



Adamantane Os(II) dissolved redox probe as an efficient ion-to-electron transducer for voltammetric ionophore-based sensing

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ABSTRACT

We present the synthesis of a new adamantane derivative containing Os(II) centers and investigate its function as a dissolved redox mediator in thin-layer ion-selective membranes for voltammetric ion sensing. The pronounced lipophilicity of the designed compound, herein termed as adamantane Os(II), ensures exceptional compatibility with the thin-layer membrane and its constituents (cation exchanger, ionophore, plasticizer, polymer), presenting complete dissolution at elevated concentrations (160 mmol/kg), absence of leaching into the sample during membrane electrode polarization, and reversible electrochemical behavior. The electrochemistry of the adamantane Os(II) is thoroughly characterized in organic medium, with variations in the counter ions of the background electrolyte and 19 distinct membrane compositions, which include control compositions, various plasticizers (DOS, o-NPOE) and polymeric matrix (PVC, PU) as well as sodium ion ionophore. The membrane composition is refined considering three interrogation strategies (namely thin-layer, diffusion, and accumulation regimes) to quantify sodium ion concentrations across several ranges (from micromolar to millimolar) in environmental samples. The accuracy of the methodology was experimentally validated using ion chromatography as the gold standard, revealing a discrepancy of < 3 % between them. Furthermore, a comprehensive theory for ionophore-based thin-layer membranes is established and supplemented by relevant numerical simulations for the three operational modes; successfully, the empirical data align closely with the proposed theoretical hypothesis. The advancement of novel lipophilic and reversible metallic-based redox mediators may create new prospects for the detection of ions and biomolecules.

1. Introduction

Coupled electron and ion-transfer (ET-IT) processes have been investigated in multiple configurations for the last decades, as these reactions are present in catalysis, energy conversion, solar cells, water splitting, and others [1–3]. However, despite incommensurable effort into the understanding of the involved reactions, few analytical and sensing concepts have been developed making use of them. An interesting configuration is that involving ion-transfer processes between two immiscible liquids (organic/aqueous phases) triggered by a redox

reaction typically occurring at the organic phase [4–7]. In essence, the ion-transfer across the interface generates to compensate for the charge imbalance created in the organic phase. Such a process is typically reversible. The first evidence of such an active interface dates back to the late eighties: Anson and coworkers deposited a micrometer-sized drop of benzonitrile onto a graphite electrode aimed at determining the electron transfer of redox couples dissolved in layers of the organic solvent with thicknesses of about 30 μm. This allows them to determine the rate of the electron/charge transfer across liquid/liquid interfaces along with the formal transfer potentials of the analyzed compounds (cobalt

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tetraphenylporphyrin, decamethylferrocene and 1,1',3,3' tetrakis (2-methyl-2-hexyl)ferrocene) [8–10].

In subsequent years, various materials have been reported to drive a charge disbalance in membrane-based arrangements, resulting in an IT at the membrane-sample interface. To the best of our knowledge, redox active conducting polymers (CPs) like poly(3-octylthiophene) (POT) and poly(3,4-ethylenedioxythiophene) (PEDOT) were the first ones to be implemented for such a purpose. Amemiya and coworkers modified a gold electrode surface with a layer of POT and a membrane on top (3 – 4.5 μm of thickness) composed of a PVC and NPOE to detect heparin and perchlorate anions [11,12]. Later, Si et al. presented a configuration based on a thin-layer membrane (calculated thickness of 340 nm) containing a mixture of cation and anion exchanger backside contacted with an electropolymerized layer of POT. Notably, the obtained voltammograms revealed two peaks associated with the transfer of sodium and chloride ions at the membrane/aqueous interface [13]. With a more applied perspective, Cuartero et al. introduced the concept of multi-ionophore thin-layer membrane to detect various cations selectively within the same voltametric scan [14,15]. For example, three different ionophores were added to the same membrane (ca. 230 nm of thickness) to detect Li^+ , Na^+ , and K^+ concurrently in the same sample because of the charge disbalance created in the system upon the oxidation of the POT underlying the membrane. A voltammogram with three well-defined peaks was observed, with the associated potentials presenting a Nernstian behavior (i.e., the peak potential was increasing with the logarithmic concentration with a slope close to 59 mV/dec) in the mM concentration range.

Bond and coworkers proposed the use of organic salts directly dissolved in the membrane as redox probes [16]. Specifically, tetracyanoquinodimethane and ferrocene compounds were incorporated in a 1 μm -thick membrane adhered to a glassy carbon surface. As a result, voltammograms with Gaussian-shaped peaks were obtained for cations as K^+ , Na^+ and Ca^{2+} , with slight deviations from one-electron surface-confined process electrochemistry. In connection to thinner membranes (~ 300 nm), Bakker and coworkers introduced a family of cationic helicenes as redox probes dissolved in membranes containing either cation or anion exchanger to promote cation (Na^+) or anion (CO_3^{2-}) transfer, respectively, at the membrane-sample interface [17, 18]. An enhancement in the electrochemical performance of the peak compared to previously reported redox probes was claimed: e.g., narrower width at half maximum (110 mV vs 210 for POT) and lower peak separation (50 mV vs 110 for POT) were observed for Na^+ . Moreover, the revealed electrochemical behavior is consistent with theoretical predictions for a surface-confined mechanism in relation to the thin-layer membrane. Cuartero et al. reported on ferrocene derivatives dissolved in membranes [19]. However, the overall application is limited by the irreversibility of the redox chemistry due to formation of non-reducible Fc^+-Cl^- complexes in chloride-based electrolytes in the aqueous phase. Ferrocene monolayers generated on glassy carbon electrodes were also explored, overcoming some drawbacks reported for previous systems, such as leaching of the redox compound when dissolved in the membrane and chloride reactivity [20]. Notably, redox-active monolayers found interesting applications, e.g., the measurement of extracellular K^+ in living cells [21]. Overall, the search relies on elements capable of mediating the IT with the sample based on its ion-to-electron transducing properties, as they can be oxidized at the electrode surface and doped by adjacent ions ultimately involving the membrane-sample interface.

An interesting niche, which has not been fully explored yet, is the use of lipophilic metal-based complexes as dissolved redox mediators in thin-layer membrane configurations. Compared to the use of redox-active layers/films, this configuration has the advantage of involving only one step for the membrane preparation, with greater control of the available redox centers, being able to operate at different conditions of excess of either the redox probe or the doping element. In this direction, Jansod et al. investigated the behavior of dinonyl bipyridyl complexes of

Os(II)/Os(III) to drive the transfer of either cations or anions, resulting in a traditional Hofmeister selectivity [22]. Nevertheless, the use of ionophores seems not plausible due to the high amount that would be needed in the membrane once the optimal membrane composition is considered. Arrigan and co-workers proposed a ruthenium-based complex, i.e., bis-tridentate ruthenium-bipod complex [23]. Despite the membrane exhibiting voltametric responses close to Nernstian behavior for lipophilic anions such as PF_6^- and ClO_4^- , instability in peak currents was observed for less lipophilic anions such as NO_3^- . All in all, these studies reported transducers with recognized electrochemical performance in voltametric ISEs; however, demonstration of trustable applicability for real samples analysis lacks. Consequently, the necessity of moving from pure conceptual developments toward tangible applied options emerges. Effectively, new strategies towards the definite ion-to-electron transducer are needed, particularly demonstrating suitability for analytical applications.

In the present paper, we report on the synthesis of an osmium (II) derivative, being this new at the time of writing, as well as its investigation as an ion-to-electron transducer when confined in 200-nm-thick ion-selective membrane for voltammetric sensing. It is the osmium (II) tris[4,4'-bis (1-adamantanylmethyl)- 2,2'- bipyridine] compound, herein termed as adamantane Os(II). A systematic study based on the electrochemical behavior of the new compound in organic media, investigation of its role in thin-layer membranes of different compositions inducing cation and/or anion transfer, demonstration of selective Na^+ transfer and tuning of the range of response by promoting initial ion accumulation is performed. Moreover, the revealed electrochemical responses were confirmed with numerical solutions obtained by modeling the thin-layer ionophore-based membrane in COMSOL Multiphysics 6.2, providing interesting fundamental insights. Finally, the developed electrode was applied to quantify Na^+ across several concentration ranges (from micromolar to millimolar) in environmental samples. The accuracy of the methodology was experimentally validated using ion chromatography (IC). Beyond demonstrating the applicability of the developed sensor in complex real matrices, the detection of Na^+ in environmental scenarios (rivers, agricultural fields, aquifers) is known to be critical because its excess or deficiency can adversely affect biogeochemical processes associated with the growth and physiology of different kinds of living beings and elements [24].

