

Studies on the Coalescence of Liquid Droplets Part IV. The Coalescence of Mercury Droplets in Mixed Solvents*

Mutsuo MATSUMOTO**

Received August 15, 1970

The range of electrical potential of coalescence was measured by using twin dropping mercury electrodes immersed into mixed solvents (methanol-water) containing potassium chloride. It was thus expected that the influence of the dielectric constant on the dispersion and coagulation of lyophobic disperse system was clarified by the present study. The potential range of coalescence became large with the decrease in the dielectric constant, *i.e.* with the increase in methanol content. This behavior was ascribed to the compression of the diffuse double layer. It was supposed from measurements of differential double layer capacities that the dielectric constant in the diffuse double layer was small in comparison with the bulk value, being proportional to the third power of the dielectric constant in the Stern layer. It was found, moreover, that the free energy of adsorption of methanol molecules at the mercury-solution interface was *ca.* -1 Kcal/mole, and hence the coalescence of mercury droplets was little affected by the formation of the adsorbed film of methanol molecules.

INTRODUCTION

Since the publication of the coagulation theory of *Derjaguin-Landau-Verwey-Overbeek*^{1,2)} (*DLVO*) on the basis of the electrostatic repulsion due to the overlap of diffuse double layers and of the van der Waals attractive force between lyophobic colloid particles many articles on the stability of lyophobic dispersions in aqueous or non-aqueous solutions were reported. However, the general proof of the theory was not sufficient, because the potential of particles could not be defined explicitly. Hence, the condition of coalescence of mercury droplets by using the twin dropping mercury electrodes immersed into the aqueous or non-aqueous solutions was studied as the model experiments of the dispersion and coagulation of lyophobic colloid particles and liquid particles, and the influence of the surface potential, ionic strength, and surface active materials on the coalescence of mercury droplets was discussed.³⁻⁵⁾ It was thus found that the interaction between macroscopic mercury droplets was essentially the same as that between submicroscopic lyophobic particles, and that the coalescence of mercury droplets was prevented by the adsorbed film of surface active materials even if the electrostatic repulsion was absent.

However, besides above considerations another problem, *i.e.* the influence of the dielectric constant on the interaction between lyophobic colloid particles, remains

* The main part of this article is a translation of the paper published in *J. Chem. Soc., Japan*, 91, No. 8 (1970) p. 708.

** 松本陸朗 Laboratory of Colloid and Surface Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

to be investigated: most papers dealt quantitatively with the interaction between such particles by using the bulk value of the dielectric constants of the solvent. Since the coagulation between lyophobic particles is governed by the electrostatic repulsion and van der Waals attractive force, the dielectric constant in the diffuse double layers must be used for the quantitative verification of the *DLVO* theory, which is smaller than the bulk value due to the dielectric saturation.⁶⁻⁹⁾

In the present paper, the *DLVO* theory was discussed by measuring potential range of coalescence and differential double layer capacities of mercury droplets in solutions of various dielectric constants.

EXPERIMENTS

Materials

Solutions were prepared by dissolving various concentrations of potassium chloride in mixed solvents of methanol and redistilled water.

The distilled water was purified by passing through ion exchange resins, and then redistilled by using an all Pyrex glass apparatus. Methanol and potassium chloride of the Analar Grade were not purified further. Mercury was purified by washing with dilute nitric acid, followed by the vacuum distillation.

Method

The Coalescence of Mercury Droplets

The condition of the coalescence of mercury droplets was studied by using the method described previously.³⁻⁵⁾ The polarizing potential was applied to the twin dropping mercury electrodes immersed in the glass cell with reference to the mercury pool by means of the potentiometer. The cell contained the solution of mixed solvent.

Mercury droplets coalesced over a certain potential region of the anodic and cathodic sides with reference to the electrocapillary maximum^{10,11)} (*ecm*), and did not coalesce outside this region owing to the electrostatic repulsion. Hence, the upper and lower limits of the polarization of the coalescence region were measured with reference to the *ecm*; these values were called critical potentials E_{\pm}^* and E^* , where the suffix shows the sign of the polarization of mercury surface.

The coalescence was judged by the dropping period by using the *a-c* bridge and synchroscope; when the coalescence took place, a slow and regular period was found, while a rapid and irregular period was found when no coalescence occurred. Thus, the influence of the dielectric constant ϵ of the solvent and the KCl concentration c_i on E_{\pm}^* was studied by changing the methanol and KCl contents of the solvent. Dielectric constants ϵ used were obtained from the literature.¹²⁾

In order to study the structure of the electrical double layer and adsorption behaviors of methanol molecules at mercury-solution interfaces, differential double layer capacities were measured by the Grahame *a-c* bridge method. The experimental method and apparatus were explained in detail in the previous paper.⁴⁾ In the present experiment the frequency and *a-c* voltage were 1 KHz and 10 mV, respectively. The mercury head of the dropping mercury electrode was 71 cm and the drop period

was *ca.* 6 sec, which depended on the polarization. Differential double layer capacities were measured at 2.5 sec after the mercury drop has started to grow. The surface area of droplets at this time was calibrated from the measurement on 0.1 mole/l KCl aqueous solution for which capacities per area were known.

