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İyon Seçici Elektrotlar için Yeni Bir Tip İyonofor Olarak Bor ve Sodyumun Bir Psödokriptand Tarafından Bağlanması

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ÖZET

İki saligenin biriminin bor koordinasyon bölgeleri olarak görev yaptığı, 15 üyeli diazatrioxa makrosiklik bir çekirdek içeren yeni ve seçici bir moleküler reseptör olan borokryptat sentezlenmiş ve karakterize edilmiştir. Bu reseptör, ortam havasında yüksek kararlılık göstermekte ve inert bir atmosfer gerektirmeden polinükleer Na-borokriptat kompleksine kolaylıkla dönüştürülebilmektedir; bu özellik, sentez sürecinin pratikliğini ortaya koymaktadır. Borokryptatın kompleks oluşturma davranışı ve iyon bağlama yeteneği, iyonofor olarak bütünüyle katı hal PVC membranlı gümüş-seçici bir elektrot içinde kullanılarak değerlendirilmiştir. Hazırlanan PVC membran elektrodu, Ag^+ iyonlarına karşı olağanüstü seçicilik göstermiş ve alkali, toprak alkali ve yaygın ağır metal iyonlarından kaynaklanan girişimlerin belirgin şekilde minimize edildiği tespit edilmiştir. Elektrot, 65 ± 25 mV/10 kat değerinde Nernst üzerinde bir eğim sergilemiş ve 10^{-2} – 10^{-5} M $AgNO_3$ aralığında doğrusal bir yanıt vermiştir. Doğrusal bölgelerin kesişimine dayalı olarak hesaplanan tespit limiti 5×10^{-6} M olarak belirlenmiş ve bu değer, düşük derişimlerde gümüş tayini için elektrodun uygunluğunu göstermektedir. Ayrıca elektrot, 4–7 pH aralığında potansiyel değerlerinde oldukça düşük sürüklenme ile mükemmel çalışma kararlılığı sunmuştur. Yaklaşık 10 saniyelik hızlı bir yanıt süresi göstermiş ve elektrot iki aya kadar yüksek tekrarlanabilirlik ve kararlı performansını korumuştur. Bu bulgular, borokryptat temelli iyonoforların güçlü seçicilik, yüksek kararlılık ve pratik uygulanabilirlik sunarak yeni nesil gümüş-seçici elektrotların geliştirilmesinde umut vaat eden adaylar olduğunu ortaya koymaktadır.

Binding of Boron and Sodium by a Pseudocryptand as a New type Ionophore for ISEs

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ABSTRACT

A novel selective molecular receptor, borocryptate, has been synthesized and characterized, consisting of a 15-membered diazatrioxa macrocyclic core linked to two saligenin moieties that serve as boron-coordination sites. This receptor exhibits notable stability under ambient conditions and can be readily transformed into a polynuclear Na-borocryptate complex without requiring an inert atmosphere, highlighting its practical synthetic accessibility. The complexation behavior and ion-binding affinity of borocryptate were evaluated through its incorporation as an ionophore in an all-solid-state poly(vinyl chloride) (PVC) membrane silver-selective electrode. The fabricated PVC membrane electrode demonstrated exceptional selectivity for Ag^+ ions, showing significantly minimized interference from alkali, alkaline earth, and common heavy metal ions. The electrode exhibited a non-Nernstian slope of 65 ± 25 mV per decade, with a linear response range spanning 10^{-2} to 10^{-5} M $AgNO_3$. The detection limit, calculated based on the intersection of the linear segments, was found to be 5×10^{-6} M, indicating strong suitability for low-level silver monitoring. Moreover, the electrode displayed excellent operational stability, maintaining consistent potential values with negligible drift across a broad pH window of 4–7. The response time was rapid, approximately 10 seconds, and the electrode retained high reproducibility and stable performance for up to two months of continuous use. These findings underscore the potential of borocryptate-based ionophores as promising candidates for the development of next-generation silver-selective electrodes, offering robust stability, strong selectivity, and practical applicability in analytical sensing.

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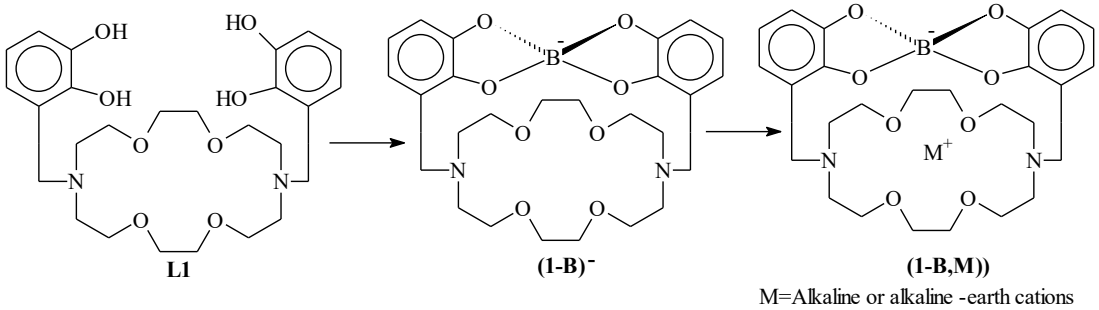
INTRODUCTION

