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Perchlorate Solid-Contact Ion-Selective Electrode Based on Dodecabenzylbambus[6]uril

Petra Itterheimová [1,2], Johan Bobacka [3], Vladimír Šindelář [1,4] and Přemysl Lubal [1,*]

1   Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic; p.itterheimova@gmail.com (P.I.); sindelar@chemi.muni.cz (V.Š.)
2   Department of Bioanalytical Instrumentation, Institute of Analytical Chemistry, Czech Academy of Sciences, 602 00 Brno, Czech Republic
3   Laboratory of Molecular Science and Engineering, Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, 20500 Turku-Åbo, Finland; johan.bobacka@abo.fi
4   Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic
*   Correspondence: lubal@chemi.muni.cz; Tel.: +420-54949-5637

Abstract: Dodecabenzylbambus[6]uril (Bn12BU[6]) is an anion receptor that binds the perchlorate ion the most tightly (stability constant ~1010 M−1) of all anions due to the excellent match between the ion size in relation to the receptor cavity. This new bambusuril compound was used as an ionophore in the ion-selective membrane (ISM) to develop ion selective electrodes (ISEs) for determination of perchlorate concentration utilizing the poly(3,4-ethylenedioxythiophene) (PEDOT) polymer film as a solid-contact material. Variation of the content of Bn12BU[6] and tridodecylmethylammonium chloride (TDMACl) in the plasticized poly(vinyl chloride)-based ISM was also tested. All the prepared solid-contact ISEs and their analytical performance were characterized by potentiometry, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronopotentiometry. The ISEs showed rapid response and a sub-Nernstian slope (~57 mV/decade) during potentiometric measurements in perchlorate solutions in the concentration range from 10−1 to 10−6 M simultaneously with their high stability and sufficient selectivity to other common inorganic anions like bromide, chloride, nitrate and sulphate. The function of the ISE was further verified by analysis of real water samples (lake, sea, and mineral water), which gave accurate and precise results.

Keywords: bambus[6]uril; ion-selective electrode (ISE); anion chemosensor; perchlorate analysis

1. Introduction

The perchlorate anion can be found in nature in some geological repositories, e.g., as a supporting compound in nitrate mines in Chile, or as a (photo)product when the water disinfection is carried out with chlorine compounds leading to the perchlorate ion [1–7]. On the contrary, the anthropogenic origin of perchlorate could be from synthetic chemical compounds employed as solid propellants in fireworks, explosives, and pyrotechnic formulations [1–3], mostly in countries where munitions are produced [1] or with a history of war, e.g., Korea [5]. Another perchlorate source could be nitrate-based fertilizers containing traces of perchlorate [1,2] or some drugs utilized for the treatment of thyroid disorders [1]. This in vivo effect of perchlorate could be dangerous for people as perchlorate may inhibit the uptake of iodide to the thyroid gland [1]. Due to its high solubility in water and low reactivity with other components, the perchlorate anion is very mobile in aqueous systems [1–7]. In the last decades the environmental impact of perchlorate was studied in detail because it could be found in surface, ground waters or other biological sources, e.g., milk, fish, soils, fresh fruits, and vegetables [2–5,7], because of water/soil pollution [1–3]. The detailed knowledge about the perchlorate concentration, mostly in water samples and food products, is a very important key parameter. An upper concentration limit of

4 $\mu g \cdot L^{-1}$ (0.04 μM) was assigned by the Environmental Protection Agency (EPA) for drinking water. Perchlorate was detected at least once in 4.1% of community drinking water systems in half of federal states in the USA, with levels ranging from a minimum of 4 $\mu g \, L^{-1}$ (0.04 μM) to a maximum of 420 $\mu g \, L^{-1}$ (4.2 μM) [2,6]. Therefore, there is a need for new sensitive analytical approaches and techniques for perchlorate analysis, especially in complex matrices. Several analytical methods, mostly separation methods—chromatography [8–12], electromigration techniques [13–17], extraction [18,19], etc., combined with a sensitive detection solve this problem effectively. For instance, there are some methods using selective membranes employed for the separation of perchlorate from other anions in mixtures followed by X-ray fluorescence [20] and surface-enhanced Raman spectroscopy [21] or electrophoresis [17]. The most employed analytical method fitting the EPA requirements is ion-chromatography with conductivity or mass-spectrometry (MS) detection [8–12]. In the case of less complex samples, it is useful to apply MS instrumentation directly in order to get semiquantitative information [22–25]. The application of methods based on molecular spectroscopy, such as absorption, luminescence, Raman, etc., is rare due to the lack of chemosensors selective for the perchlorate anion in comparison with halides [12,26–30], while most papers utilize the formation of the ionic dye-perchlorate associates in less polar solvents. This can be combined with extraction of ionic associates from aqueous solution to an immiscible organic solvent or surfactants forming micelles (cloud-point extraction) [18,19,28]. This approach has several advantages because it enables the separation of perchlorate from other anions in mixtures as well as increases the perchlorate concentration by sample preconcentration. On the contrary, the formation of ionic associates with perchlorate anions can be hampered by other anions, (e.g., nitrate, iodide) which form associates of a similar stability [18,19,28]. Such ion associates (ion exchangers) are also employed in ion-selective electrodes (ISEs) [30–39]. Potentiometric determination of perchlorate concentration by ISEs is very popular [39–57] because it enables the determination of the concentration in a broad concentration range ($-\log [ClO_4^-] = 1$–5) with simple instrumentation. There are also some attempts to enlarge the concentration range by lowering the limit of detection (LOD) for the perchlorate ion using a special methodology [37–39] or selective receptors, e.g., calixarenes [54–56], macrocyclic ligands and their metal complexes [42–44,48,49,53]. In addition, miniaturized ISEs and ISFETs could be utilized for the determination of perchlorate concentration in on-line flow mode (e.g., chromatography [9], FIA [52]), when the ISE shows a fast response and a long lifetime.

