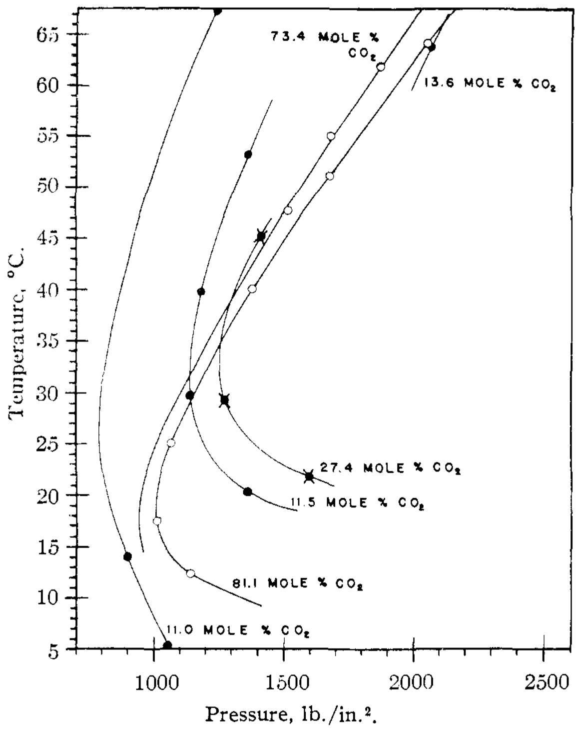

Fig. 6.—○, points on *PT* curves for mixtures *made with* 77.9 mole % alcohol–water solution; ●, points determined for mixtures *made with* 28.1 mole % alcohol–water solution; ✖, points determined for mixture *made with* 50.0 mole % alcohol–water solution.

The isobaric intersections of the region of two liquids with other planes, radiating from the CO_2 corner of Fig. 3, may be similarly plotted from the data obtained using other alcohol–water proportions (Fig. 6). An assemblage of such planes determines the surfaces of the region of two liquids. The data for other planes are necessarily more fragmentary than are those for the mixtures involving 61.0 mole % alcohol–water solutions, because of the angles at which the planes intersect the region of two liquids. However, the data are quite adequate to establish the generalizations given in the introductory discussion and to indicate the magnitudes of the effects.

Liquid–vapor critical data for CO_2, for CO_2–absolute alcohol solutions, for liquid CO_2 saturated with water, and for one ternary mixture are listed in Table I, which may be used to plot that portion of the heterobaric critical envelope illustrated in Fig. 3. These data were obtained by a technique, similar to that described, wherein the bomb was partially filled with an appropriate volume of liquid CO_2 or liquid CO_2 solution. The temperature and pressure of the separation of a gaseous phase and a liquid phase were observed upon slow cooling of the mixture from above the critical point. For each of the solutions, the point so determined is the "second critical point,"[10] *i.e.*, the temperature and pressure at which the distinction between the gaseous and the liquid phase vanishes. In this region of composition, each of these points is extremely close to the "first critical point",[10] *i.e.*, the temperature (and corresponding pressure) above which liquefication within the gaseous phase cannot be brought about by isothermal increase of pressure.

TABLE I

LIQUID–VAPOR CRITICAL DATA

Composition, mole %			Critical temp., °C.	Critical pressure, lb./in.²
CO_2	C_2H_5OH	H_2O		
100	0	0	31.0	1070
98.0	2.0	0	37.9	1150
96.4	3.6	0	40.7	1200
94.7	5.3	0	45.6	1300
93.3	6.7	0	47.8	1345
99.8	0	0.2 (satd.)	31.7	..
97.5	2.0	0.6	38.1	1195

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PHILADELPHIA 4, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Silver–Silver Chloride Reference Electrode in Acetonitrile Polarography[1]

BY ALEXANDER I. POPOV AND DAVID H. GESKE[2]

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An external reference electrode has been prepared for polarographic studies in acetonitrile. A silver–silver chloride electrode in acetonitrile solution saturated with silver chloride and trimethylethylammonium chloride was found to be reproducible and non-polarizable. Potentiometric measurements were made to relate the reference electrode to Pleskov's scale. The polarographic behavior of a number of metallic perchlorates in 0.1 *M* tetra-*n*-butylammonium perchlorate was studied. Approximate calculation of a number of half-wave potentials was done and comparison made with observed values. New data are presented for reduction of thallous and stannous ions.

Introduction

The use of acetonitrile as a solvent for polarographic measurements was first reported by Wawzonek and Runner.[3] These authors employed a mercury pool reference anode and either 0.1 *M* tetra-*n*-butylammonium iodide or 0.1 *M* tetra-*n*-butylammonium perchlorate as the supporting electrolyte. In later publications Wawzonek, *et al.*,[4] reported polarographic measurements on some organic compounds in the same solvent. The study of hydrogen ion reduction in acetonitrile has been described recently by Vlcek.[5]

After the work reported in this paper was completed, a dissertation by Coetzee[6,7] reported a comprehensive polarographic study of a number of

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(2) National Science Foundation Predoctoral Fellow.