All experiments were carried out at $28 \pm 2^\circ\text{C}$.

RESULTS

The Potential Range of Coalescence

The relation between E_{\pm}^* and $\log c_i$ for mixed solvents with the dielectric constant ϵ from 78.5 to 32.7 is shown in Fig. 1, where c_i is the molar concentration of KCl. All curves are symmetric with reference to the $E_{\pm}^* = 0$ axis. When ϵ is large, both E_{+}^* and E_{-}^* values increase with increasing c_i . While, although E_{\pm}^* values increase with the increase in c_i up to 1×10^{-2} mole/l for small ϵ values, at concentrations higher than this values pass through the maximum, and then decrease. The maximum shifts to the lower concentration with increasing methanol content.

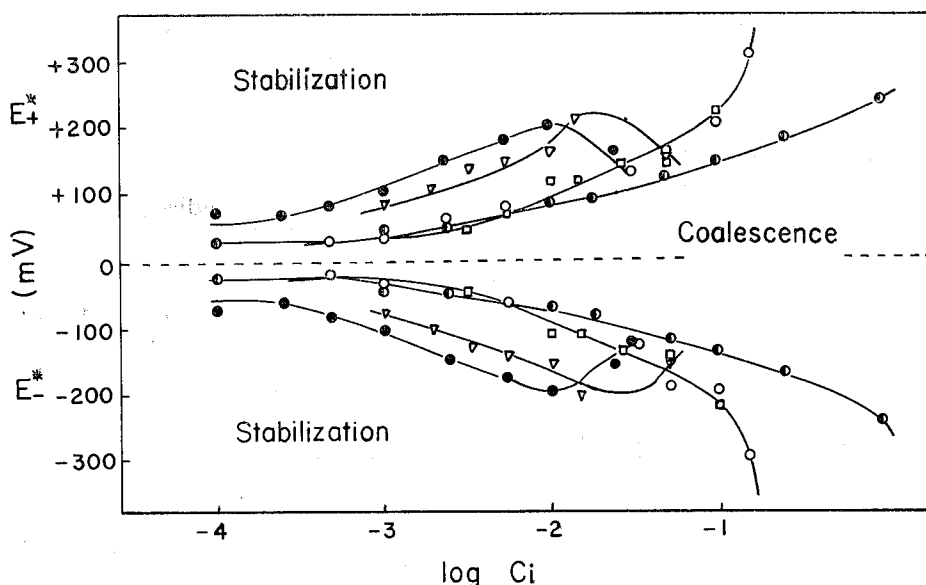


Fig. 1. E_{\pm}^* vs. $\log c_i$ curves for various concentrations of methanol. Methanol wt. %: (●), 0 ($\epsilon=78.5$); (○), 8.1 ($\epsilon=75.0$); (□), 44.1 ($\epsilon=58.9$); (▽), 64.8 ($\epsilon=49.2$); (●), 100 ($\epsilon=32.7$)

Differential Double Layer Capacities

The relation between differential double layer capacities C ($\mu\text{F}/\text{cm}^2$) and polarizations E with reference to the *ecm* is shown in Fig. 2. This is for solutions containing 1×10^{-2} mole/l KCl in mixed solvents with the methanol weight percentage $x=0$ ($\epsilon=78.5$), 8.1 ($\epsilon=75.0$), 19.8 ($\epsilon=70.1$), 44.1 ($\epsilon=58.9$), 64.8 ($\epsilon=49.2$), or 100 ($\epsilon=32.7$). Though C values of each curve are almost independent of E over the polarization range from -0.5 to 0 V, those for constant E value decrease with increasing methanol content: when E is constant, ΔC values, the difference

between C values for $x=0$ and $x=x$, increase with the increase in the concentration of methanol, and become constant for concentrations higher than 64.8%. Then, for $E \leq -0.5$ V, C values increase with increasing E values. On the other hand, they increase with increasing E values over the polarization range $E > 0$, showing a steep rise for higher methanol concentrations.

