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POLAROGRAPHIC HALF-WAVE POTENTIALS OF CATIONS IN NONAQUEOUS SOLVENTS

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Polarographic half-wave potentials of cations in nonaqueous solvents

Abstract - Polarographic half-wave potentials for the reduction of Li^+, Na^+, K^+, Rb^+, Cs^+, Cu^+, Ag^+, Tl^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Pb^{2+}, UO_2^{2+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Sm^{2+}, Eu^{3+}, Eu^{2+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Tm^{3+}, Er^{3+}, Yb^{3+} and Yb^{2+} *versus* bis(biphenyl)chromium(I)/(0) have been compiled in up to 38 nonaqueous solvents. The potentials of the silver/0.01 mol dm^{-3} silver(I) ion electrodes and the Hg/0.01 mol dm^{-3} mercury(II) ion electrodes in the respective supporting electrolytes as well as the $\frac{1}{2}(E_{pa}+E_{pc})$ values for the oxidation of ferrocene *versus* bis(biphenyl)chromium(I)/(0) are included. The accessible potential ranges on the dropping mercury electrode in polarography and on the platinum electrode in cyclic voltammetry are given together with the specific conductivities of 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in the respective solvents.

INTRODUCTION

Polarographic half-wave potentials of cations in nonaqueous solvents have been extensively reported in literature. Unfortunately there was no consistency in the use of reference electrodes *versus* which such data were measured. Quite often half-wave potentials were given *versus* aqueous reference electrodes, such as the calomel electrode, the silver/silver chloride electrode or the standard hydrogen electrode. Any measurement of half-wave potentials or any other electrode potentials, where the reference electrode is in a solvent different from the solvent in which the redox system is investigated, however, includes an unknown liquid junction potential. The liquid junction potential is associated with irreversible processes and is not a thermodynamic quantity. It cannot be determined exactly, it depends on the design of the junction and it may change during the time of the experiment. Values for half-wave potentials, which include a liquid junction potential do not allow a meaningful compilation of such data. Reference electrodes in the same solvent avoid - in cells without transference - the problems connected with the liquid junction potentials. The use of a multitude of such nonaqueous reference electrodes, however, yields only isolated data points, which prevent any comparision of electrode potentials even in the same solvent. In order to avoid the problems connected with liquid junction potentials on one hand, and with a variety of different nonaqueous reference electrodes on the other, it has been recommended that electrode potentials in nonaqueous solvents be reported *versus* either ferrocenium ion/ferrocene (bis(cyclopentadienyl)-iron(III)/(II)) or bis(biphenyl)chromium(I)/(0) as reference redox systems (ref. 1). The use of these two reference redox systems, for which the difference in electrode potentials is available for a large number of solvents, allows the establishment of one redox scale for all electrode potentials in a given nonaqueous solvent. Procedures for employing reference redox systems for *in situ* measurements were outlined in ref. 1 and need not be repeated here. Such *in situ* measurements yield electrode potentials, which are free of liquid junction potentials and are affected only by the experimental error. The data are also free of any extrathermodynamic assumptions.

Bis(biphenyl)chromium(I)/(0) was preferred in this compilation over ferrocenium ion/ferrocene, since the reduction of bis(biphenyl)chromium(I) can be observed even in solvents where the oxidation of ferrocene occurs at potentials more positive than the oxidation of the solvent itself. Thus employing ferrocene would exclude the half-wave potentials in solvents such as N,N-dimethylthioformamide, N-methyl-2-thiopyrrolidinone (N-methyl-2-pyrrolidinethione), hexamethylthiophosphoric triamide or tetrahydrothiophene. Besides the data summarized in Tables 1-7, a certain number of published half-wave potentials in nonaqueous solvents remain for which a reliable, subsequent conversion to the bis(biphenyl)chromium scale was not possible. A comprehensive summary of electrochemical data in aqueous and nonaqueous solutions can be found in the CRC Handbook in Inorganic Electrochemistry (Note a), where half-wave potentials are listed with respect to the reference electrodes used by the original authors.

It is hoped that this compilation of half-wave potentials of cations in nonaqueous solvents versus one reference redox system will encourage researchers active in the fields of electrochemistry of organometallic complexes and of organic compounds in nonaqueous solvents to report their data versus one or the other of these two reference redox systems and thus contribute to future compilations of potential data on a single redox scale.

RULES FOR ARRANGING SOLVENTS, POLAROGRAPHIC DATA AND REFERENCES

The solvents given in the tables were arranged in the following way:

i) Solvents containing only carbon, hydrogen and oxygen atoms are listed according to functional groups in the order of: alcohols; ketones; ethers; esters and lactones. Within such a group, solvents are arranged according to the number of carbon atoms.

ii) Solvents containing nitrogen in addition to carbon, hydrogen and sometimes oxygen are ordered as follows: amides; lactams and ureas; nitriles; nitro compounds; pyridine.

iii) Solvents containing halogens, sulfur or phosphorus are given in this order. Solvents with more than one of the last mentioned heteroatoms are listed according to the heteroatom that appears first in this sequence e.g. hexamethylthiophosphoric triamide is listed under sulfur compounds.

