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Abstract- The dissolution of polymers in solvents is an interest area of polymers science and technology due to their applications in films and membranes. The starting point for the preparation of polymer membranes by phase inversion is having a thermodynamically stable solution. In this work, the thermodynamic behavior of polyamide 66 (PA66) solutions in formic acid (FA) and in hydrochloric acid (HCℓ), was studied to evaluate its physical/chemistry classification. The polymer systems may be divided into five classes (types), which incorporate polymer-low molecular liquid systems, ranging from true solutions to dispersions of polymers in liquids. The polyamide 66/formic acid (PA66/FA) binary system is considered a true solution. Several experiments were performed to verify if the polyamide 66/hydrochloric acid (PA66/HCℓ) binary system has all characteristics of true solution. The analysis showed that the PA66/HCℓ binary system presents all characteristics of true solution, including the final morphology of the membranes that are similar obtained membranes by PA66/FA binary system.

Keywords: polymer-low molecular liquid systems, true solution, PA66/HCℓ binary system.

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Behavior Classification Physical/Chemistry PA66/HCℓ Binary System Utilized to Obtain Separation Membranes

Jocelei Duarte [a], Venina dos Santos [a] & Mara Zeni [a*]

Highlights

- The thermodynamic equilibrium is reached ($\Delta\mu = 0$ or $= \mu_1$) the solution becomes homogeneous.
- The PA66/HCℓ solution was frozen and thawedand the solution remained homogeneous.
- The Gibbs free energy of PA66/HCℓ system indicates to be more favorable to PA66/FA system.
- In PA66/HCℓ system dipole-dipole interactions occur, justifying the behavior similar to polyelectrolyte.
- The PA66 solution in HCℓ behaves as a true solution.

Abstract- **The dissolution of polymers in solvents is an interest area of polymers science and technology due to their applications in films and membranes. The starting point for the preparation of polymer membranes by phase inversion is having a thermodynamically stable solution. In this work, the thermodynamic behavior of polyamide 66 (PA66) solutions in formic acid (FA) and in hydrochloric acid (HCℓ), was studied to evaluate its physical/chemistry classification. The polymer systems may be divided into five classes (types), which incorporate polymer-low molecular liquid systems, ranging from true solutions to dispersions of polymers in liquids. The polyamide 66/formic acid (PA66/FA) binary system is considered a true solution. Several experiments were performed to verify if the polyamide 66/hydrochloric acid (PA66/HCℓ) binary system has all characteristics of true solution. The analysis showed that the PA66/HCℓ binary system presents all characteristics of true solution, including the final morphology of the membranes that are similar obtained membranes by PA66/FA binary system.**

Keywords: polymer-low molecular liquid systems, true solution, PA66/HCℓ binary system.

I. Introduction

The population world growth, as well as their level of requirement, both in quality and quantity, led the industry to produce ever more food, medicament, clothing and all kinds of durable goods and nondurable needed, directly and indirectly, to man. Facing this reality, new technologies have emerged to meet this demand and requirements of the population, in this context, Membrane Separation Processes (MSP) emerged as an alternative based on clean technologies, with its modular features and low energy.

The main advantage of the MSP is the separation occurs without phase change of components, different from the classical separation processes such as distillation. So, besides being economically more advantageous in a energy lower cost, the MSP can be used in very common in areas biomedical separation of thermolabile substances in juice concentration, where the use of thermal processes alter the organoleptic properties, among others[1]. Another advantage of this process is simplicity of operation, compact equipment, easy to mix with other processes and an increase in the production scale [2].

The boundary for industrial and commercial growth of MSP was the development of asymmetric membranes of cellulose acetate by researchers Loeb and Sourirajan (1961), using the phase inversion technique. These membranes are characterized by a fine surface layer compact containing pore or not (called skin or to player) responsible for the selectivity, supported by a porous structure which ensures the mechanical resistance to skin and offers little resistance to transportation. As the thickness of the skin is very thin (less than 1μm), resistance to transport through such membranes is low compared to other dense homogeneous membranes prepared from the same material [3].

