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CONTACT ANGLE STUDIES ON ANODIC POROUS ALUMINA*

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Abstract. The preparation of nanostructures using porous anodic aluminium oxide (AAO) as templates involves the introduction of solved materials into the porous of the membranes; one way to determine which are the preferred materials to fill the pores, involves the measuring of the contact angle (θ) of different solvents or test liquids on the AAOs; thus, herein we present the results of the measurements of contact angles of nine solvents on four different AAO sheets by tensiometric and goniometric methods. From the solvents tested, we found dimethyl sulfoxide (DMSO), and N, N'-dimethyl formamide (DMF) to interact with the AAOs, being the polarity of the solvents and the surfaces the driving force.

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1. INTRODUCTION

Nanoscale materials have been widely studied due to their singular properties and potential applications. In particular, one dimensional (1D) nanoscale materials have attracted much attention in recent years [1]. One of the most important methods for the preparation of 1D nanoscale materials is the template technique, which uses nanoporous membranes as templates [2-4]. In this method, anodic aluminum oxide membranes AAO, prepared by electrochemical etching aluminum foil in oxalic, sulphuric and phosphoric acid solutions are the most commonly used membranes [5-10], for the fabrication of semiconductor nanowires, superconductor nanowire arrays, carbon nanotube arrays, *etc.* These materials have been fabricated, mainly, by electro [11-13] and electroless [14] deposition, chemical vapour deposition [15], by sputtering or evaporating of the material on the surface of the AAO at high temperatures [16,17]; however, attempts to fill the pores by gravity alone, have resulted unfruitful. Therefore, it is important to perform careful studies of the liquid-solid interfaces interactions at the nanoscale in order to understand how the interfacial properties affect the introduction of molecules into the pores of membranes. For doing so, the contact angle (θ) has been used as a measure of wetting between a liquid and a solid surface. Two main techniques are commonly used for studying contact angles on a flat solid surface: a) The tensiometric or Wilhelmy method, that measures the forces that are present when a sample of solid is brought into contact with a solvent. A particular case from the tensiometric method is the Washburn technique, which is employed when the solid sample contains a porous

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structure or it is a powder. In this method, the solid is brought into contact with the testing liquid and the mass of liquid absorbed into the solid is measured as a function of time [18,19]. b) In the goniometric method, the contact angle can be assessed directly by measuring the angle formed between the solid and the tangent to the drop surface. The present investigation involves the use of these techniques. Thus, following our interest [20-22] in the properties and structure of anodic alumina oxide membranes (AAO), we would like to report our findings on the measurement of the wetting properties of different solvents towards different AAOs.

2. EXPERIMENTAL

2.1 Materials

All chemicals, unless specified otherwise, were purchased from Aldrich Chemical Co. and used as received, without further purification. The following test liquids were used: 2-propanol (99.5%), 1-butanol (99.4%), acetone (99.66%), ethyl acetate (99.5%), acetonitrile (99.5%), N,N-dimethylformamide (DMF) (99.8%), dimethylsulfoxide (DMSO) (99.9%), hexane (98.5%), benzene (99%) and Ultra pure water (18 $M\Omega cm^{-1}$) was obtained from a Barnsted E-pure deionization system.

The solvents tested were chosen according to their polarity. *Polar solvents* with large dipole moments (μsolv) and high dielectric constants (εr(solv)); *polar protic solvents*, have at least one hydrogen atom bonded to either an oxygen or a nitrogen. This creates a polar molecule that will attract other molecules or ions using hydrogen bonding, as in water (H_2O), alcohols (R-O-H), (butanol, 2-propanol) or amines ($R\text{-}NH_2$). *Polar aprotic solvents* exhibit a molecular dipole moment but, whose hydrogen atoms are not bonded to an oxygen or nitrogen atom. Examples of such solvents would include aldehydes, R-CHO, esters R-COOR' (ethyl acetate), ketones, R-CO-R' (acetone), dimethyl sulfoxide (DMSO), and N, N'-dimethyl formamide (DMF). Finally, *non-polar solvents* present low dipole moments and small dielectric constants, examples include all the hydrocarbons-alkanes, alkenes, and alkynes (hexane, toluene). Table 1 shows the selected solvents and their values of dielectric constant, dipole moment, surface tension (γsolv) and viscosity (ηsolv).

