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ELECTROCHEMICAL STUDIES IN CYCLIC ESTERS

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ELECTROCHEMICAL STUDIES IN CYCLIC ESTERS

William Sidney Harris
Thesis

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Contents

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ABSTRACT

Solubilities and conductivities of inorganic salts in the cyclic esters ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone have been studied. A number of common inorganic salts were found to be highly soluble in all of these solvents. The variation of solubility with the physical properties of the solvents is discussed. Conductivity measurements have shown that a number of salts investigated behaved as strong electrolytes. Certain solutions of highly soluble inorganic salts were found to have high viscosities in these solvents Such relatively low-melting covalent halides as $AlCl_3$, $NbCl_5$, and $FeCl_3$ were found to be quite soluble.

The solubilities and conductivities characterizing these solutions conform to present-day concepts, and are explained in the light of modern solubility theory.

Solutions of a variety of salts were electroreduced, providing further data for the characterization of these solvents. This study indicates that, in addition to those metals which may be obtained from aqueous solutions, some of the highly electropositive metals may also be electrodeposited.

These solvents are characterized by high dielectric constants, low vapor pressures, relatively low toxicity, and high chemical stability, and are relatively nonreactive with anodically liberated halogens. Such properties are desirable in an easily handled ionizing medium.

INTRODUCTION

General

Although the solvent powers of nonaqueous solvents have been recognized for centuries,[1] investigations of electrochemical properties of nonaqueous solutions were begun only in the latter part of the nineteenth century.[2] Nonaqueous electrolytes, particularly organic solutions, have received more attention in recent years. Studies have been made on conductances,[3] transference numbers,[4, 5] diffusion,[6] electrode potentials,[7] and on ionic species present in nonaqueous solutions.[8] Less quantitative explorations have been made on the electrodeposition of certain metals not now obtainable by electrolysis of aqueous solutions.[9]

The purpose of this research was to investigate a group of organic solvents with respect to certain of their electrochemical properties. Ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone (see Fig. 1) were chosen because they promised to possess many of the properties desirable for solvents used to conduct electrochemical reactions (see Table I). They have high boiling points (low vapor pressures at room temperature) and high dielectric constants (see Table I) as well as relatively low toxicity and good chemical stability. Cyclopentanone and ethylene trithiocarbonate were also included for purposes of comparison.

It seemed desirable to study solubilities in these solvents and to attempt to determine what relations exist between solubilities and certain of their physicochemical properties. Other than scattered information there has been a decided lack of characterization of this group in the literature.

In order to gain insight into what species may be present, studies were made of conductances of the various solutions. In addition, qualitative experiments were performed to determine whether certain metals may be electrodeposited.

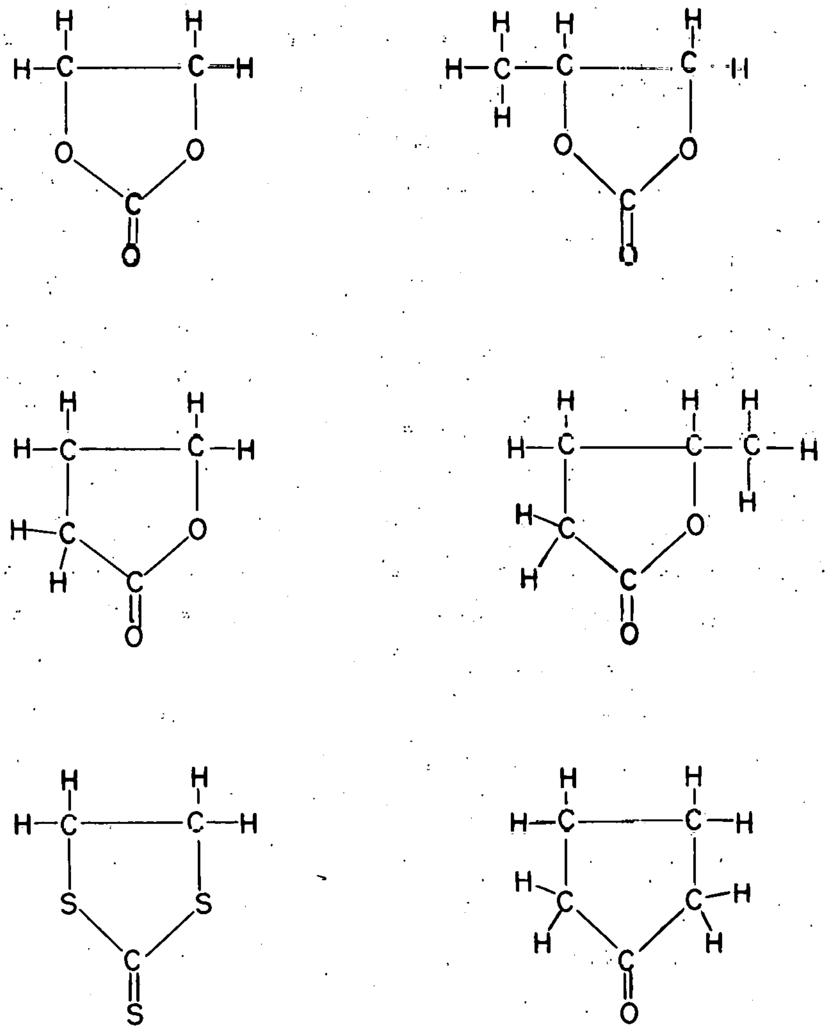

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Fig. 1. Structural formulas of selected solvents.

TABLE I

Physical properties of solvents studied[a]

Physical constants	Ethylene carbonate	Propylene carbonate	γ-butyrolactone	γ-valerolactone	Ethylene trithiocarbonate	Cyclopropanone
Melting Point (°C)	36.4 (10)	-49.2 (11)	-43.53 (12)	-31 (13)	34.5 (14)	-58.2 (15)
Boiling Point (°C)	248 (10)	241.7 (11)	204 (12)	205.9-206.6 (13)	117.5 at 0.6 mm (14)	130.6 (15)
Density of Liquid (grams ml^{-1})	1.323 at 40° 1.338 at 25°	1.183 at 40° 1.198 at 25°	1.1254 at 25° (12)	1.0518 at 25° (13)	1.48 at 25° (14)	0.9480 at 20° (15)
Dielectric constant	89.12 at 40° (16)	64.4 at 25°	39.1 at 20° (17)		58.8 at 25°	13.45 at 20° (18)
Dipole moment	4.87 D (16)		4.33 D (17)			3.00 D (19)
Refractive index	1.419 (10)	1.4209 at 20° (11)	1.4348 (12)	1.4301 (13)		1.4366 (15)
Viscosity (centipoises)	1.955 at 40° 2.547 at 25°	1.916 at 40° C 2.530 at 25° C	1.751 at 25° C	2.15 at 25° C (13)		

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[a] References to literature values are shown in parentheses.

Dielectric Properties

We may calculate the dielectric constants of these solvents, using the known values of dipole moments, refractive indices, and molar volumes, by means of Onsager's equation[20]

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \frac{4\pi N_i \mu^2}{9kT}, \qquad (1)$$

where ϵ is the dielectric constant, ϵ_∞ is the dielectric constant at infinite frequency, N_i is the number of molecules per cm^3, μ is the dipole moment, k is Boltzman's constant, and T is the absolute temperature, derived for polar liquid having spherical molecules.

We may also use an equation derived by Kirkwood[21]

$$\frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{\epsilon(\epsilon_\infty + 2)^2} = \frac{4\pi N_i \mu^2 g}{9kT} \qquad (2)$$

which is the same as the Onsager equation except for the parameter "g" which is a measure of the hindrance of rotation of the polar-solvent molecule. The parameter, g, because it was theoretically derived, may be calculated for those cases in which enough is known about the structure of the liquid. It has been evaluated for water and some of the lower aliphatic alcohols.[22]

By making the appropriate calculations from the known values of dielectric constant, dipole moment, and molar volume, and by approximating the dielectric constant at infinite frequency by the square of the refractive index for visible light, we find the folloiwng values for Kirkwood's g for the solvents listed:

Ethylene carbonate	1.19 at 40° C
Propylene carbonate	1.04 at 25° C
γ-butyrolactone	0.71 at 25° C
Cyclopropanone	0.65 at 25° C
Acetone	0.89 at 25° C
Water	2.1 at 25° C

Molecules in which the charge distribution is exposed such as those in hydrogen-bonded liquids characterized by g values differing from unity, can assume relative configurations in which there are strong interactions. When the charge distribution is not exposed but shielded as in nitrobenzene, such interactions do not take place and the orientational correlations are not great.[22] For liquids of this type, the g value should be near unity.

The values obtained for g give an indication of the type of association found in the liquids. Values of g greater than 1 indicate an association such that the dipole moments of the molecules reinforce each other, i.e., a head-to-tail association of the dipoles. Values of g for water and the lower aliphatic alcohols lie between 2 and 3.[23] Values of the parameter g less than unity are interpreted to mean that an association has taken place that reduces the effective dipole moment, i.e., a configuration in which the dipoles orient in an antiparallel manner such that their moments cancel. The values of the parameter g found for ethyl iodide, benzonitrile, and chlorobenzene lie between 0.65 and 0.70.[24]

From the calculated g values we may conclude that the solvents studied are somewhat associated. We would expect those solvents that are more strongly associated to have a more exposed charge distribution and thus to solvate better with ionic solutes.

Chemical Stability

Ethylene carbonate is decomposed slowly at temperatures between 200 and 245° C in the absence of water or catalysts. Above 125° C alkalies, and acids to a lesser extent, cause rapid decomposition. At 100° C pure ethylene carbonate is stable in the presence of water, but traces of salts such as sodium chloride accelerate its hydrolysis. At this same temperature, alkalies or strong acid cause rapid hydrolysis. Ethylene carbonate may be distilled rapidly at atmospheric pressure with only slight decomposition. Acidic materials, such as zinc chloride, aluminum chloride, or sulphuric acid at high temperatures will cause appreciable decomposition of ethylene carbonate into carbon dioxide and ethylene oxide.[11]

The stability of propylene carbonate is essentially the same as that of ethylene carbonate. Propene oxide, propionaldehyde, allyl alcohol and carbon dioxide have been found among the decomposition products.[10] Anhydrous propylene carbonate is relatively stable to attack by halogens anodically liberated at a platinum electrode. The color of bromine and iodine will persist for days, indicating a slow or negligible reaction rate. When chlorides are electrolyzed, chlorine gas is readily evolved at the platinum anode, indicating a moderate reaction rate with the solvent.

The products of decomposition of γ-valerolactone at 202° C are mostly polymerized material with the evolution of only a little gas.[25]

Background Material

The ability of nonaqueous solvents to dissolve inorganic salts has been known for a long time, but it was not until the latter part of the Nineteenth Century that any attention was given to the electrochemical aspects of nonaqueous solutions.

Of the earliest workers in this field, many gave their attention to the possibility of electrodepositing the alkali and alkaline earth metals from solutions of their halides in a variety of solvents. Such solvents as alcohols, pyridine, and acetone were employed.[26-31] As this field was further explored, a greater number of salt-solvent systems came under investigation. In 1910 electrodeposition of the metals, zinc, copper, tin, lead, cobalt, and nickel from solutions of their salts in formamid was studied by Rohler.[32]

Liquid ammonia as an electrolytic solvent also came under intensive study during this period. During the interval 1895-1909, Franklin and Kraus studied solubilities,[33] metathetical reactions,[34] conductivities[35, 36] and temperature coefficients of conductivity[37] in liquid ammonia. Conductivities in liquid ammonia were also studied by Smith in 1927.[38] Groening and Cady in 1926 studied decomposition voltages and over voltages in liquid ammonia,[39] while the deposition of metals was studied both by Audrieth and Yntema[40] and by Taft and Barnum[41] in 1930.

In the period 1922-1924 Muller and his co-workers studied the electrodeposition of metals and the decomposition potentials of a large variety of simple salts of metals in pyridine solutions. Because they took special precautions to make their materials anhydrous, they were able to discharge metals from solutions of their salts in pyridine where others had failed.[42-47]

P. Walden, one of the most intensive workers in this field during the first quarter of the century, studied electrical conductivity and solubility in various nonaqueous solvents. His book, Elektrochemie Nichtwässriger Lösungen,[48] presents the results of his own research (some of which had been previously published) along with the results of other workers. He gives a large amount of data on solubility, conductivity, and electrodeposition from nonaqueous solutions.

During the 1930's W. Plotnikow and other Russian workers conducted extensive studies on binary systems of alkali halides and aluminum halides dissolved in ethyl halides, benzene, toluene, nitrobenzene, and some of their mixtures.[49-81] Again, conductivity, solubility, and electrodeposition studies were carried out with these solutions.

