# Evidence of the adsorption of hydroxide ion at hexadecane/water interface from SHG study

Hui Fang, Wei Wu, Yajun Sang, Shunli Chen, Xuefeng Zhu, Libo Zhang, Yuanyuan Niuab and Wei Gan RSC Adv., 2015, 5, 23578

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### Motivation

<u>Known</u>: oil/water interfaces are negatively charged without the addition of any ionic surfactant and this negative charge increases rapidly with pH value and therefore with the bulk concentration of hydroxide ions

"Why Are Hydrophobic/Water Interfaces Negatively Charged?" – due to the hydroxide ions adsorb at hydrophobic/water interfaces (according to SFG spectroscopy (Jena, Angew. Chem. Int. Ed. 2012) and electrophoretic mobility (Roger, Angew. Chem. Int. Ed. 2012) measurements).



<u>Question:</u> whether the negative potential arises from the pure hexadecane/water interface or is induced by longchain carboxylic acid impurities in the hexadecane.

### Introduction

- <u>SHG</u> (total internal reflection geometry setup) was used to detect the influence of impurities in hexadecane at the hexadecane/water interface.
- <u>Oleic acid</u> was used as a model impurity.



CH<sub>37</sub>CH=CH<sub>7</sub>COOH

• Hexadecane (with 99% purity) was purified by <u>basic alumina columns</u>.



 $CH_{3}-(CH_{2})_{14}-CH_{3}$ 

# SH intensity at the hexadecane/water (pH = 7) interface affected by carboxylic acid and chemical impurities



5 passes through the basic alumina columns (Hexadecane5) reduced the amount of impurities

# SH intensity at the hexadecane/water (pH = 12) interface affected by carboxylic acid and chemical impurities

pH of the water phase was to 12 to investigate the influence of the impurities in hexadecane on the SH intensity.





The increase in the SH intensity is attributable mainly to the effect of OH<sup>-</sup> and not Na<sup>+</sup>.

The SH increased when the aqueous phase pH was changed from neutral to 12 due to the effect of OH<sup>-</sup> on the interfacial charge and molecular structure of water.

The reorientation of water molecules with their hydrogen atoms directed toward the oil phase.

### SH intensity at the hexadecane/water pH=7 and pH=12



Is the SHG radiation from the hexadecane/water interface from ordered water molecules, hexadecane molecules, or from both?

The changes in the SH signal may be from changes in <u>the surface potential and the orientational</u> <u>order of the interfacial molecules</u> or <u>the adsorbed oleic acid</u>.

### Conclusions

- The presence of impurities in the as-received hexadecane affected the molecular structure at the hexadecane/water interface
- The results provide <u>new evidence of the adsorption of OH<sup>-</sup> at oil/water interfaces</u>.



The interfacial tension of the hexadecane/water interface was also measured by the platinum slice method with an automatic tension meter.



No difference between Hexadecane3, Hexadecane4, Hexadecane5 and Hexadecane6 indicate that the interfacial tension is less sensitive to the impurities in hexadecane compared with the SHG signal

#### Purification with alumina columns

- 100 g alumina (100–200 mesh) was filled in a column shaped valval funnel with fritted disc.
- One pass through a basic alumina column: wash the column with 75 ml hexadecane to wash the column, then the column was used to purify no more than 1000 ml hexadecane with a flow speed of approximately 2 ml/min.



#### SHG (total internal reflection geometry setup)



Richmond, J. Phys. Chem. 1994

fundamental beam - 810 nm

incident angle 70°

laser power - 150 mW

high-voltage supply for the PMT -1000 V

the sample was left for 30–60 min until the SH intensity became stable