected the imbibition velocity should be [11–22]. Even so, despite the efforts made, the role of the surfactant on the imbibition dynamics is not clear enough at present.

One kind of research works carried out so far deals with the imbibition of aqueous surfactant solutions in hydrophilic porous solid [13,14,18,21,22]. These media are characterised by the spontaneous rise of water in their pores. When the surfactant is added to the solution, its adsorption at the liquid–vapour interface causes an alteration of the surface tension of the solution. On the other hand, the adsorption at the solid–liquid interface gives rise to a change of the energetic features of the solid surface that modifies the contact angle in relation to the value corresponding to water, it increasing or decreasing depending on the orientation of the adsorbed surfactant molecules. This fact could yield to a higher capillary pressure that should accelerate the rise of the solutions in the pores of the solid [21,22]. However this adsorption of the surfactant at the solid–liquid interface would cause a decrease in the surfactant concentration at the advancing meniscus that would modify again the values of the surface tension and the contact angle in relation to their equilibrium values. In consequence, the imbibition should be also affected by the new change of these parameters. The latest theoretical model proposed to describe this capillary rise process predicts that the imbibition of the solutions will be developed in the same way as the imbibition of water whenever the adsorption of the surfactant at the solid–liquid interface is strong enough as to be able to remove the whole of the surfactant molecules from the advancing meniscus [21,22]. In order to avoid the depletion of the surfactant molecules from the advancing meniscus due to the adsorption on the solid, some authors suggest the adsorption to be carried out before the imbibition experiments [16]. Thus, the maximum number of surfactant molecules compatible with the concentration of the solution would be always placed at the liquid–vapour interface during the imbibition. Under this experimental condition, the velocity of the capillary rise should show a marked dependence on the surfactant concentration. To check experimentally this situation is precisely the purpose of this work. However, instead of carrying out the adsorption of the surfactant on the solid surface before the imbibition, we have employed a solid material, calcium fluoride, unable to adsorb on its surface the surfactant, Triton X-100, selected to perform the capillary rise experiments [24]. Thus, it is sure that the solid–surfactant solutions systems verify the wanted experimental condition. We would like to throw into relief the novelty of this approach, since, until we know, no similar experimental work has been developed yet.

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. 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 throughout 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 water, distilled and deionised from a Milli-Q system, and aqueous solutions of the non-ionic surfactant Triton X-100 (Fluka, purity 99.0%). Triton X-100 consists of a 1,1,3,3-tetramethylbutyl group, a phenyl group, and a $-(\text{OCH}_2\text{CH}_2)_{9-10}\text{OH}$ chain grafted to it. The average number of oxyethylene groups is assumed to be 9.5. Its critical micelle concentration in water at 20°C is 3.0×10^{-4} M [25]. The concentration of the surfactant solutions was comprised between 10^{-4} and 10^{-9} M. Their surface tensions were measured by means of an automatic tensiometer, the du Noüy ring technique being employed. Viscosities have been considered, as elsewhere [13], equal as for water due to the low surfactant concentration.

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 [26–31], similar to those used by other authors [4,14]. Basically, it was a digital balance (Mettler AE240) with the porous column 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 by means of an Oriel motor computer controlled 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 measurements were carried out at $20 \pm 0.5^\circ\text{C}$. For each surfactant concentration, imbibition experiments were repeated done at least four times.

3. Analysis of results and discussion

The capillary rise experiments have consisted of the measurement of the increase in the weight, w_{exp} , versus time, t , as a result of the imbibition of water and aqueous solutions of

