DETERMINATION OF LEAD(II) BY ONLINE NOVEL ELECTROLYTE DROPPING ELECTRODE USING 1,10-PHENANTHROLINE IN FLOW INJECTION SYSTEM

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The transfer of Pb(II) facilitated by 1,10-phenanthroline (phen) presented in the methyl isobutyl ketone (MIBK) across the polarized water|MIBK interface was systematically investigated by novel electrolyte dropping electrode using cyclic voltammetry and square wave voltammetry. The protonation of 1,10-phenanthroline in polarized water|MIBK interface was explored. The dependence of the half-wave potential on $PbCl_2$ and phen concentration was investigated and the stoichiometry of resulting metal ligand complex was formulated. Different concentrations of $PbCl_2$ was determined online and the transfer peak current was proportional to the bulk concentration of the Pb^{2+} varied between 8 μM to 0.5 mM and 0.5 to 1 mM, and the linear regression coefficients were 0.9953 and 0.9995, respectively. The standard deviations (RSD) were 4.33, 5.80, 4.13, 3.88, 2.23, 3.39, 1.38, 2.42, 2.00, 2.73 and 2.37% for 8 times successive determinations of Pb^{2+} for the concentrations of 0.008, 0.05, 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.8, 0.9 and 1 mM, respectively. The long time stability of the electrolyte dropping electrode was tested and the result showed that this novel method was simple, rapid and efficient.
Keywords: Electrolyte dropping electrode; Liquid|liquid interface; Complex formation; Assisted ion transfer.

Lead is considered as a high toxic element because of its accumulative and persistent character in the environment. Online determination of lead as a major part of quality management of environmental monitoring has been paid more attention by the responsible authorities. Therefore different analytical techniques have been used for lead determination including atomic absorption spectrometry (AAS)[1–3], inductively coupled plasma-optical emission spectroscopy (ICP-OES)[4–7], inductively coupled plasma-mass spectrometry (ICP-MS)[8–10], atomic fluorescence spectrometry (AFS)[11–13] and electro-

analytical[14–17] methods. Among these methods, flow injection potentiometry using ion-selective electrode is widely used for several advantages, including low cost, simple instrument, rapid response, and high reproducibility, selectivity and sensitivity[18]. However, the solid electrode is usually chosen as ion-selective electrode, which has some intrinsic drawbacks. For example, solid electrode is easily to be deposited and contaminated by electrolytic products, so it is inevitable to be prepared by complicated pretreatment repeatedly. As a result it is difficult to have a reproducible fresh electrode surface and seriously affects the stability of the determination.

By opposite, the liquid electrode such as mercury electrode is well reproducible and reliable[19–21]. The continuous renewal of the droplet for electrolyte dropping electrode thoroughly avoids the deposition and contamination; moreover various complicated pretreatment is overleaped by liquid electrode. However, mercury is high toxic and the use of mercury becomes more and more restricted by the health and safety regulation.

In the last century, polarography of the electrolyte dropping electrode was pioneered by Koryta et al.[22–23], who substituted mercury with the organic solvent, such as 1,2-dichloromethane and nitrobenzene. Many articles based on the use of the dropping electrolyte electrode have been published[24–26]. However, the physicochemical properties of organic solvent, especially the conductivity and the interfacial tension, are totally different from that of the mercury. The ohmic drop of organic solvent is extremely large, and the stability of electrode is of concern because the flow rate of electrolyte dropping electrode is controlled by the height of the aqueous reservoir and the characteristics of glass capillary. All of these factors limit the analytical applications of electrolyte dropping electrode.

To address these problems our group developed a new instrument for the study of the transfer of ion at liquid|liquid interface with a classical three-electrode system[27,28]. Because of the micro-interface of the new instrument the ohmic drop of the organic solvent decreased. It is possible to measure the heavy metal ion by liquid|liquid interface indirect.

In this paper, a new instrument for the electrolyte dropping electrode was designed. Benefit from the particular mass transfer properties of microsystem and the properties of activated carbon fiber, the conductivity of aqueous phase was extremely enhanced. With the large potential windows and high conductivity, room temperature ionic liquid (RTILs) hydrophobic 1-butyl-3-methyl imidazolium hexafluorophosphate ([Bmim]PF$_6$) substituted the traditional organic electrolyte tetrabutylammonium tetraphenylborate (TBATPB). The precise roller pump was used to control the size of the liquid electrode, and the results demonstrate that this method is efficient, rapid

and simple. It is promising for online and in situ determination of heavy metal ion in practical samples.

