

The Behavior of Surface Active Agents and Dyestuffs at Oil-Water Interfaces

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The interaction between surface active agents and dyestuffs at the oil-water interface, as well as the influence of inorganic electrolytes on it, was studied by measuring electrocapillary curves. When the oil phase contained the cationic surface active agent, or the amphoteric surface active agent at the acidic side, and the aqueous phase the anionic dyestuff, the decrease in the interfacial tension over the cathodic polarization range, which is characteristic to cationic surface active agents, was suppressed due to the binding between the surface active agent and dyestuff at the interface. However, if the aqueous phase contained the anionic, instead of cationic, dyestuff, no binding was found to take place, and the ordinary builder effect, *i. e.* the increase in surface activity, was observed. When the oil phase contained the anionic surface active agent, or the amphoteric surface active agent at the alkaline side, and the aqueous phase the cationic dyestuff, the decrease in the interfacial tension over the anodic polarization range, which is characteristic to anionic surface active agents, was suppressed due to the binding between the dyestuff and surface active agent. It was also found that these bindings were strongly influenced by the species and concentration of the electrolyte in the aqueous phase.

INTRODUCTION

In recent communications¹⁻³⁾ the double layer structure of oil-water interfaces was discussed in connection with electrocapillary measurements on systems of oil phase, containing the surface active agent, in contact with the aqueous phase, containing the inorganic electrolyte. It was found that the interfacial tension decreased over the anodic polarization range when the surface active agent was anionic, while, the decrease took place over the cathodic polarization range when the surface active agent was cationic. Moreover, this decrease in interfacial tension was found to be suppressed by the counterion binding at the interface. It was thus concluded that surface active agent molecules were orientated at the interface in a manner such that the hydrophilic ionic groups are intruded into the aqueous phase.

The present paper deals with the adsorption behavior of dyestuffs at oil-water interface, together with the influence of surface active agents and inorganic electrolytes on it, by applying the same method as mentioned above. Thus, it is hoped that this study will give informations that can help to understand the dyeing process, detergency, *etc.*

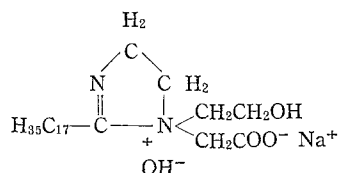
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EXPERIMENTAL

Materials

The organic solvent, methylisobutylketone (MIBK), was distilled and then saturated with water before use. Surface active agents, *i.e.* cetylpyridinium chloride (CPC), sodium cetylsulphate (SCS) and sodium dodecylbenzenesulphonate (SDBSO), were of the Analytical Grade. The amphoteric surface active agent of imidazoline type (IM), prepared in the Research Laboratory, the Lion Fat Company, Tokyo, was 92 % pure and had the following formula :



The organic supporting electrolyte added to the oil phase, tetrabutylammonium chloride (TBAC), was also of the Analytical Grade.

As for dyestuffs, the commercial Benzopurpurine 4B (BP) and Chrysophenine (CH) were purified by Robinson-Mills' method.⁴⁾ Orange II (OR) and Crystal Violet (CV) were of the Analytical Grade (Merck), which were recrystallized twice before use. Other dyestuffs, *i.e.* Methylene Orange (MO), Methylene Blue (MB) and Rodamine B (RD), as well as inorganic electrolytes, were of the Analytical Grade, which were used without further purification.

Ion exchange resin water was distilled by using an all Pyrex glass apparatus, which was used for the present experiments.

Methods

Electrocapillary curves were obtained by the same method as reported previously.¹⁾ The principle was as follows: A drop of aqueous solution was formed in the oil phase, and the interfacial tension γ calculated from the maximum drop volume. It was thus possible to obtain γ as a function of the polarization potential, E , applied to the aqueous phase, with reference to the oil phase.

The solvent of the oil phase was always MIBK, in which the anionic, cationic or amphoteric surface active agent was dissolved in addition to the organic supporting electrolyte, TBAC.

The aqueous phase, on the other hand, contained the anionic or cationic dyestuff in addition to the inorganic electrolyte. Thus, the influence of the composition of the system on the γ *vs.* E curve was examined.

These measurements were carried out at $25 \pm 1^\circ\text{C}$.

The interaction between the dyestuff and surface active agent, as well as the influence of the electrolyte on it, was also examined in the aqueous bulk phase by measuring the absorption spectra. The Shimadzu Bousch-Rohm Spectronic 20 was employed for this purpose.

RESULTS AND DISCUSSIONS

The Surface Activity of Dyestuffs

The interfacial tension between the oil phase, containing 10^{-4} M TBAC as the supporting electrolyte, and the aqueous phase containing various dyestuffs was measured as a function of the applied potential E . The aqueous phase contained 0.1 M KCl in addition to the dyestuff; this was for the purpose of increasing electric conductance of the system.

In the case of cationic dyestuffs, RD and MB, no change in γ with E was so far observed over the polarization range from -15 to $+15$ V; these dyestuffs did not show surface activity.

