



Modeling of solution thermodynamics: A method for tuning the properties of blend polymeric membranes



Krishnasri V. Kurada, Sirshendu De*

Department of Chemical Engineering, Indian Institute of Technology Kharagpur, Kharagpur 721302, India

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ABSTRACT

Thermodynamics of polymer blends are modeled and ternary phase diagrams are plotted for various blend compositions using Flory-Huggins theory for polymer solutions. Equations of spinodal curve and plait point for the quaternary systems are derived based on solution thermodynamics. Binodal curves are calculated by minimizing Gibb's free energy for blend system, poly(acrylonitrile) and poly(urethane). Effects of polymer molecular weight and interaction parameters on the phase diagram are quantified. The published data of membrane transport characteristics are correlated with the modeled phase diagram and validated using FESEM and pore-diameter analysis. The reason for increase in the permeability of blend membranes is established with structural changes with the possible formation of hydrogen bond and justified by the infrared spectra analysis of the blend membranes.

1. Introduction

Polymers are the future materials in most of the upcoming fields in science and technology. Their properties can be fine-tuned to obtain desired product characteristics meeting the specific requirement. A thorough knowledge of phase equilibrium helps in this regard [1]. Several researchers have contributed in understanding the phase separation phenomena from both kinetic and thermodynamics point of view [2–4]. Majority of work is done to study phase separation induced by nonsolvent specifically for ternary systems involving polymer, solvent and nonsolvent. Blending of polymers is the simplest way to tune the desirable properties. These blends find several applications in various fields including materials for structure of automotive parts, electric appliances [5], biomedical applications [6], water filtration for preparation of membranes using advanced polymeric materials [7]. Polymer blends find diverse applications in membrane filtration altering the porosity, electrical properties and surface hydrophilicity [7]. The addition of blending polymer can be done as a low molecular additive or in the form of another membrane forming polymer of sufficiently high molecular weight. Nunes et al., obtained an increase in membrane permeability by 14 folds by blending poly(methyl methacrylate) along with poly(vinylidene fluoride) [8]. Rahimpour et al., blended cellulose acetate phthalate with polyethersulfone (PES) to improve the hydrophilicity [9]. Roy et al., studied the application of

cellulose acetate phthalate-poly(acrylonitrile) (PAN) blend membranes for extraction of steviol glycosides [10]. Panda et al., studied the antifouling characteristics of blend membranes made with varying ratio of PAN and poly(urethane) (PU) [7]. Majority of the work is done to exploit the advantage of blend membranes compared to the single polymer membranes and to find the effect on the performance of the membranes but the work done to understand the thermodynamics of blends is scant. Phase inversion phenomena for polymeric membranes for single polymer (P)-solvent (S)-nonsolvent (NS) has been studied extensively for various polymers [3,4,11,12]. Boom et al., have done significant work in modeling the binodal curves for PES membranes with poly(vinyl pyrrolidone) as polymeric additive [13]. However, their work is limited to the analysis of only binodal curve of phase diagram. To obtain the complete phase diagram evaluation of binodal, spinodal curves and plait point are necessary. Binodal curve represents the initiation of phase separation and is calculated by minimizing the free energy. Spinodal curve signifies the limit of stability and is important in many membrane forming models [3,14]. Plait point is the point at which binodal and spinodal curves meet. The exact location of plait point at the superposition of binodal and spinodal curve signifies that the minimum point obtained by the calculation is a true minimum in the given range. The scope of this work is to model the binodal curve as a tool to predict membrane characteristics and to validate the model with experimental cloud points. Kinetic study of phase inversion

Abbreviations: DMF, *N,N*-dimethyl formamide; FESEM, Field emission scanning electron microscope; FTIR, Fourier transform infrared; IPA, Isopropyl alcohol; LLP, Liquid-liquid porometer; MWCO, Molecular weight cut off; PAN, poly(acrylonitrile); PES, polyethersulfone; PU, poly(urethane)

* Corresponding author.

E-mail address: sde@che.iitkgp.ernet.in (S. De).

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Nomenclature

a, b, c	Fitting parameters
C	Elemental carbon
g_{ij}	Concentration dependent interaction parameter for pair of components i and j
G_{ij}	Second derivative of Gibb's free energy of mixing with respect to volume fraction of i th and j th component, J
G_{ijk}	Third derivative of Gibb's free energy of mixing with respect to volume fraction of i th, j th and k th component, J
ΔG_m	Gibb's free energy of mixing, J
H	Hessian matrix
L_p	Membrane permeability ($\text{m Pa}^{-1} \text{s}$)
N	Elemental nitrogen
n_i	No. of moles of i th component
NS	Non-solvent
O	Elemental oxygen
P	Polymer
P1	Polymer in major proportion
P2	Polymer in minor proportion
PAN60	Flat sheet membranes prepared from casting solution of 60% PAN and 40% PU in DMF
PAN70	Flat sheet membranes prepared from casting solution of 70% PAN and 30% PU in DMF
PAN80	Flat sheet membranes prepared from casting solution of 80% PAN and 20% PU in DMF
PAN90	Flat sheet membranes prepared from casting solution of

