2-hydroxyethyl-2-(phenylamino) Benzoate: Synthesis, Selective Extraction and Transport of Ca^<2+> Ions

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バージョン：

2-hydroxyethyl-2-(phenylamino) Benzoate: Synthesis, Selective Extraction and Transport of Ca^{2+} Ions

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Abstract: This paper presents a detailed investigation into the design, synthesis, and characterization of 2-hydroxyethyl-2-(phenylamino) benzoate as a novel Ca^{2+} ionophore. Computational modeling elucidated a stable molecular structure after optimization with favorable electronic properties conducive to ion binding. The synthesis process involved a rigorous two-step procedure, with spectroscopic and elemental analyses confirming the successful formation of the target compound. Notably, the synthesized ionophore, distinguished by its noncyclic nature, exhibits dynamic interactions crucial for complexation-decomplexation phenomena. The paper highlights the intricate characterization of the ionophore's structure and properties, shedding light on its potential applications in diverse fields. The revealed data indicates that 1,2-dichloroethane was a promising membrane during extraction (complexation) and transport (complexation-decomplexation) of Ca^{2+} over Na^+ and K^+ than $CHCl_3$ and CCl_4 using highly lipophilic picrate salt. This research contributes to the advancement of ionophore chemistry and holds promise for various applications in environmental remediation to energy harvesting.

Keywords: Ionophore; Computational Modeling; Ca^{2+} extraction; Ca^{2+} transport

1. Introduction

Supramolecular chemistry, as described by Lehn[1)], serves as a fundamental principle governing essential life structures[2)] and mechanisms[3)]. This field encompasses interactions between host and guest through weak, reversible non-covalent interactions such as hydrogen bonding[4)], Vanderwaal forces[5)], π-π stacking, and electrostatic interactions[6)]. Ionophores, which can be either neutral or ionogenic substances, utilize the supramolecular phenomenon to selectively bind species such as cations[7)], anions[8)], or neutral molecules[9)], facilitating their extraction from one medium and transport to another. In the context of safe waste management, specific ionophores can be employed to remove targeted metal salts from industrial, agricultural, and domestic waste streams which must be properly managed. During this process ionophore acts as the host while the species acts as the guest, resulting in complexation. To support these experimental endeavors, researchers utilize computational tools such as Avogadro, GAMESS, and wxMacMolPlt. Avogadro[10)] is a tool for molecular editing and visualization offering geometry optimization and energy minimization. GAMESS[11)] is a collection of quantum chemistry programs used for initial electronic structure calculations to determine properties of molecules such as orbitals, energies, and frequencies. wxMacMolPlt[12)] is a tool for visualizing and analyzing the output generated from electronic structure calculations performed by programs like GAMESS. This computational approach plays a crucial role in advancing ionophore research enabling the rational design of molecule with improved selectivity and affinity. This paves the way for highly specific sensors and extraction techniques. A prime example is the ongoing search for improved calcium (Ca^{2+}) ionophores. These ions have crucial roles in biology, environmental monitoring, and industry. Computational design offers exciting possibilities to meet the demand for efficient and selective Ca^{2+} recognition and transport. The main objective of this study is to address these challenges by focusing on the design, synthesis, and characterization of a novel non-cyclic ionophore, 2-hydroxyethyl-2-(phenylamino) benzoate, and to optimize its selectivity and efficiency for metal ion uptake. Non-cyclic ionophores possess a pseudocyclic cavity that imparts flexibility and adaptability, accommodating metal cations of different sizes and coordination geometries. Non-cyclic ionophores possess greater sensitivity and selectivity compared to cyclic ionophores due to their dynamic properties, which makes them a compelling choice for ion transport. Using Avogadro, the structure of the compound was proposed

and optimized to achieve its lowest energy conformation. The proposed ionophore structure was further analyzed using the computational tool GAMESS and visualized using wxMacMolPlt. The synthesis of the ionophore was confirmed through elemental analysis and various spectroscopic techniques[13,14]. The utility of the ionophore was demonstrated by extracting Ca^{2+} ions into various organic solvents, followed by their transport across aqueous and organic phases using a bulk liquid membrane. The HOMO-LUMO energy gap[15] of the synthetic ionophore indicated reactivity, highlighting its significant capability for ion extraction and transport. Experimental results showed better performance for Ca^{2+} ions compared to other alkali metals, particularly when CH_2Cl_2 was utilized as the solvent in the bulk liquid membrane process[16]. The novelty of this study lies not only in the unrevealing complexities of a non-cyclic ionophore but also in highlighting the versatility and adaptability of tailored molecular recognition beyond cyclic one. The intriguing potential of this molecular architect extends to addressing challenges in various fields including ion sensing technologies[17], membrane-based separation processes, environmental remediation[18-19], and energy harvesting[20].

