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An Ionic Liquid Based Sensor for Diclofenac Determination in Water

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An ionic liquid-based sensor for diclofenac determination in water

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ABSTRACT

This paper details a miniaturised, solid state ion-selective electrode selective for diclofenac. The sensor comprises a novel ionic liquid electroactive material – an imidazolium–diclofenac ion associate. The ion associate is present in a plasticised PVC membrane on planar carbon electrodes, with an intermediate poly (3,4-ethylenedioxythiophene) layer. The sensitivity and selectivity of the sensor were determined using chronopotentiometric methods. In response to diclofenac, a slope of −53.3 ± 3.6 mV/dec was observed. A limit of detection of 2.90 × 10^{-3} g L^{-1} is reported, with a linear range of 3.18 × 10^{-3} g L^{-1} to 3.18 g L^{-1}. The sensors show good selectivity towards diclofenac against pertinent interferent molecules, with a response time of <15 s.

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Sensor; potentiometric; diclofenac; ISE; environmental; ionic liquid

1. Introduction

Diclofenac is an analgesic with both human and veterinary applications. It has been described as an emerging contaminant [1,2] due to its activity as an endocrine disruptor – even at low environmental concentrations, it affects the endocrine system of biological species. It has been banned for veterinary use in India due to links with declining vulture populations across the Indian subcontinent [3,4]. As such, improved analytical methods for its determination are essential for continuous environmental monitoring.

Where diclofenac has a carboxylate group in its structure, it is supplied and administered as its sodium salt. This enables a higher degree of ionisation, and thus dissociation, at biological pH. The ionic nature of the drug makes it ideal for quantification by ion-selective electrode (ISE).

ISEs are frequently used for environmental analysis, most commonly for pH, fluoride and nitrate. This type of electrode is selective for a target ion, ideally with minimal interference from others, and works by transducing analyte activity into electrical potential. They are typically used for quantitative analysis. Previously, we have developed ISEs for environmental ions nitrate and mercury [5,6].

Traditionally, ISEs are made of glass or plastic and contain an inner filling solution, with a selective membrane separating it from the sample solution. It is across this

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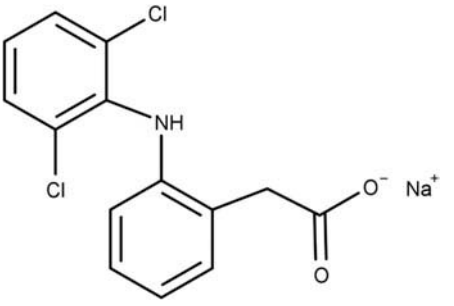

AQ10 **Figure 1.** Diclofenac sodium.

membrane that a potential is created, correlating to analyte activity in the sample. More recently, all solid state ISEs have been developed, which require no filling solution and as such are more robust. Solid state sensors are also compact – they can be any size as determined by the electrode area, making them ideal for field analysis applications [7–9].

Diclofenac-selective sensors have been investigated in the past, most commonly employing the traditional 'wet' ISE format. Kormosh et al. have developed ion associates of diclofenac and base dyes for use as sensing material in this classical sensor format [10–12]. A solid state, diclofenac-selective ISE is proposed in this paper. This type of ISE has been reported by several authors, such as polypyrrole- [13] and porphyrin-based [14] electrodes.

A novel associate of diclofenac with an imidazolium moiety, [bpim][dfc] (Figure 2), is proposed to act as diclofenac-selective material and ion exchanger in a solid contact carbon-based ISE. The associate is a room temperature ionic liquid – a salt which is molten at room temperature. Ionic liquids are conductive and have many applications, including as electrolytic solution [15] in batteries and solvents. They have been shown as effective electroactive materials in sensors [16–18].

The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) is applied as an intermediate layer, between membrane and carbon ink, acting as ion-to-electron transducer and negating the requirement for filling solution [19].

2. Experimental

2.1. *Materials and apparatus*

All materials procured from Sigma-Aldrich Ireland and used without further purification. A Lawson EMF-16 was used as potentiometer, with an Orion 900200 double junction

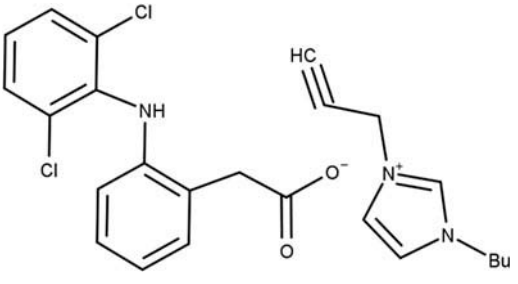

Figure 2. [bpim][dfc] structure.

