

## Application of polypyrrole for potentiometric titration of halides

Reza Ansari\*, Fatemeh Emsakpour, Majid Arvand, and Ali Mohammad-Khah

Chemistry Department, Faculty of Science, University of Guilan, Rasht, Iran

### ABSTRACT

This paper describes a potentiometric titration using a modified pencil graphite electrode with polypyrrole (PGE/PPyCl) for determination of halides at low concentrations (ppm). This indicator electrode was prepared using a pencil graphite electrode coated with a thin polypyrrole conducting polymer film and its recognition property for halides was investigated. The polypyrrole (PPy) film was prepared by the electropolymerization of pyrrole monomer in the presence of NaCl as supporting electrolyte using a pencil graphite electrode (PGE) as working electrode. The PGE/PPyCl electrode was then used as indicator electrode for determination of halide ions via potentiometric precipitation titration with silver ion. The titration curves were compared with those obtained by a normal silver wire indicator electrode. It was found that using PGE/PPyCl provides higher precision and lower detection limit in measurement of halide ions.

**KEYWORDS:** potentiometry, modified electrode, pencil graphite, polypyrrole, titration, halides

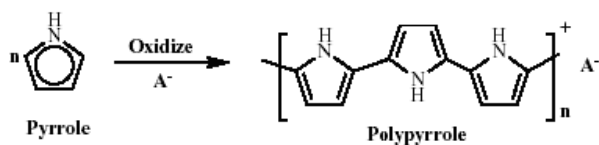
### INTRODUCTION

There has been an increasing interest in the application of conducting polymers for the development of chemical sensors. Conducting polymers show mixed ionic and electronic conductivity and therefore, act as ion-to-electron transducers [1]. This type of electrochemical

sensors could offer low limits of detection at low cost with the possibility of easy miniaturization [2]. The most important property of conducting polymers is their doping/imprinting ability with various molecular and ionic species. Because of this property, chemical recognition elements can be induced in these polymers during the preparation step. Polypyrrole is one of the most extensively used conducting polymers for the construction of various types of analytical sensors [3] and can be processed easily for many applications [4]. The different characters of PPy such as ion exchange properties [5] and environmental stability [6] and effect of dopant has been studied [7]. Polypyrrole, can be conveniently prepared by electrochemical oxidation in aqueous or organic solutions. The polymerization step is carried out by direct electropolymerization of the monomers onto the electrode surface from a solution containing a desired dopant [8, 9]. The overall polymerization reaction can be presented in a simple manner as in Fig. 1, where the  $A^-$  is the anion of the electrolyte (termed as counterion or dopant) incorporated during synthesis of the polymer. The resulting polymer is produced in the oxidised state with incorporation of counterions. The value of  $n$  has been determined to be between 2.2 and 2.4. The level of oxidation of ppy is 0.25-0.32 per pyrrole unit, depending on the type and the charge of the incorporated anion [10]. It is known that a positively charged polymer backbone is formed during the polymerization process and anions present in the medium are incorporated into the polymer structure to maintain charge neutrality.

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\*ransari@guilan.ac.ir



**Fig. 1.** Overall polymerisation reaction of polypyrrole.

The size and mobility of the doping anions influence the mechanical and electrochemical properties of the film [11-18]. A non-selective anionic response was observed for PPy films doped with small inorganic anions, such as chloride [11, 12], nitrate [13, 14], and fluoroborate [16] or perchlorate [17].

Potentiometry is an electrochemical method in which the potential of an electrochemical cell is measured while little to no current is passed through the sample [19]. The instrumentation used to perform potentiometry is simple, relatively inexpensive and the sensitivity of the electrodes allows sub-ppm concentrations to be measured. However, interferences have to be considered before analysis. This technique needs two electrodes (indicator & reference), and a potential measuring device. The end point in the measurement is characterized either by the total disappearance of one of the species (titrand) or by the appearance of an excess of one of the species (titrant).

The field of potentiometric titration procedures is the oldest yet an accurate tool to perform analyte determinations in routine analysis. Potentiometric precipitation titrations are often applied to the quantitative analysis of halides. Because the phenomenon of co-precipitation generally exists in classic precipitation titration procedures, it is difficult to use visual indicators to detect the end-point of precipitation titration. Other advantages of the potentiometric titrations are the following: 1. Colored and turbid solutions can be titrated, mixtures of species can be analysed without their preliminary separation, 2. High accuracy and precision of determinations, 3. Elimination of the visual errors in the determination of the equivalence point and 4. Intricate industrial materials can be analyzed very rapidly. In contrast to direct potentiometry, the measurement of the emf of a galvanic cell does not require the highest

possible accuracy, because only the rather large changes in the potential of an indicator electrode near the equivalence point of a titration have significance. Another advantage is the fact that we will be able to determine the equivalence point itself from the data, rather than the endpoint.

