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POLAROGRAPHY OF POTASSIUM IN BIS(2-METHOXYETHYL) ETHER-WATER MIXTURES

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INTRODUCTION

The polarographic determination of alkali, alkaline earth, and lanthanum ions in bis(2-methoxyethyl) ether (diglyme, trivial name) has been previously investigated (4). Advantages of diglyme in electrochemical measurements are its wide liquid range, low viscosity, ready miscibility with polar and non-polar solvents, inertness to reduction, and relative ease of purification. These advantages are partially offset by the slight solubility of inorganic salts in this solvent (5). Also, complications due to specific absorption at the DME were observed in the anhydrous system. When it was observed that the addition of water up to a 4:1 mole ratio of water to diglyme progressively reduces the potential span available for study without interfering with the residual current, it was suggested that a diglyme-water system, which is easier to prepare and maintain, would offer the advantage of increased salt solubility along with a portion of the more negative potential span characteristic of diglyme (4). Also, the absence of evidence for specific absorption in the current-time curves for the individual mercury drops in the diglyme-water systems suggested a system with less interference to the electrode reaction. It is shown herein that the potassium ion is reversibly reduced and obeys the Ilkovic relationship in the mixed system and qualitative observations indicate considerably less difficulty with solubility problems.

EXPERIMENTAL

Apparatus. A Beckman Electroscan 30, employing a three-electrode system to compensate for cell resistance, was used to record polarographic data. The dropping mercury electrode was a capillary approximately 21 cm long, having a drop time of 4-7 seconds at -2.2 volts in the diglyme-water systems. An ordinary polarographic H-cell was used with a platinum auxiliary electrode across the medium frit from the DME. The saturated calomel reference electrode was placed adjacent to the DME and was electrically connected via an asbestos thread. Voltages reported herein are referred to this reference and were read directly from the Electroscan 30. Cell resistances were measured

with a General Radio Company (Type 1650-A) impedance bridge.

Reagents. Ansul diglyme (Code 1206) was purified by refluxing for twelve hours over sodium and subsequent distillation in a nitrogen atmosphere. The supporting electrolyte, tetra-n-butylammonium perchlorate, was prepared from 1.0 M, polarographic grade tetra-n-butylammonium hydroxide (Southwestern Chemical Co.) by reacting the hydroxide in slight excess with reagent grade perchloric acid. Oil pumped nitrogen was used and was supplied by Air Reduction Co., Nashville, Tennessee. Other chemicals used were reagent grade.

Procedure. Deaerated, distilled water and purified diglyme were mixed in the desired ratio. Potassium perchlorate was dissolved in this mixed solvent in such concentration that aliquots of this solution could be diluted in 25 ml volumetric flasks to obtain the desired concentrations of potassium. Tetra-n-butylammonium perchlorate was added, resulting in a 0.12 M solution after the final dilution to mark. In solutions containing a very high mole percentage of water or diglyme, it was necessary to warm the solution to 50C in a water bath to effect quickly the solution of supporting electrolyte or inorganic salts. Afterwards, the solution was cooled to 25C and diluted to the mark. This solution was placed in the working compartment and the solvent and supporting electrolyte in the auxiliary-electrode compartment. After bubbling the solution with nitrogen for fifteen minutes, the polarograms were recorded. Diffusion currents were measured by extra-polating the residual currents. However, residual currents were determined from time to time on the supporting system as a check on the electrochemical purity.

RESULTS AND DISCUSSION

The results given in Table I indicate that the polarography of potassium in diglyme-water systems at 25C is essentially the same in solvent mixtures ranging between mole ratios of 0.653: 1 and 4: 1 water to diglyme. Above a 4: 1 mole ratio the polarogram is drastically altered and quickly approaches the aqueous

polarography of potassium (2). The mixed-solvent system has two advantages over the anhydrous system. First, qualitative observations indicate considerably less

TABLE I
POLAROGRAPHY OF POTASSIUM IN DIGLYME-WATER SYSTEM (25°)