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metal cations in acetonitrile. All of these measurements were done against an aqueous saturated calomel reference electrode.

Experimental Part

Reagents.—Source and purification of acetonitrile were given previously.[8] The final solvent distillation was made in a nitrogen atmosphere.

Tetra-*n*-butylammonium iodide[9] and tetra-*n*-butylammonium perchlorate[10] were prepared as described in the literature. Reagent grade potassium iodide was recrystallized from water.

Trimethylethylammonium chloride was prepared in the following way. Aqueous sodium hydroxide is added dropwise to aqueous trimethylamine. The reaction mixture was warmed to distil trimethylamine into an alcoholic solution of ethyl iodide maintained at $-50°$. The alcoholic solution was then allowed to warm to room temperature. Since the reaction is exothermic it is necessary to moderate the reaction to avoid loss of reactants. The trimethylethylammonium iodide is filtered from the reaction mixture, rinsed with ethyl acetate and recrystallized from ethyl acetate–ethanol mixture. Trimethylethylammonium chloride is produced from treatment of the iodide with silver oxide followed by titration with hydrochloric acid. The solution was evaporated and solid material recrystallized from an acetone–water mixture. Trimethylethylammonium chloride undergoes a transformation from non-cubic to cubic crystal structure at 100.0° (as observed with a hot-stage polarizing microscope). Decomposition without fusion begins at 290°. Analysis for chloride gave 28.57% compared to 28.68% calculated for $(CH_3)_3N(C_2H_5)Cl$.

Silver chloride for use in the reference electrode was precipitated from acetonitrile solutions of silver perchlorate and tetra-*n*-butylammonium chloride and washed on the filter with acetonitrile.

Silver nitrate was purified from reagent grade material by recrystallization from water followed by fusion. Anhydrous potassium, sodium, barium, strontium and silver perchlorates (G. F. Smith and Co.) were dried *in vacuo* at 25°. Anhydrous lithium perchlorate was obtained by dehydration of lithium perchlorate trihydrate.

Anhydrous lead perchlorate was obtained by preparing the hydrated material from lead monoxide and 70% perchloric acid and then dehydrating in a vacuum oven at 180°.[11] No chloride was present after the dehydration. Analysis for lead by electrodeposition of lead dioxide gave 51.5% compared to 51.02% for $Pb(ClO_4)_2$.

Thallium perchlorate was prepared anhydrous by dissolving thallium metal in perchloric acid and drying the resulting crystals at 120°. Analysis for thallium by gravimetric chromate gave 66.5% compared to 67.27% for $TlClO_4$.

Anhydrous cadmium perchlorate was prepared by dissolving cadmium oxide in perchloric acid to obtain the hexahydrate, dehydrating to the dihydrate at 25° *in vacuo*, and finally to the anhydrous compound at 120° *in vacuo*.[12] Analysis for perchlorate by precipitation of potassium perchlorate in ethanol[12] gave 63.6% perchlorate compared to 63.89% for $Cd(ClO_4)_2$.

Calcium perchlorate was obtained anhydrous by dissolving calcium hydroxide in perchloric acid and dehydrating the resulting dihydrate by heating *in vacuo* at 180°.[12] Analysis for calcium by standard Versenate titration gave 16.5% calcium compared to 16.77% for $Ca(ClO_4)_2$.

Nickel, cobaltous, ferric, ferrous, cupric and chromic perchlorates (hexahydrate) and mercuric perchlorate trihydrate (all obtained from G. F. Smith and Co.) were dried over phosphorus pentoxide *in vacuo* at 25°. Compositions were checked by precipitation of potassium perchlorate in ethanol,[12] except in the case of the cupric salt where copper was determined electrometrically. The ferrous salt was found to be free of ferric by polarographic analysis. Zinc and manganese perchlorates (hexahydrate) were prepared by action of perchloric acid on the oxide. The zinc salt was analyzed by the gravimetric perchlorate method. The manganese salt was analyzed by gravimetric determination of manganese sulfate obtained by repeated fuming with sulfuric acid. Aluminum perchlorate hexahydrate (chloride free), was obtained by action of perchloric acid on aluminum dust and was analyzed by the gravimetric perchlorate method.

The compound stannous perchlorate diacetonitrile was prepared as described by Schmidt[13] but was found to detonate on handling. It was possible to prepare an acetonitrile solution of stannous perchlorate by electrolyzing an acetonitrile solution of silver perchlorate using a tin anode. Concentration was determined from the amount of silver replaced by tin.

