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ORIGINAL PAPER

Response of a new multi-walled carbon nanotubes modified carbon paste electrode to 1-hexyl-3-methylimidazolium cation in aqueous solution

Xueli Ma[1] · Chunfeng Wang[1] · Hao Ren[1] · Yujuan Chen[1] · Kelei Zhuo[1]

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Abstract 1-Hexyl-3-methylimidazolium tetraphenylborate ([C$_6$mim]-TPB) was synthesized and explored as ion exchanger in carbon paste electrode (CPE) as an ion-selective electrode (ISE). The electrode was found to be optimal with the composition of 42 % graphite powder, 20 % paraffin oil, 30 % ion exchanger, 5 % MWCNTs, and 3 % nano-silica. The as-prepared electrode exhibits a Nernstian response (59.2 mV per decade) to 1-hexyl-3-methylimidazolium cation in the concentration range from 1.0×10^{-5} to 1.0×10^{-2} mol kg^{-1}. The novel as-prepared MWCNTs/nano-silica/CPE was successfully applied in the detection of [C$_6$mim]$^+$ in distilled water, tap water, and river water with satisfactory results.

Keywords Ionic liquid · Ion exchanger · Carbon paste electrode · Multi-walled carbon nanotubes · Potentiometry · Ion-selective electrode

Introduction

Ionic liquids (ILs) are considered as a class of promising and “green” non-molecular solvents in many processes owing to their unique chemical and physical properties, such as good solvating, non-volatility, high ionic conductivity, low vapor pressure, and low melting temperature [1]. All these interesting properties open the road to a wide range of applications, including electrochemical sensors [2], separation [3], extraction [4], inorganic synthesis [5], organic synthesis and catalysis [6, 7], nanomaterial synthesis [8], and enzymatic reactions [1, 9–14]. Because of their high ionic conductivity properties, ILs have recently been used as components for the construction of carbon paste ion-selective electrodes [15–18].

Scientists and engineers are working to delve deeply into the fundamentals and industrial application of ILs, especially, ionic liquids based on the 1-alkyl-3- methylimidazolium cation. In 1982, Wilkes et al. found that dialkylimidazolium chloroaluminate melts have more negative electrochemical reduction potential than N-alkyl pyridine salts [19]. Thereafter, many ILs containing a variety of cations and anions of different sizes have been synthesized for specific applications. Moreover, numerous properties, such as hydrophobicity, viscosity, and density, of the ILs have been studied as well as their dependence on the alkyl chain length [20–22].

The researches of ILs have become increasingly booming and thriving. However, recently, it has been demonstrated that many commonly used ionic liquids have a certain level of toxicity [23]. Their large scale use would give rise to environmental pollution through accidental spills or as effluents. The toxicity of many ionic liquids can be similar to the industrial solvents they may replace [24, 25]. While ILs pose little threat of airborne toxicity, a growing body of evidence suggests that they can be toxic to aquatic organisms, including bacteria, plants, invertebrates, and fish [26, 25, 27–29]. Most of the conventional methods for the determination of ILs reported in the literature include chromatography and electrophoresis [30, 31]. These methods are not only time consuming but also too cost intensive for most analytical laboratories. Therefore, it is desired to develop a simple, effective, and environment-friendly method for the determination of these ILs in environmental and biological samples. The interest in ion-selective

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✉ Kelei Zhuo
klzhuo@263.net; kzhuo@htu.cn

[1] Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, People’s Republic of China

electrodes (ISEs) has grown over recent years as they are easy-to-use devices that allow rapid and accurate analytical determination of chemical species at relatively low concentration, with a reasonable selectivity and low cost. However, to the best of our knowledge, there are rarely reports in the literature on the utilization of ISEs in the determination of ILs in solution [32, 33].

Carbon paste electrodes (CPEs) have attracted much attention, mainly because they have more advantages over membrane electrodes such as renewability, low ohmic resistance, stable response, and no-internal solution [34–38]. The carbon paste as an ion-selective electrode usually consists of graphite powder and ion exchanger dispersed in nonconductive paraffin oil [39–41]. They also have gained a great deal of interest owing to their additional components' low cost, good electron transfer kinetics, and biocompatibility [42].

