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# Self-Dispersion of Mercury Droplets from Saturated Calomel Electrodes into Solutions

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When mercury metal comes in quiescent contact with aqueous solution, it disperses spontaneously into the solution in micro-droplets form (J. Electroanal. Chem. 682 (2012) 66). The self-dispersion may occur from a saturated calomel electrode (SCE). This report deals with quantitative determination of mercury droplets dispersed in the solution to which the SCE was immersed quiescently for a day. The detection technique was anodic striping voltammetry at a gold electrode on which amalgam was formed spontaneously. The stripping anodic current was proportional to the periods of immersing the electrode into the solution. Calibration was made in the suspension of known concentration of mercury droplets. The concentration of self-dispersed mercury was 7 mg dm$^{-3}$ or 0.036 mmol dm$^{-3}$, which was by four orders of magnitude larger than the acceptable concentration limit in rivers.

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**Keywords:** dispersed mercury droplets; self-emulsification; saturated calomel electrodes; anodic stripping voltammetry

## 1. INTRODUCTION

Forced mixing of two immiscible solutions generates emulsions, which are unstable thermodynamically to be separated to the two phases in time [1]. Emulsions are sometimes formed even by quiescent contact of the two phases without surfactant, the process being called self-emulsification [2-8]. Emulsions are often not noticed, partly because the droplets are too small to be detected optically and partly because they are localized near the interface under quiescent conditions. Emulsifications have been sensed as unexpected electrochemical responses associated with an abnormal delay [9-12], fluctuation [13,14], pulse [15], and convection [5]. These responses are irreproducible or uncontrollable, because size and the number concentrations of droplets vary with conditions complicatedly.

Spontaneous dispersion has been observed not only for oil|water interfaces but also for gas|water interfaces [16] and mercury|water interfaces [17]. The latter can be readily inferred from the polarographic behavior which causes convection to yield polarographic maximum currents [18], as demonstrated by local velocity profiles [19,20]. The dispersion of mercury in water has also been recognized in the fields of environmental chemistry [21,22], instrumental analytical techniques [23,24] and public health [25-27].

A saturated calomel electrode (SCE) has the interfaces of Hg|$Hg_2Cl_2$ and $Hg_2Cl_2$|KCl solution. Since mercury in a SCE comes into a direct contact with the solution, mercury droplets may be formed in KCl solution, and be dispersed to solution phase through glass filter. The present report is concerned with quantitative determination of mercury droplets in solution by stripping voltammetry at a gold electrode after a long immersion of a SCE with the advantage of fast amalgam formation [28].

## 2. EXPERIMENTAL

Potassium nitrate, perchloric acid and mercury metal were of analytical grade. Water was deionized and distilled. When mercury was left in water for a period longer than a half day, floating substance which seemed to be mercury oxide was gradually recognized on the water surface. The formation of the floating was avoided by purging air from solution with nitrogen gas. Mercury in the solution was kept in nitrogen atmosphere.

An aqueous suspension of mercury was prepared by applying ultrasonication to the mixture of 200 $cm^3$ 0.1 M $HClO_4$ + 0.05 M NaCl aqueous solution + a mercury drop (0.04 g) for 30 min under nitrogen atmosphere. Then the suspension was turbid immediately after the ultrasonication, but became transparent soon without any residue.

The working electrodes were a platinum disk and a gold disk 0.50 mm in diameter. The latter was fabricated by cutting a tip of a gold wire coated with a shrinkable tube. The platinum disk electrode 1.6 mm in diameter was commercially available (BAS, Tokyo). The reference electrode was a SCE, RE-2B (BAS, Tokyo). It has a glass tube (6 mm in diameter and 45 mm in length) between Hg|$Hg_2Cl_2$ and a glass filer, in which saturated KCl solution is filled. The counter electrode was a platinum coil. The size distribution of particles in the suspension was obtained with a dynamic light scattering (DLS) instrument (Malvern Zetasizer Nano-ZS, UK).

