A priority supposition for estimation of time-dependent changes in thickness and weight of polymeric flat sheet membranes fabricated by the nonsolvent induced phase separation (NIPS) technique

**Abstract**

During the fabrication procedure of polymeric membranes using nonsolvent induced phase inversion technique, thickness and weight of the polymeric cast film change rapidly. The only available guideline just presents a qualitative criterion for thickness change in which “penetration of the denser species into the film and the elimination of the lighter ones from film to coagulation bath” has been related to the densification of the cast solution and its thickness reduction. While it is well-suited for cellulose acetate / acetone / water ternary system, but it is not applicable to our investigated systems i.e. Polyethersulfone / n-methyl-pyrolidine / water and Polysulfone / n-methyl-pyrolidine / water. Thus, here the thermo-kinetic behavior of NIPS process was discussed and then a thermodynamic model was developed, in which only initial cast film and final membrane properties were used as inputs. Two new simple suppositions were derived and examined. The use of thermodynamic modeling approach results in desirable estimation of overall changes and the proposed suppositions also can be reliably used for prediction of changes in mass and thickness experienced by cast film NIPS process. It was shown that without the implication of some serious assumptions, it is impossible to derive the old supposition from theoretical concepts. It was also found that the interpretation of film thickness reduction in literatures cannot be validated. Using the presented theoretical concept, one can obtain an overview of the decrease and/or increase in thickness and/or weight of final fabricated membrane prior to any experimental investigation.

**Keywords**: polymeric membrane; immersion precipitation; NIPS, film thickness; thermo-kinetic modeling

# Introduction

Nonsolvent induced phase separation (NIPS) process is one the most commonly used processes for commercial polymeric membrane fabrication. As shown in **Fig. 1**, [[1](#_ENREF_1)] in NIPS process, the prepared homogeneous polymeric solution (dope) is cast as a thin film on an impermeable support layer and then immersed immediately to a nonsolvent bath (immersion precipitation) or exposed to water vapor (dry casting). To obtain membranes of different internal structure, morphology and property, the operating parameters such as system temperature, dope and coagulation bath compositions, solvent/nonsolvent selection and etc. can be simply adjusted [[2](#_ENREF_2)].

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| **Fig. 1.** Dry/wet phase inversion techniques for polymeric membrane fabrication [[2](#_ENREF_2)] |

Since this process proceeds fast and experimental monitoring of changes in such a thin cast film is challenging, modeling and computer based numerical simulation of NIPS process has been considered [[1](#_ENREF_1), [3](#_ENREF_3)]. Among the different phenomenological events occurring during phase inversion process of polymeric solutions, the film thickness and mass changes have been discussed rarely and needs to be investigated in details. As reported elsewhere, when a cast solution prepared from cellulose acetate (CA) and acetone (AC) was immersed in water bath, the thickness of cast film decreased [[4-10](#_ENREF_4)] and it was attributed to the substitution of light specie (acetone) by denser one (water). These observations lead to the conclusion that the “penetration of the denser species into the film and the elimination of the lighter ones from film to coagulation bath results in densification of the cast solution” [[4](#_ENREF_4), [5](#_ENREF_5)].

However, for polymeric membranes fabricated from Polyethersulfone (PES) / n-methyl-pyrolidine (NMP) / Water and Polysulfone (PSf) / n-methyl-pyrolidine (NMP) / Water ternary systems, the aforementioned supposition [[4](#_ENREF_4), [5](#_ENREF_5)] failed to explain the observed reduction in thin film thickness. To be more specific, while in ternary system of CA/AC/water, the penetrating nonsolvent is water, with density of 0.94 gr/cm3 [[11](#_ENREF_11)], which is denser than the exiting solvent (acetone with density of 0.7857 gr/cm3 [[11](#_ENREF_11)]); in ternary systems of PES/NMP/water and PSf/NMP/water, the exiting solvent (NMP: density = 1.06 gr/cm3) is denser than the water [[12](#_ENREF_12), [13](#_ENREF_13)]. Consequently, based on the aforementioned supposition, one might expect that in such systems, the inflation of cast thin film occurs and a membrane thicker than the initial cast film would be expected, which is incorrect based on available experimental data. Therefore, this interpretation cannot be acceptable generally and no agreement to real changes can be guaranteed.

