

Optical microinterferometry method for evaluation of phase state and diffusion in ternary systems: phase separation in cellulose/N-Methylmorpholine-N-oxide/non-solvent mixtures

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Abstract. Microinterferometry technique was used to evaluate the phase state and diffusion of cellulose solutions N-Methylmorpholine-N-oxide upon contact with non-solvents (water and aqueous solutions of isopropyl alcohol). The method was helpful in visualization of the structure of the forming cellulose film in connection with the diffusivity of the components of the systems. The interdiffusion coefficient were determined. Isopropyl alcohol addition to water slows down the diffusion of the coagulant into the cellulose solution thus delaying cellulose precipitation. Increase of temperature leads to formation of less dense cellulose film morphology with large vacuoles.

1. Introduction

The membranes used in different separation processes are mainly made of a wide range of rubbery and glassy polymers due to their lower price in contrast to inorganic membranes. A typical membrane consists of the thin selective layer on top of a thick porous support layer that provides the required mechanical properties. In the case of glassy polymers with a low or moderate price like polysulfone or polyamides, the selective and porous support layers can be fabricated from the same polymeric material by phase inversion technique [1]. The polymeric solution film with a required thickness is formed on the glass plate or non-woven support by casting knife followed by immersion in the non-solvent bath. The contrariwise diffusion of non-solvent and solvent molecules leads to a change in the composition of the polymeric solution resulting in the phase separation and formation of a polymer film. At the same time, polymer precipitation and change of the viscosity of the solution affect on the further diffusion of non-solvent and solvent molecules in the bulk of polymeric solution and lead to the formation of an asymmetric porous structure. Nowadays, the greater attention is focused on the development of membrane materials and membranes from sustainable sources, and cellulose can be considered as a promising candidate due to its renewable origin and biodegradability. For example, cellulose-based membranes can be used for gas separation [2,3], organic solvent ultrafiltration [4,5] and nanofiltration processes [6,7].

The optimal casting conditions that allow obtaining the membrane with target properties such as flux, selectivity, and mechanical resistance are usually determined experimentally when the polymer solution composition, as well as solvent and non-solvent nature, is varied. It should be noticed that availability of a ternary (polymer/ solvent/non-solvent) phase diagram could significantly assist in this



approach, meanwhile, the determination of 3-component diagram for an unknown system might be time and effort costly routine. Optical methods are usually used to determine the starting moment of polymer precipitation from its solution (so-called cloud point) or to study the polymer structure (presence of crystalline regions etc.). At the same time, the optical interferometry method allows analyzing polymer-polymer and polymer-solvent interactions [8]. The principle of this method is based on the multipath interference from two surfaces of the film of the polymeric solution or the polymer placed between two glass plates having the inner surface covered with a semitransparent metallic layer to reinforce its reflection capability. By applying of monochromatic beam through the film, it is possible to obtain the interference pattern. The main requirements of the method are follows: transparency of at least one of the contacting phases and difference in refraction indices of contacting phases not less than 10^{-3} . An important advantage of microinterferometry is an opportunity to visualize the process of phase separation and the morphology of the forming phases in the course of an experiment, which seems very useful for membranes manufacturing.

Microinterferometry is generally applied for binary systems [8, 9], and the developed method of mathematical interpretation of interferograms has been regarded to be truly valid only for this case. Quite recently, however, the applicability of the microinterferometry technique was successfully extended to some cases of pseudobinary systems where one of the contacting phases was gas oil - a mixture of completely miscible components [10]

In this study optical interferometry method was used for evaluation of phase state and diffusivity in a ternary polymer/solvent/coagulant system – cellulose solution in N-methylmorpholine-N-oxide with water and isopropanol aqueous solutions selected as coagulating agents (non-solvents).