2.2. Instruments

The film surface was studied by means of scanning electron microscopy (SEM) in a microscope JEOL JSM-5900LV. The contact angle measurements by the tensiometric and Washburn methods were carried out using a Sigma 70 precision tensiometer produced by KSV Instruments. The goniometric determinations were carried out using a goniometer Rame-Hart Inc. Model 100/07/00.

2.3 Template preparation

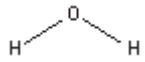
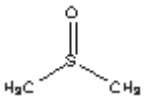
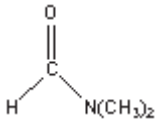
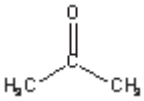
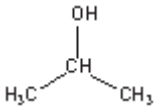
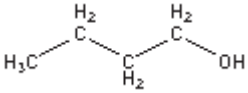
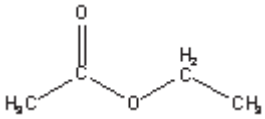
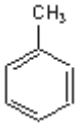
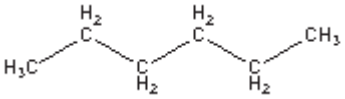
AAO templates were prepared by using the fabrication procedures reported by us and other research groups [5-10,20-22]. In this case, aluminum sheets (99.999%) (20x10 mm, thickness 0.13 mm) were annealed under air at 480 °C for 60 min and mechanically and electrochemically polished (1:5 v/v of $EtOH/HClO_4$) prior to anodization. The prepared sheets were then anodized at 40 V and 20 V in 0.3M aqueous oxalic or sulfuric acid solutions, respectively, at 10 °C, resulting in an average pore diameter for the AAO template of about 46 and 15 nm respectively. The pore length obtained by this technique exceeds the 30 mm average. In order to enlarge the pores, the sheets were placed in aqueous phosphoric acid solution (0.35M, T=30 °C, t=10 min); thus the average pore diameter obtained for the AAO template were of 52 and 26 nm respectively, remaining the length of the pores the same (about 30 mm). The pore size diameter and length were determined by SEM micrographs. Table 2.

Fig. 1 shows the surface morphology of the AAO templates, before and after pore enlarging, analyzed by scanning electron microscopy (SEM).

2.4 Contact angle measurements

The prepared AAO sheets were used to measure the contact angle. *Wilhelmy method*. The samples were immersed to a set depth, as the probe advanced into the liquid; data were collected and used to calculate an advancing contact angle (θadv). This process was reversed and, as the probe retreated from the liquid, data were collected and used to calculate the receding contact angle (θrec). In the *Washburn technique*, the sheets were brought into contact with the testing liquid and the mass of liquid absorbed into the solid was measured as a function of time working at room temperature and the immersion depth was 18.88 mm, for all samples. On the *goniometric method*, contact angles (q) were measured with sessile solvent drops. Nearly all measurements were made with drops that had a total volume of 10 μL. Advancing contact angles were measured from drops after sequential deposition. For the measurement of the receding contact

Table 1. Test liquids properties.

test liquid	structure	μsolv (debye)	ε_r*(solv) (8.85 pF/m)	γsolv (mN/m)	η⁺solv (mPa·s)
water		1.85	80.0	73.0	1.00
DMSO		3.96	47.2	25.0	2.20
DMF		3.82	38.3	25.0	0.92
acetone		2.88	20.7	23.7	0.30
2-propanol		1.68	20.1	23.8	2.86
butanol		1.66	17.8	24.6	2.95
ethyl acetate		1.78	6.02	23.9	0.46
toluene		0.36	2.4	28.5	0.59
hexane		0	2.02	18.43	0.31

*The dielectric constants of the solvents are given relative to the dielectric constant of a vacuum, 8.85 $F \cdot m^{-1}$. [Information provided by: http://www.cartage.org.lb/en/themes/Sciences/Chemistry/Electrochemis/TheoryElectrolytes/Units/Units.htm].

⁺hsolv = Viscocity.

Table 2. Conditions for the template preparation and average pore diameter.