The polarographic data and the references are given in the following manner:

i) For each cation and solvent there are three, occasionally four, entries. From top to bottom these entries give the half-wave potential in the first line, the difference in one-quarter-wave and three-quarter-wave potentials in the second line and the literature references in the third and if necessary in the fourth line. The first reference in line 3 pertains to the paper from which the value for the half-wave potential was taken. Footnotes also refer to this paper unless stated otherwise.

ii) Half-wave potentials given to three digits after the decimal point were derived from experiments in which bis(biphenyl)chromium(I) was employed in situ as an internal standard as recommended in ref. 1. Half-wave potentials given to only two digits after the decimal point were obtained from data

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Note a: L. Meites, P. Zuman and A. Narayanan, Handbook in Inorganic Electrochemistry, CRC Press Inc., Boca Raton, Florida, U.S.A. (1978)

originally reported versus an aqueous reference electrode. Conversion of such data to the bis(biphenyl)chromium scale was possible, whenever the authors had included the half-wave potentials of bis(biphenyl)chromium(I) versus the aqueous reference electrode employed in their experimental arrangement. In the absence of such data for bis(biphenyl)chromium(I)/(0), half-wave potentials of one or more cations, for which half-wave potentials were given in the respective paper, were measured versus bis(biphenyl)chromium(I)/(0) in our laboratory. Such data allowed conversion of the half-wave potentials of all other cations originally reported versus an aqueous reference electrode to the bis(biphenyl)chromium scale. Half-wave potentials reported versus ferrocene were converted using the difference in half-wave potentials between ferrocene and bis(biphenyl)chromium. In all of these conversions it was assumed that the liquid junction potential remained constant in the particular electrochemical cell employed by the respective authors.

iii) For cations, where more than one reduction wave was reported, the most positive one is included in the table, the other half-wave potentials are referred to in footnotes. The differences in one-quarter-wave and three-quarter-wave potentials are given in parenthesis in the footnotes.

iv) The data for the reduction of the lanthanide cations were obtained during the very early days of polarography in nonaqueous solvents. Conversion to the bis(biphenyl)chromium scale was made by remeasuring the half-wave potentials for the reductions of Eu^{3+} and Eu^{2+} for the solvents listed in the tables. The data given in Tables 5 - 7, however, may be uncertain by ± 0.05 V and are thus given in parenthesis.

The references, except ref. 1, are given in alphabetical order according the first author. Papers with the same first author are arranged with respect to the year of publication. Only references, which contain original data were included; review articles and papers quoting previously published data were omitted.

COMPILATION OF HALF-WAVE POTENTIALS

Half-wave potentials, the difference in one-quarter- and three-quarter-wave potentials and literature references for the above mentioned cations are summarized in Tables 1-7. The compilation of data is restricted to half-wave potentials and gives an indication of the reversibility of the electrode reactions. The difference in one-quarter- and three-quarter-wave potentials serves only as a first indication of the reversibility or irreversibility of the electrode reaction. For more detailed information on the electrochemical behaviour, on the concentrations of the electroactive species, on the purification procedures, on the purity of the solvents and on the water content, the original literature should be consulted. Occasionally, rather complex electrode processes were reported or the respective salts were found insoluble in a particular solvent. In order to avoid misleading information only literature references are given for such cases.

Included in Table 2 are the potentials of the silver/0.01 mol dm^{-3} silver(I) ion and the mercury/0.01 mol dm^{-3} mercury(II) ion electrodes in the respective supporting electrolytes and solvents. The silver/silver ion electrodes are stable in many nonaqueous solvents and may serve as reference electrodes for potentiometric studies.

Table 8 contains the approximate ranges in which polarography on the dropping mercury electrode, and cyclic voltammetry on the stationary platinum

electrode, can be carried out in supporting electrolytes of tetrabutylammonium perchlorate. These ranges are only guides, since in many solvents there is a gradual increase of the current at either the positive or the negative end of the potential window. Thus setting the limits is somewhat arbitrary for many solvents. Included in this table are the specific conductivities of 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in several nonaqueous solvents.

TABLE 1. Half-wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($\underline{E}_{1/4}$-$\underline{E}_{3/4}$)-values in millivolt (second line) and references (third and fourth line) for the reduction of alkali metal ions in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in nonaqueous solvents at 25 °C unless stated otherwise.

Solvents	Li^+	Na^+	K^+	Rb^+	Cs^+
		Alcohols			
Methanol	-1.49	-1.22	-1.24	-1.23	-1.20
		57	56	56	55
	15	15	15	15	5
Ethanol	-1.46 [a]	-1.17 [a]	-1.18 [a]	-1.18 [a]	1.18 [a]
	62	55	55	55	57
	28,15	28,15	28,15	28,15	15
		Ketones			
Acetone[a]	-1.400	-1.224	-1.281	-1.296	-1.270
	81	57	56	56	56
	21,13	21,11,13	21,11,13	21,11,13	21
		Ethers			
Tetrahydrofuran	-1.435	-1.251	-1.202	-1.204	-1.297
	88	91	85	75	118
	36	36	36	36	36
		Esters and Lactones			
Butyrolactone[a]	-1.34	-1.17	-1.26	-1.26	-1.25
	67	57	56	55	53
	28	28	28	28	28
Propylene carbonate	-1.25	-1.068	-1.189	-1.23	-1.22
(4-Methyl-1,3-dioxo-	65	63	60	56	56
lan-2-one)	43,67	63,43	63,43	43,67,3	43,67
		67,48	67,48		
		Amides, Lactams and Ureas			
N-Methylformamide[a]	-1.661	-1.321	-1.334	-1.335	-1.294
	75	56	57	57	57
	32	32	32	32	32
N,N-Dimethylformamide	-1.623	-1.349	-1.371	-1.358	-1.335
	59	58	54	52	58
	33,22,7	4,48,22	4,48,22	4,48,25	4,22,7
	67,48	7,67	7,67	22,7,67	67
N,N-Diethylformamide	-1.618	-1.332	-1.346	-1.332	-1.316
	67	69	71	76	61
	79	79	79	79	79
N,N-Dimethylacetamide	-1.690	-1.380	-1.404	-1.349	-1.344
	75	59	55	64	64
	41,42,56	41,42,56	41,42	41,42	41,42
N,N-Diethylacetamide	-1.765	-1.378	-1.375	-1.343	-1.342
	118	66	77	55	60
	4	4	4	4	4
N-Methyl-2-pyrrolidinone	-1.697	-1.367	-1.405	-1.37 [a]	-1.35 [a]
	75	60	60	56	56
	38,29,5	38,29,5	38,29,5	28,5	28,5
N,N,N,N-Tetramethylurea	-1.76	-1.391	-1.401	-1.361	
	65	57	56	56	
	72	72	72	72	