Since the seminal discoveries of cryptands by Dietrich and Lehn and crown ethers by Pedersen, supramolecular chemistry has emerged as a pivotal area of research intertwining the principles of inorganic, organic, and physical chemistry. The initial focus on the selective binding of spherical alkaline and alkaline-earth monoatomic cations has significantly advanced the molecular recognition capabilities over the years, broadening the scope of ion recognition technologies [1]. The past three decades have seen extensive investigations into the design and synthesis of binuclear complexes, enabling precise tuning of intrinsic molecular properties such as magnetic coupling, redox activity, and optical characteristics [2,3]. While initial efforts predominantly focused on heterobinuclear complexes involving either two alkaline or two transition metal cations, there is now a marked shift toward the synthesis of heterobinuclear complexes that include combinations of hard alkaline or alkaline earth with soft transition metal cations [4].

Hosseini and his collaborators have notably contributed to this evolving domain through their systematic research program focused on the design and synthesis of polynucleating ligands [5]. Their innovative strategy for developing binucleating receptors revolves around the integration of macrocyclic frameworks with two bidentate dianionic ligands. By adopting well-preorganized cores, such as diaza-macrocyclic structures, they have effectively prepared bi- and polynucleating ligands, incorporating bidentate catechol units that offer remarkable coordination properties [6]. The choice of an 18-membered ring diazatetraoxa macrocyclic core stems from its demonstrated capability to bind hard cations, which is inspired by the structural characteristics of naturally occurring antibiotics such as boromycin and aplasmomycin [7].

The original design of the borocryptand was initiated using a dual functionalization approach at both nitrogen centers of the core, integrating two catechol units, giving rise to the receptor molecule L1. Upgrades to the concept also include compounds featuring interconnected catechol units linked via polyethylene glycol spacers [8]. However, synthesis challenges emerged when incomplete oxygen removal led to the formation of a pink precipitate, which was attributed to catechol oxidation prior to binding with boron [9]. This observation necessitated specific synthesis conditions, with the free ligand L1 being converted to the (1-B,M) complex exclusively under an Ar atmosphere to mitigate oxidation concerns (Scheme 1).



Scheme 1
Synthesis of catechol-based borocryptand (L1) via dual functionalization and its subsequent complexation to (1-B,M) under controlled inert atmosphere

Potentiometric electrodes have emerged as vital analytical tools due to their capacity to provide precise measurements of ion concentrations in various applications, from clinical diagnostics to environmental monitoring. These electrodes operate based on the Nernst equation, where the potential difference across an ion-selective membrane relates to ion activity. Recent advancements have focused on novel materials and designs for the ion-selective membranes and ionophores, enhancing selectivity,

sensitivity, and stability. For instance, advancements using nanomaterials and hybrid electrodes have facilitated the development of electrodes that are not only cost-effective but also capable of detecting ions at lower concentrations with higher selectivity [10-15] .

In the present study, a novel sodium receptor was engineered using a diazatrioxa macrocyclic core combined with two saligenin units, in contrast to the previous macrocyclic core and catechol moieties employed in the (1-B,M) complex. Saligenin units not only serve as binding sites for boron, akin to catechol, but also possess enhanced stability against oxidation under atmospheric conditions. Notably, this conversion of the free ligand (pseudocryptand) to the (1-B,Na) complex was accomplished without an inert atmosphere.

The design of the pseudocryptand precursor for selective sodium receptors benefitted from a strategic reduction in the size of the borocryptand cavity, resulting in reverse selectivity, while maintaining saligenin moieties as boron-binding sites within the framework of the 15-membered diazatrioxa macrocycle [16]. Structural modifications yielded significant alterations in the ^1H and ^13C NMR spectra of the (1-B,Na) complex, particularly in the benzylic CH_2N protons, which exhibited an AB split. Cryptands and their derivatives are characterized by their high selectivity as molecular receptors capable of recognizing and reversibly transporting cations, and they have a longstanding history of integration into ion-selective electrode (ISE) membranes [17]. The heterobinuclear complexing ability and hydrophobic characteristics of the synthesized borocryptate complex position it as a promising candidate for incorporation into polymer membrane ISEs. Consequently, the potentiometric behavior of an all-solid-state silver-selective PVC membrane electrode based on this compound was thoroughly investigated, revealing unexpected selectivity profiles and potential for future applications in ion recognition [18].

MATERIALS AND METHODS

Instrumentation and Reagents

^1H NMR spectra were recorded at 400 MHz on a BRUKER DPX-400 FT-NMR spectrometer in $CDCl_3$ with TMS as the internal standard. The 13C NMR spectra were obtained at 100 MHz using the same instrument. Elemental analyses were performed using a CARLO-ERBA Model 1108 apparatus. Infrared spectra were recorded using a MIDAC-FTIR Model 1700 spectrophotometer. The melting points were measured using a GALLENKAMP apparatus with open capillaries.

