

Extraction of Alkali Ions Investigated by Conductometric and pH Measurements

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*Extraction of alkali ions from aqueous solutions of chlorides and hydroxides into a lipophilic liquid membrane composed of tetraethyl *p*-tert-butylcalix[4]arene tetraacetate (TBT) solution in hexane was investigated by means of measurements of changes in the electrolytic conductivity and pH-value of the aqueous solution. Hydrolysis of the TBT ionophore resulting in the release of the ethyl groups was proposed as the main reaction process, leading to disturbance of the known preference of TBT for sodium ions.*

Keywords: Extraction of alkali ions, calix[4]arenes, conductometric method.

1 Introduction

Analyses of the alkali ion contents in aqueous solutions are attracting considerable attention nowadays within the community of sensor developers. Information about instant, selective concentrations of Na⁺, K⁺, Mg²⁺ and Ca²⁺ ions has considerable relevance for assays of biological fluids, such as human and animal blood, sap, or, for instance, for tests of drinking water, underground water, water used in the food-processing industry, and waste water.

The most common method currently applied for alkali ion analysis is absorption or emission flame spectrophotometry. It enables selective determination of the ion concentration within the ppm range. The basic drawbacks of the method – high instrumentation and high labor costs – have stimulated the development of alternative sensing approaches based on electro-chemical and optical principles. The most important of the optical approaches, nowadays, are systems utilizing an intrinsic spectroscopic fibre optic scheme. The general physical principle for their operation employs interaction of the evanescent light field ('circling' the waveguide core and exponentially decaying along the external core normal) with the fibre cladding changing the spectral composition of the light propagating through the core, in response to diffusion of the target ions from the water phase surrounding the sensing fibre into the cladding bulk.

The cladding material (usually a polymer with a refractive index slightly lower than the core material) has to be properly sensitized to provide the desired optical absorption or fluorescence changes in the presence of the selected target ions [1]. One such sensitization method that is widely applied at present is based on enriching the cladding polymer with a carefully selected combination of an ionophore and an acid-base dye [2]. The ionophore molecules selectively create complex ions with the target ions, migrating into the cladding bulk from the water phase. The necessary condition of overall electric neutrality of the cladding material leads then to de-protonation of the dye molecules, resulting in a change in the optical absorption of the cladding. The alkalinity and lipophilicity of the dye has to be carefully tuned to get the sensing scheme working. The selectivity and reversibility of the complex ion formation is also very important. A broad range of ionophores have already been tested with the aim to optimize the latter properties, such as crown-ethers, cryptands, calix[n]arenes (n = 4, 5 or 6), validomycin derivatives, and calix-crowns [3]. Within the ionophore fam-

ily, calix[n]arenes provide an extremely flexible construction base due to their combination of stereo and electro-chemical ionic affinity [2].

The aim of the research presented here is to investigate the behavior of a typical calix[n]arene ionophore under the conditions of a restricted proton exchange between the tested aqueous solution and the sensing membrane, i.e., the case when the concentration of the proton donor is low compared to the ionophore concentration. From a practical point of view, such a situation can occur, e.g., in the vicinity of the cladding/water interface after the acidic-basic reagent has been partially washed out into the aqueous phase. A liquid, lipophilic membrane (hexane in our case) containing the dissolved ionophore has been used throughout the experiments to simplify the experimental conditions. It has already been proved that such an arrangement can be used for a realistic simulation of the ion exchange between a lipophilic polymeric membrane and water [4]. The specific conductivity and the pH of the water phase was tested to get information about the course of the complexing reaction. The measurements provided simultaneous information about the concentration changes in the target ions and protons in the tested solution.

