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"Preparation, characterization and modeling of zeolite NaA membranes for the pervaporation dehydration of alcohol mixtures"

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III.1. SYNTHESIS OF ZEOLITE NaA COMPOSITE MEMBRANES

This chapter focuses on the description of the synthesis procedures used in this work for the preparation of zeolite NaA composite membranes onto both the outer and inner sides of tubular supports. Direct in-situ and seeded hydrothermal syntheses were carried out using several methods. Moreover, the synthesized zeolite layers were also characterized by several techniques to evaluate their quality. To label the NaA membranes presented in this work, a specific nomenclature has been used, which relies on 4 fields in the following way:

Field 1 – Field 2 – Field 3 – Field 4

- **Field 1**: Kind of zeolite layer (ZA for zeolite NaA).
- **Field 2**: Outer (OUT) or inner-side (INN) tubular membranes.
- **Field 3**: CF if the membranes are prepared under a centrifugal field, SC if they are prepared in the semi-continuous synthesis system, C if a continuous synthesis system is used, or blank if they are prepared in a discontinuous glass vessel.
- **Field 4**: Number of the membrane.

For instance, the label ZA-OUT-SC-01 refers to an *outer-side zeolite NaA* membrane prepared in the *semi-continuous synthesis system* and among all the membranes prepared in these conditions, this is *number 01*.

To prevent the zeolite layers from strange elements or impurities that might reduce the reproducibility of the syntheses, great care was taken in all the preparation steps. The steps to be followed in the preparation of the membranes are described in a protocol, which has been developed after previous studies. The general steps that were always taken into account are the following ones:

1. Conditioning of the support
2. Seeding of the support
3. Preparation of the synthesis gel
4. Synthesis of the zeolite membrane
5. Characterization of the membrane

III.1.1. Conditioning of the supports

The support is the physical element onto which the synthesis of a zeolite layer takes place, which confers to the membrane the required mechanical resistance (see Figure III.1). In this work, tubular α-Al_2O_3 and TiO_2 (rutile) supports were used to grow zeolite NaA membranes, whose main characteristics are summarized in Table III.1. The tubes (7-8 mm i.d. and 10 mm o.d.) were subjected to a protocol to clean their surface and the outer- and inner-side of their both ends were enameled with commercial glaze (Duncan AN 313 Antique Blue, cone 6) diluted with deionized water or homemade glaze prepared in our laboratory, both resistant to strong alkali to define a permeation length of approximately 5 cm. **Protocol I** describes the general steps of the conditioning process:

1. Cleaning with boiling deionized water during 1-2 h.
2. Cleaning with acetone in an ultrasound bath during 1 h.
3. Drying at ambient conditions and afterwards at 373 K overnight at atmospheric pressure.

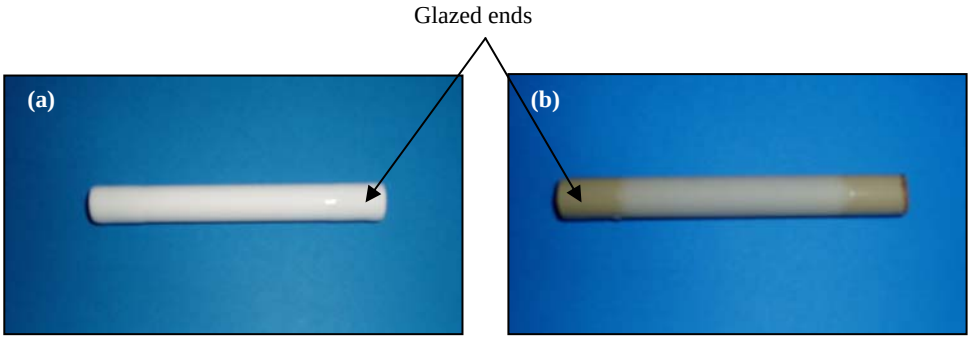


Figure III.1: Tubular supports used in the synthesis of zeolite NaA membranes. (a) α-alumina, and (b) TiO_2 (rutile).

Table III.1: Tubular supports used for the synthesis of zeolite NaA membranes

Support	*Configuration*	d_p [μm]	ε_T [-]	*o.d. [mm]*	*i.d. [mm]*	*Supplier*
α-Al_2O_3	Symmetric	1.9	25%	10	8	Inocermic (Hermsdörfer, Germany)
TiO_2 (rutile)	Asymmetric (40 μm [1])	0.8	16%	10	7	TAMI (Montpelier, France)

[1] Determined by SEM

4. Enameling both ends of the supports (the central part is wrapped with Teflon) with diluted glaze.

5. Drying the enameled tubes at ambient temperature and calcination at 1123-1273 K during 30 min in a furnace. Heating and cooling ramps of 3 K min^{-1} were used to prevent the glazed ends of the support from any thermal stress.

6. Repetition of the process at least twice to ensure the impermeability of glazed ends of the support.

7. Verification of the impermeability of the ends of the supports by means of a bubble point test.

8. Cleaning of the supports with boiling water during 1-2 h and drying at 373 K overnight (either at atmospheric pressure or under vacuum).

III.1.2. Seeding techniques

The seeding of the supports is a required process for the preparation of zeolite NaA layers by means of the secondary growth method. In this work, the rubbing technique was used to seed the outer surface of tubular supports, and the so-called brush seeding technique as a modified version of the latter was used to seed their inner sides by using a test-tube brush. Furthermore, a cross-flow filtration technique was used for seeding the inner side of tubular supports. The surface density of zeolite NaA crystals deposited onto the support after the seeding is referred in the remainder of this work as ***seeding weight gain*** (SWG) [mg cm^{-2}]. The zeolite particles used for the seeding of the supports (2 and 7 μm) were supplied by IQE (Industrias Quimicas del Ebro, Zaragoza, Spain).

III.1.2.1. *Rubbing (brush-seeding)*

Rubbing is a technique suitable for seeding the outer surface of tubular supports with zeolite NaA particles, which are manually rubbed with a powder of commercial zeolite NaA. On the other hand, the inner-side surface of tubular supports could be also rubbed with zeolite NaA powder by means of a test-brush able to penetrate the lumen of the supports (brush-seeding technique, see Figure III.2). In both cases, care was taken that all the zeolite NaA particles were attached to the surface by shaking vigorously the support. The process was repeated several times to achieve the desired SWG on the surface of the support.

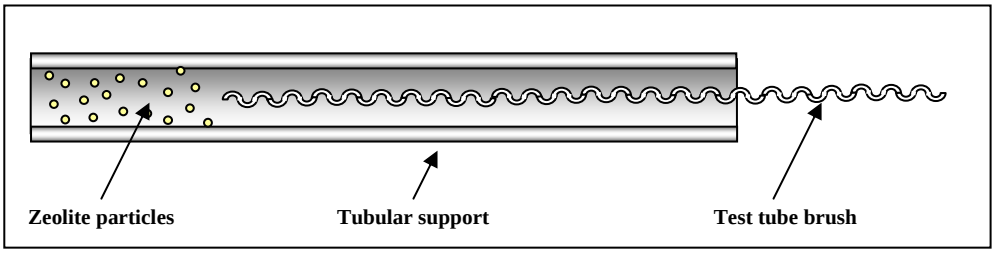


Figure III.2: General scheme of the brush-seeding process of the inner side of tubular supports

III.1.2.2. *Cross-flow filtration seeding*

The experimental set up used for seeding is depicted in Figure III.3. In the seeding process, a suspension of zeolite NaA crystals (1) was prepared, then stirred and kept in an ultrasound bath for 1 h to avoid the formation of aggregates. The pH of the suspension (Crison, micropH2002) was adjusted to the desired value and continuously controlled during the seeding process. The suspension was continuously stirred during the seeding process (2) and was fed to the lumen side of the tubular support at a given flow rate by means of a membrane pump (3). To this end, the tubular support was set inside a permeation module (5), where the desired value of transmembrane pressure, ΔP, could be fixed and continuously monitored with a manometer (6). The pressure at the retentate side was adjusted by means of a regulation valve (7) at the outlet of the module. The evolution of the seeding process was monitored from the evolution of the water permeability across the support using a graduated cylinder (8) and a chronometer (9).

Furthermore, some preliminary experiments were carried out to determine the isolectrical point (IEP) of zeolite NaA from the ζ-potential of zeolite NaA suspensions at a pH range 4-10 (below pH 4, zeolite NaA was not stable) measured by photon correlation spectroscopy (PCS) (Malvern Zetasizer 3000 HS, USA). The suspensions (500 mg L^{-1}) were stirred, immersed in an ultrasound bath for 1 h to avoid the formation of aggregates and then their pH was continuously monitored and adjusted to the desired value. Care was taken to assure that the pH was stabilized before the determination of the ζ-potential.

III.1.3. Preparation and characterization of the synthesis gels

The synthesis gels for carrying out the hydrothermal synthesis of the zeolite NaA layers must content the required Si and Al precursors in an alkali environment. The proportion of each precursor in the gel depends on the kind of zeolite to be synthesized. The influence of the relative proportion of the main species in the gel is summarized in Table III.2. On the other hand, the composition of the gels used in this work for the preparation of zeolite NaA

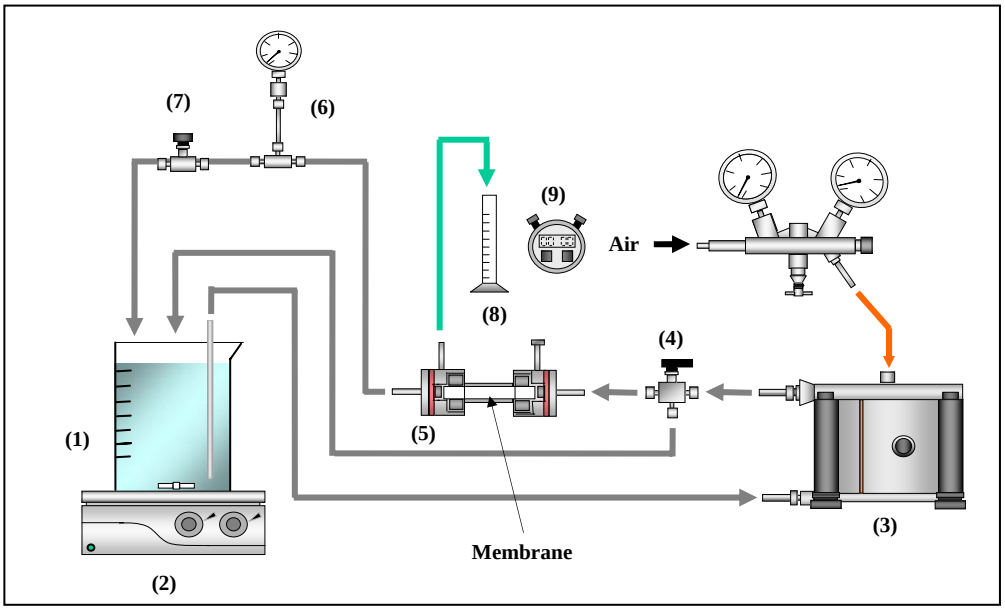


Figure III.3: Set-up used in the cross-flow seeding: (1) zeolite suspension; (2) stirrer; (3) membrane pump; (4) three-way valve; (5) membrane module; (6) manometer; (7) pressure regulation valve; (8) graduated cylinder; (9) chronometer.

Table III.2: Influence of the relative proportion of the main species in the synthesis gel of zeolite NaA membranes

MOLAR RATIO	*INFLUENCE*
SiO_2 / Al_2O_3	Structural composition
H_2O / SiO_2	Rate and mechanism of nucleation and growth
HO^- / SiO_2	Degree of polymerization of SiO_2 (decreases with an increase in the concentration of HO^- ions)
M^+ (Na^+) / SiO_2	Structure and distribution of cations

membranes is indicated in Table III.3. The reagents used for the preparation of the gels are given in Table III.4. **Protocol II** describes the process of preparation of the gels:

1. Preparation of the alumina solution: The exact amount of sodium aluminate or alumina reagents and sodium hydroxide were dissolved in the half of the total amount of water at 373 K for 30 min under vigorous stirring. After this, the solution was cooled to 323 K and filtered with a 16 μm-filter if non-dissolved alumina particles in suspension were observed.

Table III.3: Molar composition of the synthesis gels

Gel	*Al_2O_3*	*SiO_2*	*Na_2O*	*H_2O*
1	1.0	2.0	2.1	120
2	1.0	2.0	2.1	270
3	1.0	2.0	2.1	400
4	1.0	1.8	3.9	270
5	1.0	9.0	80.0	5000

Table III.4: Reagents used in the preparation of the synthesis gels

Reagent	*Composition [%wt.]*	*Formulation*	*Safe card*	*Supplier*
Sodium aluminate	53% Al_2O_3 43% Na_2O	Solid powder	Corrosive	Aldrich (Germany)
Alumina	100% $Al_2O_3 \cdot 3H_2O$	Solid powder	Corrosive	IQE * (Spain)
Sodium silicate Solution	27% SiO_2 14% NaOH	Solution	Corrosive	Sigma (Germany)
Sodium hydroxide	99% NaOH	Pellets	Corrosive	Aldrich, Merck (Germany)
Deionized water	-	Liquid	-	-

* IQE: Industrias Quimicas del Ebro (Zaragoza, Spain)

2. Preparation of the silica solution: The solution was prepared by dissolving the exact amount of the silica reagent to the rest of water at 323 K under stirring.

