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Properties of Polymer Solutions Intended for Formation of Hollow Fibers Membranes by Inversion Phases Process

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Abstract:
The gas separation process by asymmetric polymeric membranes has received much attention during the last decades because of its more energy efficiency than other conventional separation processes. Hollow fibers are the most favored membrane geometry owing to their high surface area per unit volume of membrane module. One of the key elements determining the potential and applications of asymmetric hollow-fiber membranes are the structural properties mainly including pore size, pore distribution, selective layer thickness, molecular orientation and defectiveness. These elements can generally vary depending on conditions during dry-jet wet-spinning process. Flow conditions in spinneret during extrusion are known to affect the dense-layer of hollow fibers and possibly to enhance separation performance of hollow fibers. The aim of this study was to determine flow conditions of polyetherimide/N-Methyl-2-pyrrolidone solvent/ethanol non-solvent spinning solutions flowing through concentric annulus of spinneret during hollow fiber spinning process. The rotational rheometer was used to characterize rheological properties of spinning solutions. Newtonian behavior of the spinning solutions with arbitrary composition was shown. The effect of spinning solution and spinneret dimension on flow profile in spinneret was investigated. The Newtonian character of the spinning solutions caused constant velocity profile resp. shear rate profile regardless of dope composition when flowing through a spinneret with some flowrate. It has been shown the spinneret dimensions and geometry play a crucial role in controlling the shear flow in spinneret. The phase behavior of the PEI/NMP/EtOH dope system at a temperature of the hollow fiber spinning process (40 °C) was studied.

Key words:
Hollow fiber spinning, flow profile, spinneret, phase separation, binodal curve, cloud point

1 INTRODUCTION

The gas separation process by asymmetric polymeric membranes has received much attention during the last decades because it is more energy efficient than other conventional separation processes. The membrane gas separation processes can be used in a wide range of applications, including hydrogen recovery from ammonia purge gas, enrichment of O_2 and N_2 from air and the removal of CO_2 from natural gas. Hollow fibers are the most favored membrane geometry owing to their high surface area per unit volume of membrane module. Two key elements determine the potential and applications of asymmetric hollow-fiber membranes: firstly, inherent properties of the membrane material; secondly, membrane structural properties mainly including pore size, pore distribution, selective layer thickness, molecular orientation and freedom from defects. The second key elements can generally vary depending on conditions during fabrication of fibers. Actual gas separation process occurs in dense skin layer, therefore its thickness and structure is crucial for gas separation and plays an important role in fiber separation performance. The selective layer thickness determines the membrane flux [1] and the molecular structure affects selectivity. For an asymmetric membrane fibers to be useful in separating gases, its active layer thickness must be within 10-1000 nm and have as few defects as possible [2].

It is not a trivial task to fabricate defect-free hollow fiber membranes with an ultra-thin dense-selective layer. Phase inversion is a common method to form hollow-fiber asymmetric membranes. The resulting membranes have a dense skin layer that is generally bonded in series with a thick porous substructure. Fibers are produced by the dry-jet wet-spinning process. This involves the extrusion of a more or less concentrated polymer dope solution through a spinneret annulus in

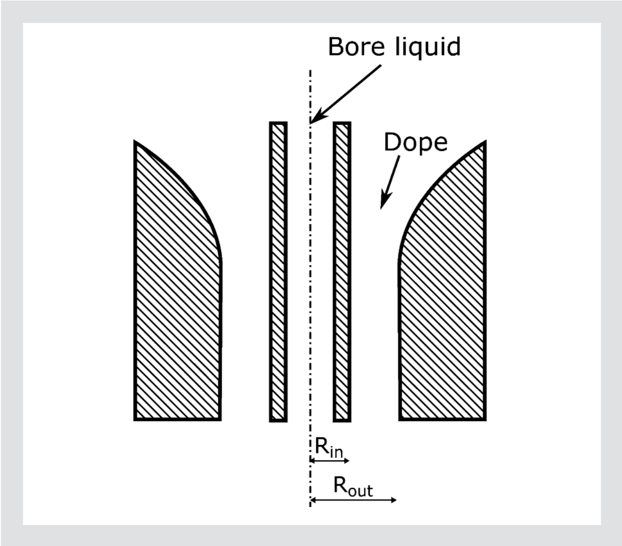

Figure 1: Spinneret profile in the phase inversion production of hollow fibers.