Table 1 continued

Solvents	Li^+	Na^+	K^+	Rb^+	Cs^+
		Nitriles			
Acetonitrile[a]	-1.200	-1.118	-1.223	-1.224	-1.207
(Ethanenitrile)	61	57	56	56	56
	28,61,20	28,61,20	28,20	28,20	28,20,22
	13,22,60	13,22	13,22	13,22	
Propanenitrile	-	-1.026 [b]		-	
	-	69		-	
	65	40,65		13	
Butanenitrile		-1.097			
		60			
		81			
Isobutyronitrile	-1.211	-1.092	-1.09 [g]	-1.11 [g]	-1.12 [g]
(2-Methylpropanenitrile)	58	65	63	52	89
	38,12,13	38,12,13	12,13	12,13	12,13
Benzonitrile	-1.115	-1.044	-1.131 [h]	-1.174 [h]	-1.183 [h]
	65	70	56	58	61
	33,20	33,20	33,20,13	33	33,20
	13,64	13,64			
Phenylacetonitrile	-1.109	-1.049	-	-	
	104	92	-	-	
	38,13,64	38,13,64	13	13	
		Aromatic Heterocycles			
Pyridine	-1.428	-1.201	-1.231	-1.232	-1.215
	68	63	70	67	65
	39,6	39,6	39,48,6	39,48,6	39,6
		Solvents Containing Sulfur			
Ethylene sulfite	-0.871	-1.081	-1.165		
	65	83	69		
	63	63	63		
Dimethyl sulfoxide	-1.86	-1.37 [a]	-1.40 [a]	-1.37 [a]	-1.361
	86	56	54	55	61
	67	48,67	48,10,67	48,10,67	33,10,67
Tetramethylene sulfone[a,c]	-1.26	-1.15	-1.25	-1.26	-1.25
(Tetrahydrothiophene-	61	57	55	59	53
1,1-dioxide)	15,14	15,14	15,14	15,14	15,14
N,N-Dimethylthio-	-0.973 [a]	-0.906 [a]	-1.021 [h]	-1.077 [h]	-1.147 [h]
formamide	58	57	53	66	62
	53	53	33	33	33
N-Methyl-2-thiopyrroli-	-1.025 [a]	0.937 [h]	-1.031 [h]	-1.091 [h]	-1.139 [h]
dinone (N-Methyl-2-	60	64	57	58	77
pyrrolidinethione)	29,38	38,33,29	33,28,38	33,28	33
Hexamethylthio-	-1.072	-0.809 [e]	-	-	-
phosphoric triamide	105	118	-	-	-
	62	62	62	62	62
		Solvents Containing Phosphorus			
Trimethyl phosphate	-1.721	-1.37 [a]	-1.36 [a]	-1.350 [a]	-1.309
	88	62	60	56	56
	33	46,48	46,48	46,48	33
Hexamethylphosphoric		-1.524	-1.421	-1.386	-1.356
triamide[d]		72	66	65	66
	56,57	62,56	62,66,56	62,66	62,66
		74,57	74,57	56,57	56,57

[a] 0.1 mol dm^{-3} tetraethylammonium perchlorate [b] 0.05 mol dm^{-3} tetrabutylammonium perchlorate [c] 30 °C [d] 0.1 mol dm^{-3} tetraheptylammonium perchlorate [e] $Na\,B(C_6H_5)_4$ in 0.05 mol dm^{-3} tetrabutylammonium tetraphenylborate [f] Iodides in 0.1 mol dm^{-3} solutions of tetrabutylammonium iodide [g] 0.05 mol dm^{-3} tetrabutylammonium iodide [h] tetraphenylborates in 0.05 mol dm^{-3} tetrabutylammonium tetraphenylborate

TABLE 2. Half-wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($E_{1/4}$-$E_{3/4}$)-values in millivolt (second line) and literature references (third and fourth line) for Cu^+, Ag^+ and Tl^+ as well as the potentials of the Ag /0.01 mol dm^{-3} Ag^+-ion (E^*Ag) and the Hg/0.01 mol dm^{-3} Hg^{2+}-ion electrodes (E^*Hg) in volt in 0.1 mol dm^{-3} tetrabutylammonium perchlorate solutions in nonaqueous solvents at 25 °C unless stated otherwise.

Solvents	Cu^+	Ag^+	Tl^+	E^*Ag	E^*Hg
		Alcohols			
Methanol			0.422	1.337	
			59	-	
			81	35,72	
Ethanol			0.449	1.275	1.349
			85	-	-
			63,28	35,72	37
Ethane-1,2-diol			0.366 [b]	1.217 [b]	
			74	-	
			78,9	78	
		Ketones			
Acetone	1.020 [a]		0.410 [a]	1.315	
	57		55	-	
	21		21,68	72	
		Ethers			
Tetrahydrofuran			0.408	1.297	1.367
			86	-	-
			36	36	37
		Esters, Lactones			
Butyrolactone			0.41 [a]	1.364	
			58	-	
			28	33	
Propylene carbonate (4-Methyl-1,3-dioxolan-2-one)			0.511	1.514	1.606
			60	-	-
			63,44,48	35,72	37
		Amides, Lactams and Ureas			
Formamide	0.718 [d]		0.375	1.200	
	-		80	-	
	41		41	41,72	
N-Methylformamide			0.286	1.120 [a]	
			57	-	
			32	32	
N,N-Dimethylformamide			0.261	1.112	1.144
			57	-	-
			4,76	4,72	37
N,N-Diethylformamide			0.272	1.143	
			91	-	
			79	79	
N,N-Dimethylacetamide			0.259	1.025	
			56	-	
			41,69	41,72	
N,N-Diethylacetamide			0.260	1.027	
			54	-	
			4	4	

