

Full Paper

Symmetric and Asymmetric PVC Membrane Potentiometric Electrodes for the Analysis of Morphine Hydrochloride

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Abstract- Two novel potentiometric Morphine sensors were designed, optimized and used for the determination of this alkaloid drug. The electrodes were based on the symmetric and asymmetric designs for the application of PVC membrane sensors. Both the symmetric membrane and the asymmetric wire coated electrodes were worked based on morphine-tetraphenyl borate ion-pair complexes which act as the sensing material and they responded based on ion exchange mechanism. The optimal response behavior was at 5% wt. of the ion-pair, 30% wt. of PVC and 65% wt. of DBP for the symmetric devices and at 25% wt. of PVC, 5% wt. of the ion-pair morphine-tetraphenyl borate, 2% wt. of ionic additive and 68% DBP. The PVC membrane sensor was found to have a Nernstian behavior in the concentration range of 5.0×10^{-5} - 1.0×10^{-2} mol L⁻¹, while the wire coated electrodes showed linear behaviors from 1.0×10^{-7} to 1.0×10^{-4} mol L⁻¹. Both devices proved to satisfactorily applicable in the analysis of Morphine hydrochloride in pharmaceutical formulation under laboratory conditions.

Keywords- Morphine hydrochloride, Potentiometry, Ion-selective electrode, Wire coated, PVC membrane, Sensor

1. INTRODUCTION

Morphine (MOR, Fig. 1) which is an opiate directly influences the central nervous system and alleviates the pain. Morphine is used in the treatment of acute and chronic pains and is also often used for treating pain caused by myocardial infarction and labor pains [1]. It has also a high potential for addiction. Morphine is primarily isolated from poppy straw of opium poppy. Most of the applications of the compound are in the developed world and in 2013, for instance, about 523,000 kilograms of morphine were produced and around 45,000 kilograms of the material were directly used for pain reduction applications, which showed a four-fold increase over the past twenty years [2]. About 70% of the produced morphine is used for the synthesis of other opioids such as hydromorphone, oxycodone and heroin [2-4]. Morphine is classified as a Schedule II pharmaceutical in the USA [5], a Class A drug in the UK [6] and a Schedule I medicine in Canada [7], and the compound is on the WHO's Model List of Essential Medicines, which illustrates the most important medications required by a basic health system [8]. The compound is highly addictive and studies comparing the physiological and subjective effects of heroin and morphine on people who had formerly been addicted to opiates revealed that these people did not reveal any preference for either drug. Further the injection of equipotent doses of heroin and morphine proved comparable action courses and identical self-rated feelings of euphoria, ambition, nervousness, relaxation, drowsiness, or sleepiness on the part of the subjects [9].

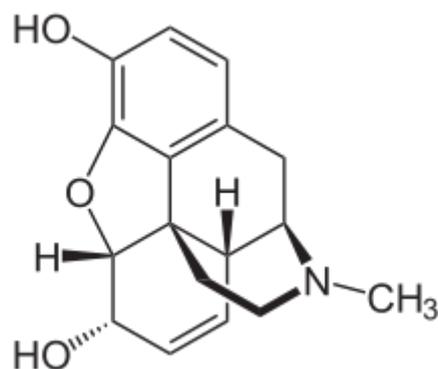


Figure 1. Chemical structure of Morphine (MOR)

The analysis of morphine in biological samples like the plasma, serum or urine specimens has been reportedly carried out through high performance liquid chromatography equipped with a UV detector (HPLC-UV) [10-13] or mass spectrometric detection (HPLC-MS) [14-16]. Also, morphine and its derivatives have been determined by gas chromatography–mass spectrometry (GC–MS) [17,18]. Other methods such as chemiluminescence [19,20], and voltammetric techniques [21,22] were used for analysis of morphine too.

The purpose of the present work has been evaluating the possibility of developing a novel selective electrochemical sensor for the determination of morphine in pharmaceutical formulations together with or without other separation methods. Such devices can offer advantages like low analysis costs, high precision, speed, wide response linearity ranges, portability, and ease of use, as reported in numerous other cases [23-28].