Bambusurils are macrocyclic ligands which were first prepared in 2010 [58,59]. These new receptors with larger cavities are capable of forming supramolecular anionic complexes exhibiting high stability in aqueous solutions or organic solvents, while their solubility can be tuned by derivatization [58–72]. The trivial name (“*bambus-uril*” [58]) originates from the simple and cheap preparation of the parent macrocyclic scaffold from urea derivatives which consist of repeating “*glycoluril*” units (usually six, less commonly four) and the resulting bambusuril shows a chemical structure similar to a bamboo (see Figure 1a). In comparison to bambus[4]urils, the derivatives of bambus[6]urils are able to accommodate larger anions (up to 4.5 Å, e.g., perchlorate, iodide) due to a larger cavity. Bambus[6]urils also bind to smaller anions (e.g., chloride) [58]) but with lower affinity compared to the larger ones. It seems that this phenomenon is preserved for solvents of different polarities as a consequence of simultaneous enthalpic and entropic contributions [64,67]. Thus, this receptor shows the highest selectivity for the perchlorate anion, which is retained for various bambus[6]uril derivatives [64,67] in different solvents, and which is unique among anionic receptors [73–77]. This extraordinary property was used to propose an optical chemosensor for perchlorate analysis in water samples [19] and for the construction of highly selective tailor-made liquid electromembrane extraction of perchlorate in the presence of other anions followed by analysis using capillary zone electrophoresis (CZE) [17]. In addition, the multicomponent quantitative analysis of anions in a mixture (e.g., perchlorate, nitrate, bromide, iodide) was carried out by NMR spectroscopy using

slow time-scale phenomena [63]. Very recently, perchlorate complexation was found to enable stabilization of the Eu$_4$L$_4$ cage [71].

(**a**)

(**b**)

Figure 1. The chemical structure of dodecabenzylbambus[6]uril (Bn$_{12}$BU[6] = ionophore) (**a**) and poly(3,4-ethylenedioxythiophene) (PEDOT, conjugated polymer in its undoped form) (**b**).

Historically, there are several types of ISEs. Generally, the ISE consists of an ion-selective membrane (ISM) containing the ionophore responsible for the electrode's selectivity [31–36]. During the last decades, the internal filling solution of ISEs is often replaced by a solid internal contact, resulting in so called solid-contact ISEs [35,36,78]. Solid-contact materials based on conducting polymers (e.g., PEDOT—see Figure 1b, poly(aniline), poly(pyrrol), etc.) are conveniently made by electrodeposition-polymerization of the monomer on an electrode, such as glassy carbon (GC) [78–92]. It has also been shown that some conducting polymers, polymerized in the presence of different anions, can behave as ISMs for cations or anions [79,85,86].

The development of anion-selective electrodes is known to be challenging due to the high free energy of solvation of anions in water. This problem is addressed in this work by exploring a relatively new group of supramolecular anion receptor molecules with high selectivity towards perchlorate. Dodecabenzylbambus[6]uril (Bn12BU[6] = BBU) was evaluated as an ionophore for perchlorate in plasticized PVC-based ISMs using PEDOT as a solid contact (electrodeposited on GC). This preliminary study shows a good selectivity of this compound for perchlorate over other anions and some of the results presented here can be used for the construction of ISE with better analytical properties in future.

2. Materials and Methods

Chemical compounds of the highest purity employed in this paper were purchased from SIGMA-Aldrich and used as received. The 3,4-ethylenedioxythiophene (EDOT, 97%) was obtained from Bayer, AG. Distilled and deionized water (ELGA Purelab Ultra; resistivity 18.2 MΩ·cm) was used to prepare all solutions. Dodecabenzylbambus[6]uril (Bn12BU[6] = BBU, $C_{114}H_{108}O_{12}N_{24}$, CAS:1308315-95-8) was synthesized and its purity validated according to laboratory procedures described elsewhere [59]. Glassy carbon (GC) rods (3 mm diameter, SIGRADUR® G, HTW Hochtemperatur-Werkstoffe GmbH, Thierhaupten, Germany) were used as counter electrodes and to prepare GC disk working electrodes (ISE) with PVC shells (8.5-mm outer diameter), as shown in Figure 2.
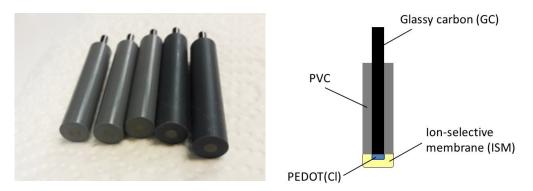

Figure 2. The disc electrodes based on the glassy-carbon (GC) material used for the preparation of the ISE (**left**). Scheme of the solid-contact ion-selective electrode (SC-ISE) employed in this paper (**right**).