2. Experimental section

2.1. Materials and equipment

Sodium chloride (NaCl), potassium chloride (KCl), tetrabutylammonium chloride (TBACl), tetrabutylammonium perchlorate (TBA-ClO_4), magnesium sulfate solution (MgSO_4), potassium osmate dihydrate ($\text{K}_2\text{O}_4\text{Os} \cdot 2 \text{H}_2\text{O}$), ammonium hexafluorophosphate (NH_4PF_6), tetrabutylammonium hexafluorophosphate (TBAPF_6), sodium tetrakis [3,5-bis(trifluoromethyl)phenyl]- borate (NaTFPB), acetonitrile (ACN), tetrahydrofuran (THF), sodium ionophore X (4-*tert*-Butylcalix[4]arene-tetraacetic acid tetraethyl ester), high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)sebacate (DOS), polyurethane (PU), 2-nitrophenyl octyl ether (NPOE), chloroform (CHCl_3), dichloromethane (DCM), methanol (MeOH), lithium diisopropylamide, 1-bromo-adamantane, ethyl acetate, acetone, ethylene glycol, and 4,4'-dimethyl-2,2'-dipyridyl were purchased from Sigma-Aldrich. Aqueous solutions were prepared with ultrapure water ($\sim 18.2 \text{ M}\Omega \text{ cm}$). Organic solutions were prepared by dissolving the osmium (II) tris[4,4'-bis (1-adamantanylmethyl)- 2,2'- bipyridine] hexafluorophosphate (for simplicity labeled as adamantane Os(II)) with several salts of different electrolytes (e.g., TBACl , TBAClO_4 , TBAPF_6 , and NaTFPB) in ACN (anhydrous, $>99.8\%$).

Glassy carbon electrodes (GCE, 6.1204.300 model) with a diameter of $3.00 \pm 0.05 \text{ mm}$, a single-junction Ag/AgCl reference electrode (3 mol L^{-1} KCl as the inner solution, 6.0726.100 model), and a platinum

electrode (6.0331.010 model) sourced from Metrohm were used in a three-electrode cell configuration for the electrochemical experiments. A rotating disk electrode device (Autolab RDE, Metrohm Autolab B.V.) was used to spin-coat the thin-layer membranes containing adamantane Os(II) on the GCE at 1500 rpm for 60 s. The ^1H NMR and ^{13}C NMR spectra of the compounds herein synthesized were acquired with a Bruker Ascend 400 NMR spectrometer. For HRMS, the corresponding samples were analyzed on an Acquity Ultra Performance Liquid Chromatograph (UPLC, Waters Corporations, MA, USA) coupled with a Waters Select Series cyclic ion mobility (CIM) mass spectrometer. Cyclic voltammograms were performed by an Autolab PGSTAT128N potentiostat (Metrohm Autolab B.V) controlled by Nova 2.10 software. Data analysis, plots, and figures were carried out using Matlab and CorelDRAW software.

2.2. Synthesis and characterization of the adamantane Os(II) compound

Synthesis of 4,4'-Bis(1-adamantantylmethyl)-2,2'-bipyridine. To achieve optimal lipophilicity of the osmium-based complex, a voluminous bis-adamantylmethyl-2,2'-bipyridine ligand was prepared. As shown in Fig. 1, a solution of 4,4'-dimethyl-2,2'-dipyridyl (0.5 g, 2.7 mmol, 1 equiv.) in dry THF (10 mL) was cooled to 0°C , followed by dropwise addition of lithium diisopropylamide solution (2 M in THF, 3.6 mL, 5.9 mmol, 2.2 equiv.). After stirring for 3 h at 0°C , a solution of 1-bromoadamantane (1.75 g, 8.1 mmol, 3 equiv.) in 5 mL THF was added dropwise, and the reaction was continued at reflux (70°C) overnight. The reaction mixture was quenched with brine and extracted with ethyl acetate. Collected organic fractions were combined, dried with MgSO_4 and evaporated to dryness. Crude product was purified by filtering through a short plug of neutral aluminum oxide (AcOEt/Hex 1:1, TLC: $R_f \sim 0.23$ in 1 % MeOH/DCM), then the collected yellow fraction was evaporated. The obtained off-white solid was washed with methanol and acetone to give pure 4,4'-Bis(1-adamantantylmethyl)-2,2'-bipyridine (II) in 20 % yield (0.200 g).

The protons of the bipyridine fragments appear on the spectrum as two doublets (8.55 and 8.15 ppm) and doublet of doublets signal at 7.03 ppm ($J = 4.9, 1.6$ Hz, 2 H) (Figure S1, top). Methylene protons appear as a singlet at 2.47 ppm, and adamantyl protons appear as a set of overlapping multiplets from 1.73 to 1.44 ppm. The number and position of the signals in the carbon ^{13}C NMR spectrum were fully consistent with the proposed structure (Figure S1, bottom). An analysis of the ligand product with high-resolution mass spectrometry (HRMS) showed a perfect match between the calculated mass (453.3264 g/mol) for $\text{C}_{32}\text{H}_{40}\text{N}_2$ ($[\text{M}^+\text{H}^+]$) and the observed mass (453.32666 g/mol). Data from the spectra: ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, $J^3 = 4.9$ Hz, 2 H), 8.15 (d, $J^4 = 1.6$ Hz, 2 H), 7.03 (dd, $J = 4.9, 1.6$ Hz, 2 H), 2.47 (s, 4 H), 1.94 (s, 6 H), 1.73–1.44 (m, 24 H). ^{13}C NMR (400 MHz, CDCl_3) δ 155.7, 148.5, 148.4, 126.1, 123.4, 50.9, 42.5, 37.0, 33.7, 28.7. HRMS (ESI-TOF) m/z calculated for $\text{C}_{32}\text{H}_{40}\text{N}_2$ ($[\text{M}^+\text{H}^+]$) was 453.3264; while the experimentally found was 453.3266.

Synthesis of osmium (II) tris[4,4'-bis (1-adamantantylmethyl)-2,2'-bipyridine] hexafluorophosphate. A mixture of 4,4'-bis (((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl)-2,2'-bipyridine (100 mg, 3.5 Eq, 221 μmol) and potassium osmate (VI) dihydrate (23.3 mg, 1 Eq, 63.1 μmol) was vigorously stirred in dry ethylene glycol (5 mL) under nitrogen at 195°C overnight. After cooling the reaction mixture, a solution of ammonium hexafluorophosphate (V) (51.4 mg, 5 Eq, 316 μmol) in 1 mL of deionized water was added, and the mixture was stirred for an additional 20 min. The reaction mixture was then diluted with 20 mL of ethyl acetate and extracted with 3×10 mL of water. The organic layer was evaporated to dryness on a rotary evaporator and then purified using chromatography (neutral alumina, $\text{CHCl}_3/\text{acetone}$ 50:1 to 10:1, TLC: $R_f = 0.16$ in 1 % MeOH/DCM). Solvent evaporation yielded the adamantane osmium (II) product (79 mg, 51 μmol , 81 %).

The ^1H and ^{13}C NMR spectra of the adamantane osmium (II) compound (Figure S2) were similar as that of the ligand (Figure S1), with the peaks of the complex strongly broadened and shifted. As a result of complexation, the signals of the protons near the bipyridine nitrogen are sharply shifted upfield (α - 7.51 ppm, marked with an orange circle on (Figure S2, top), and the methylene protons adjacent to bipyridine fragments become non-equivalent, leading to multiplet signals at 2.60 ppm. The ^{13}C NMR spectrum is consistent with the proposed structure (Figure S2, bottom). An analysis of the product m/z with HRMS showed a perfect match between the calculated mass (1548.9178 m/z) for $\text{C}_{96}\text{H}_{120}\text{N}_6\text{Os}^{2+}$ ($[\text{M}^{2+}]$) and the observed one (1548.9154 m/z) for the charged molecular ion and found agreement with the double-charged molecular ion $[\text{M}^{2+}]$ (calculated 774.4589 m/z , found 774.4590 m/z). Data from the spectra: ^1H NMR (400 MHz, CDCl_3) δ 7.89–7.85 (m, 6 H), 7.51 (d, $J^3 = 6.0$ Hz, 6 H), 7.14 (dd, $J = 6.0, 1.2$ Hz, 6 H), 2.66–2.54 (m, 12 H), 2.04–1.90 (m, 18 H), 1.71–1.62 (m, 18 H), 1.58–1.45 (m, 54 H). ^{13}C NMR (400 MHz, CDCl_3) δ 157.9, 149.6, 148.5, 130.8, 125.5, 50.5, 42.4, 36.8, 34.7, 28.6. HRMS (ESI-TOF) m/z calculated for $\text{C}_{96}\text{H}_{120}\text{N}_6\text{Os}^{2+}$ was 1548.9178 for ($[\text{M}^{2+}]$) and 774.4589 for ($[\text{M}^{2+}]$), while the experimentally found values were 1548.9154 and 774.4590 m/z , respectively.

2.3. Membrane compositions and preparation

Table 1 shows the compositions of 19 different membranes that were herein used. The corresponding membrane cocktails were prepared by dissolving each individual component in 1 mL of THF. For example, M2 contained 67 mmol adamantane Os(II) per kg of membrane, 296 mmol kg^{-1} of NaTFPB and a mixture of PVC/DOS in a ratio of 1:2. Notably, the amounts reported in table are an approximate average of the several membranes prepared to obtain the corresponding experiments. Thereafter, a dilution of each cocktail (50 μL in 250 μL of THF) was prepared. The diluted cocktail was ready to be deposited on the electrode surface: A volume of 25 μL of this was spin-coated on the surface of the GCE, resulting in a membrane thickness of around 250 nm, as demonstrated via ellipsometry experiments in previous

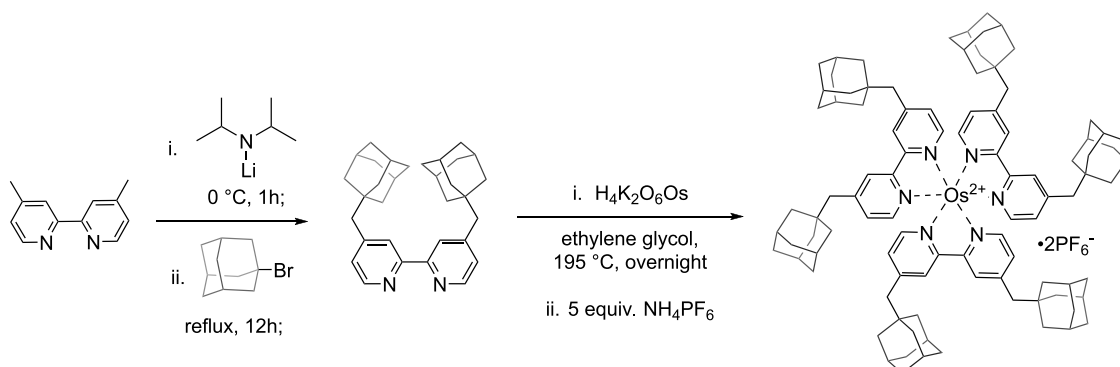


Fig. 1. Synthetic route developed for the preparation of the adamantane Os(II).