Anionic dyestuffs in the aqueous phase, on the other hand, gave rise to the decrease in γ over the anodic polarization range, thus indicating the anionic surface activity. Figure 1 shows the results for the aqueous phase containing 10^{-4} M MO, OR or BP, in addition to 0.1 M KCl. All curves are typical to anionic surface active agents, the decrease in γ over the anodic range being

$$\text{MO} < \text{OR} < \text{BP}. \quad (1)$$

This sequence coincides with that of molecular weights, the decrease in γ being the largest for the dyestuff of the highest molecular weight.

The surface activity of dyestuffs mentioned above increased with increasing electrolyte concentrations. Figure 2 shows, as an example, γ vs. E curves for various KNO_3 concentrations in the aqueous phase, which contained 5×10^{-4} M BP in addition to KNO_3 . It is noticed that the decrease in γ , and hence the adsorption of BP, is promoted by the increase in the KNO_3 concentration. This would perhaps be the similar effect as that found in the promoting influence of neutral salts on the adsorption of dyestuffs on cellulose fibres *etc.*, *i. e.* the builder effect.^{5,6)}

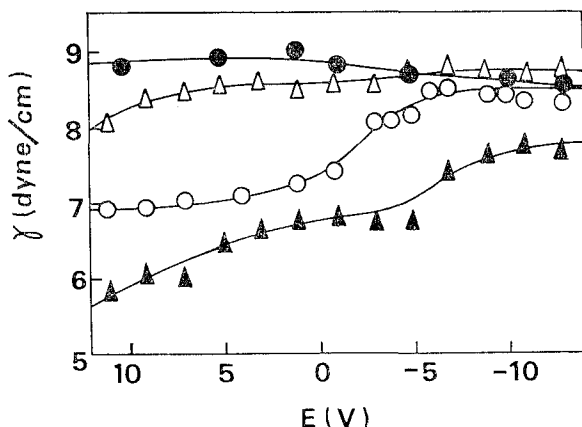


Fig. 1. The influence of dyestuffs on γ vs. E curves.
Oil phase: 1×10^{-4} M TBAC.
Aq. phase: 1×10^{-1} M KCl + 5×10^{-4} M Dyestuff.
Dyestuff: ●, none; △, MO; ○, OR; ▲, BP.

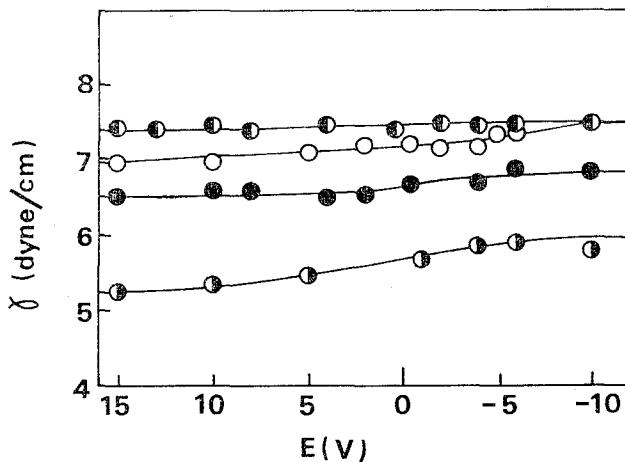


Fig. 2. The influence of the KNO_3 concentration on γ vs. E curves.
 Oil phase: $1 \times 10^{-4}\text{M}$ TBAC.
 Aq. phase: $5 \times 10^{-4}\text{M}$ BP + KNO_3 .
 $[\text{KNO}_3]$; \bullet , $1 \times 10^{-4}\text{M}$; \circ , $1 \times 10^{-3}\text{M}$;
 \bullet , $1 \times 10^{-2}\text{M}$; \bullet , $5 \times 10^{-2}\text{M}$.

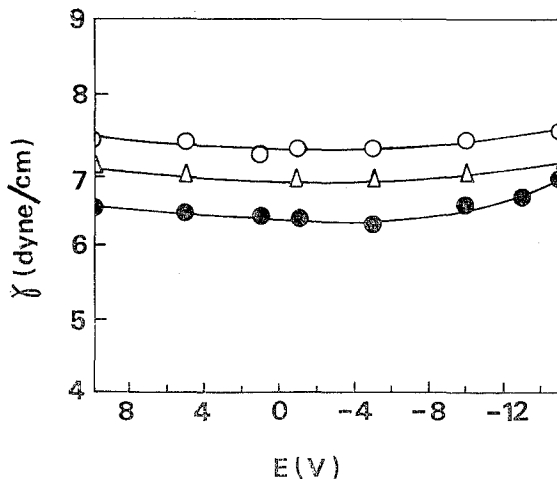
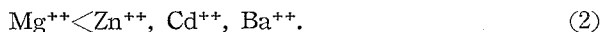


Fig. 3. The influence of the cationic valency on γ vs. E curves.
 Oil phase: $1 \times 10^{-4}\text{M}$ TBAC.
 Aq. phase: $5 \times 10^{-4}\text{M}$ BP + $1 \times 10^{-4}\text{M}$ electrolyte.
 Electrolyte; \circ , KCl ; \triangle , $\text{Cd}(\text{NO}_3)_2$; \bullet , $\text{La}(\text{NO}_3)_3$.

