INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

POLAROGRAPHIC HALF-WAVE POTENTIALS

OF INORGANIC SUBSTANCES IN

N, N'-DIMETHYLFORMAMIDE AS SOLVENT

Prepared for publication by

J. F. COETZEE

Analytical Chemistry Division

Commission on Electroanalytical Chemistry

POLAROGRAPHIC HALF-WAVE POTENTIALS OF INORGANIC SUBSTANCES IN N,N'-DIMETHYLFORMAMIDE AS SOLVENT[†]

N,N'-Dimethylformamide (DMF) is one of the most important members of the class of dipolar aprotic solvents; some other important members are dimethyl sulphoxide (DMSO), hexamethyl-phosphoramide (HMPA), acetonitrile (AN), propylene carbonate (PC) and sulpholane (SL). What all of these solvents have in common is that they have limited proton donor or even hydrogen bond donor ability. However, the Brønsted and Lewis basicities of different members vary widely. For example, their Gutmann donor numbers (Ref. 1), which are the $-\Delta H_O$ values for their interaction with antimony pentachloride in the relatively inert solvent 1,2-dichloro-ethane, are the following: AN, 14.1; SL, 14.8; DMF, 26.6; DMSO, 29.8; and HMPA, 38.8. By comparison, the donor number of the typical protic solvent methanol is 19.0; that of water is 18.0, but the effective value for the bulk solvent is uncertain. These wide variations in donor ability are reflected in the free energies of transfer of cations from water to different dipolar aprotic solvents listed in Table 1. The limited ability of the aprotic solvents to solvate small "hard" anions (e.g., chloride ion), which require hydrogen bonding for stabilisation, is also illustrated in Table 1.

TABLE 1. Gibbs Free Energies of Transfer of Ions from Water to Other Solvents[*]

	Dimethyl-formamide	Dimethyl sulphoxide	Aceto-nitrile	Sulpho-lane
H^+	-3.4	-4.5	+11.0	-
Li^+	-2.3	-3.5	+ 7.1	-
Na^+	-2.5	-3.3	+ 3.3	- 0.7
K^+	-2.3	-2.9	+ 1.9	- 1.0
Rb^+	-2.4	-2.6	+ 1.6	- 2.1
Cs^+	-2.2	-3.0	+ 1.2	- 2.4
Tl^+	-2.7	-4.9	+ 2.2	-
Ag^+	-4.1	-8.0	- 5.2	- 0.9
Cl^-	+11.0	+9.2	+10.1	+12.6
Br^-	+7.2	+6.1	+ 7.6	+ 9.5
I^-	+4.5	+2.2	+ 4.5	+ 4.9

[*]From Ref. 2 and 3; based on the extrathermodynamic assumption that values for Ph_4As^+ and Ph_4B^- are equal. All values are in kcal mol^{-1} (1 cal = 4.184 J) on the molar scale at T = 298 K (except T = 303 K for sulpholane). Negative sign (stronger solvation than in water) corresponds to negative shift in half-wave potential (on a unified emf scale for all solvents) for the electroreaction $M^{n+} + ne^- \overset{Hg}{\rightleftharpoons} M(Hg)$

Dimethylformamide has a melting point of $-61°C$ and a boiling point of $152.3°C$ (1 atm.); at $25°C$, its dynamic viscosity is 0.00796 poise and its dielectric constant is 37.0 (Ref. 4). Its useful potential range is wide, similar to those of other dipolar aprotic solvents and extending over 3.5 V at the dropping mercury electrode. It has outstanding solvent power for organic as well as many inorganic compounds. It therefore possesses many of the requisites for a useful electrochemical solvent, with the result that numerous such studies have been carried out. This report is limited to the polarography of inorganic compounds (Table 2). The extensive electrochemistry of organic compounds in DMF has been reviewed elsewhere (Ref. 5).

The principal disadvantage of DMF as a medium for chemical or electrochemical reactions is that it is far from being ideally stable. It is susceptible to both thermal and photochemical degradation, and, in presence of the ubiquitous impurity water, it rapidly produces formic acid and dimethylamine (Ref. 4). The latter impurity may drastically affect the polarographic behavior of such ions as Co^{2+} and Ni^{2+} because it is a sufficiently strong ligand to replace DMF in the coordination sphere of the metal ion. Consequently, DMF should be used as soon as possible after purification. For many of the results listed in Table 2, it is not clear whether this was the case; in still other instances, commercial DMF was used without further purification. However, the effect of impurities on the polarography of such ions as those of the alkali and alkaline earth metals is likely to be much less serious. A second possible source of error in certain measurements is the use of the aqueous saturated calomel electrode as reference, which not only may introduce water into the system, but which on prolonged exposure to DMF forms a plug of insoluble potassium chloride or potassium perchlorate (if a perchlorate is used as supporting electrolyte); such a plug changes the junction potential significantly. Consequently, the results listed in Table 2 should not be used indiscriminately, but should be viewed with some circumspection in the light of these presently known sources of error.