2 Experimental

The tetraethyl *p*-tert-butylcalix[4]arene tetraacetate ionophore (TBT, Fig. 1) was prepared from *p*-tert-butylcalix[4]arene (TB), as described in [5]. TB was purchased from Alfa Aesar. The other chemicals were obtained from Sigma-Aldrich, and they were of analytical grade purity: hexane, ethanol (EtOH), NaOH, KOH, NaCl, KCl, KClO₄, CaCl₂, and MgCl₂. Nitrogen gas (99.999 % wt) was provided by Messer Technogas CZ. De-ionized water (conductivity less than 1 μS/cm) was used for preparing of the tested solutions. The specific conductivity and pH of the aqueous solutions were measured in a thermo-stated glass test-tube (internal diameter 20 mm) kept at 20 °C and under nitrogen, with the aid of a conductance electrode (4-strip Pt electrode Gryf XB1, controlled by a Gryf XBC Magic unit attached to a PC) and a combined glass/AgCl pH-electrode (Radelkis OP-08083 attached to a Radelkis OK104 conductometer). The temperature in the test-tube was controlled by a Haake F423 thermostat. First, the electrolyte conductivity of the tested chlorides and hydroxides was determined as commensurate with the solution concentration in the interval 0.1–100 mM, and the calibration curves giving the concentration of the metallic ions in the solution versus their conductivity were cal-

culated. Full dissociation of the solutions could be assumed. Extraction of the alkali ions from an aqueous phase into a lipophilic phase was tested as follows. The test-tube was filled with 13 ml of 1 mN alkali salt or alkali hydroxide solution, the thermostat temperature was set to 20 °C, the cannula providing the nitrogen inflow was inserted deep into the solution, and the conductance and pH values were measured until stable values were obtained. Then, 6.5 ml of 2 mM TBT solution in hexane was carefully added, and the changes in alkali ion and proton concentration in the water phase were recorded for 20 hours. The nitrogen bubbles climbing from the bottom of the tube provided the moderate and stable agitation of the solutions, very important for achieving non-biased values of the stability constants characterizing the complex-ion forming reaction. Since the distribution coefficient of alkaline ions between hexane and water is negligible, the metal ions cannot penetrate into the hexane and form a complex there. Thus, the complex ions are formed only at the interface and then diffuse into the bulk hexane. If the solutions are not stirred, the equilibrium values are often misrepresented due to the restricted diffusion kinetics [5].

The development of EtOH in the aqueous solutions ob-

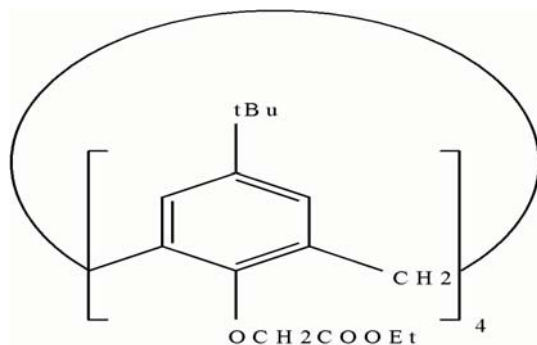


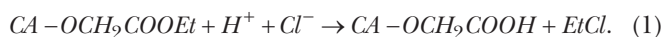
Fig. 1: Structure of Tetraethyl *p*-*tert*-Butylcalix[4]arene Tetraacetate (TBT)

served during the experiments was qualitatively evaluated using the iodoform test [6]: 10 drops of 10% (wt) NaOH solution were added to 5 ml of the tested solution. Then a 10% solution of iodine in KI was added drop-wise until a slightly yellow color was obtained. The solution was then heated up to 60 °C and left slowly to cool down. Optional precipitation of a colorless iodoform cloud gives the sought evidence of the presence of EtOH in the tested solution.

3 Results and discussion

No significant change in conductivity was observed for all the tested alkali chloride solutions (Fig. 2). However, the pH-values showed distinct variations during the inter-phase contact (Fig. 3). While an increase was observed for the solutions of NaCl, KCl, and MgCl₂, a slight fall occurred for CaCl₂ (Fig. 3).