## 3. RESULTS AND DISCUSSION

### *3.1 Evidence of dispersed mercury droplets*

The SCE was immersed into the aqueous solution of 0.5 M (= mol $dm^{-3}$) $KNO_3$ for 20 h under nitrogen atmosphere. DLS was applied to an aliquot of this solution. Figure 1 shows the curve of the scattering light intensity vs. diameters of particles.

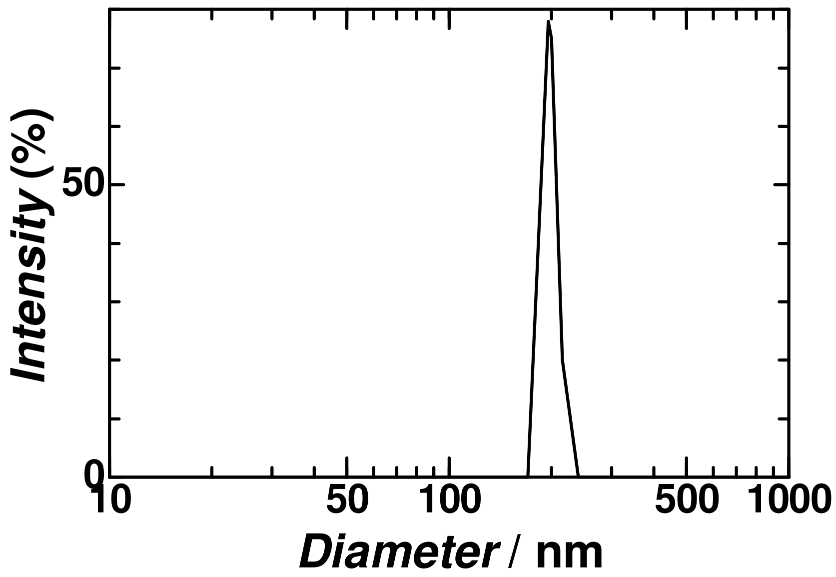

**Figure 1.** DLS signal of the solution into which the SCE was immersed.

One clear peak appeared for every sample at 0.3 ± 0.1 μm, where the error means the standard deviation. The well-defined peak indicates the presence of roughly uniform size-distribution of particles. The peak of the signal should be ascribed to either mercury droplets or particles of calomel. This value is close to 0.31 ± 0.04 μm of self-dispersed mercury droplets, which was formed by immersing a 0.04 g mercury drop into 0.5 M (= mol dm$^{-3}$) $KNO_3$ for one day [17].

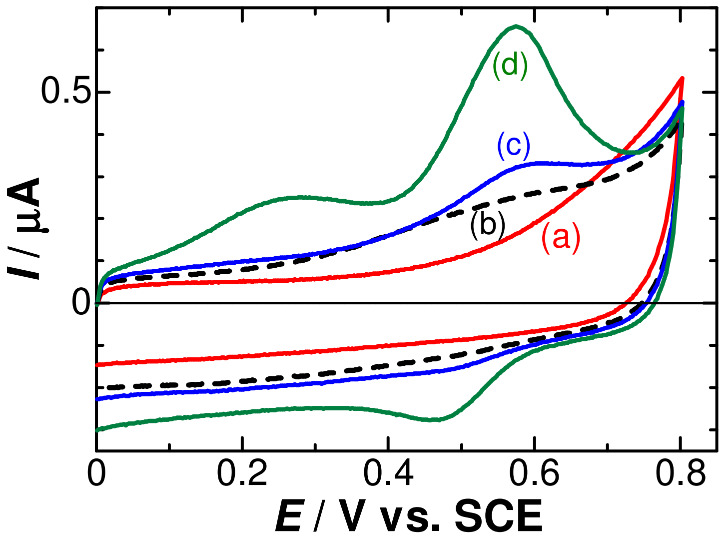

**Figure 2.** Cyclic voltammograms for $v$ = 0.1 V s$^{-1}$ in deaerated 0.5 M $KNO_3$ solution at the gold electrode (a) 0, (b) 30, (c) 50 and (d) 120 min after the gold electrode and the SCE were inserted into the solution.

