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[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Effect of the Solvent on the Polarographic Reduction of Cations[1]

BY DOUGLAS B. BRUSS AND THOMAS DE VRIES

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The effect of the solvent on the reduction of metal ions was investigated at a dropping mercury electrode with a silver-silver chloride electrode as reference. Nine cations were studied in water, ethylene glycol, formamide, dimethylformamide, pyridine, the normal alcohols through pentanol and isopropyl alcohol. The half-wave potentials were found to vary in a regular manner with the dielectric constant of the solvent, usually becoming more positive as the dielectric constant decreased. A correlation was found between the shift in half-wave potential per dielectric constant unit and the quotient of the magnetic susceptibility of the ion divided by the ionic radius. The variation of the diffusion current with the square root of the fluidity of the solvent demonstrated that, for the majority of the ions, viscosity was not the only factor affecting the diffusion coefficients.

The increasing importance and use of organic and other non-aqueous solvents in polarography has led to the need of a greater clarification of the factors affecting the reduction characteristics in such media. Hence, the principal objective in this investigation was the study of cations in organic solvents selected with a wide range of dielectric constants. There was definite correlation between the variation of the half-wave potential and the dielectric constant. The variation of the diffusion current with the viscosity of the media was related to the solvation of the ions.

A variety of organic solvents have been used by previous investigators in the polarographic reduction of selected cations. A study of the alkali metal ions was made by Peracchio and Meloche[2] in water solutions of hydroxy compounds such as methanol and trimethylene glycol. Zlotowski and Kolthoff[3] investigated the reduction of some alkali ions in 50 to 80% ethanol. The fact that they found the half-wave potentials constant with drop-time indicated that the reductions were reversible. Matyas[4] studied the variation of half-wave potential of bivalent metal ions in a variety of alcohols. He attributed a shift to more negative potentials because of the adsorption of the solvent on the mercury drops while a shift to more positive potentials in methanol and ethanol indicated that these are not adsorbed. Univalent ions were not affected. The influence of the viscosity of the solvent on the magnitude of the diffusion currents has been studied in water–ethylene glycol media,[5] in water–ethanol mixtures[6] and other non-aqueous solvents,[7] and apparently the viscosity of the solvent was not the only factor which affected the diffusion current.

Experimental

Reagents.—The organic solvents were dried over the appropriate drying agents such as metallic sodium or calcium hydride and distilled or fractionated in all glass systems equipped with drying tubes. However, it was soon found that the addition of up to 1% water did not appreciably affect the reduction characteristics. The solvents which were selected because of their wide range in dielectric constants are listed in Table I together with their properties. The viscosities there given were determined with Fenske-type glass viscometers for 0.2 *M* LiCl solutions.

All of the metal salts used were chlorides and were reagent grade. The anhydrous chlorides of bismuth, iron(II), lead and zinc were available and were used as such. The hydrated chloride of cadmium was rendered anhydrous by heating at 110°. Chromic chloride hexahydrate was obtained as a special preparation in the department. Cobaltous chloride hexahydrate, cupric chloride dihydrate and manganous chloride tetrahydrate were used as such. Nickel chloride hexahydrate was heated under reduced pressure to constant weight. The lithium chloride for the supporting electrolyte was oven dried at 110° for 24 hours.

The most suitable maximum suppressor was ethyl cellulose, but methyl red and gelatin were also used when water was the solvent.

Apparatus.—A silver–silver chloride electrode was used as anode, thus avoiding complications from liquid boundary potentials. It was prepared from 8 cm. of No. 22 platinum wire, wound into a tight spiral, which was then silver plated and anodized.[8] The same capillary was used for the dropping mercury electrode throughout this investigation. In a 0.2 *M* solution of LiCl in water on open circuit it had a drop time of 3.77 seconds and a capillary constant of 2.00 mg.$^{2/3}$ sec.$^{-1/2}$.

