TENSAMMETRY: A METHOD OF INVESTIGATING SURFACE PHENOMENA BY A.C. CURRENT MEASUREMENTS

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Summary

A new type of investigation into surface phenomena, " tensammetry ", has been developed by superimposing a small sinusoidal A.C. voltage upon the direct potential applied to a dropping mercury electrode in the presence of surface active substances and measuring the resultant A.C. currents. Wave shaped current-voltage curves are thus obtained which have their origin in adsorption processes occurring at the electrode. These waves are attributed to the movement of surface active molecules in the region of " active space " near the electrode without actual electron transfer across the electrode boundary; that is, the electrode remains polarized with respect to D.C., but is depolarized with respect to A.C. The general properties of tensammetric waves of a number of organic compounds together with their effects on one another and on D.C. and A.C. polarographic waves have been investigated. The theoretical basis and the fundamental equations governing the tensammetric process are derived and discussed.

I. INTRODUCTION

The behaviour of the electrocapillary curve of mercury in the presence of surface active organic compounds was first examined by Gouy (1903, 1906*a*, 1906*b*) who observed that generally the amount of substance adsorbed at the mercury electrode decreased with increasing field strength. Theoretical interpretations of these phenomena were attempted by various workers (e.g. Frumkin 1926; Butler 1929) who derived general equations for the variation of the amount of substance adsorbed with the potential difference at the interface of the electrode. The picture at which these authors arrived was that of the existence of layers of polar molecules (most commonly monolayers) of sparingly soluble organic substances at the electrode boundary (see, for example, Frumkin and Gorodetskaya 1928; Frumkin, Gorodetskaya, and Chugunov 1934; Proskurnin and Frumkin 1935; Gorodetskaya 1940). All the experimental evidence indicates that if the potential of the mercury electrode is made strongly positive or strongly negative, the adsorbed polar molecules at the mercury surface are displaced by the ions of the supporting electrolyte. The displacement frequently occurs over a small range of potential and a sudden change in the charge density of the double layer results. This in turn leads to a large value of the dynamic capacitance (dq/dE). Frumkin and Proskurnin (1935) thus observed two maxima with a strong depression in the middle part in the capacity-potential curve of sodium sulphate saturated with octyl alcohol. The extreme anodic and cathodic ends of the curve coincided with those obtained with

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sodium sulphate alone. Grahame (1946) repeated these experiments with similar results. The technique employed consisted in balancing out the double layer capacity with a set of variable capacitors suitably arranged in a Wheatstone network, whilst a small A.C. voltage was superimposed on the applied D.C. potential. The process of balancing was laborious and frequently the peaks of the capacity-voltage curves were not sharply defined.

When electrolytes containing small amounts of surface active substances (e.g. aniline, pyridine, phenol, cresol, benzoic acid, octyl alcohol,* etc.) were subjected to A.C. polarography (Breyer and Gutmann 1946, 1947; Breyer, Gutmann, and Hacobian 1950) current-voltage curves similar to the capacitance-voltage curves of Proskurnin and Frumkin (1935) and of Grahame (1946) were observed by the present authors. But whereas the waves in A.C. polarography are produced as a consequence of depolarization processes occurring at the dropping mercury electrode (in virtue of the applied D.C. potential), the A.C. waves obtained in the presence of surface active substances are produced without corresponding D.C. current flow. In other words: *the electrode is depolarized with respect to A.C. only and remains polarized with respect to D.C.* It is proposed to distinguish this type of electrode process, which is fundamentally different from A.C. polarography, by terming it " tensammetry ".

Tensammetric waves are basically an outcome of the same electrode phenomena as those responsible for the capacitance-voltage curves of Frumkin and Grahame. But unlike capacitance-voltage curves, tensammetric current-voltage curves are well defined and the summit potential generally can be read to better than 1 mV. Finally, the time needed to obtain a tensammetric curve is only a fraction of that required for capacitance-voltage measurements.

It is the main object of the present paper to discuss the theoretical basis and to derive the fundamental equations governing the tensammetric process.

II. THE BEHAVIOUR OF DIPOLES AT AN ELECTRODE AND THE GENERAL PROPERTIES OF TENSAMMETRIC WAVES

Consider an orientated dipole in the non-uniform field at the electrode surface (Fig. 1 (*a*)) and whose charges δ_- and δ_+ are separated by a distance l cm. Let the pole δ_- be placed a cm. from the electrode surface. $\breve{E}_1$, $\breve{E}_2$, and $\breve{E}_3$ $(E_1>E_2>E_3)$ denote the field strengths at the electrode boundary, at a cm. and at $a+l$ cm. from the electrode respectively. Considering the direction normal to the electrode surface only, the resultant force acting on the dipole is represented by

$$(E_2\delta - E_3\delta)\breve{i},$$

where $\breve{i}$ represents a unit vector in the said direction. Since $E_2 \neq E_3$ this force will always be finite and hence the dipole will behave as if it were a charged particle (cf. in this connection, Heyrovsky 1934; Ilkovič 1936; Kolthoff and Lingane 1941). It is proposed to call this type of particle an " active charge ". The magnitude and sign of the active charge depends upon the orientation of

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* 2-Ethyl hexanol was used throughout.

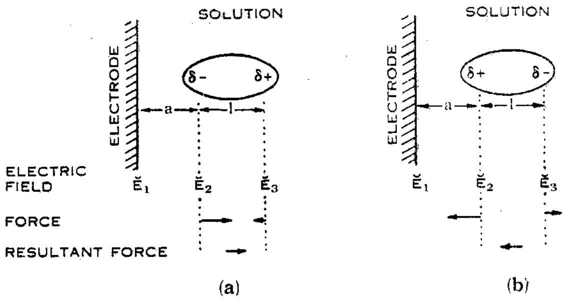

Fig. 1.—The diagrammatic representation of a dipole in a non-uniform electric field close to the electrode-solution interface.
$(E_2—E_3)\delta$, magnitude of resultant force on dipole; l, length of dipole; a, distance of one end of dipole from the electrode surface; E_1, field strength at the electrode; E_2, field strength at distance a from the electrode; E_3, field strength at distance $a+l$ from the electrode.

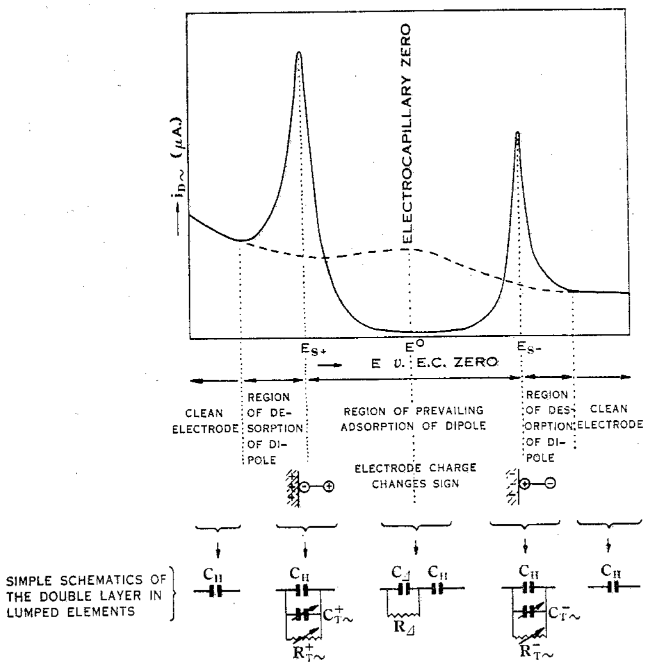

Fig. 2.—Schematic representation of tensammetric waves.
——— Tensammetric curve.
- - - - Polarogram of supporting electrolyte.
E_{s+}, E_{s-}, summit potentials of positive and negative tensammetric waves respectively; $C_{T\sim}^{+}$, $C_{T\sim}^{-}$, corresponding tensammetric capacitance; $R_{T\sim}^{+}$, $R_{T\sim}^{-}$, corresponding tensammetric leakage resistance; $C\triangle$, $R\triangle$, capacitance and leakage resistance of the electrode double layer during prevailing adsorption of dipoles; C_H, Hemlholtz-Gouy capacitance of double layer.

the dipole and is equal and opposite to that of the same dipole when orientated through 180° (cf. Figs. 1 (*a*) and 1 (*b*)).

