It can thus be concluded that the polarographic irreversibility of the reduction of this complex in the absence of excess of the ligand is caused by the *chemical decomposition* of the divalent complex formed as the result of the electron transfer reaction.

Acknowledgment.—The author is indebted to Dr. H. A. Laitinen, University of Illinois, Urbana, Ill., for valuable advice and profitable discussions in connection with this research. Part of the work was carried out under the sponsorship of the Office of Naval Research, Contract N6 ori-07136-NR 052-282 which is gratefully acknowledged.

URBANA, ILLINOIS

[CONTRIBUTION NO. 665 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Polarography in Anhydrous Ethylenediamine. I. The Mercury Pool Anode; Reduction of Some Heavy Metal Ions[1]

BY WARD B. SCHAAP, ARTHUR E. MESSNER AND FREDERIC C. SCHMIDT

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Reversible polarographic waves are obtained with the ions Tl^+, Cd^{++}, Pb^{++} and Cu^{++} in anhydrous ethylenediamine as a solvent. The mercury pool serves as a satisfactory reference electrode in spite of the absence of any depolarizing anion. The anodic reaction occurring at the pool appears to be $Hg \rightarrow Hg^{++} + 2e^-$. Diffusion coefficients for the ions studied in ethylenediamine are about 30–40% of the values in aqueous solution. The order of reduction (*i.e.*, of the half-wave potentials) of the metal ions in ethylenediamine is not the same as in aqueous solutions. The metal ions that form the more stable ethylenediamine complexes become relatively more difficult to reduce when the solvent is changed from water to ethylenediamine.

Introduction

A considerable amount of electrochemical research has been carried out in the solvent liquid ammonia. Polarographic studies,[2–8] electrode potential measurements,[9] solubility[10] and conductance[11,12] measurements have all been made in liquid ammonia as a solvent yielding results of considerable theoretical and practical significance.[13]

Electrochemical research in other amine solvents has been much more limited. For example, although ethylenediamine was isolated as a pure compound by A. W. Hoffman in 1853, it was not until 1935 that Wilson reported extensively on its physical properties.[14] Up to the present time, there have been a few reports on solubilities[15–18] and conductance measurements[18,19–24] in anhydrous ethylenediamine along with several attempts to use the solvent as a medium from which to plate active metals.[20,24] Recently, there has been an increasing amount of interest in ethylenediamine, due to its basic character, as a solvent for the potentiometric titration of weakly acidic substances.[25–28]

An investigation of several phases of electrochemistry in anhydrous ethylenediamine as the solvent medium is under way in this Laboratory. This paper is the first on polarographic studies in this solvent. Ethylenediamine is quite convenient for use as a solvent medium because of its water-like physical properties (m.p. 11.0°, b.p. 116°). Moreover, salts of many metallic elements are sufficiently soluble in ethylenediamine for polarographic study.

Experimental

Apparatus.—A Sargent Model XXI Visible Recording Polarograph was used in these studies. A Rubicon Co. portable potentiometer was employed to accurately measure the applied potential at several points during the recording of each wave. The electrolysis cell used consisted

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(1) Taken in part from a thesis submitted by Arthur E. Messner to the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Master of Arts, June, 1954. Presented in part before the 126th Meeting of the American Chemical Society. Division of Analytical Chemistry. New York. N. Y.. September 16. 1954.

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(5) H. A. Laitinen and C. E. Shoemaker, *ibid.*, **72**, 4975 (1950).

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(8) E. Vecchi. *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.*, **14**, 290 (1953); see *C. A.*, **47**, 7915f (1953).

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of a short, wide tube (*ca.* 4 × 10 cm.) through the bottom of which was sealed a platinum wire for electrical contact to the mercury pool. A three-way stopcock and inlets sealed on the tube at appropriate heights allowed nitrogen to be passed either through or over the solution. The dropping mercury electrode was held in place by means of a tightly fitting stopper.

All polarograms were run at 25 ± 0.2°. The characteristics of the capillary at this temperature and at a column height of 50.0 cm. were t = 4.99 sec. per drop (open circuit) and m = 1.069 mg. sec.$^{-1}$.

Materials.—Ethylenediamine was purchased from Eastman Kodak Co. as 98% material and was further purified and dried by double refluxing and distillation from sodium in an atmosphere of dry hydrogen. Freshly purified and distilled ethylenediamine was tapped directly from the still through a solenoid-operated ground-glass valve into a nitrogen-filled volumetric flask containing a weighed amount of the previously dried salt used for supporting electrolyte. Stock solutions of salts of the metals used in this study were similarly prepared.

