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Selective removal of sodium from alkali-metal solutions with tetraoctylammonium monensin

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Abstract

Accumulation of sodium ions in fresh water limits its use for drinking water. In the greenhouse industry reuse of irrigation water, which still contains valuable nutrients is limited due to an increasing sodium concentration, and next to this high concentrations of sodium also result in corrosion problems. Existing technologies are not yet able to selectively remove sodium to solve above mentioned problems. Therefore, it was tried to develop a novel sodium selective ionic liquid based on the monensin anion combined with the tetraoctylammonium cation. Ionic crystals were obtained instead of an ionic liquid. Nevertheless, it was proven that these crystals could selectively remove sodium. Metal extraction experiments of an aqueous solution containing Li, Na, K, Mg and Ca with the monensin ionic crystals dissolved in toluene showed a selective single stage extraction efficiency of 41 wt% for sodium, while the extraction of the other salts was negligible. Regeneration is possible by applying an acidic solution, however this also prevents its reuse.

Keywords: ionic liquids, tetraoctylammonium monensin, selective sodium extraction, sodium monensin, ionic crystals

Introduction

High concentrations of sodium in water (>20 mg/L) limit its use for drinking water [1–3]. The reuse of the irrigation water in greenhouses is limited by the accumulation of sodium ions. This irrigation water, still containing valuable plant nutrients, is often discharged to the environment as a brine stream [4,5]. Industrial water containing too much sodium on the other hand leads to corrosion problems [6]. However, up to now there is still no cost-effective industrial technology that can selectively remove sodium.

Ionic liquids (ILs) are organic solvents consisting entirely of ions. The strong electrostatic forces in these solvents result in a low volatility and low flammability. Due to these properties, ILs were selected as ideal replacements for volatile organic solvents, which are common in industry [7–13]. Furthermore, by selecting the right organic ions to synthesize the IL, one can obtain an IL that is ideal for metal extraction. It has already been proven that some ILs show excellent efficiencies for the extraction of transition and rare earth metals from aqueous phases, but less attention has been given to the extraction of alkali metals [14–20]. Attempts to facilitate alkali metal extraction have been made by adding crown ethers, aza-crown ethers and calixarenes to hydrophobic ionic liquids [21–27]. Unfortunately, analysis of the extraction mechanism showed that in these cases alkali metal extraction was based on ion-exchange, resulting in the loss of the cation of the IL into the aqueous phase, which is not sustainable [28].

Task-specific ionic liquids (TSILs) for metal extraction were developed to avoid ion-exchange processes, and the leakage of the cation of the ILs into the aqueous phases during metal extraction [29–33]. In these TSILs a metal binding functionality was incorporated into the cation or anion. In case of alkali metal extraction mostly ether functionalities were incorporated [34,35].

Monensin is an alternative organic extractant, which has specific affinity towards sodium [36,37]. Its structure is related to crown-ethers in which a sodium ion can be encircled. Monensin

and its derivatives have already been tested to make sodium selective membranes, but an IL with monensin as anion has not been reported before [38].

In this research, an ionic crystal was developed using monensin as an anion. The synthesized crystal was then tested for selective sodium removal from a mixed salt solution containing the most common metal cations in drinking and irrigation water, i.e. lithium, sodium, potassium, magnesium and calcium. Performance was compared with sodium monensin and 2-hydroxymethyl-15-crown-5, see figure 1. Additional tests were performed to characterize the regeneration and reuse of the monensin based ionic crystal.

Experimental

Materials

The extractant tetraoctylammonium monensin ($[N_{888}][\text{monensin}]$) used in this research was synthesized with reagents purchased from Sigma-Aldrich: sodium monensin (90-95%) and tetraoctylammonium chloride ($\geq 97\%$). All inorganic salts used had a purity above $>98\%$.

Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and 2-hydroxymethyl-15-crown-5 (95%) were also delivered by Sigma-Aldrich. Toluene, sodium chloride (NaCl), calcium(II) chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) and potassium chloride (KCl) were obtained from VWR-ProLabo. Lithium chloride (LiCl) was purchased from Merck. MilliQ water ($\geq 18.2 \text{ M}\Omega \cdot \text{cm}$) used throughout the synthesis was obtained by a Millipore MilliQ[®] biocel, which used a Q-grade[®] column.

