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journal or publication title	214th Meeting of the Electrochemical Society
page range	93
year	2008-10
URL	http://hdl.handle.net/10098/5211

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An air bubble mounted on an oil | water interface is a probe not only of interfacial tension but also of properties of three-phase boundary reactions. Our electrochemical cell consisted of tetramethylammonium perchlorate(TBAP)-including hemispherical nitrobenzene (NB) droplet on the glassy carbon (GC) electrode which was immersed in the aqueous solution containing sodium dodecyl sulfate (SDS). An air bubble was injected near the oil | water boundary. For [SDS] > 20mM, the bubble less than 0.3 mm in diameter kept spontaneously moving on the oil|water interface without applying any force, as is shown Fig.1 for translational motion of the bubble. The motion was irregular without decay, suggesting a contribution of Brownian motion. The bubble motion was taken by a microscope. The trajectory of the bubble by dividing the movie into each frame was obtained for several values of a bubble size and the velocity. The trajectory length was proportional to the lapse, indicating a constant average speed of the motion (Fig.2). The velocity of bubble motion was inversely proportional to a surface area of the bubble (Fig.3).

The motion may be related with interfacial tension. In order to control the potential in the oil phase, we added salt in the oil. The motion was slow down when potential was applied. However, it was difficult to find unambiguous dependence of the motion speed on potential. Clearer effects on potential were observed when ferrocene was included in oil.

When the oil droplet contained ferrocene, the voltammogram showed an anodic wave with slight hysteresis (Fig.4). This wave is ascribed to the oxidation of ferrocene to ferricenium ion. No oxidation should occur at the oil|electrode interface because of no ability of forming a double layer at this interface. No oxidation should occur either at the water|electrode interface because of absence of ferrocene in the aqueous phase. Therefore it is only the three-phase boundary which can coexist with an electric double layer ferrocene [1].

When the three-phase boundary reaction occurred, the bubble motion stopped. It was observed only in the potential domain at which ferrocene is oxidized. According to the previous work [2] on such a large air bubble that motion was not observed, the bubble moved downward in the potential domain of the oxidation of ferrocene. The down-shift has been attributed to the transfer of SDS adsorbed on the oil|water interface toward the bubble, which accumulated SDS around the bubble. This transfer of SDS may prevent instability of the adsorbed SDS layer.

[1] K.Aoki, M. Satoh, J.Chen, T. Nishiumi J. Electroanal. Chem.,595(2006)103-108.

[2] M.Satoh, K.Aoki, J.Chen, Langmuir, in press & proof 2/19

(A) (B)
Fig.1 Photograph of the TBAP-included nitrobenzene droplet on the GC electrode in 30 mM SDS aqueous solution. The sphere on the oil droplet was an air bubble. (B) was photograph after 1second from (A).

Fig.2 Σx is the cumulative sum of the length of trajectory of the motion of air bubbles $\bullet$ 0.10 mm, $\triangle$ 0.15 mm, $+$ 0.11 mm, $\times$ 0.21 mm, $\diamond$ 0.05 mm in radii.

Fig.3 Proportionality of the velocity of the bubble motion with the inverse of surface area of the bubble 30 mM SDS aqueous solution.

Fig.4 Cyclic voltammogram of the 10 mM ferrocene.