Starting in the 1930's, Audrieth and co-workers studied the preparation of rare earth amalgams by electrolysis of alcoholic solutions of rare earth salts. They did not suceed in depositing any rare earth metals directly.[82, 83] Audrieth and co-workers also investigated the electrodeposition of metals from such solvents as liquid ammonia,[40] glacial acetic acid,[84] and acetamid and formamid.[85] More recently there has been an ever-increasing amount of work done in the field of nonaqueous electrochemistry, with special emphasis on electrodeposition of metals not obtainable from aqueous solutions. Hurley and Wier investigated the electrodeposition of aluminum from nonaqueous solvents.[86] They succeeded in depositing aluminum from a fused mixture of aluminum chloride and ethyl pyridinum bromide, both with and without added benzene or toluene. Other workers using a bath similar to that of Hurley and Wier were able to obtain good aluminum deposits up to 1 mm thick.[87] Brenner and co-workers at the National Bureau of Standards have made extensive studies on the deposition of such metals as aluminum, titanium, zirconium, beryllium, and magnesium from various nonaqueous solvents.[9, 88-93]

Recently many of the fundamental physicochemical properties of nonaqueous electrolytic solutions have also been subject to investigation, Sears and Dawson, et al, have made numerous studies of conductivities, transference numbers and diffusion coefficients in a variety of solvents including amids and N-substituted amids.[94-115] Schmidt and co-workers have made conductivity, viscosity, and polarographic studies of solutions of various salts in ethylene diamine.[116-118] Griffiths, Lawrence, and Pearce have recently studied the conductivity of electrolytes in nonaqueous and mixed solvents.[119-123]

Knowledge of the electrochemical properties of nonaqueous solvents has greatly increased during the past sixty years. Although much of the first interest in nonaqueous solvents developed because of the possibility of depositing the more active metals from them, only a few nonaqueous (room-temperature) plating baths have been used outside of the laboratory. The deposition of metals from nonaqueous solvents is still of great interest. However, a greater expenditure of effort has been made lately toward an understanding of many of the physicochemical properties of such solutions.

SOLUBILITY THEORIES

The free energy of solution, which determines the solubility, results from the difference in free energy of the ions in the crystal and in the solution. The free energy of the ion in solution will be determined by electrostatic properties and by the chemical properties of the solvent. The electrostatic interactions will be influenced by dipole moment and dielectric constant of the solvent, and by the size and the charge of the ion. The chemical interactions will be affected by the charge distribution, the shape of the solvent molecule, and the availability of orbitals in the solute ions for coordination. Of the many theories and equations that have been used to predict changes in solubility with variation of solvent, the majority are dependent only upon changes in the electrostatic properties of the solvent.

J. Hildebrand, in the first edition of his monograph on solubilities, summarized a number of general factors relating to the solubility of solid electrolytes.[124] Of special note in his mention of the promotion of solubility by solvation caused by differences in acidic and basic character of the solvent and solute. This has not been given sufficient attention by many of the later investigators.

Numerous relationships between solubility of ionic salts and various functions of the dielectric constant of the solvent appear in the literature. The most commonly used relationship between solubility and dielectric constant is:

$$\log S = \text{const}_1 + \text{const}_2 \ \frac{1}{\epsilon} \ , \qquad (3)$$

where S is the solubility. Equation 3 is a simplified form of the equation originally proposed by Born to calculate the free energy of hydration (ΔF) of ions entering a medium of dielectric constant ϵ from vacuum,[125]

$$\Delta F = -\frac{N_{Av} z^2 e^2}{2r} \ (1 - \frac{1}{\epsilon}) \ . \qquad (4)$$

Here N_{Av} is Avogadro's constant, z is the charge of the ion, e is the charge of the electron, and r is the radius of the ion.

Izmailov, Krasovskii, Aleksandrov, and Vail also used this relationship [Eq. (3)] for the solubility of strong electrolytes in various solvents.[126] They obtained this equation by a consideration of the effect of the solvent on the activity coefficients. Izmailov previously showed that the activity coefficient may be split into two parts, one dependent upon the chemical properties, and the other a function of the electrostatic properties of the solvent.[127] It was assumed that by considering solvents with similar chemical properties, the activity coefficients, and hence the solubility, would depend only on the dielectric properties of the solvent. When they plotted data from the literature for the solubilities of silver chloride, silver bromide, silver iodide, strontium perchlorate, and calcium perchlorate in water, and several aliphatic alcohols, to test this equation, they obtained reasonable agreement.

S. A. Voznesenskiy and R. S. Biktimirov in their study of the solubility of inorganic salts (calcium sulphate dihydrate and strontium sulphate) in organic solvents (water, dimethylformamid, dioxane, and pyridine) and in mixtures of these solvents with water, used this same relationship,[128] obtained from Izmailov et al.[126] and Born.[125] Because the four solvents they used were of different chemical nature, they did not expect the equation to be applicable. The experimental data confirmed this. However, they did find the equation applied to solutions of calcium sulphate dihydrate and to strontium sulphate in dioxane and water mixtures over the range 0 to 50% dioxane. Dimethyl formamid increased the solubility of both salts in water; with solutions of strontium sulphate the solubility curve contained a maximum, hence the solubility equation (Eq. (3)) could not be used.

Ei Koizumi found this same equation to apply to the system lead sulphate in aqueous acetone.[129] He also studied the solubility of lead sulphate in various mixed solvents with the same dielectric constant and concluded that the solubility was not solely determined by the dielectric constant.[130]

Walden in his investigation of solubility in nonaqueous solvents found the empirical relationship:

$$3 \log \epsilon = \text{const} + \log N, \qquad (5)$$

where N is the mole fraction of the solute. As typical salts for such a study he chose tetraethyl ammonium iodide, tetramethyl ammonium iodide, tetrapropyl ammonium iodide, and tetramethyl ammonium thiocyanate. These salts were chosen because the large size of the ions would reduce the effects of solvation. Because of its smaller size, one would expect greater solvation effects in the case of the lithium ion. For solutions of lithium chloride in water and the lower aliphatic alcohols, Walden's relation is not followed.

Ricci and Davis empirically obtained the same equation (Eq. (5)). They predict $\log C = 3 \log \epsilon + \text{const.}$, where C is concentration of solute in moles/liter.[131] Their equation is based on the assumption that the Debye-Huckel limiting law will hold in more concentrated solutions and on the empirical assumption (observed for a number of solutions) that the mean activity coefficients of an electrolyte in its saturated solution is a constant, independent of the solvent.

Cleaver investigated the solubilities of some cis (flavo) and trans (croceo) dinitrotetrammine cobalt (III) salts (sulphate, iodate, picrate, permanganate, and dinitro oxalatodiammine cobaltate) in water-dioxane, water-acetone, and water-ethanol in order to determine the variation of solubility with dielectric constant in mixed solvents.[132] He then compared his results with two of the existing theories of solubility, the Born equation,[125] and the Ricci-Davis empirical equation,[131] which predict the variation of the solubility with dielectric constant. Cleaver found that the Born relationship was apparently followed only in one system, the flavo-sulphate, while for the other systems the solubility at low dielectric constants was greater than that predicted. Plots of the logarithm of solubility against the logarithm of dielectric constant were generally linear, but at the same dielectric constant the same salt in the three solvents showed different solubilities, indicating specific solvent effects. The croceo and flavo picrate had no regular change of solubility with dielectric constant, but exhibited maxima and minima as solvent composition changed from pure water to pure organic solvent.

Monk and Davis in their study on the influence of mixed solvents on the solubility of silver acetate gave data for its solubility in mixtures of water with ethanol, acetone, and with dioxane.[133] They found the function:

$$\text{log solubility-product constant} = \text{const}_1\, \epsilon + \text{const}_2 \qquad (6)$$

to be valid. Monk also observed this relationship for the systems in which calcium, barium, and lanthanum iodates were the solutes, and the solvents were water and water mixed with methanol, ethanol, acetone, propyl alcohol, ethyl acetate, dioxane, ethylene glycol, or glycerol.[134]

The theories that have been presented to explain the solubility of ionic solutes in various solvents are of only limited usefulness. Because of the important role played by specific chemical interaction, those theories which involve some function of the dielectric constant will only be valid for a group of solvents of similar coordinating ability. Water and the n-aliphatic alcohols may have similar coordinating properties. Solubilities of ionic salts in these solvents are a smooth function of the dielectric constant. Solubilities in the five solvents, ethylene carbonate, propylene carbonate, γ-butyrolactone, γ-valerolactone, and cyclopropanone, are not a smooth function of the dielectric constant.

EXPERIMENTAL PROCEDURES

Purification of Solvents

Propylene Carbonate*

The material used for making up the various solutions in this investigation was prepared by fractionating the solvent twice. The first fractionation was conducted at a pressure of 50 mm of mercury and at a reflux ratio of 5:1. A small portion containing low-boiling impurities and a smaller amount of high-boiling impurities were discarded. The total material rejected was about 5%. The remainder was refractionated at a pressure of 20 mm and a reflux ratio of between 15:1 and 25:1. The middle four-fifths of this was retained and used.

The distillation column used for the purification of the propylene carbonate, as well as for the other organic solvents used in this work, was a glass column 2.5 by 90 cm packed with 3/32-in glass helices. The column was insulated with a silvered vacuum jacket, the outside of which was electrically heated to a temperature slightly below the working temperature of the column. The reflux ratio was controlled by a stopcock. During vacuum fractionation, constant vacuum was maintained by an electrical pressure-sensing element, relay, and a solenoid valve between the system and the vacuum pump.

For subsequent analysis a special batch of propylene carbonate was prepared. The solvent received from the manufacturer was first dried by passing it through a glass crying column, 2.5 by 90 cm, packed with type 4A molecular sieves.† The material was then fractionally distilled at a pressure of 8 mm and temperature of 105° C. The distilling-pot temperature was about 140° during the distillation.

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*Received from Jefferson Chemical Co., Houston, Texas.

†Linde Air Products Co., 30 East 42nd Street, New York 17, N. Y.

The middle 4/5 of the distillate was collected in four fractions. The refractive indices of these samples were determined and found to be identical within a part in the fourth decimal value.* Two samples were analyzed using the heat-of-fusion method,† the apparatus and techniques of which have been described by Tunnicliff and Stone.[135] Sample I (the material as received and only dried by passing through a glass column containing molecular sieves) was found to contain 0.6 mole-percent impurities and had a melting point of -55.4 C. Sample II obtained at a reflux ratio of 30:1 was a center cut of the middle 4/5 of the distillate obtained by fractionation of the dried propylene carbonate as described above. This sample was found to contain 0.4 mole-perdent impurities. This sample had a freezing point of -55° C.§ The low freezing point found suggests that a metastable crystalline phase, formed by the sample pretreatment before the melting data were taken, may have interfered with the results. No prediction was made as to what effect this would have on the purity values. Other than the possibility of the formation of a metastable state, as suggested, or the formation of solid solutions of propylene carbonate with an impurity, no explanation is known for the difference in melting points. It seems very unlikely that the distilled product could be of lower purity than the starting material.

The specific conductivity of sample I was $1 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ while that of sample II was $2 \times 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. Sample I was analyzed by the Karl Fischer method for water and was found to contain 0.036 weight-percent water.[136] Sample II contained less than 0.002

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*Spencer Refractometer #2082, refractive index $n_D^{25} = 1.4196$.

†Through the courtesy of Dr. Fred Stross, Shell Development Co., Emeryville, California.

§For "material from typical production" of purity greater than 98%, the freezing point is -49.2 C.[11]

weight-percent water.[*] All the solvent as used for the experimental work contained less than 0.002 weight-percent water.[*]

Ethylene Carbonate

The starting material[†] was re-crystalized twice to eliminate a portion of the impurities and then vacuum fractionated at a pressure of 50 mm. The middle 4/5 of the distillate collected between 152.5° and 152.8° C was used.

γ-Butyrolactone

The solvent as received from the manufacturer[§] was vacuum fractionated twice, first at a pressure of 50 mm, and then at a pressure of 9 mm. The middle 4/5 of the distillate was retained and used. This material had a refractive index 1.4342 D^{25}.

γ-Valerolactone

The starting material[**] was vacuum fractionated at a pressure of 20 mm. The middle 4/5 of the distillate was retained and used.

Ethylene Trithio Carbonate

The material as received from the manufacturer[††] was flash distilled at a pressure of approximately ½ mm. The distilling-pot temperature varied from 115° C. to about 125° due to pressure fluctuations. The vapor pressure of ethylene trithiocarbonate is ½ mm at 117° C.[14]

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[*] Water was undetectable, but the limit of accuracy for the size of sample and strength of reagent was about 0.002 weight-percent water.

[†] Obtained from Jefferson Chemical Co., Houston, Texas.

[§] Obtained from Eastern Chemical Co., 34 Spring Street, Newark 2, N J.

[**] No. P6123 from Eastman Kodak Co., Rochester 3, N.Y.

[††] No. P. 6529 from Eastman Kodak Co., Rochester 3, N. Y.

Cyclopentanone

The starting material[*] was fractionated at atmospheric pressure. The middle 4/5 of the distillate which boiled at 129° C and was collected at a reflux ratio of 20:1 was used for the measurements. Analysis of this fraction by the Karl Fischer method indicated a water content of less than 0.002%.[†]

Preparation of Anhydrous Salts

Magnesium bromide, $CaBr_2$, $NiBr_2$, and $BaBr_2$ were prepared by thermal dehydration of the hydrated salt under a stream of HBr gas at atmospheric pressure at temperatures between 200° and 400° C for 4 to 8 hr.[137]

Uranium chloride, $TiBr_4$, $AlCl_3$, $FeCl_3$, $NbCl_5$, and $ThCl_4$ were obtained in an anhydrous state.