3. The silica solution was added to the alumina solution slowly at 323 K and stirred during 1 h, taking care that the hydrogel or clear solution formed was homogeneous. In the preparation of a clear solution, the final solution was filtered with a 0.05 μm-filter to remove small particles susceptible to nucleate.

4. The synthesis of the membrane began just after the preparation of the gel in order to prevent it from aging.

5. The rheological properties of the gel were characterized by a thyxotropy test at 293 ± 0.1 K using a rotational rheometer with controlled shear rate (Haake Rotovisco RV100, Germany) equipped with a concentric cylinder sensor. Shear rates ranged from 0 to 400 s^{-1} and shear stress from 0.1 to 4 Pa. After keeping the gel sample undisturbed for 2 h, the shear rate was linearly increased in 15 min from 0 to 400 s^{-1}.

This value was maintained for 15 min. Finally, the shear rate was returned to 0 in 15 min by linear decrease over time. Equilibrium was obtained independently by maintaining interjacent shear rate until constant value was achieved for the shear stress.

Prior to the preparation of the membranes, several previous studies were carried out to evaluate the possibility to hydrothermally synthesize zeolite NaA crystals with the gels listed in Table III.3. Furthermore, hydrothermal syntheses onto some planar glass supports (4 cm x 2 cm) were also carried out to assess the possibility to grow zeolite NaA layers onto them.

III.1.4. Hydrothermal syntheses

The hydrothermal syntheses were carried out both onto the outer and inner-side surfaces of the tubular supports listed in Table III.1, unseeded or previously seeded with one of the techniques described in section III.1.2. Outer-side tubular membranes were prepared statically both in a discontinuous glass vessel open to atmosphere and in a semi-continuous system. On the other hand, the syntheses of inner-side tubular membranes were carried out in a discontinuous glass vessel either with or without rotation of the support around its longitudinal axis, namely, statically or in a low-g centrifugal field, and by means of the semi-continuous and continuous synthesis systems. **Protocol III** describes the general steps followed to prepare zeolite NaA both outer and inner-side tubular membranes either with the techniques above indicated:

1. Seeding of the supports (if necessary) by means of one of the techniques described in section III.1.2 after enameling, cleaning and drying.

2. For outer-side tubular membranes, their enameled ends and the central orifice were first wrapped with Teflon to prevent the lumen of the tubes from any deposition of zeolitic material, while for inner-side tubular membranes, the whole outer surface of the supports was wrapped with Teflon.

3. Preparation of the synthesis gel.

4. The support was placed vertically either inside a synthesis glass vessel, inside an autoclave or in a metal tube depending on the set-up used to carry out the syntheses. The gel was poured into the vessel or autoclave until the support was totally covered by the synthesis gel. Afterwards, the vessel, autoclave or metal tube were immersed either in an ethyleneglycol or rhodosil oil baths.

5. Synthesis of the zeolite layer at 363-373 K during 3-7 h for each cycle.

6. After the synthesis, the membrane was taken out from the synthesis system, the Teflon wrap was removed and it was washed with boiling water during 1 h to remove the remaining gel.

7. The membrane was kept at 343 K overnight, in most cases under vacuum (<2 mmHg), with a heating ramp of 1 K min^{-1} to avoid any thermal stress in the zeolitic layer.

8. The vessel or autoclave and all the required material for the syntheses were carefully cleaned to avoid any deposition of zeolite material.

III.1.5. Synthesis of zeolite NaA membranes in a discontinuous glass vessel

A glass vessel was used as a reactor to carry out the hydrothermal synthesis of outer-side tubular zeolite NaA membranes (see Figure III.4a). However, as was indicated in section I.4.1.2.2, growing zeolite layers onto the inner-side surface of tubular supports is troublesome due to the low refreshment of the gel contained in the lumen of the support. Refreshment of the gel could be achieved by rotating the gel around its longitudinal axis (see Figure III.4b), especially that directly in contact with the surface of the support and, thus, to improve the growth of the zeolite layer. In this way, a set-up similar to that described by *Tiscareño-Lechuga et al. (2003)* was used to prepare inner-side tubular membranes (see Figure III.5).

The support with its outer surface wrapped with Teflon was attached to a rotor piece with a rigid gum tube to avoid any horizontal oscillation and was rotated around its longitudinal axis at 100 r.p.m. The membrane was immersed in the synthesis glass vessel surrounded with ethyleneglycol to keep the temperature at 363-373 K inside the vessel. The upper section of the rotor had 3 rectangular holes of an area about 10 mm^2 each.

The process that takes place inside the rotating support might be described as a segregation of the gel due to the action of a shear rate, as it is illustrated in Figure III.6a, due to the centrifugal field inside the tube that is created by the rotation of the support. Because the gel might be regarded as a pseudo plastic material (*Labanda and Llorens, 2002*), the rotation of the support might segregate the gel inside into a clear solution near its surface and into a concentrated gel or a suspension in the central part of the tube, where the shear rate is higher (see Figure III.6b). Because the clear solution is lighter than the gel provided, an upward convective flow of the former could appear due to density differences, which might be responsible for the refreshment of the gel in the nearby of the surface of the support. On the other hand, the concentrated gel in the central part of the tube might flow downwards because

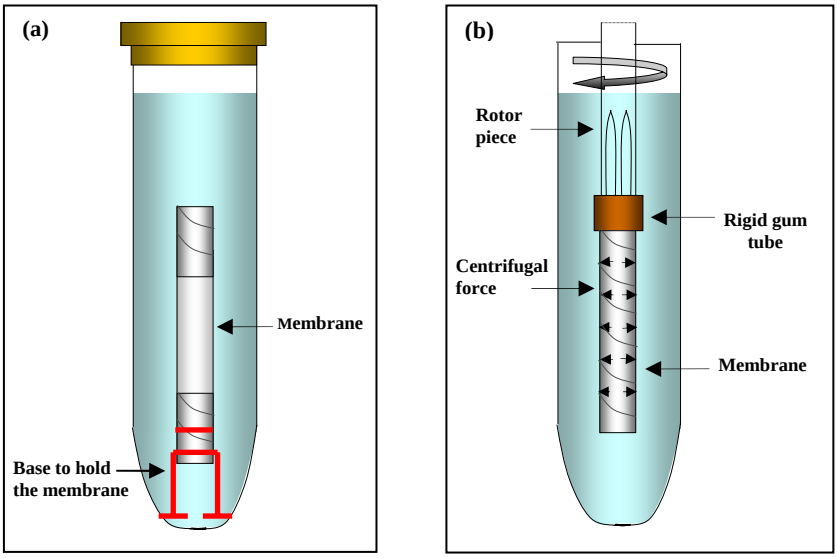


Figure III.4: Glass vessel used to carry out the synthesis of zeolite NaA membranes (a) onto the external surface of tubular supports and (b) onto the internal surface of tubular supports in a centrifugal field.

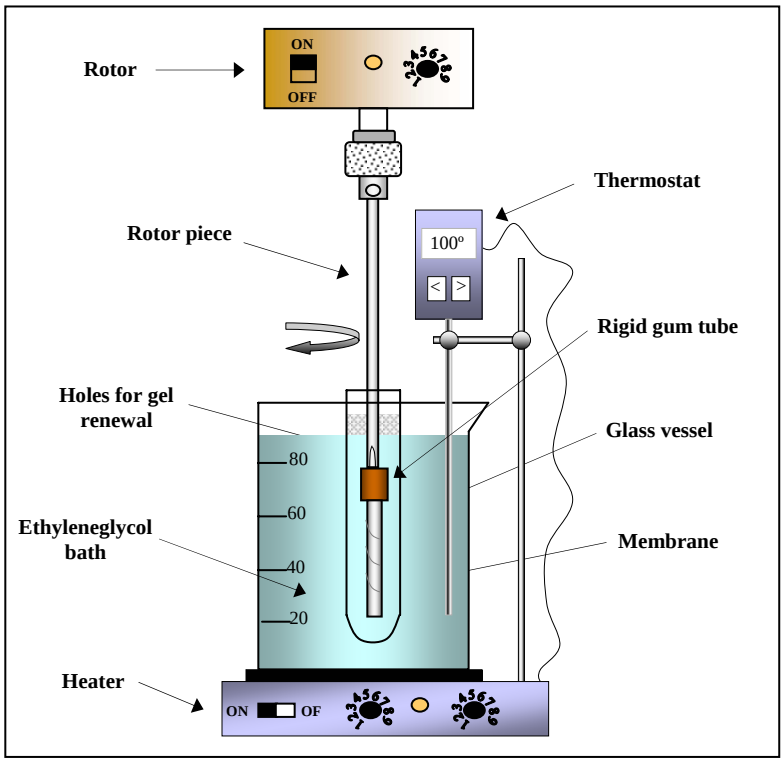


Figure III.5: Set-up used for the preparation of internal tubular zeolite NaA membranes under the influence of a centrifugal field.

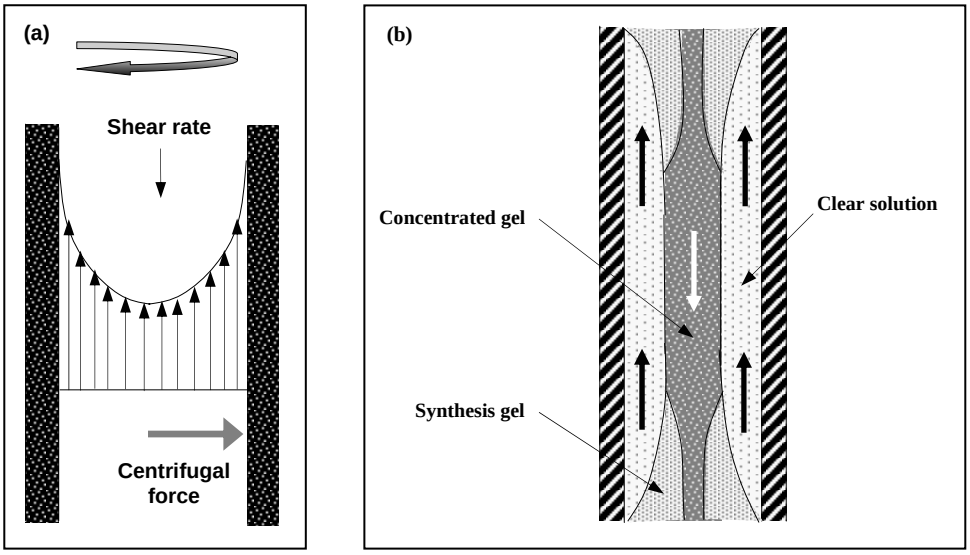


Figure III.6 (a) Shear rate inside a tube due to the action of a centrifugal field; (b) Segregation of the synthesis gel in the preparation of zeolite NaA membranes due to the action of a shear rate.

of its higher density compared to that of the gel provided. The holes in the rotor near the support might be suitable for providing gel to the its upper part. The refreshment of the gel might improve the intergrowth of the zeolite layer, because a higher concentration of nutrients might be supplied to the growing interface.

