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Fabrication and Evaluation of Selective Membrane Electrodes for the Potentiometric Determination of Diclofenac Sodium in Pure and Pharmaceutical Forms

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Annotation: This study presents a potentiometric method for determining diclofenac sodium (DIC) through the development of selective membrane electrodes. These electrodes were fabricated using a diclofenac–phosphotungstic acid (PTA) ion-pair complex as the active material, tributyl phthalate (TBPH) as the plasticizer, and polyvinyl chloride (PVC) as the polymer matrix. The fabricated DIC–PTA–TBPH electrode exhibited a near-Nernstian slope of 58.6 mV/decade over a pH range of 3 to 4. It showed a linear response within the concentration range of 1×10^{-5} to 1×10^{-1} M, with a detection limit of 0.02918 M, a response time of 5–35 seconds, and a lifespan of approximately 40 days. The electrode demostratet excellent selectivity for diclofenac ions in the presence of various mono- and divalent interfering ions, with all selectivity coefficient values (K_pot) below 1. The method was successfully applied to the analysis of diclofenac sodium in pharmaceutical tablets, yielded recovery percentages ranging from 90% to 103.5%, comparable to results obtained by HPLC.

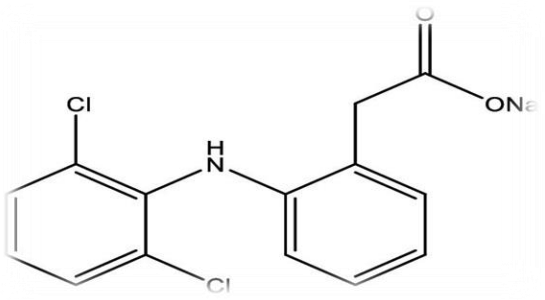
1. Introduction

Ion-selective electrodes (ISEs) are considered one of the most important modern electroanalytical techniques, characterized by the requirement that the current passing through

them must be zero [1]. They were first discovered by the researcher Wilhmost Ostwald in 1890 and operate based on the movement of ions in an electrolytic solution[2]. These electrodes utilize the same principle as semipermeable membranes, measuring the potential across a membrane where ion separation occurs between two solutions of differing concentrations of the target ion, The resulting potential change is then measured using the ion-selective electrode connected to a reference electrode with a stable potential [3].At the beginning of the 1900s, the glass electrode was developed, which has been used since then—and continues to be used today—for measuring pH (the acidity of solutions) by detecting the potential of hydrogen ions across a sensitive membrane within the glass electrode [4]. Subsequently, efforts were made to improve electrode sensitivity to specific ions[5].In 1960, Roksing and Pungor through the developmented of solid-state sensors using single crystal structures[6]. A prime example is the fluoride-selective electrode, which is based on homogeneous solid membranes [7].Since then, ion-selective electrodes have gained increasing importance in the direct determination of ions across a wide range of fields, including chemistry, environmental science, medicine, and physics.In 1966, the introduction of macrocyclic compounds as ionophores significantly improved electrode selectivity and sensitivity[8]. Compared to spectroscopic methods, ISEs offer several advantages: they are rapid, possess a wide linear response range, are unaffected by sample color, are simple to fabricate and operate, and are cost-effective.

Diclofenac sodium, chemically named (2-(2,6-dichlorophenylamino)phenyl)acetic acid, is a widely used non-steroidal anti-inflammatory drug (NSAID) with analgesic and antipyretic properties[9]. Since its approval in 1974, it has been effective in treating rheumatic and inflammatory conditions[10]. It is typically administered as sodium or potassium salts. Although generally safe within therapeutic doses (50–150 mg)[11], excessive use can lead to adverse effects such as aplastic anemia, gastrointestinal disturbances, and renal dysfunction[12].

Due to its extensive usage and poor biodegradability, diclofenac sodium has been identified as a potential environmental pollutant[13]. Its molecular formula is $C_{14}H_{10}Cl_2NNaO_2$ and chemical formula is.



Several analytical techniques have been employed to quantify diclofenac, including spectrophotometry[14-15-16-17-18], electrochemical analysis[19-20-21-22-23], and chromatographic methods[24-25-26-27-28].

2. Materials and Methods

2.1 Instruments

Jenway 3310 pH meter (UK), saturated calomel electrode (Switzerland), Precisa XB 220A analytical balance (Switzerland), ultrasonic bath and drying oven (KARL KOLB, Germany), and magnetic stirrer hot plate (Jenway, Germany).

2.2 Chemicals

All chemicals were of analytical grade and were supplied by FLUKA and BDH.

