HALF-WAVE POTENTIALS OF METAL IONS IN ORGANIC HYDROXYACID SUPPORTING ELECTROLYTES. I

by

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INTRODUCTION

Systematic information concerning the polarographic half-wave potentials of metal ions in various supporting electrolytes can be used in many ways. With its help, the practical analyst can often devise greatly simplified procedures for analysing complex solutions. It provides an immediate insight into the redox chemistry of the metal ions, and serves to indicate ways in which unfamiliar oxidation states can be prepared and stabilized. By identifying complexes which are reversibly reduced, it points the way to more detailed studies of the stoichiometry and thermodynamics of their formation.

Studies of this kind have been carried out recently by LINGANE[5], by WEST, DEAN AND BREDA[18], by PŘIBIL and co-workers[14,15,16], by DESESA, HUME, GLAMM AND DEFORD[2], and by MEITES AND MEITES[12]. The data presented in this paper were secured during the course of an investigation of the effect of the structure of an organic hydroxyacid on its ability to coordinate metal ions.

EXPERIMENTAL

The data in Table V were secured at the Louisiana State University with a photographically recording polarograph (E. H. Sargent and Co., Model XI) equipped with a d'Arsonval galvanometer. Some polarograms were obtained with a Heyrovsky-type cell, using a microcalomel reference electrode[17] as the anode; others were obtained with a conventional H-cell[6]. The concentration of the metal ion was varied from 0.01 to 10 mM, and the malonate concentration from 0.25 to 0.50M, while the concentration of gelatin was kept constant at 0.01%.

The remaining data were secured at Yale University with a pen-and-ink recording polarograph[10] whose initial and span e.m.f. voltmeters had been carefully calibrated with a Rubicon precision potentiometer. The measured half-wave potentials were corrected for the iR drops through both the polarograph and the modified H-cell[11] used. The operation of the apparatus was checked by frequently recording polarograms of cadmium(II) in 0.10M potassium nitrate. When the corrected value of $E_{1/2}$ differed by more than two or three millivolts from the literature value[1,4,7], the saturated calomel electrode and saturated potassium chloride agar bridge were replaced.

In these experiments the concentration of metal ion was always very nearly 1.0 mM, excepting that of thallous ion, which was always 0.2 mM. Unless otherwise noted in the Tables, no maximum suppressor was added.

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Reagent grade chemicals were used for the preparation of all solutions in both laboratories. The stock metal ion solutions employed at the Louisiana State University for the measurement of diffusion current constants were standardized by gravimetric or electrogravimetric methods. All solutions were deaerated with tank nitrogen or hydrogen, and Beckman Model G pH meters were used for all pH measurements. The drop times were always between 2.5 and 6 seconds.

The following symbols are used in the Tables. "$>$O" denotes a wave which begins at a potential so positive that it merges with the anodic wave due to dissolution of the electrode mercury, and carries no implication as to whether $E_{1/2}$ would actually be positive or negative if it could be measured. A value of $E_{1/2}$ enclosed in parentheses denotes an anodic wave. "NR" signifies that no wave is obtained. "w.-d." and "i.-d." mean well- and ill-defined, respectively, the criterion being the degree of accuracy with which, in our opinion, the height of the wave could be measured. A wave described as "very w.-d.", for example, is suited for the precise polarographic determination of the substance responsible for it, a "very i.-d." wave, on the other hand, merely serves to interfere with other waves, and is useless for any quantitative purpose whatever. Descriptions intermediate between these are necessarily matters of personal judgment.

The interpretation of these and other similar data derived from continuing work will be deferred until a later paper in this series.