This effect of the electrolyte on the surface activity of dyestuffs depended on the valency of the cationic component of the electrolyte. Figure 3 shows the effect of the cationic valency on γ vs. E curves for $5 \times 10^{-4}\text{M}$ BP. It is clear that the decrease in γ is the largest for La^{+++} and the smallest for K^+ ; the suppression of γ increases with the cationic valency.

For cations with the same valency, the suppression of γ is dependent on the cationic species. Thus, in the case of anionic dyestuffs, cations can be arranged

in the magnitude of the decrease in γ , over the anodic polarization, by the following sequence :



An anomalous behaviour was found in the case of Th^{4+} ion, for which the decrease in γ was even smaller than that for K^+ . This could perhaps be ascribed to the formation of insoluble thorium salt of BP at the interface.

It seems worth while to mention here that similar cationic effects as mentioned above were found in the adsorption of direct dyes to cellulose fibres.^{7,8)}

The adsorption of Dyestuffs at the Oil-Water Interface

Allowing for the electrostatic effect, Davies derived the following equation for the adsorption equilibrium of long chain ions at oil-water interfaces:⁹⁾

$$\Gamma = (B_1/B_2)c \exp \{ (mw - ze\psi_0)/kT \}, \quad (3)$$

where Γ is the number of long chain ions adsorbed at the interface per cm^2 ; B_1 and B_2 are constants characterizing the adsorption and desorption rates, respectively; c and z are the bulk concentration and valency of the long chain ion; m and w are the number of methylene groups and desorption energy per methylene group; e is the fundamental electronic charge; ψ_0 is the electric potential at the point considered in the electrical double layer; k is the Boltzmann constant; and T is the absolute temperature.

For ψ_0 higher than 100 mV and at 20°C, the Gouy equation reads

$$\psi_0 = (kT/ze) \ln (139^2 \times 4/A^2 z_e^2 c_e), \quad (4)$$

where c_e and z_e are the concentration and valency of the counterion, respectively, and A is the area per long chain ion in \AA^2 , which is given by

$$A = 10^6/\Gamma.$$

Combining equations (3) and (4), we have the following equation for uni-univalent long chain compounds :

$$\Gamma = Kc^{1/3} (z_e^2 \cdot c_e)^{1/3} \exp (mw/kT), \quad (5)$$

where K is a constant. Thus, if m and $(z_e^2 \cdot c_e)$ are constant, Γ is proportional to $c^{1/3}$, while, if c and m are constant, Γ is proportional to $(z_e^2 \cdot c_e)^{1/3}$.

Now, the interfacial excess of long chain ions can be obtained from γ vs. E curves as follows. Assuming that the thermodynamic equilibrium prevails the interface,* we can use the Gibbs adsorption isotherm,^{10,11)} *i. e.*

$$d\gamma = -\sum \Gamma_i d\bar{\mu}_i, \quad (6)$$

where γ is the interfacial tension, and Γ_i and $\bar{\mu}_i$ are the interfacial excess and electrochemical potential of the component i , respectively. The last quantity is expressed by,

* Strictly speaking, this is not true, since the electric current is passing through the interface when the polarizing potential is applied to the system. However, as the stationary state is reached in a short time after the application of polarizing potential, we can perhaps assume the partial equilibrium as far as the interfacial excess of surface active agents is concerned.

$$d\bar{\mu}_i = z_i e dE' + kT d \ln c_i, \quad (7)$$

where c_i and z_i are the bulk concentration and the valency, including the sign, of the component i , and E' is the potential difference at the interface. Since there are considerable potential drops in the oil and aqueous phases, E' is written as

$$E' = \alpha E, \quad 0 < \alpha < 1, \quad (8)$$

where E is the total applied potential. Substituting equation (7) into (6), we have for a binary surface active agent ($z_+ = -z_- = z$)

$$dr = ze(\Gamma_+ - \Gamma_-)dE' + (\Gamma_+ - \Gamma_-)kT d \ln c_i, \quad (9)$$

where Γ_+ and Γ_- are the surface excesses of cationic and anionic components of the surface active agent.

If the composition of the system is constant, the second term on the right hand side of equation (7) disappears, and hence we have

$$-dr/dE' = ze(\Gamma_+ - \Gamma_-). \quad (10)$$

Thus, the net interfacial excess $\Gamma (= \Gamma_+ - \Gamma_-)$ can be obtained from the slope of r vs. E curves, when a proper value is assumed for α . In the following estimation, we have arbitrarily taken $\alpha = 0.1$.*

