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[CONTRIBUTIONS FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Alkaline Hydrolysis of Methyl Propionate in Acetone–Water Mixtures and Solutions of Different Ionic Strength[1]

BY JOHN E. QUINLAN AND EDWARD S. AMIS

RECEIVED APRIL 1, 1955

The hydroxide ion catalyzed hydrolysis of methyl propionate has been carried out at 15.00, 25.00 and 35.03° in a number of acetone–water mixtures of known dielectric constant, and in aqueous solutions containing varying amounts of sodium nitrate. The effect of dielectric constant on reaction rate has been interpreted by a treatment of Amis based on simple electrostatic consideration of ion–dipole interactions. The effect of ionic strength on specific rate has been interpreted according to the theory of Amis and Jaffé which yields satisfactory quantitative agreement. The activation energy and logarithm of the Arrhenius frequency factor have been calculated for each of the several reaction media. A comparison of the hydrolysis has been made with the hydrolysis of ethyl acetate in ethanol–water and acetone–water solvents.

Potts and Amis[2] studied the alkaline hydrolysis of ethyl acetate in ethyl alcohol–water solvents, and in ethyl alcohol–water solutions of dielectric constant 65.0 containing sodium nitrate. Their data conformed to the requirements of the Amis–Jaffé equation[3] with respect to the salt effect, but gave an enhanced dielectric constant effect on this rate as calculated by this equation.

Amis and Siegel[4] studied the alkaline hydrolysis of ethyl acetate in acetone–water solvents and in a water–acetone solvent having a dielectric constant of 75.25 and containing different concentrations of sodium nitrate. These investigators again found agreement with the Amis–Jaffé theory with respect to the ionic strength effect upon the rate. Here again, however, the dielectric constant effects were enhanced but by an order of magnitude less than in the case of the ethyl alcohol–water media studied by Potts and Amis.

Hockersmith and Amis[5] studied the acid hydrolysis of methyl propionate in acetone–water solvents and in water containing various concentrations of sodium nitrate. The data obeyed the Amis[6] equation with respect to the dielectric constant effect upon the rate; however, the ionic strength effect was that of a catalytic catenary similar to the type "b" catenary discussed by Bell.[7]

Nair and Amis[8] found that the acid hydrolysis of ethyl acetate in dioxane–water media agreed with the Amis equation at all temperatures, and the same reaction in acetone–water agreed with the Amis theory except that at the highest temperature of 55° studied by them the parameter r calculated was unreasonably large.

It was thought to be of interest to study the alkaline hydrolysis of methyl propionate in acetone–water media and in various concentrations of sodium nitrate to ascertain whether the alkaline hydrolysis was amenable to the Amis theory as was the acid hydrolysis and also to find if the salt effect conformed to the Amis–Jaffé theory in contrast to the acid hydrolysis which did not conform to this theory. It was also thought of interest to subject the Potts–Amis and the Amis–Siegel dielectric constant data to the Amis treatment.

Experimental

Weights, volumetric apparatus, thermometers and a stopwatch were calibrated against Bureau of Standards calibrated prototypes except for the stopwatch which was calibrated against Western Union time. The constant temperature baths remained at a desired temperature within ±0.02°.

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(1) This work was done on a contract made by the Institute of Science and Technology of the University of Arkansas with the office of Naval Research. This paper is an abstract from a thesis presented by John E. Quinlan to the Graduate Faculty of the University of Arkansas in partial fulfillment for the Master of Science degree.

(2) J. E. Potts and E. S. Amis, THIS JOURNAL, **71**, 2112 (1949).

(3) E. S. Amis and G. J. Jaffé, *J. Chem. Phys.*, **10**, 598 (1942).

(4) E. S. Amis and S. Siegel, THIS JOURNAL, **72**, 674 (1950).

(5) J. L. Hockersmith and E. S. Amis, *Anal. Chim. Acta*, **9**, 101 (1953).

(6) E. S. Amis, *J. Chem. Educ.*, **30**, 351 (1953).

(7) R. P. Bell, "Acid–Base Catalysis," The Clarendon Press, Oxford, 1941, pp. 6–10, 21–35.