Therefore, the inaccurate description of film thickness reduction in literatures [[4](#_ENREF_4), [5](#_ENREF_5)] calls for an attempt to establish and develop accurate interpretation of such changes in different systems. This investigation is valuable since the results can be used for estimation of membranes thickness prior to any experimental attempt, as it has been demonstrated that the initial and final membrane thickness has remarkable influence on the separation performance of fabricated membranes [[14-16](#_ENREF_14)]. For example, Vogrin et al, [[16](#_ENREF_16)] showed that the macrovoid formation can be strongly affected by the cast film thickness as they observed macrovoid formation for initial thickness of 500 µm while for thickness lower than 300 µm, no macrovoid formation was observed [[16](#_ENREF_16)]. It was also found that the single gas permeability increases by increasing membrane thickness while the selectivity is independent of the membrane thickness.

It must be noted that the dynamic changes in cast film volume and mass are governed by the practical amount of solvent/nonsolvent exchanged between two phases which is a thermo-kinetic process depends on the operating parameters and components intrinsic characteristics [[2](#_ENREF_2), [5](#_ENREF_5)]. However, to obtain dynamic changes in volume and mass of cast film, a lot of complicated calculations are required using some computer-based computational routines and programs (for example see [[5](#_ENREF_5)]). This would be a drawback for a model intended to be used for an initial assessment of membranes overall changes in thickness and mass.

Thus establishment of a pseudo-equilibrium thermodynamic model comes to attention as covered in this work. It is worthy to mention that thermodynamic based studies consider the initial and final states of the system under consideration, so the essence of dynamic composition data would be resolved and simply accessible information regarding the initial cast solution and final fabricated membrane can be used for theoretical analysis. Then, the developed thermodynamic model was used to introduce some practical and useful simple suppositions for rapid assessment of considered changes.

In order to compare this model prediction, two case of dry and wet phase inversion of CA/AC/water were considered. Because real-time (dynamic) experimental measurement of these changes are almost inaccessible in wet phase inversion process, in this case, the comparisons are limited to the reported theoretical results, while the dry phase inversion case has the advantage of availability of such experimental data on the considered changes.

# Development of thermodynamic basis

For theoretical calculation of changes in phase inversion, three distinctive mixtures can be considered: (*1*) initial dope consisting binary mixture of solvent and polymer, (*2*) final membrane consisting binary mixture of nonsolvent and polymer and (*3*) under process cast film consisting ternary mixture of solvent, nonsolvent and polymer. Two end-points (states) of the NIPS process: i.e. (1) initial cast film (composed of polymer/solvent) and (2) final fabricated membrane (mainly composed of polymer/nonsolvent), was considered her in model development and the estimated volume and mass of these mixtures was compared with each other to analyze the cast film changes during NIPS process.

To calculate the density or any thermo-physical and physicochemical properties of polymeric systems such as membranes, a reliable thermodynamic model must be used. The Sanchez and Lacombe Lattice theory of Fluids is one of the most reliable thermodynamic theories [[17](#_ENREF_17), [18](#_ENREF_18)] for this purpose. Sanchez and Lacombe had developed [[19](#_ENREF_19), [20](#_ENREF_20)] a theory for fluids similar to that of Flory-Huggins but including empty lattice holes (hole) and the volume changes of mixing [[17](#_ENREF_17)], which can be applied for calculations of the thermodynamic properties of fluids over a wide range of temperatures and pressures [[17](#_ENREF_17), [18](#_ENREF_18)].

In view of current study, since the initial dope and final membrane (as two binary mixtures of the end points of the NIPS process) properties should be taken into account, the extension of Sanchez and Lacombe Equation of State (LS-EoS) for mixtures is required [[19](#_ENREF_19), [20](#_ENREF_20)]. As mentioned earlier, the initial dope solution is a binary mixture of solvent (*2*) + polymer (*3*), and the final fabricated membrane can be considered as a pseudo binary mixture of nonsolvent (*1*) + polymer (*3*).

The original Sanchez and Lacombe Equation of State (LS-EoS) [[17](#_ENREF_17)] was modified and rewritten by Boudouris et al. [[21](#_ENREF_21)] as presented in Eq. 1 for polymeric solutions, where,,  and  are reduced pressure, temperature, density and volume as defined by Eq. 2, in which ,  and  are characteristic pressure, temperature and density.

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To apply LS-EOS to the two consider end-points of NIPS process, it is required to determine the characteristic parameters for initial dope and final membrane binary mixtures. For calculation of the reduced density of mixture using Eq. 1 [[18-20](#_ENREF_18)], it must be noted that the characteristic pressure, temperature and density (,  and) of mixture must be employed as defined in Eq. 3 [[18-20](#_ENREF_18)], where,  and are mass fraction and volume faction of component “*i*” and are interrelated by .

