Studies on the Coalescence of Liquid Droplets

Part I. The Influence of the Polarizing Potential on the Coalescence of Mercury Droplets in Oil Solutions

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In order to study the dispersion and coagulation on the hydrophobic disperse system in the non-aqueous solution and emulsion, the range of the electrical potential of coalescence in the oil phase was measured by using the twin dropping mercury electrodes. When an organic electrolyte was contained in the oil phase, the coalescence of mercury droplets was prevented over the potential range which was characteristic to the material. The potential range of coalescence became narrow with increasing ionic strength of the oil phase. Since this was closely related to the adsorbed amount of organic electrolyte ions, as was obtained from the electrocapillary curve, it was concluded that the coalescence of the droplets was prevented by the adsorption layer of the ions.

I. INTRODUCTION

The study on the coalescence of mercury droplets in the aqueous phase was previously made by Watanabe *et al.*[1] by using a pair of dropping mercury electrodes, who discussed the influence of the composition of the aqueous solution and the surface potential of these droplets. According to their results, the condition of coalescence in the aqueous solution containing inorganic electrolytes was in good agreement with the coagulation theory of Derjaguin-Landau-Verwey–Overbeek (DLVO),[2] and the interaction between such large particles as mercury droplets was essentially the same as that between hydrophobic colloid particles. Moreover, if surface active agents were added to the aqueous solution,[3] the condition of coalescence became independent of the polarizing potential. If the concentration of these materials exceeded a certain critical value, the coalescence did not take place even at the zero potential. This was explained by the protecting action of adsorbed layers of surface active agents.

It is a problem whether the same kind of electrostatic repulsion and protection is also found in non-aqueous solutions. Moreover, it is expected that the investigation on the condition of coalescence of mercury droplets in the oil phase provides us with informations concerning not only the applicability of DLVO theory to non-aqueous systems, but also the stabilization mechanism in emulsions and foams.

In the present paper the mechanism of coalescence of mercury droplets is discussed by studying the potential range of coalescence of the droplets in the

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oil phase.

II. EXPERIMENTS

Materials

Analar reagent of methylisobutylketone (MIBK) was distilled and then saturated with redistilled water, which was used as the solvent of the oil phase.

Analar reagents of tributylammonium picrate (TBAPi), tetrabutylammonium chloride (TBAC), dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC), cetyltrimethylammonium chloride (CTAC) and octadecyltrimethylammonium bromide (OTAB) was used as electrolytes of the oil phase.

The mercury was purified by washing with dilute nitric acid, followed by the vacuum distillation.

Method

The experimental apparatus used in the present study is the same as that used in experiments[1,3] on aqueous solutions. The principal part is shown in Fig. 1. Glass capillary tips of a pair of dropping mercury electrodes, are bent horizontally and then attached to the support which can move to three directions. The tips are confronted each other, and then immersed into the oil phase containing various electrolytes. Then, mercury droplets are formed at the tips, and the dropping is repeated.
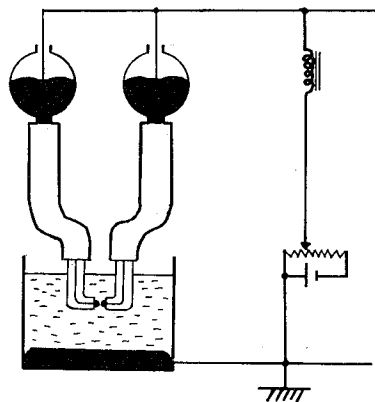

Fig. 1. The schematic diagram of the experimental apparatus.

The potential difference E is applied to the mercury droplets with reference to the mercury pool by using the potentiometer. If these mercury droplets are brought to the distance of contact, there occurs either coalescence or repulsion. If the constituent of the oil phase is constant, the repulsion takes place at cathodic or anodic E values larger than a certain critical value. This value is called "the critical potential difference E^*" at which the prevention of the coalescence takes place. This potential can be consider as the measure of the stability against coalescence. Here, the sign of E is taken as that of dropping mercury electrodes with reference to the mercury pool.

The electrocapillary curve of the mercury-oil interface is obtained by measuring the relation between the maximum volume of the mercury droplet and the polarizing potential E; at a constant flow rate of the mercury, the relation between the dropping period t and E is determined. In order to convert t to the interfacial tension γ, the calibration was made for the mercury droplet in the aqueous phase containing $0.1\,M$ NH$_4$Cl, for which accurate γ values are known.[4]

