

## Cathode Overpotential and Electrosorption Effects of Straight-Chain Carboxylic Acids during Electrodeposition of Copper

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## Cathode Overpotential and Electrosorption Effects of Straight-Chain Carboxylic Acids during Electrodeposition of Copper

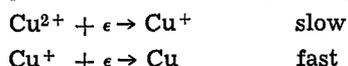
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## ABSTRACT

The effects of straight-chain carboxylic acids on cathode overpotential during electrodeposition of copper were studied by galvanostatic methods at current densities up to 0.020 A-cm<sup>-2</sup>. No modification of the charge-transfer mechanism of copper deposition occurred. Overpotential increments caused by lengthening of the carbon chain can be correlated with the reduced concentrations of the carboxylic acids in accordance with Traube's rule. This can be rationalized in terms of the general relation between adsorbability and solubility of the additive. The general behavior is consistent with the blocking theory of additive function according to which overpotential increments are directly dependent on additive adsorbability. The fractional surface coverage calculated from overpotential increments appears to fit a Langmuir-type isotherm from which the free energies of adsorption of the carboxylic acids can be determined. The magnitudes of these free energies are consistent with physical adsorption forces. A relation was derived between the free energy of adsorption and the free energy contributions from the carboxyl group and the carbon chain. This shows that the longer the chain, the higher the adsorbability.

*Overpotential and adsorbed additives.*—The rate-determining step in electrodeposition varies with the overpotential region (1). The charge-transfer process is believed to be rate-determining at high overpotentials (2) and the accepted mechanism in the case of copper deposition is the two step charge transfer



The charge-transfer overpotential  $\eta$  is related to the current density  $i$  by the Tafel equation (3)

$$\eta = a + b \ln i \quad [1]$$

Under high overpotential conditions, the measured overpotential will represent the magnitude of  $\eta$  if other sources of overpotential can be eliminated or sufficiently minimized.

The presence in the solution of surface-active additives results in a considerable increase in cathode overpotential in many instances (4-7), due primarily to adsorption of the additive on the cathode surface (4-6, 8, 9). Since this adsorption undoubtedly modifies the surface conditions for electrodeposition, it is essential to try to correlate the resulting overpotential increment and the additive adsorbability.

In metal deposition, overpotential increments caused by additives are generally believed to arise

from an increased true current density because of partial blocking of the electrode by adsorbed additive. If a fraction  $\theta$  of the cathode surface is covered by additive molecules, and if electrodeposition occurs only on the uncovered fraction  $1 - \theta$ , then the true current density will be increased from  $i$  in the absence of additive to  $i'$ , in the presence of additive, such that

$$i' = \frac{i}{1 - \theta} \quad [2]$$

If the charge-transfer process remains rate-determining, the increased charge-transfer overpotential  $\eta'$  in the presence of additive will be given by

$$\begin{aligned} \eta' &= a + b \ln i' \\ &= a + b \ln \left( \frac{i}{1 - \theta} \right) \end{aligned} \quad [3]$$

An expression relating the overpotential increment and the fractional surface coverage can then be obtained by subtracting Eq. [1] and [3] to give

$$\theta = 1 - \exp(-\Delta\eta/b) \quad [4]$$

Equation [4], based on the simple blocking theory, has been used in the study of hydrogen overvoltage at solid electrodes (8, 10) and values of  $\theta$  calculated in this way from overvoltage data have been found to agree satisfactorily with values obtained from double-layer capacity measurements (10). If it can be as-

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sumed that this equation applies equally well to metal deposition, then the fractional surface coverage for additives which adsorb randomly on the electrolytically active sites is readily calculable from experimental measurements of  $\Delta\eta$ .

It should be pointed out that overpotential is not always increased by the presence of additive. Certain alkaloids have been found to lower the hydrogen overvoltage of mercury and lead, but presumably because the specifically adsorbed alkaloid acts as a low-stability source of electroactive hydrogen (11).

**Electrosorption of additives.**—Various aspects of electrosorption have been reviewed by Frumkin (12). Mercury electrodes have been used for much of this work because they allow the extent of adsorption to be determined from electrocapillary data. In the case of solid electrodes, radiotracer methods have been used with some success (13, 14), but useful information can also be derived from studies of ordinary adsorption (15, 16), particularly concerning the adsorbability of additive and the type of bonding with the electrode surface. It is known that adsorbability in ordinary adsorption depends on the solubility of the adsorbate (15). In general, the lower the solubility, the higher the adsorbability.

