Studies on the Coalescence of Liquid Droplets

Part II. The Influence of the Polarizing Potential on the Coalescence of Aqueous Droplets in Oil Solutions

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The range of electrical potential of coalescence of aqueous droplets in the oil phase was studied, and was compared with the electrocapillary phenomena at the oil-water inter-face. The experimental method was essentially the same as that of the coalescence of mercury droplets mentioned previously. If neither the aqueous nor oil phase contained the surface active material, aqueous droplets in the oil phase always coalesced over the whole range of the applied electrical potential. On the other hand, when the oil phase contained an ionic surface active agent, the repulsion of the aqueous droplets was observed at po-tentials higher than a certain value. This potential was governed by the ionic strength of the oil phase; the range of electrical potential of coalescence increased with increasing ionic strength of the oil phase. This tendency was similar to that of the coalescence of mercury droplets in the inorganic electrolyte solution. In the latter case the coalescence was prevented by the electrostatic repulsion between mercury droplets. When the oil phase contained the nonionic, instead of ionic, surface active agent, the condition of coalescence of aqueous droplets was independent of the ionic strength of the oil phase as well as the electrical potential, but depended on the concentration of the nonionic surface active agent; the coalescence was prevented only if the concentration of the agent exceeded a certain value. It was thus concluded that aqueous droplets in the nonionic surface active agent solution was protected by the adsorbed layer.

I. INTRODUCTION

In previous papers,[1~3] the coagulation mechanism of hydrophobic dispersions was discussed in relation to the coalescence of liquid droplets. They treated with the condition under which the coalescence of mercury droplets took place in aqueous or non-aqueous media. It was found that the coalescence of mercury droplets in the aqueous solution containing an inorganic electrolyte was prevent-ed by the electrostatic repulsion between them. It was proved that Derjaguin–Landau-Verwey-Overbeek's theory[4] of coagulation, which dealt with the electro-static and the van der Waals interaction between particles, held not only systems of colloid particles, but also in systems of hydrophobic dispersions and of liquid droplets.

If, on the other hand, the aqueous or non-aqueous solution contained either surface active agents or organic electrolytes, the coalescence of mercury drop-lets[2,3] was prevented by the protection due to the adsorbed film of these ma-

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terials. This fact is particularly important, since no stable emulsions are formed without the addition of surface active materials.

In the present communication, therefore, experiments on the coalescence of aqueous droplets in the oil phase will be treated. This is in close relation to electrocapillary phenomena at oil-water interfaces.[5~7]

II. EXPERIMENTS

Materials

The methylisobutyl ketone (MIBK) of the Analar Grade was distilled and then saturated with redistilled water, which was used as the solvent of the oil phase.

The surface active agents, dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC) and cetyltrimethylammonium chloride (CTAC), were of the Analar Grade, with the exception of sodium cetylsulfate (SCS), octadecyltrimethylammonium bromide (OTAB), and nonypole-100 (N-100), a nonionic surface active agent of the nonylphenyl type with the molecular formula $C_9H_{19}C_6H_4O(C_2H_4O)_{10}H$, which were of the Guaranteed Grade. Octadecyltrimethylammonium bromide was used after twice recrystallizations.

Tetrabutylammonium bromide (TBAB) of the Analar Grade was used as the supporting electrolyte of the oil phase.

The distilled water was purified by passing through ion-exchange resins, and then redistilled by using an all Pyrex glass apparatus. The specific conductivity of the water was about 10^{-6} mho cm^{-1}.

Inorganic electrolytes of the aqueous phase, potassium fluoride, potassium chloride, potassium bromide, potassium iodide and sodium malonate, were of the Analar Grade, and potassium ferricyanide was of the Guaranteed Grade. These materials were not purified further.