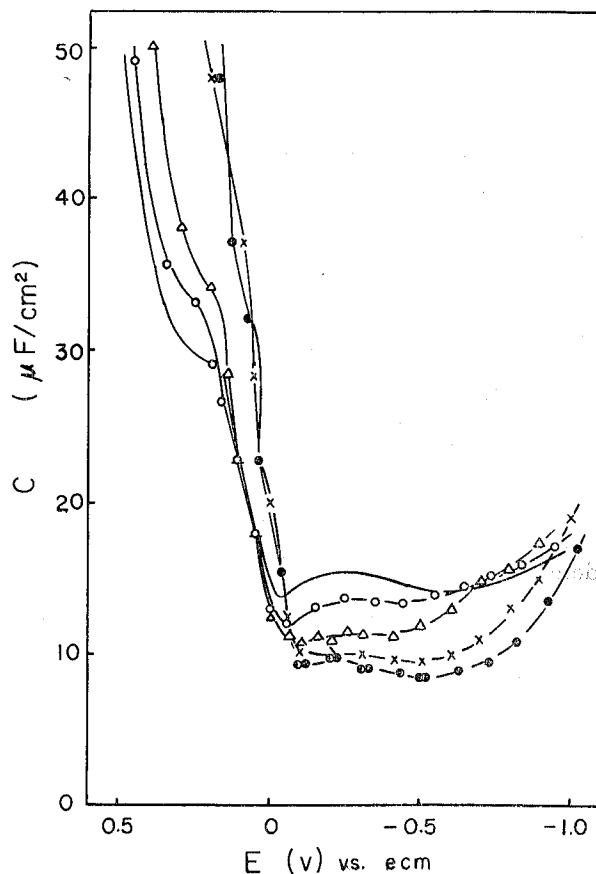


Fig. 2. C vs. E curves in the presence of methanol and 1×10^{-2} mole/l KCl.
Methanol wt. %: —, 0 ($\epsilon=78.5$); ○, 8.1 ($\epsilon=75.0$); △, 19.8 ($\epsilon=70.1$);
×, 44.1 ($\epsilon=58.9$); ●, 64.8 ($\epsilon=49.2$); ●, 100 ($\epsilon=32.7$)

Differential double layer capacities were also measured for $c_i=1.8 \times 10^{-1}$ mole/l and $x=0\%$, $c_i=5.6 \times 10^{-2}$ mole/l and $x=44.1\%$, as well as $c_i=8.9 \times 10^{-3}$ mole/l and $x=64.8\%$, though the results are not shown here.

DISCUSSIONS

The Interaction between Mercury Droplets

It is evident from the above that the condition of coalescence of mercury droplets is governed by the polarization, the electrolyte concentration, and the solvent com-

position. This condition can be explained by the free energy¹³⁾ V due to the electrostatic repulsion V_r and the van der Waals attraction V_a , *i.e.*

$$V = V_r + V_a \quad (1)$$

Since mercury droplets are large, *DLVO's* expressions¹⁴⁾ on V_r and V_a for two approaching planes can be used, *i.e.*

$$V_r = (64 \mathbf{c}_i N kT/1000\kappa) \cdot r^2 \cdot \exp(-2\kappa h) \quad (2)$$

$$r = \{\exp(\mathbf{e}\psi_s Z/2kT) - 1\} / \{\exp(\mathbf{e}\psi_s Z/2kT) + 1\}$$

$$V_a = -A/48\pi h^2 \quad (3)$$

Here, \mathbf{c}_i is the electrolyte concentration (mole/l), N the Avogadro number, k the Boltzmann constant, T the absolute temperature, \mathbf{e} the electronic charge, Z the valency of the counter ion, A the Hamaker constant,¹⁵⁾ h the distance between planes, and ψ_s the Stern potential. Here, ψ_s is equal to E under the assumption of no specific adsorption of counter ions. κ in equation (2) is the reciprocal thickness of the diffuse double layer, *i.e.*

$$\kappa = (8\pi \mathbf{c}_i N \mathbf{e}^2 Z^2/1000\epsilon kT)^{1/2} \quad (4)$$

If, in the absence of protecting action by the adsorbed film of methanol molecules, mercury droplets approach each other to the distance at which the van der Waals attraction is predominant, these droplets always coalesce. Therefore, in order to prevent the coalescence of droplets, V_r must be larger than V_a , *i.e.* $V > 0$. It is clear from equations (2) and (3) that, though V_a is independent of E , \mathbf{c}_i , and ϵ , V_r depends on them. Particularly, in equation (2) the thickness of diffuse double layer $1/\kappa$ becomes thin with increasing \mathbf{c}_i and decreasing ϵ ; when the solvent is water ($\epsilon=78.5$), $1/\kappa$ is *ca.* 100, 30 and 10 \AA for $\mathbf{c}_i=1 \times 10^{-1}$ mole/l, 1×10^{-2} mole/l, and 1×10^{-3} mole/l, respectively. While, in pure methanol ($\epsilon=32.7$), $1/\kappa$ is *ca.* 42, 13 and 4.2 \AA for $\mathbf{c}_i=1 \times 10^{-1}$ mole/l, 1×10^{-2} mole/l, and 1×10^{-3} mole/l, respectively.

Therefore, we must increase the r value by increasing the E_{\pm}^* value to have the large V_r for the system of small ϵ . It can, thus, be explained qualitatively that E_{\pm}^* values in Fig. 1 increase with increasing \mathbf{c}_i and decreasing ϵ .

On the other hand, for systems of $\epsilon=49.2$ and 32.7 in Fig. 1 the decrease in E_{\pm}^* is found at concentrations higher than $\mathbf{c}_i=1 \times 10^{-2}$ mole/l. This appears to be related to the fact that KCl dissociates weakly, and ion pairs^{16, 17)} of KCl are formed at high concentrations. In this connection, the author examined the relation between the equivalent conductance and $\sqrt{\mathbf{c}_i}$. It was found that for concentrations lower than $\mathbf{c}_i=1 \times 10^{-2}$ mole/l the equivalent conductance is a linear decreasing function of $\sqrt{\mathbf{c}_i}$ in agreement with Onsager's strong electrolyte theory,¹⁸⁾ but that over the region $1 \times 10^{-2} < \mathbf{c}_i < 1 \times 10^{-1}$ mole/l the equivalent conductance deviates considerably from the linearity. This supports the idea of incomplete dissociation of KCl .