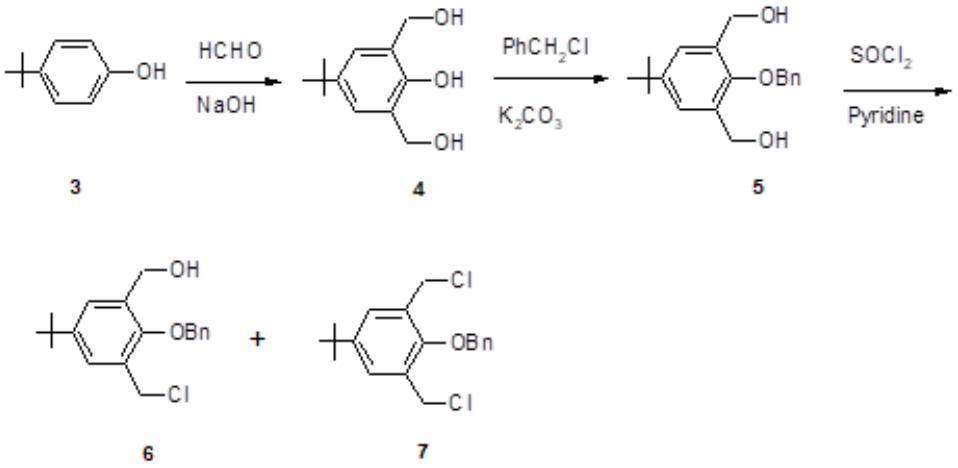
Potential measurements were conducted using a custom-built analog/output board and an electrode interface module (Molspin Instruments, Newcastle-upon-Tyne, UK) controlled via laboratory-written software. All measurements were referenced to a porous-plug double-junction saturated calomel electrode (Russel, Auchtermuchty, Fife, UK) in stirred solutions.

All chemicals, including $AgNO_3$, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cu^2, Ni^2, Pb^2, Zn^2, Cd^2, Hg^2, Co^2, $Fe^{2/3}$, Cr^3, and Al^3 salts, were of analytical grade and purchased from Merck (Darmstadt, Germany). Deionized water was used throughout the study. All PVC membrane components, except the synthesized Na-borocryptate ionophore, were purchased from Fluka. Membrane cocktail composition: borocryptate 20 mg; 2-nitrophenyloctyl ether (o-NPOE) 340 mg; Polyvinychloride (PVC) 140 mg; (Potasium tetrakis(p-chlorophenyl)borate) KTpClPB 2 mg in 5 mL of tetrahydrofuran (THF).

Synthesis of Ligands and Complexes

The synthesis of saligenin derivatives (4–7) (Scheme 2), pseudocryptand, and sodium borocryptate (1-B,Na) followed classical procedures with minor modifications. The key steps included hydroxymethylation, benzyl protection, selective chloromethylation, nucleophilic substitution with

diaza-15-crown-5, and final coordination with B/Na $^{+}$ under ambient conditions, resulting in nearly quantitative yields. Spectroscopic characterization (^1H/^13C NMR, IR, elemental analysis) confirmed the structures and purities of all compounds.



Scheme 2
Multistep synthetic pathway for saligenin derivatives (4–7) and the ambient-condition assembly of the sodium borocryptate (1-B,Na) complex

The compounds 4-tert-Butyl-2,6-Dihydroxymethyl Phenol (4), 4-tert-Butyl-2,6-Dihydroxymethyl Phenyl Benzyl Ether (5), 4-tert-Butyl-2-hydroxymethyl-6-Chloromethyl Phenyl Benzyl Ether (6) and 4-tert-Butyl-2,6-dichloromethyl Phenyl Benzyl Ether (7) were obtained following previously established methods [19].

Synthesis of Pseudocryptand

The saligenin-armed diaza-15-crown-5 derivative (pseudocryptand) was synthesized by reacting commercially available diaza-15-crown-5 (1.0 g, 45.87 mmol) with 4-tert-butyl-2-hydroxymethyl-6-chloromethyl phenyl benzyl ether (6) (4.64 g, 45.87 mmol) in the presence of triethylamine (Et3N) in toluene (75 mL). The reaction mixture was stirred at 80-85°C for 16 h. Upon cooling, the mixture was filtered, and the crude product was obtained as an oil (2:3.26 g, 91%). This crude residue was directly debenzylated using Pd/C in a dry ethanol-ethyl acetate mixture, yielding a colorless liquid in almost quantitative yield. Characterization by ^1H NMR (CDCl3) revealed shifts at δ 1.16 (s, 18H); 2.65-2.75 (m, 8H); 3.46-3.67 (m, 16H), 4.56 (s, 4H), 4.66 (bs, 4H), and 7.07 (dd, 4H). ^13C NMR (CDCl3) showed δ 18.40, 31.87, 34.21, 54.55, 54.67, 57.77, 59.74, 61.98, 68.50, 69.11, 70.77, 124.84, 125.00, 125.18, 127.45, 141.77, 153.65 ppm.

Analytical calculations provided the following for C34H56N2O7: C, 67.55; H, 9.27; N, 4.64; found: C, 67.18; H, 9.34; N, 4.58, which aligns with previous findings on similar structures [19,20].