Table 2 continued

Solvents	Cu^+	Ag^+	Tl^+	E^*Ag	E^*Hg
N-Methyl-2-pyrrolidinone			0.232	1.032	1.118
			55	-	-
			38,29	34,33,72	37
N,N,N,N-Tetramethylurea	0.765		0.223	1.036	
	56		56	-	
	72		72	72,33	
Nitriles					
Acetonitrile	0.420	1.155	0.480	1.030	1.336
(Ethanenitrile)	61	67	65	-	-
	30,18	33,61,65	28	33,72,18	37
	23,61				
Propanenitrile[b]	0.412	1.104	0.485	1.026	1.423
	58	76	57	-	-
	40,65	40,65	40	40	37
Butanenitrile	0.441	1.189	0.489	1.059	1.427
	56	70	59	-	-
	69	35	69,13	35	37
Isobutyronitrile	0.440	1.143	0.467	1.071	
(2-Methylpropanenitrile)	60	62	59	-	
	38,12	38,12	38,12	38	
Benzonitrile	0.495	1.253	0.495	1.112	1.448
	57	64	58	-	-
	33,18,64	33,18,64	33	34,33	37
Phenylacetonitrile	0.512	1.186	0.508	1.136	1.469
	55	97	60	-	-
	38,64	38,64	38	38	37
Nitro Compounds					
Nitromethane	1.025	-	0.569	1.571	1.686
	59	-	59	-	-
	63,2	2	63,75,59	63,72	37,13
Nitrobenzene			0.556	1.546	1.601
			65	-	-
			63,52	63	37
Aromatic Heterocycles					
Pyridine	-0.009		0.242	0.611	0.783
	71		58	-	-
	39		39	39	37
Solvents Containing Halogens					
Benzoyl fluoride			0.55		
			56		
			51		
Dichloromethane				1.562	
				-	
				38	
1,2-Dichloroethane			0.531	1.503	
			66	-	
			38	38	
Solvents Containing Sulfur					
Ethylene sulfite			0.501	1.481	1.595
			57	-	-
			63,47	63	37
2-Mercaptoethanol	0.455		0.409		
	89		62		
	78		78		

Table 2 continued

Solvents	Cu^+	Ag^+	Tl^+	E^*Ag	E^*Hg
Dimethyl sulfoxide	0.595		0.18	0.958	1.022
	55		53	-	-
	33,18		48,10,76	34,72	37
Tetramethylene sulfone[a,c]	-	-	0.41	1.349	
(Tetrahydrothiophene-	-	-	56	-	
1,1-dioxide)	17	15,55,17	15,55,17	72	
2,2'-Thiodiethanol			0.350	0.691	0.979
			60	-	-
			30	30,72	37
Tetrahydrothiophene[b]	0.117		0.355	0.700	0.784
	58		66	-	-
	36		36	36	37
N,N-Dimethylthio-	-0.077 [a]	0.396	0.173 [a]	0.261	0.501
formamide	57	56	58	-	-
	53	33,53	53	34,33	37
N-Methyl-2-thiopyrroli-	-0.119	0.325	0.149	0.181	0.452
dinone (N-Methyl-2-	55	56	55	-	-
pyrrolidinethione)	34,33,29	34,33,29	38,29	34,33,72	37
Hexamethylthiophos-	0.204	0.58	0.311	0.445	0.699
phoric triamide	65	66	67	-	-
	62	62	62	62	37
Solvents Containing Phosphorus					
Trimethyl phosphate			0.31	1.179	1.292
			58	-	-
			46	63	37
Hexamethylphosphoric	-		0.131	0.891	0.929
triamide	-		54	-	-
	70		62,66,73	62,72,73	37

[a]0.1 mol dm^{-3} tetraethylammonium perchlorate [b]0.05 mol dm^{-3} tetrabutylammonium perchlorate [c]30 °C [d]double wave

TABLE 3. Half-wave potentials in volt versus bis(biphenyl)chromium (first line), ($E_{1/4}$-$E_{3/4}$)-values in millivolt (second line) and literature references (third and fourth line) for the reduction of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in nonaqueous solvents at 25 °C unless stated otherwise.

Solvents	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Alcohols					
Methanol	-	-		0.963	-0.397
	-	-		33	72
	9	9		35	35
Ethanol	-		-	0.936 [f]	-0.180 [g]
	-		-	33	127
	9		9	30	30,9
Ethane-1,2-diol	-0.644	-0.614	-0.763	0.651	-0.361
	63	74	70	175	130
	78,9	78,9	78,9	78,9	78,9
Ketones					
Acetone	-0.410 [a]	0.00 [a]	- [j]	1.23 [a,k]	0.130 [a]
	57	95	-	57	36
	21	21	21	21	21