Figure 2 shows a typical tensammetric current-voltage curve. It can be seen that the curve consists essentially of two waves situated on either side of the electrocapillary zero point. In the following, these waves will be called the positive and the negative tensammetric wave respectively and their summit potentials will be distinguished by the symbols E_{s+} and E_{s-}. At high positive or high negative polarizations of the dropping mercury electrode, the tensammetric curve coincides with that of the supporting electrolyte. As is well known, maximum adsorption of the dipole occurs at the electrocapillary zero point and hence both the double-layer capacity and the A.C. current are appreciably lowered in this region (cf. Fig. 2).

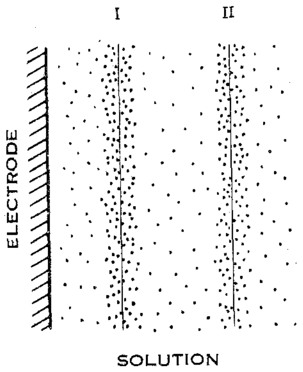

Fig. 3.—Distribution of " active charges " near the electrode-solution interface.

The reason for the large changes in differential current ($i_{D\sim}$) in the neighbourhood of E_{s+} and E_{s-} can be found in reorientation of the dipole molecules in the double layer with the change of the applied potential. These reorientation changes are discussed in detail in Section III (*a*).

Figure 2 shows also the various electrical equivalents of the electrode-double-layer system represented as lumped loss-free capacitors with leakage resistors in parallel. Following the nomenclature proposed by Grahame (1946), $C_\triangle$ represents the capacity and $R_\triangle$ the leakage resistance of an uncompressed layer of surface active molecules at the electrode-solution boundary.

III. THE SIGNIFICANCE OF THE TENSAMMETRIC POTENTIAL (E_s) AND OF THE TENSAMMETRIC CAPACITANCE ($C_{T\sim}$)

As shown in Section II, dipoles behave as " active charges " when in a non-uniform electric field like that encountered between the electrode surface and the bulk of the solution. Consider now these active charges to be distributed between regions I and II (Fig. 3) near the surface of the electrode. The picture is that of a variable condenser whose plates are situated at I and II and whose dielectric contains active charges.

It is the object of the following treatment to show that the capacitance of the variable condenser system becomes a maximum at the applied D.C. potential E_s.

Let the volume charge density of active charges be q_v^{I} (coulombs/cm.^{3}) in region I and q_v^{II} in region II and let their sum be equal to Q. The particles in the spaces I and II are in equilibrium

$$\mathrm{I} \rightleftharpoons \mathrm{II}. \tag{1}$$

Let a^{I} and a^{II} denote the activities, γ^{I} and γ^{II} the activity coefficients, c^{I} and c^{II} the concentrations (moles/cm.^{3}) of the active substance participating in the equilibrium process and contained in spaces I and II respectively. The dynamic capacitance is determined by the relation

$$C=\frac{dq_v}{d\psi}, \tag{2}$$

ψ being the potential difference between the regions I and II. As we are only concerned with changes of ψ and not with its absolute value, we can write

$$C=\frac{dq_v}{dE}, \tag{3}$$

where E is the applied potential between the electrode and the bulk of the solution.

If (**1**) is reversible then

$$Q_0E=RT\ln K-RT\ln K', \tag{4}$$

where K is the ratio of the activities of the charges in regions I and II at the potential $E=0$, K' denotes the same ratio at any potential E, and Q_0 represents the charge associated with 1 gram mole of active substance. The relationship between Q_0 and Q is given by

$$Q_0=\frac{Q}{c^{\mathrm{I}}+c^{\mathrm{II}}}, \tag{5}$$

and

$$Q=|q_v^{\mathrm{I}}|+|q_v^{\mathrm{II}}|. \tag{6}$$

If E_x represents that potential at which $a^{\mathrm{I}}/a^{\mathrm{II}}=1$ the following relationship is obtained:

$$E=E_x-\frac{RT}{Q_0}\ln K'. \tag{7}$$

Since

$$K'=\frac{\gamma^{\mathrm{I}}c^{\mathrm{I}}}{\gamma^{\mathrm{II}}c^{\mathrm{II}}}=\frac{q_v^{\mathrm{I}}}{q_v^{\mathrm{II}}}, \tag{8}$$

and from (**7**)

$$K'=e^{-Q_0(E-Ex)/RT}, \tag{9}$$

the dynamic capacitance of the condenser system follows as

$$C=\frac{dq_v}{dK'}\cdot\frac{dK'}{dE}. \tag{10}$$

For small deviations of E from E_x, Q and Q_0 can be considered independent of E. Combining (**6**) and (**8**) we obtain

$$K' = \frac{Q}{q_v^{\mathrm{II}}} - 1, \qquad (\mathbf{11})$$

and

$$\frac{dK'}{dq_v^{\mathrm{II}}} = -Q(q_v^{\mathrm{II}})^{-2},$$

or

$$\frac{dq_v^{\mathrm{II}}}{dK'} = -\frac{(q_v^{\mathrm{II}})^2}{Q}. \qquad (\mathbf{12})$$

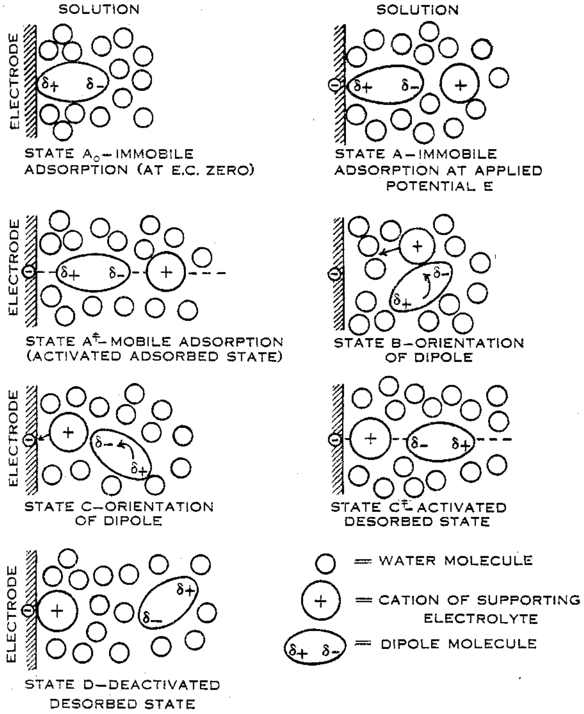

Fig. 4.—Schematic representation of the adsorption-desorption process.

