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Abstract

The performance of thallium amalgam-thalious halide electrodes with thallium concentrations from 1 to 20 atomic percent has been investigated in propylene carbonate (PC). Measurements of bias potentials, polarization measurements, and comparison of emf's of amalgam concentration cells without transference with data on cells in aqueous solutions show reversibility and good stability of the electrodes. The solubilities of thalious chloride, bromide, and iodide were found in the order of 1 to 5×10^{-6} moles/1000 ml.

The pure thallium-thalious chloride electrode was also found to be suitable for reference purposes in propylene carbonate.

Introduction

In recent years propylene carbonate (mp: -48°C , bp: 242°C , dielectric constant: 64.5 at 25°C) has attracted much interest as an ionizing solvent for application in high energy density batteries. For measurements of thermodynamic properties of electrolytes and for studies of electrode processes in this solvent a reversible reference electrode of the second kind is required, which, for practical reasons, should involve a halide as sparingly soluble salt since this allows the experimental establishment of concentration cells without transference. Halides of sufficiently low solubilities in PC include mercurous, silver, and thallous halides.

At first sight the calomel and the mercury-mercurous bromide electrodes promise to be suitable systems. Mercurous chloride and bromide, however, disproportionate instantaneously when they are added to solutions of the corresponding alkali halides in propylene carbonate. Disproportionation also takes place in absence of indifferent halides; only the reaction rate is very low. Slow disproportionation of mercurous chloride has been reported to occur in contact with solutions of the corresponding halides in acetonitrile⁴ and in dimethyl sulfoxide⁵. Rapid spontaneous reaction, however, has not been reported thus far.

The solubility of silver chloride (2×10^{-5} moles/1000 ml)¹¹ in propylene carbonate suggests the application of the silver-silver chloride electrode in this solvent. However, excess chloride ions increase the solubility to such an extent that it becomes approximately equal to the excess chloride concentration¹¹. We have, therefore, not investigated further the application of this electrode in propylene carbonate.

The thallium amalgam-thallos chloride electrode is a reliable reference electrode in aqueous solutions, especially for measurements above 80°C, and is commercially available with 40 wt percent thallium as "Thalamid-Elektrode"⁷. Recently it has been shown by Smyrl and Tobias⁵ and by Cogley and Butler⁸ that it is also reversible and well suited as a reference electrode in dimethylsulfoxide solutions. Furthermore, the solubilities of thallos chloride, bromide, and iodide determined by means of emission spectroscopy are in the order of 5×10^{-6} (TlCl), 1×10^{-6} (TlBr), and 2×10^{-6} (TlI) moles/1000 ml solvent and hence an order of magnitude below that of silver chloride. These values yield solubility products in the order of 10^{-12} to 10^{-11} (moles/1000 ml)², if complete dissociation and no complex formation of the salts at these low concentrations is assumed. Quantitative tests on the effect of excess halides on the solubility of thallos halides have not been performed in the frame of this study. Unlike in the case of silver chloride, however, no effect could be discerned by visual observation.

Therefore it seemed promising to examine the behavior of thallium amalgam electrodes in connection with thallos halides in propylene carbonate. Lithium chloride (10^{-3} M), lithium bromide (0.1M), and potassium iodide (0.1M) were chosen as indifferent electrolytes because of their relatively high solubility in PC; the thallium concentration of the amalgams ranged from 1 to 20 atomic percent. The experiments also included measurements on oxide free thallium metal electrodes covered with an electrolytically formed layer of thallos chloride.

Experimental

Propylene carbonate (Jefferson Chemical Company, Houston, Texas) was distilled at 0.5 mm Hg by means of a commercially available column^{*} packed with stainless steel helices^{**}. The reflux ratio was 50 to 60, the head temperature 65°C. The first 10 percent and the last 20 percent of the solvent were discarded.

Because of the high tendency of the solvent to dissolve stopcock greases the receiver system of the column was designed with glass drip tips and needle valve stopcocks[†] equipped with Teflon "O"-rings.

