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Efficient liquid-liquid extraction of NaCl governed by simultaneous cation and anion coordination

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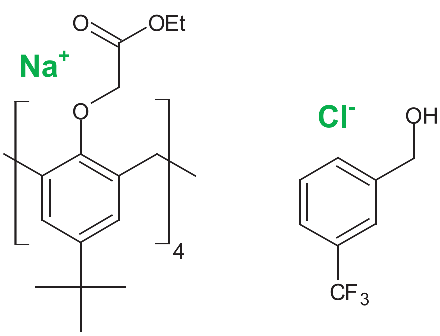
GRAPHICAL ABSTRACT



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ABSTRACT

In the frame of solvent extraction processes, rather quick and efficient extraction of NaCl and some other salts from water was realized by simultaneous coordination of both cations and anions in the organic phase. A calixarene type compound **1** was used for cation complexation, while functionalized benzyl alcohol **2** acted as anion binding agent in organic phase. Importance of both extractants for efficient extraction was shown. A possibility of separation of different cations and anions was further demonstrated. X-ray structural study proved that extraction always takes place on molecular level. The NMR and μ-Raman spectroscopy studies displayed the character of ion binding by extractants molecules. By carrying out several cycles and changing temperature, the process is efficient for extraction and separation of different ions, and has found already its pilot industrial application.

1. Introduction

Lack of freshwater for personal consumption and irrigation is of huge importance. Natural supplies of freshwater in form of rain, surface-water and ground-water reserves quickly become insufficient in view of population and technological growth, thus the desalination techniques attract rising interest [1,2]. These techniques include mainly thermal and membrane-based methods [3–7]. However, a great

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motivation consists in finding more energy saving and environmentally friendly solutions. In particular different approaches based on extraction have been examined [8–13].

In this context Adionics® patented AquaOmnes®, a liquid-liquid extraction process to remove, massively or selectively, salts from water (seawater, industrial produced waters or else) thanks to different versions of an organic formula so called Flionex® [14,15]. Liquid-liquid extraction is a well-known separation method used to transfer some species from one liquid phase to another one (usually from aqueous to organic one) by intensive contact between these two phases [16,17]. Flionex® takes up the challenge to bind the rather hydrophilic inorganic cations and anions present in the aqueous phase and extract them towards the organic phase.

Concerning cation complexation, famous calixarenes are well-documented molecules [18,19]. These hydrophobic macrocycles show high affinity and high complexation constants for alkali and alkaline earth metal species, allowing the transfer of picrate salts into organic phase [20]. By varying a number of phenol units and their functionalization, changing the polar cavity size, efficiency and selectivity towards certain cations may be achieved [21–25].

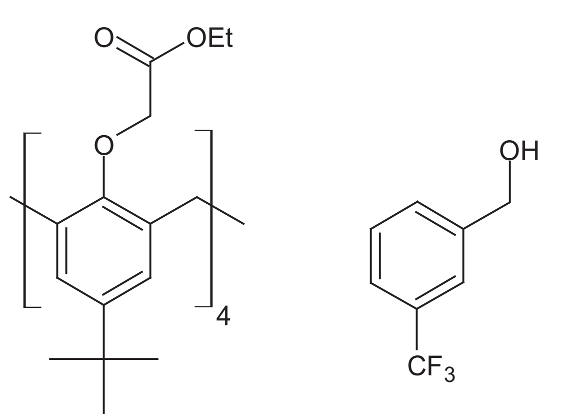
Regarding anion coordination, the story is more recent compared to cation, however largely reviewed [26–29]. Anions possess donor character, have larger size, higher hydration energy, and are often polyatomic which make their extraction more challenging than cations. Nevertheless different approaches for anion coordination and extraction have been proposed, based mainly on hydrogen bonds formation or π-interaction [30–36].

The present work reports on extraction of NaCl and some other common salts from water solutions using two extractants in organic phase, for cation and anion. The cation extractant (noted CE) is 4-tert-butylcalix[4]arene-O,O′,O″,O‴-tetraacetic acid tetraethyl ester **1**, the anion extractant (noted AE) is 3-(trifluoromethyl)benzyl alcohol **2** (Fig. 1). The latter serves as solvent as well.