In 1996, Britto et al. [43] demonstrated for the first time that the use of carbon nanotubes (CNTs) in the study of dopamine detection. Recently, a new family of nanoporous carbons prepared by thermal conversion of metal organic frameworks (MOFs) has been utilized as sensors and electrode materials [44–46]. Multi-walled carbon nanotubes (MWCNTs) have also been used in composition of carbon paste electrodes [16, 47, 48]. Due to their special physicochemical properties such as metallic or semi-metallic behavior, ultra-light weight, thermal conductivity, mechanical strength, surface area, and electrical conductivity, the MWCNTs-based sensors generally have higher sensitivities, lower limits of detection, and faster electron transfer kinetics than traditional carbon electrodes [49–53].

In our previous work [33], a type of PVC membrane electrodes were made for determination of the 1-alkyl-3-methylimidazolium bromide ionic liquids ([$C_n$mim]Br, n=3–8). However, the main problem of PVC membrane ion-selective electrode is their low physical and mechanical stability after a series of experiments. In order to improve the performance and low physical and mechanical stability of the electrode, a novel MWCNTs/nano-silica/CPE was prepared. The electrode could be used for a long term and renewed easily by mechanical polishing whenever needed. The paste electrode works based on the ion exchanger ([C_6mim]-TPB) which was made from the reaction between [C_6mim]Br and NaTPB (sodium tetraphenylborate).

Experimental

Materials and reagents

Sodium tetraphenylborate (A.R.; Aladdin), graphite powder with a small particle size (<30 μm; Shanghai Colloid Chemical Plant, China), nano-silica (Sigma), and high-purity paraffin oil (Sigma) were used. Ionic liquids [C_6mim]Cl, [$C_n$mim]Br (n=2–8) (>99 %), and [C_nPy]Br (n=2, 4) (>99 %) were purchased from Lanzhou Greenchem. Co., LICP, China. MWCNTs with 10–20 nm diameter, 10–30 μm length, 5–10 nm core diameter, >200 m^2 g^{-1} SSA, 0.22 g cm^{-3} tap density, 2.1 g cm^{-3} true density, and with 95 % purity were purchased from Boyu Gaoke Co., Beijing, China. All these materials (except paraffin oil) were dried under vacuum for 3 days before use. De-ionized water with a conductivity of 1.0×10^{-4}–1.2×10^{-4} S m^{-1} was used throughout all experiments.

Preparation of sensing element (ion exchanger) [33]

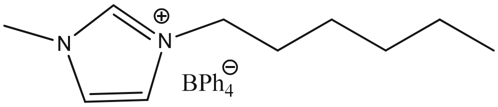
The ion exchanger, [C_6mim]-TPB (Scheme 1), was prepared from the reaction of [C_6mim]Cl and NaTPB: 150 mL of 1.0×10^{-2} mol kg^{-1} NaTPB solution was dropwise added into 120 mL of aqueous [C_6mim]Cl solution with the same molality under stirring at 323.15 K. After the mixture stood for 24 h at room temperature, white sediment (C_6mim-TPB) generated. Then the sediment was washed by ethanol and redistilled water in sequence, and was dried under vacuum for 6 h at 338.15 K.

Preparation of the carbon paste electrode (CPE)

The modified CPE was prepared as follows [16, 54–57]: the paraffin oil along with an appropriate amount of ion exchanger ([C_6mim]-TPB), graphite powder, MWCNTs, and nano-silica were thoroughly mixed. After homogenization of the mixture, the resulting carbon paste was carefully transferred into a plastic tube with 2.5 mm inner diameter and a height of 5 cm. The paste piled into the tube must avoid possible air gaps, which often enhance the electrode resistant. A copper wire was inserted into the opposite end of the CPE to establish electrical contact. External surface of the carbon paste electrode was smoothed with soft paper. A new surface can be renewed by scraping out the old surface and replaced by the new carbon paste. The CPE was finally conditioned for 48 h by soaking it into a solution of 1.0×10^{-3} mol kg^{-1} [C_6mim]Br.

