

SUMMARY

1. The dependence of the frequencies of the vibration spectrum of water on the force constants of its potential function has been analysed.
2. It has been established on the basis of a comparison of the results of this analysis with the vibration spectrum of water adsorbed by zeolites that two principal classes of states of adsorbed water molecules exist. These states are characterised by strong perturbation of either only one (first class) or both (second class) O-H bonds.
3. The nature of the vibrations and the displacements of atoms in these two states have been examined. In-phase and out-of-phase vibrations are retained in both cases. In the first case the vibrations are mainly concentrated in one of the bonds.

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EFFECT OF THE ADSORPTION OF SURFACE-ACTIVE ORGANIC COM- POUNDS ON THE KINETICS OF THE ELECTROCHEMICAL REDUCTION OF ANIONS

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A comparatively large amount of information has been published on the effect of the adsorption of organic compounds on the electrochemical reduction of anions¹⁻⁷, but

these results are mainly qualitative in character. Plots of the current flowing to the drop against the time of growth of the drop have recently begun to be used to study the effect of such adsorption on the kinetics of electrode processes. A theory has been developed⁸⁻¹² of the effect of adsorption on the shape of the current-time curves when the rate of the electrochemical reduction varies either linearly or exponentially with increase in surface coverage.

The present paper deals with the effect of the adsorption of n-valeric acid and diethyl ketone on the electrochemical reduction of the anion $S_2O_8^{2-}$, and also the effect of the adsorption of n-pentanol on the reduction of this anion and of $Fe(CN)_6^{3-}$.

EXPERIMENTAL

We have studied the adsorption of n-valeric acid and diethyl ketone by measuring differential capacitance with the use of theoretical relationships obtained in previous work^{13,14}. Data on the adsorption of n-pentanol, obtained by a similar method, have been taken from Ref. 15.

Polarisation curves for the reduction of anions at the dropping mercury electrode were determined by first recording current-time curves at various electrode potentials by means of a TsLA oscillograph of PO-5122 brand, correcting for the charging current, and constructing current-potential curves from values of the current at a definite time after detachment of the mercury drop. Differential capacitance curves were determined by means of the a.c. bridge described previously¹⁶.

All reagents were carefully purified. Inorganic salts were recrystallised twice from twice distilled water and ignited, and the organic compounds were redistilled twice in an atmosphere of an inert gas.

Fig. 1 shows polarisation curves for the reduction of $S_2O_8^{2-}$ in the presence of various additions of diethyl ketone. It is seen that adsorption of the latter results in an appreciable decrease in the rate of the electrode process. The

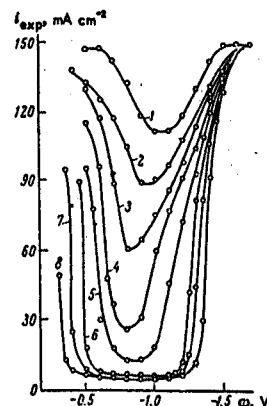


Fig. 1. Polarisation curves in solution of 0.001 N $K_2S_2O_8$ + 0.05 N Na_2SO_4 containing different additions (M) of diethyl ketone:
1) 0; 2) 0.005; 3) 0.01; 4) 0.013;
5) 0.02; 6) 0.04; 7) 0.07; 8) 0.10.

adsorption of n-valeric acid and n-pentanol exerts a similar influence on the electrochemical reduction of both $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$.

Differential capacitance curves in 0.05 N Na_2SO_4 solutions containing different additions of valeric acid and diethyl ketone are reproduced in Figs. 2 and 3.

We have assumed the adsorption of these organic compounds to be consistent with the Frumkin isotherm¹⁷

$$Bc = \frac{\theta}{1-\theta} \exp(-2a\theta), \quad (1)$$

where θ is the surface coverage, c the concentration, a the attraction constant, and B the adsorption equilibrium constant, which, provided that the charge ϵ on the electrode is a linear function of θ , can be written

$$B = B_0 \exp \left[- \frac{\int_0^{\varphi} \epsilon_0 d\varphi + C' \varphi \left(\varphi_N^0 - \frac{\varphi}{2} \right)}{A} \right], \quad (2)$$