Concentration KClO ₄ , mmolar	Diffusion Current, μ Amp	Drop Time Seconds/Drop	Mercury Flow Rate mg/second	Diffusion Current Constant	Standard Deviation
(0.653 Mole Water—1.00 Mole Diglyme)					
1.00	0.74	4.81	0.393	1.06	
2.50	1.77	4.27	0.398	1.03	
5.00	3.50	4.52	0.403	0.998	
7.50	5.46	5.16	0.393	1.02	
10.00	7.08	6.47	0.376	0.996	
				Ave. 1.02	0.02
(1.14 Moles Water—1.00 Moles Diglyme)					
5.00	3.49	5.40	0.392	0.985	
10.00	7.44	7.00	0.403	0.998	
				Ave. 0.99	
(1.46 Moles Water—1.00 Mole Diglyme)					
1.00	0.72	6.69	0.386	0.989	
2.50	1.76	6.56	0.393	0.958	
5.00	3.47	5.88	0.352	1.04	
7.50	5.39	6.45	0.403	0.965	
10.00	7.10	5.90	0.385	1.03	
				Ave. 1.00	0.04
(2.92 Moles Water—1.00 Mole Diglyme)					
1.01	0.71	4.90	0.384	1.02	
5.02	3.43	6.13	0.391	0.945	
7.54	5.28	6.14	0.386	0.977	
10.08	7.40	5.14	0.374	1.08	
				Ave. 1.01	0.06
(3.94 Moles Water—1.00 Mole Diglyme)					
1.01	0.91	6.64	0.429	1.16	
2.52	1.72	6.88	0.393	0.930	
5.04	3.64	6.92	0.386	0.995	
10.08	7.46	6.44	0.394	1.01	
				Ave. 1.02	0.09
				Total Ave. 1.01	0.05

Average Diffusion Coefficient $2.04 \times 10^{-6} \text{ cm}^2/\text{sec}$

difficulty in the dissolution of salts. For example, solutions of 0.01 M potassium perchlorate were easily prepared. In contrast it was necessary to heat the anhydrous system to 90°C to achieve this concentration (4). Second, the diglyme-water system is easier to

prepare and maintain. It is not necessary to keep the mixed solvent from contact with the air as in the case with the 90°C, anhydrous system. If the diglyme is cooled after distillation under nitrogen, it can be mixed with water in the presence of air with no deleterious effect on the residual current provided the mixture is bubbled with nitrogen for fifteen minutes prior to a polarographic run. This system was polarographically stable for at least eight hours. An unanswered question presently being investigated is how long both the purified diglyme and the diglyme-water mixtures can be stored without affecting the residual current.

Residual currents of less than 1μ amp were routinely obtained provided a slight excess of tetra-n-butylammonium hydroxide over the perchloric acid was used in the preparation of the supporting electrolyte, tetra-n-butylammonium perchlorate.

Half-wave potentials were determined by plotting $\log(i - i_0)/i$ vs potential and reading the potential intercepts. The half-wave potential for potassium was found to be -2.04 ± 0.03 volts and was the same regardless of the ratio of water to diglyme up to a 4:1 mole ratio. The limits on the half-wave potential are imposed by the polarograph used as the potentials were obtained from the chart recordings. Resistances measured were 7,550 ohms between two platinum electrodes across the glass frit, 10,790 ohms between DME and auxiliary electrode, and 114,000 ohms between DME and reference electrode, indicating the voltage compensation required by the three-electrode system was well within the instrument capabilities.

The slope of the $\log(i - i_0)/i$ vs potential plots indicated a reversible reduction in all systems and concentrations studied.

In all of the systems studied controlled potential electrolysis established that potassium was reduced to the amalgam. A micro drop of mercury was polarized to -2.2 volts vs the reference electrode in a 10^{-4} M solution of potassium. Electrolysis was carried out for twenty-four hours, during which time the current decayed exponentially. After washing, the mercury drop was treated with dilute hydrochloric acid. The sodium cobaltinitrate test confirmed the presence of potassium and yielded negative results in blank runs.

A slight disadvantage observed in the diglyme-water systems is the somewhat irregular form of the polarographic envelope. This is due to a small irregularity in drop time. With a fresh capillary a smooth polarogram is obtained with only slight irregularities showing in the region more negative than -2.2 volts. After about six polarizations in the region more negative than -2.0 volts, the irregularities are more pronounced and occur at more positive potentials. Breaking off about 2 cm of the electrode tip restores a fresh capillary performance. This result has been observed by others in different solvents and is likely due to changes in the glass-mercury interface at such negative potentials (1, 3).

