

ions, and (iii) increased mobility of charged units. Lawrence and Pearson¹², using Na⁺ ion selective electrodes, have found that increase in the conductivity of 2% aqueous solutions of SDS is due to the presence of alcohols (essentially because of the release of the counter ions from the micelles) and partly due to the release of a few surfactant ions from the micelles. But as the chain-length of alcohol increases upto five carbon atoms, the increase in the specific conductivity is caused entirely by the released counter ions. Though the additive may cause a change in the shape and size of the micelles, it seems unlikely, especially in concentrated solutions of surfactants where micelles have high aggregation numbers, that micelles of much different shapes will be formed. Therefore, increase in the mobility of the micelles cannot be considered as a significant factor in accounting for such a sharp increase in the conductivity of the solution. When the alcohol content is at a certain level, hydrophobization of micelle as a consequence of the appearance on its surface of alcohol hydroxyl groups, which are less polar than ionic groups of the surfactant, leads to pronounced turbidity of the solution. The turbidity is induced by the separation of a mesomorphic phase consisting of surfactant-alcohol and water.

As mentioned above, the contribution of monomeric surfactant ion to the observed increase in conductivity decreases with increasing chain-length. With *n*-pentanol the increase is entirely due to the released counter-ions, thus the lower heights of maxima observed in the cases of *n*-hexanol and *n*-heptanol may partially be due to the lack of any contribution of conductivity by the monomeric ions. Comparing the effectiveness of *m*-cresol and aniline with those of alcohols, it seems that the former additives lie between *n*-pentanol and *n*-hexanol (Table 1). It is, therefore, obvious that the nature of the polar groups and size of nonpolar moiety both together determine the effectiveness of these compounds.

It may be interesting to mention that *n*-octanol¹¹ does not give rise to any maximum in conductance. The higher alcohols being completely insoluble in water will completely solubilize in the micelle interior and therefore will not cause any perturbation in the electrical double layer where the counterions are held. Octanol, though having a polar-OH group, behaves exactly as the completely non-polar solutes like *n*-hexane and toluene. It will, however, be interesting to see what effect *iso*-octanol will have since the —OH group in the molecule occupies a middle position in the chain. Further work with compounds containing multiple groups and branched chain structures is being carried out in our laboratory.

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Standard Rate Constant of Sb(III)/Sb(Hg) Exchange in Alkaline Medium

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Apparent standard rate constant values (k_s) for the reduction Sb(III)/Sb(Hg) in 1M NaOH and KOH have been determined using faradaic impedance measurements. From the values of the reaction rate constants at different temperatures in 1M NaOH, it is concluded that the reduction is irreversible under the experimental conditions used. The enthalpy of activation ΔH^\ddagger has been calculated from the slope of the linear plot between k_s and $1/T$.

STUDIES using oscillographic polarography showed that the reduction of trivalent antimony was irreversible in the presence of certain base electrolytes¹. This conclusion was also confirmed by Norakidze *et al.*². The rate constant values for the reduction of Sb(III) in acid solutions were also reported³. In this note are reported the apparent standard rate constant values (k_s) of Sb(III)/Sb(Hg) exchange in 1 M NaOH and KOH. The technique employed is essentially polarography with superimposed alternating voltage.

The capacitive and resistive components of the mercury surface were measured on an a.c. bridge similar to that used by Grahame⁴. The bridge, polarization cell and d.c. polarizing circuit were essentially the same as described previously⁵. In the presence of trivalent antimony and with no current-maxima suppressor added, the pseudocapacity and over-all polarization resistance were traced over an appropriate potential range at a normal working frequency of 1000 Hz. The effect of a higher frequency i.e. 3000 Hz on the peak C_m and R_m values was also studied. The results were analysed vectorially to determine the components of the impedance

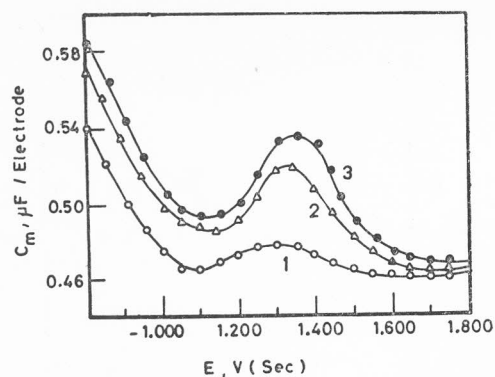


Fig. 1 — Variation of pseudocapacity as a function of polarization for the reduction of Sb(III) in 1M NaOH [Curve 1, [Sb(III)] = 1 mM; curve 2, [Sb(III)] = 2mM; curve 3, [Sb(III)] = 3mM].