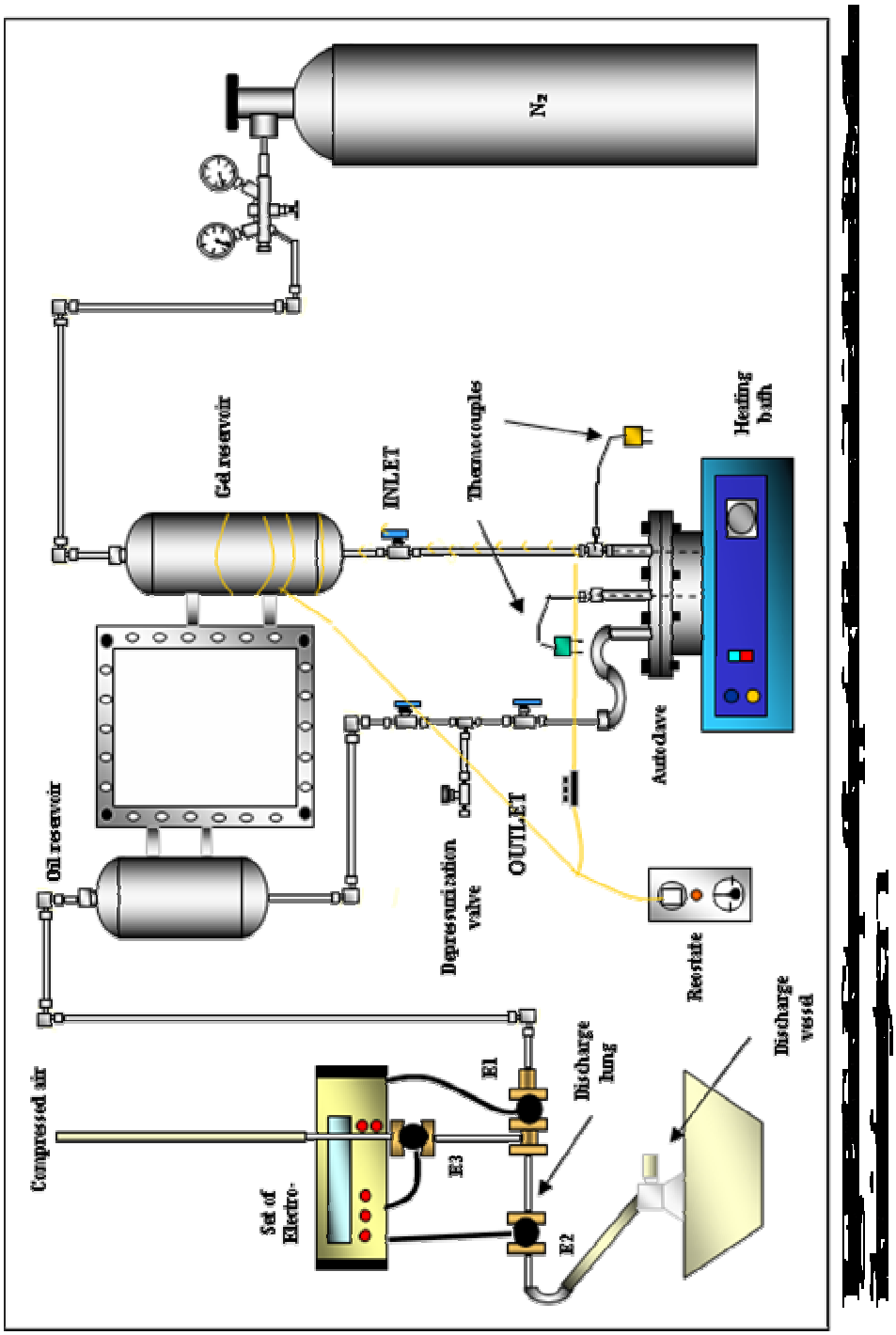
III.1.6. Synthesis of zeolite NaA membranes in a semi-continuous system [1]

III.1.6.1. Experimental set up

Zeolite NaA membranes grown onto both the outer and inner-side of the supports were also prepared by means of the semi-continuous synthesis set up. The general scheme of the set-up used is depicted in Figure III.7 As can be seen, the set-up consisted of the following elements:

1. Teflon-lined autoclave: The autoclave contains a Teflon flask (volume = 155 cm^3) in which the synthesis is carried out. The support is placed in the Teflon flask either vertically on the bottom with the help of a base for outer-side membranes, or subjected to its inlet or outlet gel tubes for inner-side membranes (see Figure III.8). Two thermocouples were used to measure the temperature up and down the flask. A thermostated bath (Selecta, Spain) with rhodosil oil was used to control the temperature in the autoclave.

[1] This study was done at the Catalysis and Reactor Engineering Group at the Department of Chemical and Environmental Engineering, Faculty of Sciences, University of Zaragoza (Spain).


N2
Gel reservoir
INLET
Thermocouples
Heating bath
Autoclave
Oil reservoir
Depressurization valve
OUTLET
Restrate
Discharge vessel
Discharge lung
E1
E3
E2
Compressed air
Set of Electro-

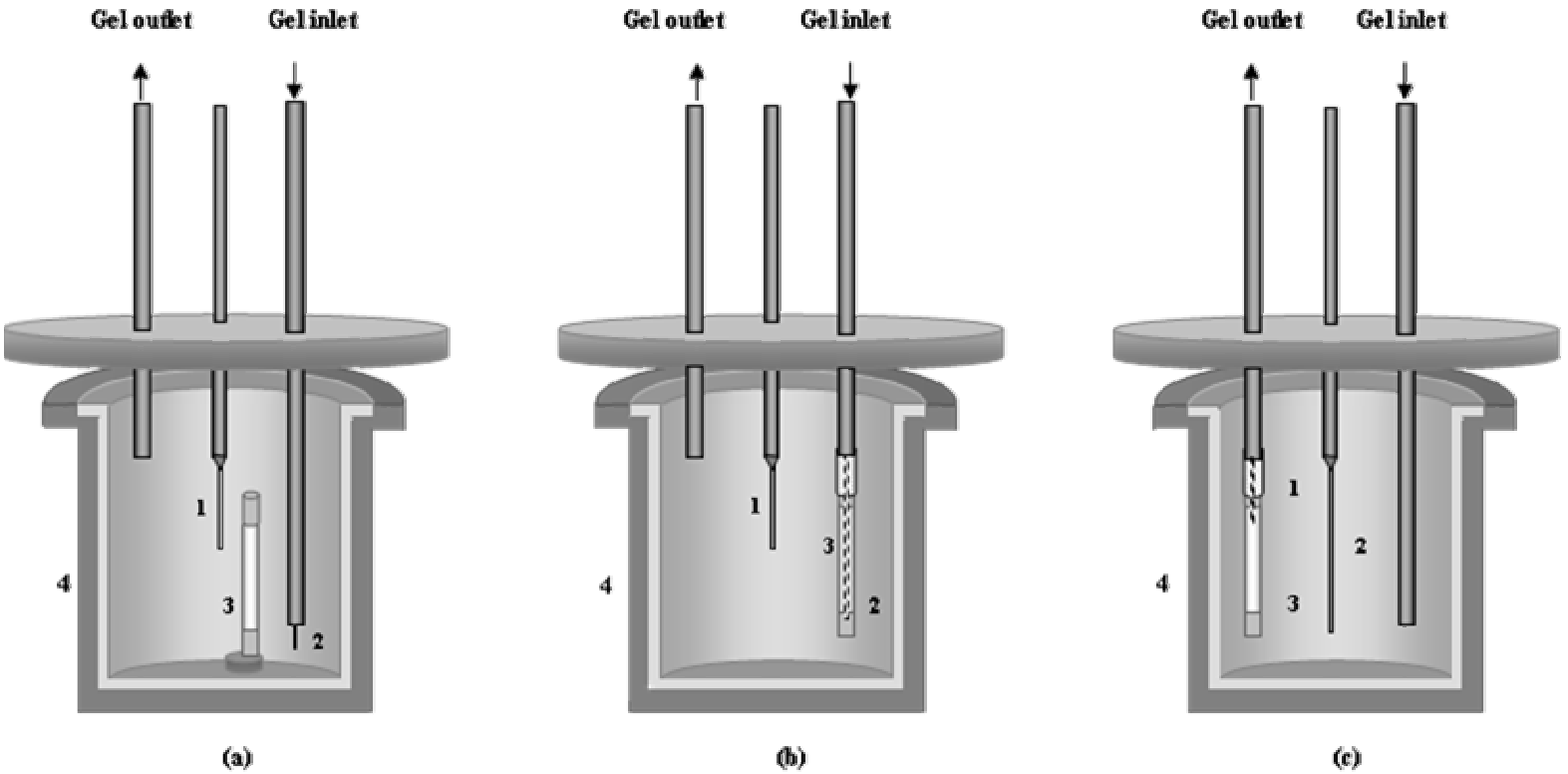


Figure III.8: Different membrane arrangements used in semi-continuous synthesis. (a) membrane set in an intermediate vertical position; (b) membrane attached to gel inlet tube; (c) membrane attached to gel outlet tube. Nomenclature: (1) upper thermocouple, (2) lower thermocouple, (3) seeded support, and (4) autoclave.

2. Gel reservoir (volume = 2 L): Its main function was to store the synthesis gel that entered the autoclave. A valve between the outlet of the gel reservoir and the intlet of the autoclave allowed controlling the entrance of the gel. The reservoir and the whole set-up were pressurized with dry N_2 to 5-10 bar to let the gel flow throughout the set-up along the synthesis. The gel reservoir and the upper part of the autoclave were surrounded by an electrical resistance to preheat the gel at ~343 K and not to reduce the temperature of the gel inside the autoclave after each gel renewal.

3. Oil reservoir (volume = 1 L): It stored paraffin oil, which was used to avoid any contact of the gel with the electro-pneumatic valves to prevent the set up from any deterioration due to the alkalinity of the gel. This reservoir was attached to the outlet of the autoclave and to the set of electro-pneumatic valves.

4. Set of electro-pneumatic valves and discharge system: The set of electro-pneumatic valves (E1, E2, E3) (Tecyser, USA) was used to control the gel renewal in the autoclave. The system was attached to the outlet of the oil reservoir to allow the discharge lung (length=5-10 cm; ϕ = ¼ in) to be filled with an exact volume of paraffin oil from the oil reservoir, because the whole set-up was pressurized.

5. Control box: It was used to control the time of opening and close of the electro-pneumatic valves.

6. Discharge Vessel: It is placed at the end of the set-up and its function was to recover the oil removed from the oil reservoir, which was later recycled.

III.1.6.2. Experimental procedure

The principle of operation of the semi-continuous flow set-up is based on the renewal of a determined volume of the gel in the autoclave at periodic intervals from the gel reservoir. The gel renewal rate could be fixed at the desired value by programming the appropriate switching sequence in a set of electro-pneumatic valves. The ***renewal rate*** [min^{-1}] is defined in the remainder of this work as the inverse of the time between two consecutive gel renewals, that is, the rate at which fresh gel is introduced into (and used gel removed out of) the autoclave. Thus, a renewal rate of 1/10 min^{-1} indicates the introduction of a fixed amount of fresh gel every 10 min. An increase in the renewal rate implies a reduction of the amount of gel refreshed in the autoclave.

At given times according to the renewal rate, valve E1 was opened and the fixed volume of the discharge lung was filled with paraffin oil from the oil reservoir. At the same time, the same volume of the gel was evacuated from the autoclave to the oil reservoir, being

replaced by fresh gel from the gel reservoir. This process of gel renewal was programmed, so that the gel from the gel reservoir could refresh regularly the gel contained in the autoclave. After valve E1 was closed, valve E2 was opened and communicated the discharge lung to the discharge vessel, which removed the oil placed in the lung. Oil removal was helped by the opening of valve E3 due to the action of compressed air. After the refreshment process, all the electro-pneumatic valves were closed and the process was repeated until the end of the synthesis time. **Protocol IV** was used for the synthesis of membranes by means of the semi-continuous synthesis system, which broadens the information given in step 5 of **protocol III**:

1. After placing in the autoclave the (seeded) support wrapped with Teflon tape in all the parts where no zeolite layer should grow, this was closed and immersed inside the heating bath.

2. After placing and attaching the autoclave to the set-up, the gel and oil reservoirs were filled, respectively, with the synthesis gel and the paraffin oil.

3. The attachments between the autoclave and the reservoirs were opened and the set-up was pressurized. As a result, the gel flowed from the gel to the oil reservoir and the autoclave was filled with gel.

4. According to *Pina et al. (2004)*, the autoclave was heated to 368 K with a ramp of 1 K min^{-1} to avoid any thermal stress. When the temperature reacheed this value, the synthesis began. The temperature was regularly controlled to assure that it remained at a stable value along the synthesis.

5. The set of electro-pneumatic valves was programmed by means of the control box. Valve E2 was programmed with the desired renewal rate.

6. After the synthesis time (5 h), the set-up was depressurized and all the gel was removed. The autoclave was disconnected, cooled in a cold water bath and washed. The gel placed in the oil reservoir after the synthesis was removed from the plant and the autoclave was carefully cleaned for further syntheses.

7. The *as*-synthesized membrane was taken out of the autoclave, washed with boiling water for 1 h and dried in air at 373 K overnight under a temperature ramp of 1 K min^{-1} to minimize thermal stress in the zeolitic layer.

Three different positions of the seeded support inside the autoclave were studied (see Figure III.8): (a) membrane fixed in a vertical position by means of a Teflon plug, (b) membrane attached to gel inlet tube, and (c) membrane attached to gel outlet tube. Two thermocouples positioned in the upper and lower sections of the autoclave were used to

monitor any temperature fluctuation with gel introduction. For attachments (b) and (c), the upper thermocouple was placed inside the tube. Attachment (a) was used for both outer and inner-side zeolite membrane synthesis, while attachments (b) and (c) were only used for inner-side synthesis. Furthermore, in each renewal step, a gel volume of 12 mL was removed from the autoclave for attachments (a) and (c); however, for attachment (b), a gel volume of 6.3 mL was removed from the autoclave, corresponding to roughly twice the total amount of gel contained in the lumen of the support (3.2 mL). In attachment (b) the bulk gel volume in the autoclave is not a relevant factor because this volume only plays a part on the autoclave residence time of the consumed gel. The use of a smaller volume of gel renewal under arrangement (b) was necessary to avoid pronounced temperature fluctuations in the vicinity of the growing layer due to the introduction of gel at lower temperature (343 K), a problem that was pointed out by *Pina et al. (2004)*. In arrangements (a) and (c) the gel introduced was mixed with the gel existing in the autoclave before reaching the membrane surface, and the thermal effect was reduced. In addition, for attachment (b), the system was gradually pressurized at the beginning of the synthesis process to prevent zeolite seeds from being swept away by a sudden flush of the renewal solution.