2. Computational details

2.1 Optimization

The Optimized structure of 2-hydroxyethyl-2-(phenylamino) benzoate (Fig. 1) was obtained from Avogadro. In the Avogadro tool, the overall energy associated with the arrangement of atoms in the molecule is determined to be 268.361 kJ/mol. Additionally, there is no change in energy during the optimization[21] process, signifying stability in the molecular configuration.

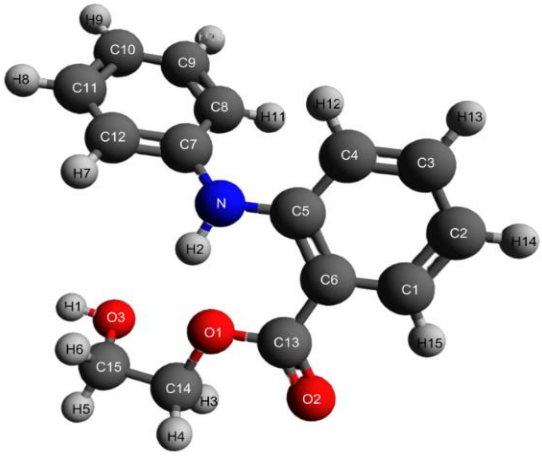


Fig. 1: Optimized structure of 2-hydroxyethyl-2-(phenylamino) benzoate

2.2 Quantum chemical calculations

DFT[22] quantum chemical calculations were performed using the GAMESS tool in which B3LYP functional and 6-311+G(d,p) basis sets were applied to optimize the geometry of the compound. The computed energy components and thermodynamic parameters are summarized in Tables 1 and 2 respectively.

Table 1. Energy components for ionophore

Parameter	E (Kcal/Mol)
Heat of formation	-61.4506
One electron energy	-3883.3990
Two electron energy	1667.6825
Nuclear repulsion energy	1370.6710
Total energy	-845.0454
Electron-electron potential energy	1667.6825
Nucleus-electron potential energy	-4720.7791
Nucleus-nucleus potential energy	1370.6710
Total potential energy	-1682.4255
Total kinetic energy	837.3801
virial ratio = -2.0092	

Table 2. Thermodynamic parameters of ionophore

Energy	E Kcal/mol	H Kcal/mol	G Kcal/mol	C_V cal/mol/K	C_P cal/mol/K	S cal/mol/K
Elec.	0.000	0.000	0.000	0.000	0.000	0.000
Trans.	0.889	1.481	-11.200	2.981	4.968	42.533
Rot.	0.889	0.889	-9.205	2.981	2.981	33.855
Vib.	181.617	181.617	171.283	46.264	46.264	34.658
Total	183.394	183.987	150.878	52.225	54.212	111.045
Vib.Thermal correction E(T)-E(0)=H(T)-H(0)=5970.368 cal/mol						

2.3 Electronic visualization

HOMO-LUMO and 3D electron density[23] from the output generated by GAMESS were depicted by the wxMacMolPlt tool (Fig. 2-4). The energy of HOMO and LUMO were found to be -0.209 and 0.218 eV respectively.