Table 3 continued

Solvents	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
		Ethers			
Tetrahydrofuran	-0.594	-0.420	-0.453	0.817	-0.049
	58	130	190	55	80
	36	36	36	36	36
		Esters, Lactones			
Butyrolactone				1.128	0.138
				57	47
				33	33
Propylene carbonate[a,h]	-1.08	0.02 [p]	-0.16 [p]	1.25	0.21 [p]
(4-Methyl-1,3-dioxo-	-	61	126	60	40
lan-2-one)	48	44,48	44,48	18,44	44,48
		Amides, Lactams and Ureas			
Formamide	-	-	-	0.858 [d]	-
	-	-	-	-	-
	8	8	8	41,8	8,9
N-Methylformamide	-			0.723	-0.390
	-			37	88
	48			32	32
N,N-Dimethylformamide	-0.86	-0.55	-0.22	0.706	-0.291
	34	91	57	30	38
	23,76	76,7	76,23,7	4,18,23	23,7,76
N,N-Diethylformamide	-0.809	-0.642	-1.358	0.718	-0.291
	38	198	87	46	47
	79	79	79	79	79
N,N-Dimethylacetamide	-0.88	-0.35	-0.14	0.725	-0.233
	- [e]	- [e]	- [e]	58	47
	41	41	41	41	41,69
N,N-Diethylacetamide		-0.319	-0.131	0.736	-0.231
		55	68	77	31
		4	4	4	4
Hexamethylphosphoric		-0.082	0.551	-0.7	-
triamide		-	75	62	-
		62,66	62,66	62,66	62,66
		73	73	73,70	73
N-Methyl-2-pyrrolidinone	-0.4 [a]	-0.13 [a]	-0.12 [a]	0.751 [n]	-0.26 [a]
	220	180	80	73	30
	29	29	29	38,29	29
N,N,N,N-Tetramethylurea		-0.164	0.13	0.950 [l]	-0.140
		38	360	58	29
		72	72	72	72
		Nitriles			
Acetonitrile	-0.34 [a]	0.12 [a]	0.44 [a]		0.104
(Ethanenitrile)	27	35	30		73
	61,23,48	61,48	61,23		30,23,48
			48		65,60
Propanenitrile	-	-	-		
	-	-	-		
	65	65	65		
Butanenitrile					0.136
					42
					35
Isobutyronitrile		0.08 [q]	0.35 [q]		0.126
(2-Methylpropanenitrile)		32	190		42
		12	12		38

Table 3 continued

Solvents	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Benzonitrile	-0.28 [a]	0.21 [a,e]	0.41 [a]		0.243
	31	-	56		30
	64	64	64		33,64
Phenylacetonitrile	-0.29 [a]	0.21 [a]			0.205
	38	35			34
	65	64			38
Nitro Compounds					
Nitromethane[a]	0.43	0.50	0.57	- [o]	0.50
	68	72	124	-	50
	75	75	75	63	75
Nitrobenzene	0.42	0.56	0.54	1.393	0.59
	100	90	59	61	28
	52	52	52	63,59	52
Aromatic Heterocycles					
Pyridine	-0.728	-0.277	0.007	-	-0.315
	38	36	35	-	32
	39	39	39	39	39
Solvents Containing Halogens					
Benzoyl fluoride	0.40	0.50	0.56		0.48
	81	104	71		41
	51	51	51		51
Dichloromethane				1.358	
				48	
				38	
Solvents Containing Sulfur					
Ethylene sulfite	-0.18 [a,i]	0.06 [a]	- [a,j]	1.243	0.10 [a]
	107	59	-	41	83
	47	47	47	63,47	47
2-Mercaptoethanol					0.082
					36
					78
Dimethyl sulfoxide[a]	-1.00	-0.71	-0.35	0.724 [m]	-0.37
	49	89	72	62	27
	48,76	76,48	76,48	33,18,10	48,76
Tetramethylene sulfone[c]	-0.29	0.07 [a]		1.234	0.28
(Tetrahydrothiophene-	30			67	28
1,1-dioxide)	15,55,17	15,55,17		33,15,55	15,55,17
2,2'-Thiodiethanol	-0.435	-0.029	0.100	0.405	-0.013
	43	60	87	40	37
	30	30	30	30	30
N,N-Dimethylthio-	-0.410	0.040	0.178	-	-0.243
formamide[a]		38	33	-	31
	53	53	53	53	53,33
N-Methyl-2-thiopyrroli-	-0.365 [a]	-0.05 [a]	-		-0.245 [a]
dinone (N-Methyl-2-	60	40	-		32
pyrrolidinethione)	29	29	29		29
Hexamethylthiophosphoric		-0.434	-0.561		-0.327
triamide		158	200		110
		62	62		62
Solvents Containing Phosphorus					
Trimethyl phosphate[a]	-1.15	-0.69	-0.20	0.929	-0.12
	210	205	115	71	30
	46	46	46	33	46

Table 3 continued

Solvents	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Hexamethylphosphoric triamide		-	-0.082	0.551	-0.7
		-	75	62	- [e]
		62,66	62,66	62,66	62,66
		73	73	73,70	73

[a]0.1 mol dm^{-3} tetraethylammonium perchlorate [b]0.05 mol dm^{-3} tetrabutylammonium perchlorate [c]30 °C [d]additional wave $E_{\frac{1}{2}}$: 0.718 V [e]maximum [f]small adsorption prewave $E_{\frac{1}{2}}$: 0.997 [g]additional wave $E_{\frac{1}{2}}$: -0.312 V (144 mV) [h]aqueous perchlorates [i]additional wave $E_{\frac{1}{2}}$: -0.46 V (28 mV) [j]$E_{\frac{1}{2}}$ concentration dependent [k]additional wave $E_{\frac{1}{2}}$: 1.02 V (57 mV) [l]additional wave $E_{\frac{1}{2}}$: 0.765 V (56 mV) [m]additional wave $E_{\frac{1}{2}}$: 0.595 V (55 mV) [n]poorly resolved double wave [o]first wave with a maximum, $E_{\frac{1}{2}}$ approximately at 1.03 V, additional one electron wave $E_{\frac{1}{2}}$: 0.785 V (52 mV) [p]aqueous perchlorate [q]0.05 mol dm^{-3} tetraethylammonium perchlorate

TABLE 4. Half-wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($E_{1/4}$-$E_{3/4}$)-values in millivolt (second line) and literature references (third and fourth line) for the reduction of Cd^{2+}, Ba^{2+}, Pb^{2+} and UO_2^{2+} as well as $\frac{1}{2}(E_{pa} + E_{pc})$ values for the oxidation of ferrocene (Fc) in 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in nonaqueous solvents at 25 °C unless stated otherwise.