Lithium chloride (reagent grade) was chosen as the supporting electrolyte because of the very negative discharge potential of the lithium ion. (Although in these studies saturated LiCl (*ca.* 0.29 *M*) solutions were used, it would probably be more convenient to use a lower concentration, *e.g.*, 0.1 or 0.2 *M* LiCl, because of the considerable length of time needed to reach saturation.) Salts of other metals used were usually chlorides or nitrates and were the best commercially available grades.

Procedure.—Dry, oxygen-free nitrogen was passed through the clean, dry, stoppered polarographic cell for several minutes, after which the ethylenediamine solution and mercury for the pool were poured into the cell and the tightly fitting stopper holding the dropping electrode was placed in position. Nitrogen was bubbled through the ethylenediamine solution for at least 20 minutes to remove dissolved gases. The three-way stopcock was then turned so that the nitrogen passed over the solution while the polarogram was being recorded.

The electrical resistance of the complete cell arrangement including the dropping electrode and the saturated ethylenediamine solution of LiCl was quite high and was measured to be about 1100 ohms even when the lower end of the capillary was placed close to the mercury pool (within 1 cm.). Correction for this electrical resistance was made whenever the iR drop exceeded a millivolt or two.

Discussion and Results

The Mercury Pool Anode.—The polarographic set-up requires a reference electrode which maintains a constant and reproducible potential and against which the potential of the dropping mercury electrode is measured.

The reference electrodes most commonly used in aqueous solutions do not function properly in ethylenediamine because of changed solubility relationships. Thus, since silver chloride is soluble in ethylenediamine, the silver–silver chloride electrode is not depolarized by chloride ion, but acts as a simple silver metal electrode. Also, calomel reacts vigorously when mixed with ethylenediamine producing a grey-black precipitate and droplets of metallic mercury. This behavior suggests that calomel disproportionates in ethylenediamine into mercury and soluble mercuric chloride, which is similar to its behavior in liquid ammonia as reported by Laitinen and Shoemaker[4] and others. No suitable reference electrode of the type: metal, insoluble metal salt (in which the anion of the insoluble salt is the anion of a suitable supporting electrolyte) has been found as yet for use in ethylenediamine, but the problem is being investigated further.

Laitinen and Shoemaker[4] found that the mercury pool anode serves as a fairly satisfactory reference electrode in liquid ammonia, remaining constant to within ten millivolts in spite of the absence of any depolarizing anion. It was decided, therefore, to employ the mercury pool as a temporary, unproved reference electrode in ethylenediamine and then to attempt to find some ion that is reversibly reduced. Since the half-wave potential of a reversibly reduced ion should be constant in a given solution, this ion could then serve as a "pilot ion" and could be used to study the variation in potential of the pool (or any other electrode) and to establish suitability as a reference electrode.

Table I

Reversibility and Reproducibility of Thallium Wave Measured *versus* the Mercury Pool in Ethylenediamine[a]

Concn. Tl^+, mmol./l.	$-E_{1/2}$ (*vs.* Hg pool), *v.*	id/C, μamp./mmole	Slope of Ed.e. *vs.* log $(id - i)/i$
0.173	0.186	2.01	0.061
.342	.191	2.10	.067
.518	.188	2.01	.057
.690	.190	2.03	.061
1.710	.185	2.02	.052

[a] Supporting electrolyte is satd. LiCl (*ca.* 0.29 *M*).

Thallous ion was the first selected for study and possible use as a pilot ion. Table I shows the polarographic data for solutions of varying concentration of thallous ion (added as $TlClO_4$) and containing satd. lithium chloride as supporting electrolyte.

The data in Table I show that thallous ion is reversibly reduced at the dropping electrode *via* a one-electron process with an average half-wave potential of −0.188 volt *versus* the pool. Moreover, the constancy of the $E_{1/2}$ values implies that the mercury pool maintains a fairly constant and reproducible potential.

To investigate further the behavior of the mercury pool, a second series of polarograms was run with a constant concentration of Tl^+ as pilot ion and a varying concentration of mercuric ion. Since the $E_{1/2}$ of reversible thallous waves is itself constant, changes in the apparent $E_{1/2}$ values with added mercuric ion actually represent changes in the potential of the mercury pool reference electrode. The results are presented in Table II.