The importance of halide is immense in many areas such as in industry, agriculture and environment. In addition to being used in the production of industrial chemicals, they are also useful in the production of fertilizers. The source of environmental chlorides includes leaching from several types of rocks through weathering, before it is transported into groundwater [20]. In this paper, we report a new solid-state polypyrrole film electrodeposited onto pencil graphite used as indicator electrode for potentiometric precipitation titration of halide ions successfully.

## EXPERIMENTAL

### Reagents and samples

All chemicals used were of analytical reagent grade. Silver nitrate, potassium iodide, sodium chloride, potassium boromide obtained from Merck. All experiments were performed in aqueous solutions using deionised water. Standard  $\text{AgNO}_3$  solutions were obtained by gradual dilution of a 0.10 M  $\text{AgNO}_3$  solution. The  $\text{AgNO}_3$  solution was standardized using NaCl as a primary standard.

### Synthesis of polypyrrole

All electrochemical growth and characterisation experiments were carried out using a Digital Coulometer/Electrolysis System ZCM 761 (potentiostat/galvanostat). A two-electrode system comprised of a pencil graphite electrode (0.5 mm diameter) and silver wire as working and counter electrodes respectively. Polypyrrole film was prepared by galvanostatic methods using a constant current of 0.5 mA for 20 min. The concentration of pyrrole present in all polymerisation solutions was 0.10 M, while the concentration of dopant (NaCl) was 0.20 M. Before polymerization, the pencil graphite was finally immersed in acetonitrile and carefully rinsed with distilled water. Next, the electrode to be covered with PPy was immersed in ethanol, after this the electrode was rinsed

with distilled water. Before potential measurement, freshly prepared PPy film electrodes were doped with aqueous NaCl solutions of different concentrations and using various doping times. Using 0.01M NaCl solution and conditioning time of 6 hours were found to be the most suitable conditions. Chloride ion was used for doping of the polymer due to its higher effective mobility compared to the other halides.

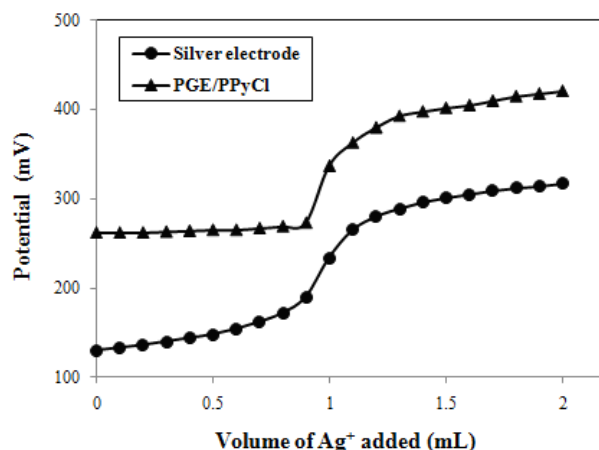
### Potentiometric titrations

The indicator electrodes were PGE/PPyCl or silver electrodes. All titrations were performed manually by adding the titrant, silver nitrate, to halide solutions while stirring continuously using a magnetic stirrer. A calomel electrode was used as reference electrode employing KNO<sub>3</sub> salt bridge to prevent diffusion of potassium chloride solution into the sample and avoid any chance of chloride contamination of the sample. A digital multimeter was used for the potential measurements. Potentiometric titration for halide ions was carried out by taking a halide solution (10.0 mL) in a vessel and silver ion was added from a burette as titrant. The concentration of AgNO<sub>3</sub> (titrant) was 10-fold to halide ions being titrated in all of titrations. Addition of titrant was performed using a 10 mL glass burette graduated each 0.05 mL. The potential values were recorded when a constant value was achieved. Knowing the stoichiometry of the reaction, and the volume and concentration of titrant, the concentration of the halide ions can be found.