The ion-pair ionophore was prepared through reacting morphine hydrochloride and sodium tetraphenyl borate, and the evaluations showed that the constructed sensors reveal a behavior according to the ion-exchange mechanism.

Generally speaking, different ion selective electrodes (ISEs) are used as the indicator electrodes in potentiometric procedures. These range from PVC membrane electrodes (PME) and coated-wire electrodes (CWE) to carbon paste electrodes (CPE), all-solid-state electrodes (ASS) and field effective transistors (FET). Potentiometric indicator electrodes (PIEs) have been classified into two general classes of symmetrical and asymmetrical ion selective electrodes (SISEs and AISEs). SISEs are constructed by placing an ion selective membrane between an internal and an external analyte solution. In AISEs, on the other hand, the inner surface of the ion selective membrane is in contact with a solid state transducer, and only its outer surface is in contact with the sample solution [29-33]. Based on the structural constraints, the SISEs suffer two main weaknesses; i.e. the potential-time behavior of SISEs is rather considerable, and these devices require the application of an internal reference electrode and inner solution. Coated wire electrodes (CWEs), that are categorized as AISEs based on coating a carbonic or metallic conductor with an ion-selective membrane [29-33], suffer from potential drifts, due to the high charge-transfer resistance and low double-layer capacitance present between the solid state conductor and the membranes.

2. EXPERIMENTAL SECTION

2.1. Materials

Chemicals were of the highest purity available and they were used any further treatments. The high-molecular weight polyvinylchloride (PVC) (Fluka Co., USA), sodium tetraphenyl borate (NaTPB), dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), and tetrahydrofuran (THF) (Merck Co., Germany) were of analytical reagent grade purity. Morphine hydrochloride and its pharmaceutical formulation were the courtesy of a local pharmaceutical manufacturer (Tehran, Iran).

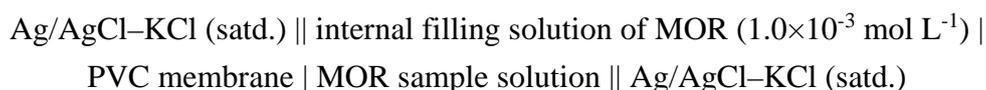
2.2. Synthesis of the Ion-pair complex

The ionophore used in the sensing elements of the SISEs and SISEs was an ion-pair complex of morphine hydrochloride (MOR) and sodium tetraphenyl borate (NaTPB). The ion-pair was prepared through admixing about 20 mL of a 0.01 mol L⁻¹ MOR solution an equivalent volume of NaTPB, and filtering the resulting precipitate. The MOR-TPB ion-pair

was then washed with distilled water, and dried under ambient conditions and stored for used in the construction of the sensors [23,24].

2.3. Devices

A glass cell equipped with an Ag/AgCl reference electrode (Azar electrode, Iran), and morphine sensors as the indicator electrodes was used for the measurements and the electrodes were externally in contact through a mili-voltmeter (± 0.1). The resulting cells based on the symmetric and asymmetric indicator electrodes could be illustrated as:



and



respectively. All measurements were carried out based on the calibration method using various standard solutions.

2.4. Preparation of the electrodes

2.4.1. PVC membrane sensors

The overall procedure for preparing the SISEs, i.e. the PVC membrane electrodes included admixing various amounts of the MOR-TPB ion-pair, with appropriate amounts of the other ingredients (i.e PVC, plasticizer and additive) in a small volume of tetrahydrofuran (THF). This mixture was then thoroughly mixed to reach a homogenous solution and was rested under room temperature so that some of its THF content was evaporated to yield an oily solution. Next a plastic tube (of around 3 mm in o.d.) was dipped into the resulting mixture for around 10 s. This way a 0.3 mm membrane was formed at the tip of the tube. The membranes were next rested under ambient temperature for about 5 hours to dry and then the tubes were filled with a 1.0×10^{-3} mol L⁻¹ of MOR solution to act as the inner filling solution. The outer surfaces of the membranes were also treated by soaking the electrodes in an identical solution for 15 hours, before the electrodes were ready for use [23-28].