(8) P. M. Nair and E. S. Amis, *Anal. Chim. Acta*, **9**, 111 (1953).

Commercial methyl propionate was treated 24 hours with Drierite and fractionated using a fractionating column packed with glass helices. The fraction distilled between 79.5 and 79.6° corrected to standard pressure was retained. This fraction had a refractive index at 25.00° of 1.3742, and at 25.00, 34.98 and 45.04° had the respective densities of 0.9081, 0.8944 and 0.8787 g./cm.^{3}. Munch[9] reported the boiling point of methyl propionate to be 79.0° and its refractive index and density at 25° to be 1.373 and 0.9107, respectively.

Reagent grade acetone was treated with solid potassium permanganate for 48 hours and distilled. The heart cut of the distillate was dried for 24 hours over anhydrous potassium carbonate and fractionated through the column packed with glass helices. The fraction distilling between 55.7 and 55.8° corrected to standard pressure was collected. The refractive index of this fraction was 1.3562 at 25.00°, and its densities were 0.7950, 0.7838 and 0.7729 g./cm.^{3} at 15.00, 25.00 and 35.03°, respectively. Values[10] of 0.7958 and 0.7844 g./cm.^{3} at 15 and 25°, respectively, for the density of the acetone were found in the literature.

All stock solutions of sodium hydroxide were prepared from freshly boiled distilled water and were protected from carbon dioxide by tubes of Ascarite.

Solutions containing the reactants were prepared for rate studies as described below. A sufficient volume of standard sodium hydroxide to yield a 0.0200 M solution of the alkali upon dilution was pipetted into a 500-ml. volumetric flask. In the dielectric constant effect studies the desired volume of acetone was then pipetted into the flask. In the case of ionic strength studies, the requisite amount of standard sodium nitrate solution was added to the flask. The flask was filled with distilled water to within about 20 ml. of the mark and allowed to come to temperature equilibrium in the bath. To initiate the reaction there was added to the flask 10 ml. of freshly prepared aqueous solution of methyl propionate at the proper temperature and of such a concentration as to yield a reaction solution of 0.0100 M in the ester. Zero time for the reaction was taken as the mid-point of addition of the ester solution. The flask was quickly filled to the mark with distilled water, well shaken, and its contents poured into a clean, dry 500-ml. bottle immersed in the bath. Bringing the flask to volume and mixing the contents required about 90 seconds after which the first sample was taken.

Difficulty in handling the volatile ester resulted in poorer control of its concentration than of any other factor in the rate studies. This factor, it was estimated, could be off by ±0.0002 part in 0.0100.

When the reaction temperature was 35°, six 50-ml. samples were taken as quickly as possible. At 15 and 25° samples were withdrawn at appropriate intervals during the first 85% of the reaction. The samples in all cases were pipetted into a measured excess of hydrochloric acid to inhibit the hydrolysis. Each sample was timed when half its volume had been added to the acid. The excess acid was titrated to the emerald green end-point of brom thymol blue with dilute standard sodium hydroxide. After the sixth sampling, the reaction was allowed to stand for at least 20 half lives, when three 50-ml. samples were withdrawn and titrated as explained above. From these last three titrations, the final sodium hydroxide concentration was determined.

Because of the uncertainty in the concentration (±2%) of the ester solution due to the difficulty in handling the volatile material the difference in the initial and final amounts of sodium hydroxide was taken as the initial amount of the ester and the difference in the sodium hydroxide concentrations at any time and finally was taken as the ester concentration at that time.

The values of the specific velocity constant k' were calculated using the second-order rate equation

$$k' = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \qquad (1)$$

where a and b are the moles per liter of base and ester, respectively, and x is the moles per liter of each reactant that has reacted in t seconds. The units of k' then are liters/mole-second. If a plot of log $(a - b)/(b - x)$ *versus* t is made the slope of the line is $(a - b)k'/2.303$. Thus k' equals the slope of the line multiplied by $2.303/(a - b)$. Now $a - x = C_t$ the concentration of sodium hydroxide at time t, hence $(a - x)/(b - x) = C_t/(C_t - C_f)$. The log $C_t/(C_t - C_f)$ or its equivalent $[(M_a/N_b) - T_t]/(T_f - T_f)$ was actually plotted *versus* t in the calculations of k'.