It is well known [2] that TBT can undergo hydrolysis in acid and basic solutions, so that an acidic hydrolysis process following reaction schema (2) is likely compatible with the observed behavior:



Here CA denotes the upper rim and central annulus of the TBT molecule. The validity of the proposed mechanism was supported by the remarkable development of a gas (the

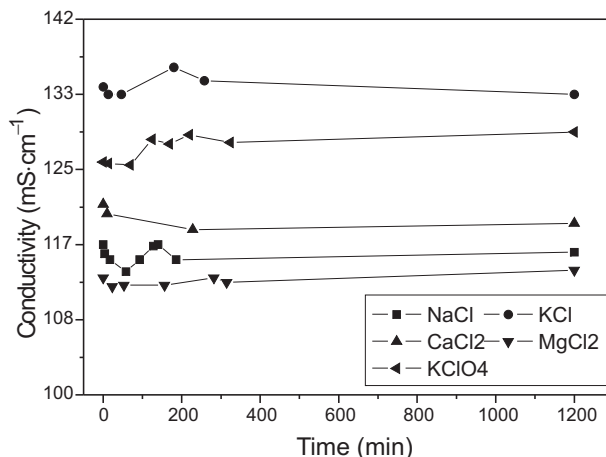


Fig. 2: Temporal evolution of the electrolyte conductivity of the tested chloride solutions during the extraction process (temperature 20 °C, initial concentration of the chloride solutions and the TBT solution 1 mN and 2mM, respectively)

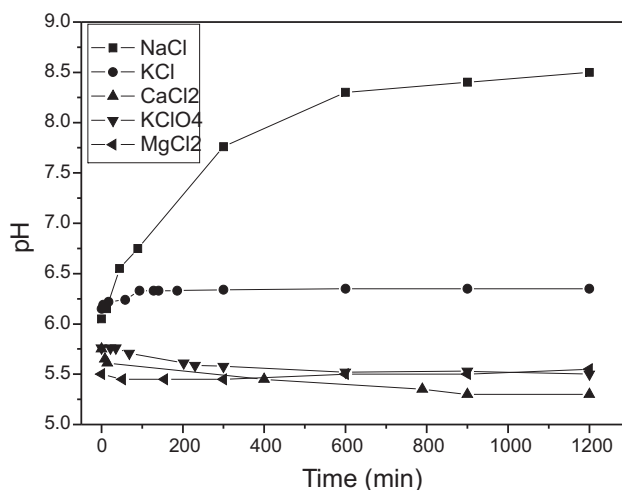


Fig. 3: Temporal evolution of the pH value of the tested chloride solutions during the extraction process (temperature 20 °C, initial concentration of the chloride solutions and the TBT solution 1 mN and 2mM, respectively)

boiling temperature of the ethyl chloride is ~ 12 °C at room temperature and atmospheric pressure) observed after shaking the solutions together. The observed behavior of the potassium perchlorate and calcium chloride solutions is also conformal with (1). Both the solutions showed a lower starting pH-value (~ 5.6–5.7) than the other tested chlorides. The less electro-negative perchlorate ions did not react according to scheme (1). In the case of calcium chloride, reaction (1) took place but the shift in the balance towards the basic conditions led to the creation of calcium hydroxide. This precipitated due to its very limited solubility, forming an observable white cloud in the solution. The equilibrium concentration of Ca²⁺ in the solution remained unchanged in the same time, since it is buffered by the incomplete dissociation of the CaCl₂ present in the solution.

NaOH and KOH solutions showed remarkable decay of the conductivity value with time. This was accompanied by a decrease in the pH of the solutions (Fig. 4, Fig. 5).

Magnesium and calcium hydroxides were not tested because of their low solubility in water. The observed data can