III.1.7. Synthesis of zeolite NaA membranes in a continuous synthesis system

III.1.7.1. Experimental set up

The continuous synthesis set-up was used to grow inner-side tubular zeolite NaA membranes, where the synthesis gel in the lumen of the tubes was continuously refreshed by the action of gravity. The scheme of the set-up used is depicted in Figure III.9. As can be seen, the set-up is constituted by the following elements:

1. Metal tube (length=10 cm, ϕ = ¼ in): It contains the support with the outer surface wrapped with Teflon tape onto the inner side surface of which grew the zeolite layer. The tube with the support was connected to the inlet and outer tubes where the gel flows and immersed in a rhodosil oil thermostatic bath (*Haake, Germany*) at 353-363 K. The temperature at the inlet of the tube was controlled by a thermocouple.

2. Gel reservoir (volume = 2 L): Its main function was to store the synthesis gel that enters the lumen of the support, which was vigorously stirred in order to avoid phase segregation. The gel reservoir and the upper part of the metal tube were surrounded by an electrical resistance to preheat the gel (~333 K). The gel reservoir could be pressurized with compressed air.

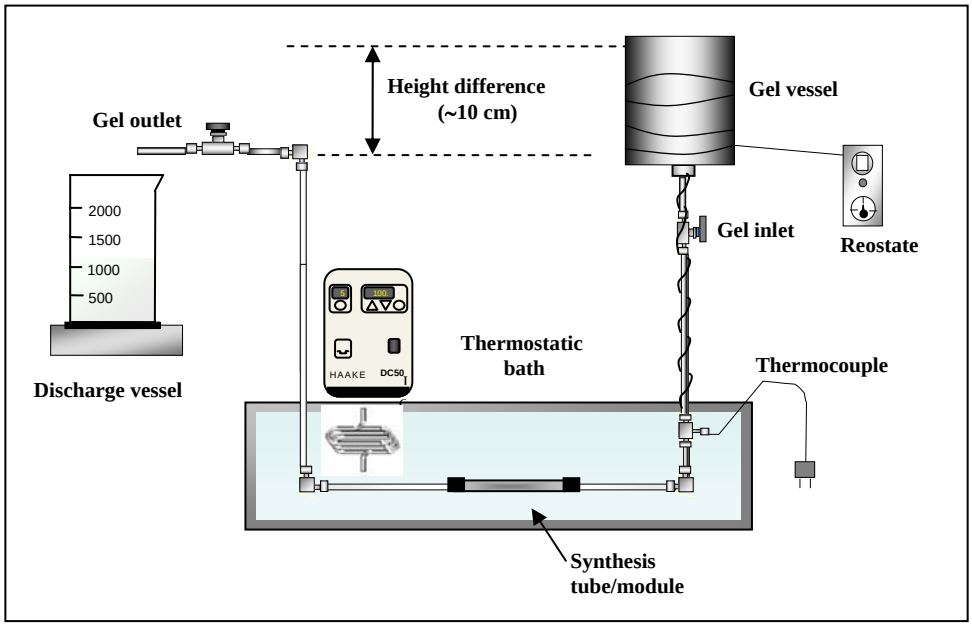


Figure III.9: Scheme of the set-up used for the preparation of inner-side tubular zeolite NaA membranes in the continuous system.

3. Discharge vessel: It was placed at the end of the experimental set-up to recover the synthesis gel that flowed across the lumen of the support and that could be recirculated if it was properly considered.

III.1.7.2. Experimental procedure

The principle of operation of the continuous synthesis set-up is based on a continuous flow of the synthesis gel across the lumen of the support at a high enough flow to allow the gel not to crystallize in the bulk of the solution, but low enough not to remove the growing zeolite layer on the inner surface of the support. The flow rate could be regulated by means of the difference between the height of the gel in the gel reservoir and that in the lumen of the support. The height difference between both positions was regulated along the synthesis of the membrane layers to compensate the height reduction of the gel contained in the reservoir. On the other hand, the gel flow rate could be also regulated by means of the total pressure of the gel reservoir by means of compressed air. The gel flow rate for all the membranes prepared with this technique was ~1.5 mL min^{-1}, which was approximately constant for all the synthesized membranes. **Protocol V** describes the general steps followed to synthesize inner-side zeolite membranes by means of the continuous system. This protocol completes the information provided in step 5 of **protocol III**:

1. The outer surface of the support was wrapped with Teflon tape to avoid the deposition of zeolite crystals and placed inside the metal tube.

2. The metal tube was connected to the set-up, immersed in the bath and this was filled with rhodosil oil. The oil bath was heated to ~368 K, so that the synthesis gel that entered the lumen of the support was kept at a temperature in the range 353-363 K. When the temperature reached ~353 K, the synthesis of the zeolite layer began. The temperature was monitored along the synthesis process to assure that it was approximately constant along the synthesis process (oscillation: ± 5 K).

3. The height difference between the gel in the reservoir and in the lumen of the support or the pressure in the gel reservoir were regulated to allow the gel to circulate at ~1.5 mL min^{-1} and to keep the temperature approximately constant in the lumen of the support along the synthesis time (3-7 h).

4. After the synthesis, the valve between the gel reservoir and the metal tube was closed and the metal tube was removed from the set-up.

5. The membrane was removed from the metal tube, cleaned with boiling water and kept in an oven overnight at 373 K under vacuum. The set-up was carefully cleaned for further syntheses.

III.2. MEMBRANE CHARACTERIZATION TECHNIQUES

III.2.1. Characterization of *as*-synthesized zeolite NaA membranes

After the synthesis, the *as*-synthesized membranes were first characterized by means of their ***weight gain*** [mg cm^{-2}] to evaluate the growth of zeolite material onto the support. In a similar manner as the SWG, the weight gain of a membrane was defined as the density of zeolite NaA material covering the support. Moreover, in terms of permeation, the membranes were characterized by a N_2 permeance test, He/N_2 selectivity, Knudsen-laminar test and pervaporation tests.

III.2.1.1. Permeation of pure gases at near ambient pressure

The *as*-synthesized membranes were first characterized by means of N_2 and He single gas permeance tests [mol m^2 s^{-1} Pa^{-1}] to evaluate the compactness of the layer and to assess the presence of large pores or pinholes in the zeolite layer. The set-up used to carry out these experiments is described in Figure III.10. Care was taken that the membranes were completely

dry before the measurements to avoid any interference of water. Single gas permeance tests give information concerning the growth of the layer, indicating that a significant resistance towards the permeance of gaseous species was present due to the layer grown. However, these data do not give information related to the mechanism of permeation, but this can be evaluated in terms of He/N_2 or N_2/SF_6 ideal selectivities by calculating, respectively, the ratio of the He and N_2 and the ratio of N_2 and SF_6 single permeances (kinetic diameters: $d_{m,He}$ = 0.26 nm; $d_{m,N2}$= 0.36 nm; $d_{m,SF6}$= 0.55 nm). In both cases, a ratio near 1 would reflect that no gas separation exists in the membrane due to the presence of a viscous mechanism related to great number of defects in the grown layer, while a value higher than 1 would reflect the presence of other mass transfer mechanisms, such as Knudsen or molecular sieve, where the separation of different species could be achieved (see Figure III.11). Moreover, a rough calculation of the viscous or laminar contribution of the *as*-synthesized zeolite NaA layer to the overall permeance (the contribution of the support is neglected) was also determined for some of the membranes prepared by fitting N_2 permeance data, $\mathbf{N_G^T}$ [mol m^{-2} s^{-1} Pa^{-1}], measured at different mean pressures [2], P_m [Pa], to the expression:

$$N_G^T = \frac{1}{3}\bar{d}_P \frac{\varepsilon_T}{\tau}\sqrt{\frac{8}{\pi MRT}} + \frac{1}{32}\frac{\bar{d}_P^2}{\mu_G RT}P_m = A + B\,P_m \qquad \text{(Eq. III.1)}$$

where the first term is related to the Knudsen contribution and the second one to the viscous contribution. In this work, for P_m=1.0 bar, the viscous contribution is given as follows:

$$\%VISCOUS = \frac{N_G^V}{N_G^T}\cdot 100 = \frac{N_G^V}{N_G^V + N_G^{Kn}}\cdot 100 = \frac{B\cdot 1.0}{A + B\cdot 1.0}\cdot 100 = \frac{B}{A+B}\cdot 100 \qquad \text{(Eq. III.2)}$$

III.2.1.2. Vacuum pervaporation (VPV)

The set-up used to carry out the vacuum pervaporation tests is shown in Figure III.12. The membrane was placed in a module (7) immersed in a temperature-controlled silicone oil bath (6). The temperature and pressure at the retentate side were measured, respectively, with a thermopar (8) and a manometer (5) and were continuously monitored and maintained at constant values. 300 mL min^{-1} of a ethanol/water liquid mixture measured with a calibrated rotameter (3) were fed to the retentate side of the membrane by means of a magnetically coupled centrifugal pump (Ismatec BVP-Z, Glattbrugg, Switzerland) (2), and recirculated to the feed tank (1). Samples of the feed could be taken at the inlet and outlet of the membrane module by means of two needle valves (4 and 9). The pressure at the permeate side of the module was measured by a vacuum gauge (Schlee Gmbh & CoV-D3, Witten, Germany) (11)

[2] The mean pressure is calculated as the arithmetic mean of the pressures in the retentate and permeate sides of the membrane

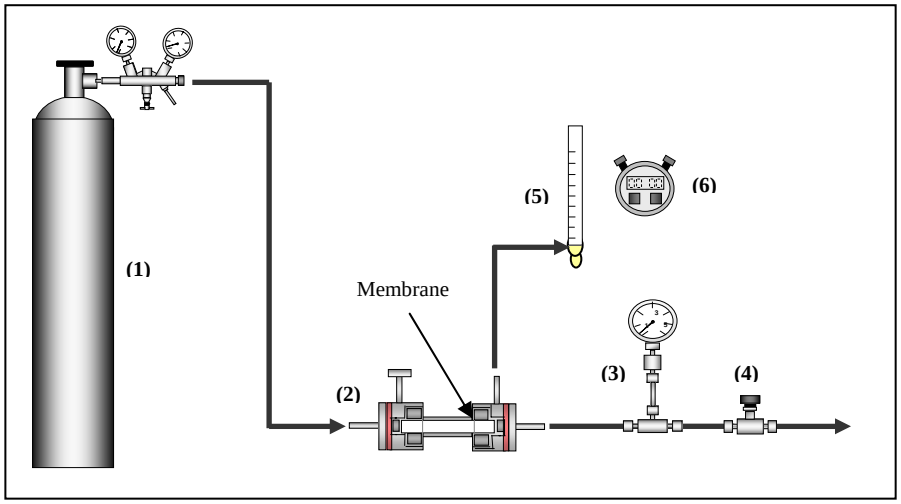


Figure III.10: Set-up used for the single gas permeance tests (1) gas cylinder (N_2, He, CO_2); (2) module; (3) manometer; (4) regulation valve; (5) bubble-meter; (6) chronometer.

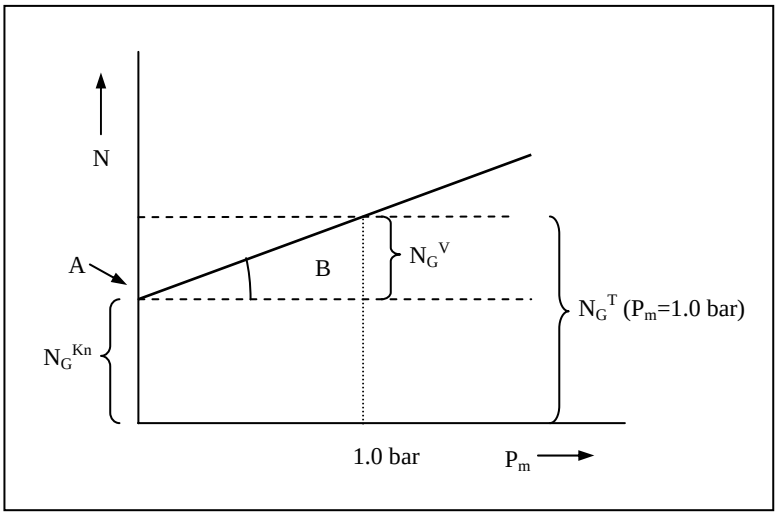


Figure III.11: Evolution of the gas permeance with the mean pressure according to Eq. III.1.

and maintained at <2 mbar by the action of an oil vacuum pump (Telstar 2G-6, Sabadell, Spain) (12). The permeated vapors were condensed and collected in a set of cold traps (10) cooled with liquid nitrogen. Both the feed and the collected liquid were analyzed in a gas chromatograph (HP 6890 series equipped with a TCD detector, Germany). The selectivity of the membrane was calculated as the ratio of the weight fractions of water and ethanol in the permeate side to that in the feed. The final values correspond to the mean of two consecutive steady-state measurements taken after 12 h of stabilization.