Standard 1-hexyl-3-methylimidazoliumbromine solutions

A stock solution of 1.0 mol kg^{-1} [C_6mim]Br was prepared. The working standard solutions (1.0×10^{-7}–5.0×10^{-2} mol kg^{-1}) were prepared by appropriately dilution of the stock solution with de-ionized water. The working



Scheme 1 Chemical structure of ion exchanger [C_6mim]-TPB (TPB=BPh_4^-)

standard solutions of pH=6.5 was used throughout all experiments.

Experimental measurements

The as-prepared imidazolium cation selective electrode (CPE) and Ag/AgCl reference electrode (Jiangsu Electronical Instrument Co.) were used in the experiments. Cell potentials were measured by a PH/ISE meter (model 920A+; Orion) with a resolution of 0.1 mV. The test solution was continuously stirred with a magnetic stirrer. The CPE and the reference electrode were immersed in test solutions. The temperature of all test solutions in cell was controlled at T=298.15± 0.05 K with a low-temperature thermostat (model DC-2006; Shanghai Hengping Instrument Factory, China). The following electrochemical cells were set up to measure cell potentials for the sample systems.

$$\mathrm{CPE}|sample\ solution|Ag/AgCl{-}KCl(satd.)$$

The micrographs of the surface of as-prepared electrode were obtained at 30.0 kV on a JSM-5610LV scanning electron microscope (SEM; JEOL, Japan). The electrochemical impedance spectroscopy (EIS) was performed using an Autolab Potentiostat/Galvanostat (Model 600 D; CH Instruments, Inc.). A conventional three-electrode system was used with a carbon paste working electrode, a saturated calomel electrode (SCE; Jiangsu Electronical Instrument Co.) as the reference electrode, and a Pt wire as the counter electrode.

Results and discussion

Carbon paste composition selection

For potentiometric sensors or ion selective electrodes, the ionophore impeded in the sensing composition of the electrode largely determines sensitivity and selectivity of the electrode. The ionophore (or ion exchanger) is the most important sensing component in an ion-selective electrode. It binds selectively the target ion while discriminating against interfering ions [58–61]. The ion exchanger ([C_6mim]-TPB) was used to fabricate different CPEs with a variety of compositions. The results for these CPEs are given in Table 1. Obviously, the CPE no-containing ion exchanger showed almost no Nernst response (electrode No. 1, in Table 1). At the use of the ion exchanger as a modifier but the absence of MWCNTs and nano-silica in the composition of paste, the response slope first increased and then decreased. With the increase of the amount of the ion exchanger, the efficient exchange between cations in the electrode and solution increased. But over some threshold, the conductivity decreased due to the decrease in the amount of graphite, and consequently the response slope decreased. It can be clearly seen from the comparison among the electrodes (Nos. 2–4). The CPE (No. 3) showed a sub-Nernstian slope of 24.8 mV per decade. Along with the increase of paraffin, the impedance of the electrode increased, and thus the response of the electrode decreased (Nos. 3, 5, 6).

The MWCNTs can improve the conductivity and convert the chemical signal to an electrical signal. Moreover, their unique dimensions and unusual current conduction mechanism make the carbon nanotubes, especially multi-walled carbon nanotubes, become an ideal component in electrical circuits. The influence of the MWCNTs to the response of the electrode was similar to the ion exchanger (Nos. 7–9). Higher amounts of MWCNTs in the matrix of the modified electrode did not show an expected change in the Nernstian slope. The CPE (No. 8) showed a sub-Nernstian slope of 46.2 mV per decade. Rechanging the amount of the ion exchanger (Nos. 8, 10, 11), we observed that No. 11 was the best modified CPE and showed a Nernstian slope 57.6 mV per decade. So the best ratio of the ion exchanger in carbon nanotube paste composition was fixed at 30 % (*w*/*w*).