### *3.2 Determination of concentration*

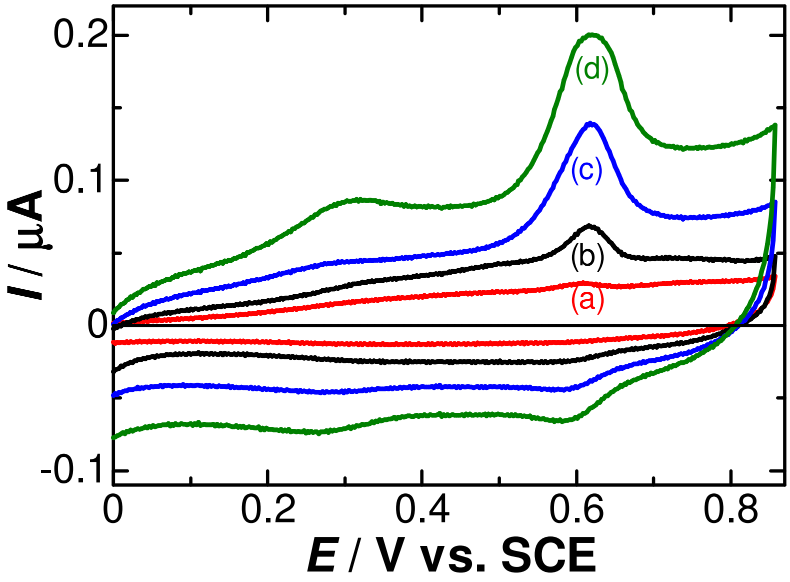

**Figure 3.** Cyclic voltammograms for $v$ = 0.1 V $s^{-1}$ in deaerated 0.5 M $KNO_3$ solution at the gold electrode which was immersed into the suspension for (a) 0, (b) 50, (c) 130 and (d) 170 s before each voltammetric run. They were obtained by use of the Ag|AgCl reference electrode, but the voltage was presented on the SCE scale.

We inserted the SCE into 0.5 M $KNO_3$ solution for one day under nitrogen atmosphere. The gold electrode was immersed into this solution in a given period for amalgam formation during bubbling nitrogen gas, and then anodic linear scan voltammetry was made in a fresh 0.5 M $KNO_3$ solution by use of the Ag|AgCl reference electrode. The electrode surface was renewed by cutting the electrode tip before each insertion of the SCE. Figure 3 shows voltammograms of the above solution after several immersion periods. A peak appeared at ca. 0.6 V, which is caused by oxidation of mercury [17]. The peak current increased with an increase in the immersion period, and the anodic wave at 0.3 V also increased. The latter wave disappeared when NaCl was added to the aliquot up to [NaCl] = 0.05 M, as was made previously [17]. Therefore the wave at 0.3 V may be due to the participation of $Cl^-$, which may leak from the reference electrode.

We took the net peak current by subtracting the linear background current in the domain from 0.5 to 0.8 V. The net peak current was proportional to the period of the immersion, as shown in Fig. 4. The proportionality implies that the mercury droplets should be supplied to the electrode with convection forced by bubbling of nitrogen gas. When the suspension was diluted by 25 times, the plot showed also the proportionality, of which slope was 25 times smaller than the former. Therefore the peak current represents quantitatively concentration of mercury droplets.