2.3 Preparation of Solutions

Diclofenac sodium (0.1 M): 3.1915 g dissolved in deionized water, diluted to 100 mL.

Phosphotungstic acid (PTA, 0.1 M): 28.802 g dissolved and diluted to 100 mL.

2.4 Preparation of Pharmaceutical Sample

Ten tablets (50 mg each) were weighed, crushed, and a portion equivalent to 12.306 g was transferred to a 100 mL volumetric flask. After shaking with 10 mL distilled water for 10 minutes, the volume was completed to the mark. Dilutions from 10^{-1} M to 10^{-3} M were prepared.

2.5 Preparation of Ion-Pair Complex

30 mL of 0.1 M DIC solution was mixed with 10 mL of 0.1 M PTA. The greenish-blue precipitate was filtered, washed with deionized water, and dried at room temperature.

2.6 Membrane Fabrication

0.1 g of the complex was mixed with 0.45 g PVC and 0.46 g TBPH in 10 mL butanone and 20 mL THF. The solution was poured into a petri dish and left at room temperature for 2 days to form a ~0.3 mm membrane.

2.7 Electrode Assembly

A PVC tube (3–4 cm) was polished. A membrane disc was glued to one end using PVC–THF adhesive, and excess membrane was trimmed.

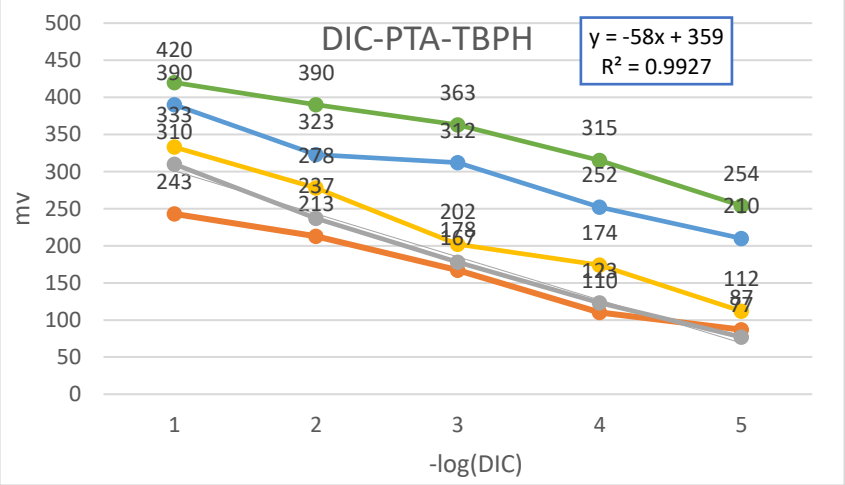
3. Results and Discussion

3.1 Electrode Construction

The DIC–PTA–TBPH ion-selective membrane electrode was fabricated using diclofenac-phosphotungstic acid complex as the active material, PVC as a matrix, and TBPH as a plasticizer. Prior to measurements, the electrodes were conditioned in 0.1 M DIC solution for two hours.

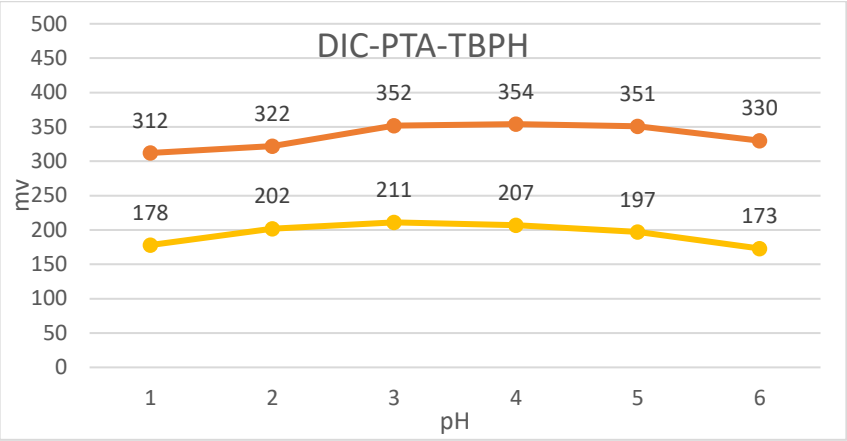
3.2 Effect of Internal Filling Solution

Different internal solutions (10^{-5} to 10^{-1} M) were tested. The best response was observed at 10^{-2} M, which produced a stable near-Nernstian slope. Lower concentrations provided poor linearity.



