Thermodynamic modeling behavior of cellulose acetate / polyvinyl chloride blend membrane preparation

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Outline:

- Introduction
- Objectives
- Experimental work
- Model Equations
- Results
- Conclusions

Introduction

- Polymer Membranes are widely used in different applications, high selectivity and high permeability are principal requirements.

➔Polymeric Membranes:

- high mechanical properties
- good chemical stability
- Tunable microstructures

➔Asymmetric Membranes:

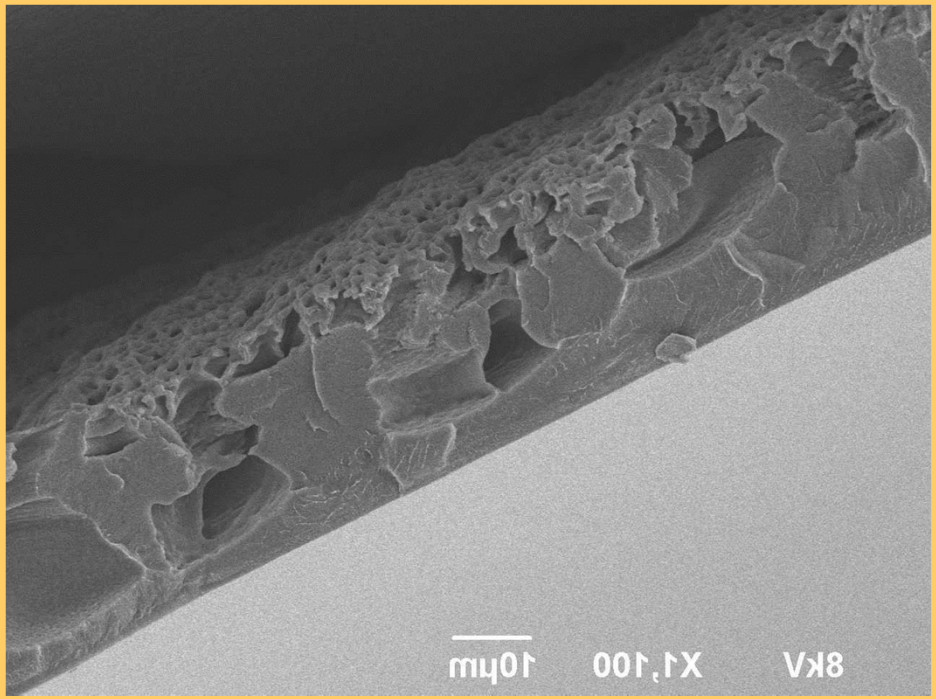
- to get High J_{water}
- to achieve liquid molecular separation

- The phase inversion technique is the most popular membrane fabrication method, especially for commercial membrane manufacturing.

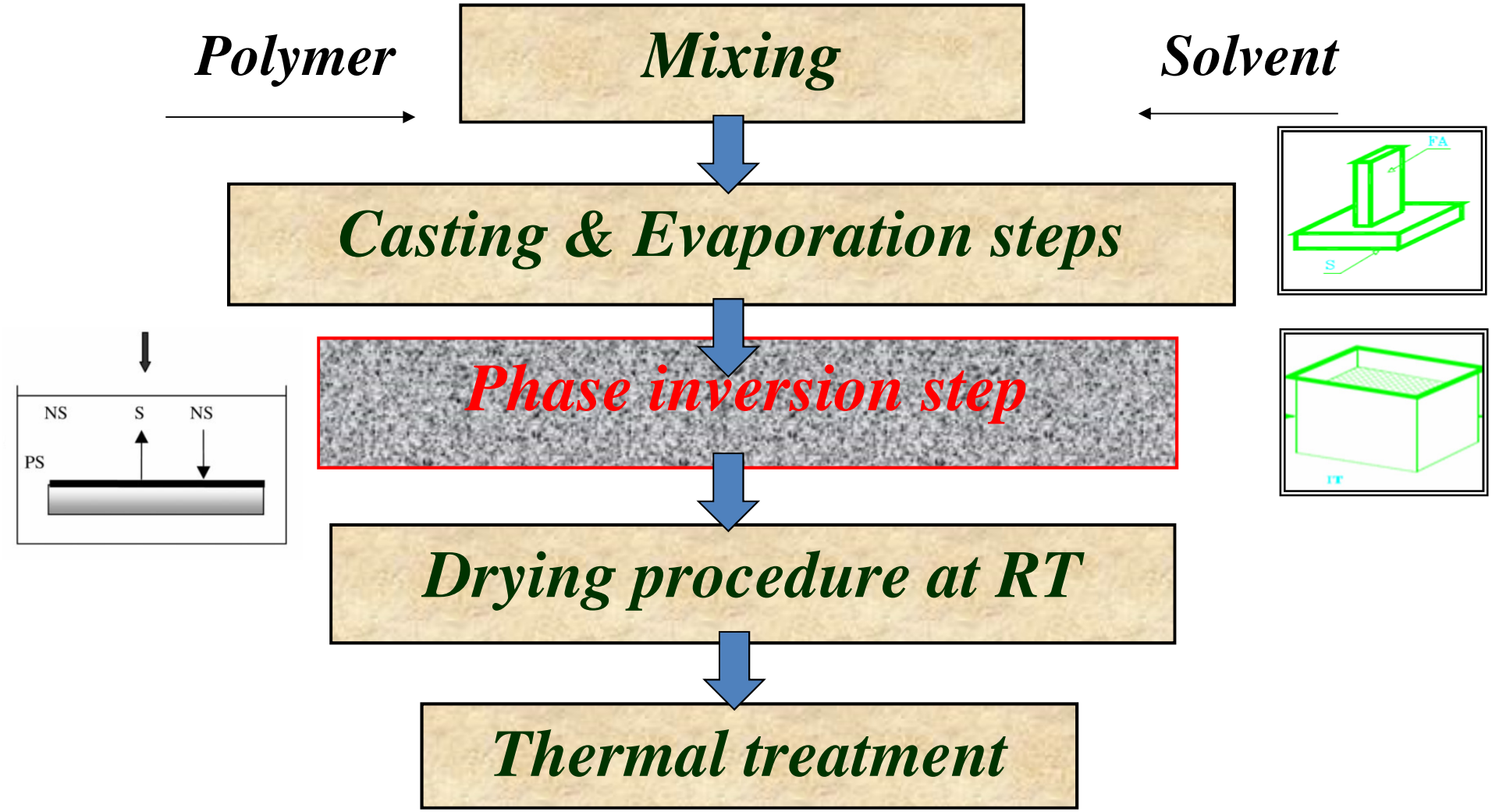
Objectives

- The goal of this work is to discuss the basis of solubility parameters, and their use in predicting polymer dissolution for polymers blends and solvents.
- The modeling results can be used to develop a better understanding of the experimental results and the precipitation process.