2. Experimental part

Sulfate viscose cellulose with a polymerization degree of 600 produced by the Baikal pulp-and-paper plant (Russian Federation) was used in this work and have the following properties in a accordance to manufacturer specification: the α -cellulose content of 94.96 wt%, the equilibrium moisture content 8 wt% at RH 60%. Cellulose was used as a powder with 200 μm average particles size. N-methylmorpholine-N-oxide (NMMO) monohydrate with 10-13 wt% water was supplied by Demochem (China). Solid-phase cellulose solutions in NMMO were prepared by the grinding in a mortar of cellulose and NMMO monohydrate powders for 7-10 min for activation of the mixture as described elsewhere [11]. The cellulose concentration in NMMO solutions was 12 wt% as a typical composition used for films, fibers, and membrane formation. The films of 12wt% cellulose solution in NMMO were prepared using a HLCL-1000 coater-laminator (Cheminstruments, USA). The completion of the dissolution of cellulose in NMMO was controlled by the using the optical polarizing microscope Boetius equipped with the heating table. Distilled water and 20 and 50 wt% isopropyl alcohol (IPA) aqueous solutions were selected as coagulating agents (non-solvent for cellulose).

Cellulose coagulation from the solution in NMMO at contact with coagulating agents was studied at 25 and 65°C. Before the experiments, the diffusion cell with the solid-phase solutions was thermostated for 15 min at 90°C until complete cellulose dissolution in NMMO. Then the cell was cooled down to the required temperature, and then the coagulation agent was brought in contact with the system. The interference patterns (interferograms) were recorded by the digital camera. Mutual diffusion of the components leads to the drift of the refraction index ion the diffusion zone and consequently, to bending of interference bands. Using interferograms and refractions indices of the contacting phases, it was possible to plot the concentration profiles of components in the diffusion zone. The resulting concentration profiles were then used to calculate the diffusion coefficients following the Matano-Boltzmann method [12, 13] The schematic representation of the principle of the optical microinterferometry method and obtained data are shown in Fig. 1 and 2, respectively.

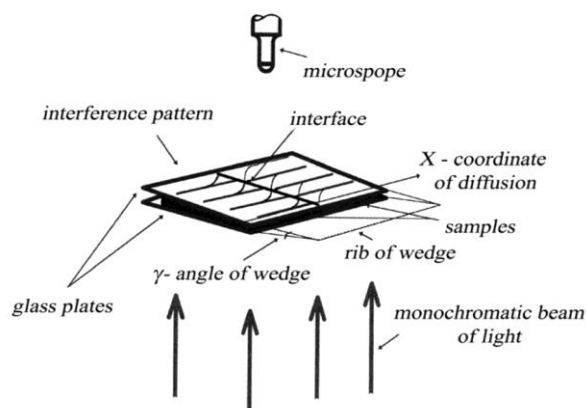


Figure 1. Principle of the optical microinterferometry method (interferometer).

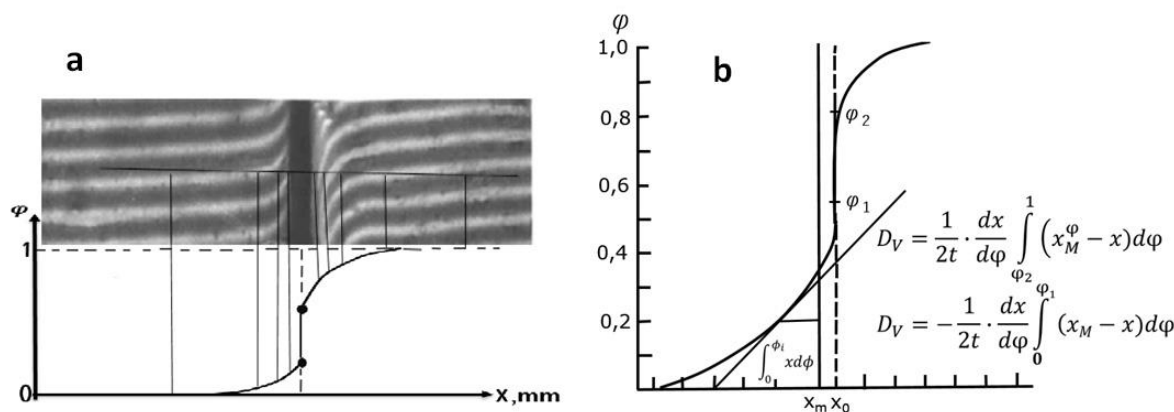


Figure 2. An example of plotting the concentration profile from the interferogram (a) and calculation of the interdiffusion coefficients (b).