Reagent-grade NaI, which was found to contain 3% water, was effectively dehydrated under vacuum (0.1 to 1.0 μ pressure) at temperatures between 50° and 100° C. The standard procedure for all other salts which do not hydrolyze with water was to dry them on a vacuum line (0.1 to 1.0 μ pressure) as a precautionary measure to remove adsorbed water before use.

The purity and the sources of the various salts appear in Appendix II.

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[*] Obtained from Arapahoe Chemicals Inc., Boulder, Colo. and also as No. 2543 from Eastman Kodak Co., Rochester 3, N. Y.

[†] Water was undetectable, but the limit of accuracy for the size of sample and strength of reagent was about 0.002 weight-percent water.

Physical Measurements

Viscosimetry

All viscosity measurements were made by the use of Ubbelohde suspended-level viscosimeters.[138] [*] The approximate calibration factors[†] of the three viscosimeters were 0.01, 0.1, and 1 respectively.

The viscosimeter with constant 0.01 was calibrated with water at 25° C and then compared to the one with constant 0.1 by the use of di-n-butyl pthalate. The viscosimeters with constants 0.1 and 1.0 were compared with an 85% glycerol, 15% water mixture. The final calibration constants were 0.00974, 0.1063, and 0.938. The value of the viscosity of water at 25° was taken as 0.8902 centipoise.[139, 140] Corrections for kinetic energy of flow were used as tabulated by Ubbelohde.[138]

Density Measurements

Densities were determined by weighing the solutions in calibrated 25-ml volumetric flasks. For our purposes this method gave sufficient accuracy. Air buoyancy corrections were applied to the density determinations.

Solubilities

A water bath of 175 liters capacity was used as a thermostat for both solubility and conductivity measurements. The temperature of the bath was controlled at 25° C ± 0.01. Saturated solutions of the various salts in the solvents were prepared by agitation of 5 to 15 gr of the salt with approximately 75 ml of solvent in a special glass cell shaped in the form of an inverted T. (See Fig. 2). The solubility cell

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[*] Obtained from Arthur H. Thomas Co., West Washington Square, Philadelphia 5, Pa.

[†] Kinematic viscosity equals calibration factor multiplied by observed efflux time in seconds.

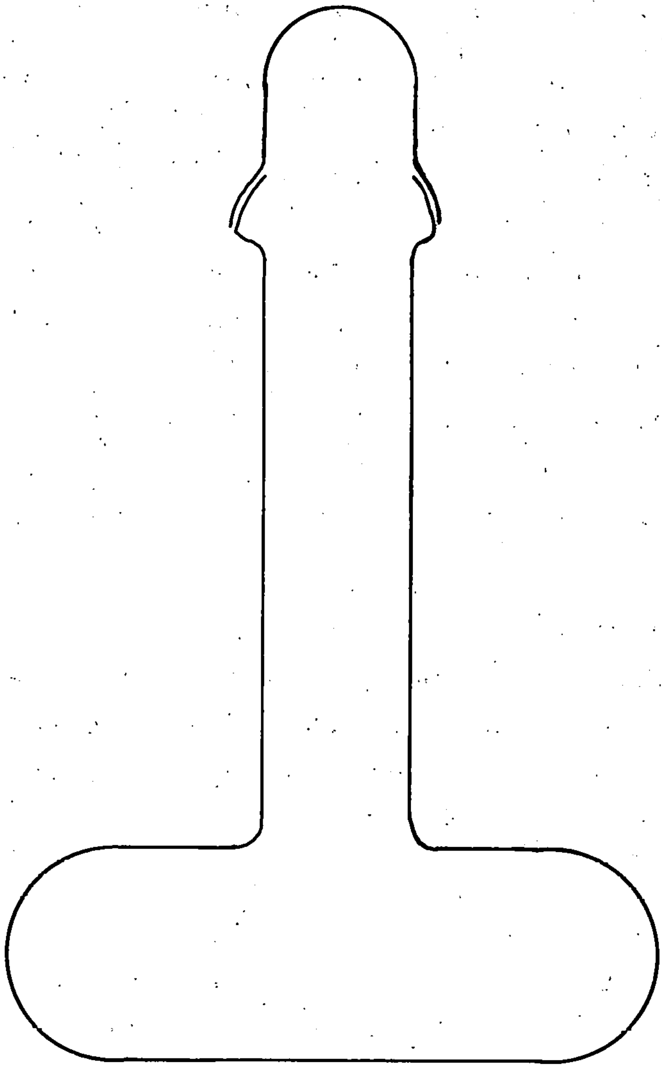

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Fig. 2. Solubility cell.

was constructed with a size 35/20 ball joint and cap, thus when fitted with a clamp this could be transferred when necessary through the vacuum lock of the dry box.[*] The solutions were made by rocking the solubility cells with the horizontal section of the cell completely submerged in the thermostat bath. Agitation was continued for a minimum of three days, with longer periods for more viscous solutions.

In order to determine solubilities a weighed portion of the saturated solution was withdrawn and analyzed. The solubilities of certain relatively nonhygroscopic salts were determined by vacuum evaporation of approximately 1 ml of saturated solution (it was found that when the solutions were evaporated in air at 100° C, oxidation of solvent gave relatively nonvolatile products which gave high solubility values.)

The solubility of a majority of the salts was determined by analysis by the use of accepted standard methods.[†] Others which contained only traces of salts were analyzed by optical spectrometric means.[§]

Conductivity Measurements

Conductivities of solutions were determined with a Wheatsone-type bridge by the use of an oscilloscope as a null-detecting instrument.

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[*] The dry box is of a design developed at the Livermore Laboratory of University of California Radiation Laboratory. The box, constructed of steel, has two glove ports and an antechamber. The total enclosed volume (about 350 liters) was dried by evacuation with an oil-diffusion pump, and then filled with dry argon.

[†] By Dr. Eugene Huffman's analytical group, University of California Radiation Laboratory.

[§] By Dr. John Conway's group, University of California Radiation Laboratory.

(See circuit in Fig. 3.) Smooth platinum electrodes were used in the conductivity cells to facilitate handling and eliminate need for frequent replatinization. It was recognized that the omission of platinization can cause a small relative error in the conductivities.[141, 142] The specially constructed cells had cell constants of 1.608 cm^{-1} and 0.04200 cm^{-1}. (See Figs. 4 and 5.)

For the conductance concentration curves the concentration was varied experimentally by stepwise addition of a solution containing a known concentration of salt to a given weight of pure solvent, or to a more dilute solution of the same salt in the conductivity cell.

Dielectric Constants

The dielectric constant of propylene carbonate was determined at 100 kc, and that of ethylene trithiocarbonate at 50 kc*. The results appear in Table I.

Electrodeposition Experiments

The qualitative electrodeposition experiments were performed in an H-shaped cell (Fig. 6). The cathode and anode compartments were separated by a sintered-glass diaphram. Provision was made for magnetic stirring of both sides. The two electrode chambers were closed with ball joints which gave vacuum-tight seals. The cell, as normally used, contained a total of 30 ml of solution. Unless otherwise specified, platinum electrodes (0.06 mm thick) each of 3 cm^2 area, were employed.

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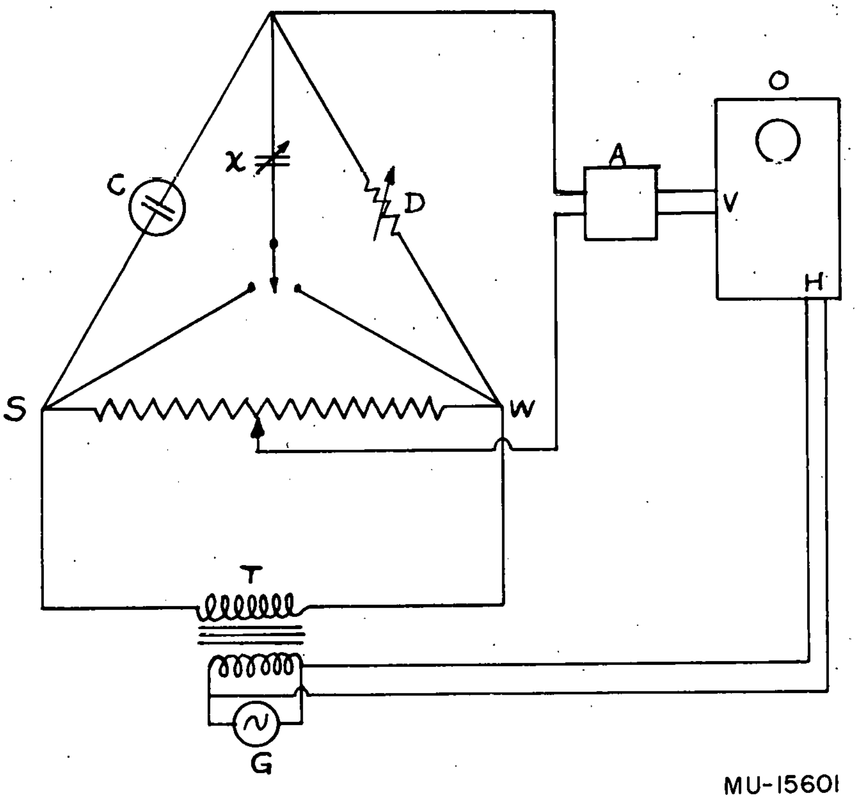
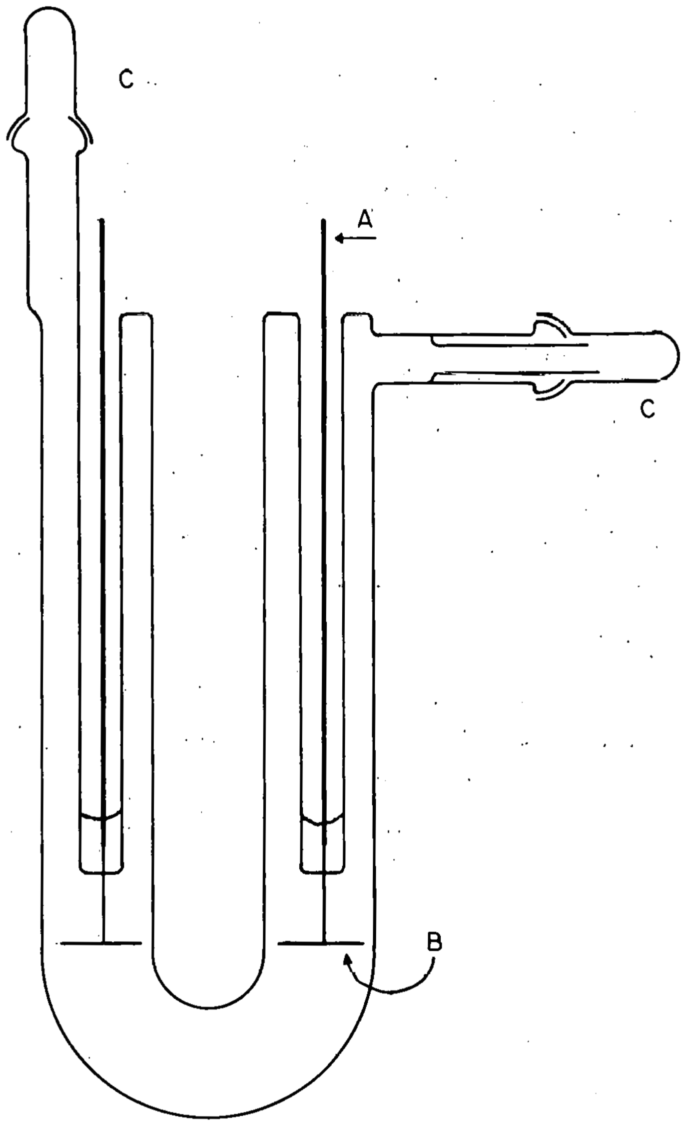
*Measurements were performed by William Ortung at the University of California, using a wide-range capacitance bridge employing the best features of Cole and Gross, J. Sci. Instr. 20, 252 (1949), and O'Konski, J. Amer. Chem. Soc. 73, 5093 (1951).



MU-15601

Fig. 3. Circuit diagram of conductivity bridge, showing:

a.	1000-cycle tuned amplifier
c.	conductivity cell
d.	decade resistance box, General Radio Type 602-M.
g.	oscillator, Hewlett-Packard type 200C
h.	horizontal input to oscilloscope
o.	oscilloscope - RCA type 155A
s-w.	slide wire, Leeds and Northrup type 4258
t.	isolating transformer, 1:1, 600 Ω
v.	vertical input to oscilloscope
x.	variable capacitance box.



