

On the Coalescence of Mercury Droplets in Aqueous Solutions

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The potential range of polarization of the twin dropping mercury electrodes, over which the coalescence of two mercury droplets in aqueous solutions took place, was measured as a function of the solution composition. For simple inorganic electrolyte solutions, the condition of coalescence obtained was in quantitative agreement with the Verwey-Overbeek theory of coagulation. Thus, the interaction between macroscopic mercury droplets was proved to be essentially the same as that between submicroscopic hydrophobic particles in these cases, providing at the same time the most direct proof of the theory. For solutions, however, in which ionic or nonionic surface active materials were added in addition to the supporting inorganic electrolyte, no coalescence occurred even at the zero polarization for surface active material concentrations higher than certain values, *i.e.* a perfect stabilization took place. These critical concentrations were found to depend on the HLB values of the surface active materials added; the stabilizing power increased with increasing hydrophilic property of the molecule. It was proved by differential double layer capacity measurements that such a stabilization was related to the formation of interfacial films of these materials, which protect the droplets from coalescence.

1. INTRODUCTION

It is generally accepted that the separation of unstable emulsions into two separate phases usually takes place in two consecutive processes, the coagulation and coalescence of dispersed liquid particles^{1,2)}. Hence, the stability of emulsions, or liquid droplets in liquid media in general, is increased by the inhibition of either of these two processes. These processes depend markedly on the electrical state, *i.e.* the thickness of and the potential distribution in the electrical double layer around each emulsion particle, the van der Waals attraction between particles and the property of the interfacial film formed by emulsifier molecules. It is therefore hoped to carry out experiments under the condition in which these factors are well defined at particle-solvent interfaces for the elucidation of the mechanism of the stabilization of emulsions, and dispersed systems in general.

Being a metallic conductor in the liquid state at room temperatures, the mercury droplet is suited to the investigation of the type mentioned above in a macroscopic manner, since we can define the condition of the electrical double layer around a mercury droplet in an aqueous solution of a known composition by applying various polarizing potentials of a wide range by means of a potentiometer. It is due to such an ideally polarized property, with a high hydrogen overpotential, of the mercury electrode that so many

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experimental studies on the electrocapillarity have been made by using this electrode^{3,4,5,6}. The present authors took advantage of this fact and devised successfully the twin dropping mercury electrodes (TDME), a couple of dropping mercury electrodes, in contact with various inorganic as well as surface active agent solutions, in order to examine the condition of coalescence of mercury droplets. It was thus hoped that, by comparing the condition obtained experimentally with that obtained by the theory of coagulation of hydrophobic colloids, we could distinguish the conditions of coagulation and coalescence in a narrow sense. The present paper is the review of present authors' studies, the details of experimental and theoretical treatments having been published elsewhere^{7,8}.

2. THE COALESCENCE OF MERCURY DROPLETS IN INORGANIC ELECTROLYTE SOLUTIONS⁷⁾

The critical electrical potential of the TDME in aqueous inorganic electrolyte solutions, at which an abrupt change from the repulsion to the coalescence of droplets occurred, was measured. The experiments had a feature in a sense that the electrical potential of droplets was defined by an outside circuit in a distinct manner; no considerations had been made on the potential of droplet surfaces in most of the experiments which had so far been carried out⁹⁻¹⁸. Thus, it was possible in the experiments, under the assumption of the coincidence of coalescence and coagulation, to examine whether the theory of coagulation¹⁹⁻²² which had been proved to hold for hydrophobic sols²⁰⁻²⁵, was also applicable to TDME, in which the theory of the diffuse double layer had been established⁴.

The tips of a couple of dropping mercury electrodes are bent horizontally and confronted each other with a small gap distance between them; thus the two mercury droplets grown from these two capillaries can get in touch with each other after a certain period of time, see Fig. 1. This system is the

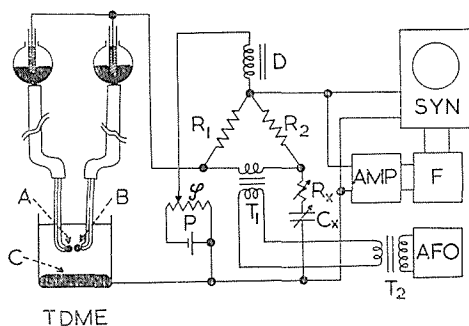


Fig. 1. The coalescence experiment of mercury droplets. A, B, mercury droplets; C, reference (pool) electrode; D, choke coil; F, filter circuit; P, potentiometer; R₁, R₂, resistors; T₁, T₂, transformers; R_v, standard variable resistor; C_v, standard variable capacitor; AMP, amplifier; AFO audiofrequency oscillator, 1,000 cps; SYN, synchroscope; TDME, twin dropping mercury electrodes.