Firstly, the working (GC) disc electrodes were polished using abrasive paper (P400, P600, P800, P1000, P1200, P2500, P4000), diamond paste (1 μM) and an aqueous suspension of alumina (0.3 μM) and then the electrodes were cleaned by ultrasonication in water for 15 min. Secondly, the surface of the GC-electrode was coated by a layer of conducting polymer (PEDOT) achieved by galvanostatic electropolymerization of the EDOT monomer (0.01 M EDOT + 0.10 M KCl solution bubbled by nitrogen for 15 min prior electrolysis) applying a constant current of 14 μA (0.2 mA·cm^{-2}) during 714 s, equal to a charge of 10 mC [79–84].

The ISM layer was prepared by pipetting 50 μL of the ISM cocktail (Table 1) in order to cover the whole PEDOT surface of the body of the electrode (Figure 2 right). After THF evaporation (about 15 min) this procedure was repeated once. The composition of the cocktail solution was varied (see Table 1) to study the effect of ionophore concentration on the ISE performance. The electrodes with ISM were left to dry overnight and then were used for potentiometric measurements or let in solution of anions (~0.01 M) for conditioning. The GC/PEDOT electrodes with and without ISM, immersed in 0.1 M NaClO$_4$, were characterized by CV, EIS and chronopotentiometry using an Autolab PGSTAT 20 potentiostat (Eco Chemie, Utrecht, The Netherlands). CV and EIS experiments were carried out in a nitrogen atmosphere in solutions bubbled by nitrogen for 15 min prior to measurements. The potentiometric response of newly prepared GC/PEDOT electrodes, with and without ISM, was measured on a multichannel mV-meter (EMF 16, Lawson Labs, Malvern, PA, USA) at laboratory temperature in the NaClO$_4$ concentration range of 10^{-1}–10^{-8} M. The potential reading of the ISE was taken after 5 min in each solution, using a double-junction reference electrode (Ag | AgCl | 3 M KCl || 1 M CH$_3$COOLi). The selectivity coefficients were determined by potentiometric measurements in 0.01 M solutions of potential interfering anions by the separate solution method (SSM) [35,82,83]. The EIS data were plotted as Nyquist plots and analyzed by using equivalent electrical circuits.

The activity of perchlorate was calculated using the extended Debye Huckel equation [35]. Natural waters of different origin in Finland (e.g., Littoinen Lake, the sea close to Vepsä Island) were analyzed by adding known amounts of perchlorate solutions. In

the case of mineral water (Värska), the sample was bubbled by nitrogen gas for 5 min to eliminate carbon dioxide and other dissolved gases before analysis.

Table 1. Cocktail compositions for ISM preparation (compounds were dissolved in 1.0 mL THF solution, the molar ratio TDMACl/Bn12BU[6] ~1.75).

Cocktail for ISM	Composition of Compounds in Membrane (ISM)/% (*m/m*)			
	Bn12BU[6] [a]	TDMACl [b]	DOS [c]	PVC [d]
1% BBU	1.0	0.5	65.2	33.3
2% BBU	2.0	1.0	64.2	32.8
3% BBU	3.0	1.5	63.2	32.3
0% BBU	—	0.6	66.0	33.4

[a] Bn12BU[6] = dodecabenzylbambus[6]uril (BBU), [b] TDMACl = tridodecylmethylammonium chloride, [c] DOS = bis(2-ethylhexyl)sebacate, [d] PVC = poly(vinylchloride).

3. Results and Discussion

3.1. Development of Perchlorate SC-ISE

PEDOT was selected as a solid-contact material due to its well-known electrochemical characteristics and its versatility for solid-contact ISEs [79–81,84,87–92]. PEDOT can be electrosynthesized from its monomer dissolved in aqueous solutions of various electrolytes. Electrolytes with large multivalent anions (e.g., poly(4-styrenesulphonate)—PSS) are known to give PEDOT cationic sensitivity (due to anions trapped in PEDOT), while electrolytes with small anions (e.g., KCl) results in PEDOT showing anion sensitivity (due to the positively charged backbone of PEDOT) [86,87]. Hence, for the perchlorate ISEs developed in this work, PEDOT was electro-synthesized on GC in a 0.1 M KCl electrolyte, resulting in GC/PEDOT(Cl) as a solid contact.

The potentiometric response of the GC/PEDOT(Cl) electrode to perchlorate is shown in Figure 3. Three replicates of GC/PEDOT(Cl) electrodes show identical potentiometric behavior, which is a proof of high reproducibility of the prepared PEDOT(Cl) polymer. The calculated slope of the calibration plot for GC/PEDOT is close to the Nernstian slope (*ca* $-58.3 \, \text{mV}/\log a(\text{ClO}_4^-)$) in the concentration range 10^{-5}–10^{-1} M (see Table 2—Electrode 1).
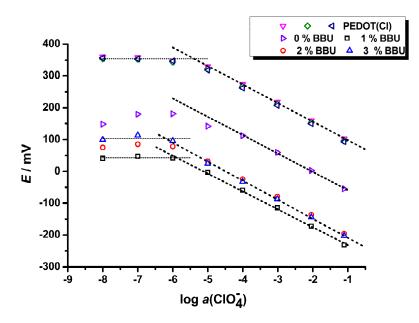

Figure 3. Calibration plots of GC/PEDOT(Cl) electrodes without ISM and with ISM containing TDMACl only and ISMs containing 1–3% BBU at a constant TDMACl/BBU ratio (Table 1). The potential of ISE with ISM containing TDMACl (0% BBU, violet triangles) were shifted with a constant value (+100 mV) for the sake of clarity.