Differentiating (**9**)

$$\frac{dK'}{dE} = -\frac{Q_0}{RT} e^{-Q_0(E-Ex)/RT}, \qquad (\mathbf{13})$$

and combining (**10**), (**12**), and (**13**)

$$C = \frac{(q_v^{\mathrm{II}})^2}{RT} \cdot \frac{Q_0}{Q} e^{-Q_0(E-Ex)/RT}. \qquad (\mathbf{14})$$

Since

$$q_v^{\mathrm{II}} = \frac{Q}{1+e^{-\varphi}}, \qquad (\mathbf{15})$$

where

$$\varphi=\frac{Q_0(E-E_x)}{RT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (16)$$

it follows that

$$C=\frac{Q^2 \, . \, e^{-\varphi}}{(c^{\mathrm{I}}+c^{\mathrm{II}})RT(1+e^{-\varphi})^2}=\frac{QQ_0e^{-\varphi}}{RT(1+e^{-\varphi})^2}, \quad \ldots\ldots\ldots\ldots \quad (17)$$

C is therefore a maximum when $\varphi=0$, that is, when $E=E_x$ and hence when $K'=1$.

To a maximum capacitance corresponds a maximum A.C. current and it follows therefore from the tensammetric curve that E_x is identical with the summit potential E_s (Fig. 2). It can thus be concluded that at this point of the curve the concentrations (activities) of the active charges in regions I and II are equal.

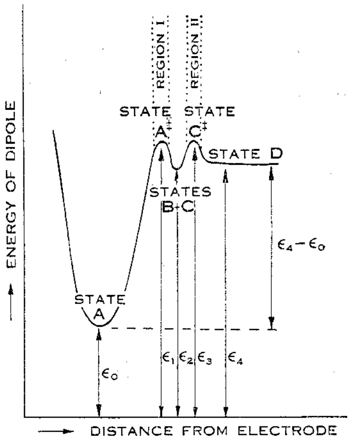

Fig. 5.—Energy states of dipole molecule during the adsorption-desorption process (after Fig. 4).
ε_0, energy of dipole in adsorbed state A (immobile adsorption) ; ε_1, energy of dipole in region I (state $A‡$ activated adsorption) ; ε_2, energy of dipole in states B and C (orientation) ; ε_3, energy of dipole in region II (state $C‡$ activated desorption) ; ε_4, energy of dipole in state D (deactivated desorption).

(*a*) *The Tensammetric Potential* (E_S)

The equilibrium between the active charges in regions I and II is actually the equilibrium between adsorbed and desorbed dipoles. The mechanism of this adsorption-desorption process is shown in Figures 4 and 5 and discussed in the following.

At the electrocapillary zero point the greatest number of dipoles at the electrode surface is in a state of immobile adsorption (state A_0) (cf. Glasstone, Laidler, and Eyring 1941). When a potential is applied between the electrode and the bulk of the solution a double layer is formed consisting of ions and dipoles on the one hand and the electrode on the other. The arrangement is such that most of the dipoles find themselves between the electrode and the ions. At the same time the dipoles are distorted due to the presence of a non-uniform electric field (state A). As the potential difference between solution and electrode is further increased, desorption begins. The majority of dipoles now find themselves in a state of " mobile adsorption " (cf. Glasstone, Laidler, and Eyring 1941) (state $A^{\ddagger}$), which is followed by reorientation (states B and C), by the activated desorbed state (state $C^{\ddagger}$), and finally by the deactivated desorbed state (state D).

The equilibrium between the active charges in regions I and II is actually the equilibrium between the *activated* adsorbed state $A^{\ddagger}$ and the *activated* desorbed state $C^{\ddagger}$. The complete mechanism can be represented by

$$A \rightleftharpoons A^{\ddagger} \rightleftharpoons B \rightleftharpoons C \rightleftharpoons C^{\ddagger} \rightleftharpoons D. \quad \dots\dots\dots\dots\dots\dots \quad (18)$$

If reorientation is relatively fast compared with $A \rightleftharpoons A^{\ddagger}$ and $C^{\ddagger} \rightleftharpoons D$, then (**18**) can be written as

$$A \rightleftharpoons A^{\ddagger} \rightleftharpoons C^{\ddagger} \rightleftharpoons D. \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (19)$$

Since adsorption is the spontaneous process, a molecule in the immobile adsorbed state will possess minimum energy (ε_0, Fig. 5). The desorption rate is determined by the number of molecules in state A per unit volume (c_A) and is given by (Glasstone, Laidler, and Eyring 1941):

$$v_{\text{Des}} = c_A \frac{kT}{h} \cdot \frac{F_A^{\ddagger}}{F_A} e^{-(\varepsilon_1 - \varepsilon_0)/kT}, \quad \dots\dots\dots\dots\dots\dots \quad (20)$$

where k=Boltzmann's constant,
T=absolute temperature,
h=Planck's constant,
F_A=partition function of the molecules in state A,
$F_A^{\ddagger}$=partition function of the molecules in state $A^{\ddagger}$,
ε_0=energy of molecule in state A,
ε_1=energy of molecule in state $A^{\ddagger}$.

The adsorption rate, on the other hand, will be determined by the number of molecules (c_D) in state D after the establishment of an equilibrium. Thus

$$v_{\text{Ads}} = c_D \frac{kT}{h} \cdot \frac{F_C^{\ddagger}}{F_D} e^{-(\varepsilon_3 - \varepsilon_4)/kT}, \quad \dots\dots\dots\dots\dots\dots \quad (21)$$

in which F_D=partition function of the molecules in state D,
$F_C^{\ddagger}$=partition function of the molecules in state $C^{\ddagger}$,
ε_3=energy of molecule in state $C^{\ddagger}$,
ε_4=energy of molecule in state D.

At E_s the adsorption and desorption rates are the same

$$v_{\text{Des}} = v_{\text{Ads}}, \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (22)$$

and both the concentrations of active charges in regions I and II and their respective energy states are equal, so that

$$\varepsilon_1 = \varepsilon_2 \quad \text{and} \quad F_C^{\ddagger} = F_A^{\ddagger}, \quad \dots\dots\dots\dots\dots\dots \quad (23)$$

and therefore

$$\frac{c_D}{c_A}=K_1=\frac{F_A}{F_D}e^{(\varepsilon_A-\varepsilon_0)/kT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (24)$$

or

$$K_1=\frac{F_A}{F_D}e^{Q_0E_s/RT}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (25)$$

where Q_0E_s represents the work done in desorbing 1 gram mole of dipole from state A to state D. It follows that

$$Q_0E_s=RT\ln K_1+RT\ln\frac{F_D}{F_A},$$

or

$$E_s=\frac{RT}{Q_0}(\ln K_1+\ln K_2)=\frac{RT}{Q_0}\ln M, \quad \ldots\ldots \quad (26)$$

where

$$M=K_1\cdot K_2 \text{ and } K_2=F_D/F_A. \quad \ldots\ldots\ldots\ldots \quad (27)$$

E_s is expressed with respect to the electrocapillary zero point.

