

RESULTS AND CONCLUSIONS

From Figure 5, it is evident that the maximum error produced by a transformed spectrum occurs at shifts of 0.5 channel. Figure 6 allows one to predict the maximum error which will occur when a peak of given aspect ratio appears in a shifted composite spectrum, is transformed, and is subjected to a least squares analysis. The significance of these results is that they are exact—the errors here are divorced entirely from errors produced by statistical fluctuations in the spectra.

By applying a transformation to composite spectra before application of least squares spectral analysis, a significant

improvement will occur for those cases where the composite spectrum is shifted by more than 0.5 channel with respect to the standards.

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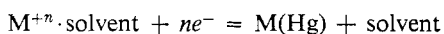
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Relative Polarographic Half-Wave Potential Scales in Dimethyl Sulfoxide and Dimethylformamide

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IN RECENT YEARS the popularity of nonaqueous solvents as reaction promoters and reaction media has vastly expanded. Accordingly, the opportunity and the interest in characterizing solvent-solute interaction has also increased. Often solvents are compared with each other by noting the physical properties, but to make a worthwhile study of solvent-solute interaction one must consider chemical equilibria. In this study an electrochemical approach has been used to gather data that may become useful for comparison of donor atom effects of related solvents. Specifically, polarographic half-wave potentials of several metal ions have been determined in dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) at the dropping mercury electrode. Basically, half-wave potentials are a measure of the relative strengths of the metal ion-solvent bonds (compared to the reference electrode reaction) according to this reaction:



However, in multistep or irreversible reductions, other equations must be written to fit the individual cases. Further, previously determined half-wave potentials in water and ethylenediamine are compared with those in DMSO and DMF by the use of relative potential scales.

Schaap *et al.* (1) reported the results of work done in liquid ammonia and ethylenediamine and compared these two solvents with results in water. Depending upon the solvent, the potential scales become condensed or expanded and some metal ions are shifted to different relative positions. Also, since the half-wave potentials are always reported *vs.* the reference electrode used, these numerical values will, of course, be different for the different solvents.

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Previous polarographic work in DMSO is limited to work done by Reddy (2, 3) and Gutman *et al.* (4-11), who both used a modified aqueous saturated calomel electrode for their reference electrode. Further work was done by Burrus (12) who used both an H-cell with a built-in aqueous saturated calomel electrode and a Heyrovsky single compartment cell with a mercury pool as a reference electrode.

The amount of polarographic data available in DMF is more extensive. Most of it has been organic polarography, but some, of more relevancy to this discussion, has been with metal ions. Previous work in this more limited area has been done by Bruss and DeVries (13), Given and Peover (14), Brown and Al-Urfale (15), Hale and Parsons (16) and Gorman

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(17), all of whom used a mercury pool type reference electrode, except for Gorman who used a mercury/0.1M mercuric nitrate electrode.

EXPERIMENTAL

Apparatus. All polarograms were recorded on a Sargent Model XXI Visible Recording Polarograph in conjunction with a Sargent IR Compensator (S-29320) and a Sargent electrolysis vessel (S-29322).

In DMSO, the reference electrode compartment of the electrolysis vessel contained a saturated solution of zinc perchlorate · 4DMSO in contact with a saturated zinc amalgam. In DMF, the reference electrode consisted of a saturated solution of anhydrous sodium perchlorate in contact with a saturated sodium amalgam.

The three-compartmented electrolysis vessel is fitted with high-resistance asbestos fibers which adequately curtail the diffusion of ions between compartments; consequently, the composition of the reference electrode was not limited by the composition of the solution in the working compartment.

Conductance data indicated that both zinc perchlorate · 4DMSO in DMSO and sodium perchlorate in DMF are strong electrolytes.

Reagents. Zinc perchlorate · 4DMSO, copper perchlorate · 4DMSO and nickel perchlorate · 4DMSO were all prepared by the 2,2-dimethoxypropane method as explained by Starke (18) and applied by Meek, Drago, and Piper (19). This same technique proved successful in the preparation of the corresponding DMF-solvated forms of zinc, copper, and nickel perchlorate. Quantitative analysis using $(\text{NH}_4)_2\text{HPO}_4$ indicated that six molecules of DMF are associated with each molecule of zinc perchlorate.

Cadmium nitrate · 3DMSO (assumed) was prepared from cadmium nitrate · 6 HOH by dissolving the hydrated salt in DMSO and then evaporating under vacuum. This method of preparation is effective because water and DMSO seem to compete fairly evenly for places in the coordination sphere with the concentration of water being insignificant (20).

The saturated zinc amalgam was prepared by the electrolytic deposition of zinc into a layer of pure mercury from an aqueous zinc sulfate solution. The saturated sodium amalgam was prepared by dissolving sodium metal in pure mercury.