EIS results for GC/PEDOT in 0.1 M NaClO$_4$ are shown in Figure S1. The electrical parameters (C_d, R_s—see Table 2) obtained from the equivalent circuit shown in Scheme S1 were determined from the Nyquist plots (Figure S1). As can be seen in Table 2, the capacitance values of GC/PEDOT in 0.1 M NaClO$_4$ obtained by EIS (C_d = 375 +/− 55 µF) agree with those obtained by CV (C_{CV} = 327 +/− 35 µF). The sum of the solution resistance and the ohmic resistance of GC/PEDOT is low (R_s = 183 +/− 11 Ω) in agreement with the high electronic and ionic conductivity of PEDOT. The obtained capacitance and resistance values are typical for PEDOT electrodes prepared with a charge of 10 mC [80,81]. These results show that GC/PEDOT is a proper solid-contact material for perchlorate ISEs and thus the GC/PEDOT electrodes were further coated with the ISM to obtain solid-contact ISEs.

The preparation of the ISM proved to be difficult due to the low solubility of BBU in organic solvents [59,64]. However, it is known that the solubility of BBU can be significantly improved in the presence of anions that form supramolecular complexes with BBU [64]. TDMACl was chosen because chloride forms stable supramolecular complexes with BBU and the tridodecylmethylammonium cation is capable of forming ion associates with anions. Furthermore, the {Cl$^-$@BBU} complexes are of lower stability than the {ClO$_4^-$@BBU} complexes [64], so that the Cl$^-$ initially present in the ISM can be exchanged with ClO$_4^-$. The addition of TDMACl in excess (the molar TDMACl/BBU ratio is ~1.75) improved the BBU solubility in THF to get homogenous ISM cocktails consisting of PVC, DOS, TDMACl and BBU, which could be drop cast on top of the GC/PEDOT electrode. After THF evaporation, the GC/PEDOT/ISM electrodes were characterized.

Unfortunately, decreasing the molar ratio of TDMACl/BBU to about 0.5 (which may be favorable for the ISE selectivity) led to a decrease in the BBU solubility to such an extent that it was not possible to use such a cocktail for the ISM preparation. Therefore, the molar ratio (TDMACl/BBU~1.75) for ISM preparation was kept, while the BBU content was varied between 1–3% (*m/m*) (see Table 1).

The solid-contact ISEs (GC/PEDOT/ISM) with different BBU content in the ISM exhibit a Nernstian slope (−56 to −60 mV/log a(ClO$_4^-$)) which is close to the theoretical value (Table 2—Electrodes 3–7). In addition, the limit of detection for the GC/PEDOT/ISMs with BBU is about 1 µM, which is *ca* two orders of magnitude lower than for the GC/PEDOT/ISMs without BBU and it is lower by *ca* one order of magnitude compared to the GC/PEDOT electrode (Figure 3). These results show that the presence of BBU in the ISM significantly extends the linear response range of the ISE to perchlorate.

Chronopotentiometric and EIS results for GC/PEDOT/ISM in 0.1 M NaClO$_4$ are shown in Figures S2–S4. The chronopotentiometric traces (Figures S2a–S4a) and impedance spectra (Figures S2b–S4b) are typical for solid-contact PVC-based ISEs [80,84,88,92]. The electrical parameters (R_b, C_g, C_L—see Scheme S2 [92]) obtained by EIS for ISEs containing the BBU ionophore in the ISM show a large contribution from the bulk resistance of the ISM (R_b~6–9 MΩ) in parallel with the geometric capacitance of the ISM (C_g~7.4–8.5 pF). The electrode resistance values obtained by chronopotentiometry (R~6–11 MΩ) agree well with R_b obtained by EIS. The capacitance values obtained by chronopotentiometry for the GC/PEDOT/ISM (C_L~14–92 µF), which originate from the redox capacitance of PEDOT, are smaller than for the GC/PEDOT electrode without ISM, in agreement with earlier observations [80].

As illustrated in Figure 4, the electrodes with ISM show a fast and stable potentiometric response in the concentration range 10^{-6}–10^{-1} M, while the GC/PEDOT electrode responds in a narrower range 10^{-5}–10^{-1} M, which was also observed elsewhere [84]. To elucidate the function of BBU as an ionophore, the ISM containing only TDMACl (Table 2—Electrode 2) was used for comparison because of the anion-exchange properties of TDMA$^+$. The calibration plots show that the Nernstian slope (~−57.7 mV/log a(ClO$_4^-$)) is valid for a narrow concentration region 10^{-4}–10^{-1} M (see Figure 3 and [84]) in comparison with ISM containing the BBU ionophore (Figure 3), which suggests the important role of the BBU receptor. The impact of BBU as an ionophore is important because it extends the linear response range from 10^{-4} M to 10^{-6} M (Figure 4).