EXPERIMENTAL

Apparatus

All electrochemical experiments were performed with the CHI 660A electrochemical workstation (CHI Instruments, Shanghai, China). A conventional three-electrode system was employed for the voltammetric measurements. An electrolyte dropping electrode was used as the working electrode, platinum wire and Ag|AgCl (3 M KCl) (both from CHI Instruments, Shanghai, China) were used for the counter electrode and reference electrode, respectively. The pH values were measured with a Mettler Toledo LE438 meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). The flow rate of the electrolyte dropping electrode was controlled by cole parmer ismatec precise roller pump (Ismatec, AG, Glattbrugg, Switzerland), a home-made glass capillary with internal tip area 2.44 mm^2, a home-made two-port stainless valve and a carbon fiber (prepared as previously reported[29]) were used to fabricate the electrolyte dropping electrode.

Reagents

The stock standard solutions of 1×10^{-2} M Pb^{2+}, Cd^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+}, Ca^{2+} and Ni^{2+} were prepared by dissolving appropriated amounts of $PbCl_2$, $CdCl_2$, $MgCl_2$, $CuCl_2$, $FeCl_3$, $CaCl_2$ and $NiSO_4$, respectively (Shanghai Reagent Corporation, China) in ultrapure water, and then diluted to various concentrations of the working solutions. Organic electrolyte [Bmim]PF$_6$ was purchased from Henan Lihua Pharmaceutical Co., Ltd. All reagents used, including 1,10-phenanthroline (phen) and methyl isobutyl ketone (MIBK) (Shanghai Reagent Corporation, China), were of analytical grade. Organic solvents were saturated with 1 M HCl. The
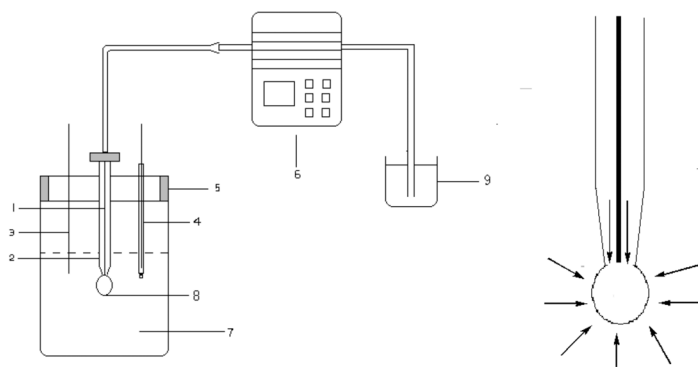

Fig. 1

Schematic diagrams of the electrochemical cell: 1 activated carbon fiber, 2 burette, 3 Pt counter electrode, 4 Ag|AgCl reference electrode, 5 lid, 6 precise roller pump, 7 organic phase, 8 liquid|liquid interface, 9 sample cell

phen solution was prepared daily by dissolving appropriated amount of phen in MIBK. All other chemicals were used without further purification. Ultrapure water (18 MΩ cm) was used throughout.

Working Electrode

Figure 1 illustrates the schematic of the working electrode. A capillary glass tube was pulled in the middle for making a pipette with a short shank and fine tip 1.2 mm in diameter. Activated carbon fibers 8 cm long (treated according to published methods[29]) embedded in a glass capillary were connected to a home-made two-port stainless valve. The flow rate and the size of electrolyte dropping electrode were controlled by precise roller pump. As the density of water is higher than that of MIBK, after the measurement it was waited for the droplet dripped down, and the next measurement was carried out.

Procedure

Cyclic voltammetry was used for the investigation of the electrochemical behavior of Pb^{2+} transfer across the water|MIBK interface assisted by phen. The size of the droplet of electrolyte dropping electrode was 0.01 ml.

Unless stated otherwise, the cyclic voltammetry waveform parameters were as follows: scan rate 50 mV/s, quiet time 150 s.

In order to obtain better detection limit, square wave voltammetry was used for the measurement of Pb^{2+} transfer across liquid|liquid interface. The square wave voltammetry waveform parameters were as follows: amplitude 100 mV, frequency 15 Hz, increment 8 mV, quiet time 150 s.

Unless stated otherwise, 0.01 M NaAc–HAc buffer solution containing 0.01 M LiCl was used for the supporting electrolyte. The cyclic voltammograms and square wave voltammograms were recorded between –1.2 and 0.4 V. The electrochemical experiments were performed at room temperature (25 ± 3) °C, and the pH of aqueous phase was at 4.5 ± 0.05.

