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Membrane surface characterisation by contact angle measurements using the immersed method

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Abstract

A new concept of contact angle measurements by the immersed method is applied to membrane surface characterisation. The general system of two immiscible liquids is used wherein a droplet of CCl_4 is deposited on the membrane surface immersed in an aqueous solution. When the solution is pure water, membrane hydrophilicity is evaluated. With aqueous solutions of a cationic surfactant (below its critical micelle concentration) at different pH values, membrane titration curves are obtained. From these curves we obtain the acid–base behaviour of each membrane and the pH value at which half of the membrane surface groups are ionised, $pK_{1/2}$. This method is tested with five nanofiltration membranes, a series of three cellulose acetate membranes, CA-316, with increasing hydraulic permeabilities and two commercial thin film composite membranes, CD-NF-50 of poly(*trans*-2,5-dimethyl)piperazin thiofurazanamide/polyethersulfone and HR-98-PP of polyamide/polysulfone. The results show that the method (i) is easy to perform and avoids dynamic measurements (requires 5 min of drop deposition); (ii) is reproducible (maximal deviations of 7°); (iii) simulates multiple membrane technical environments (e.g. pure water, aqueous solutions); (iv) is not affected by the presence of pores in the nanofiltration range of operation; and (v) is sensitive to membrane hydrophilicity and membrane acidity/basicity (titration curves and $pK_{1/2}$ values). Furthermore, the results show the direct effect of the annealing treatment on the acidity of the CA-316 membranes and they evidence the importance of the membrane chemical properties (hydrophilicity, acidity/basicity) on the membrane permeation performance.

Keywords: Membrane surface characterisation; Contact angles; Immersed method; Hydrophilicity; Surfactant; Acid–base interactions; Nanofiltration

1. State of the art

Characterisation of the surface chemistry is a crucial issue in membrane science and technology, because it is well known that membrane performance depends not only on feed hydrodynamics and steric hindrances, but also on membrane surface chemistry (hydrophilicity, membrane surface charge) and on membrane–solute(s)–solvent chemical interactions.

Contact angle is a measure of the wettability of an ideal surface. It is one of the most easy, common and reliable methods of determining solid surface properties when it is possible to separate intrinsic variations from apparent variations. These apparent variations are induced by surface porosity and roughness, surface morphologic alterations during the measurement (e.g.

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resulting from surface drying), surface heterogeneity and contaminations of the solution(s) and/or solid surface.

Until now, most of the contact angle measurements for membrane characterisation have been made on hydrophobic membranes used for pervaporation or gas permeation [1–4] and on porous hydrophilic or hydrophobic membranes used in microfiltration (MF) or ultrafiltration (UF) [5,6]. Fane et al. [5] correlated flux decline with the variation of membrane hydrophilicity while Oldani and Schock [6] showed that hydrophilic membranes do have better flux recoveries. However, these studies have some drawbacks because they are performed with dry MF or UF membrane samples, measuring the contact angle of a droplet of water on membrane surface. Using dry samples, the information is less relevant than that collected in a technical environment of a MF/UF operation, i.e. membrane in contact with an aqueous stream. Besides, drying may irreversibly damage the morphological structure of some membranes, e.g. cellulose acetate membranes prepared by phase-inversion using the wet process. In addition, for MF/UF membranes, the surface porosity and surface roughness may affect the contact angle and under cover intrinsic variations of membrane hydrophilicity.

In the 70's, Hamilton [7] proposed the immersed contact angle method whereby he obtained the magnitude of the polar interaction by measurement of the contact angle of *n*-octane (compound with a dispersive surface tension equal to water) on solid surfaces immersed in water. David and Misra [8] used the reversed system, they measured the contact angle of water on the surfaces immersed in *n*-octane. Matsunaga and Ikada [9] and Toussaint and Luner [10] evaluated the dispersive component of the surface free energy of cellulose materials and their non-dispersive interaction with different polar liquids (water, glycerol, among others) based on a series of contact angle values of the polar liquid on solid surfaces immersed in different hydrocarbons. This solid–water–hydrocarbon system is very advantageous. It allows the determination of both dispersive and non-dispersive interactions (since hydrocarbons do not interact specifically with the solid surface) and it does not require dynamic measurements as the equilibrium between the two immiscible liquids and the solid surface is promptly reached [9,10]. Moreover, it thoroughly avoids the polymer contact with air moisture (since saturated immersion liquids are used) and therefore, the surface spreading pressure may be neglected [9,11].

Instead of using the two-liquids immersion system, Zhang and Hallström [4] and Gekas et al. [12] measured contact angles of air on membrane surface immersed in water (captive bubble method). However, this system, as well as the Hamilton's method require a more sophisticated *apparatus* where the membrane is suspended on the top of the immersion chamber [4] (in the case of asymmetric membrane suspended up-side down with the active layer facing the bulk solution), because the air bubble or the *n*-octane droplet are both less denser than the immersion solution of water.

Still with the air bubble–liquid–membrane system, Keurentjes et al. [13] developed a simple method for indirect determination of the contact angle. They used the sticking bubble technique, i.e. they measured the percentage of air bubbles that stick to the membrane surface placed on the bottom of a cell, using different immersion liquids. Plotting the percentage of sticking bubbles vs. the surface tension of the liquid they obtained the surface tension of the liquid at the point of detachment, from which, using the force balance, they compute the contact angle. This method is not influenced by the presence of the pores and so it is especially adequate to evaluate the hydrophobicity of porous materials, such as MF and UF membranes. However, it is much too laborious and time consuming and it is not worth for dense membranes, such as those of nanofiltration and reverse osmosis. In addition, the air bubbles would not stick to hydrophilic membranes immersed in aqueous solutions because the water wets the surface (almost) completely [13], rendering this method inadequate for most practical situations.