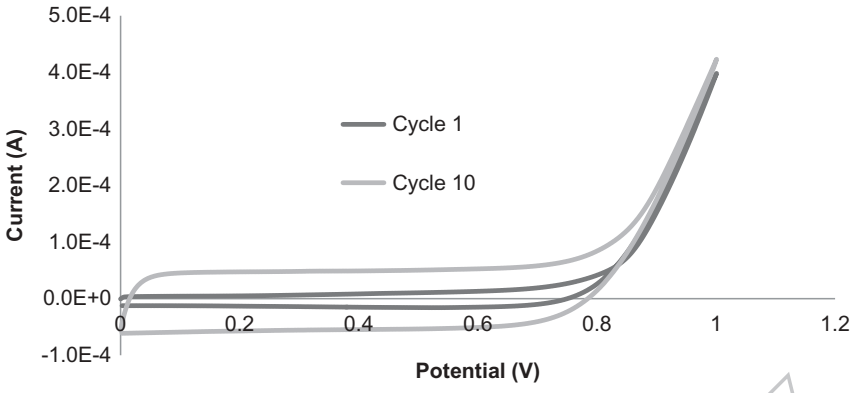

Figure 3. Cyclic voltammograms depicting PEDOT electropolymerisation. The rising current with cycle number indicates formation of the electroactive layer on the electrode surface.

reference electrode. An Autolab PGSTAT12 potentiostat was used for cyclic voltammetry. ERCON E31078 as carbon ink and Electrodag 452SS as dielectric ink were used to fabricate screen-printed carbon electrodes, using a DEK 248 semi-automatic screen printer to print carbon 'lollipop' tracks. Ultrapure Milli-Q water (14.0 MΩ cm^{-1}) was used for all experiments and solutions. A Bruker Avance 400MHz NMR was used to obtain spectra.

2.2. *Preparation of [bpim][dfc]*

Butyl imidazole (3.7255 g, 30 mmol) was chilled on ice for 5 min. Propargyl bromide solution (3.9450 cm^3, 35 mmol) was added dropwise under nitrogen and stirred for 10 min.

The mixture was brought to 70°C and stirred for 10 min, then stirred at room temperature for 14 h under nitrogen. The resulting amber, viscous fluid was dried by rotary evaporation to yield the ionic liquid 1-butyl-3-propargyl imidazolium bromide (6.1920 g, 86% yield). ^{1}H-NMR: δ/ppm (400 MHz, d-DMSO) = 9.55 (s, 1H), 7.98 (t, 1H, J = 1.8), 7.89 (t, 1H, J = 1.8), 5.32 (d, 2H, J = 2.6), 4.26 (t, 2H, J = 7.2), 3.86 (t, 1H, J = 2.6), 1.75 (m, 2H), 1.22 (m, 2H), 0.84 (m, 3H). ^{13}C-NMR: δ/ppm (400 MHz, d-DMSO) = 136.0, 122.8, 122.2, 78.9, 75.9, 48.7, 38.6, 31.4, 18.7, 13.2.

Aqueous solution of diclofenac sodium (10 mmol in 65.0 cm^3) was added dropwise to a solution of aqueous 1-butyl-3-propargyl imidazolium bromide (3 mmol in 6.0 cm^3) and stirred for 4 h. This was extracted with diethyl ether/ethyl acetate and dried under vacuum. The resulting brown oil was oven dried at 80°C for 4 h. The complex (520 mg) was dark brown in colour, with a sticky, tar-like consistency and 37% yield.

^{1}H-NMR (400 MHz, d-DMSO) δ/ppm: 9.91 (s, 1H), 9.78 (s, 1H), 7.70 (dt, 2H, J = 5.8, 1.8), 7.38 (d, 2H, J = 8.0), 7.18 (d, 1H, J = 7.4), 7.04 (t, 1H, J = 8.1), 6.96 (t, 1H, J = 7.6), 6.76 (t, 1H, J = 7.4), 6.39 (d, 1H, J = 7.9), 5.33 (d, 2H, J = 2.6), 4.23 (t, 2H, J = 4.2), 3.60 (s, 2H), 3.32 (t, 1H, J = 2.6), 1.77 (m, 2H), 1.21 (m, 2H), 0.84 (t, 3H, J = 7.6). ^{13}C-NMR: 178.2, 143.2, 138.4, 129.5, 128.8, 127.0, 126.3, 123.1, 122.6, 122.0, 121.3, 120.9, 120.6, 116.7, 98.1, 90.2, 74.8, 49.7, 43.4, 39.1, 31.9, 31.0, 19.4, 13.4.

