# Water characterization in composite organic membranes by thermal analysis

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## Abstract

We describe a dehydration study of ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) organic composite membranes. This study gives an original description of the state of water in polymer composite membranes by differential thermal analysis (DTA). Usually three types of water are present in polymer membranes described by spectroscopic studies: first shell of water hydrate (type 1 water), second shell of disturbed liquid like water and liquid like water (type 2 and 3 water). These experiments cannot permit to clearly distinguish these different types of water but only two. Ours results show that strongly bounded water, corresponding to the type 1 water, has a high departure temperature. Types 2 and 3 water cannot be differentiated and their departure occurs around the boiling point temperature of free water. © 1998 Elsevier Science B.V.

*Keywords:* Composite organic membranes; Ultrafiltration; Nanofiltration; Reverse osmosis; Thermal analysis; High bonded water

## 1. Introduction

The study of the state of water in polymer membranes has been fully described in symmetrical cellulose acetate membranes [1,2a,2b–6]. From all these studies a crystal like structure has been deduced for the water in the pores. This structure is intermediate between that of ice and free water. As a consequence water in the pores exhibit different properties as in the bulk such as higher viscosity and smaller permittivity....[3,5,6]. Murphy et al. [7] have found that the structure of water in asymmetrical cellulosic membranes is dependant on the heterogeneity of the membrane. Water in big pores (ultrafiltration, UF, microfilteration, MF) seems to aggregate in clusters of water molecules as in small pores the percentage of clusters is very small [6]. The active layer of dense reverse osmosis (RO) membranes contain weakly aggregated water. In UF membranes water contained is rather like free water.

There are many models to describe the water structure in polymers [8–14]. Three types of water have been found in polymer membranes from spectroscopic studies [2a,2b,5,6,15–18] or thermoporometry [19]: first shell of water hydrate (type 1 water), second shell of disturbed liquid like water and liquid like water

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(type 2 and 3 water). The hydration of organic membranes happened in 2 steps [19,20]: (i) a layer of water monomer is adsorbed on the surface of the polymeric membrane, (ii) other water molecules are adsorbed on the first monolayer with weak hydrogen bonding. The first layer of adsorbed water has lost its hydration properties toward solutes, especially in RO, where the pore diameter is very small as compared to the thickness of the adsorbed film. In that case, the first layer of water monomers acts as a new membrane which can be a selective barrier for solutes. As a consequence the mechanism of solute transfer in RO is a solvation–diffusion mechanism. In UF, the thickness of the first layer of monomers is very small compared to the pores diameter and solutes mass transfer mechanism is mainly convective [19–21].

The present paper deals with thermal analysis of organic membrane swollen by water. The work aims at describing the water structure in polymeric membranes by mean differential thermal analysis (DTA). Membranes used for this study are polymer composite membranes in the range of molar weight cut-off

(MWCO) from UF (<200,000 Da) to RO (<100 Da) membranes.

## 2. Materials and method

The organic membranes under study are polyamide (PA) NF membranes (NF70 with a molar weight cut-off (MWCO) near 180 Da (average pore diameter: 0.62 nm) from Filmtec (Denmark) and polyethersulfone (PES) UF membranes (MWCO: 1000, 30,000, 100,000 and 200,000 Da; average pore size respectively: 0.8±0.2, 5.1±1.0, 10±1, 28±5 nm) from Tech-Sep (France). In addition, a polyamide RO dense membrane from Barnstead (USA) has been used for comparison (RO pure). The membrane materials are reported on Fig. 1. All are composite with a support layer in polysulfone (PS).