III. RESULTS

Electrocapillary Curves

The relation between the interfacial tension γ and the polarizing potential E was measured in MIBK containing various electrolytes. Figure 2 shows γ *vs.* E curves for TBAPi. Each curve shows the maximum near the $E=-0.2\,V$.
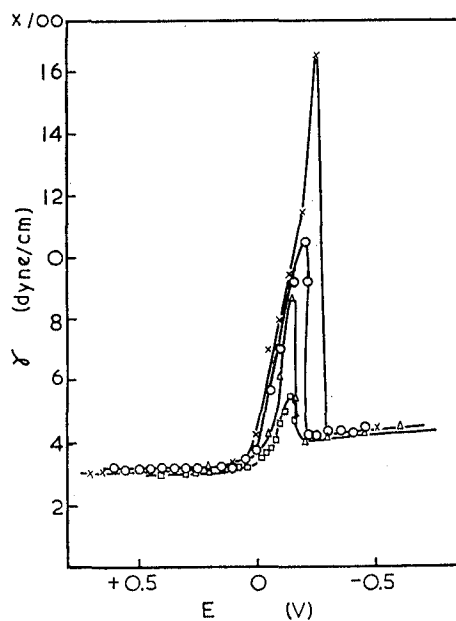
Fig. 2. The influence of the TBAPi concentration on electrocapillary curves.
Oil Phase : $\times$, $5\times10^{-4}\,M$ TBAPi; $\bigcirc$, $1\times10^{-3}\,M$ TBAPi;
$\triangle$, $2.5\times10^{-3}\,M$ TBAPi; $\square$, $5\times10^{-3}\,M$ TBAPi.

When, instead of TBAPi, TBAC was used as the electrolyte of the oil phase, γ decreased over the cathodic range, while remained constant over the anodic range. This tendency was found for other cationic surface active agents as well.

The Potential Range of Coalescence

In Fig. 3 the E^* *vs.* $\log C$ curve for TBAPi is shown, where C is the concentration. Here, the critical potential E^*_+ or E^*_- is given with reference to the electrocapillary maximum, which was obtained by curves in Fig. 2. Two critical potentials E^*_+ and E^*_- are observed, absolute values of which decreasing with increasing the TBAPi concentration; the potential range of coalescence becomes
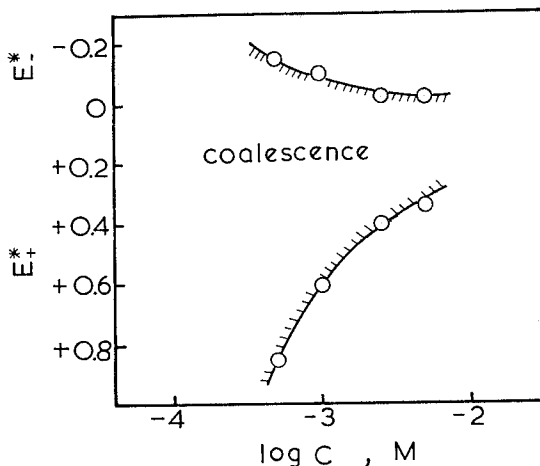
Fig. 3.　The influence of the TBAPi concentration on the coalescence of the mercury droplet.
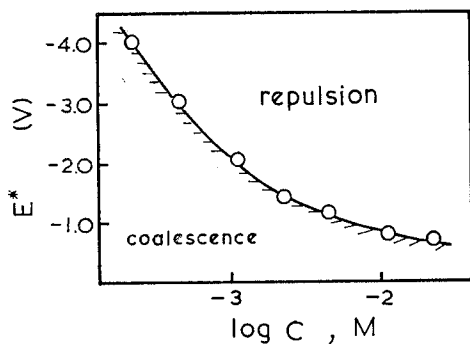

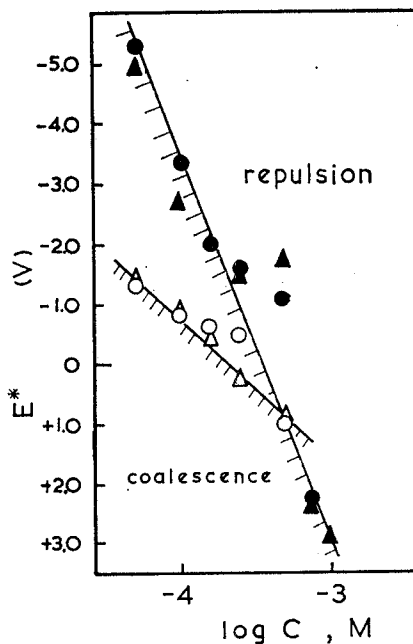Fig. 4.　The influence of the TBAC concentration on the coalescence of the mercury droplet.

Fig. 5.　The influence of the cationic surface active agent concentration on the coalescence of the mercury droplet.
Oil Phase : ●, CTAC ; ▲, OTAB ;
　　　　　　 ○, DPC ; △, CPC.

small.　This tendency is the opposite to that found for the coalescence[1] in the aqueous phase containing the inorganic electrolyte.　In the latter case, the width of potential range of coalescence increases with increasing electrolyte concentration.

　　Figure 4 and 5 show E^* vs. $\log C$ curves for TBAC and cationic surface active agents, respectively.　Since the electrocapillary curves have no maxima

in these cases, E^* values are given here by the readings of the potentiometer. It is noticed that the absolute value of E^* decreases with increasing electrolyte concentration. Critical potentials are found over the cathodic range only, no repulsion taking place over the anodic range.