Asymmetric membranes preparation



Procedure overview



Principales of phase inversion

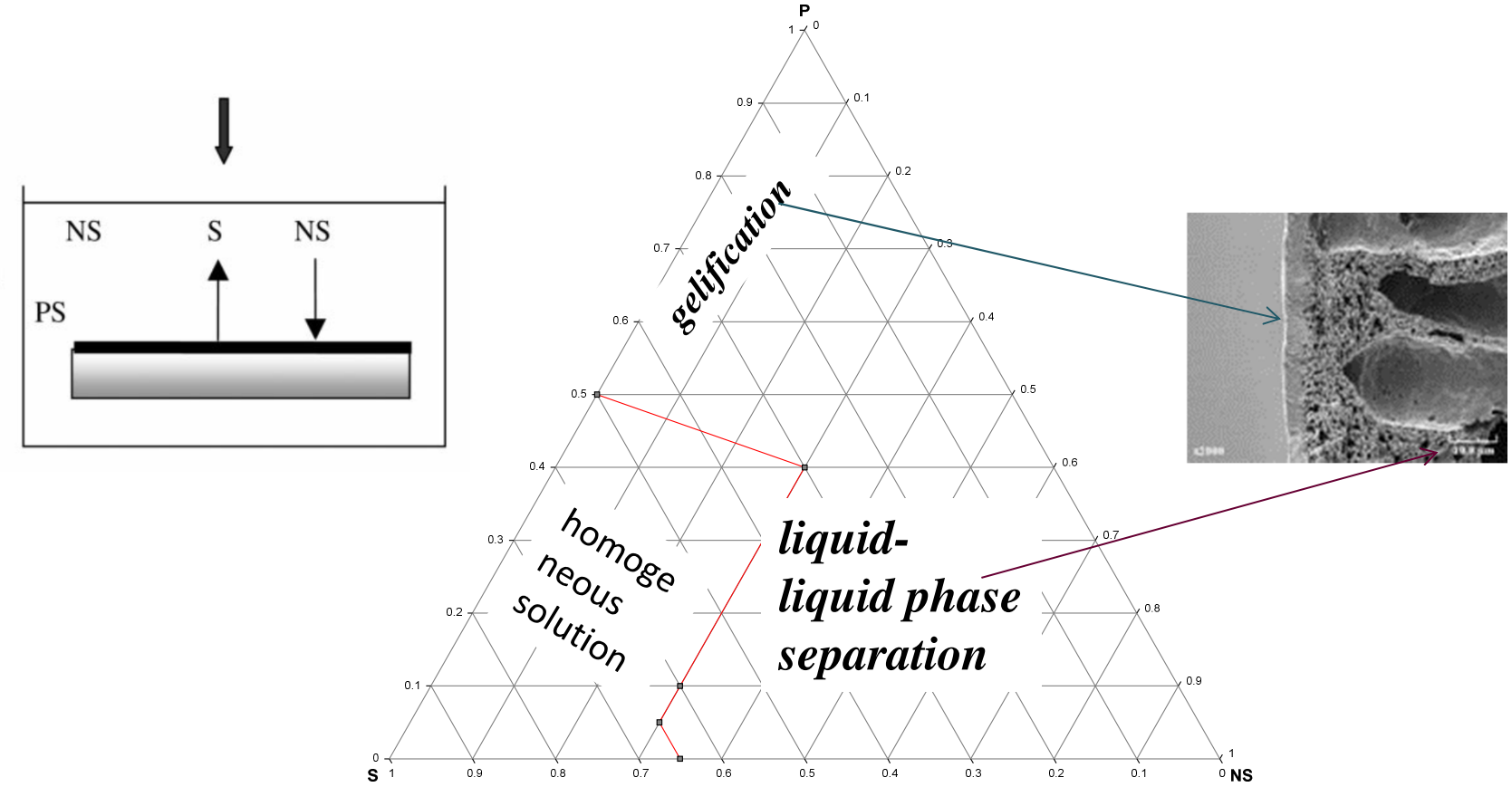
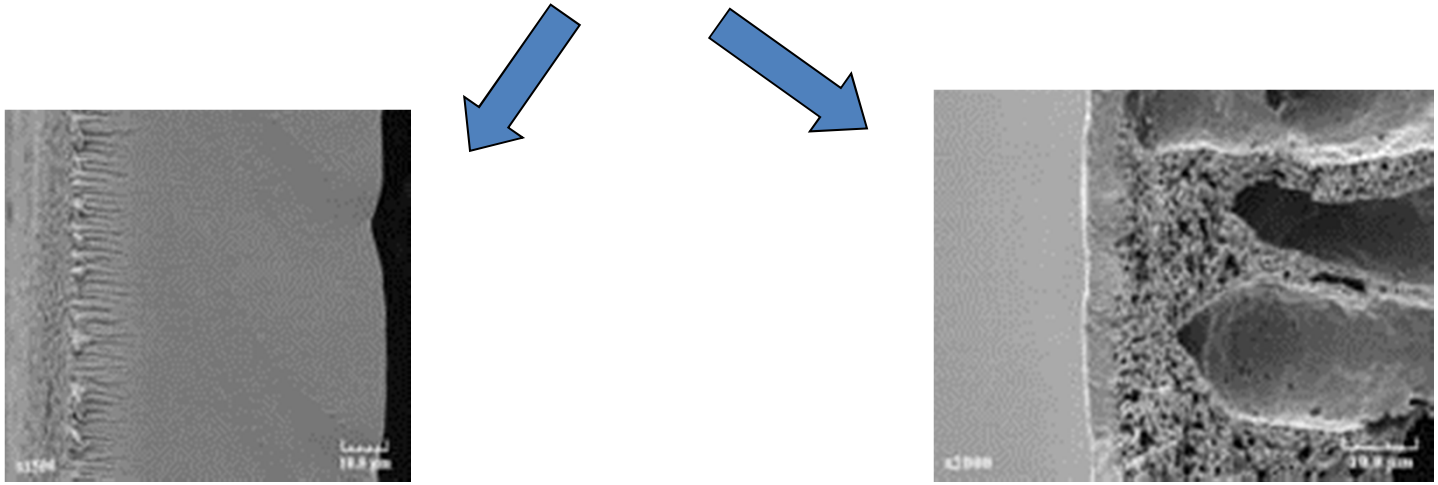


Fig.: Ternary phase diagram containing***; P: polymer; S: solvent; NS: non-solvent***