Table 1
Membrane compositions.

Membrane	Os(II) ^a	NaTFPB ^a	Ionophore ^a	Molar ratio	PVC ^b	PU ^b	DOS ^b	NPOE ^b
M1	75			75:0:0	29.4		58.8	
M2	67	296		1:4:0	21.1		42.2	
M3	67	150		1:2:0	24.8		49.5	
M4	30	296		1:10:0	23.0		46.0	
M5	20	296		1:15:0	23.5		47.0	
M6	10	296		1:30:0	24.0		48.0	
M7	10	100		1:10:0	29.9		59.7	
M8	10	90		1:9:0	30.2		60.3	
M9	10	80		1:8:0	30.5		60.9	
M10	10	70		1:7:0	30.8		61.5	
M11	10	50		1:5:0	31.9		63.7	
M12	10	40		1:4:0	31.6		63.3	
M13	10	50	50	1:5:5	29.6		59.1	
M14	10	50		1:5:0	29.6			59.1
M15	10	50	50	1:5:5	29.6			59.1
M16	10	50		1:5:0		29.6	59.1	
M17	10	50	50	1:5:5		29.6	59.1	
M18	10	50		1:5:0		29.6		59.1
M19	10	50	50	1:5:5		29.6		59.1

^a mmol kg⁻¹. ^b mass percentage.

papers [25].

All the membranes were prepared with NaTFPB as the cation exchanger, meaning that, before any contact with the sample solution, Na⁺ will be the only cation present in the membrane. Subsequently, upon interaction with the KCl solution (background electrolyte) at a comparatively high concentration (10 mM), K⁺ will completely substitute Na⁺ in the membrane. The time needed for such a phenomenon has been calculated to be in the order of milliseconds; hence, the electrode does not need any previous conditioning step. Later, when a calibration is performed at increasing Na⁺ concentrations, K⁺ is gradually exchanged in the membrane by Na⁺ entering from the solution. This mechanism has been already elucidated for analogous systems based on POT [26]. Regarding membranes M2–M10, the NaTFPB amount is unusually high, specially comparing with the traditional compositions used in potentiometry. However, such amounts were soluble in the THF cocktail, and we observe no evidence of a leaching when in contact with the sample solution, considering the timeframe of the conducted experiments.”

3. Results and discussion

3.1. Electrochemical characterization of the adamantane Os(II) redox probe

First, the electrochemical performance of the newly synthesized adamantane Os(II) was investigated in a typical polar aprotic organic solvent (ACN), using some representative doping anions such as PF₆⁻ and TFPB⁻. This latter was selected because it will be the anion present in the membrane-based experiments herein studied, i.e., NaTFPB is used as the cation exchanger. Fig. 2 shows the cyclic voltammograms obtained at 100 mV s⁻¹ for 1 mM adamantane Os(II) in ACN supplemented with (a) 100 mM TBAPF₆, and (b) 5 mM NaTFPB on a GCE electrode as a working electrode. The adamantane Os(II) was found to be oxidized to adamantane Os(III) in the anodic (or forward, f) scan, being reduced back in the cathodic sweep (backward, b). Moreover, the electrochemistry followed a Nernstian behavior associated with one electron transfer process (difference between the peak potentials, ΔE_{pp} ~ 60 mV). The charge ratio calculated as the area under the forward and backward peaks (Q_f/Q_b) was close to 1, indicated the electrochemistry reversibility and that both redox species were largely stable in the time window of the experiment.

To assess the stability of the redox system in more detail, five consecutive voltammograms were obtained (the first scan was always discarded, Fig. 2). As observed, there was no difference between the

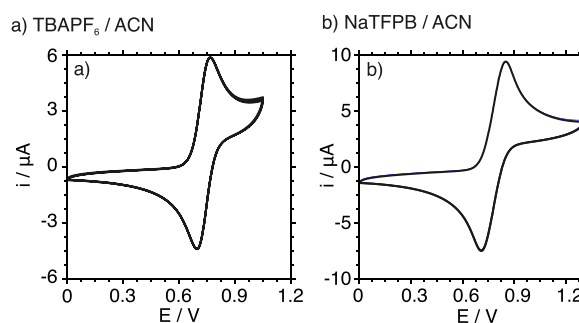


Fig. 2. Consecutive cyclic voltammograms (from the 2nd to 5th cycle) in a solution containing 1 mM adamantane Os(II) and (a) 100 mM TBAPF₆ or (b) 5 mM NaTFPB in ACN. Initial potential: 0 V, switching potential: 1.2 V, scan rate: 100 mV s⁻¹.

second and fifth scans, confirming the stability of the redox species as well as the repeatability of the electrochemical process. Notably, in previous works using other redox materials (e.g., helicene or ferrocene compounds)[18,19], it was reported that the nature of the counter anion (size, spatial conformation, lipophilicity) plays a key role in the modulation of the resulting electrochemical signal. Interestingly, when using 20 times less concentrated doping agent (5 mM TFPB⁻ vs. 100 mM PF₆⁻), the calculated charge was indeed three times larger. This suggested that TFPB⁻ enhance the number of moles that are electrochemically converted in the adamantane from Os(II) to Os(III) compared to PF₆⁻. Effectively, this is a key result to confirm a priori the adequate functioning of the adamantane Os(II) as an ion transfer redox mediator when incorporated in thin-layer membranes.

3.2. Membrane-based electrodes with adamantane Os(II)

The adamantane Os(II) was directly dissolved in the membrane cocktail, which was afterwards deposited on GCE electrodes as explained in the Experimental section. Preliminary experiments were performed using membranes M1, M2 and M3 formulated with three distinct concentration ratios of adamantane Os(II) with respect to NaTFPB in a PVC/DOS matrix. At such, M1 only contained adamantane Os(II), while M2 and M3 were prepared with quadruple and double the molar amount of TFPB⁻ respect to adamantane Os(II), respectively. Cyclic voltammetric experiments were conducted in 10 mM NaCl solutions, and the outcomes are shown in Fig. 3 together with the working

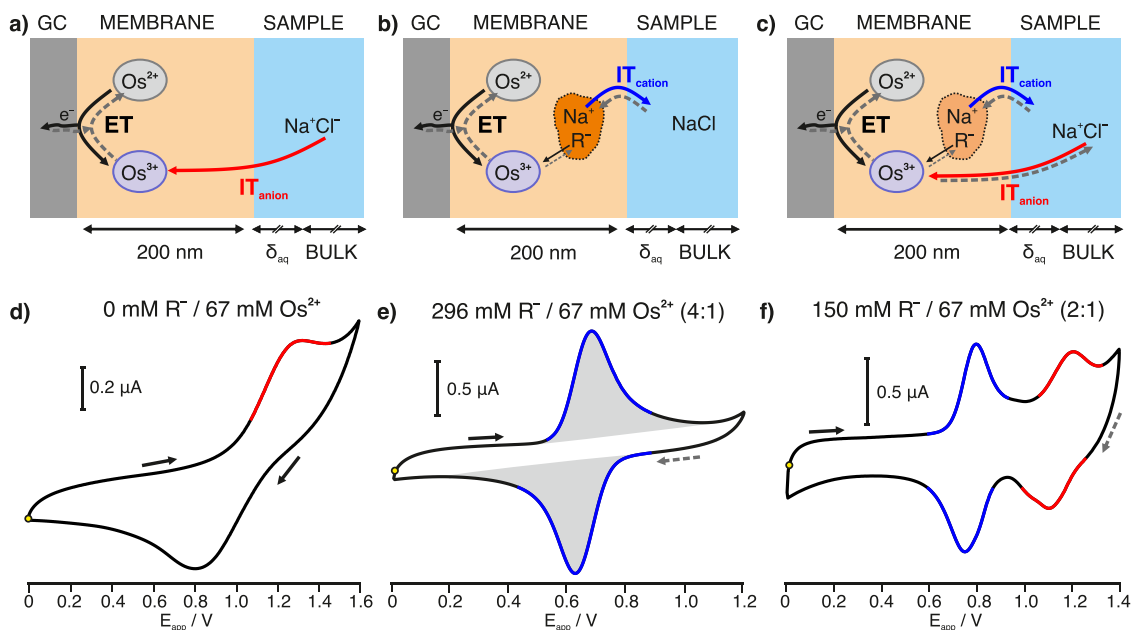


Fig. 3. Top: working mechanisms underlying the three membranes formulated with different adamantane Os(II) and NaTFPB ratios (in mmol kg⁻¹): (a) M1 (67:0), (b) M2 (67:296), and (c) M3 (67:150). Cyclic voltammograms in 10 mM NaCl for membranes (d) M1, (e) M2 and (f) M3. Scan rate = 100 mV s⁻¹; initial potential = 0 V; switching potential in the range of 1.2–1.6 V; end potential = 0 V. Arrows indicate the scanning direction.

mechanism that we hypothesized to occur in each case. In the positive scan direction, the adamantane Os(II) is oxidized to adamantane Os(III) creating a charge disbalance inside the membrane domain that is ultimately compensated by either Cl⁻ anions entering the membrane (Fig. 3a) from the aqueous solution, TFPB⁻ already present in the membrane (which is in turn coupled with the Na⁺ transfer from the membrane to the solution, Fig. 3b), or both (i.e., Os(III) doping with Cl⁻ and TFPB⁻, Fig. 3c).