Nano-silica-based materials are robust inorganic solids displaying both high specific surface area and a three-dimensional structure made of highly open spaces interconnected to each other. This would impart high diffusion rates of selected targets to a large number of accessible binding sites, which constitutes a definite key factor in designing sensor devices with high sensitivity [62]. The research about electroanalysis with pure, chemically modified, and sol–gel-derived silica-based materials has been reported by Walcarius in 2001 [63]. Also, nano-silica in the composition of the carbon paste can improve the response of the electrode. In addition, the use of nano-silica in carbon paste enhances the mechanical properties of the electrode. Generally, the nano-silica had a similar influence trend with MWCNTs (Nos. 11–14).

Ultimately, the electrode was found to be optimal with the composition of 42 % graphite powder, 20 % paraffin oil, 30 % ion exchanger, 5 % MWCNTs, and 3 % nano-silica. Therefore, this electrode (No. 13) was chosen for further examination.

Scanning electron microscope (SEM) characterization

Figure 1 shows the SEM images for CPE and MWCNTs/CPE. As can be seen from Fig. 1a, the layer of irregular flakes of graphite powder was present and isolated from each other in the surface of CPE. By addition of MWCNTs to the carbon paste (Fig. 1b), it can be seen that most of the MWCNTs were in the form of small bundles or single tubes and were distributed on the surface of the electrode.

Table 1 Optimization of carbon paste electrode composition[a]

Number	Composition (%)					Slope (mV per decade)	Line range (mol kg^{-1})	R^2
	Graphite	Paraffin	[C_6mim]-TPB	MWCNTs	Nano-silica			
1	80	20	–	–	–	9.0±0.1	–	–
2	70	20	10	–	–	15.0±0.1	1.0×10^{-5}–1.0×10^{-2}	0.989
3	60	20	20	–	–	24.8±0.3	1.0×10^{-4}–1.0×10^{-2}	0.980
4	55	20	25	–	–	12.0±0.2	1.0×10^{-5}–5.0×10^{-2}	0.892
5	55	25	20	–	–	22.3±0.3	1.0×10^{-5}–1.0×10^{-2}	0.967
6	50	30	20	–	–	9.6±0.1	1.0×10^{-5}–1.0×10^{-2}	0.899
7	57	20	20	3	–	38.6±0.1	1.0×10^{-5}–1.0×10^{-2}	0.988
8	55	20	20	5	–	46.2±0.2	1.0×10^{-5}–1.0×10^{-2}	0.982
9	53	20	20	7	–	36.7±0.3	1.0×10^{-4}–1.0×10^{-2}	0.991
10	50	20	25	5	–	54.9±0.3	1.0×10^{-5}–1.0×10^{-2}	0.963
11	45	20	30	5	–	57.6±0.2	1.0×10^{-5}–1.0×10^{-2}	0.992
12	44	20	30	5	1	57.2±0.2	1.0×10^{-5}–1.0×10^{-2}	0.997
13	42	20	30	5	3	59.2±0.2	1.0×10^{-5}–1.0×10^{-2}	0.998
14	40	20	30	5	5	56.1±0.1	1.0×10^{-5}–1.0×10^{-2}	0.987

