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Journal of Electroanalytical Chemistry 581 (2005) 16–21

Journal of Electroanalytical Chemistry

www.elsevier.com/locate/jelechem

Selective transfer of Ag^+ at the water|1,2-dichloroethane interface facilitated by complex formation with a calixarene derivative

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Received 14 December 2004; received in revised form 28 March 2005; accepted 31 March 2005
Available online 23 May 2005

Abstract

The facilitated transfer of silver, Ag^+, has been studied at the Interface between Two Immiscible Electrolyte Solutions (ITIES). The transfer was achieved with the assistance of a calixarene-based silver ionophore. An investigation of the mechanistic details of the transfer was conducted using cyclic voltammetry at both micro and macro liquid|liquid interfaces. The mechanism was found to follow a Transfer by Interfacial Complexation (TIC)/Transfer by Organic phase Complexation (TOC) mechanism. The complex stoichiometry was found to shift from 1:1 to 1:2, metal:ligand, with increasing ionophore concentration. The logarithms of the complex association constants, $\log\beta_1^o$ and $\log\beta_2^o$, were estimated at 12.4 and 14.5, respectively. The charge transfer current was also found to be limited by diffusion of the transferring species and was unchanged by the presence of a range of interferents. The system thus shows promise for selective analytical applications.

Keywords: Liquid|liquid interfaces; Ion-selective electrode; Micropipette; Association constants; Calixarene; Ion transfer

1. Introduction

The study of facilitated ion transfer at the liquid|liquid interface (ITIES) has received extensive treatment since it was first reported in 1979 [1]. These studies have involved the transfer of mainly alkali metal and alkaline earth metal ions using a range of ionophores including valinomycin [1,2], dibenzo-18-crown-6 [3–6], nonactin [7], nigericin [8], naphtho-15-crown-5 [9,10], and monensin [11–13].

Studies of the facilitated transfer of Ag^+ at the ITIES have, however, been limited to only a small number of systems. Cunnane and co-workers [14] made use of *N*-phenylpyrrole, a heterocyclic monomer, to facilitate Ag^+ transfer. This charge transfer was followed by a slow, homogeneous electron transfer reaction from *N*-phenylpyrrole to the silver ion followed by polymerisation and metal cluster growth. Tetrakis(4-chlorophenyl)borate ($TPBCl^-$), an organic base electrolyte anion commonly used at the ITIES, has also been shown to facilitate Ag^+ transfer [15,16]. A similar observation had been made by Hundhammer et al. [17] while investigating a related Ag^+ system with tetraphenylborate (TPB^-) in place of $TPBCl^-$. However, it was found in that case that the observed charge transfer was, in fact, that of TPB^- from the organic to the aqueous phase. TPB^- has also been to associate with Cs^+ at the liquid|liquid interface [18].

Related work on Ag^+ transfer has involved the use of dicyclo-18-crown-6 to extract the cation as a neutral complex with a nitrate counterion [19]. Cyclic and acyclic tetrathiazaalkanes bearing a proton-dissociable

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doi:10.1016/j.jelechem.2005.03.043

hydrazone moiety have also been used for Ag^+ extraction into an organic medium in a process driven by proton loss from the ionophore [20].

The goal of the work outlined in this paper is to develop an amperometric sensor for the continuous in-process monitoring of Ag^+ concentrations in an industrial environment, based on facilitated ion transfer at the liquid|liquid interface. The potential advantages of ion-selective electrodes (ISEs) based on amperometry at the ITIES as opposed to the more conventional method of potentiometry at polymeric membranes have been well documented [21–24]. Such a system would necessitate the use of a highly lipophilic ionophore to avoid ionophore losses due to leaching. The ionophore would also have to be redox stable to avoid degradation of the sensoric response due to oxidation by Ag^+. It is envisaged that the final sensor construction would involve the use of a supported liquid membrane (SLM) [25–33].

Calixarenes have been studied extensively for use in ion-selective, potentiometric membrane sensors [34–43]. Various studies also indicate a high degree of redox stability [44,45]. Recently the electrochemical recognition of alkali metal ions at the micro water/1,2-dichloroethane interface using a calix[4]arene derivative has been reported [46]. Calixarenes were therefore an obvious choice for investigation of interaction with Ag^+ ions. The commercially available silver ionophore O,O″-Bis[2-(methylthio)ethyl]-*tert*-butylcalix[4]arene [47] was utilised for this study (Fig. 1).