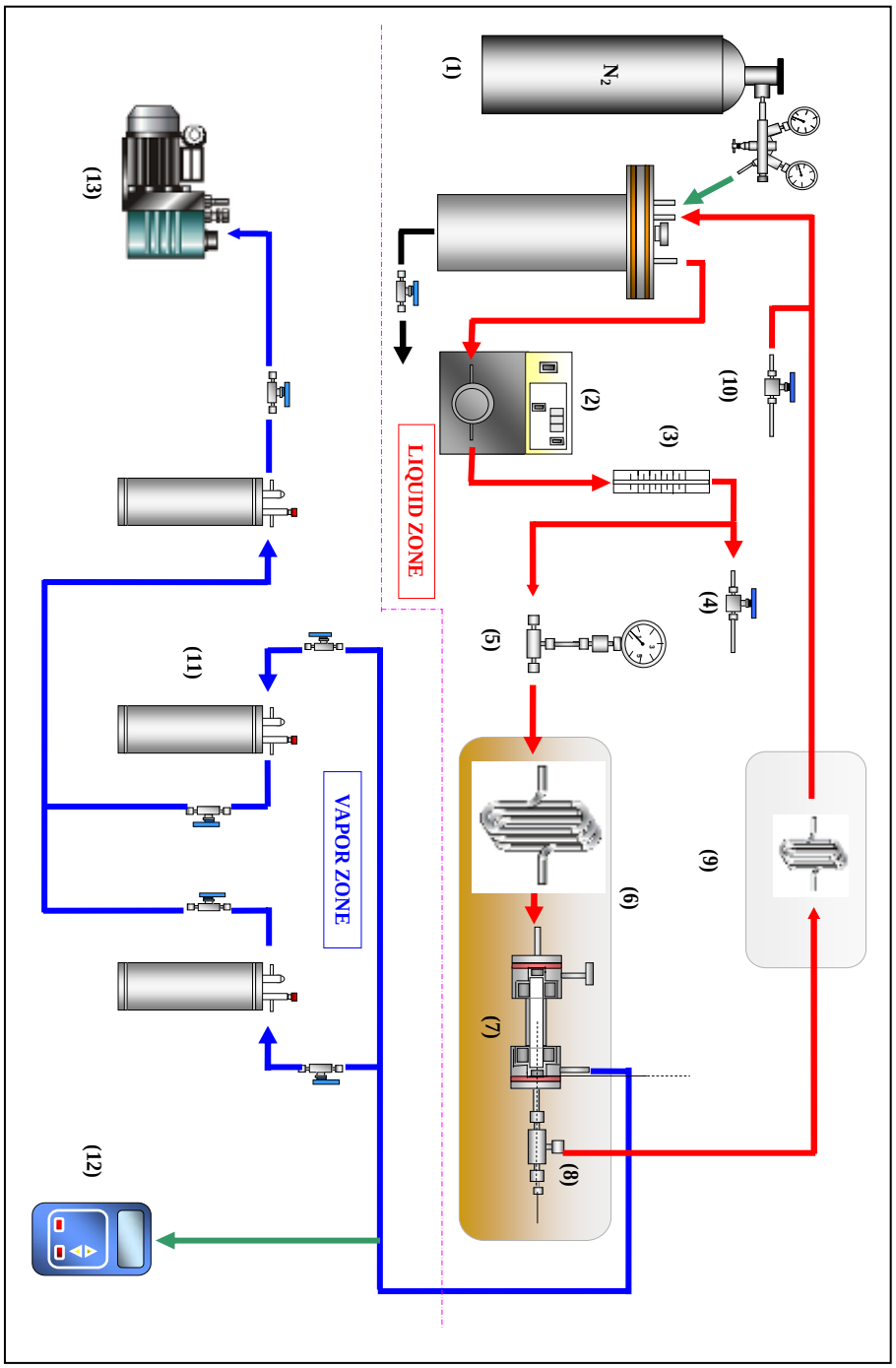


Figure III.12: Set-up used for the pervaporation test. (1) Feed tank; (2) Magnetically coupled centrifugal pump; (3) Rotameter; (4) Needle valve; (5) Manometer; (6) Thermostated bath; (7) Module; (8) Thermopar; (9) Cooling bath; (10) Needle valve; (11) Cold traps; (12) Vacuum pressure gauge; (13) Oil vacuum pump.

The pervaporation performance of the membranes was evaluated in terms of total flux ($\mathbf{N^T}$ [kg m^{-2} h^{-1}]) and selectivity (α [-]). The former is related to the total flux through the membrane, while the latter gives information concerning the ability of the membrane to separate two different species with respect to the feed concentration, which is calculated as follows:

$$\alpha_{i/j} = \frac{Y_i / Y_j}{X_i / X_j} \qquad \text{(Eq. III.3)}$$

where $\mathbf{X_i}$ and $\mathbf{X_j}$ correspond, respectively, to the weight fractions of species **i** and **j** in the feed (or retentate) [-], and $\mathbf{Y_i}$ and $\mathbf{Y_j}$ are the weight fractions of both species in the permeate [-]. In this work, several alcohol/water mixtures and ternary mixtures were studied, whose main characteristics are summarized in Table III.5. It should be noted that DNPE is immiscible with water, while 1-pentanol and 1-butanol are miscible with water for water compositions <10 wt.% at temperatures >373 K (*Pera-Titus et al., 2001*). Therefore, for 1-butanol, 1-pentanol/water mixtures and 1-pentanol/water/DNPE mixtures, the temperature in the whole PV plant was kept >373 K.

Table III.5: Chemicals used for the PV experiments

Reagent	*Purity [wt.%]*	*Density (293 K) [g cm^{-3}]*	*M [g mol^{-1}]*	*Safe card*	*Supplier*
Water	-	1.0	32.04	Flammable	Fluka (Germany)
Methanol (C1)	99.5	0.792	32.04	Flammable	Fluka (Germany)
Ethanol (C2)	99.5 (PRS)	0.789-0.790	46.07	Flammable	Panreac (Spain)
1-propanol (C3)	99.5 (PS)	0.808-0.810	60.10	Flammable	Panreac (Spain)
1-butanol (C4)	99.7	0.810	74.12	Harmful	Romil (England)
1-pentanol (C5)	99.0	0.815	88.15	Harmful	Aldrich (Germany)
di-n-pentylether (DNPE)	98	0.787	158.28	-	Prepared in our laboratory from the etherification reaction of 1-pentanol

III.2.1.3. Other analyses

In addition to the characterization methods aforementioned, the phases present in the zeolite NaA layers were characterized by X-ray diffraction (XRD). Furthermore, the surface morphology and thickness of the synthesized membranes was also visualized by scanning

electron microscopy. Some elemental Si microanalyses were also performed by SEM/EDS to determine its distribution in the zeolite layers. For further details concerning the equipments used and the experimental conditions surveyed for both techniques see sections III.4.1 and III.4.2.

III.2.2. Determination of PSDs in meso- and macroporous ceramic membranes in terms of flux measurements

The method presented in this work allows the determination of PSDs in meso- and macroporous commercial tubular ceramic asymmetric membranes from the experimental determination of a pure Knudsen single-gas diffusion permeance, the permeability of a pure liquid, and the non-hindered diffusion permeance of an electrolyte through the membranes. The membranes, all made of TiO_2 (rutile) supplied by TAMI (Montpellier, France), covered the range of applications arising from UF (1-300 kDa) to MF (0.10-0.80 μm)

III.2.2.1. Procedure I: pure Knudsen diffusion of a single gas

The set-up for the determination of single gas pure diffusion fluxes is depicted schematically in Figure III.13. The experimental procedure involves the following steps:

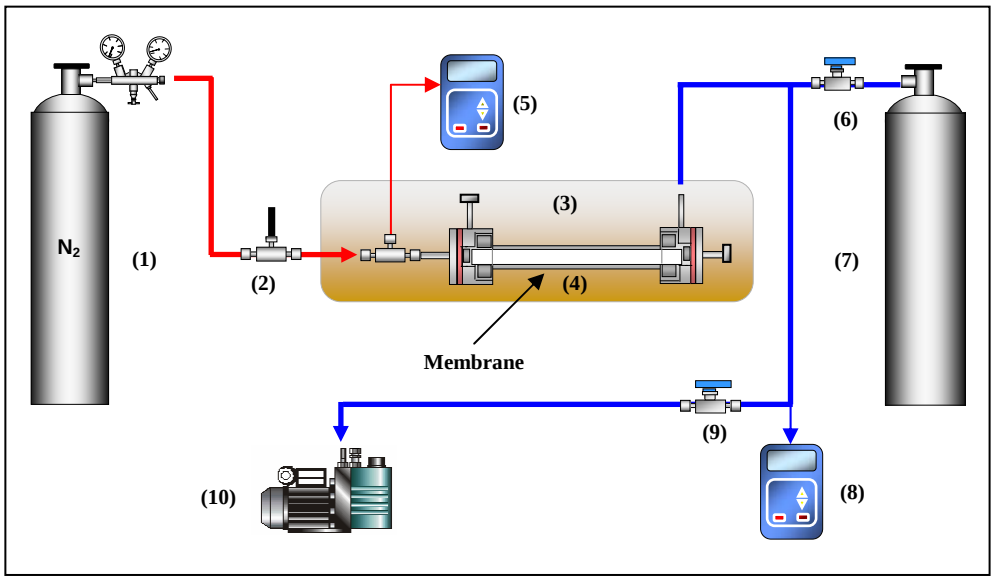


Figure III.13: Set up used for the determination of single gas pure Knudsen diffusion flows. (1) N_2 cylinder; (2) needle valve; (3) thermostatic bath; (4) module; (5) vacuum pressure gauge; (6) on/off valve; (7) vacuum lung; (8) vacuum pressure gauge; (9) on/off valve; (10) membrane vacuum pump.

1. The ***membrane*** previously dried in an oven at 373 K under vacuum was placed inside the ***module*** (4) and this was attached to the set-up.

2. ***Stabilization of temperature***: The module was immersed in an ethyleneglycol bath and the temperature stabilized in the range 303-363 K.

3. ***Depressurization of the system***: Valves (2) and (6) were closed, valve (9) was opened, and the vacuum pump started to depressurize the whole set-up.

4. ***Vacuum stabilization***: Once vacuum pressure reached a stable value (ca. 3 kPa) measured both at the retentate and permeate sides of the membrane, valve (9) was closed and the pressure between both valves monitored during 15 min to ensure the stability of vacuum pressure inside the system.

5. ***Connection of the vacuum lung***: Valves (6) and (9) were opened and the vacuum pressure was again stabilized for the whole system (ca. 3 kPa). The function of the vacuum lung was to provide a high enough permeate volume (~48 L, measured in our laboratory) to allow a more accurate monitoring of the vacuum pressure at the permeate side of the membrane.

6. ***Beginning of the experiment***: The experiment began by opening valve (2) and thus filling stepwise the retentate side of the membrane with the selected gas at a desired pressure (from ~5 to 10-30 kPa). Both the retentate and permeate pressures were continuously monitored by means of vacuum pressure gauges (5) and (7) and registered. Care was taken that the retentate pressure was constant along the experiment (maximum oscillation: ± 1 mbar). In the end, a breakthrough curve of permeate pressure was obtained.

7. ***End of the experiment***: The experiment was considered to end once the permeate pressure reached a steady-state asymptotic value (retentate pressure).

8. ***Replicates***: Steps 1-7 were repeated at least three times more to ensure optimal reproducibility of the experiments.

9. **Removal of the module from the set-up** and the membrane was again stored in an oven at 373 K under vacuum.

A typical curve obtained following procedure I is shown in Figure III.14. In addition, the details concerning the derivation of pure Knudsen diffusion fluxes from the experimental breakthrough curves of permeate pressure are outlined in chapter VI.

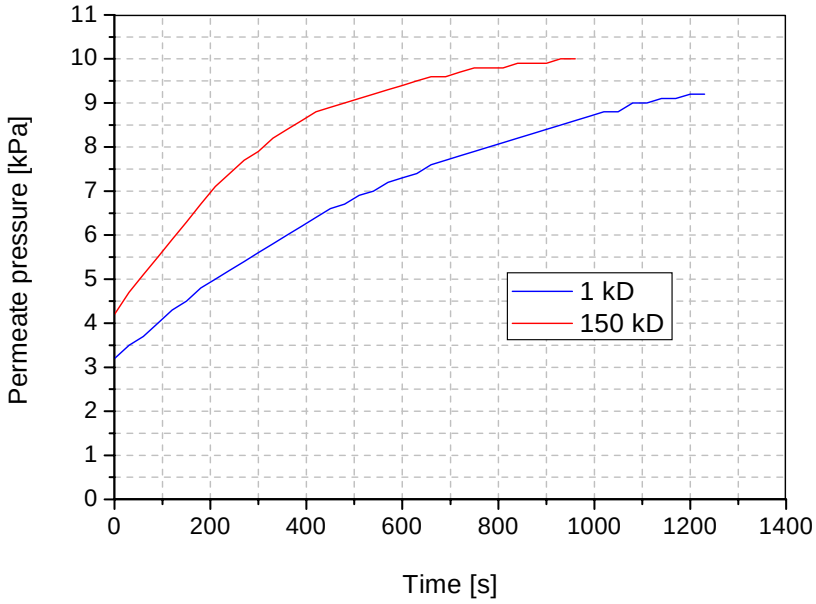


Figure III.14: Temporal evolution of the permeate pressure for two mesoporous ceramic membranes in a typical experimental according to procedure I. Conditions: T = 303 K; Retentate pressure = 10.2 kPa.