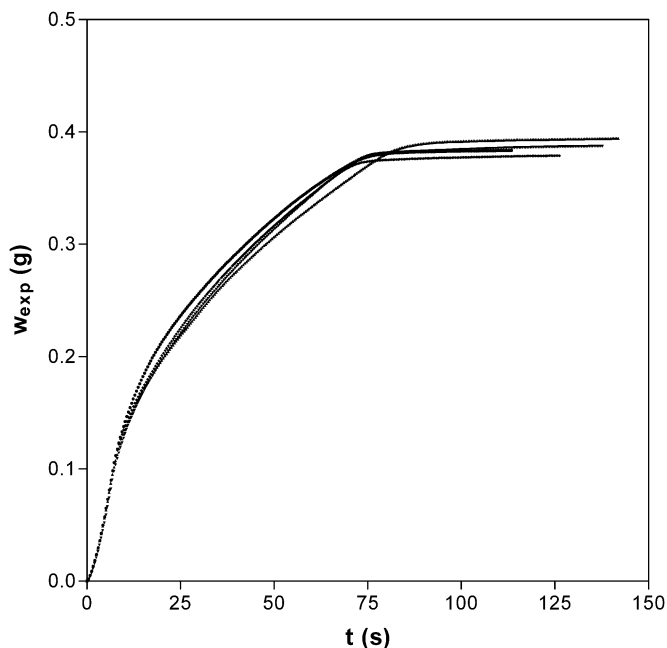


Fig. 1. Experimental weight vs time corresponding to the imbibition carried out with the aqueous solutions whose Triton X-100 concentration is 5.9×10^{-5} M.

Triton X-100 in porous columns of calcium fluoride. As an example, the experimental curves corresponding to the results of the experiments carried out with the solution whose surfactant concentration is 5.9×10^{-5} M are in Fig. 1. As shown exhaustively elsewhere [26–30], the graphical shape of these curves indicates that two simultaneous physical processes happening during the experiments are the responsible for the observed increase in the weight: the first of them, the imbibition in the interstices of the solid; the second one, the formation and the subsequent evolution of a liquid meniscus at the bottom of the glass columns. As the influence of the surfactant concentration on the imbibition is reflected only in the increase in the weight caused by the movement of the liquid inside the solid substrate, the weight contribution due to the meniscus has to be removed from the experimental results. The adequate analytical procedure is described in detail in some previous papers [26–30]. Basically, it leans on the fact that the weight contribution due to the meniscus reaches a constant value few seconds after the beginning of the experiments. Thus, it can be eliminated by subtracting a large enough weight value from the experimental data. Once this procedure has been carried out on the experimental results, the deduced weight data can be analysed by fitting them to Washburn's equation in order to determine the values the contact angle acquires as a function of the surfactant concentration. However, this has to be made by a modified expression of this equation that takes into account that the time, t , and the weight increase due to the imbibition, w_{imb} , are evaluated after w_{exp} reaches the value chosen to remove the effect of the meniscus [26–30]:

$$t = Bw_{\text{imb}}^2 + 2Bw_{0,\text{imb}}w_{\text{imb}}(t), \quad (1)$$

$w_{0,\text{imb}}$ being the weight of liquid acquired by the porous columns before the time selected to rescale the experimental

Table 1

Average values of the parameters B and A of Eqs. (4) and (5), as well as surface tension, γ_{LV} , free energy reduction per surface unit, Δg , and contact angle, θ , vs surfactant concentration C of the aqueous solutions

C (M)	γ_{LV} (mJ m^{-2})	B (10^6 s kg^{-2})	A (10^4 s m^{-2})	$R\Delta g$ (10^8 J m^{-1})	$R \cos \theta$ (10^7 m)
0 (water)	72.80	644 ± 64	5.4 ± 0.5	3.7 ± 0.3	5.1 ± 0.4
5.9×10^{-9}	71.24	674 ± 72	5.9 ± 0.8	3.5 ± 0.5	4.8 ± 0.6
3.2×10^{-7}	69.03	686 ± 74	5.8 ± 0.5	3.5 ± 0.3	5.0 ± 0.4
6.5×10^{-7}	65.54	684 ± 102	5.9 ± 0.6	3.4 ± 0.3	5.2 ± 0.5
1.3×10^{-6}	59.55	623 ± 90	5.2 ± 0.5	3.9 ± 0.4	6.5 ± 0.6
1.9×10^{-6}	53.27	759 ± 80	6.2 ± 0.6	3.3 ± 0.3	6.1 ± 0.6
1.8×10^{-5}	48.62	728 ± 75	6.2 ± 0.4	3.2 ± 0.2	6.7 ± 0.5
2.9×10^{-5}	42.82	673 ± 76	5.5 ± 0.6	3.7 ± 0.4	8.6 ± 0.9
3.2×10^{-5}	41.03	625 ± 26	5.2 ± 0.1	3.8 ± 0.1	9.3 ± 0.2
5.9×10^{-5}	40.18	636 ± 65	5.4 ± 0.5	3.7 ± 0.3	9.2 ± 0.9
6.5×10^{-5}	36.02	655 ± 17	5.7 ± 0.3	3.5 ± 0.2	9.8 ± 0.6
1.2×10^{-4}	33.54	691 ± 82	5.7 ± 0.7	3.5 ± 0.4	10.5 ± 1.2
1.5×10^{-4}	32.78	712 ± 85	6.0 ± 0.5	3.3 ± 0.3	10.2 ± 0.9