LITERATURE CITED

1. W. D. Cooke, M. T. Kelley and D. J. Fischer. 1961. Capillary behavior in high sensitivity polarography, *Anal. Chem.* 33:1200-1215.
2. I. M. Kolthoff and J. J. Lingane. 1952. "Polarography," Second Edition, Interscience Publishers Inc., New York.
3. F. L. Lambert. 1958. Polarography at very negative potentials. Improvement of polarograms by use of N,N-dimethylformamide and tetra butylammonium iodide, *Anal. Chem.* 30:1018.
4. J. T. Netterville. 1965. Polarography of alkali, magnesium, alkaline earth, and lanthanum ions in bis(2-methoxyethyl) ether (diglyme), Ph.D. Thesis, Vanderbilt University.
5. W. J. Wallace. 1963. Private Communication, University at Mississippi.

NEWS OF TENNESSEE SCIENCE

Austin Peay State University, Clarksville:

A grant of \$60,830 has been received for support of 'Physics: The Program for Teachers.' The grant, the first installment of a three-year NSF grant of \$162,000 under the direction of M. R. Mayfield, Professor and Chairman of the Department of Physics, will allow for the addition of new faculty, staff, apparatus and facilities for experimental work in secondary physics education.

King College, Bristol:

Dr. Edward W. Burke, Jr., Physics Department, and Mr. William Boy of the Mathematics Department left on May 29 for Tucson, Arizona, to utilize the 16-inch telescope of the Kitt Peak National Observatory in their work on a variable star program. This is the third visit by King College personnel: Dr. William W. Rolland and two students observed there in May and June, 1967, and Dr. Burke and Dr. Rolland in January, 1968.

Professor R. Dean Blevins of the Biology Department has been spending his second summer as a research participant in the cooperative University of Tennessee-Atomic Energy Commission Research Laboratory at Oak Ridge studying the effects of radiation on reproductive physiology.

Dr. Earl Taylor Wallick, Associate Professor of Chemistry, has been spending the summer as a Research Associate at the Savannah River Laboratory, Aiken, S. C.

Memphis State University, Memphis:

Dr. Donald Schwartz, formerly Program Director for the special project programs of NSF and consultant for HEW, has been appointed to the new position of Associate Dean of the Graduate School. The new position deals with the problems of the advanced graduate research program.

Southwestern-at-Memphis:

The Challenge Campaign has achieved its goal of matching two-for-one a 1965 Ford Foundation grant of \$1.9 million. A portion of the funds will be utilized in the construction of a \$3 million Science Center.

Tennessee Technological University, Cookeville:

NSF has awarded a grant of \$10,000 to the Biology Department under the direction of Dr. Gordon E.

Hunter for the purchase of instructional scientific equipment. The funds have been used to equip new laboratories for ecology and plant physiology.

A NSF grant of \$8,900 has been awarded to the Department of Mechanical Engineering under the direction of Dr. Hudy Hewitt for the purchase of instructional scientific equipment.

The College Science Improvement Program (COSIP) of NSF has awarded Tennessee Tech a grant of \$138,200 for the improvement of instruction in the Departments of Biology, Chemistry, Earth Sciences, Mathematics, Physics, and Sociology. The program is under the general direction of Dr. Don Caplenor.

The University of the South, Seawanee:

Dr. Nelson S. Loftus, Jr., formerly of the Southeastern Forest Experiment Station at Macon, Ga., is the new Research Soil Scientist at the U. S. Forestry Research Station at Seawanee. He and Glendon Smalley will be concentrating on soil research relating the success of tree species to fundamental properties of the soils.

The University of Tennessee, Medical Units, Memphis:

Dr. Cyrus Erickson was appointed Acting Chairman of the Department of Pathology, effective July 1, replacing Dr. Douglas H. Sprunt who will retire on August 31.

Dr. Clark M. Blatteis, Associate Professor of Physiology and Biophysics, is a visiting lecturer for approximately six months at the University of Arequipa in Arequipa, Peru, on a grant awarded by the Exchange of Scientists Program of the Organization of American States.

Dr. Kenneth E. Avis, Professor and Vice Chairman of Pharmaceutics, has been appointed a visiting scientist professor of the American Association of Colleges of Pharmacy. Dr. John Autian, Professor of Dentistry and Pharmacy and Director of the Materials Science Toxicology Laboratory, was appointed to a fourth year as a visiting professor.

Dr. W. R. Kukoverts, Associate Professor of Pharmacology at the Pharmacology Institute, University of Graz, Austria, will spend a year at the Medical Units on a Senior Foreign Scientist Fellowship awarded by NSF. His research will concern cardiovascular pharmacology.

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