SEM Control of membrane structure

Asymmetric membranes

- phase inversion procedures



Membrane characterizations

- *SEM*

-**Water content**

-***Porosity***

-**Mechanical test.**

-***Performance test(as: Flux, Separation)***

Mathematical Model

- Thermodynamic Model

- The Flory–Huggins theory is chosen as a basis for the thermodynamic model since it is the most relevant theory for modeling the free energy of binary and ternary polymer mixtures.
- The quaternary system has two low molecular weight component; as (S1 –S2), and two high molecular weight polymers (P1 and P2).
- The diffusion model is used to investigate the immersion/precipitation process.
- The phase behavior of polymer blends can be described by the Gibb's free energy of mixing (ΔG_{mix})

Model Equations - 1

-The model main equation is an equation for calculating the Gibbs free energy change for mixing a polymer with a solvent

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

Where:

ΔH_m: Change in enthalpy during the mixing process, J/mol

ΔS_m: Change in entropy during the mixing process, J/mol/K

T: Temperature, K

the critical value of the interaction parameter:

$$X_{ij} = \frac{V_r(\delta_i - \delta_j)^2}{RT} \quad (2)$$

Where;

δ_i : Solubility parameterof component i, $kJ^{1/2}/m^{3/2}$

V_r: Reference volume which was chosen to be 100 cm^3/mol

R : Universal gas constant, J/mol/K

Model Equations - 2

- The general expression of the extended Flory-Huggins model for quaternary polymer solutions

$$\Delta G_m = RT\left[\sum_{i=1,2,3,4} n_i ln\emptyset_i + n_1\emptyset_2 X_{12} + n_1\sum_{i=1,2,3}\emptyset_i\sum_{\substack{i=1\\j=2,3,4}} X_{ij} + n_2\sum_{i=3,4}\emptyset_i\sum_{\substack{i=2\\j=3,4}} X_{ij} + n_3\sum_{i=4}\emptyset_i\sum_{\substack{i=3\\j=4}} X_{ij}\right] \quad (3)$$

Where;

n_i : Number of moles of component i, mole

$\emptyset_i$: Volume fraction of component i

- **Chemical potential** was calculated taking the first derivative of the Gibbs free energy of mixing equation with respect to the mole

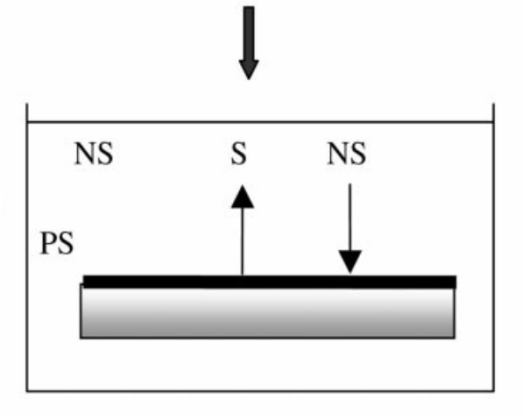
$$\frac{\Delta\mu_1}{RT} = a + b(1-\emptyset_1) - c - \emptyset_2 u_2(1-u_2)\left[\frac{\partial X_{12}}{\partial u_2}\right] - \emptyset_3 u_3(1-u_3)\left[\frac{\partial X_{23}}{\partial u_3}\right] - \emptyset_4 u_4(1-u_4)\left[\frac{\partial X_{24}}{\partial u_4}\right] \quad (4)$$

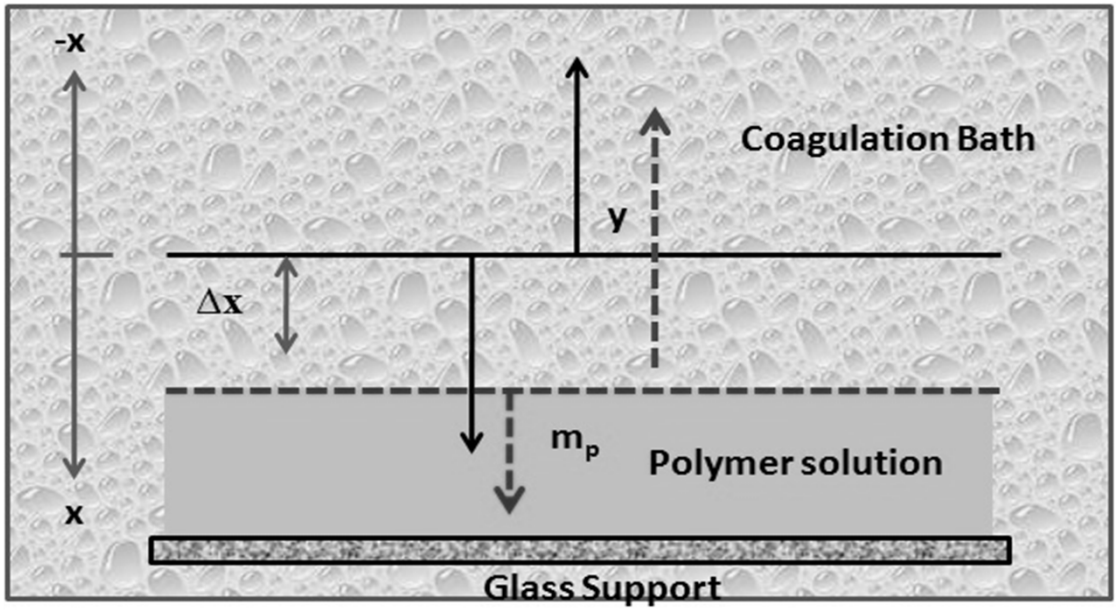
Model Equations – 3 Diffusion model of immersion precipitation step

Model assumptions

1. The reference system is chosen centered around the interface between coagulation bath and polymer film.
2. The interface of the casted blend membrane in the coagulation bath has an initial composition similar to the original coagulation bath (distilled water).
3. The polymers blend is considered as a matrix phase in which the two other components diffuse.
4. The polymer solution doesn't form a closed system, and the volume of the polymer solution is not constant.
5. According to diffusion path of solvent from polymer film and until the spinodal is reached, one phase system is assumed.
6. The mobility of the polymer is much slower compared to the low molecular weight components.
7. The concentration of components in the coagulation bath depends on the diffusion coefficients.
8. The fluxes are independent of the film thickness.