	90% PAN and 10% PU in DMF
PAN100	Flat sheet membranes prepared from casting solution of 100% PAN in DMF
PU100	Flat sheet membranes prepared from casting solution of 100% PU in DMF
R	Universal gas constant, J/mol K
r, s, t	Ratio of molar volumes
S	Solvent
T	Absolute temperature, K
u_2	Concentration function
v_i	Molar volume of i th pure component, $\text{m}^3 \text{mol}^{-1}$
v_{ref}	Molar volume of reference component, $\text{m}^3 \text{mol}^{-1}$
w	Equilibrium water content (%)
χ_{ij}	Concentration independent interaction parameter for pair of components i and j
Z	Optimization function

Greek letters

α, β	Polymer rich and lean phase respectively
δ	Hansen solubility parameter, $(\text{MPa}^{1/2})$
$\delta_{i,D}$	Energy from dispersion forces, $(\text{MPa}^{1/2})$
$\delta_{i,P}$	Energy from dipolar forces, $(\text{MPa}^{1/2})$
$\delta_{i,H}$	Energy from intermolecular forces, $(\text{MPa}^{1/2})$
$\Delta\mu_i^\alpha$	Chemical potential of i th component in α phase, (J Kg^{-1})
λ	Ratio of P1 to P2
ϕ_i	Volume fraction of i th component

phenomena requires the knowledge of complete phase diagram to identify the phase inversion mechanism as spinodal demixing or nucleation and growth phenomena [15]. This mechanism of phase inversion in turn explains the formation of asymmetric structure in case of spinodal demixing and symmetric structure in case of nucleation and growth. The plait point also represents the concentration at which the phase inversion always takes place by spinodal demixing. However, thermodynamic modeling of blend polymeric system to such detail is not available in literature. The present work aims to fill this gap to obtain the complete phase diagram for a polymer blend system including calculation of binodal, spinodal and plait point which can be used as a tool to predict membrane characteristics more accurately. To the best of our knowledge, the theory and modeling the spinodal and plait point for blend membranes are not available in literature.

Present work focuses on developing the equations for binodal, spinodal curves and plait point and locating the complete phase diagram for a quaternary membrane forming system, where the second polymer is a polymer of higher molecular weight. Binodal and spinodal curves indicate the two limits of stability enclosing the metastable region in between them. PAN membranes are widely used due to their good thermal stability and chemical resistance against organic solvents, chlorine and its derivatives [16–19]. PU has been extensively studied for their antimicrobial and anti fouling properties in specific biomedical and drug delivery applications. Blending of polymers is a proven method to fine-tune membrane properties [20–24]. PAN-PU blend membranes are reported to be an excellent choice for removal of suspended particles and organic foulants [7]. Based on these facts, PAN and PU are selected as primary and secondary polymer of the blend respectively. The model equations are derived for the four quaternary system having water as nonsolvent, N, N-dimethyl formamide (DMF) as solvent, PAN as membrane forming polymer (P1) and PU as the secondary polymer used for blend (P2). The cloud point data for PAN-PU system available in literature [7] is used for validating the modeled work.

2. Theory**2.1. Development of equations**

The scope of present work is to study the changes taking place during the phase inversion of polymeric membranes for quaternary systems involving polymer blends, solvent and nonsolvent. The four components are referred to hereafter as 1 for nonsolvent, 2 for solvent, 3 for polymer present in major proportion and 4 for the polymer present in smaller proportion. The changes taking place during the phase inversion can be correlated with the corresponding change in free energy of the system. The Gibb's free energy of system is calculated based on the Flory-Huggins [25] theory for polymer solutions extended to ternary components by Tompa [26]. However, for quaternary systems the one to one interaction of the three components with the 4th component also needs to be considered. The Gibb's free energy of mixing for quaternary system is given by the following expression:

$$\Delta G_m/RT = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_4 \ln \phi_4 + n_1 \phi_2 g_{12}(u_2) + n_1 \phi_3 g_{13} + n_1 \phi_4 g_{14} + n_2 \phi_3 g_{23} + n_2 \phi_4 g_{24} + n_3 \phi_4 g_{34} \quad (1)$$

where, ΔG_m is the change in free energy, R is the universal gas constant, T is the temperature in absolute scale, g_{ij} is the Flory-Huggins binary interaction parameter for the pair of components i and j , n_i is the no. of moles of component i and ϕ_i is the volume fraction of i^{th} component for $i, j = 1, 2, 3$ and 4. The ternary and quaternary interactions are the manifestations of van der Waals forces and the net effect of these multi-body interactions on free energy curve is usually small [27]. Hence, for simplification, only the binary interactions are considered and all combinations of ternary and quaternary interactions (g_{123} , g_{124} , g_{134} , g_{234} and g_{1234}) are not included in free energy calculations. Previous studies on ternary systems also did not consider the ternary interaction terms owing to the lack of sufficient knowledge of the methods to determine these parameters [3,15,28]. Determination of the multi-body interaction in polymer systems is itself an interesting area of study. The computation of binodal curves with active higher

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