Sample	Acid solution	Temperature (°C)	Voltage (V)	Pore enlarging conditions	Average pore diameter (nm)
1	0.3M sulfuric acid	10	20	-	15
2	0.3M sulfuric acid	10	20	0.35M H_3PO_4, 30 °C, 10 min	26
3	0.3M oxalic acid	10	40	-	46
4	0.3M oxalic acid	10	40	0.35M H_3PO_4, 30 °C, 10 min	52

angles, solvent was withdrawn. The AAO sheets were dried at 100 °C in a closed oven for 1 hr after the treatment with each solvent and allow them to reach room temperature in a desiccator for one extra hour before the next solvent was used.

3. RESULTS AND DISCUSSION

3.1. Wilhelmy Method

The interaction between the liquid and the surface can be estimated by contact angle (q) measurements. The details of the interactions between the surface and the solvents were explored by analysis of the effect of the properties of the liquid on varying the equilibrium contact angle (θeq) with the different surfaces. These θeq values were determined from the intersection of the fits for advancing and receding angles *versus* contact angle hysteresis (Δq, which is the difference between the advancing and the receding angles) with the ordinate at Δq=0, one finds the equilibrium angle θeq [23]. Fig. 2 presents the plots of ethyl acetate contact angle as a function of the dynamic hysteresis for one of the AAOs (sample **2**) and Table 3, summarizes the results for all four AAOs.

If Eq. (1) is used to calculate θeq using the θadv and qrec data obtained in the present investigation, the qeq values thus obtained result very similar to those obtained experimentally Table 3. The tendencies and results discussed further are the same with both values.

$$\cos\theta eq = 0.5(\cos\theta adv + \cos\theta rec) \quad (1)$$

Where the terms *adv* and *rec* stand for advancing and receding [24].

As will be discussed further, the most definitive and meaningful properties affecting the qeq were

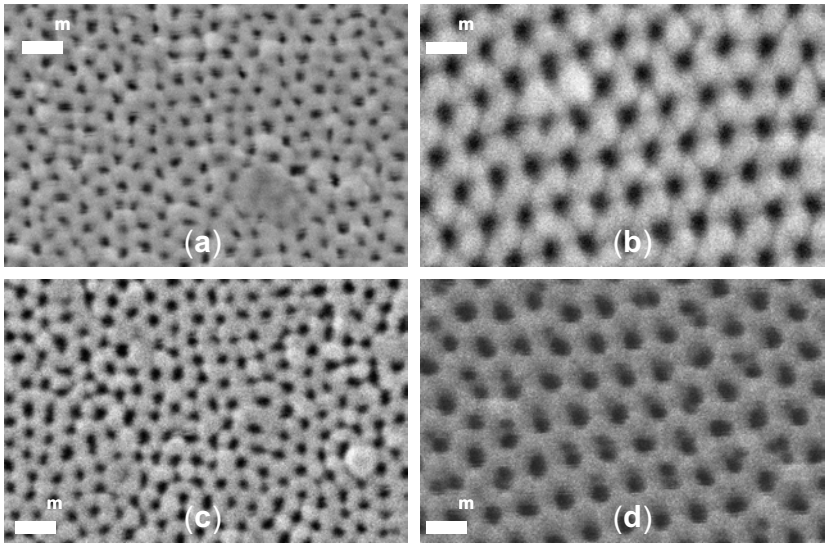


Fig.1. SEM micrographs of the top view of anodic alumina sheets. Anodization was conducted in (a) 0.3M sulfuric acid at 10 °C and 20 V (sample **1**), b 0.3M oxalic acid at 10 C° and 40 V (sample **3**). Pore opening was carried out in 0.35M phosphoric acid at 30 °C for 10 min (c) sulphuric acid anodized (sample **2**), (d) oxalic acid anodized (sample **4**).