•Diffusion model of immersion precipitation





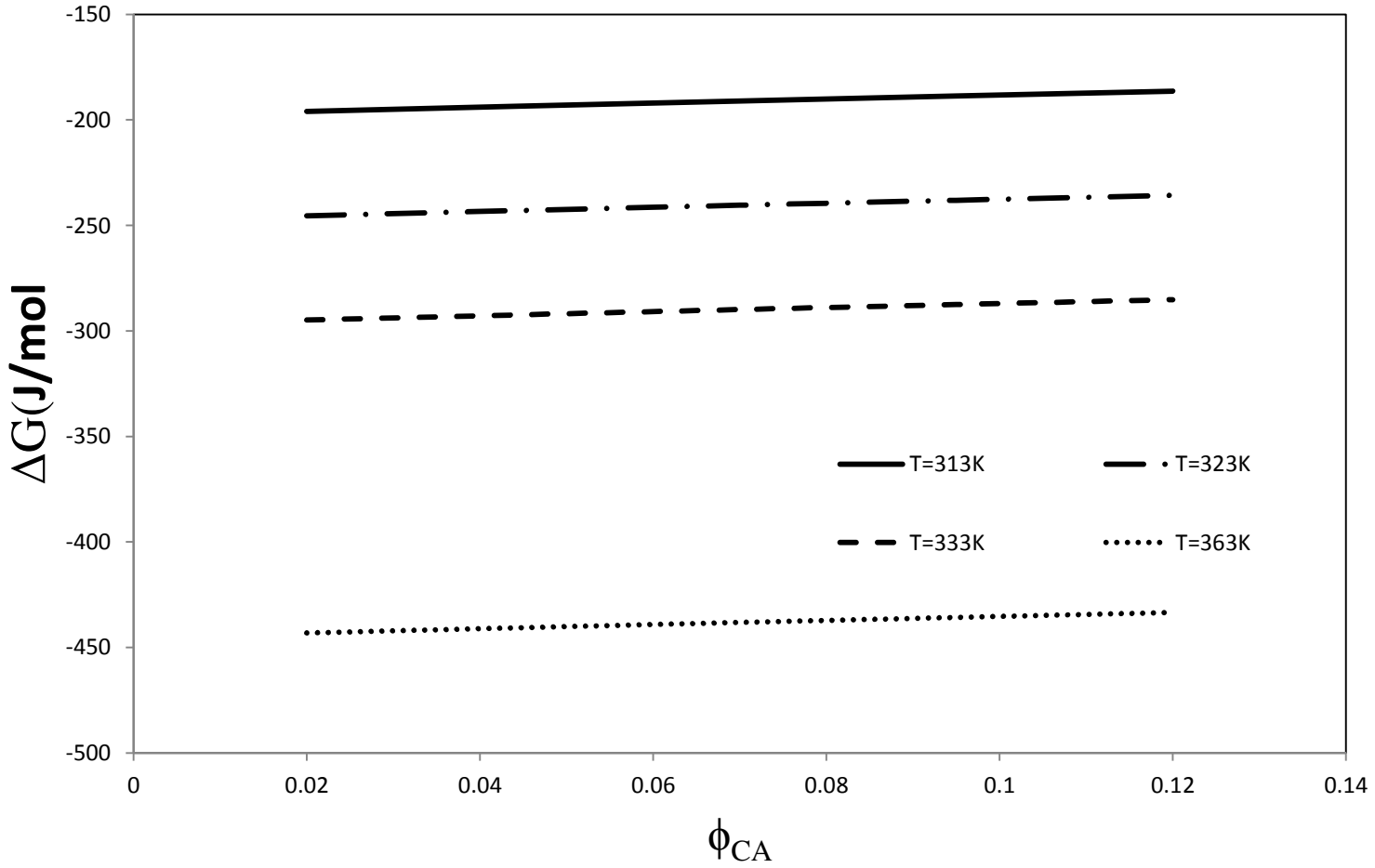
$$\frac{d\left(\frac{\emptyset_i}{\emptyset_n}\right)}{dt} = \bar{v}_i \frac{\partial}{\partial m}\left\{\sum_{j=1:n-1} \emptyset_n L_{ij} \frac{\partial \mu_j}{\partial m}\right\}$$

describes diffusion in the polymer solution (i) represents polymer

$$\frac{d\emptyset_i}{dt} = \bar{v}_i \frac{\partial}{\partial y}\left\{\sum_{j=1:n-1} L'_{ij} \frac{\partial \mu_j}{\partial y}\right\} - \frac{\partial \emptyset_i}{\partial y} \sum_{k=1:n-1} J_k$$

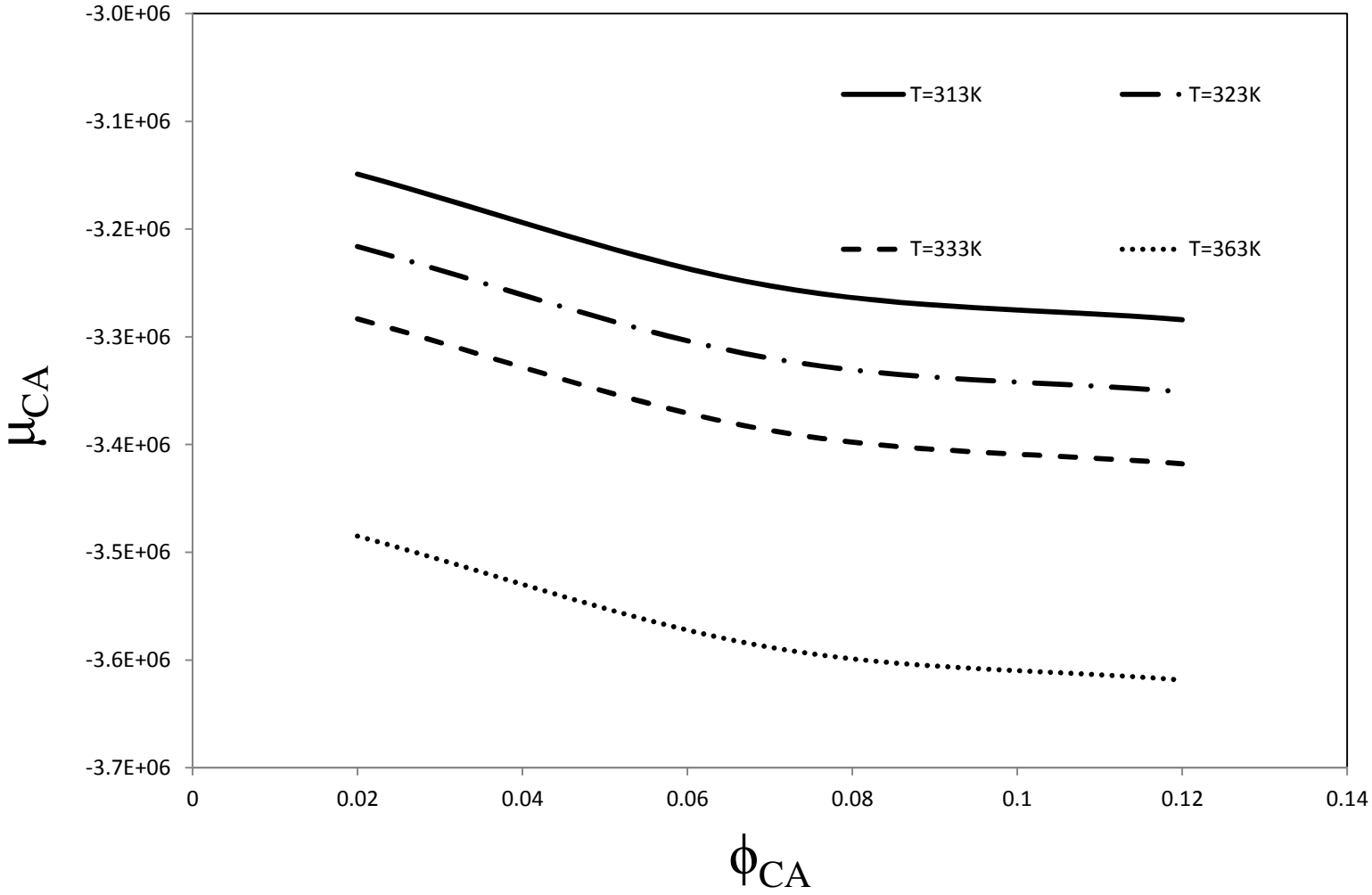
the diffusion of solvent component (j) represents solvent