In electrosorption, as in ordinary adsorption, solvent adsorption occurs at the electrode, and adsorption of additive involves a displacement of solvent molecules (17-19). Competition between solvent and additives for the electrode surface therefore occurs. Generally, if the adsorbed molecules are polar, their orientation might be expected to depend on the sign of the electrode charge, and the competition for adsorption sites between water and an organic additive might be expected to be potential dependent (20, 21). Accordingly, water molecules should be least strongly attached to the electrode at the point of zero charge, with maximum adsorption of the organic additive the expected result, but this is not always the case (17, 20, 22). In chemisorption particularly, the orientation of an adsorbed molecule will depend on the functional group that determines the point of attachment (15), and so the potential dependence of such adsorption would be relatively unimportant.

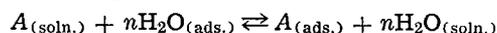
The equilibrium between adsorbed additive on an electrode surface and additive in the solution phase can be described in the customary way by an adsorption isotherm. In general, since the major difference between gas-phase and liquid-phase adsorption is merely that the substrate surface is bare in the former and solvated in the latter, it follows that isotherms originally derived for gas-phase adsorption also find application in electrosorption studies. In these studies, the Langmuir isotherm has been found useful.

**Langmuir adsorption isotherm.**—The Langmuir isotherm, derivable from either a kinetic or statistical treatment (23, 24), can be written in the form

$$\frac{\theta}{1-\theta} = CK = C \cdot \exp\left(-\frac{\Delta G^{\circ}_a}{RT}\right) \quad [5]$$

where  $\theta$  and  $C$  are the fractional surface coverage and concentration of additive, respectively,  $K$  is the equilibrium constant (the adsorbability), and  $\Delta G^{\circ}_a$  is the standard free energy of adsorption. From the model and assumptions made in the derivation, this isotherm can be expected to apply to localized monolayer adsorption with no lateral interference (i.e., free energy of adsorption is not coverage dependent) and to the condition where each adsorbed molecule occupies a single site on the surface. At low coverage, Eq. [5] describes many electrosorption systems to a good approximation (13, 25, 26).

**Langmuir adsorption from solution.**—Adsorption of an additive  $A$  on a solvated electrode surface can be written as a displacement reaction



where  $n$  is the number of water molecules displaced by a molecule of additive. A Langmuir-type isotherm for this kind of displacement adsorption has been formulated as (17)

$$\frac{\theta}{(1-\theta)^n} \frac{\{\theta + n(1-\theta)\}^{n-1}}{n^n} = CK = \frac{C}{55.5} \exp\left(\frac{-\Delta G^{\circ}_a}{RT}\right) \quad [6]$$

When  $n$  is unity, Eq. [6] reduces to the ordinary Langmuir isotherm

$$\frac{\theta}{1-\theta} = \frac{C}{55.5} \exp\left(\frac{-\Delta G^{\circ}_a}{RT}\right) \quad [7]$$

This is essentially the same form as Eq. [5] except that it contains the factor 1/55.5 which arises from taking unit mole fraction of adsorbed species as standard state.

### Experimental

Some of the overpotential measurements in this work were made with a Haring cell (5), while others were made with a Luggin probe in contact with the bottom end of a copper-wire cathode (about 2.0 mm diameter) in a specially constructed H-cell similar to one described by Turner and Johnson (7). The Haring cell was designed to contain 150 ml of solution with 10 cm<sup>2</sup> of electrode area immersed. The cathode compartment of the H-cell contained about 65 ml of solution with 1 cm<sup>2</sup> of cathode surface immersed. Cathode overpotentials were measured with a Sargent SR recorder in some cases and with a Leeds and Northrup Type K potentiometer in others. Overpotential increments were determined for several straight-chain carboxylic acids added to the standard reference solution of copper sulfate and sulfuric acid (4, 5). Effects of additive concentration and current density were determined.

Electrolyte containing 0.5M CuSO<sub>4</sub> and 1.0M H<sub>2</sub>SO<sub>4</sub>, both reagent grade, was used as the standard solution. The water was triply distilled in all-glass apparatus. Precautions were taken to remove possible organic contaminants from the copper sulfate pentahydrate solid before preparing the solutions. This was done by heating at 750°C for several days to cause complete decomposition to copper oxide, which was then dissolved in the required amount of sulfuric acid. All copper electrodes were heated to redness before use to remove any organic substances. Solutions containing the additives were always freshly prepared and only high-purity compounds were used.