The perchloric acid solution used for polarographic study was prepared by dilution of 70% stock followed by titration against standard base.

Tank nitrogen was purified by passage through concentrated sulfuric acid, barium oxide, hot copper turnings, another barium oxide column, and finally an acetonitrile presaturator.

Apparatus.—A Sargent Model XXI recording polarograph was used to obtain all data reported here. Calibration of current sensitivity was done as described by Kolthoff and Lingane.[14] Current measurements were made by using the average of the pen deflections with the instrument circuit undamped. Recorder lag was negligible with the circuit undamped. Potential settings for scanning were checked with a potentiometer. Polarograms were corrected for iR drop through the cell and instrument resistances.

The dropping mercury electrode had a drop time of $t = 4.02$ sec. and $m = 1.75$ mg. sec.$^{-1}$ at a pressure of 60.0 cm. Hg (uncor.) on open circuit in 0.1 M tetra-*n*-butylammonium perchlorate solution. Diffusion current constants were evaluated using m and t values obtained at the potential of the reduction wave.

Resistance measurements were made using a Wheatstone bridge powered by a 1000 cycle audio oscillator. Resistance of the cell circuit was taken at maximum mercury drop size.

Electromotive force measurements of circuits of high resistance were made using a Leeds and Northrup #7673 thermionic amplifier and a type K potentiometer.

Temperature of polarographic cell was maintained at 25.0 ± 0.1° by circulation of water from a constant temperature reservoir through a smaller auxiliary bath in which the cell was placed.

Stock solutions were prepared in 50-ml. quantities. Weighings of extremely hygroscopic solutes were done in stoppered vials.

Reference Electrode.—Polarography in non-aqueous solvents requires a suitable reference electrode. The use of an external aqueous calomel reference electrode has been reported with formamide,[15] acetamide–formamide mixtures,[16] and acetonitrile.[7] Such a procedure is convenient but nevertheless magnifies the question of liquid junction potentials and the possibility of contamination of sample system with water.

External polarographic reference electrodes have been prepared in acetone[17] and formic acid.[18] A search was made for a half-cell reaction suitable for use as an external polarographic reference electrode in acetonitrile.

An acetonitrile analog of the aqueous calomel electrode was investigated. Mercurous chloride, although insoluble in acetonitrile, undergoes a disproportionation reaction in the presence of excess chloride ion present either from lithium chloride or tetra-*n*-butylammonium chloride.

$$Hg_2Cl_2 + Cl^- \longrightarrow Hg^0 + HgCl_3^-$$

Particles of finely divided mercury appear and mercuric ion is detected in solution. The enhanced stability of the chloromercurate complex anion is apparently responsible for

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this reaction in acetonitrile as well as in a number of other organic solvents. These observations agree with those reported by Ulich and Spiegel[19] and Cruse, Goertz and Petermoller.[20]

The mercury–mercurous sulfate electrode, with sulfate ion furnished by tetraethylammonium sulfate, was found to be entirely unsatisfactory.

A silver–silver nitrate electrode was unsatisfactory because of polarization when current flowed.

Janz and Taniguchi[21] comment that the tendency of silver chloride to form complexes in acetonitrile makes the silver–silver chloride electrode unsuitable as a reference electrode. A preliminary study in this Laboratory indicated that the solubility of silver chloride is indeed greatly increased in the presence of free chloride ion, thus indicating complex formation. This increased stability of silver polychloride anions in acetonitrile by comparison with water is in accord with observations by Kratohvil.[22] However it was found possible to achieve equilibrium conditions such that the potential of a silver–silver chloride electrode did not change.

A silver electrode was prepared by deposition of silver on a platinum cylinder with a surface area of 23.4 cm.². The silver deposition was done as described by Brown.[23]

The reference electrode consisted of the silver electrode placed in acetonitrile saturated with respect to silver chloride and trimethylethylammonium chloride. The solubility of silver chloride in acetonitrile is limited by the amount of free chloride ion present, which in turn is governed by the solubility of trimethylethylammonium chloride. It is this saturation condition that prevents the electrode potential from drifting as further complexation occurs. Equilibrium conditions for a 250-ml. quantity of reference electrolyte are achieved in approximately 80 hours at 25°.

Analysis of such solutions equilibrated at 25.0° was carried out by digesting an aliquot portion in aqueous nitric acid and filtering. This gave the amount of silver chloride present. Excess chloride was determined in the filtrate by the usual means. The composition of the reference electrolyte was found to be 0.015 *M* silver chloride and 0.118 *M* trimethylethylammonium chloride.