TDME. A polarizing potential φ vs. pool is applied to the mercury droplets A and B by means of the potentiometer, P. If we put the electrocapillary maximum (ecm) φ_0 , then the polarization E vs. ecm can be expressed as $E = \varphi - \varphi_0$. Then the polarization of the TDME is classified into three regions, *i.e.* the anodic, zero and cathodic regions according to conditions $E \gg 0$, $E \approx 0$ and $E \ll 0$, respectively²⁰.

If the absolute value of E is sufficiently large for the electrostatic repulsion between the droplets A and B to be very strong, the two droplets do not coalesce even if their surfaces are in apparent contact, and then detach the tips and fall as separate particles, see Fig. 2 B. However, over the potential

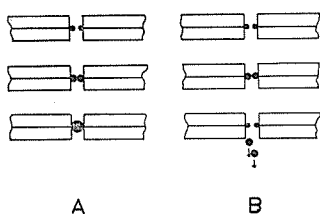


Fig. 2. The behaviour of twin mercury droplets.
A, coalescence; B, repulsion.

range $E_+ > E > E_-$ in the zero polarization region, the electrostatic repulsion is sufficiently small for the van der Waals attraction to become predominant, thus giving rise to the coalescence of droplets, Fig. 2 A. Thus, the critical potentials of coalescence E_+ and E_- , the upper and lower limits of the coalescence region, can be measured. In practice an abrupt change in the drop

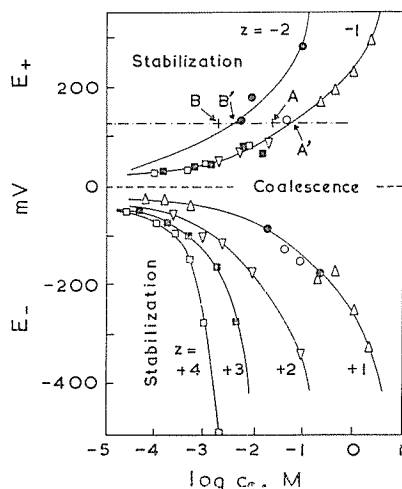


Fig. 3. Critical potential vs. log concentration curves for the coalescence of mercury droplets.

\triangle KCl; \circ KF; \bullet Na_2SO_4 ; ∇ $\text{Zn}(\text{NO}_3)_2$; \blacksquare $\text{La}(\text{NO}_3)_3$; \square $\text{Th}(\text{NO}_3)_4$.
A, B, the coagulation concentrations for the positive silver iodide sol, $\zeta = +130$ mV; A', B', the concentrations of mono- and divalent anions, corresponding to the critical potential $E_+ = +130$ mV.

period, which occurs at the critical potential E_+ or E_- , is used for this measurement. The a-c bridge circuit in Fig. 1 is employed for this purpose^{27, 28, 29}.

Values of E_+ and E_- depend markedly on the type and concentration of the electrolyte contained in the solution phase of the TDME. E_+ and E_- values are plotted in Fig. 3 as functions of $\log c_e$ for various aqueous inorganic salt solutions, where c_e is the concentration of electrolytes in M. It is noticed that both E_+ and E_- are increasing functions of $\log c_e$, the positions and shapes depending on the type of electrolytes. In particular, E_+ is primarily determined by the valency of the anionic species, while E_- by that of cationic species, no obvious ionic specificity being observed. It is also found that, if absolute values of the valency are the same, the E_+ vs. $\log c_e$ and E_- vs. $\log c_e$ curves are symmetrical to each other with reference to the horizontal axis $E=0$.