### Results

All overpotentials reported in this paper are steady-state total values reproducible to within  $\pm 5\%$ . Minor variations in electrode surfaces appeared to be the main factor affecting the reproducibility. In the electrolysis of the standard solution at 25°  $\pm 0.1^\circ\text{C}$  and 20 mA-cm<sup>-2</sup>, the total cathode overpotential was 100  $\pm 5$  mV (4, 5). Some overpotential decay measurements indicate that under these conditions with natural free convection, the concentration overpotential, which is less than 5 mV, is not significantly affected by the additives employed in this work (27). It may therefore be assumed that the main effect of the additives is to increase the charge-transfer overpotential only. The overpotential increment in each case was obtained by subtracting 100 mV from the measured total value.

**Steady-state overpotential.**—The total steady-state cathode overpotential is shown in Fig. 1 as a function of additive concentration for several straight-chain carboxylic acids, methanoic, propanoic, pentanoic, heptanoic, and hexanedioic acids. These compounds were chosen to show the effect of carbon chain length on overpotential, the only variation in functional

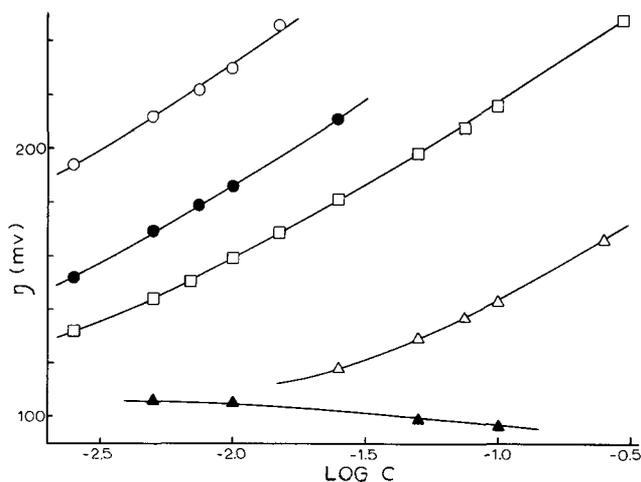


Fig. 1. Steady-state cathode overpotential and additive concentration. Temperature,  $25^\circ \pm 0.1^\circ\text{C}$ ; current density,  $20 \text{ mA}\cdot\text{cm}^{-2}$ .  $\circ$ , Heptanoic acid;  $\bullet$ , hexanedioic acid;  $\square$ , pentanoic acid;  $\triangle$ , propanoic acid;  $\blacktriangle$ , methanoic acid.

group being in the dicarboxylic hexanedioic acid. Additives differing by two methylene groups were chosen to cover a wide range of chain length with a minimum of experimental data. The curves in Fig. 1 show that cathode overpotential generally increases with increasing concentration and with increasing chain length of these additives. No effect on overpotential was found with methanoic acid up to about 0.1M, apart from a tendency to decrease the overpotential slightly though not significantly.

In the measurement of cathode overpotential at constant current density and with different concentrations of additive, it was found that, apart from the overpotential increase, the carboxylic acids had no effect on the time variation of overpotential. Good steady states were obtained in most cases in about 1 hr, after which prolonged electrolysis for several hours produced no further change. An exception was observed with heptanoic acid at a concentration close to saturation (0.015M). In this case the time required for steady state was about 8 hr.

**Overpotential-current density effects.**—Overpotential measurements at different apparent current densities were made by reducing the current density in 2-mA steps from  $20 \text{ mA}\cdot\text{cm}^{-2}$  down to  $2 \text{ mA}\cdot\text{cm}^{-2}$  with no current interruption during the step. The time required for steady state at each new current density varied from about 5 to 10 min. Typical overpotential-current density data are shown as Tafel plots in Fig. 2. These show a linear behavior extending from about  $8 \text{ mA}\cdot\text{cm}^{-2}$  to about  $20 \text{ mA}\cdot\text{cm}^{-2}$ , with the additives having no marked effect on the Tafel slope. In accordance with Eq. [3] and the natural logarithm of current density, this slope was found to be  $50 \pm 1 \text{ mV}$ , in agreement with the theoretical value calculated from the relation

$$b = RT/\alpha zF$$

with the transfer coefficient  $\alpha$  taken as 0.5 and  $z$  taken as unity (2). Therefore, under conditions where charge transfer is rate-determining, carboxylic acids have no significant effect on the kinetics of copper deposition. Their primary effect is merely to increase the charge-transfer overpotential by increasing the true current density.