When hydrophilic polar groups of cationic surface active agents are the same, plottings of E^* *vs.* $\log C$ show the same straight line, regardless of the chain length of hydrophobic groups and the kind of counterions, see Fig. 5.
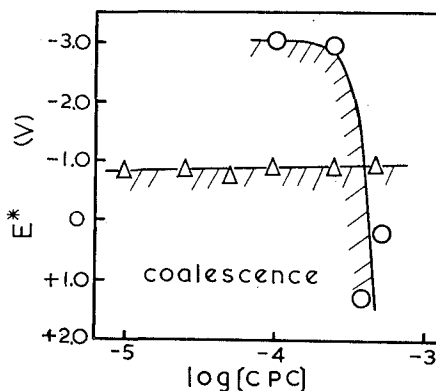

Fig. 6. Critical potentail *vs.* log [CPC] curves for the oil phase
containing two kinds of electrolytes.
Oil Phase: △, $1.15 \times 10^{-2}\,M$ TBAC ; ○, $5 \times 10^{-4}\,M$ TBAC.

Figure 6 shows E^* *vs.* log [CPC] curves for oil phases, containing various concentrations of CPC in addition to a constant concentration of TBAC. When the CPC concentration is much smaller than the TBAC concentration (1.15×10^{-2} M), the E^* value is constant at ca. $-0.9\,V$ for [CPC] from $1 \times 10^{-5}\,M$ to $5 \times 10^{-4}\,M$. This constant value is nealy equal to $E^*(=-0.8\,V)$ for the oil phase containing TBAC only, see Fig. 4. However, the curve for the TBAC concentration 5×10^{-4} M, gives a constant E^* value of ca. $-0.3\,V$ over the concentration range [CPC] <[TBAC]. This value is equal to E^* for the TBAC concentration $5 \times 10^{-4}\,M$, *i.e.* $-0.3\,V$, see Fig. 4. When concentrations of CPC and TBAC are comparable, the E^* value becomes positive, which corresponds to the result for the system containing CPC only, see Fig. 5.

IV. DISCUSSION

The maxima of γ *vs.* E curves in Fig. 2 are the so-called electrocapillary maxima (ecm)[5,6], at which the surface charge density $q = -d\gamma/dE$ equals zero. It is concluded, therefore, that the adsorptions of Pi$^-$ and TBA$^+$ ions are absent, or the same in magnitude. As can be seen from this figure, however, the maximum value decreases with increasing TBAPi concentration. It has been confirmed by electrical conductivity measurements on MIBK containing various TBAPi concentration that the TBAPi is weakly dissociated. It appears, therefore, that the γ depression at ecm is due to the adsorption of undissociated TBAPi molecules.

On the other hand, the adsorption of picrate ions (Pi⁻) and tributylammonium ions (TBA⁺) takes place over the anodic and cathodic polarization range, respectively, thus depressing the interfacial tension. If absolute values of the slope $d\bar{r}/dE$ for the cathodic and anodic sides are compared, the former is stronger than the latter. This shows that the chemical affinity of TBA⁺ ions to the mercury surface is stronger than that of Pi⁻ ions. In this connection, two critical potentials ranging the coalescence region are found at each concentration in Fig. 3. Absolute values of E^* at the cathodic polarization side (adsorption of TBA⁺ ions) are smaller than those at the anodic polarization side (adsorption of Pi⁻ ions). These critical potentials decreases with increasing TBAPi concentration. Hence, there appears to exist a correlation between electrocapillary curves and critical potential values of coalescence in this system, the coalescence of mercury droplets being prevented by the adsorbed layer of TBA⁺ and Pi⁻ ions. This is similar to the coalescence of mercury droplets in the aqueous phase containing surface active agents, which was already reported.[3]

When, instead of TBAPi, tetrabutylammonium chloride or various cationic surface active agents are used as the electrolyte of the oil phase, the r value over the anodic polarization range remains constant independent of E.

E^* values are only found over the cathodic side in Fig. 4 and 5. Hence, it is supposed that the specific adsorption of capillary active ions strongly prevents the coalescence.

In the case of the oil phase containing two kinds of electrolytes, TBAC and CPC, critical potentials are governed by the concentration of the ionic component present in excess, see Fig. 6. When the concentration of TBA⁺ ions is higher than that of CP⁺ ions, the coalescence of mercury droplets in the oil phase is prevented by the adsorbed film of TBA⁺ ions. Whereas, in the opposite case the adsorbed film of CP⁺ ions gives rise to the protection.

As for the coalescence of mercury droplets in the non-aqueous media, Sonntag's experiment[7] with respect to the xylene containing stearic acid can be cited. According to his result, when a mercury column in this solution is cut through with a mica knife, the coalescence of mercury column is prevented by the formation of interfacial film of stearic acid on freshly created mercury surfaces. This can be compared with present results. It is hence considered that the protection by various electrolytes in the present experiments is due to the same mechanism as in Sonntag's experiment.

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