If we assume that the conditions of the coagulation and coalescence of mercury droplets coincide in the present case, the experimental facts here obtained agree with the Schulze-Hardy rule of coagulation.³⁰⁻³² Thus, for a constant positive electrical potential of mercury surfaces, the critical concentration of coalescence c^+ is almost entirely dependent on the valency of anionic species, while for a negative constant potential, on the valency of cationic species. It is also noticed that the c^+ value decreases with increasing valency. The points A and B in Fig. 3 are coagulation concentrations for the positive silver iodide sol with zeta potential +130 mV, which was measured by using the turbidimetry and ultramicroelectrophoresis.²⁴⁻²⁵ Points A' and B' in the same figure represent c^+ values of mono- and divalent anions when the mercury surface is polarized at the same potential, +130 mV. The agreements between A and A' and also between B and B' are sufficiently good to lead to the conclusion that the so called Schulze-Hardy rule holds in both cases of the coagulation of positive silver iodide sols and the coalescence of mercury droplets; the small deviations would be explained by the difference between the van der Waals attraction constants of silver iodide and mercury.

On the other hand, the change in the potential with keeping the electrolyte concentration constant, as was actually the procedure of present experiments, corresponds to the so called adsorption coagulation, *i. e.* the change in the potential of the surface by changing potential determining ion concentrations,³⁵ or in the Stern potential by the addition of an ionic surface active agent having the charge opposite to the surface of colloid particles.²¹⁻²³ All these changes decrease the effective electrical potential at interfaces, thus giving rise to the coagulation over the potential range around the zero polarization, *i. e.* $E_+ > E > E_-$. It is therefore concluded that the present experiments as are summarized in Fig. 3 do represent the general aspect of coagulation of lyophobic colloids,³⁶⁻³⁷ including the nonspecific Schulze-Hardy and the specific adsorption coagulations.

Now, the free energy of interaction between mercury droplets V is given by the algebraic sum of the terms due to the electrostatic repulsion V_R and the van der Waals attraction V_A , *viz.*³⁸

$$V = V_R + V_A \quad (1)$$

Since we are treating liquid droplets of macroscopic sizes, we can employ Verwey-Overbeek's expressions for V which are applicable in the case of two approaching planes, *i. e.*¹⁹⁾

$$V = \frac{4.62 \times 10^{-6} a \gamma^2 \exp(-\kappa au)}{z^2} - \frac{A}{12u} \quad (2)$$

Here a is the radius of droplets; z is the valency of the counter ion; A is the van der Waals constant; and u is the parameter standing for the distance of droplets, *i. e.*

$$u = x/a \quad (3)$$

where x is the closest distance between the droplet surfaces. The electrical potential of surfaces is implicitly contained in equation (2) by a relation

$$\gamma = \frac{\exp(ze\psi_1/2kT) - 1}{\exp(ze\psi_1/2kT) + 1} \quad (4)$$

where e is the electronic charge; k is the Boltzmann constant; T is the absolute temperature; and ψ_1 is the Stern potential. While, the electrolyte concentration c_e , or the ionic strength of the solution $z^2 c_e$, is contained in equation (2) by a relation between the reciprocal thickness of the diffuse double layer κ , *viz.*

$$\kappa = \sqrt{8\pi c_e e^2 z^2 N / 1000 DkT} \quad (5)$$

where D is the dielectric constant of the diffuse double layer, and N the Avogadro constant.

Now, if we assume that curves in Fig. 3 represent the condition of the so called rapid coagulation, that is if we assume that the condition of coalescence of droplets coincides with that of the coagulation, the critical Stern potentials of coalescence ψ_+ and ψ_- are given by the following conditions,²⁰⁾

$$dV/du = 0 \quad \text{and} \quad V = 0 \quad (6)$$

This means that there is no potential energy barrier between droplets, and hence the two surfaces can approach each other to the distance within which the van der Waals attractive force is strong enough for the coalescence to take place, when these come into contact with each other. From equations (2) and (6) we obtain

$$\frac{1.70 \times 10^{-6} a \gamma_{\pm}^2}{z^2} = \frac{A a c_e z^2}{12} \sqrt{\frac{8\pi e^2 N}{1000 DkT}} \quad (7)$$