3. Results and discussion

3.1. Cellulose coagulation at 25°C

Interferograms obtained at the contact of 12 wt% cellulose in NMMO solution with water, 20 and 50 wt% of IPA in water at 25°C are presented in Fig. 3. It could be noticed that all of them are quite alike with continuous interference bands which indicate on the complete miscibility of all components except for cellulose which forms a transparent and almost invisible film in the diffusion zone. However, the boundary of the film (depicted in Fig. 3) is quite distinct, so it can be speculated that a dense surface sublayer is formed at the initial contact of the cellulose solution with a non-solvent. The increase of IPA in the coagulating bath seems to slow down the non-solvent diffusion and cellulose film formation and can explain less pronounced film boundary in the case of 50 wt% IPA solution.

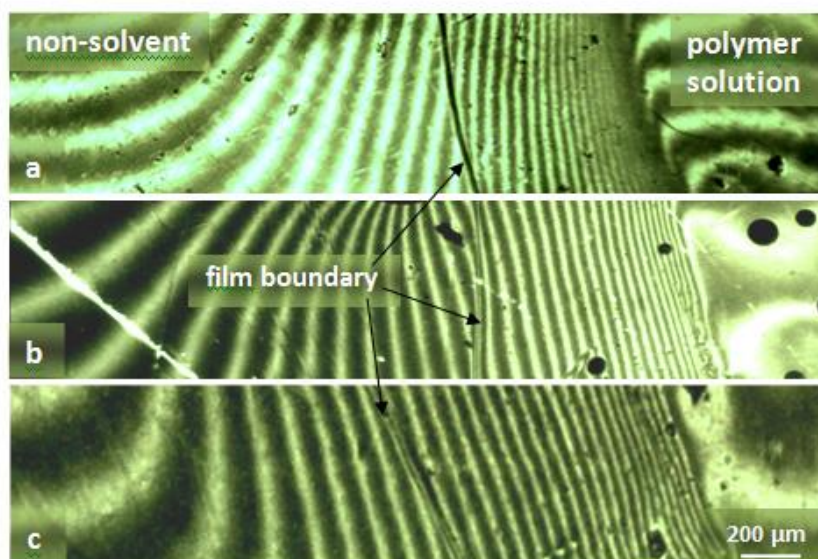


Figure 3. Interferograms obtained at the contact of 12 wt% cellulose in NMMO solution with water (a), 20 (b) and 50 (c) wt% IPA aqueous solutions at 25°C. Dark circles on the photos are air bubbles entrapped at melting of the cellulose in NMMO solid solution

The concentration profiles in the diffusion zones can be used to estimate the process kinetics. An example of such profiles is shown in Fig. 4 for the case of 50 wt% IPA solution used as the coagulating agent. The presented curves demonstrate widening of the diffusion zone in time. The data similar to those presented in Fig. 4 were then used to plot isoconcentration dependences in coordinates x vs. $t^{1/2}$ (here x is diffusion coordinate, t is time after the initial contact of phases). All such dependences for all the systems under investigation were linear which indicates on the truly diffusive mixing of the components without chemical interaction.

It should be noted that Fig. 4, in fact, presumes system to be quasi-binary and uses “polymer solution” and “non-solvent” as independent basic components of the system. Therefore, the concentration and of interdiffusion coefficients profiles presented below should be regarded as some effective ones describing the overall kinetics of the process. The calculated interdiffusion coefficients for the systems are shown in Fig. 5.

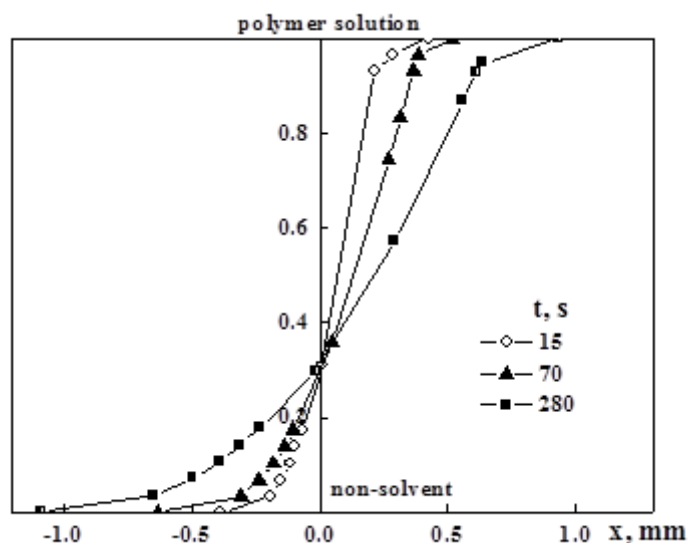


Figure 4. Concentration profiles of components for 50 wt% IPA solution at 25°C and 15, 70, 280 s after contact