2. Development of a new immersion system for contact angle measurement

The main objective of the present work is to develop a simple method of determining the surface chemical properties, namely relative hydrophilicity and acidity/basicity, of nanofiltration membranes. The method should preferably allow the evaluation of membrane–solvent–solute(s) chemical interactions. Therefore, based on the previous work reported in the

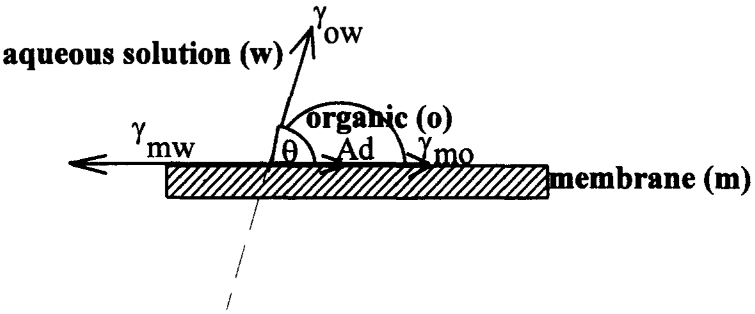

Fig. 1. Final form of a droplet of an organic (CCl_4) on a membrane immersed in an aqueous solution: contact angle and membrane–CCl_4–solution interfacial forces.

literature, we designed a two-liquids immersion system sensitive to pH variations and to the presence of a dissolved solute.

The general system consists of a drop of a neutral organic (o), which is water immiscible and heavier than water, e.g. carbon tetrachloride, placed on the membrane surface (m) immersed in an aqueous solution (w). Fig. 1 illustrates the contact angle, θ, of CCl_4 on the membrane surface immersed in the aqueous solution and the interfacial forces: membrane–CCl_4, γ_{mo}; membrane–solution, γ_{mw}; and CCl_4–solution, γ_{ow}. The surface free energy which is lost when solute is adsorbed on membrane surface is represented by Ad (when the immersion solution is pure water there is no contaminant and solute adsorption (Ad) is zero). Contact angles smaller than 90° correspond to hydrophobic membranes while contact angles larger than 90° correspond to hydrophilic membranes.

There are two main reasons for choosing this system:

(i) the need to simulate the membrane technical environment (water immersed) and, simultaneously, to keep the membranes wet, avoiding risky and time consuming drying processes;

(ii) the opportunity to take advantage from surface contamination (usually an undesired effect) with solute adsorption.

The force balance to the interface yields the Young–Dupré equation, modified to include solute adsorption (Ad)

$$\gamma_{\mathrm{ow}}\cos\theta = \gamma_{\mathrm{mw}} - \gamma_{\mathrm{mo}} - \mathrm{Ad} \quad (1)$$

For hydrophilic surfaces (such as most of the membranes) and polar liquids (such as water), the adhesive forces acting on the interface are now-a-days considered to have a non-polar Lifshitz–Van-der-Waals and an acid–base (such as hydrogen bonding) component [14–16]. The acid–base interaction requires that acidic sites of one phase interact with basic sites of the other, so that if either phase is neutral or if both phases have only basic or only acidic sites, there can be no acid–base interaction [16].

Most membrane polymers have acidic (usually, carboxylic, sulphonic) and basic (usually, amine) groups and the global character is dependent on the pH of the immersion solution. With increasing pH, the membrane can go from positively charged (basic character) to negatively charged (acidic character). When the membrane is immersed in an aqueous solution, this global character determines membrane–solute adsorption, therefore conditioning the final contact angle of CCl_4. Fig. 2 illustrates the relationship between cationic surfactant adsorption on an ionisable membrane surface and the contact angle of CCl_4 when (a) the membrane and the surfactant are both positive; (b) the membrane is neutral, low adsorption; (c) the membrane has a negative charge, complete monolayer formation. Depending on membrane and surfactant characteristics, when the membrane surface is highly negatively charged the formation of a double layer (Fig. 2(d)) may occur [17].

Plotting contact angles against solution pH results in membrane titration curve generally represented in Fig. 3 for a basic membrane (Fig. 3(a)), for an acidic membrane (Fig. 3(b)) and for an amphoteric (both acidic and basic) membrane (Fig. 3(c)). In this figure, the notes 2(a)–2(d) correspond to the situations illustrated in Fig. 2 and $\mathrm{p}K_{1/2}$ is the pH value at which