This can be abbreviated into a form,

$$c_e = B \gamma_{\pm}^4 / z^6 \quad (8)$$

Here B is a constant containing A and a . γ_+ and γ_- are γ values obtained by substituting $\psi_1 = \psi_+$ and $\psi_1 = \psi_-$ in equation (4), respectively. It is clear from equation (4) that for small values of ψ_{\pm} , $\gamma_{\pm} \cong z e \psi_1 / 4kT$ and hence

$$c_e = B' \psi_{\pm}^4 / z^2 \quad (9)$$

While, for a large value of ψ_{\pm} , $\gamma_{\pm} \cong 1$, and hence

$$c_e = B''/z^6 \tag{10}$$

Here, B' and B'' are constants containing A and a .³⁷⁾ Then, under the assumption that $\psi_1 = E$, for the discussion of which see later, equations (8), (9) and (10) can be written in logarithmic forms as,

$$\log c_e = 4 \log |E_{\pm}| - 9 \log z + \log B \tag{11}$$

for small $|E_{\pm}|$ values

$$\log |E_{\pm}| = (1/4) \log c_e + (1/2) \log z - \log B' \tag{12}$$

and for large $|E_{\pm}|$ values,

$$\log c_e = -6 \log z + \log B'' \tag{13}$$

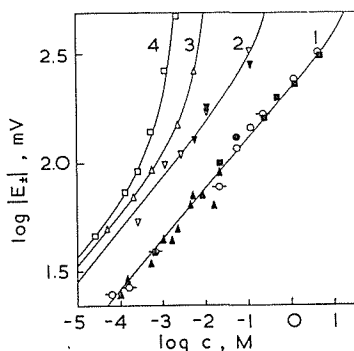


Fig. 4. Log critical potential *vs.* log ionic concentration for simple inorganic electrolyte solutions.
 ○ K⁺; -○- Na⁺; ▽ Zn⁺⁺; △ La⁺⁺⁺; □ Th⁺⁺⁺⁺;
 ● F⁻; ■ Cl⁻; ▲ NO₃⁻; ▼ SO₄⁻⁻; 1, 2, 3, 4, the absolute values of ionic valencies.

Curves in Fig. 4 are typical plottings indicating that these theoretical equations hold in the present experiments. From the behaviour of curves for low values of $\log |E_{\pm}|$, straight lines are obtained with a constant slope 1/4. It is also noticed that the position of curves shifts to the left with increasing z . These behaviours agree well with equation (12). For high values of $|E_{\pm}|$ each curve becomes independent of $|E_{\pm}|$, approaching asymptotically to a value which is dependent on the valency z of the counter ion, *vide* equation (13). It can also be confirmed that, in agreement with equation (13), these asymptotic values of $\log c_e$ for $|E_{\pm}| \rightarrow \infty$ are in linear relation to $\log z$ with a slope -6. It is possible in this connexion to estimate the van der Waals constant A , which is $0.2 \sim 0.3 \times 10^{-12}$ erg in the present case. This value is quite reasonable, since experimentally obtained values of A for various materials generally scatter between 10 and 0.1×10^{-12} erg.^{19,20,24,25)}

It is thus proved that the coalescence of mercury droplets in aqueous inorganic electrolyte solutions can be explained quantitatively by the Verwey-Overbeek theory of coagulation of lyophobic colloids.¹⁹⁾ In other words, the interaction between macroscopic mercury droplets is substantially the same as

that between submicroscopic hydrophobic colloid particles, if we assume that the conditions of coagulation and coalescence coincide with each other in the former case. Since the theory mentioned above is based on the electrostatic repulsion between the superposed electrical double layers as well as on the van der Waals attraction, the present experiments appear to give at the same time a partial verification of the existence of the electrical double layers around mercury droplets in aqueous solutions.

3. THE PROTECTION BY ORGANIC MATERIALS⁹⁾

It is well known that citrate salts are effective in preventing the coagulation of the blood or milk. Such stabilizations of dispersed systems by the addition of citrates are not restricted to the organic particles but can also be found in the case of inorganic silver iodide sols. It was found that a strong stabilization of the positive silver iodide sol took place over the concentration range higher than *ca.* 10^{-6} M, which was defined as the minimum of the stability *vs.* concentration curve obtained by turbidity measurements, was much lower than expected from the Schulze-Hardy rule, *i.e.* *ca.* 10^{-4} M in the case of trivalent ions in general.

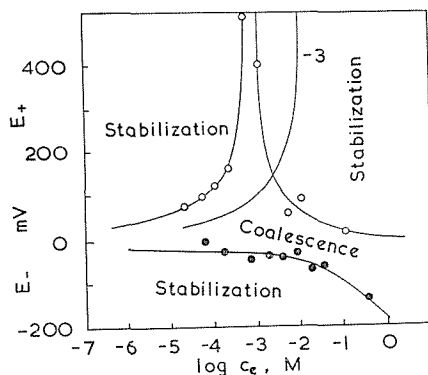


Fig. 5. Critical potential *vs.* log ionic concentration curves for sodium citrate solutions.