which it is subjected to shear flow (Figure 1). The fluid then passes through an air gap in which the dominant mode of deformation is elongational, moreover the separation layer may begin to form by solvent and non-solvent evaporation. Simultaneously, the coagulant (the bore fluid) flowing through the center of the liquid filament starts to cause coagulation from the center outwards. Next, the fluid passes into the coagulating bath, where the coagulation front passing from the outside inwards ultimately meets the inside front, and coagulation is completed to form a skin on the outer surface.

Flow conditions during extrusion are known to affect the properties of hollow fibers by altering dense-layer polymer molecular orientation [3 – 5]. Two dominant mechanisms were found to induce molecular orientation during the phase inversion of hollow fiber formation. One is mainly due to the elongational stress in the air gap and coagulation bath and the other is due to the shear stress inside spinneret [6]. It was found there exists an optimal shear rate to yield hollow fiber membranes with balanced permeance and selectivity [7]. Enhanced molecular orientation of the active layer was observed with an increase in shear rate [8, 9]. Since dope rheology clearly plays an important role in determining and enhancing the separation characteristics of hollow fiber membranes, it is a subject of interest to conduct a study on this topic. Hollow-fiber spinning process is usually carried out at wider range of temperatures (25 – 50 °C) because of various reasons. The influence of spinning temperature during phase inversion was investigated considering structure of the final fibers [10, 11]. Easier and less energy consuming transport of highly concentrated dope solutions to spinneret may be another point for higher operating temperatures. The polymer solutions consist of three or more additives. Besides polymer and solvent, the non-solvent component is usually added in order to bring dope composition near the cloud point. Phase behavior respective binodal curves knowledge of the dope mixtures are thus needed for phase inversion technology.

The aim of this study was to determine flow conditions of polyetherimide/N-Methyl-2-pyrrolidone solvent – ethanol non-solvent dope solutions, flowing through concentric annulus of spinneret. More spinnerets with variable inner radius R_{in} and outer radius R_{out} were considered. The flow of the dope solutions in spinneret was at a temperature of 40°C. The binodal curve of this ternary dope mixture was determinated for this temperature.

2 EXPERIMENTAL

2.1 MATERIALS

Polyetherimide (PEI, Ultem® 1000) from Sabic, in form of brown transparent cylindrical pieces, used as the base polymer, was dried overnight at 105°C. N-methyl-2-pyrrolidone (NMP) from Sigma Aldrich with purity more than 99 % was used as a solvent without further purification. Ethanol (EtOH) from Penta Chemicals with purity more than 99.8 % was used as a nonsolvent additive without further purification. PEI/NMP/EtOH solutions were prepared in Plas Labs 850-NB dry-box with nitrogen atmosphere. The solutions were stirred with an overhead stirrer at higher temperatures of 50 – 70°C. Measurements of the rheological properties were carried out first day after solution preparations.

2.2 CHARACTERIZATION OF RHEOLOGICAL PROPERTIES OF SPINNING SOLUTIONS

During steady rotational shear deformation with plate-plate geometry, the shear rate $\dot{\gamma}$ of the sample layer touching the rotating element depends on the rotational angular velocity Ω, on the radius from rotation axis *r* and on the characteristic geometry factor *R*. With cone plate geometry, the shear rate $\dot{\gamma}$ of the sample layer touching the rotating element depends on the rotational angular velocity Ω and on another characteristic geometry factor *R*:

$$\dot{\gamma} = \Omega R \tag{1}$$

For achieving and maintaining the desired shear rate, the appropriate shear force and the torque *M* of the rotating element has to act on the abutting sample layer. With plate-plate geometry, the shear stress σ acting on the abutting sample layer is proportional to the torque *M*, to the radius r from the rotation axis and to the characteristic geometry stress factor *S*. With cone-plate geo-