## RESULT AND DISCUSSION

### Potentiometric titration of chloride ion

Titration curves of potentiometric titration of Cl<sup>-</sup> ion obtained with PGE/PPyCl and silver electrodes are indicated in Fig. 2. The resulting titration curve expressed as a plot of potential vs. volume of the titrant is characterized by a sigmoidal shape and a sharp change of the potential at the equivalence point. For reliable determinations, a fairly rapid response of the indicator electrode is required at the equivalence point. The PGE/PPyCl indicator electrode properly fulfils this requirement.



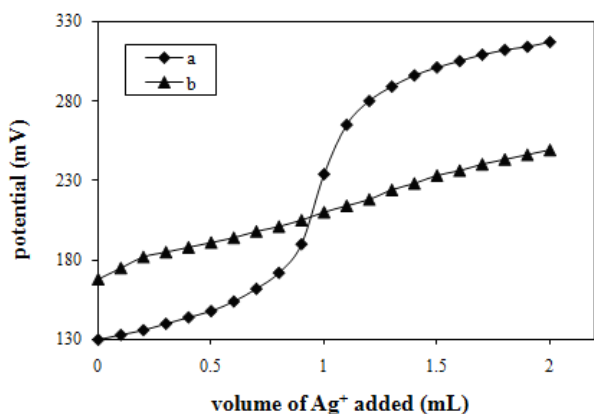
**Fig. 2.** Potentiometric titration of 10.0 ml of  $1.0 \times 10^{-3}$  NaCl with 0.010M AgNO<sub>3</sub>.

As can be seen, the potentiometric titration curve with PGE/PPyCl indicator electrode compared favorably with the potentiometric titration performed with the aid of a silver electrode. The change of the potential around the equivalence point obtained with PGE/PPyCl indicator electrode ( $\Delta E=64$  mV) is greater than that obtained using a silver electrode ( $\Delta E=44$  mV). It might be concluded that PGE/PPyCl indicator electrode is more sensitive for determination of chloride ion compared to silver electrode. This might be attributed to the high mobility and therefore fast ion exchange process between chloride ions in the analyte solution and dopant chloride ions in the polymer film.

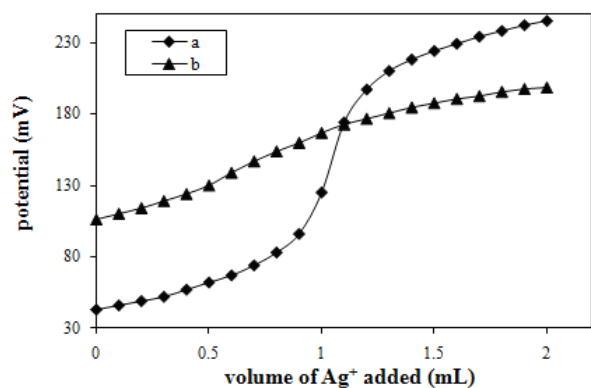
### Detection limit

Lower limits correspond to the lowest concentration of halide ions that are needed to obtain an equivalence point using the proposed procedure. The detection limit was evaluated by method based on potentiometric titrations of different concentrations of halide ions against the AgNO<sub>3</sub> solution. Potentiometric titration for halide ions was carried out by choosing 10.0 mL of halide solution for analysis.

As the results show, using the commonly used silver electrode, it is only possible to measure the concentration of chloride ion up to  $10^{-3}$  M and bromide and iodide ions up to  $10^{-4}$  M with desired precision (Figs. 3-5). However; as we have shown in Figs. 6-8, the modified electrode



**Fig. 3.** Potentiometric titration of 10.0 mL of : (a) NaCl  $10^{-3}$  M, (b) NaCl  $10^{-4}$  M with  $\text{AgNO}_3$ , using silver indicator electrode.

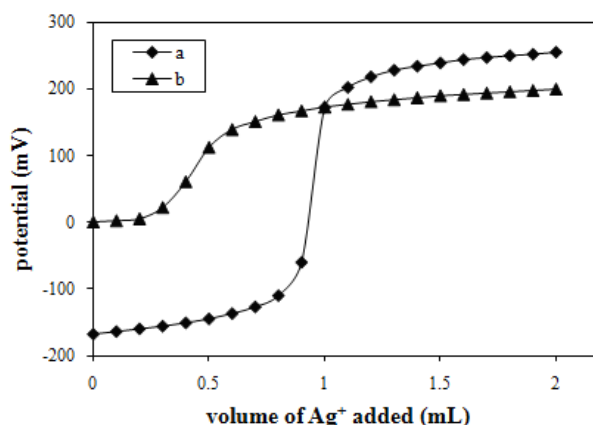


**Fig. 4.** Potentiometric titration of 10.0 mL of KBr (a)  $10^{-4}$  M, (b)  $10^{-5}$  M with  $\text{AgNO}_3$  using silver indicator electrode.

introduced in this paper (PGE/PPy/Cl) allows us to measure concentration of halide ions at lower concentrations with clear equivalent points which implies the higher sensitivity of the PGE/PPy/Cl electrode compared to normal silver electrode.