TABLE I

HALF-WAVE POTENTIALS IN SATURATED CITRIC ACID

Element and oxidation state	*$E_{1/2}$ vs S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)	>0	0	Rounded max., very w.-d.
As(III)	-0.58	0(film?(3,9))	Very i.-d.
	-0.73	0	I.-d.
	-1.02	$-$III	I.-d., max. not suppressed by 0.002% Triton X-100
As(V)	NR		
Bi(III)	-0.025	0	W.-d., slightly irreversible
Cd(II)	-0.514	0	Very w.-d., reversible
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	NR		
Cr(III)	-0.78	II	I.-d., reversible
Cr(VI)	>0	III	Large rounded max., w.-d., no indication of wave at -0.78 V
Cu(II)	$+0.03$	0	Small max., very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	$+0.23$	II	W.-d., reversible
In(III)	-0.54_0	0	W.-d., irreversible
Mn(II)	NR		
Mo(VI)	$+0.038$	V	Very w.-d., reversible
	-0.43_7	III	Very w.-d., irreversible
Ni(II)	-0.98	0	I.-d., irreversible
Pb(II)	-0.358	0	W.-d., reversible
Sb(III)	-0.37_6	0	Very w.-d., irreversible
Sb(V)	NR		
Sn(II)	(-0.05)	IV	Fairly w.-d., reversible
	-0.40	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR		
Tl(I)	-0.442	0	Very w.-d., reversible
U(VI)	-0.122	IV(?)	Very w.-d.; $E_{3/4}-E_{1/4} = -63$ mV
V(IV)	-0.67	?	Small i.-d. pre-wave
	-1.05	II	I.-d., irreversible
V(V)	$+0.10_8$	IV	Very w.-d., reversible
	-0.63	II	Fairly i.-d., irreversible
W(VI)	NR		
Zn(II)	-0.930	0	Fairly i.-d., reversible

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TABLE II

HALF-WAVE POTENTIALS IN SATURATED MALONIC ACID

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
As(III)	−0.70	0(?)	Fairly i.-d., irreversible; may actually be poorly resolved double wave
As(V)	NR		
Bi(III)	+0.010	0	Large max. nearly unaffected by 0.002% Triton X-100, very w.-d.
Cd(II)	−0.519	0	Reversible, very w.-d.
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	NR		
Cr(III)	-0.8_5	II(?)	Very small, very i.-d.
Cr(VI)	>0	III	Huge max., very w.-d.; height is only about 2/3 the predicted value for $n = 3$
Cu(II)	+0.081	0	Very w.-d., slightly irreversible
Fe(II)	NR		
Fe(III)	>0	II	Very w.-d.
Fe(III)[a]	+0.202	II	Very w.-d., reversible
In(III)	−0.504		Very i.-d.
	−0.61	0	Plateau has abnormally large positive slope. Waves are due to two species in sluggish equilibrium.
Mn(II)	NR		
Mo(VI)	+0.073	V	Very w.-d., irreversible
	−0.228	III	Very w.-d., slightly irreversible
Ni(II)	−0.97	0	I.-d., irreversible
Pb(II)	NR		Complete pptn.; $E_{1/2} = -0.375$ V for very w.-d. reversible wave in half-saturated malonic acid
Sb(III)	−0.118	0	Very w.-d., nearly reversible
Sb(V)	NR		
Sn(II)	(+0.015)	IV	Fairly w.-d., nearly reversible
	−0.397	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	NR(?)		Final current rise starts abnormally early, at −0.95 V
Tl(I)	−0.440	0	Reversible
U(VI)	−0.12	IV	Very w.-d.; $E_{3/4}-E_{1/4} = -57$ mV
	−1.1(?)		Some indication of an i.-d. irreversible wave
V(IV)	−0.64		Pre-wave
	−1.08	II	Very i.-d., very irreversible
V(V)	>0	IV	Fairly w.-d.
	−0.67	II(?)	
W(VI)	NR(?)		Final current rise starts at −0.8 V, but no plateau is found: catalytic reduction of H^+?
Zn(II)	-0.9_4	0	Very i.-d.