Note. It must be noted that, despite the fact that some of these coefficients are multiplied by the average radius of the interstices of the porous columns, R , the deduced conclusions do not depend on it.

data has spent. The parameter B is connected with the free energy reduction per surface unit accompanying the imbibition process Δg as

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

where R and η are the average radius of the pores of the solid on the assumption that they are considered as an assembly of identical parallel cylindrical capillaries and the viscosity of the liquid, respectively. On the other hand, $w_{\text{imb-max}}$ represents the maximum weight increase caused by the imbibition (experimental parameter) and h_{max} is the maximum height the liquid reaches in the porous columns, which is equal to the length of the solid inside it.

If this analysis procedure is carried out on the results originating in the imbibition experiments made with water and the surfactant solutions, the particular values of the coefficient B can be deduced. On the other hand, if Eq. (2) is taken into account, a coefficient A can be determined as

$$A = \left(\frac{w_{\text{imb-max}}}{h_{\text{max}}} \right)^2 B, \quad (3)$$

which permits to deduce the free energy reduction per surface unit, Δg , as a function of the surfactant concentration through

$$R\Delta g = \frac{2\eta}{A}. \quad (4)$$

Finally, the contact angle values can be derived from Δg and the surface tension of the liquids, γ_{LV} , through the next equation:

$$\Delta g = \gamma_{\text{LV}} \cos \theta. \quad (5)$$

In Table 1, the values of all these parameters are shown as a function of the surfactant concentration. The first fact deduced from them is the constancy of the free energy reduction per surface unit, it taking values similar to the corresponding to water. This means that the force that drives the liquids

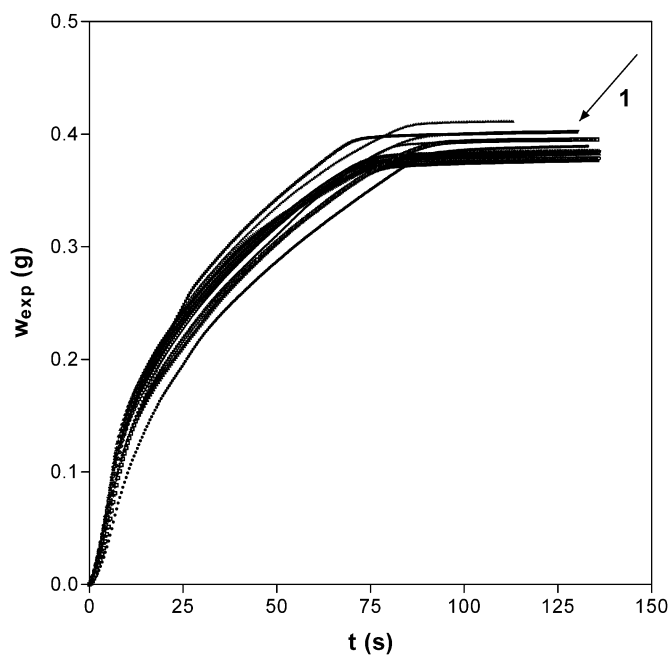


Fig. 2. Experimental weight vs time for one experiment carried out with each Triton X-100 solution of different concentration and with water (marked as 1).