According to the *DLVO* theory, results of Fig. 1 show that the flocculation concentration of lyophobic particles with the Stern potential E_{\pm}^* or E_{\pm}^* in the

medium of the dielectric constant ϵ is \mathbf{c}_i . In this case, following conditions must be satisfied:¹⁹⁾

$$\frac{d\mathbf{V}(h)}{dh} = 0 \tag{5.1}$$

$$\mathbf{V}(h) = 0 \tag{5.2}$$

Equations (2) and (3) are substituted into the term \mathbf{V} in the equation (5.1), and we obtain

$$\frac{d\mathbf{V}(h)}{dh} = -2 \mathbf{V}_a/h - 2\kappa \mathbf{V}_r = 0 \tag{6.1}$$

$$\kappa h = 1. \tag{6.2}$$

Equation (6.2) is substituted into (5.2), and we have,

$$\mathbf{c}_i = \mathbf{B} \cdot \gamma^4 / Z^6 \tag{7}$$

$$\mathbf{B} = 107 \cdot 10^3 \epsilon^3 \kappa^5 T^5 / N A^2 \mathbf{e}^6.$$

Here, γ takes the following form by Debye's approximation when $|\mathbf{E}_{\pm}^*|$ is small:

$$\gamma \simeq \mathbf{e} \mathbf{E}_{\pm}^* / 4 \text{ kT} \tag{8}$$

Then, equation (7) reads,

$$\mathbf{c}_i = \mathbf{B}' \cdot \mathbf{E}_{\pm}^{*4} / Z^2 \tag{9}$$

where $\mathbf{B}' = 107 \cdot 10^3 \epsilon^3 \text{ kT} / 256 N A^2 \mathbf{e}^2$. Since $|\mathbf{E}_{\pm}^*|$ is equal to $|\mathbf{E}_{\mp}^*|$ for constant

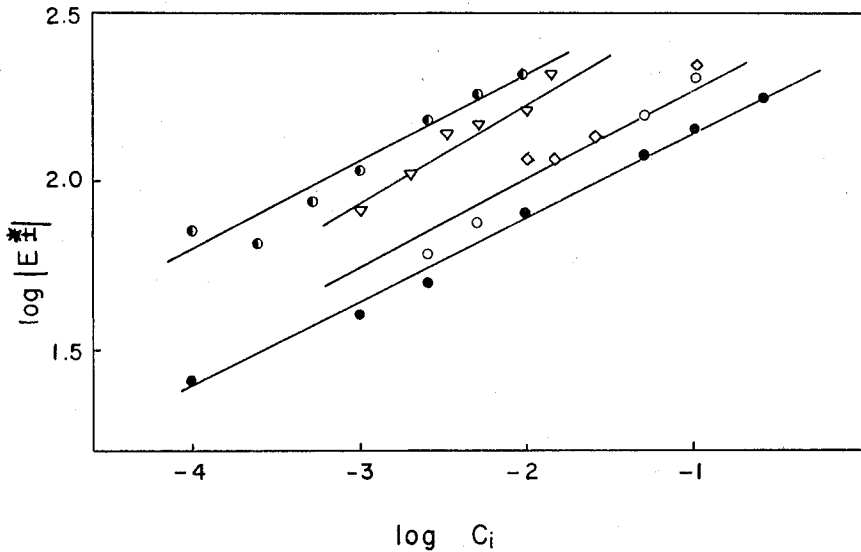


Fig. 3. The relation between $\log |\mathbf{E}_{\pm}^*|$ and $\log \mathbf{c}_i$ in the presence of methanol. Methanol wt. %: ●, 0; ○, 8.1; ◇, 44.1; ▽, 64.8; ●, 100

c_i and ϵ in Fig. 1, equation (9) can be rewritten in a logarithmic form as follows:

$$\log |E_{\pm}^*| = 1/4 \cdot (\log c_i - \log B') \quad (10)$$

Results of Fig. 3, showing the relation between $\log |E_{\pm}^*|$ and $\log c_i$, shows a linear relation with the slope *ca.* 1/4 for each solution, in agreement with equation (10), see Fig. 3. It was thus proved that the mechanism of the coalescence of mercury droplets in mixed solvents also could be explained by the theory of the stability of lyophobic particles.

Moreover, according to equation (8) the relation between $\log c_i$ and $\log \epsilon$ at a constant $|E_{\pm}^*|$ value should be a straight line with the slope 3. This is shown in Fig. 4 for $|E_{\pm}^*| = 79, 100,$ and 158 mV. Though the linear relation is found to hold except for a few points, the slopes are about 5, instead of the theoretical value 3. The reason appears to be explained by the fact that the bulk value of ϵ was used. Since the concentration of the rapid coagulation is governed by the interaction between diffuse double layers, the dielectric constant in these layers ϵ_g should be used.