It is interesting to note that when the concentration of halide ion is very low, the direction titration curve is changed (Fig. 6d, 7c, 7d, 8c and 8d). As the results show, it is possible to determine concentration of KI at lower concentration with clear equivalence point (Fig. 8d). This can be due to the lower solubility of AgI compared to other silver halides.

In the course of titration of the halide ions, the potential jump at the end-point and the total



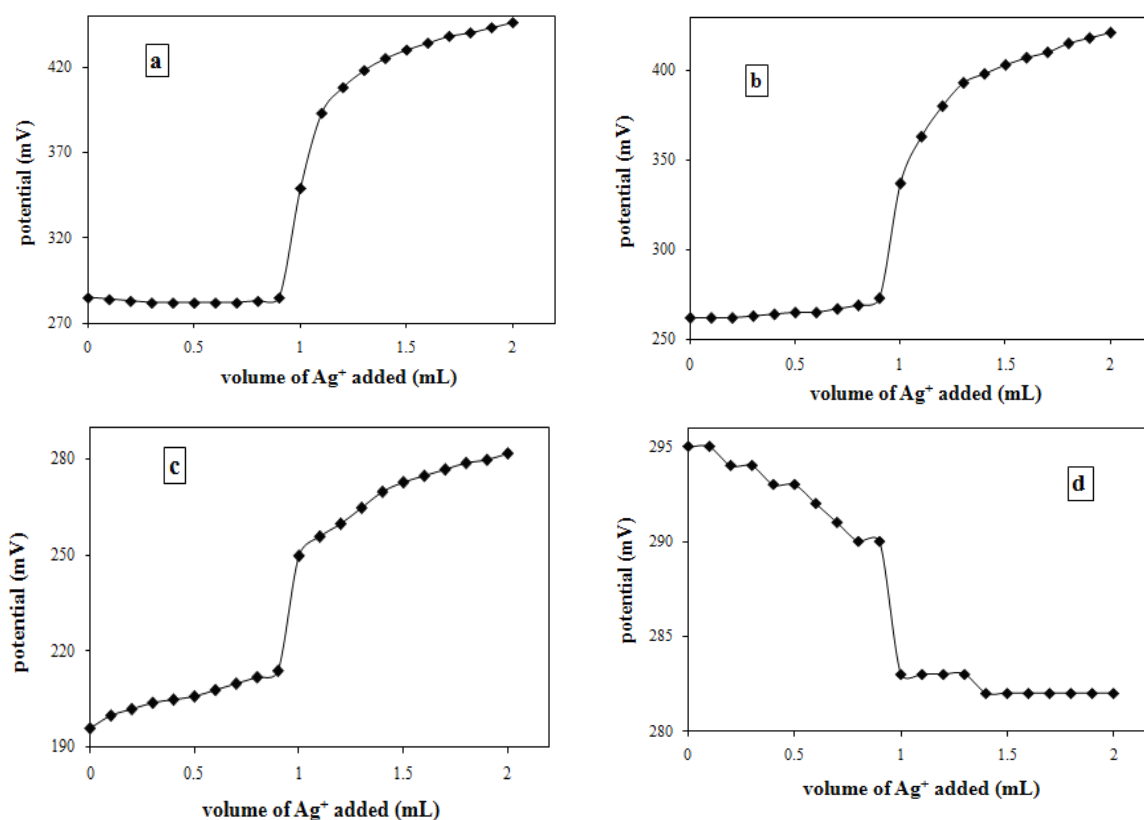
**Fig. 5.** Potentiometric titration of 10.0 mL of KI (a)  $10^{-4}$  M, (b)  $10^{-5}$  M with  $\text{AgNO}_3$  using silver indicator electrode.

potential change decrease proportionally with the decrease of the concentration of halide ( $10^{-2}$  M  $> 10^{-3}$  M  $> 10^{-4}$  M) (Figs. 6-8). The plots between emf and volume of  $\text{AgNO}_3$  are a perfect sigmoid curve and exhibit 1:1 stoichiometry of halide - metal complex up to a concentration of  $10^{-4}$  M of the  $\text{Cl}^-$  and  $\text{Br}^-$  ions (Fig. 7c & Fig. 8c) and  $10^{-5}$  M in the case of  $\text{I}^-$  ion (Fig. 8d).