A Leeds and Northrup Type E Electrochemograph was used to record the polarograms. A Rubicon potentiometer was used to check the half-wave potentials to one millivolt. The cell resistances which are listed in Table I were determined for 0.2 *M* LiCl solutions at 1000 cycles using a General Radio Co. Amplifier and Null Detector in a conventional

TABLE I

SOLVENTS USED AND THEIR PROPERTIES

		Dielectric constant	Viscosity, poise	Fluidity$^{1/2}$	Cell resistance
1	Formamide	109.5	0.03532	5.33	510
2	Water	78.5	.00917	10.44	170
3	Ethylene glycol	37.7	.1854	2.32	2,300
4	Dimethylformamide	36.7	.00931	10.38	3,000
5	Methanol	31.5	.00626	12.62	350
6	Ethanol	24.3	.01333	8.66	1,050
7	Propanol	20.1	.02478	6.36	2,200
8	Isopropyl alc	18.0	.02624	6.19	6,400
9	Butanol	18.0	.03304	5.77	7,200
10	Pentanol	15.8	.04370	4.79	20,000

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[1] Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy. February, 1955. Fron the Ph.D. thesis of D. B. Bruss, Purdue University, June, 1954.

[2] E. S. Peracchio and V. W. Meloche, THIS JOURNAL, **60**, 1770 (1938).

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[7] N. Radin and T. De Vries, *Anal. Chem.*, **24**, 971 (1952).

[8] A. S. Brown, THIS JOURNAL, **56**, 646 (1934).

Table II

Half-wave Potentials of Cations

	Bi	Cd	Cr(III)	Cr(II)	Co	Cu	Fe(II)	Mn	Ni	Zn
Formamide	0.152	0.672	0.830							1.044
Water		.638	.868	1.469	1.170	0.169	1.524	1.516	1.070	1.032
Ethylene glycol	.088	.600		1.317	1.148	.218	1.240	1.396	0.926	1.028
Dimethylformamide			.290	1.15						
Methanol	.076	.595	.531	1.301	1.136	.246	1.214	1.357	.917	1.140
Ethanol	.056	.590	.508	1.238	1.082	.280	1.126	1.294	.478 .797	1.209
Propanol	.048	.585	.487		1.066	.291	1.112	1.272	.439	
Isopropyl alc.			.396	1.218		.284	1.128	1.298		
Butanol	.040	.581	.471	1.200	1.063		1.103	1.266	.422	
Pentanol				1.223	1.030		1.120	1.265	.328	

Wheatstone bridge circuit. All measurements were made at 25.0° in a thermostatically controlled water-bath.

Procedure.—The cell solution was prepared by pipetting 10 ml. of 0.05 *M* LiCl stock solution in the appropriate solvent, 5 ml. of the reducible ion stock solution and one ml. of a solution of the maximum suppressor when desired, and diluting to 25.0 ml. in a volumetric flask. Thus a solution was obtained containing 0.2 *M* LiCl which was sufficient to give a relatively low cell resistance. The concentration of the reducible species was approximately 0.0005 *M* and that of the suppressor about 0.001%. As the polarograph cell required only 10 ml., the above dilution gave sufficient solution to rinse the cell and provide for the gas presaturator. Traces of oxygen were removed from the nitrogen used for degassing the cells with vanadous sulfate solutions.[9] The nitrogen was presaturated with solvent before entering the cell solutions.

The values of the half-wave potentials here reported are the averages of three or more determinations and the polarograms were run in both the forward and reverse directions to cancel out recorder lag. The potentials were also corrected for the potential drop through the cell.

Discussion and Results

It may be assumed that there is a relationship between the dielectric constant of a solvent, the solubility of a salt in it and the degree of ionization. Ionic mobility, however, depends on the viscosity of the medium and other factors, hence it is not unreasonable that the cell resistances which varied from 170 to 20,000 ohms are not in the same sequence as the dielectric constants (see Table I). A solvent not listed in the table but used for a limited number of experiments was pyridine with a dielectric constant of 12.5 and a viscosity of 0.00988 poise, which also gave solutions with 20,000 ohm cell resistance.

No difficulty was experienced in obtaining good polarograms. When maxima occurred on the curves, they were generally suppressed with ethyl cellulose. Much trouble was experienced, however, both with formamide and pyridine as solvents.