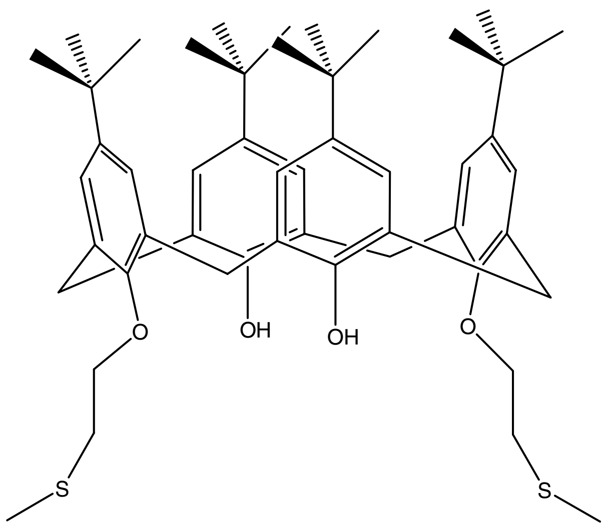

Fig. 1. Structure of the silver ionophore; O,O″-Bis[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene.

2. Experimental

2.1. Reagents

The calixarene-based silver ionophore, O,O″-Bis[2-(methylthio)ethyl]-*tert*-butylcalix[4]arene, was prepared at the University of Bangor, Wales. Bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)-borate (BTPPATPFPB) was used as organic base electrolyte throughout. This was prepared by metathesis of bis(triphenylphosphoranylidene)ammonium chloride (BTPPACl, Fluka ⩾98%) and lithium tetrakis(pentafluorophenyl)borate etherate (LiTPFPB, Boulder Scientific Company, USA) in methanol/water (1:1) solutions. The resulting precipitate was filtered, dried and twice recrystallised from ethanol. 1,2-Dichloroethane (1,2-DCE, Fluka ⩾99.5% G.C. Grade) was employed as organic solvent in all electrochemical experiments. 18.2 MΩ water (Maxima ultra pure water system, Elga) was used throughout. Sulphuric acid (H_2SO_4, Fluka >95%), silver sulphate (Ag_2SO_4, Aldrich 99%), and tetramethylammonium sulphate (TMA_2SO_4, Fluka ⩾99%) were used as received.

2.2. Procedures

All electrochemical investigations involved the use of an Autolab PSTAT100 (Eco Chemie B.V., Netherlands). Four-electrode measurements were carried out in a conventional cell (Samec et al. [48], 0.2 cm^2). The electrochemical cell is represented by

$$\text{Cell 1: Pt}\,|\,\underset{\text{(aq ref)}}{1\ \text{mM LiTPFPB}}\,|\,\underset{\text{(DCE)}}{5\ \text{mM BTPPATPFPB},\ x\ \text{mM Iono}}\,\|\,\underset{\text{(w)}}{10\ \text{mM}\ H_2SO_4,\ y\ \text{mM}\ Ag^+,\ z\ \text{mM}\ TMA^+}\,|\,\text{Pt}$$

where (w) and (DCE) represent the aqueous and organic phases, respectively, and ‖ denotes the electrochemically polarisable liquid|liquid interface. The cell potential difference is measured between the two platinum quasi-reference electrodes. The organic phase is placed in contact with an aqueous reference phase containing 1×10^{-3} M LiTPFPB. The presence of a common ion ($TPFPB^-$) in the aqueous reference and organic phases creates an electrochemically reversible, non-polarisable interface between the two. The Galvani potential difference across the liquid|liquid interface ($\Delta_o^w\phi$) is defined as the difference of the Galvani potentials in the aqueous and organic phases, respectively.

$$\Delta_o^w\phi = \phi^w - \phi^o. \tag{1}$$

All measured experimental half-wave ion transfer potentials ($E_i^{1/2}$) were corrected to their corresponding half-wave Galvani ion transfer potentials ($\Delta_o^w\phi_i^{1/2}$), following established methods. The measured experimental