Solvents	Cd^{2+}	Ba^{2+}	Pb^{2+}	UO_2^{2+}	Fc
		Alcohols			
Methanol	0.285	-1.06 [a]	0.467 [a]		1.134 [a]
	55	31	48		-
	35	20,15	35,31		28,19
Ethanol	0.224 [a]	-0.991	0.525	-	1.134 [a]
	-	42	33	-	-
	30,9	37,15	30,31	80	28
Ethane-1,2-diol	0.271 [b]		0.413 [b]		1.132 [b]
	47		41		74
	78		78		78
		Ketones			
Acetone	0.510 [a]	-1.075 [a]	0.708	-	1.131 [a,l]
	33	33	29	-	56
	21,13	21	31	80	21,19
		Ethers			
Tetrahydrofuran	0.320	-1.102	0.511	-	1.209 [l]
	99	41	49	-	100
	36	37,36	36	80	36
		Esters, Lactones			
Butyrolactone	0.511		- [f]		1.112 [a]
	32		-		-
	33		31		28
Propylene carbonate (4-Methyl-1,3-dioxolan-2-one)	0.64 [a,h]	-0.941	0.691	0.37 [k]	1.114 [a]
	40	42	43	62	-
	44	37,43,20	31	3,77	28,19
		Amides, Lactams and Ureas			
Formamide	0.156		0.387		1.135
	71		46		-
	41,8		41,31		41

Table 4 continued

Solvents	Cd^{2+}	Ba^{2+}	Pb^{2+}	UO_2^{2+}	Fc
N-Methylformamide	0.132	-1.33 [a,d]	0.282		1.135
	35	-	32		-
	32	32	31,32		32
N,N-Dimethylformamide	0.126	-1.305	0.270	0.22 [i]	1.127 [a]
	31	35	30	-	-
	4,76	37,23	31,23	68,80	28,19
		7,76			
N,N-Diethylformamide	0.135		0.270		1.142
	33		34		-
	79		79		79
N,N-Dimethylacetamide	0.129	-1.34	0.259	0.14 [j]	1.135
	32	[d]	36	66	-
	41,69	41,45	41,69	3	41
N,N-Diethylacetamide	0.109	-1.354	0.272		1.137
	31	54	33		-
	4	4	31,4		4
N-Methyl-2-pyrrolidinone	0.118	-1.39	0.266		1.126 [a]
	35	40	32		-
	38,29	29,37	31		28
N,N,N,N-Tetramethylurea	0.249	-1.321	0.220		1.129 [m]
	32	46	64		-
	72	72	72		72
Nitriles					
Acetonitrile	0.460	-0.883	0.686		1.119
(Ethanenitrile)	33	28	31		-
	30,61,60	37,20,23	30,31	80	28,19
	48,65	60,48	23		
Propanenitrile[b]	0.471		0.669		1.132
	32		35		-
	40,65	65	40		40
Butanenitrile	0.469	-0.941	0.686		1.145 [m]
	35	48	34		-
	35	37	35		81
Isobutyronitrile	0.417		0.658		1.131 [l]
(2-Methylpropanenitrile)	76		40		60
	38		38		38
Benzonitrile	0.543 [a]	-0.88 [a]	0.705	-	1.149
	39	31	36	-	-
	33,64	64,20	33	80	81,19
Phenylacetonitrile	0.559	-0.85	0.732		1.150
	34	31	43		-
	38,65	65	38		38
Nitro Compounds					
Nitromethane	0.824		0.850		1.112 [a]
	33		32		-
	63,75		31	80	28,2,19
Nitrobenzene	0.781		0.812		1.140 [l]
	33		32		59
	63,52		63		63,19,52
Aromatic Heterocycles					
Pyridine	0.031	-1.036	0.337	-	1.149
	40	33	43	-	-
	39	37,39	39	80	39

Table 4 continued

Solvents	Cd^{2+}	Ba^{2+}	Pb^{2+}	UO_2^{2+}	Fc
Solvents Containing Halogens					
Benzoyl fluoride	0.75				1.14 [1]
	30				60
	51				51
Dichloromethane			0.803	-	1.148 [1]
			35	-	81
			38,31	80	38
1,2-Dichloroethane			0.714		1.131
			30		-
			31		28
Solvents Containing Sulfur					
Ethylene sulfite	0.592		0.685		1.135 [1]
	36		32		56
	63,47		63		63
2-Mercaptoethanol	0.391		0.497		
	38		45		
	78		78		
Dimethyl sulfoxide	0.02	-1.36 [a]	0.179	0.14	1.123 [a]
	29	29	29	56	-
	10,76	76	31	68,26,80	28,19
Tetramethylene sulfone[c]	0.581	-1.01 [a]	0.641		1.114 [a]
(Tetrahydrothiophene-	46	29	32		-
1,1-dioxide)	33,15	15,55,17	31,55		28
	55,17				
2,2'-Thiodiethanol	0.319		0.443		1.121
	38		35		-
	30		30		30
Tetrahydrothiophene[b]	0.328		0.391		-
	116		83		-
	36		36		36
N,N-Dimethylthio-	0.054	-0.778 [a]	0.283		
formamide	35	66	33		
	53	53	31		
N-Methyl-2-thiopyrroli-	0.059	-0.811	0.272		
dinone (N-Methyl-2-	35	95	46		
pyrrolidinethione)	38,29	63	31		
Hexamethylthiophos-	0.252		0.437		1.153
phoric triamide	41		43		-
	62		62		62
Solvents Containing Phosphorus					
Trimethyl phosphate	0.21 [a]	-1.33 [a]	0.345		1.131
	50	48	69		-
	46	46	31		81
Hexamethylphosphoric	0.055	-1.485	0.158		1.140
triamide	27	82	50		-
	62,66	62,58	62,66		62

