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Adsorption of *n*-Aliphatic Alcohols on Mercury Electrode and Their Effect on Electrode Kinetics

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The adsorption parameters of butyl alcohol, amyl alcohol, and hexyl alcohol at mercury electrode were evaluated by means of the electrocapillary measurements and compared with those obtained by differential capacity measurements. A marked difference is observed both in the interaction parameters between adsorbed molecules and in the maximum surface excess, Γ_{max}. The inhibition effect by these alcohols on the electrode kinetics of the vanadium(III)/vanadium(II) couple in 0.5 M H_2SO_4 and of the europium(III)/europium(II) couple in 1.0 M HCl depends only on the surface coverage, $\theta=\Gamma/\Gamma_{\text{max}}$, of the electrode and is independent of the chain length of the adsorbed alcohol. The blocking effect is predominant in the inhibition of the electrode process by these alcohols.

The neutral surfactants adsorbed on the electrode surface often have a marked influence on electrode kinetics. The role of these surfactants can be interpreted by one of three classes of inhibition mechanisms. These involve: (a) a blocking effect, (b) an electrostatic effect, the change in the ϕ_2 potential, and (c) the effect on the activation energy for the charge transfer step. Lipkowski and Galus extensively discussed and compared the present theories with the available experimental data.1) It has been shown that the interaction between the activated complex and the adsorbed surfactants may be described by the equation derived from Flory-Huggins, Frumkin or Blomgren-Bockris adsorption isotherms for the activated complex. It was found from the statistical analysis of the experimental data that the Flory-Huggins type equation2,3) was better than the other two, namely:

$$k_\theta = k_0(1-\theta)^n \qquad (1)$$

where k_θ is the apparent rate constant in the presence of adsorbed layer, k_0 the rate constant without surfactants, θ the surface coverage, and n is a constant.

In the present work, the effect of aliphatic alcohols on the electrode kinetics of the V(III)/V(II) and Eu(III)/Eu(II) couples has been studied in connection with the adsorption behavior of these alcohols on the dropping mercury electrode.

Experimental

Reagent grade butyl, amyl, and hexy alcohols (Tokyo Kasei) were used without further purification after their purity had been checked by gas chromatography. These alcohols were dissolved in either 0.5 M H_2SO_4 or 1.0 M HCl solutions. The base solutions were pre-treated with a purified activated charcoal. The electrocapillary curves for these solutions were obtained with a modified capillary electrometer and the radius of the capillary was determined by standardization against a solution of known surface tension as previously described.4)

The V(III)/V(II) system in 0.5 M H_2SO_4 solution was prepared by reducing $VOSO_4$ *in situ* on a mercury pool cathode. The Eu(III)/Eu(II) system in 1.0 M HCl solution was prepared by dissolving Eu_2O_3 (electronic grade, 99.9%) and Eu(II) was generated cathodically *in situ*. The electrode kinetic parameters of the V(III)/V(II) and Eu(III)/Eu(II) systems were measured by conventional dc polarographic and pulse polarographic methods (Fuso Model 312 Polarograph). The detailed experimental procedure has been previously described.5)

Measurements were made at (25±0.5) °C and, the electrode potential was referred to SCE.

Results and Discussion

Adsorption Isotherms. As shown in Table 1, the maximum surface excess of these alcohols is considerably smaller than that calculated from the projected area of the perpendicular orientation (7.90×10^{-10} mol cm^{-2}) and decreases linearly with the chain length of the alcohol. This is probably due to either the deviation of the alcohol dipole from vertical orientation at the electrode surface or the contamination of water molecules in the electrical double layer saturated by the alcohol. These results also suggest that the shift of the point of zero charge with respect to the surface excess of these alcohols at the electrode surface deviates from the curve predicted by the Frumkin model.7)

The adsorption isotherms are well characterized by the Frumkin isotherm5)

$$B_0 c = \frac{\theta}{1-\theta}\exp(-2a_0\theta) \qquad (2)$$

and

$$-\Delta G_A^\circ = RT\ln(55.5\,B_0) \qquad (3)$$

where B_0 is the adsorption equilibrium constant, a_0 is the attraction constant between adsorbed molecules (a positive value of a_0 corresponds to the presence attraction between the adsorbed species, and *vice versa*), θ ($=\Gamma/\Gamma_{\text{max}}$) is the surface coverage of the mercury electrode, ΔG_A° is the standard free energy of adsorption of the alcohol, and c is the bulk concentration of the alcohol. The values of these parameters listed in Table 1 were obtained at the point of zero charge. The free energies of adsorption obtained by the present work agrees reasonably well with those obtained by Damaskin *et al.* from the differential capacity measurements.8) However, both the maximum values of surface excess Γ_{max}, and the attraction constants a_0, in the present results differ markedly from their values.8)