In the absence of the cation exchanger NaTFPB (M1), the voltammogram revealed one peak in the forward and another in the backward scans: $E_{peak,f}$ 1.33 V and $E_{peak,b}$ 0.81 V (Fig. 3d). Focusing on the anodic scan, the adamantane Os(II) is oxidized at the surface of the GCE electrode via an electron transfer reaction (ET), and this process is coupled to a Cl⁻ transfer from the solution to the membrane (ion transfer, IT) to maintain the electroneutrality of the system. To unequivocally associate the observed peak to the Cl⁻ in the solution, its concentration was increased from 10 to 100 mM. A shift of the peak to less positive potentials (from 1.33 to 1.26 V) with increasing NaCl concentration in the bulk solution, the easiest (energetically speaking) is to incorporate the anion into the membrane (anodic scan) and vice versa, since its availability is locally (at the membrane-sample interface) facilitated. The related potential shift was ca. 64 mV, a bit higher to the Nernstian behavior expected when both the membrane and solution behaves with a thin layer effect. Effectively, this latter is expected at the concentration conditions used in our experiments, allowing the neglect of mass transport contribution in the solution. The resistance found in the voltammetric peak might be related to the absence of any cation exchanger in the membrane favoring its ionic conductivity.

By incorporating a TFPB⁻ amount four times larger in molar relation to the adamantane Os(II) in the membrane (M2), the voltammogram displayed a reversible wave with a Gaussian shape typical of thin layer conditions, half-wave width of ~150 mV, ΔE_{pp} ~ 60 mV and Q_f/Q_b ~ 1, revealing reversibility (Fig. 3e). Compared to M1, the anodic and cathodic peaks appeared at much lower potentials ($E_{peak,f}$ = 0.676 V, $E_{peak,b}$ = 0.615 V), being related to a cation transfer at the sample-membrane interface rather than an anion one. The overall process to compensate the charge generated in the conversion of Os(II) to Os(III) (anodic scan) is more thermodynamically favorable and hence, the

doping anion is not coming from the solution but directly from the anion present in the membrane (TFPB⁻). Accordingly, the accompanied cation (Na⁺) is transferred from the membrane to the solution. Such a transfer permits the system to entirely manifest a thin-layer behavior, with the ultimately produced IT at the membrane-sample interface not generating a significant resistance anymore (Na⁺ versus Cl⁻, M2 versus M1). Furthermore, the described mechanism is fully reversible (RSD < 3 % at both the peak current and charge over 50 consecutive scans).

Subsequently, the effect of reducing the TFPB⁻ amount in the membrane (ratio 2:1, membrane M3) was explored. Under this condition, two pairs of reversible voltammetric waves were obtained (Fig. 3f). These are likely assigned to cation ($E_{1/2}$ = 0.774 V) and anion ($E_{1/2}$ = 1.152 V) transfer processes when comparing the peak potentials with those observed in M2 and M1 respectively. Indeed, once the concentration of NaCl was increased 10-fold, a positive shift was observed for the first peak from 0.796 to 0.840 V; whereas a shift to lower potentials was found for the second one from 1.196 to 1.118 V (Fig. S4). This confirmed the respective character of cation and anion transfer. Furthermore, the waves were reproducible during consecutive scans and rather reversible, with the integrated charges from the anodic and cathodic peaks being significantly similar (<10 % of difference).

Overall, the results observed for membranes M1–M3 demonstrated the possibility of membrane tuning towards observation of either anion or cation transfer (red and blue portions of the voltammograms in Fig. 3) or even both, depending on the Os(II)/NaTFPB molar ratio. In further experiments, we focused on the optimization of the membrane composition towards isolated cation transfer voltammetric wave (M2, and M4–12, Table 1), reducing the peak width and making it selective to Na⁺. To achieve this latter, the optimization aimed at minimizing both the concentration of the adamantane Os(II) and TFPB⁻ in the membrane, serving to guarantee the adequate incorporation of a selective receptor, i.e., in a molar amount compatible with membrane solubility and minimizing its leaching (M13–M19).

Fig. 4a presents the voltammograms observed with membranes containing a fix amount of NaTFPB (296 mmol kg⁻¹) within the range of 10–67 mmol kg⁻¹ for adamantane Os(II). Specifically, the NaTFPB/Os(II) molar ratios were: 4:1 for M2, 10:1 for M4, 15:1 for M5, and 30:1 for M6. As observed, decreasing the adamantane Os(II) resulted in slight variations in the peak potential (e.g., 14.2 mV shift from M2 to M6)

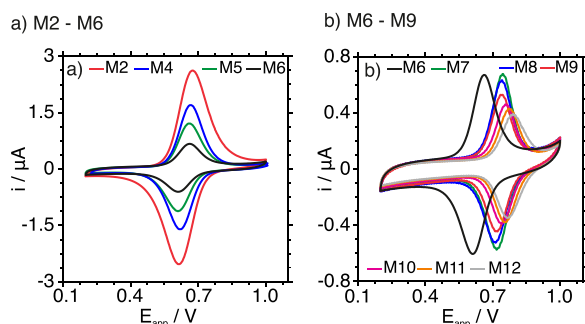


Fig. 4. (a) Cyclic voltammograms in 10 mM NaCl for membranes M2, M4, M5 and M6. (b) Cyclic voltammograms in 10 mM NaCl for membranes M6–12. Scan rate = 100 mV s^{-1} , initial potential = 0.2 V, switching potential = 1 V, end potential 0.2 V.

accompanied by a significant reduction in the peak current, and so the peak charge. For example, from M4 to M6, the relative current intensity in the anodic peak decreased by a factor of 3 (from $1.7 \mu A$ to $0.67 \mu A$). According to this trend, the NaTFPB is in excess with respect to the adamantane Os(II) in all these membranes, with a smaller molar amount being consumed as the Os(II) is decreased in the membrane. We did not further reduce the adamantane Os(II) amount to ensure a certain peak magnitude that allows for adequate electrochemical characterization and later analytical application.

Inspecting more in detail the electrochemistry of M6, containing the lower amount of adamantane Os(II) (10 mmol kg^{-1} membrane), an excellent reversibility was observed ($\Delta E_{pp} = 56.0 \text{ mV}$ and $I_{peak,f}/I_{peak,b} = 1.1$) with a narrower peak feature compared to M2 ($W_{1/2}$ of 123 mV vs. 152 mV). Thus, acknowledging the adequate performance of M6, we considered an Os(II) concentration of 10 mmol kg^{-1} to understand if the concentration of TFPB[−] may be reduced in the membrane, since it is in principle in excess. Fig. 4b shows the cyclic voltammograms of seven membrane compositions (from M6 to M12, Table 1) in which the TFPB[−] was gradually reduced from 296 mmol kg^{-1} to 40 mmol kg^{-1} , using a constant amount of adamantane Os(II) of 10 mmol kg^{-1} . Notably, even narrower $W_{1/2}$ values were observed when decreasing the amount of NaTFPB, reaching a minimum value of ca. 100 mV for M11 (50 mmol kg^{-1} of NaTFPB) and increasing a little bit for M12 (40 mmol kg^{-1} of NaTFPB). However, it was evidenced that the peak position shifted to more positive potentials, pointing out that the overall ET-IT process became less energetically favorable. The peak shifted in 81.6 mV from M6 to M7 and 127.8 mV to M12. On the other hand, the thin-layer behavior was confirmed to be maintained in membranes M6–M12 by the linearity found between the peak current and scan rate (Figure S5). Building upon these results, M11 showed a compromised feature among readable current intensity, redox potential, and content of components to be used; thereby, a composition comprising 50 mmol kg^{-1} of NaTFPB and 10 mmol kg^{-1} of the adamantane Os(II) was selected for the following investigations.

The fact that decreasing the NaTFPB amount from M6 to M8 did not drastically affect the peak current and charge, but it was from M9 that this trend was observed, may indicate that the TFPB[−] is initially invested in pairing the adamantane Os(II), therefore replacing the initial PF₆[−] counter anion. It is expected that PF₆[−] is coextracted to the sample phase in the form of NaPF₆, with the Na⁺ coming from the NaTFPB compound in the membrane. Thus, the effective NaTFPB moles available in the membrane from the doping process of the Os(III) are not affected as far as this is in excess (M6–M8) but then, it starts decreasing and so the Os(II) moles that are oxidized, manifested this in a decrease of the peak. Notably, the NaTFPB amount was not decrease further than that used in membrane M12 to guarantee a certain peak magnitude permitting adequate electrochemical characterization and later analytical application.