Table II

Variation of Pool Potential with Added Mercuric Ion[a]

Added Hg^{++}, mmole/l.	0.00	0.017	0.034	0.065	0.166	0.334	0.500
$-E_{1/2}$ of Tl^+ *vs.* pool, v.	.188	.191	.193	.206	.212	.216	.225

[a] Saturated LiCl used as supporting electrolyte; Hg^{++} added as $HgCl_2$.

The potential of the mercury pool in ethylenediamine is a function of mercuric ion concentration, showing that in ethylenediamine the concentration of chloride ion due to the supporting electrolyte does not determine the potential of the pool as is the case with aqueous solutions. The data from the more concentrated mercuric ion solutions show that the shift in potential of the pool approaches, but is somewhat less than, thirty millivolts for a tenfold change in Hg^{++} concentration. It seems certain, therefore, that the potential determining reaction at the mercury pool electrode in ethylenediamine is $Hg \rightleftarrows Hg^{++} + 2e^-$.

With the smaller quantities of added Hg^{++} the shift in potential of the pool becomes less and the potential gradually approaches the value for no added Hg^{++}. Actually, there is a small concentration of Hg^{++} produced at the surface of the pool due to its functioning as the anode in the polarographic cell and due to reaction of reducible impurities with the mercury. (In view of the great stability of the solvated Hg^{++} ion in ethylenediamine, as evidenced by an over-all stability constant, k_1k_2, of $10^{23.4}$ for the aqueous mercuric–ethylenediamine complex,[29] mercury is undoubtedly a stronger reducing agent in ethylenediamine than it is in water.) The concentration of Hg^{++} which is produced at the mercury pool surface and which establishes the constant and reproducible potential of the pool even when no Hg^{++} is added or no depolarizing anion is present can be estimated by plotting the data for the more concentrated solutions (Table II) and extrapolating back to -0.188 volts, the $E_{1/2}$ of Tl^+ *versus* the pool with no added Hg^{++}. This concentration is approximately 2×10^{-5} molar mercuric ion.

Reduction of Some Heavy Metal Ions.—Since the mercury pool functions as a reasonably reproducible reference electrode in ethylenediamine, it was used in studying the polarographic characteristics of a number of heavy metal ions. The data in Table III were obtained with solutions containing satd. LiCl as supporting electrolyte and varying concentrations of the ion being studied. The figures listed are average values from at least six polarograms.

TABLE III

POLAROGRAPHIC CHARACTERISTICS OF A NUMBER OF METAL IONS IN ETHYLENEDIAMINE

Ion	$-E_{1/2}$ (*vs.* Hg pool), v.	Slope of $E_{1/2}$ *vs.* log $(id - i)/i$	$id/Cm^{2/3}t^{1/6}$	D, cm.^{2} sec.$^{-1}$ $\times 10^7$
Tl^+	0.188	0.059	1.47	5.88
Cu^{++} (1st)	.219	.060	..	
(2nd)	.350	.052	2.12[a]	3.05[a]
Pb^{++}	.333	.031	2.25	3.43
Cd^{++}	.696	.034	2.14	3.10
Hg^{++}	(0.0)[b]	...	2.12	3.05

[a] This value is calculated from the combined heights of both waves. [b] The reduction of Hg^{++} always begins at zero applied potential when referred to the mercury pool as reference electrode. However, the potential of the pool itself is a function of Hg^{++} concentration as shown in Table II.

Lead and cadmium are reversibly reduced *via* two-electron processes. Solutions of Cu^{++} give two waves quite close together which are not completely resolved. Since the combined heights of the two waves lead to a value of $i_d/Cm^{2/3}t^{1/6}$ very close to that of Cd^{++} and Pb^{++} and different from that of Tl^+, it is obvious that in ethylenediamine, as in liquid ammonia,[5] the solvated cupric ion first reduces to the cuprous ion and then to the amalgam. In the analysis of the two copper waves for reversibility, the height of the first wave was assumed to be exactly one-half the total wave height. With this assumption, the plots of $E_{d.e.}$ *versus* $\log(i_d - i)/i$ indicate reversible one-electron reactions for each of the two waves. The second copper wave appears to be slightly steeper than a reversible wave, but this may be due to the presence of a slight maximum (see below).