Results – 1 Model verification: Effect of polymer blend composition(CA/PVC membrane)



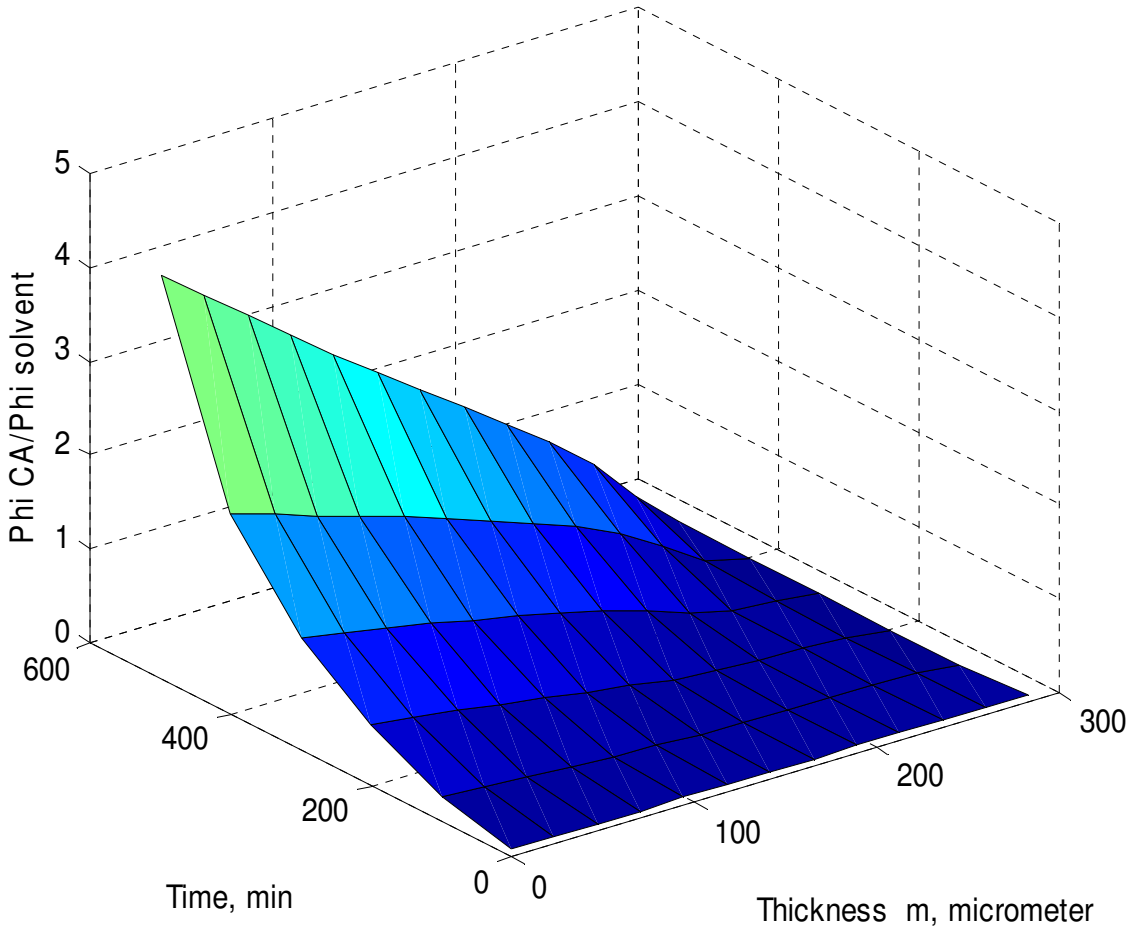
ΔG as a function of ϕ_{CA} at different temperatures