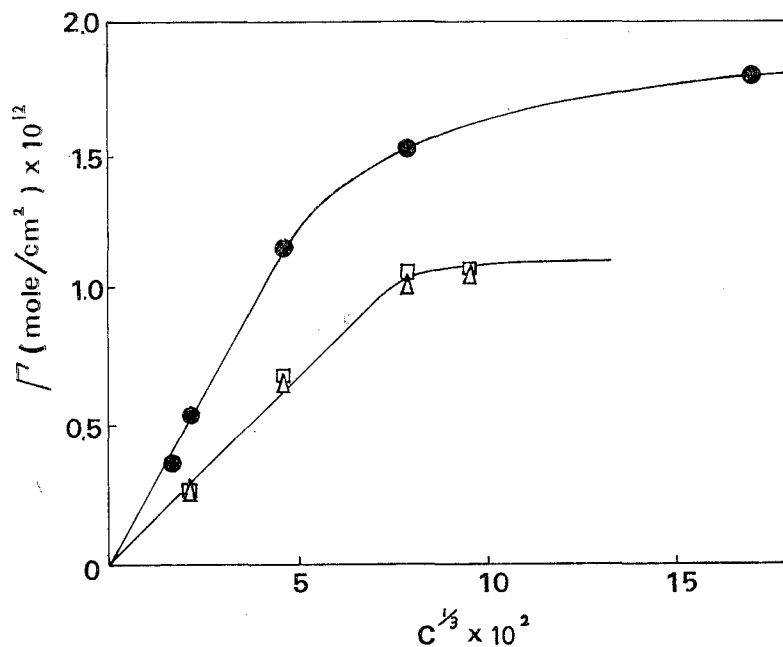


Fig. 4. Plottings of Γ against $c^{1/3}$ for the adsorption of dyestuffs at oil-water interfaces.

[KCl] = 1×10^{-2} M.

Dyestuff: ●, BP; △, CH; □, CV.

* Since deposition potentials of various ionic species in non-aqueous systems are in general of the same order of magnitude as those in aqueous systems, the actual potential difference at the interface between oil and water in present systems would perhaps be of the order of several hundred mV.¹²⁾

Figure 4 shows plottings of Γ as functions of $c^{1/3}$ for BP, CH and CV at $E=15$ or -15 V and the ionic strength 10^{-2} M. For low c values, linear relations hold in agreement with equation (5). It is interesting to find in this connection that the slope is the largest for BP.

It has been found by present authors that, in the case of surface active agents, the slope increased with increasing chain length, when polar groups were the same.¹³⁾ This can be explained by the increase in m of equation (5). However, since polar groups of dyestuffs are different in the present case, we must allow for the term (B_1/B_2) in equation (3), or K in equation (5), in addition to m . Thus, we can conclude that the adsorbability of BP is the largest at the oil-water interface.¹⁴⁾

The linearity does not hold for high c values, see Fig. 4. This can perhaps be explained by the association of dyestuff molecules at such high concentrations.

Figure 5 shows the influence of metal ions on the adsorption of BP, *i. e.* the relation between Γ at $E=15$ V and $(z_e^2 \cdot c_e)^{1/3}$ for a constant BP concentration. Linear relations with positive slopes are obtained, which is in agreement with equation (5). The same relation has already been found for the influence of

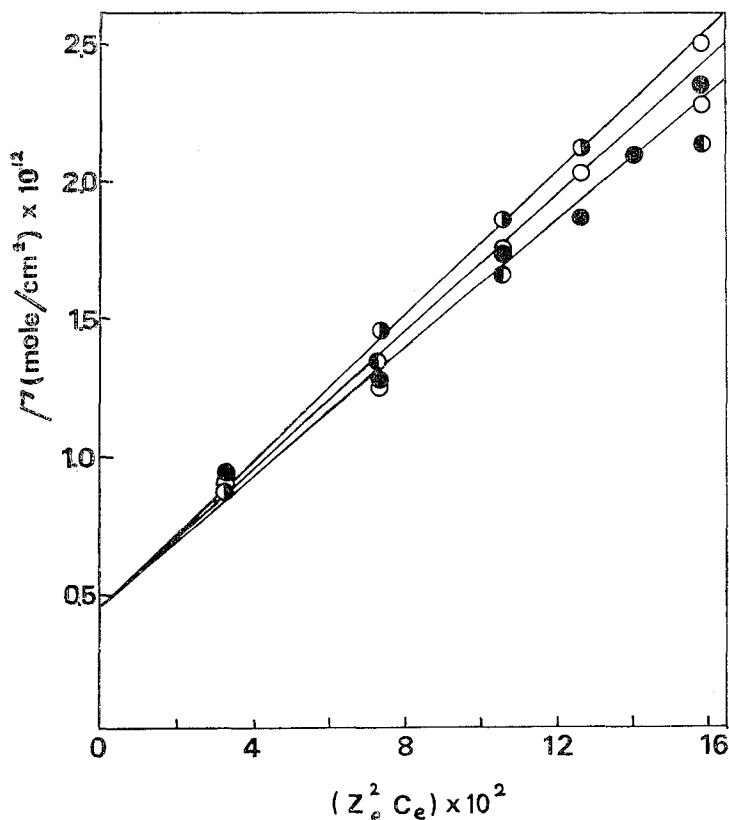


Fig. 5. Plottings of Γ against $(z_e^2 c_e)^{1/3}$ for the adsorption of BP at oil-water interfaces.

[BP] = 5×10^{-4} M.

