

The Electrocapillarity of Oil-Water Interfaces*

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When a potential difference is applied to two immiscible liquids in contact with each other, the interfacial tension changes with it. Such an electrocapillary phenomenon takes place over a reasonable potential range, *i. e.* from *ca.* -20 to +20V, only when the system has a sufficiently high electric conductance and contains surface active agents. For a system of an organic solvent (oil phase) in contact with an aqueous solution (aqueous phase), the electrocapillary curve has a characteristic shape depending on the ionic type of the surface active agents; the interfacial tension is suppressed over the cathodic or anodic polarization range according as the surface active agent is cationic or anionic. Here, the sign of polarization is taken as that of the aqueous phase with respect to the oil phase. In the case of amphoteric surface active agents the shape of curves depends on the pH value of the aqueous phase, being the anionic or cationic type according as the pH value is higher or lower than a certain value, the interfacial isoelectric point. The electrolyte in the aqueous phase not only enhances the electric conductance, but also changes the shape of the electrocapillary curve. This is ascribed to the counterion binding of the polar head group of the surface active agent immersed in the aqueous side of the interface.

INTRODUCTION

The electrocapillary phenomenon is in general defined as the change in interfacial tension induced by the application of a potential difference between two phases. Although this has been studied mainly for systems of a liquid metal, *e. g.* mercury, in contact with various aqueous solutions and very helpful in the study on the double layer structure at interfaces,¹⁻⁵⁾ it is not restricted to such systems; it is supposed to take place at any immiscible liquid phases in contact with each other.

Such an extension of the scope of electrocapillarity to oil-water interfaces was first made by Guastalla.⁶⁾ Thus, he obtained the electrocapillary curve for an oil phase, consisting of cetyltrimethylammonium bromide dissolved in nitrobenzene, in contact with a dilute aqueous solution of KCl or KBr. It was found that the interfacial tension decreased when the aqueous phase was polarized cathodically with respect to the oil phase. He also noticed the same kind of interfacial tension suppression over the anodic range, when the oil phase contained sodium alkylsulphate.

Although, as far as we know, no further extension of experimental conditions

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has so far been made by him, this work is important in the sense that an extra variable, *i. e.* the interfacial polarization, has been introduced as a factor which can easily be controlled experimentally. It is then expected that the structure of adsorption layers and adsorption processes at oil-water interfaces can be studied as the functions of electrical conditions. This consideration has led the present authors to further the experiment on more or less the same lines by extending the concept of the electrocapillarity to include various liquid-liquid interfaces. In Chapter I the confirmation of Guastalla's conclusion will be made by using different oil-water systems, Chapter II will deal with the effect of counterions on the electrocapillarity, *i. e.* the counterion binding, and Chapter III will be devoted to the description of the interfacial behaviour of a biologically important amphoteric surface active agent, lecithin.

I ELECTROCAPILLARY CURVES OF OIL-WATER SYSTEMS CONTAINING SURFACE ACTIVE AGENTS

The drop volume method for interfacial tension measurements⁷⁾ was modified so that a polarizing potential difference could be applied to the interface by means of an outer circuit. A drop of electrolyte solution (aqueous phase) was formed in an oil phase from the tip of a glass capillary needle by using a micrometer syringe. Here, the "oil phase" means that of an organic solvent in which various organic electrolytes, say ionic surface active agents, were dissolved. The glass capillary was equipped with a platinum electrode sealed to its wall, by means of which the polarizing potential E from 0 to $\pm ca. 20$ V was applied to the aqueous phase with reference to the mercury pool at the bottom of the oil phase. It was thus possible to measure the interfacial tension γ as a function of E from measurements of the maximum drop volume V at various polarizations. The details of the experimentation has been given elsewhere.⁸⁾

In order to minimize the ohmic potential drop in bulk phases, the electrical conductance of the oil phase as well as that of the aqueous phase must be kept as high as possible. The first experiment was, therefore, made by using an oil phase of tetramethylammonium iodide (TMAI) dissolved in methylisobutylketone (MIBK), the aqueous phase being 1 M KCl. However, no interfacial tension change was found to occur over the polarization range from 0 to ± 20 V by thus simply enhancing the electrical conductance of the system, see Fig. 1.