Synthesis of the extractant

$[N_{888}][\text{monensin}]$ was obtained by adding tetraoctylammonium chloride (1.17 g, 2.33 mmol) diluted in 50 mL toluene to an aqueous solution of an equimolar amount of monensin salt (1.61 g, 2.33 mmol, 50 mL). The solution was then stirred for 3 h at room temperature. The

organic phase was washed with water in order to remove the remaining sodium and chloride (6 times with 50 mL MilliQ water). The residual chloride content was confirmed to be negligibly low by adding AgNO_3 to the last water phase and observing that no AgCl precipitated. Toluene was removed under reduced pressure using a rotary evaporator (BUNCHI Rotavapor[®] R-3) at 50 °C.

The product was obtained in the form of a white powder (2.936 g). Yield: 92% MS (ESI):

Calculated for $[\text{N}_{888}(\text{C}_{32}\text{H}_{68}\text{N})]^+$ m/z: 467.0; found m/z: 466.7 and calculated for $[\text{Monensin}(\text{C}_{36}\text{H}_{61}\text{O}_{11})]^-$ m/z: 669.9; found m/z: 669.4. Elemental analysis found (%): C, 73.0; H, 11.6; N, 1.41; calc. for $\text{C}_{68}\text{H}_{129}\text{O}_{11}\text{N}$: C, 71.85; H, 11.44; N, 1.23; O, 15.48. $T_m > 378$ K, two degradation points were observed $T_d = 463$ K and 552 K.

Figure 1. A) the extractant tetraoctylammonium monensin, $[\text{N}_{888}][\text{monensin}]$ first reported here B) the structure of 2-hydroxymethyl-15-crown-5.

Characterization of the ionic crystal $[\text{N}_{888}][\text{monensin}]$

The purity of the ionic crystal was determined using ^1H NMR on a 400 MHz Bruker nuclear magnetic resonance (NMR) spectrometer. The decomposition temperature was determined with a thermogravimetric analysis (TGA) Q 500 apparatus (TA instruments, USA) at a scan rate of 10 $\text{K}\cdot\text{min}^{-1}$ under a nitrogen flow. The thermograms were analyzed with TG instruments software. Differential scanning calorimetry (DSC) Q 1000, and Perkin Elmer Pyris 1 were used to obtain the melting temperature with a scan rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Electrospray-ionisation combined with mass

spectrometry (ESI-MS) was used to analyze the ionic crystal after synthesis with acetonitrile as eluent. An Agilent Technologies 1200 series ESI-MS was used with acetonitrile:water 90:10 as eluent working with an Agilent mass hunter workstation data acquisition.

Salt extraction and regeneration tests

Three different metal salt solutions were used to test the extraction efficiency of [N₈₈₈][monensin]. (I) An aqueous sodium chloride solution containing 1 g/L Na, (II) an alkali solution containing 1 g/L of KCl, NaCl and LiCl and, (III) a mixed alkali and earth alkali solution containing 1 g/L of Li and 2 g/L of Na, K, Mg and Ca from their chloride salts. 0.5 g of [N₈₈₈][monensin] was dissolved in 10 mL of toluene. For solutions (I) and (III) 1 mL of the toluene solution and 1 mL of the salt solution was used. For solution (II) 5 mL of the toluene solution was mixed with 5 mL salt solution. Extraction of the first salt solution was also repeated for an equimolar amount of sodium monensin or 2-hydroxymethyl-15-crown-5 dissolved in toluene. To quantify regeneration, 1 mL aliquots were taken from used extractant (5mL toluene exposed to salt (II)) and subsequently mixed with either: 1 mL of a 0.1 M HCl solution, a 0.1 M acetic acid solution or, MilliQ water. These samples were stirred for 2 h on a vortex mixer (Heidolph multireax) and then placed in a centrifuge (Allegra TM X-12R, Beckman coulter) for 5 min at 3750 rpm.

Analysis of the water phase after extraction

Cations present in the water phase were measured with a Perkin Elmer, Induced Coupled Plasma Optical Emission Spectrometer (ICP-OES) optima 5300DV (Perkin Elmer, Massachusetts). Results were obtained via a Winlab 32 ICP continuous automated analysis. The ICP-OES has a detection limit of 25-250 $\mu\text{g}\cdot\text{L}^{-1}$, with an uncertainty of 1.4-2%. Anions were

analyzed via a Metrohm 761 Compact ion chromatography (IC) and 762 IC interface with a detection limit of 0.1 mg/L.