[a]: with 0.002% Triton X-100

TABLE III

HALF-WAVE POTENTIALS IN SATURATED TARTARIC ACID

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)	>0	0	Small rounded max., w.-d.
As(III)	−0.37		Fairly w.-d.
	−0.45		Rounded max., i.-d.
	−0.62	−III	Fairly w.-d.

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TABLE III (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(V)	−1.0		Very i.-d.
Bi(III)	-0.06_0	0	W.-d., slightly irreversible
Cd(II)	−0.564	0	Very w.-d., reversible
Ce(IV)	+0.25	III	
Co(II)	NR		
Cr(III)	−0.91	II	Very i.-d., irreversible
Cr(VI)	—		Rapidly reduced to Cr(III), *q.v.*
Cu(II)	>0		I.-d
	−0.08		I.-d.
	−0.34		Very w.-d.
Fe(II)	NR		
Fe(III)	>0	II	W.-d.
In(III)	−0.527	0	Reversible; plateau has abnormally large positive slope
Mn(II)	NR		
Mo(VI)	-0.08_4	V	Fairly w.-d., irreversible
	−0.391	III	Very w.-d., irreversible
Ni(II)	−1.05	0	Fairly i.-d.
Pb(II)	−0.40	0	Very w.-d., reversible
Sb(III)	−0.41	0	Very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(−0.08)	IV	W.-d., reversible
	−0.44	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	−0.83	?	Abnormally small
Tl(I)	−0.473	0	Very w.-d., reversible
U(VI)	-0.11_5	IV(?)	W.-d., rounded max.; $E_{3/4}-E_{1/4}$ = −51 mV
V(IV)	+0.03		Two small i.-d irreversible waves
	−0.40		
	−0.75	II	I.-d., very irreversible
V(V)	+0.25	IV	Fairly w.-d.
	−0.75	II	I.-d., very irreversible
W(VI)	−0.9		Some indication of a very irreversible wave; *cf.* Table II
Zn(II)	−1.03	0	Fairly w.-d

TABLE IV

HALF-WAVE POTENTIALS IN 0.5*M* SODIUM HYDROGEN MALONATE — 0.5*M* DISODIUM MALONATE, pH 4.8

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	−1.00	?	Very i.-d.
As(V)	NR		
Bi(III)	−0.195	0	Very w.-d., slightly irreversible
	−1.20		Anomalous[a,8,13]
Cd(II)	−0.648	0	Very w.-d., reversible
	−1.17		Anomalous[a]
Ce(IV)	>0	III	Very w.-d.
	−1.16		Anomalous[a]
Co(II)	NR		
Cr(III)	−1.0	II	Small, i.-d., very irreversible[a]
Cr(VI)	>0	III	Large max., very w.-d
	−1.16		Anomalous[a]
Cu(II)	−0.170	0	Very w.-d., reversible
	−1.16		Anomalous[a]

TABLE IV (cotinued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Fe(II)	(−0.250)	III	Very w.-d., reversible
Fe(III)	−0.255	II	Very w.-d., reversible
	−1.16		Anomalous[a]
Fe(III)[b]	−0.250	II	Very w.-d., reversible
In(III)	−0.19	?	Both very i.-d. and almost completely
	−0.72	?	eliminated by 0.004% Triton X-100
Mn(II)	NR		
Mo(VI)	−0.67	IV	Fairly i.-d., very irreversible
	−1.21	III	Fairly i.-d., irreversible
Ni(II)	−1.13		I.-d. triple wave[a]
	−1.28		
	−1.50		
Pb(II)	−0.481	0	Very w.-d., reversible
	−1.16		Anomalous[a]
Sb(III)	-0.47_8	0	Small acute max. on rising portion of wave simulates double wave; very w.-d., slightly irreversible
Sb(V)	NR		
Sn(II)	(−0.293)	IV	Very w.-d., reversible
	−0.605	0	Very w.-d., reversible
Sn(IV)	NR		
Te(VI)	−1.17		Fairly i.-d., irreversible
Tl(I)	−0.474	0	Very w.-d., reversible
	−1.16		Anomalous[a]
U(VI)	−0.437	IV	Very w.-d.; $E_{3/4}-E_{1/4}$ = −51 mV
	−1.19	III	Very i.-d., very irreversible
V(IV)	−1.34	II	Very i.-d., irreversible
V(V)	>0	IV	Very w.-d.
	−1.33	II	I.-d., irreversible
W(VI)	−1.38	?	Large acute max., i.-d.
W(VI)[b]	−1.39	III(?)	Fairly w.-d.; $E_{3/4}-E_{1/4}$ = −46 mV
Zn(II)	-1.14_6	0	Fairly w.-d., reversible