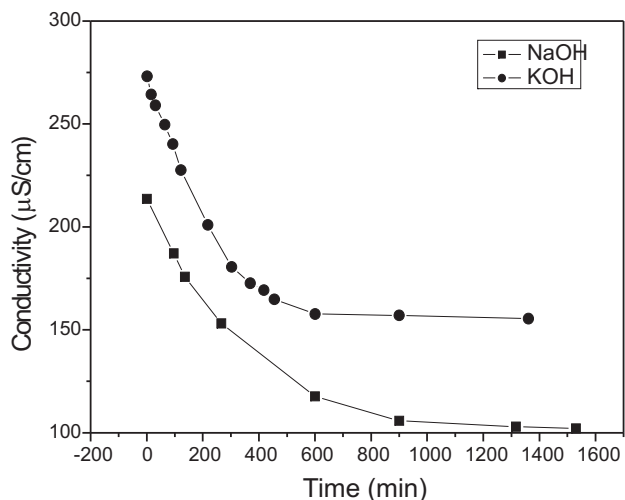


Fig. 4: Temporal evolution of the electrolyte conductivity of the tested hydroxide solutions during the extraction process (temperature 20 °C, initial concentration of the chloride solutions and the TBT solution 1 mM and 2mM, respectively)

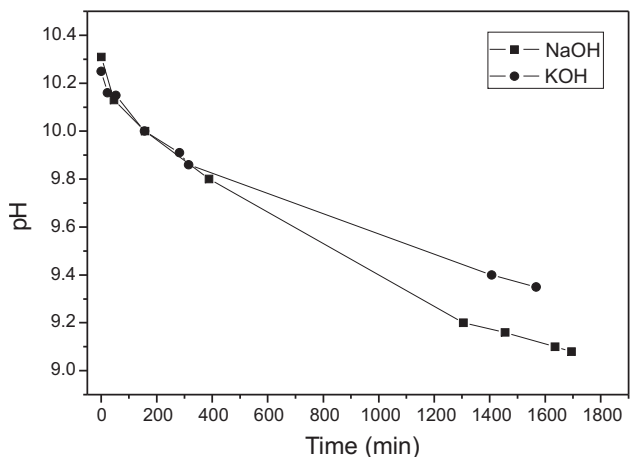
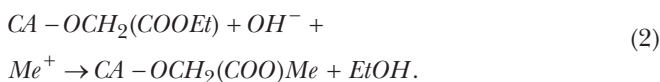


Fig. 5: Temporal evolution of the pH value of the tested hydroxide solutions during the extraction process (temperature 20 °C, initial concentration of the chloride solutions and the TBT solution 1 mM and 2mM, respectively)

in this case likely be explained by basic hydrolysis of the ionophore side groups:



Me^+ stands for the Na^+ and K^+ ions. The relevance of reaction scheme (2) was supported by the observed presence of ethanol in the resulting aqueous solutions, qualitatively verified by the iodoform test. The following stability constants were calculated from the obtained conductivity data, using relation (2): $K_{Na^+} = 7.3 \times 10^{-7}$, $K_{K^+} = 6.5 \times 10^{-8}$, $K_{Ca^{2+}} = 1.6 \times 10^{-5}$, $K_{Mg^{2+}}$: no measurable reaction. Thus, the highest selectivity (β , $\beta=1/K$) toward the target ion was obtained for the potassium ions: $\beta(K^+)/\beta(Na^+) = 11.1$. This result confirms again that the observed extraction process differs from the expected creation of complex ions $[TBT-Me]^+$ known to take place, e.g., in methanol solutions. The latter process shows remarkable preference for Na^+ ions with the selectivity ratio $\beta(Na^+)/\beta(K^+) \sim 400$ [7].

4 Conclusions

The results presented here show that the nature of the chemical reaction of the tested TBT calix[4]arene derivative with alkali ions can be strongly changed in a lipophilic solvent, such as hexane, and depends on the pH value of the water phase. When no free protons are available for an effective charge exchange at the water/hexane interface, there is a hydrolytic attack on the ionophore molecules. In case of alkaline solutions, this results in extraction of the target ions to the hexane phase; for slightly acidic solutions of chlorides, no observable ionic extraction can be observed. The proposed hydrolytic mechanism only includes the ethyl ester side groups, so it cannot be directly extended to other calix[n]arene derivatives bearing other substituents at the bottom rim. However, if hydrolysis of the side groups may occur, the effect has to be seriously considered as a possible parasitic reaction disturbing function of, e.g., intrinsic fibre optic sensors utilizing calix[n]arenes ionophores as the selective reacting centers for alkali metal detection.

5 Acknowledgment

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