It was observed that the half-wave potentials became more positive for the solvents having the smaller dielectric constants. The change per unit of dielectric constant varied from 0.2 (in millivolts) in the case of zinc, to the highest value 6.98 in the case of ferrous iron. This is discussed more fully later. It is to be expected that the potential of the AgCl reference electrode in non-aqueous solvents will shift since the activity of the chloride ion will decrease as the dielectric constant decreases. Furthermore, changes in the solubility of the AgCl in the various solvents will also contribute to the effect. However, in any given solvent, the reference electrode will remain the same, and a comparison between ions can be obtained. The half-wave potentials for the different ions in the various solvents are collected in Table II.

A resume of the results follows. Bismuth ion exhibited maxima in all the solvents. A small, sharply pointed maximum occurred on the diffusion plateaus in propanol, butanol, ethylene glycol and in formamide, and could not be suppressed with ethyl cellulose or methyl red. The variation of half-wave potential with dielectric constant was regular. The plot of the diffusion current with the square root of the fluidity of the solvent gave a straight line indicating that the viscosity was the only factor affecting the diffusion coefficients. Bismuth chloride was insoluble in isopropyl alcohol and gave erratic results in pentanol.

Cadmium ion exhibited excellent waves in all of the solvents except isopropyl alcohol and pentanol in which it was insoluble. The variation of half-wave potential with dielectric constant was stricly linear but the variation of the diffusion current with the square root of the fluidity of the solvent split the solvents into two groups as shown in Fig. 2. The alcohols form one group, and water, ethylene glycol and formamide form the second group.

Chromium chloride produced a well-defined two-step reduction wave in most of the solvents. The data in Table II indicate in which solvents only one wave was obtained. Variation of the half-wave potential for both the chromous and chromic ions was regular. The diffusion currents exhibited the same effect as was noted for cadmium in that two distinct lines were produced in a plot with the square root of the fluidity as the abscissa.

Reductions of cobalt ion were not satisfactory in isopropyl alcohol and formamide. The variations of half-wave potential exhibited a definite curvature in regions of high dielectric constant. The variation of diffusion current with solvent viscosity showed a behavior analogous to that of cadmium.

The reduction of the cupric ion was characterized by a short residual current and a large anodic wave occurring before the reduction (cathodic) wave. The diffusion current constant was only about one-half the value reported for the reduction of cupric ion to the metallic state, hence it was assumed that the single reduction wave measured was that for the reduction of a stable cuprous chloride complex. Cuprous ion exhibited the reverse be-

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(9) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

havior from the other ions in that the reductions occurred at more negative potentials with decreasing dielectric constant. Like bismuth, it exhibited a single line in a plot involving the viscosity of the solvents. Reductions in butanol, pentanol and formamide proved unsuccessful due to the large irrepressible maxima which occurred.

Ferrous chloride gave well defined waves in all the solvents except formamide. The variation of the diffusion current with the square root of the fluidity showed a curvature for the data from the alcohol solutions which gradually became parallel to the water–ethylene glycol line at higher viscosities.

Manganous ion exhibited well defined waves in all the solvents except formamide and dimethylformamide. The maxima were easily suppressed with ethyl cellulose.

Nickel ion produced a well defined two-step wave in ethanol in the presence of 0.001 *M* acetic acid. With no acid present the waves were more indefinite. If 0.001% methyl red was added, the first wave became more distinct with an increased diffusion current. Temperature variation studies have shown that the first wave is stable at higher temperatures and that the second wave is stable at the lower temperatures. In 1.0 *N* LiCl the first wave became predominant. Reductions in the other solvents were normal, though there was some evidence for the presence of a second small wave in some of the other alcohols. Variation of the diffusion current with solvent fluidity was similar to that obtained for cadmium.

No waves were obtained for the reduction of zinc in any of the higher alcohols above ethanol. In regions of low dielectric constant the reduction became more negative with decreasing dielectric constant. The plot of the diffusion current *versus* the square root of the fluidity gave a line for the alcohols which intercepted the fluidity axis at a much greater value than for any of the other ions.

The relative shifts of the half-wave potentials for the different ions as the dielectric constant changes can be attributed to changes in complexation or solvation. The double wave of the nickel ion in ethanol appears to be the result of a slow equilibrium between two species of chloride ion complex as evidenced by the effect of temperature and chloride ion activity on the phenomenon. For all of the ions, except the cuprous and the zinc ion in the regions of low dielectric constant, the reductions became more positive as the dielectric constant decreased. This could seem to indicate that the complexes formed in the low dielectric media are less stable and require less energy for the reduction than those formed in media of high dielectric constant. The decrease of the effective chloride ion concentration in media of lower dielectric constant will also tend to shift the potentials in a positive direction.