MU-15602

Fig. 4. Conductivity cell, showing:
a. tungsten lead to electrode
b. platinum electrode
c. caps, size $\frac{18}{9}$

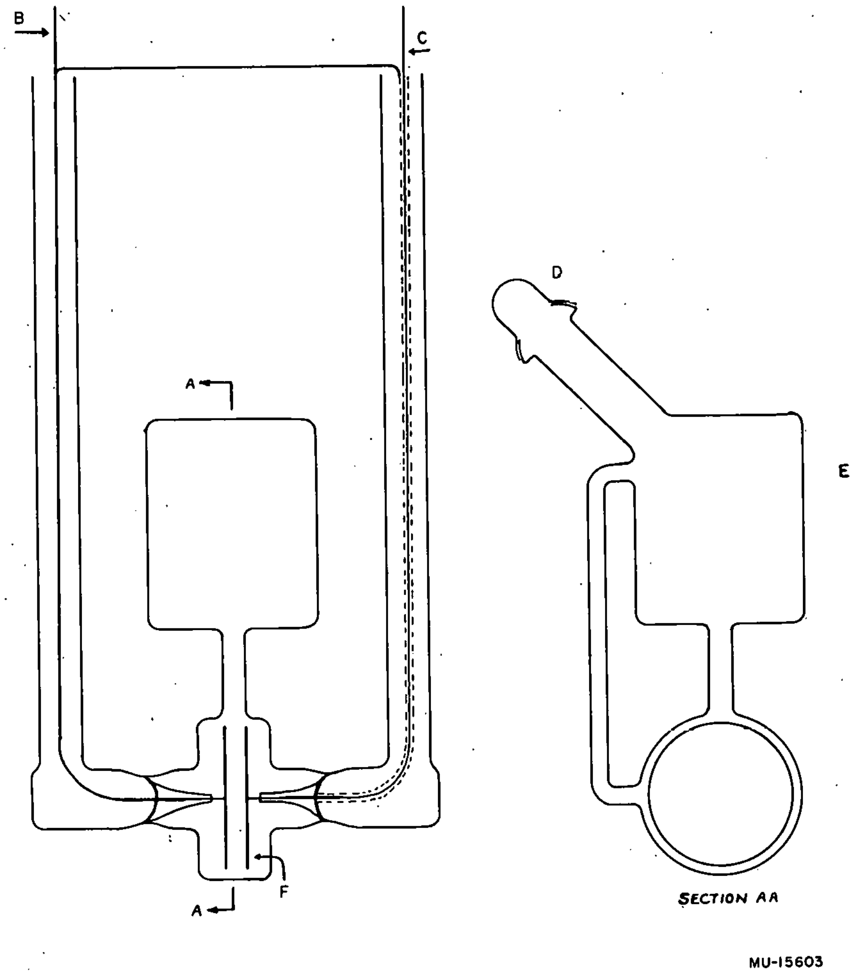


Fig. 5. Conductivity cell, showing:
  b. grounded electrodes and nickel lead-in
  c. shielded lead-in
  d. cap, size $\frac{28}{15}$
  e. mixing chamber
  f. platinum electrodes.

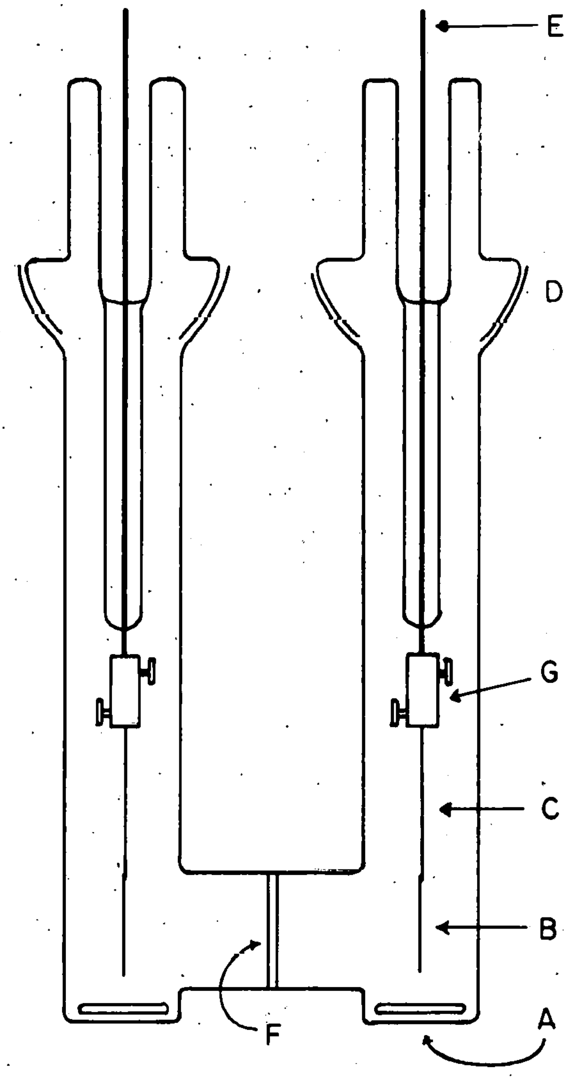


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Fig. 6. Electrolysis cell showing:
a. magnetic stirrer
b. platinum electrode
c. platinum lead
d. ball joint, size $\frac{35}{25}$
e. tungsten lead-in
f. sintered-glass diaphragm
g. connector.

SOLUBILITY AND CONDUCTIVITY DATA

The most recent extensive compilation of solubilities of inorganic salts in nonaqueous solvents was made by Walden in 1924.[48] He gave both qualitative and quantitative data for a large variety of solvents. More recently Seidel has given some data for the more common solvent-solute combinations.[143] Solubilities for a more limited number of solvents have been given by Audrieth and Kleinberg.[144]

There are no published quantitative solubilities for the solvents ethylene carbonate, propylene carbonate, γ-butyrolactone, γ-valerolactone, ethylene trithio carbonate, or cyclopropanone except for the data appearing in Jefferson Chemical Co.'s Technical Bulletins for ethylene carbonate and propylene carbonate.[10, 11]

The solubilities of salts in propylene carbonate, the results of this work, are compiled in Table II. Solubilities in the other solvents studied appear in Table III.

In the solution of lead iodide and potassium iodides (composition of solid phase(s) unknown, but solution was not saturated with respect to PbI_2), the mole ratio of K:Pb was 0.748:1. The presence of polynuclear complexes of lead is indicated by this ratio, because lead iodide is insoluble in propylene carbonate. The solution probably consists of potassium ions, PbI_3- ions, and polynuclear lead iodide complex ions. In aqueous solutions at 25° C potassium iodide is always in excess of lead iodide, when the solid phases are KI and double salt or when the phases are PbI_2 and double salt.

The viscosities and densities of a number of typical solutions were determined and their values appear in Table IV.

Effect of Impurities on Solubility

Cadmium iodide is quite soluble and forms a viscous solution in propylene carbonate that has not been specially purified (purity > 98%, as received from the manufacturer, but subsequently dried.) The solubility in carefully purified propylene carbonate is low (0.166 g/ 100 g solvent). Potassium iodide has virtually the same

TABLE II

Solubilities and conductivities of various anhydrous salts in propylene carbonate[a]

Salt	Temp. (°C)	Solubility gr/100 g solvent	Solubility moles/100 g solvent	Method for determining solubility	Specific conductivity (κ)	1000κ/moles per 1 solvent
<u>Group I Metals</u>						
LiCl	25	0.003	7.7×10^{-5}	k	1.91×10^{-5}	
LiBr	25	21.12	0.243	h	4.99×10^{-4}	0.247
LiI	25	18.2	0.1365	h		
NaF	25	$\sim 2 \times 10^{-4}$	$5. \times 10^{-6}$	c		
NaCl	25	$\sim 2 \times 10^{-5}$	3×10^{-7}	c	1.56×10^{-6}	
NaBr	25	0.08	0.008	e	1.79×10^{-4}	24
NaI	25	16.63	0.111	e	5.8×10^{-3}	6.25
NaOMe	25	i		q		
$NaBH_4$	25	i		q		
Na_2SiF_6	25	i		q		
$NaSO_3NH_2$	25	i		q		
$NaBF_4$	25	1.02	0.00935	e	1.7×10^{-3}	21.8
KCl	25	~0.002	4×10^{-5}	c	1.06×10^{-5}	33.6
KBr	25	0.07	6×10^{-4}	e	1.48×10^{-4}	30
KI	25	3.71	0.0223	e	4.41×10^{-3}	23.6
KI	40	3.42	0.0206	e	5.71×10^{-3}	33.3
KBF_4	25	0.18	0.0012	e	1.9×10^{-4}	19
$CuCl_2$	25	0.12	8.7×10^{-4}	k	7.07×10^{-5}	
$CuBr_2$	25	0.14	6.2×10^{-4}	e	5.03×10^{-5}	9.7

TABLE II (cont'd)

Solubilities and conductivities of various anhydrous salts in propylene carbonate[a]

Salt	Temp (^{o}C)	Solubility gr/100 g solvent	Solubility moles/ 100 g solvent	Method for determining solubility	Specific conductivity (κ)	1000 κ/ moles per l solvent
Group II Metals						
$MgBr_2$	25	v. s.		q		
$CaCl_2$	25	~0.06	5×10^{-4}	c	2.26×10^{-5}	5
$CaBr_2$	25	14.9	0.0745	h	3.32×10^{-4}	0.530
$Ca(BF_4)_2$	25	1.44	0.00678	e	2.02×10^{-3}	35.6
$BaBr_2$	25	0.0232	0.000780	h	3.98×10^{-5}	6.1
$ZnCl_2$	25	72.0	0.528	h	7.18×10^{-5}	0.0163
$CdCl_2$	25	i		q		
$CdBr_2$	25	0.12	4.5×10^{-3}	k	3.94×10^{-5}	
CdI_2	25	0.166	4.54×10^{-3}	h	4.00×10^{-5}	1.1
$Cd(SO_3NH_3)_2$	25	i		q		
$HgCl_2$[11]	25	21	0.078			
Group III Metals						
$AlCl_3$	25	v. s.		q		
AlI_3	25	v. s.		q		
Actinide Series						
$ThCl_4$	25	1.25	0.00334	h	2.1×10^{-4}	7.48
UCl_4	25	3.89	0.0102	h	8.79×10^{-4}	10.1

TABLE II (cont'd)

Solubilities and conductivities of various anhydrous salts in propylene carbonate[a]

Salt	Temp (°C)	Solubility gr/100 g solvent	Solubility moles/100 g solvent	Method for determining solubility	Specific conductivity (κ)	1000 κ/moles per 1 solvent
Group IV Metals						
$TiCl_2$	25	i		q		
$TiBr_4$	25	v. s.		q		
TiI_2	25	i		q		
$SnCl_2$	25	i		q		
$SnCl_4$	25	26.70	0.102	h	low	
$PbCl_2$	25	~0.0006	2×10^{-6}	c	$\sim 5 \times 10^{-7}$	
$PbBr_2$	25	~0.04	$\sim 1 \times 10^{-4}$	k	4.73×10^{-5}	
PbI_2	25	$\sim 7 \times 10^{-6}$	$\sim 2 \times 10^{-8}$	h	2.3×10^{-6}	
K, Pb, I Complex	25	KI-15.56 PbI_2-58.47	0.0875 0.124	h	4.84×10^{-3}	
Group V Metals						
$NbCl_5$	25	~85	0.315	*		
Same, not saturated		6.023	0.0224	h	3.71×10^{-4}	1.65
$BiCl_3$	25	24.41	0.0774	h	1.86×10^{-5}	0.0318
Group VII Metals						
$MnCl_2$	25	~0.03	2×10^{-4}	k	6.5×10^{-5}	
$MnBr_2$	25	32.28		h		

TABLE II (cont'd)

Solubilities and conductivities of various anhydrous salts in propylene carbonate[a]

Salt	Temp	Solubility		Method for determining solubility	Specific conductivity (κ)	1000 κ/moles per l solvent
		gr/100 g solvent	moles/100 g solvent			
Group VII Metals (cont'd)						
Same, not saturated		~19	0.089	e	2.6×10^{-3}	3.5
Group VIII Metals						
$FeCl_3$	25	v. s.		q		
$FeBr_2$	25	s		q		
FeI_2	25	v. s.		q		
$CoCl_2$	25	0.0845	6.5×10^{-4}	h	1.74×10^{-4}	28
$NiCl_2$	25	i		k	$< 10^{-6}$	
$NiBr_2$	25	0.1	5×10^{-4}	k	1.39×10^{-4}	

---

[a] Key to solubility and conductivity tables:

q	Qualitative observation	k	Estimated from conductivity
v. s.	Very soluble	e	Analyzed by vacuum drying of solution
s.	Soluble		
sl. s.	Slightly soluble	h	Analyzed by Dr. Eugene Huffman's group, University of California Radition Laboratory
i.	Insoluble		
		c	Analyzed by Dr. John Conway's group, University of California Radiation Laboratory
		*	Estimated

TABLE III

Solubilities of anhydrous salts in solvents structurally related to propylene carbonate[a]

Salt	Temp (°C)	Solubility gr/100 g solvent	Solubility moles/100 g solvent	Method for determining solubility[a]	Specific conductivity (κ)	1000 κ/moles per l solvent
			Solvent: ethylene carbonate			
$ZnCl_2$[10]	40	33	0.242			
$HgCl_2$[10]	40	49	0.181			
KCNS[16]	40	s				
$KMnO_4$[16]	40	s				
$K_2Cr_2O_7$[16]	40	s				
$Cu(Br)_2$[16]	40	s				
NaI	40	37.60	0.251	h	1.1×10^{-2}	4.38
NaBr	40	0.31	0.0030	e	9.46×10^{-4}	36
$CaCl_2$	40	0.2	2×10^{-3}	k	8.66×10^{-5}	
KI	40	11.16	0.0671	e	1.50×10^{-2}	26.8
			Solvent: γ-butyrolactone			
NaBr	25	0.23	0.0022	e	4.29×10^{-4}	24
KI	25	12.5	0.0755	e	1.34×10^{-2}	21.2
NaI	25	58.15	0.388	h	7.56×10^{-5}	2.34
$CaCl_2$	25	0.05	4×10^{-4}	k	1.38×10^{-5}	

TABLE III (cont'd)

Solubilities of anhydrous salts in solvents structurally related to propylene carbonate[a]

Salt	Temp (°C)	Solubility gr/100 g solvent	Solubility moles/100 g solvent	Method for determining solubility[a]	Specific conductivity (κ)	1000 κ/moles per 1 solvent
			Solvent: γ-valerolactone			
NaI	25	30.03	0.200	h	5.47×10^{-3}	3.3
KI	25	4.24	0.0255	h	4.57×10^{-3}	21.5
			Solvent: ethylene trithiocarbonate			
NaI	40	< 0.006		c		
KI	40	< 0.02		c		
$CuBr_2$	40	s		q		
CdI_2	40	sl. s.		q		
			Solvent: cyclopentanone			
NaI	25	26.0	0.173	h		
KI	25	0.43	0.0026	e	1.69×10^{-4}	7.8

[a] Symbols are same as those in footnote a of Table II.