Method

The experimental method on the coalescence of aqueous droplets in the oil phase is essentially the same as that of mercury droplets in the aqueous phase.[1~3]
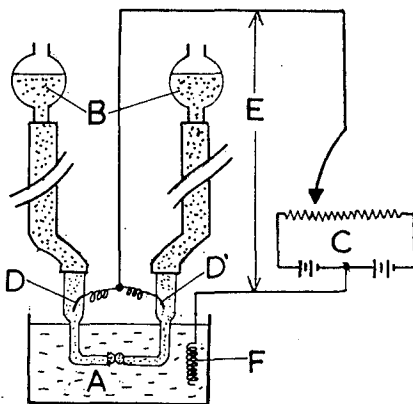

Fig. 1. The schematic diagram of the experimental apparatus.

In Fig. 1 the schematic diagram is shown. A pair of glass capillaries, the tips of which are bent horizontally, are immersed into the oil phase (A) containing an organic electrolyte. Aqueous droplets, *i.e.* aqueous solutions (B) of an inorganic electrolyte, are then formed in the oil phase from the glass capillary tips. A polarizing potential E is applied to the droplets by using the platinum electrodes D, D' sealed into the glass capillaries with reference to the platinum electrode F in the oil phase. When E is zero, the coalescence of aqueous droplets takes place as soon as they become in contact with each other. Whereas, if E is increased gradually towards the anodic or cathodic direction, the repulsion of droplets is observed at potentials higher than a critical value. This potential is called* "the critical potential E^*." The value of E^* is the average of five to ten experiments. Here, the sign of E is conventionally taken as that of the aqueous phase with respect to the oil phase.

Electrocapillary curves are obtained by measuring the maximum drop volume, from which the interfacial tension can be calculated by Harkins-Brown's equation.[8]

All experiments were carried out at the room temperature.

<div align="center">III. RESULTS</div>
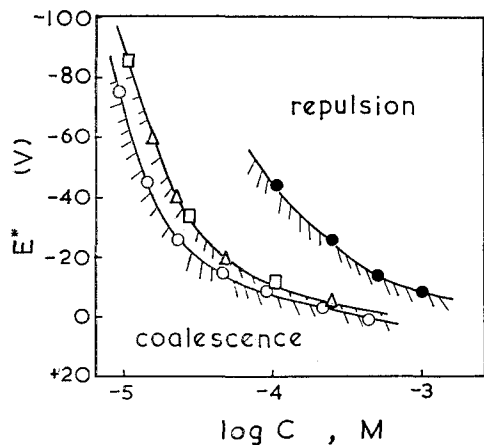
The Critical Potential Range of Coalescence

Fig. 2. The influence of the surface active agent concentration on the coalescence of the aqueous droplet in the oil phase.
Aqueous phase : 0.1 M KCl.
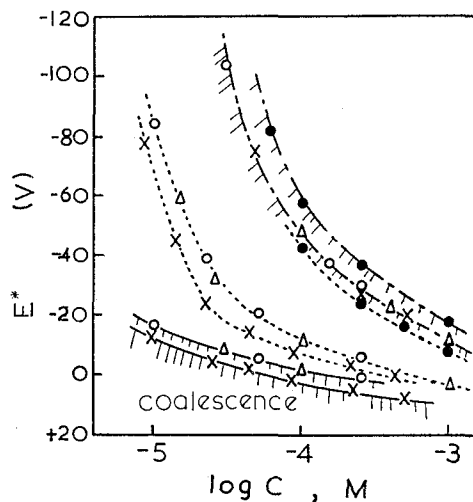Oil phase : ●, DPC ; △, CPC ;
□, CTAC ; ○, OTAB.

Fig. 3. The influence of the composition of the aqueous and oil phases on the coalescence of the aqueous droplet.
Aqueous phase : —·—, 0.1 M KBr ;
······, 0.1 M KCl ;
——, 0.1 M KF.
Oil phase : ●, DPC ; △, CPC ;
○, CTAC ; ×, OTAB.

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* E and E^* are readings of the potentiometer C and not the true polarizing potential at the oil-water interface. They contain ohmic drops in the aqueous and oil phases.

In order to increase the electrical conductivity of the system, $2.5 \times 10^{-4}\,M$ TBAB and $0.1\,M$ KCl were added to the oil and aqueous phases, respectively. In this system, no repulsion between aqueous droplets was found over the entire potential range between $+100$ and $-100\,V$.

