Phase Inversion Kinetics of Polymer-Ionic Liquid Solutions in Relation with Membrane Morphology and Macrovoid Formation

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Cellulose is an abundant bio-polymer and it is stable against dissolution in many solvents due to its inter- and intra- molecular hydrogen bonds. Ionic liquids can dissolve cellulose and allow membrane fabrication via phase inversion. On the other hand, it is known that morphology of membranes made by using ionic liquid solvents can be quite different than those made using conventional solvents such as polar aprotic solvents [1].

The aim of this study is to understand the relationship between phase inversion kinetics of three different polymers in their ionic liquid solutions and the morphology of resultant membranes. Eight different solutions with different polymers and solvents were chosen to be studied and these solutions were coagulated either in water or in ethanol which were chosen as two readily available solvents of different nonsolvent strength. 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) is the primary solvent for all solutions and dimethyl sulfoxide (DMSO) is the co-solvent (Table 1). To estimate solvent or nonsolvent strength Hansen solubility parameters were used and relative energy difference (RED) values were calculated in order to get better understanding of affinity between two components [2]. RED values of less and more than 1.0 represent high and low affinity, respectively. Therefore, for a good solvent RED value is expected to be less than 1.0 and similarly for a good nonsolvent, it is expected to be much higher. RED value is found by dividing the solubility parameter distance value, Ra to radius of interaction, Ro of the solute; which is the limit of solubility parameter distance, above which solvent does not dissolve the polymer [2]. In Table-1 RED values of polymer-solvent, polymer-water and polymer-ethanol is given. Since Ro values are not available for solvent-nonsolvent pairs, to assess the interaction between solvents and nonsolvent solubility parameter distance (Ra) values are used.

Table 1: Composition and relevant RED values for polymer solutions used [2,3]

Solution Code	Polymer	Solvent	$RED_{P/S}$	$RED_{P/W}$	$RED_{P/E}$	Ra_{S-W}	Ra_{S-E}
A	8.0% Cellulose	92.0% [EMIM]OAc	0.922	1.027	1.024	9.44	7.52
B	8.0% Cellulose	46.0% DMSO 46.0% [EMIM]OAc	0.921	1.027	1.024	9.29	10.16
C	8.0% Cellulose	61.3 % DMSO 30.7% [EMIM]OAc	0.924	1.027	1.024	9.42	11.10
D	10.6% Cellulose	59.6% DMSO 29.8% [EMIM]OAc	0.924	1.027	1.024	9.42	11.10
E	8.0% Cellulose Acetate	92.0% [EMIM]OAc	0.523	0.999	1.347	9.44	7.52
F	8.0% Cellulose Acetate	46.0% DMSO 46.0% [EMIM]OAc	0.244	0.999	1.347	9.29	10.16
G	8.0% Polyether Sulfone (PES)	92.0% [EMIM]OAc	1.066	2.427	2.077	9.44	7.52
H	8.0% Polyether Sulfone (PES)	46.0% DMSO 46.0% [EMIM]OAc	0.930	2.427	2.077	9.29	10.16

All membranes were prepared via immersion precipitation and to measure phase inversion rate, light transmission through the solution during coagulation was measured. The light transmission data were normalized in the form of I/I_0 where I_0 is the initial value for illuminance before the polymer solution is immersed and the I is the value at any time after the immersion. The magnitude of the slope of normalized light transmission (I/I_0) against time graphs were expressed as the phase inversion rate (Figure 1).