2.4.2. Wire coated sensor

To construct the AISEs, similar mixtures were prepared and coated on a copper wire, by dipping the wire into the viscose mixtures for 5 s. The membrane coated wires were next rested in room temperature for about 10 hours and finally soaked in a 1.0×10^{-3} mol L⁻¹ MOR solution for two days before they were fit for use [29-30].

2.5. Preparing the standard MOR solutions

A 0.1 mol L⁻¹ MOR solution was prepared and used as the stock solution for preparing 1×10⁻⁸ to 1×10⁻² mol L⁻¹ MOR solutions through diluting proper amounts thereof with distilled water, to be used as the standard working solutions.

3. RESULTS AND DISCUSSION

The synthesized MOR-TPB ion-pair used in the preparation of the sensing elements of the PVC membrane and wire coated electrodes. The experiments revealed that the presence of the MOR-TPB played an important role in the responses of the SISEs and AISEs. Further the other ingredients of the membranes were found to leave particular effects in the electrode response. In this light, the type and weight percent of each component in the membrane composition were optimized, and the results were summarized in Tables 1 and 2.

3.1. The Optimal PVC Membrane Composition

It is ineluctable to state that the polymeric membrane is the major element of every membrane based ISE. Given that the previous experiments had proven PVC as an ideal choice for being used as the polymeric matrix, this polymer was used for this purpose. Also, since it has been experimentally established that membranes with plasticizer/PVC ratios of around 2.2 lead to best results [31-39], this ratio was used in all compositions. The weight percent of the PVC powder was kept at 30% in all compositions, for the sake of simplicity.

The plasticizer, on the other hand, is a low vapor-pressure water-immiscible liquid, which does not chemically react with the PVC matrix and bears no functional groups and is used to homogenize the membrane composition as well as increasing the diffusional mobility of the ion-pair through the membrane. The nature of these solvents greatly influences the selectivity of electrodes due to their grave effects on the ion-exchange mechanisms of the membranes [34-37]. The type of the plasticizer greatly influences the slope and linear range of the calibration curve as well as the selectivity of the electrodes.

In this study, three plasticizers with different dielectric constants (DCs) were, i.e. dibutyl phthalate (DBP, DC=6.4), nitrobenzene (NB, DC=35.7), and benzylacetate (BA, DC=5.7) were evaluated, and DBP was found to yield an effective linear range and a lower detection limit. This was attributed to the enhanced extraction of MOR ions, which is a hydrophobic ion, into the DBP plasticizer. In case of NB, the sensor did not any respond. Addition of more NaTPB as an ionic additive was also done but no improvement in the response of the membrane was seen. Table 1, on the other hand, shows that a membrane lacking of the MOR-TPB ion-pair produces a very poor responses (membrane no. 7). This can be held as proof that of the significance of the ion-pair in the response of the electrodes. The best Nernstian slope (i.e. 57.2±0.4 mV per decade) was observed with membrane no. 2 with a composition of 30% PVC, 5% ion-pair, and 65% DBP which was chosen as the optimum composition.