III.2.2.2. Procedure II: permeability of a pure liquid

The experimental set-up used to determine pure liquid permeabilities is depicted in Figure III.15. As can be seen, in general terms, it is similar to that used for cross-flow filtration seeding (see Figure III.3). The procedure to determine liquid permeabilities involves the following steps:

1. The ***membrane*** previously wetted in deionized water (Milli-Q Millipore with 18 MΩ cm^{-1} resistivity) overnight was placed inside the ***module*** (4) and this was attached to the set-up.

2. ***Stabilization of temperature***: The temperature was measured by means of a thermocouple in the feed beaker and stabilized in the range 288-299 K.

3. ***Circulation of deionized water***: Deionized water flowed across the retentate side of the membrane keeping the regulation valve (7) open and was recirculated to the feed beaker at a high flow rate (1 L min^{-1}) to avoid the presence of fouling.

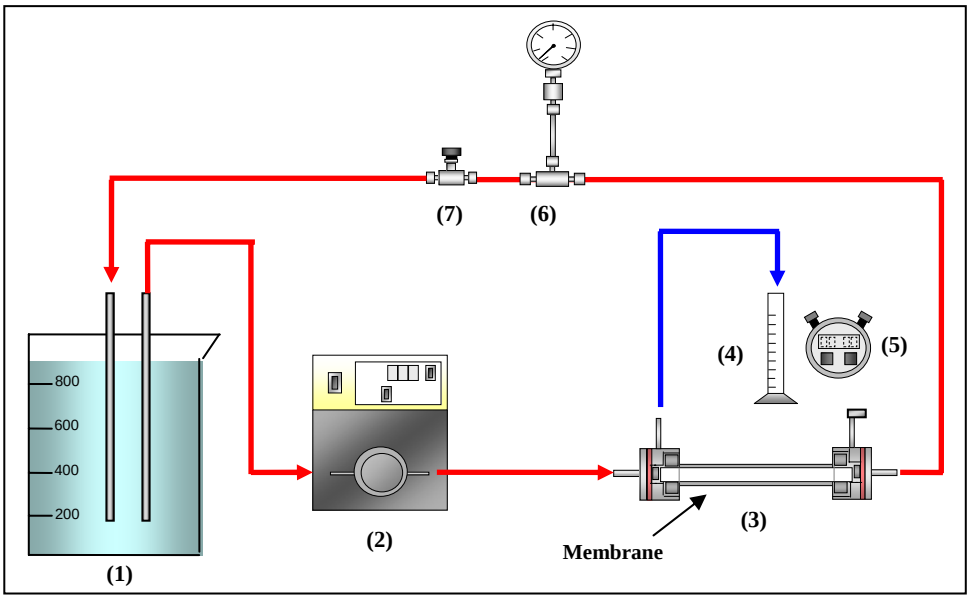


Figure III.15: Set up used for the determination of the permeability of water. (1) beaker filled with deionized water; (2) magnetic pump; (3) module; (4) graduated cylinder; (5) chronometer; (6) manometer; (7) regulation valve.

4. ***Transmembrane pressure***: After 15 min, the retention valve (7) was partially closed to achieve a fixed value of transmembrane pressure in the range 5-240 kPa depending on the MWCO and porosity of the membrane studied. The water permeability of the membrane [m^3 m^{-2} s^{-1} Pa^{-1}] was experimentally determined with a graduated cylinder and a chronometer as the ratio between the volume permeated by a given time. The water permeability was monitored during at least 1 h to assure that the value was constant, that is, no fouling occurred.

III.2.2.3. Procedure III: non-hindered electrolyte diffusion

The set-up used for the determination of non-hindered electrolyte diffusion permeances is schematically depicted in Figure III.16. As can be seen, it consisted of two closed retentate and permeate cycles with a perfectly known volume, whose pH was continuously monitored close to the module to avoid any delay in the signals. A saline solution was pumped in each cycle, respectively, by the action of a peristaltic and a magnetic pump. The main characteristics of the reagents used in this study are summarized in Table III.6. The experimental procedure to determine non-hindered electrolyte diffusivities involves the following steps:

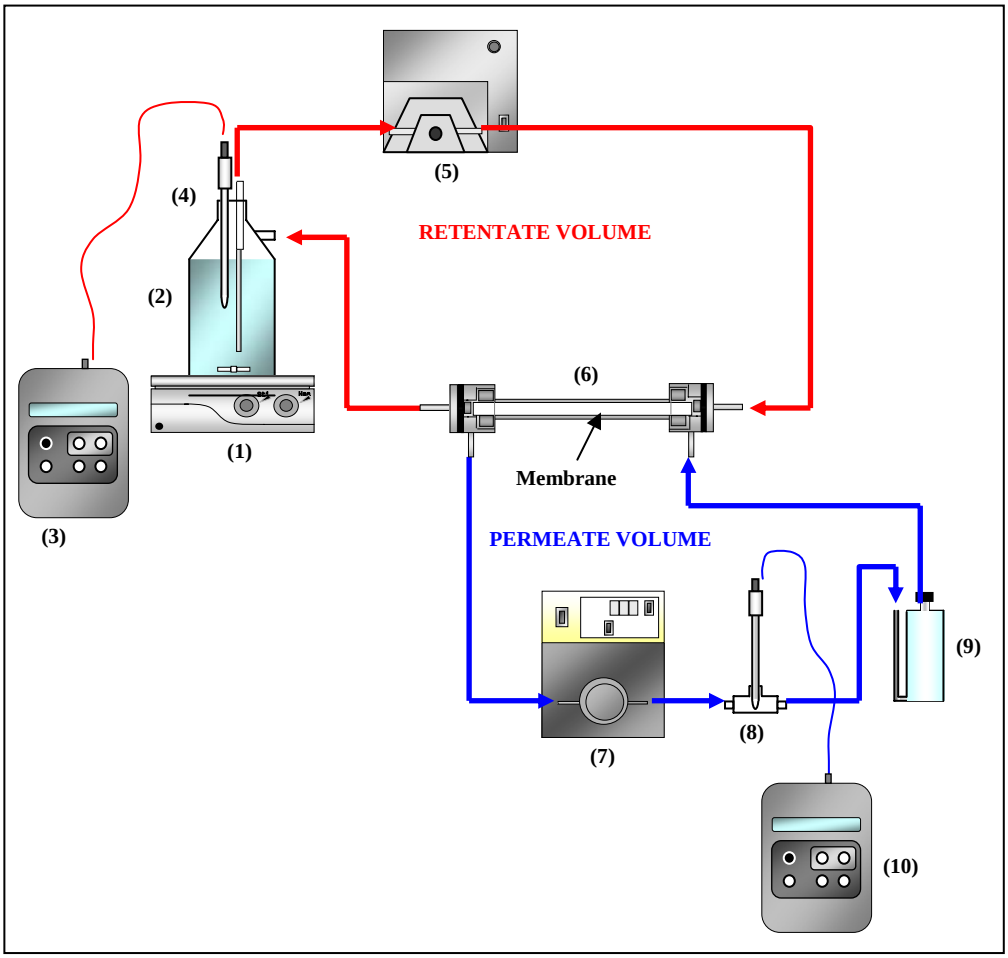


Figure III.16: Set up used for the determination of the non-hindered electrolyte diffusivities. (1) magnetic stirrer; (2) feed tank; (3) pH meter; (4) electrode; (5) Peristaltic pump; (6) module; (7) magnetic pump; (8) electrode; (9) permeate volume; (10) pH meter.

Table III.6: Reagents used according to procedure III

Reagent	*Purity*	*MW [g mol^{-1}]*	*Safe card*	*Supplier*
Lithium chloride	99%	42.39	Harmful	Merck (Germany)
Sodium chloride	99.5% (PA)	58.44	-	Panreac (Spain)
Potassium chloride	99.5% (PA)	74.56	-	Panreac (Spain)
Potassium hydroxide	85% (ACS)	56.11	Corrosive	Aldrich (Germany)
Hydrogen chloride	1 M *	36.46	Corrosive	Panreac (Spain)

* Concentration

1. The ***membrane*** previously wetted in a solution of KCl, NaCl or LiCl salts (see Table III.6) in deionized water (Milli-Q Millipore with 18 MΩ cm^{-1} resistivity) (100-500 mM) overnight to stabilize the ζ-potential of the surface of the pores was placed inside the module (6) and this was attached to the set-up.

2. ***Stabilization of temperature***: The temperature was measured by means of a thermocouple in the feed beaker and stabilized in the range 298-303 K.

3. ***Circulation of saline solution***: The same saline solution used to wet the membrane was recirculated (1 L min^{-1}) from the feed tank (2) across the retentate side of the membrane by the action of a peristaltic pump (5).

4. ***Filling the permeate volume***: On the basis of hydrostatic pressure differences, the closed permeate volume (V = 380 mL) (9) was filled with the saline solution. When the volume reached half the total value, the magnetic pump (7) started and the permeate solution was recirculated (300 mL min^{-1}). After filling the closed permeate volume with the saline solution, the remaining volume occupied by air was removed. Care was taken that no bubbles were present in the permeate volume.

5. ***Beginning of the experiment***: After stabilization of the volumes and the pH in the permeate and retentate sides of the membranes, an exact volume of acid (HCl) or alkali (LiOH, NaOH) measured with a volumetric pipette was supplied to the feed tank and the pH in both the permeate and retentate volumes were continuously monitored and registered, respectively, by pH-meters (3) and (10). In the end, a breakthrough curve of pH was obtained.

6. ***End of the experiment***: The experiment was considered to end once the pH in the permeate volume reached a steady-state value.

7. ***Replicates***: Steps 1-5 were repeated at least three times more to assure optimal reproducibility of the experiments.

8. ***Cleaning the system***: Deionized water was circulated in both permeate and retentate volumes to neutralize the pH.

9. **Removal of the module from the set-up** and the membrane was again stored in a saline environment overnight.

A typical curve obtained following procedure III is shown in Figure III.17. The details concerning the derivation of non-hindered electrolyte diffusivities from the experimental breakthrough curves of pH are outlined in chapter VI.

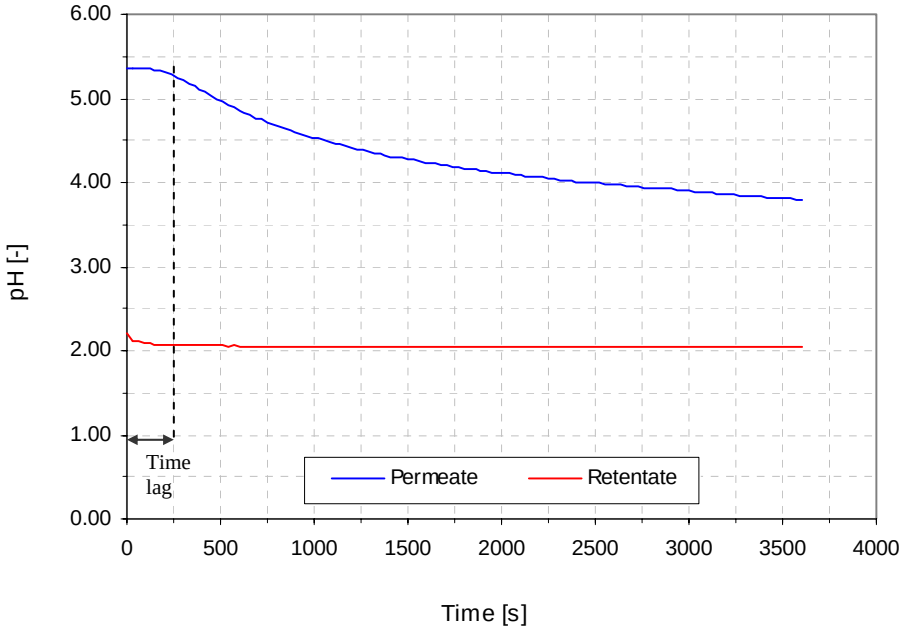


Figure III.17: Temporal evolution of the permeate and retentate pH for a mesoporous ceramic membrane (MWCO = 1 kD) in a typical experimental according to procedure III. Conditions: T = 300 K; c_{KCl} = 500 mM.

III.3. DETERMINATION OF EQUILIBRIUM AND KINETICS OF ADSORPTION

III.3.1. Weight uptake in a microbalance (TGA) [3]

III.3.1.1. Experimental set-up

The experiments were carried out in a thermogravimetric analyzer (TGA), whose schematic diagram is presented in Figure III.18. A microbalance (*Sartorius M 25 D, Germany*) with an accuracy of 0.001 mg was placed at the top. The sample holder was connected to the balance via a chain. The temperature was fixed by means of an oven. All the variables of the system were controlled and continuously monitored by means of a personal computer (PC) equipped with LABVIEW® software.