On the other hand, if the oil phase contained a surface active agent, the repulsion of aqueous droplets was observed. Some examples are shown in Fig. 2, together with the E^* *vs.* $\log C$ curve. Here, the oil phase contained cationic surface active agents at various concentrations C and the aqueous phase was $0.1\,M$ KCl. It is found that the absolute value of E^* decreases with increasing concentration C and chain length of cationic surface active agents.

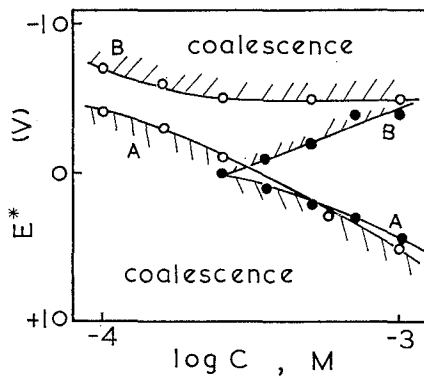The same tendency was found for all potassium halides as the constituent of

Fig. 4. The influence of anion valencies in the aqueous phase on the coalescence of the aqueous droplet.
Aqueous phase: $\bigcirc$, $0.1\,M$ $CH_2(COONa)_2$; $\bullet$, $K_3[Fe(CN)_6]$
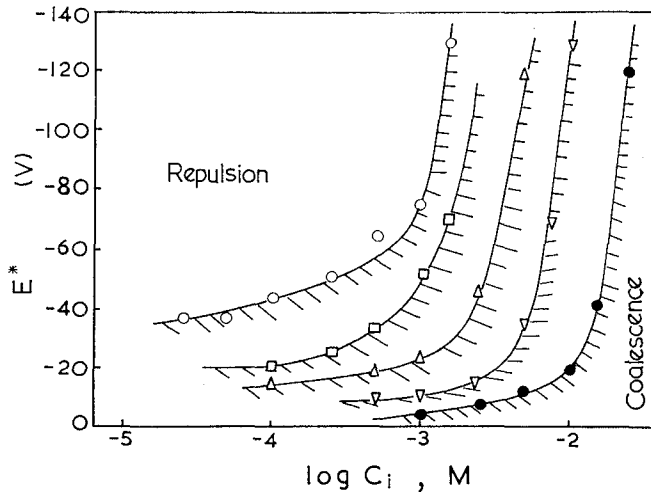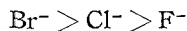Oil phase: CPC

Fig. 5. The influence of the ionic strength in the oil phase on the coalescence of the aqueous droplet.
Aqueous phase: $0.1\,M$ KCl
Oil phase: CPC; $\bigcirc$, $2.5 \times 10^{-5}\,M$; $\square$, $5 \times 10^{-5}\,M$; $\triangle$, $1 \times 10^{-4}\,M$; $\triangledown$, $2.5 \times 10^{-4}\,M$; $\bullet$, $5 \times 10^{-4}\,M$

the aqueous phase, with a considerable specificity (Fig. 3). For example, the value of E^* for CPC in Fig. 3 can be arranged in the decreasing magnitude by the following sequence:

$$Br^- > Cl^- > F^-$$

The same sequence was obtained for DPC, CTAC and OTAB.

If the oil phase contained CPC at various concentrations C, and the aqueous phase contained polyvalent anions, $CH_2(COONa)_2$ or $K_3[Fe(CN)_6]$, E^* vs. $\log C$ curves obtained were very different from those given above. This is shown in Fig. 4. The region of repulsion is arranged by two regions of coalescence in this case.

Now, when TBAB was added to the oil phase at various concentrations C_i in addition to CPC at a constant concentration, E^* vs. $\log C_i$ curves were obtained as shown in Fig. 5. Here, the aqueous phase was $0.1\,M$ KCl. It is noticed that the absolute value of E^* increases with increasing ionic strength of the oil phase. Moreover, provided that the TBAB concentration of the oil phase is constant, the absolute value of E^* decreases with increasing CPC concentration.