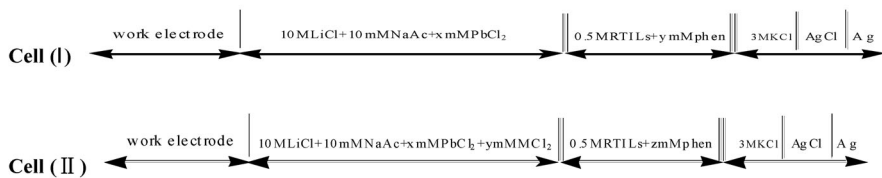For a simple and fast online determination, the quiet time of the measurement of Pb^{2+} was 0 s and the electrochemistry stripping was continuously without regarding the influence of the peak current by the size of droplet. The electrolyte dropping electrode was washed with deionized water several times before determination. The autosampler of electrochemistry system was performed and the flow rate for precise roller pump was 1.2 ml/min for 10 min, then the flow rate was adjusted to 0.3 ml/min and recorded the experimental data simultaneously. After the measurement, the sample was replaced with the next one without rinsing.

RESULTS AND DISCUSSION

Facilitated Ion Transfer

Scheme 1 describes the electrochemical cells used for the experiments presented here. Unless stated otherwise, the cell (I) was used for the measurement. When the potential increased between two phase, the peak current was taken as positive increases, due to the transfer of the cation from the

aqueous phase to the organic phase or the anion from the organic phase to the aqueous phase, otherwise a negative current was the result of the transfer of a cation from the organic phase to the aqueous phase or an anion from the aqueous phase to the organic phase.

Cell (I)

| work electrode | 10 M LiCl + 10 mM NaAc + x mM PbCl$_2$ | 0.5 M RTILs + y mM phen | 3 M KCl | Ag Cl | A g |

Cell (II)

| work electrode | 10 M LiCl + 10 mM NaAc + x mM PbCl$_2$ + ymM MMCl$_2$ | 0.5 M RTILs + zmM phen | 3 M KCl | Ag Cl | A g |

SCHEME 1
Electrochemical cell

From Fig. 2a it is clear that without the Pb^{2+} no current peak appears. The cyclic voltammograms of the supporting electrolyte show an available potential window. At the positive potentials, the potential window is limited by the excess transfer of Li$^+$ from the aqueous phase to the organic phase or by transfer of [PF$_6$]$^-$ ion from the organic phase to the aqueous phase. Conversely, at negative potentials the window is limited by either Bmim$^+$ or Cl$^-$ presented in the organic and liquid phase, respectively. The electrochemical window for this electrochemical system is from –1.2 to 0.4 V.
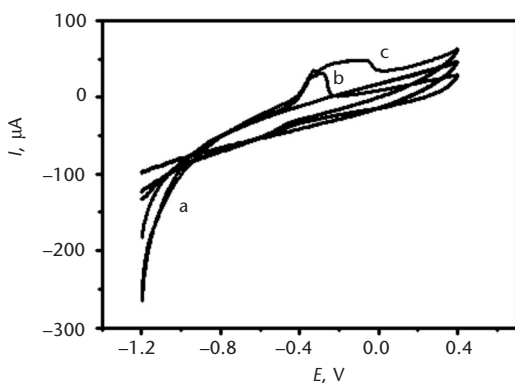

FIG. 2
Cyclic voltammogram of facilitated Pb^{2+} transfer across the water|MIBK interface for assisted ion transfer $x = 1$ mM, $y = 5$ mM, non-assisted ion transfer $x = 1$ mM, $y = 0$ mM, blank $x = 0$ mM, $y = 5$ mM

A non-assisted transfer of Pb^{2+} from the aqueous to the MIBK phase was carried out. The resulting voltammogram in Fig. 2b represents an irreversible wave from which the transfer potential of Pb^{2+} is evaluated at –0.352 V. Obviously, Pb^{2+} could transfer from the aqueous to the MIBK phase without the presence of phen in the organic phase. On the contrary, from Fig. 2c with the presence of phen in the organic phase, the transfer potential of the Pb^{2+} is shifted to more positive potential at –0.331 V and the peak current is higher. The non-assisted transfer potential of Pb^{2+} from water to 1,2-DCE phase is 505 mV [30]. So it is different with the non-assisted transfer potential of Pb^{2+} from the aqueous to the MIBK phase. Compare the MIBK and 1,2-DCE, as a conventional extractant, MIBK has been saturated with 1 M HCl. It has the ability to extract the Pb^{2+} from the aqueous to the organic phase. Compared with non-assisted transfer, the peak current of Pb^{2+} assisted transfer increases sharply which imples that phen efficiently facilitates the transfer of Pb^{2+}.