If Q_s represents the surface charge density (coulombs/cm.^{2}) of the electrode surface then the work done in desorbing the dipole from the electrode surface is given by

$$Q_sE_s=\tfrac{1}{2}(C_{H(E_S)}-C\Delta_0)E_s^2,$$

that is

$$Q_s=\tfrac{1}{2}(C_{H(E_S)}-C\Delta_0)E_s, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (28)$$

where $C_{H(E_S)}$ refers to the capacitance of the rigid double layer at the potential E_s, and $C\Delta_0$ represents the capacitance of the electrode-solution system at the electrocapillary zero, E^0, respectively (both in F./cm.^{2}). Regarding the adsorbed molecules as of roughly cylindrical shape, perpendicularly orientated to the surface of the electrode and having a charge separation of l cm., Q, the volume charge density at the electrode surface will be approximately equal to Q_s/l. Remembering that

$$Q_0=\frac{Q}{(c^{\mathrm{I}}+c^{\mathrm{II}})},$$

we have

$$Q_0=\frac{Q_s}{l(c^{\mathrm{I}}+c^{\mathrm{II}})}=\frac{1}{2}\frac{(C_{H(E_S)}-C\Delta_0)}{l(c^{\mathrm{I}}+c^{\mathrm{II}})}E_s, \text{ (coulombs/mole)} \quad \ldots\ldots \quad (29)$$

and since $c^{\mathrm{I}}=c^{\mathrm{II}}$ at E_s

$$Q_0=\frac{(C_{H(E_S)}-C\Delta_0)}{4lc^{\mathrm{II}}}E_s. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (30)$$

The total number of active charges in regions I and II depends upon the applied potential and upon the nature and concentration of the ions at the interface. Hence the concentration of active charges $(c^{\mathrm{I}}+c^{\mathrm{II}})$ participating in the process at E_s, for a given supporting electrolyte, can be expressed as

$$c^{\mathrm{I}}+c^{\mathrm{II}}=\mathrm{K}f(E_s), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

where K is a dimensional constant. Considering the special case when $f(E_s)=E_s$ equation (**31**) becomes

$$c^{\mathrm{I}}+c^{\mathrm{II}}=\mathrm{K}E_s. \qquad (\mathbf{31a})$$

Substituting equation (**31a**) in (**29**) we obtain

$$Q_0=\frac{(C_{H(E_s)}-C\Delta_0)}{2l\mathrm{K}}. \qquad (\mathbf{32})$$

The magnitude of Q_0, the number of active charges associated with 1 gram mole of active dipole, depends upon the polarization of the dipole at the electrode interface so that

$$Q_0=\mathrm{L}[g(P_{\mathrm{Di}},\ P_{\mathrm{Oi}})], \qquad (\mathbf{32a})$$

where L is a dimensional constant and $g(P_{\mathrm{Di}}, P_{\mathrm{Oi}})$ is a function of the distortion polarization, P_{Di} and the orientation polarization P_{Oi} of the dipole at the interface.

The excess desorption work (Φ) done at the potential E_s over that done at the electrocapillary zero point, where $E=0$, is connected with the respective bulk concentration of dipole, c_B (after Frumkin 1926) by

$$|\ln c_B|_0^{E_s}=\frac{\Phi S}{RT}, \qquad (\mathbf{33})$$

where S is the surface area requirement of 1 gram molecular weight of dipole. Since Φ represents the additional work of desorption done by the electrical forces we can write

$$\Phi=\tfrac{1}{2}(C_{H(E_s)}-C\Delta_0)E_s^2, \qquad (\mathbf{34})$$

and substituting in equation (**33**)

$$|\ln c_B|_0^{E_s}=\frac{S(C_{H(E_s)}-C\Delta_0)E_s^2}{2RT}. \qquad (\mathbf{35})$$

Combining (**35**) with (**32**) we obtain

$$Q_0=\frac{RT\,|\ln c_B|_0^{E_s}}{lS\mathrm{K}E_s^2}=\frac{RT\,|\ln c_B|_0^{E_s}}{V\mathrm{K}E_s^2}, \qquad (\mathbf{36})$$

where V is the volume occupied by 1 mole of dipole at the interface.

Substituting Q_0 in equation (**26**)

$$E_s=\frac{|\ln c_B|_0^{E_s}}{V\mathrm{K}\ln M}, \qquad (\mathbf{37})$$

or

$$E_s=\frac{\ln c_B-\mathrm{const.}}{V\mathrm{K}\ln M}. \qquad (\mathbf{38})$$

This equation shows that the tensammetric potential should be a logarithmic function of the bulk concentration of dipole, a result which was confirmed experimentally. Figure 6 shows that the relationship between E_s and log c_{Bulk} for pyridine, octyl alcohol, and *cyclo*hexanol is linear as demanded by equation (**38**).

(*b*) *The Tensammetric Capacitance* ($C_{T\sim}$)

Superimposing a small sinusoidal potential

$$\triangle V=\triangle V_0 \sin \omega\tau, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{39})$$

onto the applied direct potential E_s, an A.C. current ($\triangle i$) is produced in accordance with

$$\triangle i=\triangle i_0 \cos (\omega\tau+\theta). \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{40})$$

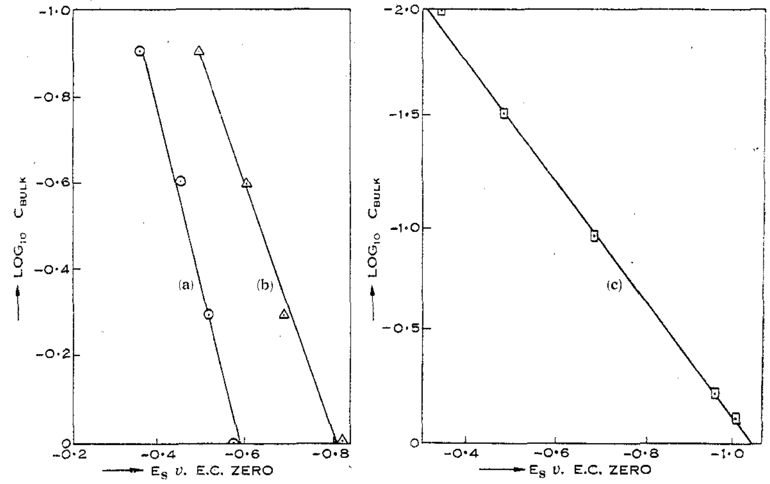

Fig. 6.—Relation between log c_{Bulk} and E_s for pyridine, octyl alcohol, and *cyclo*hexanol.
(*a*) Octyl alcohol in 0·5N $NaClO_4$: *T*, 25 °C., $c_{\text{Bulk}}=1$ for saturated octyl alcohol solution; (*b*) *cyclo*hexanol in 0·5N $NaClO_4$: *T*, 25 °C., $c_{\text{Bulk}}=1$ for saturated *cyclo*hexanol solution; (*c*) pyridine in 0·1M KCl: *T*, 25 °C., c_{Bulk} in molar concentrations.

Due to the applied A.C. field, the concentration of active charges at the electrode surface will vary sinusoidally, so that we can write

$$\triangle c=\triangle c_0 \cos (\omega\tau+\theta'), \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{41})$$

where θ and θ' represent the phase angles relative to the A.C. voltage of the current and of the concentration changes ($\triangle c$) respectively.