[a]: Eliminated by 0.002% Triton X-100
[b]: With 0.002% Triton X-100

TABLE V

HALF-WAVE POTENTIALS IN 0.5*M* MALONATE — 0.01% GELATIN, pH 0.1-9

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Ag(I)	>0	0	Rapidly reduced by Hg pool
Al(III)	NR		
Au(III) ($AuCl_4^-$)	NR		
Bi(III)	−0.084	0	pH 2.18, w.-d., irreversible. I = 3.72. Unsatisfactory at pH<2
Bi(III)	−0.196	0	pH 4.54, w.-d., irreversible. I = 3.72
Bi(III)	−0.248	0	pH 5.69, w.-d., irreversible. I = 3.72
Cd(II)	$-0.65_7 \pm 0.01_2$	0	pH 4.6-6, w.-d., reversible. I = 2.93 Unsatisfactory at pH<4.5
Co(II)	NR		
Cr(III)	NR		
Cu(II)	−0.006±0.002	0	pH 0.1-1.5, very w.-d., reversible. I = 3.55. Unsatisfactory with < 0.1 m*M* Cu(II)

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TABLE V (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
I(V) (IO_3^-)	−0.77	−I	pH < 4.0, w.-d., irreversible. I = 9.94
I(V) (IO_3^-)	−0.77 −1.14	 −I	4.0 ⩽ pH ⩽ 6.0. I_{total} = 9.94
I(V) (IO_3^-)	−1.14	−I	pH > 6.0. I = 9.94
Ir(IV)	NR		
Mn(II)	NR		
Ni(II)	NR		
Os(VIII)	NR		
Pb(II)	−0.495 ± 0.002	0	pH 5.7-6.0, 1 mM Pb(II), w.-d., reversible. I = 3.29
Pt(IV)	NR		
Sb(III)	not satisfactorily measurable		Poorly resolved double wave (second wave begins at *ca.* −0.3 V)
Se(IV)	−0.742	0(?)	pH 5.2-5.8, 1 mM Se(IV), fairly w.-d., irreversible. I = 5.06
Se(IV)	−0.802	0(?)	pH 5.2-5.8, 5 mM Se(IV), fairly w.-d., irreversible
Se(IV)	−0.74 −1.41	0(?) ?	pH > 5.8 $E_{1/2}$ independent of Se concn.
Se(VI)			Virtually identical with Se(IV) in every respect
Sn(II)	(−0.265) −0.664	IV 0	
Sn(IV)	NR		
Te(VI)	−1.57	0(?)	pH 5.7-8.7, 0.06 mM Te(VI), w.-d., irreversible. $\Delta E_{1/2}/\Delta \log$ [Te(VI)] = −0.060 V
Te(VI	−1.33	0(?)	pH 5.64, 0.06 mM Te(VI), w.-d., irreversible. $\Delta E_{1/2}/\Delta \log$ [Te(VI)] = −0.060 V
Te(VI)	−1.30	0(?)	pH 4.95, 0.06 mM Te(VI), w.-d., irreversible. $\Delta E_{1/2}/\Delta \log$ [Te(VI)] = −0.060 V
Te(VI)	—		pH 4.07, 0.06 mM Te(VI), very i.-d.
Tl(I)	−0.492 ± 0.006	0	pH 2.2-5.6, 0.01 mM Tl(I), very w.-d., reversible. I = 2.46