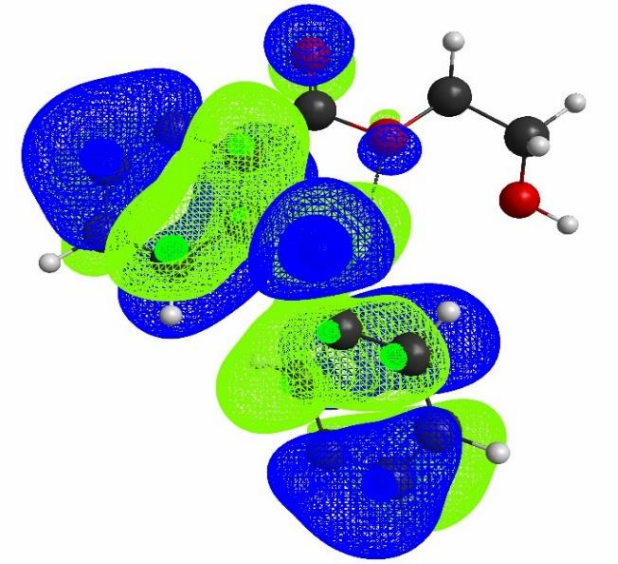


Fig. 2: HOMO of the ionophore

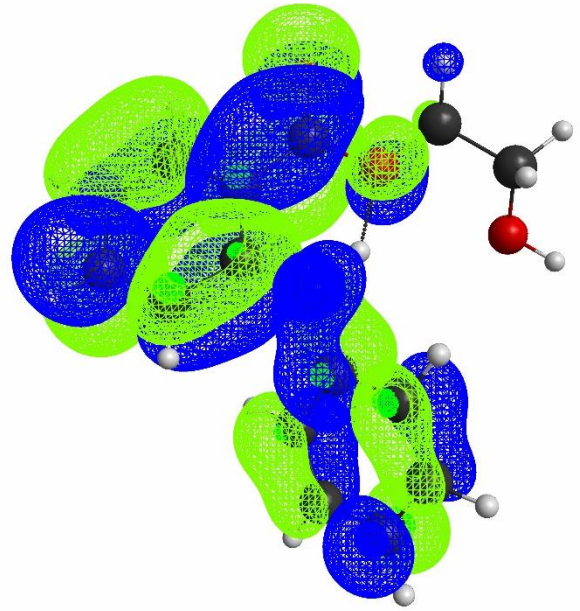


Fig. 3: LUMO of the ionophore

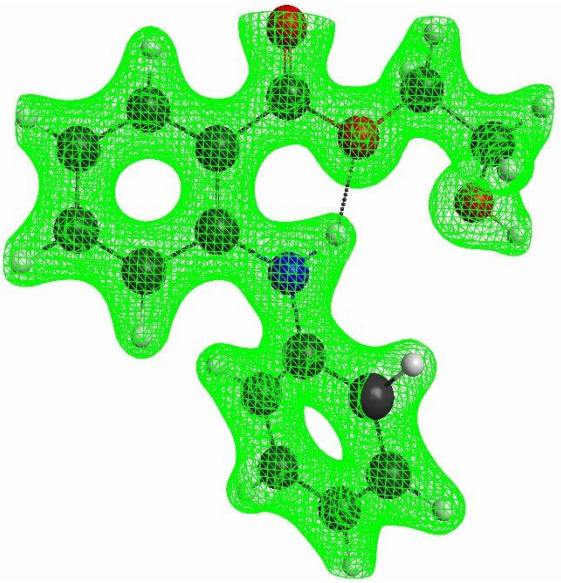


Fig. 4: 3D-electron density of the ionophore

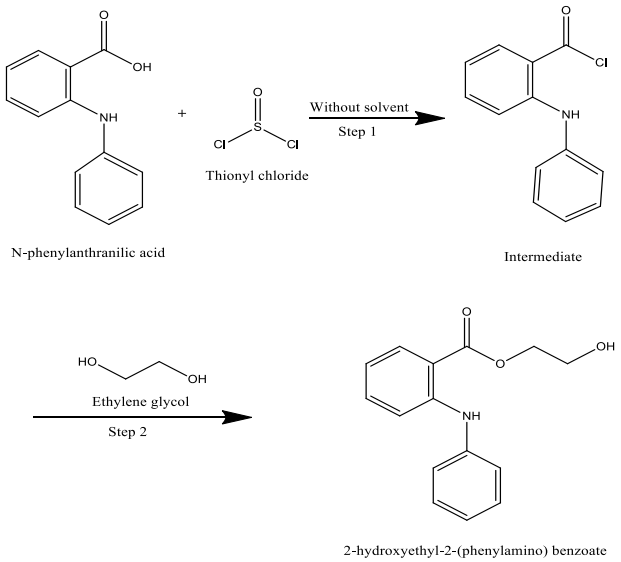
3. Experimental details

3.1 Material and Methods

All chemicals were purchased from Qualigens and Merck and were used without further purification. N-phenyl anthranilic acid, thionyl chloride, and ethylene glycol were used to synthesize ionophore. 1,2-DCE, chloroform and carbon tetrachloride were used to prepare the liquid membrane. Picrate salts of metal ions were prepared according to the reported method[24]. The liquid membrane was prepared by dissolving the appropriate amount of ionophore in the organic solvent.

3.2 Synthesis of ionophore

The desired ionophore, 2-hydroxyethyl-2-(phenylamino) benzoate, was synthesized through a two-step process outlined in scheme 1. The first step involved the refluxing of N-phenyl anthranilic acid (4.26 g/0.02 mol) and thionyl chloride (5.95 g/0.05 mol) in a flask for 2 hours[25], yielding an intermediate product[26]. This intermediate was then subsequently refluxed with ethylene glycol for 1 hour, affording the target ionophore (7.55 g/0.029 mol). Further optimization of the synthesis was explored by investigating various reaction conditions, including modifications in the molar excess of thionyl chloride and solventless alternatives.



Scheme 1: Synthetic route of ionophore

3.3 Extraction

Experiments were conducted to investigate the complexation between metal salts and ionophores in solution[27], focusing on the ability of ionophore to extract metal cations from an aqueous phase into an organic phase through complexation. In liquid-liquid extraction studies[28], a 50 ml solution of 1.0×10^{-3} M aqueous picrate salts of Na^+, K^+, and Ca^{2+} were vigorously stirred with 50 ml of 1.0×10^{-3} M ionophore solution in CCl_4, $CHCl_3$, and $C_2H_4Cl_2$[29] using a magnetic stirrer (150 rpm). The