Table 2. The characteristic electrical parameters of the ISM layer and metrological parameters of ISE.

Electrode	1	2	3	4	5	6	7
ISM	—	0% BBU	1% BBU	2% BBU	3% BBU	3% BBU [a]	2% BBU [b]
CV (GC/PEDOT(Cl))							
$C_{CV}/\mu F$	393	261	420	408	401	394	345
EIS (GC/PEDOT(Cl))							
R_s/Ω	184.5	204.3	177.3	178.9	178.5	171.0	186.2
$C_d/\mu F$	314.2	391.3	350.4	327.1	316.5	313.8	277.9
EIS (ISM)							
$R_b/M\Omega$	—	10.66	5.91	8.98	—	—	8.31
C_g/pF	—	7.44	8.50	8.41	—	—	8.19
ChP (ISM)							
$R/M\Omega$	—	10.7	5.95	9.20	6.91	6.97	8.50
$C_L/\mu F$	—	86.3	91.5	46.9	39.2	14.1	27.5
Slope							
mV/log $a(ClO_4^-)$	-58.3 ± 0.7	-57.7 ± 1.4	-56.2 ± 1.4	-56.3 ± 1.3	-59.9 ± 1.1	-57.3 ± 0.4	-57.1 ± 1.5
Conc. range							
$-\log a(ClO_4^-)$	5–1	4–1	6–1	6–1	6–1	6–1	6–1
Limit of detection							
μM	6.3	100	~1	~1	~1	~1	~1

[a] Conditioning solution—0.01 M $NaClO_4$, [b] used for analysis of real samples.
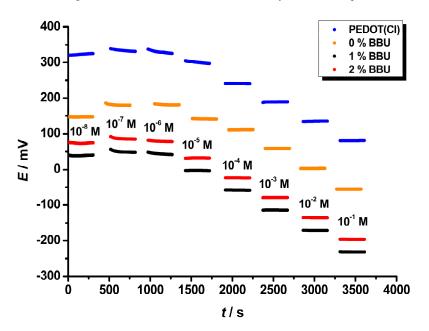

Figure 4. The time traces of electric potential for the GC/PEDOT electrode without ISM (blue) and the GC/PEDOT/ISM electrodes with ISMs containing 0% BBU (orange), 1% BBU (black), and 2% BBU (red), corresponding to electrodes 1–4 (Table 2). The potential of the ISE with ISM containing 0% BBU (orange) was shifted with constant value (+100 mV) for the sake of clarity.

3.2. Selectivity of Perchlorate SC-ISE

To elucidate the response mechanism of ISEs for the detection of perchlorate, the selectivity coefficients were estimated (see Figure 5). The content of BBU ionophore does not influence the values of selectivity coefficients. On the contrary, in comparison with GC/PEDOT electrode, the presence of BBU ionophore in ISM seems to be crucial due to the formation of strong supramolecular complexes with studied anions.

Concerning the values of selectivity coefficients for halides (Figure 5), there is a noticeable order ($Cl^- < Br^- < I^-$) for all studied ISEs. The GC/PEDOT electrode is

more selective for halides than for perchlorate, while the selectivity is retained for other anions (nitrate, sulphate) (Figure 5) [84]. On the contrary, electrodes with ISM effectively discriminates the halides (Figure 5) due to the formation of stable ionic {TDMA$^+$.X$^-$} associates in ISM. The results for the electrode with ISM containing TDMACl only are also in rough agreement with values of selectivity coefficients and the calibration plot for the concentration 10^{-4}–10^{-1} M region published elsewhere [84] where it was also demonstrated that this ISM is not practically redox sensitive. This fact is important for practical application in oxygen containing water samples. Adding the BBU ionophore to the ISM of the ISE, the selectivity retains (Figure 5). The selectivity of ISE with ISM towards sulphate, nitrate and chloride is also high (Figure 5), which is especially important for the analysis of mineral water samples. In addition, the nitrate anion is often an interfering anion for many perchlorate-ISEs described in literature [40–57].
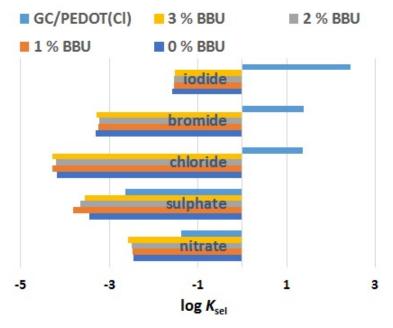

Figure 5. Selectivity coefficients for different anions related to perchlorate ISE (log K_{sel} (X$^-$/ClO$_4$$^-$)) with different content of BBU in the ISM.