Displacement of dipoles from the electrode surface with increasing D.C. potential results in an excess concentration of dipoles near the electrode as compared with the bulk of the solution. Hence a concentration gradient is set up and the dipoles will diffuse from the electrode into the bulk. This diffusion process, which is slow compared with the rate of adsorption : desorption (cf. Frumkin and Melik-Gaĭkazyan 1951) is thus the rate determining step. By applying Fick's diffusion equation

$$\frac{\partial c}{\partial \tau}=D\frac{\partial^2 c}{\partial x^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (\mathbf{42})$$

and combining with equation (**41**) we obtain (after Randles 1947)

$$\left.\frac{\partial(\triangle c)}{\partial x}\right|_{x=0}=-\frac{\triangle c}{2}\sqrt{\frac{\omega}{D}}\cos\left(\omega\tau+\theta'+\frac{\pi}{4}\right), \quad \ldots\ldots\ldots \quad (\mathbf{43})$$

where the distance x is reckoned from an imaginary boundary drawn across the region of active charges near the electrode and the bulk of the solution.

The alternating current is also given by $\triangle i = Q_0 A$. flux, where

$$\text{flux} = D\frac{\partial(\triangle c)}{\partial x}, \quad \dots\dots\dots\dots\dots\dots\dots \quad (44)$$

A is the area of the electrode surface and D the diffusion coefficient of the dipole in the aqueous phase.

Combining (**43**) and (**44**) we obtain

$$\triangle i = Q_0 A\frac{\triangle c_0}{2}\sqrt{\omega D}\cos\left(\omega\tau + \theta' + \frac{\pi}{4}\right). \quad \dots\dots\dots \quad (45)$$

The amplitude of the A.C., $\triangle i_0$, is therefore expressed as

$$\triangle i_0 = Q_0 A\frac{\triangle c_0}{2}\sqrt{\omega D}, \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (46)$$

where

$$\theta = \theta' + \pi/4. \quad \dots\dots\dots\dots\dots\dots\dots \quad (47)$$

The concentration changes in virtue of the superimposed A.C. potential, $\triangle V$, and at the applied D.C. potential, E_s, are given by

$$\triangle V_0 \cos\omega\tau = \frac{RT}{Q_0}\ln\frac{c - \triangle c_0\cos(\omega\tau + \theta')}{c + \triangle c_0\cos(\omega\tau + \theta')}, \quad \dots\dots\dots \quad (48)$$

where c refers to the concentrations of active charges in regions I and II which at E_s are equal, that is, $c^{\text{I}} = c^{\text{II}} = c$.

Rearranging,

$$\triangle c_0 \cos(\omega\tau + \theta') = -c\tanh\left(\frac{\psi}{2}\right), \quad \dots\dots\dots\dots \quad (49)$$

where

$$\psi = \frac{Q_0 \triangle V_0 \cos\omega\tau}{RT}. \quad \dots\dots\dots\dots\dots\dots \quad (50)$$

At $\tau = 0$

$$\triangle c_0 = \frac{c}{\cos\theta'} \cdot \tanh\left(\frac{\psi_0}{2}\right), \quad \dots\dots\dots\dots\dots \quad (51)$$

where

$$\psi_0 = \frac{Q_0 \triangle V_0}{RT}. \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (52)$$

Applying a theoretical treatment similar to that used in deriving the A.C. active space and the dynamic capacitance of electrode reactions in alternating fields (cf. Breyer and Hacobian 1952*a*, 1952*b*) the tensammetric capacitance results as

$$C_{T\sim} = \frac{\pi Q_0 b(mt)^{2/3}D^{1/2}c}{8\sqrt{2}\,\triangle V_0\,\omega^{1/2}}\left(\tanh\frac{\psi_0}{2}\right)(1 - \tan\theta'), \quad \dots\dots \quad (53)$$

where $b = 8{\cdot}5 \times 10^{-1}$, involving the specific gravity of mercury and having the dimensions $M^{-2/3}\text{L}^2$, m is the mass of mercury (g./sec.), and t is the drop time of the capillary (in sec.).

Combining (**53**) with (**31a**) and (**32a**) we obtain

$$C_{T\sim}=\frac{\pi \mathrm{K} b(mt)^{2/3}D^{1/2}\mathrm{L}[g(P_{\mathrm{Di}}, P_{\mathrm{Oi}})]E_s}{8\sqrt{2}\,\triangle V_0\,\omega^{1/2}}\left(\tanh\frac{\psi_0}{2}\right)[1-\tan(\theta-\pi/4)]. \qquad \text{(54)}$$

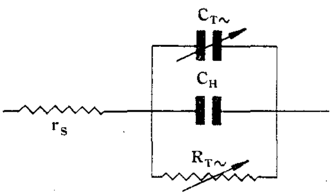

Fig. 7.—Equivalent circuit of the electrode system at E_s. r_s, ohmic series resistance of the cell ; $C_{T\sim}$, tensammetric capacitance ; C_H, Helmholtz-Gouy capacitance ; $R_{T\sim}$, leakage resistance at the standard tensammetric potential.

The phase angle of the A.C., θ, is a measure of the reversibility of the adsorption-desorption process at the particular A.C. frequency (ω) and varies between $\pi/4$ and $\pi/2$ (**47**). For a perfectly reversible process, concentration changes and A.C. voltage are in phase so that $\theta=\pi/4$ and $\theta'=0$. With decreasing reversibility the charge transfer will lag behind the superimposed A.C. voltage and $\theta>\pi/4$ whilst $\theta'>0$. θ can be determined experimentally by the relation

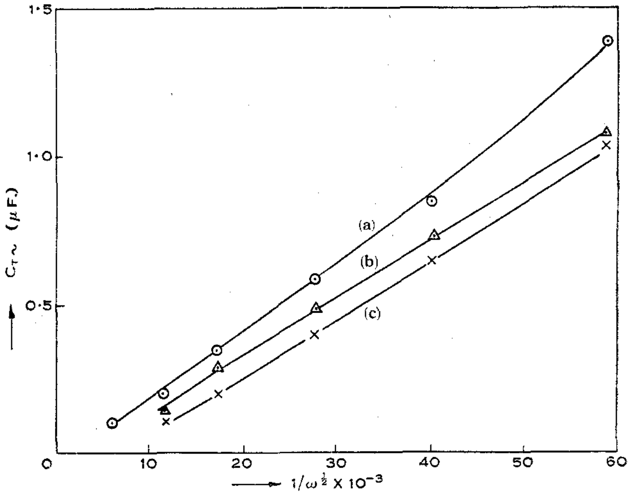

Fig. 8.—The linear relationship between the tensammetric capacitance ($C_{T\sim}$) and $1/\omega^{\frac{1}{2}}$ for pyridine, octyl alcohol, and *cyclo*hexanol. A.C. 10 mV. r.m.s. ; T, 20 °C. ; capillary characteristics : m, 1·5 mg. sec.$^{-1}$, t, 3·5 sec.
(*a*) 0·1M pyridine in 0·1 KCl ; (*b*) saturated octyl alcohol in 0·5N NaClO$_4$; (*c*) saturated *cyclo*hexanol in 0·5N NaClO$_4$.

$$\tan\theta=\omega C_{\sim}R_{T\sim}. \qquad \text{(55)}$$

As shown in Figure 7, $C_{\sim}$ represents the total capacity of the network and is equal to the sum of the Helmholtz-Gouy capacity (C_H) and the tensammetric capacitance ($C_{T\sim}$). $R_{T\sim}$ is the corresponding leakage resistance. $C_{T\sim}$ reaches a maximum when $\theta=\pi/4$.