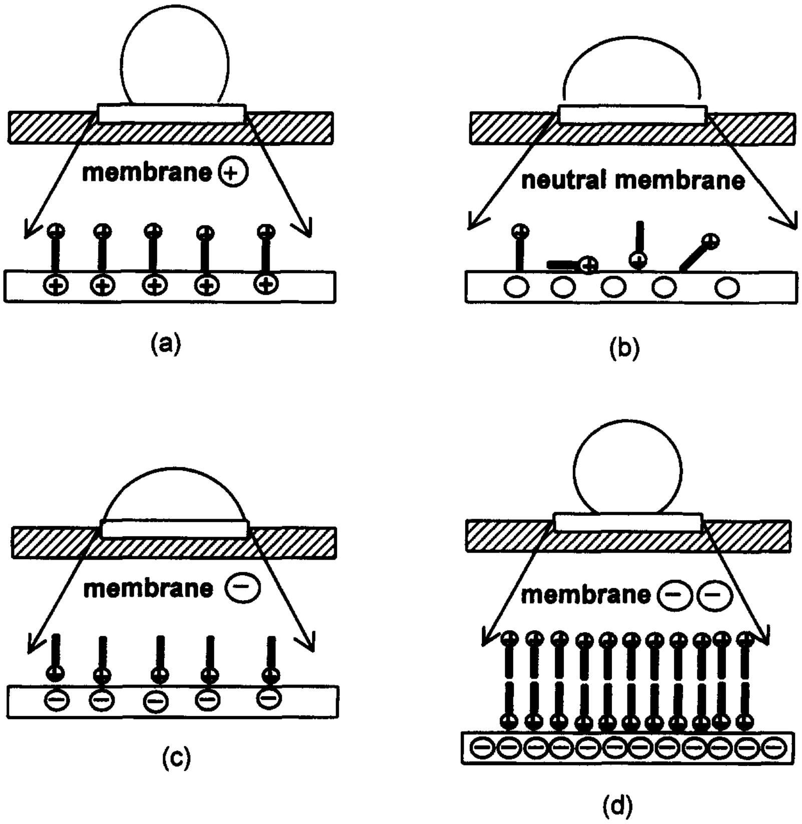

Fig. 2. Illustration of the relationship between cationic surfactant adsorption on a ionisable membrane surface and the contact angle of CCl_4: (a) membrane and surfactant with the same charge; (b) neutral membrane; (c) membrane with opposite charge, complete monolayer formation; (d) membrane with maximum opposite charge, double layer formation.

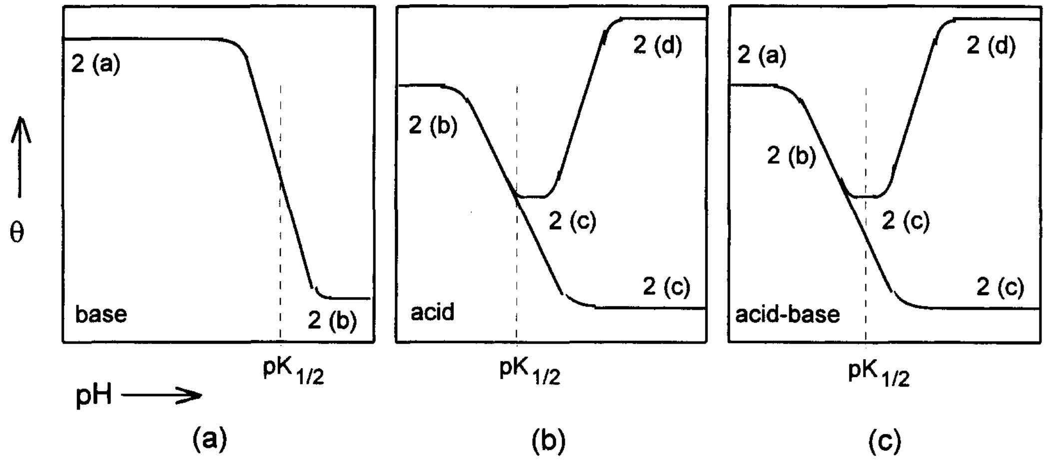

Fig. 3. Membrane titration curves obtained with contact angle of CCl_4 on membrane surface immersed in a cationic surfactant solution at several pH values for (a) basic membrane; (b) acidic membrane; (c) amphoteric membrane (2(a)–2(d) are the situations illustrated in Fig. 2).

50% of the groups are ionised [18]. For example, for an AH acid, the equilibria involved are:

$$\mathrm{pH} < \mathrm{p}K_{1/2} \quad [\mathrm{AH}] \gg [\mathrm{A}^-]$$
$$\mathrm{pH} = \mathrm{p}K_{1/2} \quad [\mathrm{AH}] = [\mathrm{A}^-]$$
$$\mathrm{pH} > \mathrm{p}K_{1/2} \quad [\mathrm{AH}] \ll [\mathrm{A}^-]$$

Other types of titration curves were obtained by Whitesides et al. [18] based on contact angle measurements using buffered water as immersion solution.

In the present work, two types of immersion solutions are used (i) pure water, to evaluate membrane relative hydrophilicity, and (ii) an aqueous solution of a cationic surfactant at different pH values to evaluate membrane acidity/basicity.

The method is tested with five nanofiltration (NF) membranes (pore diameter in the range of 10^{-9} m) of different materials and porosities. A CA-316 series of three cellulose acetate (CA) membranes with increasing hydraulic permeabilities (i.e. with increasing porosities) are prepared in the laboratory by the phase inversion method. Two commercial thin film composite membranes are used, CD-NF-50 of poly(*trans*-2,5-dimethyl)piperazinthiofurazanamide/polyethersulfone (TFZ/PES) and HR-98-PP of polyamide/polysulfone (PA/PS). With the set of membranes chosen, we test the method for weakly acidic (CA), predominantly acidic (TFZ) and predominantly basic (PA) polymers and, for the same polymer, we study the effect of porosity in the range of nanometers (CA-316 series).

3. Experimental

3.1. Membranes

Laboratory-made and commercial membranes were investigated.

A series of flat-sheet cellulose acetate asymmetric membranes, labelled CA-316 series, were prepared in the laboratory by the phase inversion method as described by Kunst and Sourirajan [19]. The individual CA-316 membranes are identified by the numbers 50, 68, and 86 that correspond to the annealing temperature in °C. This annealing was performed to obtain membranes of different permeabilities. Details on the preparation and annealing conditions are listed in Table 1.