To shed light on the exchange reaction mechanism of perchlorate-ISEs with BBU ionophore, the correlation of selectivity coefficients with equilibrium constants of the {X$^-$@BBU} complex was evaluated (Figure 6). To make a correlation with selectivity coefficients, the absolute values of the equilibrium constants of the {X$^-$@BBU} complex given in literature [64] were recalculated to get values relative to perchlorate (K_{rel}). Due to the low solubility of BBU in some organic solvents, the set of stability constants measured in chloroform to prepare solutions in mM concentrations [64] has been used. In addition, chloroform as a solvent of low polarity is like a solid lipophilic phase. Firstly, the log-log correlation gives the following equation (Figure 6):
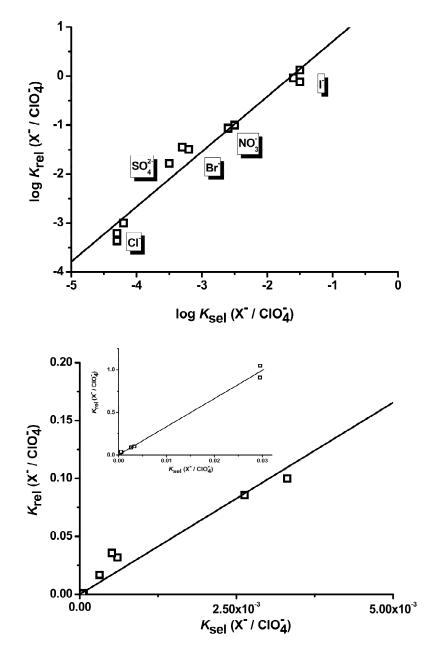
$$\log K_{rel} \ (X^-/ClO_4^-) = 1.12(8) \times (\log K_{sel} \ (X^-/ClO_4^-) + 1.8(2) \tag{1}$$

The term corresponding to the intercept in Equation (1) represents the energetic contribution (ΔG°) related to the anion transfer: X$^-$(aq) $\rightarrow$ X$^-$(s). Since the slope is close to unity within the uncertainty of calculation, the normal correlation (Figure 6) was also obtained:

$$K_{rel} \ (X^-/ClO_4^-) = 33.1(8) \times K_{sel} \ (X^-/ClO_4^-) \tag{2}$$

and the new equation in reverse form

$$K_{sel} \ (X^-/ClO_4^-) = 0.030(1) \times K_{rel} \ (X^-/ClO_4^-) \tag{3}$$

Thus, the slope 0.03 in Equation (3) is related to lower activities of all species present in the ISM.

Figure 6. Linear free energy relationship (LFER) plots: $\log K_{rel}$ (X^-/ClO_4^-) = 1.12(8) × ($\log K_{sel}$ (X^-/ClO_4^-) + 1.8(2) (**up**); K_{rel} (X^-/ClO_4^-) = 33.1(8) × K_{sel} (X^-/ClO_4^-) (**down**). The experimental data of equilibrium constants for various anions were taken from literature [64].

The following exchange reaction can be postulated supposing that the TDMA$^+$.{Cl$^-$@BBU} ionic associate is soluble in the ISM:

$$ClO_4^- \text{ (aq)} + TDMA^+.\{Cl^-@BBU\} \text{ (s)} \Leftrightarrow Cl^- \text{ (aq)} + TDMA^+.\{ ClO_4^- @BBU\} \text{ (s)} \quad K_{extr,perchlorate} \qquad (4)$$

The formation of this complex is highly probable because the analogous supramolecular {Lucigenin^{2+}.2ClO$_4^-$@BBU} complex formed in dichloromethane, a solvent of low polarity, has been already described [19]. From the thermodynamic point of view, the previous reaction is more preferred than the following exchange reaction:

$$ClO_4^- \text{ (aq)} + TDMA^+.Cl^- \text{ (s)} \Leftrightarrow Cl^- \text{ (aq)} + TDMA^+.ClO_4^- \text{ (s)} \qquad (5)$$

The chemical Equation (4) could be defined in general form

$$X^- \text{ (aq)} + TDMA^+.\{Cl^-@BBU\} \text{ (s)} \Leftrightarrow Cl^- \text{ (aq)} + TDMA^+.\{X^-@BBU\} \text{ (s)} \quad K_{extr,X-} \quad (6)$$

Assuming that the stability constants of supramolecular complexes $\{X^-@BBU\}$ measured in chloroform are proportionally lower in the ISM, and the validity of the equation ($K_{sel} = K_{extr,X-}/K_{extr,perchlorate}$), then the above-obtained linear free energy relationship (LFER) correlation can be obtained.

$$K_{sel} \text{ } (X^-/ClO_4^-) = a \times [K \text{ } (X^-@BBU)/K \text{ } (ClO_4^-@BBU)] \quad (7)$$

This correlation is a proof that the stability of supramolecular complexes is probably a very important factor determining the selectivity of perchlorate-ISE towards other anions. The increase of solubility of the BBU ionophore can also be explained by formation of stable $\{Cl^-@BBU\}$ supramolecular complex:

$$TDMACl(l) + BBU \text{ (l)} \Leftrightarrow TDMA^+.\{Cl^-@BBU\} \text{ (s)} \quad (8)$$

Equations (1) and (3) can be also utilized for the estimation of stability constant of the supramolecular $\{HCO_3^-@BBU\}$ complex. The value ($\log K_{sel} \text{ } (HCO_3^-/ClO_4^-) \sim -2$) is of the same order of magnitude as for nitrate (see Figure 6), which after substitution into Equation (1) leads to $\log K_{rel} \text{ } (HCO_3^-/ClO_4^-) \sim -2.2$, and then to the equilibrium constant $K(HCO_3^-@BBU) \sim 1 \times 10^8$. This value is two orders of magnitude higher than for chloride and this ratio ensures a highly efficient and selective transmembrane Cl^-/HCO_3^- exchange-antiport process [69,72]; however, this value is not available for acetonitrile due to low BBU solubility [69].

