Enhancement of Formation of Polar Microenvironment in Polymer by Compressed CO₂

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Abstract: The copolymer $(EO)_{22}(PO)_{52}(EO)_{22}$ in *p*-xylene can solubilize much more water in the presence of compressed CO₂ than the case without CO₂.

Keywords: Reverse micelles, polymer surfactant, carbon dioxide.

To date, polar microenvironments in apolar solvents have been successfully used in different ways, such as separation of proteins¹, enzymatic or catalytic reactions in reverse micelles². It is obvious that investigation of new method to create polar microenvironments is of great importance to both pure and applied sciences, and it is desirable that forming and breaking the microenvironments can be easily controlled. Compressed CO₂ can dissolve in many organic solvents and the solubility can be tuned continuously by its pressure³. Thus the solvent power of the solvents can be controlled by pressure. In this work, we studied the effect of compressed CO₂ on the solubilization of water in nonionic polymer (EO)₂₂(PO)₅₂(EO)₂₂ (P103) in *p*-xylene. It was found that compressed CO₂ could enhance the formation of polar microenvironment in the polymer.

The apparatus used was similar to that reported previously⁴. All experiments were carried out at 313.15 \pm 0.5 K. In a typical experiment, 5 g solution of the polymer in *p*-xylene and the desired amount of double distilled water were loaded into the high-pressure view cell. The stirrer was started and CO₂ was charged into the cell slowly after thermal equilibrium had been reached. With the addition of CO₂, the hazy and milky solution became transparent and completely clear as the pressure reached certain value, which is defined as dissolution pressure.

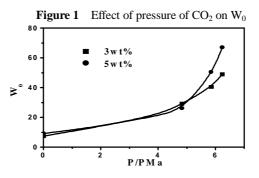
 W_0 , the molar ratio of excess water to polymer, can be used to characterize the amount of loaded water in the polar environments. In the calculation process of W_0 , the trace amount of water dissolved in the solvent at the same temperature and pressure has been corrected by subtracting the amount of water in the CO₂-saturated solvent from the corresponding polymer solution. The effect of CO₂ pressure on the W_0 of the polymer solutions of 3wt% and 5wt% is illustrated in **Figure 1**. The results in the **Figure** show that the W_0 increases slowly with increasing pressure in the lower pressure range.

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However, W_0 increases sharply with the increase of pressure as pressure is high enough. In other words, the CO₂ dissolved in the solvent can enhance the formation of polar microenvironment in the polymer. At suitable conditions W_0 can be as high as 67, *i.e.*, strong polar microenvironments are formed in the polymer molecules. The reasons for this interesting phenomenon need to be studied further. One of the main reasons may be that *p*-xylene is a good solvent for the polymer, and its hydrophilic-hydrophobic balance is not suitable to forming polar environment in the polymer. Thus the polymer is more extended in the solution. CO₂ is a poor solvent of the polymer, and dissolution of CO₂ reduces the solvent power of the solvent. It is well known that polymers become more coiled in poorer solvents, and the polar heads are closer in the coiled polymer molecules. Thus, dissolution of CO₂ is favorable to the formation of polar environment, which can solubilize more water.

Our experiments showed that the water solubilized could be precipitated after pressure was reduced, and was solubilized again after compression. Thus, in this new method, formation and breaking of the polar environment can be easily controlled by pressure of CO_2 , which is of special advantages for applications such as chemical reaction engineering, separation science, and nano-particle preparation.



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