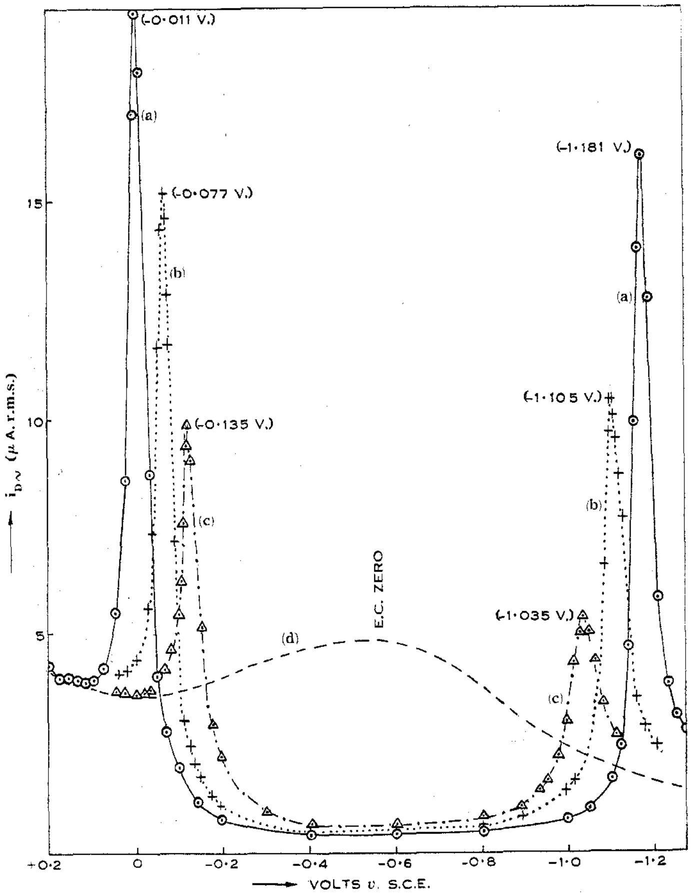

Fig. 9.—Tensammetric waves of octyl alcohol in 0·5N $NaClO_4$. A.C. 15 mV. r.m.s.; *T*, 20 °C. (*a*) Saturated octyl alcohol in 0·5N $NaClO_4$; (*b*) half-saturated octyl alcohol in 0·5N $NaClO_4$; (*c*) quarter-saturated octyl alcohol in 0·5N $NaClO_4$; (*d*) supporting electrolyte alone (0·5N $NaClO_4$).

Equation (**54**) shows that the tensammetric capacitance is a measure of the distortion and orientation polarization of the molecule at the electrode interface. In addition, $C_{T\sim}$ appears to be linearly proportional to E_s and inversely proportional to the square root of the A.C. frequency. Since, however, P_{Di}, the distortion polarization of the dipole at the interface, is a function of the applied potential it is obvious that E_s and $C_{T\sim}$ will not in actual fact have a linear relationship. It follows also from equation (**54**) that no tensammetric wave can occur at the electrocapillary zero point as for $E_s \to 0$ also $C_{T\sim} \to 0$.

It should be stressed that the theoretical treatment given above applies for a given polarization only, that is, the values of $C_{T\sim}$ are different for one and the same substance at E_{s+} and E_{s-}. The reason is that K, L and the polarization function $g(P_{\mathrm{Di}}, P_{\mathrm{Oi}})$ ((**31**) and (**32a**)) assume different values depending, for example, on the nature of the double layer which is different at positive and negative polarizations of the electrode. For the same reason also E_{s+} and E_{s-} are not, strictly speaking, equally removed from the electrocapillary zero point (E^0).

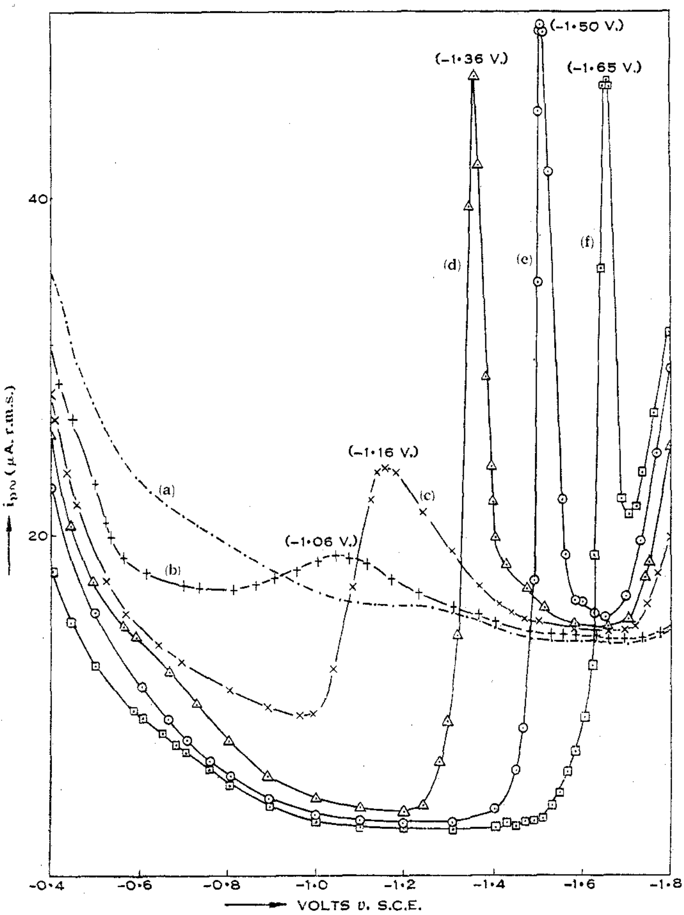

Fig. 10.—Tensammetric waves of pyridine in 0·1N KCl as supporting electrolyte. A.C. 45 mV. r.m.s.; *T*, 25 °C.
(*a*) 0·1N KCl; (*b*) 0·1N KCl+0·01M pyridine; (*c*) 0·1N KCl+0·05M pyridine; (*d*) 0·1N KCl+0·1M pyridine; (*e*) 0·1N KCl+0·2M pyridine; (*f*) 0·1N KCl+0·5M pyridine.

The relationship between $\omega^{-\frac{1}{2}}$ and $C_{T\sim}$ for pyridine, octyl alcohol, and *cyclo*hexanol is shown in Figure 8. A practically linear dependence as demanded by equation (**54**) was obtained.

IV. VARIATION OF TENSAMMETRIC SUMMIT POTENTIALS AND WAVE HEIGHTS WITH CONCENTRATION AND TEMPERATURE CHANGES

Saturated *cyclo*hexanol solution in N K_2SO_4 (20 °C.) gave two well-defined tensammetric waves at +0·045 V. and −1·243 V. *v.* S.C.E. respectively. In half-saturated *cyclo*hexanol solution the waves shifted to −0·015 and −1·159 V. *v.* S.C.E. respectively with corresponding reduction in the wave heights. As demanded by equation (**38**) both the positive and the negative waves shifted towards the electrocapillary zero point on dilution. A similar behaviour was observed with saturated *cyclo*hexanol solution in 0·5N $NaClO_4$. The shifts of the positive and negative tensammetric potentials of octyl alcohol with dilution are shown in Figure 9.