3.3. Study of ionophore-based membrane containing adamantane Os(II)

Sodium ionophore was incorporated in the formulation of the membranes aiming at a facilitated Na⁺ transfer at the membrane-sample interface. On one hand, an effect in the interfacial equilibrium is expected, since the ionophore presents a higher association constant for Na⁺ than for the rest of cations. On the other hand, a kinetic effect is also expected as modeled by previous theories about ion-ionophore interactions in plasticized polymeric membranes[27], decreasing the activation barrier for the interfacial transfer of Na⁺. A series of membranes in the absence and presence of sodium ionophore (M11, and M14–M19, see Table 1) were investigated. The polymer matrix and plasticizer used in the membranes were systematically varied (i.e., PVC-DOS, PVC-NPOE, PU-DOS, and PU-NPOE) to obtain an optimal configuration. Fig. 5 shows the cyclic voltammograms in 10 mM NaCl solution using membranes considering DOS/PVC and DOS/PU matrix (Figs. 5a, b) as well as o-NPOE/PVC and o-NPOE/PU (Figs. 5c, d).

In the absence of sodium ionophore, the peaks presented by DOS-based membranes (Fig. 5a) appeared at more positive peak potentials (0.781 V for PVC/DOS and 0.886 V for PU/DOS-based membranes) compared with those displayed by the NPOE-based membranes (Fig. 5c, 0.364 V for PVC/NPOE and 0.625 V for PU/NPOE). This indicated that the overall ET-IT process in DOS-based membranes scanned in the anodic direction was more energetically favorable compared with NPOE-based membranes, demonstrating that the plasticizer significantly influences the performance of the system. In particular, the plasticized polymeric matrix is expected to affect the mobility of ions within the membrane phase, influencing the doping of the oxidized Os(III) centers, which ultimately will affect the cation transfer at the membrane-sample interface since all the charge processes are interconnected in the system. Effectively, the chemical nature and inherent properties of the two plasticizers herein used are different. NPOE possesses a high dielectric constant (~ 14) due to its high polarity, attributed

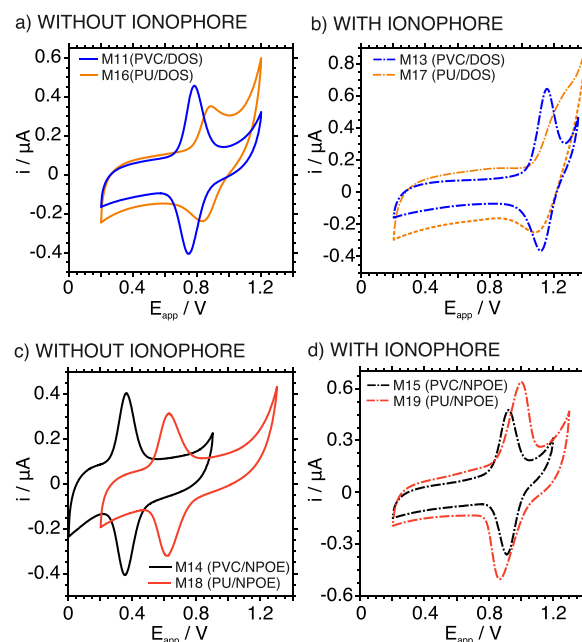


Fig. 5. Cyclic voltammograms in 10 mM NaCl for: (a) DOS-based membranes without sodium ionophore (M11 and M16); (b) DOS-based membranes with sodium ionophore (M13 and M17); (c) NPOE-based membranes without sodium ionophore (M14 and M18); (d) NPOE-based membranes with sodium ionophore (M15 and M19). All the membranes contained 10 mmol kg^{-1} adamantane Os(II) and 50 mmol kg^{-1} NaTFPB, in the absence or presence of 50 mmol kg^{-1} of the sodium ionophore. Scan rate = 100 mV s^{-1} , initial potential in the range of 0–0.2 V, switching potential = 1.2 V, end potential in the range of 0–0.2 V.

to the presence of the nitrophenyl group; whereas DOS has a considerably low dielectric constant (~ 6) due to its aliphatic structure and low polarity [28]. In our system, a higher dielectric constant improved the ion conductivity within the polymer matrix, thereby facilitating the membrane processes connected to the cation transfer at the membrane-sample interface and hence, enhancing in turn the overall electrochemical performance.

Also, the polymer was found to have an influence in the peak position and shape. The voltammograms obtained with PVC-based membranes exhibited slightly narrower peaks at more positive potentials than those obtained with PU-based membranes. Notably, plasticized PVC is known to be a polymer with free volume homogeneously distributed within the membrane phase. This structural feature enhances flexibility, improving the ionic mobility and the diffusion of dissolved species, such as the redox probe and cation exchanger [29]. Unlike PVC, PU is a polymer with a two-segmented structure consisting of soft and hard domains, which confer flexibility and stiffness, respectively. The plasticization effect in this polymer primarily enhances the soft domain, while having minimal impact on the hard one. This results in a heterogeneous organization of the polymer chains, with reduced ion mobility compared to plasticized PVC [30]. On the other hand, the PU favors other aspects, such as the membrane lifetime upon rinsing processes because of a cushioning leaching process of the membrane components [31].

Upon incorporation of the sodium ionophore, the anodic peaks shifted to more positive potential for all the membranes. For example, in M11 and M13 (PVC/DOS without and with the ionophore), the peak shifted from 0.780 V to 1.161 V respectively. This behavior was in principle expected, because a higher energy is required to release Na^+ from the membrane to the solution when it is complexed with its corresponding ionophore rather than when just ion paired with the TFPB $^-$. Among all membranes comprising the sodium ionophore (M13, M15, M17 and M19), the peaks obtained with NPOE-based membranes showed the narrowest peaks ($W_{1/2}$ of 103 mV for PVC/NPOE and 138 mV for PU/NPOE) compared with the DOS-based membranes (165 mV for PVC/DOS and 151 mV for PU/DOS). Notably, a sharper peak is indicative of a fast and reversible electron transfer process, with a theoretical $W_{1/2}$ value of 90 mV for a one-electron reversible redox reaction, as that expected in the oxidation of the adamantane Os(II). Furthermore, a sharper peak may enhance the resolution of the voltammetric electrode in view of an analytical application. Accordingly, we used NPOE-based membranes for subsequent analysis.

The operational robustness of the thin-layer membranes formulated with o-NPOE and either PVC or PU was investigated upon repetitive rinsing conditions. Figure S6 displays the voltammograms for M15 (PVC) and M19 (PU) in 10 mM NaCl solution before and after rinsing with ultrapure water. As observed, they remained rather constant for PU, presenting minimal differences (0.2 % in peak current, and 0.3 % in peak potential). However, less repeatability was obtained with PVC: current decrease of 10.3 % in the first rinsing but reaching a relatively constant value from the second rinsing onwards (0.5 % of deviation). Additionally, a slight shift in the peak potential (0.9 %) was found. The superior reversibility found for PU-based membranes likely originates from enhanced compound entrapment due to interactions between the cross-linked PU matrix and additional covalent bonds from amine functional groups [32,33]. Nevertheless, both polymers may be used for electroanalytical purposes at millimolar concentrations as far as the rinsing effect is appropriately considered in the experimental procedures. Overall, the operational lifetime of PU-based membranes was found to be at least 5 days, with the final lifetime strongly depending on the measurements story and how many times the electrode is rinsed.

3.4. Electroanalytical protocols for Na^+ within various concentration ranges

Having demonstrated the robust electrochemistry as well as the compatibility of the adamantane Os(II) among sodium ionophore,

plasticizers and polymeric matrices, we put forward diverse electroanalytical protocols to measure Na^+ at different concentration ranges, labeled as modes 1, 2 and 3. The experiments were conducted using either M15 or M19 (PVC or PU) containing a ratio of 1:5:5 (adamantane Os(II):TFPB $^-$: sodium ionophore). The PVC-based membrane could be used only in the case of millimolar concentrations of Na^+ (Mode I), since not very reproducible results between subsequent additions were observed in case of micromolar concentrations. Accordingly, M15 was selected for Mode I and M19 for Mode II and Mode III. Notably, stability issues may be found not only after rinsing but for continue usage, affecting the decrease of the signal more in the case of micromolar concentrations [34]. The experimental results (Fig. 6) are accompanied with the corresponding numerical simulations (Table S1, Figure S7, Figure S8 and Figure S9).