TABLE IV

Viscosities of selected solutions

Solvent	Solute	Solubility (moles/100 g solvent)	Temp (^{o}C)	Kinematic viscosity (centistokes)	Density (g/ml)	Viscosity (centipoise)
Ethylene carbonate			40	1.478	1.323	1.955
Propylene carbonate			40	1.620	1.183	1.916
Ethylene carbonate (super-cooled)			25	1.904	1.338	2.547
Propylene carbonate			25	2.111	1.198	2.530
γ-butyrolactone			25	1.556	1.1254	1.751
Propylene carbonate	KI	0.0223	25	2.588	1.2277	3.177
Propylene carbonate	NaI	0.111	25	7.175	1.336	9.5858
Propylene carbonate	LiBr	0.243	25	62.73	1.372	86.07
Propylene carbonate	$ZnCl_2$	0.528	25	1084.	1.602	1736.
Propylene carbonate	KI PbI_2	0.0875 0.124	25	157.2	1.901	298.8

solubility in solvent of both purities (3.65 g and 3.71 g/100 g solvent, for impure and purified solvent respectively). Because the impurities in the impure solvent are unknown, one can only speculate as to the reasons for this different behavior.

Salt-Induced Solvent Decomposition

The solution of a number of inorganic salts in propylene carbonate appeared to cause its decomposition. A slow pressure build-up over solutions of $CaBr_2$, and $MgBr_2$ evidenced the decomposition of the solvent. This reaction was further characterized by a distinct change in odor. Magnesium and calcium bromides were probably acting as Lewis acids and were coordinating to the carbonyl carbon of propylene carbonate, consequently causing the bond between the secondary carbon and the oxygen adjoining it to cleave. A strong coordination was further evidenced by inability to electrodeposit these metals (see page 59). This cleavage resulted either in the formation of propene oxide and carbon dioxide, or possibly the formation of propionaldehyde and carbon dioxide. Because this decomposition as characterized by pressure build-up and odor change was not evident for solutions of LiBr, $MnBr_2$, $ZnCl_2$, and $BiCl_3$, it therefore may have been a result of the specific combination of alkaline earth ion with bromide ion. Zinc chloride and aluminum chloride are known to cause the decomposition of propylene carbonate into propene oxide and carbon dioxide at elevated temperatures.

A nearly saturated solution of aluminum chloride reacted more rapidly; a darkening of the colorless solution was noticeable after several hours. A ferric chloride solution reacted slowly and formed an insoluble precipitate. Uranium tetrachloride, niobium pentachloride and stannic chloride solutions gradually darkened after a number of weeks. It is likely that these salts also coordinated strongly to the solvent molecule and caused its slow decomposition. UCl_4 is known to dissolve irreversibly in certain oxygen containing solvents such as methyl alcohol, ethyl alcohol, and acetone.[145]

DISCUSSION OF SOLUBILITY

By examination of the table of solubility of inorganic salts in propylene carbonate (Table II), we find that, as could be expected, the relatively low-melting covalent salts are quite soluble.

Great differences of solubility exist between various salts, all of which are relatively soluble in water. Consider sodium and potassium halides, the iodides being the only ones that are really soluble. Peacock, Schmidt, Davis, and Schaap have proposed that this enhancement of solubility (in amine solvents) may be due to solvation of the iodide ion by expansion of its outer valency shell.[8] The possible formation of such complexes, however, has not been investigated. The much larger solubility of iodides as compared with the other halides (and most other salts) is probably due in part to their low lattice energies.

We may split up the free energy of solvation of gaseous ions into two parts: the first is an electrostatic term due to the separation of ions in a dielectric medium; the second is due to specific chemical interaction between the ions and the polar-solvent molecules.[127]

The electrostatic part of the free energy can be approximately evaluated by the use of the Born equation:[125]

$$\Delta F = - \frac{N_{Av} z^2 e^2}{2r} \left(1 - \frac{1}{\epsilon}\right). \tag{4}$$

Verwey in his calculations of free energies of hydration of ions applies the Born equation only to the ion with its first solvation shell in its interaction with the test of the solvent. In this calculation the macroscopic dielectric constant of water is used. The energy of interaction of the ion with its first hydration shell is based on the interaction between solvent dipoles and the ion, obtained with the help of a detailed consideration of the structure of liquid water.[146] The ion dipole interaction will be enhanced by solvents having larger dipole moments, by ions of higher charge density, and by a more exposed charge distribution in the solvent molecule.

Coordination between ion and solvent will be increased by differences in acid-base character between the solvent molecule and the ions. A "small" solvent molecule will promote a greater amount of coordination and a greater ion—dipole interaction because of greater number of molecules that may surround a given ion in solution.

It is generally true that the greater the difference between the lattice-energy and the energy of solvation of a salt, the greater the solubility will be. Higher solvation energies will in general be favored by ions of high charge density (which also increases the lattice energy), a solvent of high dielectric constant, greater separation of charge in the solvent molecule, and by greater specific chemical interaction between the ion and solvent.

The cyclic esters studied will solvate cations to a much larger degree than anions. The carbonyl oxygen with its relatively high negative charge and exposed position will solvate cations without great difficulty. The positive end of the solvant's dipole will, however, be spread over a number of atoms and will be much less accessible than in the case of water which, in contrast, because of the exposed charge distribution, solvates both anions and cations to comparable degrees.

In water all the sodium halides are soluble. This is because the increase in lattice energy in going from iodide to fluoride is largely compensated by a corresponding gain in the solvent-anion interaction. With the solvents studied, and many other organic solvents, such is not the case. Because the anions are less solvated, in going from iodide to fluoride the increase in the lattice energy is not compensated by a corresponding increase in the anion solvation. Hence those sodium halides with high lattice energies are insoluble. With sodium and potassium only the iodides have a low enough lattice energy to be appreciable soluble in the solvents studied.

Consider solubility relations for the salt potassium iodide in the solvents studied (Table V). In arranging the solvents studied in order of their solvent power for potassium iodide, we find the order (based on mole fractions): γ-butyrolactone > ethylene

Table V

Comparative Solubilities of NaI and KI in Selected Solvents

Solvent	Temperature (°C)	ϵ	Solubility g/100g solvent NaI	Solubility g/100g solvent KI	Solubility Mole fraction NaI	Solubility Mole fraction KI
Ethylene Carbonate	40	89.12	37.6	11.16	0.180	0.0557
Propylene Carbonate	25	64.4	16.83	3.71	0.103	0.0223
γ-butyrolactone	25	39.1	58.15	12.5	0.250	0.0607
γ-valerolactone	25		30.03	4.24	0.171	0.0247
Cyclopropanone	25	13.45	26.0	0.43	0.128	0.0022
Ethylene trithiocarbonate	25	58.5	<0.0065	<0.021		

carbonate > γ-valerolactone > propylene carbonate >> cyclopropanone >> ethylene trithiocarbonate. If solubilities were solely determined by dielectric constant we would have predicted the following order: ethylene carbonate > propylene carbonate > ethylene trithiocarbonate > γ-butyrolactone > γ-valerolactone > cyclepropanone. It is seen that the effect of the dielectric constant, although a significant factor, is overshadowed by other properties of the solvents.

The fact that γ-butyrolactone and ethylene carbonate dissolve comparable amounts of NaI, KI, and NaBr, in spite of its much lower dielectric constant may be explained by a consideration of the charge distribution and bond moment of the carbonyl group. In γ-butyrolactone a greater separation of charge and a greater bond moment for the carbonyl group are attained. The methylene group adjacent to the carbonyl group in γ-butyrolactone has a much higher positive charge on it than either of the methylene groups in ethylene carbonate. The structural formulas of the solvents under consideration appear in Fig. 1. The value of Kirkwoods g for γ-butyrolactone (discussed on pages 7 and 8) which diverges further from unity than the values of ethylene and propylene carbonates gives support to the belief that γ-butyrolactone possesses a more exposed charge distribution. Thus with γ-butyrolactone there will be a stronger ion-dipole interaction or stronger coordination with both positive and negative ions of an ionic solute. If an ethylene carbonate molecule is coordinated to a positive ion by its carbonyl oxygen, one would expect the negative charges on the two ether oxygens to repel subsequent molecules, or to limit the number that will coordinate. In contrast, γ-butyrolactone has in the position corresponding to these two oxygens, one methylene group which bears a positive charge, and one negative oxygen. Thus one would expect less repulsion of succeeding solvent molecules as they are attracted to a positive ion. This effect will also contribute to a greater solvation of ions by γ-butyrolactone than by ethylene carbonate. The comparable solvent properties of γ-valerolactone and propylene carbonate may also be explained by the above reasoning. Ethylene carbonate and γ-butyrolactone are better solvents (for KI and NaI) than the solvents in which a methyl group has been substituted. Because of the very close similarity between the substituted and unsubstituted solvents, the major effect is probably due to the difference in dielectric constant caused by the increase in size of the substituted solvents. With cyclopropanone the major effect appears to be its low dielectric constant. In spite of its high dielectric constant ethylene trithiocarbonate does not dissolve sodium or potassium iodide. It is probably a poor solvent for these solutes because of the lack of coordination between sodium or potassium and sulphur. Oxygen is known to be the donor atom for nearly all of the complexes of the light metal ions (Periodic groups IA, IIA, IIIB, IVB) which seldom coordinate with sulphur.[147] The alkali halides are also known to be insoluble in liquid hydrogen sulphide (dielectric constant is 10.2 at -60°C).[148] This lack of coordination with sulphur is due to its larger size, as compared with oxygen, which greatly decreases the electrostatic attraction between cations and this solvent. Because cadmium and copper are expected to coordinate with sulphur as the donor atom,[147] it is not surprising that cadmium iodide and cupric bromide are soluble in ethylene trithiocarbonate.

With sodium iodide as the solute, the order of the solvents from greatest to least solubility is γ-butryolactone, ethylene carbonate, γ-valerolactone, cyclopropanone, propylene carbonate, and ethylene trithiocarbonate. All of the compounds, with the exception of ethylene trithiocarbonate, are relatively good solvents for NaI. There is little apparent dependence of solubility on the dielectric constant. Ethylene trithiocarbonate is probably a poor solvent for this solute for the same reason that it is a poor solvent for potassium iodide, that is, because of lack of coordination with sodium ion.

Several generalizations concerning the effect of different solutes in these solvents may be noted. With the alkali halides increases in solubility in the series K, Na, and Li are due to the relative gain in solvation energy compared with lattice energy as the cation size decreases (in propylene carbonate solubility of iodides are 0.0223, 0.111, and 0.136

respectively, and bromides 6×10^{-4}, 8×10^{-3}, and 0.243 respectively[*]). The same is true of barium and calcium (solubilities of their bromides in propylene carbonate are 7.8×10^{-4} and 0.0745 respectively[*]). Solubility also increases in the series Cl, Br, I for sodium, potassium, and lithium salts (solubilities in propylene carbonate for sodium salts are 3×10^{-7}, 8×10^{-3}, and 0.111; for potassium salts 4×10^{-6}, 6×10^{-4}, and 0.0223; and for lithium salts 7.7×10^{-5}, 0.243, and 0.1365 respectively[*]), lithium bromide being an exception. Potassium and sodium borofluorides are intermediate in solubility between the bromides and iodides. From the data, no multivalent ions appear to exist in propylene carbonate solutions with the possible exception of calcium ion in $Ca(BF_4)_2$.

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[*] Moles/100 grams solvent.