In MSP often are used polymeric membranes and polyamide 66 (PA66), one of the polymers used for this application [4]. These are mainly obtained by the technique of phase inversion, since this technique allows controlling important variables that govern the morphology of these membranes thus improving process performance [5-6].

A variety of separation membranes are available on the market today for various applications. Distinct separation processes require membranes with different characteristics. In microfiltration and ultra filtration processes where filtration occurs by size difference, porous membranes that act as sieves are used. Processes such as gas separation and pervaporation, where the transport mechanism and selectivity, involves gas diffusion and solubility, require dense membranes.

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In the literature there is a large number of works addressing studies both of the thermodynamics of polymer solutions, as kinetics of mass transfer, formation of the filter skin and the sublayer of the polymeric asymmetric membranes [7].

Knowledge of the thermodynamic properties of a ternary system is relevant to understand and predict the membranes formation [8]. Many researchers have studied the morphology and properties of polyamide membranes [4,9–11] as well as the physicochemical interactions between components in the polymer solution and thermodynamic properties non-solvent (1) / solvent (2) / polymer (3) systems[12–15].

The study of the behavior of polymer solutions require a thermodynamic approach exhibit different aspects of those usually employed in the study of solutions formed by only low molecular mass components [16]. The size and shape of the macromolecules introduce changes in the thermodynamic behavior as well, show large deviations from ideality. From this, it is possible to relate the solubility properties of the components forming part of the system to obtain PA66 in formic acid and/or hydrochloric acid membranes, using water as non-solvent.

a) True Solutions of Polymers

i. *Specific Properties of True Solutions*

According to Tager[17], a true solution is a multi component system which has the following characteristic features: (a) affinity between components; (b) spontaneous formation; (c) constant concentration in time; (d) homogeneity, i.e., presence of only one phase e (e) thermodynamic stability.

Second Lucas et al.[16], the components may mix in any proportion (complete miscibility) or in definite proportions (partial miscibility). If the external conditions (pressure and/or temperature) do not vary, the true solution concentration remains constant in time. A true solution is a system consisting of a single phase. The solution phase may be separated from the other phases (precipitate, vapor or solution) by an interface, but within the solution itself there is no interface, i.e., the system is homogeneous.

The most important feature of a true solution is its thermodynamic stability or equilibrium state. A system is called thermodynamically stable if its formation is accompanied by a decrease in the Helmholtz free energy (at constant volume and temperature) or by a decrease in the Gibbs free energy - ΔG (at constant pressure and temperature). The Gibbs free energy decreases to a definite equilibrium value which does not change subsequently with time[16-17].

ii. *Dissolution and Swelling of Polymers*

According to Schuld & Wolf [18], a polymer does not dissolve in all liquids. In some cases, the polymer and the low molecular liquid (solvent) possess mutual affinity, while in others no such affinity exists. In the former case, the formation of a true solution may be expected, but, in the latter case only a colloidal solution can be formed. The polymer solutions formed spontaneously have all the characteristics of true solutions, including reversibility, equilibrium, swelling before dissolving, high viscosity and slow diffusion. All these features are due to the great difference in size between the particles of the components mixed [19].

Second Canevarolo[20], before dissolving the polymer "swells", i.e., absorbs the low molecular liquid, increasing in mass and volume. Swelling inevitably involves a change in polymer structure, which sharply increases the volume of the samples. Swelling may be limited (it is interaction of the polymer with a low molecular liquid in which the polymer chains are not completely separate from each other) or unlimited (where dissolution occurs spontaneously).

For Tager[17], the degree of swelling can be determined only for polymers with limited swelling, because upon unlimited swelling the polymer itself begins to dissolve and the mass of the sample decreases. Sometimes a phenomenon called negative swelling is observed in polymers, involving decrease rather than increase of sample mass in time.

Polymers may absorb low molecular substances not only from the liquid, but also from the gaseous phase; if the polymer swells on a liquid, it will swell on its vapors as well[16].

Describe the influence of thermodynamic properties in water / hydrochloric acid (HCℓ) / polyamide 66 (PA66) ternary systems with the morphology of the PA66 membranes; starting by characterization of PA66 in HCℓsolutions has motivated this work.