TABLE VI

HALF-WAVE POTENTIALS IN 1 M DISODIUM MALONATE — 0.2 M SODIUM CARBONATE — 0.2 M SODIUM BICARBONATE, pH 10.0

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	(−0.02)	V	Very i.-d., slightly irreversible
As(V)	NR		
Bi(III)[a]	-0.51_9 −1.29	0	Very w.-d., slightly irreversible Anomalous[b]
Cd(II)[a]	−0.692 −1.28	0	Very w.-d., reversible Anomalous[b]
Ce(IV)	−0.058 −1.25	III	W.-d., reversible Anomalous[c]
Co(II)	−1.59	0	Fairly w.-d., very irreversible
Cr(III)	NR		
Cr(VI)	−0.40	III	I.-d.; shape greatly improved by 0.002% Triton X-100
Cu(II)	−0.220 −1.31	0	Very w.-d., reversible Anomalous[b]

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TABLE VI (continued)

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
Fe(II)	(−0.512)	III	Very w.-d., reversible
	−1.62	0	Fairly w.-d., irreversible
Fe(III)	−0.518	II	W.-d., reversible
	−1.65	0	I.-d., irreversible
In(III)	−1.32	0	Very w.-d., irreversible, probably includes anomalous wave
In(III)[d]	−1.30	0(?)	Very i.-d., very irreversible
	−1.61		Probably anomalous
Mn(II)	NR		
Mo(VI)	NR		
Ni(II)	−1.14		Very i.-d., irreversible
	−1.36		Fairly i.-d., irreversible
Pb(II)[a]	−0.616	0	Very w.-d., reversible
	−1.28		Anomalous[c]
Sb(III)	(-0.12_2)	V	W.-d., irreversible
	−0.864	0	W.-d., nearly reversible
Sb(V)	-0.1_4		Four very small, fairly w.-d., irreversible waves
	-0.4_6		
	-0.8_8		
	-1.2_6		
Sn(II)	(−0.638)	IV	Very w.-d., irreversible
	−0.817	0	Very w.-d., reversible
	−1.28		Anomalous
Sn(IV)	−1.25	0(?)	I.-d., very irreversible
Sn(IV)[d]	−1.22	II(?)	Very i.-d., irreversible
	−1.64	0(?)	Probably not anomalous; total wave height is unaffected by Triton
Te(VI)	−1.38	?	Fairly i.-d.
Tl(I)	−0.483	0	Very w.-d., reversible
	−1.30		Anomalous[b]
U(VI)	−0.90	V	Fairly i.-d., irreversible
	−1.29		Anomalous[b]
V(IV)	(−0.380)	V	Very w.-d., slightly irreversible
	−1.17		Very irreversible pre-wave
	−1.59	II	Fairly i.-d., irreversible
V(V)	−1.18	IV	Very i.-d., irreversible
	−1.59	II	Fairly w.-d., irreversible
W(VI)	NR		
Zn(II)	-1.28_6	0	W.-d., irreversible

a: Extensive precipitation from a 1 m*M* solution
b: Shifted to −1.62±0.02 V and considerably decreased in height by 0.002% Triton X-100
c: Eliminated by 0.002% Triton X-100
d: With 0.002% Triton X-100

TABLE VII

HALF-WAVE POTENTIALS IN 1*M* DISODIUM MALONATE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ vs. S.C.E. volts	Formula or oxidation state of product	Notes
As(III)	(−0.273)	V	W.-d., reversible
As(V)	-1.1_4		Very small, i.-d.
Bi(III)	-0.68_6	0	W.-d., slightly irreversible
	−1.23		Anomalous
Cd(II)[a]	−0.94		Decreases on standing (all i.-d.)
	−1.20		Probably anomalous (all i.-d.)
	−1.55		Increases on standing (all i.-d.)

