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VOLTAMMETRIC HALF-WAVE POTENTIALS IN SULPHOLANE AS SOLVENT

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Sulpholane (tetrahydrothiophene-1,1-dioxide, tetramethylenesulphone) is a dipolar aprotic solvent which provides a number of attractive features for voltammetry and other measurements. Some of its physical properties are given in Table 1. Several procedures for its

TABLE 1. Physical properties of sulpholane

Property[a]	Value	Ref.
Freezing temperature, °C	28.45	1
Boiling temperature, °C (1 atm., decomp.)	285	2
Density, g cm^{-3}	1.2625	3
	1.2623	4
Dynamic viscosity, poise	0.1029	4
Refractive index, n_D^{30}	1.4820	5
Dipole moment, μ (in benzene)	4.7	1
Relative permittivity, ε	43.3	3,4

[a]For temperature-dependent properties, temp. = 30°C.

purification and tests for impurities have been described (Ref. 3).

The principal advantage of sulpholane for electrochemical measurements is that it combines a fairly high relative permittivity (dielectric constant) with moderate solvating power and outstanding resistance to electrolytic oxidation or reduction and to chemical degradation. Its donor strength towards metal ions is generally similar to that of acetonitrile (Ref. 6 and 7), except that it does not provide any unusual stabilization of silver (I) and copper(I) ions. However, its proton basicity is much lower than that of acetonitrile (Ref. 5 and 8). It generally resembles acetonitrile in being a poor solvator of those anions having low polarisability and/or a localised charge, e.g., chloride and acetate ions.

The most significant disadvantage of sulpholane for many (but not all) electrochemical techniques is its high viscosity, which reduces the sensitivity of many measurements. Sulpholane also exhibits certain peculiarities. For example, for polarograms given by the alkali metal ions (Ref. 3), plots of log $[i/(i_d-i)]$ vs. -E are linear with slopes near the theoretical value of 60 mV for a reversible one-electron reaction, provided that current values corresponding to maximum drop size are used. However, if mean current values are used, the plots exhibit much greater scatter and the best straight lines have slopes considerably greater than 60 mV, typically near 70 mV. The current-potential trace for the rising part of the wave also deviates from that normally encountered, in that as the diffusion plateau is approached, the current at minimum drop size increases proportionately much less than the maximum current does, giving a pronounced flare to the current-potential envelope. Consequently, the polarogram is more drawn-out for mean than for maximum current values. This behavior may be the result of adsorption of an unidentified impurity on the electrode surface.

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The useful potential range of sulpholane is wide. Discharge potentials in 0.1 M Et_4NClO_4 vs. an Ag/(0.1 M $AgClO_4$ in sulpholane) reference electrode were found to be as follows (Ref. 3): +0.04 and -3.50 V at the dropping mercury electrode, and +2.3 and -2.9 V for a current of 2 μA at a platinum electrode of 9 mm^2 area rotated at 60 rad sec^{-1}.

Half-wave potentials for the reduction or oxidation of inorganic electroactive species are listed in Table II, while those for the oxidation of a number of polynuclear aromatic hydrocarbons are given in Table III.

KEY TO TABLE II

1.   The first entry in Table II is the actual electroactive species, the second entry is its source. The concentration is $0.5 - 3 \times 10^{-3}$ M for measurements at the dropping mercury electrode, and ca. 1×10^{-4} M for those at the rotated platinum electrode.

2.   The supporting electrolyte is 0.1 M Et_4NClO_4, except where noted otherwise.

3.   The temperature is 30°C for Ref. 3 and 7, and 40°C for Ref. 6.

4.   All potentials are reduction potentials, and are referred to the following reference electrode (A): Ag/(0.1 M $AgClO_4$ in sulpholane). Headridge et al. (Ref. 6) used the following reference electrode (B): Ag, AgCl/(Et$_4$NCl[sat.] + AgCl[sat.] in sulpholane), having a potential of -1.14 V vs. reference electrode A. The potential of A is +0.700 V vs. SCE(aq.); this directly measured value naturally includes the sulpholane-water liquid junction potential. Attempts to refer potentials in different solvents to a common standard state are controversial. Nevertheless, it may be mentioned that one such procedure (Ref. 3), based on an empirical modification of the Born equation, predicts that the potential of A is +0.66 V vs. SCE(aq.) and, hence, that the liquid junction potential is relatively small (-0.04 V). A more widely accepted procedure, based on the assumption that the free energies of transfer of tetraphenylarsonium and tetraphenylborate ions are equal (Ref. 9), predicts that the potential of A is +0.46 V vs. SCE(aq.), so that the liquid junction potential is quite large (-0.24 V).

5.   All potentials were measured at the dropping mercury electrode, except where otherwise noted.

6.   The majority of measurements reported in Ref. 3 and 7 were made with 3-electrode polarographs under conditions of negligible uncompensated IR-drop. Certain earlier measurements, as well as those reported in Ref. 6, were made with 2-electrode polarographs; IR corrections were large and have been applied.

7.   Slopes of waves reported from Ref. 3 refer to log $[i/(i_d-i)]$ vs. -E plots and are indicated by asterisks, while those from Ref. 6 are $E_{1/4}-E_{3/4}$ values. For entries from Ref. 7, waves were arbitrarily designated as reversible (R) when slopes were within ±10% of the theoretical value (60/n mV). Waves were analyzed using currents at maximum drop size; mean currents exhibited the perturbation described above.