II. Experimental

a) Materials

The polymer used for the solutions and membranes preparation it is the polyamide 66 (PA66) commercial supplied by Alfa Chem. Co.(Brazil), in pellets.

The solvents used in the solutions and membranes preparation were fuming hydrochloric acid (HCℓ) with purity of 37-38% and formic acid (FA) with purity 98-100%, both supplied by Merck (Brazil).

The non-solvent used in the membranes preparation was distilled water. The information of the PA66 and the solvent properties are listed in Table 1.

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Table 1: Characteristic data of the solvents and polymer investigated

Materials	Molar volume ($cm^3 \cdot mol^{-1}$)	Molar mass ($g \cdot mol^{-1}$)	Density ($g \cdot cm^{-3}$)
PA 66	10,642.20	11,600[a]	1.22[b] e 1.09[c]
HCℓ (37-38%)	30.67	36.5	1.19
FA (98-100%)	37.7	46	1.22

a = viscosimetric average molar mass (M_v)
b = PA66 density solid (arranged)
c = PA66 density in solution (amorphous)
Source: BRANDRUP & IMMERGUT, 1989

b) Methods

PA66 was dried for 2 hours at 90°C prior to each procedure performed [21].

i. *Preparation of asymmetric flat sheet membranes*

To obtain asymmetric flat sheet membranes two different casting solutions were prepared: PA66 / formic acid / water and PA66 / hydrochloric acid / water, by the phase inversion method(PI) [2].

PA66/HCℓand PA66/FA solutions were prepared using 20 g of PA66 dissolved in 100 cm^3 of each solvent for both systems, at controlled room temperature 25 ± 2°C and at atmospheric pressure (1 atm), under magnetic stirring for 2h. The magnetic stirrer was isolated with glass wool.

The homogeneous casting solutions were cast on glass plate with a knife casting of approximately 200 µm, after was taken solvent evaporation under controlled temperature depending of the solvent used, then immersed in the coagulation bath. The membranes preparation conditions are shown in Table 2.

Table 2 : PA66 Membrane spreparation conditions

	Evaporation conditions		PI* bath conditions	
Membranes	Time (mim)	Temperature (°C)	Time (mim)	Temperature (°C)
FA	10	20	120	25±2
HCℓ	60	60	120	25±2

**PI = phase inversion*

The prepared membranes were washed with distilled water to remove residual solvent and maintained at temperature of 25 ± 2°C for drying. The membranes were called as FA and HCℓ, according use of formic or hydrochloric acid respectively, and them were dried for 24 h at 60°C and characterized by Scanning Electron Microscopy (SEM).

ii. *Scanning Electron Microscopy (SEM)*

Analysis by Scanning Electron Microscopy (SEM) of the surface and the cross section of the membranes were performed on Shimadzu Model SSX550 microscope. Samples were fractured in N_2 liquid at –196°C and metalized by means of a sputtering with a thin gold layer prior to its characterization.

iii. *Solutions preparation and techniques to prove be the polyamide 66 / hydrochloric acid system a true solution*

a. *Affinity between components*

To observe the affinity between components, a solution was prepared using PA66 (20 g) and placed in flat-bottomed flask, to which was added 100 cm^3 hydrochloric acid (HCℓ).

b. *Spontaneous formation*

In order to demonstrate do not be necessary the use of heat or other external force for dissolving the polymer, PA66 (20 g) solution was prepared and placed in double-jacket reactor to which was added 100 cm^3 of hydrochloric acid (HCℓ). In the inner part of the double-jacket was adapted a thermocouple to impart the bath temperature. In contact with the solution, a thermometer measured the temperature of the same during the dissolution process. The system was coupled in a thermostatic bath (25°C).

This experiment was also performed under the same conditions, but with isolated system with glass wool and vacuum in the double-jacket to prevent the heat transfer between the system and the environment.

c. *Constant concentration in time*

To investigate the precipitation possibility (phase separation) of the solution by temperature, PA66 (20 g) solution in 100 cm^3 HCℓ, was frozen in liquid nitrogen(-196°C). Once frozen, the solution was allowed to stand at controlled room temperature (25 ± 2°C) and, when liquid again placed under stirring.