The thermal analytical system employed is a Mettler TA-Thermosystème FP800 associated to an FP85 oven and an EPSON HX20 data system. Membrane samples have been heated at a rate of 2°C/min or
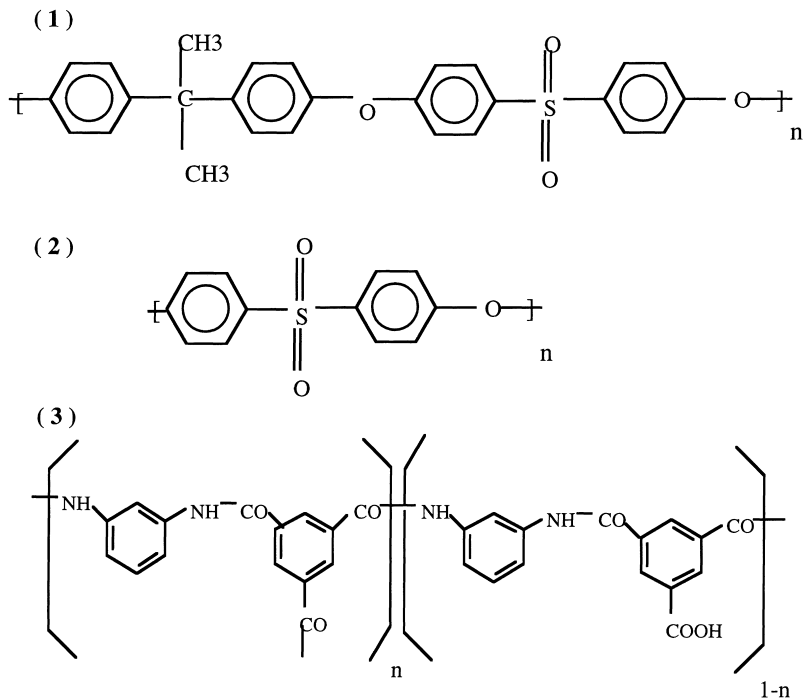
Fig. 1. Membrane materials: (1) polysulfone (PS), (2) polyethersulfone (PES) and (3) polyamide.

5°C/min in sealed aluminium pans (volume: 40 μl, $P_{max}$=2 bar). The sample weight is in the range of 15–20 mg. The skin and the sublayer parts of the membranes studied, have been separated by manual pealing using an adhesive double tape. The samples are immersed in liquid water at room temperature during 24–48 h. Before experiments all samples are drained off the excess of water in the air. Then the samples are cut in pieces small enough to fill the pan in which the DTA will be done.

## 3. Results and discussion

### 3.1. Thermal analysis of the components of a NF70 membrane

In order to investigate the contributions of the different layers of these composite membranes, the skin and the sublayer of the membranes have been separated and analyzed separately by means of DTA. The results are reported in Table 1 and Fig. 2.

Table 1
Characteristics of the DTA endothermic peaks

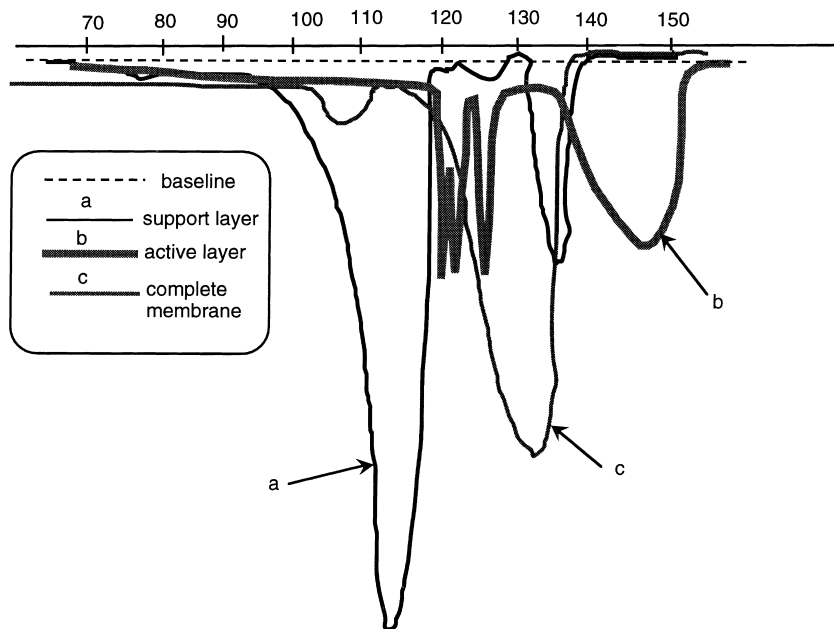|  |  | Temperature transition (°C) | | |
| --- | --- | --- | --- | --- |
|  |  | Peak onset | Peak maximum | Peak endset |
| Whole membrane | peak 1 | (96)[a] | (110)[a] | (118)[a] |
|  | peak 2 | 120 | 137 | 144 |
| Skin | peak 1 | 122 | 123; 125; 128 | 129 |
|  | peak 2 | 134 | 144 | 149 |
| Sublayer | peak 1 | 105 | 115 | 118 |
|  | peak 2 | 134 | 140 | 142 |

[a] Peak occasionally observed.