[a] Average of three replicate measurements for every electrode

Calibration graph and statistical data

As shown in Fig. 2, MWCNTs/nano-silica/CPE with the optimum composition (No. 13) exhibited Nernstian response to [C_6mim]$^+$ in aqueous solution in the range from 1.0×10^{-5} to 1.0×10^{-2} mol kg^{-1} and the slope was 59.2 mV per decade. To calculate the detection limit of the CPE, the extrapolation of the linear portion of the electrode's calibration curve was used and the detection limit was obtained to be 1×10^{-5} mol kg^{-1}.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is always used to further study the characterization of the electrodes, which can reflect the surface properties of the modified electrodes. The curve of the EIS can be regarded as two parts: one is a semicircular part at higher frequencies and the other is a linear part at lower frequencies. The semicircular part corresponds to an electron-transfer limited process, which controls the electron transfer kinetics of the redox probe at the electrode interface. Usually, the diameter of semicircular is equal to the electron transfer resistance (R_{et}). Meanwhile, the linear part at lower frequencies represents diffusion limited process [64–66]. Figure 3 shows the Nyquist diagrams of different electrodes (Nos. 3, 8, 13 and PVC membrane electrode [33]) in 2.5 mmol dm^{-3} $K_3[Fe(CN)_6]^+$ 100 mmol dm^{-3} KCl solution in the frequency ranging from 1 Hz to 100 kHz. The PVC membrane electrode showed a larger semicircle in the high frequencies range and had a larger resistance of electron transference than the CPE, indicating a sluggish electrochemical performance of the PVC membrane electrode. Meanwhile, the carbon paste electrode decreased the resistance of the $Fe(CN)_6^{3-/4-}$ redox couple. However, the MWCNTs/nano-silica/CPE (No. 13) suggested a much smaller diameter in the high frequencies range and can be used for the further study.

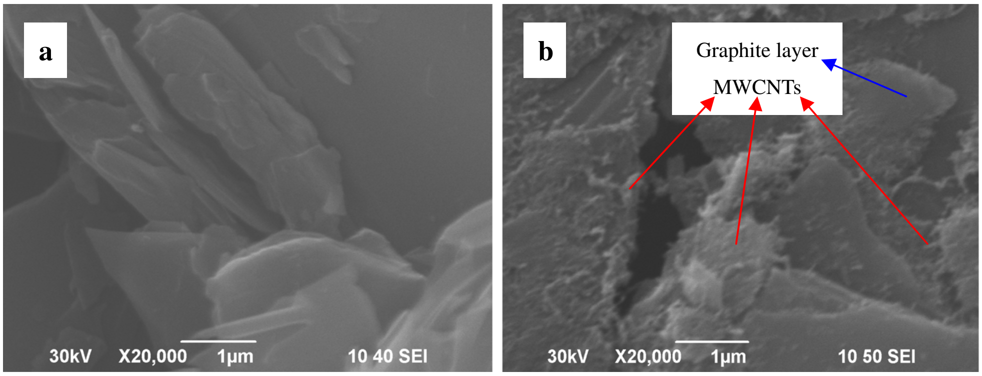


Fig. 1 SEM images of CPE (**a**) and MWCNTs/CPE (**b**)

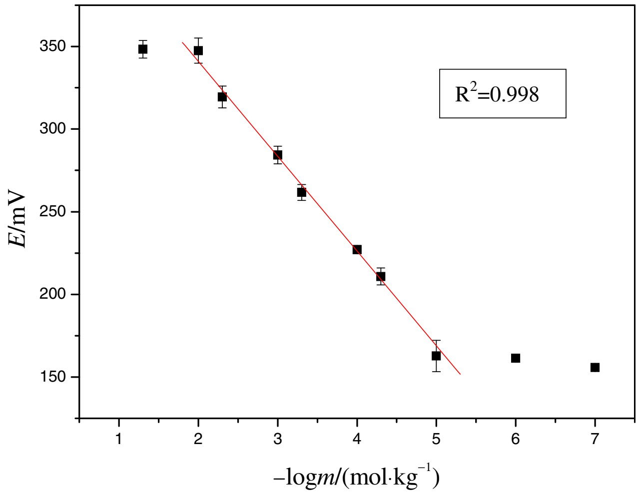


Fig. 2 The calibration curve of the MWCNTs/nano-silica/CPE based on $[C_6mim]$-TPB (No. 13)