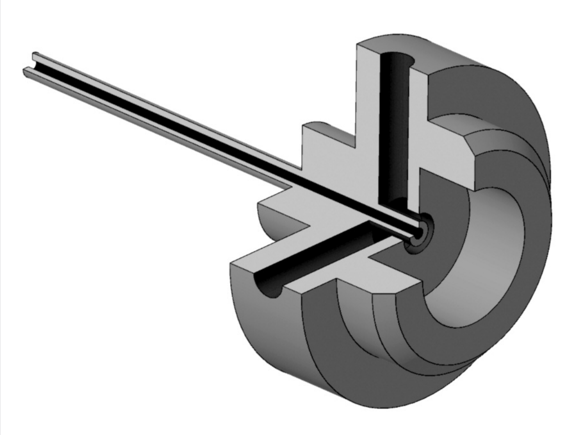

Figure 2: Typical spinneret construction.

metry, the shear stress σ acting on the abutting sample layer is proportional to the torque M and to another characteristic geometry stress factor *S*:

$$\sigma = MS \tag{2}$$

For Newtonian fluids the dynamic viscosity η during shear flow does not change with shear rate and it is a material constant that depends mainly on the temperature:

$$\sigma(\dot{\gamma}) = \eta\dot{\gamma} \tag{3}$$

The HAAKE MARS III rheometer from Thermo Fisher Scientific was used to examine the rheological properties of PEI/NMP/EtOH spinning solutions. The measurements were carried out at a temperature of 40 ± 0.03°C in a nitrogen atmosphere with flow rate of 300–400 ml/min. Dry inert atmosphere prevents precipitation of polymer from solution by air humidity. The plate-plate respective coaxial cylinder geometry was used. The P20 TiL plate-plate geometry had a diameter of 20 mm with gap height 0.4 mm, with maximal shear rate 3900 1/s and maximal shear stress 127.4 kPa. TM-PE-P (Peltier) temperature module was utilized with this geometry. The viscosity function points were determined in unsteady constant-rotation mode (the shear rate of the plate was continuously increasing with time and shear stress applied to the sample was measured immediately). The Z40 DIN coaxial cylinder geometry had a rotor diameter of 40 mm with gap height 8 mm (filling volume was 64.5 ml), with maximal shear rate 1300 1/s and maximal shear stress 1115 Pa. TM-LI-C (liquid) temperature module was utilized with this geometry. The viscosity function points were determined in steady constant-rotation mode (the constant shear rates of the cone were stabilized and after 10-30 seconds the steady shear stresses applied to the sample were measured).

2.3 EVALUATION OF FLOW PROFILE IN SPINNERETS

The typical spinneret construction is shown in Figure 2. The spinning solution enters the spinneret through four inlets in radial direction, then flows to the intrinsic concentric annulus with inner radius R_{in}, outer radius R_{out}, and length l and finally exits the system through the single outlet. The flow conditions of spinning solutions are of interest primarily in the concentric annulus and for this area the flow profiles were evaluated in this study. The flow in a spinneret during hollow fiber spinning is normally steady and laminar: A Reynolds number of 0.5 is typical. Assuming steady laminar flow of incompressible Newtonian fluid vertically downwards in a straight concentric annulus with inner radius R_{in} and outer radius R_{out} with no-slip condition at the wall boundaries, the following equations can be analytically derived from a force balance considering gravitational, pressure, and stress forces [12]. The downstream pressure drop of the fluid is:

$$\frac{dp}{dx} = \frac{8Q\eta}{\pi} \frac{1}{\frac{\left(R_{out}^2 - R_{in}^2\right)^2}{\ln\left(R_{out}/R_{in}\right)} - \left(R_{out}^4 - R_{in}^4\right)} + \rho g \tag{4}$$

where Q is the volumetric flow rate, ρ the fluid density, and g the gravitational acceleration. This shows that pressure drop is constant along the full length of annulus. The fluid linear velocity in the annulus as a function of a distance r from the center line is:

$$u_x(r) = \frac{2Q}{\pi} \frac{\frac{\left(R_{out}^2 - R_{in}^2\right)\ln\left(\left(R_{out}/r\right)\right)}{\ln\left(\left(R_{out}/R_{in}\right)\right)} - \left(R_{out}^2 - r^2\right)}{\frac{\left(R_{out}^2 - R_{in}^2\right)^2}{\ln\left(\left(R_{out}/R_{in}\right)\right)} - \left(R_{out}^4 - R_{in}^4\right)} \tag{5}$$