Table 1. Optimization of PVC membrane components of the sensor

Membrane no.	PVC (% wt.)	Plasticizer (% wt.)	Ion-pair (% wt.)	Slope* (mV decade ⁻¹)	Linear Range (mol L ⁻¹)	Detection Limit (mol L ⁻¹)	Response time
1	30	DBP, 66	3	43.6±0.5	1.0×10 ⁻⁴ - 1.0×10 ⁻²	9.0×10 ⁻⁵	50 s
2	30	DBP, 65	5	57.2±0.4	5.0×10 ⁻⁵ - 1.0×10 ⁻²	3.5×10 ⁻⁵	25 s
3	30	DBP,64	7	53.5±0.3	5.0×10 ⁻⁵ - 1.0×10 ⁻²	1.0×10 ⁻⁵	30 s
4	30	NB, 63	5	No response	-	-	-
5	30	BA, 63	5	42.1±0.4	1.0×10 ⁻⁴ - 1.0×10 ⁻²	1.0×10 ⁻⁴	32 s
6	30	DBP, 65	5 + 2% NaTPB	54.2±0.5	5.0×10 ⁻⁵ - 1.0×10 ⁻²	5.0×10 ⁻⁵	21 s
7	30	DBP, 70	-	3.7±0.7	1.0×10 ⁻⁴ - 5.0×10 ⁻³	-	3 min

*there results are based on 5 replicate measurements.

3.2. Wire coated Composition

The optimal wire coated electrodes (CWEs), were based on membranes containing 25% wt. of PVC, 5% wt. of MOR-TPB, 2%wt. of NaTPB and 68% wt. of DBP (no. 2) and used for further evaluations.

Table 2. Optimization of wire coated sensor ingredients

No.	Composition, % wt.				Slope* (mV decade ⁻¹)	Linear Range (mol L ⁻¹)
	PVC	Plasticizer	MOR-TPB	NaTPB		
1	25	DBP,70	5	--	32.7±0.7	5.0×10 ⁻⁶ -5.0×10 ⁻⁴
2	25	DBP,68	5	2	57.5±0.5	1.0×10 ⁻⁷ -1.0×10 ⁻⁴
3	25	DBP,69	5	1	52.6±0.5	5.0×10 ⁻⁷ -1.0×10 ⁻⁴

*the results are based on 5 replicate measurements.

3.3. Characterization of the sensors

The calibration curve of the optimal SISEs is shown in Fig. 2, which reveals that the sensor has a linear response behavior in the range of 5.0×10⁻⁵-1.0×10⁻² mol L⁻¹. The detection limit of the device was estimated through the extrapolation of the two linear segments of the calibration

graph and was found to be around $3.5 \times 10^{-5} \text{ mol L}^{-1}$. The slope of the calibration curve was also evaluated at $57.2 \pm 0.4 \text{ mV}$ per decade of the MOR concentration for 5 replicate measurements.

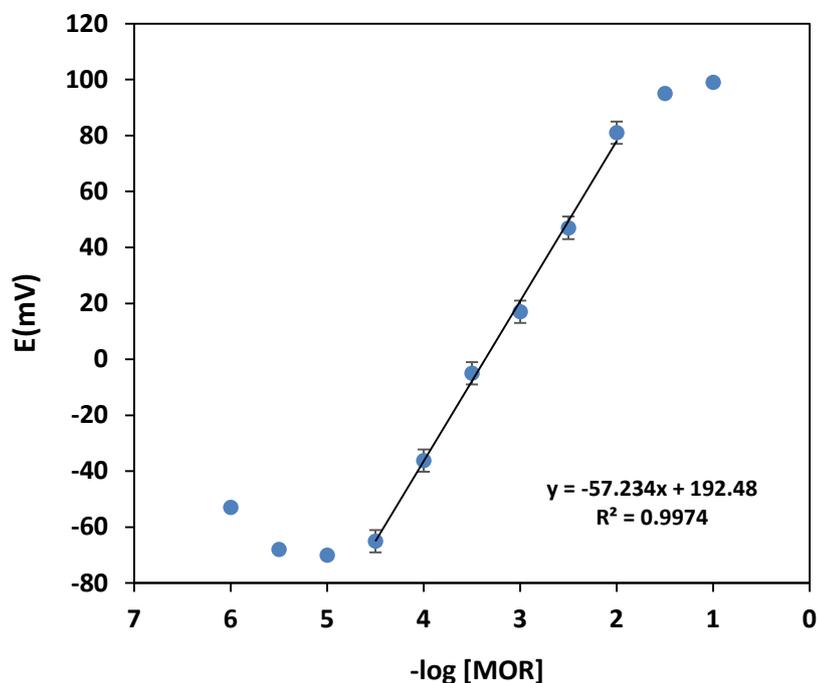


Figure 2. Calibration curves of MOR-HCl PVC membrane electrode (no. 2). The results are based on 5 replicate measurements.