All other chemicals were anhydrous.

Procedure. Previous papers (21, 22) describe the details of the procedures for recording and analyzing the polarograms for half-wave potentials. The oxidation potentials of mercury and the reduction potentials of the supporting electrolyte or solvent were obtained by noting the potentials at the intersections of lines drawn tangent to the residual current portion and to the sharply rising portion of the polarograms.

In DMSO the half-wave potentials of antimony(III), copper(II) (two waves), lead(II), cadmium(II), nickel(II), oxygen (two waves), and thallium(I) were determined using 0.1M sodium nitrate as a supporting electrolyte. Barium(II), strontium(II), ammonium, lithium, sodium, and potassium ions were determined in 0.1M tetraethyl ammonium perchlorate.

Table I. Half-Wave Potentials and Slopes of Several Metal Ions in Dimethyl Sulfoxide and Literature Values Where Available

Metal Ion	$E_{1/2}^a$	Slope	$E_{1/2}^b$	$\Delta E_{1/2}$	$E_{1/2}^c$
Na ⁺	-1.001	0.062	-2.07*	1.08	-2.12
K ⁺	-1.016	0.062	-2.11*	1.09	-2.14
Li ⁺	-1.447	0.097	-2.45*	1.00	-2.33
NH ₄ ⁺	-1.031	0.063	-2.13*	1.10	...
Ba ⁺⁺	-0.992	0.034	-2.09*	1.10	-1.92
Sr ⁺⁺	-1.229	0.047	-2.10*	0.87	-2.11
O ₂ (1st)	+0.352	0.067	-0.72**	1.07	-0.05
O ₂ (2nd)	-0.027	0.135	-1.13**	1.10	-0.9
Ni ⁺²	+0.032	0.069	-1.08**	1.05	-0.92
Tl ⁺	+0.542	0.052			-0.46
Cu ⁺² (1st)	+1.084	0.059			+0.04
Cu ⁺² (2nd)	+0.960	0.057			+0.04
Cd ⁺²	+0.384	0.031			-0.60
Pb ⁺²	+0.526	0.032			-0.40
Zn ⁺²	+0.018	0.028			-1.0
Sb ⁺³	+0.786	0.039			-0.30

^a Volts vs. zinc reference electrode as determined in this research.

^b Volts vs. aqueous calomel electrode as determined by Gutmann *et al.* (*) and Reddy (**).

^c Volts vs. calomel electrode in aqueous medium from Meites (23).

In DMF and half-wave potentials of copper(II) (two waves), lead(II), cadmium(II), zinc(II), oxygen (two waves), and thallium(I) were determined using 0.1M sodium nitrate as a supporting electrolyte. Ammonium, lithium, sodium, and potassium ions were determined in 0.1M tetraethyl ammonium perchlorate. In both DMSO and DMF, the concentration of the reducible metal ion was approximately $5 \times 10^{-4}M$.

RESULTS AND DISCUSSION

The reliability and stability of the reference electrodes have been substantiated by the following experimental results. The half-wave potentials of the metal ions were reproducible to ± 2 mv (or better) over a span of several months.

In DMSO the polarographic voltage span was 2.16 v (from +1.33 to -0.83 v) when 0.1M NaNO₃ was used as the supporting electrolyte and 3.05 v (from +1.36 to -1.69 v) when 0.1M Et₄NClO₄ was used as the supporting electrolyte. In DMF the figures are 2.32 v (from +2.48 to +0.16 v) using 0.1M NaNO₃ and 3.20 v (from +2.42 to -0.78 v) using 0.1M Et₄NClO₄. These data were recorded at the beginning and at the end of each working day and they remained constant even though the electrodes were used continuously for 12 to 14 hours at a time. Furthermore, these values remained constant for a period of several months.

In DMSO the electrocapillary point remained at a constant value of $+0.69 \pm 0.01$ v.

By maintaining one of the reference electrodes at 25° C and varying the temperature of the other, a temperature coefficient of 2.2 mv per degree for the DMSO reference electrode and 2.3 mv per degree for the DMF reference electrode was found.

DMSO. In most cases the relative half-wave potentials for metal ions in DMSO agree favorably with those results obtained by Gutmann and Reddy. See Table I. All the discrepancies that do exist are associated with those ions which have irreversible reductions. Also, Reddy was unable

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to suppress the intense maximum observed in the reduction of nickel(II), although several maximum suppressors were tried (including gelatin). However, the nickel maximum was suppressed in this laboratory by using a 0.05% solution of gelatin. The solution was prepared by dissolving the required amount of gelatin in warm DMSO.