Using membrane M15 (PVC), cyclic voltammetry experiments were conducted at increasing NaCl concentrations ranging from 1 μM to

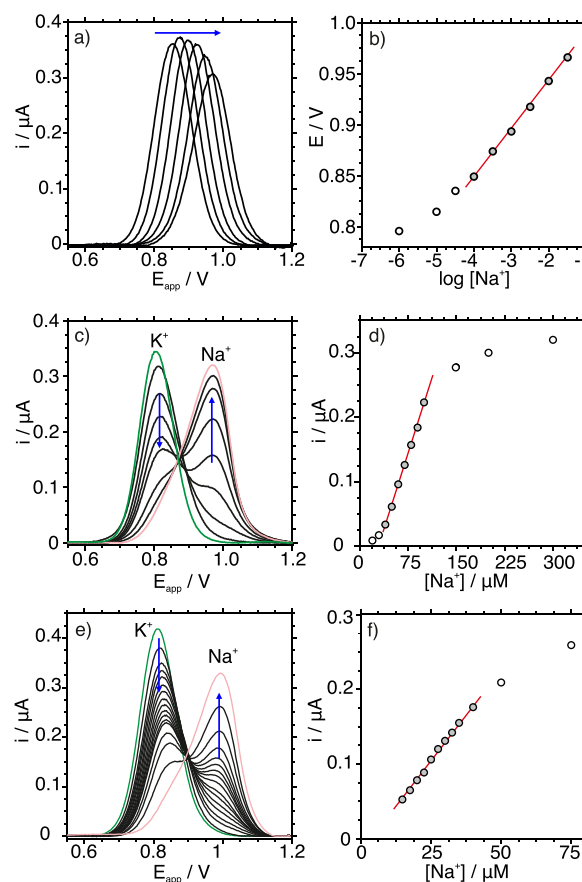


Fig. 6. Mode I: (a) Baseline-corrected voltammograms at increasing NaCl concentrations (from 1 μM to 10 mM) in 10 mM KCl background. Only voltammograms of those concentrations in the linear range of response are shown as a matter of clarity. Notably, the charge under the peak was maintained. Membrane=M15 (1:5:5 Os:NaTFPB:Ionophore molar ratio, PVC, NPOE). (b) Corresponding calibration curve considering the peak potential. Mode II: (c) Background-corrected voltammograms at increasing NaCl concentrations (from 10 to 300 μM) in 10 mM KCl background. Voltammograms of some concentrations are not shown as a matter of clarity. Membrane=M19 (1:5:5 Os:NaTFPB:Ionophore molar ratio, PU, NPOE). (d) Corresponding calibration curve using the peak current intensity. Mode III: (e) Background-corrected voltammograms at increasing NaCl concentrations (from 5 μM to 200 μM) in 10 mM KCl background. Voltammograms of some concentrations are not shown as a matter of clarity. Membrane=M19 (1:5:5 Os:NaTFPB:Ionophore molar ratio, PU, NPOE). (f) Corresponding calibration curve using the peak current intensity. The accumulation step ($E_{\text{app}} = 0$ V for 700 s, 400 rpm) was followed by the application of an anodic linear sweep potential from 0 to 1.2 V. Scan rate = 100 mV s^{-1} .

10 mM (considering a traditional response range observed for potentiometric ISEs) in 10 mM KCl as the background electrolyte (needed to ensure the conductivity of the voltammetric experiment regardless the cation analyte concentration). To ensure the homogeneity of the solution, the sample was stirred at 200 rpm for 30 s after each Na^+ addition. Immediately after turning down the stirring, the voltammetry experiment started. The protocol is herein called as Mode I. At the selected concentration range, the mass transport of Na^+ in the solution was sufficiently fast and did not limit the overall process. The corresponding voltammograms are shown in Fig. 6a. As the concentration of Na^+ increased, the voltammetric peak shifted to more positive potentials, showing a typical close-to-Nernstian response (Fig. 6b): a linear correlation was found between the peak potentials and the logarithmic Na^+ concentration from 0.1–100 mM ($E_{\text{PEAK}}(\text{mV}) = 58.3 * \log c_{\text{Na}^+}(\text{mM}) + 1050.66 \text{mV}$). While the linear fitting could be performed from the 10–5 M concentration, the best adjustment was obtained from 0.1 mM. In any case, this linear range is slightly narrower than that traditionally found for analogous potentiometric sensors based on the same Na^+ ionophore. We believe that this performance is a consequence of the use of a relatively high concentrated KCl background electrolyte.

Mode I works under a thin-layer regime so that the diffusional contribution of Na^+ at both the membrane and aqueous phases is not the rate-limiting step [17]. This was confirmed by the calculations, wherein a model comprising two distinct domains in one-dimensional system representing the membrane (200 nm) and the aqueous phase (3 mm) was simulated. Two interfacial points representing the electrode/membrane and membrane/aqueous interface were in turn defined. Then, a system of boundary conditions was defined for each domain in order to consider the transport of chemical species as finite and semi-infinite linear diffusion for the membrane and aqueous domain, respectively. The redox reaction of the adamantane Os(II) (electron transfer) is treated with the Nernst condition (fast kinetics), while the ion transfers of K^+ and Na^+ with a concentration dependent kinetics with Butler-Volmer equation (slow kinetic). Notably, the equation system needs to build the model are detailed in Section 3.6.

The simulated voltammograms for Mode I are presented in Figure S7a with the corresponding calibration graph in Figure S7b. A potential shift of the calculated gaussian peak is observed as the Na^+ concentration increases. The corresponding calibration curve shows a linear response, exhibiting a close-Nernstian slope of 54.9 mV/dec for the peak potential as a function of the logarithmic Na^+ concentration. Additionally, the width of the simulated peaks ($W_{1/2} = 119 \text{ mV}$) closely matched the experimentally obtained value ($W_{1/2} = 126 \text{ mV}$), confirming the deviation from the theoretical value (90 mV) because of the influence of the ion transfer in the electron transfer generated in the Os moieties.

Next, using membrane M19 with a similar membrane composition to M15 but using PU instead of PVC, the response at lower concentrations of Na^+ (from 10 to 300 μM) was explored. The experimental protocol is the same as in Mode I but at a lower concentration range, which creates a diffusion limiting process. Thereby, a new regime (Mode II) is established. Notably, the PU-based membrane (M19) is preferred under accumulation conditions (see Mode III) in order to preserve the membrane lifetime under long stirring conditions so that to ensure analytical precision along the entire calibration experiment. For a fully comparative situation, considering or not such an accumulation, PU (M19) was selected for Mode II as well, despite PVC (M15) being also suitable.

As observed in Fig. 6c, only one peak appeared for the 10 mM KCl background solution, which was ascribed to K^+ expelling from the membrane to the solution (green voltammogram). It is important to mention that all the Na^+ initially present in the membrane due to the cation exchanger is quickly replaced by the K^+ coming from the background solution, as previously demonstrated [25]. After adding Na^+ to the solution, the appearance of an unclear second wave was noticed at more positive potentials (ca. 1.00 V versus 0.81 V for the first peak). As binding with the ionophore made the expulsion of Na^+ from the

membrane less energetically favorable, a higher potential is needed for Na^+ transfer compared with K^+ . The total charge adding K^+ and Na^+ transfers did not change significantly for the different concentrations ($0.45 \pm 0.3 \mu\text{C}$), meaning the total available charge in the membrane is always divided into these two transfers. Moreover, the $W_{1/2}$ of the K^+ peak was $115.4 \pm 2.8 \text{ mV}$ for all the tested concentrations, and 130.5

$\pm 2.3 \text{ mV}$ for the Na^+ transfer. By a further increase of Na^+ in the sample, then a clear Na^+ peak was developed, reaching a scenario in which only one peak was distinguishable (pink voltammogram obtained at 300 μM of Na^+). Fig. 6d depicts the linear calibration curve for Na^+ ranging from 30 to 100 μM ($i_{\text{PEAK}}(\mu\text{A}) = 3.03 * 10^{-2} * c_{\text{Na}^+}(\mu\text{M}) + 0.065$).

The performed simulations shed light into the underlying working mechanism. Effectively, the initial replacement of Na^+ in the membrane by K^+ from the sample only containing the background electrolyte (KCl) is achieved by considering the initial concentration set by the corresponding ion exchange equilibrium at the membrane-sample interface. This is illustrated in Figures S8a–S8c, which depict the concentration profile within the membrane for K^+ , not-complexed Na^+ and ionophore-complexed Na^+ along the potential scan. Then, at low NaCl concentrations in the aqueous solution, the K^+ pre-fixed in the membrane by initial exchange is replaced by Na^+ . As NaCl concentration increases, this replacement increases until it becomes total, eventually leaving Na^+ as the sole compensating cation within the membrane, primarily in the ionophore-complexed form. Notably, the ionophore- Na^+ interaction is reversible and the related equilibrium fast enough to allow for its transfer at the membrane-sample interface when reaching the appropriate potential [35].

Figure S8d shows the electrochemical behavior calculated for Mode II and Figure S8e the corresponding calibration graph considering the peak current. Initially, there is a single peak associated with the K^+ transfer. A second peak appears as the Na^+ concentration is present and increases, indicating that the electrochemical response is controlled by the initial mass transfer of Na^+ mentioned above. The total charge from the simulated voltammograms did not change appreciably across different Na^+ concentrations, confirming that the ion transfer capacity of the system remains constant. This aligns with the voltammograms obtained at increasing NaCl concentrations ranging from 10 to 300 μM in 10 mM KCl background solution. Furthermore, being consistent with the experimental calibration curve, the simulation demonstrates a linear correlation between Na^+ concentration (in the range from 40 to 100 μM) and the current intensity of the Na^+ peak.

Finally, we run Mode III with membrane M19 at increasing Na^+ concentrations (from 5 μM to 200 μM) in 10 mM KCl background solution. An initial accumulation step ($E_{\text{app}} = 0 \text{ V}$, for 700 s, sample stirred at 400 rpm) to promote the accumulation of Na^+ from the solution to the membrane, followed by the application of an anodic linear sweep potential (from 0 to 1.2 V at a scan rate of 100 mV s^{-1}) was implemented. The accumulation step was aimed at enhancing the mass transport of Na^+ from the solution to the membrane-solution interface, and so to facilitate the ion-exchange equilibrium, while the application of 0 V was to ensure that all the adamantane Os(II) in the membrane was in its reduced state. Then, in the following stripping step (i.e., the anodic linear sweep), the adamantane Os(II) was oxidized, accompanied by the release of all the cation species (K^+ and Na^+ in distinct proportions) from the membrane to the solution.