2.3. *Preparation of electrodes*

2.3.1. *PEDOT coating*

To a potentiostat, two electrodes were connected in tandem, with a saturated calomel reference electrode and graphite auxiliary electrode. The electrodes were immersed in a mixed solution of EDOT (0.01 M) and KNO_3 (0.1 M), with stirring. At 50 mV s^{-1} scan rate, the cell was cycled from 0 to 1.2 V, for a total of 20 scans.

2.3.2. *Membrane formulation*

AQ4 [bpim][dfc] (6.4 mg), PVC (125 mg) and NPOE (250 mg) were dissolved in THF (~2 cm^3), until a homogenous, viscous mixture was obtained. This was dropcasted in µL quantities onto PEDOT-coated electrodes.

2.4. *Electrode function*

The electrodes were conditioned in diclofenac solution (10^{-4} M) for 1.5 h, then water for 30 min, prior to testing. Potentiometric titration with diclofenac sodium was carried out, and selectivity was determined using the separate solutions method (SSM). Potentiometric response to chloride, fluoride, sulphate, bromide, acetate, nitrate, salicylate, ibuprofen and aspirin was examined. The electrodes were also alternated between 3.18 and 3.18 × 10^{-2} g L^{-1} diclofenac solutions to determine signal reversibility.

A standard addition method was employed for sample evaluation, where aliquots of diclofenac sodium standard were added to sample solutions.

3. Results and discussion

3.1. *Membrane composition*

The structure of the ion associate was verified by ^{1}H- and ^{13}C-NMR. Deviation in chemical shift relative to starting materials is indicative of associate formation, and peak integrations are evidential of a 1:1 complex. The complex is dark brown in colour, with a thick gel-like consistency. It is sparingly soluble in water and soluble in tetrahydrofuran and ethyl acetate. The relative insolubility of the complex in water is ideal for analysis in aqueous matrices (i.e. environmental and biological samples), as the integrity of the membrane is most likely to remain intact. Four identical electrodes were tested regularly over a 2-month period with no evidence of electrode deterioration (or leaching) observed. The [bpim][dfc] complex acts as ion exchanger in the membrane, negating the requirement for an additional ion exchanger – a fundamental component of many ISEs that can be costly. This means a simpler electrode configuration.

NPOE was chosen for formulation to decrease resistance and lipophilicity of the PVC membrane. As diclofenac is similarly lipophilic, migration of the analyte to the membrane is further promoted, with suppression of interferent signals from hydrophilic anions.

3.2. *Response to diclofenac*

The sensors (n = 4) exhibit a linear response to diclofenac, at concentrations above log a ≥−5 (Figure 4). The slope of the calibration curve is sufficiently Nernstian, at

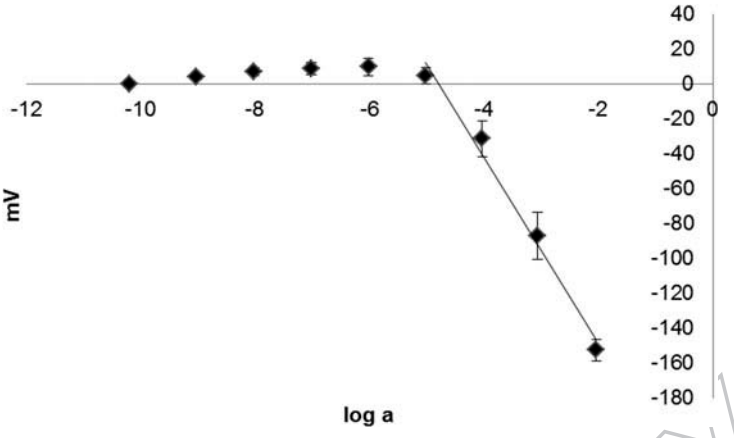

Figure 4. Sensor response to diclofenac (n = 4 separate electrodes).

−53.3 ± 3.6 mV/dec, with a linear range of 3.18 × 10^{-3} g L^{-1} to 3.18 g L^{-1}. An limit of detection (LOD) of 2.90 × 10^{-3} g L^{-1} is reported.