Performance of the electrode was tested by placing identical half-cells in the arms of an H cell with a fine sintered glass frit separating the arms. A linear current–voltage relationship was found from 0 to 2 volts and 0 to 100 μa. Polarization was less than 1 mv. on such a run, and less than 2 mv. when a current of 100 μa. was passed through the cell for 20 minutes. There was no variation of potential on shaking the cell. These results indicated that the electrode was suitable as a non-polarizable polarographic reference electrode.

Pleskov[11] has measured formal electrode potentials in acetonitrile using a silver–silver nitrate (0.01 *M*) half-cell as a primary zero reference. It seemed desirable to relate the saturated silver chloride electrode to this primary reference, thus allowing comparison of half-wave potentials with electrode potentials.

This measurement was made in an H cell whose arms were separated by a ground glass plug. Junction between the two half-cells formed around the plug. The high resistance of the cell necessitated the use of the amplified potentiometer circuit previously described.

Six measurements with different electrolyte preparations over a period of six months gave a value of 0.638 ± 0.001 v. for this cell at 25.0°.

$$-\text{Ag, AgCl } (0.015\ M),\ \text{Me}_3\text{NEt}^+\text{Cl}^-\ (0.118\ M)//\text{AgNO}_3\ (0.01\ M),\ \text{Ag} +$$

The temperature coefficient was 0.6 mv. deg.$^{-1}$. Half-wave potentials reported in this paper are all referred to the silver–silver nitrate scale by the above measurement.

Following completion of this investigation a publication by Hanselman and Streuli[24] reported use of a silver–silver chloride in saturated lithium chloride as a potentiometric reference electrode in acetonitrile. Pavlopoulos and Strehlow[25] found the solubility of lithium chloride in acetonitrile to be 0.14 g./100 ml. at 25°, corresponding to a 0.026 *M* solution. It appears reasonable that a silver chloride electrode saturated with lithium chloride could be adapted for use as a polarographic reference electrode. Such an electrode would undoubtedly have a higher resistance than the cell employing trimethylethylammonium chloride as electrolyte. On the other hand, lithium chloride is more readily available. Transference numbers for estimation of liquid junction potentials are not available for ionic species in the reference electrolyte. The following limiting ionic conductances were reported by Walden[26] and are of interest here: lithium, 59.3; chloride, 88.8; tetramethylammonium, 92.9; and tetraethylammonium, 86.1 (trimethylethylammonium limiting conductance assumed intermediate to tetraethyl- and tetramethylammonium ions). From these data it seems probable that the saturated solution of trimethylethylammonium chloride minimizes the liquid junction potential more effectively than a saturated solution of lithium chloride.

Cell Construction.—A satisfactory polarographic cell was obtained by modification of the design of Pecsok and Juvet.[27] Reference electrolyte and electrode are separated from a junction compartment by a sintered glass disk (fine porosity). The junction compartment is in turn separated from the test solution by another disk (coarse porosity).

Formation of the liquid–liquid junction in this manner proved quite successful. There was no contamination of the test solution by chloride ion from the reference electrolyte.

An external electrical contact into the test solution compartment was provided for the studies of the mercury pool reference electrode. Resistance of the cell using the external reference electrode was 1500 ohms.

A gravity-flow closed system was designed in which it was possible to distil solvent, prepare and dilute solutions and transfer into the polarographic cell under dry nitrogen. It was found unnecessary to use this apparatus since the solvent which had been distilled under nitrogen required only ten minutes of degassing to remove traces of oxygen. The minor effect of small amounts of water is described later.

Results

Polarographic data were obtained in acetonitrile using the reference electrode described above. These data are summarized in Table I, with half-wave potentials reported *versus* the silver–silver nitrate (0.01 *M*) electrode. Data presented represent the average of at least three determinations. Diffusion current was proportional to concentration in the range studied, 1 to 0.1 millimolar. All polarographic waves were examined by plotting log $i/(i_d - i)$ *vs.* the applied e.m.f. corrected for iR drop (except for ferrous ion reduction, where $\log(i_d - i)$ *vs.* ϵ was plotted). The slope of such lines gives $n\alpha/0.059$. Values of $n\alpha$ are listed in Table I for those waves which gave straight line plots. The effect of addition of 0.5% water on half-wave potential is also listed in Table I.