Such a stabilizing effect was observed by the addition of a citrate salt in the case of mercury droplets in aqueous solutions as well. Fig. 5 shows E_+ and E_- *vs.* $\log c_e$ curves for sodium citrate solutions. As is expected from the results given in the former section, the E_- *vs.* $\log c_e$ curve is normal in the sense that the shape and position correspond to the monovalent cation, *i.e.* Na^+ . However, the E_+ *vs.* $\log c_e$ curve, which is supposed to depend on the anionic species, shows certain anomalies. Although the shape of the curve over the concentration range lower than $10^{-3.2}$ M is quite in accord with that expected for trivalent anions, *i.e.* the curve -3 in the figure, its position is shifted to a much lower concentration range. This can be explained if we assume that the Stern potential ψ_1 is much more negative than the potential of the surfaces E due to the specific adsorption of citrate ions.³⁹⁾ However, we can

not explain by this mechanism another tremendous effect of stabilization observed over the concentration range higher than $10^{-3.2}$ M. Thus, the E_+ value is now a decreasing function of $\log c$. This is, however, a phenomenon which was also observed at silver iodide sols as well as many other colloids. It would appear, therefore, that the stabilization of dispersed systems in general by the addition of citrate salts can not be explained by the specific adsorption of citrate ions only.

We should refer in this connexion to the suggestion made by Becher who proposes the stabilization by the formation of insoluble salt films at the interface¹⁾. It is quite reasonable to assume that the formation of some sort of citrate salts at the interface between mercury and solution protects the droplets from coalescence, thus giving rise to the stability mentioned above.

Such a kind of protection by the interfacial film is very common in the case of emulsions stabilized by emulsifiers. We shall quote here the present authors' model experiments of this kind by using various surface active materials at the TDME. In Fig. 6 E_+ and E_- values, the critical potentials of

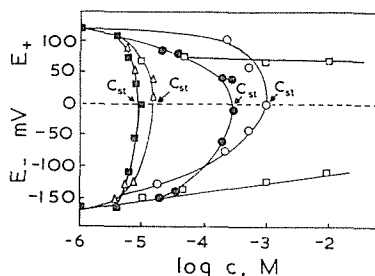


Fig. 6. The effect of various agents on the coalescence of twin dropping mercury electrodes. Supporting electrolyte, 10^{-1} M/l KCl.

■ Polyvinyl alcohol ($\bar{P}=1,400$), \triangle EPAN (copolymer of ethylene oxide and propylene oxide); ● SDS; ○ Cetylpyridinium chloride; □ Glycine.

coalescence, are plotted as functions of $\log c$ for the TDME with 0.1 M KCl as the supporting electrolyte, where c is the concentration of surface active materials added in M. It is noticed that over the concentration range higher than a certain critical value c_{st} , which is characteristic of each material used, no coalescence takes place even at the zero value of E , that is even if the electrostatic repulsion is supposed to be minimum. This behaviour of curves, that is the closure against higher concentrations, is quite common with either of cationic, anionic, or nonionic surface active materials. Since there is very little chance in the case of nonionic surface active materials for the Stern potential to increase in magnitude by the specific adsorption, it would be reasonable in these cases to propose some mechanism other than the increase in the electrostatic repulsion. This would also be applicable to cases of stabilization by the addition of ionic surface active materials as well, since the E_+ and E_- vs. $\log c$ curves in Fig. 6 show a behaviour similar to nonionic materials.

It is then concluded that in cases of this section the condition of coalescence does not coincide with that of coagulation. In other words even if the condition of coagulation is satisfied, and hence the droplet surfaces can approach each other to a certain distance, some kind of protection acts to prevent the further approach to the distance within which the van der Waals attractive force is effective to give rise to coalescence.

In the case of nonionic surface active materials of high molecular weights, *i.e.* the EPANs, the critical stabilizing concentration c_{st} is related to the so called HLB value of the substance, as is shown in Table 1^{40,41)}. Here EPANs are a group of commercial nonionic surface active polymers of the Pluronic type⁴²⁾, consisting of polypropylene glycol (PO) as the hydrophobic and the polyethylene glycol (EO) as the hydrophilic groups at different mole ratios, see Table 2. As is noticed in Fig. 7 $\log c_{st}$ is a linear decreasing function of

Table 1. The critical stabilizing concentration of various surface active materials with 0.1 M KCl as the supporting electrolyte.