Results – 2 Effect of polymer blend composition



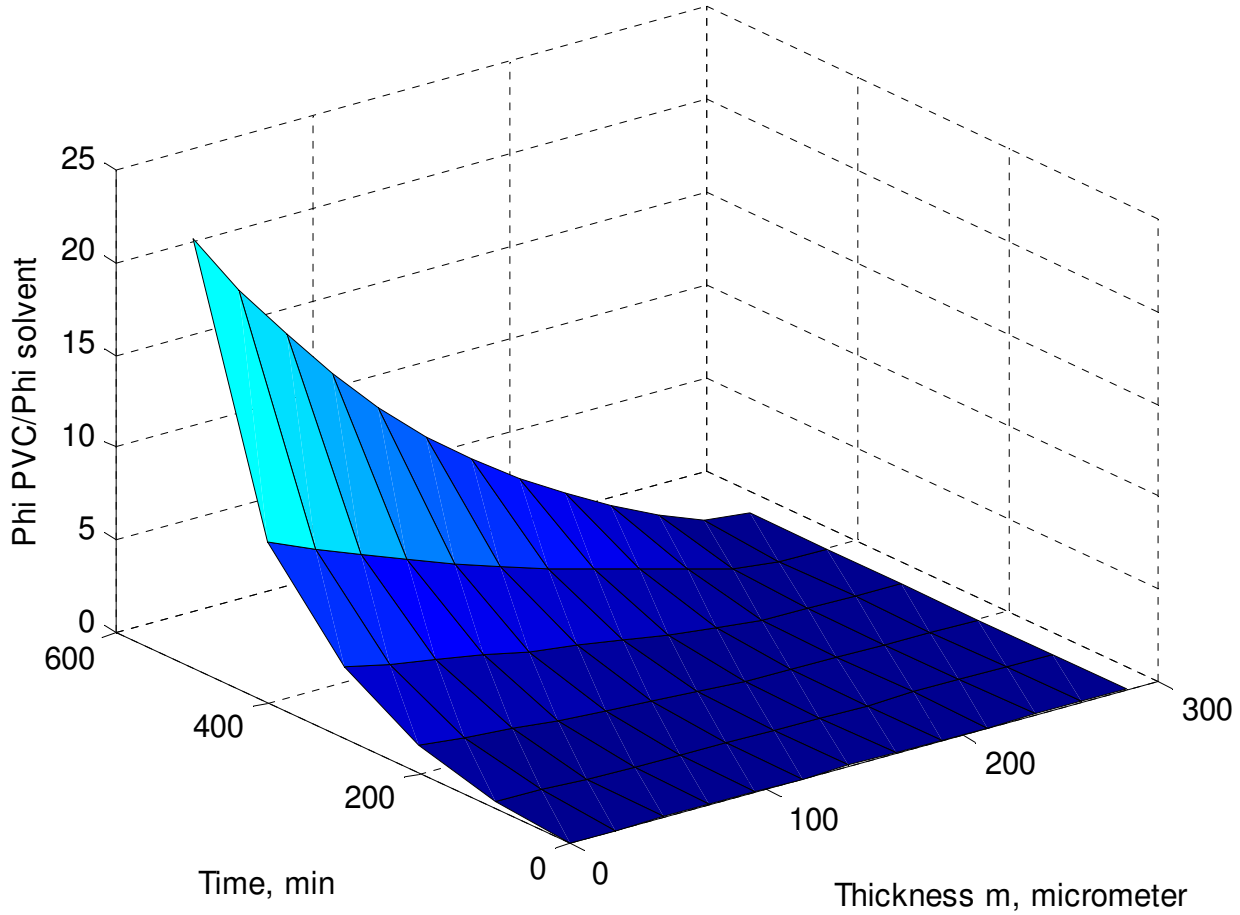
μ_{CA} as a function of ϕ_{CA} at different temperatures

Results - 3Verification of diffusion model of immersion precipitation



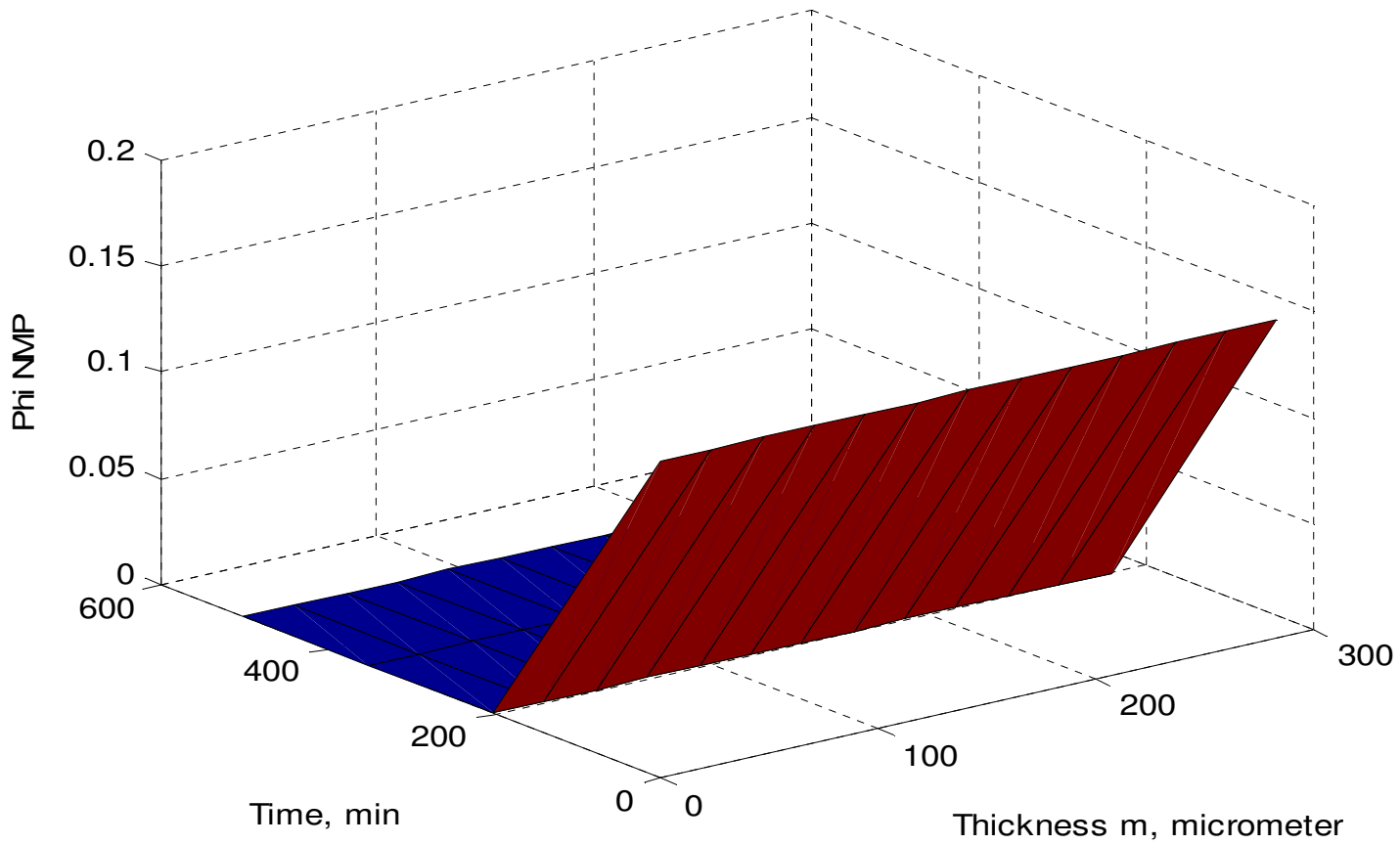
$\phi_{CA}/\phi_{solvent}$as a function of time and thickness of membrane at T=298K, Initially; ϕ_{CA}= 0.07, ϕ_{PVC}= 0.07, ϕ_{NMP}=0.15, ϕ_{THF}=0.71