Effect of Experimental Parameters

Preconcentration Time

The effect of preconcentration time on the peak current of cyclic voltammetry and square wave voltammetry was investigated. Square wave voltammetry and cyclic voltammetry (Fig. 3) show that the peak current of Pb^{2+} transfer across the water|MIBK interface increase rapidly with the preconcentration time increase from 0 to 90 s. When the preconcentration time is longer than 90 s, the current response remains unchanged because of the excess deposition of the metal ligand complex at liquid|liquid interface. The preconcentration time of metal ion transfer was 150 s for the further experiments.

Scan Rate of Cyclic Voltammetry

Scan rate dependence of cyclic voltammetry was investigated in order to prove the diffusion control of Pb^{2+} transfer at liquid|liquid interface. Cyclic voltammogram was recorded for various scan rates. The positive peak current versus the square root of the scan rate (Fig. 4) were plotted for the ligand and the metal ion excess, giving a straight line with regression coefficients 0.9972 and 0.9976, respectively.

These results indicate that the transfer process is controlled by diffusion. When the ligand is in a large excess, the current is controlled by the metal ion diffusion, otherwise it is controlled by the ligand diffusion. In this experimental system, the evaluation and mathematical treatment were simplified by either the metal ion or the ligand in the large excess and the facilitated metal ion transfer was controlled by the diffusion of metal ion in the aqueous phase and ligand in the organic phase.
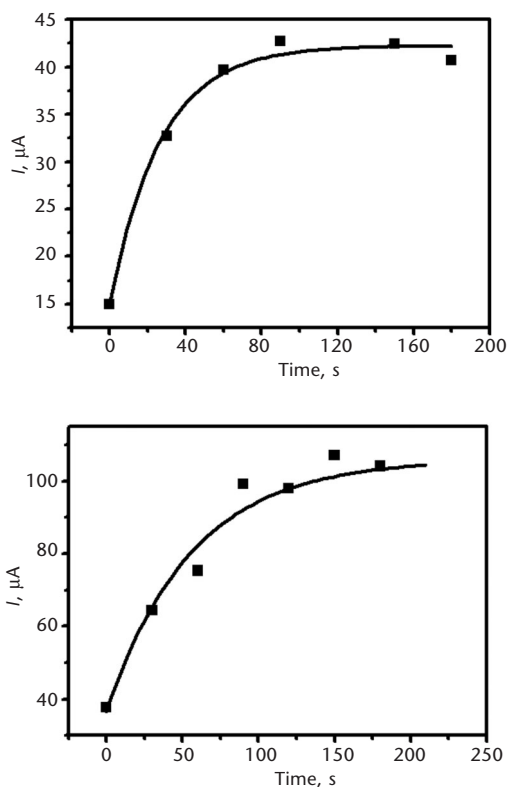

Fig. 3
Effect of preconcentration time on peak current for $x = 1$ mM, $y = 5$ mM by cyclic voltammetry (a) and for $x = 1$ mM, $y = 5$ mM by square wave voltammetry (b)
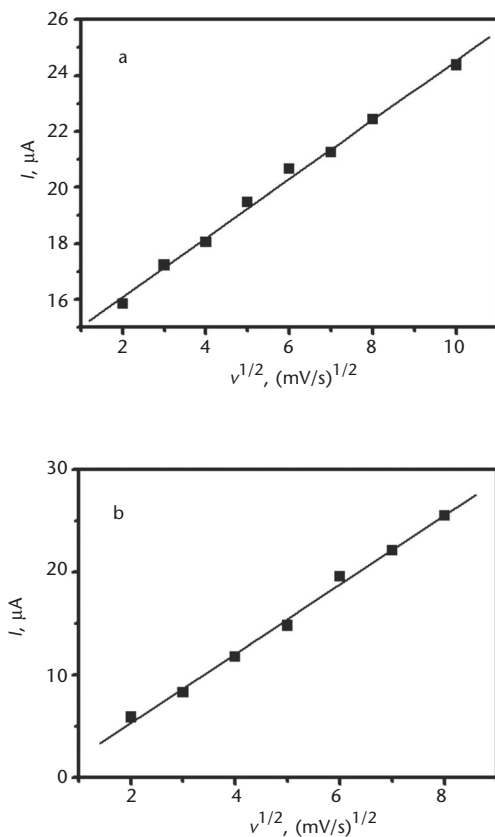
FIG. 4

The dependence of transfer peak current on the square root of the scan rate for x = 0.5 mM, y = 5 mM (a) and x = 0.5 mM, y = 0.1 mM (b) at scan rates of 4, 9, 16, 25, 49, 64 mV/s

Preliminary Study of Phen

As a popular organic metal chelator, phen could form highly stable colored complexes with many heavy metal ions. The structure of phen is showed in Fig. 5.
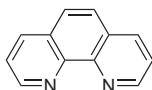

FIG. 5

Structure of 1,10-phenanthroline

The ability of phen to facilitate the electrochemical transfer of the metal ions through the liquid|liquid polarized interface was investigated. A preliminary study was focused on the form of phen in water|MIBK interface. Because of the precipitation of Pb^{2+}, the pH of aqueous phase was adjusted from 1.44 to 5.42.

