Synthesis of Insoluble β -Cyclodextrin Polymer and Its Application in Removal of Surfactant in Aqueous Solution

Guangming Bai, Bin Xu [a]

College of Chemical Engineering and Safety, Binzhou University, Binzhou, 256600, China.

[a] cnxubin@126.com

Abstract

Insoluble β-cyclodextrin-epichlorohydrin polymers have received more and more attention in many kinds of environmental applications such as organic's removal in aqueous solutions. In this paper, an insoluble β-cyclodextrin-epichlorohydrin polymer was synthesized and the inclusion property toward surfactants was studied. The FT-IR results showed that the basic structural units of β-CD were preserved in insoluble β-CD polymer. The Uv-vis spectrometry results showed that phenolphthalein can be encapsulated in cyclodextrin cavity of the insoluble β-cyclodextrin polymer and the host-guest inclusion complex in aqueous solution was formed at a host: guest mole ratio of 1:1. Phenolphthalein can be released from cyclodextrin cavity under the competitive inclusion of SDS and the release rate of phenolphthalein increased with the increasing SDS/CD molar ratio. The above results exhibit a possible way to remove surfactants in aqueous solution.

Keywords

Insoluble β-Cyclodextrin polymer, surfactant, removal, inclusion, competitive Uv-Vis spectrometry.

1. Introduction

The discharge of chemical substances into environment has become a more and more serious problem all over the world. The pollutants can affect both water and soil quality and many pollutants exert toxic effects on the environment and humans. Increasingly strict legislation has been made to protect water resources [1]. As in petroleum industry, several kinds of chemical flooding methods were employed to enhance oil recovery [2] , such as polymer flooding [3], surfactant flooding [4], SP flooding [5], ASP flooding [6], etc. Due to the use of alkali, surfactant and polymer as flooding agents in the injected water, the produced liquid of the chemical flooding wells is seriously emulsified and hard to treat [7].

A lot of treatment methods for chemical flooding produced liquid have been reported and tested. These methods mainly include demulsification process to separate oil and water and the subsequent wastewater treatment process. Water-insoluble β-cyclodextrin-epichlorohydrin polymers have received more and more attention in many kinds of environmental applications recent years and the polymers show good prospects for application in organic's removal, recycling and utilization from aqueous solutions or gas [1].

In this paper, a kind of insoluble β-cyclodextrin polymer was synthesized and the inclusion property of the insoluble β-cyclodextrin polymer toward surfactants was studied using competitive Uv-vis spectrometry to find a possible way to remove surfactants in aqueous solution.

2. Experimental

2.1 Materials

Acrylamide (AM, AR) was twice recrystallized from acetone (AR) and then dried under vacuum. β-cyclodextrin (β-CD, AR), epichlorohydrin and (EP, AR), sodium hydroxide (NaOH, AR), sodium carbonate (Na_2CO_3, AR), sodium bicarbonate ($NaHCO_3$, AR), phenolphthalein (PP, AR), Sodium dodecyl sulphate (SDS, AR) and ethanol (AR) were obtained from Sino pharm Chemical Reagent Co., Ltd. SDS was twice recrystallized from ethanol. All aqueous solutions were prepared using deionized water.

2.2 Synthesis of Insoluble B-Cyclodextrin Polymer

Preparation of water insoluble β-CD polymers (β-CD-EP polymer) was achieved by the reaction of β-CD with epichlorohydrin (EP) in an alkaline medium by a two-step procedure [8]. The polycondensation conditions are: EP/B-CD = 10, NaOH =33%, T= 30°C, t = 300 min. The products were washed and purified by excessive acetone for 3 times and then dried in vacuum at 45 ℃ for 48 h.

2.3 Inclusion Interaction of Insoluble B-CD Polymer and Surfactant By Competitive UV-Vis Spectrophtometric Method

The competitive UV-Vis spectrophtometric method was applied to study the inclusion interaction and determine the inclusion constant of β-CD derivatives with surfactant using phenolphthalein (PP) as a spectral probe in aqueous buffer solution (pH=10.50) at room temperature.