T_t = ml. of sodium hydroxide to titrate sample at time t
T_f = ml. of sodium hydroxide required to titrate final sample
N_b = sodium hydroxide titrant, N
M_a = mequiv. of hydrochloric acid used per sample

All runs were repeated two or more times and the specific rate constants reported are average values of the constants.

From the volume of acetone at a given temperature in a solution, the density of acetone at that temperature, like quantities with respect to water, and the total volume of the solution the weight per cent. of the acetone in that solution was calculated. Table I contains the average values of the rate constants determined in acetone–water media. The average per cent. precision for each determined k' value is included in the last column of the table. The dielectric constants recorded in the table were taken from the work of Åkerlöf.[11]

TABLE I

SPECIFIC RATE CONSTANTS IN ACETONE–WATER MEDIA

Wt. % acetone	Dielectric constant D	Av. k', l./mole sec.	Av. % dev.
0.00	82.26	0.0937	0.2
8.12	77.64	.0910	0.7
16.59	72.51	.0850	0.0
25.43	67.06	.0737	1.0
34.66	61.06	.0615	0.1
44.31	57.70	.0510	0.7
54.42	47.97	.0415	0.1
65.00	40.83	.0353	2.6
0.00	78.54	0.187	0.9
8.03	74.16	.172	.3
16.42	69.25	.157	1.7
25.20	63.99	.136	0.4
34.39	58.16	.114	.4
44.00	52.09	.0929	0.3
54.09	45.60	.0780	.0
64.70	39.00	.0679	.7
0.00	74.92	0.341	0.7
7.95	70.78	.305	.6
16.27	66.01	.275	2.2
24.99	60.90	.236	1.3
34.13	55.57	.199	1.3
43.75	49.77	.171	1.2
53.85	43.48	.144	1.9
64.45	37.20	.125	1.2

Table II contains the average values of the specific velocities together with their average per cent. precision as determined in solutions containing various concentrations of electrolytes.

Discussion of Data

The treatment developed by Amis[12] to explain the effect of changing dielectric constant on the rates of ion–dipolar molecule reactions was applied to the data in Table II. The equation used was

$$\ln k'_{D=D} = \ln k'_{D=\infty} + \frac{Z\epsilon\mu}{2.303DkTr^2} \qquad (2)$$

where $k'_{D=D}$ is the specific rate constant at any dielectric constant, D, $k'_{D=\infty}$ is the specific rate constant at reference dielectric constant infinity, Z is the valence of the reacting ion, ϵ is the electronic

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(9) J. C. Munch, THIS JOURNAL, **48**, 994 (1926).

(10) "International Critical Tables," Vol. VIII, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 33.

(11) G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

(12) E. S. Amis, *J. Chem. Educ.*, **30**, 351 (1953).

TABLE II

SPECIFIC RATE CONSTANTS IN SOLUTIONS OF VARYING ELECTROLYTE CONCENTRATIONS

Temp. (°C.)	Total electrolyte concn.	Av. k', l./mole sec.)	Av. % precision
15.00	0.0200	0.0937	0.2
	.0550	.0920	.5
	.1000	.0899	.3
	.2000	.0860	.1
	.3000	.0841	1.2
	.6000	.0759	1.3
25.00	0.0200	0.185	0.9
	.0500	.183	1.1
	.1000	.175	1.1
	.2000	.170	1.5
	.3000	.164	1.4
	.6000	.158	0.6
35.03	0.0200	0.341	0.7
	.0500	.327	1.0
	.1000	.320	1.8
	.2000	.309	1.5
	.3000	.307	1.7
	.6000	.278	0.5

charge, μ is the dipole moment of the reacting molecule, k is the Boltzmann constant and r is the distance of approach necessary for reaction to occur between the ion and the molecule.