3.3 *Selectivity*

Selectivity testing was also carried out via titration with common anions in the Hofmeister series of lipophilicity. This is a measure of how well the electrodes perform in the presence of interferent ions, as in a real sample matrix. Figure 5 also demonstrates that in addition to providing ion exchange functionality, the IL used induces selectivity for diclofenac obviating the need for an additional ionophore, normally present in ISE membranes. This represents a further simplification of the ISE construct [20–22].

The SSM was used to determine the selectivity coefficient, $K_{i,j}^{pot}$, following IUPAC recommended methods [23] (Equation 1), where i = diclofenac, and j = interfering ion.

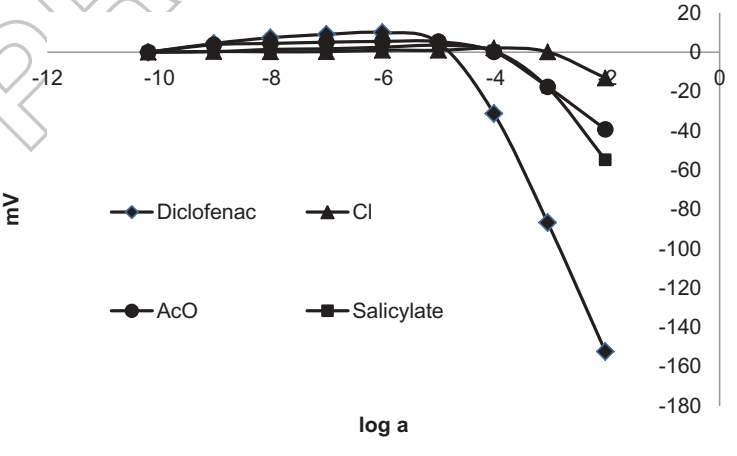

Figure 5. Response of sensors (n = 4) to diclofenac and some interferent anions. Some tested anions have been omitted for clarity (refer to Table 1).

$$K_{i,j}^{pot} = \exp\left\{\frac{E_j - E_i}{RT} z_1 F\right\} \quad (1)$$

$K_{i,j}^{pot}$ is presented as its logarithm for accessibility (Table 1). The negative values indicate the sensor's preferential detection of diclofenac over the interferent anions tested. The order of selectivity shows slight deviation from the Hofmeister (lyotropic) series of ions [24], where the response sequence is $F^- = SO_4^{2-} < AcO^- < Cl^- < NO_3^-$. Diclofenac is expected to occur after nitrate in the series. The sensors are shown to be least selective to chloride, a prominent anion in both environmental and biological systems. Selectivity for diclofenac over other small organic molecules with carboxylate functionality, represented by acetate and salicylate, is also practically relevant, along with the analgesics ibuprofen and aspirin (Table 1). The sensors exhibit a negligible response to ascorbic acid.

A summary of electrode data is presented (Table 2) in comparison with published diclofenac-selective electrochemical sensors. The proposed sensors compare well to existing potentiometric sensors in terms of linear range and lower detection limits, with good selectivity observed. It should be noted that selectivity coefficients are not calculable for voltammetric methods. By nature, voltammetric studies exhibit low detection limits and linear ranges, where potentiometric sensors tend to utilise a simpler format and are more appropriate for longer term monitoring applications.

3.4. *Reversibility study*

It is essential that a sensor can quickly detect changes in diclofenac concentration, with consistent values. Reversibility studies were carried out by shifting between different diclofenac concentrations and recording the signal.

Table 1. Selectivity coefficients for interferent molecules.

Interferent molecules	log $K_{i,j}^{pot}$
Cl^-	−3.85
NO_3^-	−3.45
SO_4^{2-}	−3.46
F^-	−3.54
AcO^-	−2.97
Salicylate	−2.46
Br^-	−3.95
Paracetamol	−1.99
Aspirin	−2.51
Ibuprofen	−2.04

Table 2. Comparison with literature values.