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Then, the volume of mixture can be obtained as  [[19](#_ENREF_19), [20](#_ENREF_20)] where, ,  and  can be calculated by using Eq. 4 [[19](#_ENREF_19), [20](#_ENREF_20)], in which  is the molecular weight of component “*i*”, and  is the Boltzmann constant [[19](#_ENREF_19), [20](#_ENREF_20)].

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The comparison of mixture volumes, mass and density before and after the immersion of cast film in nonsolvent bath can be made by defining following ratios (*R*) as defined in Eq. 5, where subscripts *m* and *d* indicate the mixture properties corresponding to **m**embrane and **d**ope, respectively.

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Eq. 5, in the context of lattice fluid theory [[20](#_ENREF_20)], can be rewritten as given by Eq. 6;

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These expressions can be used for comparison of changes in volume and mass of membrane before and after the immersion.,,and are characteristics parameters of corresponding mixtures and  and  are calculated from modified LS-EOS using characteristics parameters of corresponding mixtures.

# Developing Suppositions

## Discussion on old supposition

Here first, it has been shown that the old supposition [[4](#_ENREF_4), [5](#_ENREF_5)] can be recovered in terms of pre-defined solvent (*2*) and nonsolvent (*1*) ratios described in previous section. Then the new suppositions are developed.

To differ from the aforementioned ratios defined in previous section, here to show the recovery of old supposition, we refer to the new ratios as polymer-free ratio and the superscript  indicates the pure state properties. By term “polymer-free”, we intend to point out that the comparisons are being made by solvent and nonsolvent themselves. Thus, in this case, subscripts *m* and *d* that respectively indicate the mixture properties corresponding to **m**embrane and **d**ope in defined ratios, can be replaced by 1 and 2 that respectively accounts for nonsolvent and solvent as given in Eq. 7, where ,  and  re where polymer-free ratio of changes in volume, mass and density before and after the immersion.

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,  and in the context of lattice fluid theory [[20](#_ENREF_20)], can be rewritten as given by Eqs. 8-10;

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As seen, the old supposition can be recovered theoretically provided that the contribution of polymer is being ignored and the comparisons be done only based on solvent and nonsolvent as if there were no mixture. Therefore, it cannot reveal the real changes in mass and volume as it is shown numerically in next sections.

## Our new suppositions

To have an estimate of studied changes instead of exact numerical results or the use of procedures described in previous sections, it would be beneficiating to obtain some correlations/suppositions. Therefore, attempts were made to obtain simple suppositions using molecular properties of components as illustrated in next paragraphs based on the aforementioned thermodynamic basis. Our initial screening of these systems indicated that the film thickness reduction can be related to molecular volume of exchanged components. Therefore, ratio of exchanged volumes of solvent (*2*) and nonsolvent (*1*) and ratio of exchanged mass of solvent (*2*) and nonsolvent (*1*) upon immersion process can be defined as presented by Eq. 11;

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The volume of each component can be related to its molecular volume () as  in which  is number of moles and  is the Avogadro number. Thus, Eq. 11 can be rewritten as Eq. 12;

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Practically, the number of moles exchanged is governed by the **kinetic** of phase inversion process. Along the immersion time of *t*, the ratio of number of exchanged moles of solvent to nonsolvent per immersion time *t* equals the flux ratio of solvent to nonsolvent indicated by *k* as described in Ref. [[22](#_ENREF_22)] by Young and Chen. Thus, Eq. 12 can be rewritten as given by Eq. 13. In this equation (Eq. 13),  reveals the progress of phase inversion process while and  account for components properties. While the later ones (and) have a fixed and constant value over immersion process and are independent of process dynamics/kinetics, a time-dependent and time-varying form can be realized for  [[22](#_ENREF_22)].

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It must be obvious that the definition of density ratio results in a **static** comparison of two exchanging components disregarding the process of concern as it eliminates *k*. In other words, if we define the density ratio of solvent to nonsolvent as, then we can show that Eq. 14 is obtained.

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This ratio measures nothing regarding the NIPS process, and only gives simple comparison of individual components properties. It even leads to incorrect estimation of changes in cast film. For precise prediction of changes in volume (thickness) and mass of polymeric cast film, one must use ratios defined in Eq. 13.