An interesting correlation was found between the shift in half-wave potential per unit of dielectric constant and the quotient of the magnetic susceptibility divided by the ionic radius. The data for the correlation are given in Table III and represented in Fig. 1. This correlation seems reasonable if both

TABLE III

VARIATION OF HALF-WAVE POTENTIAL WITH DIELECTRIC CONSTANT

	$\Delta E_{1/2}$, mv.	ΔD dielectric constant	$\Delta E/\Delta D$	Ionic radius, Å.	Magnet. suscep.	χ/r
Bi	112	91.5	1.22	1.20	−0.32	−0.27
Cd	91	91.5	1.00	1.03	−0.32	−0.31
Cr(III)	360	91.5	3.93	0.65	44.3	68
Cr(II)	246	62	3.96			
Co	118	22	5.36	.82	90.5	111
Fe(II)	404	62	6.53	.83	101	122
Mn	131	20	6.55	.91	107	118
Ni	153	47	3.25	.78	44.7	57
Zn	16	71	0.23	.83	−0.47	−0.57

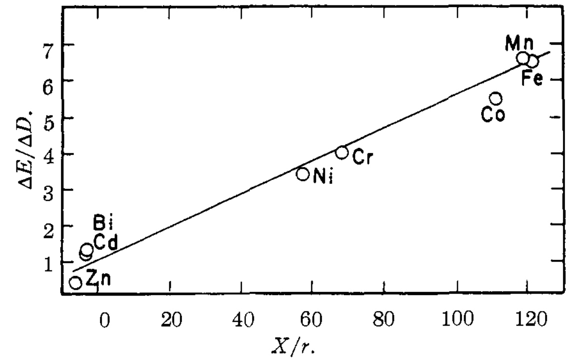

Fig. 1.—Correlation between change of half-wave potential per unit of dielectric constant, magnetic susceptibility and the radius of ion reduced.

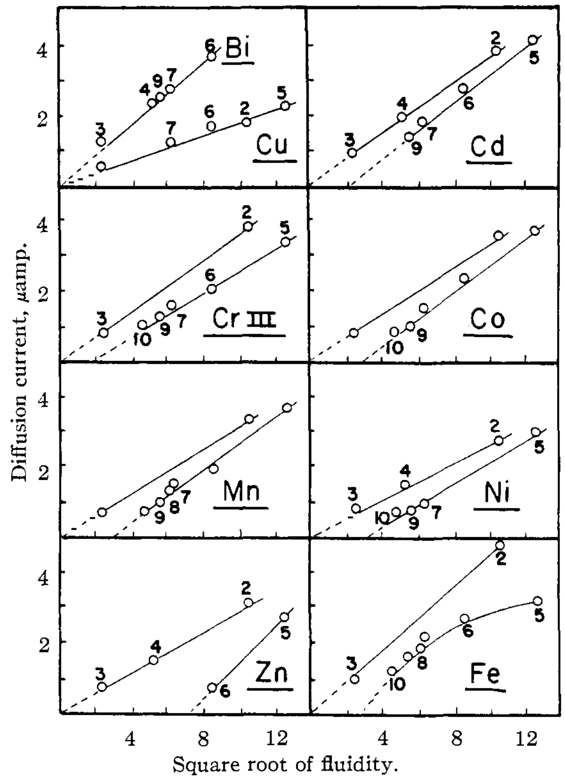

Fig. 2.—Dependence of diffusion current on square root of fluidity. Diffusion current for 5.00 × 10^{-4} molar solutions. Numbers identify solvents as listed in Table I.