Extraction efficiency ($E\%$) is calculated by:

$$E(\%) = \left\{ \frac{c_0 - c_1}{c_0} \right\} \times 100 \quad (1)$$

where c_0 and c_1 are the total metal concentration (mg L^{-1}) in the aqueous phase before and after metal extraction, respectively. Furthermore, the mole ratio x_i of salt extracted over the amount of extractant applied was calculated via:

$$x_i = \frac{n_i}{n_{ex}} \quad (2)$$

in which n_i stands for the molar amount of salt extracted and n_{ex} is the molar amount of extractant being applied. The relative selectivity is calculated by dividing $E\%$ of sodium over $E\%$ of the salt of interest from the same experiment.

Regeneration percentage ($R\%$) is calculated by:

$$R(\%) = \left\{ \frac{c_2}{c_3} \right\} \times 100 \quad (3)$$

where c_2 stand for the metal concentration (mg L^{-1}) observed in the aqueous phase after regeneration and c_3 is the metal concentration (mg L^{-1}) in the organic phase and is determined by $c_0 - c_1$.

The molar concentration of the salt removed was calculated from the difference of the total cation concentrations in the aqueous metal solution before and after the extraction.

Results and discussion

A white solid powder was obtained after the synthesis of the extractant, $[\text{N}_{888}][\text{monensin}]$. The melting point was determined to be above 100°C . Because all experiments with this

compound were conducted at room temperature, and thus below the melting point, we refer to the product as an ionic crystal instead of IL.

The assumed sodium extraction process with the extractant $[N_{888}][\text{monensin}]$ can be written as:

The extraction efficiency for a pure sodium solution (I) was found to be $6.1 \pm 0.4\%$ for the sodium cation and $4.0 \pm 1.7\%$ for the chloride anion. This gives a molar ratio of chloride to sodium of 0.86, indicating that the process is mainly based on ion-pair extraction as assumed by equation (4) and not on ion-exchange.

Table 1. Extraction efficiencies ($E\%$) and mole ratio of salt extracted (x_i) for $[N_{888}][\text{monensin}]$ dissolved in toluene (A) of a salt (Li, Na, K) solution compared to the extraction efficiencies of $[\text{Na}][\text{monensin}]$ (B) and 2-hydroxymethyl-15-crown-5 (C).

	$E_A (\%)$	x_{iA}	$E_B (\%)$	x_{iB}	$E_C (\%)$	x_{iC}
K	10.0 ± 1.0	0.062	2.8 ± 0.3	0.0093	2.3 ± 1.4	0.000013
Na	50.8 ± 0.8	0.54	-4.1 ± 0.9	-0.020	2.6 ± 1.5	0.000029
Li	9.4 ± 1.0	0.29	1.1 ± 0.4	0.0049	3.2 ± 1.8	0.00047

Extraction efficiency tests performed with a mixed alkali solution (II) provide a measure of ion specificity for sodium, the results are shown in Table 1. It was observed that the extractant was selective towards Na compared to Li and K. The extraction results for $[N_{888}][\text{monensin}]$ were also compared with the selective removal of Na by the precursor, sodium monensin ($[\text{Na}][\text{monensin}]$) (Table 1). It was found that $[\text{Na}][\text{monensin}]$ requires sonication to be dissolved in toluene at room temperature. Moreover, the Na extraction efficiency was found to be negative. This is most likely due to some exchange of the Na in the $[\text{Na}][\text{monensin}]$ by K or Li. The extraction with the crown ether 2-hydroxymethyl-15-crown-5, which is known as a good sodium selective extractant [39], showed poor extraction and exhibited no selectivity for Na using the same alkali salt solution and conditions as for $[N_{888}][\text{monensin}]$. This indicates once more the remarkable selectivity for

sodium by the $[N_{888}][\text{monensin}]$ ionic crystal. Removing 40% of the dissolved sodium would already be sufficient to reuse irrigation water and significantly reduce corrosion as previously discussed. Furthermore, x_{iA} for $[N_{888}][\text{monensin}]$ indicates that for this specific case only half of the ionic crystals extracts a sodium ion. This means that in theory even much more sodium could be extracted, if one could minimize the co-extraction of lithium.

Table 2. Extraction efficiencies ($E\%$) and mole ratio of salt extracted (x_i) for a test solution containing the metals Li, Na, K, Mg and Ca.