Synthesis of Sodium Borocryptate (1-B, Na)

For Sodium Borocryptate (1-B, Na), pseudocryptand (2.51 g, 4.17 mmol) was dissolved in ethanol and treated with one equivalent each of NaOH and 1 equivalent of B(OH)3 in a water/ethanol mixture at room temperature. This reaction afforded the (1-B, Na) complex as a precipitate, which was subsequently filtered and recrystallized using methanol. The final product (1-B, Na) was obtained as white crystals in nearly quantitative yield, with a melting point of 300°C (decomposed). The IR spectrum revealed significant absorption bands at v 3384, 2952, 2870, 2825, 1613, 1485, and 1365 cm^{-1}.

^1H NMR (CDCl3) analysis showed peaks at δ 1.24 (s, 9H); 1.27 (s, 9H); 2.33-3.03 (m, 8H);

3.28-4.12 (m, 12H); 3.52 (dd, 2H); 3.55 (dd, 2H); 4.78 (dd, 2H); 5.00 (dd, 2H); 6.87 (dd, 4H). ^13C NMR (CDCl3) provided data at δ 32.11, 34.12, 34.15, 50.79, 53.71, 54.85, 55.57, 58.18, 58.51, 61.38, 62.81, 63.62, 67.18, 67.28, 68.40, 68.76, 69.05, 69.20, 121.95, 122.05, 123.63, 125.03, 125.32, 125.38, 125.87, 126.92, 139.53, 139.69, 152.78, 152.90 ppm.

Analytical data for C34H52N2O7BNa confirmed C, 64.35; H, 8.20; N, 4.42; found C, 64.12; H, 8.37; N, 4.34, aligning well with established methodologies in the field of boron chemistry [21].

Electrode Preparation and Measurements

All-solid-state PVC membrane electrodes were fabricated as previously described [22], with 1-B,Na as the ionophore. Briefly, the PVC membrane cocktails had the following composition: orocryptate, 20.0 mg; 2-nitrophenyloctylether (o-NPOE), 340.0 mg; polyvinyl chloride (PVC), 140.0 mg; and potassium tetrakis p-chlorophenylborate (KTpClPB), 2.0 mg. The membrane components were dissolved in 5 ml tetrahydrofuran (THF), and the resulting solution was maintained until an appropriate viscosity was attained. The electrode performance was evaluated using potentiometric measurements of standard Ag^+ solutions ($0.1–10^{-7}$ M). The selectivity coefficients were determined with standard solutions of each ion using the separate-solution method [23]. The electrochemical cell configuration was Cu/all-solid-state polyvinyl chloride (PVC) membrane/test solution/reference electrode.

RESULTS AND DISCUSSION

Synthesis of Sodium Borocryptate (1-B,Na)

The transition from catechol-based ligands to the saligenin-armed pseudocryptand represents a significant shift in the practical synthesis of boron-centered molecular receptors. While previous L1-type borocryptands required strictly inert conditions to prevent the oxidation of catechol units, often evidenced by the formation of a pink precipitate, the saligenin moieties utilized in this study demonstrated exceptional atmospheric stability. This allowed for the nearly quantitative conversion of the free ligand to the (1-B,Na) complex under ambient conditions. The saligenin precursors were obtained in good yields using classical hydroxymethylation and benzyl protection strategies, confirming the robustness of the synthetic methodology. The selective mono-chloromethylation of compound 5 to form compound 6, despite the concurrent formation of the dichlorinated by-product 7, highlights the sensitivity of benzylic positions toward electrophilic substitution, particularly under thionyl chloride activation [24,25]. Nevertheless, purification via column chromatography afforded analytically pure compound 6, demonstrating that the reaction remains both reproducible and scalable for ligand synthesis.

The key step in constructing the pseudocryptand structure involved the nucleophilic substitution between diaza-15-crown-5 and the chloromethylated saligenin derivative. The high yield (91%) of the crude macrocycle attachment suggests that the macrocyclic nitrogen atoms possess appropriate nucleophilicity for efficient tether formation, consistent with the behavior of diaza-crown ethers in previous polynucleating ligand systems [26]. Subsequent debenzylation under mild hydrogenolysis conditions proceeded cleanly, avoiding decomposition of the macrocyclic framework and preserving the integrity of the saligenin units. Spectroscopic data (1H and 13C NMR) indicated successful attachment and correct structural assembly, with chemical shifts corresponding to intact aromatic, benzylic, and crown ether segments [27].

Formation of the sodium borocryptate (1-B,Na) from L1 represents an important synthetic advancement compared with earlier borocryptands [28]. Notably, saligenin groups eliminated the need for an inert atmosphere, addressing a major drawback of catechol-based systems [29] that are highly

prone to oxidative degradation. The rigidification of the 15-membered diazatrioxa macrocycle upon boron coordination was confirmed via NMR spectroscopy. The observed changes in the NMR spectra, particularly the emergence of well-resolved AB patterns in benzylic CH_2 groups, provide strong evidence for successful boron coordination and rigidification of the ligand framework upon metal binding. The nearly quantitative yield and high stability of the complex demonstrate that saligenin substitution not only improves synthetic practicality but also enhances the suitability of such borocryptates for real-world applications where air-stability is essential.

The strategic alteration of the macrocyclic cavity and the introduction of saligenin groups appear to have substantial implications for the chemical stability and metal-binding behavior of the resulting ligand, shaping future investigations aimed at designing boron-based multinuclear receptors. Such modifications may facilitate the development of tailored functional architectures that improve ion recognition capabilities and performance in electrochemical technologies.