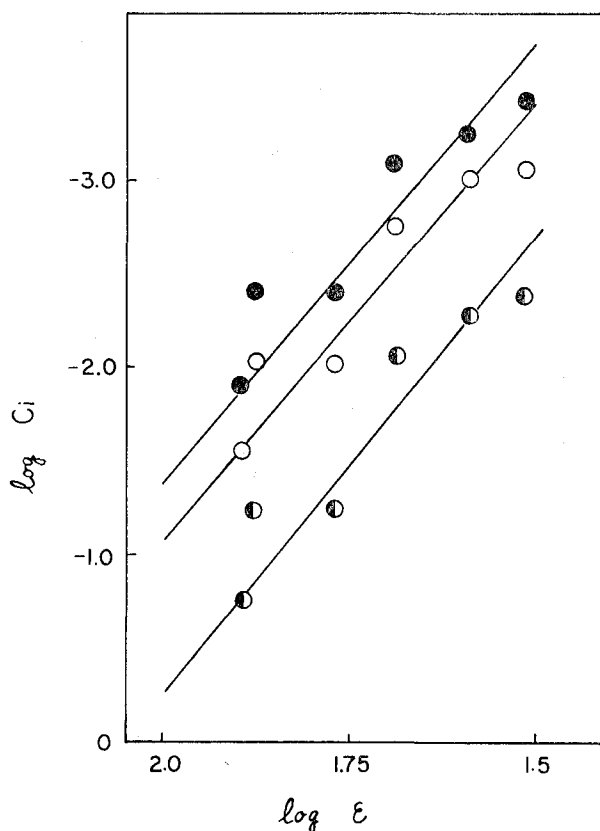


Fig. 4. The relation between $\log c_i$ and $\log \epsilon$ at constant $|E_{\pm}^*|$.
 $|E_{\pm}^*|$: ●, 158 mV; ○, 100 mV; ●, 79 mV

The Dielectric Constant in the Double Layer

According to Stern's theory²⁰⁾ the differential double layer capacity C at mercury-

solution interfaces consists of the series combination of the capacity of specific adsorption layer (Stern layer) C_s and that of diffuse double layer C_g ; C is given by the following equation:

$$1/C = 1/C_s + 1/C_g \quad (11)$$

The capacity of diffuse layer is a function of the electrolyte concentration, the dielectric constant in diffuse layer, and the charge density of the Stern plane. For $C_g \gg C_s$, equation (11) reduces to

$$C \simeq C_s \quad (12)$$

If equation (12) holds in the present experiment, C_s is equivalent to the parallel combination of the capacity of counter ions and methanol molecules in the Stern layer. This is expressed by the following relation on the basis of the electrostatic theory:

$$C = C_s = 1/4 \pi \cdot \{ \epsilon_1/d_1 - (\epsilon_1/d_1 - \epsilon_2/d_2) \theta \} \quad (13)$$

Here, d_1 and ϵ_1 are the effective diameter of the hydrated counter ion and its dielectric constant, and d_2 and ϵ_2 are respective quantities for methanol molecules, which are considered to have the vertical orientation towards the mercury surface. Then, θ expressed the degree of coverage of methanol molecules in the Stern layer.

Equation (13) can be written as follows when d_1 is equal to d_2 :

$$4\pi d C_s = \epsilon_1 - (\epsilon_1 - \epsilon_2) \theta = \epsilon_s \quad (14)$$

where ϵ_s is the dielectric constant in the Stern layer.

Equation (14) means that C decreases with the increase in θ , for ϵ_1 is generally larger than ϵ_2 . This is clear from Fig. 2, in which C values decrease with the increase in methanol content over the polarization range from 0 to -1.0 V.

As will be explained later, θ has a maximum at the absolute zero potential difference, and decreases with the increase in the absolute potential. In the present case, ϵ_s was calculated by using the average value^{9,21)} 4.2 \AA for d , with C values

Table. The Comparison of Dielectric Constants.

C _i = 1 × 10 ⁻² mole/l		
MeOH (wt.%)	ε	ε _s
0	78.5	7.2
8.1	75.0	6.5
19.8	70.1	5.4
44.1	58.9	4.8
64.3	49.2	4.6

of $E = -275$ mV under the condition that the complete adsorption of methanol molecules occurred. This is shown in the table with dielectric constants of the solvent. Dielectric constants in the Stern layer in this table are of an order smaller than those of the solvents. Such small values appear to be due to the dielectric saturation owing to the high field strength in the Stern layer.^{8, 9)} Then, the decrease of ϵ_s with increasing methanol concentration is ascribed to the increase in the degree of coverage of methanol molecules in the Stern layer. It has been shown by Webb⁶⁾ that the effective dielectric constant of water is considerably lower than its macroscopic value in the vicinity of an ion, owing to the dielectric saturation produced by the high field strength due to the ion, *i.e.* 7.8. This value agrees with the value 7.2 for the aqueous solution in the table.