PA66 solutionin HCℓ was placed in double-jacket reactor coupled to temperature controller at -5°C (Frigomix), under magnetic stirring for 2h. After this time, the temperature was raised to 96°C, still under stirring.

d. *Homogenity*

An aliquot of PA66/HCℓ [PA66 (20 g) in 100 cm^3 HCℓ]solution, was placed on a glass coverslip and examined under an optical microscope Carl Zeiss

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AxioScope A1 to analyze the presence of interface within the solution.

e. Thermodynamic stability

For to measurethe most important feature of a true solution that is its thermodynamic stability or equilibrium state[16-17], for the PA66/HCℓ and PA66/FAbinary systems, the Gibbs free energy of mixing(ΔG_m) was calculated by the following equation (1):

$$\frac{\Delta G_m}{RT} = x_1 ln\varphi_1 + x_2 ln\varphi_2 + g_{12}(\varphi)x_1\varphi_2 \qquad (1)$$

where φeχ are volume fraction and molar fraction of components; T is the temperature (K) e R is the gas constant. The g_{12} parameter can be considered a free energy term containing contributions enthalpy and entropy[18]. The Gibbs free energy of mixing was calculated as a function of volume fraction of polymer for both solvents.

iv. *Determination degree of swelling*

In order to determine the degree of swelling of PA66, were placed 100 cm^3 of solvent (HCℓ) in flat-bottomed flask. In the mouth flask was adapted polyester fabric, with enough closed mesh to allow the passage of solvent vapor. On the screen a few PA66 pellets was placed. The flask was kept under magnetic stirring for 5h. This method was adapted from Tager[17].

III. Results and Discussion

a) Polymer solution

i. *Specific Properties - True Polymer Solutions*

According to Papkov e Iovleva[22], all systems can be divided into five classes (true solutions containing predominantly solvent; plasticized systems; gels; systems with complete phase separation and polymer dispersions) that comprise polymer with low molecular liquid systems, ranging from true solutions to polymer dispersions in liquids. The low molecular liquid terminology is adopted for solvents, thinners, non-solvents, plasticizers and liquid dispersion media.

Following the concepts of Papkov and Iovleva[22], formic acid (FA) is considered a low molecular liquid (46 $g \cdot mol^{-1}$) when compared with polyamide 66 (11,600 $g \cdot mol^{-1}$), this system (PA66/FA) is considered by Lin et al. [9] as a true solution.

In order to check if the PA66/HCℓ system displays all the characteristics of true solution such as: affinity between components; spontaneous formation; constant concentration in time; homogeneity and thermodynamic stability, several experiments were performed.

ii. *Affinity between components with spontaneous formation of solution*

To prove affinity between components PA66/HCℓ, the polyamide 66 (PA66) was placed in contact with hydrochloric acid (HCℓ)(Figure 1a)for 2h under magnetic stirring, and the polymer molecules absorbed the solvent, the polymer chains diffused slowly, acquiring mobility and making the homogeneous solution, as can be seen in Figure 1b.