Well-defined peak currents appear in the cyclic voltammogram. As described by Reymond et al.[31], Fig. 6 can be used to predict qualitatively the influence of the aqueous pH on the variation of the half-wave potential and on the nature of transferring species across the water|MIBK interface. In Fig. 6, the effect of half-peak potential on the pH shows three independent measurements. A plot presents two lines with the same slope of 53 mV/decade and it shows that there is a proton being exchanged in the transfer process. The other line is horizontal from pH 2.2 to 4.1 representing the exchange of HL^+ through the liquid|liquid interface. From Fig. 6, different species responsible for the transfer of protons are proposed.

Calculation of the Stoichiometry of Metal Ligand Complex

To evaluate the charge and stoichiometry of the metal ion complexes, the cyclic voltammetric behavior of the Pb^{2+} transfer across the liquid|liquid interface was studied. From Fig. 6 it is clear that the neutral form of ligand is predominant when the pH of aqueous phase is higher than 4.1. The pH of aqueous phase was adjusted to 5.5 with the HCl and NaOH.
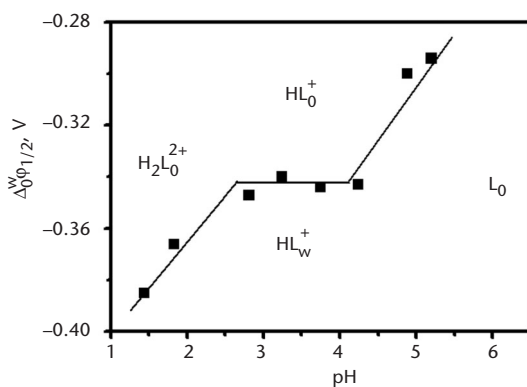

FIG. 6
Dependence of half-wave potential on the pH in the case of phen excess for x = 0.5 mM, y = 5 mM

The transfer peak current is proportional to the bulk concentration of the Pb^{2+} for the case of ligand excess. By opposite when the concentration of excess Pb^{2+} is varied, from Fig. 7 the half-wave potential is linear with the $\log C_{Pb^{2+}}$ and the slope is +32 mV. According to the model for evaluation of the charge and stoichiometry of the metal ion complexes proposed by Matsuda et al.[32] and Reymond et al.[33], from the slopes +32 mV, a charge of +2 for the complex could be deduced. The dependence of the half-wave potential on the change of the ligand concentration in the presence of excess Pb^{2+} has been monitored. Since the plot of the half-wave transfer potential as a function of $\log C_{phen}$ is linear with a slope of –27 mV (Fig. 8), the stoichiometry of the complex must be 1:2.
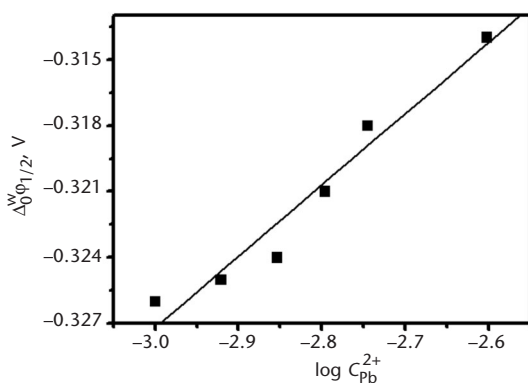

Fig. 7
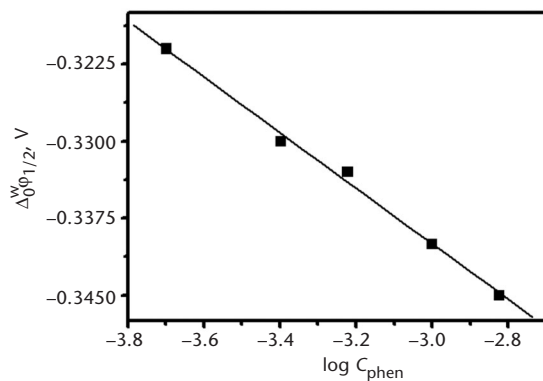Dependence of the half-wave potential on the $\log C_{Pb^{2+}}$ in the case of Pb^{2+} excess

Fig. 8
Dependence of the half-wave potential on the $\log C_{phen}$ in the case of Pb^{2+} excess

Figure 6 shows that the neutral form of ligand is predominant when the pH of aqueous phase is 5.5 and the ligand involved in interface complexation is L. The stoichiometry of complex must be 1:2 and complex $[Pb(L)_2]^{2+}$ forms in the liquid|liquid interface and it is consistent with the literature reported[34].