The ionic surface active agent dissolved in the oil phase, on the other hand, has a substantial influence on the electrocapillary curve, γ *vs.* E , as is shown in Fig. 1. For anionic surface active agents, *e. g.* sodium cetylsulphate (SCS) or sodium dodecylbenzenesulphonate (SDBSO), the interfacial tension γ is suppressed over the anodic polarization range, *i. e.* for $E > 0$, while, for cationic surface active agents, *e. g.* cetyltrimethylammonium chloride (CTAC) or cetylpyridinium chloride (CPC), the suppression occurs over the cathodic polarization range. It is interesting to notice in this connexion that the coexistence of SCS and CTAC in the oil phase has an additive effect, thus producing an ordinary type of electrocapillary curve usually obtained for mercury-aqueous solution interfaces; the electrocapillary

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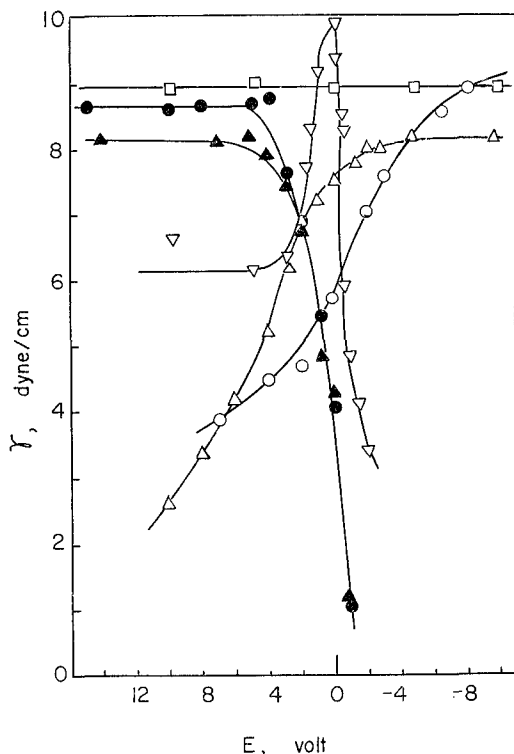


Fig. 1. Typical electrocapillary curves. Aqueous phase: 1 M KCl. Oil phase: □, $1 \times 10^{-4} M$ TMAC; ▲, $2.5 \times 10^{-4} M$ CTAC; ●, $2.5 \times 10^{-4} M$ CPC; ○, $2.5 \times 10^{-4} M$ SCS; △, $1 \times 10^{-4} M$ SDBSO; ▽, $5 \times 10^{-5} M$ SCS + $5 \times 10^{-5} M$ CTAC in MIBK.

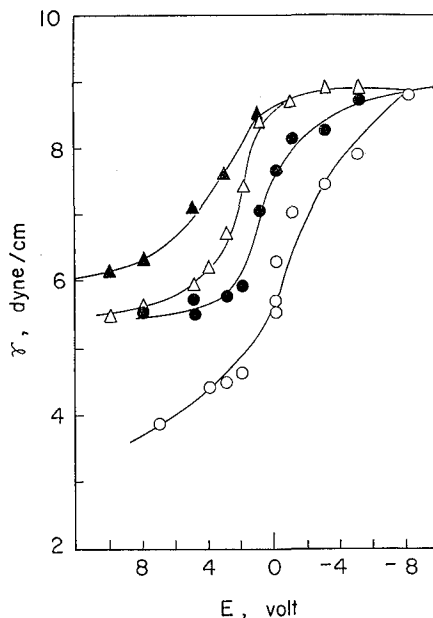


Fig. 2. The influence of the concentration of SCS on γ vs. E curves. Aqueous phase: 1 M KCl. Oil phase: SCS in MIBK; ▲, $1 \times 10^{-6} M$; △, $1 \times 10^{-5} M$; ●, $1 \times 10^{-4} M$; ○, $2.5 \times 10^{-4} M$.

maximum is found to be at around $E=0$ in the present case.

Fig. 2 shows the effect of the surface active agent concentration on γ vs. E curves for SCS dissolved in MIBK in contact with 1 M KCl aq. It is noticed that the γ suppression over the anodic polarization range starts to take place at a less anodic polarization, *i. e.* the curve is shifted to the right, for the higher SCS concentration. The same kind of concentration effect, but of the opposite direction, was obtained for the cationic surface active agent as well over the cathodic polarization range. It is worth pointing out the fact that, although the suppression of γ by the addition of surface active agents is in general negligible at $E=0$, *i. e.* in the absence of polarization, for very small surface active agent concentrations, say for $[SCS]=10^{-6}$ to $10^{-5} M$, a marked change in γ is found even for such low concentrations, if a polarizing potential of sufficient amount is applied to the interface.