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TABLE VII (continued)

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Cd(II)[a,b]	−0.86		Very small, i.-d., irreversible
	−1.59		I.-d., probably anomalous
Ce(III)[a]	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	−1.52	0	Small, very i.-d., irreversible
Cr(III)	−0.92	II	Small, w.-d., reversible
Cr(VI)	−0.75	III	Fairly w.-d., irreversible
	−1.16		Probably anomalous
Cr(VI)[b]	-0.77_0	III	W.-d., irreversible
Cu(II)	-0.35_7		Very i.-d. } both reversible; two complexes
	-0.44_7	0	Very w.-d. } in sluggish equilibrium
	−1.26		Anomalous
Cu(II)[b]	-0.36_6		I.-d. } *vide supra*
	-0.44_8	0	Very w.-d. }
	−1.55		Anomalous
Fe(II)[a]	(−0.96)	III	
	−1.56	0	Very small; fairly w.-d.
Fe(III)	−0.90	II	Fairly i.-d., irreversible
	−1.19		Anomalous
	−1.57	0	Fairly i.-d., slightly irreversible
Fe(III)[b]	−0.89	II	Fairly w.-d., irreversible
	−1.61	0	I.-d., irreversible, includes anomalous wave
In(III)	−1.12	0(?)	W.-d., irreversible, includes anomalous wave
Mn(II)[a]	(−0.43)	III(?)	Very small, i.-d., irreversible
	−1.72	0	Very i.-d., slightly irreversible
Mo(VI)	−0.90	?	Very small, irreversible
Ni(II)	NR		
Pb(II)	−0.754	0	Very w.-d., reversible
	−1.29		Anomalous
Pb(II)[b]	−0.757	0	Very w.-d., reversible
Sb(III)	(-0.47_5)	V	Very w.-d., slightly irreversible
	-1.13_7	0	Fairly i.-d., irreversible
	−1.41		Possibly anomalous
Sb(V)	NR		
Sn(II)	(-0.95_2)	IV	Large acute max., very w.-d.
	-1.13_7	0	Large acute max., i.-d
	−1.39		Anomalous
Sn(II)[b]	(−0.934)	IV	Very w.-d., slightly irreversible
	-1.14_8	0	W.-d., slightly irreversible
	−1.60		Anomalous
Sn(IV)	NR		
Te(VI)	−1.52		Fairly i.-d., irreversible
Tl(I)	−0.477	0	Very w.-d., reversible
	−1.29		Anomalous
U(VI)	−0.908	V(?)	Fairly w.-d., reversible (?)
	−1.24		} Two i.-d. very irreversible waves of approxi-
	−1.63		} mately equal heights
U(VI)[b]	−0.906	V(?)	Very w.-d., reversible (?)
	−1.60	IV(?)	I.-d., very irreversible
V(IV)	(-0.44_0)	V	Very w.-d., irreversible
	−1.68	II	Very i.-d., irreversible
V(V)	-1.67_4	II	Very i.-d., irreversible
W(VI)	−0.90	?	Small, fairly w.-d.
	−1.22		Probably anomalous
W(VI)[b]	−0.90	?	Small, w.-d.
Zn(II)	−1.482	0	Very w.-d., irreversible