CONDUCTIVITIES

No previous conductance studies have been reported for the solvents propylene carbonate and γ-butyrolactone. In order to determine the equivalent conductance, the conductivity of several salts in these solvents was obtained as a function of concentration. The values obtained for the equivalent conductance at infinite dilution, and the observed and calculated Onsager limiting law slopes of the Kohlrausch plots are presented in Table VI. From the Kohlrausch plots (Figs. 7, 8, and 9) it is seen that for the systems sodium iodide—propylene carbonate and potassium iodide—γ-butyrolactone the curve of equivalent conductance versus square root of concentration approaches the Onsager limiting law from above, while in the system potassium iodide—propylene carbonate the approach is from below the Onsager limiting law. The curve of a completely dissociated electrolyte would approach asymptotically from above, while that of an incompletely dissociated electrolyte would approach asymptotically from below the limiting law.[149]

For potassium iodide that portion of the Kohlrausch plot lying below a concentration of 0.017M may be adequately represented by a straight line. The equivalent conductance at infinite dilution, λ_o, was evaluated at zero concentration by means of the Shedlovsky extrapolation (Fig. 10).[150]

The degree of dissociation, α, of potassium iodide in propylene carbonate at a concentration of 1×10^{-2} $\underline{M}$ was approximated by means of the equations:[151]

$$\frac{\Lambda}{\Lambda'} = \alpha \qquad (7)$$

and

$$\Lambda'_o = \Lambda_o - (A + B\lambda_o)\sqrt{\frac{\Lambda}{\Lambda'} C} \; . \qquad (8)$$

Where Λ is the equivalent conductance, Λ' is hypothetical equivalent conductance if all of a weak electrolyte had ionized, A and B are constants of the Onsager equation, and Λ_o is the equivalent conductance at infinite dilution. A value of 0.98 was found, indicating little association to form ion pairs.

Table VI

Conductance Data at 25°C

Solvent	Salt	λ_o	Onsager slope	Observed slope
Propylene carbonate	KI	31	-32.3	-37
	NaI	28	-31.6	-27
γ-butyrolactone	KI	46	-66	-54

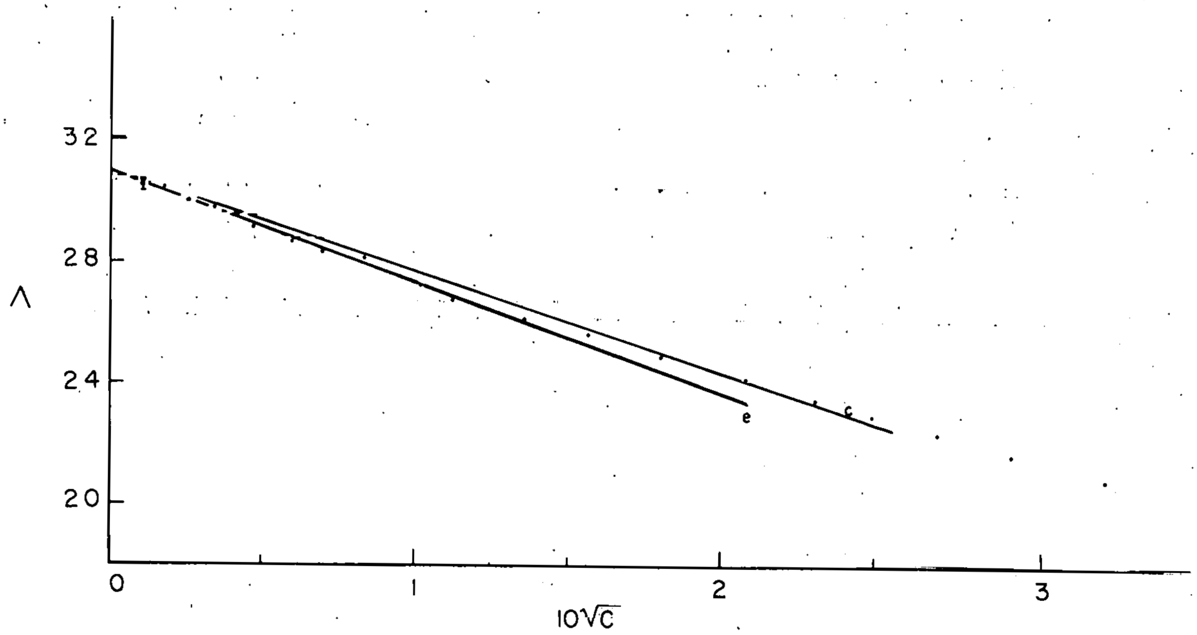

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Fig. 7. Kohlrausch plot for potassium iodide in propylene carbonate.

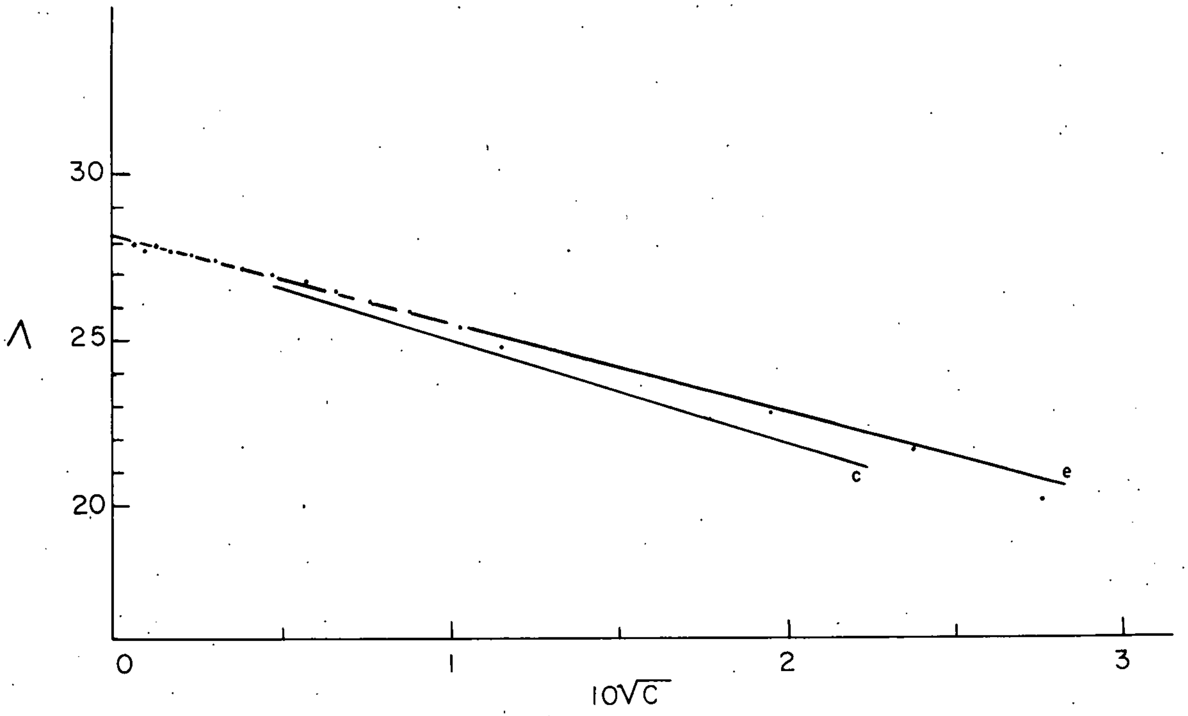

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Fig. 8. Kohlrausch plot for sodium iodide in propylene carbonate.

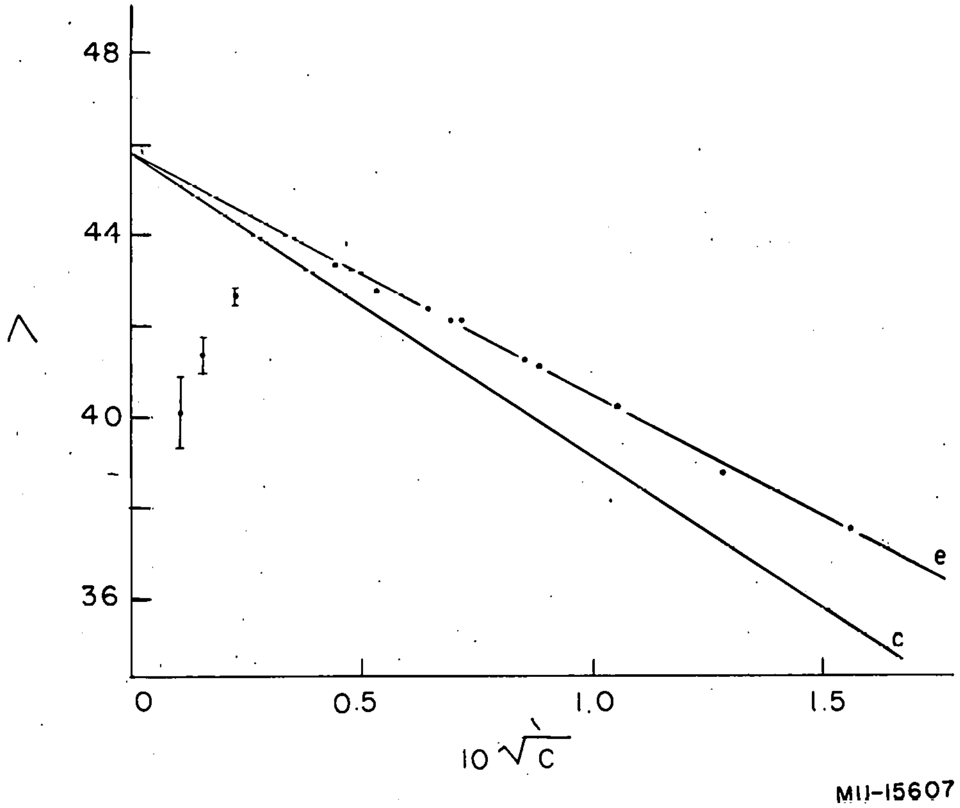

Fig. 9. Kohlrausch plot for potassium iodide in γ-butyrolacyone.

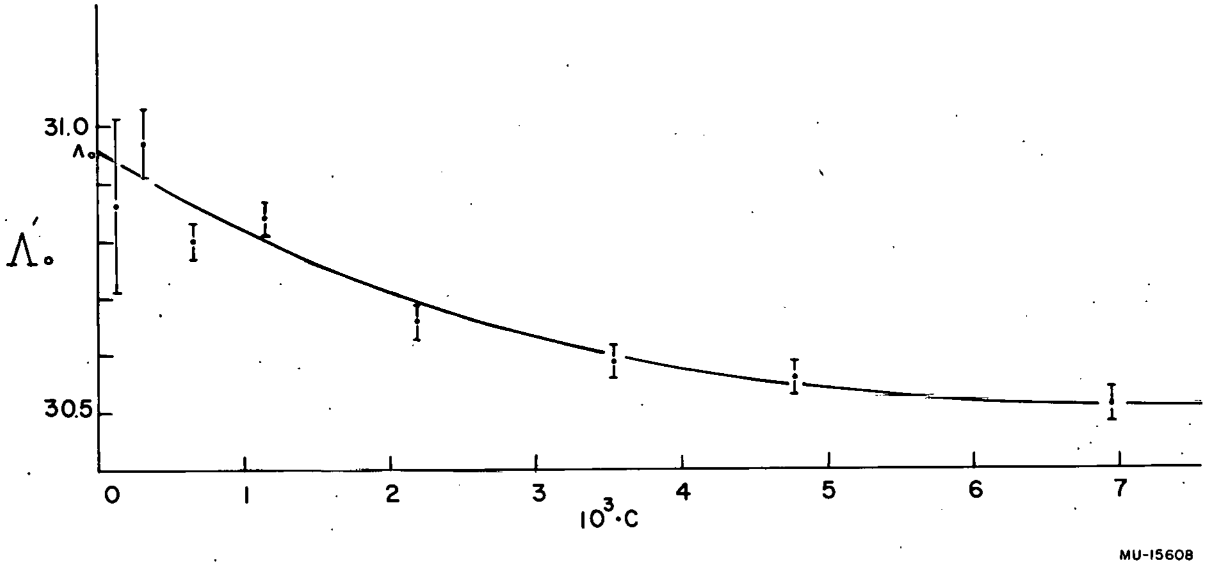

Fig. 10. Shedlovsky extrapolation for potassium iodide in propylene carbonate solution.

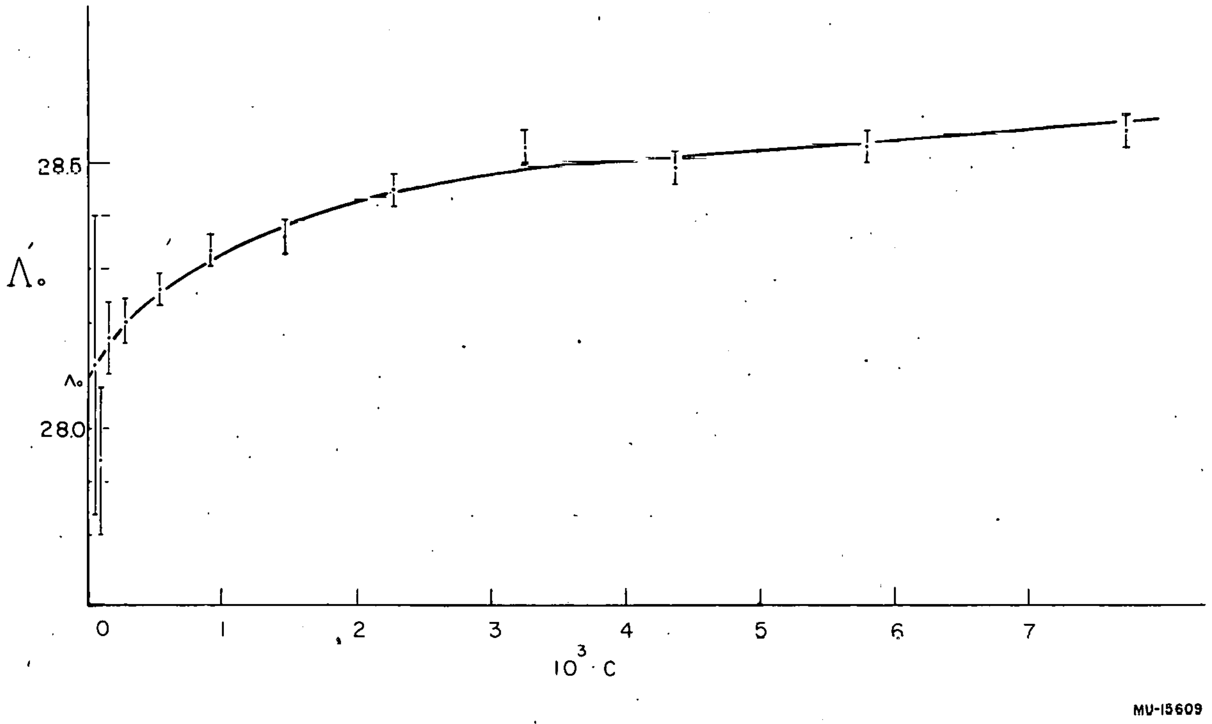

Fig. 11. Shedlovsky extrapolation for sodium iodide in propylene carbonate solution.