The opposite approach can be applied for the estimation of selectivity coefficients when all selectivity coefficients cannot be determined directly. Substituting the equilibrium constants measured in chloroform for F^-, CN^-, SCN^-, IO_4^- and acetate anions [64] into Equation (3), leads to the following estimated selectivity coefficients $\log K_{sel} \text{ } (X^-/ClO_4^-)$: -5.13, -4.52, -3.10, -4.34 and -5.58 for F^-, CN^-, SCN^-, IO_4^- and acetate anions, respectively. One can see that fluoride has the lowest value of all halides while thiocyanate, with a value comparable to bromide, is higher than cyanide and acetate. On the contrary, the periodate anion has a value three orders of magnitude lower than iodide. This knowledge could be used for masking of iodide by its oxidation with permanganate.

3.3. Analysis of Real Samples

The previous results are very important for the analysis of real samples because some water samples could contain some of these anions, e.g., bicarbonate, sulphate, chloride. The determined selectivity coeffiicents for these interfering ions are low for this perchlorate-ISE; therefore, it can be utilized for the sensitive and selective determination of perchlorate. The LOD of the ISE (~1.0 µM) is comparable with the value (~3.7 µM) found for spectrophotometric determination of perchlorate [19].

There are several critical points for practical long-term analysis of perchlorate in water samples, notably how to store the ISE carefully between measurements and the effect of interfering anions on the response of the ISE?

Firstly, the effect between ISEs prepared in different ways was studied. Electrodes 5 and 6 (see Table 2) exhibit the same metrological parameters, e.g., the Nernstian slope, LOD; however, the latter was conditioned in 0.01 M NaClO$_4$ overnight. The same behavior was described in the previous section. Because of similar properties of iodide and perchlorate, e.g., $\log K(I^-@BBU) \sim \log K(ClO_4^-@BBU)$ in chloroform [64], the ISE was also soaked in 0.01 M KI solution. As can be seen, the response of the ISE is the same, when the electrode was equilibrated in 0.01 M NaClO$_4$ (Figure 7a,b). Analogous experiments were carried out for the response of the ISE towards iodide (Figure 7c,d), when the electrode was soaked in 0.01 M solution of both salts. One can notice in both cases that the linear concentration

region of the calibration plot for iodide was narrower (compare Figure 7a,c and Figure 7b,d) for electrodes with and without ISM. It is interesting that the ISE based on the BBU ionophore can be employed for analysis of iodide in special cases when the perchlorate concentration is negligible. In the opposite case, the perchlorate analysis by ISE could be carried out for samples with low concentration of iodide. This is fulfilled usually for water samples which contain only trace concentrations of iodide. If the concentration becomes higher, there is a possibility of masking iodide by precipitating it as AgI via the addition of silver-nitrate or silver-sulphate solution. If the perchlorate-ISE is stored in 0.01 M NaBr solution, it leads to worse results (e.g., higher LOD, narrower concentration region) than in case when the electrode is soaked in 0.01 M NaClO$_4$ or NaI solution. In addition, this ISE could not be used for bromide and bicarbonate analysis due to its lower selectivity in comparison with perchlorate and iodide. Analogously, the presence of bicarbonate as an interfering anion in samples could be resolved by change of solution pH < 5.
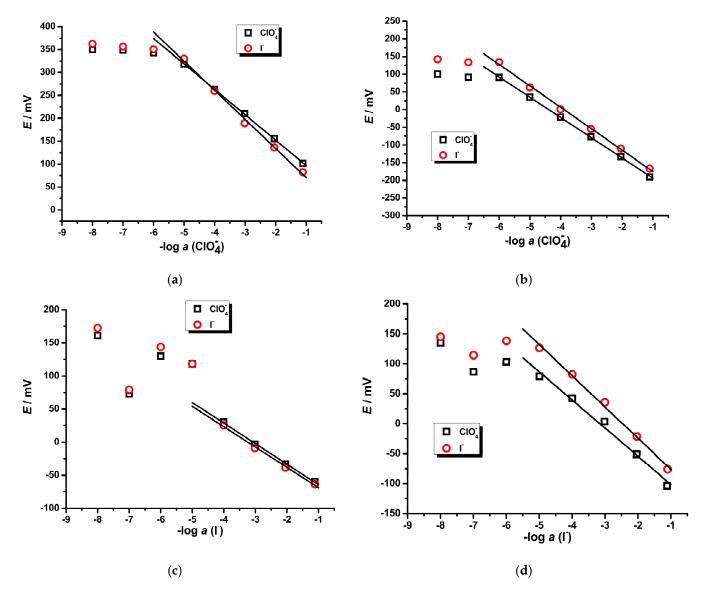

Figure 7. The calibration plot of perchlorate-ISE (**a,b**) or iodide-ISE (**c,d**) equilibrated in 0.01-M solution of anion (ClO$_4^-$/I$^-$): GC/PEDOT(Cl) electrode (**a,c**); GC/PEDOT(Cl)/ISM(3% BBU) (**b,d**).

In the last step, the perchlorate-ISE was evaluated for analysis of real samples (Table 3). Water samples of different origins were chosen to simulate the variation of concentration of different interfering ions which contribute to the total ionic strength of the solution.