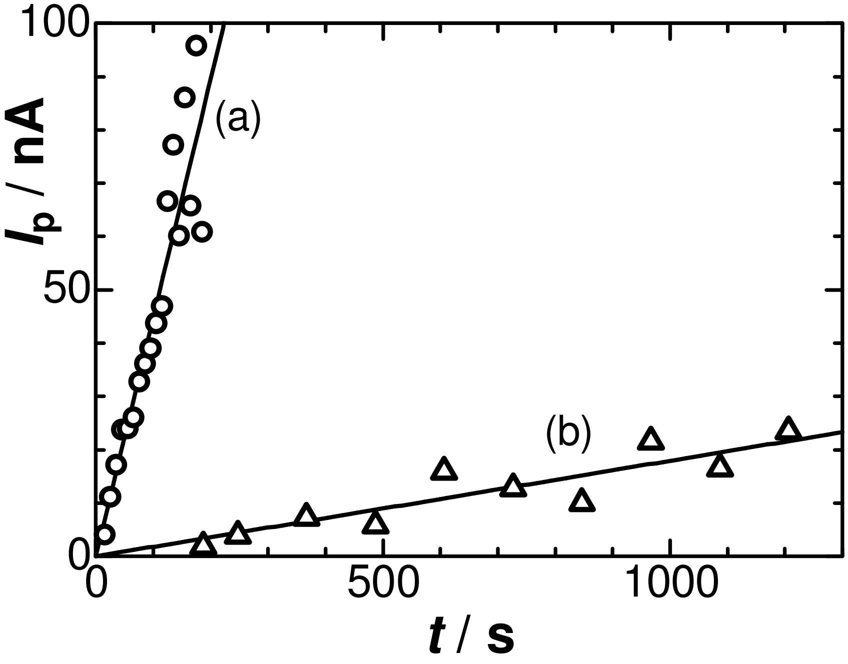

**Figure 4.** Plots of peak currents of anodic waves of stripping voltammograms against the periods of immersing the electrode into (a) the suspension of Fig. (3) and (b) the 25 times diluted suspension.

In order to determine the concentration of the self-dispersed mercury droplets, we prepared a suspension with known concentration by dispersing 4.61 mg mercury in 15 cm$^3$ $KNO_3$ solution with 10 min's ultrasonication. The concentration of this suspension would be 0.05 mM if the mercury were to be dissolved uniformly in the aqueous solution. Voltammograms of the suspension at the gold electrode were close to in Fig. 3. The net peak currents were proportional to the periods of immersing the electrode. The suspension diluted by 10 times showed the proportionality, of which slope was 10 times smaller than the above. Therefore the calibration line provides a quantitative relationship between the peak current and the concentration. Then the concentration of mercury leaking from the SCE is 0.036 mM or 7 mg / dm$^3$ water. This value is 30 times larger than the concentration at which a mercury drop 1 mm diameter was immersed in 2 cm$^3$ aqueous solution for one day [17], probably because the area of the Hg|solution boundary of the SCE is at least ten times larger than the area of the boundary in the previous experiment. The concentration (7 mg dm$^{-3}$) is by four orders of magnitude larger than the environmental limit 0.0005 mg dm$^{-3}$ of revers in Japan.

Anodic stripping determination of dispersed mercury droplets was made at the gold electrode but could not at the platinum electrode. Amalgam formation is obviously a key step of accumulating of mercury on the electrode. Amalgam is initially formed on the gold surface, and then it proceeds on the amalgamated gold. Therefore, the accumulating rate is predicted to decrease with the immersion time. We examined the relation between the amount of the amalgam and concentration of dispersed mercury instead of the relation between the accumulation rate with the time. Concentrations over ten times larger than 0.05 mM (4.61 mg / 15 $cm^3$ $KNO_3$) showed the saturated anodic charge of mercury deposit by the anodic stripping voltammetry. A constant amalgam formation rate is limited to the concentration less than 0.5 mM. The largest charge density in Fig. 3 is 0.5 μC $mm^{-2}$, which corresponds to $5\times10^{-10}$ mol $cm^{-2}$ or the occupied area of 0.3 $nm^2$ per mercury atom. These values suggest the monolayer formation of amalgam. Therefore, the proportionality in Fig. 4 is restricted to the thickness of the amalgam less than the monolayer. This fact may be relevant to selectivity of adsorption on amalgam electrodes and stability of amalgam [29-32].

## 4. CONCLUSIONS

A SCE disperses mercury droplets spontaneously into aqueous solution. The droplets are 0.3 μm in diameter, and are invisible. The dispersion can be observed not only DLS but also anodic stripping voltammetry in which deposition occurs spontaneously by amalgam formation at a gold electrode. The dispersion occurs by self-emulsification at the mercury|KCl solution interface in the SCE, and the droplets pass through the glass filter of the SCE. The concentration of dispersed mercury is 7 mg $dm^{-3}$ when the SCE was immersed for one day. It is extremely larger than the standard of the environmental limit.