Now, the nonionic surface active agent, N-100, was added to the oil phase containing various concentrations C_i of TBAB, and its effect on the coalescence of $0.1\,M$ KCl aq. was examined. The results are shown in Fig. 6; the ordinate and abscissa are concentrations of N-100 and TBAB, respectively. It is found that the repulsion of aqueous droplets occurred at concentrations of N-100 higher than a critical value, i.e. $2.5 \times 10^{-2}\,M$, which was independent of C_i and E $(0 \sim \pm 50\,V)$.
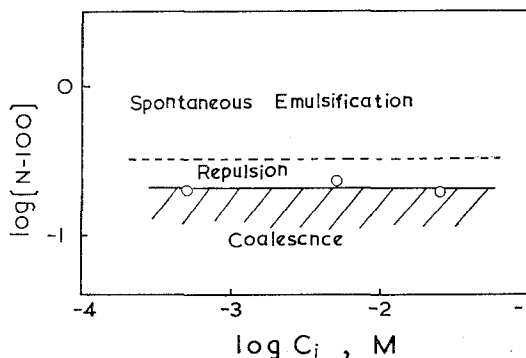

Fig. 6. The influence of the nonionic surface active agent concentration in the oil phase on the coalescence of the aqueous droplet.
Aqueous phase: $0.1\,M$ KCl
Oil phase: N-100+TBAB

The spontaneous emulsification was observed at concentrations slightly higher than this critical value.

The coalescence of aqueous droplets was examined also in the oil phase containing the anionic surface active agent. For instance, when the oil phase was $2.5 \times 10^{-4}\,M$ SCS and the aqueous phase $0.1\,M$ KCl, aqueous droplets always coalesced for E from -10 to $+4.0\,V$. If the anodic potential was increased

further, the experiment became impossible to carry out due to the formation of insoluble surface film on the droplets.

Electrocapillary Curves

The change in the interfacial tension γ with E, for the oil phase containing $2.5 \times 10^{-4} M$ CPC in contact with the aqueous phase containing $0.1 M$ potassium halides, is shown in Fig. 7. All curves are depressed over the cathodic range of E. The value of γ for halide ions can be arranged in the increasing magnitude by the following sequence:
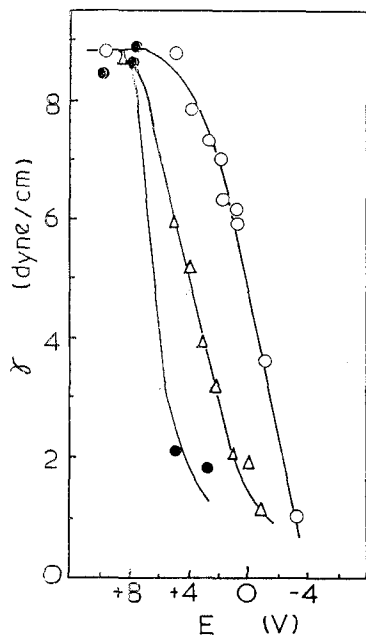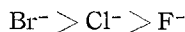
$$Br^- > Cl^- > F^-$$

Fig. 7. The influence of halide ion species in the aqueous phase on γ vs. E curves.
Aqueous phase: ●, $0.1 M$ KF;
△, $0.1 M$ KCl;
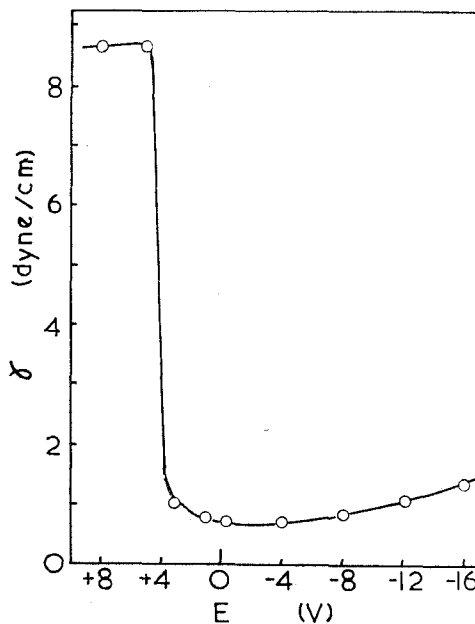○, $0.1 M$ KBr
Oil phase: $2.5 \times 10^{-4} M$ CPC