Figure 1 shows the dependence of θ on the relative concentration $c/c_{\theta=0.5}$ calculated from Eq. 2 in terms of the attraction constant. It is obvious from these plots that the higher the values of a_0 are, the lower the values of θ when $c<c_{\theta=0.5}$ and *vice versa* when

Table 1. Adsorption parameters of aliphatic alcohols on mercury electrode

	Γ_{max} / 10^{-10} mol cm^{-2}	$-\Delta G^\circ_A$ / kcal mol^{-1}	a_0
Butyl alcohol	6.67 (5.18)[a)]	3.88 (3.83)[a)]	0.39^3 (1.28)[a)]
Amyl alcohol	5.9 (4.85)[a)]	4.76 (4.58)[a)]	0.42^6 (1.48)[a)]
Hexyl alcohol	5.0 (4.64)[a)]	5.68 (5.39)[a)]	0.69^5 (1.68)[a)]

a) The values in the parentheses are quoted from Ref. 8.

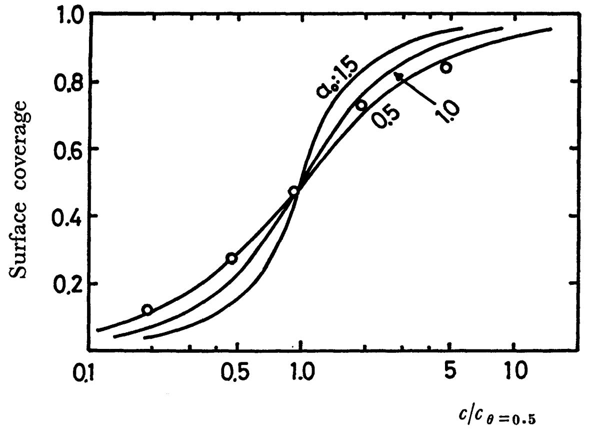

Fig. 1. Dependence of surface coverage of mercury electrode on the relative concentration, $c/c_{\theta=0.5}$, for butyl alcohol in 0.5 M H_2SO_4.

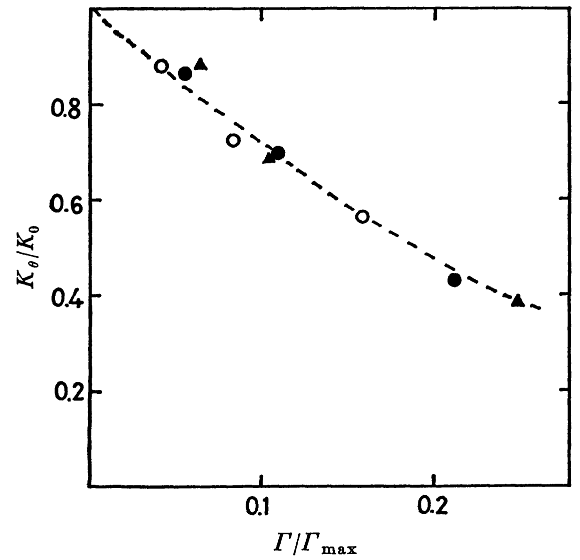

Fig. 2. Variation of the standard rate constants of V(III)+e=V(II) in 0.5 M H_2SO_4 with the surface coverage by alcohols.

○: Butyl alcohol, ●: amyl alcohol, ▲: hexyl alcohol.
----: $k_\theta = k_0(1-\theta)^{3.3}$.

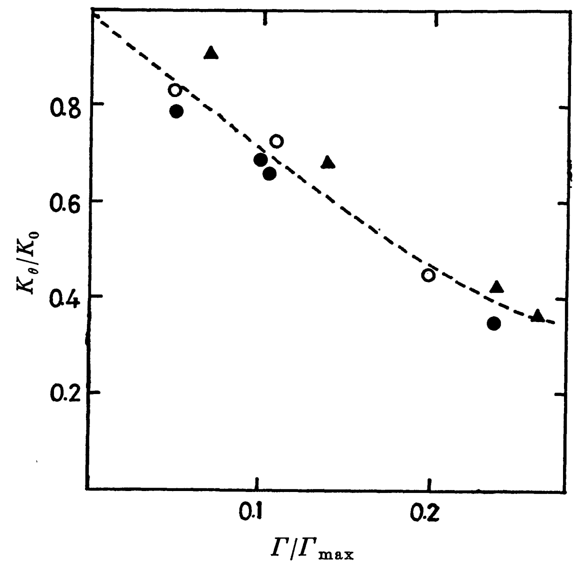

Fig. 3. Variation of the standard rate constants of Eu(III)+e=Eu(II) in 1.0 M HCl with the surface coverage by alcohols.

○: Butyl acohol, ●: amyl acohol, ▲: hexyl alcohol.
----: $k_\theta = k_0(1-\theta)^{3.3}$.