Table 3. Contact angle tensiometric measurements. Experimental (θeq) and arithmetic mean data (0.5(cosθadv+cosθrec)).

test liquid	sample 1		sample 2		sample 3		sample 4	
	θ_{eq}	$0.5(\theta_{av}+\theta_{rec})$	θ_{eq}	$0.5(\theta_{av}+\theta_{rec})$	θ_{eq}	$0.5(\theta_{av}+\theta_{rec})$	θ_{eq}	$0.5(\theta_{av}+\theta_{rec})$
water	68.1±0.3	77.5±0.3	65.8±0.0	78.2±0.2	73.3±0.1	82.2±0.4	62.6±0.2	81.6±0.3
DMSO	32.7±0.3	26.2±0.2	36.9±0.3	35.3±0.3	50.6±0.1	56.0±0.6	48.5±0.1	54.2±0.4
DMF	36.6±0.3	40.1±0.6	45.7±0.4	45.0±0.3	56.2±0.1	56.8±0.2	54.4±0.3	54.6±0.6
acetone	57.8±0.1	57.3±0.3	59.3±0.4	61.3±0.4	63.7±0.2	63.7±0.6	67.6±0.1	67.8±1.2
2-propanol	63.3±0.2	62.3±0.2	53.5±0.8	63.3±0.2	69.2±0.0	68.7±0.2	69.5±0.3	69.5±0.2
butanol	61.2±0.1	58.2±0.5	60.8±0.1	61.6±1.0	67.3±0.1	66.5±0.3	66.6±0.0	67.0±0.3
ethyl acetate	59.1±0.3	58.2±0.3	59.9±0.0	61.2±0.3	67.4±0.4	66.8±0.6	64.5±0.4	65.1±0.3
toluene	61.9±0.3	63.9±0.5	58.3±0.4	62.6±0.5	68.9±0.1	68.4±0.1	69.0±0.1	69.2±0.4
hexane	57.9±0.2	57.9±0.2	59.2±0.8	61.4±0.7	64.5±0.3	66.1±0.4	68.0±0.1	67.1±0.5

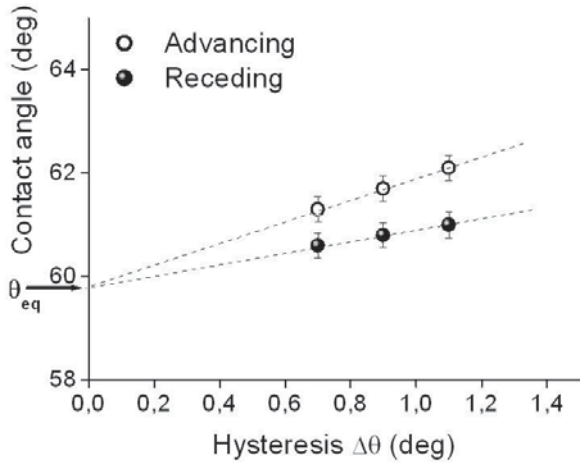


Fig. 2. Advancing (open circles) and receding (filled circles) contact angles *versus* contact angle hysteresis for ethyl acetate on sample 2. The dashed lines correspond to the linear regressions. The equilibrium contact angle is 59.9 in this case.

