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The Influence of Lanthanide Ions on the Polarographic Minima of Peroxodisulfate Ions

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It is generally known, from a report by Frumkin[1] on the effect of cations on the minimum wave of peroxodisulfate ions, that when the cationic charge is constant, the effect is more pronounced for larger ionic radii (r_c). This seems to demonstrate that the mutual electrostatic interaction between depolarizer and electrode depends on the size of the hydrated cations adsorbed on the electrode. The aim of the present study is to examine the behavior of this minimum wave of the $S_2O_8{}^{2-}$ anion in the presence of the lanthanide cations, which have similar ionic radii, in order to obtain some information about the hydration structure of these cations as they are adsorbed on the electrode surface. For comparison, the aluminum ion was also investigated.

Experimental

D. c. polarograms were recorded using a Yanagimoto Polarograph PB, Type 4. The capillary constants used were: $m=1.432$ mg/sec, $t=5.1$ sec/drop, $m^{2/3}t^{1/6}=1.667$ mg$^{2/3}$ sec$^{-1/2}$ in a 0.1 N KCl solution with a mercury column height of 58.4 cm at -1.15 V *vs.* SCE. The temperature was 25 ± 0.1°C in all cases. The dissolved oxygen was removed by passing through nitrogen gas.

To prepare the 0.01 M $K_2S_2O_8$ solution, $K_2S_2O_8$ of an analytical grade was dissolved in distilled water without further purification; the concentration was determined by indirect titration using a $KMnO_4$ standard solution. 0.01 M lanthanide ion solutions and an aluminum ion solution were prepared by dissolving in 0.001 N HCl the corresponding amounts of their chloride compounds, which had been prepared from the oxides (99.9% pure) by treatment with HCl. The concentrations were determined by chelatometric titration using an EDTA

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[1] A. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

standard solution. Each solution described above was diluted to the required concentration before use. All the other reagents used were reagent-grade.

Results and Discussion

D. C. Polarogram of Peroxodisulfate in the Presence of the Lanthanide Ion or the Aluminum Ion. In order to obtain a proper minimum wave of $S_2O_8^{2-}$, 0.01 M LiCl was chosen as the supporting electrolyte. D. c. polarograms of solutions containing 4.2×10^{-4}M $S_2O_8^{2-}$, 1×10^{-4}M HCl, and 1×10^{-5}M of Al, La, and Yb ions respectively are shown in Fig. 1. The current-voltage curves were recorded by sweeping the voltage in the negative direction from −0.45 V, since the maxima appeared at *ca.* −0.3 V. In this case the plateau of the limiting current lay within a very small region, −0.45—−0.50 V. The minimum current, i_{dep}, was obtained by measuring the current corresponding to the depth from the limiting current at −0.45 V to the minimum point. The voltage corresponding to the minimum was approximately −1.15 V. As is obvious from Fig. 1, i_{dep} increases in the order: $Al^{3+} < La^{3+} < Yb^{3+}$. The effect of cations on the minimum phenomena (for $S_2O_8^{2-}$) is due to their adsorption, as was noted by Frumkin. Also, the effect of the concentrations of La or Tb ions (Fig. 2) obviously shows that the relation between the persulfate current at the minimum and their concentration gives a saturated curve and that the adsorption equilibrium is of a Langmuir type. The temperature coefficient of i_{dep} was also examined between 30°C and 50°C in the presence of lanthanide ions, but no well-defined wave was observed.

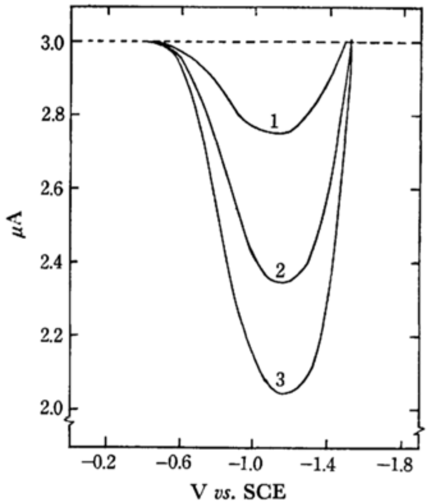

Fig. 1. D.c. polarograms of 0.42 mM $K_2S_2O_8$ in 0.01 M lithium chloride and 0.1 M hydrochloric acid, in the presence of 0.01 mM of (1) Al, (2) La, and (3) Yb.