Fig. 6e presents the observed voltammograms. In analogy to Mode II, first, the peak for K^+ appeared, followed by a second wave that developed at increasing Na^+ concentrations until a sole well-defined peak is identified at 15 μM . This concentration was significantly lower than that found in Mode II (150 μM) due to the accumulation step. Then, once more, the increase in the Na^+ peak current coincided with a decrease in the K^+ peak one, with the former exhibited excellent linearity for 15–40 μM Na^+ (Fig. 6f): $i_{\text{PEAK}}(\mu\text{A}) = 5.7 * c_{\text{Na}^+}(\mu\text{M}) + 0.1325$, $R^2 = 0.9974$. Regarding the theoretical simulation of this mode, the

accumulation step of Na^+ into the membrane was achieved by increasing the equilibrium constant related to the exchange between K^+ and Na^+ . Then, in analogy to Mode II, the simulated experiments for Mode III exhibit a peak for K^+ and the appearance of a second peak at higher potentials for Na^+ while the K^+ peak decreases due to increasing Na^+ concentrations in the sample (Figure S9a). The corresponding calibration curve (Figure S9b) showed linearity between the peak current and the Na^+ concentration in the range from 15 to 30 μM , lowering the limit of detection for Na^+ compared to Mode II. Comparing the overall simulations with the experimental results, it can be concluded that the established theory (Section 3.6) properly describes the Os(II) system herein developed.

The reversibility of the electrodes under Mode II and Mode III was evaluated in view of a potential analytical application. The voltammetric measurements were carried out alternating low and high Na^+ concentrations. The electrodes were rinsed with ultrapure water when changing the solution. As shown in Figure S10a, under Mode II, the cyclic voltammograms were obtained according to the following order: 50, 90, 50, 90, 50, and 90 μM NaCl in 10 mM KCl background solution. Negligible variations were found at both concentration levels in terms of peak current ($<1\%$) and peak potential ($<2\%$). Under Mode III (Figure S10b), the voltammograms were obtained by measuring the solutions with different Na^+ concentrations in the following order: 10, 20, 10, 20, 10, 20 μM . In analogy to Mode II, a significant overlap of the voltammograms was obtained for the same concentration levels (less than $<2\%$ RSD in peak current and position).

3.5. Analytical application in real environmental samples

To demonstrate the analytical implementation of the developed membrane electrode, we quantified the Na^+ content in different water samples (seawater, lake water and tap water) and a standard NaCl solution under Mode II and Mode III, since these two cover the expected levels of all the water samples when diluted. The measures were always conducted in 10 mM KCl as the background solution, ensuring an appropriate medium for the voltammetric measurement while performing the needed dilution. The accuracy of the analysis was validated by performing measurements with ion chromatography (IC), a reference technique for this purpose. Figs. 7a and b show the voltammograms and

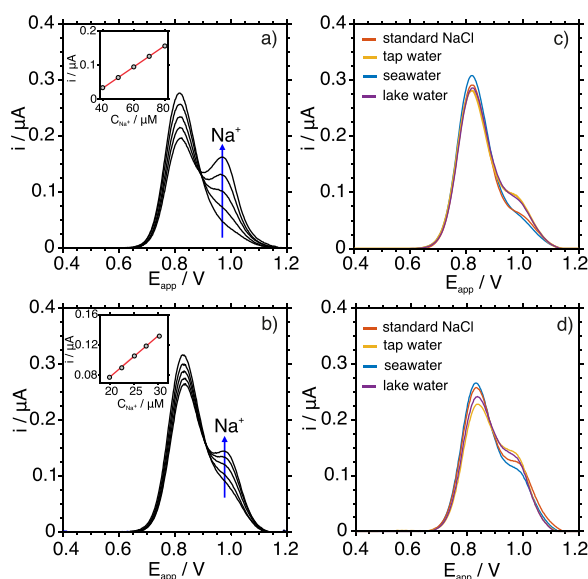


Fig. 7. Background-corrected voltammograms of: (a) Sodium calibrants (40, 50, 60, 70, 80 μM) used in Mode II. (b) Sodium calibrants (20, 22.5, 25, 27.5, 30 μM), used in Mode III. (c) Diluted water samples analyzed with Mode II. (d) Diluted water samples analyzed with Mode III.

the corresponding linear fitting of the peak current used as the external calibration curves for Mode II and Mode III respectively (K^+ peak ~ 0.80 V and Na^+ peak ~ 0.95 V); while Figs. 7c and d display voltammogram outputs randomly selected from the triplicates obtained for the four samples. The adequate separation between the two peaks revealed in the voltammograms allowed the determination of Na^+ in each of them by comparison with the preliminary calibration graph. In essence, the first peak corresponds to the transfer of all the cations present in the sample rather than Na^+ (the cation analyte), which will appear at a lower potential similar as that for the K^+ peak in the calibration experiments. Notably, POT-based electrodes revealed the same behavior when measuring in real samples[34]. All the quantitative results are listed in Table 2. Overall, the differences between IC and the electrodes were less than 4 %, demonstrating the excellent accuracy of the new all-solid-state concept.

3.6. Theoretical framework and simulations

The computational study was carried out using COMSOL Multiphysics 6.2. We set the simulation considering the surface of the working electrode (we), the membrane (m) and the aqueous phase (aq). Two domains were used to represent the membrane and aqueous phases (grid construction) in a one-dimensional space (x), see Figure S11. In addition, Table S1 depicts the abbreviation of each variable used in this section.

The processes illustrated in Fig. 3b are summarizing in the following set of equations (Eqs. 1–6). The electrochemical oxidation of the adamantane Os(II) compound at the electrode/membrane interface (electron transfer, ET with a formal reduction potential, E^0),



which is coupled with the Na^+ and K^+ transfers at the membrane/aqueous interface (ion transfer, IT)



For membranes formulated with sodium ionophore (L), Eq. 4 describes the binding process between Na^+ and the ionophore in the membrane, and k_1 and k_2 correspond to the kinetic constants of such a process.



The role of the anion counter part of the cation exchanger (R^-) is described by Eqs. 5 and 6.



where $\text{LNa}_{(m)}^+$ is the sodium cation complexed with the ionophore; $\text{LNaR}_{(m)}$ denotes the sodium-ionophore complex paired with the anion in the cation exchanger, while $\text{OsR}_{(m)}^{2+}$ refers to the adamantane Osmium (III) paired with the anion in the cation exchanger. Note that we considered formal first- and second-order kinetics to set out the Eqs. 4, 5 and 6, whereby k_3 , k_4 , k_5 and k_6 represent the corresponding kinetic constants.

Table 2

Sodium quantification in water samples (n = 3) and comparison of the results obtained with IC.

Sample	Membrane electrode ^a				IC ^b		(%) RE ^c	
	Mode II		Mode III		Dilution	c _{Na} ⁺ (μM)	Mode II-IC	Mode III-IC
	Dilution	c _{Na} ⁺ (μM)	Dilution	c _{Na} ⁺ (μM)				
Sea water	1:1000	47.18 ± 0.03	1:2000	23.80 ± 0.05	1:100	458.80 ± 0.74	2.81	3.70
	-	47,180 ± 30	-	44,600 ± 100	-	45,880 ± 74	-	-
Standard NaCl (1 mM)	1:20	50.72 ± 0.04	1:40	25.76 ± 0.10	-	-	2.10	3.71
	-	1014.4 ± 0.8	-	1030.4 ± 4.0	-	993.52 ± 0.46	-	-
Lake water	1:10	54.12 ± 0.15	1:20	28.43 ± 0.10	-	-	3.48	1.41
	-	541.2 ± 1.5	-	568.6 ± 2.0	-	560.71 ± 0.27	-	-
Tap water	1:10	58.04 ± 0.28	1:20	30.88 ± 0.11	-	-	2.49	3.78
	-	580.4 ± 2.8	-	617.6 ± 2.2	-	595.15 ± 0.75	-	-

^a Average±SD (n = 3 electrodes). ^b Average±SD (n = 3 measurements). ^c %RE = relative error

Subsequently, we calculate the concentration profiles of the participating species over time for both membrane and aqueous domains; thus, linear diffusion conditions were applied using the second Fick's law expanded with the corresponding kinetic terms for the aside reactions in the Eqs. 4–6 (see Eqs. 7–17). Furthermore, boundary conditions including initial conditions (Eqs. 18–19), interfacial conditions (Eqs. 20–26), bulk conditions (Eq. 27) and charge neutrality (Eq. 28) are necessary to solve the set of PDEs.