### Discussion

**Adsorption isotherm and surface coverage.**—The fractional surface coverage  $\theta$  due to additive adsorbed on the cathode was calculated from the overpotential increment  $\Delta\eta$  by applying Eq. [4] to the data for propanoic, pentanoic, heptanoic, and hexanedioic acids. For these calculations, the Tafel slope  $b$  was taken as

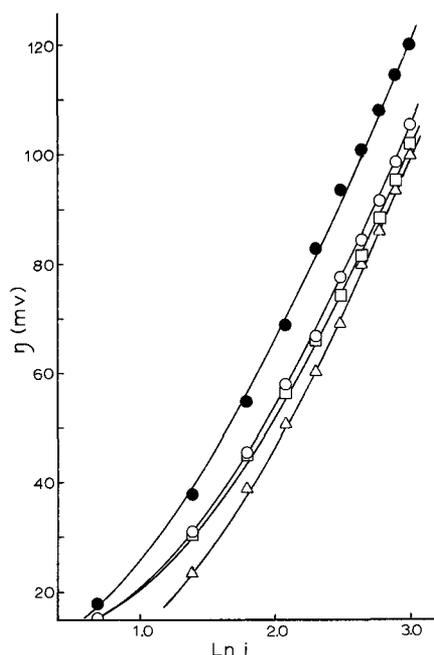


Fig. 2. Overpotential-current density relations. Temperature,  $25^\circ \pm 0.1^\circ\text{C}$ .  $\triangle$ , Standard solution;  $\square$ ,  $1.0 \times 10^{-3} \text{ M}$  methanoic acid;  $\circ$ ,  $1.0 \times 10^{-2} \text{ M}$  methanoic acid;  $\bullet$ ,  $3.0 \times 10^{-2} \text{ M}$  propanoic acid.

the experimental 50 mV, with results as shown in Table I. A test was made for Langmuir adsorption by plotting the left hand side of Eq. [6] against additive concentration, and it was found that if  $n$ , the number of water molecules replaced by a molecule of adsorbed additive, is taken as 2, a straight line passing through the origin is obtained for each of the four additives. Typical results are shown in Fig. 3.

**Free energy of adsorption.**—Since the behavior of carboxylic acids shown in Table I and Fig. 3 appears to be consistent with Langmuir adsorption, Eq. [6] may be used to evaluate the standard free energy of adsorption of these additives. The values of the adsorbability  $K$  and standard free energy  $\Delta G^\circ_a$ , calculated from the slopes of the lines as illustrated in Fig. 3, are listed in Table II. The results show that, with other things being equal, the free energy of adsorption and the adsorbability increase with the length of the carbon chain. From the magnitude of the net standard free energy, it would appear that physical forces are primarily involved in the adsorption process.

Table I. Adsorption data

Temperature = $25^\circ \pm 0.1^\circ\text{C}$ Current density = $20 \text{ mA}\cdot\text{cm}^{-2}$				
Additive	C (moles l <sup>-1</sup> )	$\Delta\eta$ (mV)	$\theta$	$f(\theta)$
Propanoic acid	$2.5 \times 10^{-2}$	18.0	0.302	0.263
	$5.0 \times 10^{-2}$	29.4	0.445	0.562
	$7.5 \times 10^{-2}$	37.2	0.525	0.851
	$1.0 \times 10^{-1}$	43.0	0.577	1.145
Pentanoic acid	$2.5 \times 10^{-3}$	31.9	0.472	0.645
	$5.0 \times 10^{-3}$	44.0	0.585	1.20
	$6.9 \times 10^{-3}$	50.4	0.635	1.63
	$1.0 \times 10^{-2}$	59.2	0.693	2.41
Heptanoic acid	$2.5 \times 10^{-3}$	94	0.848	10.6
	$5.0 \times 10^{-3}$	112	0.894	22.1
	$7.5 \times 10^{-3}$	122	0.913	32.6
	$1.0 \times 10^{-2}$	130	0.926	45.0
Hexanedioic acid	$2.5 \times 10^{-3}$	52.0	0.647	1.75
	$5.0 \times 10^{-3}$	69.5	0.751	3.78
	$7.5 \times 10^{-3}$	79.0	0.794	5.65
	$1.0 \times 10^{-2}$	86.0	0.821	7.56

$$f(\theta) = \frac{\theta}{(1-\theta)^2} \left[ \frac{\theta + 2(1-\theta)}{4} \right]$$