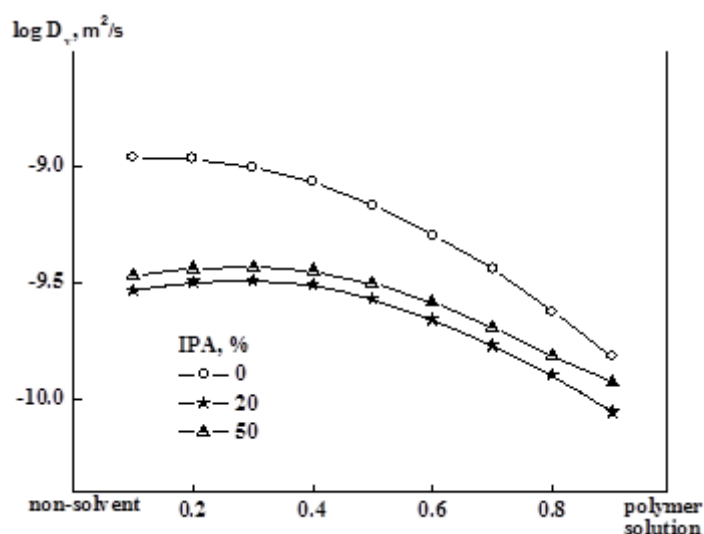


Figure 5. Interdiffusion coefficients for cellulose solution – non-solvent systems at 25°C

The cellulose film precipitated from the solution at contact with a non-solvent works as a membrane between the solution and non-solvent, so its morphology would influence on the diffusion process kinetics. D_v values in the region enriched with a non-solvent (left part of Fig. 5) are half an order of magnitude higher than those in the region of the polymer solution (right part of the plot). This is true for all the systems studied and may be explained either by higher viscosity of the polymer solution or by the dense morphology of the forming cellulose film. IPA addition leads to a noticeable decrease in the interdiffusion coefficients which may be connected with some increase in the non-solvent viscosity [14].

3.2. Cellulose coagulation at 65°C

The interferograms of the same systems obtained at 65°C (Fig. 6) look different as compared with those at 25°C (Fig. 3). One may notice large vacuoles in the forming cellulose film beyond the dense surface layer followed by a network-like structure. The vacuoles are oriented in the diffusion direction. The addition of IPA changes the pattern; vacuoles become less distinct and quite rare.

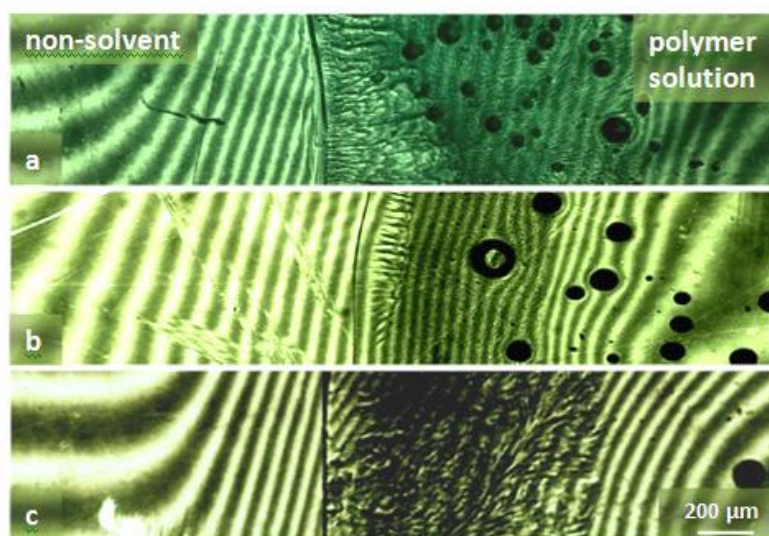


Figure 6. Interferograms obtained at the contact of 12 wt% cellulose in NMMO solution with water (a), 20 (b) and 50 (c) wt% IPA aqueous solutions at 65°C. Dark circles on the photos are air bubbles entrapped at melting of the cellulose in NMMO solid solution.