3. Results and Discussion

FT-IR spectra of the synthesized insoluble β-CD polymer shown in Fig. 1. The peaks of O-H stretching vibration (3419 cm^{-1}), C-H stretching (2925 cm^{-1}), C-H deformation vibration at 1412 cm^{-1} and C-H deformation vibrations and glucopyranose stretching vibrations at 938 cm^{-1}, 851 cm^{-1} were observed. The results showed that the basic structural units of β-CD were preserved in insoluble β-CD polymer.

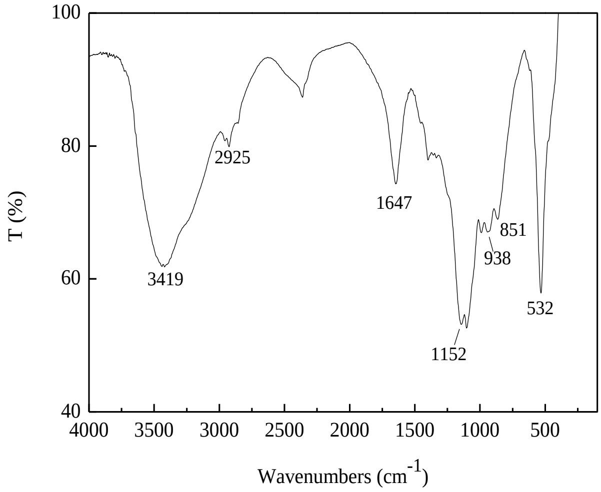
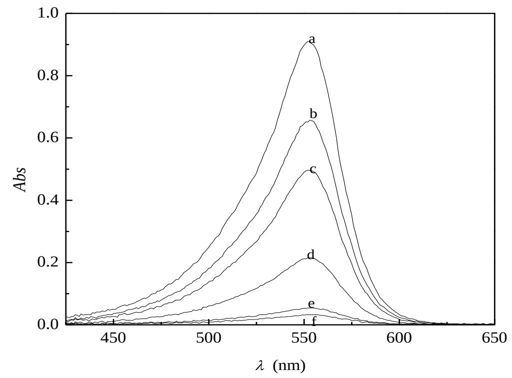


Fig. 1 FT-IR spectrum of β-CD-EP microsphere

Fig. 2 showed the Uv-vis spectrum of phenolphthalein with and without insoluble β-CD polymer. The absorbance of phenolphthalein fell down with the increasing β-CD-EP polymer concentration which indicated that phenolphthalein can be encapsulated in cyclodextrin cavity.



a.3.000×10^{-5} mol/L PP; b. a+1.000×10^{-5} mol/L β-CD-EP; c. a+2.000×10^{-5} mol/L β-CD-EP; d. a+3.000×10^{-5} mol/L β-CD-EP; e. a+4.000×10^{-5} mol/L β-CD-EP; f. a+5.000 ×10^{-5} mol/L β-CD-EP

Fig. 2 Uv-vis spectrum of phenolphthalein with and without insoluble β-CD polymer

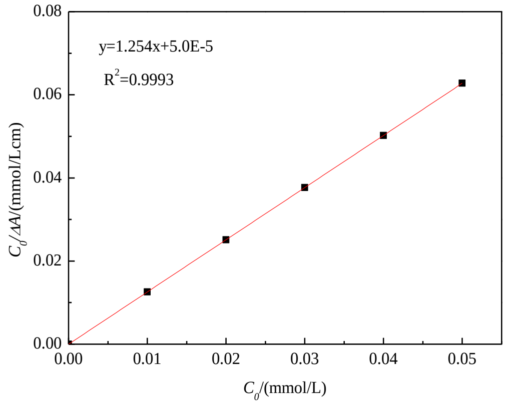


Fig. 3 $C_{\beta\text{-CD-EP, 0}}$ /ΔA as a function of $C_{\beta\text{-CD-EP, 0}}$ of insoluble β-CD-EP polymer /PP inclusion system

Fig. 3 showed the linear regression curve by mapping $C_{\beta\text{-CD-EP, 0}}/\Delta A$ with $C_{\beta\text{-CD-EP, 0}}$ of insoluble β-CD-EP polymer/phenolphthalein inclusion system. The linear relationship showed that the host-guest inclusion complex in aqueous solution was formed at a host:guest mole ratio of 1:1.