The shear rate of the fluid profile in the annulus is:

$$\dot{\gamma}(r) = \frac{8Q}{\pi} \frac{1}{\frac{\left(R_{out}^2 - R_{in}^2\right)^2}{\ln\left(R_{out}/R_{in}\right)} - \left(R_{out}^4 - R_{in}^4\right)} \left(\frac{r}{2} + \frac{\left(R_{out}^2 - R_{in}^2\right)}{4r\ln\left(R_{out}/R_{in}\right)}\right) \tag{6}$$

The shear stress profile of the fluid in the annulus is:

$$\sigma(r) = \eta\dot{\gamma}(r) \tag{7}$$

It implies that for arbitrary Newtonian liquid passing

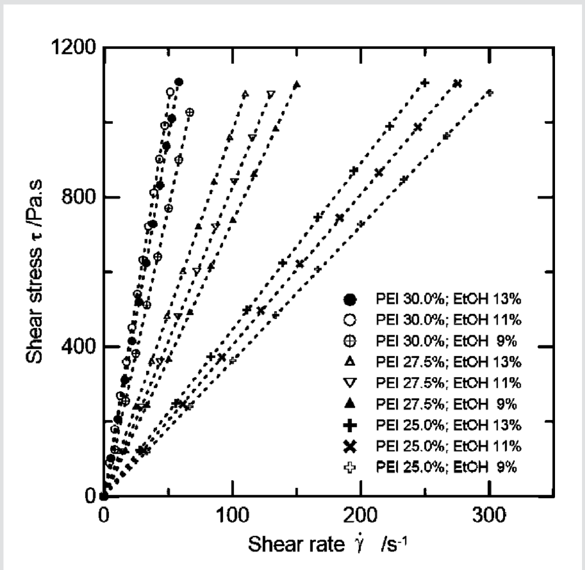

Figure 3: Flow curves for the spinning solutions with compositions (w/w) given in the legend.

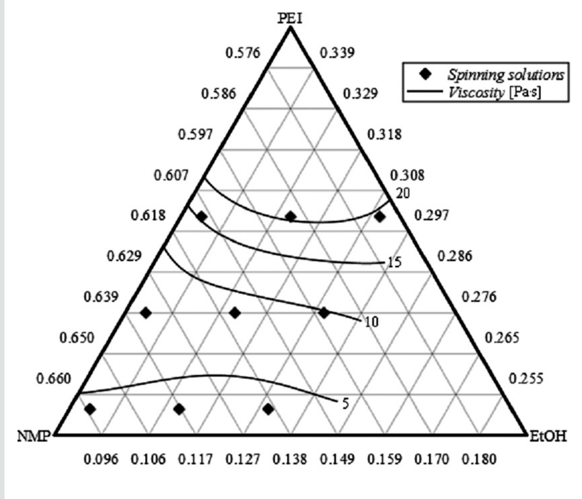

Figure 4: Viscosity contour lines (equidistance is 5 Pas) in the composition area of examined solutions on the PEI/NMP/EtOH ternary diagram.

through some spinneret with some volumetric flowrate the actual velocity profile respective shear rate profile does not differ. The Maple software was used to calculate the flow stress curves, the flow profiles in spinnerets and the binodal curves for the ternary spinning solution system. The PTC Creo Parametric software was used to create the 3D spinneret model.