The characteristic effect of ionic type of the surface active agent on γ vs. E curves obtained above is in general found for any polar solvents. This is clear from γ vs. E curves in Fig. 3 for oil phase of SCS dissolved in various polar

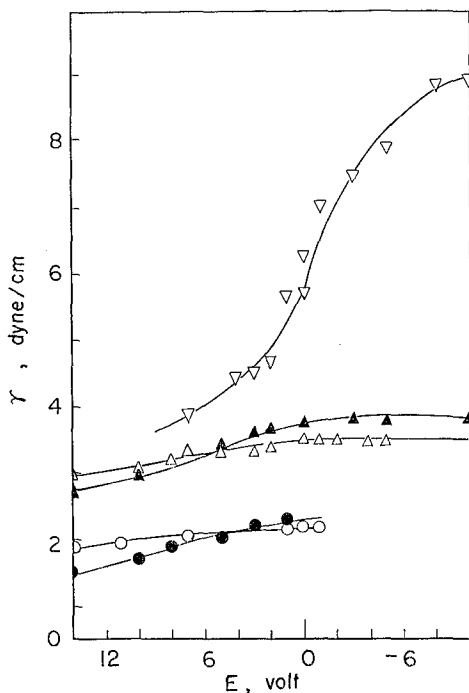


Fig. 3. The influence of solvents on γ vs. E curves.

Aqueous phase: 1 M KCl

Oil phase: ∇ , $2.5 \times 10^{-4} M$ SCS in MIBK;
 \blacktriangle , $1 \times 10^{-5} M$ SCS in MIBK;
 \triangle , $2.5 \times 10^{-4} M$ SCS in pentanol;
 \circ , $2.5 \times 10^{-4} M$ SCS in butanol;
 \bullet , $1 \times 10^{-5} M$ SCS in pentanol.

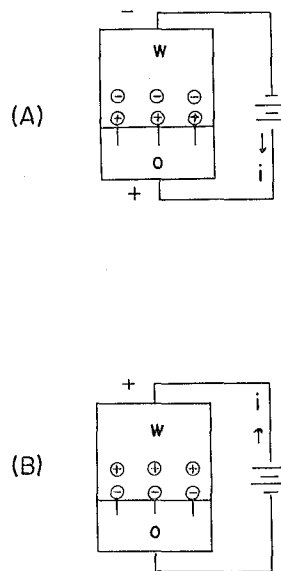


Fig. 4. The schematic representation of double layers at the oilwater interface.

(A) Cationic surface active agent.
 (B) Anionic surface active agent.

solvents, *i.e.* pentanol, butanol and MIBK, the aqueous phase being 1 M KCl throughout. All curves have the shape characteristic of anionic surface active agents; the γ suppression takes place over the anodic polarization range.

Now, under the assumption that the thermodynamic equilibrium is established at interfaces, which is however not valid in the present cases (see later), the Gibbs adsorption isotherm holds, *viz.*^{4,9)}

$$-d\gamma = \sum_i \Gamma_i RT d \ln c_i + q dE', \quad (1)$$

where Γ_i is the surface excess of the component i , c_i its bulk concentration, q the surface charge density on the aqueous side of the interface, R the gas constant, T the absolute temperature, and E' the interfacial potential drop. E' is usually smaller than E in the present cases, although $E \cong E'$ in most cases of mercury-aqueous solution interfaces, since the electrical conductance of the system is usually high enough in latter cases. Anyway, we shall assume that E' is an approximately linear increasing function of E .

For a constant composition, *i.e.* for $d \ln c_i = 0$, equation (1) reduces to the form:-

$$-(\partial\gamma/\partial E')_{c_i} = q, \quad (2)$$

which is the Lippmann-Helmholtz equation of electrocapillarity.

It has been shown by the present experiments that $(\partial\gamma/\partial E')_{c_i}$ is positive or negative according as the surface active agent used is cationic or anionic. It is then concluded that q is negative or positive in the respective case. We have therefore a picture of the interfacial electrical double layer as is shown in Fig. 4 A and B. For the system containing cationic surface active agents, these cations are adsorbed on the oil side of the interface, which together with the inorganic counterions, here anions, constitute the interfacial electrical double layer (A). While, a double layer of the opposite polarity is formed in the case of anionic surface active agents (B).

Such a double layer model is somewhat different from that of the mercury-solution interfaces. Since the latter is considered to be an ideal polarized electrode, the equivalent circuit being a perfect condenser without leakage, the interfacial polarization is ascribed to the excess or deficit of electrons at the mercury surface and to the unsymmetrical distribution of ions on the solution side of the interface. The interfacial charge transfer is usually negligible in this system.^{4,5)}

Since, on the other hand, we can not expect the presence of the free electronic charge at an oil-water interface, the double layer of present systems will almost completely be ascribed to the unsymmetrical distribution of ions at the interface.