The calculated interdiffusion coefficients (Fig. 7) agree with these observations. First, the values of diffusion coefficients are substantially higher than those at 25°C. The difference between D_v values in areas with high and low polymer solution content is lower than at 25°C and decreases with IPA content.

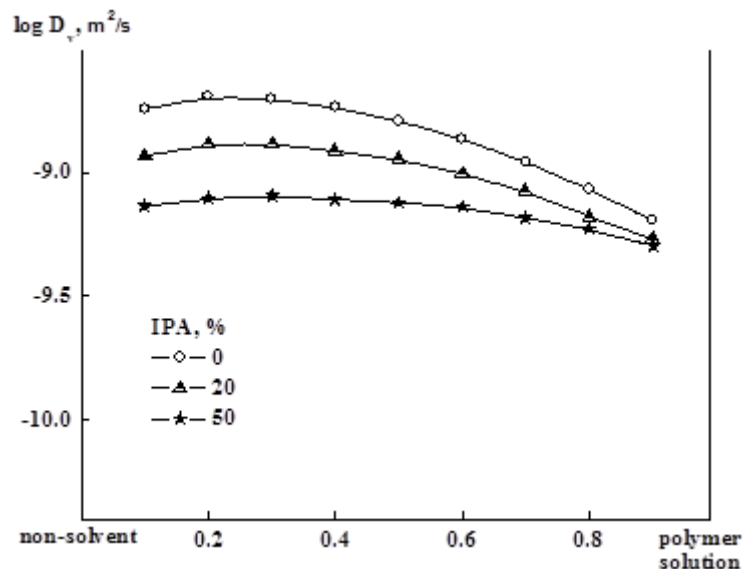


Figure 7. Interdiffusion coefficients for cellulose solution – non-solvent systems at 65°C

4. Conclusions

Application of microinterferometry for studying polymer/solvent/non-solvent systems may be very helpful as a means of visualization of the structure of the precipitating polymer as well as assessing the kinetics of the process in spite of intrinsic limitations of the method.

Acknowledgments

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References

- [1] Mulder J 2012 *Basic principles of membrane technology* (Kluwer Academic Publishers Dordrecht, Boston, London) p 75.
- [2] Wu J and Yuan Q 2002 *J. Membr. Sci.* **204** 185.
- [3] Jie X, Cao Y, Lin B and Yuan Q 2004 *J. Membr. Sci.* **91** 1873.
- [4] Zhang Y, Shao H, Wu Ch and Hu X 2001 *Macromol. Biosci.* **1** 141.
- [5] Li J H, Cao M T, Qin J J, Jie M X, Wang H T, Liu H J, Yuan Q, Zhang Y 2006 *J. Membr. Sci.* **279** 328.
- [6] Anokhina T S, Yushkin A A, Volkov V V, Antonov S V, Volkov A V 2015 *Phys. Proc.* **72** 171.
- [7] Yushkin A A, Anokhina T S and Volkov A V 2015 *Pet. Chem.* **55** 746.
- [8] Makarova V and Kulichikhin V 2012 *Application of Interferometry to Analysis of Polymer-Polymer and Polymer-Solvent Interactions* (InTech) ed I Padron p 395.
- [9] Malkin A Ya, Chalykh A E 1979 *Diffusion and viscosity of polymers. Measurement techniques* (Moscow: Khimia) in Russian.
- [10] Pakhmanova O A 2012 *Catalytic cracking of polymer-containing oil feedstock* (Moscow: PhD thesis, A.V. Topchiev Institute of Petrochemical Synthesis, RAS) in Russian.
- [11] Golova L K, Romanov V V, Lunina O B, Platonov V A, Parkov S P, Khorozova O D, Yashkin V V, Belasheva T P, Sokira A N 1992 Patent SU 1645308.
- [12] Boltzmann L 1894 *Ann. Phys* **289** 959.
- [13] Matano C 1993 *Jap. J. Phys* **8**. 109.
- [14] Lide D R 2007 *CRC Handbook of Chemistry and Physics* (Boca Raton: Taylor and Francis).