(It is of interest to note that Laitinen and Shoemaker[5] found that Cu^{++} is reduced *via* two one-electron steps in liquid ammonia also. However, in that solvent the two waves for copper are much more widely separated than in ethylenediamine, the $E_{1/2}$ values being -0.15 and -0.52 volt *versus* the mercury pool in liquid ammonia. This indicates that solvated Cu^+ is more stable relative to solvated Cu^{++} in liquid ammonia than it is in ethylenediamine. Thus, in liquid ammonia the first reduction will be easier compared to the second. The probable reason for this difference in the relative stabilities of Cu^+ and Cu^{++} in the two amine solvents lies in the fact that Cu^+, which prefers a linear configuration in its coördination compounds, cannot "chelate" the bidentate ethylenediamine without strain and thus is less stable in this solvent relative to Cu^{++} which forms very stable chelates with ethylenediamine.)

The data for Tl^+ and Hg^{++} are included in Table III for comparison. Since the mercuric ion wave begins at zero applied potential and residual current values are difficult to choose so near to the threshold of the anodic dissolution wave, no attempt was made to analyze for the reversibility of the mercuric reduction wave.

Some difficulty was encountered due to the appearance of maxima in the waves with the more concentrated solutions. Pronounced maxima were observed with Tl^+ solutions at concentrations greater than 1.5 millimolar, and with Pb^{++} solutions greater than 1.0 m*M*. Slight irregularities appeared in the Cd^{++} waves at concentrations above 2.0 m*M*. The second copper wave showed a large maximum above 0.6 m*M*, but the first wave showed none even at much higher concentrations. In the case of each of the above ions the maxima disappeared when the concentration of the ion was decreased sufficiently.

The diffusion coefficients calculated from the polarographic data for the cations listed in Table III parallel the values given for the ions (at infinite dilution) in aqueous solution,[30] but are only about 30–40% as large. For a given cation at a given concentration, the height of the polarographic wave in ethylenediamine will be about two-thirds the height of the wave for the same concentration of the cation in aqueous solution, capillary characteristics remaining constant.

Several investigators[18–24] have carried out conductance measurements on solutions of uni-univalent salts in ethylenediamine. Limiting equivalent conductances at infinite dilution for some of these salts in ethylenediamine are estimated and the

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(29) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 518–519.

(30) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., Vol. I, Interscience Publishers, New York, N. Y., 1952, p. 52.

values are about 50% of the limiting equivalent conductances for the same salts in aqueous solution. No data have been reported on conductances of bi-univalent salts; nor have any values for individual ionic conductances been reported from which diffusion coefficients of ions could be calculated for comparison with our polarographic values.

The half-wave potentials in ethylenediamine given in Table III show some interesting differences in order of reduction compared to aqueous solutions. In aqueous solutions the order of ease of reduction is $Cu^{++} > Pb^{++} > Tl^{+} > Cd^{++}$ while in ethylenediamine the order is $Tl^{+} > Cu^{++} \geq Pb^{++} > Cd^{++}$.

When comparing the half-wave potentials in aqueous and ethylenediamine solutions it must be remembered that the numerical values for $E_{1/2}$ for one particular cation in each of the two solvents cannot be expected to be the same or even to be directly related in any absolute sense for the reasons listed below. (Relative comparisons for a series of cations do have significance, however, as explained below.)

(1) The potentials in ethylenediamine reported here are referred to the mercury pool in a satd. LiCl (ethylenediamine) solution, while the potentials in aqueous solution are referred to a mercury pool in satd. KCl (aqueous) solution, *i.e.*, the satd. calomel electrode. However, the potential determining reactions occurring at the mercury pool in the two solvents (and the reference electrode potentials themselves) are entirely different, since Hg^{++} is the oxidation product in ethylenediamine while Hg_2^{++} or an insoluble mercurous salt is the product in aqueous solution.

(2) An unknown and probably large liquid junction potential is included implicitly when the numerical values of $E_{1/2}$ for a given cation in the two solvents are compared, and any attempt to relate the potentials in the two solvents to the same reference electrode would always encounter the junction potential.

(3) The interaction of the solute cations with the solvent (energy of solvation) may not vary uniformly for all cations between the two different solvents, causing the $E_{1/2}$ values for the various cations to be shifted relative to each other.