Domain 1: $0 \leq x \leq l$ (membrane, m)

$$\frac{\partial C_{Os^{2+}}}{\partial t} = D_{Os^{2+}} \frac{\partial^2 C_{Os^{2+}}}{\partial x^2} \quad (7)$$

$$\frac{\partial C_{Os^{3+}}}{\partial t} = D_{Os^{3+}} \frac{\partial^2 C_{Os^{3+}}}{\partial x^2} + k_6 C_{OsR^{2+}} - k_5 C_{Os^{3+}} C_{R^-} \quad (8)$$

$$\frac{\partial C_{Na^+}}{\partial t} = D_{Na^+} \frac{\partial^2 C_{Na^+}}{\partial x^2} + k_2 C_{LNa^+} - k_1 C_{Na^+} C_L + k_4 C_{LNaR} - k_3 C_{LNa^+} C_{R^-} \quad (9)$$

$$\frac{\partial C_{K^+}}{\partial t} = D_{K^+} \frac{\partial^2 C_{K^+}}{\partial x^2} \quad (10)$$

$$\frac{\partial C_{R^-}}{\partial t} = D_{R^-} \frac{\partial^2 C_{R^-}}{\partial x^2} - k_3 C_{LNa^+} C_{R^-} + k_4 C_{LNaR} + k_6 C_{OsR^{2+}} - k_5 C_{Os^{3+}} C_{R^-} \quad (11)$$

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial x^2} + k_2 C_{LNa^+} - k_1 C_L C_{Na^+} \quad (12)$$

$$\frac{\partial C_{LNa^+}}{\partial t} = D_{LNa^+} \frac{\partial^2 C_{LNa^+}}{\partial x^2} - k_2 C_{LNa^+} + k_1 C_{Na^+} C_L - k_3 C_{LNa^+} C_{R^-} + k_4 C_{LNaR} \quad (13)$$

$$\frac{\partial C_{LNaR}}{\partial t} = D_{LNaR} \frac{\partial^2 C_{LNaR}}{\partial x^2} - k_4 C_{LNaR} + k_3 C_{LNa^+} C_{R^-} \quad (14)$$

$$\frac{\partial C_{OsR^{2+}}}{\partial t} = D_{OsR^{2+}} \frac{\partial^2 C_{OsR^{2+}}}{\partial x^2} - k_6 C_{OsR^{2+}} + k_5 C_{Os^{3+}} C_{R^-} \quad (15)$$

Domain 2: $l \leq x \leq x_{max}$ (aqueous solution, aq)

$$\frac{\partial C_{Na^+}}{\partial t} = D_{Na^+} \frac{\partial^2 C_{Na^+}}{\partial x^2} \quad (16)$$

$$\frac{\partial C_{K^+}}{\partial t} = D_{K^+} \frac{\partial^2 C_{K^+}}{\partial x^2} \quad (17)$$

Eqs. 18 and 19 define that initial concentration of each specie at the beginning of the experiment correspond to the concentrations defined in input parameters of the model, which are in accordance with experimental data (see input parameters in table S1).

Boundary conditionsInitial condition: $t = 0$ Domain 1: $0 \leq x \leq l$

$$C_i(0, x) = C_i^* \left(i \equiv Os^{2+}, Os^{3+}, OsR^{2+}, R^-, L, Na_{(m)}^+, K_{(m)}^+, LNa, LNaR \right) \quad (18)$$

where the initial concentrations of $Na_{(m)}^+$, $K_{(m)}^+$, L and LNa^+ are set according to the ion-exchange equilibrium $LNa^+ + K_{aq}^+ \rightleftharpoons L + Na_{aq}^+ + K_m^+$ (Eqs. 2–4).

Domain 2: $l \leq x \leq x_{max}$

$$C_i(0, x) = C_i^* \left(i \equiv Na_{(aq)}^+, K_{(aq)}^+ \right) \quad (19)$$

The Nernst condition (Eq. 20) is applied to the redox reaction of Adamantane Os(II) (electron transfer) since it is considered a process kinetically favorable with a high current density exchange. Eq. 21 defines a condition of reversibility, stating that all Osmium(II) oxidize to form Osmium(III). On other hand, Eq. 22 states that these species do not react electrochemically at the interface working electrode / membrane.

Interfacial condition at $x = 0$ (we/m):

$$C_{Os^{3+}} = C_{Os^{2+}} e^{\frac{F}{RT} \left(E_{we/m} - E'_{Os^{2+}/Os^{3+}} \right)} \quad (20)$$

$$D_{Os^{2+}} \left(\frac{\partial C_{Os^{2+}}}{\partial x} \right)_{x=0} = -D_{Os^{3+}} \left(\frac{\partial C_{Os^{3+}}}{\partial x} \right)_{x=0} \quad (21)$$

$$D_i \left(\frac{\partial C_i}{\partial x} \right)_{x=0} = 0 \left(i \equiv OsR^{2+}, R^-, L, Na_{(m)}^+, K_{(m)}^+, LNa, LNaR \right) \quad (22)$$

In contrast to electron transfer, the ion transfer processes of sodium and potassium are considered the limiting process of the coupled transfer. Therefore, their kinetics are modeled using the Butler-Volmer formalism.

Interfacial condition at $x = l$ (m/aq):

$$D_{Na_{(m)}^+} \left(\frac{\partial C_{Na_{(m)}^+}}{\partial x} \right)_{x=l} = k_{Na^+}^0 e^{-\frac{0.5F}{RT} \left(\frac{E_m - \Delta\phi_{Na^+}'}{we} \right)} C_{Na_{(aq)}^+} - k_{Na^+}^0 e^{\frac{0.5F}{RT} \left(\frac{E_m - \Delta\phi_{Na^+}'}{we} \right)} C_{Na_{(m)}^+} \quad (23)$$

$$D_{K^+_{(m)}} \left(\frac{\partial C_{K^+_{(m)}}}{\partial x} \right)_{x=l} = k_{K^+}^0 e^{-\frac{0.5 F}{RT} \left(\frac{E_m - \Delta \phi_{K^+}^{0'}}{w_e} \right)} C_{K^+_{(aq)}} - k_{K^+}^0 e^{-\frac{0.5 F}{RT} \left(\frac{E_m - \Delta \phi_{K^+}^{0'}}{w_e} \right)} C_{K^+_{(m)}} \quad (24)$$

$$D_{i_{(m)}} \left(\frac{\partial C_{i_{(m)}}}{\partial x} \right)_{x=l} = D_{i_{(aq)}} \left(\frac{\partial C_{i_{(aq)}}}{\partial x} \right)_{x=l} \quad (i \equiv Na^+, K^+) \quad (25)$$

$$D_i \left(\frac{\partial C_i}{\partial x} \right)_{x=l} = 0 \quad (i \equiv Os^{2+}, Os^{3+}, OsR^{2+}, R^-, L, LNa, LNaR) \quad (26)$$

Bulk condition at $x = x_{\max}$: (Semi-infinite diffusion domain)

$$C_{i_{(aq)}} = C_{i_{(aq)}}^* \quad (i \equiv Na^+, K^+) \quad (27)$$

Charge neutrality (equal current across both interfaces):

$$D_{Os^{2+}} \left(\frac{\partial C_{Os^{2+}}}{\partial x} \right)_{x=0} = -D_{i_{(m)}} \left(\frac{\partial C_{i_{(m)}}}{\partial x} \right)_{x=l} \quad (i \equiv Na^+, K^+) \quad (28)$$

Ultimately, the current flow across the system (Eq. 29) may be computed from the concentration profiles and represented as a function of the applied potential and concentration of Na^+ in aqueous phase, yielding Figures S5-S7.

$$i = FAD_{Os^{2+}} \left(\frac{\partial C_{Os^{2+}}}{\partial x} \right)_{x=0} \quad (29)$$

4. Conclusions

We have demonstrated the redox capability of a newly synthesized adamantane Os(II) compound for its use in thin-layer voltammetry ionophore-based membranes. The adamantane Os(II) compound showed excellent redox features, being a promising candidate for sensing purposes when incorporated in voltammetric ISEs. Importantly, we have found experimental evidence of the interconnection between the oxidation-reduction of the Os(II) moieties and the ion transfer established at the membrane-sample interface. The resulting process is dependent on many variables, such as membrane composition and the concentration of the analyte in the sample, providing different analytical opportunities. To support the experimental findings, we have developed a theory considering the redox reaction of the adamantane osmium (II) at the interface of the electrode/membrane (electron transfer) coupled with the cation exchange at the membrane-aqueous interface (ion transfer) during the electrochemical interrogation. From the analytical point of view, we have quantified the Na^+ concentration from μM to mM levels in environmental samples, validating the proposed methodology with chromatography measurements. The selectivity of the sensor is adequate for the sample analysis as well as stability when using the PU-based membrane. Future work will be accomplished in the direction of multianalyte detection and the nanoconfinement of the dissolved adamantane Os(II) in nanopipettes for single-cell ion detection. Evidently, these directions expand the analytical application of the voltammetric ISEs reported until the time of writing.

CRedit authorship contribution statement

Eduardo Laborda: Writing – original draft, Supervision, Methodology, Investigation, Conceptualization. **Yujie Liu:** Methodology, Investigation. **Edward Zamudio:** Writing – review & editing, Writing – original draft, Visualization, Software, Investigation, Formal analysis. **Ziwei Fan:** Writing – original draft, Visualization, Methodology, Investigation. **Cuartero Maria:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Funding acquisition, Conceptualization. **Gastón A. Crespo:** Writing –

review & editing, Writing – original draft, Visualization, Supervision, Methodology, Investigation, Conceptualization. **Ruzal Sitdikov:** Methodology, Investigation. **Adam Tillo:** Methodology, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.snb.2025.138359](https://doi.org/10.1016/j.snb.2025.138359).

Data availability

Data will be made available on request.

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