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Effect of chemical reaction causing contact angle variation on the spontaneous motion of an I<sub>2</sub>-containing nitrobenzene droplet



# O Aim of study

Quantification of droplet motion

Previous researchers have presented discussions using only phase diagrams indicating the existence/non-existence of motion or the type of motion.

Determination of chemical components

Previous researchers investigated this phenomenon using a physical or mathematical approach.

Verification of proposed mechanism



#### Quantitative determination of droplet motion





The rotational direction was not constant.

The droplet ran on the glass substrate at a constant velocity.

- $I_2$  concentration in oil droplet
  - : Absorptiometry (550 nm) or RGB value analysis
- Iodic ion (I<sup>-</sup>, I<sub>3</sub><sup>-</sup>, IO<sub>3</sub><sup>-</sup>) concentration in aqueous solution
   : Ion chromatography

#### Running distance and duration of motion

Droplet motion was observed under alkaline conditions with the addition of NaOH, although no remarkable motion was observed in an aqueous solution of NaCl or HCl.



An intermittent motion consisting of the running state and resting state was exhibited below 0.8 mM.

The running distance and duration increased with increasing NaOH conc.

Iodine disproportionate in the alkaline conditions

 $I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$ 

The droplet motion was probably induced by the ionic association between TSA<sup>+</sup> and **iodic ions** such as I<sup>-</sup> and  $IO_3^-$ .

#### Quantitative determination of chemical components



The mass balance between  $I_2$  and  $I^-$  was not break-even.

 $I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$ 

The formed I<sup>-</sup> would induce further reaction with  $I_2$ on the oil–water interface to produce  $I_3^-$ :

 $\mathrm{I_2} + \mathrm{I^-} \rightarrow \mathrm{I_3^-}$ 

The contributions of I<sup>-</sup> and  $I_3^-$  to the consumption of  $I_2$  are almost equal.

The presence of  $I^-$  in aqueous solution was only identified in the system without TSA<sup>+</sup>.

*Matsushita et al.* reported in relation to the formation of TSA-I in a similar system. *Colloid Surface A* 395 (2012) 233.

These results support the reaction between TSA<sup>+</sup> and I<sup>-</sup> at the interface.



## **I**<sub>2</sub> consumption rate



These results agree well with the prediction that the reaction between TSA<sup>+</sup> and iodic ions at the interface induces the droplet motion.

The consumption rate of  $I_2$  increased with increasing NaOH conc.

The concentration equilibrium was achieved earlier under the condition of higher NaOH conc.

The rate of  ${\rm I_2}$  consumption correlated with the velocity of droplet motion.



## O Droplet contact angle

For discussion in terms of the variation of the interfacial energy of oil–glass interface, we considered the interfacial tensions and contact angles within the three phase water–oil–glass substrate in this study.



The oil droplet contact angle stayed high (~160 deg) in the aqueous solution without surfactant TSAC.



### Variation of contact angle



The contact angle would be controlled by competition between TSA<sup>+</sup> adsorption on the oil–glass interface and the ion aggregation derived from iodic ion generation.

$$I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$$



The interfacial energy increased with more TSA<sup>+</sup> desorbing from the oil–glass interface.

In fact, the contact angle in the aqueous solution without TSAC corresponded with the upper limit.



The interfacial energy decreased with more TSA<sup>+</sup> adsorption on the oil–glass interface.

 $I_{\rm 2}$  was consumed over time, becoming scarce for the ion aggregation with TSA+.

#### **Difference of interfacial tensions**



However, the left side of equation was smaller than the right side .

Young's equation

$\gamma_{\rm ow} \cos \theta_{\rm wso} + \gamma_{\rm so} = \gamma_{\rm sw}$	
Yow	oil-water interfacial tension
$\gamma_{\rm SW}$	substrate-water
$\gamma_{\rm SO}$	substrate-oil
$ heta_{wso}$	contact angle of droplet

The difference of interfacial tensions generated around the oil droplet at non-equilibrium.

$$\Delta F = \gamma_{sw} - \gamma_{ow} \cos \theta_{wso} - \gamma_{so}$$

$$\gamma_{sw} = \gamma_{sa} - \gamma_{aw} \cos \theta_{asw}$$

$$\gamma_{so} = \gamma_{sa} - \gamma_{ao} \cos \theta_{aso}$$
Young's equation in air
$$\Delta F = \gamma_{ao} \cos \theta_{aso} - \gamma_{ow} \cos \theta_{wso} - \gamma_{aw} \cos \theta_{asw}$$

## Effect of △*F* on droplet motion



The **threshold** for the occurrence of droplet motion existed.

 $\Delta F_{\rm th} \approx 23.5 \ {\rm mN \ m^{-1}}$ 

 $\Delta F$  increased to almost 50 mN m<sup>-1</sup> with increasing NaOH conc.

 $\Delta F$  increased slightly with increasing NaCl conc. under the condition with addition of NaCl in which the droplet motion was not observed.

 $\Delta F$  was not 0 mN m<sup>-1</sup>, even in the case without droplet motion.



## Trigger for droplet motion

We expect that a small trigger exists for the deformation of oil droplets, called "contact angle hysteresis". such as...

1 An instability of droplet during the injection

(2) The interfacial instability caused by the interfacial reaction

③ The generation of emulsion around the droplet.



#### 17 msec/frame

# **Conclusion**

**(1)** Iodic ions such as I<sup>-</sup>, IO<sub>3</sub><sup>-</sup>, and I<sub>3</sub><sup>-</sup> were produced from the disproportionate reaction of I<sub>2</sub> under alkaline conditions.

② These ions reacted with cationic surfactant TSA<sup>+</sup> at the oil—water interface on the glass substrate.

③ The aggregate of these ions desorbed from the glass surface. The oil–glass interfacial tension increased.

**④** The oil droplet contact angle increased.

**(5)** The disruption of balance of the interfacial tension around the droplet induced spontaneous droplet motion.