For a series of cations whose half-wave potentials are determined in both ethylenediamine and water, the first two of the factors in the preceding paragraphs will remain constant over the entire series and will contribute a constant amount to the difference (shift) in the numerical values for $E_{1/2}$ of each cation in the two solvents. Thus, any relative changes in the difference in $E_{1/2}$ values, or in the order of reduction between the two solvents, must reflect changes in relative energies of solvation of the various cations in the two solvents.[31] The half-wave potentials at 25° in ethylenediamine and in aqueous solutions for the cations included in this study are listed in Table IV. Also shown is the shift in the half-wave potentials for each cation between the two solvents, *i.e.*, $\Delta E_{1/2}$(en-aq). Since no values for the free energies of ions in ethylenediamine solution are available for comparison with the relative shifts in the half-wave potentials, we have chosen instead to compare the shifts with the over-all stability constants of the metal–ethylenediamine complexes as measured in aqueous solution at 25°. The stability constants are a measure of the tendency of ethylenediamine to replace the water in the coördination sphere of the cation, and as such are a measure of the comparative energies of attraction of the cations for ethylenediamine and water. (It is immaterial whether the shifts in $E_{1/2}$ are compared with the ΔF values for the complex forming reaction, or with the logarithm of the stability constant, since these quantities are related by a constant term, $-\Delta F = RT \ln K_N$.)

TABLE IV

COMPARISON OF HALF-WAVE POTENTIAL SHIFTS FOR METAL IONS BETWEEN ETHYLENEDIAMINE AND WATER WITH STABILITY CONSTANTS OF THE METAL–ETHYLENEDIAMINE COMPLEXES

Ion	$E_{1/2}$ in ethylenediamine,[a] (*vs.* Hg pool), v.	$E_{1/2}$ in aqueous soln.[b] (*vs.* S.C.E.), v.	Relative shift, $\Delta E_{1/2}$ (en-aq), v.	Log K_N of aqueous metal–ethylenediamine complex
Tl^{+}	−0.188	−0.459	+0.269	0.4[c]
Pb^{++}	− .333	− .388	+ .055	...
Cd^{++}	− .696	− .578	− .118	12.2[d]
$Cu^{++}(\rightarrow Cu^{\circ})$	(− .28)[e]	+ .02	− .305	20.0[d]
$Cu^{++}(\rightarrow Cu^{+})$	− .22	(− .093)[f]		
$Cu^{+}(Cu^{\circ})$	− .35	(+ .275)[f]	− .62	...
Hg^{++}	(.0)[g]	(+ .47)[h]	− .47	23.5[d]

[a] Supporting electrolyte is satd. LiCl (*ca.* 0.29 *M*) in ethylenediamine. [b] Supporting electrolyte is KNO_3, usually 0.1 *N* KNO_3 if such data were available. [c] Taken from J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 177–178. [d] Values taken from Martell and Calvin, reference 29. [e] The two-electron reduction of Cu^{++} to the amalgam does not occur in ethylenediamine. The value given is calculated by the usual procedure from the volt-faradays of the two one-electron reactions. [f] This reaction does not occur in aqueous solution. The value listed is the calculated value given by Latimer[32] for the E° of this reaction *vs.* the S.C.E., which in turn is taken to be +0.246 volt *versus* the hydrogen electrode. [g] To be consistent with the $E_{1/2}$ values for the other cations in ethylenediamine, this potential must be considered to be the potential of the mercury pool in ethylenediamine with no Hg^{++} added. Actually, as discussed above, there is probably a concentration of about 2×10^{-6} *M* Hg^{++} present at the surface of the anode which depolarizes the mercury pool anode and establishes its fairly reproducible potential. [h] This is the value calculated by the Nernst equation for the potential of a mercury pool in an aqueous solution containing 2×10^{-6} *M* Hg^{++}, *i.e.*, under the same conditions as presumably obtain in ethylenediamine. (It is also approximately the potential at which the anodic dissolution current becomes large in an aqueous solution that contains no anions that precipitate or complex either Hg_2^{++} or Hg^{++}.)

The data in Table IV show that the ions which become relatively more difficult to reduce when the solvent is changed from water to ethylenediamine are precisely those that form the more stable coördination complexes with ethylenediamine. In fact, the relationship between the half-wave po-

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(31) W. A. Pleskov and A. M. Monasson (*Acta Physicochim., U.R.S.S.*, **2**, 621 (1935)) compared electrode potentials of a series of ions in liquid ammonia at −50° and in aqueous solution at 20°. See also H. Strehlow, *Z. Elektrochem.*, **56**, 827 (1952).

(32) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 185.

tential shift and log K_N appears to be linear, as shown in Fig. 1.