Fig. 8. The γ vs. E curve on the aqueous phase containing the polyvalent anion.
Aqueous phase: $0.1 M$ K$_3$[Fe(CN)$_6$]
Oil phase: $1 \times 10^{-3} M$ CPC

When the oil phase contains $1 \times 10^{-3} M$ CPC and the aqueous phase $0.1 M$ K$_3$[Fe(CN)$_6$], a rapid decrease in the γ value is found for E between $+5$ and $+4 V$, after which a constant value is found over the potential range from $+4$ to $-4 V$, and then the γ value increases gradually by increasing the cathodic polarization further than $-4 V$, see Fig. 8.

When the oil phase contains TBAB at various concentrations C_i in addition to $1 \times 10^{-4} M$ CPC, and the aqueous phase is $0.1 M$ KCl, γ vs. E curves as shown in Fig. 9 are obtained. In this case, slopes $d\gamma/dE$ do not change over the concentration range of TBAB from 0 to $1.6 \times 10^{-3} M$, and a small change is found over the range from $3.2 \times 10^{-3} M$ to $1 \times 10^{-2} M$.

IV. DISCUSSION

It was previously found that, the adsorption layer starts to take place at a lower polarizing potential for a higher concentration of agents with a strong surface activity, and that these surface active agent ions orientate at the oil-water interface[6,7]; hydrophilic polar groups are in the aqueous phase and hydrophobic groups in the oil phase. Therefore, since the electrostatic repulsion between these polar groups is not influenced by the addition of the supporting electrolyte TBAB in the oil phase, the adsorbed amount of these ions should not change by it. Actually, the slope of γ vs. E curves in Fig. 9, which is the measure of the
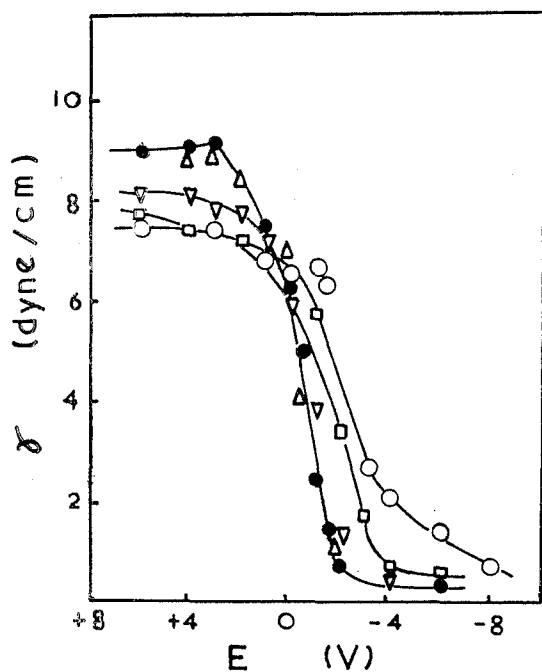