KEY TO TABLE 2

1.   The concentration of the supporting electrolyte is 0.1 M, that of the electroactive species is typically 0.5 - 1 mM, and the temperature is $25°C$, except where otherwise noted.

2.   The following abbreviations are used for reference electrodes:

     2.1 Hg: mercury pool internal reference electrode
     2.2 Ag: Ag,AgCl/Et_4NCl (saturated, in DMF)
     2.3 Na: Na amalgam (saturated)/$NaClO_4$(saturated, in DMF)
     2.4 SCE(DMF): calomel electrode with NaCl (saturated, in DMF)
     2.5 SCE(W): aqueous saturated calomel electrode

3.   Slopes are those of plots of $-E$ vs. $\log [i/(i_d-i)]$ except that values with asterisks are those of $E_{1/4} - E_{3/4}$.

4.   In each case, the first entry in the first column is the actual electroactive species, the second entry is its source.

5.   Salts such as $Cu(ClO_4)_2 \cdot aq$, which are not easily dehydrated, were probably introduced as the hydrates in most cases; however, most authors did not include this information.

TABLE 2. Half-Wave Potentials of Inorganic Species at the Dropping Mercury Electrode in N,N'-Dimethylformamide as Solvent

Electroactive Species	Supporting Electrolyte	Reference Electrode	Half-Wave Potential V	Slope, mV	Ref.
Li^+;LiCl	Bu_4NI	Hg	-1.81	62	7
Li^+;$LiClO_4$	Et_4NClO_4	Na	-0.354	83	8
Li^+;$LiClO_4$	Et_4NClO_4	Ag	-1.92	66*	9
Na^+;NaI	Bu_4NI	Hg	-1.53	62	7
Na^+;$NaClO_4$	Et_4NClO_4	Na	+0.018	58	8
Na^+;$NaClO_4$	Et_4NClO_4	Ag	-1.63	54*	9

TABLE 2 (continued)

Electroactive Species	Supporting Electrolyte	Reference Electrode	Half-Wave Potential, V	Slope, mV	Ref.
K^+; KI	Bu_4NI	Hg	-1.55	69	7
K^+; $KClO_4$	Et_4NClO_4	Na	-0.006	54	8
K^+; $KClO_4$	Et_4NClO_4	Ag	-1.67	54*	9
Rb^+; RbI	Bu_4NI	Hg	<u>ca.</u> -1.52	–	7
Rb^+; $RbClO_4$	Et_4NClO_4	Ag	-1.65	55*	9
Cs^+; CsCl	Bu_4NI	Hg	<u>ca.</u> -1.53	–	7
Cs^+; $CsClO_4$	Et_4NClO_4	Ag	-1.62	57*	9
NH_4^+; NH_4ClO_4	Et_4NClO_4	Na	-0.169	179	8
Tl^+; $TlClO_4$	$NaNO_3$	Na	+1.628	59	8
Tl^+; $TlClO_4$	$NaClO_4$	Ag	-0.07	60*	9
$Tl°$; Tl(Hg)	$NaClO_4$	Ag	-0.07	-63*	9
Mg^{2+}; $Mg(ClO_4)_2$	Et_4NClO_4	Ag	-2.05	–	9
Ca^{2+}; $CaCl_2$	Bu_4NI	Hg	-1.78	–	7
Ca^{2+}; $Ca(ClO_4)_2$	Et_4NClO_4	Ag	-1.95	45*	9
Sr^{2+}; $Sr(ClO_4)_2$	Bu_4NI	Hg	-1.68	59	7
Sr^{2+}; $Sr(ClO_4)_2$	Et_4NClO_4	Ag	-1.80	44*	9
Ba^{2+}; $Ba(ClO_4)_2$	Bu_4NI	Hg	-1.49	43	7
Ba^{2+}; $Ba(ClO_4)_2$	Et_4NClO_4	Ag	-1.62	33*	9
$Ga°$; Ga(Hg)	$NaClO_4$	Ag	-0.37	-27*	9
$In°$; In(Hg)	$NaClO_4$	Ag	+0.03	-32*	9
Pb^{2+}; $Pb(ClO_4)_2$	$NaNO_3$	Na	+1.629	37	8
Pb^{2+}; $Pb(ClO_4)_2$	Et_4NClO_4	Ag	-0.03	40*	9
$Pb°$; Pb(Hg)	$NaClO_4$	Ag	-0.03	-32*	9
$Bi°$; Bi(Hg)	$NaClO_4$	Ag	+0.038	-114*	9