As suggested by this equation plots of ln $k'_{D=D}$ *versus* $1/D$ were made and gave the requisite straight lines in the region of higher dielectric constants as can be seen from Fig. 1. From the slope, S, of the straight line portion of the curve r was calculated using the expression

$$r = \sqrt{\frac{Z\mu\epsilon}{2.303kTS}} \quad (3)$$

The dipole moment of methyl propionate was taken as 1.8 Debye units in agreement with the recorded values[13] of 1.7, 1.8 and 1.79 Debye units for methyl acetate, ethyl acetate and ethyl propionate, respectively. The values of r were calculated in this manner also for the Potts and Amis and Amis and Siegel data which as already mentioned gave enhanced dielectric constant effects upon the rate as calculated by the Amis–Jaffé theory. The values of r calculated for the three data are recorded in Table III.

Although the values for r are rather small especially in the case of the ethyl acetate in water and ethanol–water, the results are as a whole gratifying; and this treatment gives considerably better agreement with data on the dielectric constant effect with respect to the alkaline hydrolysis of these esters than does the Amis–Jaffé treatment.

TABLE III

THE VALUES OF r CALCULATED FOR THE ALKALINE HYDROLYSIS OF METHYL PROPIONATE AND OF ETHYL ACETATE

Ester	Solvent	Temp., °C.	$r \times 10^8$, cm.
Methyl propionate	Water and acetone–water	15.00	1.4
		25.00	1.4
		35.03	1.3
Ethyl acetate	Water and acetone–water	0.00	1.5
		15.87	1.8
		26.10	2.0
Ethyl acetate	Water and ethanol–water	0.00	0.9
		9.80	0.9
		19.10	1.0

A word might be said about the difference in the assumptions made in deriving the Amis and the Amis–Jaffé equations. The former equation was derived from purely electrostatic considerations without particular assumptions as to the formation of an intermediate complex. On the other hand Amis and Jaffé assumed that a critical complex was formed and followed the procedures of Christiansen[14] and of Scatchard[15] in calculating the concentration of this complex.

A plot of the specific rate constant *versus* ionic strength is given in Fig. 2.

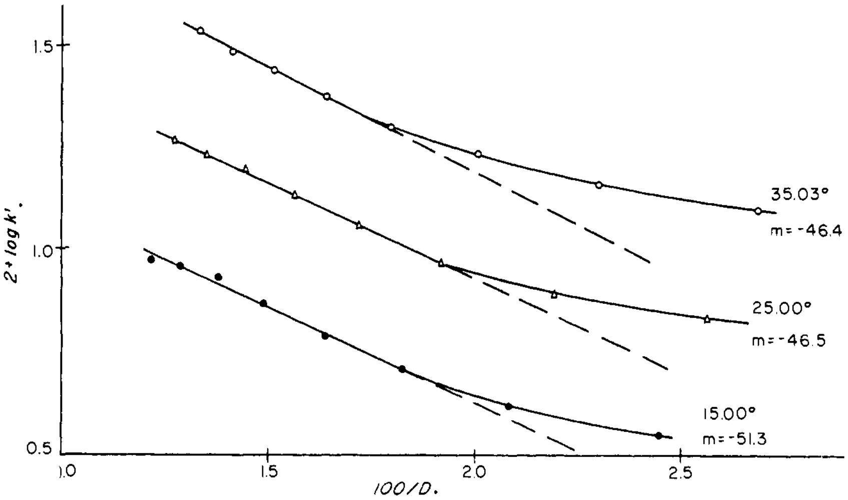

Fig. 1.—Variation of the logarithm of specific rate constant with reciprocal of dielectric constant.

Interpretation of the data for the ionic strength effect upon the alkaline hydrolysis of methyl propionate was made by the Amis–Jaffé[3] equation which is

$$\ln k' = \ln k'_{\kappa=0} + \frac{\epsilon Z_{\mathrm{B}} \cos \Theta}{DkTr_0{}^2}\left(\mu_0^* - \frac{\mu^*(1 + Dr_0)}{e^{Dr_0}}\right) \quad (4)$$

By substituting the dimensionless quantities

$$Z = \kappa a = \kappa r_0 \quad (5)$$

and

$$W = \frac{(\ln k' - \ln k'_{\kappa=0})\, 2DkTr_0^2}{\epsilon Z_{\mathrm{B}} \mu_0^* \cos \Theta} \quad (6)$$

we can write equation 4 in the form

$$W = \frac{Z^2}{1 + Z + Z^2/2 + (N^2/2D)(1 + Z)} \quad (7)$$

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(13) C. P. Smyth, "Dielectric Constant and Molecular Structures," Chemical Catalog Company, Inc., New York, N. Y., 1931, pp. 193–199.