Surface active material	critical stabilizing concentration (M)	HLB	ΔG (Kcal/M)
EPANs :			
E-720	7.0×10^{-5}	5.57	-7.9
E-740	5.9×10^{-5}	11.92	-8.0
E-750	4.5×10^{-5}	16.82	-8.4
E-785	1.4×10^{-5}	86.91	-9.1
E-420	5.8×10^{-5}	5.20	
E-450	5.0×10^{-5}	11.97	
E-485	2.3×10^{-5}	53.95	
PVA*	1.1×10^{-5}		
SDS	3.0×10^{-4}		
CPC	1.1×10^{-3}		

* Average degree of polymerization, 1,380; acetyl groups, 11.3 mole per cent.

Table 2. The EPANs.

EPAN*	Molecular weight	Molecular weight of PO groups	Molecular weight of EO groups
E-710	2,222	2,000	222
E-720	2,500	2,000	500
E-740	3,333	2,000	1,333
E-750	4,000	2,000	2,000
E-785	13,333	2,000	11,333
E-410	1,333	1,200	133
E-420	1,500	1,200	300
E-450	2,400	1,200	1,200
E-485	8,000	1,200	6,800

* $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_a(\overset{\text{CH}_3}{\text{C}}\text{HCH}_2\text{O})_b(\text{CH}_2\text{CH}_2\text{O})_c\text{H}$

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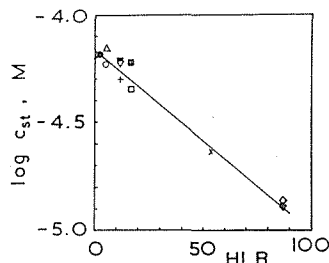


Fig. 7. The logarithm of the critical stabilizing concentration as a function of HLB.

The supporting electrolyte, 0.1M KCl; \triangle , E-720; \triangle , E-740; \square , E-750; \diamond , E-785; \circ , E-410; $+$, E-450; \times , E-485. $5 \times 10^{-3}M$ $La(NO_3)_3$; \bullet , E-710; \blacktriangledown , E-740; \blacksquare , E-750; \blacklozenge , E-785

HLB; the stabilizing power increases with increasing hydrophilic property of the material added.

The fact that these protections due to the addition of EPANs are intimately related to the formation of interfacial adsorption layers is clearly indicated by the differential double layer capacity of mercury-solution interfaces $C(\mu F/cm^2)$. In Fig. 8 C vs. E curves for E-785 are shown with c values as the

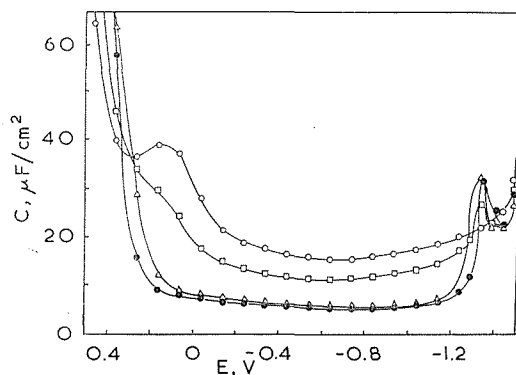


Fig. 8. The differential double layer capacity vs. polarization curves in the presence of E-785 with 0.1M KCl as the supporting electrolyte. EPAN concentrations: \bullet , $1.4 \times 10^{-5}M$; \triangle , $3.9 \times 10^{-6}M$; \square , $1.5 \times 10^{-6}M$, \circ , 0 M.

parameter. It is noticed that typical capacity suppressions take place over the potential range near the $E=0$ region, thus indicating the formation of interfacial films^(4,43-47). The protection of the mercury droplets from coalescence, therefore, accompanies with it the formation of the interfacial adsorption layer of EPAN molecules.

The capacity suppression as a function of the surface active material concentration can be used to the estimation of the free energy of adsorption of this material on the mercury surface $\Delta G^{(4)}$. ΔG values thus obtained are summarized in Table 1. It is clear that the higher the hydrophilic property

of the molecule, the larger is the absolute value of ΔG , that is the easier is the molecule to be adsorbed. It is then concluded that the stabilization strongly depends on the adsorbability on the mercury surface in the present experiments. It would appear that the desorption of the surface active material must take place before the coalescence of droplets to take place, and hence this process is the rate-determining step in the entire coalescence process.

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