through the interstices of the porous columns remains invariable despite the change in the surfactant concentration, which indicates that the development of the imbibition is not affected by the surfactant addition. This result can be corroborated by drawing one of the experimental curves (arbitrarily chosen) associated with each experiment carried out both with water and with the aqueous solutions of Triton X-100 (Fig. 2). As it is observed, their behaviour is practically indistinguishable despite the change of the surfactant concentration. Besides, the total durations of the different imbibition processes are similar, which confirms that the capillary rise velocity does not depend on the surfactant concentration. On the other hand, the values of the parameter $R \cos \theta$ shown in Table 1 indicate that the contact angle certainly depends on the Triton X-100 concentration. As it is seen, the contact angle becomes smaller as surface tension decreases. These two findings can be revealed more clearly if the values of $R \Delta g$ and $R \cos \theta$ are plotted as a function of the surface tension of the solutions (Fig. 3). As it is shown, the first of them remains constant in spite of the increase the surfactant concentration whereas the second one increases as the surface tension of the solutions decreases.

In order to analyse why the imbibition remains unaltered and however the contact angle decreases as surfactant concentration increases, the role of the interfacial adsorption in the imbibition of aqueous solutions will be considered next. It should be noticed that the depletion of the surfactant molecules from the advancing liquid front, which is the cause normally adduced to explain the independence the imbibition shows with regard to the surfactant concentration [21,22], cannot be assumed for explaining our experimental findings. This is so because the adsorption of the surfactant at the solid–liquid interface, which

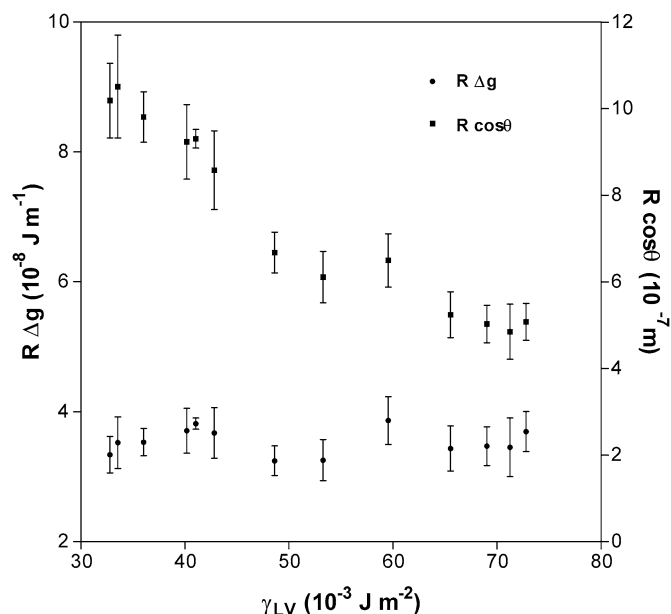


Fig. 3. $R \Delta g$ and $R \cos \theta$ vs surface tension, γ_{LV} , of the aqueous solutions.

does not happen in this case, is precisely the basis of this hypothesis.

With the mentioned aim, let us remind that the free energy reduction per surface unit, Δg , can be written as the difference between the free energies of the solid–vapour and solid–liquid interfaces:

$$\Delta g = \gamma_{SV} - \gamma_{SL}. \quad (6)$$

This equation indicates that the driving force causing the capillary movement proceeds from the energetic excess produced by the continuous replacement of the solid–vapour interface by the solid–liquid interface during the imbibition. In order to deduce the influence of the surfactant concentration on this quantity, let us differentiate this last equation in relation to the natural logarithm of the concentration, $\ln C$, and let us take into account the Gibbs' adsorption equations that relate the interfacial free energies with the surfactant concentration, C [32]:

$$\frac{d(\Delta g)}{d \ln C} = -RT(\Gamma_{SV} - \Gamma_{SL}). \quad (7)$$

In this last equation, Γ_{SV} and Γ_{SL} are the surface excess concentrations of the solid–vapour and solid–liquid interfaces for a given concentration C of the bulk solution, respectively, and R and T have their habitual meaning. From this equation it is deduced that the imbibition will be independent of the surfactant concentration whenever the adsorption at the solid–vapour interface is equal to that at the solid–liquid interface ($\Gamma_{SV} = \Gamma_{SL}$), results that is in agreement with the values of the free energy reduction per surface unit during imbibition, Δg , shown in Table 1. On the other hand, let us remind that Triton X-100 does not adsorb on calcium fluoride surface when it is immersed in aqueous solution of this surfactant [24]. So, $\Gamma_{SL} = 0$ independent of the surfactant concentration. This fact implies that the adsorption of this surfactant at the solid–vapour interface can be