(14) J. A. Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

(15) G. Scatchard, *Chem. Revs.*, **10**, 229 (1932).

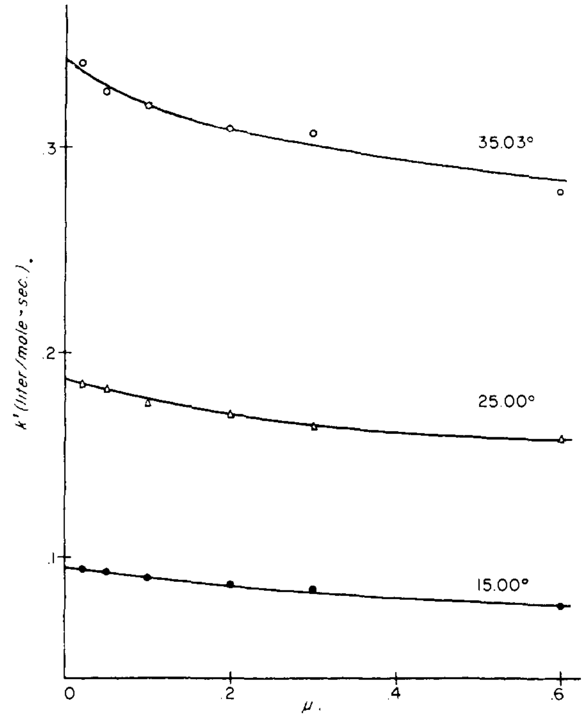

Fig. 2.—Variation of specific rate constant with ionic strength.

This equation brings out the dependence on electrolyte concentration in a general way.

To check the agreement of data with theory a plot of W *versus* Z^2 was made and the data were made to fit the curve by adjusting the values of the parameters $k'\kappa = 0$, μ_0^* and r_0 (see Fig. 3). These values together with the value of the square of the refractive index calculated from the enhanced moment μ_0^* at zero ionic strength are recorded in Table IV. These values are reasonable in magnitude and agree in magnitude with values of these parameters found in previous applications of this theory.[2-4]

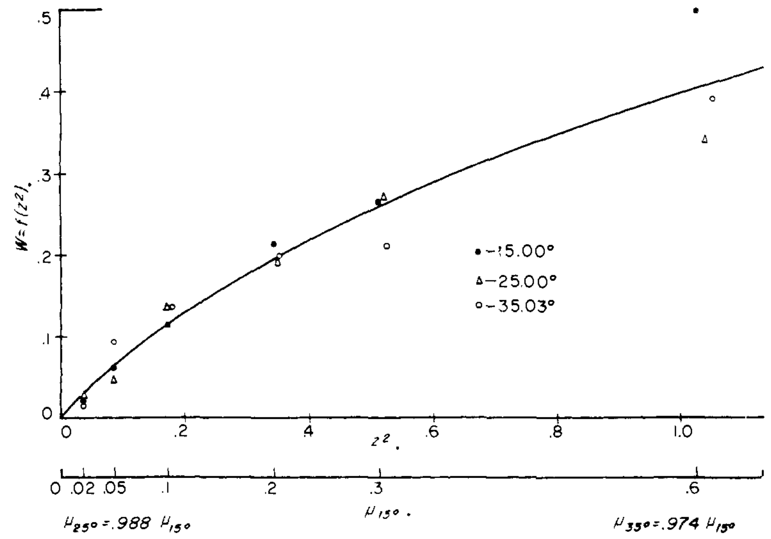

Fig. 3.—Agreement of ionic strength data with theoretical curve: $W = f(z^2)$ *vs.* z^2.