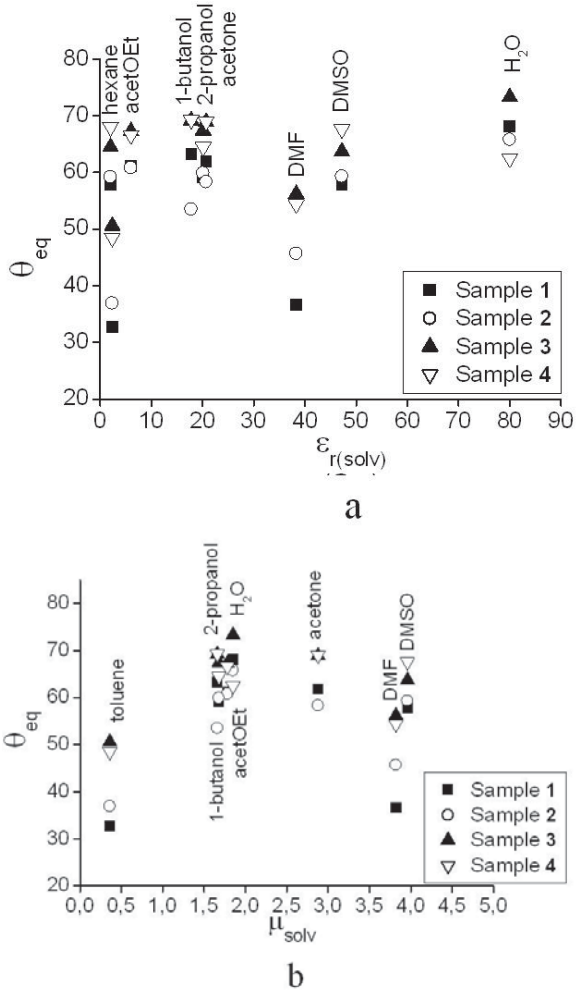


Fig. 3. Effect of $\varepsilon_{r(solv)}$ (2a) and μ_{solv} (2b) on the contact angle (θeq) obtained with the dynamic tensiometric method.

the dielectric constants and the dipolar moments of the solvents as it is shown in Fig. 3.

Table 3 shows the experimental values of qeq obtained for samples **1** to **4**. A general inspection of the θ_{eq} values show that DMSO and DMF, in this order, are the solvents which best wet the porous anodic aluminium oxide sheets. On the other hand, for a given solvent, the sulphuric AAOs have a lower θ_{eq} than oxalic AAOs; thus, it can be conclude that the influence of the widening is less significant than the type of alumina. Whereas, the highest θ_{eq} values are systematically obtained for the case of water. Thus, it seems clear that, water due to its highest surface tension value, practically does not wet any of the samples. These findings have a practical importance and clearly show the convenience of using DMSO and DMF as solvents for an easier filling of the anodic alumina porous, as well as the inherent difficulty of introducing aqueous solutions into the pores.

The θ_{eq} values for the four AAO sheets evaluated with the tensiometric method on the different test liquids are summarized in Table 3. Closer consideration on this group reveals that there is a dependence on the values of polar parameters (μ_{solv} and $\varepsilon_{r(solv)}$, Fig. 3) from solvents and surfaces. Noticing that the main difference between the AAOs studied in this work is the surface composition, this is, the amount of hydroxide, sulphate, and oxalate groups formed during the anodized process. The AAOs surfaces interact with the liquid phase *via* surface groups, thus, the polar component defines, in part, the strength of the interaction between the test liquid and the AAO surface [25]. None to medium polar tested solvents result in higher values of θ_{eq} and, thus, into a poorer interaction with the AAO surface. Water, exhibits high values of $\varepsilon_{r(solv)}$ and μ_{solv}, but it also has the highest value of γ_{solv} which results in the worst interaction with the AAO surface. Whereas, DMSO and DMF have the higher values of $\varepsilon_{r(solv)}$ and μ_{solv}, with γ_{solv} = 25. Therefore these solvents present stronger interactions with the surface groups, in particular, with the hydroxide groups from the AAO surfaces, which can explain the observable values of qeq for these solvents. This interaction also exists in water but, once again the high value of gsolv prevents water from spreading to afford the highest θ_{eq} values. These results suggest that there is a delicate balance between the properties of the tested liquids and the high component

Table 4. Wetting force values.

test liquid	***Wf***			
	1	2	3	4
water	32.2±0.7	31.2±3.2	21.2±0.2	22.6±0.7
DMSO	25.6±0.1	27.5±2.5	22.2±1.3	21.4±0.8
DMF	39.0±0.2	37.0±2.2	29.0±3.1	30.6±0.6
acetone	45.7±1.4	42.7±0.7	29.6±0.8	30.8±1.4
2-propanol	26.4±4.6	24.5±1.9	20.8±1.8	20.3±1.4
butanol	25.7±0.5	24.0±2.2	20.0±1.6	21.2±1.4
ethyl acetate	22.5±0.3	22.4±3.7	18.3±1.1	17.6±0.6
toluene	26.1±0.7	23.8±1.4	22.2±0.4	18.9±0.8
hexane	20.0±0.9	18.5±2.1	15.8±0.6	15.2±1.4

on the dipolar contribution of the solvents and their surface tension, referred as 'disjoining pressure' [26].