Electrolytes: ○, Ba(NO₃)₂; ●, Cd(NO₃)₂; ◐, Zn(NO₃)₂; ◑, Mg(NO₃)₂.

inorganic ions on the adsorption of surface active agents.⁵⁾

It must be added here that straight lines in Fig. 5 do not pass through the origin, and hence, equation (5) must be corrected for it. In equations (4) and (5) the ionic strength of the system is considered to be governed by the concentration of the indifferent electrolyte only. However, since dyestuffs themselves are also electrolytes, we must use the term $(z^2c+z_e^2c_e)$ instead of $(z_e^2c_e)$. This must be taken into account at low electrolyte concentrations in order to explain the deviation mentioned above.

The Interaction between Dyestuffs and Surface Active Agents.

The counterion binding was found to take place at the interface between the oil phase, containing 10^{-4} M CPC, and the aqueous phase, containing the anionic dyestuff in addition to 10^{-3} M KCl. An example is shown by Fig. 6, in which γ values are plotted against E for various concentrations of OR. It is noticed that the depression of γ over the cathodic polarization range, which is characteristic to cationic surface active agents in general, here CPC, is inhibited by OR. The same effect was also found for the dyestuff MO. Such a suppression of the decrease in γ was also found for surface active agents and ascribed by present authors to the counterion binding at the interface, *i. e.* the neutralization of the ionic charge of surface active materials.²⁾

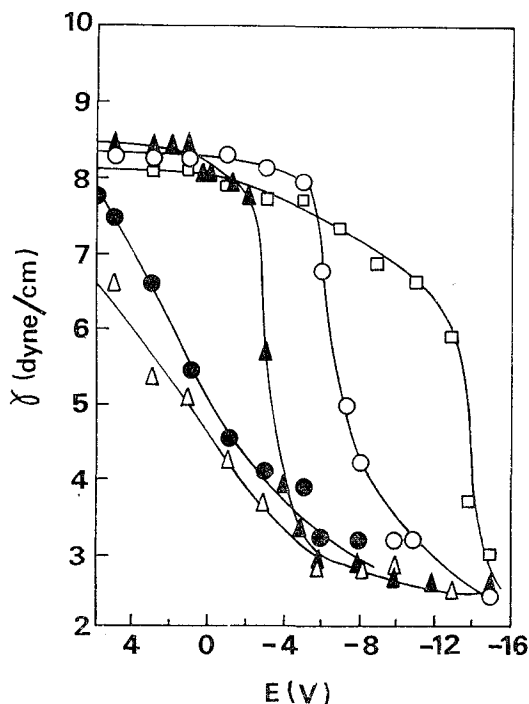


Fig. 6. The interaction between OR and CPC at oil-water interfaces.

Oil phase: 1×10^{-4} M CPC.

Aq. phase: 1×10^{-3} M KCl+OR.

[OR]; \square , 9×10^{-4} M; \circ , 5×10^{-4} M; \blacktriangle , 2×10^{-4} M;

\bullet , 1×10^{-4} M; \triangle , 8×10^{-5} M.

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The effect of counterion binding was also found to take place at the interface between the oil phase, containing the anionic surface active agent, 10^{-4} M SCS, and the aqueous phase, containing the cationic dyestuff, MB or RD, in addition to 10^{-3} M KCl. Figure 7 shows the results obtained for MB.

It was thus proved that polar groups of ionic surface active agents are intruded into the aqueous side of the oil-water interface, offering the sites for the binding of oppositely charged dyestuff ions.

It is worth mentioning in this connection that the complex formation between dyestuffs and oppositely charged surface active agents often takes place in the aqueous bulk phase.¹⁵⁻¹⁸⁾ This was proved, for instance, by electric conductance measurements for solutions containing OR, MB or RD in addition to various surface active agents.¹⁸⁾

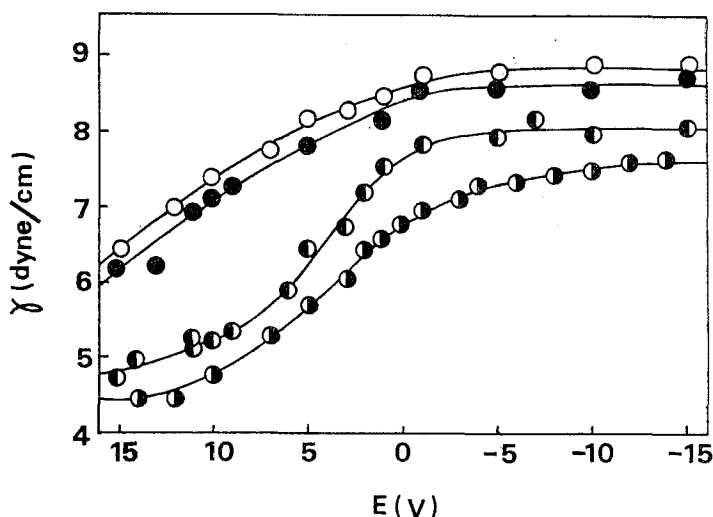


Fig. 7. The interaction between MB and SCS at oil-water interfaces.
Oil phase; 1×10^{-4} M SCS.
Aq. phase: 1×10^{-3} M KCl+MB.
[MB]; ○, 9×10^{-4} M; ●, 5×10^{-4} M; ◐, 1×10^{-4} M; ●, 0 M.