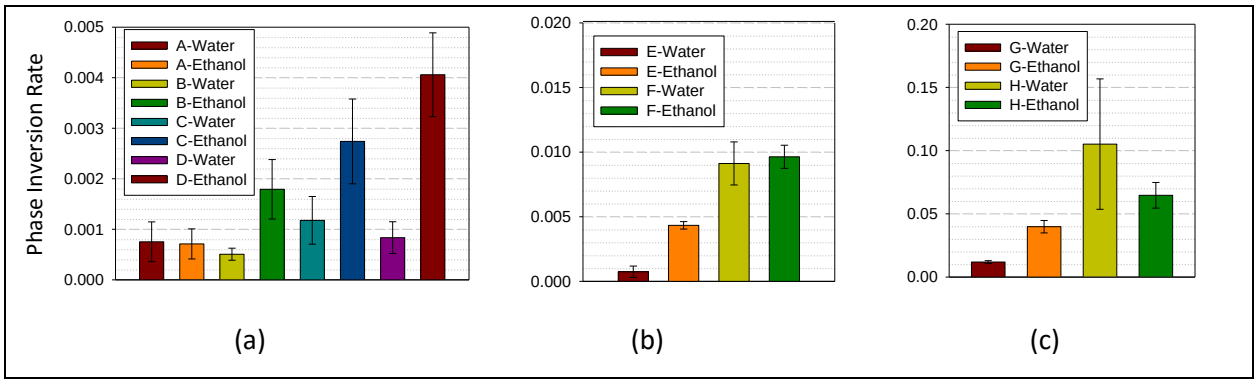


Figure 1: Phase inversion rates of solutions with (a) Cellulose, (b) Cellulose Acetate, (c) PES

Phase inversion rates for cellulose solutions coagulated in water are very close to each other (Figure 1-a). SEM images of these membranes indicate that morphologies are nodular and quite dense. Bovine Serum Albumin (BSA) rejections of these membranes are all measured to be above 90%. Although there is a small increase in phase separation rate for the solutions coagulated in ethanol when DMSO is used as cosolvent, SEM images show that the morphologies are still similar to each other and to solutions coagulated in water (Figure 2). The nodular morphologies are typically attributed to low diffusivities of nonsolvent in solvent due to the high viscosity of ionic liquids compared to conventional polymer solvents [4].

On the other hand, there is a considerable increase in phase inversion rate of cellulose acetate solutions when compared to cellulose solutions in both nonsolvents (Figure 1-b). For *Solution E* which is 8% cellulose acetate in [EMIM]OAc, SEM images show a nodular morphology with large circular macrovoids near the bottom of the membrane facing the substrate during coagulation in water. Although the phase inversion rate is very similar to *Solution A* coagulated in water, the presence of macrovoids in *Solution E*, may be attributed to difference in non-solvent quality of water for cellulose and cellulose acetate. When DMSO was added as cosolvent, and water was the coagulant, a typical asymmetric membrane morphology with a selective layer and macrovoids was observed. For cellulose acetate solutions coagulated in ethanol, phase inversion begins after a time delay of approximately 1 minute. When *Solution E* is considered there is a clear increase in phase inversion rate when compared to the solution coagulated in water. This may be attributed to the nonsolvent strength of ethanol being higher than water as RED values indicate, assuming diffusivities of ethanol and water in [EMIM]OAc are similar. On the other hand, phase inversion rates are similar for *Solution F* for both nonsolvents. Resultant membranes of cellulose acetate solutions coagulated in ethanol could not be broken with liquid nitrogen disabling to examine cross-section morphology via SEM. However, surface images indicate that those membranes are macroporous with lacy and open structure.