in which B_0 , C' , φ_N^0 , and A are constants whose physical significance and methods of determination have been discussed previously¹³, ϵ_0 is the value of ϵ at $\theta = 0$, and φ the electrode potential reckoned from the zero-charge point at $\theta = 0$. As shown previously¹³, if

$$a = a_0 + \beta \varphi, \quad (3)$$

a_0 and β being constants, the differential capacitance C in the presence of the organic substance is given by

$$C = C_0(1-\theta) + C'\theta + \frac{[\epsilon_0 + C'(\varphi_N^0 - \varphi) - 2A\beta\theta]^2}{A} \times \frac{\theta(1-\theta)}{1-2a\theta(1-\theta)}, \quad (4)$$

where C_0 is the value of C at $\theta = 0$. Values of the constants B_0 , C' , φ_N^0 , A , a_0 , and β are given in Table 1.

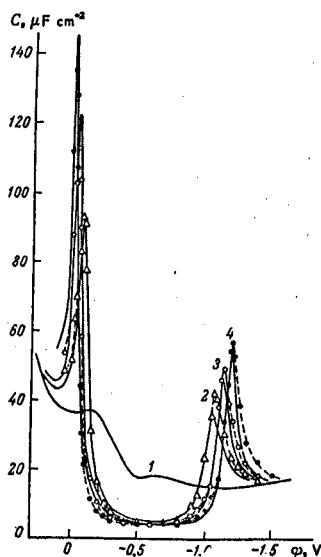


Fig. 2. Differential capacitance curves in 0.05 N Na_2SO_4 with different additions (M) of n-valeric acid:

1) 0; 2) 0.05; 3) 0.08; 4) 0.12.

The full curves represent experimental results at 400 c/s and 25°; the points and the broken curves represent capacitance values calculated by means of Eqn. (4).

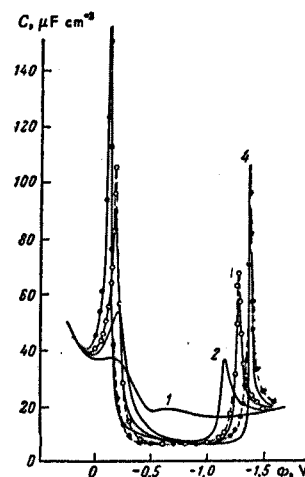


Fig. 3. Differential capacitance curves in 0.05 N Na_2SO_4 with different additions (M) of diethyl ketone:

1) 0; 2) 0.03; 3) 0.05; 4) 0.10.

The full curves represent experimental results at 400 c/s and 25°; the points and the broken curves represent capacitance values calculated by means of Eqn. (4).

TABLE.

Compound	Constant					
	A	B_0	C'	φ_N^0	a_0	β
n-C ₄ H ₉ COOH	1.155	29.50	4.17	0.18	1.30	0.08
C ₂ H ₅ COC ₂ H ₅	0.99	12.25	5.75	0.51	1.61	0.058

Figs. 2 and 3 show good agreement between $C-\varphi$ curves, calculated from Eqns. (1)–(4) for several concentrations of valeric acid and diethyl ketone, and the experimental curves. This indicates that the adsorption of these compounds on mercury obeys the Frumkin isotherm¹⁷, while the constants in Table 1 characterise the adsorbed state of n-C₄H₉COOH and C₂H₅COC₂H₅, and can be used to calculate the charge on the electrode in the presence of these compounds:

$$s = s_0(1-\theta) + C'\theta(\varphi - \varphi_N^0) + A\beta\theta^2. \quad (5)$$

Fig. 4 shows $\epsilon-\varphi$ curves calculate by means of Eqn. (5) for 0.05 N Na_2SO_4 solutions with various additions of diethyl ketone. In a similar manner $\epsilon-\varphi$ curves have been calculated for solutions of valeric acid and pentanol (in the latter case data obtained previously¹⁵ were used).