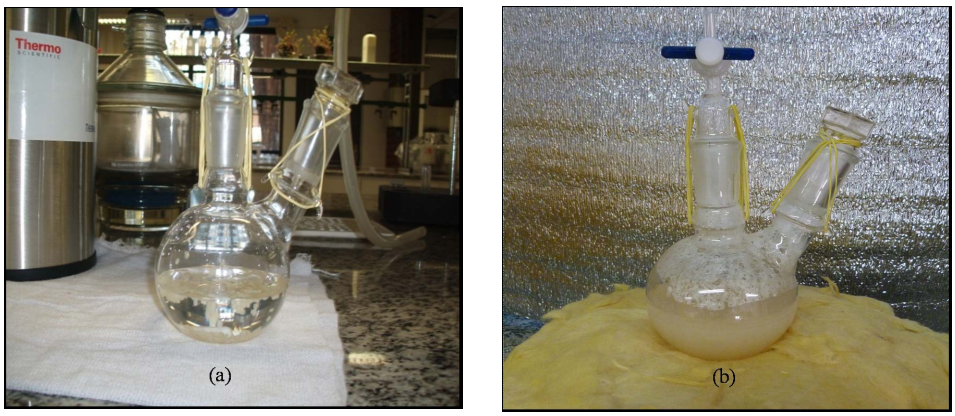

Figure 1: Homogeneous solution of PA66 in HCℓ after testing affinity between components with spontaneous solution formation

According to Tager[17], form true solutions when there is affinity, i.e., there is interaction between components; them disperse spontaneously in direct contact, without the use of heat and/or pressure. Second Lucas et al. [16] this is because the chemical potential of the pure solvent (μ_0) is larger than the chemical potential of the solvent in the solution (μ_1), and when the thermodynamic equilibrium is reached ($\Delta\mu = 0$ or $= \mu_1$) the solution becomes homogeneous. This is corroborated by Gundert & Wolf [23] who claim that HCℓ and FA are good solvents for polyamide at room temperature and atmospheric pressure.

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iii. *Constant concentration in time and homogeneity*

Also according Tager[17], if the external conditions (pressure and temperature) do not vary, the concentration of a true solution remains constant over time. In studies by Mulder [2], in most cases, polymer/solvent solutions are characterized by an upper critical solution temperature (UCST), or when cooled (T_0 to T_1) induce phase separation, altering the concentration.

From tests carried out it was observed that when the PA66/HCℓ solution was frozen and thawed, there was no phase separation, the solution remained homogeneous without the presence of precipitates or interface within the solution, as can be seen in Figure 2, only with the presence of air bubbles due to magnetic stirring.

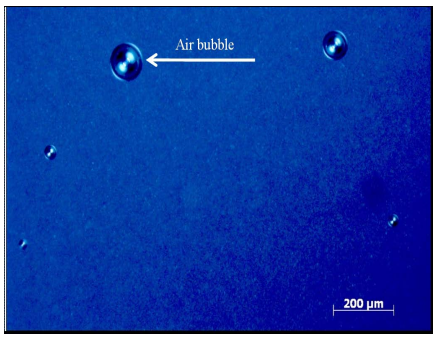

Figure 2: Optical microscopy of the PA66/HCℓ solution - 20 g/100 cm³ (10x)

iv. *Thermodynamic stability*

Second Tager[17]and Lucas et al. [16], a system is called thermodynamically stable if their formation is accompanied by a decrease in the Gibbs free energy of mixing - ΔG_m (constant pressure and temperature), which reduces to a definite value of equilibrium which does not change with time.

So that PA66/HCℓ and PA66/FA binary systems form a homogeneous system (one phase), the Gibbs free energy is negative, as can be seen in Figure 3.The Gibbs free energy of mixing was calculated as a function of volume fraction of polymer for both solvents. The PA66/HCℓ system indicates be more favorable in all concentrations compared to PA66/FA system as values obtained fromΔG_m.