[a] 0.1 mol dm^{-3} tetraethylammonium perchlorate [b] 0.05 mol dm^{-3} tetrabutylammonium perchlorate [c] 30 °C [d] maximum [e] possibly a double wave [f] double wave $E_{\frac{1}{2}}$: 0.621 V and 0.555 V [g] Ref. 31 two waves $E_{\frac{1}{2}}$: 0.487 V (31 mV) and $E_{\frac{1}{2}}$: 0.392 V (31 mV) [h] aqueous perchlorates [i] additional waves $E_{\frac{1}{2}}$: -0.15 V and -0.70 V, half-wave potentials concentration dependent [j] $UO_2(ClO_4)_2.2H_2O$,

additional wave $\underline{E}_{\frac{1}{2}}$: -0.36 V (267 mV) [k]$UO_2(ClO_4)_2.2H_2O$, additional wave $\underline{E}_{\frac{1}{2}}$: 0.19 V (115 mV) [l]$\underline{E}_{\frac{1}{2}}$ measured at the dropping mercury electrode [m]pulse polarography

TABLE 5. Half wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($\underline{E}_{1/4}$-$\underline{E}_{3/4}$)-values in millivolt (second line) and literature references (third line) for the reduction of La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Sm^{2+} in 0.1 mol dm^{-3} solutions of tetraethylammonium perchlorate in nonaqueous solvents at 25 °C.

Solvents	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Sm^{3+}	Sm^{2+}
			Ketones			
Acetone			(-0.81)	(-0.83)	(-0.47)	(-1.04)
			-	-	-	-
			11	11	11	11
			Esters			
Propylene carbonate	(-0.89)	(-0.87)	(-0.87)	(-0.89)	(-0.34)	(-0.91)
(4-Methyl-1,3-dioxo-	70	82	65	92	124	33
lan-2-one)	71	71	71	71	71	71
			Amides			
N,N-Dimethylformamide[a]	(-1.37)	(-1.37)	(-1.37)	(-1.37)	(-1.17)	(-1.34)
	18	23	26	26	55	49
	24	24	24	24	24	24
N,N-Dimethylacetamide	(-1.36)	(-1.35)	(-1.31)	(-1.32)	(-0.96)	(-1.33)
	-	-	-	-	-	-
	49	49	49	49	49	49
			Nitriles			
Acetonitrile[b]	(-0.7)		(-0.7)	(-0.7)	(-0.84)	(-0.72)
(Ethanenitrile)	-		-	-	-	-
	61		61	61,16	61,16	16
Benzonitrile			(-0.77)	(-0.73)	(-0.23)	(-0.81)
			170	175	58	79
			54	54	54	54
			Sulfur Compounds			
Dimethyl sulfoxide[a]	(-1.59)	(-1.57)	(-1.53)	(1.53)	(-1.35)	(-1.45)
	70	100	100	-	51	39
	24,25	24,25	24,25	24,25	24,25	24,25

[a]anhydrous chlorides [b]aqueous perchlorates

TABLE 6. Half-wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($\underline{E}_{1/4}$- $\underline{E}_{3/4}$)-values in millivolt (second line) and literature references (third and fourth line) for the reduction of Eu^{3+}, Eu^{2+}, Gd^{3+}, Tb^{3+} and Dy^{3+} in 0.1 mol dm^{-3} solutions of tetraethylammonium perchlorate in nonaqueous solvents at 25 °C.

Solvents	Eu^{3+}	Eu^{2+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
		Ketones			
Acetone	0.630	(-1.13)	(-0.83)	(-0.72)	(-0.78)
	56	74	-	-	-
	81,11	81,11	11	11	11
		Esters			
Propylene carbonate	0.844	(-0.95)	(-0.86)	(-0.83)	(-0.84)
(4-Methyl-1,3-dioxo-	71	40	111	123	128
lan-2-one)	81,71,50	81,71,50	71	71	71

Table 6 continued

Solvents	Eu^{3+}	Eu^{2+}	Gd^{3+}	Tb^{3+}	Dy^{3+}
		Amides			
N,N-Dimethylformamide[a]	0.002	(-1.36)	(-1.46)	(-1.46)	(-1.58)
	62	51	26	21	32
	81,24,50	81,24,50	24	24	24
N,N-Dimethylacetamide	0.146	(-1.41)	(-1.43)	(-1.45)	(-1.49)
	59	-	-	-	-
	81,49,50	81,49	49	49	49
		Nitriles			
Acetonitrile[b]	0.93	(-0.89)	(-0.7)		
(Ethanenitrile)	57	-	-		
	81,16	81,61	61		
	11,50	16,50			
Benzonitrile	0.95	(-0.93)			
	72	44			
	81,54	81			
		Sulfur Compounds			
Dimethyl sulfoxide[a]	-0.143	(-1.45)	(-1.49)	(-1.52)	(-1.41)
	57	43	150	260	190
	81,24	81,24	24,25	24,25	24,25
	25,50	25,50			

[a]anhydrous chlorides [b]aqueous perchlorates

TABLE 7. Half-wave potentials in volt versus bis(biphenyl)chromium(I)/(0) (first line), ($E_{1/4}$ - $E_{3/4}$)-values in millivolt (second line) and literature references (third line) for the reduction of Ho^{3+}, Tm^{3+}, Er^{3+}, Yb^{3+} and Yb^{2+} in 0.1 mol dm^{-3} solutions of tetraethylammonium perchlorate in nonaqueous solvents at 25 °C.