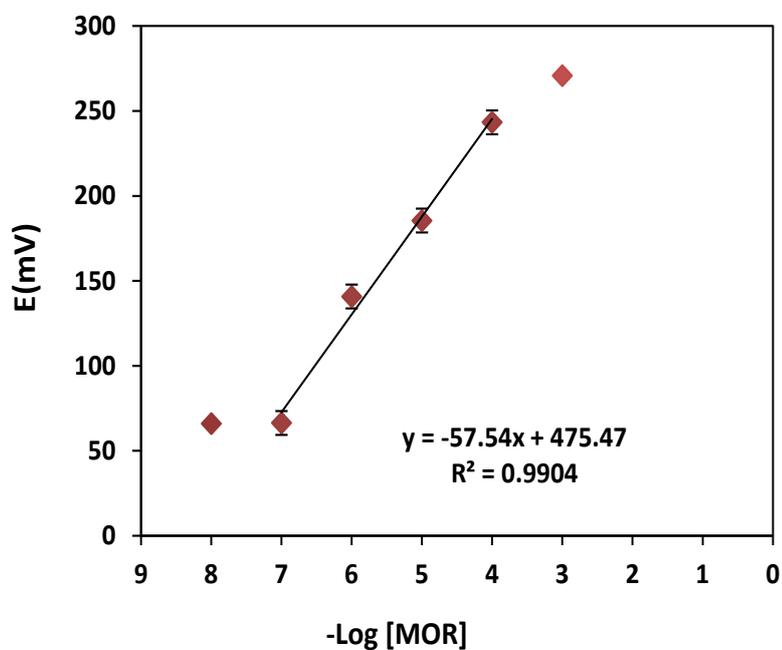


Figure 3. Calibration curves of MOR-HCl wire coated electrode (no. 2). The results are based on 5 replicate measurements.

In the case of the wire coated sensors (i.e. the AISEs) the calibration curve shown in Fig. 3, indicates a linear response range from 1.0×10^{-7} to 1.0×10^{-4} mol L⁻¹ and a detection limit as low as 1.0×10^{-7} mol L⁻¹. The slope of the calibration curve was in about 57.5 mV per decade of the MOR concentration with a standard deviation of ± 0.5 mV for 5 replicate measurements.

The dynamic response of the sensor, which is defined as the time required for reaching response values within ± 1 mV of the corresponding equilibrium potential after a 10-fold increase in the concentration of the analyte solution was evaluated through the successive immersions of the sensors in different sample solutions and making potential readings until reaching the equilibrium response [39-43]. In this case MOR solutions in the range of 1.0×10^{-4} to 1.0×10^{-2} mol L⁻¹ and 1.0×10^{-7} to 1.0×10^{-4} mol L⁻¹ were used in the experiments by SISE and AISE, respectively. The results revealed that the SISEs reached their equilibrium response values after about 25 s throughout the tested concentration range and in case of AISE was 13 s.

The life time of the sensors was also estimated by monitoring the slope of the calibration curve and detection limits of devices which were used for 1 hour/day for 10 weeks. It was observed that after 4 weeks of use of SISE and 5 weeks of AISE, the slopes slightly decreased while the detection limits increased, which can be attributed to the leakage of the membrane ingredients from the organic layer.

3.5. The pH Effect

The effect of pH on the responses of the SISEs and AISES is illustrated in Figure 4. To perform this study the electrode potentials were measured at a fixed MH solution concentration (1.0×10^{-4} mol L⁻¹) while varying the pH from 1.0 to 9.0 using concentrated NaOH or HCl solutions to avoid considerable volume and concentration changes. It was found that the potential is pH-independent in the range of 3.0 to 6.0, which can be translated to the fact that pH changes do not influence the response of the sensors in this range.