The surface excess Γ_s of surface active ions in the interfacial double layer can be estimated from the slope of γ vs. $\ln c$ curves at a constant E' , since we obtain from equation (1) the following expression :-

$$-(1/RT)(\partial\gamma/\partial \ln c_s)_{E'} = \Gamma_s. \quad (3)$$

Here, c_s is the surface active agent concentration. Now, an assumption will be made that, if E is constant, E' is also constant. We then obtain Γ_s for SCS or CTAC dissolved in MIBK as a function of E , see Fig. 5. It will be noticed that the adsorption starts to take place at the lower absolute value of polarization for the higher surface active agent concentration. It is also noticed that the Γ_s value

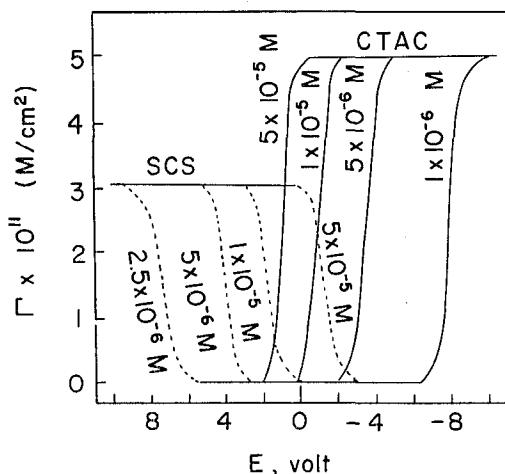


Fig. 5. Interfacial excess vs. polarization.

for the saturated adsorption, *i. e.* for sufficiently high values of $|E|$, is independent of the concentration c_s ; it is characteristic of the system used. Molecular cross sections estimated from such saturation values are *ca.* 300 and $500 \text{ \AA}^2/\text{molecule}$ for CTAC and SCS, respectively. These are of an order larger than the limiting area, *i. e.* $20 \text{ \AA}^2/\text{molecule}$, of saturated fatty acids at air-water interfaces,^{10,11)} and are rather close to the areas obtained at the solid-liquid interfaces.^{12,13)} It must be added, however, that above calculations were made on the assumption that the thermodynamic equilibrium is established at the interface. That this is not valid in the present systems is clear from the fact that an appreciable amount of electric current is passing through the system during the application of polarizing potential. Hence, these calculations give only a rough idea of the order of magnitude of adsorption at the stationary state of adsorption processes.

The limiting value γ_∞ of γ in the opposite direction, *e. g.* those for very large negative values of E in Fig. 2, gives, according to the present reasoning, the interfacial tension in the absence of adsorbed surface active agents. The values are 10.9, 3.9 and 2.3 for MIBK, pentanol and butanol, respectively; these can be compared with interfacial tensions γ_i measured without applying a potential difference, *i. e.* with the open circuit, which are 10.8, 4.4 and 1.6 for the respective interfaces.¹⁴⁻¹⁶⁾ The agreement between γ_∞ and γ_i is considered to be sufficient to support the present authors' opinion.

In Fig. 6 current densities i are plotted as functions of E for 1 M KCl aq in

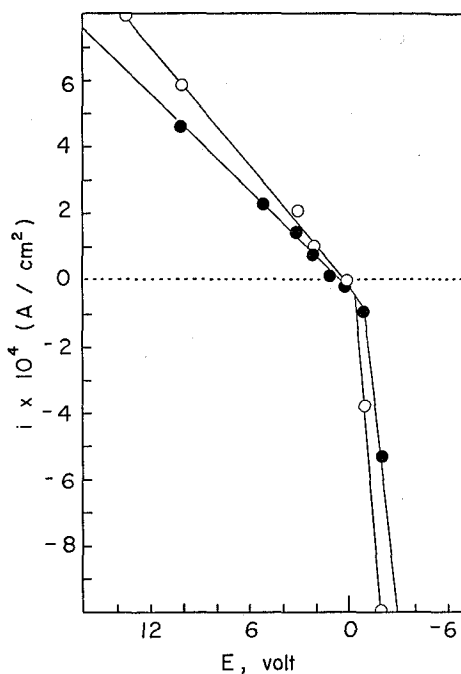


Fig. 6. Current density vs. polarization curves.

Aqueous phase: 1 M KCl

Oil phase: CPC in MIBK;

O, $5 \times 10^{-4} M$ ●, $2.5 \times 10^{-4} M$

contact with the oil phase containing CPC in MIBK. It is found that for such system, *i. e.* if the surface active agent is cationic, the slope di/dE is greater in magnitude over the cathodic than the anodic polarizations. Such a rectification, *i. e.* the nonlinear relationship between the current density and E , was found at almost every interfaces of the present study. The rectification of opposite direction was found for anionic surface active agents. These rectifications would probably be due also to the formation of interfacial charged layers of surface active agents.