also considered negligible during the development of the imbibition ($\Gamma_{SV} = 0$), since, as pointed elsewhere, it is unlikely it happens either because the speed of the imbibition impedes the transfer of the surfactant molecules onto the bare surface of the solid ahead the advancing liquid front [21,22], or because normally there is not surfactant in the vapour phase [18]. Therefore, the equality $\Gamma_{SV} = \Gamma_{SL} = 0$ justifies why the imbibition does not depend on the surfactant concentration on the basis of the absence of adsorption at the solid interfaces. Besides, this result indicates that only if the adsorption of the surfactant at the solid surface happened, it could be expected that the imbibition in a hydrophilic media was influenced by the surfactant concentration.

On the other hand, if Young's equation is differentiated with regard to the natural logarithm of the concentration, $\ln C$, and if it is again taken into account Gibbs' equations for adsorption [32], the dependence between the contact angle and the surfactant concentration is easily obtained [33]:

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

From this last equation, it is deduced that the contact angle decreases whenever

$$\Gamma_{SV} < \Gamma_{SL} + \Gamma_{LV} \cos \theta. \quad (9)$$

If the absence of adsorptions at the solid–liquid and solid–vapour interfaces is again considered, it is deduced from Eq. (9) that the contact angle decreases if $\Gamma_{LV} \cos \theta > 0$, inequality that the imbibition of the Triton X-100 solutions verified, since, on the one hand, the parameter $\cos \theta$ is always positive, and, on the other hand, the increase in the Triton X-100 concentration causes a decrease in the surface tension of the solutions (Table 1) that indicates that the specific adsorption at the liquid–vapour interface is also positive ($\Gamma_{LV} > 0$). This fact means that the behaviour associated with the contact angle is exclusively due to the decrease in the surface tension of the solutions caused by the surfactant addition, fact compatible with the lack of adsorption at the solid–liquid and solid–vapour interfaces, reason needed to understand the independence of the imbibition from the surfactant concentration.

4. Summary

A study about the imbibition of aqueous solution of Triton X-100 in porous columns made from a hydrophilic solid, calcium fluoride, has been carried out in order to describe the influence of this surfactant on the capillary rise through the pores of the medium. This solution–solid system has been chosen because this surfactant behaves as non-adsorbable at the surface of this solid when it is in aqueous solution. Thus, it is expected that the imbibition is strongly affected by the surfactant molecules placed at the advancing meniscus, since they cannot be removed from it as a result of its adsorption at the solid–liquid interface. With this aim, experiments where the increase in the weight of the porous columns as a result of the imbibition is measured have been made. The results have been analysed by a procedure that allows isolating the weight contribution caused

by the imbibition from the experimental weight increase. From such analysis, it has been deduced that the surfactant concentration does not modify the velocity of the imbibition, this rate being similar to the observed in the experiments carried out with water. However, the surfactant addition alters the contact angle, fact apparently incompatible if it is taken into account that the contact angle is one of the physical quantities that drives the imbibition.

In order to analyse these two findings, a theoretical study about the influence of the interfacial adsorption on the imbibition has been carried out. On the basis of the Young's and Gibbs' equations, it has been proved that the absence of adsorption at the solid–liquid interface is precisely the reason that justifies both the independence of the imbibition rate from the surfactant concentration and the decrease of the contact angle, this last physical effect being produced exclusively by the decrease of the surface tension of the aqueous solution caused by the adsorption of the surfactant at the liquid–vapour interface. On the other hand, this conclusion indicates that the hypothesis that is normally employed to explain this phenomenon, the depletion of the surfactant from the liquid–vapour interface, has to be ruled out because of the lack of the adsorption at the solid interfaces. Finally, it is stated from this experimental study that only if the free energies of the solid–vapour and the solid–liquid interfaces were modified as a result of the adsorption of the surfactant molecules on the solid surface, the imbibition of aqueous solutions in hydrophilic media could be influenced by the surfactant concentration.

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