(See Eq. [6])

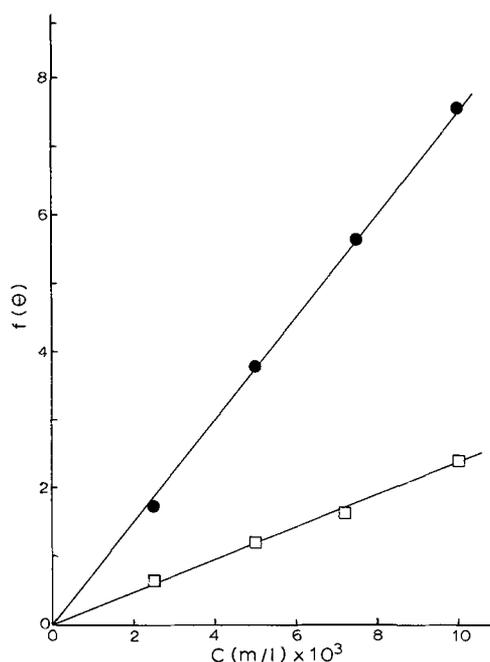


Fig. 3. Langmuir isotherm plots. ●, Hexanedioic acid; □, pentanoic acid.

Since the net free energy of adsorption shown in Table II is in every case significantly greater than the molal thermal energy  $RT$ , it may be argued that adsorption of carboxylic acids on a copper cathode is localized to a degree such that the effective blocking is the primary factor responsible for the overpotential increment. Delocalized (i.e., mobile) adsorption of additive would presumably not contribute greatly to this increment.

With carboxylic acids as additives, the affinity of the carboxyl group for the copper surface is presumably sufficient to assure localized adsorption provided that the carbon chain is of sufficient size to have the necessary effect on the free energy of the process. Considerable surface coverages can be expected, as shown by the experimental results (Table I). The small or nearly zero overpotential effect of methanoic acid presumably arises from the hydrophilic nature of this compound, resulting in relatively ineffective competition with the solvent in the adsorption process, with a consequent low adsorbability. This view is supported by some studies of hydrogen evolution on a copper cathode with ethanoic acid as additive (10) which indicate that little or no adsorption occurs up to a concentration of 2.5M.

**Components of adsorption free energy.**—In the adsorption of carboxylic acids at the electrode surface, the polar functional group probably determines the energy required for appropriate bonding or physical attraction with the surface, while the hydrophobic carbon chain contributes part of the free energy to assist the adsorption process. The adsorption energy of the functional group presumably depends in part on the nature of the adsorbent (the electrode surface), while the adsorption energy of the carbon chain depends primarily on the solution. For the additives studied, the increase in adsorption free energy is found to be the same for each increase in chain length

Table II. Net free energy of adsorption

Additive	Temperature = 25° ± 0.1°C	
	K (1 mole <sup>-1</sup> )	$\Delta G^{\circ}_a$ (cal mole <sup>-1</sup> )
Propanoic acid	11.2	-3812
Pentanoic acid	243	-5597
Heptanoic acid	4400	-7351
Hexanedioic acid	758	-6309

by two methylene groups, within experimental error. If the free energy of adsorption of the functional group,  $\Delta G^{\circ}_p$ , remains unchanged as the carbon chain is varied, the free energy due to each added methylene group,  $\Delta G^{\circ}_{CH_2}$ , may be calculated from the data for the monocarboxylic acids in Table II by applying the equation

$$\Delta G^{\circ}_a = \Delta G^{\circ}_p + n_{CH_2} \cdot \Delta G^{\circ}_{CH_2} \quad [8]$$

where  $n_{CH_2}$  is the number of methylene groups in the molecule (including the terminal methyl). The mean values of  $\Delta G^{\circ}_p$  and  $\Delta G^{\circ}_{CH_2}$  were found to be 2047 and 885 cal-mole<sup>-1</sup>, respectively. However, if these values are used for hexanedioic acid, taking into account the two carboxyl groups, the calculated  $\Delta G^{\circ}_a$  is found to be 7634 cal-mole<sup>-1</sup>, significantly higher than the experimental 6309 cal-mole<sup>-1</sup>. Steric effects and possible cyclization are probable factors in preventing adsorption of this compound to the extent predicted from the monocarboxylic behavior.