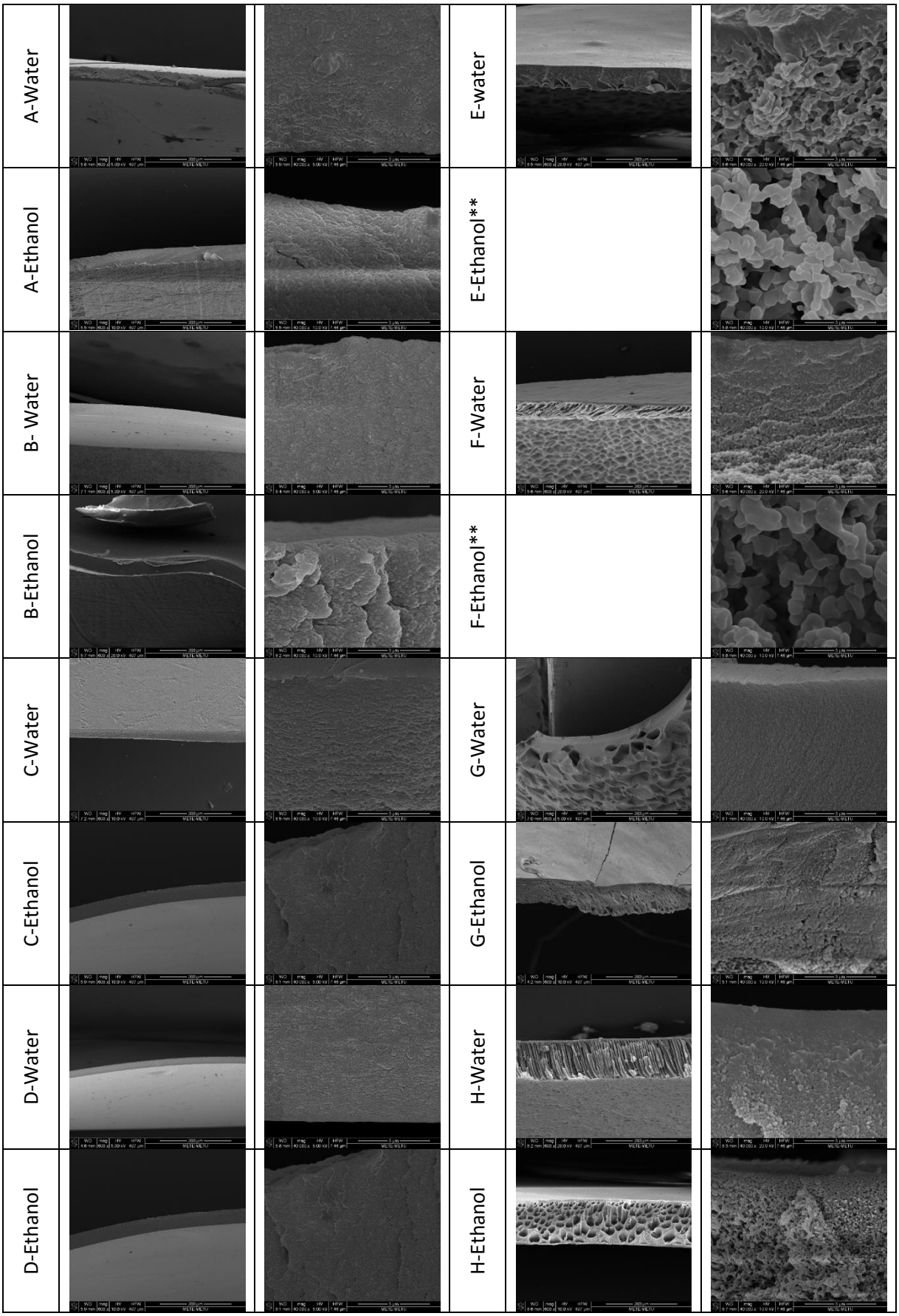


Figure 2: SEM images of membranes

*** SEM image of top surface, not the cross section; because those membranes could not be broken with liquid nitrogen.*

Phase inversion rate of PES solutions was the fastest when compared to other polymer solutions. Coagulation in ethanol was faster than in water in PES-[EMIM]OAc solutions as with Cellulose Acetate-[EMIM]OAc solutions. The rate is increased when DMSO is added to the solution; and, water and ethanol result in similar phase inversion rates and morphologies with selective layer and macrovoids. (Figure 1-c). SEM images of the top of the membranes show that coagulation in ethanol results in a looser skin layer for PES solutions, in both solvents.

In general, it was concluded that the phase inversion rate of solutions was faster in ethanol, with the exception of solution A. Phase inversion rates of Solution A in water and ethanol is very close to each other and RED values of these nonsolvents with cellulose indicate that the nonsolvent strengths are also very similar. Among the three polymers, the rate increased in the order of Cellulose < Cellulose Acetate < PES, which in general again agrees with increasing nonsolvent strength for the polymer. All cellulose solutions with or without DMSO as cosolvent resulted in membranes with nodular morphology with no macrovoids. For cellulose acetate and PES, on the other hand, addition of DMSO resulted in typical asymmetric membrane morphologies, whereas the solutions in [EMIM]OAc only resulted in nodular morphologies with large circular macrovoids only near the bottom of the membranes.

REFERENCES

[1] Xing, D., Peng, N. and Chung, T. (2010). Formation of Cellulose Acetate Membranes via Phase Inversion Using Ionic Liquid, [BMIM]SCN, As the Solvent. *Industrial & Engineering Chemistry Research*, 49(18), pp.8761-8769.

[2] Hansen, C. (2007). *Hansen solubility parameters*. 2nd ed. Boca Raton: CRC Press.

[3] Weerachanchai, P., Wong, Y., Lim, K., Tan, T. and Lee, J. (2014). Determination of Solubility Parameters of Ionic Liquids and Ionic Liquid/Solvent Mixtures from Intrinsic Viscosity. *ChemPhysChem*, 15(16), pp.3580-3591.

[4] Xing, D., Chan, S. and Chung, T. (2013). Fabrication of porous and interconnected PBI/P84 ultrafiltration membranes using [EMIM]OAc as the green solvent. *Chemical Engineering Science*, 87, pp.194-203.