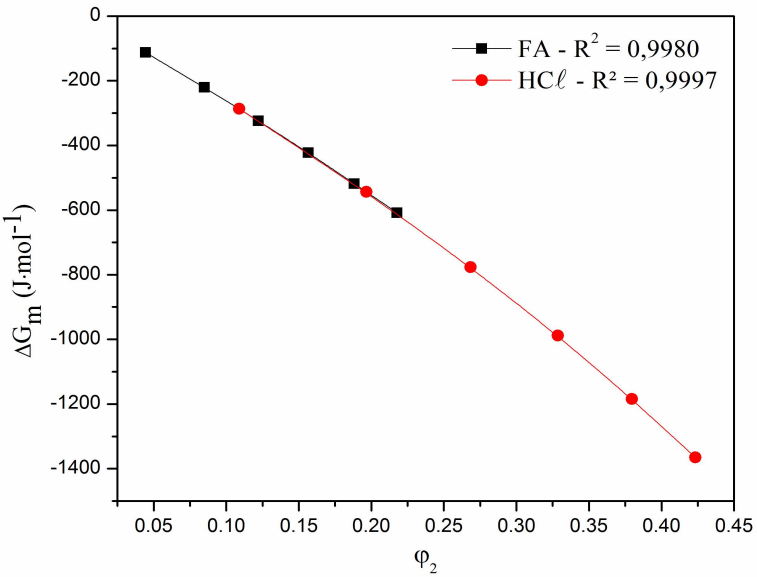

Figure 3: Gibbs free energy of mixing (ΔGm) for PA66/FA and PA66/ HCℓbinary systems as a function of volume fraction of PA66 (φ_2), which is different between systems depending on the concentration of the solvents

The HCℓ (37-38%) is a solution and does not a pure solvent, indicating the presence of water in the PA66 solution, while FA is purity solvent with 98-100%. In the PA66/FA system occur hydrogen bonds between polymer and formic acid, which explains the Gibbs free energy to be negative; in the PA66/HCℓ system dipole-dipole interactions occur, which are also strong interactions. What likely explain the energy of mixing PA66/HCℓ be more negative with respect to PA66/FA system is the acid strength (Ka = acidity constant).

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While the HCℓ Ka = 1 x 10^{7}[24-25], formic acid Ka = 1, 77 x 10^{-4}[25], justifying the similar behavior to the polyelectrolyte solution[26-27].

v. *Dissolution and swelling degree of polymers*

According to results obtained for the specific properties of true solutions of the PA66/HCℓ system, confirmed that this is a polymer with low molecular liquid system (HCℓ = 36, 5 g·mol^{-1}) and also is it a true solution, such as PA66/FA system [9]. Being PA66/HCℓ spontaneous system, requiring no external force (pressure and/or temperature) to dissolve the polymer, it was investigated the swelling degree, and according to Lucas et al. [16], if the polymer swells in contact with the low-molecular liquid, also swell in contact with its vapor. The Figure 4 shows the swelling test of the PA66pellets in contact with HCℓ vapor.

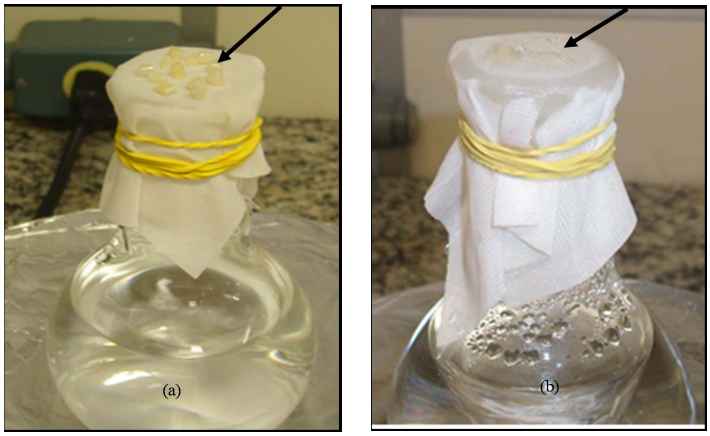

Figure 4 : Dissolution test of the PA66pellets in contact with HCℓ vapor: (a) before and (b) after the test

After 5h the PA66 in contact with HCℓ vapor showed unlimited swelling, i.e. dissolved before swell (Figure 4b). Tager[17] attributed this behavior to interaction between polymer/solvent and solvent strength.

b) Morphological analysis by Scanning Electron Microscopy (SEM) of PA66films

The surface and cross section of the PA66 films were analyzed by scanning electron microscopy (SEM).

The upper surfaces of the films showed dense layer, nonporous, homogeneous and composed of polygonal grains, as can be seen in Figure 5.