The stability of experimental system, for NaAc–HAc buffer solutions the voltammetric behavior of Pb^{2+} facilitated by phen was investigated at pH 4.5 for the following determination, and the ligand involved in interface complex is neutral L.

APPLICATIONS

Selectivity and Stability of the Online Determination

The peak current of Pb^{2+} transfer across the liquid|liquid interface was determined by square wave voltammetry. In order to meet the requirement of simple and rapid, the quiet time was 0 s. The flow rate of precise roller pump was 1.2 ml/min for 10 min, then the flow rate was adjusted to 0.3 ml/min and the peak current of Pb^{2+} was recorded continuously.

The peak current versus the concentration of Pb^{2+} has been plotted for the excess ligand case. The transfer peak current is proportional to the bulk concentration of the Pb^{2+} between 0.008 to 0.5 mM and 0.5 to 1 mM (Fig. 9) and the linear coefficients are 0.9953 and 0.9995, respectively. The relative standard deviations (RSD) are 4.33, 5.80, 4.13, 3.88, 2.23, 3.39, 1.38, 2.42, 2.00, 2.73 and 2.37% for 8 times successive determinations in the solutions
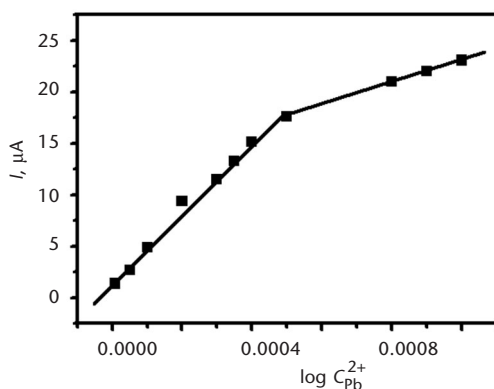

FIG. 9
Dependence of the peak current on the log $C_{Pb^{2+}}$

of 0.008, 0.05, 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.8, 0.9 and 1 mM Pb^{2+}, respectively.

The selectivity is very important for determination of heavy metal ion and ligand is the chemical base for the design of reliable sensor for the particular determination of ions. The interference of some metal ions to the Pb^{2+} transfer across the liquid|liquid interface was studied. The electrochemical cell (II) was used in this experimental system.

Square wave voltammetry of the solution containing 1 mM $PbCl_2$, and 1 mM $PbCl_2$ with the same concentration of $CaCl_2$, $NiSO_4$, $MgCl_2$, $FeCl_3$, $CuCl_2$ and $CdCl_2$ are shown in Fig. 10. As Fig. 10 shows, in these voltammograms forward peaks are separated clearly and the recoveries of the Pb^{2+} concentration are 97.00% (1 mM $PbCl_2$ + 1 mM $CaCl_2$), 90.05% (1 mM $PbCl_2$ + 1 mM $CuCl_2$), 99.12% (1 mM $PbCl_2$ + 1 mM $MgCl_2$), 80.30% (1 mM $PbCl_2$ + 1 mM $FeCl_3$), 98.60% (1 mM $PbCl_2$ + 1 mM $CdCl_2$) and 90.85% (1 mM $PbCl_2$ + 1 mM $NiSO_4$).

From the recovery of the Pb^{2+} concentration, Cu^{2+} and Fe^{3+} have a great influence on the square wave voltammetry and it may be due to the competition between Pb^{2+}, Cu^{2+} and Fe^{3+} at the water|MIBK interface. In the absence of Cu^{2+} and Fe^{3+}, well-defined square wave voltammograms of magnesium, calcium, nickel and cadmium are observed.
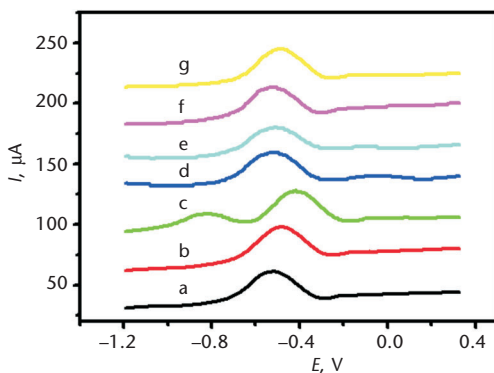