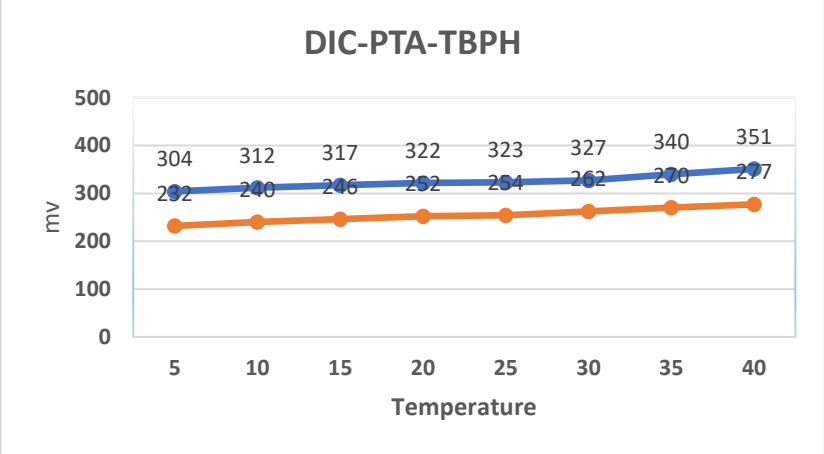
3.3 Effect of pH

The electrode response was investigated in the pH range 1.0–7.0 using DIC solutions at 10^{-1} and 10^{-3} M. Optimal performance was observed between pH 3–4. At higher pH, alkaline error and precipitation affected the potential readings.



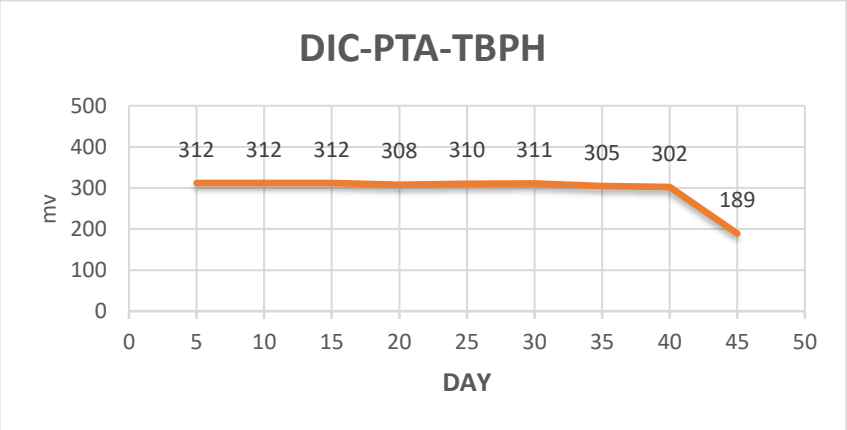
3.4 Effect of Temperature

Potential readings were recorded at different temperatures. Optimal electrode performance was noted between 20–30 °C. Above 50 °C, potential increased due to enhanced diffusion and membrane swelling.



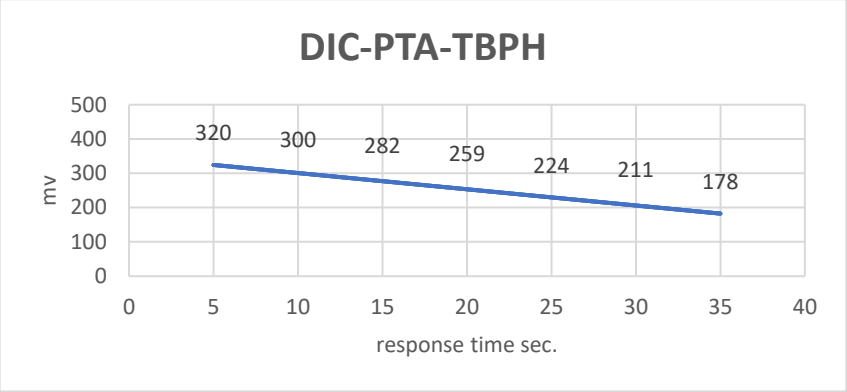
3.5 Electrode Lifetime

The electrode maintained a stable response for 40 days before signal drift occurred, attributed to leaching of the active components.