Previous workers[3] have obtained half-wave potentials of various cations in 0.1 *M* tetra-*n*-butylammonium iodide employing a mercury pool anode. It is of interest to correlate these data with those reported in this paper. Measurement of the half-wave potential of potassium ion (in iodide supporting electrolyte) *versus* both the mercury pool and silver–silver chloride reference electrodes showed a difference of 0.25 v. Combining this measurement with the potential of the cell, Ag,AgCl,Me_3NEtCl(satd.) // AgNO_3 (0.01 *M*), Ag, the half-wave potentials in 0.1 *M* iodide are referred to the silver nitrate electrode by addition of

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TABLE I

POLAROGRAPHIC DATA

Compound	$-E_{1/2}$, volts Ref. 7[a]	$-E_{1/2}$, volts This paper[b]	I[c]	$n\alpha$	Effect of water[e]
$LiClO_4$	2.24	2.26	2.68	0.90	0.04
$KClO_4$		2.24	3.23	0.95	0.00
$NaClO_4$	2.14	2.14	3.00	0.94	
$Ca(ClO_4)_2$	2.11	2.14	4.34	..	
$Sr(ClO_4)_2$	2.05	(2.08)[f]	4.56	..[f]	
$Ba(ClO_4)_2$	1.92	1.92	4.62	1.68	
$Al(ClO_4)_3 \cdot 6H_2O$	1.71	1.64	5.22	0.64	
$Mn(ClO_4)_2 \cdot 6H_2O$	1.41	1.40	4.44	1.89	
$Cr(ClO_4)_3 \cdot 6H_2O$	1.41	1.39	3.79	1.27	
	0.29	(0.3)	..	..	
$Fe(ClO_4)_2 \cdot 6H_2O$	1.29	1.33	4.25	..[g]	0.13
$Fe(ClO_4)_3 \cdot 6H_2O$	1.29	1.33	4.25	..[g]	
		> −0.36	1.91	..[h]	
$Co(ClO_4)_2 \cdot 6H_2O$	0.94	0.96	4.55	1.45	
$Zn(ClO_4)_2 \cdot 6H_2O$	0.99	0.91	4.59	0.94	0.07
$HClO_4$	0.70	0.78	1.65	1.08	0.68
$Cu(ClO_4)_2 \cdot 6H_2O$	0.65	0.62	2.54	0.96	−0.01
		> −0.36	2.27	..[h]	
$TlClO_4$		0.55	3.19	0.93	
$Cd(ClO_4)_2$	0.56	0.55	4.10	1.89	0.03
$Pb(ClO_4)_2$		0.33	5.38	1.25	0.03
$Sn(ClO_4)_2$		0.23	4.50	1.63	
$AgClO_4$	−0.03	−0.13	3.10	0.94	0.005
$Hg(ClO_4)_2 \cdot 3H_2O$		> −0.36	4.70	..[h]	

[a] Metallic perchlorates in 0.1 *M* sodium perchlorate, except Li, Na, Ca, Sr, Ba in 0.1 *M* tetraethylammonium perchlorate. [b] Metallic perchlorates in 0.1 *M* tetra-*n*-butylammonium perchlorate. [c] $I = i_d/cm^{2/3}t^{1/6}$. Where multiple waves occur, *I* values given for separate waves, not total wave. [d] Slope value defined in text. [e] Values given are for $E_{1/2} - E_{1/2}^{H_2O}$ where $E_{1/2}^{H_2O}$ is the half-wave potential for solutions containing 0.5% water (except $HClO_4$, where 1% water was added). [f] Maxima. [g] No straight line when log $(i_d - i)$ plotted *vs.* ϵ. [h] Current phenomenon described in text.

−0.89 volt. Potentiometric measurement of the cell, Hg, $Bu_4NI(0.10\ M)$ // $AgNO_3(0.01\ M)$, Ag, also gave 0.89 v. These recalculated values are shown in Table II.

TABLE II

COMPARISON OF HALF-WAVE POTENTIALS

Ion	Present work[a]	$-E_{1/2}$ Ref. 3[b]	Ref. 7
Li	2.26	2.31	2.24[d]
Na	2.14	2.14	2.14[d]
K	2.24	2.23	2.23[b]
Rb		2.25	2.24[b]
Cs		(2.23)[c]	
Ca	2.14	2.13	2.11[d]

[a] Metallic perchlorates in 0.1 *M* tetra-*n*-butylammonium perchlorate. [b] Metallic halides in 0.1 *M* tetra-*n*-butylammonium iodide. [c] Maxima. [d] Metallic perchlorate in 0.1 *M* tetraethylammonium perchlorate.

Half-wave potentials for a number of ions in 0.1 *M* tetra-*n*-butylammonium perchlorate measured with a mercury pool anode have been reported.[3] Comparison of these data with data in this publication did not show an exactly constant difference between the two sets of measurements. The possibility that the mercury pool anode was polarizable was verified by passing a current of 50 μa. for 2 minutes through the cell: Ag, AgCl reference / / 0.1 *M* Bu_4NClO_4, Hg. Polarization of 60 mv. occurred.

The potential of the mercury pool anode in iodide media is controlled by the activity of mercuric ion present largely as tetraiodomercurate, $HgI_4^{=}$. In the case of perchlorate media, the absence of mercury complexes may account for the polarizability of the pool electrode.