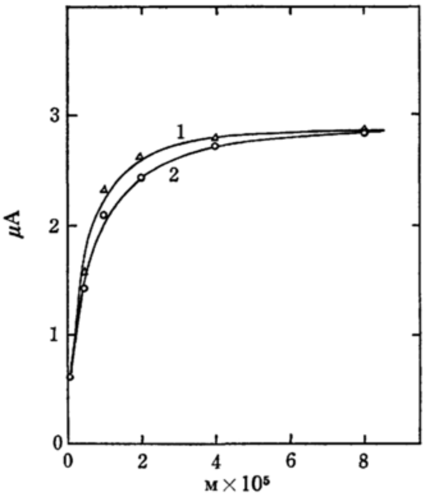

Fig. 2. Effects of (1) lanthanum and (2) terbium concentrations on persulfate current at the minimum in solutions containing 0.42 mM $K_2S_2O_8$ plus 10 mM LiCl and 0.1 mM HCl.

The Relation between the Size of the Cation (III) and the Minimum Current. i_{dep}, measured in solutions containing 1×10^{-5}M cation (III), 4.2×10^{-4}M $K_2S_2O_8$, 1×10^{-2}M LiCl and 1×10^{-4}N HCl, and the Stokes radii,[2] r_s, of the cations(III) at 25°C are shown in Table 1. The r_s values were calculated from the equation: $r_s = (Z\varepsilon\times1/300)/6\pi\eta\mu$. The lanthanide ion mobilities used in

TABLE 1. RELATIONSHIP OF i_{dep} TO THE IONIC RADIUS
0.42 mM $K_2S_2O_8$; 10 mM LiCl; 0.1 mM HCl;
0.01 mM lanthanide.

Cation(III)	i_{dep} (μA)	r_c Å	r_s Å	$r_s - r_c$ Å
La	0.67	1.22	3.92	2.70
Pr	0.75	1.16	3.93	2.77
Nd	0.78	1.15	3.94	2.79
Sm	0.76	1.13	3.99	2.86
Eu	1.84	1.13	4.03	2.90
Gd	0.85	1.11	4.06	2.95
Tb	0.88	1.09		
Dy	0.85	1.07	4.16	3.09
Ho	0.89	1.05	4.12	3.07
Er	0.88	1.04	4.15	3.11
Tm	0.93	1.04	4.18	3.14
Yb	0.96	1.00	4.16	3.16
Lu	0.96	0.99		
Al	0.25	0.57	3.60	3.03

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[2] I. Oshita, "Electrophysical Property of Liquid," Maki Co., Tokyo (1964), p. 13.

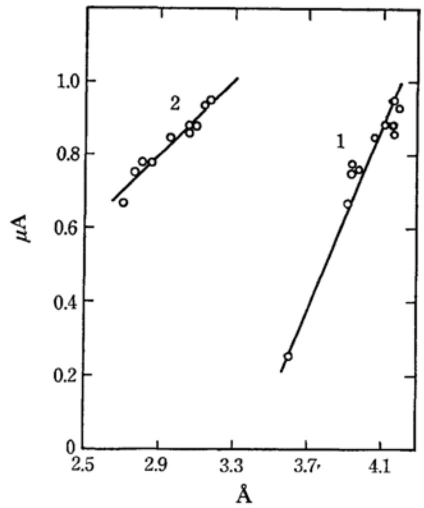

Fig. 3. Relation between i_{dep} and ionic radius: (1), r_s; (2), r_s-r_c.

calculating μ were obtained from the literature.[3] In Table 1, r_c are the ionic radii reported by Goldschmidt.[4] The value of r_s for the aluminum ion was calculated as follows. First, the value of the equivalent conductivity[5] of $AlCl_3$ at an infinite dilution was obtained by extrapolation. Second, the value of the Cl^- mobility, 76.3, was subtracted from the value obtained above. The value of the Al^{3+} mobility was then found to be 75.5 (at 25°C). Figure 3 shows the relation between i_{dep} and r_s. All the points on curve 1 in Fig. 3 apparently lie on an approximately straight line drawn from Al to La. However, the values of r_s in Table 1 are almost unchanged for La, Pr, and Nd, although there is a clear difference between the i_{dep} values of La and Pr. The same phenomenon is recognized in Dy, Ho, Er, Tm, and Yb. Curve 2 in Fig. 3 is a plot of the radius difference (r_s-r_c) *vs.* i_{dep}; this shows a better linear relation than does 1 (except for Al). Consequently, among the lanthanide ions with the same r_s values, it seems probable that the charge-transfer process of $S_2O_8{}^{2-}$ is more suppressed by thicker hydration layers. The increase in i_{dep}value in the presence of the Eu(III) ion can be interpreted as follows: the Eu(III) ion is reduced immediately to the Eu(II) ion at −1.15 V and is adsorbed as a bivalent hydrated cation, so it gives a relatively large value of i_{dep}.

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[3] R. A. Robinson and R. H. Stokes, "Electrolyte Solution," Butterworths Scientific Publications, London (1959).

[4] R. G. Vickery, "Chemistry of the Lanthanons," Butterworths Scientific Publications, London (1953), p. 204.

[5] Chem. Soc. of Japan, "Handbook of Chemistry," Maruzen Co., Tokyo (1952), p. 609.