TABLE IV

PARAMETERS USED TO FIT IONIC STRENGTH DATA TO THEORETICAL CURVE

Temp., °C.	$r \times 10^8$ cm.	μ_0^*, Debye units	N^2	$k'\kappa = 0$
15.00	4	9.8	9.5	0.0947
25.00	4	10.6	11.6	.187
35.03	4	11.6	11.6	.344

TABLE V

ACTIVATION ENERGIES AND LOGARITHMS OF FREQUENCY FACTORS IN VARIOUS MEDIA

Wt. % acetone μ = 0.0200	ΔE (kcal./mole) 15–25°	25–35°	Log Z 15–25°	25–35°
0.0	11.6	11.2	7.77	7.44
8.0	10.9	10.4	7.22	6.85
16.4	10.5	10.2	6.89	6.66
25.2	10.5	10.0	6.83	6.47
34.4	10.5	10.1	6.78	6.49
44.0	10.2	11.1	6.47	7.10
54.1	10.8	11.2	6.79	7.06
64.7	11.2	11.1	7.02	6.97
Ionic strength in water soln.				
0.0200	11.6	11.2	7.77	7.44
.0500	11.7	10.6	7.85	7.03
.1000	11.4	11.0	7.58	7.28
.2000	11.6	10.9	7.73	7.21
.3000	11.4	11.4	7.57	7.57
.6000	12.5	10.3	8.39	6.72

The energies of activation ΔE and logarithms of the Arrhenius frequency factors, log Z, were calculated for the alkaline hydrolysis of methyl propionate using the respective equations

$$\log \frac{k_2'}{k_1'} = \frac{\Delta E(T_2 - T_1)}{2.303RT_1T_2} \tag{8}$$

and

$$\log Z = \frac{T_2 \log k_2' - T_1 \log k_1'}{T_2 - T_1} \tag{9}$$

The values of these functions are recorded in Table V. The energies of activation are comparable to those found for the alkaline hydrolysis of ethyl acetate in acetone–water media by Amis and Siegel.[4] The frequency factors are somewhat low compared to the values recorded in the literature[2,4,5] for these quantities in other ester hydrolysis investigations.

It appears that an equation which combines the dielectric constant effect as given by equation 2 with the salt effect as given by equation 4 would best represent the data from ion–dipole reaction rates. The resulting equation is

$$\ln k = \ln k_{\substack{D=0\\D=\infty}} + \frac{Z\epsilon\mu}{DkTr_0^2} + \frac{Z_B\cos\Theta}{DkTr_0^2}\left(\mu_0{}^* - \frac{\mu^*(1 + \kappa r_0)}{e^{\kappa r_0}}\right)$$

The data presented here and elsewhere[2,4,16] support this suggestion.

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(16) W. J. Broach and E. S. Amis, *J. Chem. Phys.*, **22**, 39 (1954).

Landskoener and Laidler[17] have derived another equation for the dielectric constant dependence of the rate of ion–dipole reaction rates. This equation purportedly takes proper cognizance of the charge distribution in the reactants and activated complex.

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[17] P. A. Landskoener, Dissertation submitted to the Graduate School of Arts and Sciences of the Catholic University of America, Washington, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON][1]

Polarographic Investigation of the Ethylenediamine, 1,2-Propanediamine and Diethylenetriamine Complexes of Mercury(II)

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The complex ions formed by mercury(II) ion with three polyamines at 25° were investigated by a modification of the polarographic method. The data were interpreted as indicating the existence of the ions $[Hg(en)_2]^{++}$, $K_2 = 1.5 \times 10^{23}$; $[Hg(pn)_2]^{++}$, $K_2 = 3.4 \times 10^{23}$; and $[Hg(dien)_2]^{++}$, $K_2 = 1.15 \times 10^{25}$. A value of 1.2×10^{18} was calculated for the formation constant of the ion $[Hg(dien)]^{++}$. These complex ions alone do not allow a complete interpretation of the data. An interpretation based on the possible existence of complexes containing more than two amine molecules per mercury(II) ion is presented.