The surface activity of amphoteric surface active agents dissolved in the oil phase depends on the pH of the aqueous phase in contact with it. It behaves as a cationic or anionic surface active agent depending upon whether the pH is lower or higher than the interfacial isoelectric point.³⁾ Figure 8 shows γ vs. E curves for the oil phase, containing the amphoteric surface active agent IM at the concentration 10^{-4} M, in contact with 10^{-2} M KCl *aq* at various pH's. The pH was adjusted by adding HCl or KOH to the aqueous phase. It is noticed that the curve is of the anionic type, *i. e.* γ decreases over the anodic polarization range, for the pH higher than 8.8, while, the curve is of the cationic type for the pH lower than 7.3.

Figure 9 shows γ vs. E curves for various concentrations of OR at a constant pH, 5.8. It is noticed that the decrease in γ over the anodic polarization range

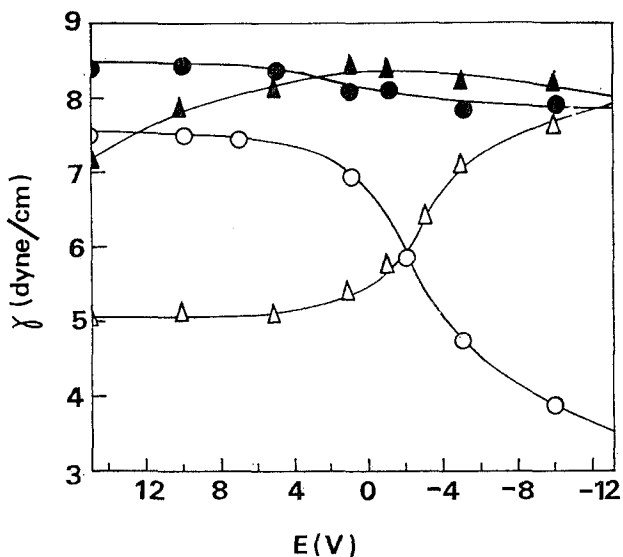


Fig. 8. The influence of pH on γ vs. E curves for IM.
 Oil phase: 1×10^{-4} M IM.
 Aq. phase: 1×10^{-2} M KCl.
 pH: \circ , 5.80; \bullet , 7.32; \blacktriangle , 8.84; \triangle , 10.50.

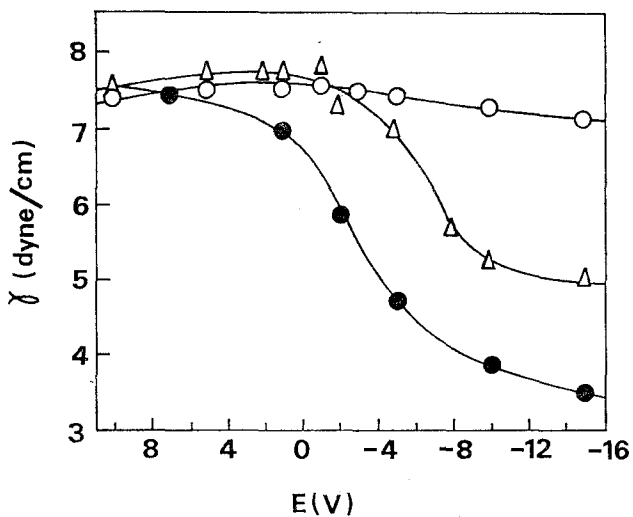


Fig. 9. The interaction between OR and IM at pH 5.8.
 Oil phase: 1×10^{-4} M IM.
 Aq. phase: 1×10^{-2} M KCl+OR.
 [OR]; \circ , 3×10^{-4} M; \triangle , 1×10^{-4} M; \bullet , 0 M.

becomes smaller with increasing OR concentration. This is similar to its effect on CPC, see Fig. 6. It is thus concluded that the binding between IM and OR molecules is taking place at the interface.

Figure 10 shows γ vs. E curves for the cationic dyestuff RD at the pH 10.5.

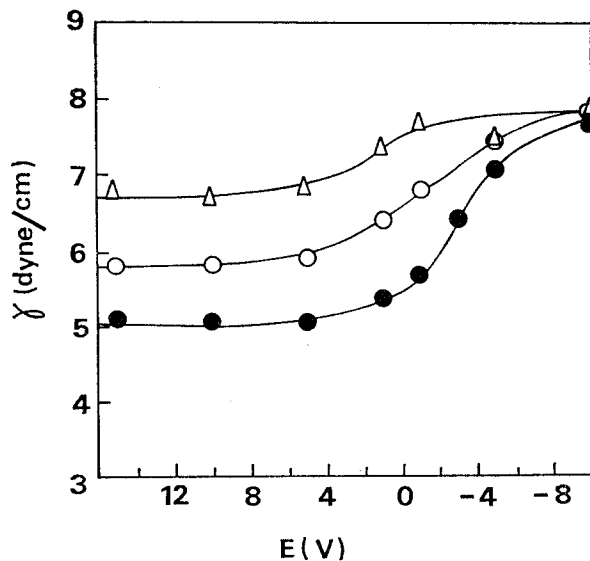


Fig. 10. The interaction between RD and IM at pH 10.5.
 Oil phase: $1 \times 10^{-4} M$ IM.
 Aq. phase: $1 \times 10^{-2} M$ KCl+RD.
 [RD]; Δ , $5 \times 10^{-4} M$; \circ , $3 \times 10^{-4} M$. \bullet , 0 M.