**Calculation of  $\Delta G^{\circ}_a$ .**—Since adsorption of additive from solution is a water-replacement process as stated previously, the net standard free energy of adsorption will be the difference between the free energies of adsorption of additive and water from solution

$$\Delta G^{\circ}_a = \Delta G^{\circ}_{A(soln)} - n\Delta G^{\circ}_{W(soln)} \quad [9]$$

But adsorption of additive at an electrode-solution interface can be regarded as the sum of two processes: (i) the transfer of additive from the solution bulk to the pre-electrode layer, and (ii) the attachment of additive, physically or chemically, to the electrode surface from the pre-electrode layer.

The first of these processes appears to be analogous to the adsorption of additive at a liquid-water interface (28, 29). In the adsorption of carboxylic acids on an electrode surface, the carboxyl group probably has a higher affinity for the metal than it does for the solvent, while the hydrophobic carbon chain is effectively rejected by the solvent. Due to this solvent rejection, the additive will transfer spontaneously to the pre-electrode layer and thus make further interaction with the electrode surface possible. The first term on the right in Eq. [9] is then given by

$$\Delta G^{\circ}_{A(soln)} = \lambda + \Delta G^{\circ}_{A,M} \quad [10]$$

where  $\lambda$  is the free energy due to solvent rejection and  $\Delta G^{\circ}_{A,M}$  is the free energy due to additive-metal interaction. The quantity  $\lambda$  may in turn be regarded as the sum of the energies required to bring both the polar and nonpolar portions of the additive molecule from the bulk to the pre-electrode layer

$$\lambda = \lambda_P + n_{CH_2} \lambda_{CH_2} \quad [11]$$

This equation, which has been generally accepted as valid for adsorption at the air-water and liquid-water interfaces (29, 30), can be used with adsorption data from such studies to provide useful information in the interpretation of additive adsorption on electrodes.

Combination of Eq. [9], [10], and [11] gives

$$\Delta G^{\circ}_a = \Delta G^{\circ}_{A,M} + \lambda_P - n\Delta G^{\circ}_{W(soln)} + n_{CH_2} \lambda_{CH_2} \quad [12]$$

Accordingly, for a given functional group, the net standard free energy of adsorption  $\Delta G^{\circ}_a$  increases as the number of methylene groups increases, provided of course that the signs of  $\Delta G^{\circ}_a$  and  $\lambda_{CH_2}$  are the same. The magnitude of  $\Delta G^{\circ}_{A,M}$  may be considered to depend primarily on the nature of the functional group as suggested earlier. Generally, the magnitude of  $\lambda_P$  is small relative to that of  $n_{CH_2} \lambda_{CH_2}$ . For an organic polar molecule with a long carbon chain, it may be expected that the greatest contribution to the free energy of adsorption from solution to the pre-electrode layer comes from the carbon chain. Thus, with other factors equal, the longer the carbon chain, the greater the adsorbability.

To compare the quantities in Eq. [12] with the values calculated for  $\Delta G^\circ_{\text{CH}_2}$  and  $\Delta G^\circ_{\text{P}}$  (885 and 2047 cal-mole<sup>-1</sup>), we may write, in view of Eq. [8]

$$\Delta G^\circ_{\text{P}} = \Delta G^\circ_{\text{A,M}} + \lambda_{\text{P}} - n\Delta G^\circ_{\text{W(soln.)}} \quad [13]$$

and

$$\Delta G^\circ_{\text{CH}_2} = \lambda_{\text{CH}_2} \quad [14]$$

The experimental value of  $\Delta G^\circ_{\text{CH}_2}$  for the carboxylic acids studied, 885 cal-mole<sup>-1</sup>, may be compared with the value 820 cal-mole<sup>-1</sup> for the oil-water interface (29) and 625 cal-mole<sup>-1</sup> for the air-water interface (30). Hence, the value of  $\Delta G^\circ_{\text{CH}_2}$  for an electrode-solution interface may be approximately predicted from data for the liquid-water interface, which are readily available and known for many systems (15).