Calibration plots were constructed for the concentration range 10^{-6}–10^{-4} M, while the spiked artificial samples (~20 µM) were prepared in the middle of this concentration range. The results show that the slope was close to the Nernstian one for water samples originating from the lake and underground. On the contrary, the lowest value was determined in the case of sea water, probably due to high chloride concentration in the Baltic Sea. The value of the Nernstian slope is reflected in the precision of ISE analysis of real samples, when the results are not loaded by any systematic error (see Table 3).

Table 3. Results of real samples analyzed by means of the perchlorate ISE (Table 2—Electrode 7).

Sample	Concentration of Perchlorate/µM			Slope/mV/$-\log c(\text{ClO}_4{}^-)$ [b]
	Added	Found	t_{exp} [a]	
Lake water	20.0	19.5 ± 0.6	1.44	55.1 ± 0.5
Mineral water	20.0	20.05 ± 0.05	1.73	58.5 ± 0.1
Sea water	20.0	16 ± 3	2.31	50 ± 2

[a] t_{tab} (2, 95%) = 4.30; [b] the calibration plot in concentration region 10^{-6}–10^{-4} M.

4. Conclusions

In this paper, it was demonstrated that the BBU anionic receptor could be successfully employed as an ionophore in the construction of ISEs which could be applied for fast determination of the perchlorate anion in various water samples in the concentration region 10^{-6}–10^{-1} M. The limit of detection of ISEs is comparable to values obtained for the extraction-spectrophotometric method using the lucigenin-BBU assay running in dichloromethane [19]. The electrode is selective for the perchlorate anion due to the formation of the stable supramolecular TDMA$^+$\{ClO$_4{}^-$@BBU\} complex. In addition, it was shown that the selectivity of the perchlorate-ISE is driven by stability of other supramolecular \{X$^-$@BBU\} complexes while the exchange reaction:

$$\text{ClO}_4{}^- \text{ (aq)} + \{\text{Cl}^-\text{@BBU}\} \text{ (s, ISM)} \Leftrightarrow \text{Cl}^- \text{ (s, ISM)} + \{\text{ClO}_4{}^- \text{@BBU}\} \text{ (s, ISM)} \quad (9)$$

is responsible for producing the analytical signal via the PEDOT ion-to-electron transducer. This new perchlorate-ISE exhibits the metrological parameters like other electrodes with ISM's concerning macrocycle-based ionophores (see Table 4).

The results presented in this contribution could be used for the improvement of the selectivity of perchlorate-ISEs using other ionophores based on BBU derivatives, by using information about the stability constants of supramolecular complexes measured in chloroform. This approach was also recently applied in the research of transmembrane transport [17]. This knowledge could be utilized for the optimization of perchlorate transport on the (s)-(aq) interface which leads to a decrease of LOD of the ISE [36–39]. The formation of the ionic colored \{Lucigenin^{2+}.2ClO$_4{}^-$@BBU\} associate can also be used for the construction of perchlorate-opt(r)ode. We hope that this paper opens doors for the development of new chemosensors based on the BBU ionophore selective for perchlorate and other anions.

Table 4. Comparison of the perchlorate-ISE's with ISM containing ionophore of macrocycle compound. The charges of ionophores are omitted for the sake of clarity.

Ionophore	Electrode Type	Conc. Range (M)	Detection Limit (μM)	Slope (mV·decade^{-1})	Ref.
Bambusuril	A	1×10^{-6}–1×10^{-1}	~1	-57.3 ± 0.4	This work
L^1	B	1.4×10^{-5}–1×10^{-1}	6.6	-57.3	[44]
L^2	B	1×10^{-5}–1×10^{-1}	5.4	-54.5	[44]
L^3	B	6.3×10^{-5}–1×10^{-1}	22	-70.2	[47]
	B	1×10^{-5}–1×10^{-1}	5.6	-55.0	[44]
L^4	A	1×10^{-6}–1×10^{-2}	0.8	-56	[40]
	C	6×10^{-7}–1×10^{-2}	0.3	54	[40]
L^5	B	1×10^{-6}–1×10^{-1}	0.5	-56.3	[56]
NiL^6	B	5×10^{-7}–1×10^{-1}	0.2	-59.3	[42]
ZnL^7	B	1.0×10^{-7}–1.0×10^{-2}	0.09	-59.3	[56]
CuL^1	B	7.9×10^{-5}–1.0×10^{-1}	13	-67.6	[47]

A—all solid-state PVC-membrane electrode, B—PVC-membrane electrode, C—ISE—CHEMFET; Ionophore: L^1—1,4,8,11-tetra(*n*-octyl)-1,4,8,11-tetraazacyclotetradecane, L^2—1,4,7,10,13-penta(*n*-octyl)-1,4,7,10,13-pentaaza-cyclopentadecane, L^3—1,4,7,10,13,16-hexa(*n*-octyl)-1,4,7,10,13,16-hexaazacyclooctadecane, L^4—7-phenyl-7-phospha-3,11-dithiabicyclo[l1,4,0]heptadeca-13(1),14,16-triene, L^5—calix[4]arene derivative, L^6—1,8-dibutyl-1,3,5,8,10,13-hexaazacyclotetradecane, L^7—1,5,8,12-tetra-azacyclotetradecane-6,13-diene derivative.

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