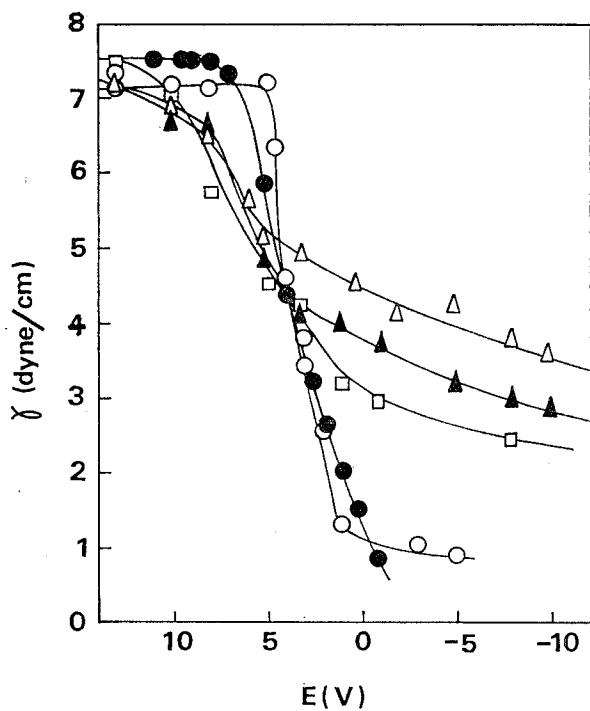


Fig. 11. The interaction between BP and CPC at oil-water interfaces.
 Oil phase: $1 \times 10^{-4} M$ CPC.
 Aq. phase: $1 \times 10^{-3} M$ KCl+BP.
 [BP]; Δ , $7 \times 10^{-5} M$. \blacktriangle , $1 \times 10^{-4} M$; \square , $3 \times 10^{-4} M$;
 \bullet , $5 \times 10^{-4} M$; \circ , $9 \times 10^{-4} M$.

The same effect is found in the case of SDBSO in MIBK, thus indicating the occurrence of binding between RD and IM. The same applies to MB.

It was thus proved that the binding between oppositely charged species, including hydrogen ions, dyestuffs and surface active agents, takes place at oil-water interfaces.^{2,3)}

In the case of BP, however, no binding to IM or CPC was so far found to take place. Figure 11 shows the results for CPC. The decrease in γ over the cathodic polarization range is not inhibited, but rather promoted, by the increase in the BP concentration. The binding was thus proved to be absent. It appears, therefore, that, like ordinary inorganic electrolytes, BP acts here as the builder for the adsorption of CPC.

Now, let us consider the case in which the dyestuff and surface active agent are of the same sign.

Figure 12 shows γ vs. E curves for the oil phase, containing 9.5×10^{-5} M-SDBSO, in contact with the aqueous phase containing 5×10^{-4} M MO, OR or BP, in addition to 10^{-3} M KCl. Contrary to the case of oppositely charged species mentioned above, the decrease in γ over the anodic polarization range is promoted by the addition of the anionic dyestuff. Dyestuffs can be arranged in the magnitude of this effect by the following sequence :

$$\text{MO} < \text{OR} < \text{BP}. \quad (11)$$

This sequence coincides with that of the surface activity of respective dyestuffs, see the inequality (1). It appears to show the additive effect of surface active agents and dyestuffs. In fact, the decrease in γ over the anodic polarization range is equal to the sum of the decreases due to the surface active agent and to the dyestuff.

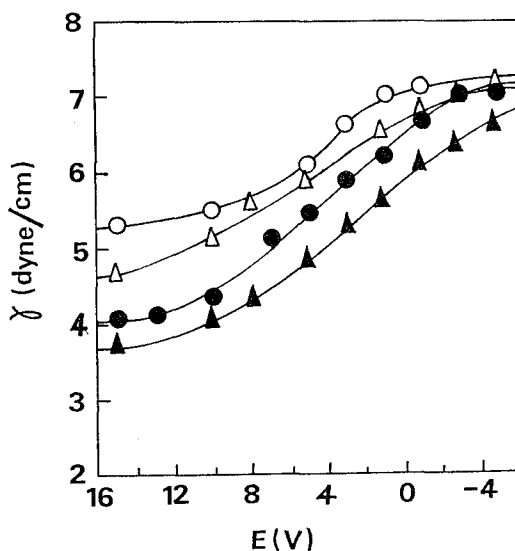


Fig. 12. The interaction between dyestuffs and SDBSO at oil-water interfaces.
 Oil phase : 9.5×10^{-5} M SDBSO.
 Aq. phase : 1×10^{-3} M KCl + 5×10^{-4} M Dyestuff.
 Dyestuff ; ○, none ; △, MO ; ●, OR ; ▲, BP.