Polarographic measurements were made by Coetzee[7] using 0.1 *M* solutions of tetraethylammonium perchlorate and sodium perchlorate as supporting electrolyte. These measurements were related to Pleskov's electromotive force series[11] by measurement of the cell, saturated calomel(aq.) / / $AgNO_3(0.01\ M)_{CH_3CN}$ Ag; $E = 0.29$ volt. Although both this measurement and the polarographic measurements involve an unknown liquid junction potential, if the junction potentials are assumed equal, the half-wave potentials obtained by Coetzee[7] are satisfactorily placed on the silver–silver nitrate (acetonitrile) scale. Thus comparison may be made between Coetzee's work (listed in Tables I and II) and the data in this paper.

Generally good agreement is found between the two sets of data, even though the supporting electrolytes were not the same.

Coetzee[7] reports a well-defined wave for the chromic–chromous reduction, while in this work the wave is ill-defined ($E_{1/2}$ approximate only) and the diffusion current plateau was not accurately measurable.

Difficulty was encountered in the study of nickel perchlorate. Two reducible species appeared to be present, since one wave occurred at −0.69 v. and another at −1.22 v. The total diffusion current was proportional to concentration but the height of the individual waves was not reproducible.

A systematic study has been made by Vlcek[5] of the effect of small amounts of water on the reduction of hydrogen ion. By using potassium as a pilot ion, hydrogen ion reductions were carried out in acetonitrile–water solutions of up to 6.2% water. The solution was saturated with tetramethylammonium iodide to provide supporting electrolyte. The reduction wave shifted to increasingly negative potentials with increasing water concentration. A plot of difference between half-wave potentials of potassium and hydrogen ions ($\Delta E_{1/2}$) *vs.* water concentration was extrapolated to zero water concentration. This value 1.55 v., represented the $\Delta E_{1/2}$ in anhydrous acetonitrile. In practice, in the solution of lowest water content, 0.05%, Vlcek found that the hydrogen ion reduction wave did not show a knee, but the current rose sharply from zero applied voltage (*vs.* mercury pool). At slightly higher water concentrations, 0.2%, the wave was normally formed.

The present work in 0.1 *M* perchlorate media shows a $\Delta E_{1/2}$ (as defined above) of 1.46 v. with the wave normally formed. Similarly, addition of 1% water shifted the half-wave potential 0.68 v. to more negative potentials. It has been suggested[3] that reduction waves observed for copper, cadmium and zinc perchlorates might actually be due to hydrogen ion reduction. Table I includes data for the shift of these reduction waves upon addition of 0.5% water. It is seen that these shifts are extremely small compared to the shift observed with addition of water to perchloric acid solution. This seems to offer conclusive proof that the reduction waves observed for the metallic cations are due to that cation and not a hydrogen ion reduction.

Stannous perchlorate shows only a single reduction wave and no oxidation to stannic ion in the potential range studied (limited by anodic dissolution of mercury).

A curious current phenomenon was encountered in the case of mercuric, cupric (first step) and ferric (first step) ion reductions. Polarograms were scanned both from the most positive potential possible (limited by anodic dissolution of mercury) toward more negative potentials and *vice versa.* In the case of the ions mentioned, at the higher concentrations (approximately 1×10^{-3} *M*) the current rose sharply at the most positive potentials and then broke abruptly several hundred millivolts more negative to a limiting current plateau. The behavior of copper as shown in Fig. 1 is typical. This behavior is somewhat similar to that described by Bachman and Astle,[28] who suggest that the discontinuity is due to adsorption processes. A more likely explanation is that there is interaction of the oxidants with the mercury drop causing a "mercury" maxima. Adsorption reactions would not account for the current in excess of the diffusion current. No studies were made in the present work to differentiate between diffusion and kinetic control of the limiting currents. At concentrations of less than approximately 5×10^{-4} *M* the discontinuous current rise was absent and the wave appeared to be normal. However, subtraction of residual current obtained from polarogram of the supporting electrolyte showed that the apparent wave was caused by the beginning of the mercury dissolution. From this it is concluded that actual half-wave potentials of cupric and ferric ions occur at more positive potentials than +0.36 v.