Fig. 2. Differential thermal analysis thermograms of a nanofiltration composite membrane: (a) support layer; (b) active layer; (c) complete membrane (membrane NF70; scan rate: 2°C/min).
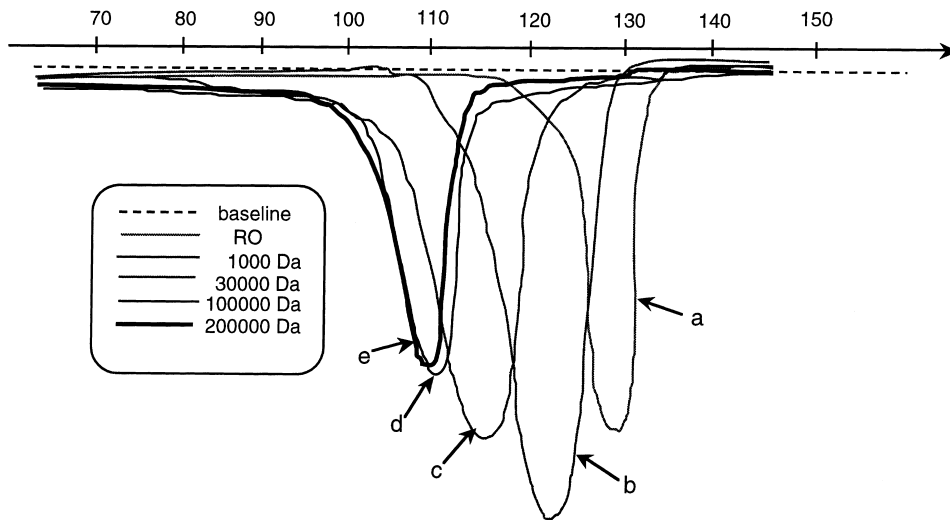
Fig. 3. DTA of PES membranes with different cut-off (scan rate: 5°C/min).

Thermal analysis of the whole membranes in sealed pan reveals a large endothermic peak beginning at 120°C and stopping at 144°C ($T_{max}$=137°C). The small endothermic peak, occasionally observed below or near 100°C, is attributed to surface humidity. The skin layer exhibits, at least 3 narrow peaks between 122°C and 129°C and a large peak at $T_{max}$=144°C. The sublayer presents two well defined peaks at $T_{max}$=115°C and $T_{max}$=140°C. These results show that the thermogram of the whole membrane does not correspond to the sum of the skin and the sublayer. This could be due to water exchange between the two layers in the composite membrane during the analysis. The difference in thermal analysis of the components of the membrane could be attributed to their different chemical nature: polyamide (skin) and polysulfone (sublayer).

## 3.2. DTA of PES membranes with different MWCO

In order to investigate the influence of the pore size on the temperature of water departure, we have used a set of PES mesoporous membranes with cut-off ranging between 1000–200,000 Da, 1 Da=1 g/mole). As seen in Fig. 3, the $T_{max}$ values of the large endothermic peak decrease with the cut-off. Although the RO membrane is made from PA and not PES, this membrane exhibits the highest

temperature for water departure. As the PES membranes are identical in nature, the shift of $T_{max}$ towards higher temperature could be clearly related to their mean pore size.

## 4. Conclusion

Referring to authors [2a,6,14,15,17], three types of water are present in polymer membranes. Our DTA experiments cannot permit to clearly distinguish these three different types of water but only two. For a composite membrane, water state is best determined by separating membrane support and active layer. Ours results show that strongly bounded water, corresponding to the type 1 water, has a high maximum temperature and the smaller the average pore size, the higher the departure temperature occurs. Types 2 and 3 water cannot be differentiated and have a temperature departure around the boiling point of free water.

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