Gas chromatographic analysis^{††} of the product showed the presence of two impurities at very low concentration, one of which could be identified as water. The concentration of water as determined by K. Fischer method was below 5 ppm.

Thallous chloride (reagent grade, Fisher Scientific Company, New York) and thallous bromide and iodide (prepared by precipitation from aqueous solutions of thallous nitrate with the corresponding alkali halides) were dried in vacuo with phosphorous pentoxide. In contact with PC they are slightly sensitive to light; the effect increases with increasing molecular weight of the halides. Solutions and galvanic cells were, therefore, kept in dark as far as possible.

Thallium wire used for preparation of amalgams and thallium electrodes was 99.999 percent pure (United Mineral and Chemical Corporation, New York).

* Semi-CAL Series 3650, Podbielniak, Franklin Park, Illinois.

** Helipak, Podbielniak.

† Delmar Scientific Laboratories, Inc., Maywood, Illinois.

†† Conditions of these runs were: Ucon HB 2000 (polar) on graphite in glass columns, at 152°C, carrier gas: Helium; 5 μ l samples. Propylene carbonate did not decompose in this column.

The surface was freed from oxide by washing with oxygen-free water under argon atmosphere. The silvery white metal dissolved readily in mercury. The thallium concentrations of the amalgams were determined by the acidimetric titration method given by Richards and Daniels¹.

Electrolyte solutions, amalgams, and cells were prepared in dry argon atmosphere inside a glove box, which could be evacuated to below 1μ Hg. The argon passed a U-tube with dried magnesium perchlorate for removal of water and a U-tube with BTS catalyst* for removal of oxygen. The water content was 1 ppm by volume^{**}.

The Pyrex cells used for equilibrium emf and polarization measurements consisted of six compartments, five of which were equidistant from a center compartment. This arrangement permitted the combination of any two of six reference electrodes for test purposes.

Electrode cups containing about 5 ml of the amalgam exposed 0.5 and 1 cm^2 of the metal surface to the electrolyte. The amalgams were covered with a thin adherent layer of thallous halide. Since it was found that propylene carbonate tends to creep between glass and amalgams, a tightly fitting Teflon "O"-ring was attached to the glass stem of the platinum contact below the mercury surface preventing contact between electrolyte and platinum.

The cells were tightly sealed, and 1 atm of argon was maintained over the solution throughout the measurements. The temperature was kept at $30 \pm 0.02^\circ\text{C}$.[†]

* BASF, Ludwigshafen, Germany.

** "Moisture Monitor", Consolidated Electrodynamics Corp., Pasadena, Calif.

† This temperature was chosen for the purpose of direct comparison of the data in PC with those given by Richards and Daniels for 30°C .¹

Thallium-thallic chloride electrodes were prepared from thallium wire. Thallic chloride well adhering to the metal surface was formed by anodization inside the sealed cells with current densities of 0.2 ma/cm^2 for a period of 30 minutes, yielding an amount of $0.85 \text{ mg TlCl/cm}^2$ and an average layer thickness of $1.2 \times 10^{-3} \text{ mm}$. Dissolution of this layer was prevented by presaturating the electrolyte solutions with thallic chloride.

Electrode potentials and overvoltages were measured with a potentiometric electrometer^{*}. Constant current was supplied by a constant current power supply^{**} and measured with a multirange electrometer[†]. Each of the six electrodes of each cell studied was subjected to positive and negative galvanostatic polarization (from 10^{-8} to 10^{-6} amp/cm^2), as counter and reference electrodes served any two of the other amalgam- or thallium-thallic chloride electrodes.

Results

Bias Potentials

Thallium amalgam (1 to 20 atomic percent)-thallic halide and thallium-thallic chloride electrodes were set up in propylene carbonate solutions of the corresponding alkali halides. Measurements of bias potentials and electromotive forces were conducted at 30°C for at least six months.

Bias potentials of "good" amalgam electrodes never exceeded 0.05 mv, and it could be foretold from the appearance of the surface when, in few

* Keithley potentiometric electrometer, Model 630.