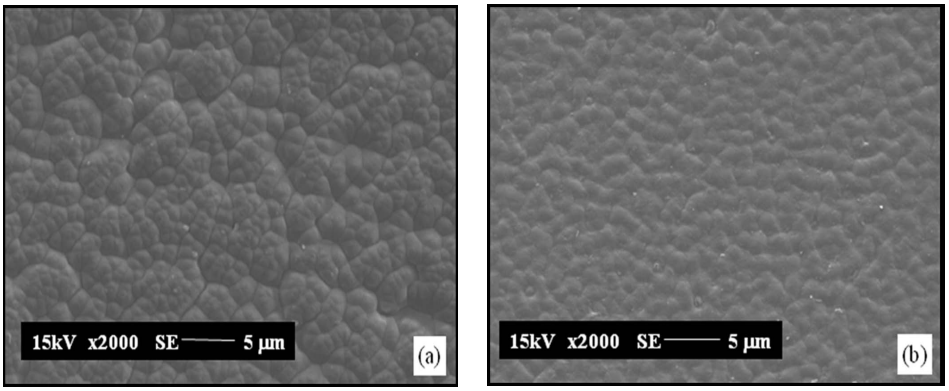

Figure 5: Micrograph (SEM) of surface of PA66 membranes in the form of films prepared in FA (a) and prepared in HCℓ (b) (2000x)

Shih et al.[28]and Lin et al.[9], also studied the mechanisms of phase separation on PA66 membranes in FA and, this polygonal characteristic with limits almost linear are similar to spherulites, that are obtained for phase separation solid-liquid (S-L) (crystallization).

The morphology of the PA66films in formic acid and hydrochloric acid is typical of polyamide films precipitate on considered aggressive bath (water), with dense layer and cellular and pore structure. The micrograph (Figure 6a) shows a PA66film in FA with a dense layer of approximately 4 µmthickness and pores cell small surrounded by a polymer matrix. The micrograph (Figure 6b) shows a PA66 film in HCℓ with dense layer of approximately 23 µm in thickness and

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also has pores cell small surrounded by a polymer matrix.

Figure 6 shows the cross section of the PA66 films in FA and HCℓ which present similar morphologies.

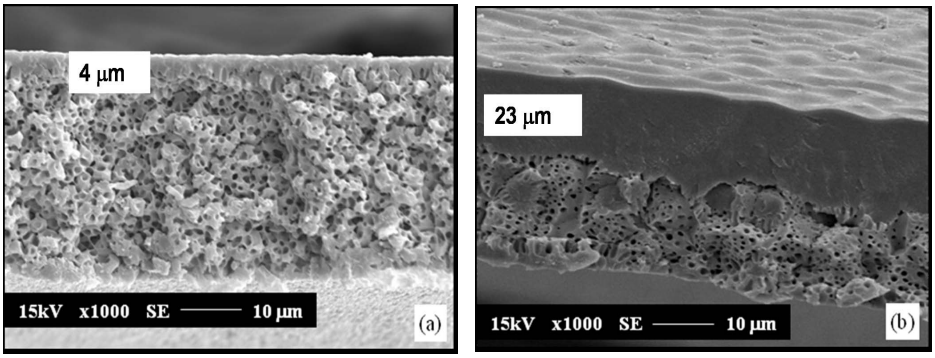

Figure 6: Micrograph(SEM) of the cross section of the PA66 films in: FA (a) and HCℓ (b) (1000X)

Looking at Figure 6 of the standpoint of Lin et al. [9], the non-porous dense layer formation is due to the increased concentration of polymer in the film interface with the bath (water). During precipitation a thick gel layer was formed on the surface excluding the possibility of nucleation liquid micelles in the region (pore formation). This process was more intense in PA66/HCℓ films, but these films were subjected to a solvent evaporation step, where according Mulder [2] is the beginning of precipitation, prior to the immersion bath. This probably favored the polymer concentration highest on the surface, resulting in increased thickness of the dense layer (23 μm) in relation to PA66/FA films (4 μm).

IV. Conclusions

The solution of PA66 in FA is considered a true solution in the literature, however, to solution PA66 in HCℓ was not found reference. The specific properties analyzed proved that the solution of PA66 in HCℓ behaves as a true solution, including the final morphology of the membranes that are similar membranes obtained by binary system PA66/FA.

V. Acknowledgements

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