The cellulose acetate (39.8% acetyl content) was supplied by Eastmann Kodak, MW 30270. This is a linear glassy polymer with a degree of substitution of 2.5, i.e. 2.5 of the three hydroxyl groups on the anhydroglucose ring bear an acetyl (CH_3CO–) substituent instead of the hydrogen that is found in the native cellulose. Hydroxyl groups are responsible for CA-316 membrane hydrophilicity and weakly acidic character (–OH dissociation constant is around 10^{-10} to 10^{-12}). Acetyl substituents are responsible for

Table 1
Film casting conditions of the CA-316 series membranes

Membrane	CA-316-50	CA-316-68	CA-316-86
Casting solution (wt%)			
Polymer: CA 398	17 (in all cases)		
Solvent: Acetone	69.2 (in all cases)		
Additive: $Mg(ClO_4)_2/H_2O$	1.45/12.35 (in all cases)		
Casting conditions			
Temperature of solution (°C)	9–12 (in all cases)		
Temperature of atmosphere (°C)	22–23 (in all cases)		
Humidity of atmosphere (%)	50–65 (in all cases)		
Solvent evaporation time (min)	1 (in all cases)		
Gelation medium	Ice cold water (1 - 2 h) (in all cases)		
Annealing conditions			
Annealing medium	Hot water (in all cases)		
Annealing time (min)	11 (in all cases)		
Temperature of medium (°C)	50	67.5	86

membrane hydrophobicity. At extreme pH values (acid or alkaline) the acetyl groups may hydrolyse to hydroxyl groups and, therefore, CA-316 membranes cannot be subjected to severe pH for long periods of time to avoid irreversible changes in membrane characteristics. Membrane hydrophilicity would increase and the pore radius as well, because the –OH steric hindrance is lower than that of CH_3CO–. Usually, the recommended pH limits of operation are 2–8, to ensure a reasonable membrane lifetime, which is 2–3 years in most cases. For very short time periods (e.g. 1–2 days), it is safe to use a pH interval of 3–11.

The two commercial membranes are both thin film composite membranes.

The CD-NF-50 membrane (supplied by Separem, Italy) has an active layer of TFZ (poly(*trans*-2,5-dimethyl)piperazinthiofurazanamide) casted on an ultrafiltration PES (polyethersulfone) membrane. The CD-NF-50 is an amphoteric membrane with a predominant acidic character from the carbonyl and sulphur groups of TFZ.

The HR-98-PP membrane (supplied by Dow/DDS, Denmark) has an active layer of PA (polyamide) casted on a PS (polysulfone) support. It is an amphoteric membrane with a predominant basic character from the amide groups.

The five membranes are all nanofiltration/reverse osmosis membranes as expressed by their hydraulic permeabilities and average pore radii shown in Table 2.

Hydraulic permeability was determined by the slope of the pure water flux vs. transmembrane pressure [20]. Membrane pore radius was determined by modelling the experimental data of dilute solutions of sugars (ethanol, glycerol, glucose, saccharose and raffinose) by an integrated transport model for UF/NF. In this model, the average pore radius is a global parameter related to the membrane morphological structure (i.e. polymer molecular arrangement) responsible for the diffusive and convective steric hindrances and for the membrane–solute–water chemical interactions. The integrated transport model, as well as the NF experimental set-up and procedure have been already described by Rosa and de Pinho [20,21].

Table 2
Membrane permeation characteristics (from [20,21] (pressure= 3 MPa, temperature =298 K, feed tangential velocity=0.11 m/s, feed concentration=0.3 kg/m^3, membrane surface area= 13.2×10^{-4} m^2)

Membrane	Hydraulic permeability (m)	Average ore radius (Å)
CA-316-50	1.55	4.4
CA-316-68	0.90	4.0
CA-316-86	0.16	3.3
CD-NF-50	2.34	4.2
HR-98-PP	1.63	2.8

3.2. Surfactant solution

A cationic surfactant was selected because most commercial NF membranes have an acidic character and we wanted to promote membrane–surfactant attraction. The surfactant used was *N*-cetyl-*N,N,N*-trimethylammonium bromide (C16TAB), pro analysis, from Merck. In the pH range studied of 3–11 this surfactant presents little or no significant pH sensitivity [17]. The surfactant solution has to be below the value of critical micelle concentration (CMC). Otherwise, the surfactant molecules will interact with each other forming micelles instead of interacting with the membrane surface forming adsorption layers. Using the Klevens equation [17] the value of CMC for C16TAB is 0.83 mM. For safety reasons, and because for most ionic surfactants CMC decreases with the ionic strength of the solution (promoted by the pH adjustment), a concentration of 0.3 mM was used, well below the CMC of 0.83 mM.

Solution pH was adjusted with NaOH and HNO_3 covering the range of 3 to 11. Deionised water with a conductivity lower than 0.2 μS/cm was used.

Concerning the ability to form a double layer, although this is not a typical behaviour of this class of surfactants due to the high volume of the polar head, C16TAB can form a double layer because of its long aliphatic chain. In fact, it is 32 times a C–C length against the sphere radius of the polar head. In addition, there is always an excess of surfactant in solution. For a minimal volume of solution of 1 ml and a minimal polar head radius of 1 Å and for a maximal membrane area of 2 cm^2, there are ca. 30 times more *adsorbable material area* (polar heads) than *adsorbent area* (area available for adsorption) (i.e. 0.3×10^{-3} ×

$10^{-3}\times 6.022\times 10^{23}\times 3.14\times 10^{-20}/2\times 10^{-4}=29.3$). The formation of a third layer of adsorption is not possible because the polar heads of the double layer are facing the bulk solution, therefore repelling the surfactant in solution.

3.3. Contact angles measurements

Membrane samples have 0.5–1 cm^2 of surface area. Prior to the measurements and between different solutions, the membranes were washed in an ultrasound bath with deionised water (<0.2 μS/cm) for two times, 15 min each. The membranes were then immersed in the aqueous solution, at room temperature (20°C), for a time period optimised to ensure the stabilisation of membrane–solution interactions. Afterwards, they were put on a sintered glass plate, with the active layer up, and transferred to a spectrophotometric quartz cell filled with the immersion solution. A droplet (2–5 mm height) of CCl_4 (pro analysis, Merck) was delivered by a microsyringe. After a fixed deposition time, the image was recorded. Both stabilisation and deposition times were optimised in prior experiments described below (point 3.4.). Special care was taken when manipulating CCl_4, being always avoided the direct contact (using eye, skin and clothes protection) and vapours inhalation.