Table IV

Values of $n\alpha$ from Slopes of Log Plots

	Bi	Cd	Cr(III)	Cr(II)	Co	Cu	Fe(II)	Mn	Ni	Zn
Formamide	2.48	1.55	0.63							1.82
Water		1.70	0.68	1.27	0.68	1.50	1.79	1.98	0.61	1.89
Ethylene glycol	2.07	1.75		1.15	.59	0.43		2.25		0.68
Methanol	2.30	1.62	1.12	1.06	.72	1.70	1.02	2.07	.54	.68
Ethanol	2.47	1.45	1.02	1.09	.53	0.99	1.37	1.54		.44
Propanol	2.16	1.50	0.94		.51	1.10	1.07	1.35	.88	
Isopropyl alc.			1.11	0.79		0.86	1.07	0.79		
Butanol	2.04	1.28	1.19	.95	.49		1.27	1.05	.81	
Pentanol				.82	.43		1.13	0.93	.55	

magnetic susceptibility and large ionic radius contribute to complexation of the cation and this in turn contributes to the shift in the half-wave potential.

The Stokes–Einstein relation predicts that the diffusion coefficient is a linear function of the viscosity of the medium provided the diffusing species is large in comparison with the solvent molecules. Hence the ratio of the polarographic diffusion current and the square root of the fluidity should be a constant and such has been observed by others.[5–7] If the factors such as the change in the size of the solvated species are operative then the above ratio may not be constant. Such results were observed. The values used for the diffusion current were those obtained in 0.0005 M solutions and the results are shown in Fig. 2 where three separate effects seem to be evident. For the bismuth and copper ions, a plot of the diffusion current *versus* the square root of the fluidity gave a single line passing through the origin indicating that the viscosity of the solvent was the major factor affecting the diffusion coefficient. For cadmium, chromium, cobalt, ferrous iron, manganese and nickel, two parallel lines were obtained. These ions in water, formamide and ethylene glycol gave results which fell on a line which intercepted the origin. The results from the alcohol solutions fell on a parallel line which intercepted the fluidity axis. These data seem to suggest that for these ions the solvation species formed in the alcohols are similar but of a much larger sort than formed in the other solvents. A third effect can be seen for the results with zinc. The line formed by the alcohols was divergent and also intercepted the fluidity axis. The fact that reduction of zinc could not be obtained in the higher molecular weight alcohols seems to indicate a very large solvation species.

All of the polarographic waves were examined by plotting log $i/(i_d - i)$ *versus* the applied voltage, corrected for the potential drop through the solution. The slope of such lines gives $n\alpha/0.059$ and the values of $n\alpha$, when straight lines were obtained, are tabulated in Table IV. The reduction of chromium(III) in the alcohols, and manganese and zinc in water and formamide, gave values corresponding to the valence, but cobalt and zinc in the alcohols show some of the lowest values in the table.

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LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarographic and Coulometric Study of *p*-Dimethylaminoazobenzene

BY H. A. LAITINEN AND T. J. KNEIP[1]

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In acid solution *p*H 1.9 in 50% ethanol, the polarographic reduction of *p*-dimethylaminoazobenzene involves a four-electron reaction to yield the amines, followed by a catalytic hydrogen wave. Coulometric measurements with a mercury poo cathode led to the same result. In strongly alkaline solution, *p*H 13.5, a two-electron polarographic wave was observed. Coulometric measurements indicated an unstable hydrazo compound, which gave an anodic polarographic wave, and which disproportionated slowly to give the original azo compound and the amines. At a *p*H of 9.5, the polarographic wave height corresponded to a little more than two electrons, while the coulometric measurement indicated a four-electron reduction. This disagreement is caused by a disproportionation rate which is slow compared to the polarographic drop life, but fast compared with the duration of a coulometric experiment. (NOTE: The *Chemical Abstracts* name of *p*-dimethylaminoazobenzene would be N,N-dimethyl-*p*-phenylazoaniline.)

The reduction of *p*-dimethylaminoazobenzene by chemical methods has been studied by Jacobson and Kunz.[1,2] They found that the products of zinc reduction in hydrochloric acid medium were amines from the splitting of the azo bond by the addition of four hydrogen atoms, an O-semidine and 2,4′-diamino-5-dimethylaminobiphenyl from the rearrangement of the intermediate hydrazo compound. Catalytic reduction of azo compounds to the amines or hydrazo compounds can be achieved by proper choice of catalyst.[3,4]

Water-soluble sulfonated azo dyes have been re-

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(1) P. Jacobson, *Ann.*, **428**, 76 (1922).

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