As a special case of Eq. [13], if the magnitude of  $\Delta G^\circ_{\text{A,M}}$  is comparable to that of  $n\Delta G^\circ_{\text{W(soln.)}}$ ,  $\Delta G^\circ_{\text{P}}$  is approximately equal to  $\lambda_{\text{P}}$ . For the carboxyl group, the values of  $\lambda_{\text{P}}$  for the oil-water interface, 1630 cal-mole<sup>-1</sup> (29), and for the air-water interface, 437 cal-mole<sup>-1</sup> (30), are relatively small compared to the value of  $\Delta G^\circ_{\text{W(soln.)}}$ , 4800 cal-mole<sup>-1</sup> (26, 31) calculated from data for adsorption of water vapor on mercury. Obviously, the magnitude of  $\Delta G^\circ_{\text{P}}$  depends largely on the number of water molecules replaced, i.e.,  $n$ . If other factors are equal, additives will tend to adsorb on an electrode surface in such a way that the least number of water molecules will be replaced.

For the carboxylic acids employed in this study, the number of water molecules replaced is taken as 2 (see Fig. 3). If the value of  $\lambda_{\text{P}}$  for the oil-water interface, 1630 cal-mole<sup>-1</sup> (29), is applicable to the electrode-solution interface, and if the value of  $\Delta G^\circ_{\text{W(soln.)}}$  quoted above, 4800 cal-mole<sup>-1</sup> (26, 31), is also applicable, the value of  $\Delta G^\circ_{\text{A,M}}$  may be found from Eq. [13], using the experimental value, 2047 cal-mole<sup>-1</sup>, for  $\Delta G^\circ_{\text{P}}$ . The value obtained is 10,020 cal-mole<sup>-1</sup>.

Since  $\Delta G^\circ_{\text{A,M}}$  and  $2\Delta G^\circ_{\text{W(soln.)}}$  differ by only 420 cal-mole<sup>-1</sup>, an approximate prediction may be made of the net standard free energy of adsorption of an additive on an electrode surface, using adsorption data from liquid-water interfacial studies. This is seen by writing Eq. [12] in the approximate form

$$\Delta G^\circ_{\text{a}} \approx \lambda_{\text{P}} + n_{\text{CH}_2} \lambda_{\text{CH}_2} \quad [15]$$

Accordingly, with additives having a long carbon chain, the greatest contribution to the net free energy of adsorption comes from this chain.

*Correlation between overpotential increment and additive solubility.*—Since the adsorbability of a carboxylic acid depends to a considerable extent on the carbon chain length, for a given functional group, and since it is known that the solubility of a hydrocarbon compound is also carbon chain dependent, then it may be expected that a direct correlation can be derived between overpotential increment and additive solubility. If the simple blocking action arising from adsorption of additive is the primary cause of overpotential increase, then such a correlation should be possible between overpotential increment, a function of additive concentration, and the reduced concentration of additive, which accounts for the effect of solubility. The reduced concentration has been defined as (32, 33)

$$C_r = \frac{C}{C_s} \quad [16]$$

where  $C$  and  $C_s$  are the concentrations of bulk and saturated solution, respectively.

If overpotential increments are plotted against reduced concentration calculated from known solubilities (34, 35) of the additives used in this study, a generalized behavior results as shown in Fig. 4. It is seen that the overpotential increment for a given reduced concentration is approximately the same for all the carboxylic acids employed. These results may be compared with those obtained for the adsorption of

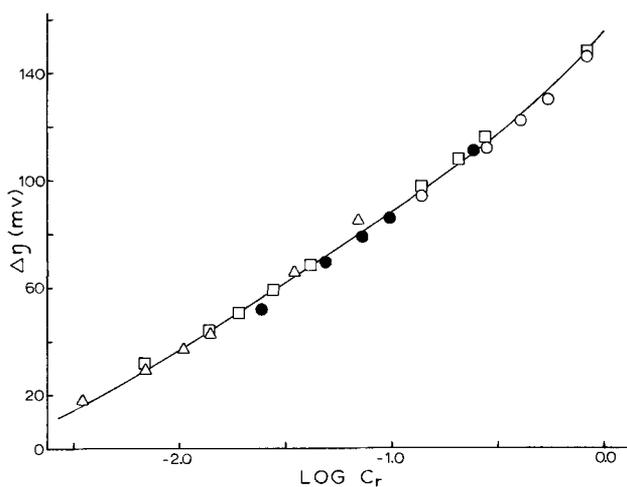


Fig. 4. Overpotential increment as a function of reduced concentration. Temperature,  $25^\circ \pm 0.1^\circ\text{C}$ .  $\circ$ , Heptanoic acid;  $\bullet$ , hexanedioic acid;  $\square$ , pentanoic acid;  $\triangle$ , propanoic acid.

carboxylic acids on graphite (33). The relation between overpotential increment and the chain length of the carboxylic acids can therefore be generalized if the solubilities are taken into account.