The Kohlrausch plot for sodium iodide in propylene carbonate may be adequately represented by a straight line up to concentrations of 0.01 M (Fig. 8). The value of λ_o was obtained by the Shedlovsky extrapolation. As with potassium iodide in propylene carbonate, the curve could not be represented by a straight line (Fig. 11).

The conductivity data for potassium iodide in γ-butyrolactone were plotted in a Kohlrausch plot. (Fig. 9). The curve may be represented by a straight line between 0.0025 and 0.0225 M. Because of erratic results in the data no further refinements were made in the extrapolation to infinite dilution. The solutions when mixed developed the color of iodine; therefore the erratic results may have been due in part to chemical reaction.

Thus we see that certain ionic salts are essentially completely ionized in two of these solvents. For these salts one would expect the solvent ethylene carbonate to behave like propylene carbonate because of its higher dielectric constant and chemical similarity. γ-valerolactone should behave comparably to γ-butyrolactone. However, because of the lower dielectric constant of γ-valerolactone, some ion association may occur.

Equivalent conductivity of many of the saturated solutions were calculated and appear in Tables II and III. Examination of this data (with that of Table VI) indicates that in propylene carbonate solutions, NaBr, NaI, $NaBF_4$, KCl, KBr, KI, and KBF_4 are highly ionized. In their saturated solutions, $CaCl_2$, $BaBr_2$, CdI_2, $ThCl_4$, UCl_4, $ZnCl_4$, $CuBr_2$, $BiCl_3$, $NbCl_5$ are only partly ionized. Cobalt chloride and $Ca(BF_4)_2$ appear to behave as uni-univalent electrolytes. Because of the increased viscosity of many of the more highly soluble solutions it is difficult to state with accuracy whether the salts--LiBr, $CaBr_2$, $ZnCl_2$, and $MnBr_2$--are highly ionized. Potassium iodide is highly ionized in ethylene carbonate, γ-butyrolactone, and γ-valerolactone, but not in cyclopentanone, where it is only partly ionized. Sodium bromide is highly ionized in its solutions in ethylene carbonate and γ-butyrolactone.

ELECTRODEPOSITION

Introduction

Because only about 30 of the 70 known metallic elements have been deposited from aqueous solution, electrochemists have turned their attention to nonaqueous electrolyte-solute systems. Both organic compounds that are liquid near room temperature, and fused inorganic salts have been employed as solvents. We will consider only those organic solvents (also ammonia) that are liquid at temperatures less than 100°C.

Three groups of metals have received the greatest amount of research. Experimental work in the early part of the century on the electrodeposition of metals from nonaqueous solutions concerned mainly the very electropositive metals such as potassium, lithium, and calcium. The electrodeposition of aluminum from organic plating baths has received the attention of many investigators in the past quarter century. More recently the deposition of certain transition metals, such as titanium, zirconium, and molybdenum, has been of special interest. Because of the corrosion resistance of these metals, the ability to deposit them in thin films on base metals would be very desirable.

Certainly many metals such as the alkali and alkaline earth metals cannot be electrodeposited from aqueous solution because it is impossible to reach a high enough potential to discharge these metals before hydrogen preferentially evolves. Some other metals are not deposited from aqueous solution, although, from thermodynamic consideration, one would expect them to be deposited.

A very large number of solvent-solute combinations have been tried for the electrodeposition of various metals. Many of these attempts failed completely, and many of those that were reported as being successful produced only small amounts of deposit, largely contaminated with metal compounds and unidentified organic residues. Frequently the authors did not report such important data as current densities, composition of deposits, solvent-decomposition products, and hydrodynamic conditions. Only a few authors appear to have made relatively systematic studies.

Alkali Metals

The alkali metals may be deposited from a large variety of solvents, the only requirements apparently being that the solvent not react too quickly with the metal and that one be able to reach high enough potential for the electrodeposition, i.e. the solvent should not be reduced at a lower potential. Alkali metals have been deposited from pyridine,[44, 30, 28, 152] propyl amine,[153] ethylene diamine,[154] alcohols,[30, 155] acetone,[30, 29] and $POCl_3$.[156]

Alkaline Earth Metals

Wood and Brenner succeeded in obtaining electrodeposits of beryllium (95% pure) and beryllium alloys containing boron or aluminum from ethyl ether solutions of such solutes as dimethyl beryllium, beryllium chloride, beryllium borohydride, and beryllium aluminohydride.[9]

Magnesium has been deposited by electrolysis of Grignard reagent.[157] Putnam and Kobe obtained "nearly pure" magnesium by the electrolysis of a 20% solution of magnesium perchlorate in ethylene diamine.[154] Connor, Reid and Wood described the electrodeposition of magnesium and magnesium alloys from various organic baths. They reported metallic deposits composed of 90% magnesium and 10% boron obtained from an ether solution of $MgBr_2$ and $LiBH_4$. Although these deposits could not be built up from a bath containing $MgBr_2$, $AlBr_3$, and $LiAlH_3$, it was possible to get thick deposits of an alloy (7% magnesium—93% aluminum).[9]

Patten and Mott obtained electrodeposits of strontium from solutions of its salts in acetone.[158] Barium has been electrodeposited from $Ba(ClO_4)_2$ in 2-ethoxyethanol (cellosolve).[159]

Rare-Earth Metals

Several of the rare earths have been obtained as amalgams by electrodeposition from alcoholic solutions by the use of a mercury cathode.[82] Rare-earth deposits containing only 50% metal have been obtained by cathodic reduction of solutions of their salts in ethylene diamine and monoethanolamine.[160] Deposits have also been reported from solutions of rare-earth nitrates in ethylene diamine.

Aluminum

A number of workers have obtained electrodeposits of aluminum using $AlBr_3$ and $AlCl_3$ as solutes alone or in combination with alkali halides and such solvents as ethyl bromide and benzene.[49, 53, 161—164] Aluminum deposits described as bright and adherent have been obtained from an aluminum chloride-amine-ethyl ether system.[165, 166] Menzel reported having obtained aluminum deposits from baths consisting of aluminum chloride and xylene.[167] Deposits of aluminum have also occurred by electroreduction of solutions of aluminum Grignard compound in dry ethyl ether.[168] Ziegler found that solutions of alkali-metal methyls or sodium fluoride in aluminum alkyls may be used for the deposition of aluminum.[169] According to Hurley and Wier aluminum may also be deposited from a fused mixture of ethyl pyridinium bromide and $AlCl_3$ and from this mixture plus benzene or toluene.[86, 170] Safranck, Schichner, and Faust reported the deposition of dense strong ductile aluminum 0.65 to 1.0 mm thick from plating baths similar to those of Hurley and Wier.[87] One may also obtain electrodeposits of aluminum, although only partly adherent, from a bath consisting of aluminum bromide dissolved in a tetraalkyl ammonium bromide at 100°C.[168] Smooth ductile and coherent deposits of aluminum may be obtained from an ethereal solution of $AlCl_3$ and LiH. This process was developed at the National Bureau of Standards and is used commercially.[88, 92]

Metals Obtainable from Aqueous Solution

Many of the common metals that are easily reduced from aqueous solution can also be obtained in nonaqueous solvents.

Zinc and cadmium. Zinc and cadmium have been obtained by electrodeposition from a large variety of nonaqueous solvents such as liquid ammonia,[41, 40] acetone,[171, 172] formamid at 100°C, and acetamid at 100°C.[85] Zinc has also been deposited from pyridine solution.[45]

Tin, bismuth, antimony and arsenic. Tin, bismuth, antimony, and arsenic have been obtained from solutions of their chlorides in acetone[158] and in glacial acetic acid.[84, 173] Tin has been deposited from solutions in formamid and acetamid at 100°,[85] and from liquid ammonia.[40]

The iron transition metals. In aqueous solution the iron metals are deposited with high irreversibility from many of their salt solutions. Iron, nickel, and cobalt have been obtained from a wide variety of solvents. Cobalt and nickel have been deposited from liquid ammonia,[41, 40] as well as formamid at 100°C, and acetamid at 100°C.[85] Iron has been deposited from pyridine[45] and acetone.[158]

Silver and copper. As one would expect because of their ease of reduction, silver and copper have been obtained from many solvents.

Chromium. The deposition of chromium has also been reported from nonaqueous solutions.[174] More effective deposits have been obtained from solutions containing chromium III compounds than from those containing chromium VI compounds. Of the solvents tried, formamid, acetamid, and an acetonitrile-urea mixture were most satisfactory. Less satisfactory were acetic acid and ethanolamine; dimethylformamid and acetonitrile gave little success.

Transition Metals Unobtainable from Aqueous Solutions

Because of the desirable properties that electrodeposits of certain of the transition metals (Ti, Zr, Ta, W, etc) possess, much effort has been expended on attempts to electrodeposit them. Lowenheim has reviewed the electrodeposition of the less common metals, and includes many references for the deposition of these metals from nonaqueous solvents.[175] Sein and Holt have reviewed and critically examined the published literature concerning the deposition of tantalum. They found they were unable to electrodeposit tantalum from any of the described baths or from numerous other aqueous and nonaqueous solutions.[176] Brenner and co-workers have briefly reviewed the electrodeposition of titanium and zirconium from aqueous and nonaqueous media and concluded that these metals had not been deposited up to the time of their work.[93]

Exploratory investigations of the deposition of titanium by Sherfey and Senderoff at the National Bureau of Standards in 1951-1952 indicated that it cannot be deposited successfully from solutions of titanium halides in any of the many solvents tried. Solvents considered included aromatic hydrocarbons, halogenated hydrocarbons, alcohols, ethers, acetone, acids, amines, amides, nitrides, organometallic solvents, and several inorganic compounds.[93]

Recently A. Brenner and co-workers at the National Bureau of Standards succeeded in electrodepositing titanium and zirconium alloys from solutions of their tetrachlorides in conjunction with aluminum borohydride, aluminum chloride, and lithium hydride in ethyl ether solutions. Alloys containing up to 6% titanium and up to 45% zirconium were obtained, the rest of the alloy being mostly aluminum and some boron.[93]

Electrodeposition of Metals from Solutions of their Salts in Cyclic Esters

The electroreduction experiments were undertaken as they were believed to be one of the simplest kinds of reactions that could be advantageously employed in characterizing a new solvent. Although quite qualitative in nature, they provide information concerning species present and indicate the range of metals that may be electrodeposited from propylene carbonate solutions. Because of the similarity between propylene carbonate and ethylene carbonate, the results are also expected to apply closely to ethylene carbonate solutions. Somewhat similar results are expected to apply to the lactones that were studied. The experimental procedure and equipment used was that described on page 23 .

Lithium was obtained by electrolysis from a saturated solution of lithium bromide. Metal was deposited with only slight evolution of gas at current densities as low as 1 ma/cm^2. The electrodeposition of the lithium distorted the electrode (0.06 mm thick) and caused it to curve convexly toward the side on which the electrodeposition was taking place.

By the electrolysis of a solution of sodium iodide in unpurified propylene carbonate containing about 0.2% water and 0.5 to 1% of organic impurities, metallic sodium was not obtained. Small amounts of sodium were produced after the addition of anhydrous $AlCl_3$. From the same quality of propylene carbonate small amounts of sodium were obtained from $NaBF_4$ solution. By the electrolysis of a solution of sodium iodide in carefully puried propylene carbonate no deposit was obtained at current densities up to 3 ma/cm^2, but a light grey layer of sodium was deposited at a current density of 10 ma/cm^2 with the evolution of a small amount of gas.

Potassium was not obtained at current densities up to 5 ma/cm^2 from a saturated solution of potassium iodide in propylene carbonate, but was produced at a current density of 20 ma/cm^2, again with the evolution of a few bubbles.