θ is greater than 0.5. The isotherms obtained by various investigators with the capillary electrometer generally agreed well[6)] and the attraction constants calculated from these adsorption isotherms were always smaller than unity. On the other hand, the attraction constants evaluated from the differential capactiy measurements were much greater than unity. As was mentioned in the previous work,[6)] the surface coverages evaluated from the differential capacity measurements are smaller than those evaluated from the electrocapillary measurements when the surface coverage of the electrode surface is less than 0.5 and *vice versa* when θ is greater than 0.5.

The concentration of the alcohol needed to give a certain coverage ($\theta = \Gamma/\Gamma_{\text{max}}$) at the point of zero charge decreases regularly with an increase in the chain length of the alcohols. This factor, Traube's factor, is about 5.1. On the other hand, the value reported by Kaganovich and Gerovich[9)] and Damaskin *et al.*[8)] were 3.0 and 3.7, respectively.

There are certain regularities in the solubility of n-aliphatic alcohols in water and in electrolyte solutions. The solubility of these alcohols decreases by the ratio of 3.9 in water[8)] and 4.5 in 1 M KCl[9)] for each additional CH_2 group. Therefore, the adsorption isotherms (the electrocapillary curves) are superimposable when the relative concentration, c/c_{satd} where c_{satd} is the solubility of the alcohol, of these alcohols is used as a measure of the concentration.

Electrode Kinetics. The standard rate constant of the V(III)/V(II) ($E^\circ = -0.505$ V, 0.5 M H_2SO_4) and Eu(III)/Eu(II) ($E^\circ = -0.612$ V, 1 M HCl) couples is not proportional to the uncovered electrode area, $1-\theta$, as stated in the previous work.[3)] The inhibition effect of butyl alcohol on the electrode kinetics is the least among these alcohols and that of hexyl alcohol is the highest at a given surface excess. In the plot of the ratio of the standard rate constants, k_θ/k_0, against the surface coverage, θ, however, the variation of the rate constants of the V(III)/V(II) and Eu(III)/Eu(II) couples with respect to the surface coverage are superimposable regardless of the chain length of the alcohol as shown in Figs. 2 and 3. The standard rate constant of the uncovered electrode is denoted by k_0 and that at the electrode with the coverage of θ is denoted by k_θ. The plots of Figs. 2 and 3 are also superimposable. A similar electrode kinetic behavior of the vanadium couple to the europium couple is reasonable because the ionic charges of these couples are identical and the ionic sizes of these systems are roughly the same.

The transfer coefficient of the vanadium system and of the europium system does not depend on the nature of the alcohols and the extent of the coverage of the electrode surface. The transfer coefficient in the presence of the alcohols coincides with that without alcohols.

Andreev and his coworkers[13] noticed that the transfer coefficient decreases in the presence of the alcohols and is almost twice smaller than that in the solutions without alcohols in the reduction of cadmium ions in 0.5 M H_2SO_4. In the plot of $\log k_\theta$ against θ^2 in the range of θ=0.4—0.9, the experimental data fit well on straight lines.[12] However, the linear plots with different alcohols were not superimposable. In the reduction of zinc ion in 0.1 M $NaClO_4$, on the other hand, amyl and hexyl alcohols have about equal inhibiting effect whereas the effect of butyl alcohol is somewhat weaker.[13]

The inhibition effect on the electrode kinetics depends only on the surface coverage, θ, of the electrode and is independent of the chain length of the adsorbed alcohol molecule. This evidence suggests that the "blocking effect" is predominant in the inhibition of the electrode process when aliphatic alcohols adsorbed on the electrode surface. The effect due to the interaction between the adsorbed alcohol molecules predicted by Biegler and Laitinen,[14] Sathyanarayana,[2] and Parsons[3] is negligible in the present experiments.

It is also interesting to note that the values of n in Eq. 1 calculated by Lipkowski and Galus[1] for various systems agree reasonably well when we employ the surface excess of the alcohols determined by the present work. The results are shown in Table 2. In the previous work,[5] on the other hand, the value of the closed packed coverage, $\Gamma_{max}=7.9\times10^{-10}$ mol cm^{-2} was used so that large values of n were obtained.

TABLE 2. THE n VALUE FOR THE ELECTRODE REACTION RATE CONSTANT EQUATION OF $k_\theta=k_0(1-\theta)^n$

System	Alcohol	n	Ref.
V(III)/V(II)	amyl	4.2[a]	
		6.4	5
V(III)/V(II)	butyl amyl hexyl	3.3	present work
Eu(III)/Eu(II)	butyl amyl hexyl	3.3	present work
Cd(II)	butyl	4.0[a]	
		4.5	5
$HPbO_2^-$	butyl	4.8[a]	
		4.9	5
		2.8	1
$Fe(CN)_6^{3-}$	amyl	5.1[a]	
		3.0	1
Cu(II)	butyl	3.6[a]	
		2.1	1
$S_2O_8^{2-}$	amyl	6.0[a]	
		3.5	1

a) The n values were calculated by using the data in Ref. 6.

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