## References

[1] A. W. Adamson, *Physical Chemistry of Surfaces*, 3rd ed. John Wiley & Sons, New York 1976, pp.491-508.
[2] Y. A. Shchipunov, O. Schmiedel, *Langmuir*, 12 (1996) 6443.
[3] S. Pautot, B. J. Frisken, J.-X. Cheng, X. S. Xie and D. A. Weitz, *Langmuir*, 19 (2003) 10281.
[4] H. Gonza´lez-Ochoa, L. Ibarra-Bracamontes and J. L. Arauz-Lara, *Langmuir*, 19 (2003) 7837.
[5] J. Chen and M. Satoh, *J. Electroanal. Chem.* 572 (2004) 153.
[6] K. Aoki, M. Li, J. Chen and T. Nishiumi, *Electrochem. Commn.* 11 (2009) 239.
[7] M. Li, K. Aoki, J. Chen and T. Nishiumi, *J. Electroanal. Chem.* 655 (2011) 159.
[8] S. Sacanna, W. K. Kegel and A. P. Philipse, *Langmuir*, 23 (2007) 10486.
[9] K. Maeda, S. Kihara, M. Suzuki and M. Matsui, *J. Electroanal. Chem.* 295 (1990) 183.
[10] Y. Shao, A.A. Atewart and H.H. Girault, *J. Chem. Soc. Faraday Trans.* 87 (1991) 2593.
[11] M. Tsionsky, A.J. Bard adn M.V. Mirkin, *J. Phys. Chem.* 100 (1996) 17881.
[12] W. Hyk and Z. Stojek, *J. Phys. Chem. B* 102 (1998) 577.
[13] K. Aoki, M. Satoh, J. Chen and T. Nishiumi, *J. Electroanal. Chem.* 595 (2006) 103.
[14] T. Kakiuchi, *Electrochem. Commun.* 2 (2000) 317.
[15] M. Nakagawa, N. Sezaki and T. Kakiuchi, *J. Electroanal. Chem.* 501 (2001) 260.
[16] K. Aoki, H. Toda, J. Yamamoto, J. Chen and T. Nishiumi, *J. Electroanal. Chem.* 668 (2012) 83.
[17] K. Aoki , C. Li, T. Nishiumi and J. Chen, *J. Electroanal. Chem.* 682 (2012) 66.
[18] J. Heyrovsky and J. Kuta, *Principles of Polarography*, Academic Press, New York, 1966, pp. 429-463
[19] R. N. O'Brien and F. P. Dieken, *Can. J. Chem.* 48 (1970) 2651.
[20] Md. M. Islam, T. Okajima and T. Ohsaka, *J. Electroanal. Chem.* 618 (2008) 1.
[21] M. C. Canela, W. F. Jardim and *J. Brazil. Chem. Soc.* 8 (1997) 421.
[22] D.Sarkar, *Envir. Geo.* 10 (2003) 151.

[23] E. Onat, *J. Inorg. Nuclear Chem.* 36 (1974) 2029.
[24] Yu.V. Zelyukova and T.O. Didorenko, *Zh. Anal. Khim.* 42 (1987) 1431.
[25] T. Okabe, J. Ferracane, C. Cooper, H. Matsumoto and M. Wagner, *J. Dent. Res.* 66 (1987) 33.
[26] M. Marek, *J. Dent. Res.* 69 (1990) 1167.
[27] Y. Takahashi, J. Hasegawa and Y. Kameyama, *Dent. Mat.* 5 (1989) 256.
[28] M. Vasjari, Y.M. Shirshov, A. V. Samoylov and V. M. Mirsky, *J. Electroanal. Chem.* 605 (2007) 73.
[29] B. Yosypchuk and V. Mareček, *J. Electroanal. Chem.* 653 (2011) 7.
[30] D. Deylova, V. Vyskocil and J. Barek, *Electrochim. Acta* 62 (2012) 335.
[31] R. Piech and W. W. Kubiak, *Electrochim. Acta* 53 (2007) 584.
[32] M. Prato, C. Toccafondi, G. Maidecchi, V. Chaudhari, M.N. K. Harish, S. Sampath, R. Parodi, V.A. Esaulov and M. Canepa, *J. Phys. Chem. C*, 116 (2012) 2431.