Sodium and potassium were also successfully deposited from other cyclic esters. A solution of sodium iodide in ethylene carbonate was electrolyzed at a temperature between 40° and 60°. Although no deposit was obtained at current densities up to 2 ma/cm^2, a powdery deposit was electrodeposited at a current density of 15 ma/cm^2. Electrolysis for a short time at a higher current density gave enough sodium to produce a yellow flame when the electrode was immersed in water. Metallic sodium was also obtained from a saturated solution of sodium iodide in γ-valerolactone. A greyish crystalline deposit was produced at a current density of 30 ma/cm^2, but none was obtained at 3 ma/cm^2. Only gas evolution was observed at the cathode when enough water was added to make its concentration 0.75% and the solution was electrolyzed at 50 ma/cm^2. With a saturated solution of potassium iodide in γ-valerolactone only relatively small amounts of potassium were produced at current densities between 40 and 100 ma/cm^2. A few gas bubbles were observed.

No deposit of magnesium occurred when a solution of magnesium bromide in propylene carbonate was electrolyzed at current densities up to 35 ma/cm^2. In one case a small amount of gelatinous precipitate appeared on the cathode. A few bubbles were also observed on the cathode.

Solutions of calcium bromide in propylene carbonate, some of which had been treated with calcium hydride, were electrolyzed at current densities up to 50 ma/cm^2. No conclusive evidence of metal deposition was obtained. Significant bubble formation at the cathode was not observed during electrolysis except when 0.5% water was added to the catholyte.

No deposition of aluminum was produced from $AlCl_3$ solutions in propylene carbonate at current densities up to 125 ma/cm^2. During electrolysis some bubbles were observed on the cathode.

From an ~40% saturated solution of zinc chloride in propylene carbonate, a grey crystalline adherent deposit of zinc was obtained at a current density of 5 ma/cm^2.

Cadmium was obtained at low current densities from solutions of cadmium iodide in both propylene carbonate and γ-butyrolactone.

Metallic iron was produced by electrolysis of a solution of ferrous iodide in propylene carbonate; deposits were obtained at current densities less than 30 ma/cm^2. From a solution of manganous bromide in propylene carbonate, manganese electrodeposited in the form of dark nodules at a current density of 5 ma/cm^2. Cobalt was obtained as a nonuniform, moderately adherent deposit when a solution of cobaltous chloride in propylene carbonate was electrolyzed at a current density of 4 ma/cm^2.

Titanium was not obtained electrolytically from a solution of $TiBr_4$ in propylene carbonate at current densities up to 32 ma/cm^2, nor from the solution resulting when sodium borohydride reacted with a solution of $TiBr_4$ in propylene carbonate.

A solution of niobium pentachloride was electrolyzed without deposition at current densities up to 7 ma/cm^2. Niobium pentachloride in solution was reacted with sodium borohydride in propylene carbonate. The resulting solution, virtually a nonconductor, was electrolyzed at current densities of 1 ma/cm^2 without apparent success.

Electrolysis of a propylene carbonate solution of UCl_4 gave no evidence of depositing metal at current densities up to 15 ma/cm^2. Electrolysis in the presence of potassium iodide or sodium chloride apparently gave only traces of the alkali metals.

Bismuth was obtained from a solution of bismuth trichloride in propylene carbonate by electrolysis at a current density of 1 ma/cm^2. The deposit was matte black and easily burnished to a metallic luster.

From the viscous and saturated (or nearly so) propylene carbonate solution of lead iodide and potassium iodide, (mole ratio $KI:PbI_2 = 0.738:1$) a less viscous solution containing about 20 g lead iodide per 100 g of solvent was prepared. When this solution was electrolyzed at a current density of 2 ma/cm^2 by the use of a platinum cathode, a deposit of lead was obtained on widely spaced nuclei. The distance between the nuclei varied from about 1/10 mm to 1 mm.

Electrolysis of a propylene carbonate solution of stannic chloride at current densities up to 6 ma/cm^2 gave no evidence of metal deposition.

Discussion of Electrodeposition from Cyclic Esters

The alkali metals were readily obtained by electrolysis from solutions of their halide salts in propylene carbonate, but the alkaline earth metals were not deposited under like conditions. The free energies of formation at 25° of $CaBr_2$ and $MgBr_2$ are almost twice the value for the free energy of formations of LiBr, NaI, and KI. On this basis one would expect that because the alkali metals can be deposited from propylene carbonate solutions of their salts, calcium and magnesium will also be deposited. The nondeposition of magnesium and calcium may best be explained by the existence of a high overvoltage for metal deposition. Aluminum, which one would expect to be deposited at a lower potential than Li, Na, or K on the basis of its free energy of formation, is not deposited. This also is due to a high overvoltage for process of metal deposition. If reduction of ions of titanium, niobium, uranium, and tin of higher valence to species of lower valence proceeds more rapidly than the reduction of species of higher valence to metal, no deposition of metal will be observed until all of the high-valence species has been reduced. In the exploratory electrodeposition experiments, only a small fraction of the metal ions present could have been reduced to a lower valance state. If reduction to the metal proceeds through an intermediate lower valence state, electrodeposition will not occur if any step in the process has so high an activation potential that the solvent would be destroyed first. For tin either of these possibilities may be true. In aqueous solution deposition of tin doubtless passes through the divalent state. The reduction from tin (IV) to tin (II) is irreversible, but the reduction from tin (II) to metal is reversible.[177]

A. Brenner divides the metallic elements into two groups: (1) those which may be electrodeposited from aqueous solution, and (2) those which cannot be so electrodeposited. This latter group he further subdivides into two groups depending upon the cause of the inability to be deposited from aqueous solution. In the first group, the inability to be deposited stems from being unable to reach a high enough electrode potential to deposit the metal because of hydrogen evolution; in the second a high activation potential in the electrodeposition process prohibits a deposition that otherwise would be thermodynamically possible.[91]

To the first subgroup belong lithium, sodium, potassium, magnesium, calcium, and possibly aluminum and beryllium. The alkali metals may be electrodeposited from a rather large variety of organic solvents in which the hydrogen is more tightly bound than in water.

To the second subgroup probably belong molybdenum, tantalum, niobium, zirconium, hafnium, vanadium, tungsten, and titanium. Estimates of the electrode potential of molybdenum and tungsten in aqueous solution indicate that it should be thermodynamically possible to electrodeposit these metals from aqueous solution.[91]

Brenner concludes that the prime factor which determines whether a solution will conduct or whether a metal can be deposited from it is not the dielectric constant of the solvent or the crystal structure of the compound, but the chemical nature of the solvent and solute combination. An example is the case of the aluminum hydride plating bath. The two components $AlCl_3$ and $LiAlH_4$ when dissolved separately in ether give a poorly donducting solution, but when they are mixed the result is a good conductor which gives good deposits upon electrolysis. To form a plating bath, a loose complex must form between solute and solvent. The solution will not be a conductor if a complex does not form. However, if the complex is too stable conductivity may occur, but not metal deposition. Ethyl ether was found to be the best organic solvent for the deposition of the metals which Brenner et al. have studied (Mg, Be, Ti, Al, and Zr). Only a few of the many conducting solutions obtained with a variety of organic solvents yielded metal on electrolysis.[91]

E.H. Lyons has investigated the deposition of metals from aqueous solutions with special reference to the electronic structure of complexes that exist in solution.[178-181] He concludes that only those metals that form outer orbital complexes[182] will be reversibly deposited from aqueous solution. Those that form inner orbital complexes[182] will in general not be deposited, or will be deposited only with a high degree of irreversibility (high overvoltage) from aqueous solution.

Lyons and Parry list Ti, V, Zr, Nb, Mo, Hf, Ta, W, Th, Pa, and U as forming only inner orbital complexes.[183] In view of this it is not surprising that in aqueous solutions these metals cannot be deposited. We may assume that in propylene carbonate solutions because of a high activation energy for deposition resulting from an inner orbital configuration, the solvent is decomposed before the metal is deposited at a finite rate.

These qualitative electrodeposition studies have shown that these solvents-ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone- are promising as ionizing media for carrying out electrochemical reactions. The need for further study of several aspects of electrodeposition is indicated. A detailed and quantitative investigation of the deposition and solution of metals in these solvents would be desirable, as would be a study of the oxidation and reduction products of the solvent itself.

SUMMARY

The five-membered cyclic esters, ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolactone, have been characterized as solvents for electrochemical reactions. They possess the following desirable properties: low vapor pressures, relatively low toxicity, high chemical stability, high dielectric constants, and high solvent power for certain ionic salts. In addition, they are relatively nonreactive with anodically liberated halogens. Such properties are desirable in an easily handled nonaqueous ionizing medium.

The solubilities and conductivities of saturated solutions of a large number of both covalent and ionic inorganic compounds were determined. Of the ionic halides, the bromides and iodides were found to be the most soluble.

The variation of solvent power of the solvent was discussed with reference to the solvent variables, dielectric constant, solvent size, dipole moment, and charge distribution. Contrary to predictions of many solubility theories, the solubility of ionic salts was not found to be a smooth function of the dielectric constant. As could be expected, a number of relatively covalent halides such as $FeCl_3$, $AlCl_3$, $NbCl_5$, and $TiBr_4$ were found to be quite soluble.

A study of the dependence of conductivity upon concentration indicated that certain alkali halides behave as strong electrolytes in both propylene carbonate and γ-butyrolactone. Further studies of solubilities and conductivities in these solvents seems desirable, both with reference to additional solutes and the use of these solvents with various substituted groups.

The electrolysis of a variety of inorganic compounds further characterized these solvents as ionizing media. In addition to many of those metals that are reducible from aqueous solutions, certain of the very electropositive elements (Li, Na, and K) were also deposited.

Because these solvents possess good solvent power for a great number of other organic compounds, they may also prove very useful for the preparation of organic compounds by the electrolysis of suitable soluble intermediates. With further investigation these solvents may prove to be advantageous for the electrowinning of pure metals or the plating of protective films. It is unfortunate that although a great deal of work has been done in aqueous systems, so little has been done in nonaqueous solutions. It is believed that studies in solvents other than water will facilitate the better understanding of electrochemical processes in aqueous solutions.

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APPENDIX I

Symbols and Abbreviations

A	constant of Onsager equation
B	constant of Onsager equation
C	concentration moles/liter
D	Debye units
<u>M</u>	molar
N	mole fraction
N_{Av}	Avagadro's number
N_i	number of molecules per cm^3
S	solubility
T	degrees Kelvin
e	electronic charge
k	Boltzman's constant
n_D^{25}	refractive index, D line at 25°C
r	radius of ion
z	charge of ion
Λ	equivalent conductance
Λ_o	equivalent conductance at infinte dilution
Λ'	hypothetical equivalent conductance if all of a weak electrolyte had ionized
Λ'_o	used in Shedlovsky extrapolation defined by Eq. (8)
Ω	ohm
α	degree of dissociation
ϵ	dielectric constant
ϵ_∞	dielectric constant at infinte frequency
k	specific conductivity
μ	dipole moment
const.	numerical constant for a given equation

APPENDIX II

Sources and Purity of Salts

Salt	Purity	Source
$BiCl_3$	Reagent	Baker and Adamson
$CaBr_2 \cdot 2H_2O$	Reagent	General Chemical Division
$CaCl_2$	Reagent	Allied Chem. and Dye Corp.
$CdCl_2 \cdot 2\frac{1}{2}H_2O$	Reagent	New York, N. Y.
$CuBr_2$	Reagent	
KBr	Reagent	
$MnCl_2 \cdot 4H_2O$	Reagent	
$NiCl_2 \cdot 6H_2O$	Reagent	
$NiBr_2$	C. P.	
KBF_4	Tech.	
CdI_2	Reagent	J. T. Baker Chem. Co.,
$SnCl_4$		Phillipsburg, N. J.
$AlCl_3$	C. P.	
$CuCl_2 \cdot 6H_2O$	C. P.	
$CuCl_2 \cdot 2H_2O$	C. P.	
KCl	C. P.	
LiCl	C. P.	
NaCl	C. P.	
NaF	C. P.	

APPENDIX II (cont'd)

Sources and Purity of Salts

Salt	Purity	Source
LiBr	Reagent	Matheson, Coleman, and Bell Div. The Matheson Company, Inc. East Rutherford, N. J.
$MnBr_2 \cdot 4H_2O$	Purified	Fischer Scientific Co.
NaI	C. P.	Pittsburgh, Pa.
NaOMe	Pure	
$Ca(RF_4)_2$	Technical	Kawecki Chem. Co. P. O. Box 57 Boyertown, Pa.
$NaSiF_6$	Technical	Braun-Knecht-Heimann Co. San Francisco, Calif.
$PbBr_2$	Pure	Eimer and Amend New York, N. Y.
$FeBr_2$		Powers-Weightman-Rosengarten Co. Philadelphia, Pa.
$BaBr_2 \cdot xH_2O$		Amend Drug and Chemical Co.
		117-119 East 24th St.
LiI	Pure	New York 10, N. Y.

APPENDIX II (cont'd)

Sources and Purity of Salts

Salt	Purity	Source
FeI_2		Mallinkrodt Chem. Works St. Louis and New York
KI	Reagent	
$NaBH_4$		Obtained through the courtesy of Stauffer Chemical Co. Richmond, Calif.
$NbCl_5$		
$TiBr_4$		
$TiCl_2$		
TiI_2		
NaBr	Reagent	Merck and Co. Inc. Rahway, N. J.
$ZnCl_2$	C. P.	
$NaBF_4$		City Chemical Corp. 132 West 22nd St. New York 11, N. Y.
$ThCl_4$		
UCl_4		A. D. Mackay Inc. 198 Broadway New York, N. Y.

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