II COUNTERION BINDING AT OIL-WATER INTERFACES

In the discussion of the last chapter we have adopted for the sake of simplicity the Helmholtz double layer model, *cf.* Fig. 5. However, since the Gouy-Chapman diffuse double layers are supposed to exist on both sides of the interface, the situation is much more complicated. Moreover, we can suppose with a good reason that surface active agent ions are orientated at the interface with the hydrophilic polar head groups directed towards the aqueous phase and with the hydrophobic chains towards the oil phase. We shall give an experimental evidence of this double layer picture in this chapter. We have in addition an evidence to suggest that the polar groups are immersed in the aqueous phase to a considerable depth from the interface.

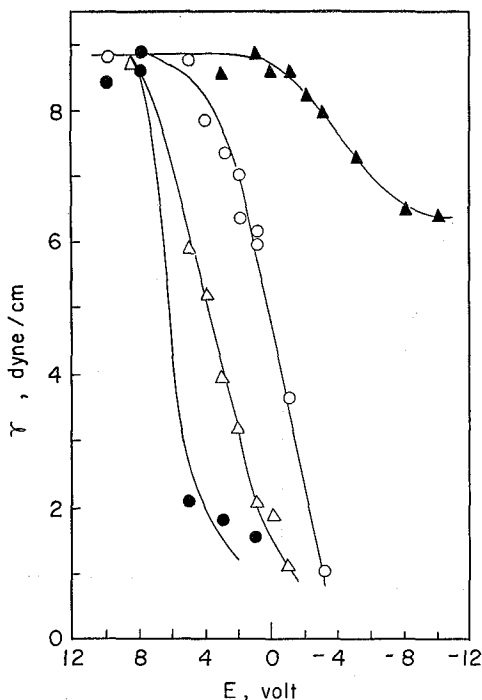


Fig. 7. The influence of halide ions in the aqueous phase on γ vs. E curves.

Oil phase: $2.5 \times 10^{-4} M$ CPC in MIBK.

Aqueous phase: $1 \times 10^{-1} M$;

▲, KI; ○, KBr; △, KCl; ●, KF.

According to the modern theory of electrical double layers, the so called Stern layer is formed by the specific adsorption just in front of the charged surface, if the system contains capillary active components. In the present systems this layer corresponds to the array of counterions bound to the orientated head groups of surface active agent ions at the interface.

In Fig. 7 γ vs. E curves for interfaces between the oil phase of $5 \times 10^{-4} M$ CPC dissolved in MIBK and various $0.1 M$ potassium halides aq., *i.e.* KF, KCl, KBr and KI are given. It is noticed that anions are arranged in ascending magnitudes of the suppression of γ over the cathodic region in the following sequence:-



The same anionic sequence has also been obtained when the oil phase contained CTAC, but not for oil phases containing anionic surface active agents. The above sequence agrees with the Hofmeister lyotropic series, thus showing that ions of larger crystallographic radii have stronger tendencies to prevent the γ suppression caused by cationic surface active agents. Such an antagonism would perhaps be explained by the neutralization of the charge of adsorbed surface active ions due to the counterion binding, here of halides, since the surface active ions would then no longer behave as *charged* films at interfaces, *cf.* Chapter III. It is a well known

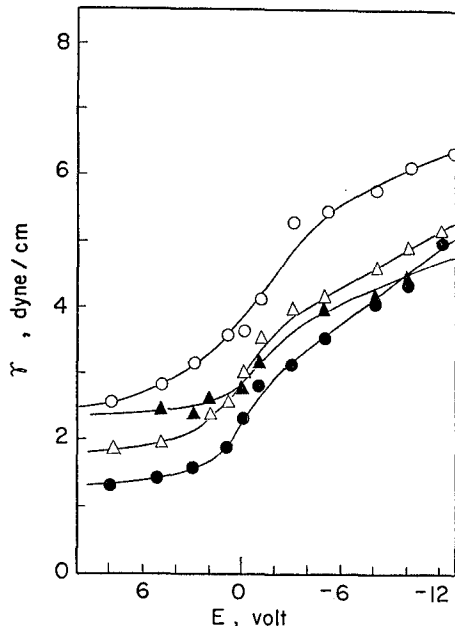


Fig. 8. The influence of bivalent cations on γ vs. E curves.

Oil phase: $5 \times 10^{-4} M$ SDBSO in MIBK.

Aqueous phase: $1 \times 10^{-2} M$;

○, $Cd(NO_3)_2$; △, $Zn(NO_3)_2$;

▲, $MgSO_4$; ●, $Ba(NO_3)_2$.