The experimental set-up integrates a colour video camera JVCO mounted on a microscope Wild M3Z where the quartz cell was adapted. The video signal is transmitted to a Video Pix Framegrabler from Sun Microsystems, using a computer Sun Sparcstation IPC to import the drop image. The contact angles were obtained by the sessile drop method using the software ADSA-P (Axisymmetric Drop Shap Analysis-Profile) developed by Neumann and co-workers.

Each value presented is the result of a statistical t-test analysis (95% confidence), $\overline{\theta}\pm(\sigma_{n-1}\,t_{95\%}/\sqrt{n})$. The number of samples, n, is relative to the number of droplets deposited in two different membrane samples and n is always equal or higher than 8 ($n\geq 8$).

3.4. Optimisation of the drop deposition time and stabilisation time

Contact angles of CCl_4 on membrane active layer immersed in pure water (<0.2 μS/cm) were measured after 1, 5, 60 and 90 min of drop deposition. The results are shown in Table 3. We tested only two membranes, CA-316-50 and CD-NF-50, because among the five membranes studied they have the larger pores (see Table 2), thus because the ones for whom there is a possible variation of the contact angle with deposition time. The membranes were fully hydrated since they had been stored in water for, at least, one week (the water being changed every day).

Table 3
Contact angles of CCl_4 on membrane active layer immersed in pure water (<0.2 μS/cm, pH=6.5, immersion time>1 week, water daily changed) measured after 1, 5, 60 and 90 min of drop deposition

Membrane	Time (min)	θ (°)
CA-316-50	1	99±2
	5	100±3
	60	99±3
	90	100±3
CD-NF-50	1	126±3
	5	127±2
	60	125±1
	90	127±3

From Table 3, five minutes are more than sufficient to reach the equilibrium between the two immiscible solutions and the surface. Therefore, dynamic measurements are not necessary, this being one of the great advantages of the two-liquids immersion method, as discussed previously.

The stabilisation time was optimised with a dilute (0.3 kg/m^3) aqueous solution of 2-chlorobenzoic acid (pro analysis, Merck), one of the solutes that will be important to study in terms of membrane–solute chemical interactions. Contact angles of CCl_4 on membrane active layer immersed in chlorobenzoic acid solution for different periods of time were measured after 5 min of drop deposition time. The results are presented in Table 4.

From Table 4 we conclude that the optimum stabilisation time is 24–48 h. Longer time periods may cause negative side effects, such as solute degradation and/or membrane degradation.

Comparing Tables 3 and 4 we conclude that the values obtained with pure water are different from those obtained with 2-chlorobenzoic acid solution, i.e. the two-liquids immersion method developed is sensitive to the variation of the immersion solution (presence of solute and/or solution pH).

Table 4
Contact angles of CCl_4 on membrane active layer immersed in 2-chlorobenzoic acid solution (pH=2.9) for different periods of time (values measured at room temperature, after 5 min of drop deposition)

Membrane	Time (h)	θ (°)
CA-316-50	1	94±5
	24	95±3
	48	94±3
CA-316-68	1	98±3
	24	97±4
	48	95±3
CA-316-86	1	99±3
	24	102±4
	48	101±9
CD-NF-50	14	139±5
	38	141±5
	86	141±3
HR-98-PP	14	140±10
	38	145±5
	86	147±6

Table 5
Contact angles of CCl_4 on membrane active layer immersed in pure water (<0.2 μS/cm, pH=6.5, immersion time>1 week, water daily changed, values measured at room temperature, after 5 min of drop deposition)

Membrane	θ (°)
CA-316-50	100±3
CA-316-68	104±2
CA-316-86	107±1
CD-NF-50	127±2
HR-98-PP	146±3

4. Results and discussion

4.1. Immersion system I: CCl_4–membrane–water

Table 5 shows the results relative to the CCl_4–membrane–water system. Four main conclusions can be drawn.

First, the method is reproducible and hysteresis is controlled as the values of $\sigma_{n-1}\, t_{95\%}/\sqrt{n}$ range from 1 to 3°. These values are similar to (or even lower than) those reported in the literature (e.g. 0.5–2° [9], 4–16° [12]) and considered to be possible to obtain by author (i.e. 2° [22]). Because they are relative to, at least, two membrane samples they indicate the macroscopic homogeneity of the membrane active layer.

Second, the contact angles are larger than 90° for all the membranes, thereby the membranes do prefer the aqueous solution to CCl_4, i.e. the five membranes studied are hydrophilic. In addition, these results indicate the relative hydrophilicity order of the membranes:

$$\text{CA-316-50} \leq \text{CA-316-68} \leq \text{CA-316-86} < \text{CD-NF-50} < \text{HR-98-PP}$$

Third, for the CA-316 series the contact angle increases with the increase of the annealing temperature. According to Table 2, the membrane pore radius decreases with the annealing temperature. As a result, in this series of homologous membranes of the same polymer the contact angle decreases with the increase of membrane pore radius (see Tables 2 and 5). In turn, the contact angle deviation, $\sigma_{n-1}\, t_{95\%}/\sqrt{n}$, decreases through CA-316 series, which must be due to the higher membrane surface homogeneity observed for membranes with lower average pore radius [22].

The variation of the contact angle through CA-316 series, although it is not much pronounced (7°), reveals an intrinsic decrease of the membrane hydrophilicity with the pore radius. If an apparent effect such as membrane roughness was in question, the opposite trend would be observed, i.e. the contact angle would increase with pore radius, because when the true angle is >90° the apparent angle on a rough surface is greater than the true value [17].