Fig. 9. The influence of the ionic strength in the oil phase on γ vs. E curves.
Aqueous phase: 0.1 M KCl
Oil phase: 1×10^{-4} M CPC+TBAB;
$\bigcirc$, 1×10^{-2} M TBAB;
$\square$, 3.2×10^{-3} M TBAB;
$\bigtriangledown$, 1.6×10^{-3} M TBAB;
$\triangle$, 5×10^{-4} M TBAB;
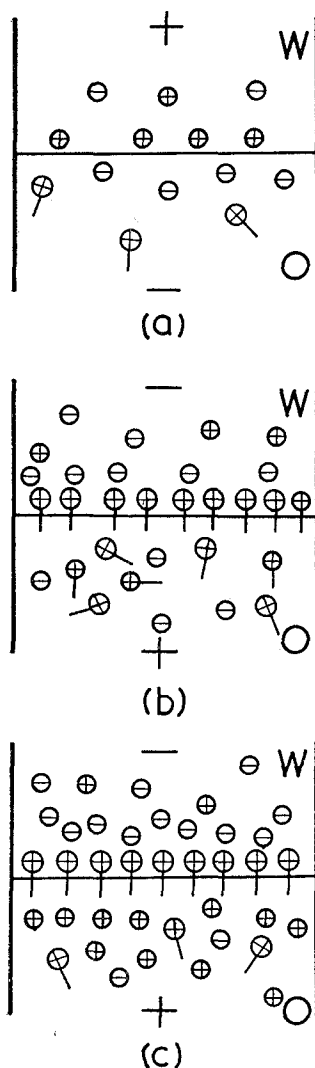$\bullet$, 0 M TBAB

Fig. 10. The schematic representation of double layers at the oil-water interface.

adsorbed amount, is almost independent of the TBAB concentration. On the other hand, absolute values of E^* increase with the increase in C_i. This can be explained as follows.

When the cationic surface active agent and the inorganic electrolyte are dissolved in the oil phase and the aqueous phase, respectively, the oil-water interface is not polarized over the anodic polarization range, because the adsorption of the surface active agent at the interface does not take place,[5] see Fig. 10a. Whereas, the oil-water interface is polarized over the cathodic polarization range, owing to the adsorption of cationic surface active agent ions, thus giving rise to the γ depression, see Fig. 10b. It appears that the surface excesses of inorganic anions and surface active agent ions are formed respectively on the aqueous and oil sides of the interface. Then, electrical double layers are formed towards bulks of both phases. Since the present investigation discusses the mechanism of coalescence of water droplets in the oil phase, the consideration will be restricted to the double layer in the oil phase.

If the ionic strength of the oil phase is low, the thickness of diffuse double layers around the aqueous droplets is large. Therefore, the approach of the droplets is prevented by the electrostatic repulsion owing to the overlap of double layers[4]; these droplets can not approach each other within the range of the van der Waals force. However, if the thickness of diffuse double layer is compressed by increasing the ionic strength in the oil phase, the repulsion decreases. Hence, so long as the polarizing potential is not high enough, no electrostatic repulsion acts to prevent the coalescence of aqueous droplets, see Fig. 10c. The E^* value thus increases with increasing C_i (Fig. 5).

On the other hand, Fig. 2 and 3 show the opposite tendency compared with that mentioned above; the absolute value of E^* decreases with the increase in the concentration of cationic surface active agents. This can be explained as follows. Since the oil phase does not contain the supporting electrolyte in this case, the electrical conductivity is low at the low concentration of surface active agents. Hence, it appears that most part of the applied potential is consumed by the ohmic drop* in the oil phase, the actual potential difference at the interface being very small.[6] Therefore, it is supposed that the absolute value of E^* increases with the decrease in the concentration of cationic surface active agents.

In this connection, Albers and Overbeek's experiments,[9] on the stability of emulsions of water in oil by measuring the electrophoretic mobility, are cited. According to their results, aqueous droplets with a small surface potential are more stable against flocculation than those with a high surface potential in benzene containing the various kinds of the metal soap. They interpreted this by the protection owing to the hydrophobic chain of the metal soap adsorbed on surfaces of aqueous droplets.

This conclusion contradicts the consideration of the present study. It is sup-

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* Concerning the ohmic drop in the oil phase, the contribution of the aqueous part to the total ohmic drop was examined by measuring E^* values for the aqueous phase of various concentrations of KCl in contact with the oil phase containing a constant concentration of CPC. It was found, in this case, that E^* values coincided with in Fig. 2.

posed that, the adsorbed film on aqueous droplets is present as the mobile mono-layer, if the hydrolysis of the metal soap does not occur at the oil-water inter-face. Hence, if the aqueous droplets approach each other, the droplets deform and hence the plane of the part confronted each other becomes flat, the adsorbed film of the metal soap being locally compressed at once. Moreover, as the con-tinuous oil phase between aqueous droplets is drained,[10] the flow will also promote the localized compression of the monolayer. Then, it becomes doubtful whether the surface potential of aqueous droplets measured by Albers and Over-beek is equal to that at the confronted part of the surface, when the droplets approach each other. It is also a problem whether the thickness of the electrical double layer, which gives the electrostatic repulsion between aqueous droplets, is uniform on the surface, or not.