2. Experimental

2.1. Samples

The solutions of calix[4]arene **1** in 3-(trifluoromethyl)benzyl alcohol **2** (both supplied by Adionics) at 0.03–0.3 M concentration range were prepared by direct solubilization at 80 °C with stirring. The high concentration range was limited by 0.3 M because of issues with calixarene solubility and high viscosity of resulting solutions. For the 0.3 M case, the weight fraction of **2** is 77% (5.7 M). It gets of course higher when concentration of **1** is reduced down to 0.03 M. Most of measurements were done by using a 0.15 M solution of **1**.



1 **2**

Fig. 1. Chemical structures of extractants for the cation with **1** the 4-*tert*-butylcalix[4]arene-O,O′,O″,O‴-tetraacetic acid tetraethyl ester and for the anion with **2** the 3-(trifluoromethyl)benzyl alcohol.

As for the aqueous phase concentration, two salt concentration regimes were studied: the concentrated one with 0.6 M of salt ($c_{salt} >> c_{calix[4]arene}$), for which the organic phase saturation by salt is achieved, as well as diluted one with 0.06 M of salt ($c_{salt} << c_{calix[4]arene}$), for which the extraction equilibrium should be reached with no saturation of calix[4]arene sites by sodium. The interest of the first regime consists in studying the extraction capacity of formulation, with the salt concentration being chosen close to the one in sea water. For the second regime (the diluted one), the tendency of ions to pass into organic phase may be characterized by using the distribution coefficient $D = c^{org} / c^{aq}$, which is proportional in this case to the equilibrium constant. Thus the concentrated regime has more practical interest, while the diluted one is mainly of fundamental importance.

2.2. Methods

The extraction was conducted by introducing 200 μL of each phase (aqueous and organic ones) in contact at magnetic stirring (700 min^{-1}) for 90 min.

Ion chromatography on a Dionex ICS 5000 device was used for the quantification of ion concentration in solution. The concentration range was within 5–20 ppm. The 10 μL volume of aqueous phase was further diluted 100–1000 times to match the required concentration range. The amount of extracted salt is calculated by difference of aqueous concentrations before and after extraction. The standard solutions from CPAchem Ltd. were used for calibration.

Coulometric Karl Fischer titration was applied for the water content determination in organic phase by using 831 KF Coulometer from Metrohm.

Small and wide angle X-ray scattering (SWAXS) experiments were performed on a home-built SAXS camera. The setup involves a Molybdenum source delivering a beam of 17.4 keV. Fine Monochromatization and focusing (12:∞) were performed using a Fox-3D multilayer mirror and the beam collimation and scattering background reduction were achieved using two sets of "scatterless" slits. The diffraction pattern was recorded using a MAR345 2D imaging plate for typical acquisition time of 30 min. The measurements were performed on samples placed in 2 mm thick glass capillaries.

X-ray data for single crystals were collected on a SMART APEX II system with Mo radiation. An Oxford Cryostream 700 low-temperature device set to 150 K was used to control temperature.

NMR study was performed on a Bruker AVANCE III 400 spectrometer equipped with a two channels probe. Formulations in purely hydrogenated form were used for investigation, while the DMSO-d_6 was used as an external reference.

Infrared spectra of samples were recorded between 380 and 4000 cm^{-1} at a resolution of 4 cm^{-1} with a Bruker Equinoxe 55 Fourier Transform Infrared Spectrometer equipped with a Golden Gate diamond ATR reflection unit.

All the experiments were carried out under standard conditions for pressure and temperature (20–21 °C).

3. Results and discussion

3.1. Efficiency of formulations for the NaCl extraction

Before studying the extraction capacity of formulations, a preliminary measurement of the extraction kinetics was conducted.

The salt extraction from 0.6 M NaCl solution by 0.15 M solution of calix[4]arene **1** in alcohol **2** was followed in time to explore the extraction kinetics. There is double interest: firstly to establish correct extraction conditions, secondly to probe the industrial process potential. Thus we have determined that the extraction equilibrium is achieved in 30 min when mixing was done at 700 min^{-1}, so the process is quite fast. However we used 90 min as extraction time for all