The water vapor required in the experiments was supplied by bubbling N_2 measured with a mass flow controller (Bronkhorst Hi-Tec, F-201C-FA-22-V, The Netherlands) in deionized water at room temperature. The gas phase was forced to circulate through a porous

[3] This study was done at the Catalysis and Reactor Engineering Group at the Department of Chemical and Environmental Engineering, Centro Politecnico Superior, University of Zaragoza (Spain).

plate to reduce the size of the bubbles and to improve the contact between both phases. The approach to saturation of the humidified stream was measured by a gas chromatograph, where a value in the range 80 ± 2% was obtained for all the conditions tested. Furthermore, the vapor partial pressure in the humidified stream was continuously monitored by means of a humidity sensor (Testo 605-H, The Netherlands).

The resulting stream was mixed with pure N_2 and supplied stepwise to the microbalance by the action of a 3-way electrovalve (3V-2) to achieve the desired water partial pressure. The gases were heated before entering the microbalance. Furthermore, a balance and a protective purge flows were used to avoid water vapor approach the microbalance. To prevent the system from water condensation, the tubes downstream the bubbler were wiped up with an electric resistance. In the course of an experiment, the sample mass, the temperature, and the total pressure were continuously monitored and registered in the PC.

III.3.1.2. Experimental procedure

The experimental procedure used in this section was similar to that reported by *Bausach et al. (2004)* for the study of the gas-solid non-catalytic reaction of HCl with $Ca(OH)_2$ in the presence of water vapor, which involved of the following steps:

1. ***Loading the sample holder***: The zeolite A powder (IQE, Zaragoza, Spain) (m_{ZA} ~50 mg) kept overnight at 373 K is set on the sample holder and subsequently introduced to the TGA, where the sample remained hanging during the following steps. The system was closed and dry N_2 circulates over the sample until constant weight was reached (~1 h).

2. ***Warming*** the sample holder at the 473 K with a ramp of 1 K min^{-1} for by the action of the oven until constant weight was newly reached (~5-6 h). For all the tested samples, a decrease in weight in the range 16-18% was observed. This value (Δm_w [mg]) was used to correct the weight of zeolite powder and has been termed "outgassed weight" in the remainder of this work.

3. ***Warming*** the sample holder at the desired temperature (298-423 K), ***heating*** the pipes upstream to avoid further water condensation, and ***turning on*** the balance and protective flows (200 and 0-1000 cm^3 (STP) min^{-1}, respectively).

4. ***Humidification*** of N_2 (carrier gas) by bubbling in deionized water during 30 min to obtain a constant water flow. The temperature of the water contained in the bubbler was measured with a thermocouple several times in the course of an experiment to ensure constancy in its value.

5. ***Beginning of the experiment***: The feeding stream (H_2O/N_2) (total flow = 0-1000 cm^3 (STP) min^{-1}) was supplied to the TGA by changing the position of electrovalve 3V-2 and the adsorption process started. All the data concerning the operational variables were continuously monitored and registered in the PC.

6. ***End of the experiment***: The experiment was considered to end once the total weight reached a constant value (1-2 h).

7. ***Replicates***: Steps 1-6 were repeated at least twice to ensure good reproducibility of the experiments.

8. ***Cooling of the system***: The oven was withdrawn from the sample holder and cooled at room temperature.

9. ***Removal of the sample***: Once the sample holder was at room temperature, the zeolite sample was removed from the TGA.

The total weight change during an adsorption experiment is shown in Figure III.19. The water molar loading on the zeolite powder, $\mathbf{q_w}$ [mol kg^{-1}], could be measured as the ratio between the weight uptake of the sample until constancy due to water adsorption and the dry zeolite weight (Eq. III.3)

$$q_w = \frac{m_w}{(m_{ZA} - \Delta m_w)} \frac{18.0148}{1000} \text{ [mol kg}^{-1}\text{]} \qquad \text{(Eq. III.3)}$$

Finally, to evaluate the experimental error, some experiments were replicated twice. Both water and ethanol loadings measured at selected vapor pressures were accurate to within ±15%.

III.3.2. Breakthrough curve analysis by mass spectrometry (MS) [4]

III.3.2.1. Experimental set-up

The experiments were carried out in the apparatus depicted schematically in Figure III.20, which basically consisted of four main parts:

1. ***Feeding system***: N_2 and Ar gases were obtained from two gas cylinders and were regulated employing 4 mass flow controllers (Bronkhorst Hi-Tec, F-201C-FA-22-V,

[4] This study was done at the Catalysis and Reactor Engineering Group at the Department of Chemical and Environmental Engineering, Centro Politecnico Superior, University of Zaragoza (Spain).

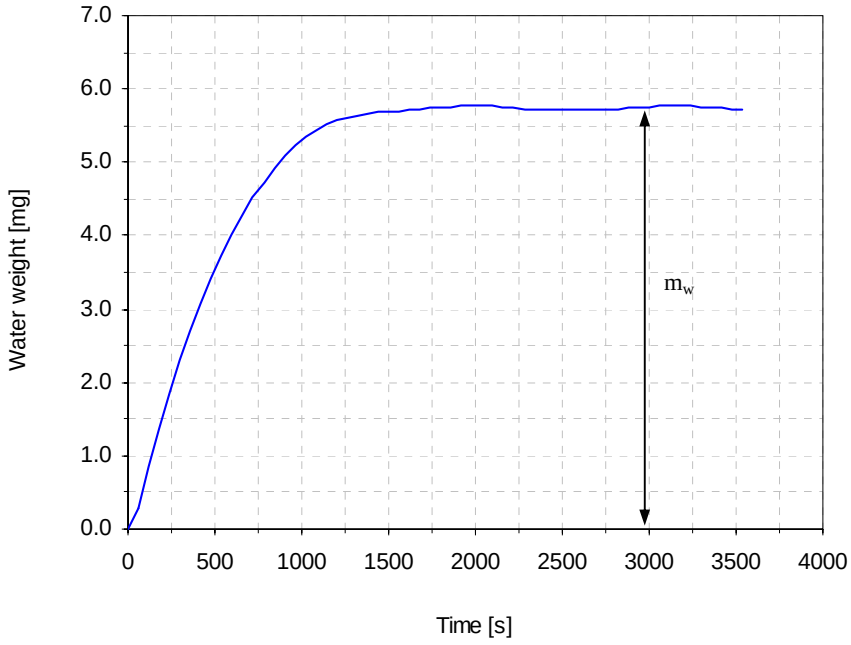


Figure III.19: Water uptake by zeolite A. Conditions: T = 393 K; P_w^{in} = 1.70 kPa; m_{ZA} = 50.0 mg.

2. The Netherlands). The water/ethanol vapors required in the experiments were fed into the system by bubbling N_2 in deionized water and in ethanol (>99.5 wt.%, Panreac, Spain), respectively, at room temperature in a similar manner as that outlined in section III.3.1.1. The resulting streams were mixed with pure N_2 and supplied stepwise to the adsorption system by the action of a 6-way and a 4-way electrovalves, 6V and 4V, respectively to achieve the desired water and ethanol partial pressures to carry out unary and binary adsorption experiments. Furthermore, to prevent from vapor condensation, the tubes downstream the bubblers were wiped up with an electric resistance.

3. ***Adsorption system***: The adsorption process took place in an isothermal packed bed with downward flow operated under differential conditions, which consisted of a Pyrex tube (200 mm height, 12.5 mm o.d., 7.5 mm i.d.) with a porous plate to hold the zeolite powder. The temperature in the bed was regulated by an oven.

4. ***Analytical system***: H_2O, EtOH, N_2 and Ar were analyzed by means of an on-line mass spectrometer (Omnistar^{TM}, Pfeiffer Vacuum QMS 200) with an Enclosed Ion Source and a triple mass filter, and equipped with a dual detector (Faraday and Electron Multiplier). The detection limit was <10 ppm and <10 ppb for Faraday and

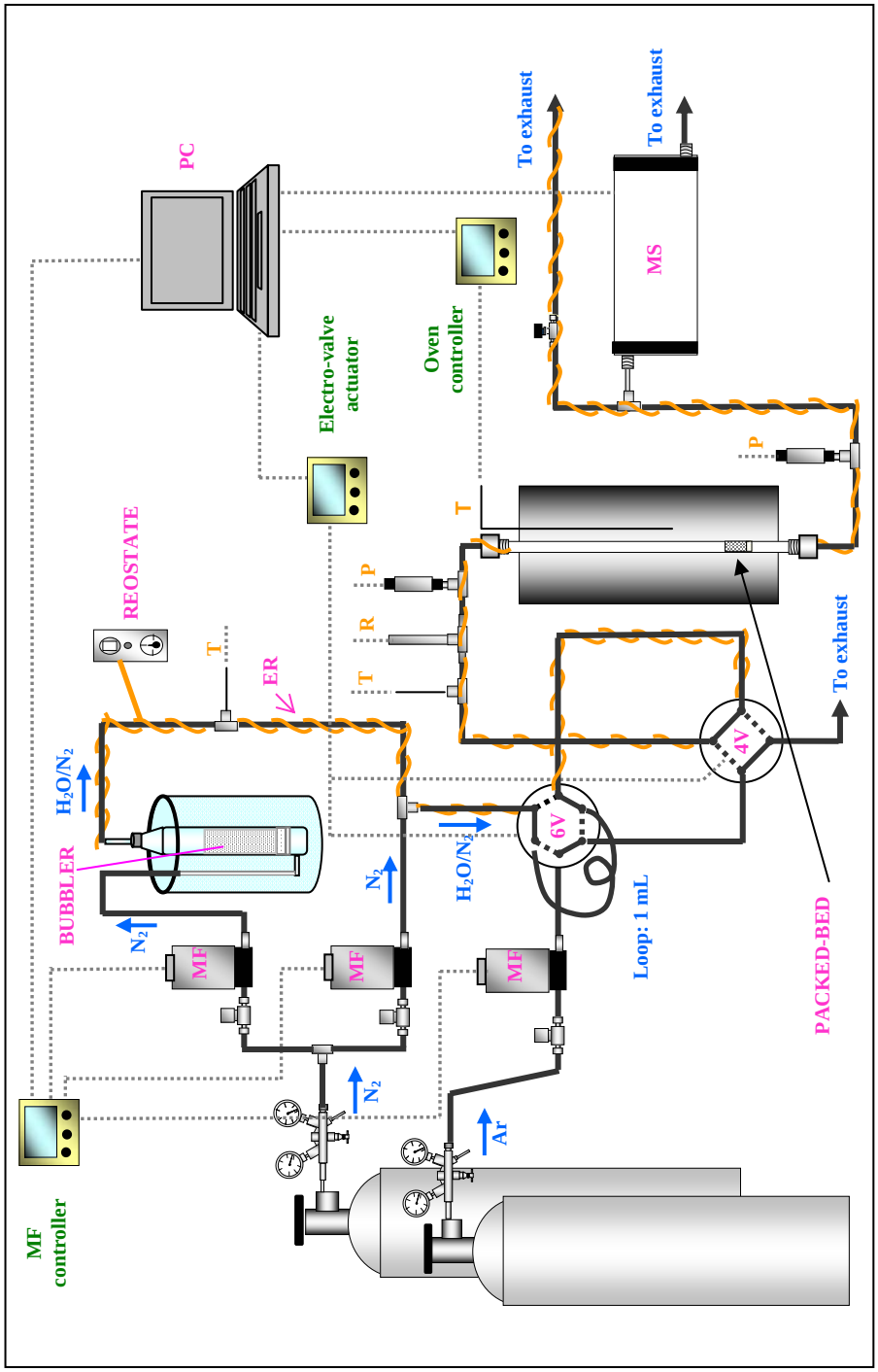


Figure III.20: Schematic representation of the set-up used for the determination of equilibrium and kinetics of adsorption on zeolite powder with MS analysis.

5. Electron Multiplier detectors, respectively. Vacuum was generated by means of rotatory and turbo-molecular pumps. Signals corresponding to mass / charge ratios (m/z) of 18, 28, 40 and 45 were chosen to follow the evolution of concentration of H_2O, N_2, Ar and EtOH, respectively, at the outlet of the fixed-bed reactor.

6. ***Personal computer***: All the data concerning the operational variables, that is, temperature, gas signals, and gas flows were continuously monitored and registered by a PC equipped with LABVIEW® software.

III.3.2.2. Experimental procedure

The procedure of each experiment is similar to that reported by *Bausach et al. (2005)* for the study of the gas-solid non-catalytic reaction of SO_2 with $Ca(OH)_2$ in the presence of water vapor, which consisted of the following steps:

1. ***Loading the bed***: The zeolite powder (~100 mg) outgassed overnight at 373 K was packed in the glass column with apparent porosity of 60-70%. Compared to the study reported by *Bausach et al. (2005)*, in the present study, no inert solid was introduced to the reactor to avoid the channeling of the gas because of the low amount of solid loaded to the reactor.

2. ***Outgassing the solid***: The bed was warmed up to 623 K with a ramp of 1 K min^{-1} (~2 h) by the action of an oven under the presence of an Ar sweep gas stream (200 cm^3 (STP) min^{-1}) in order to remove strongly bound humidity in the solid.

3. ***Warming*** the sample holder at the desired temperature (298-423 K) and ***heating*** the pipes upstream to avoid water condensation.