initial concentration of Ca^{2+} in the aqueous phase was measured using complexometric titration[30] while Na^+ and K^+ were by flame photometer. After 4 hours of stirring, the mixture was allowed to stand for 5 minutes for phase separation. The depleted aqueous phases were analyzed using the same methods mentioned above. Ionophore-extracted cations were quantified by measuring the difference in the aqueous phase before and after extraction (Table 3). A blank experiment without the receptor was conducted simultaneously to determine metal ion leakage from the aqueous to the organic phase. All measurements were duplicated for reproducibility.

Table 3. Extraction and Transport of Ca^{2+}, Na^{+} and K^{+} ions

Metal ion	Extracted amount in ppm (%)			D_M			Transported amount in ppm (%)		
	$C_2H_4Cl_2$	$CHCl_3$	CCl_4	$C_2H_4Cl_2$	$CHCl_3$	CCl_4	$C_2H_4Cl_2$	$CHCl_3$	CCl_4
Ca^{2+}	0.52 (17.05)	0.27 (8.85)	0.22 (7.21)	0.17	0.08	0.06	2.24 (62.57)	1.08 (30.17)	0.56 (15.64)
Na^{+}	0.31 (9.63)	0.14 (4.35)	0.09 (2.95)	0.09	0.04	0.03	0.83 (23.51)	0.67 (18.98)	0.48 (13.6)
K^{+}	0.38 (12.34)	0.17 (5.52)	0.18 (5.84)	0.12	0.05	0.05	0.45 (13.01)	0.30 (10.69)	0.28 (8.09)

The distribution ratio (D_M) between both phases was determined by the following formula[31]:

$$D_M = \frac{\text{Total concentration of metal ions in organic phase}}{\text{Total concentration of metal ions in aqueous phase}}$$

3.4 Transport

In the bulk liquid membrane[32] transport experiment, a 'U' tube cell was utilized, separating a 10 ml aqueous source phase from a 10 ml receiving phase with a 25 ml organic phase ($C_2H_4Cl_2$, $CHCl_3$, or CCl_4). The U tube, covered at both ends, was placed on a magnetic stirrer. The aqueous source phase contained picrate salts of Na^{+}, K^{+}, and Ca^{2+} at a concentration of 1.0×10^{-3} M, and the organic phase held the ionophore at a concentration of 1.0×10^{-3} M. After 24 hours, samples from the receiving phase were withdrawn and subjected to complexometric titration to analyze cation transport (Table 3).