	Li	Na	K	Mg	Ca
$E(\%)$	1.0 ± 1.4	41.1 ± 0.8	2.1 ± 1.6	1.5 ± 1.5	1.2 ± 1.6
x_i	0.028	0.80	0.023	0.026	0.014

Checking the extraction efficiency of the ionic crystal $[N_{888}][\text{monensin}]$ for a mixed alkali and earth alkali solution (III) containing the most common metal cations in drinking and irrigation water confirms again the very high selectivity for Na (Table 2). In this case, the Na removal corresponded to a ratio of 0.80 mol Na per mol of extractant. Comparing these results to membranes containing monensin or monenin derivatives previously reported in literature confirms that this ionic crystal has a unique selectivity for Na. For example, 0.2M of $[Na][\text{monensin}]$ in octanol has a relative selectivity of 8:1 for Na:Li and 3:1 for Na:K [38], while in this research 0.0004M of $[N_{888}][\text{monensin}]$ dissolved in toluene has a relative selectivity of 41:1 for Na:Li and 10:1 for Na:K.

Table 3. Regeneration efficiencies ($R\%$) of the $[N_{888}][\text{monensin}]$ solution after the extraction of alkali metals presented in Table 1 (E_A) and there extraction efficiencies ($E\%$) afterwards towards the same alkali solution (II) applied in Table 1.

	$R_{HCl} (\%)$	$R_{\text{acetic acid}} (\%)$	$R_{H_2O} (\%)$	$E_{HCl} (\%)$	$E_{\text{acetic acid}} (\%)$	$E_{H_2O} (\%)$
K	32.1 ± 3.3	30.4 ± 2.9	28.8 ± 3.0	8.5 ± 1.6	8.8 ± 1.8	11.2 ± 1.2
Na	100.0 ± 2.8	100.0 ± 2.7	56.0 ± 1.4	6.6 ± 0.9	8.8 ± 1.2	38.5 ± 0.7
Li	9.8 ± 0.1	9.4 ± 0.1	9.3 ± 0.1	9.0 ± 0.6	9.3 ± 1.1	9.6 ± 1.1

Regeneration and reuse of the extractant was investigated with 0.1 M HCl, 0.1 M acetic acid and MilliQ water (Table 3). Tests were performed on the toluene solution containing [N₈₈₈][monensin] that was applied for extraction of a aqueous solution of 1 g/L of LiCl, KCl and NaCl presented in Table 1. Results show that recovery of sodium can efficiently be done by applying an acid (i.e. acetic acid or HCl). However, the extractant loses its selective extraction capability following regeneration. It is assumed that the higher regeneration with acids is caused by the protonation of monensin together with the formation of a very water soluble sodium salt. It can be observed from the results given in Table 3 that recovery of the sodium selective form is not possible following acid regeneration. It is thus considered that the ionic crystal should either first be deprotonated before reuse or that the monensin ion is not stable towards acids. Regeneration using MilliQ water retains some sodium selectivity but suffers a lower from reduced overall capacity. Although the levels of extraction and regeneration look very promising, further experiments are necessary to investigate why the ionic crystals cannot be reused. This would indicate if alternative regeneration mechanisms have to be applied or if more stable monensin based complexes have to be developed that still show a high sodium selectivity. Understanding and overcoming this problem will then result in a high selective ionic crystal that can be implemented in ion-exchange resins or membranes.

The solubility of [Na][monensin] in water was also compared to that of [N₈₈₈][monensin] in water. When mixing the two compounds with the salt (Li, Na and K) solution, it was noticed that [Na][monesin] formed a white emulsion with the water phase, whereas [N₈₈₈][monensin] did not and preferred to stick to the inner wall of the test tube. Analysis of the water phase showed that [Na][monensin] has a low solubility in water of 71.6 mg·L⁻¹ due to its rather hydrophobic character, while [N₈₈₈][monensin] has an even lower water solubility of 43.6 mg·L⁻¹. From this result, it can be concluded that replacing the sodium ion by the [N₈₈₈] cation in the monensin salt

results in an almost twofold decrease of the solubility in water, thereby preventing the loss of this valuable ionic crystal.

Conclusions

Results showed that the ionic crystal, [N₈₈₈][monensin] is an ideal extraction agent for selective Na removal. Mixing the ionic crystal with a mixed salt solution containing LiCl, NaCl, KCl, MgCl₂ and CaCl₂ results in a 41% sodium removal. The extraction mechanism of [N₈₈₈][monensin] is mainly based on ion-pair extraction. Comparing the sodium selectivity and extraction kinetics with [Na][monensin] or with the known sodium extractant 2-hydroxymethyl-15-crown-5 stresses the high selectivity of this novel ionic crystal. Furthermore, changing the Na cation for [N₈₈₈] to obtain the ionic crystal [N₈₈₈][monensin] resulted in a lower solubility of this ionic crystal into the aqueous phase. Full sodium regeneration of this ionic crystal is possible by applying acidic solutions (0.1 M HCl or 0.1 M acetic acid). However, this regeneration step limits its reuse.

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