Other experimental parameter, derived directly from the contact angle and surface tension is the wetting force (*Wf*), which is related with the strength of the interaction between liquid and solid phases, and calculated from Eq. (2)

$$Wf = \theta solv\ P\cos\theta_{eq}, \quad (2)$$

where, $\theta_{solv} = \theta_{lv}$, is the surface tension for the liquid-vapour phase and P is the perimeter of the probe (2.1 cm for this work).

As can be seen from data in Table 4, there are three well distinguishable regions. Since *Wf* is proportional to the surface tension, it can be observed a linear correlation of the solvents with $\theta solv \approx 25$ mN/m (graphics not shown). Within this group of solvents, DMSO and DMF show the highest *Wf* values and water ($\theta_{solv} = 73$), toluene ($\theta_{solv} = 28.5$) and hexane ($\theta_{solv} = 18.4$) do not fit for this linear correlation being away from the main solvents group.

The hydrogen bond interactions from DMSO and DMF that interact with the hydroxide groups from the AAO surfaces can explain the observable values of *Wf* for these solvents. This interaction also exists in water, which would explain the high values of *Wf* for this solvent; however, once again the high value of gsolv prevents water from spreading to afford the highest qeq values.

Besides the chemical composition of the AAOs, there is the porosity factor. Sample **1** present average porous diameters of 15 nm; while sample **3** has 46 nm as an average diameter (Fig. 1). The widening process does not seem to affect the *Wf* values of the samples. Comparison of the values of the samples **1** and **2** with those of the sheets **3** and **4** reveals not observable tendency. Thus, these results can not be used to explain the solid-liquid interactions. Nevertheless, the differences between oxalic and sulphuric AAOs are more important, so the values of *Wf* from **1** and **2** are higher than the *Wf* values for **3** and **4**; this can be explained in terms of the proportion of contact area and the holes present in the surfaces. Since, there are more contact area in **1** and **2**, there are more interaction with the solvent. So, taking into account both factors, the chemical composition and contact area, the resulting wetting force is higher in the AAOs anodized with sulphuric acid (samples **1** and **2**) than in **3** and **4** (AAOs anodized with oxalic acid).

These results can be resumed as follows: the wetting force between sheets with or without widening is basically the same, this is: *Wf*(**1**) ≈ *Wf*(**2**) and *Wf*(**3**) ≈ *Wf*(**4**); but, between different anodized sheets, the *Wf* values are notably different, expressing this as; *Wf*(sulphuric anodized AAO; **1** and **2**) > *Wf*(oxalic anodized AAO; **3** and **4**) and, in consequence, θ_{eq}(**1** and **2**) < θ_{eq}(**3** and **4**).

3.2 Goniometric and Washburn determinations

θ_{eq} were evaluated using both goniometric and Washburn techniques. However, goniometric measurements are extremely sensitive to variations in the local heterogeneity of the chemistry and topography of the surface, and this results in a large standard deviation in the experimental data, and the values of θeq, except for water, are too low (0 - 10°).

And *ii)* the results obtained by the Washburn method reveal no spontaneous penetration into the pores for none of the applied liquids. Therefore, it is clear that these methods are inadequate and/or not sensible enough to analyze the effect of the contact angle on the nanopores of AAO surfaces.

3.3. Wetting of porous templates

Nanoscale wetting phenomena can be depicted considering a small liquid droplet deposited on a smooth solid substrate, its wetting behaviour can be described by the spreading parameter, defined as $S = \gamma_{sv}-\gamma_{sl}-\gamma_{lv}$ (with γ_{sv}, γ_{sl}, γ_{lv}, respectively the solid-vapour, solid-liquid and liquid-vapour interfacial tensions). If *S* is negative, a liquid drop deposited on the solid adopts an equilibrium shape corresponding to a finite contact angle θeq defined by the Young's condition $\cos\theta_{eq} = (\gamma_{sl}-\gamma_{sv})/\gamma_{lv}$; if *S* is positive, spontaneous spreading occurs, and the equilibrium situation corresponds to a complete coverage of the solid by a thin liquid film. *S* measures the interfacial energy per unit area gained during the spreading [27] Thus we propose the following explanation for the wetting of AAOs subject of study in the present investigation. If a liquid is allowed to spread on the pore walls of AAOs (Figs. 4a-c); first the test liquid is brought into contact with the membrane (Fig. 4a). Organic materials and most solvents are considered as low energy materials with respect to their surface energies, whereas inorganic materials are referred as high energy materials (covalent, ionic and metallic). Low energy liquids spread rapidly on high energy surfaces. Therefore, the pore walls will be covered by a mesoscopic film if they exhibit a high surface energy (Fig. 4b) [28]. We suggest that the underlying driving forces are due to short range as well as long range polar interactions between the wetting liquid and the pore walls. Thus, if the adhesive force (γ_{sl}) is strong enough to overcome the cohesive force (γ_{lv}), the pores will be complete filling as in the case of DMSO and DMF (Fig. 4c). On the contrary if cohesive force is stronger than the adhesive, the equilibrium could be reached on a time scale from several months up to several years. This could be the case of water. We have previously reported on the obtaining of nanostructures by immersion only, after 15 days [29].