4. Results and Discussion

4.1 Computational

The computational study affirms the stability of the optimized molecular stability and provides valuable insight into the electronic structure of the molecule which is essential for understanding its reactivity and potential applications. Energy data ensure that the molecule is energetically stable, with strong electron affinity and attractive forces with its components. These conclusions suggest that the molecule's structure is well-formed and likely to be stable under the conditions described. The interactions between electrons, nuclei, and the overall structure of the molecule seem intricate and well-balanced, contributing to its stability. The negative virial ratio can imply an attractive force between the particles, which could contribute to the stability of the molecule. Thermodynamical data also indicate the stability and feasibility of the molecule with positive enthalpy, Gibb's free energy, and entropy values. The heat capacities and vibrational thermal correction provides further insight into the molecule. A Positive value like this indicates that the molecule's vibrational energy increased with the temperature which is a general trend in all stable molecules. The energy gap between HOMO and LUMO is 0.427 eV which is quite smaller indicating potential reactivity and ion binding *via* interaction with metal ions in its pseudocyclic cavity. 3D-electron density diagram shows concentrated electron density around the lone pairs on the oxygen and nitrogen. These high-density regions are potential binding sites for metal ions.

4.2 Experimental

The experimentally obtained ionophore was as an oily liquid, displaying a brown-yellow hue, and was obtained with a yield of 74%. Confirmation of product formation was established through IR[33] (recorded on PerkinElmer Spectrum Version 10.4.00 and drawn using OriginPro), H-NMR (recorded on JEOL Delta2 NMR spectrometer), Mass spectrum[34] (recorded on TOF mass spectrometer) and Elemental Analysis (recorded on Thermo-Fisher element analyzer) (Fig. 5-8) Analysis of Vibrational frequencies, H-NMR peaks, mass fragmentations, and elemental percentages are given in Table 4.