We have used the values of the surface charge on the electrode to find the dependence of the ψ_1 potential at constant φ on the concentration of the organic compound. It was assumed, as in Ref. 18, that, in the presence of the organic substance, just as in the pure supporting electrolyte, the ψ_1 potential could be determined by means of the equation of the kinetic theory of the diffuse layer¹⁹

$$\psi_1 = 51.2 \sinh^{-1} \left(\frac{\epsilon}{11.73 \sqrt{c_{Na}^+}} \right), \quad (6)$$

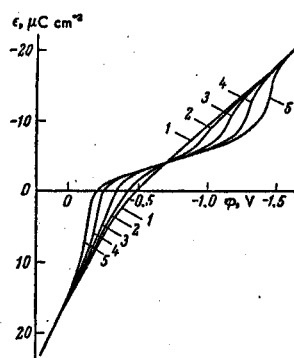


Fig. 4. Dependence of charge on potential of electrode in 0.05 N Na_2SO_4 containing various additions (M) of diethyl ketone: 1) 0; 2) 0.01; 3) 0.02; 4) 0.05; 5) 0.10. Curves (2)–(5) calculated by means of Eqn. (5).

where ψ_1 is measured in millivolts, c_{Na^+} is the concentration (M) of Na^+ cations, and the numerical coefficients correspond to a temperature of 25° . Fig. 5 shows the variation of the ψ_1 potential with the concentration of diethyl ketone at various potentials. Knowledge of the concentration dependence of ψ_1 has enabled us to calculate the degree of inhibition of the electrochemical reaction $\Delta i/i_0 = (i_0 - i)/i_0$, where i_0 is the kinetic current density in the absence of the organic compound and i the current in its presence, the latter corrected for the change in ψ_1 caused by the organic addition. For the determination of i experimental values i_{exp} of the polarographic current (less the charging current) were first corrected for concentration polarisation by means of the approximate equation

$$i_k = \frac{i_{\text{exp}} i_d}{i_d - i_{\text{exp}}} \quad (7)$$

where i_d is the limiting diffusion current, and then values of the kinetic current already obtained from Eqn. (7) were corrected for the change $\Delta\psi_1$ in the ψ_1 potential due to the

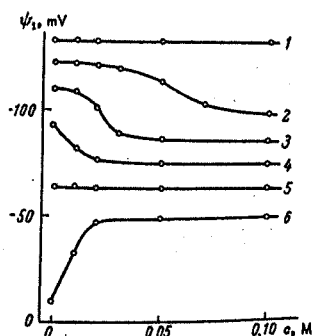


Fig. 5. Dependence of ψ_1 potential on concentration of diethyl ketone in 0.05 N Na_2SO_4 at various electrode potentials (V, relative to saturated calomel electrode, s.c.e.): 1) 1.5; 2) 1.3; 3) 1.1; 4) 0.9; 5) 0.7; 6) 0.5.

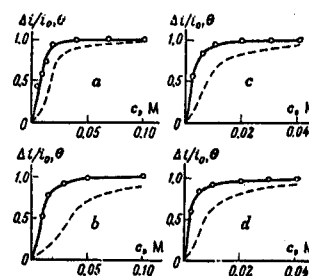


Fig. 6. Comparison of dependence of degree of inhibition (full curves) and surface coverage (broken curves) on concentration of organic compounds in 0.05 N Na_2SO_4 containing:

- a) 0.001 N $\text{K}_2\text{S}_2\text{O}_8$ + diethyl ketone ($\varphi = -1.10$ V, s.c.e.);
- b) 0.001 N $\text{K}_2\text{S}_2\text{O}_8$ + n-valeric acid (-1.00 V);
- c) 0.001 N $\text{K}_2\text{S}_2\text{O}_8$ + n-pentanol (-0.90 V);
- d) 0.001 N $\text{K}_3\text{Fe}(\text{CN})_6$ + n-pentanol (-0.90 V).

change in the charge on the electrode with the concentration of the organic compound²⁰

$$i = i_k \exp \left[\frac{(-n + \alpha) F \Delta \psi_1}{RT} \right] \quad (8)$$

where n is the charge on the species undergoing discharge with the sign taken into account, and α is the transfer coefficient (for $\text{S}_2\text{O}_8^{2-}$ the values of n and α are -2 and 0.28 respectively, the corresponding values of $\text{Fe}(\text{CN})_6^{3-}$ being -3 and 0.16).