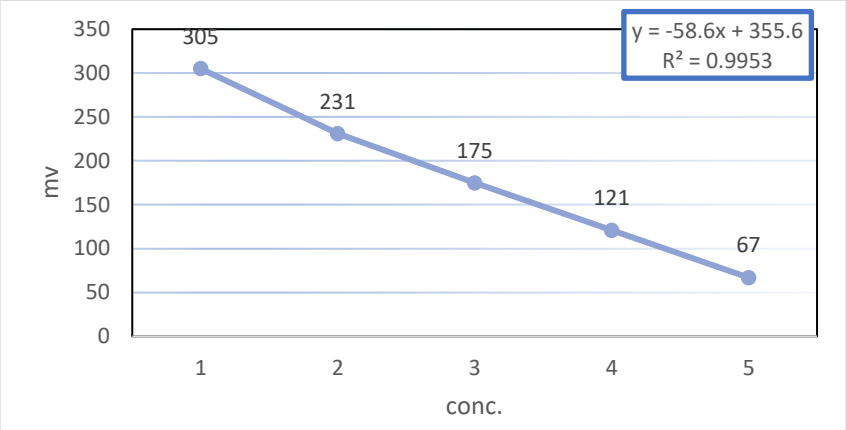
3.6 Response Time

The response time, recorded under optimized conditions ranged from 5 to 35 seconds for concentrations between 10^{-5} and 10^{-1} M.



3.7 Calibration Curve

A linear response was observed over the concentration range 10^{-5} to 10^{-1} M with a slope of 58.6 mV/decade and correlation coefficient of 0.9953.



3.8 Accuracy and Precision

Recovery values ranged between 98.3% and 100%, indicating high analytical accuracy.

LOD	Recovery %	Calc. response	Std. .Dev	Response (mv)	Drug .conc	Electrode type
0.02918	100	4.009	0.57	121	10^{-4}	DIC-PTA-TBPH-
	98.3	4.919	0.57	67	10^{-5}	

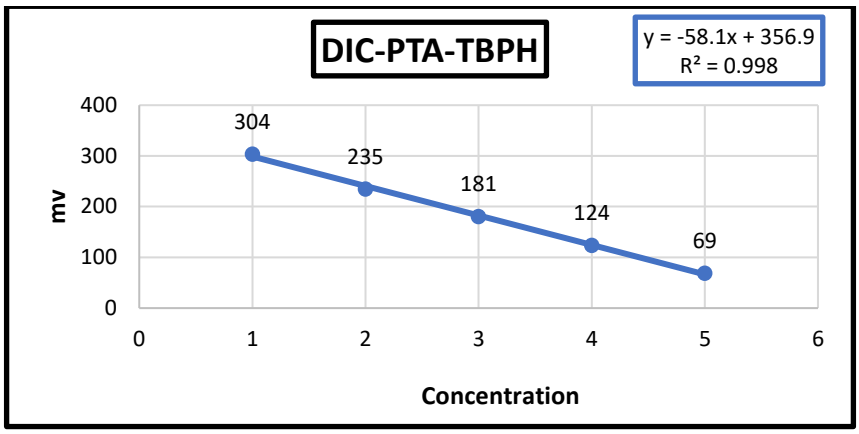
3.9 Selectivity Measurements

Selectivity coefficients (K_pot) for interfering ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, and Ba^{2+} were all <1, indicating excellent selectivity.

Interfering ion 10^{-3}	Interfering ion 10^{-2}	Interfering ion 10^{-1}	Interfering ion
-0.1234	-0.285	-0.0255	Na^{+1}
-0.1258	0.1083	-0.0278	K^{+1}
-0.2597	-0.0462	0.0214	Ca^{+2}
-0.2573	-0.0657	-0.0081	Mg^{+2}
-0.1885	-0.0657	-0.0081	Ba^{+2}

3.10 Practical Applications

The electrode was applied to the analysis of diclofenac in pharmaceutical tablets.



HPLC Recovery %	Recovery %	Calc. response	Std. .Dev	response (mv)	Drug .conc	Electrode type
90	**90**	**0.9**	**0.57**	**304.6**	**10^{-1}**	**DIC-PTA-TBPH**
99	**103.5**	**2.07**	**0.57**	**236.3**	**10^{-2}**	
100	**100.5**	**3.02**	**0.57**	**181.3**	**10^{-3}**	

Recovery values ranged from 90% to 103.5%, which were comparable to HPLC results.

4. Conclusion

The developed DIC–PTA–TBPH membrane electrode exhibited excellent selectivity, sensitivity, and stability for the potentiometric determination of diclofenac sodium in pharmaceutical preparations. Its performance is comparable to that of HPLC, making it a reliable and cost-effective tool for routine analysis in pharmaceutical laboratories.

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