2.4 CLOUD POINT MEASUREMENT OF DOPE SOLUTIONS

A predetermined amount of PEI/NMP/EtOH dope solutions with known composition were transferred into a phial and were thermostated at 40 ± 1 °C under gentle stirring in above mentioned dry-box with nitrogen atmosphere. The next ethanol as a coagulant was then added dropwise from a pipette until the solutions became cloudy. The cloud point was detected visually (brown transparent solutions turned opaque with brighter brown grey colour). From the weight of the added coagulant, the compositions at the cloud points were determined.

Solution ID	w/w composition /% PEI	NMP	EtOH	η /Pa.s	Coefficient of determination R^2 /-
1	10	90	0	0.057	0.9972
2	15	85	0	0.344	0.9998
3	20	80	0	1.040	0.9997
					95% two-sided confidence interval /Pa.s
4	25	66	9	3.61	0.008
5	25	64	11	4.03	0.017
6	25	62	13	4.44	0.017
7	27.5	63.5	9	7.34	0.072
8	27.5	61.5	11	8.28	0.031
9	27.5	59.5	13	9.80	0.043
10	30	61	9	15.4	0.137
11	30	59	11	20.6	0.387
12	30	57	13	19.2	0.194

Table 1: Effect of PEI/NMP/EtOH spinning solution composition on viscosity.

3 RESULTS AND DISCUSSION

3.1 RHEOLOGICAL CHARACTERISTICS OF DOPE SOLUTIONS

The viscosities for PEI/NMP/EtOH dope solutions with different composition were measured. Newtonian behaviour of these solutions is obvious from the shear stress as a function of the shear rate (Figure 3). Viscosity data points of PEI/NMP/EtOH ternary spinning dopes were taken in steady constant rotation mode. Five measurements were performed for every composition. All the spinning solutions behaved as Newtonian liquids. For every data point set the viscosity was calculated using least square fit. Figure 3 shows the resulting flow curves of the PEI/NMP/EtOH spinning dopes. The calculated viscosities are listed in Table 1. The results clearly show increasing viscosity with more concentrated dope solutions. The N methylpyrrolidone possesses higher viscosity compared to ethanol at given temperature [13, 14]. For 25 % respective 27.5 % of polymer the

a_{ij}		i = 0	1	2
j	0	-32996	653949	-2999288
	1	106596	-2101342	9611700
	2	-85922	1685760	-7692000

Table 2: Least square parameters matrix (Equation 8, n = 2] for fitting composition dependence of viscosity of the spinning solution.