Fig. 10
Square-wave voltammograms for 1 mM $PbCl_2$ (a), 1 mM $PbCl_2$ + 1 mM $CaCl_2$ (b), 1 mM $CdCl_2$ + 1 mM $PbCl_2$ (c), 1 mM $PbCl_2$ + 1 mM $CuCl_2$ (d), 1 mM $PbCl_2$ + 1 mM $FeCl_3$ (e), 1 mM $CdCl_2$ + 1 mM $MgCl_2$ (f), 1 mM $CdCl_2$ + 1 mM $NiSO_4$ (g) transfer across water|MIBK interface

Online Determinations

Because of the requirement of practical application, the stability of flow injection system was investigated. Autoinjection was performed and electrolyte dropping electrode was rinsed with 0.5 mM $PbCl_2$. The flow rate of precise roller pump was adjusted to 1.2 ml/min to rinse the tube, after 15 min the flow rate was adjusted to 0.3 ml/min and the electrochemistry determination of Pb^{2+} transfer across the liquid|liquid was researched. The transfer peak current was recorded. From Fig. 11 it is clear that when the Pb^{2+} concentration increases, the transfer peak current increases accordingly and then reaches the maximum value and keeps mostly unchangeable until the next sample is injected. Because the difference of concentration is high when the tube is filled with ultrapure water, it takes 15 min to reach the equilibrium. But in most cases it takes 10 min to reach the equilibrium. Figure 11 shows that the flow inject system has a very excellent stability.
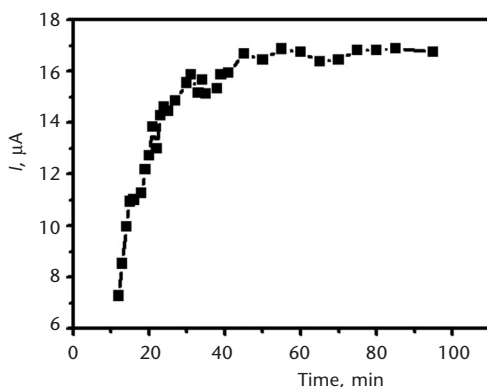

Fɪɢ. 11
Online determination

CONCLUSION

A novel electrolyte dropping electrode was designed to investigate the Pb^{2+} assisted transfer across the water|MIBK interface by phen. The form of phen at water|MIBK interface was investigated. The dependence of the half-wave potential on the ligand and the metal ion concentration was investigated to calculate the charge and stoichiometry of the metal ligand complex. The Cu^{2+} and Fe^{3+} have great influence on Pb^{2+} transfer across the water|MIBK interface. The stability of electrolyte dropping electrode was monitored and

the relative standard deviations (RSD) were 4.33, 5.80, 4.13, 3.88, 2.23, 3.39, 1.38, 2.42, 2.00, 2.73 and 2.37% for 8 times successive determinations in the solutions of 0.008, 0.05, 0.1, 0.2, 0.3, 0.35, 0.4, 0.5, 0.8, 0.9 and 1 mM Pb^{2+}, respectively.

As a liquid electrode, the interface of electrolyte dropping electrode is refreshed continually which effectively avoids the contamination from electrolyte, and the volume of droplet is controlled by a precise roller pump accurately and it ensures the stability of the determination. Complicated pretreatment of solid electrode, such as polished sequentially with different size of slurries of alumina powder, modified with a great diversity of chemicals, is not need. RTIL used as organic electrolyte extremely increased the conductively of organic electrode.

Compared with traditional organic electrolyte TPATPB, the detection limit of this electrochemistry is two orders of magnitude higher than that used in conventional electrolyte[30,31]. The measurement time for each sample is smaller than 1 min, and the electrochemistry apparatus of electrolyte dropping electrode is easy to portable and adapt to automate. It is simple and effective. As a novel approach, it allows the direct and simultaneously determination of several trace metals in a short time, and has prospective application in the online and in situ determination of heavy metal ions.