Such an additivity was also found in the bulk phase, in which the similarly charged surface active agent and dyestuff coexisted in the aqueous phase.

The Influence of the Electrolyte on the Interaction

Figure 13 shows γ vs. E curves for the oil phase, containing 10^{-4} M CPC, in contact with the aqueous phase, containing 5×10^{-4} M OR in addition to various concentrations of KCl. The decrease in γ over the cathodic polarization range is promoted by the increase in the salt concentration. Although the decrease in γ could be explained by the increase in the surface activity of OR due to the increase in the salt concentration, it might as well be due to the inhibition of the binding between CPC and OR.

In this connection we can refer to the following fact. Figure 14 shows the effect of the KCl concentration on the absorption spectrum of OR. The solution contained 10^{-5} M OR and 10^{-4} M CPC, in addition to various concentrations of KCl. It is noticed that the absorption maximum increases with increasing KCl concentration, approaching the value in the absence of CPC. This is in accordance with the general consideration, *i. e.* the electrostatic attraction between oppositely charged species in a solution is weakened by the increase in the ionic strength.

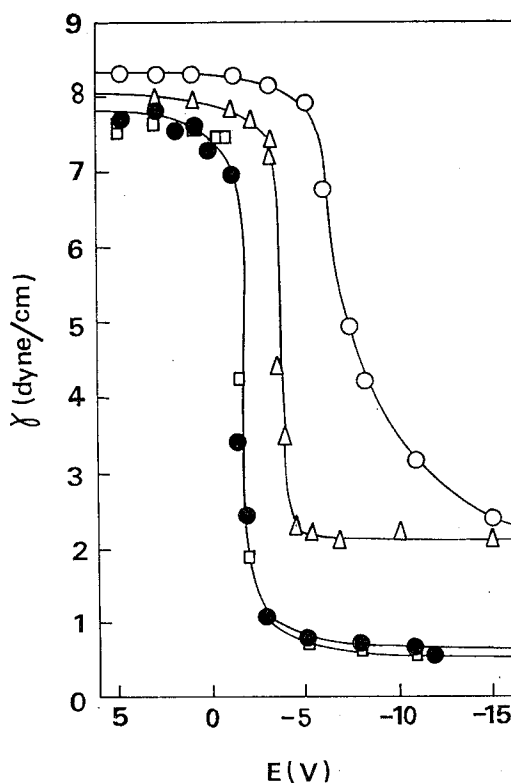


Fig. 13. The influence of the KCl concentration on the interaction between OR and CPC at oil-water interfaces.

Oil phase: 1×10^{-4} M CPC.

Aq. phase: 5×10^{-4} M OR + KCl.

[KCl]; □, 1×10^{-1} M; ●, 1×10^{-2} M; △, 3×10^{-3} M; ○, 1×10^{-3} M.

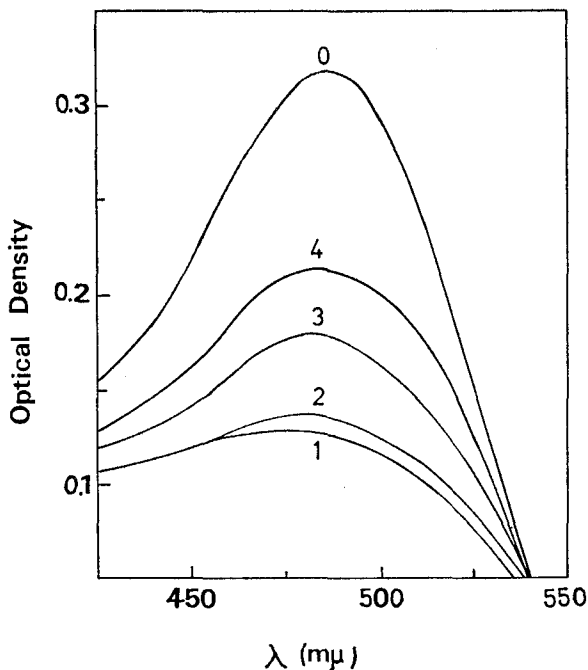


Fig. 14. The influence of the KCl concentration on absorption spectra of aqueous solutions containing OR and CPC.
 $[\text{OR}] = 1 \times 10^{-5} \text{M}$, $[\text{CPC}] = 1 \times 10^{-4} \text{M}$ and
 $[\text{KCl}]$; 1, 0 M; 2, $1 \times 10^{-3} \text{M}$; 3, $1 \times 10^{-2} \text{M}$; 4, $1 \times 10^{-1} \text{M}$.
 Curve 0; $0 \sim 1 \times 10^{-1} \text{M}$ KCl + $1 \times 10^{-5} \text{M}$ OR.

Hence, the above result would perhaps be explained by the weakening of the bond between CPC and OR molecules by the increase in the KCl concentration.

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