The changes in the response of the sensors at pH values over 6.0 could be due attributed to the elimination of positively charged MOR molecules, while the fluctuations below pH=3.0 were considered as the result of the enhanced leakage of the membrane ingredients or the analyte into the solution.

3.6. Selectivity

The selectivity of the sensor response, which illustrates its preference toward the target ion as opposed to other "interfering ions", can be regarded as the most prominent characteristic any ISE. Consequently the potentiometric selectivity coefficients of the MOR SISEs and AISEs were evaluated through the matched potential method (MPM) [40-45]. MPM suggests adding a specified concentration of the target ion (A) to a reference solution

and measuring the potential. In another experiment, the interfering ions (B) are successively added to an identical reference solution, until the potential response of the sensor reaches that obtained in the first experiment. Finally, the MPM selectivity coefficient is calculated finding the ratio of the concentrations of the primary and interfering ions. The MPM values obtained in this case are summarized in Table 3, indicating that the interference caused by all tested species is negligible with both the SISE and AISEs.

Table 3. Selectivity coefficients of various interfering compounds for Morphine hydrochloride sensors

Interfering ion	Log K_{MPM} (SISE)	Log K_{MPM} (AISE)
Na ⁺	-3.4	-3.5
K ⁺	-3.1	-3.1
NH ₄ ⁺	-2.8	-2.9
Ca ²⁺	-3.5	-3.7
Mg ²⁺	-3.9	-4.0
Lactose	-4.1	-4.3
Glucose	-4.0	-4.0

3.6. Analysis of Morphine in pharmaceutical formulations

The proposed SISEs and AISEs were used in the analysis of the morphine content of 10 mg/mL of injections using calibration method with direct potentiometry (Table 4) and the results were found to be in good agreement with the labeled values.

Table 4. Potentiometric determination of Morphine in pharmaceutical formulations

Sample	Found by SISE*	Found by AISE*
Sample 1	10.17±1.27 mg/mL	10.09±1.44 mg/mL
Sample 2	10.21±1.63 mg/mL	9.72±1.50 mg/mL
Sample 3	9.84±1.22 mg/mL	10.11±2.13 mg/mL

* The results are based on 3 replicate measurements.

3.7. Evaluation of precision, accuracy, and ruggedness/robustness

In further studies 3 standard samples were prepared and subjected to analysis to evaluate the repeatability of the tests and the RSD values were found to be 3.3, 3.7, and 3.4% for the SISEs and 3.2, 3.1, and 3.6% for the AISEs.

To evaluate the ruggedness of the devices the intra- and inter-day assay results for MOR samples were obtained using two analysts and the RSD values of the intra- and inter-day assays performed in the same laboratory were found not to exceed 4.3%. Further the robustness of the devices was examined while solution pH and laboratory temperature changed slightly. The studies showed that morphine hydrochloride recovery values were good under most of the experimental conditions, and no significant changes were observed upon modifying the critical parameters.

4. Conclusion

In this work two types of symmetric and asymmetric ISEs for Morphine hydrochloride were constructed and evaluated. The devices showed excellent performances and short response times. The SISEs had a lower detection limit of 3.5×10^{-5} mol L⁻¹, while that of the AISEs was estimated at 7.0×10^{-7} mol L⁻¹ and the respective potential response of the two electrodes was found to be linear in the two ranges of 5.0×10^{-5} - 1.0×10^{-2} mol L⁻¹ and 1.0×10^{-7} - 1.0×10^{-4} mol L⁻¹. Using the devices MOR could be determined in pharmaceutical formulations and both the SISEs and AISEs work based on the ion-exchange mechanism. The best performance was achieved at a membrane composition of 30% wt. of PVC, 65% wt. of DBP and 5% wt. of the MOR-TPB for the SISEs and 25% wt. of PVC, 5% wt. of Ion-pair, 2% wt. of the additive and 68% of the plasticizer in the case of the AISEs.

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