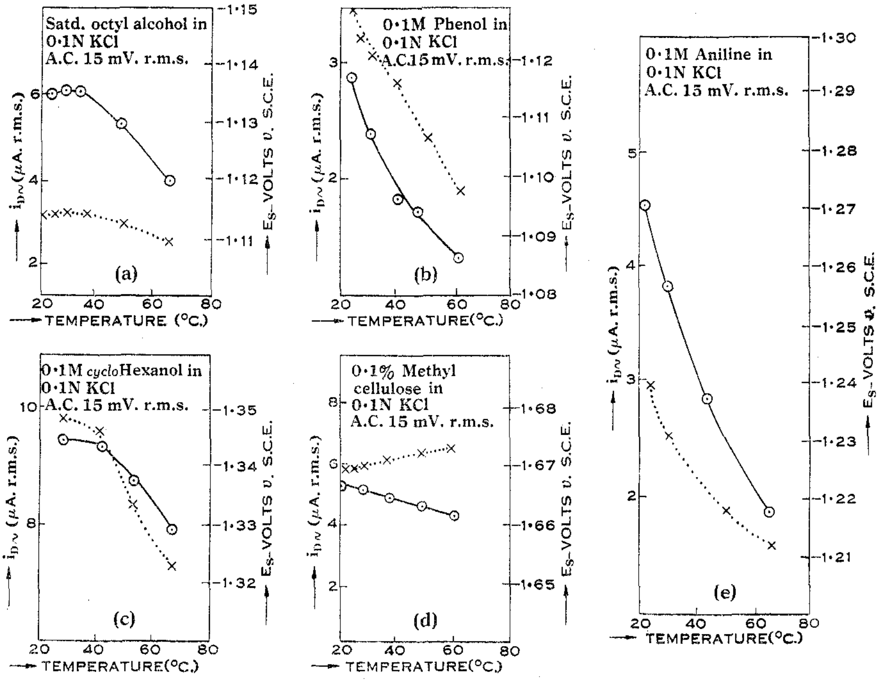

Fig. 11.—Variation of tensammetric wave height ($i_{D\sim}$) and negative tensammetric potential (E_{s-}) with temperature.

⊙——⊙ E_{s-}-temperature curves.

×····× $i_{D\sim}$-temperature curves.

Figure 10 shows the effect of dilution on the pyridine waves. A shift of as much as 0·6 V. was observed when the concentration of pyridine was changed from 0·5 to 0·01 molar (in 0·1 N KCl). Figure 10 also shows the corresponding increase of the base current in the region of the electrocapillary zero point with dilution of the pyridine, indicating that less pyridine is adsorbed at the interface as the dilution increases. The wave heights of pyridine were not greatly affected in the concentration range between 0·1 and 0·5 molar.

The influence of temperature changes on the wave heights of 2-methyl hexanol, phenol, *cyclo*hexanol, methyl cellulose, and aniline are shown in Figures 11 (*a*), (*b*), (*c*), (*d*), and (*e*). It can be seen that generally both the wave heights and the E_s values decrease with increasing temperature. This behaviour is best explained by remembering that both the kinetic energy and the solubility of the surface active substance increase with increasing temperature, facts which lead to easier desorption from the interface.

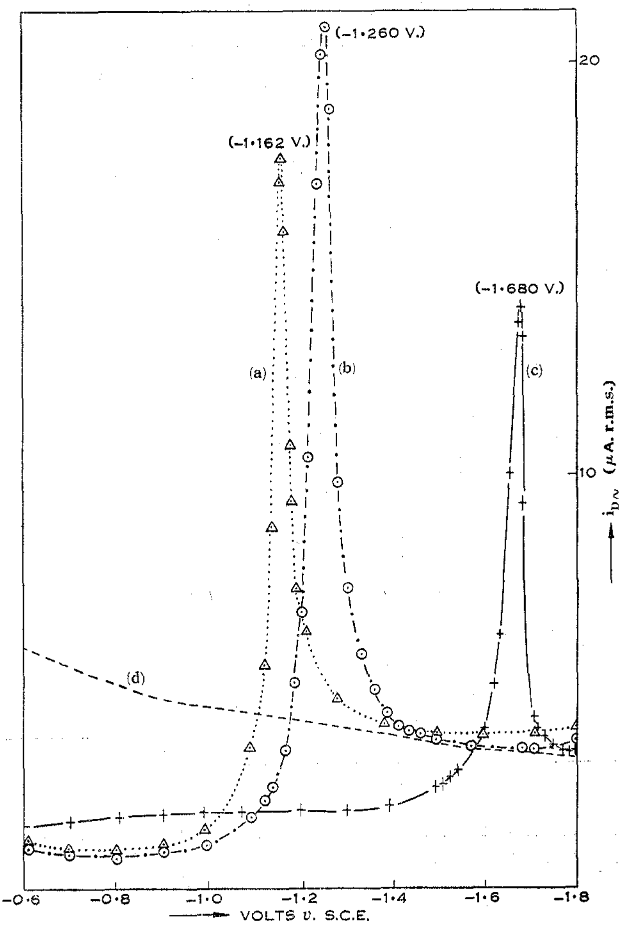

Fig. 12.—Influence of tensammetric waves on one another. (*a*) Saturated octyl alcohol in 0·1N KCl; (*b*) same as (*a*)+0·1M *cyclo*hexanol; (*c*) same as (*b*)+0·1 per cent. methyl cellulose; (*d*) 0·1N KCl (supporting electrolyte).

That solubility changes are at least partly responsible for the observed changes in tensammetric waves with change in temperature is shown by the behaviour of methyl cellulose: as is well known the solubility of this substance decreases with increasing temperature and it was found accordingly that in this case the wave height increased with a rise of temperature. The E_s values changed but very little. The behaviour of weak acids (phenol, cresol, etc.) and weak bases (e.g. aniline, pyridine) also showed how the wave height varies with solubility changes : whereas the free acids and bases gave good tensammetric waves, no waves were obtained in media of such pH that the respective salts were formed. Due to the greater solubility of the salt compared with that of the free acid or base, practically complete desorption from the interface takes place.