On the other hand, it is not reasonable to justify the observed trend based on drop penetration effects. The membrane pore radii approach molecular dimensions and it is not possible for a CCl_4 drop to penetrate the pores only by capillary forces. When immersed in water, a CCl_4 droplet 5 mm height will exert a gravitational force of about 30 N/m^2 ($\Delta P = \Delta\rho$ g h, with $\Delta\rho \sim 600$ kg/m^3). According to the Laplace equation for cylindrical pores (which, in fact, is more adequate for microporous surfaces with $r_{\max} \sim 10^{-6}$ m), this gravitational force would correspond to a $\gamma_{\mathrm{ow}} \cos\theta$ variation of 75×10^{-10} N/m (i.e. 1/2 $\Delta P\, r_{\max}$ with $r_{\max}$=5 Å), a rather small value compared to the usual γ_{ow} range of 10^{-3} N/m.

Thus, the intrinsic variation of the hydrophilicity in CA-316 series must be related to the annealing temperature used to obtain membranes with different pore radius.

Actually, it is reported in the literature that membranes of the same polymer can present significant variations of hydrophilicity [13] because different conditions of preparation (e.g. annealing temperatures) can induce conformational changes in the membrane polymeric matrix [23–26]. In addition, the authors observed recently the influence of the annealing temperature on the optical anisotropy, and therefore on the macromolecular organisation of the active layer of these CA-316 membranes [27].

In fact, the annealing consists on the introduction of thermal energy which causes translational motion of the macromolecules and allows the approach of the polar groups to form virtual cross-links by dipole–dipole interactions [25]. These cross-links tend to decrease the chain mobility and, as the annealing is performed in a water bath (a non-solvent medium for cellulose acetate), they result in an irreversible membrane shrinkage. This shrinkage is responsible for a decrease in the average pore radius (see Table 3) which hinders the water transport through the membrane matrix and thus reduces the membrane water permeability. ATR/FTIR studies with these CA-316 membranes showed that, in fact, both the water content and the state of water sorbed in the membrane active layer vary with the annealing (i.e. with increasing temperature there is a lost in water content together with a decrease in hydrogen bonding and cluster size of the water sorbed by the active layer of the membrane) [28]. Nevertheless, the membrane shrinkage is also responsible for a macroscopic increase of the –OH surface density, which increases the membrane surface hydrophilicity (i.e. increases the contact angle).

This increase in membrane hydrophilicity with the annealing temperature is a very important result because it chemically favours the water transport (membrane–water chemical interactions are favoured, and so are the water transport and the membrane cleaning with aqueous solution), thus enhancing the relative membrane permeation performance. This is, CA-316-86 membrane is less permeable than CA-316-50 membrane (CA-316-86 has a denser polymeric structure, with higher steric hindrances) but it would probably present higher relative fluxes (permeate flux with the aqueous solution over the pure water flux) and flux recoveries (ratio of final to initial pure water fluxes determined, respectively, after and before permeating the solution) than CA-316-50 membrane.

The fourth conclusion to be taken concerns the correlation of membrane permeation performance (in terms of hydraulic permeability, Table 2) with membrane hydrophilicity (Table 5). The results relative to CD-NF-50 and HR-98-PP clearly illustrate that the steric hindrances are not the only factor playing an important role on water transport. Other effects such as membrane–water chemical interactions, i.e. hydrophilicity (and/or the number of pores in the active layer) are most important and can be evaluated by contact angle measurements (hydraulic resistance due to membrane thickness also intervenes and is not accounted in superficial measurements such as contact angles). CD-NF-50 has an average pore radius of 4.2 Å, an intermediate value between those of CA-316-50 and CA-316-68 membranes (respectively, between 4.4 and 4.0 Å) but it is more hydrophilic than these membranes, i.e. it has a contact angle of 127°, well above those of CA-316 membranes (100° and 104° for CA-316-50 and CA-316-68, respectively). Therefore, although with intermediate steric hindrances, CD-NF-50 has stronger membrane–water chemical interactions than CA-316 membranes which results in the high membrane hydraulic permeability of CD-NF-50 membrane over the CA-316 membranes (2.34 m against 1.55 m and 0.90 m, respectively for CA-316-50 and CA-316-68 membranes). The same effect, but even more pronounced, is found with HR-98-PP membrane over CA-316-86 membrane. HR-98-PP has a smaller pore radius but it is much more hydrophilic and 10 times more water permeable than CA-316-86 (pore radius of 2.8 Å, contact angle of 146° and hydraulic permeability of 1.63 m for HR-98-PP against 3.3 Å, 107° and 0.16 m for CA-316-86). These results contribute both to the comprehension of transport phenomena through NF/RO membranes and to membrane selection for a given application.

Similar comparison of the membrane performance with aqueous solutions (other than pure water at natural pH) and the results in Table 5 is not possible. As discussed previously, in most cases, membrane and solute are both ionisable substances and, therefore, the membrane–solute–solvent chemical interactions have

