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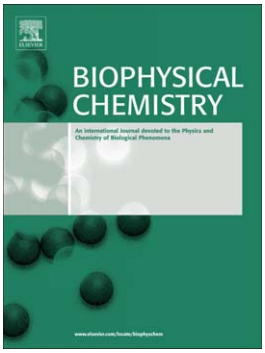

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Hydrostatic pressure effect on PNIPAM cononsolvency in water-methanol solutions

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Abstract

When methanol is added to water at room temperature and 1 atm, poly(*N*-isopropylacrylamide), PNIPAM, undergoes a coil-to-globule collapse transition. This intriguing phenomenon is called cononsolvency. Spectroscopic measurements have shown that application of high hydrostatic pressure destroys PNIPAM cononsolvency in water-methanol solutions. We have developed a theoretical approach that identifies the decrease in solvent-excluded volume effect as the driving force of PNIPAM collapse on increasing the temperature. The same approach indicates that cononsolvency, at room temperature and P = 1 atm, is caused by the inability of PNIPAM to make all the attractive energetic interactions that it could be engaged in, due to competition between water and methanol molecules. The present analysis suggests that high hydrostatic pressure destroys cononsolvency because the coil state becomes more compact, and the quantity measuring PNIPAM-solvent attractions increases in magnitude due to the solution density increase, and the ability of small water molecules to substitute methanol molecules on PNIPAM surface.

Key-words: PNIPAM; polymer collapse; cononsolvency; hydrostatic pressure.

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