a: Extensive precipitation from a 1 m*M* solution
b: With 0.002% Triton X-100

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TABLE VIII

HALF-WAVE POTENTIALS IN 1*M* SODIUM LACTATE — 1*M* SODIUM HYDROXIDE

Element and oxidation state	$E_{1/2}$ *vs. S.C.E. volts*	*Formula or oxidation state of product*	*Notes*
Ag(I)[a]	>0	0	
As(III)	(−0.27)	V	Fairly w.-d., nearly reversible
As(V)	NR		
Bi(III)	-0.71_5	0	Fairly i.-d., slightly irreversible
	−1.10		Anomalous
Cd(II)	−0.83	0	Small, fairly w.-d.
	−1.12		Anomalous
Ce(III)	NR		
Ce(IV)	—		Rapidly reduced to Ce(III), *q.v.*
Co(II)	−1.62	0	Very i.-d., irreversible
Cr(III)	NR		
Cr(VI)	−0.80	III	Very w.-d.
Cu(II)	-0.51_6	0	W.-d., slightly irreversible
	−1.13		Anomalous
Fe(II)	(−0.98)	III	W.-d., reversible
	−1.66	0	Fairly w.-d., slightly irreversible
Fe(III)	−1.00	II	Irreversible
	−1.67	0	Slightly irreversible
Mn(II)	(−0.46)	III(?)	Abnormally small, irreversible
	−1.76	0	Fairly w.-d., nearly reversible
Mo(VI)	NR		
Ni(II)[a]	NR		
Pb(II)	−0.772	0	I.-d., reversible
	−1.11		Anomalous
Pb(II)[b]	−0.771	0	Very w.-d., reversible
	−1.41		Anomalous
Sb(III)	(−0.46)	V	Very w.-d., slightly irreversible
	−1.17	0	W.-d., irreversible
Sb(V)	NR		
Sn(II)	(−0.95)	IV	Very w.-d., nearly reversible
	−1.15	0	Very w.-d., nearly reversible, includes anomalous wave ($i_c > i_a$)
Sn(IV)	>0		Three small waves of approximately equal heights. No waves observed with 5 m*M* Sn(IV)
	−1.09		
	−1.48		
Sn(IV)[b]	>0		Very small
	−1.6		I.-d., very irreversible. Total wave height is greatly decreased by Triton
Te(VI)	−1.54	0(?)	Fairly w.-d., irreversible
Tl(I)	−0.485	0	Fairly w.-d., reversible
	−1.09		Two very irreversible waves
	−1.34		
Tl(I)[b]	−0.485	0	Very w.-d., reversible
	−1.40		Fairly w.-d., irreversible
	−1.66		
U(VI)	−0.95	V(?)	I.-d.
	−1.7	IV(?)	Very i.-d.
U(VI)[b]	−0.93	V	Fairly w.-d., reversible
	−1.67	IV(?)	Fairly i.-d., irreversible
V(IV)	(−0.51)	V	W.-d., reversible
	−1.70	II	Very i.-d., irreversible
V(V)	−1.71	II(?)	Very i.-d., very irreversible
W(VI)	−1.1	?	Abnormally small, irreversible, eliminated by 0.002% Triton X-100
Zn(II)	−1.50	0	W.-d., slightly irreversible

[a]: Extensive precipitation from a 1 m*M* solution
[b]: With 0.002% Triton X-100

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SUMMARY

Eight new media containing organic hydroxyacids and their anions have been investigated as supporting electrolytes for polarographic analysis. For over 25 metal ions in each of these media there are tabulated the half-wave potentials, reversibilities and probable products of the electrode reactions, descriptions of the wave forms, and other data of polarographic importance.

RÉSUMÉ

Huit nouveaux milieux, renfermant des hydroxyacides et leurs sels, ont été étudiés comme électrolytes de base dans l'analyse polarographique, pour plus de 25 cations. Les potentiels de demi-onde, les réversibilités et les produits de réaction aux électrodes, les descriptions des formes des ondes et d'autres renseignements polarographiques sont donnés dans des tableaux.

ZUSAMMENFASSUNG

Es wurden acht neue Medien, welche Hydroxysäuren und ihre Salze enthalten, als Basiselektrolyte in polarographischen Analysen fur mehr als 25 Kationen untersucht. Die Halbwertspotentiale, die Reversibilität und die Reaktionsprodukte an den Elektroden, die Beschreibung der Form der Wellen und andere polarographische Einzelheiten werden in Tabellen angegeben.

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