TABLE 2 (continued)

Electroactive Species	Supporting Electrolyte	Reference Electrode	Half-Wave Potential, V	Slope, mV	Ref.
Ti(III);$TiCl_3$	Et_4NClO_4	SCE(W)	-1.53(1)	irrev.	10
			-1.91(2)	irrev.	
Ti(IV);$TiOCl_2$ or	Et_4NClO_4	SCE(W)	-1.22(1)	110[*]	10
$TiO(ClO_4)_2$			-1.76(2)	130[*]	
Ti(IV);	Et_4NClO_4	SCE(W)	-0.57(1)	irrev.	10
$TiCl_4 \cdot 2DMF$			-1.34(2)	irrev.	
			-1.59(3)	irrev.	
			-1.72(4)	irrev.	
			-1.93(5)	irrev.	
V(III);VCl_3	Et_4NClO_4	SCE(W)	-0.62(1)	58	11
			-0.76(2)	60	
V(IV);					
$VO(ClO_4)_2 \cdot 5DMF$	Et_4NClO_4	SCE(W)	-1.40(1)	62	11
			-0.735(2)	60	
Zr(IV);$ZrCl_4$	Et_4NClO_4	SCE(W)	-1.32(1)	95	12
			-1.86(2)	130	
Zr(IV);					
$ZrOCl_2 \cdot 8aq$	Et_4NClO_4	SCE(W)	-1.33(1)	100	12
			-1.86(2)	140	
Cr(III);$CrCl_3$	Et_4NClO_4	SCE(W)	-0.915(1)	115	11
			-1.54(2)	73	
Cr(III);	LiCl(0.2 M)	Ag	-0.290(1)	–	13
$CrCl_3 \cdot 6aq$			-1.15(2)		
Fe(II);$Fe(ClO_4)_2$	Et_4NClO_4	SCE(DMF)	-1.43	–	14
Fe(II);FeX_4^{2-},	Et_4NClO_4	SCE(DMF)	-2.3 to	–	14
X = Cl,Br,I			-2.6		
Fe(II);ferrocene	$NaClO_4$	Ag	+0.88(II→III)	65	9
Mn(II);$Mn(ClO_4)_2$	Et_4NClO_4	Ag	-1.12	34[*]	9
Mn(II);$Mn(ClO_4)_2$	$NaClO_4$	SCE(DMF)	-1.476	43	15
Mn(II);$Mn(ClO_4)_2$	Et_4NClO_4	SCE(DMF)	-1.55	–	14
Mn(II);$MnCl_4^{2-}$	Et_4NClO_4	SCE(DMF)	ca. -2.1	–	14

TABLE 2 (continued)

Electroactive Species	Supporting Electrolyte	Reference Electrode	Half-Wave Potential,V	Slope, mV	Ref.
Co(II);Co(ClO$_4$)$_2$	NaClO$_4$	Ag	-0.81	89[*]	9
Co(II);Co(ClO$_4$)$_2$	Et$_4$NClO$_4$	SCE(DMF)	-1.37	–	14
Co(II); Co(ClO$_4$)$_2$·6aq	NaClO$_4$(0.2 M)	Hg	-1.32	116	7
Ni(II);Ni(ClO$_4$)$_2$	NaClO$_4$	Ag	-0.53	64[*]	9
Ni(II);Ni(ClO$_4$)$_2$	NaClO$_4$	SCE(DMF)	-0.856	100	16
Ni(II); Ni(ClO$_4$)$_2$·6aq	NaClO$_4$(0.2 M)	Hg	-1.06	105	7
Cu(II);Cu(ClO$_4$)$_2$	NaClO$_4$	Ag	+0.41	33[*]	9
Cu(II); Cu(ClO$_4$)$_2$·6aq	NaClO$_4$(0.2 M)	Hg	-0.15	49	7
Cu(II)	NaNO$_3$	Na	+2.050(1)	37	8
			+1.777(2)	87	
Cu(I)	LiClO$_4$	SCE(W)	+0.05(I→II)	-65	17
Cu(I) (at Pt)	LiClO$_4$	SCE(W)	0.00(I→0)	270	17
Cu(I)	LiClO$_4$	SCE(W)	0.00(I→0)	65	8
Zn(II);Zn(ClO$_4$)$_2$	Et$_4$NClO$_4$	Ag	-0.59	38[*]	9
Zn(II); Zn(ClO$_4$)$_2$·6aq	NaClO$_4$(0.2 M)	Hg	-1.12	48	7
Zn(II)	NaNO$_3$	Na	+1.062	36	8
Zn°;Zn(Hg)	NaClO$_4$	Ag	-0.59	-30[*]	9
Cd(II);Cd(ClO$_4$)$_2$	Et$_4$NClO$_4$	Ag	-0.17	33[*]	9
Cd(II)	NaNO$_3$	Na	+1.453	22	8
Cd°;Cd(Hg)	NaClO$_4$	Ag	-0.17	-28[*]	9
Eu(III);EuCl$_3$	Et$_4$NClO$_4$	SCE(W)	-0.70(III→II)	60	18
			-2.05(II→0)	–	
Yb(III);YbCl$_3$	Et$_4$NClO$_4$	SCE(W)	-1.39(III→II)	59	18
			-2.14(II→0)	–	
Sm(III);SmCl$_3$	Et$_4$NClO$_4$	SCE(W)	-1.87(III→II)	–	18
			-2.04(II→0)	–	