### Simultaneous titration of halides

PGE/PPyCl microelectrode has been successfully applied as indicator electrode in the potentiometric determination of mixture of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) simultaneously, with  $\text{AgNO}_3$ . The results presented in Fig. 9 show that the simultaneous determination of chloride, bromide and iodide reveals sharp inflection breaks at the equivalent points and consequently, perfect stoichiometry. However, in the case of silver wire indicator electrode, when two or more halides are determined in solution by precipitation titration with silver nitrate as the titrant, significant errors can occur at the first equivalence point as a result of coprecipitation.

Chloride, iodide and bromide ions promote the quantitative reaction with  $\text{Ag}^+$  ion, resulting in the formation of a precipitate under stoichiometric conditions. Since the solubility products ( $K_{sp}$ ) of the resulting precipitates are quite different,  $3.2 \times 10^{-10}$  for AgCl and  $8.7 \times 10^{-13}$  for AgBr and  $1.5 \times 10^{-16}$  for AgI in 0.10 molar ionic strength adjusted media, it should be possible to have three



**Fig. 6.** Potentiometric titration of 10.0 ml of NaCl (a)  $10^{-2}$  M (b)  $10^{-3}$  M (c)  $10^{-4}$  M (d)  $10^{-5}$  M with  $\text{AgNO}_3$  using PGE/PPyCl indicator electrode. Concentration of  $\text{AgNO}_3$  is 10-fold to NaCl solution.

well-defined equivalence points in the titration curves using PGE/PPyCl.

#### Titration of silver ion using normal silver and PGE/PPyCl indicator electrodes

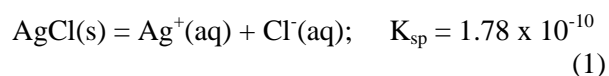
Potentiometric titration for silver ion was carried out by a 10.0 mL of silver solution (titrand) and standard solution of NaCl (with concentration 10-fold to silver ion) as titrant using silver and PGE/PPyCl indicator electrodes. As the results show, using both silver and PGE/PPyCl indicator electrodes, it is able to measure the concentration of silver ion up to  $10^{-3}$  M with desired precision (Figs. 10 and 11).

As the results show, PGE/PPyCl indicator electrode can be used for determination of silver ions from liquid samples via potentiometric titration with comparable precision as commonly used silver electrode. However in the case of analysis of halide ions, it was more sensitive, so

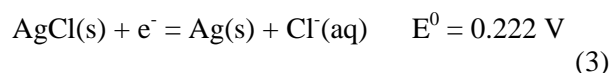
lower concentration of halides ions can be determined successfully.

#### Mechanism of the response

Silver works as halide indicator electrode if coated with silver halide (Electrode of the second kind). The two relevant equilibria at this electrode are:

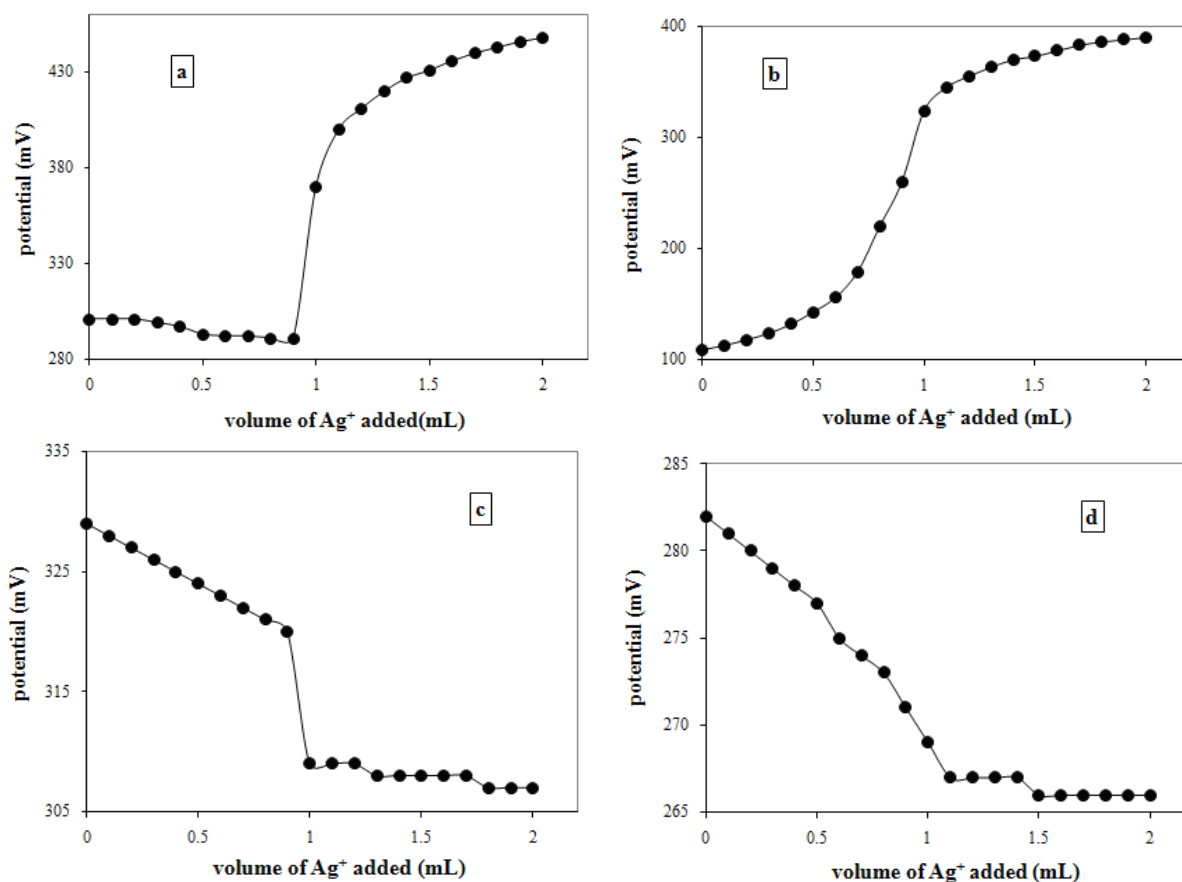


These two equations can be combined to yield a third half-reaction:



The Nernst equation for this half-reaction is as follows:

$$E = 0.222 \text{ V} - 0.059 \log [\text{Cl}^-] = 0.222 + 0.059 \text{ pCl} \quad (4)$$

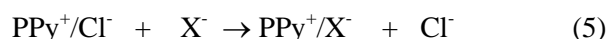


**Fig. 7.** Potentiometric titration of 10.0 ml of KBr (a)  $10^{-2}$  M (b)  $10^{-3}$  M, (c)  $10^{-4}$  M (d)  $10^{-5}$  M with  $\text{AgNO}_3$  using PGE/PPyCl indicator electrode. Concentration of  $\text{AgNO}_3$  is 10-fold to KBr solution.