4. ***Humidification*** of N_2 (carrier gas) by bubbling in deionized water/ethanol during 30 min to obtain constant water and ethanol flows. Both flows were later diluted with dry N_2 to achieve the desired values of water and ethanol vapor pressures.

5. ***Beginning of the experiment***: The feeding streams (H_2O/N_2) and ($EtOH/N_2$) (0-200 cm^3 (STP) min^{-1} both of them) were supplied to the bed and the adsorption process started. All the data concerning the relevant operational variables were continuously monitored and registered in the PC.

6. ***End of the experiment***: The experiment was considered to end once all the mass signals visualized in the mass spectrometer showed constant values. Then, the Ar stream was again supplied

7. ***Replicates***: Steps 1-6 were repeated at least twice to ensure good reproducibility of the experiments.

8. ***Cooling of the system***: The oven was withdrawn from the packed bed and cooled at room temperature.

9. ***Removal of the sample***: Once the bed was at room temperature, the zeolite sample was removed from the TGA.

The evolution of the signals (Faraday) obtained for H_2O, N_2 and Ar in a typical experiment is plotted in Figure III.21. After each experiment, normalized adsorption breakthrough curves of water and/or ethanol leaving the packed bed could be plotted. Furthermore, normalized blank breakthrough curves of water and/or ethanol could be also obtained from experiments performed following the same procedure, but with no presence of solid in the bed. These experiments were carried out both before and after each experiment to assure that the steady-state water and ethanol signals at the end of each experiment corresponded exactly, respectively, to the water and ethanol vapor pressures supplied to the packed bed.

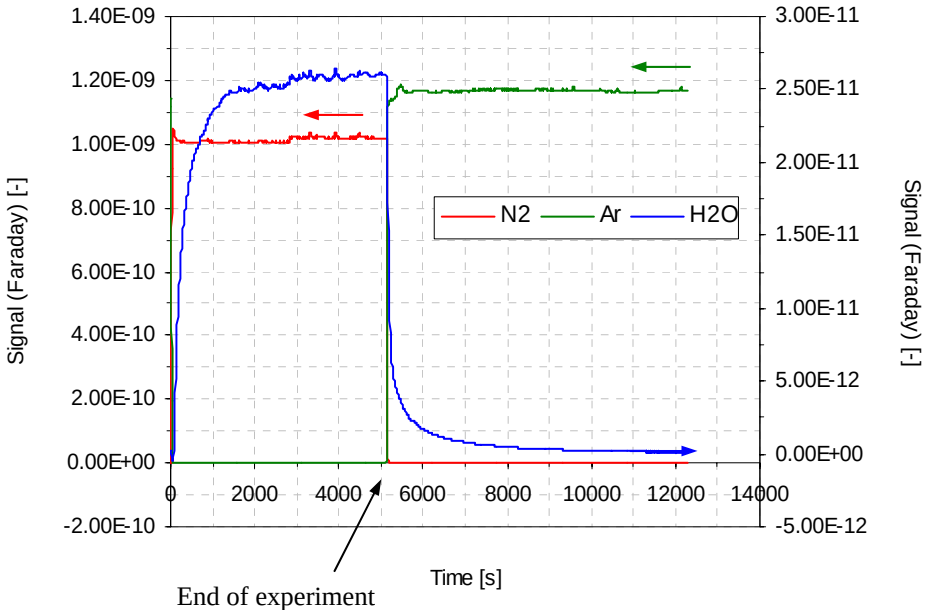


Figure III.21: Evolution of signals in the Faraday detector with time for water, N_2 and Ar. Conditions: T = 393 K; P_w^{in} = 1350 Pa; m_{ZA} = 103.2 mg.

An example of a normalized adsorption and blank breakthrough curves are shown in Figure III.22, where $\mathbf{P_i^{in}}$ and $\mathbf{P_i^{out}}$ correspond, respectively, to the partial pressure of species **i** at the inlet and outlet of the bed [kPa]. Thus, when all the species **i** (water or ethanol) that enters the bed is retained, the ratio P_i^{out} / P_i^{in} [-] becomes zero. In the same way, when the ratio P_i^{out}/P_i^{in} tends to one, no adsorption is expected. On the other hand, the total amount of species **i** removed from the feeding stream can be evaluated from the area drawn between normalized blank and adsorption breakthrough curves. The amount of species **i** retained per kg of zeolite A at a time t is given by Eq. III.4

$$q_i(t) = \left[A_{bl,i}(t) - A_{ads,i}(t)\right]\frac{P_i^{in}}{P}\frac{(\phi_v/60)}{22.4}\frac{10^3}{(m_{ZA} - \Delta m_{ZA})} \text{ [mol kg}^{-1}\text{]} \qquad \text{(Eq. III.4)}$$

where $\mathbf{A_{bl,i}}$ and $\mathbf{A_{ads,i}}$ correspond to the areas drawn, respectively, by the normalized blank and adsorption breakthrough curves until time t [s^{-1}], $\boldsymbol{\phi_v}$ is the total volumetric flow of the feeding stream [cm^3 (STP) min^{-1}], **P** is the total pressure [kPa], $\mathbf{m_{ZA}}$ is the weight of zeolite A loaded to the bed [mg], and $\mathbf{\Delta m_{ZA}}$ is the decrease in weight of the zeolite sample due to outgassing (step 2 of the experimental procedure) [mg] determined by the TGA analyzer (16-18% m_{ZA}) (see section III.3.1.2). Both water and ethanol loadings measured at selected vapor pressures were accurate to within ±15% and were not be dependent on the total flow in the packed bed reactor for the operational range 50 – 300 cm^3 (STP) min^{-1}. A more detailed calculation of the amount of each species retained per kg of zeolite A for a given experiment can be found in Appendix A.

III.3.3. Adsorption isotherms of N_2 at 77 K

In addition to the unary and binary adsorption isotherms of water and/or ethanol on zeolite A at high temperatures (298-423 K), N_2 adsorption isotherms were also obtained on a set of several amorphous active carbons and zeolite powders at 77 K and at very low relative vapor pressures in order to obtain data concerning the interaction between adsorbent-adsorbate by applying solution thermodynamics to the system. The details of the equipment used to carry out the adsorption measurements can be found in section III.4.5. Prior to the analyses, the samples were subjected to a strict heating protocol to ensure complete outgassing of strongly bounded water in the micropores (see Figure III.23). For further modeling information see chapter VI.

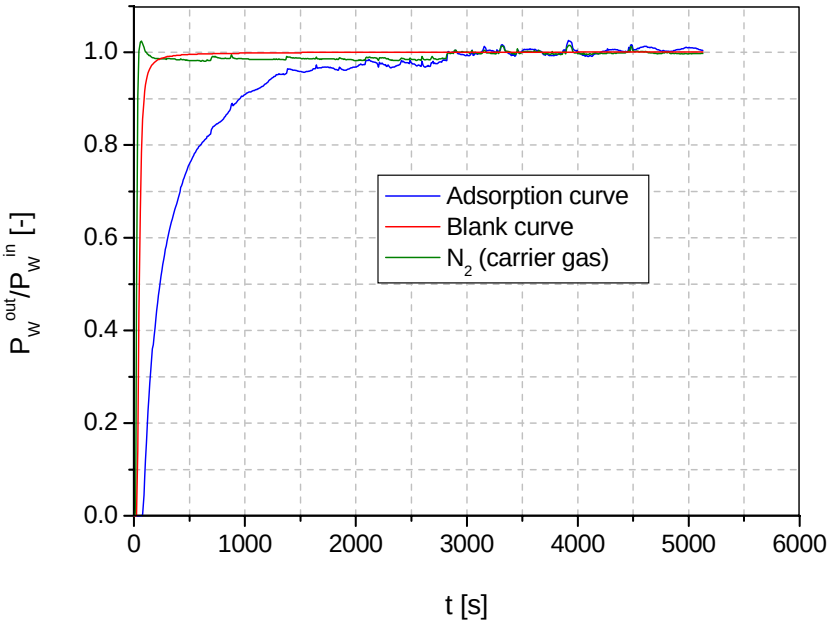


Figure III.22: Breakthrough curves of water and N_2. Conditions as in Figure III.21.

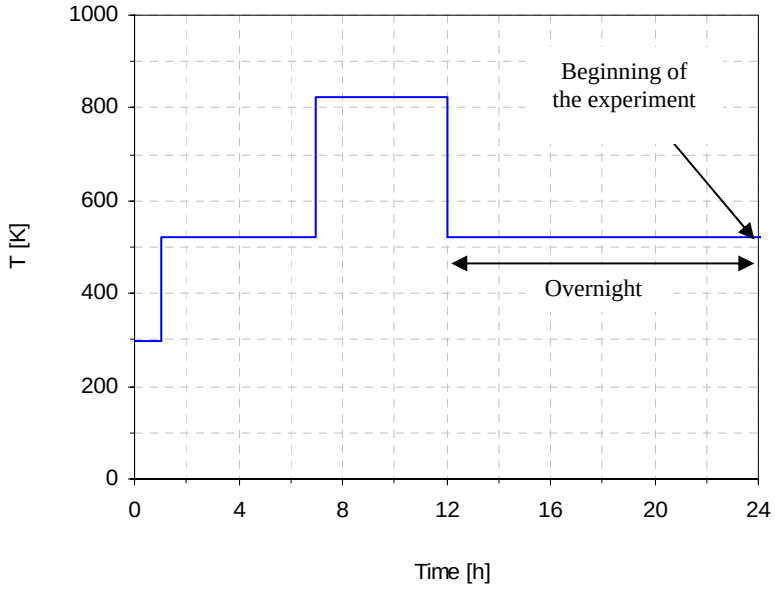


Figure III.23: Heating curve used for outgassing the zeolite powder samples prior to the N_2 adsorption isotherms at 77 K.

III.4. SOLID CHARACTERIZATION TECHNIQUES[5,6]

The following techniques were used to carry out the different analyses concerning the solid powders (zeolites) and granulate (active carbons) used in this work:

III.4.1. X-ray diffraction (XRD)

Qualitative analysis of the solid powders used in this work and synthesized zeolite NaA membranes were done to identify the phases present in the samples. The interpretation of the XRD patterns was done by comparison with data published by the "Joint Committee of Powder Diffraction Standards (2002)."

- *Equipment used*: Diffractometer (Siemens D-500, Germany) using Cu Kα radiation (α=1.5128 Å) and a secondary graphite monochromator, angle (2θ [º]) swept in the range 5-40º with a step in the range 0.03-0.05º.

III.4.2. Scanning electron microscopy (SEM) – Energy dispersive spectroscopy (EDS)

The surface morphology of the solid particles and zeolite NaA membranes was also inspected by scanning electron microscopy (SEM) and field electron scanning electron microscopy (FESEM). Furthermore, some elemental microanalyses by EDS were also carried out to determine the distribution of Si in the zeolite layers.

- *Equipments used*: Hitachi H-4100FE, Hitachi S-2300, JEOL JSM-840 and Stereoscan S-360, all operating at 10-35 kV.

III.4.3. Transmission electron microscopy (TEM)

This technique was used for the determination of mean particle size from the inspections of TEM micrographs.

- *Equipment used*: JEOL 1010 equipped with Bioscan (Gatan) image processor

III.4.4. X-ray fluorescence (XRF)

This technique allows doing semi-quantitative analyses of 78 elements of atomic weight larger or equal to that of boron (B). This technique was used for the determination of SiO_2/Al_2O_3 ratios in commercial zeolite powders.

[5] These experiments were carried out at Serveis Científico-Tècnics at the University of Barcelona (UB).
[6] These experiments were carried out at Servicios de Apoyo a la Investigación (UniZar)

- *Equipment used*: X-ray spectrophotometer Philips PW 2400 equipped with UniQuant v. 2.53 software for semi-quantitative analysis.

III.4.5. Photon correlation spectroscopy (PCS)

This technique allows the determination of particle size distributions and ζ-potential of solid powders prepared in a suspension of a fixed concentration (~500 mg L^{-1}) and pH.

- *Equipments used*: Malvern Zetasizer 3000 HS

III.4.6. BET surface area and N_2 adsorption isotherms at 77 K

This technique was used to determine BET surface areas, pore volumes, pore size distributions and N_2 adsorption isotherms of solid powders and granulates at 77 K. The equipment included a low pressure microdose system that allowed micropore analysis. Table III.7 summarizes the analysis conditions for the determination of adsorption isotherms in the micropore region ($P/P^o < 10^{-3}$) for zeolites.

- *Equipment used*: Porosimeter Micromeritics ASAP 2010 using liquid N_2 (77 K).

Table III.7: Analysis conditions for the determination of N_2 adsorption isotherms at 77 K in the micropore region

Sample weight [g]	0.1 – 0.2
Equilibrium interval [s]	40
Low pressure dose [cm^3 (STP) g^{-1}]	3-6
Time min. [min]	0
Time max. [min]	999
Backfill gas [-]	N_2
Outgassing	See heating protocol in Figure III.23

III.4.7. Helium pycnometry

The density of the solid powders was analysed by helium picnometry at room temperature (301-302 K) after drying the samples at 373 K under vacuum (<13 Pa) overnight.

- *Equipment used*: Helium pycnometer Accupic 1330.