Selectivity of the CPE

Selectivity, the most important characteristic of ion-selective electrodes, describes an electrode's specificity toward the target ion in the presence of interfering ions. In this work, the selectivity coefficient of the new MWCNTs/nano-silica/CPE was determined by the separate solution method (SSM) [50, 67, 68]. The values of the selectivity coefficient were calculated by the following equation:

$$\log K_{ij}^{pot} = \frac{E_2 - E_1}{2.303RT/Z_iF} + \left(1 - \frac{Z_i}{Z_j}\right)\log a_i$$

where E_1, E_2, Z_i, and Z_j are the measured potentials and charges on the ions i and j, respectively. a_i is the activity of ion i of interest (but no j) and j is the interfering ion at the same activity $a_j = a_i$ (but no i). The resulting values of selectivity coefficients are given in Table 2. For the alkylmethylimidazolium cations, the extent of interference is lower, when the number of carbon atoms of alkyl side chain of the interfering ions is less than six ($[C_nmim]^+$, $n<6$). However, it is higher when $n>6$. The alkylmethylimidazolium cation with a longer alkyl side chain ($n=7$, 8) as an interfering ion would interfere badly with the selectivity of the electrode to the target ion ($[C_6mim]^+$). For the pyridinium cations, the extent of interference with a shorter alkyl side chain is also lower ($[C_2Py]^+ < [C_4Py]^+$). For the inorganic cations, the extent of divalent cation (Ca^{2+}) is lower than the univalent inorganic cations (Na^+, K^+, NH_4^+). Overall, it can be clearly seen that the electrode has a relatively good selectivity except for $[C_7mim]^+$ and $[C_8mim]^+$.

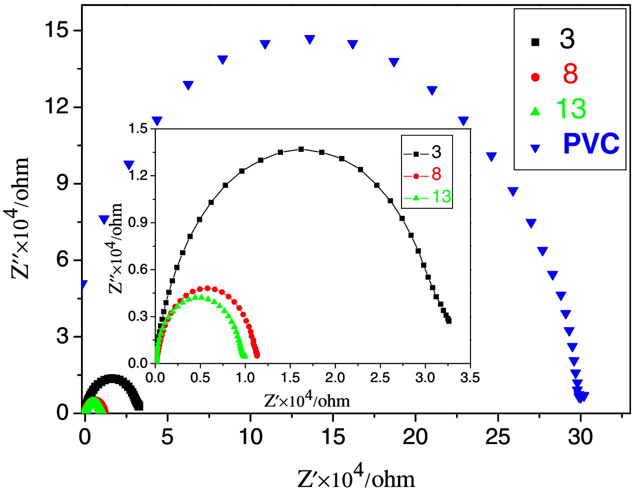


Fig. 3 Electrochemical impedance spectroscopy (EIS) for the CPE [Nos. 3 (*filled squares*), 8 (*filled circles*), 13 (*filled triangles*)] and PVC membrane electrode (*filled down-pointing triangles*) in 2.5 mmol dm^{-3} $K_3[Fe(CN)_6]^+$, 100 mmol dm^{-3} KCl. Frequency range: 1–10^5 Hz

pH effect on the electrode response

To investigate the pH effect on the potential response of the electrode, the potentials were measured for a given concentration of $[C_6mim]Br$ solution at different pH values and the pH of solution was adjusted by the addition of NaOH or HCl solution. The potential variation as a function of pH was plotted (Fig. 4). The results indicated that the potential remains approximately constant when the pH values change in the range of 5 to 8.

Response time and lifetime of the CPE

The response time of an ion-selective electrode is an important factor for any analytical application. The response time is defined in this work by measuring the average time required to achieve values within ±1 mV of the final equilibrium potential (steady-state potential) [69, 70]. The resulting response time for the electrode (No. 13) was obtained upon changing the concentration of $[C_6mim]Br$ solution from 1.0×10^{-7} to 5.0×10^{-2} mol kg^{-1}. The response time of the electrode was less than 20 s.