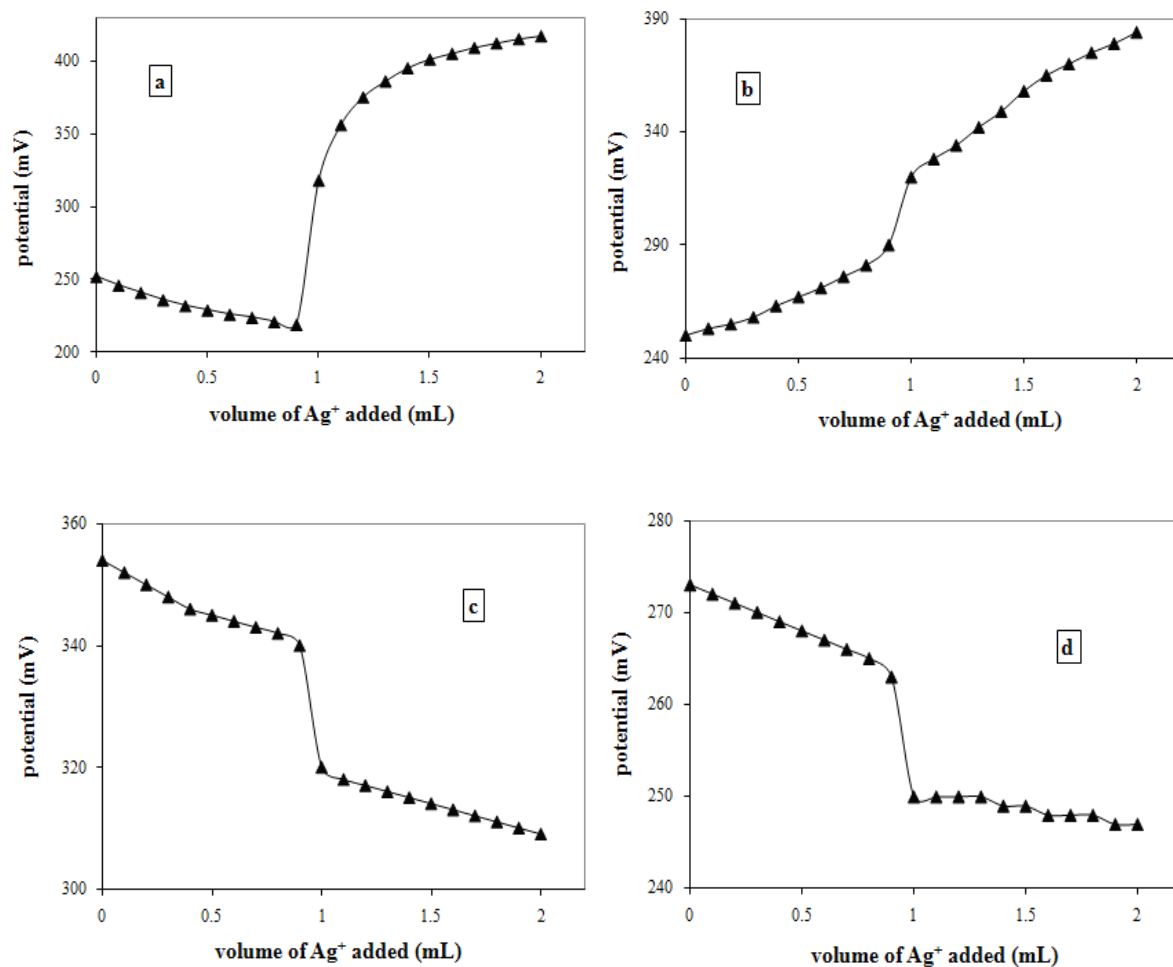
Thus using a silver indicator electrode, a linear relationship exists between the value of  $\text{pCl}$  and the emf of the cell. The indicator electrode's potential will be determined by the concentration of chloride ion in the cell solution. Of course, the potential will be influenced by other species in the solution, especially if their silver salts have  $K_{\text{sp}}$  values smaller than silver chloride. To use this electrode to measure chloride concentrations directly would require a series of standards and a calibration curve. However, this electrode can be used as an indicator electrode in a titration without any special calibration procedure. This advantage is due to the fact that we will be looking for the largest change in the potential, rather than the absolute value of the potential. The same response mechanism can be suggested for polypyrrole chloride electrode. A simple halide ion sensitive electrode is constructed during

titration with silver ion because of formation of silver chloride on the surface of PGE/PPyCl electrode. On the other hand, PGE/PPyCl the same as the second kind electrodes, works as halide indicator electrode if coated with silver halide. The potential variation during titration can be obtained from equation 4.

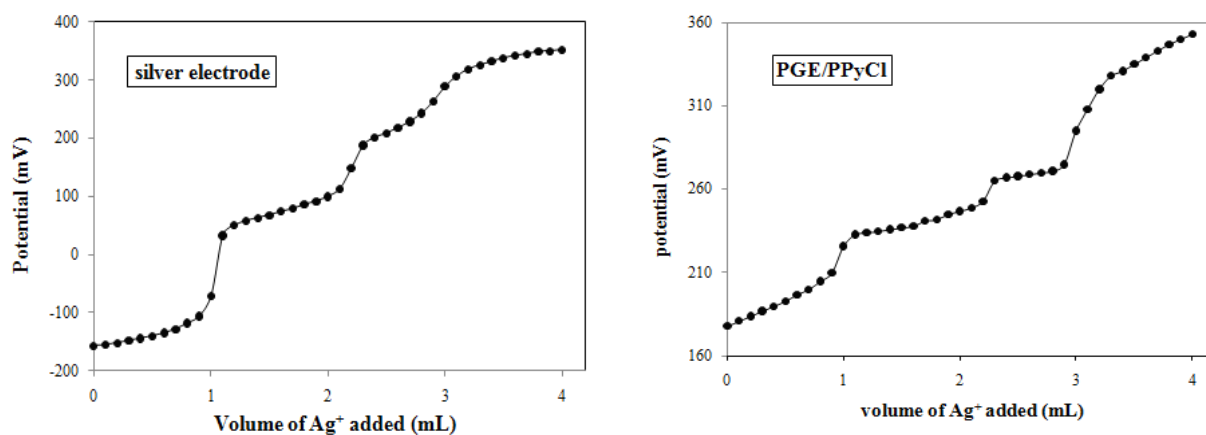
Another response mechanism of polypyrrole chloride to halide ions, might be attributed to the anion exchange properties of PPy conducting polymers when doped with small size dopants (releasable) such as chloride ion [21-28]. The ion exchange processes occurring on polypyrrole (PPy) can be represented as:



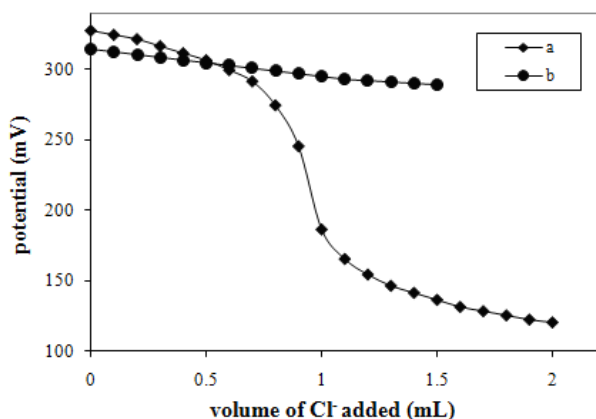
PPy conducting polymers doped with small counterions, exhibit anion exchange behavior due to the high mobility of the chloride ions in the



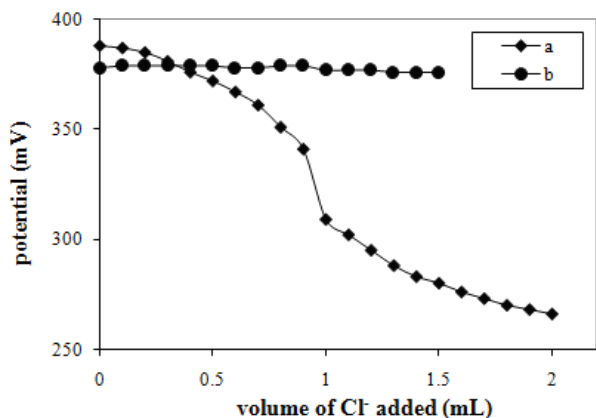
**Fig. 8.** Potentiometric titration of 10.0 ml of KI (a)  $10^{-2}$  M, (b)  $10^{-3}$  M, (c)  $10^{-4}$  M (d)  $10^{-5}$  M with AgNO<sub>3</sub> using PGE/PPyCl indicator electrode.



**Fig. 9.** Potentiometric titration mixture of halides with AgNO<sub>3</sub>. 10 mL of each salt (KI, KBr, NaCl) with concentration of  $10^{-3}$ . PGE/PPyCl and silver electrodes were used as indicator electrodes.



**Fig. 10.** Potentiometric titration of 10.0 mL of  $\text{AgNO}_3$  (a)  $10^{-3}$  M, (b)  $5 \times 10^{-4}$  M with NaCl (titrant) using silver indicator electrode.



**Fig. 11.** Potentiometric titration of 10.0 ml of  $\text{AgNO}_3$  (a)  $10^{-3}$  M, (b)  $5 \times 10^{-4}$  M, with NaCl (titrant) using PGE/PPyCl indicator electrode.

polymer matrix. Ion exchange processes on polypyrrole has been found to be reversible and the selectivity also depends on the size of the originally incorporated anions [26]. The ion exchange properties of the PPy composites are in fact the basis of many of its applications in preparation of sensors, actuators, and electrically switchable ion exchange membranes [29, 30].

## CONCLUSIONS

The proposed PGE/PPyCl indicator electrode enables low concentrations of halide ions to be determined using the potentiometric titration method which is not usually possible using

normal silver wire electrode. The sensing property of PGE/PPyCl to the halide ions seems to be mainly due to the ion exchange of halide with chloride ions (dopant of polymer). PGE/PPyCl indicator electrode was found to be more suitable than silver indicator electrode especially in the determination of low halide ion concentration since the potential change around the equivalence point was greater. The PGE/PPyCl microelectrode can be simply prepared and its performance is comparable with commonly used silver electrode in potentiometric determination of halides and silver ion. The currently introduced PPy modified electrode can also be successfully applied for simultaneous determination of mixed halides ions with high accuracy.

## ACKNOWLEDGEMENTS

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