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

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 behaviour of polyamide 66 (PA66) solutions in formic acid (FA) and in hydrochloric acid (HC), 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/HC) binary system has all characteristics of true solution. The analysis showed that the PA66/HC 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/HC binary system

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 thermo labile 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 top layer) 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 1 μm), 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 ultrafiltration processes where filtration occurs by size difference, porous membranes that act as sieves are used. Processes such as gas separation and evaporation, where the transport mechanism and selectivity,
involves gas diffusion and solubility, require dense membranes. 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 sub layer 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 behaviour 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 behaviour 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.

**True Solutions of Polymers**

*Specific Properties of True Solutions:* According to Tagger [17], a true solution is a multicomponent 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) 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, vapour 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 - G (at constant pressure and temperature). The Gibbs free energy decreases to a definite equilibrium value which does not change subsequently with time [16,17].

**Dissolution and Swelling of Polymers:** According to Schuld and 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 Caneverarlo [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 Tagger [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 vapours as well [16].

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

**Experimental**

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

**Methods**

**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 (IF) [2]. PA66/HC and PA66/FA solutions were prepared using 20g of PA66 dissolved in 100 cm³ 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. 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 HC, according use of formic or hydrochloric acid respectively, and

![Table 1 Characteristic data of the solvents and polymer investigated.](http://polymerscience.imedpub.com/archive.php)

**Table 1** Characteristic data of the solvents and polymer investigated.

| Materials | Molar volume(cm³·mol⁻¹) | Molar mass(g·mol⁻¹) | Density(g·cm⁻³) |
|-----------|------------------------|---------------------|----------------|
| PA 66     | 10,642.20              | 11,600a             | 1.22b e 1.09c  |
| HC (37-38%) | 30.67                  | 36.5                | 1.19           |
| FA (98-100%) | 37.7                   | 46                  | 1.22           |

a = viscometric average molar mass (Mᵥ)  
b = PA66 density solid (arranged)  
c = PA66 density in solution (amorphous) Source: BRANDRUP & IMMERMUT, 1989
them were dried for 24 h at 60°C and characterized by Scanning Electron Microscopy (SEM).

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 prepared in N2 liquid at 196°C and metalized by means of a sputtering with a thin gold layer prior to its characterization.

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

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 cm³ hydrochloric acid (HC).

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 cm³ of hydrochloric acid (HC). 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.

Constant concentration in time: To investigate the precipitation possibility (phase separation) of the solution by temperature, PA66 (20 g) solution in 100 cm³ HC, 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 solution in HC was placed in double-jacket reactor coupled to temperature controller at -5°C (Frigomix), under magnetic stirring for 2 h. After this time, the temperature was raised to 96°C, still under stirring.

Homogenity: An aliquot of PA66/HC [PA66 (20 g) in 100 cm³ HC] solution, was placed on a glass coverslip and examined under an optical microscope Carl Zeiss AxioScope A1 to analyze the presence of interface within the solution.

Thermodynamic stability: For to measure the most important feature of a true solution that is its thermodynamic stability or equilibrium state [16,17], for the PA66/HC and PA66/FA binary systems, the Gibbs free energy of mixing (G_m) was calculated by the following equation (1):

$$\frac{\Delta G_m}{RT} = x_1 \ln \Psi_1 + x_2 \ln \Psi_2 + g_{12}(\Psi)x_1\Psi_2$$

(1)

where e are volume fraction and molar fraction of components;
T is the temperature (K) e R is the gas constant. The g_e 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.

Determination degree of swelling: In order to determine the degree of swelling of PA66, were placed 100 cm² of solvent (HC) in flat-bottomed flask. In the mouth flask was adapted polyester fabric, with enough closed mesh to allow the passage of solvent vapour. On the screen a few PA66 pellets was placed. The flask was kept under magnetic stirring for 5h. This method was adapted from Target [17].