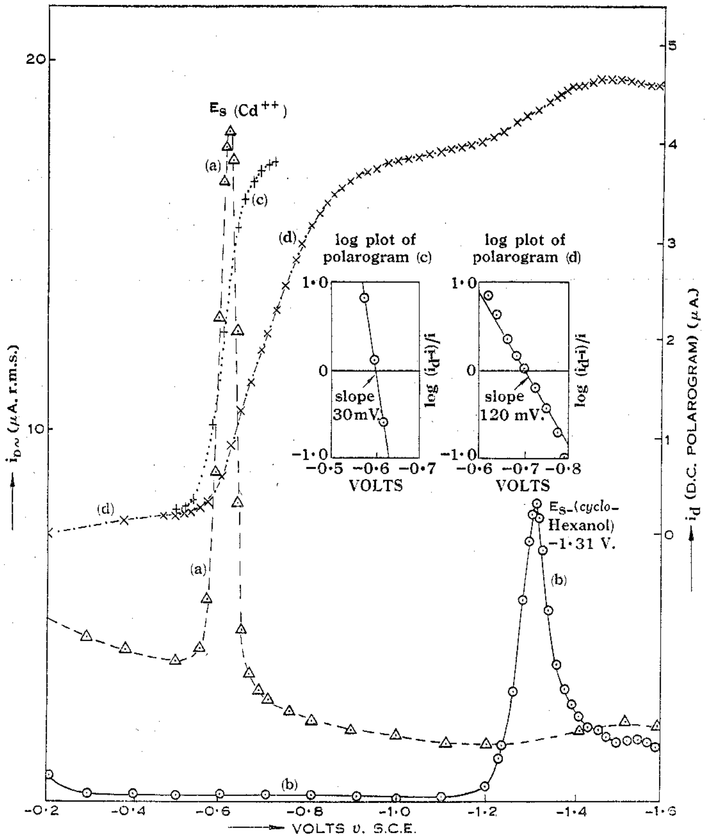

Fig. 13.—Effect of the presence of *cyclo*hexanol on the A.C.-D.C. polarograms of Cd^{++}. The polarograms show that the discharge of Cd^{++} becomes irreversible in the presence of the adsorbed molecules of *cyclo*hexanol.
(*a*) A.C. polarogram of 10^{-3}N Cd^{++} in 0·1N KCl (air-free) : A.C. 15 mV. r.m.s. ; *T*, 20 °C.
(*b*) A.C. polarogram of (*a*)+0·1M *cyclo*hexanol : only the tensammetric wave of *cyclo*-hexanol appears ; (*c*) D.C. polarogram of solution as under (*a*) ; (*d*) D.C. polarogram of solution as under (*b*).

V. INFLUENCE OF TENSAMMETRIC WAVES ON ONE ANOTHER AND ON CATHODIC A.C. AND D.C. POLAROGRAPHIC WAVES

Examining the region of negative polarizations, it was observed that when a mixture of two surface active substances was present in an indifferent supporting electrolyte, only one tensammetric wave was obtained corresponding to that substance whose E_s occurred at a more negative potential. In other words, only that substance which was more strongly adsorbed at the mercury-solution interface produced a tensammetric wave. The phenomenon is illustrated in Figure 12. Curve (*a*) shows the negative tensammetric wave of saturated octyl alcohol in 0·1N KCl with the summit potential at —1·162 V. *v.* S.C.E. In the presence of 0·1M *cyclo*hexanol, however, curve (*a*) disappears and only a single wave (*b*), corresponding to the tensammetric wave of *cyclo*hexanol alone (E_{s-} = —1·260 V. *v.* S.C.E.), is obtained, probably because *cyclo*hexanol is more

TABLE 1

TENSAMMETRIC POTENTIALS (E_s) AND WAVE HEIGHTS ($i_{D\sim}$) OF A NUMBER OF SURFACE ACTIVE SUBSTANCES IN VARIOUS SUPPORTING ELECTROLYTES (AIR-FREE)

Capillary characteristics: *m*, 1·5 mg. sec.$^{-1}$; *t*, 3·5 sec. (open circuit); A.C. 15 mV. r.m.s.; *T*, 25 °C.

Compound	Concn.	Supporting Electrolyte	Tensammetric Potential		Max. Differential Current ($i_{D\sim}$)	
			E_{s+} *v.* S.C.E. (V.)	E_{s-} *v.* S.C.E. (V.)	+ve Wave (μA. r.m.s.)	—ve Wave (μA. r.m.s.)
Octyl alcohol ..	Satd.	N Na_2SO_4	0·00	—1·140	17·1	4·2
,, ,, ..	,,	N $NaNO_3$	0·00	—1·140	30·5	9·2
,, ,, ..	,,	N KCl	—	—1·15	—	9·3
,, ,, ..	,,	N $MgSO_4$	0·00	—1·16	17·5	6·5
*cyclo*Hexanol ..	Satd.	N Na_2SO_4	+0·06	—1·30	34·0	10·8
,, ..	,,	N $NaNO_3$	—0·105	—1·18	14·0	8·2
,, ..	,,	N KCl	—	—1·28	—	14·0
,, ..	,,	N $MgSO_4$	+0·06	—1·35	34·6	9·1
n-Propyl alcohol	M	N Na_2SO_4	—0·015	—1·290	22·0	3·7
n-Butyl alcohol ..	0·1M	,,	—	—1·16	—	3·2
Octyl alcohol ..	0·1M	0·1N KCl	—	—1·135	—	7·3
Benzyl alcohol ..	Satd.	N Na_2SO_4	+0·275	—1·450	24·5	13·5
Anisole	,,	,,	0·0	—1·140	5·5	6·5
Phenol	0·1M	,,	—	—1·130	—	3·0
o-Cresol	Satd.	,,	—	—1·270	—	10·5
Catechol ..	0·1M	,,	—	—1·100	—	3·6
Resorcinol ..	,,	,,	—	—1·070	—	3·6
Hydroquinone ..	,,	,,	—	—1·060	—	3·6
Pyrogallol ..	M	,,	—0·02	—1·290	<0·5	3·0
Benzoic acid ..	0·01M	,,	—	—1·015	—	6·5
Gallic acid ..	Satd.	,,	—	—1·080	—	<0·5
Aniline	0·1M	,,	—0·03	—1·335	9·0	7·3
Pyridine	,,	,,	—	—1·383	—	32·5
Piperidine ..	Satd.	10N NaOH	—	—1·413	—	15·5
Methyl cellulose ..	0·1%	0·1N KCl	—	—1·665	—	6·0
,, ,, ..	Satd.	,,	—	—1·681	—	20·5

strongly adsorbed at the electrode surface than octyl alcohol. Adding now approximately 0·1 per cent. methyl cellulose to the mixture, the *cyclo*hexanol in turn is displaced by the more strongly adsorbed methyl cellulose molecules as shown by the disappearance of the *cyclo*hexanol wave and the appearance of the methyl cellulose wave only ($E_{s-} = -1{\cdot}680$ V. *v.* S.C.E.).

In order to test the validity of the schematic representation of the various electrical equivalents of the electrode-double-layer system as shown in Figure 2, experiments were carried out studying the influence of tensammetric waves on A.C. and D.C. polarography. The results are illustrated in Figure 13. A.C. polarogram (*a*) was obtained by the reversible discharge of 10^{-3}N Cd^{++} in 0·1N KCl (air-free solution). Its corresponding D.C. polarogram is represented by curve (*c*). Plotting log $(i_d - i)/i$ against E gave a straight line with a nearly theoretical slope of 30 mV./log unit. In the presence of *cyclo*hexanol, however, the discharge of Cd^{++} was rendered irreversible as shown by the absence of the A.C. polarogram. Only the tensammetric wave of *cyclo*hexanol ($E_{s-} = -1{\cdot}31$ V.*v.* S.C.E.) appeared. The D.C. polarogram also revealed that the Cd^{++} reduction had become irreversible: the " log plot " of the Cd^{++} step was non-linear with an approximate slope of 120 mV. In contradistinction to Cd^{++} the discharge of Mn^{++} (−1·5 V. *v.* S.C.E.) was completely unaffected by the presence of *cyclo*hexanol. The experiments clearly demonstrate that a reversible reduction process occurring within the region of dipole adsorption is rendered irreversible by the presence of a surface film at the electrode. In the case of Mn^{++} the reduction occurs at a potential at which the film is already desorbed (Fig. 2) and consequently both A.C. and D.C. polarograms remain unaffected. Thus in the presence of an adsorption layer the deposition of ions is impeded owing to the presence of a charged barrier at the electrode (see, for example, Heyrovsky, Sorm, and Forejt 1947 ; Loshkarev and Kryukova 1951 ; Maites and Maites 1951).

Tensammetric potentials and wave heights of a number of substances in various supporting electrolytes are given in Table 1.

VI. ACKNOWLEDGMENT

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