It is, thus, clear from the above that, in order to prove experimentally the *DLVO* theory, the dielectric constant in the double layer must be used. Since, moreover, the coalescence between mercury droplets or the coagulation between lyophobic particles are governed by the interaction between diffuse double layers, values ϵ_g in the diffuse layer must be used. However, as no direct method of measuring ϵ_g is available at the moment, the relation between the coagulation concentration and the dielectric constant is examined by the temporary use of ϵ_s instead of ϵ_g . It is found from Fig. 3 that concentrations of KCl for the coalescence between mercury droplets to take place at $E_{\pm}^* = -158$ mV are 1.8×10^{-1} mole/l for the aqueous solution, 5.6×10^{-2} mole/l for 44.1% methanol, and 8.9×10^{-3} mole/l for 64.8% methanol, respectively. ϵ_s values at these concentration have been calculated from equation (14) by using C values under the assumption that C values are equal to C_s . In Fig. 5 $\log c_i$ is plotted as the function of $\log \epsilon_s$, which shows a

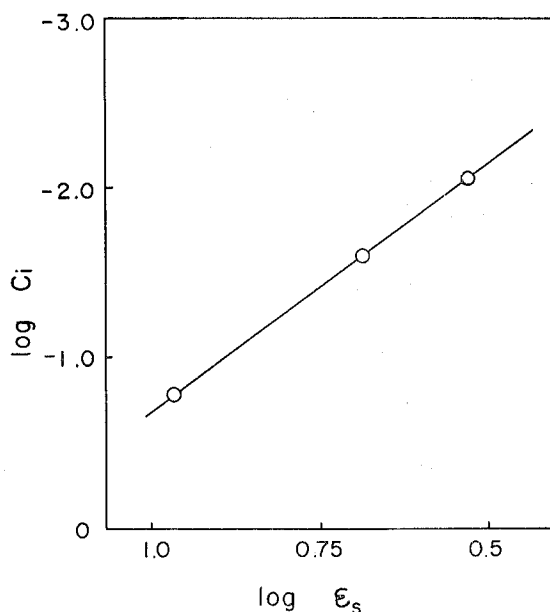


Fig. 5. The relation between $\log c_i$ and $\log \epsilon_s$ at $E^* = -158$ mV.

straight line with the slope 2.8. This value agrees fairly well with the theoretical one 3.

The Protection

The mechanism of the coalescence of mercury droplets was discussed on the basis of the electrostatic repulsion and van der Waals attraction. However, since, as can be seen from double layer capacity measurements, methanol molecules adsorb on the mercury surface, they are expected to protect the mercury droplets.

Now, if C values in Fig. 2 were equal to C_s , the ionic double layer and the adsorbed layer of methanol coexisted in the Stern layer. Hence, C_s values can be obtained as the parallel combination of capacities C_I and C_{II} :

$$C_s = C_I(1-\theta) + C_{II}\theta \quad (15)$$

For the Langmuir-Stern type of adsorption the degree of coverage is given by the following relation:

$$\theta = \frac{bN}{1+bN} \quad (16)$$

Here, N is the mole fraction of methanol and b the equilibrium constant of adsorption, the latter of which is related to the electrochemical free energy of adsorption $\Delta\bar{G}$ by

$$\Delta\bar{G} = -RT \ln b, \quad (17)$$

where R is the gas content, and T the absolute temperature. According to electrostatic considerations, the following equation is obtained for the adsorption of neutral molecules like the dioxane and methanol:^{4,22)}

$$\Delta\bar{G} = a(E-E_m)^2 + \Delta G_c \quad (18)$$

Here, ΔG_c is the chemical free energy of adsorption for neutral molecules. The first term of the right hand side of equation (18) is the electrostatic free energy of adsorption, which effects to weaken the adsorption of neutral molecules with the increase in E . a is a constant which contains dielectric constants of the neutral molecule and water, and E_m the polarization at which the potential difference becomes zero.

Equation (18) for $E-E_m=0$ is given by the following expression:

$$\Delta\bar{G} = \Delta G_c = -RT \ln b \quad (19)$$

Moreover, the following relation is obtained from equations (15) and (16):

$$\frac{1}{\Delta C'} = \frac{1}{\Delta C''} \left(1 + \frac{1}{bN} \right) \quad (20)$$

where $\Delta C' = C_I - C_s$

and $\Delta C'' = C_I - C_{II}$.

The adsorbed amount of methanol is, thus, given by the capacity suppression, $\Delta C' = C_I - C_s$. Figure 6 shows the relation between $\Delta C'$ and E obtained from Fig. 2. All curves show maxima, and $\Delta C'$ decreases to zero for high values of $|E|$. This behavior can be explained by the competition between methanol and water molecules; when the double layer electrical field is strong, methanol molecules with the low dielectric constant are displaced by water molecules with the high dielectric constant.