8.   The effect of low concentrations of water has been described in Ref. 6 and 7.

TABLE 2. Half-wave potentials for reduction or oxidation of inorganic substances in sulpholane as solvent

Electroactive Species	Half-Wave Potential, V	Slope, mV	Ref.
Li^+; $LiClO_4$	-2.67	64*	3
Na^+; $NaClO_4$	-2.56	60*	3
	-2.58	64	6
K^+; $KClO_4$	-2.66	58*	3
	-2.69	67	6
Rb^+; $RbClO_4$	-2.67	62*	3
	-2.67	66	6
Cs^+; $CsClO_4$	-2.66	56*	3
NH_4^+; NH_4ClO_4	-2.6[a]	-	7
Tl^+; $TlClO_4$	-1.00	R	7
	-1.00[b]	56	6
Ag^+; $AgClO_4$	-0.19[c]	-	7
	-0.15[b,c]	45	6
Mg^{2+}; $Mg(ClO_4)_2$	-2.59	100	6

Table 2. (continued)

Electroactive Species	Half-Wave Potential, V	Slope, mV	Ref.
Ba^{2+}; $Ba(ClO_4)_2$	−2.42	R	7
	−2.47	41	6
Cu^{2+}; $Cu(ClO_4)_2$	−0.15[d]	−	7
(n=2)	−0.14[b,d]	ca. 90	6
	−0.37[c]	−	7
Zn^{2+}; $Zn(ClO_4)_2$·aq	−1.13	R	7
	−1.13[b]	36	6
Cd^{2+}; $Cd(ClO_4)_2$·aq	−0.81[b]	29	6
Pb^{2+}; $Pb(ClO_4)_2$·aq	−0.76[b,d]	−	6
Mn^{2+}; $Mn(ClO_4)_2$	−1.70	R	7
$Mn(ClO_4)_2$·aq	−1.70[b]	28	6
Co^{2+}; $Co(ClO_4)_2$	−1.34[d]	−	7
$Co(ClO_4)_2$·aq	−1.29[b,d]	ca. 70	6
Ni^{2+}; $Ni(ClO_4)_2$·aq	−0.82[b]	120	6
Al^{3+}; $Al(ClO_4)_3$	−1.78[b]	140	6
La^{3+}; $La(ClO_4)_3$·aq	−2.23	−	7
Sm^{3+}; $Sm(ClO_4)_3$·aq	−1.70,−2.42	−,−	7
(n=1,n=2)	−1.65[b], −2.36[b]	70,35	6
Eu^{3+}; $Eu(ClO_4)_3$·aq	−0.45[b]	87	6
(n=1)			
Ferrocene	−0.30	R	7
	−0.30[c]	R	7
	−0.31[b,c]	−58	6
Cobalticinium perchlorate(reduction)	−1.64[b]	56	6
Ferroin perchlorate(oxidation)	+0.34[b]	R	7
Cl^-; LiCl	+1.39[c,e,f]	−240	6
Br^-; LiBr	+0.20[c,e,f],+0.74[c,e,g]	−260,−150	6
I^-; Et_4NI	−1.01[h], −0.5[i]	R, −	7
	−0.34[c,f], −0.02[c,g]	R, R	7
H_3O^+; $HClO_4$·H_2O	−1.23	−	7
H_2SO_4	−1.9[a]	−	7
$(C_6H_5COOH$	−3.0[a]	−	7)
O_2	−1.56	−	7
(n=1,n=1)	−1.18[b],−1.78[b]	63, 220	6

[a] Measured with 2-electrode polarograph

[b] Supporting electrolyte: 0.1 M $NaClO_4$

[c] Measured at rotated platinum electrode

[d] Maximum present

[e] Supporting electrolyte: 0.1M $LiClO_4$

[f] Electrode reaction probably: $3X^- - 2e \rightarrow X_3^-$

[g] Electrode reaction probably: $2X_3^- - 2e \rightarrow 3X_2$

[h] Electrode reaction probably: $3I^- + Hg - 2e \rightarrow HgI_3^-$

[i] Electrode reaction probably: $2HgI_3^- + Hg - 2e \rightarrow 3HgI_2$

TABLE 3. Anodic differential pulse voltammetry of polynuclear aromatic hydrocarbons
at the glassy carbon electrode in sulpholane as solvent at 30°C (Ref. 10)

Hydrocarbon	$E_{1/2}$[a]	$W_{1/2}$[b]
Anthracene	0.57	47
Benz[a]anthracene	0.68	90
Benz[ghi]perylene	0.51	102
Benz[a]pyrene	0.44	76
Chrysene	0.82	83
Coronene	0.77	83
Dibenz[a,h]anthracene	0.75	78
9,10-Diphenylanthracene	0.53[c]	102
Perylene	0.34[c]	100
Pyrene	0.57	62
Triphenylene	1.09	106
(Ferrocene	-0.31[c]	106)

[a]Evaluated by extrapolating peak potentials to zero pulse amplitude. In V vs.
Ag/(0.1 M AgClO4 in sulpholane) external reference electrode. Supporting electro-
lyte: 0.1 M Bu4NPF6.

[b]Limiting value (for small pulse amplitudes) of width at half peak height, in mV.

[c]Reversible one-electron oxidation. In all other cases ECE reactions perturb half-
wave potentials.

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