It might be worthwhile to mention that the higher values of *k* (*k>3*) are mainly restricted to a small region around the interface of cast film and coagulation bath which is no more than 1 micron in thickness [[2](#_ENREF_2), [5](#_ENREF_5)]. On the other hand, the underlying layers and regions within the polymeric film, mainly have lower numeric values for *k* (*k<1.5*). Therefore, the determination of exact numerical value of *k* would be a challenge itself. Thus, we defined the scaled ratios of changes in volume (thickness) and mass in polymeric film by dividing Eq. 13 by *k* as presented by Eq. 15.

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# Results and discussion

## Validation of thermodynamic based modeling

The application of thermodynamic based modeling requires the determination of components composition of systems. Three ternary systems have been considered in this study, namely (i) Cellulose acetate (CA) / acetone (AC) / water, (ii) Polyethersulfone (PES) / n-methyl-pyrolidine (NMP) / water and (iii) Polysulfone (PSf) / n-methyl-pyrolidine (NMP) / water [[2](#_ENREF_2), [5](#_ENREF_5), [6](#_ENREF_6), [8](#_ENREF_8), [23](#_ENREF_23)]. The details of initial dope composition and thickness of cast film and those of final fabricated membrane for these three ternary systems are summarized in Table 1. The converted composition of vitrification was used as composition of fabricated membranes for each case [[2](#_ENREF_2), [5](#_ENREF_5)]. The properties of the pure components that are required in model was obtained from [[2](#_ENREF_2)] in where they were calculated using the Boudouris et al. [[21](#_ENREF_21)] group contribution method.

**Table 1.** Details of **d**ope and **m**embrane composition and thickness

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| No. | **D**ope | | **M**embrane[[2](#_ENREF_2)] | | |
| Composition (*ω*) | Thickness (*µm*) | Composition (*ω*) † | Composition (*ω*)‡ | Thickness (*µm*) |
| 1 | CA/AC  0.15/0.85 | 75 | CA/AC/water  0.71/0.16/0.13 | CA/water  0.845/0.155 | 64.27 |
| 2 | PES/NMP  0.20/0.80 | PES/NMP/water  0.71/0.17/0.11 | PES/NMP  0.855/0.145 | 67.31 |
| 3 | PSf/NMP  0.20/0.80 | PSf/NMP/water  0.81/0.13/0.06 | PSf/NMP  0.93/0.07 | 67.92 |
| † the vitrification composition from literatures [[2](#_ENREF_2)] | | | | | |
| ‡ converted vitrification composition by eliminating the solvent using formula *ωnew= ωold/(1- ω2)* | | | | | |

The practical changes in volume upon immersion precipitation process for each membrane can be calculated using Eq. 5 through the application of SL-EOS. The obtained results are summarized in **Table 2**.

**Table 2.** Details of dope and membrane volumes

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| No. | **D**ope | |  | **M**embrane | |  |
| Composition (*ω*) | Calculated volume (cm3/gmol) |  | Composition (*ω*)‡ | Calculated volume (cm3/gmol) |
| 1 | CA/AC  0.15/0.85 | 82.3522 |  | CA/water  0.845/0.155 | 82.2012 | ***0.89*** |
| 2 | PES/NMP  0.20/0.80 | 90.4482 |  | PES/ water  0.855/0.145 | 22.6313 | ***0.25*** |
| 3 | PSf/NMP  0.20/0.80 | 101.9414 |  | PSf/ water  0.93/0.07 | 57.7584 | ***0.56*** |

As seen in **Table 2**, membranes fabricated from wet phase inversion of all three dope solutions in water coagulation bath experience a densification according to the ratio of dope solution and fabricated membrane (*of mixture based*) densities, which themselves are obtained using the volumes calculated by the prescribed thermodynamic model. The comparison of densities must be based on the mixture properties but not the pure solvent and nonsolvent ratio as mentioned in literatures [[4](#_ENREF_4), [5](#_ENREF_5)]. It can be obviously seen that while the ratio of solvent/nonsolvent defined in literatures for these considered system predicts unreliable and inaccurate changes in film thickness and volume, the thermodynamic modeling gives the physically consistent results.

## Validation of new proposed suppositions

To specify the reliability of proposed suppositions and discuss numerically the issue of concern, three ternary systems have been considered, for which the required components molecular properties are listed in **Table 3**.