Potentiometric Performance and Sensitivity

Given the established role of molecular receptors in ion recognition, newly synthesized Sodium Borocryptate (1-B,Na) was evaluated as an ionophore in all-solid-state PVC membrane electrodes for electroanalytical applications. The need for advanced electrochemical electrodes that reliably detect ions, particularly silver ions (Ag^+), has prompted research into functional materials such as borocryptates owing to their unique structural properties and interactions with metal ions. The three-dimensional cage-like framework of boron-based materials allows for enhanced selectivity and interaction, which is essential for high-performance electrodes in practical applications.

The integration of such supramolecular hosts into ion-selective membranes is expected to improve their sensitivity and stability compared to traditional ionophores. Such advancements are crucial for developing reliable and efficient electrodes capable of rapid and precise ion detection, particularly in environments where low concentrations of heavy metals, such as silver, pose significant risks to health and safety. Ongoing efforts to optimize the chemical and structural properties of Sodium Borocryptate reaffirm its potential as a leading candidate for future electrode technology.

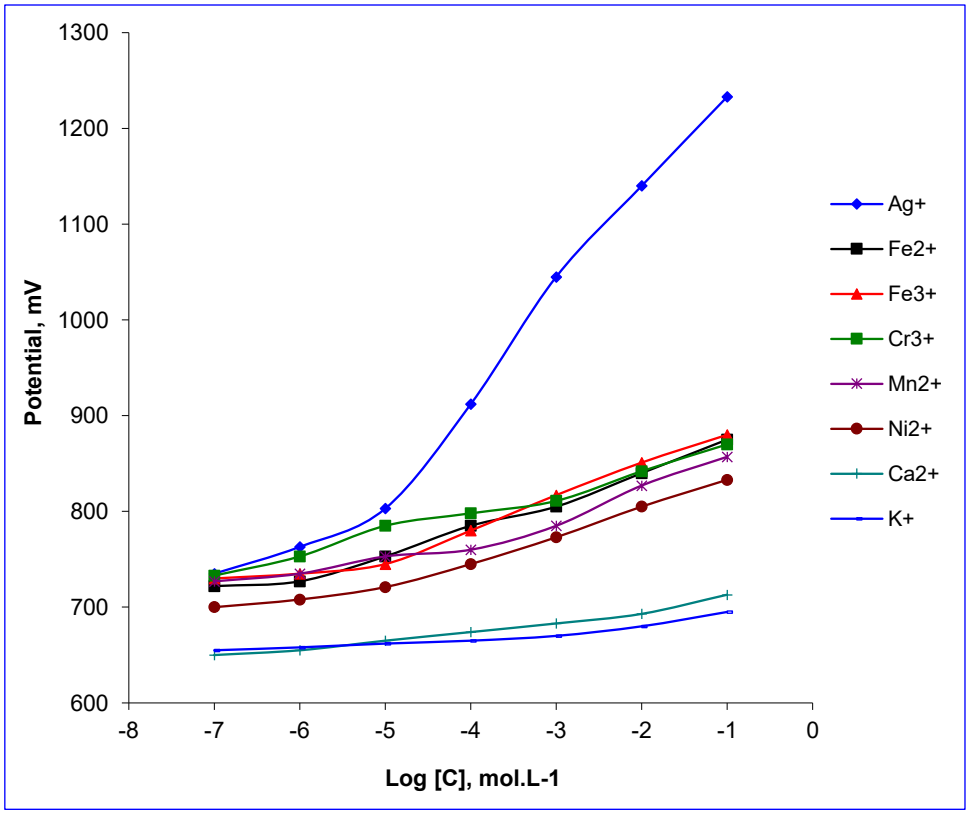


Figure 1

Potentiometric selectivity profile of the all-solid-state contact PVC membrane electrode based on sodium borocryptate (1-B,Na) toward various interfering cations

The potentiometric performance of the all-solid-state PVC membrane electrode incorporating Sodium Borocryptate (1-B,Na) was comprehensively assessed in terms of sensitivity, linear dynamic range, response time, detection limit, and selectivity. As shown in Figure 1, The electrode exhibited a near-Nernstian slope of approximately 65 ± 25 mV/decade over the concentration range of (10^{-2}–10^{-5} M) Ag^{+}, indicating an efficient and stable interaction between silver ions and the borocryptate-based sensing layer. While the calculated slope of 65 ± 25 mV/decade is significantly higher than the theoretical Nernstian value of 59.2 mV $decade^{-1}$ for a monovalent cation. Such non-Nernstian behavior is often observed in solid-state contacts where super-sensitivity may be triggered by specific ion-exchange kinetics or surface-limited interactions [22].