Method	Limit of detection (LOD) (g L^{-1})	Linear range (g L^{-1})	Slope (mV/dec)	log$K_{dfc,Cl}^{pot}$	Reference
Ion-selective electrode (potentiometric)	6.36×10^{-2}	9.86×10^{-2} to 3.49	48.2 ± 1.7	< −2	[13]
	3.20×10^{-3}	0.16 to 15.91	38.0 ± 1.2	−5	[11]
	10.20×10^{-3}	1.59×10^{-2} to 3.18	58.1 ± 0.8	+0.36	[25]
	2.90×10^{-3}	3.20×10^{-3} to 3.18	−53.3 ± 3.6	−3.85	This paper
Differential pulse voltammetry	6.0×10^{-5}	1.60×10^{-4} to 9.50×10^{-2}	-	-	[26]
	1.27×10^{-5}	5.70×10^{-5} to 37.85×10^{-4}	-	-	[27]
Square wave voltammetry	1.97×10^{-6}	3.18×10^{-6} to 3.20×10^{-4}	-	-	[28]
HPLC	7.27×10^{-5}	1.24×10^{-4} to 6.0×10^{-4}	-	-	[29]

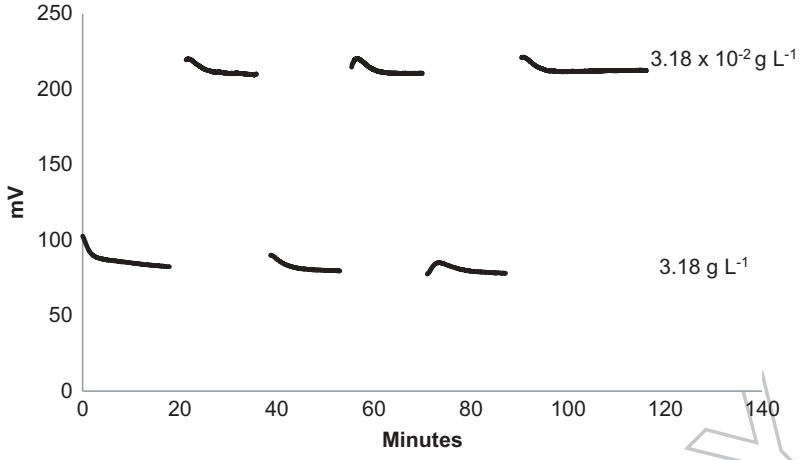

Figure 6. Typical sensor response with changing diclofenac concentration.

Table 3. Reversibility of signal response (n = 4).

Concentration (g L^{-1})	Response (mV)	% RSD
3.18	83.0 ± 2.9	3.45
3.18 × 10^{-2}	212.7 ± 0.3	0.14

The sensors were switched between two diclofenac solutions (3.18 and 3.18 × 10^{-2} g L^{-1}; Figure 6). The sensors exhibit excellent signal reversibility between different concentrations of diclofenac (Table 3), with a < 15 s response time.

For alternate concentrations of 3.18 and 3.18 × 10^{-2} g L^{-1} diclofenac, relative standard deviations (RSD) of <5% were observed, indicating precise measurements. This suggests that diclofenac ions are not immobilised permanently in the membrane, even at relatively high concentrations, and exchange with sample solutions occurs on a practical timescale. The high degree of precision demonstrates the sensors' functionality over a wide range of concentrations.

3.5. *Real sample assay*

The sensors were used to determine diclofenac in both a topical pharmaceutical gel and spiked spring water (Table 4) to assess electrode function in both pharmaceutical and environmental sample matrices. A standard addition method was employed to negate matrix effects in samples. Good accuracy, indicative of selectivity, and inter-electrode precision were observed compared to those in literature. The favourable selectivity demonstrated in the samples is in accordance with calculated selectivity coefficients (Table 1).

Table 4. Diclofenac determination in samples (RSD <3.5% for n = 4).

Sample	Nominal content	Content determined by electrode	Recovery (%)	Reference
Diclac® gel	1% w/w	0.99 ± 0.02% w/w	99.0	This paper
Spring water	6.4 × 10^{-2} g L^{-1} (spike)	6.21 × 10^{-2} ± 2.40 × 10^{-3} g L^{-1}	97.0	
Dicloran® tablet	100 mg/tablet	101.20 ± 1.60 mg	101.2	[11]
Tablet sample	6.4 × 10^{-3} g L^{-1}	6.56 × 10^{-3} ± 2.55 × 10^{-4} g L^{-1}	103.0	[26]

4. Conclusions

This paper presents a novel, solid state membrane sensor for use in diclofenac determination. The sensors are compact and can be produced at a low cost. Given the favourable selectivity and good reversibility, both environmental and pharmaceutical applications are envisaged for the sensor.

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Disclosure statement

AQ7 No potential conflict of interest was reported by the authors.

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