TABLE 2. (continued)

Electroactive Species	Supporting Electrolyte	Reference Electrode	Half-Wave Potential,V	Slope, mV	Ref.
Other lanthanides	Et_4NClO_4	SCE(W)	-2.1 to -2.2(III→0?)	-	18
Hf(IV);$HfCl_4$	Et_4NClO_4	SCE(W)	-1.32(1)	85*	13
			-1.86(2)	88*	
Th(IV);$ThCl_4$	Et_4NClO_4	SCE(W)	-1.96(1)	-	19
			-2.10(2)	-	
O_2	$NaNO_3$	Na	+1.661(1)	33	8
			+1.469(2)	48	
O_2	Bu_4NClO_4	SCE(W)	-0.80(1)	-	20
			-2.8(2)	-	
O_2	Bu_4NClO_4 (0.2 M)	SCE(W)	-0.87	-	21
Cl^-;LiCl	$LiClO_4$	SCE(W)	-0.17(1)	-	22
			+0.125(2)	-	
I^-;Et_4NI	$LiClO_4$	SCE(W)	-0.32(1)	-	22
			+0.10(2)	-	

REFERENCES

1. V. Gutmann and R. Schmid, Coord. Chem. Rev. 12, 263 (1974).
2. B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, Aust. J. Chem. 27, 477 (1974).
3. I. M. Kolthoff and M. K. Chantooni, Jr., J. Phys. Chem. 76, 2026 (1972).
4. J. Juillard, "Dimethylformamide: Purification, Tests for Purity and Physical Properties", Pure Appl. Chem. (1977).
5. C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, Inc., New York, N. Y., 1970.
6. J. F. Coetzee and G. R. Padmanabhan, J. Phys. Chem. 66, 1708 (1962).
7. G. H. Brown and R. Al-Urfali, J. Am. Chem. Soc. 80, 2113 (1958).
8. D. L. McMasters, R. B. Dunlap, J. R. Kuempel, L. W. Kreider and R. T. Shearer, Anal. Chem. 39, 103 (1967).
9. J. B. Headridge, M. Ashraf and H. L. H. Dodds, J. Electroanal. Chem. 16, 114 (1968).
10. V. Gutmann and M. Michlmayer, Monatsh. Chem. 99, 316 (1968).
11. M. Michlmayer and V. Gutmann, Inorg. Chim. Acta 1, 471 (1967).
12. D. B. Bruss and T. DeVries, J. Am. Chem. Soc. 78, 733 (1956).
13. M. Michlmayer and V. Gutmann, Electrochim. Acta 13, 1671 (1968).
14. A. Ciana and C. Furlani, Electrochim. Acta 10, 1149 (1965).
15. J. N. Gaur and N. K. Goswami, Electrochim. Acta 12, 1489 (1967).
16. J. N. Gaur and N. K. Goswami, Electrochim. Acta 11, 939 (1966).
17. K. W. Boyer and R. T. Iwamoto, J. Electroanal. Chem. 7, 458 (1964).
18. G. Gritzner, V. Gutmann and G. Schöber, Monatsh. Chem. 96, 1056 (1965).
19. G. Gritzner, V. Gutmann and M. Michlmayer, Z. Anal. Chem. 224, 245 (1967).
20. D. L. Maricle and W. G. Hodgson, Anal. Chem. 37, 1562 (1965).
21. M. E. Peover and B. S. White, Electrochim. Acta 11, 1061 (1966).
22. P. H. Given and M. E. Peover, J. Chem. Soc., 1602 (1959).