Table 1

Potentiometric selectivity coefficients (K_{Ag+}^{Pot}, M^{n+}) of the sodium borocryptate-based PVC membrane electrode determined by the separate solution method

Interfering Ion (M^{n+})	$-\log K^{pot}_{(Ag^+,M^{n+})}$	$K^{pot}_{(Ag^+,M^{n+})}$ (approx.)
Fe^{2+}	**2.8**	1.6×10^{-3}
Fe^{3+}	**3.0**	1.0×10^{-3}
Cr^{3+}	**3.3**	5.0×10^{-4}
Mn^{2+}	**3.6**	2.5×10^{-4}
Ni^{2+}	**4.2**	6.3×10^{-5}
Ca^{2+}	**5.9**	1.3×10^{-6}
K^+	**6.2**	6.3×10^{-7}

Table 1 exhibits selectivity coefficients of the Ag-selective electrode. The selectivity coefficients determined via the separate solution method, expressed as ($-\log K_{Ag^+/M^{n+}}$), demonstrated a pronounced preference for Ag^+ over various competing cations, including alkali, alkaline earth, transition, and heavy-metal ions. The $-\log K^{pot}$ values increase in the order $Fe^{2+} < Fe^{3+} < Cr^{3+} < Mn^{2+} < Ni^{2+} < Ca^{2+} < K^+$, demonstrating progressively lower interference from these ions. Particularly high $-\log K^{pot}$ values for K^+ and Ca^{2+} (~6) confirm excellent discrimination against alkali and alkaline earth metals, which are commonly present in environmental and biological matrices. Transition metal ions such as Ni^{2+}, Mn^{2+}, Cr^{3+}, and Fe^{3+} show moderate but still acceptable interference levels, confirming that the borocryptate cavity provides a favorable coordination environment for Ag^+ compared to competing species. Notably, Hg^{2+} was the only ion that exhibited significant interference because of its strong binding affinity for soft donor atoms, which aligns with the findings on thiacrown ether binding properties [7]. This selectivity pattern suggests that the borocryptate host, although initially designed for hard cation coordination, provides an unexpectedly favorable microenvironment for stabilizing Ag^+, likely due to the synergistic effects of the macrocyclic cavity geometry and boron coordination site.

The calibration curve of the electrode constructed using n = 7 data points demonstrated a linear relationship between the potential (mV) and the logarithm of concentration over the range of 10^{-7}–10^{-1} M (Figure 2). The potential values increased from 735 mV to 1233 mV as the concentration increased. Linear regression analysis yielded a slope of almost 88mV per decade and a coefficient of determination (R^2) of 0.9652, indicating good linearity within the studied concentration range. Although the calculated slope is higher than the theoretical Nernstian slope, the results confirm that the electrode exhibits a strong and concentration-dependent potentiometric response.

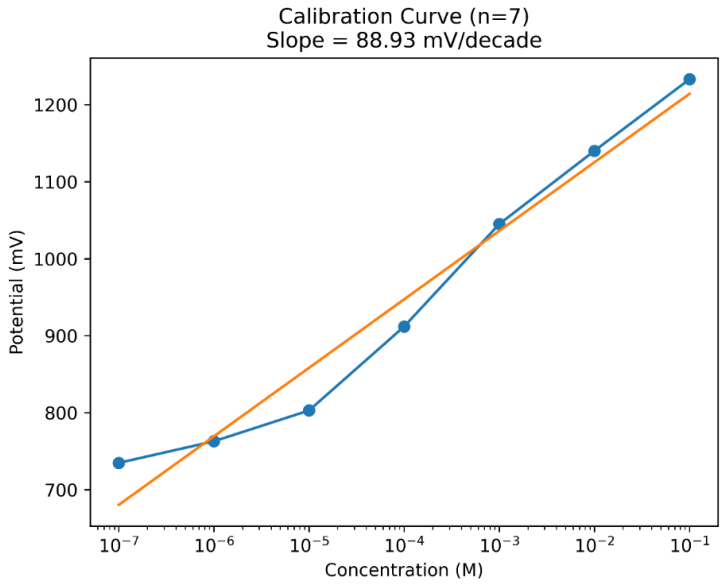


Figure 2

Potentiometric calibration plot of the all-solid-state contact Ag^{+}-selective electrode illustrating the linear dynamic range and sensitivity

The detection limit (LOD) for the ion-selective electrode in this study was determined using the standard intersection of linear segments method, where a calibration curve of electrode potential versus the logarithm of Ag^{+} concentration is plotted. This plot typically shows a linear Nernstian response segment at higher concentrations and a flatter baseline segment at very low concentrations; the LOD is defined as the Ag^{+} concentration at the point where extrapolations of these two linear segments intersect. The detection limit of 5×10^{-6} M and a rapid response time of less than 10 seconds underscore the efficient ion-exchange processes at the polymeric membrane interface. This fast kinetics is likely facilitated by the unique microenvironment of the borocryptate host, which balances the "soft" nature of $Ag^{+}$with the structural cavity geometry [1,2]. This is crucial for achieving high sensitivity in environmental and analytical applications.

The response time of the electrode was experimentally determined to be below 10 s for a tenfold change in Ag^{+} concentration. This fast potentiometric response can be attributed to the efficient ion-exchange process at the polymeric membrane-solution interface, as supported by the dynamic behavior of ion interactions within the stable borocryptate environment, akin to previously reported systems using calixarenes for heavy metal ion detection [3,30]. However, a dynamic potential-time curve is not presented. This is because the primary focus of this study was the evaluation of steady-state potentiometric performance parameters, including sensitivity, linear range, detection limit, repeatability, and selectivity. Since the electrode exhibited rapid stabilization within a few seconds and no anomalous transient behavior was observed, detailed time-resolved analysis was not considered essential for performance validation. The reported response time (<10 s) is consistent with the behavior of solid-contact PVC membrane ion-selective electrodes reported in the literature, where fast ion-exchange kinetics at the membrane–solution interface typically lead to stabilization within seconds.