** Electronics Measurements, Inc., Model 613.

† Keithley multirange electrometer, Model 601.

cases, they had higher values (up to 3 mv). "Good" electrodes had a certain appearance: Their surface was completely covered with a thin layer of very fine crystals of thallous halide. The velvet layer was produced by shaking the amalgam before it was immersed into the solution; the salt spread readily over its surface and was not removed on wetting with propylene carbonate solution. Salt in excess over the adherent quantity was usually ejected out of the electrode cups by this procedure; its presence was found to be unnecessary for a good performance of the electrodes. Only a few amalgam electrodes could either not completely be covered with thallous halide or lost the coherence of the adherent film on wetting with propylene carbonate. They showed patches of shiny amalgam, and their bias potentials were up to 3 mv and not quite constant.

Solid thallium wires employed as metal phases for thallium-thallous chloride electrodes were immersed in the PC solutions saturated with thallous chloride. Acting as electrodes of the first kind they exhibited bias potentials of less than 0.2 mv and constant emf's with amalgam-thallous chloride electrodes showing identical states of metal and surfaces. Directly after anodization and formation of the thallous chloride layer the potentials were usually off by several hundred millivolts; they changed, however, rapidly returning to their preceding value: Bias potentials were below 1 mv after two hours and below 0.2 mv after six hours. The erroneous potentials directly after anodization seem to be caused by nonuniform concentrations of electrolytes in the freshly formed layer of thallous chloride.

Polarization Measurements

In order to characterize their actual performance and reversibility, the electrodes were subjected to positive and negative polarization with current densities from 10^{-8} to 10^{-6} amp/cm².

The overvoltages of amalgam-thallic halide electrodes were in every case proportional to the current flowing; no hysteresis could be observed. Overvoltages of electrodes with 9 atomic percent thallium were corrected for the iR -drop obtained from resistance measurements at 10,000 cycles/sec between corresponding electrodes and the electrode in the center compartment. The corrected overvoltages allow the calculation of i_o^* , the effective exchange current density

$$i_o^* = \frac{RT}{nF} \left(\frac{\partial i}{\partial \eta} \right)_{\eta \rightarrow \infty}$$

Its magnitude is determined by the slowest reaction at the electrode surface. For the electrode

i_o^* is in the order of 2 to 5×10^{-5} amp/cm².

Concentration Cells

Richards and Daniels investigated thermodynamic properties of thallium and its amalgam from 0.33 wt percent to saturation (over 40 wt percent) in concentration cells without transference and used aqueous 2 percent thallic sulfate as electrolyte¹. As long as only the reversible electrode reaction determines the potential of the electrodes, the electromotive forces of these cells should be independent of the electrolyte, its concentration, the solvent, and whether the electrodes

are of the first or second kind. The emf's should only depend on the ratio of the thallium activities of the amalgam.

Accordingly, electromotive forces between thallium amalgam electrodes of the second kind with different thallium concentrations (1 to 20 atomic percent) and with thallous chloride, bromide, and iodide as sparingly soluble salts and also thallium-thallous chloride electrodes were measured in concentration cells without transference in solutions of corresponding alkali halides at 30°C. The values were compared with those for aqueous solutions at the same temperature given by Richards and Daniels. For more correct interpolation the literature data were treated by a method used by Lewis and Randall. Agreement of these interpolated values with our measurements was in every case better than 0.1 mv.

Conclusion

The results reported indicate that thallium amalgam electrodes in connection with thallous chloride, bromide, and iodide as sparingly soluble salts as well as thallium-thallous chloride electrodes with electrolytically formed thallous chloride layer are well suitable as constant, reproducible, and reversible reference electrodes of the second kind in propylene carbonate solutions. The three amalgam electrodes provide a wide and useful range of applicability, especially for thermodynamic measurements in cells without transference, since they allow the selection of the most soluble and most suited halide of a given cation to be studied. It is to be emphasized, however, that oxygen has strictly to be excluded from the system, since solid thallium and its amalgams undergo oxidation very rapidly. Preliminary experiments indicate, that

the thallium amalgam-thalious chloride reference electrode is also suitable for work in acetonitrile solutions.

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