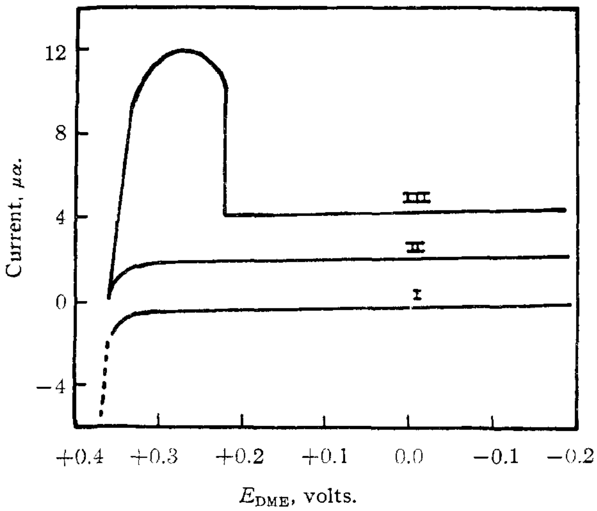

Fig. 1.—Polarograms, current *vs.* applied voltage: I, residual current, 0.1 *M* tetra-*n*-butylammonium perchlorate; II, cupric perchlorate, 0.55×10^{-3} *M*; III, cupric perchlorate, 1.10×10^{-3} *M*.

Discussion

The half-wave potentials observed in acetonitrile are generally in the same order as in aqueous solution (non-complexing supporting electrolyte). Two important exceptions are copper and silver. While the reduction of silver in water occurs at such positive potentials that mercury oxidation occurs first, the reduction is observed easily in acetonitrile. An indication of the solvated nature of silver ion in acetonitrile is seen in the fact that dipyridinesilver(I) perchlorate shows the same half-wave potential as silver perchlorate (the coordinated pyridines are undoubtedly largely displaced by acetonitrile).

Stabilization of the cuprous state in acetonitrile, as indicated by the two-step reduction of cupric ion, is shown by other observations. Morgan[29] isolated cuprous nitrate tetra-acetonitrile, $CuNO_3 \cdot 4CH_3CN$, from reaction between an acetonitrile solution of silver nitrate and metallic copper.

It is of interest to compare observed half-wave potentials with calculated values. Where measurements are made with solid metal electrodes, the half-wave potential is given by the expression[14]

$$E_{1/2} \backsimeq E^0{}_M + E_S + \frac{0.059}{n} \log C_{satd} f_{satd}$$

The normal electrode potential is given by $E^0{}_M$, E_S is the potential of the cell, $M(s)/M^{n+}/M(Hg)_{satd}$, and C_{satd} and f_{satd} are the concentration and activity coefficient, respectively, of the metal in the saturated amalgam. Since these last three terms are independent of solvent, calculation of half-wave potentials only requires evaluation of $E^0{}_M$.

Values of $E^0{}_M$ were obtained by assuming the Nernst equation to hold, and then calculating $E^0{}_M$ from e.m.f. data for the lowest concentration of solute as given in the publication by Pleskov.[11] This estimate of $E^0{}_M$ should be reasonably accurate since the activity coefficient approaches unity at zero concentration.

Using Pleskov's[11] data for 5×10^{-4} *N* CdI_2 with $E = -0.7327$ v. (*vs.* $AgNO_3$ reference), E^0 is -0.626 v. For cadmium $E_S = 0.051$ v.,[30] $C_{satd} = 6.40$ moles/l.,[31] $f_{satd} = 1.15$[32] giving a calculated half-wave potential of -0.550 v. which compares favorably to the observed -0.553 v. Similar calculations can be made for zinc and lead but are not presented here since the polarographic waves are irreversible.

Calculation of half-wave potentials of some metal ions in acetonitrile from Pleskov's amalgam electrodes has been done.[7] Employing the expression developed by von Stackelberg[33] and using Pleskov's[11] potentiometric data, the half-wave potential of cesium is found to be -2.20 v., which compares well with the recalculated value, -2.23 v., given in Table II as obtained by Wawzonek and Runner.[3]

Vlcek[34] has suggested that the half-wave potential of potassium is the same in all solvents. Un-

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[31] C. E. Teeter, Jr., This Journal, **53**, 3927 (1931).

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der this assumption, comparison of reduction of cations in differing solvents can be made by noting the difference, $\Delta E_{1/2}$, between the potassium half-wave potential and the half-wave potential of the particular metal. This is at least a reasonable approach to absolute comparison of half-wave potentials. Tabulation of these data for acetonitrile and aqueous solutions (non-complexing supporting electrolyte) shows several interesting points. Of the ions studied (outside of the alkali metals) the $\Delta E_{1/2}$ values are most similar for thallium, 1.70 v. in acetonitrile and 1.66 v. in water. This is reasonable when one considers that thallous ion does not form complex ions and presumably is not highly solvated, or at least the degree of solvation is the same in water as in acetonitrile.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF ARKANSAS]

The Neutral and Acid Hydrolysis of Ethyl Dibromoacetate in Acetone–Water Solvents[1]

BY FREDERICK N. HORNYAK AND EDWARD S. AMIS

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The neutral and acid hydrolysis of ethyl dibromoacetate was carried out at three temperatures and in water-acetone solvents containing various percentages of acetone. In the neutral hydrolysis the acid formed produced a departure from the first-order law at greater than 8% reaction. The acid-catalyzed runs followed the pseudo first-order law strictly for at least 85% of completion of reaction. The parameters of the Arrhenius equation are presented and discussed. The dependence of the rates on the dielectric constant of the media is compared with that of the acid hydrolysis of ethyl dichloroacetate in acetone–water solvent.

