CYCLIC VOLTAMMETRY OF IODINE AT THE ORGANIC LIQUID/ AQUEOUS SOLUTION INTERFACE

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The electrochemical behavior of iodine extracted with an organic solvent at the liquid/liquid interface was studied using a new composite electrode. The effects of various solvents and supporting electrolyte on the electrochemical reaction of iodine were analyzed by cyclic voltammetric curves. The formation of a polar solvent complex of iodine and a strong donor solvent in organic solution was comfirmed by UV-VIS spectra. A possible mechanism was suggested based on experiments. This method makes it possible to measure heavy metal ion in solution indirectly.

Keywords: Liquid/liquid interface; Iodine; Solvent extraction; Cyclic voltammetry; Electrochemistry; Solvent effects.

Electrochemistry at liquid/liquid (L/L) interfaces is mostly studying charge (ion and charge) transfer across an interface between two immiscible electrolyte solutions and the associated chemical reactions. The studies in this area are fuelled by the importance of L/L interfaces in separation membranes, ion-selective electrodes, solvent extraction, and mimicking biological membranes[1–4].

Voltammetric techniques appear to be a simple and powerful tool for studying the thermodynamics and kinetics of charge transfer processes. There are always problems regarding the *iR* drop effect resulting from the high-resistivity of nonaqueous solvents used and of how to distinguish double-layer charging from faradic currents. In order to solve these problems, supporting electrolytes are generally added, both aqueous and nonaqueous, and the system is usually studied by utilizing a four-electrode potentiostat[5]. Another way is to support an L/L interface at the tip of a glass micro- and nanopipette or in the microhole of a polyester thin membrane[6–8]. Due to some a priori limitations of such an experimental arrange-

ment, which is mainly related to the narrow potential window, the transfer of many organic and inorganic ions has not been accessible so far. In recent years, Shi et al.[9,10] developed a voltammetric method to study the ion transfer by using electrodes covered with the film of an immiscible organic liquid. Scholz et al.[11] reported a novel approach to study of the ion transfer between two immiscible electrolyte solutions. According to the method they employed, a single droplet of a water-immiscible organic solvent containing an electroactive compound was attached to the surface of a paraffin-impregnated graphite electrode, and immersed in an aqueous electrolyte. They assumed that the electrochemical reactions of the electroactive compound could only proceed along the three-phase junction line graphite|water|organic phase.

The aim of this paper was to design a simple method of investigation of electrochemical reactions of iodine at the L/L interface. We prepared a composite electrode by inserting a Pt wire electrode into a micropipette and injecting an organic solvent containing extracted iodine. Based on the experimental results, a possible mechanism was proposed, in which the reactions might no longer be confined to the three-phase junction line as Mirčeski reported[12]. In addition, this approach could also be applied to the indirect determination of the heavy metal ion content in terms of the reductive properties of iodide ion.

EXPERIMENTAL

Instruments and Chemicals

All the salts used for preparation of the supporting electrolytes were used as purchased and all the chemicals used were of analytical grade. Tetrabutylammonium tetraphenylborate (TBATPB) was prepared according to the method reported in ref.[13]. The aqueous solutions were prepared in deionized water. Organic solvents were saturated with deionized water prior to experiments. A triiodide stock aqueous solution was obtained by the reaction of H_2O_2 and excess KI. The exact concentration of iodine was determined by iodometry. Certain concentrations of iodine in organic solvents were prepared by extraction from triiodide stock solution with an organic solvent saturated with water (e.g. methyl isobutyl ketone (MIBK), nitrobenzene (NB), acetophenone, 1,2-dichloroethane (DCE), tetrachloromethane). A comparison of the physical properties of these solvents studied is given in Table I.

The electrochemical experiments were performed at room temperature (25 ± 1) °C with an electrochemical measuring system Autolab (PGSTAT30, Ecochemie, Netherlands).

UV-VIS spectra were measured with a UV-VIS Tu-1901 (Beijing Purkinje General Instrument Co. Ltd.) spectrophotometer.