REFERENCES

1. Duarte A. T., Dessuy M. B., Silva M. M., Vale M. G. R., Welz B.: *Microchem. J.* **2010**, *96*, 102.
2. Anthemidis A. N., Ioannou K.-I. G.: *Anal. Chim. Acta* **2010**, *668*, 35.
3. Anthemidis A. N., Adama I. S. I., Zachariadis G. A.: *Talanta* **2010**, *81*, 996.
4. Meche A., Martins M. C., Lofrano B. E. S. N., Hardaway C. J., Merchant M., Verdade L.: *Microchem. J.* **2010**, *94*, 171.
5. Grigoletto T., de Oliveira E., Gutz I. G. R.: *Talanta* **2005**, *67*, 791.
6. Kulkarni P., Chellam S., Mittlefehldt D. W.: *Anal. Chim. Acta* **2007**, *581*, 247.
7. Wang J., Nakazato T., Sakanishi K., Yamada O., Tao H., Saito I.: *Anal. Chim. Acta* **2004**, *514*, 115.
8. Lam J. C., Chan K.-K., Yip Y.-C., Tong W.-F., Sin D. W.-M.: *Food Chem.* **2010**, *121*, 552.
9. Aydin F. A., Soylak M.: *J. Hazardous Mater.* **2010**, *173*, 669.
10. Kaiser J., Galiová M., Novotný K., Červenka R., Reale L., Novotný J., Liška M., Samek O., Kanický V., Hrdlička A., Stejskal K., Adam V., Kizek R.: *Spectrochim. Acta., Part B* **2009**, *64*, 67.

11. D'Ilio S., Petrucci F., D'Amato M., di Gregorio M., Senofonte O., Violante N.: *Anal. Chim. Acta* **2008**, *624*, 59.
12. Neuhauser R. E., Panne U., Niessner R., Petrucci G. A., Cavalli P., Omenetto N.: *Anal. Chim. Acta* **1997**, *346*, 37.
13. Neuhauser R. E., Panne U., Niessner R., Petrucci G. A., Cavalli P., Omenetto N.: *Sens. Actuators, B* **1997**, *38–39*, 344.
14. Nasraoui R., Floner D., Paul-Roth Ch., Geneste F.: *J. Electroanal. Chem.* **2010**, *638*, 9.
15. El Mhammedi M. A., Achak M., Bakasse M., Chtaini A.: *Chemosphere* **2009**, *76*, 1130.
16. Nasraoui R., Floner D., Geneste F.: *J. Electroanal. Chem.* **2009**, *629*, 30.
17. Hwang G. H., Han W. K., Hong S. J., Park J. S., Kang S. G.: *Talanta* **2009**, *77*, 1432.
18. Siriangkhawut W., Pencharee S., Grudpan K., Jakmunee J.: *Talanta* **2009**, *79*, 1118.
19. Winkler K., Mojsa R., Costa D. A., Balch A. L.: *Anal. Chem.* **1998**, *70*, 5244.
20. Lee T. S.: *J. Am. Chem. Soc.* **1952**, *74*, 5001.
21. Serrano N., Díaz-Cruz M. J., Ariño C., Esteban M., Serrano N.: *J. Electroanal. Chem.* **2003**, *560*, 105.
22. Koryta J., Vanýsek P., Březina M.: *J. Electroanal. Chem.* **1976**, *67*, 263.
23. Koryta J., Vanýsek P., Březina M.: *J. Electroanal. Chem.* **1977**, *75*, 211.
24. Samec Z., Papoff P.: *Anal. Chem.* **1990**, *62*, 1010.
25. Sinru L., Freiser H.: *Anal. Chem.* **1987**, *59*, 2834.
26. Yoshida Z., Freiser H.: *Inorg. Chem.* **1984**, *23*, 3931.
27. Xie S. A., Jia J. P., Chen H. J.: *Collect. Czech. Chem. Commun.* **2007**, *27*, 917.
28. Chen K., Xie S. A., Jia J. P.: *Acta Chim. Sin.* **2006**, *64*, 532.
29. Sun T. H., Jia J. P., Fang N. H., Wang Y. L.: *Anal. Chim. Acta* **2005**, *530*, 33.
30. Lagger G., Tomaszewski L., Osborne M. D., Seddon B. J., Girault H. H.: *J. Electroanal. Chem.* **1998**, *451*, 29.
31. Reymond F., Steyaert G., Carrupt P., Testa B., Girault H. H.: *J. Am. Chem. Soc.* **1996**, *118*, 11951.
32. Matsuda H., Yamada Y., Kanamori K., Kudo Y., Takeda Y.: *Bull. Chem. Soc. Jpn.* **1991**, *64*, 59.
33. Reymond F., Lagger G., Carrupt P. A., Girault H. H.: *J. Electroanal. Chem.* **1998**, *451*, 59.
34. Ferreira E. S., Garau A., Lippolis V., Pereira C. M., Silva F.: *J. Electroanal. Chem.* **2006**, *587*, 155.