Introduction

As part of the general problem of the effect of solvent and molecular substituent changes upon reaction rate in solution, a study of the neutral and acid-catalyzed hydrolysis of ethyl dibromoacetate was carried out.

Experimental

Materials.—All water was twice distilled; the last distillation employed alkaline potassium permanganate. The water was then boiled to ensure carbon dioxide removal and was stored and delivered from vessels protected with ascarite tubes.

A. C. S. reagent grade acetone was purified according to the procedure of Åkerlöf.[2]

Ethyl dibromoacetate (product of Sapon Laboratories, Inc.) was washed briefly with concentrated sodium bicarbonate and then with calcium chloride solution. After drying over drierite, distillation at 14.5 mm. gave the ester with b.p. 81–82.5° (reported[3] 66–70° at 7 mm.); d^{22} 1.9081; $n^{22}{}_{D}$ 1.4973; $n^{12.5}{}_{D}$ 1.5018 (reported[4] $d^{20}{}_{20}$ 1.9025; $n^{12.5}{}_{D}$ 1.50167). Observed molar refraction and neutralization equivalent were 37.72 and 244 ± 2, respectively (calculated 37.86 and 246).

Barium hydroxide solutions, 0.002500 and 0.02500 *N*, were made up periodically from concentrated stock solution and were checked frequently against aliquots of standard potassium acid phthalate solutions. The hydrochloric acid solution was 0.3700 *N*. C.P. chemicals were used and all normalities were determined to four significant figures.

Methods and Apparatus.—Reaction temperatures were kept constant to ±0.03° and were determined with a NBS thermometer.

All pipets and burets were calibrated.

Hydrolysis were carried out in glass-stoppered 100-ml. volumetric flasks. By lightly greasing the stoppers (Fisher Rubber Compound Stopcock Lubricant) and fastening them down with rubber bands evaporation of solvent was made negligible. The grease was insoluble and had no apparent effect.

The reaction solution for a kinetic study was prepared as follows. Appropriate amounts of acetone, water and hydrochloric acid (if any) were weighed into a tared volumetric flask. The flask was then stoppered and placed in the constant temperature bath for several hours to reach thermal equilibrium. Weighings were made to 0.02 g. and the weight of hydrogen chloride (if any) was taken into account when calculating the weight of water present. The reaction was started by adding 10.00 ml. of a standard acetone–ester solution and adjusting to the mark with water at the temperature of the experiment. The flask was then shaken and the time noted. At convenient intervals 10.00-ml. samples were withdrawn, run into 25 ml. of ice-cold water and titrated with standard base. Sufficient accuracy in the times of starting and of sample withdrawal was easily attained because of the slowness of the reaction. The actual sample volume delivered by the pipetting procedure was checked by weight and also by titration and allowance was made in subsequent calculations.

The concentration of ester in all runs was 0.0500 molar and the concentration of hydrochloric acid in the acid runs was 0.0500 molar. The acetone percentages employed are shown in the tables of results.

In this work it was found that the standard base, during the titration of an ice-cold reaction sample, reacted in part with unhydrolyzed ester giving an acid value that was too high. It was found that identical samples of reaction mixture gave widely different acid values depending on the strength of the base used; the stronger base gave the highest value. In the titration of standard acid with standard base the addition of pure ester and acetone vitiated the results even under ice-cold conditions. An ester solution alone, without the presence of acid showed a zero acid value on titration with standard base (immediate end-point).

Because of these facts it was necessary to standardize the titration procedure and determine the errors involved. The titrating base solution was run in always at approximately the same rate and the reaction sample was stirred constantly in an ice-bath.

A series of mixtures of standard acid phthalate, acetone, water and ester were made up to correspond to compositions which would be obtained for titration at various stages of reaction. These mixtures were freshly made up and titrated ice-cold in the same manner as the actual run samples. The errors obtained were reproducible and found for acid hydrolyses to be a linear function of the amount of unhydrolyzed ester present. These corrections were applied to the actual run titrations to determine the true amount of acid present.

The acid runs employed the stronger 0.02500 *N* base and the titration error was about 5% in the early stages of reaction where the amount of unhydrolyzed ester is large.

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(1) The authors wish to thank the National Science Foundation for a grant which made this research possible.

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