Experimental Procedures

A conventional three-electrode cell was used, with saturated calomel electrode (SCE) as the reference electrode ($E = 0.241$ V vs standard hydrogen electrode) and a platinum electrode as the auxiliary electrode. The working electrode was a platinum wire ($d = 0.1$ mm) sealed in a classical capillary ($d = 1.0$ mm). Before experiment, it was polished with sheepskin, cleaned successively with alcohol and acetone, and then dried with a hair drier. After that, 20–40 μl of an organic solution containing iodine was injected into a pipette using a microsyringe, and the platinum wire electrode was immersed into it. Then the combined electrode was immediately set just on the surface of the aqueous solution. The schematic diagram of the experimental assembly is shown in Fig. 1. The cell employed had an interfacial area of 0.8 mm^2. During cyclic voltammetric experiments, neither a significant distortion nor a change of the

TABLE I
Physical properties[14] of organic solvents (293 K)

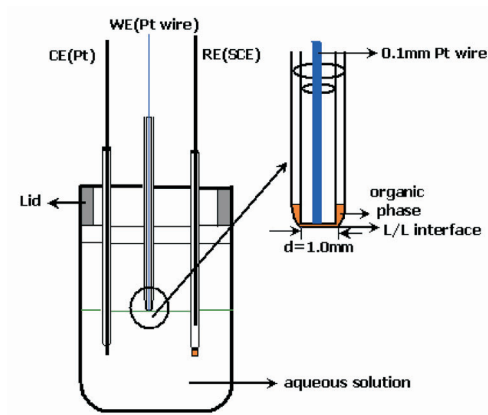|	MIBK	1,2-DCE	NB	Acetophenone	Tetrachloromethane
Density g cm^{-3}	0.8006	1.2465	1.2032	1.026	1.595
Viscosity 10^3 kg m^{-1} s^{-1}	0.59	0.84	1.98	1.617	1.458
Dielectric constant	13.10	10.45	35.96	17.44	2.2
Solubility in water % (w/w)	1.75	0.81	0.19	–	0.08

FIG. 1
Schematic diagrams of the electrochemical cell

color of the organic phase has been observed. The interfacial area influences only the measured currents, where both the position of the response (peak potential) and the shapes are not affected.

RESULTS AND DISCUSSION

Organic Solvent Without Supporting Electrolyte

As shown in Fig. 2, cyclic voltammograms of iodine extracted into different organic solvents, i.e. acetophenone (*1*), methyl isobutyl ketone (*2*) and nitrobenzene (*3*), were similar. However, in the cyclic voltammograms with tetrachloromethane (*4*) and 1,2-dichloroethane (*5*), no obvious current changes were observed in the same potential range. This was different from the results that Mirčeski[12] reported using a three-phase electrode system.

Based on the properties of the voltammetric response, the second oxidation peak at about +0.7 V vs SCE and reduction peak at about +0.4 V vs SCE would be a quasi-reversible electrochemical process. It was due to the transfer of chloride ion initially present in the aqueous phase into organic solvent in accordance with ref.[12]
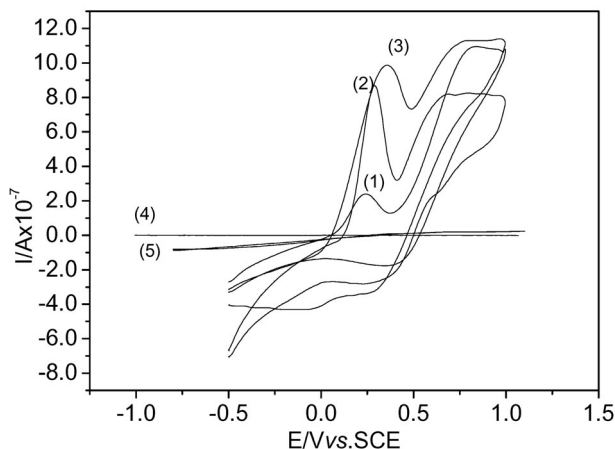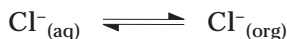
$$Cl^-_{(aq)} \rightleftharpoons Cl^-_{(org)}$$