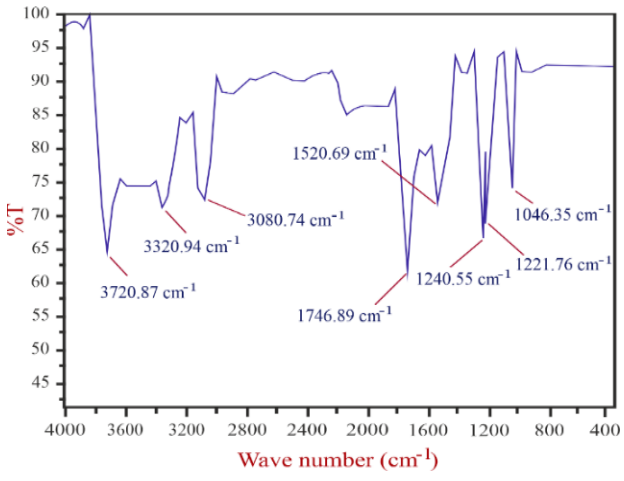


Fig. 5: IR spectrum of ionophore

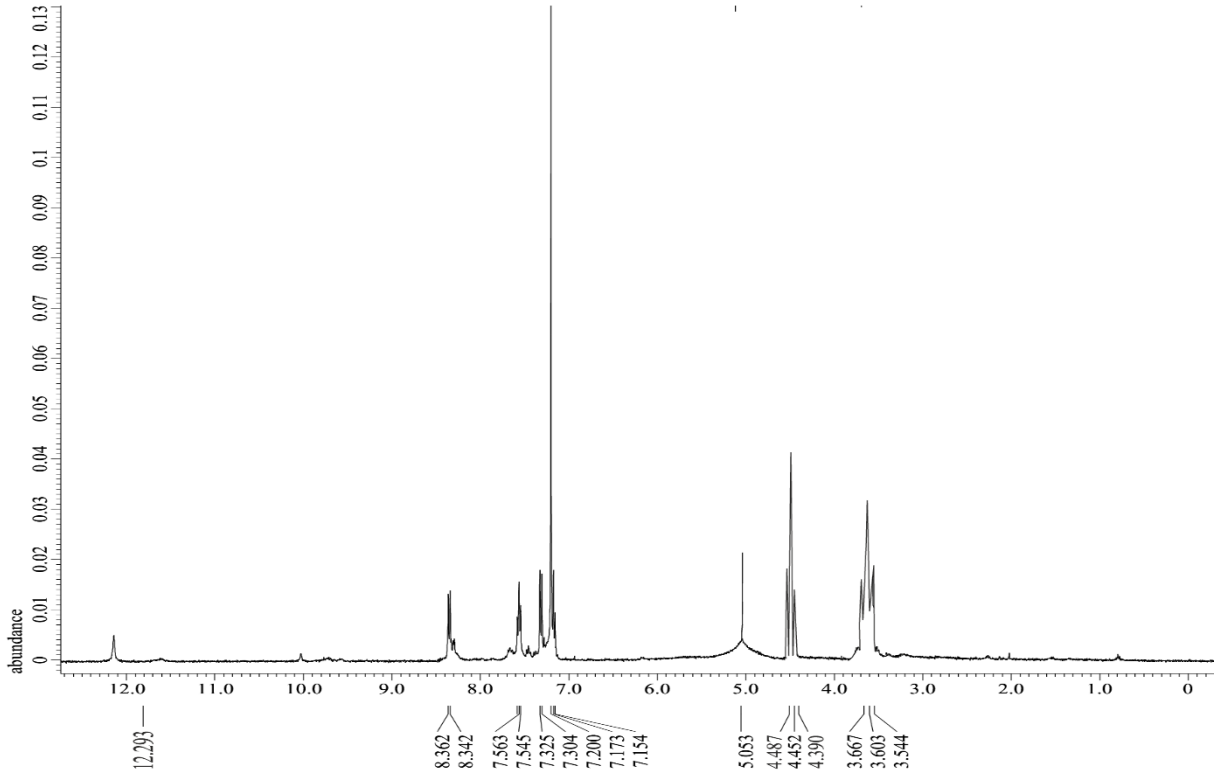


Fig. 6: ^{1}H-NMR spectrum of ionophore

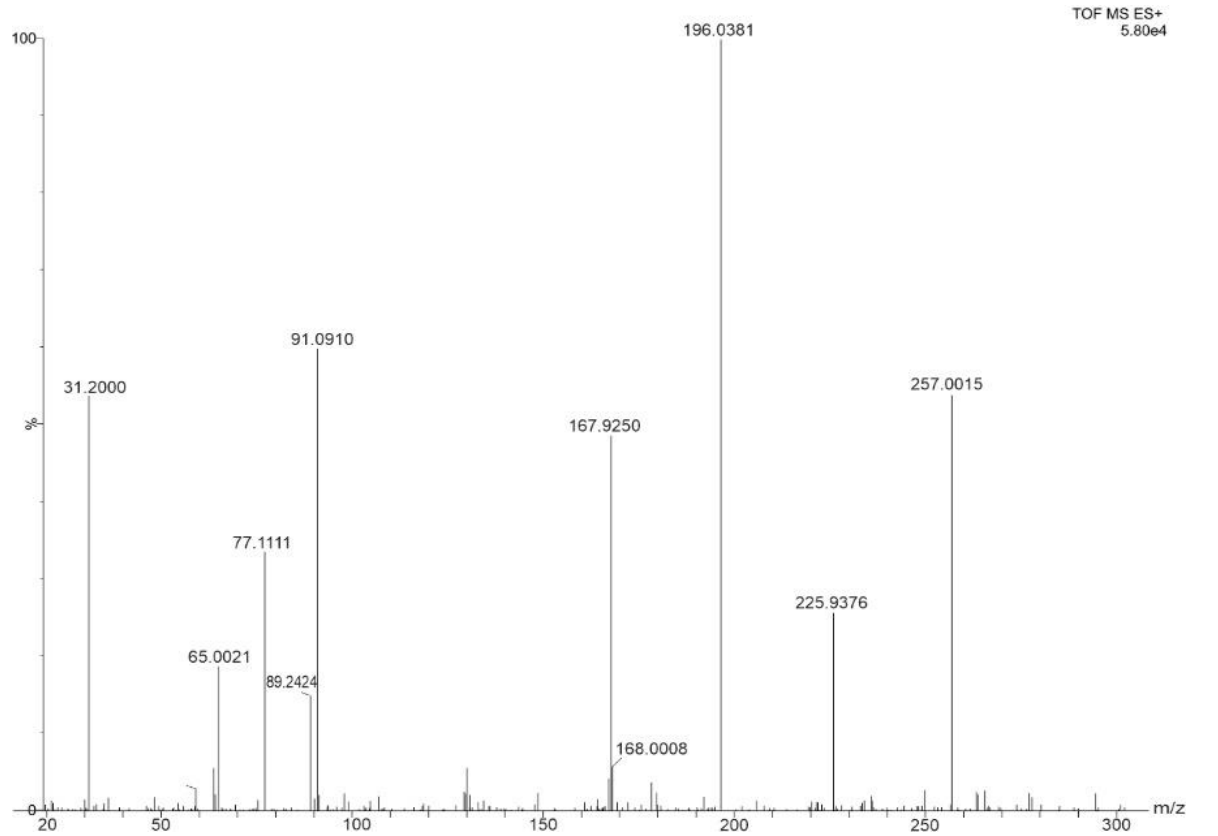
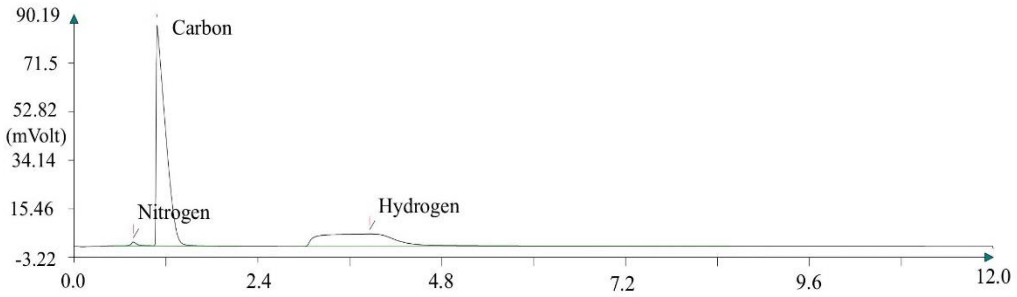


Fig. 7: Mass spectrum of ionophore



Peak Number (#)	Retention Time (min)	Area (.1* uV * sec)	Element %	Component Name
1	0.775	86055	05.346	Nitrogen
2	1.083	7136097	70.221	Carbon
3	3.858	5405822	05.646	Hydrogen
		13401974	81.213	

Fig. 8: Elemental analysis of ionophore

Table 4. Spectral and elemental analysis of the reported compound

IR frequencies (cm^{-1})	3720.87	3320.94	3080.74	1746.89	1520.69	1240.55	1221.76	1046.35
	free O-H	N-H	Ar C-H	C=O Ester	Ar C=C	C-C-O	C-N	O-C-C
^{1}H-NMR (δ)	12.293 (s, 1H, NH)	7.154-7.325 (m, 5H, ArH)		7.545-8.362 (m, 4H ArH)	5.053 (s, 1H, OH)	4.390-4.487 (t, 2H, CH_2)		3.544-3.667 (t, 2H, CH_2)
Mass	257.0015	225.9376	196.038	167.925	91.091	89.242	77.11	65.002	31.2
	M^+	M^+-31	M^+-61 (Base peak)	M^+-89	M^+-166	M^+-168	M^+-180	M^+-192	M^+-226
Elemental	Calculated (%)			Obtained (%)		
	C	H	N	C	H	N
	70.04	5.84	5.45	70.22	5.65	5.35

4.2.1 Effect of membrane

The extractability and selectivity of ionophore-metal complexes were investigated using different organic solvents for extraction. Notably, 1,2-dichloroethane proved to be the most effective organic phase for extracting metal ions (Fig. 9). The main property that influences the extraction is the highest dipole moment of $C_2H_4Cl_2$ (DCE). The polarity of 1,2-dichloroethane favors the dipole-ion interaction to bind the metal ion in the pseudo-cyclic cavity. Comparisons between DCE, chloroform, and carbon tetrachloride membranes revealed varying ion transport abilities: $C_2H_4Cl_2 > CHCl_3 > CCl_4$ (Fig. 10). This is also due to the higher dipole moment of DCE which solvates ions the best. In the presence of an aqueous metal salt solution, a fraction of $C_2H_4Cl_2$ forms 1,2-ethanediol, which acts as a supporting ionophore with the used non-cyclic ionophore. So, it enhances the transport of metal ions across the membrane towards the receiving phase than the other two membranes.