In the present investigation, however, the surface potential of aqueous drop-lets was well-defined by applying the polarization from the outer circuit. Hence, the problem as mentioned above is considered to be absent.

So far, the coalescence of aqueous droplets has been discussed without con-sidering the interaction between counterions and surface active agents. However, inorganic electrolytes, especially those with anions of high polarizability, in the aqueous phase show strong bindings to polar groups of surface active agents.[6,7]

Therefore, if such counterion bindings take place, the interfacial charge de-creases. Hence, a higher polarizing potential must be applied in order to prevent the coalescence of aqueous droplets. This is found in Fig. 3, where E^* values are influenced by the kind of halide ions. The anions can be arranged in the order of the magnitude of E^* by the following sequence: $Br^- > Cl^- > F^-$. This sequence is also found in r $vs.$ E curves in Fig. 7.

The concept of counterion binding also explains results on the coalescence of aqueous droplets containing divalent or trivalent anions in Fig. 4. Since the charge of polyvalent anions is high, a small polarizing potential is expected to be sufficient to give the interfacial charge density required for the repulsion. In contradiction to the above consideration, the critical potential over the anodic region, $i.e.$ curve A in Fig. 4, is almost the same as that for the system contain-ing KF, see Fig. 3. This shows that polyvalent anions bind to polar groups of cationic surface active agents, although F^- ions do not bind to them.[5]

If a high cathodic potential is applied to the present system, a reaction takes place between inorganic ions and cationic surface active agents. For instance, the formation of a slightly yellowish insoluble film is formed at $E=-4.0\,V$. Con-sequently, since the formation of this film leads to a considerable decrease in the surface charge density, the electrostatic repulsion between aqueous droplets is small. Therefore, if the protection of this film is small, the coalescence of droplets is considered to take place. In fact, over the cathodic region in Fig. 4, another critical potential curve (curve B) is found, the aqueous droplets showing coalescence over the potential range higher than this.

On the other hand, when the oil phase contains the nonionic surface active agent, N-100, the coalescence of aqueous droplets is independent of the applied polarizing potential and the supporting electrolyte concentration in the oil phase;

it depends on the N-100 concentration only. Therefore, it appears that the stability of aqueous droplets is not due to the electrostatic repulsion between them, but to the protection of the adsorbed film in this case.

ACKNOWLEDGMENT

REFERENCES

(1) A. Watanabe and R. Gotoh, *Kolloid-Z.*, **191**, 36 (1963).
(2) A. Watanabe and M. Matsumoto, R. Gotoh, *Kolloid-Z.*, **201**, 147 (1965).
(3) M. Matsumoto, *This Bulletin*, **47**, 354 (1969).
(4) E. J. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948).
(5) A. Watanabe, M. Matsumoto, H. Tamai and R. Gotoh, *Kolloid-Z.*, **220**, 152 (1967).
(6) A. Watanabe, M. Matsumoto, H. Tamai and R. Gotoh, *Kolloid-Z.*, **221**, 47 (1967).
(7) A. Watanabe, M. Matsumoto, H. Tamai and R. Gotoh, *Kolloid-Z.*, **228**, 58 (1968).
(8) W. D. Harkins and F. E. Brown, *J. Amer. Chem. Soc.*, **38**, 288 (1916); **41**, 499 (1919).
(9) W. Albers and J. Th. G. Overbeek, *J. Colloid Sci.*, **14**, 501 (1959).
(10) K. J. Mysels and K. Shinoda, "Soap Films," Pergamon Press, New York (1959).