There are several reports of investigations of the complex ions of mercury(II) ion with polyamines which are pertinent to this investigation. A report of the stability of complex ions formed between mercury(II) ion and ethylenediamine[2] was made by Bjerrum.[3] For the logarithm of the mean complexity constant, Bjerrum reported the value 11.71. Thus, for the ion $[Hg(en)_2]^{++}$, an over-all formation constant of 2.6×10^{23} is indicated. A polarographic investigation by Mason and Watters[4] indicated the formation constant of this same ion to have a value of 4.5×10^{22}.

Prue and Schwarzenbach[5,6] have investigated by *p*H methods the complex ions formed by mercury(II) ion with diethylenetriamine. In chloride and in bromide media, the complex ion formed appeared to contain both halide and diethylenetriamine. In 0.5 *N* sodium perchlorate, the data could not be interpreted to obtain a formation constant for $[Hg(dien)]^{++}$. However, an equilibrium constant of approximately 1×10^7 for the reaction of $[Hg(dien)]^{++}$ with diethylenetriamine to form $[Hg(dien)_2]^{++}$ was obtained.

This paper reports the results of a polarographic investigation of the complexes of mercury(II) ion with three polyamines. A preliminary investigation of the ethylenediamine complexes[7] was completed about the time that the work of Mason and Watters was reported. It was undertaken initially in order to compare the formation constants obtained by the method employed with those obtained by Bjerrum, presumably from *p*H measurements. The diethylenetriamine system was reinvestigated in an attempt to obtain a value for the formation constant of $[Hg(dien)_2]^{++}$ from mercury(II) ion and diethylenetriamine in the absence of halogen. There appeared to be no reports of previous investigations of the stability of mercury–1,2-propanediamine complexes, and so this system was also studied.

Data and Discussion

General.—The usual procedure followed in the polarographic investigation of complex ions is to determine the effect of different concentrations of complexing agent on the half-wave potential of the metal ion. In such a case, the relationship between the half-wave potential of the metal ion and the concentration of complexing agent is given by eq. 1. $(E_{1/2})_c$ and $(E_{1/2})_s$ are half-wave potentials of the complex and simple metal ions; C_x is the concentration of the complexing agent; and K_j is the formation constant of the complex ion MX_j from the simple metal ion and *j* molecules of the complexing agent.[8,9]

$$(E_{1/2})_s = (E_{1/2})_c + \frac{RT}{nF} \ln (C_x)^j K_j \qquad (1)$$

In this investigation, the effect of changing the concentration of complexing agent on the oxidation potential of mercury to mercuric ion was determined. The difference in oxidation potentials of the complex and simple mercuric ions is given by an equation entirely analogous to equation 1, with the exception that the potentials involved are not half-wave potentials, but the potentials of the electrode at an arbitrary current. As has been pointed out by Kolthoff and Miller,[10] the potential of a mercury electrode in equilibrium with the surrounding liquid is given by equation 2. In this expression

$$E_{d.e.} = E^\circ_{Hg_2^{++}} + \frac{RT}{nF} \ln [Hg_2^{++}]_0 = E^\circ_{Hg^{++}} + \frac{RT}{nF} \ln [Hg^{++}]_0 \qquad (2)$$

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[1] This project carried out in part under support of the Office of Ordnance Research, U. S. Army, Project No. DA-04-200-ORD-65.

[2] The names of ethylenediamine, 1,2-propanediamine and diethylenetriamine have been abbreviated (en), (pn) and (dien), respectively.

[3] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

[4] J. Mason and J. I. Watters, Paper No. 91 presented before the Division of Physical and Inorganic Chemistry at the 125th National A.C.S. Meeting, Kansas City, Mo., March 23 to April 1, 1954.

[5] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 947 (1950).

[6] J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 985 (1950).

[7] C. J. Nyman, Progress Report No. 7 to Office of Ordnance Research, Project No. DA-04-200-ORD-65, March 1, 1953.

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

[9] D. D. DeFord and D. N. Hume, THIS JOURNAL, **73**, 5321 (1951).

[10] I. M. Kolthoff and C. S. Miller, *ibid.*, **63**, 1405 (1941).