Long-term stability tests confirmed that the electrode remains robust for up to eight weeks. The slight initial decrease in slope observed in the first week followed by stabilization at 55 mV/decade indicates good mechanical and electrochemical integrity of the PVC membrane over time. This behavior underscores the importance of optimizing pH conditions for accurate measurements in practical applications.

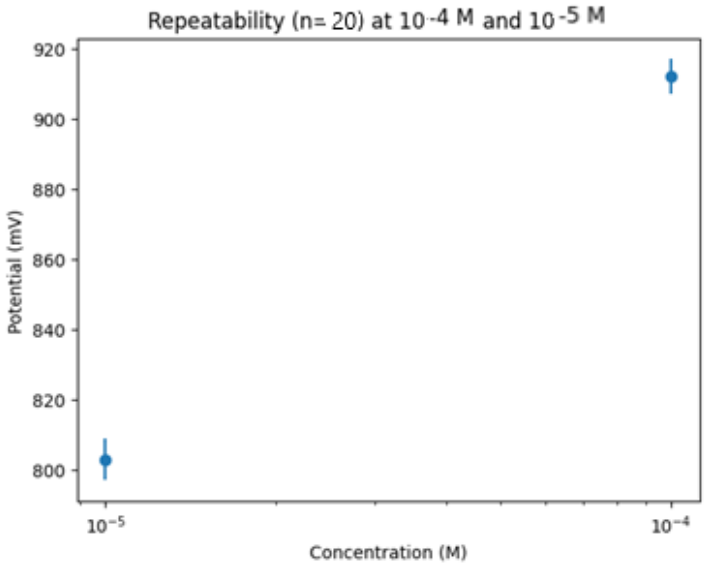


Figure 3
Statistical repeatability analysis of the Ag^+-selective electrode response based on 20 consecutive measurements (n=20) at 10^{-4} M and 10^{-5} M $AgNO_3$ concentrations

Repeatability of the electrode response was evaluated based on 20 consecutive measurements (n = 20) at 10^{-4} M and 10^{-5} M concentrations (Figure 3). The mean potential value at 10^{-4} M was 912 ± 5 mV, corresponding to a relative standard deviation (%RSD) of 0.55%. At 10^{-5} M, the mean potential was 803 ± 6 mV, yielding a %RSD of 0.75%. In both cases, the %RSD values were below 1%, indicating excellent repeatability and high measurement precision of the electrode. These results demonstrate the stability and reliability of the developed system under repeated measurement conditions.

The electrode exhibited stable potentials within the pH range of 4–7, indicating that the sensing mechanism operates under optimal conditions where Ag^+ remains in its free ionic form and the borocryptate ionophore is not protonated. At pH values above 7, the observed decrease in potential can be attributed to the formation of silver hydroxide species and Ag_2O precipitation, which reduce the free Ag^+ activity in solution. Conversely, at pH values below 4 suggests a competition between H+ and Ag+ for the coordination sites or partial protonation of the ionophore, altering the phase boundary potential at the membrane-solution interface. This behavior underscores the importance of optimizing pH conditions for accurate measurements in practical applications [6].

The Ag^+-selective electrode was not applied to real samples in this study because the primary objective was to evaluate its fundamental analytical performance under controlled laboratory conditions. The work focused on optimizing membrane composition, determining sensitivity, selectivity, detection limit, and repeatability in standard solutions to establish proof of concept. Application to complex real matrices (e.g., environmental or biological samples) requires additional validation steps, including matrix effect evaluation, recovery studies, and interference assessment, which are planned for future investigations. Overall, the low detection limit (10^{-6} M), fast response (< 10 s), high selectivity, wide usable pH range, and long-term stability of the electrode make it a promising candidate for practical Ag^+ monitoring, particularly in environmental, industrial, and analytical applications where rapid and selective Ag^+ detection is paramount [31].

In conclusion, the implementation of Sodium Borocryptate (1-B,Na) in electrochemical electrodes not only enhances the detection capabilities for silver ions but also provides insights into the design of future electrode technologies. The continued exploration of boron-centered materials promises

to advance the broader field of ion-selective electrodes through novel molecular architectures suited for diverse analytical challenges.

Comparative Discussion

As shown in Table 2, the Na-borocryptate (1-B,Na) based electrode exhibits analytical performance comparable to or slightly improved over previously reported Ag^+-selective ionophores. The detection limit (5×10^{-6} M) falls within the same order of magnitude as dilactam crown ethers, calixarene derivatives, and porphyrin-based systems, indicating competitive sensitivity.

Although its linear range (10^{-5}–10^{-2} M) is somewhat narrower than that of certain literature examples extending to 10^{-1} M, the electrode demonstrates a relatively fast response time (<10 s), which is advantageous for real-time monitoring applications. Notably, the observed slope (65 ± 25 mV /decade) approaches or exceeds near-Nernstian behavior, suggesting efficient ion-exchange dynamics at the membrane interface.