The data in Fig. 1 compare reactions involving two chemical equivalents. This is done because most of the cations being compared are bivalent and their reductions involve two electrons. The reactions involving monovalent cations must therefore be doubled and their equilibrium constants squared in order to conform to this basis. Thus, the value plotted for K_N of Tl^+ is $(10^{0.4})^2 = 10^{0.8}$. *Moreover, the equation of the straight line shown in Fig. 1 has the form of a Nernst equation for a two-electron process and is* $\Delta E_{1/2}(\text{en-aq}) = E' - 0.059/2 \log K_N$. In this equation E' is a constant term which includes both the liquid junction potential and the difference in potential arising from the fact that the electrode reaction at the mercury pool is different in the two solvents. K_N is the over-all stability constant on the basis of two chemical equivalents. A more detailed examination of the thermodynamic significance of this linear relationship will be given in a subsequent paper.

The stability constant of the aqueous lead–ethylenediamine complex has not been previously reported. From Fig. 1, its over-all stability constant may be estimated to be $10^{7.5\pm1}$.

Similarly, the square of the stability constant of the cuprous complex can be obtained from Fig. 1 (if the straight line is extended sufficiently) and is $10^{29\pm1}$. Thus, its stability constant (which cannot be measured in aqueous solution) is estimated from these polarographic data to be $10^{14.5\pm0.5}$.

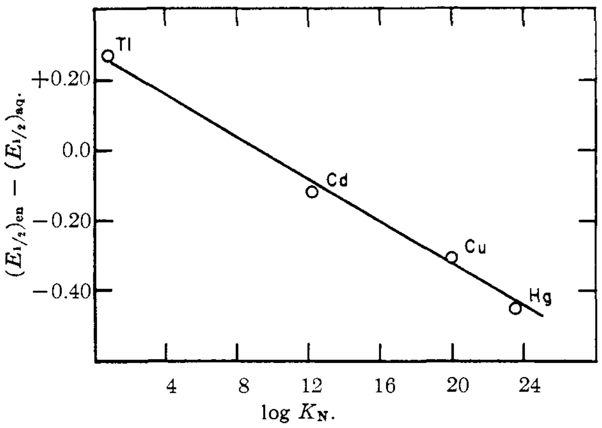

Fig. 1.—Plot of shift in half-wave potentials between ethylenediamine and aqueous solutions for several metal ions *versus* the logarithm of the over-all stability constants of their aqueous ethylenediamine complexes.

Approximate over-all stability constants of other cations with ethylenediamine can be estimated similarly if reversible potentials are known for the reduction of the cations in anhydrous ethylenediamine as a solvent. Furthermore, there seems to be no reason why this method of obtaining approximate over-all stability constants cannot be extended to other liquid solvents whose molecules can serve as coördinating ligands for metal ions.

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BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Interaction of β-Particles with Organic Liquids in the Presence of Vinyl Monomers[1]

BY W. H. SEITZER[2] AND A. V. TOBOLSKY

RECEIVED DECEMBER 20, 1954

Solutions of common organic liquids with vinyl monomers (either styrene or methyl methacrylate) have been exposed to a point source of β-particles, and the resulting rates of polymerization were measured for several monomer concentrations. An expression was derived which relates rate of chain initiation to the measured rate of polymerization in terms of the average absorption coefficient for the β-particles. The number of radical chain starters produced in the various organic liquids per 100 e.v. of energy absorbed was thereby calculated.

One method of studying the effects of high energy β-particles on organic liquids is to allow the resulting fragments to react with a known concentration of an active substance which undergoes a simple and measurable chemical change. In the experiments here reported the active substance is a vinyl monomer, either styrene or methyl methacrylate, which polymerized under these conditions. Various concentrations of monomer in organic liquids have been irradiated by placing a source of pure β-radiation in the center of a spherical container having a diameter large enough to stop all of the particles. The resulting rates of polymerization of the monomers have been measured.

The Source.—The source of radiation was an equilibrium mixture of Sr^{90} and Y^{90} chlorides deposited in a thin glass bulb 3 mm. in diameter. The bulb was blown on the end of a 1 mm. diameter capillary, the other end of which was ring-sealed to a 7/25 standard taper joint. This apparatus was inserted into a spherical flask in such a manner that the bulb was in the center of the flask.

Both Sr^{90} and Y^{90} are pure β-emitters with energies of 0.61 and 2.24 Mev., respectively. The half-life of Sr^{90} is 19.9 years. By measuring the activity of an aliquot portion, the total activity of these isotopes in the bulb was estimated to be 1.74×10^{10} counts/min. The average thickness of the glass bulb was shown from absorption measure-

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[1] This article is based upon a dissertation submitted by W. H. Seitzer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. Allied Chemical and Dye Corporation Fellow, 1952–1953; General Electric Company Fellow, 1953–1954.

[2] Sun Oil Company Laboratories, Norwood, Pennsylvania.