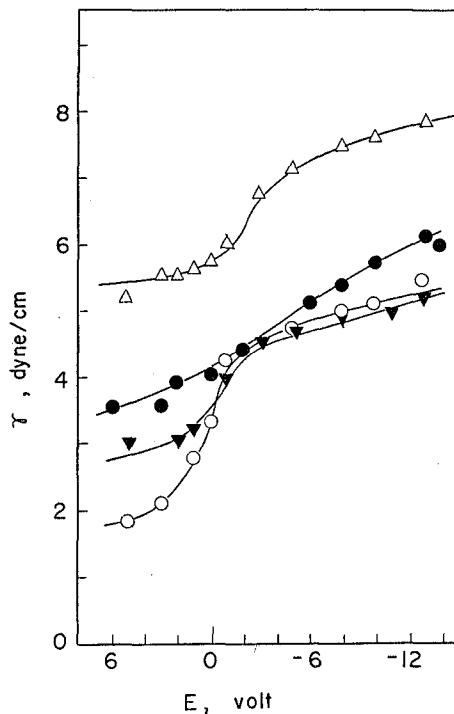


Fig. 9. The influence of cationic valencies on γ vs. E curves.

Oil phase: $5 \times 10^{-4} M$ SDBSO in MIBK.

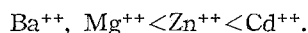
Aqueous phase: $1 \times 10^{-2} M$;

△, $Th(NO_3)_4$; ●, $La(NO_3)_3$;

▼, $Ba(NO_3)_2$; ○, KCl.

fact that the anion of a large ionic radius, like I^- , has a high binding tendency, due to the larger polarizability as compared with the smaller ions, like F^- .^{4,17)}

An example of the binding of divalent cations to anionic surface active ions is shown in Fig. 8, in which γ vs. E curves are given for interfaces between $5 \times 10^{-4} M$ SDBSO dissolved in MIBK and various $10^{-2} M$ salts aq., *i. e.* $Ba(NO_3)_2$, $MgSO_4$, $Zn(NO_3)_2$, and $Cd(NO_3)_2$. Cations are arranged in ascending order of magnitude of the suppression of γ over the anodic polarization range as follows :-



This cationic sequence has been found to agree with the binding ability of these cations with chondroitin sulphate.¹⁸⁾

Fig. 9 shows the effect of the cationic valency on γ vs. E curves for interfaces between the oil phase of $5 \times 10^{-4} M$ SDBSO dissolved in MIBK and various $10^{-2} M$ salt solutions, *i. e.* $Th(NO_3)_4$, $La(NO_3)_3$, $Ba(NO_3)_2$ and KCl. It is noticed that cations of the higher valency shows the stronger inhibition of the γ suppression over the anodic polarization range.

It can easily be supposed that the above mentioned antagonism due to the counterion binding can take place only when the polar head group of orientated ionic surface active agent is immersed into the aqueous side of the interface. As in the case of the specific adsorption of ions from the solution to mercury surface, the counterion binding is supposed to take place not only by the electrostatic attraction but also by the chemical binding between the head group and the counterion.¹⁹⁾

III THE ELECTROCAPILLARITY OF LECITHIN AT OIL-WATER INTERFACES

In Chapters I and II the effect of ionic surface active agents on electrocapillary curves of oil-water interfaces has been discussed. Then, it is natural to extend the scope of experiments to include amphoteric surface active agents. For this purpose we have adopted lecithin, not only because this substance is widely employed as oleophilic emulsifier and dispersant²⁰⁾ but also because it is biologically very important as the constituent of cell membranes.²¹⁾ It was thus hoped to study the adsorption behaviour and the counterion binding of lecithin at oil-water interfaces and to understand the basic mechanism of the emulsification and dispersion as well as the ionization of amphoteric substances at interfaces.

Fig. 10 shows typical γ vs. E curves for interfaces between the oil phase of 0.001% lecithin dissolved in MIBK and aqueous phases of 1 M KCl plus varying amounts of HCl. It is found that the lecithin originally added to the oil phase behaves at the oil-water interface as an anion at $pH > 1.2$ and as a cation at $pH < 0.88$. At $pH 1.1$ γ did not change with E over the entire polarization range examined. It is thus concluded that $pH 1.1$ is the interfacial isoelectric point of lecithin for the MIBK-water system. Such a high sensitivity of the dissociation state of lecithin at the interface on pH as observed here is characteristic of the present experiments and provides us with an accurate isoelectric point measurements at interfaces.