The operational pH window (4–7) aligns well with practical aqueous conditions and ensures stable Ag^+ detection without significant proton interference or hydroxide precipitation effects. Overall, the borocryptate ionophore provides a balanced combination of sensitivity, selectivity, and operational stability, supporting its potential as a viable alternative to conventional macrocyclic Ag^+-selective systems.

Table 2
Comparative evaluation of analytical performance parameters for the proposed sodium borocryptate (1-B,Na) ionophore against previously reported Ag^+-selective sensing systems.

Ionophore	Linear Concentration Range (M)	Limit of Detection (M)	pH Working Range	Response Time (s)	Slope (mV/decade)	Ref.
5,10,15,20-Tetra(4-pyridyl)-21H,23H-porphine	$1.0 \times 10^{-6} – 1.0 \times 10^{-1}$	1.9×10^{-6}	4 – 10	8	~51	[32]
Dilactam Crown Ether	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	6.8×10^{-6}	5.1 – 7.2	~20	59.8 ± 0.2	[33]
2-Phenylethylammonium Benzoate	$1.0 \times 10^{-5} – 1.0 \times 10^{-1}$	7.14×10^{-6}	4.0 – 10.0	< 7	59.3 ± 3.7	[34]
Schiff base–p-tert-butylcalix[4]arene	1.0×10^{-5}–1.0×10^{-1}	3.0×10^{-6}	1.0–5.6	20	59.7	[35]
Na-Borocryptate (1-B,Na)	$1.0 \times 10^{-5} – 1.0 \times 10^{-2}$	5×10^{-6}	4 – 7	< 10	65 ± 25	This work

CONCLUSION

Silver-selective electrodes have been traditionally developed using various macrocyclic

ionophores, including calixarenes, azacrowns, thiacrowns, and lariat ethers. These systems have demonstrated notable affinity and selectivity towards Ag^+ ions, highlighting their potential applications in analytical chemistry and environmental monitoring. Recent developments, particularly boron-centered polynuclear cryptands, suggest a novel direction for the design of silver-selective electrodes. Borocryptates exhibit unique structural characteristics, including a three-dimensional cage-like framework and an electron-rich coordination environment, suggesting enhanced selectivity through tailored host–guest interactions. This structural feature is crucial for achieving high-performance electrodes capable of differentiating between various ions in complex matrices.

Preliminary findings indicate the feasibility of integrating borocryptate-based ionophores into all-solid-state contact PVC membrane ion-selective electrodes, opening new possibilities for improved analytical performance in various applications. Potentiometric evaluations revealed a detection limit of approximately $\times 10^{-6}$ M for Ag^+ ions, which is comparable to that of existing macrocyclic ionophores, indicating robust interaction dynamics between Ag^+ ions and the borocryptate-based sensing layer. This is particularly relevant in settings that require rapid and precise monitoring. These electrodes demonstrate rapid response times, approximate stability over extended use, and broad usable pH ranges, making borocryptate ionophores promising candidates for practical applications in environmental and industrial contexts requiring swift and accurate silver ion detection [36], which is essential given silver's economic importance and its potential adverse effects on human health and the environment due to long-term toxicity. Ongoing research focused on the synthesis, structural optimization, and comprehensive electrochemical evaluation of borocryptate derivatives is vital for enhancing our understanding of the mechanisms of metal-ion binding. These insights will likely lead to further improvements in the applicability of these materials for selective and stable Ag^+ sensing systems, reinforcing their importance in various analytical contexts. Overall, this study lays the foundation for the development of a new class of boron-based electroactive materials and has the potential to significantly advance silver-sensing technologies.

In conclusion, the exploration of borocryptate-based ionophores represents a transformative step in the design of effective electrodes for silver ions. Exploiting the distinct characteristics of these structures holds considerable promise for enhancing the efficiency of ion-selective electrodes, thus facilitating more advanced detection methods for both research and industrial applications in the future. This advancement in electrode technology highlights the crucial importance of interdisciplinary strategies in improving chemical electrode design by combining materials science, supramolecular chemistry, and analytical methods to address ion detection issues.

Ethical Statement

The present study is an original research article designed and produced by the authors.

Author Contributions

Research Design (CRediT 1) M.Y. (%40) – Ö.T. (%20) – İ.I. (%40)

Data Collection (CRediT 2) M.Y. (%20) – Ö.T. (%20) – İ.I. (%60)

Research – Data Analysis – Validation (CRediT 3-4-6-11): M.T. (%20) – M.Y. (%40) – Ö.T. (%20) – H.H. (%10) – G.T. (%10) – İ.I. (%20)

Manuscript Writing (CRediT 12-13): Ö.T. (%80) – İ.I. (%20)

Text Revision and Improvement (CRediT 14): M.T. (%10) – M.Y. (%10) – Ö.T. (%20) – İ.I. (%60)

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Conflictof Interest

There are no conflicts of interest among the authors of this article.

Sustainable Development

This study contributes primarily to Sustainable Development Goal 9 (Industry, Innovation and Infrastructure) through the development of a novel pseudocryptand ionophore for ion-selective electrodes. The work also supports SDG 3 (Good Health and Well-being) by improving analytical tools for chemical sensing.

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