Efficient one-pot conversion of biomass to ethanol in liquid zwitterion/ DMSO mixtures

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我々はこれまでに、常温で液体のカルボン酸系 liquid zwitterion（OE_2imC_3C）が「セルロース溶解能」および「低毒性」という性質を有することから、ワンポットエタノール発酵を達成した。しかし、OE_2imC_3C は粘性が非常に高く、セルロースの溶解量が限られている。そこで本検討ではジメチルスルホキシド（DMSO）を共溶媒として加え、粘性の低下を試みた。その結果、より多くのセルロースを溶解できた。また、DMSO を加えることで溶液の毒性を低下させることもできた。

1. Introduction

Ionic liquids (ILs) can dissolve cellulose efficiently. However ILs are toxic to microorganisms, because cation inserts into hydrophobic part of lipid bilayer membrane of microorganisms.[1)] We have developed a carboxylic acid-type of liquid zwitterion (ZI), OE_2imC_3C (Figure 1), which satisfy both low toxicity and dissolution of cellulose. This advantage allows a one-pot conversion process of biomass into ethanol via pretreatment, hydrolysis, and fermentation. However, the OE_2imC_3C has a problem: high viscosity. In this study, a co-solvent, dimethyl sulfoxide (DMSO), was added to decrease the viscosity.

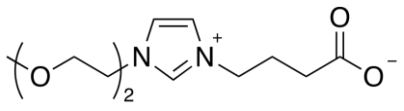

Figure 1. A structure of OE_2imC_3C.

2. Experimental

We used a recombinant *Escherichia coli* (*E. coli*) KO11, which can convert glucose into ethanol, for growth assay. Growth assay was conducted in LB medium containing of various concentration of OE_2imC_3C/DMSO.

3. Result and Discussion

Cellulose dissolution into OE_2imC_3C/DMSO mixtures

A pure solution of OE_2imC_3C dissolved cellulose at 100 ºC. However, the solution cannot to be stirred anymore after dissolving 1 wt% of cellulose due to its high viscosity. Therefore, we could not confirm whether over 1 wt% of cellulose can be dissolved or not. On the other hand, DMSO accelerates the dissolution of cellulose: OE_2imC_3C with 40 wt% of DMSO can dissolve cellulose up to 12 wt%. Dissolution ability of OE_2imC_3C/DMSO mixtures decreased when over 40 wt% of DMSO was added. To clarify the reason for this phenomenon, we investigated the viscosity and hydrogen bonding basicity (β value of Kamlet-Taft parameters). The viscosity almost exponentially decreased

with adding DMSO: this is the reason for high dissolution ability of the OE_2imC_3C/DMSO (60/40) mixture. From viewpoint of polarity, β value somewhat decreased when 80 wt% of DMSO was added: this may be a reason for low dissolution ability of the OE_2imC_3C/DMSO (20/80) mixture.

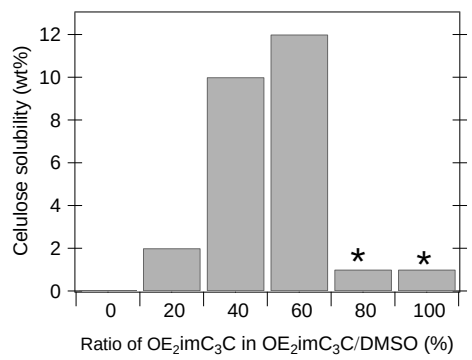

Figure 2. Dissolution of cellulose in mixture of OE_2imC_3C/DMSO (%) at 100ºC. *cellulose solubility cannot be confirmed clearly due to high viscosity.

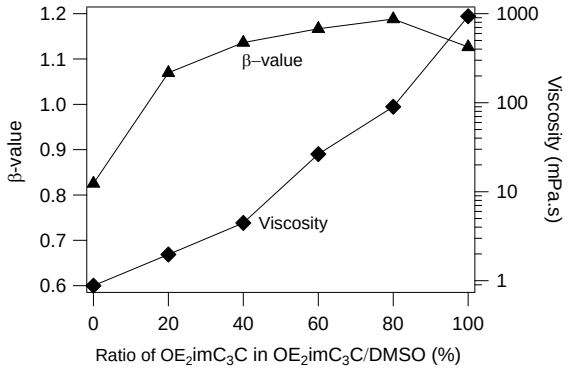

Figure 3. Viscosity and β–value of mixtures OE_2imC_3C/DMSO. The viscosity was measured at 80 ºC.

<u>Toxicity of OE_2imC_3C/DMSO mixtures to *E. coli* KO11</u>

Toxicity was investigated with EC_{50}, which is a critical concentration of chemical compounds for growth of microorganisms. Toxicity of OE_2imC_3C to *E. coli* KO11 was lower than that of DMSO despite that DMSO is known as a low toxic organic solvent. Therefore addition of DMSO is expected to cause decrease of EC_{50}. However, 20 wt% of DMSO increased EC_{50} of the mixture, compared to pure OE_2imC_3C. The reason may be as follows: mechanisms to show toxicity of OE_2imC_3C and DMSO are different, and tolerances of *E. coli* KO11 to OE_2imC_3C and DMSO are independent. We will discuss about it in detail in poster session.

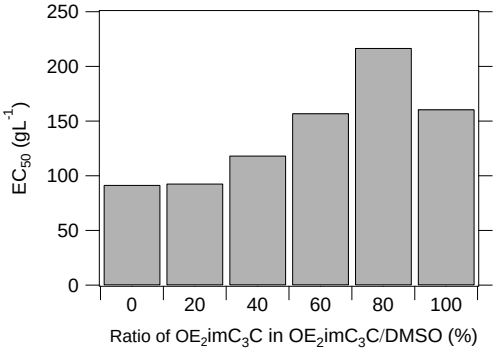

Figure 3. EC_{50} of OE_2imC_3C/DMSO mixtures to *E.coli* KO11.

4. Reference

1) G.S. Lim, J. Zidar, D.W. Cheong, S. Jaenicke, M. Klähn, J. Phys. Chem B., 2014, 118, 10444-10459.

5. Acknowledgements

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