Table . Component molecular properties

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| **Components** | **Density (gr/cm³)** | **Molecular weight (gr/mole)** | **molecular properties ×1023** | |
| † | ‡ |
| NMP | 1.026 [[12](#_ENREF_12), [13](#_ENREF_13)] | 99.13 [[24](#_ENREF_24)] | 16.4609 | 16.0437 |
| AC | 0.7857 [[11](#_ENREF_11)] | 58.0791 [[25](#_ENREF_25)] | 9.6442 | 12.2747 |
| ***H2O*** | ***0.94 [***[***11***](#_ENREF_11)***]*** | ***18.0153 [***[***26***](#_ENREF_26)***]*** | ***2.9915*** | ***3.1824*** |
| ‡ Calculated as , where *NAv* = 6.02214129×1023 mol−1 is the Avogadro number  † Calculated as | | | | |

The calculated ratios as defined are listed in **Table 4**.

Table . Calculated ratios

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| **No.†** |  | |  | **×1023** | |  |  | **×1023** | |  |
|  | **1** | **2** | **1** | **2** | **1** | **2** |
| 1 | H2O | NMP | 2.9915 | 16.4609 | ***0.1817*** | 3.1824 | 16.0437 | ***0.1979*** |
| 2 |
| 3 | H2O | AC | 2.9915 | 9.6442 | ***0.4502*** | 3.1824 | 12.2747 | ***0.2592*** |
| † Systems number according to **Table 1**. | | | | | | | | | | |

As shown in **Table 4**, for membranes fabricated from a ternary solution containing NMP-water pair as solvent-nonsolvent, the molecular volume () of pure NMP and pure water are 16.044×10-23 *mL/molecule* and 3.182×10-23 *mL/molecule* respectively. In other words, molecular volume of NMP is approximately 5 times of molecular volume of water. In addition, the mass of pure NMP and pure water are 16.46×10-23 *gr/molecule* and 2.99×10-23 *gr/molecule*, in other words, molecular mass of NMP is approximately 5 times of molecular mass of water. The application of the scaled ratios of proposed suppositions predicts a reduction in both volume and mass of polymeric film, which can be validated based on available data for PSf/NMP/water ternary system as reported elsewhere [[23](#_ENREF_23)]. It is necessary to note that NMP is denser than H2O, and the old supposition suggests a membrane thicker than initial cast film after phase separation (inflation). In addition, it must be obvious that the use of old supposition cannot reveal the correct changes.

In practice, elimination of one NMP molecule from thin film, during phase inversion process (solvent/nonsolvent exchange), provides a large free space for water molecules to be replaced. As both molecules must diffuse in opposite directions through the skin layer at the interface of coagulation bath and dope phase, it would be expected that water molecules mostly have no such a chance to completely fill in this available free space, and a part of it might remain in the form of voids or etc. Therefore a weight loss for such systems due to solvent/nonsolvent exchange during phase inversion process is expected for PSf/NMP/water ternary system as reported elsewhere [[23](#_ENREF_23)].

For the ternary system of CA/AC/water, as calculated in **Table 4**, molecule volume of AC is nearly 4 times of molecular volume of water. Therefore, penetration of water to dope and the elimination of acetone (from dope to nonsolvent bath) result in a decrease in total film’s volume. It is necessary to note that in this case, a decrease in total film’s mass (weight) is expected since molecular mass of pure AC is approximately equivalent with 3 molecular mass of water). The mass and thickness changes suggested by our proposed interpretation for system of CA/AC/water are in accordance with the available data in literatures [[5](#_ENREF_5), [9](#_ENREF_9)].

As seen, the new proposed concept, for film thickness reduction interpretation, requires only widely available molecular information of components, in particular molecular weight (*Mw*) and density (*ρ*) of solvent and nonsolvent, to give a qualitative justification on film thickness and weight variations.

# Concluding remarks

To interpret the changes in cast film thickness and weight observed during NIPS process, theoretical methods were developed, and then applied, examined and discussed using the collected systems data from literatures and our experimental data to assess their reliability and correctness. It was shown that without the implication of some serious assumptions, it is impossible to derive the old supposition from theoretical concepts. It was also found that the interpretation of film thickness reduction in literatures cannot be validated. In addition, two new simple suppositions were proposed for the film thickness (volume) and weight (mass) changes of cast film during NIPS process. Using the presented theoretical concept, one can obtain an overview of the decrease and/or increase in thickness and/or weight of final fabricated polymeric membranes, fabricated by NIPS process, prior to any experimental investigation.

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**Conflict of Interest**

The authors declare that they have no conflict of interest.

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