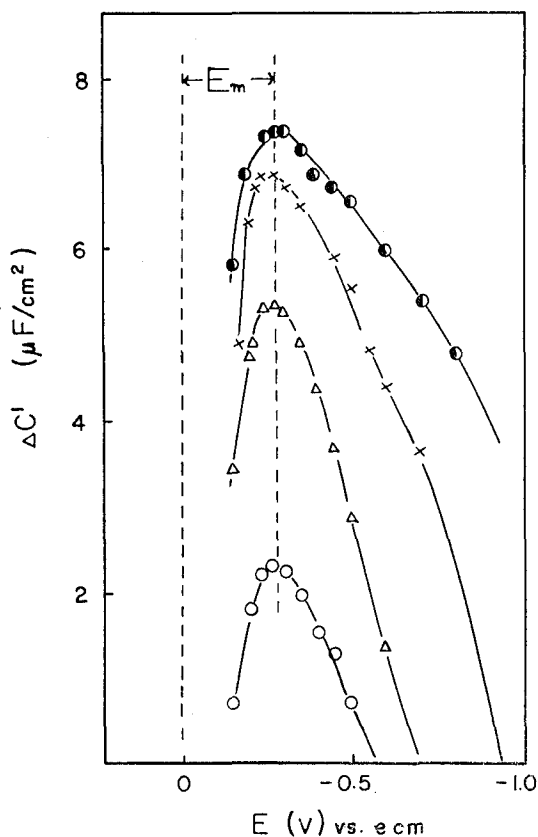


Fig. 6. $\Delta C'$ vs. E curves in the presence of methanol and 1×10^{-2} mole/l KCl.
Methanol wt. %: \circ , 8.1; \triangle , 19.8; \times , 44.1; \bullet , 64.8

It is clear from Fig. 6, moreover, that the maximum adsorption of methanol molecules takes place at -275 mV. This is the E_m , and does not agree with the polarization $E=0$, the zero point of charge. The disagreement can be explained by the orientation of water dipoles with their negative poles directed towards the mercury surface at the *ecm*; an additional negative polarization E_m must be applied to the mercury surface in order for the water dipoles to take the random orientation.²²⁾

It is expected from equation (20) that the plotting of the reciprocal capacity suppression at E_m , $1/\Delta C'_m$ against the reciprocal mole fraction $1/N$ shows a straight line with the slope $1/b$. This relation is shown in Fig. 7. The linearity holds at

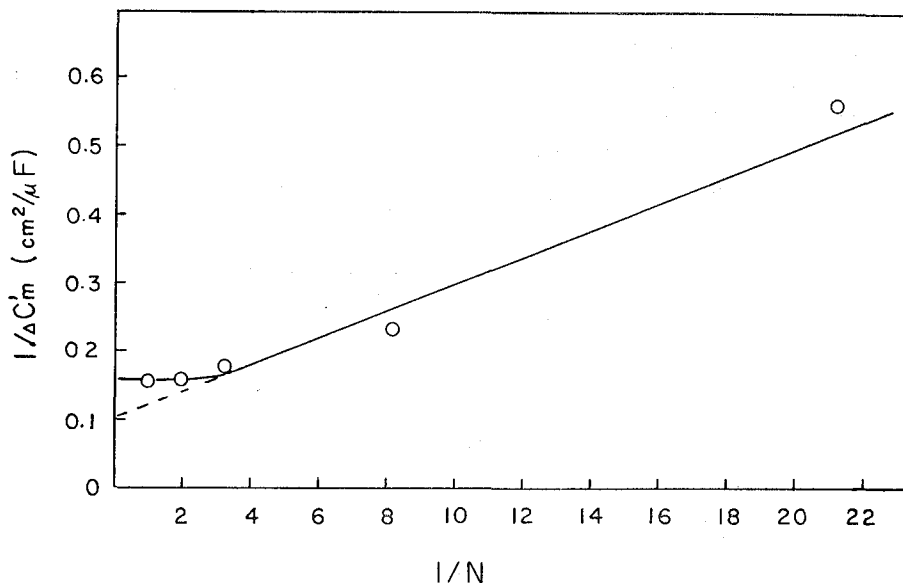


Fig. 7. The relation between $1/\Delta C'_m$ and $1/N$ for 1×10^{-2} mole/l KCl.

high $1/N$ values, thus indicating the Langmuir-Stern type of adsorption. However, marked deviations from the linearity are found at low $1/N$ values, the plotting becoming parallel to the horizontal axis. The same behavior was also observed in the case of nonionic surface active agents,⁴⁾ the interaction between adsorbed molecules taking place at high degree of coverage.

Now, as the first term of the right hand side of equation (18) is zero at $E=E_m$, the calculation of ΔG_c by using equation (19) is possible. Substituting the b value 5.3 obtained from the slope of the straight line, $-\Delta G_c$ is about 1 Kcal/mole (1.7 RT). This is only about 1/10 of the value for nonionic surface active agents in the aqueous solution which was reported previously.⁴⁾ Thus, the free energy of adsorption is small, even if the adsorbability of methanol molecules is not weakened by the electrostatic force.

According to the theory of the coagulation of lyophobic particles, the potential barrier of at least 15 RT is necessary to prevent electrostatically the flocculation between particles.²³⁾ The free energy of adsorption of methanol molecules given above is too small to prevent the coalescence of mercury droplets.

