Synthesis and Characterization of Oil-Soluble Dispersants

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Abstract

Dispersants are important additives in the oil industry. A type of oil-soluble dispersants consisting of a polyamine and two polyisobutylene chains will be synthesized and their efficiency for stabilizing carbon-rich particles found in engine oils will be investigated. This efficiency can be described as "associative strength", which represents the dispersant ability to self-associate in solution into reverse micelles. It will be characterized by determining the critical micelle concentration (CMC). These studies are expected to provide a correlation between the structure and the efficiency of the dispersants.

Introduction

Over time, carbonaceous deposits composed of carbon-rich particles are produced during the normal operation of the engine. The role of a dispersant is to adsorb onto the polar surface of the particles and reduce the driving force towards aggregation. As two particles coated with dispersant get close, interpenetration of the shells occurs, resulting in the non-polar layer loosing disorder which is thermodynamically unfavorable. This further leads to interparticle repulsion, or in other words, stabilization of the particles.

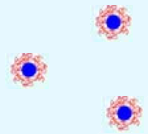


Fig. 1 CRPs coated with dispersant

deposit formation without dispersant

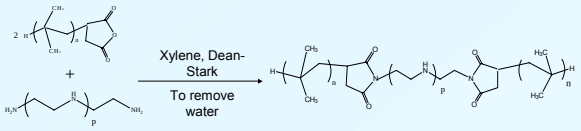
no deposit formation with dispersant

Fig. 2 Comparison of Intake valve of a Mercedes Benz M102E engine after 60 test hours

Proposal

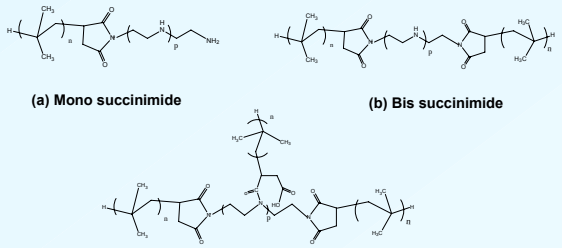
In this project, a family of succinimide dispersants will be studied. They are BAB triblock copolymers synthesized by reacting polyamines with polyisobutylene terminated with one succinic anhydride at one end (PIBSA).

Scheme 1 Synthesis of the dispersants (p=0-3)



Characterization of Dispersant

The reaction with polyamines exhibiting secondary amines can generate several structures, so that the dispersant becomes a mixture of succinimide derivatives. The proportion of each derivative in the dispersant mixture can be determined by FT-IR and UV-vis absorption.



(a) Mono succinimide **(b) Bis succinimide**

(c) Tris succinimide

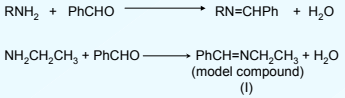
Fig. 3 Mono-, bis-, and tris- succinimide derivatives

➢ **Characterization of succinimide content by FT-IR**

(Internal Standard) + polyisobutylene (PIB)

The succinimide content of the dispersant can be determined by a calibration curve correlating the absorption ratio (1717cm^{-1} / 1390 cm^{-1}) with the concentration of methyl succinimide.

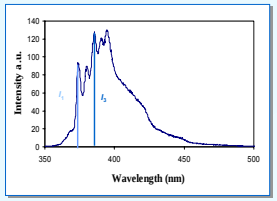
➢ **Characterization of primary amine content by UV-vis absorption**



The model compound (I) will be used to determine the extinction coefficient of benzylidene.

Scheme 2 Characterization of succinimide derivatives

Characterization of the Associative Strength of the Dispersant



The ratio of the fluorescence intensity I_1/I_3 is a parameter sensitive to the polarity of the environment of the chromophore.

Fig. 4 Steady-state fluorescence spectrum of 1-pyrenemethanol excited at λ_{ex} = 344 nm

At CMC, a sudden change occurs in the fluorescence spectrum due to the partial association of the chromophore with the reverse micelles.

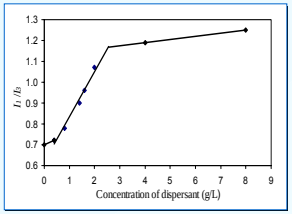
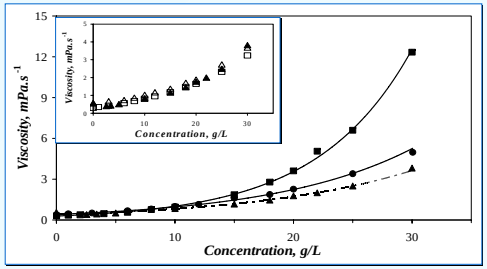


Fig. 5 Determination of the CMC of the dispersant with 1-pyrenemethanol



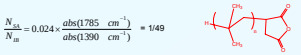
Viscosity of Py-EP (solid traces) and naked EP (dashed traces). Py-EP in hexane (■), toluene (▲), and hexane/toluene mixture (70 vol% hexane) (●), naked EP in hexane (□) and toluene (△).

Fig. 6 Effect of aromatic compounds in oil

An increase of the content of aromatic compounds has been shown to result in a viscosity decrease in the presence of a dispersant. This is believe to be due to a decrease in the associative strength of the dispersant when aromatics are present in the oils (cf. Fig. 6).Toluene will be used as a mimic of the aromatic compounds found in oils, and the effect of its concentration on the CMC of the dispersants will be investigated.

Preliminary Results

Determination of the number of isobutylene (IB) units in PIBSA



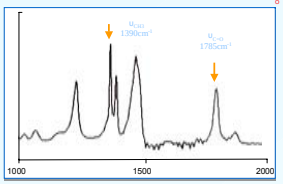


Fig. 7 Determination of PIB units by FT-IR

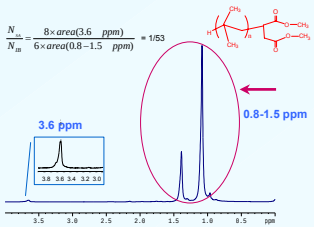


Fig. 8 Determination of PIB units by ^{1}H NMR through methylation

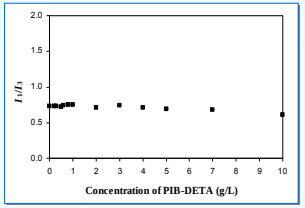


Fig. 9 CMC measurement of PIB-DETA synthesized by PIBSA and diethylenetriamine

Conclusion

- The number of isobutylene units in polyisobutylene succinic anhydride has been calculated.
- There is no polar microdomain generated in hexane by the dispersant PIB-DETA.

Acknowledgements

➢Imperial Oil

www.basf.com/automotive-oil
Zhang M. Z; Duhamel J Macromolecules 2005, ASAP
Mathew, A. K.; Internal Report to Imperial Oil, Nov. 17, 1999