Since the effect of the carbon chain on the overpotential increment can be related to additive solubility, then Traube's rule which relates the effect of carbon chain on surface tension (36) might be applicable to overpotential data. This was verified for the monocarboxylic acids used in this study, and it was found that by adding one methylene group to the carbon chain, the additive concentration required to cause the same overpotential increment reduces to approximately 1/4.3. The value 4.3 can therefore be regarded as the approximate Traube coefficient in this instance. The relation can be generalized as

$$\Delta\eta(n_{\text{CH}_2}C) = \Delta\eta(n_{\text{CH}_2-s,(\omega)^sC}) \quad [17]$$

where  $\Delta\eta(n_{\text{CH}_2}C)$  is the overpotential increment due to additive containing  $n_{\text{CH}_2}$  methylene groups at concentration  $C$ , and  $\Delta\eta(n_{\text{CH}_2-s,(\omega)^sC})$  is the overpotential increment due to additive containing  $n_{\text{CH}_2-s}$  methylene groups at concentration  $(\omega)^sC$ ,  $\omega$  being the Traube coefficient 4.3. As an example, the overpotential increment caused by pentanoic acid can be predicted from data for propanoic acid by writing

$$\Delta\eta C(\text{pentanoic}) = \Delta\eta(4.3)^2 C(\text{propanoic})$$

since  $s = 2$ . This prediction can be generalized further in the form

$$C_1 = (4.3)^s C_2 \quad [18]$$

for straight-chain monocarboxylic acids 1 and 2 such that the chain length of 2 is longer than that of 1 by  $s$  methylene groups, and where  $C_1$  and  $C_2$  are concentrations that give the same overpotential increment. It is immediately apparent that Eq. [18] is consistent with the obvious parallelism of the overpotential *vs.*  $\log C$  curves in Fig. 1. Since the difference between  $\log C$ -values remains constant for any two of the monocarboxylic additives, then the ratio of the concentrations will also be constant.

Overpotential increments predicted in accordance with Eq. [17] and [18] are compared with experimentally measured values in Fig. 5. Satisfactory agreement is found. In a similar manner, a theoretical prediction can be made concerning the concentration of methanoic acid that would be required to cause a given overpotential increment. As an example, for an increment of 50 mV (total overpotential 150 mV), the methanoic acid concentration would have to be about 2.5M, high enough to have a significant effect on the solvent activity.

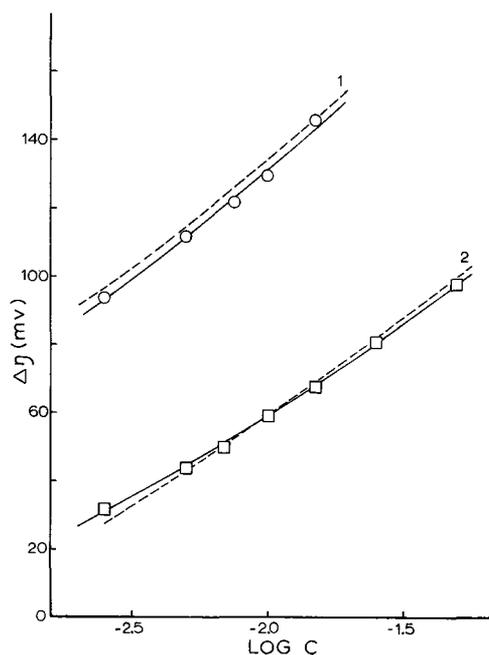


Fig. 5. Overpotential increment and additive concentration.  $\circ$ , Heptanoic acid. Curve 1, calculated for heptanoic acid from pentanoic data.  $\square$ , Pentanoic acid. Curve 2, calculated for pentanoic acid from propanoic data.

Another observation concerns the overpotential effects of hexanedioic acid shown in Fig. 1. According to Eq. [17] and [18], the  $\eta$  vs.  $\log C$  curve for hexanedioic acid should lie halfway between the curves for heptanoic and pentanoic acids, meaning that the overpotential effect of hexanedioic acid is less than that expected for hexanoic acid. This difference might be rationalized on the basis of partial cyclization of the hexanedioic acid in the aqueous solution. Studies are in progress to compare overpotential effects of a series of straight-chain dicarboxylic acids with their monocarboxylic counterparts.

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