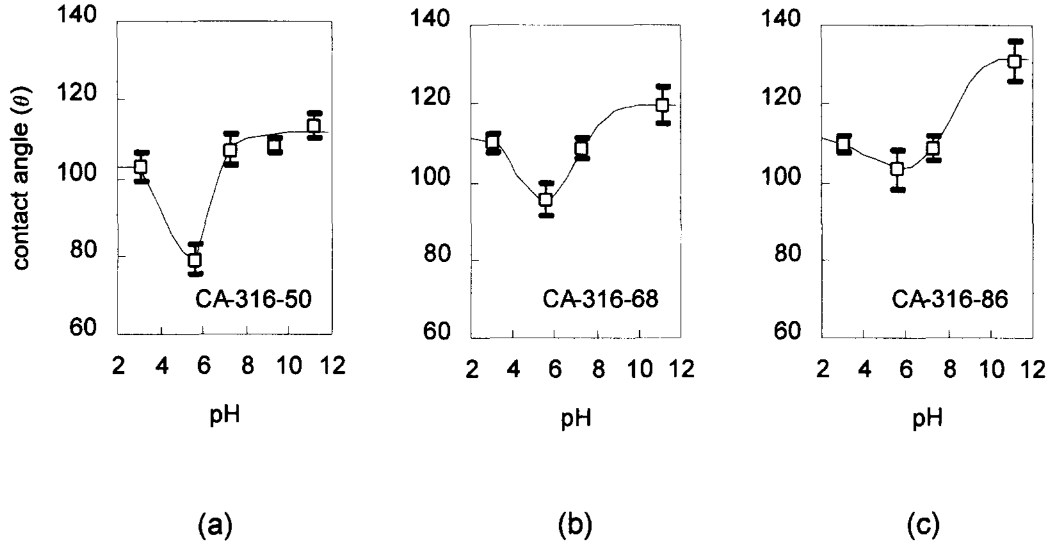

Fig. 4. Titration curves of the three CA-316 membranes: (a) CA-316-50, (b) CA-316-68, (c) CA-316-86 (contact angles measured at room temperature, after 5 min of drop deposition, immersion time=24–48 h).

Lifshitz–Van-der-Waals and acid–base contributions. Thus, to estimate membrane–solute interactions the contact angles obtained with water at only one pH value do not suffice. They do not indicate membrane charge signal but only the relative surface charge density. To evaluate membrane acidity/basicity one has to have values at different pH values either with pure water or, as in the present work, with a surfactant solution.

4.2. Immersion system II: CCl_4–membrane–surfactant solution

Figs. 4–6 show the results relative to CCl_4–membrane–C16TAB solution at different pH values, i.e. the titration curves of CA-316, CD-NF-50 and HR-98-PP membranes, respectively. Two immediate conclusions can be drawn.

First, the contact angle hysteresis is not much increased when pure water is replaced by C16TAB dilute solutions. The values of $\sigma_{n-1}\, t_{95\%}/\sqrt{n}$ are 1–3° in the first case and 2–7° in the second.

Second, all the membranes present a variation of the contact angle with the solution pH as expected from the chemical nature of the membrane polymers involved.

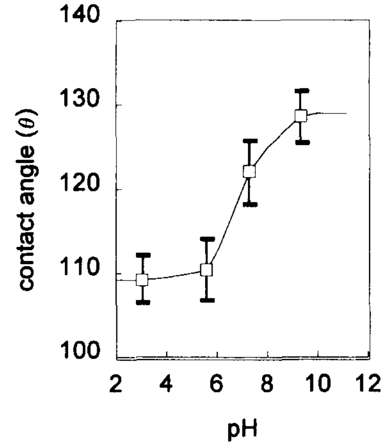

Fig. 5. Titration curve of CD-NF-50 membrane (contact angles measured at room temperature, after 5 min of drop deposition, immersion time=24–48 h).

Fig. 4 presents the titration curves of the CA-316 membranes, a series of weakly acidic membranes due to the –OH groups of cellulose acetate (see Section 3.1). As illustrated in this figure, the three CA-316 membranes present similar titration curves with a minimum at pH 5–6, the pH that corresponds to the ionisation of 50% of the –OH groups (the acidity constant of a weak acid such as an alcohol is around 10^{-10} to 10^{-12}, i.e. p$K_{1/2}$ is 5–6). The curves in Fig. 4 have the expected shape of the theoretical titration curve shown in Fig. 3(b) for acidic membranes with double layer formation. Besides the same shape,

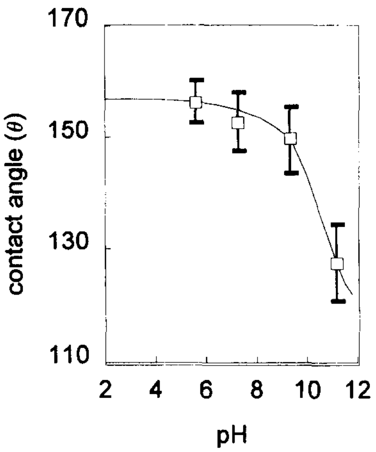

Fig. 6. Titration curve of HR-98-PP membrane (contact angles measured at room temperature, after 5 min of drop deposition, immersion time=24–48 h).

curves 4(a), 4(b) and 4(c) display significant differences. The first plateau is identical for the three membranes, 103° for CA-316-50 and 110° for CA-316-68 and CA-316-86, but the minimal value of the contact angle increases in the series, being 80°, 95° and 105° for CA-316-50, CA-316-68 and CA-316-86, respectively. Furthermore, the pH at which the second plateau (complete double layer formation) is reached also increases, 7.5, 9 and 10 for CA-316-50, CA-316-68 and CA-316-86, respectively. These observations indicate that the membrane surface acidity increases in this series, in agreement with the results relative to the membrane–CCl_4–water system. At low pH values, the –OH groups are mainly not ionised, thereby the contact angles are similar for the three membranes. For pH values corresponding to the ionisation of the –OH groups, i.e. for pH >3, the membrane with higher –OH surface density (higher acidity) presents a higher negative charge, therefore presenting higher CCl_4 contact angles.