The effect of pH of the aqueous phase on the ionization of lecithin added to the oil phase mentioned above clearly shows that this substance is orientated at the

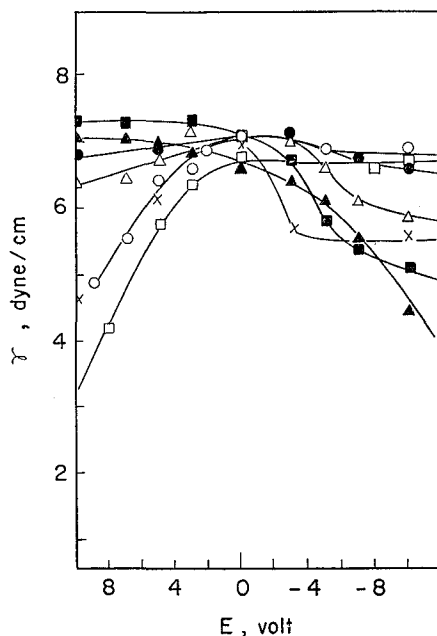


Fig. 10. The influence of pH of the aqueous phase containing 1M KCl on γ vs. E curves for lecithin.
Oil phase: $1 \times 10^{-3}\%$ lecithin in MIBK.
Aqueous phase: 1 M KCl;
pH: \square , 2.2; \times , 1.45; \circ , 1.20;
 \bullet , 1.10, \triangle , 1.00; \blacksquare , 0.88.

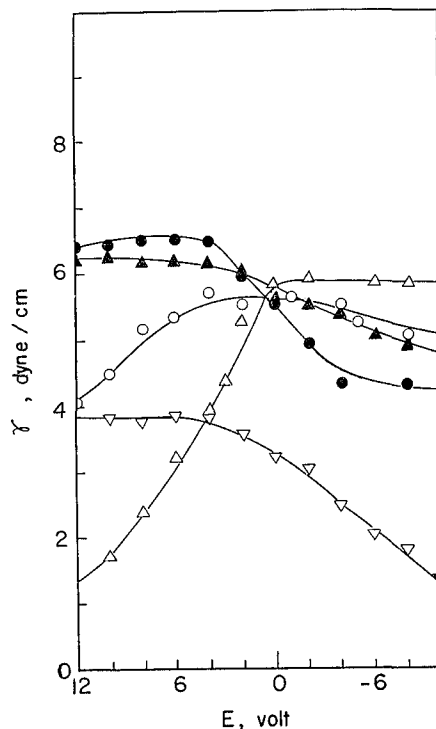


Fig. 11. The influence of the concentration of $\text{Cd}(\text{NO}_3)_2$ on γ vs. E curves for lecithin.
Oil phase: $1 \times 10^{-3}\%$ lecithin in MIBK.
Aqueous phase: $\text{Cd}(\text{NO}_3)_2$;
 ∇ , 1 M (pH 1.75); \blacktriangle , $5 \times 10^{-2} M$;
 \bullet , $3 \times 10^{-2} M$; \circ , $2 \times 10^{-2} M$ (pH 4.2);
 \triangle , $1 \times 10^{-2} M$ (pH 4.1).

interface with its polar groups, *i. e.* $-\text{N}(\text{CH}_3)_3^+\text{OH}^-$ and $-\text{PO}_3^-\text{H}^+$, immersed in the aqueous phase. It is then expected that metal ions, if present in the aqueous phase, would be bound to the anionic head group, just as in Chapter II. Such a counterion binding is shown by Fig. 11, in which γ vs. E curves are given for the oil phase of lecithin in contact with aqueous phases containing various concentrations of $\text{Cd}(\text{NO}_3)_2$. It is noticed that for low $\text{Cd}(\text{NO}_3)_2$ concentrations the anionic type of electrocapillary curves, while for high $\text{Cd}(\text{NO}_3)_2$ concentrations the cationic type of curves, are obtained. The reversal of charge is found to take place at $[\text{Cd}^{++}] = 2 \sim 3 \times 10^{-2} M$. The same kind of behaviour was also found for aqueous phases containing $\text{Th}(\text{NO}_3)_4$ or $\text{La}(\text{NO}_3)_3$, the charge reversal points being 10^{-4} and *ca.* $3 \times 10^{-2} M$, respectively. It was also found that no charge reversal took place when the aqueous phase contained KCl only, since both K^+ and Cl^- do not bind so much as to change the sign of the film.

It must be mentioned in this connexion that the hydrolysis takes place when a high valent cation, such as Th^{++} *etc.*, is contained in the aqueous phase, thus giving rise to the change in pH of the aqueous phase. Then it is highly probable that such a pH change has an influence on the ionization state of the lecithin at

the interface. However, the charge reversal due to the presence of a high valent cation can not entirely be ascribed to this pH change. This can be shown, for instance, by the pH value of $10^{-4}M$ $\text{Th}(\text{NO}_3)_4$ aq., *i. e.* pH 3.92, which is still higher than the interfacial isoelectric point, pH 1.1, obtained above for KCl aq.

In order to find the effect of the supporting electrolyte on the interfacial isoelectric point pH_i^* , γ vs. E curves for aqueous phases of various salt contents were examined. As an illustration γ vs. E curves for interfaces between lecithin dissolved in MIBK and $10^{-5}M$ $\text{Th}(\text{NO}_3)_4$ aq. of various pH are shown in Fig. 12. It is noticed that the charge reversal takes place at pH 3.92 for this salt concentration. This is different from the value $\text{pH}_i^* 1.1$ for KCl.