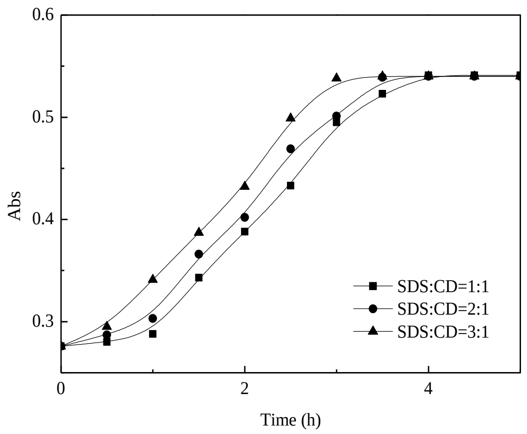


Fig. 4 The absorbance of insoluble β-CD-EP polymer/phenolphthalein inclusion system with SDS

Fig. 4 showed the absorbance of insoluble β-CD-EP polymer/phenolphthalein inclusion system with SDS at different SDS/CD molar ratios. The results showed that phenolphthalein can be released from cyclodextrin cavity under the competitive inclusion of SDS and the release rate of phenolphthalein increased with the increasing SDS/CD molar ratio.

4. Conclusion

Insoluble β-cyclodextrin-epichlorohydrin polymer was synthesized in an alkaline medium. The basic structural units of β-CD were preserved in insoluble β-CD polymer. Phenolphthalein can be encapsulated in cyclodextrin cavity of the insoluble β-cyclodextrin polymer and the host-guest inclusion complex in aqueous solution was formed at a host: guest mole ratio of 1:1. phenolphthalein can be released from cyclodextrin cavity under the competitive inclusion of SDS and the release rate of phenolphthalein increased with the increasing SDS/CD molar ratio.

Acknowledgements

This research was supported by National Training Program of Innovation and Entrepreneurship for Undergraduates (No. 201610449036) and the Major Project Foundation of Binzhou University (2017ZDL01).

References

[1] N. Morin-Crini, G. Crini. Environmental applications of water-insoluble β-cyclodextrin-epichlorohydrin polymers. Prog. Polym. Sci., Vol. 38 (2013) No. 2, p. 344-368.
[2] V. Alvarado, E. Manrique. Enhanced Oil Recovery: An Update Review. Energies, Vol. 3 (2010) No. 9, p.1529-1575.
[3] J.J. Sheng, B. Leonhardt, N. Azri. Status of Polymer-Flooding Technology. J. Can. Petrol. Technol., Vol. 54 (2015) No. 2, p. 116-126.
[4] Q. Liu, M. Dong, S. Ma, et al. Surfactant enhanced alkaline flooding for western Canadian heavy oil recovery. Colloid Surface A, Vol. 293(2007) No. 1-3, p.63-71.
[5] H. Liu, Y. Zhang, Y. Li, et al. Influence on emulsification in binary flooding of oil displacement effect. J. Disper. Sci. Technol., Vol. 37(2016), No. 1, p. 89-96.
[6] J. Hou, Z. Liu, M. Dong, et al. Effect of Viscosity of Alkaline/Surfactant/ Polymer (ASP) Solution on Enhanced Oil Recovery in Heterogeneous Reservoirs. J. Can. Petrol. Technol., Vol. 45(2006) No.11, p. 27-33.
[7] S. Deng, G. Yu, Z. Jiang, et al. Destabilization of oil droplets in produced water from asp flooding. Colloid Surface A, Vol. 252(2005) No. 2-3, p. 113-119.
[8] E. Renard, A. Deratani, G Volet, et al. Preparation and characterization of water soluble high molecular weight β-cyclodextrin-epichlorohydrin polymers. Eur. Polym. J., Vol. 33(1997) No. 1, p. 49-57.