The experimental results suggest that the water only occupies the very top of the nanopores as is shown in Fig. 4a. Due to the lack of detailed structural information for the 'nanointerface' solid-liquid, this interpretation would need further investigation.

Despite the fact, that the effect of the small differences between the values of θeq from the four AAO sheets can be ruled out by experimental error, an alternative explanation can be based on the amount of anions on the surface. Since the widened process eliminates, in part, hydroxyl, sulphate and/or oxalate anions 30,31] this would result in a less inorganic and polar surface, lowering the energy surfaces and so the interaction liquid-solid. Thus, the alumina that has been widened (**2** and **4**) had a poorer interaction with the test liquids than those not widened (**1** and **3**). Finally, alumina sheets **1** and **2** can be considered as more polar than **3** and **4**, since the later have oxalate anions in contrast with **1** and **2,** which contain sulphate anions on their surfaces.

4. SUMMARY

Specific polar parameters were identified to describe the effect of the contact angle on porous anodic alumina oxide sheets. The best correlation was found between the polar contribution of the test liquids trough ε_r(solv) and msolv values and the equilibrium contact angle (θ_{eq}). The solvents DMSO and DMF have the perfect equilibrium between polar and

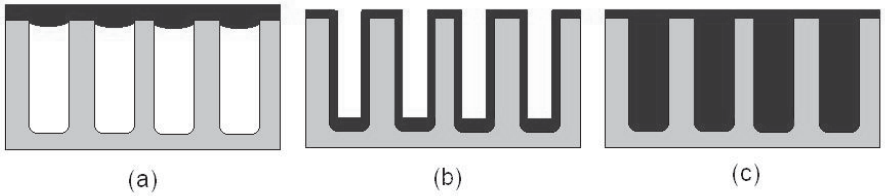


Figure 4. Schematic representation of the different stages of pore wetting. (a) A test liquid is brought into contact with the AAO membrane and the liquid spreads on the substrate. (b) A mesoscopic film of the liquid rapidly wets the pore walls. (c) The liquid wetted the nanostructured layer.

surface tension properties for a complete filling of the porous surface, opposite from water which has high values of $\varepsilon_{r(solv)}$ and μ_{solv}, but too high surface tension (γ_{solv}), thus preventing water from filling the pores causing an increase on the contact angle value. Liquids with low $\varepsilon_{r(solv)}$ and μ_{solv} values do not fill completely the pores of the membranes and presented values of qeq around 60°. The wetting force between sheets with or without widening is basically the same, this is: *Wf*(**1**) ≈ *Wf*(**3**) and *Wf*(**2**) ≈ *Wf*(**4**); but, between different anodized sheets, the *Wf* values are notably different, expressing this as; *Wf*(**1** and **3**) > *Wf*(**2** and **4**) and, in consequence, θ_{eq}(**1** and **3**) < θ_{eq} (**2** and **4**); θ_{eq} (**1**) ≈ θ_{eq}(**3**) and θ_{eq}(**2**) ≈ θ_{eq}(**4**). These findings have a practical importance and clearly show the convenience of using DMSO and DMF as a solvent for an easier filling of the anodic alumina porous, as well as the inherent difficulty of introducing aqueous solutions into these pores.

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