Fig. 5 presents the titration curve of the CD-NF-50 membrane, an amphoteric membrane with a predominantly acidic behaviour due to the carbonyl and sulphur groups of TFZ (see Section 3.1). The titration curve of this membrane shows a plateau for pH ranging from 3 to 5, then an increase up to pH 9 after which a second plateau is probably reached. This curve agrees with the theoretical curve shown in Fig. 3(c) for acid–base membrane with double layer formation. Both facts, the absence of the minimum and the high slope of the curve indicate the strong acidic character of the membrane (carbonyl and sulphur groups) responsible for the fast change from a neutral to a highly negative membrane charge (double layer formation). The value of $pK_{1/2}$ is around 5–6 (carbonyl and sulphur groups) and the maximum negative charge is attained at pH above 9. Actually, Fig. 5 extends the tendency observed through CA-316 series (Fig. 4(a–c)), i.e. CD-NF-50 (carbonyl and sulphur groups) has an acidic character stronger than that of CA-316-86 membrane (hydroxyl groups).

Fig. 6 presents the titration curve of the HR-98-PP membrane, an amphoteric membrane with a predominantly basic behaviour from the amide groups of PA (see Section 3.1). The titration curve of this membrane shows a slight decrease of the contact angle for pH ranging from 5.6 to 9 and then a steep decrease from pH 9 to 11. This curve agrees with the theoretical curve for basic membranes shown in Fig. 3(a) (the variation of the contact angle occurs for pH values above neutrality). This indicates that, in fact, the basic character of the membrane surface far exceeds its acidic character, being the ionisation of the acidic groups only significant for pH above 10 (for comparison, carboxylic groups are 100% ionised at pH 11).

Summarising, from Figs. 4–6, one obtains the acid–base behaviour of the five membranes:

- CA-316 membrane series present an acidic character (from the –OH groups of cellulose) with a $pK_{1/2} \sim 5$–6 and with maximum negative charge at pH above 7.5, 9 and 10 for the annealing temperatures of 50, 68 and 86°C, respectively. This trend represents the increase in the surface concentration of –OH groups promoted by the annealing treatment;
- CD-NF-50 membrane presents an acidic character (from the carbonyl and sulphur groups of TFZ) stronger than the CA-316 membranes: $pK_{1/2} \sim 5$–6 and maximum negative charge at pH >9;
- HR-98-PP membrane has a basic character (from the amide groups of PA) presenting neutral or weakly negative charge at pH 9.

These data indicate that, when permeating pure water (i.e. at pH 6.5), HR-98-PP membrane is positively charged while the other four membranes are negatively charged. Based on the magnitude of the contact angle values, at pH 6.5 the membrane surface charge density follows the sequence:

$$\begin{aligned}&\text{CA-316-50}(-) < \text{CA-316-68}(-)\\&\quad < \text{CA-316-86}(-) < \text{CD-NF-50}(-)\\&\quad < \text{HR-98-PP}(+)\end{aligned}$$

These results are in agreement with those relative to pure water and they explain the high water permeabilities of the strongly acidic CD-NF-50 membrane and the strongly basic HR-98-PP membrane over the less energetic CA-316 membranes of equivalent pore radius.

Due to their acidic character, CD-NF-50 and CA-316 membranes are adequate to process alkaline aqueous solutions of anionic solutes (e.g. alcohols, organic acids). The membrane and the solute(s) would be both highly negatively charged which maximises membrane–solute(s) repulsion and increases membrane permeability and solute rejection. For analogous reasons, HR-98-PP is adequate to process acid aqueous streams with cationic solutes.

5. Conclusions

A new method for membrane surface characterisation is developed based on the two-liquids immersion system. The general system CCl_4–membrane–aqueous solution is adapted to give membrane relative hydrophilicity and membrane acidity/basicity. In the first case the immersion solution is pure water and in the second case is an aqueous solution of a cationic surfactant (below its critical micelle concentration) at different pH values.

The experimental results with five nanofiltration membranes of different polymers demonstrated that:

- the method is reproducible, presenting maximal deviation values, $\sigma_{n-1}\, t_{95\%}/\sqrt{n}$, of 7° (corresponding to 5%);
- it is easy to perform and avoids dynamic measurements as 5 min of drop deposition are sufficient to ensure equilibrium;
- measurements can be performed with membranes immersed in their natural operating environment, e.g. water, solutions of cationic surfactants, solutions of organochlorinated compounds;
- the method is not affected by the presence of pores in the nanofiltration range of operation;
- it is sensitive to membrane hydrophilicity and membrane acidity/basicity;
- it gives the membrane titration curves and the $pK_{1/2}$ values for weakly acidic, predominantly acidic and predominantly basic membranes.

Furthermore, the experimental data show the effect of the annealing treatment on CA-316 membrane acidity, which suggests an increase of the surface density of –OH groups with annealing temperature. These data also show the importance of the chemical properties of membrane surface on membrane permeability – i.e. membranes with equivalent pore radii but more hydrophilic do have much (2–10 times) higher hydraulic permeabilities.

This method therefore represents a contribution to the characterisation of membrane surface chemistry and its relation with membrane permeation performance.

6. List of symbols

Ad	membrane surface energy spent on solute adsorption, mJ/m^2
CA	cellulose acetate
C16TAB	*N*-Cetyl-*N*,*N*,*N*-trimethyl-ammonium bromide
CMC	critical micelle concentration
MF	microfiltration
n	number of samples
NF	nanofiltration
PA	polyamide
PES	polyethersulfone
$pK_{1/2}$	pH at which 50% of the polymer groups are ionised
PS	polysulfone
r_{max}	maximal membrane pore radius
RO	reverse osmosis
TFZ	poly(*trans*-2,5-dimethyl)piperazinthiofurazanamide
UF	ultrafiltration

6.1. Greek letters

ΔP	gravitational force exerted by the CCl_4 droplet on membrane surface, N/m^2
γ_{ij}	interfacial tension between substances i and j, mJ/m^2

θ	membrane–CCl_4–solution contact angle

6.2. Subscripts

mo	interface membrane–organic
mw	interface membrane–water
ow	interface organic–water

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