Results - 4



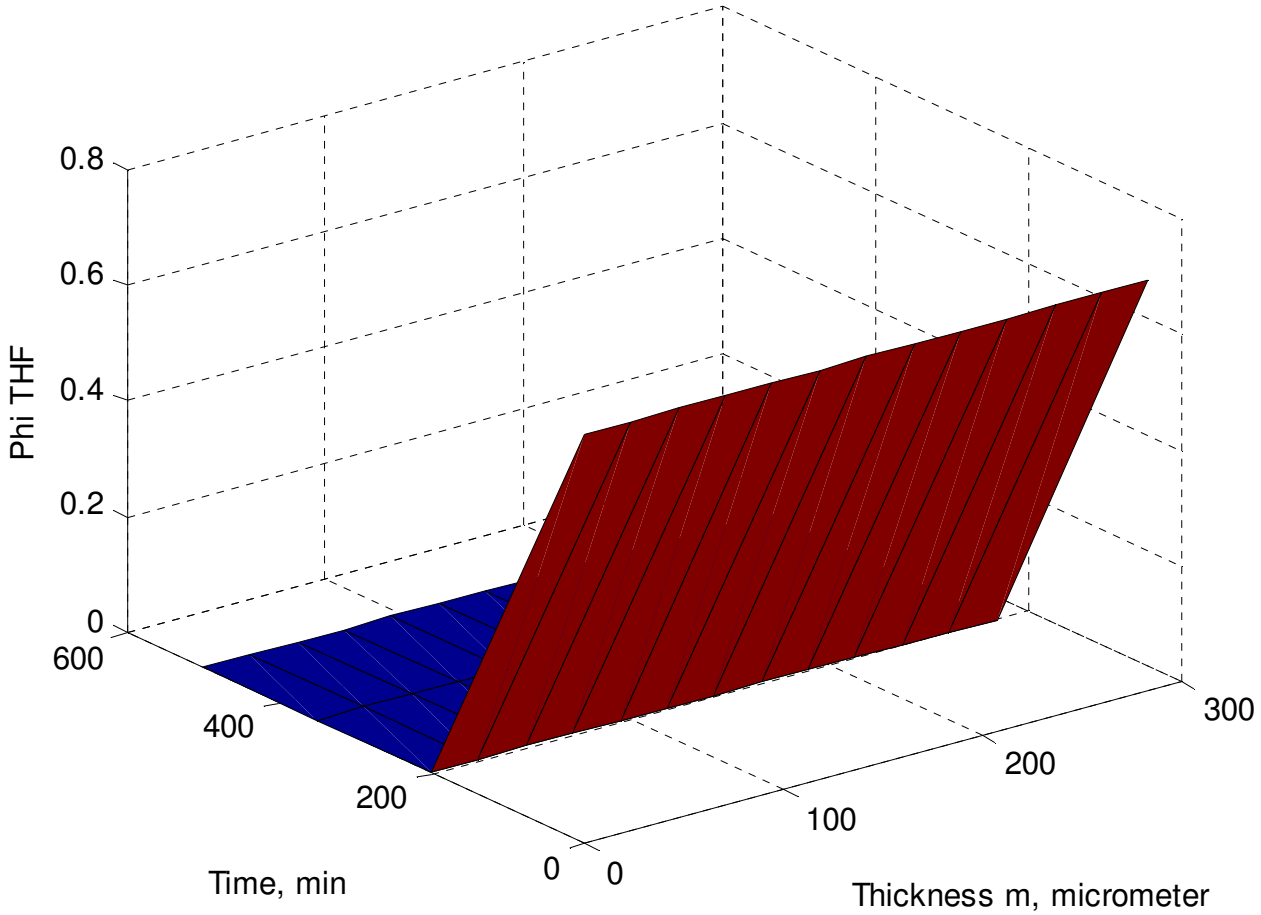
$\phi_{PVC}/\phi_{solvent}$ as a function of time and thickness of membrane at T=298K, Initially; ϕ_{CA}= 0.07, ϕ_{PVC}= 0.07, ϕ_{NMP}=0.15, ϕ_{THF}=0.71

Results - 5



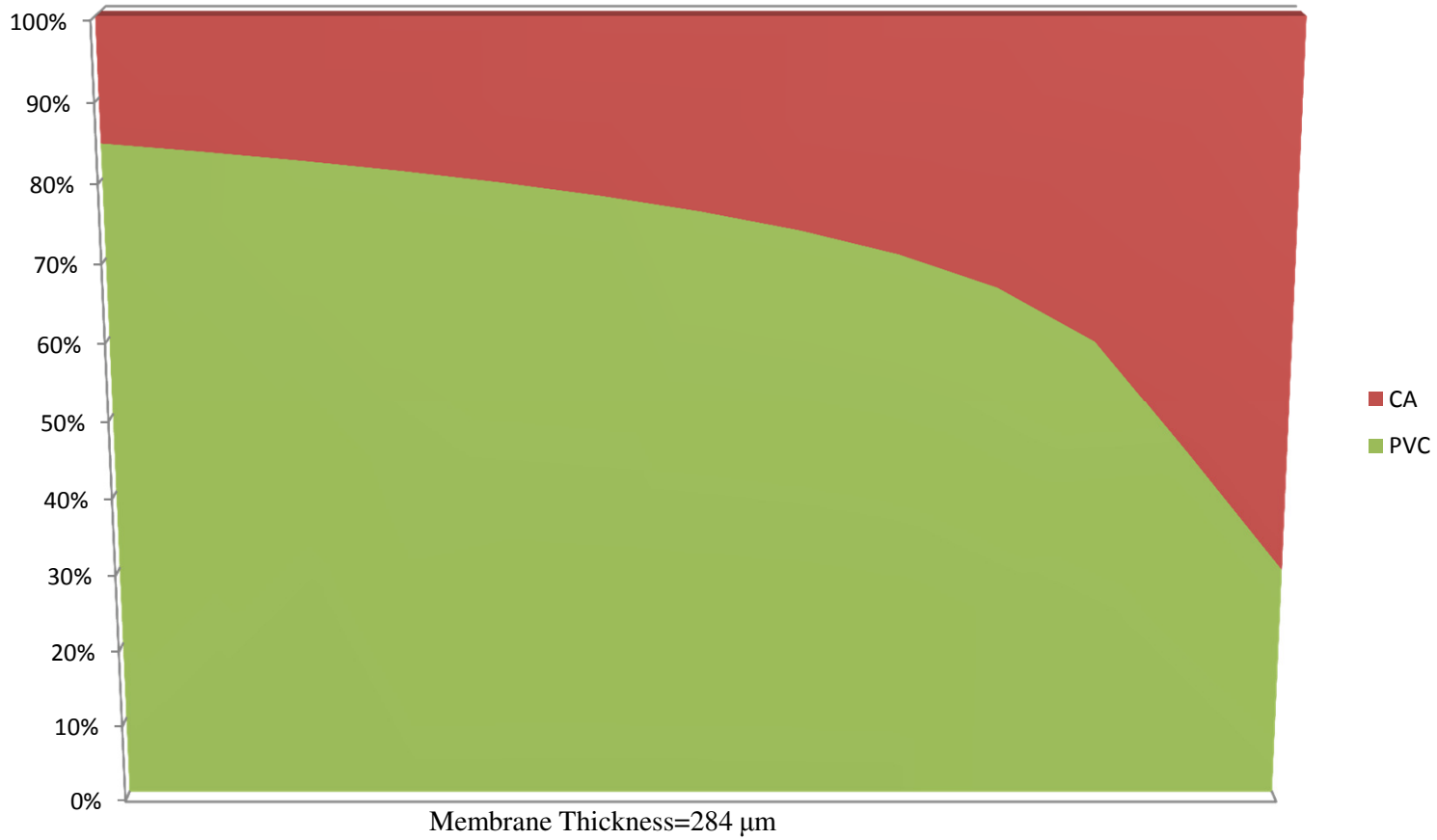
ϕ_{NMP}as a function of time and thickness of membrane at T=298K,
Initially; ϕ_{CA}= 0.07, ϕ_{PVC}= 0.07, ϕ_{NMP}=0.15, ϕ_{THF}=0.71