FIG. 2

Cyclic voltammograms of different solvents: *1* acetophenone, *2* methyl isobutyl ketone, *3* nitrobenzene, *4* tetrachloromethane and *5* 1,2-dichloroethane containing 0.0232 M iodine in 1 M solution of KCl; scan rate 50 mV/s

To elucidate the mechanism of iodine oxidation at the electrode surface, the electroneutrality of the organic phase had to be taken into account. Due to an analogy of features of the oxidation to the reaction of iodide on an electrode in aqueous medium[15], it was reasonable to assure that the reaction could be described as follows:

$$2\ I^-_{(org)} - 2\ e \rightleftharpoons I_{2(org)}\ .$$

The first oxidation peak appeared at a potential of +0.3 V vs SCE close to the standard potential of the reaction in water ($E^{\theta}_{I_2/I^-}$ = 0.290 V vs SCE).

Figure 2 also revealed that no reduction peak of iodine occurred in the organic phase and that the origin of the iodide was critical to explain the mechanism. If the iodide ion was extracted from the stock triiodide solution into organic phase, all the organic solutions we used might generate similar voltammograms. However, this was not in agreement with our results. Therefore, the origin of iodide ion coming from aqueous solution could be ruled out.

The most notable feature of organic solutions was the dependence of their color on the nature of the solvent. As it was seen in Figs 3a and 3b, the solution of iodine in CCl_4 or 1,2-DCE showed the maximum absorbance at ~500 nm, appearing pink or reddish brown, while iodine in stronger donor solvent such as MIBK, NB displayed maximum absorbance at wavelengths lower than 400 nm (Figs 3c and 3d), and was deep brown. This variation could be explained as follows: a weak donor–acceptor interaction led to the formation of a complex between the solvent (donor) and iodine (acceptor), [Org·I_2], alters the optical transition energy[16]. Such donor solvents could be classified as (i) weak π-donors (e.g. MIBK) and (ii) strong σ-donors such as NB. Further interactions may also occur in polar solvents leading to ion dissociation, which rendered the solutions electrically conductive, e.g.:
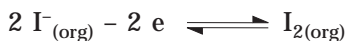
$$2\ Org·I_2 \rightleftharpoons [Org_2·I]^+ + I_3^-\ .$$

Due to no weak donor–acceptor interactions between iodine and CCl_4 or 1,2-DCE, no complex was generated in organic solutions.

Considering the iodide–iodine–triiodide equilibrium[17]

$$I_3^- \rightleftharpoons I_2 + I^-\ , \qquad K_{eq} = 0.0127\ .$$
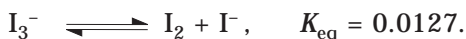
With the complex formation when iodine was extracted into a strong donor organic solvent, such as MIBK, the triiodide was successively produced. The oxidation of iodide could be accompanied by transfer of Cl^- from water

to organic phase to compensate the decrease in negative charge in organic phase. At the same time, the ion-pairs ($[Org \cdot I]^+[X^-]$) might be formed at the L/L interface. Therefore, the whole mechanism could be described as a sequence of the following reactions:

$$2 \ Org \cdot I_2 \ \rightleftharpoons \ [Org_2 \cdot I]^+ + I_3^-$$

$$I_3^- \ \rightleftharpoons \ I_2 + I^-$$

$$2 \ I^-_{(org)} - 2 \ e \ \rightleftharpoons \ I_{2(org)}$$

$$Cl^-_{(aq)} \ \rightleftharpoons \ Cl^-_{(org)} \ .$$

No complex was formed in CCl_4 and 1,2-DCE weak-donor solvents, which showed no interaction with iodine. No similar electrochemical behavior of iodine was observed in them.
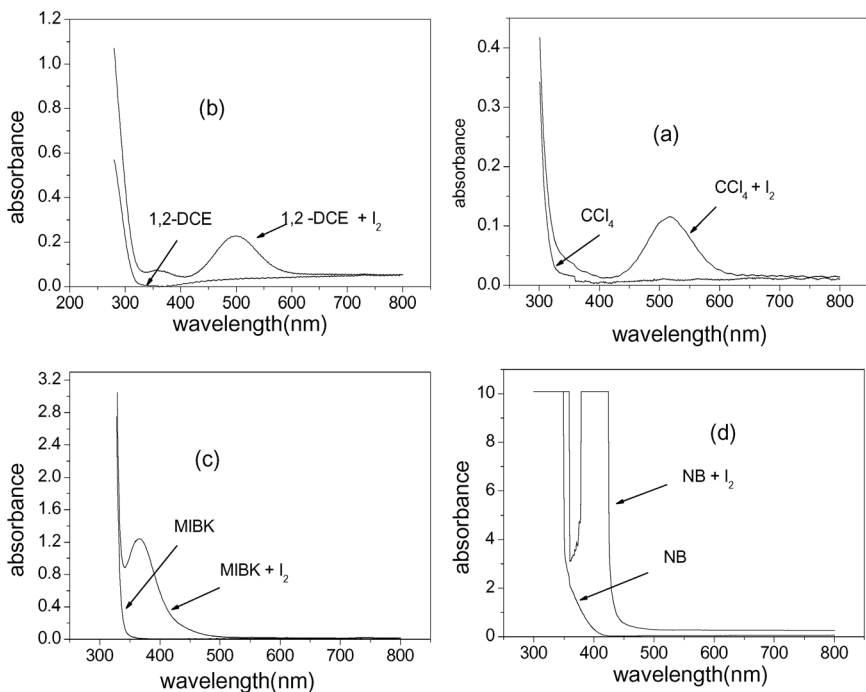

Fig. 3
UV-VIS spectra of iodine in different organic solvents

Organic Solvent with Supporting Electrolyte

We also investigated the effects of adding TBATPB as the supporting electrolyte to MIBK. The cyclic voltammograms in Fig. 4 showed the relationship between the oxidation peak currents of cyclic voltammograms and the scan rates in the potential range from –0.5 to +0.7 V vs SCE. Only one oxidation peak was observed at +0.3 V vs SCE, caused by oxidation of iodide, but no reduction peak appeared. The peak currents were proportional to square root of sweep rate, which indicated that the electrode reaction of iodide in this system was a diffusion-controlled and irreversible electrochemical process. The results of experiments are in accord with the equation of peak current I_p of irreversible process[18]:

$$I_p = 0.4463 \; nFAC_A^0 \, v^{1/2} D^{1/2} (nF/RT)^{1/2}.$$

For a stationary system, A and D were constants, when the v did not change. The peak current was directly proportional to the concentration of iodine in organic solution. This is the basis of quantitative cyclic voltammetry. Therefore, the iodine obtained by chemical reactions between excess iodide and oxidizing metal ions (e.g. Cu(II)) in solution determines its content indirectly in this method.
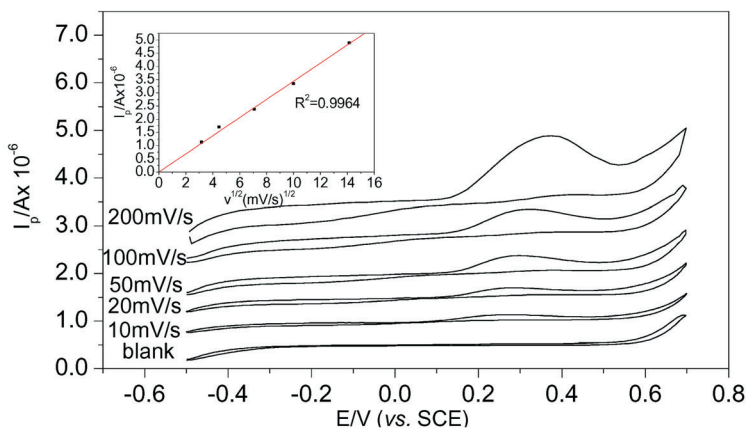