Comparison of the concentration dependence of degree of inhibition $\Delta i/i_0$ calculated in this way with the corresponding adsorption isotherms calculated from Eqns. (1) and (2) shows (Fig. 6) that the $(\Delta i/i_0)-c$ and $\theta-c$ curves are similar in shape in all the systems. This indicates that the principal cause of retardation of the electrochemical reduction of anions is coverage of the electrode surface by the organic substance. However, in all cases the retardation of the reaction increases more rapidly with concentration of the organic compound than does θ . This is probably because the calculations of the ψ_1 potential took into account only those changes caused by the decrease in surface charge in the presence of the organic substance, and could not allow for the changes in ψ_1 potential associated with oriented adsorption of dipoles of the compound. In fact, the adsorption potential difference $\varphi_{\text{No}} > 0$ in all cases, and therefore the adsorbed organic molecules were oriented with the negative end towards the solution. These negative ends of the dipoles will then prevent negatively charged species — $\text{S}_2\text{O}_8^{2-}$ and $\text{Fe}(\text{CN})_6^{3-}$ — from approaching the electrode, which produces an additional retarding effect on the electrochemical process apart from that due to coverage of part of the electrode surface. However, further work is needed to confirm this explanation. Thus, for example, on this interpretation, the degree of inhibition should vary less strongly than the degree of surface coverage with concentration if the organic molecules are oriented with the positive end of the dipole towards the solution, or if a positively charged species is undergoing reduction.

We are very grateful to Academician A. N. Frumkin for his constant interest in the work and for discussing the experimental results.

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SUMMARY

1. The adsorption of n-valeric acid and of diethyl ketone has been investigated, and shown to follow the Frumkin adsorption isotherm.
2. All the compounds investigated are shown to retard reduction of the anions $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$. Comparison of the dependence of degree of inhibition and of surface coverage on the concentration of organic compound in solution suggests that the decrease in the rate of electrochemical reduction of the anions is due to coverage of the electrode surface by the organic compound and to the change in ψ_1 potential due to oriented adsorption of the organic dipoles.

IMPROVEMENT OF CATHODIC METAL ELECTRODEPOSITS BY ADDITION OF SURFACE-ACTIVE AGENTS

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The heightened interest shown recently¹⁻¹³ in the addition of certain organic substances to electrolyte solutions is explained by the desire to broaden ideas on the phenomena occurring at the metal-solution interface, and to control the electrical crystallisation of metals. Some workers^{7,14} have examined the effect of the synthetic surface-active agent OP-10, which contains derivatives of polyethylene glycol ethers, on the electrodeposition of metals. However, the adsorption and desorption of the wetting agent was not linked with the state of aggregation of the additive in solutions of strong electrolytes. Workers who have investigated the mechanism of the adsorption of surface-active substances have suggested that they form true solutions.

The effect of several surface-active agents on the kinetics of electrode processes has now been examined, and the great significance of the micellar structure of wetting agents noted.

EXPERIMENTAL

The surface-active agents investigated are described in the Table. Industrial specimens were used without further purification.

Standard acid electrolytes for the deposition of copper, zinc, and cadmium¹⁵ have been examined; additives which would increase polarisation (glue, dextrin, etc.) were not introduced. The electrolyte solutions were made up with distilled water from "chemically pure" samples which were further purified by filtration through activated charcoal. The pH of the electrolyte was measured by means of an LP-58 valve potentiometer. In all cases the reference electrode was a saturated calomel half-cell (s.c.e.).

TABLE.

Class	Component	Chemical nature of component
Cation-active	smoothing agent A	quaternary ammonium salts of diethylaminomethyl derivatives of polyethylene glycol ethers of 6-methylheptylphenols
	Alkamon D	quaternary ammonium salts of decyl (and dodecyl) diethylaminomethyl ethers
Anion-active	"Novost" wetting agent	mixture of sodium salts of the sulphates of higher aliphatic alcohols with a filler (sodium sulphate)
	Sulphonol NP-1	mixture of sodium alkylbenzenesulphonates
Non-lonogenic	preparation OS-20	reaction product from 20 moles of ethylene oxide with a mixture of higher aliphatic alcohols
	wetting agent SV-105	reaction product of 10 moles of ethylene oxide with a mixture of monoalkylphenols in which the alkyl groups contain 8-10 C

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