Table 2 Selective coefficients (K_{SSM}) of the electrode (No. 13) to 1-hexyl-3-methylimidazolium cation ($[C_6mim]^+$) for various interfering cations[a]

Interfering cation	$\log K_{SSM}$	Interfering cation	$\log K_{SSM}$
$[C_2mim]^+$	−1.2	$[C_2Py]^+$	−1.3
$[C_3mim]^+$	−1.5	$[C_4Py]^+$	−0.8
$[C_4mim]^+$	−1.1	Na^+	−1.1
$[C_5mim]^+$	−1.1	K^+	−1.3
$[C_6mim]^+$	0	Ca^{2+}	−2.1
$[C_7mim]^+$	0.2	NH_4^+	−1.4
$[C_8mim]^+$	0.3		

[a] Average of three replicate measurements

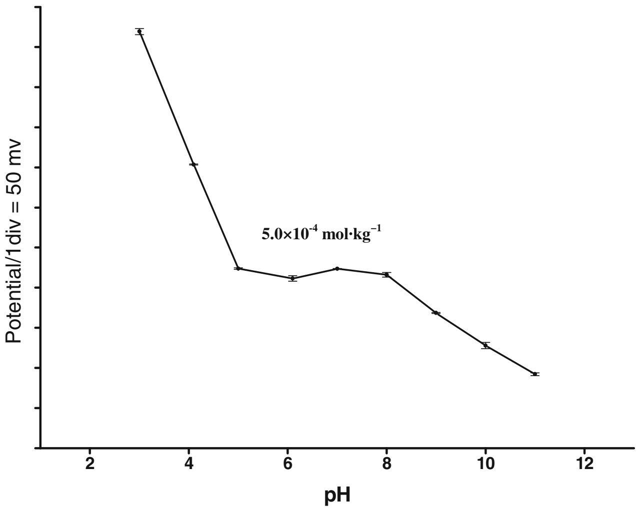


Fig. 4 Effect of pH on the potential response of the $[C_6mim]^+$ modified CPE (No. 13)

Lifetime is another important issue for the ion-selective electrode. The average lifetime for most sensors ranges from 3 to 10 weeks. After this time, the slope of the sensor decreases and the detection limit increases. In this work, the as-prepared CPE can be renewed by scraping the surface of the used electrode, and the obtained results indicated that the as-prepared CPE can be used for at least 5 months.

Analytical application

The as-prepared MWCNTs/nano-silica/CPE was successfully applied to obtain recoveries of $[C_6mim]Br$ in distilled water, tap water, and river water, respectively. The analysis was performed by the standard addition technique. The results are given in Table 3. Satisfactory results were observed in all the cases. Therefore, the potentiometric sensor provides a good alternative for the determination of $[C_6mim]^+$ in real samples.

Table 3 Determination of $[C_6mim]Br$ recovery by the proposed electrode (No. 13) in the real samples

Samples	Content of $[C_6mim]Br$ (mol kg^{-1})	% Recovery±SD[a]
Distilled water	1.50×10^{-4}	96.0±0.7
	4.00×10^{-4}	100.3±1.5
	7.50×10^{-4}	98.9±0.4
	9.50×10^{-4}	100.2±0.4
Tap water	1.50×10^{-4}	96.7±2.0
	4.00×10^{-4}	100.5±0.2
	7.50×10^{-4}	96.9±0.4
	9.50×10^{-4}	101.8±1.2
River water	1.50×10^{-4}	97.3±0.7
	4.00×10^{-4}	96.8±3.5
	7.50×10^{-4}	98.5±1.9
	9.50×10^{-4}	100.6±0.4

SD standard deviation

[a] Average of three replicate measurements

Conclusions

The MWCNTs/nano-silica/CPE, a new potentiometric sensor, was constructed for the determination of 1-hexyl-3-methylimidazolium cation. The as-prepared CPE exhibited excellent performances especially in lifetime and response time. The $[C_6mim]$-TPB as the ion exchanger was used in construction of CPE and thus its response is based on ion-exchange mechanism. The CPE was also used for the determination of $[C_6mim]Br$ in three real water samples with good recoveries. It can be expected that the CPE would be applied widely to the detection of ILs and the determination of properties of ILs in aqueous solutions.

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