Solvents	Ho^{3+}	Tm^{3+}	Er^{3+}	Yb^{3+}	Yb^{2+}
		Ketones			
Acetone	(-0.78)	(-0.78)	(-0.77)	(-0.05)	(-1.05)
	-	-	-	-	-
	11	11	11	11	11
		Esters			
Propylene carbonate	(-0.85)		(-0.84)	(0.11)	(-0.97)
(4-Methyl-1,3-dioxo-	118		157	88	41
lan-2-one)	71		71	71	71
		Amides			
N,N-Dimethylformamide[a]	(-1.50)		(-1.51)	(-0.69)	(-1.44)
	32		35	56	40
	24		24	24	24
N,N-Dimethylacetamide	(-1.50)		(-1.52)	(-0.52)	(-1.48)
	-		-	-	-
	49		49	49	49
		Nitriles			
Acetonitrile[b]				(0.21)	(-0.91)
(Ethanenitrile)				59	-
				61 16	61 16
Benzonitrile		(-0.75)		(0.14)	(-0.87)
		150		80	126
		54		54	54
		Sulfur Compounds			
Dimethyl sulfoxide[a]	(-1.42)		(-1.42)	(-0.810)	(-1.54)
	190		190	62	37
	24,25		24,25	24,25	24,25

[a]anhydrous chlorides [b]aqueous perchlorates

TABLE 8. Potential ranges on the dropping mercury electrode and on the stationary platinum electrode versus bis(biphenyl)chromium(I)/(0) in volt as well as specific conductivities of 0.1 mol dm^{-3} solutions of tetrabutylammonium perchlorate in nonaqueous solvents at 25 °C unless stated otherwise (first line) and literature references (second line).

Solvents	dropping mercury electrode		stationary platinum electrode		specific conductivity $10^5\ \Omega^{-1}\ cm^{-1}$
		Alcohols			
Methanol	1.27	-1.43	2.32		
	27	27	27		
Ethanol	1.28	-1.47	1.92		
	27	27	27		
Ethane-1,2-diol[b]	1.25	-0.95	1.82	-0.55	6.3 [b]
	78	78	78	78	78
		Ethers			
Tetrahydrofuran	0.99	-2.02	1.88	-1.49	27.2
	36	36	36	36	36
		Esters, Lactones			
Butyrolactone	1.37	-2.13	2.67		
	27	27	27		
Propylene carbonate(4-Methyl-1,3-dioxolan-2-one)	1.48	-1.94	2.55		
	63,27	63,27	27		
		Amides, Lactams and Ureas			
Formamide	0.95	-0.5	1.7	0.5	184
	41	41	41	41	41
N-Methylformamide	1.10 [a]	-2.00 [a]	2.74 [a]		
	32	32	32		
N,N-Dimethylformamide	1.07	-2.23	2.19		
	27	27	27		
N,N-Diethylformamide	0.98	-1.94	1.6	-1.4	
	79	79	79	79	
N,N-Dimethylacetamide	1.1	-2.2	2.00	-0.5	158
	41	41	41	41	41
N,N-Diethylacetamide	1.05	-2.34	2.00	-1.70	
	4	4	4	4	
N-Methyl-2-pyrrolidinone	1.07	-2.14	2.15		
	27,29	27,29	27,29		
N,N,N,N-Tetramethylurea	1.05	-2.1	2.0		
	72	72	72		
		Nitriles			
Acetonitrile (Ethanenitrile)	1.07	-2.14	2.15	-1.26	
	81,50	81,50	81,50	81	
Propanenitrile	1.23	-1.9	2.15	-1.30	
	40	40	40	40	
Butanenitrile	1.13	-1.42			
	81	81			
Isobutyronitrile (2-Methylpropanenitrile)	1.34	-1.58	2.08	-1.35	
	38	38	38	38	

Table 8 continued

Solvents	dropping mercury electrode		stationary platinum electrode		specific conductivity $10^5\ \Omega^{-1}\ cm^{-1}$
Benzonitrile	1.35	-1.42	2.47	-1.17	
	81	81	81	81	
Phenylacetonitrile	1.43	-1.81	2.66	-1.24	
	38	38	38	38	
Nitro Compounds					
Nitromethane	1.65	-0.29	2.85	-0.29	
	63	63	63	63	
Nitrobenzene	1.6	-0.21	2.98	-0.18	
	63	63	63	63	
Aromatic Heterocycles					
Pyridine	0.72	-1.62	2.36	-1.6	204
	39	39	39	39	39
Solvents Containing Halogens					
Benzoyl fluoride	1.64	-1.96			
	51	51			
Dichloromethane	1.61	-1.24	2.78	-0.55	
	38	38	38	38	
1,2-Dichloroethane	1.61	-1.39	3.11		
	27	27	27		
Solvents Containing Sulfur					
Ethylene sulfite	1.43	-1.34	2.76	-1.12	
	63	63	63	63	
2-Mercaptoethanol	0.55	-0.56	1.4	-0.3	74.1
	78	78	78	78	78
Dimethyl sulfoxide	0.95	-2.23	2.12		
	27	27	27		
2,2'-Thiodiethanol	0.92	-1.31	1.91		11.4
	30	30	30		30
Tetrahydrothiophene[b]	0.68	-0.78	1.15	-0.62	5.8 [b]
	36	36	36	36	36
N,N-Dimethylthio-[a] formamide	0.3	-1.45	1.0	-1.40	
	53	53	53	53	
N-Methyl-2-thio pyrrolidinone	-0.4	-1.6	1.0		
	29	29	29		
Hexamethylthiophosphoric triamide	0.5	-2.2	1.3	-1.7	34.7
	62	62	62	62	62
Solvents Containing Phosphorus					
Trimethyl phosphate	1.15 [a]	-1.4 [a]			
	46	46			
Hexamethylphosphoric triamide	0.9	-1.9	1.7	-1.7	108
	62	62	62	62	62

[a] 0.1 mol dm^{-3} tetraethylammonium perchlorate [b] 0.05 mol dm^{-3} tetrabutylammonium perchlorate

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