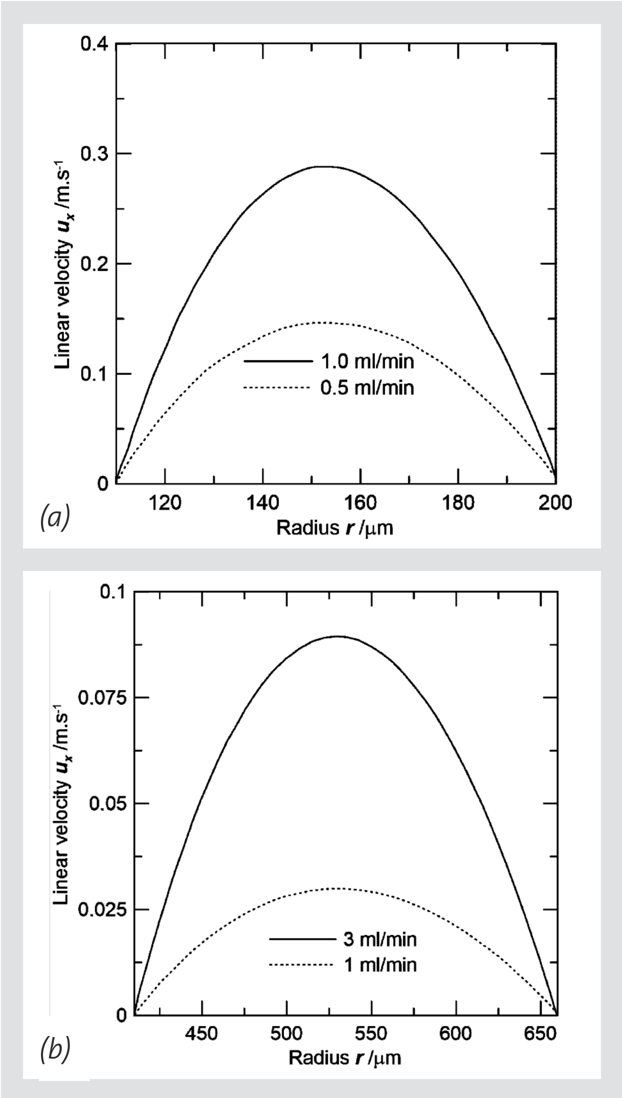

Figure 5: The linear velocity profiles of examined spinning solutions in the annulus of small spinneret (a) and big spinneret (b).

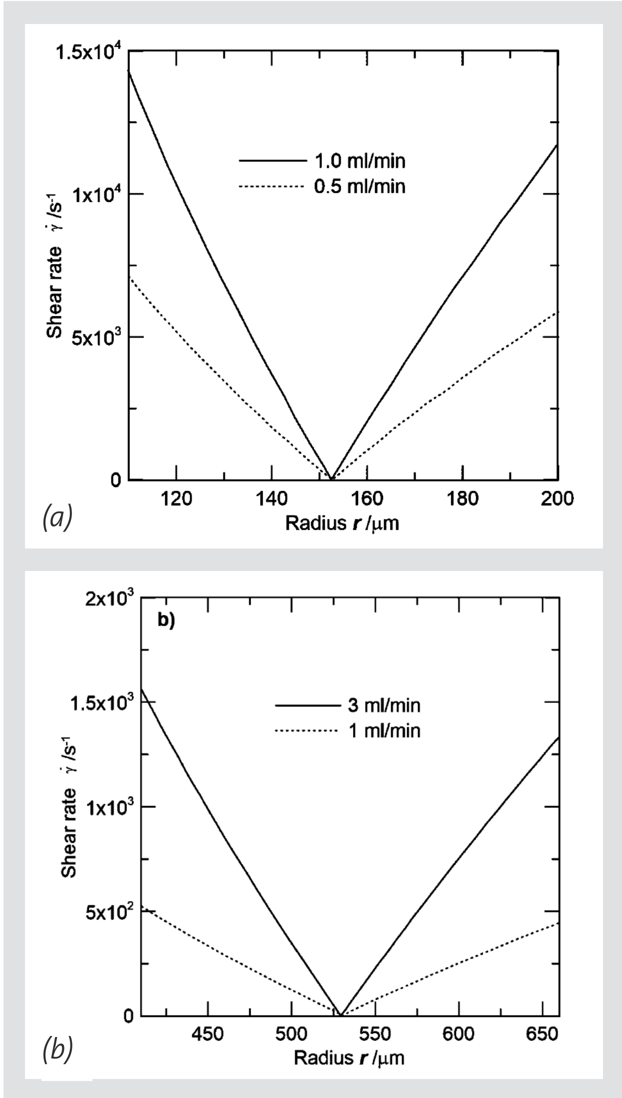

Figure 6: The shear rate profiles of examined spinning solutions in the annulus of small spinneret (a) and big spinneret (b) with variable flowrates.

dope solutions are becoming more viscous with higher percentage of ethanol nonsolvent and the trend is thus opposite to a simple additive model. For 30 % of polymer this trend appears no longer to apply and so another factor plays a dominant role in solution's viscosity. For the composition dependence of viscosity of the spinning solutions the appropriate bivariate polynomial was generated using least square fit where n = 2 was the order of the polynomial.

$$\eta\left(w(NMP),w(EtOH)\right)=\sum_{j=o}^{n}\sum_{i=o}^{n}a_{ij}w^{i}(EtOH)w^{j}(NMP) \quad (8)$$

Spinneret	R_{in} [µm]	R_{out} [µm]	l [µm]
Small	110	200	400
Big	410	660	500

Table 3: Spinneret dimensions.

The best fit parameters matrix is evaluated in Table 2. The contour lines (isoviscosity line) of the polynomial are displayed within the relevant composition area in Figure 4.

