Ternary phase diagrams of polyimide/solvent/non-solvent systems

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A popular method to synthesize polymeric membranes is the phase inversion process. To obtain a membrane through that process, a homogeneous solution of a polymer in an appropriate solvent is formed and then a non-solvent is added, so that the exchange between solvent and non-solvent occurs until the polymer precipitates. Then phase separation takes place, which induces the formation of polymer-rich and polymer-lean phases. Beyond the knowledge we have already obtained, it is crucial to create reliable predictions on membrane formation and structure interpretation so that the fabrication of optimal membranes could be achieved. The experimental way to plot a ternary phase diagram is by collecting the cloud points from polymer solutions with different concentrations. The cloud point corresponds to the binodal or the coexistence curve of the ternary phase diagram.

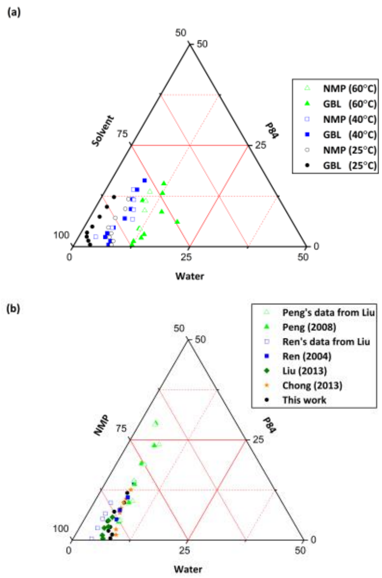

Figure 1: (a) Ternary phase diagram of PI/Solvents/Water system at 25, 40 and 60°C, (b) Ternary phase diagram of PI/NMP/Water compared to bibliography data at 25°C.

In the present work, the systems of polyimide (PI) polymer with NMP and GBL as organic solvents were studied as well as deionized water was used as non-solvent. The cloud point data were determined by the titration method. For this purpose, PI/NMP, PI/GBL, PI/GBL/NMP (Figure 1) solutions with PI concentration from 0.5 wt.% to 17.5 wt.% were prepared and the respective ternary phase diagrams were plotted at three equilibrium temperatures. As it is shown in Figure 1b, there are slight differences in the location of the binodal curve between our experimental results and the bibliographic data at 25°C. These differences may be attributed to inaccurate observation of the turbidity onset. Moreover, in the case of NMP solvent (Fig. 1a), the temperature has little effect on the experimental binodal curve (small shift from the PI-NMP axis, mainly at 60°C), whereas in the case of GBL solvent, the temperature has remarkable effect on this curve. Finally, the three systems presented differences concerning the needed amount of water in order to achieve phase separation in the system. The smallest amount of water needed was in the case of GBL solvent (1-3.5 wt.%), the highest for the NMP solvent (5-8 wt.%) and the intermediate for the NMP/GBL mixture (2.5-4.5 wt.%) at 25°C.

References: [1] A. Chong Lua, Y. Shen, *J. of Mem. Sci.* **429**, 155 (2013); [2] Li-Qi Liu et al., *Tex. Res. J.* **83**, 553 (2013); [3] J. Ren, Z. Li, F.-S. Wong, *J. of Mem. Sci*. **241**, 305 (2004); [4] N. Peng, T.-S. Chung, K.Y. Wang, *J. of Mem. Sci.* **318**, 363 (2008)