Results - 6



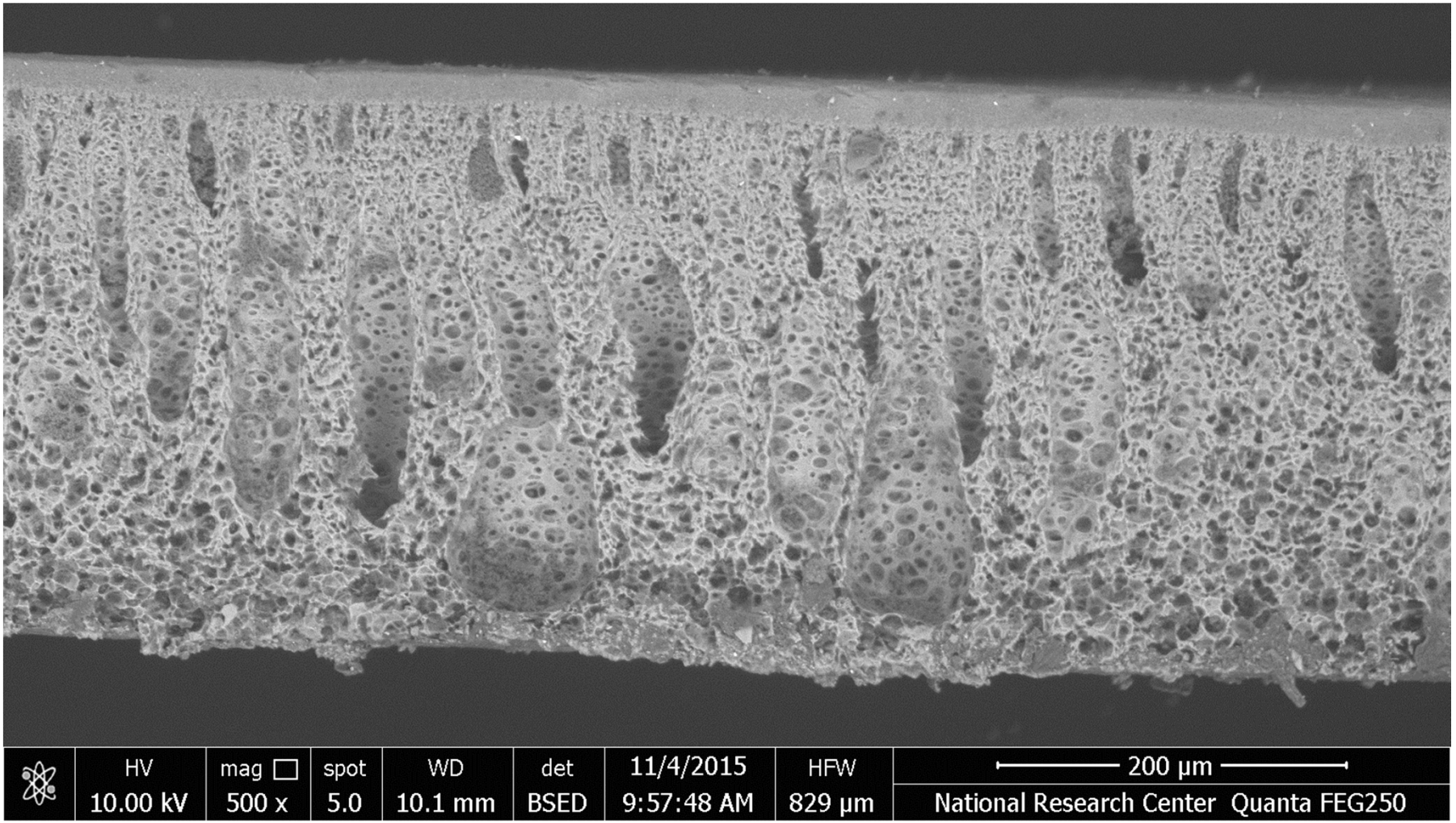
ϕ_{THF} as a function of time and thickness of membrane at T=298K, Initially; ϕ_{CA}= 0.07, ϕ_{PVC}= 0.07, ϕ_{NMP}=0.15, ϕ_{THF}=0.71

Results - 7



Representation of membrane constituents after 500 min of coagulation

Results - 8



Cross section of PVC/CA membrane

Conclusions - 1

- A quaternary thermodynamic model was developed to describe a cases study of blend membrane formation using the phase inversion process. The model was verified and the following conclusions can be drawn from the present study:

- The effect of polymer blend composition on the change of Gibbs free energy was observed, however the mixing was stable for all the polymers compositions at different solution temperatures .

- The diffusion model was developed to study the effect of immersion/ precipitation time in the coagulation bath on the blend membrane formation.

Conclusions - 2

- The model indicated that the solvent was segregated from polymer solution dissolving in the coagulation bath during precipitation time.

- The volume fraction of solvent increased in the bath and the volume fraction of polymer solution decreased as a result of the membrane formation.

THANK YOU