3.2 THE EFFECTS OF SPINNING SOLUTION AND SPINNERET DIMENSIONS ON FLOW PROFILES IN SPINNERET

Two spinnerets with different dimensions were considered. Table 3 shows the dimensions of their concentric annuli. Because of Newtonian character of the examined spinning solutions, their compositions have no impact on the linear velocity profiles (Equation 5) respective shear rate profiles (Equation 6) when flowing through a spinneret annulus with some flowrate. Figure 5 and 6 show those velocity respective shear rate profiles for small and big spinneret and with variable flowrates. The shear stress profiles of the spinning solutions can be evaluated using Equation 7.

3.3 PHASE DIAGRAM FOR PEI/NMP/ETOH SYSTEM

The phase behavior of the ternary system PEI/NMP/EtOH was determined by four cloud point measurements at a temperature of 40 °C. The compositions of the cloud points refer to the position of the binodal curve (Figure 7). From obtained cloud points the appropriate linear cloud point correlation (LCP) in Equation 9 describing the binodal curve was generated using least square fit. The LCP parameters for this ternary system at room temperature were also reported [15].

$$ln\frac{w(EtOH)}{w(PEI)} = a\,ln\frac{w(NMP)}{w(PEI)} + b \qquad (9)$$

4 CONCLUSIONS

In order to develop asymmetric PEI hollow fiber membranes with high performance for gas separation, the influence of dope composition on rheology was studied for PEI/NMP/EtOH dope system. The effect of spinning solution and spinneret dimension on flow profile in spinneret was investigated. The phase behavior of the PEI/NMP/EtOH dope system was examined. Newtonian behavior of the spinning solutions with composition in range 25 – 30 wt% of polyetherimide and 9 – 13 wt% of ethanol in N-methylpyrrolidone was shown. The viscosity of the dope solutions increases non-linearly with polymer mass fraction. The Newtonian character of the spinning solutions causes constant linear velocity profile and shear rate profile regardless of its composition when flowing through a spinneret with some flowrate. The spinneret dimensions and geometry play a crucial role in controlling the shear flow in a spinneret. For considered spinnerets the shear rates on the wall significantly differ during flow of the same flowrates (for example from 500 1/s in big spinneret to 14000 1/s in small spinneret with flowrate of 1 ml/min). The Newtonian character of the spinning solutions causes linear relation between the shear rate respective shear stress and the distance from the axis of rotation (the radius) in a concentric annulus of spinneret. The phase behavior of the dope system at a temperature of the hollow fiber spinning process (40 °C) has shown there is some more "space" for the solution composition to get closer to the relevant binodal curve. Obtain data will be used to optimize in production of hollow fibers membrane for gas separation.

	Temperature /°C	
	25	40
a	1.3113	1.2559
b	−2.1619	-1.4661
R^2	0.9991	0.9958

Table 4: The LCP parameters for PEI/NMP/EtOH system.

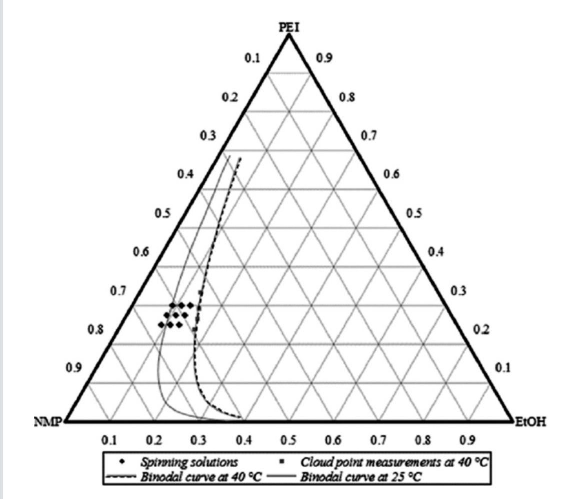

Figure 7: The binodal curves for PEI/NMP/EtOH system. Binodal curve for 25 °C (Data from [15]).

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