GENERAL DISCUSSION ON THE COALESCENCE OF LIQUID DROPLETS

So far, the coalescence mechanism of liquid droplets was studied by using the mercury,⁵⁾ aqueous,²⁴⁾ or oil droplets.²⁵⁾ Though the mercury droplets are considered as the model of lyophobic colloid particles and emulsions, the coalescence mechanism of mercury droplets is not necessarily consistent with that of the aqueous or oil droplets, the latter of which give the direct model for emulsions. For example, the coalescence

of mercury droplets in the oil phase, as the model of water-in-oil type emulsions, is explained by a mechanism which is different from that of aqueous droplets in the oil phase. The mercury droplets are prevented from coalescence by the adsorbed film of the organic electrolyte, while, the aqueous droplets by the electrostatic repulsion owing to the overlap of diffuse double layers. The organic electrolyte, *e.g.* tetrabutylammonium bromide, strongly adsorbs at the mercury-oil solution interface, even if it is inactive at the oil-water interface. Therefore, the coalescence of mercury droplets is prevented by the barrier of the adsorbed film of the organic electrolyte even if mercury droplets can approach within the operative region of the van der Waals attraction in the absence of the electrostatic repulsion. On the other hand, since tetrabutylammonium bromide is surface inactive at the oil-water interface, it only supplies counter ions in the diffuse double layers of aqueous droplets. Hence, these droplets coalesce unless an electrostatic repulsion occurs which is sufficient to prevent the coalescence.

Now, oil droplets in the aqueous solution and also mercury droplets in the aqueous solution containing a surface active agent, the model system of oil-in-water type emulsions, are prevented from coalescence by the protecting action of the adsorbed surface active agent. Here, the protection of oil droplets is similar to the mechanism of the stability of the lyophilic colloid particle, and is due to the hydration of polar groups of the surface active agent. While, it is not clear whether the protection of mercury droplets is due to hydrophobic groups or to the hydration of polar groups.

If the coalescence of liquid droplets is only governed by the electrostatic repulsion and the van der Waals attraction, the coalescence of these droplets is prevented by the increase in the electrostatic repulsion. The electrostatic repulsion between liquid droplets increases with increasing diffuse double layer thickness and surface potential. The thickness of diffuse double layer depends on the ionic strength in the solution and the dielectric constant. The influence of ionic strength on the coalescence of liquid droplets at a constant dielectric constant was studied in detail by Watanabe *et al.* by using mercury droplets. They concluded from their experimental results that the mechanism of coalescence between mercury droplets is the same as that of the rapid coagulation of lyophobic particles. The same conclusion should also be obtained by changing the dielectric constant in the solution. This is treated in the present paper, and experimental results clearly show that the coalescence mechanism of mercury droplets in mixed solvents can be explained by the same mechanism.

ACKNOWLEDGMENTS

The author wishes to express his gratitude to Dr. Rempei Gotoh, Emeritus Professor of Kyoto University, Dr. Eiji Suito, Professor of Kyoto University, and Dr. Akira Watanabe, Professor of Kyoto University of Industrial Arts and Textile Fibres, for their kind supervision and valuable discussions during the course of this study. Thanks are also due to the Ministry of Education, Japan, for the Grant of the Fundamental Scientific Research to carry out a part of this work.

REFERENCES

- (1) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948).
- (2) H. R. Kruyt, "Colloid Science I," Elsevier, London (1952).
- (3) A. Watanabe and R. Gotoh, *Kolloid-Z.*, **191**, 36 (1963).
- (4) A. Watanabe, M. Matsumoto, and R. Gotoh, *Kolloid-Z.*, **201**, 147 (1965).
- (5) M. Matsumoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 354 (1969).
- (6) J. Webb, *J. Amer. Chem. Soc.*, **48**, 2589 (1926).
- (7) B. E. Conway, J. O'M. Bockris, and I. A. Ammar, *Trans. Faraday Soc.*, **47**, 756 (1951).
- (8) A. Watanabe, F. Tsuji, and S. Ueda, *Proc. Intern. Congr. Surface Activity*, 2nd, III, 94 (1957).
- (9) J. O'M. Bockris, M. A. V. Devanathan, and K. Müller, *Proc. Roy. Soc.*, **274**, 55 (1963).
- (10) N. K. Adam, "Physics and Chemistry of Surfaces," Oxford Univ. Press (1938) pp. 336.
- (11) J. A. V. Butler, "Electrocapillarity," Methuen, London (1940) pp. 57.
- (12) B. E. Conway, "Electrochemical Data," Elsevier, London (1952) pp. 45.
- (13) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948) pp. 107.
- (14) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948) pp. 95, 101.
- (15) J. Lyklema, *Advance in Colloid and Interface Sci.*, **2**, 65 (1968).
- (16) G. D. Parfitt and A. L. Smith, *Trans. Faraday Soc.*, **59**, 257 (1963).
- (17) R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience, London (1959) pp. 207.
- (18) S. Glasstone, "Elements of Physical Chemistry," Maruzen, Tokyo (1954) pp. 419.
- (19) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948) pp. 117.
- (20) O. Stern, *Z. Electrochem.*, **30**, 508 (1927).
- (21) L. E. Sutton, "Tables of Interatomic Distance and Configuration in Molecules and Ions," Chem. Soc. Purlington House, London (1965) pp. S-8, S-16.
- (22) A. Watanabe, F. Tsuji, and S. Ueda, *Kolloid-Z.*, **191**, 147 (1963).
- (23) E. J. W. Verwey and J. Th. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, London (1948) pp. 169.
- (24) M. Matsumoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 361 (1969).
- (25) M. Matsumoto, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 371 (1969).