Results and discussion

Polymer solution

Specific properties - True polymer solutions: According to Papkov e lovleva [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·mol⁻¹) when compared with polyamide 66 (11,600 g·mol⁻¹), this system (PA66/FA) is considered by Lin et al. [9] as a true solution. In order to check if the PA66/HC 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.

Affinity between components with spontaneous formation of solution: To prove affinity between components PA66/HC, the polyamide 66 (PA66) was placed in contact with hydrochloric acid (HC) (Figure 1a) for 2h under magnetic stirring, and the polymer molecules absorbed the solvent, the polymer chains diffused

Table 2: PA66 Membranes preparation conditions.

| Membranes | Evaporation conditions | IF* bath conditions |
|-----------|------------------------|---------------------|
|           | Time (mim) | Temperature (°C) | Time (mim) | Temperature (°C) |
| FA        | 10         | 20                 | 120        | 25±2               |
| HC        | 60         | 60                 | 120        | 25±2               |

*IF = phase inversion

Figure 1: Homogeneous solution of PA66 in HC after testing affinity between components with spontaneous solution formation.
slowly, acquiring mobility and making the homogenous solution, as can be seen in Figure 1b. According to Tagger [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] is this because the chemical potential of the pure solvent (μ\text{solvent}) is larger than the chemical potential of the solvent in the solution (μ\text{solvent in solution}), and when the thermodynamic equilibrium is reached (Δμ = 0 or = μ\text{solvent}), the solution becomes homogenous. This is corroborated by Gundert and Wolf [23] who claim that HC and FA are good solvents for polyamide at room temperature and atmospheric pressure.

**Constant concentration in time and homogeneity:** Also according Tagger [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\text{UCST} < T\text{solvent}) induce phase separation, altering the concentration. From tests carried out it was observed that when the PA66/HC solution was frozen and thawed, there was no phase separation, the solution remained homogenous 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.

**Thermodynamic stability:** Second Tagger [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 - Gm (constant pressure and temperature), which reduces to a definite value of equilibrium which does not change with time. So that PA66/HC 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/HC system indicates be more favourable in all concentrations compared to PA66/FA system as values obtained from Gm. The HC (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/HC system dipole-dipole interactions occur, which are also strong interactions. What likely explain the energy of mixing PA66/HC be more negative with respect to PA66/FA system is the acid strength (Ka = acidity constant). While the HC Ka = 1 x 10^7 [24, 25], formic acid Ka = 1, 77 x 10^-3 [25], justifying the similar behaviour to the polyelectrolyte solution [26, 27].

**Dissolution and swelling degree of polymers:** According to results obtained for the specific properties of true solutions of the PA66/HC system, confirmed that this is a polymer with low molecular liquid system (HC = 36, 5 g·mol^{-1}) and also is it a true solution, such as PA66/FA system [9]. Being PA66/HC 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 vapour. The Figure 4 shows the swelling test of the PA66 pellets in contact with HC vapour (Figure 4). After 5h the PA66 in contact with HC vapour showed unlimited swelling, i.e. dissolved before swell (Figure 4b). Tagger [17] attributed this behaviour to interaction between polymer/solvent and solvent strength.

**Morphological analysis by Scanning Electron Microscopy (SEM) of PA66 films**

The surface and cross section of the PA66 films were analysed 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. 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 spherules, that are obtained for phase separation solid-liquid (S-L) (crystallization). The morphology of the PA66 films 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 PA66 film in FA with a dense layer of approximately 4 μm thickness and pores cell small surrounded by a polymer matrix. The micrograph (Figure 6b, 6c) shows a PA66 film in HC with cell small surrounded by a polymer matrix.
6b) shows a PA66 film in HC with dense layer of approximately 23 μm in thickness and also has pores cell small surrounded by a polymer matrix. Figure 6 shows the cross section of the PA66 films in AF and HC which present similar morphologies. Looking at Figure 6 of the stand point 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/HC 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 favoured 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).

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