R_r and C_r . The method is a direct one and has been shown to lead to quite reliable results⁶. Potentials were measured against a saturated calomel electrode and solutions were de-aerated with purified hydrogen.

According to Grahame's analysis of the theory of the faradaic admittance⁷, the magnitude of the pseudocapacity peak C_m may be taken as a qualitative measure of the intrinsic speed of the electrode reaction in this medium. The results for the pseudocapacity at 1000 Hz as a function of polarization as obtained during the reduction of trivalent antimony in 1 M NaOH are shown in Fig. 1. Similar curves are obtained in 1 M KOH. In these media, the pseudocapacities appear as humps and shift slightly towards more negative potentials with increase in antimony concentration. C_m tends to increase in magnitude with increase in [Sb(III)]. The half wave potential for the reduction of trivalent antimony to the metal is -1.255 and -1.260 V in 1 M NaOH and 1 M KOH respectively, in agreement with the already reported value in 1 M NaOH⁸.

The specific rate constant for the exchange $\text{Sb(III)}/\text{Sb(Hg)}$ was calculated following the simple model of the faradaic impedance⁹. According to this model,

$$R_r - 1/\omega C_r = \frac{RT}{n^2 f^2 AC} \cdot \frac{1}{k_s}$$

where k_s is the standard rate constant in cm sec^{-1} , C the concentration in g ion/cm^3 , A the area in cm^2 , n the number of electrons involved in the reduction, R_r and C_r are respectively the resistive and capacitive components of the faradaic admittance. The various quantities involved in the calculation together with the calculated k_s values at 25°C in 1 M NaOH are shown in Table 1. Similar results are obtained in 1 M KOH. The rate constant for the reduction of trivalent antimony is the same in the two media being $\sim 3.3 \times 10^{-4}$ cm/sec.

The values of k_s at different temperatures in 1 M NaOH show that k_s increases with increase in temperature. By plotting $\log k_s$ against $1/T$ an approximate straight line is obtained. The energy of activation as obtained from the slope is 4.8 ± 0.5

TABLE 1 — APPARENT STANDARD RATE CONSTANT (k_s) OF THE EXCHANGE $\text{Sb(III)} + 3e \rightleftharpoons \text{Sb(Hg)}$ in 1 M NaOH AT 25°C

[A=0.0300, $R_s = 40$, $C_d = 0.45$]

C(mM)	Freq. (Hz)	C_m	R_m	R_r	$\frac{1}{\omega C_r}$	$k_s \times 10^4$
1.0	1000	0.480	84	3271	270	3.3
	3000	0.470	51	3123	29	3.3
2.0	1000	0.498	105	1600	80	3.3
	3000	0.484	51	1579	80	3.3
3.0	1000	0.526	130	1029	29	3.3
	3000	0.474	50	1025	28	3.3

kcal. From the values of reaction rate constants at different temperatures, it may be concluded that reduction of Sb(III) under these experimental conditions is irreversible¹⁰.

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Spectrophotometric Determination of Basicities of Substituted Acetonaphthones

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The basicities of several 6-substituted 2-acetonaphthones and of 4-substituted 1-acetonaphthones have been determined spectrophotometrically in sulphuric acid media at 30°. The Hammett equation has been applied in both series. The point for the methoxy group deviates considerably from the Hammett plot in both the series. A very good linear correlation exists between pK_{BH^+} and σ_p^+ in the case of 4-substituted 1-acetonaphthones.

THE linear free-energy relationships are successful in correlating reactivities of many side-chain reactions in benzene derivatives¹. The applicability of these relationships to naphthalene derivatives has been tested in only a few cases²⁻⁷. The basicities of several 6-substituted 2-acetonaphthones and 4-substituted 1-acetonaphthones have now been deter-

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