The work by Burrus was done at several different concentrations of several different supporting electrolytes, using two different reference electrodes and at two different temperatures; therefore, a comparison is more difficult. However, relative potential differences within a given set of conditions were similar to those in this paper with two exceptions: Burrus obtained only one wave for the reduction of copper(II) and, therefore, a comparison cannot be made and nickel and zinc are switched in the order of their reduction, which points out the difficulty of obtaining reliable data for the irreversible reduction of nickel.

DMF. The correlation between the reduction potentials for metal ions obtained in our laboratory and the work done by Brown (15) and Gorman (17) is generally good. See Table II. The actual differences in half-wave potentials are due to the use of different reference electrodes, but the fact that these differences are constant points to similar results. (The reason for the two different sets of delta values by Gorman is that he used two different reference electrodes.)

Table II. Half-Wave Potentials and Slopes of Several Metal Ions in Dimethylformide and Literature Where Available

Metal ion	$E_{1/2}^a$	Slope	$E_{1/2}^b$	$\Delta E_{1/2}$	$E_{1/2}^c$	$\Delta E_{1/2}$
Li ⁺	-0.354	0.083			-1.81	-1.46
NH ₄ ⁺	-0.169	0.179				
K ⁺	-0.006	0.054			-1.55	-1.54
Na ⁺	+0.018	0.058			-1.53	-1.51
Zn ²⁺	+1.062	0.036	-1.41	2.47	-1.12	+2.18
Ni ²⁺	max.		-1.33		-1.06	
Cd ²⁺	+1.453	0.022	-1.02	2.47		
O ₂ (2nd)	+1.469	0.048				
Pb ²⁺	+1.629	0.037	-0.90	2.53		
Tl ⁺	+1.628	0.059	-0.88	2.51		
O ₂ (1st)	+1.661	0.033				
Cu ²⁺ (2nd)	+1.777	0.087				
Cu ²⁺ (1st)	+2.050	0.037	-0.43	2.48	-0.15	+2.20

^a In volts vs. Na(Hg), NaClO₄ reference electrode as determined in this research.

^b In volts vs. mercury pool by Brown (15).

^c In volts vs. mercury pool by Gorman (17).

Relative Potential Scales. The horizontal voltage scales used in Figure 1 are the same for all solvents. Since the values are relative, the identities of the reference electrodes used are immaterial. Also, the vertical relationship of the scales is arbitrary. We have chosen to position the scales so that the potentials of sodium in the solvents are connected by a vertical line. This implies that the potentials of the Na, Na⁺ electrodes in the solvents are the same. The reduction potentials of sodium were chosen because they occur reversibly in each solvent and because of the noncomplexing nature of the sodium ion in solution.

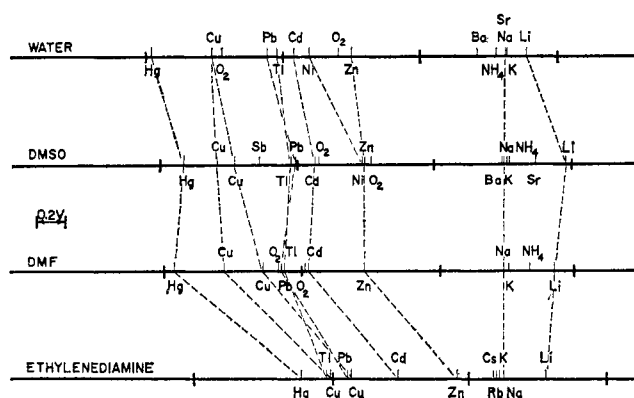


Figure 1. Relative reduction potential scales

The range of reduction in water, DMF, and DMSO is larger than that in ethylenediamine. This demonstrates the weak complexing role of the first three solvents as compared to the strong complexing ability of ethylenediamine.

In DMF the two waves that represent the two-step reduction of oxygen are closer together than those that occur in DMSO, with water showing an even larger separation in these two waves. The reduction of oxygen in DMSO and DMF has been described by Maricle and Hodgson (24). A detailed study of oxygen reduction in DMSO has been done by Johnson *et al.* (25).

The reduction of copper(II) in water occurs in one step. However, copper(II) reduces in two steps in DMSO, DMF, and ethylenediamine. Therefore, all these solvents tend to stabilize the cuprous ion relative to the cupric ion.

As a solvent, DMF appears to be very much like water in its relative solvating ability of various ions (compared to Na⁺, the arbitrary standard). DMSO seems to possess slightly stronger solvating ability for divalent ions than either DMF or H₂O. Ethylenediamine is quite different from water in its solvating properties and is the most strongly solvating of these solvents for the heavy metal ions.

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