Fig. 13 is the summary of interfacial isoelectric points for various salts of various concentrations, *i. e.* the cation binding spectra. It is noticed that the interfacial isoelectric point is almost independent of the salt concentration, although it is strongly dependent on the cationic species of the salt. Such a cationic specificity can be compared with that obtained by various authors. Seaman and Pethica,²²⁾ for instance, measured by the electrophoresis the charge reversal point of normal blood red cells suspended in 0.85% NaCl aq. containing $\text{Th}(\text{NO}_3)_4$ or $\text{La}(\text{NO}_3)_3$. Although their cation binding spectra appear to agree with the cationic sequence of Fig. 13 of the present authors, there is a difference in experimental conditions between them. Although Seaman and Pethica did not adjust the pH of the system, our conclusion is that the change in pH by the hydrolysis must be taken into

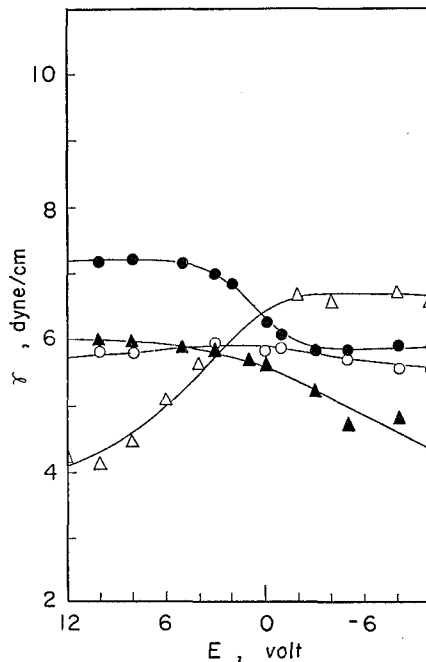


Fig. 12. The influence of pH of the aqueous phase containing $1 \times 10^{-5}M$ $\text{Th}(\text{NO}_3)_4$ on γ vs. E curves for lecithin.
Oil phase: $1 \times 10^{-3}\%$ lecithin in MIBK.
Aqueous Phase: $1 \times 10^{-5}M$ $\text{Th}(\text{NO}_3)_4$:
pH; \triangle , 4.45; \circ , 3.92; \bullet , 2.55; \blacktriangle , 1.82.

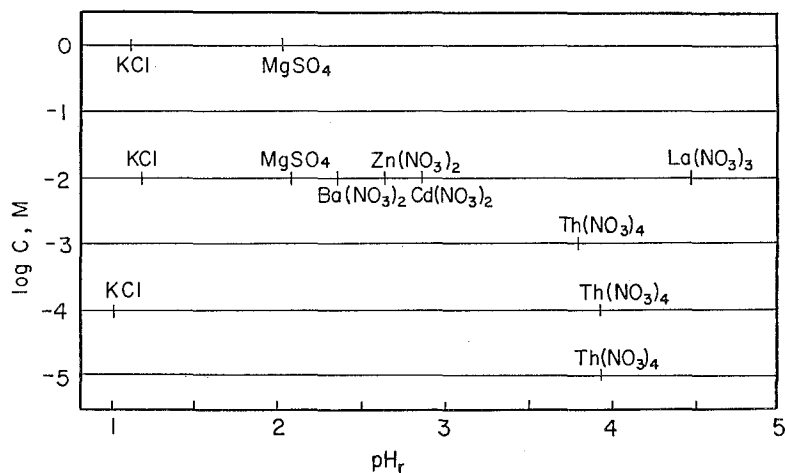


Fig. 13. Reversal of charge spectra of lecithin at oil-water interfaces.

account. The cation binding spectra of Fig. 13 for the salt concentration $10^{-2}M$ give a cationic sequence of ascending pH_i^* values which is the same as that obtained by Bungenberg de Jong for the cation binding to lecithin in the presence of the cholesterol.²³⁾ It is thus supposed that bindings of the hydrogen ion and other cations are competing at the interface for the head group of lecithin.

The bulk isoelectric points pH_i of lecithin in pure water and KCl aq. were estimated approximately by using the turbidity method. It was found that the isoelectric point did not change by the addition of KCl to the lecithin solution, the pH_i value being from 1 to 2. It was thus concluded that the interfacial and the bulk isoelectric points are almost the same in the case of KCl solutions. The present method of the bulk isoelectric point measurement was not accurate enough to allow a further comparison of the pH_i and pH_i^* , and of the difference in pH values of the interface and bulk phase.

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