4.2.2 Effect of metal

A significant discovery in this investigation revealed that the ionophore is most efficient and sensitive for Ca^{2+} ions. The large charge density of Ca^{2+} ion over Na^+ and K^+ makes it suitable for extraction additionally moderate ionic radius and high tendency to distribute itself between two phases make it suitable for transport. High solvation of the small Na^+ ions reduces the attraction between lone pairs of the ionophore and the charge of the cation is the reason for its less extraction but high transport. The large size of K^+ ions makes it suitable more than Na^+ ions but less than Ca^{2+} ions for extraction furthermore its large size

hinders movement within the membrane resulting in the lowest transport efficiency among the three ions.

4.2.3 Effect of associated anion

The reason for choosing picrate salt of metal ions is the consistent charge delocalization due to the presence of three electron-withdrawing nitro groups in the picrate ring as well as high solubility in organic solvents which enables faster and more efficient mobility of the cation carrier complex and thus improving the extraction and transport efficiency of podand.

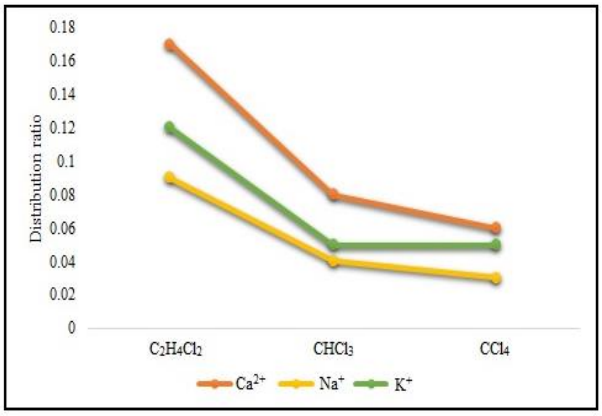


Fig. 9: Distribution ratio of metal ions

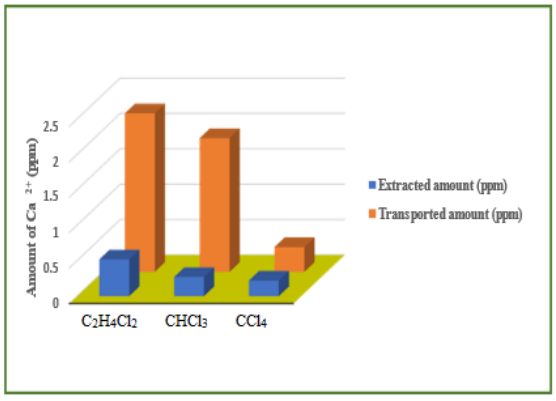


Fig. 10: Extracted and Transported amount of metal ions

Conclusions

The present study successfully established the design, synthesis, and functional characterization of a novel non-cyclic ionophore for Ca^{2+} extraction and transport. Computational modeling provided valuable insights into the molecule's stability and electronic structure, while experimental analysis confirmed its synthesis and revealed excellent extraction and transport capabilities. The solvent-dependent extraction and transport efficiency emphasize the importance of careful solvent selection for optimal performance. Ion sensing technologies utilize ionophores to selectively detect and quantify specific ions in various environments. Membrane-based separation processes rely on ionophores to facilitate the selective transport of ions across membranes, especially in the case of non-cyclic ionophores with enhanced selectivity and sensitivity. Environmental remediation efforts can benefit from the use of ionophores for the selective extraction and removal of harmful ions or pollutants from soil, water, and air. Energy harvesting technologies, such as ion-selective membranes in fuel cells and batteries, rely on the efficient transport of ions to generate electrical energy.

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