Fig. 4

Dependence of peak current on the scan rate of cyclic voltammogram: organic phase 2.032 × 10^{-3} M iodine and 3.2 × 10^{-3} M TBATPB in MIBK, water phase 1.0 M KCl, organic phase 3.2 × 10^{-3} M TBATPB in MIBK

*Solvent Extraction of Iodine from Aqueous into MIBK and
Determination of Cu(II) by Voltammetry*

As it is well known, an oxidizing analyte is added to excess I^- to produce
iodine and then the iodine is titrated with standard thiosulfate solution[15].
In this method, an indicator and standard solution are prepared. Here, we
improve the method of measuring the content of iodine in solution. Iodine
is prepared according by the chemical reactions as follows:

$$2\ Cu^{2+} + 5\ I^- \rightleftharpoons 2\ CuI(s) + I_3^-\ .$$

Then various concentrations of iodine are extracted into MIBK. Solvent extraction is a well established separation technique based on the principle
that a solute can distribute itself in a certain ratio between two immiscible
solvents, one of which is usually water and the other organic solvent. This
method is widely used because of its simplicity, speed, and applicability to
low analyte concentrations. However, voltammetric detection in organic
solvent with conventionally sized electrodes is restricted by the *iR* drop,
but as data in this work imply, this limitation should not apply to microelectrode system. Extraction of iodine from aqueous media into MIBK is
easily performed in a volumetric conical flask. The MIBK phase separates
above the water phase, and delivers the MIBK phase with syringe.
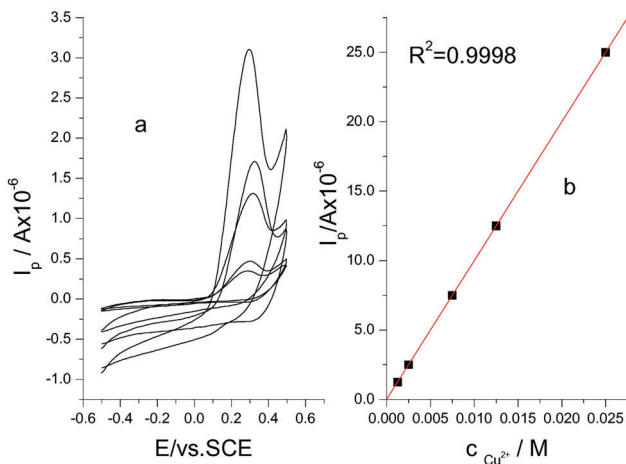

Fig. 5
a Cyclic voltammograms of various iodine concentrations in MIBK; scan rate 50 mV/s. b The
peak current vs concentration of copper ion in solution; the Cu^{2+} concentrations (in M): 0.025,
0.0125, 0.0075, 0.00025, 0.000125

The cyclic voltammograms (CVs) of the iodine prepared by reaction of various concentrations of copper ion and excess I^- in a neutral electrolyte, are shown in Fig. 5a. The peak current was directly proportional to Cu^{2+} concentration as shown in Fig. 5b. The proportionality coefficient was close to 1.0. The limit of detection for the determination of copper(II) indirectly was found to be 1.0×10^{-5} mol/l, and the concentration range up to 2.0×10^{-2} mol/l gave a linear limiting current versus concentration response.

CONCLUSIONS

We have characterized a method of study of the oxidation of iodide in organic solvent at the L/L interface, in which the ion transfer from aqueous solution to organic phase proceeds, and compared the effects of various solvents and supporting electrolytes on electrochemical behavior of iodine. The preliminary results show that iodide in the organic phase came from ionic dissociation of a polar solvent complex formed by interaction of iodine and solvent. In a certain potential range, this electrochemical reaction was an irreversible process controlled by diffusion. Considering the strong reductive properties of iodide in aqueous solution, we can obtain iodine by chemical reactions between excess iodide and heavy metal ions (e.g. Cu(II)) in solution, and then determine its content indirectly using the present method. The measurement could be performed easily with a classical three-electrode potentiostat.

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