



Extractive concentration of aqueous salt solutions in aqueous two phase systems



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HIGHLIGHTS

- 53 commercial polymers were screened for formation of aqueous biphasic systems with FeCl₃, NaCl and Na₂SO₄.
- (Block co)polyethers were found suitable for concentration of NaCl and Na₂SO₄ solutions.
- Single step concentration factors of up to 7.7 in the raffinate were measured.
- Distributions were temperature dependent.
- Thermally induced phase splitting could be used for recovery of the polymers.

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ABSTRACT

Concentration of aqueous salt solutions is among the most energy intensive processes in the chemical industry. We here report on extractive concentration as an alternative for the traditional technologies based on water evaporation or reverse osmosis. Extractive technologies are potentially energy-efficient, key is avoiding evaporation of (co-)extracted water during the recovery of the solvent. Polymers have been applied as solvents, because recovery may be done through mild temperature swing. For in total 53 commercially available polymers, the phase behavior of ternary systems containing water, salt (NaCl, Na₂SO₄, and FeCl₃) and polymer was studied at room temperature (294 K) and atmospheric pressure. Formation of aqueous two phase systems (ATPS) was studied for various solvent/feed ratios (mass) of (0.25 < S/F < 0.75), and initial salt concentrations of 5 wt.% < [salt]_{initial} < 30 wt.%. Several polyether (block co)polymers were found suitable for creating ATPS with NaCl and Na₂SO₄ with reasonable distributions of water and these systems were analyzed more detailed at 294 K and 314 K, showing concentration factors up to 7.70 in a single extraction step, and strong temperature dependency. Temperature responsive recovery by induced phase splitting was shown to be a promising option.

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1. Introduction

Salt production concerns large scale operations [1]. Often, salts are produced in dilute streams that need to be concentrated. For concentration of aqueous salt solutions, mostly evaporative technologies have been deployed [2–4]. Evaporation of water is highly energy demanding due to the high heat of evaporation of water, and alternatives like liquid–liquid extraction can potentially save a lot of energy [5,6] if water evaporation is limited or even excluded. The applicability of alternative concentration technologies based on liquid–liquid operations in different salt productions is conditional to the properties of the salts and their aqueous solution. Under varying conditions, different technologies may be optimal. In this study, the applicability of liquid–

liquid extraction using polymers as solvents to form aqueous two phase systems (ATPS) was investigated for concentration of three salts (ferric chloride, sodium chloride, and sodium sulfate) that were selected as model salts, because of their relevance for industry and society.

Ferric chloride is used in many different municipal and industrial water treatment applications [7], such as phosphorus removal, hydrogen sulfide control, sludge thickening, conditioning and dewatering agent, and chemically enhanced clarification [8–12]. It is also utilized as a primary coagulant in drinking water treatment [13–15]. The yearly production is 2.2 million metric tons of aqueous FeCl₃ (typically 45 wt.%) per year (in 2010) [16,17]. Usually, the production involves the reaction between ferric oxide and hydrochloric acid resulting in 5–30 wt.% aqueous FeCl₃-solutions that also contain 2.45 wt.% HCl as stabilizer. Concentrations of over 40 wt.% FeCl₃ are desired for economic reasons, which is currently done through triple effect evaporation.

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Sodium chloride, mostly known for its domestic use, is also used in several production processes in the chemical industries, for de-icing and for softening of water [18]. These demands together require a massive production volume of 220 million metric tons per annum, mostly provided by brines from mines and seawater. Concentrating these brines is done mostly by distillation-based technologies and membrane-based technologies. Where the evaporative technologies are energy demanding because of the high heat of evaporation of water, the membrane based separations require high pressures.

Sodium sulfate has a wide range of use, from the home-care industry, to the glass industry, in textile manufacturing industries and as a thermal storage of solar heat, making use of its high heat of melting. A large amount of energy can be stored in this working fluid by phase changing from solid to liquid, and subsequently the energy can be released from the material during liquid–solid transition [19]. This salt is produced from natural resources where crushed glauberite rocks are fed into a tank and the salt is leached into an aqueous solution. After removing the impurities the clean extract is evaporated and centrifuged. Finally the wet sodium sulfate is dried by multi-effect evaporation to obtain the final product. The estimated yearly production in 2013 is 6.8 million metric tons [20].

Thus, production of all three salts involves concentration of the aqueous salt solution, for which liquid extraction [21,22] could be applied. We have previously studied liquid–liquid extraction of ferric chloride from aqueous solutions using a wide range of solvents [6], and found ethers to be interesting for the extractive concentration of ferric chloride. Besides the ethers, polymers may also be used for extractive concentration of salts [5,23,24]. Formation of ATPS systems has been reported for a range of polymers with different salts [25], and ATPS systems are usually mentioned in conjunction with separation of biomolecules [26–29]. However, because of the difference in distributions of water and salt over the two aqueous phases, ATPS might also be suitable to concentrate aqueous salt solutions. The use of polymers in extractive salt concentrations is specifically interesting if the ATPS is temperature responsive, i.e. the miscibility gap between the two aqueous phases changes with changing temperature. By increasing the miscibility gap, a phase separation may be induced. In a polymer based extraction process followed by induced phase separation (IPS) for recovery, the polymer is added to an aqueous salt solution, thereby forming an ATPS containing a polymer rich extract phase, and a polymer lean raffinate phase. After the extraction, the phases are allowed to settle and are collected separately. The separated extract and raffinate phases are then subjected to a change in temperature to induce phase separations in order to recover the polymer without evaporation of water. Such extraction plus induced phase separation processes (LLE + IPS process) may be very

economic due to the use of inexpensive polymers that are available on bulk scale, and avoiding the evaporation of water. Fig. 1 displays the process concept for the proposed LLE + IPS process.

In order to develop LLE–IPS based processes to concentrate aqueous salt solutions, three key conditions need to be satisfied.

- 1) a biphasic system needs to be formed;
- 2) the salt and the water need to distribute differently, i.e. the polymer should extract either the water or the salt preferentially, so that a separation can be realized;
- 3) the polymer should be recoverable from both the extract phase and the raffinate phase, e.g. by temperature swing induced phase separation.

In the study here presented, all three criteria (formation of a biphasic system, differentiation in distribution of salt and water, and recoverability through temperature swing) have been investigated. In the first part, formation of aqueous biphasic systems was studied, and the most promising systems in which biphasic systems were formed were studied in more detail by measuring the distributions of the salt, the polymer and water at different temperatures to study on the separability of water and the salt, and the possibility to recover the polymer by temperature induced phase separation. The polymers that were studied are listed in Table 1.

2. Experimental section

2.1. Chemicals

The following chemicals were purchased from Sigma Aldrich: solid anhydrous ferric chloride (reagent grade, >97%), nitric acid, sodium chloride (reagent grade, >99%), and sodium sulfate (reagent grade, >99%). The water used was milli Q from MILLIPAK® Express 20 Millipore (0.22 μm). All polymers in this study were used as supplied, and are listed in Table 1.

2.2. Experimental procedures

2.2.1. Phase behavior screening experiments

ATPS-formation experiments were carried out in glass vessels of 16 mL placed in an oil bath to control the temperature. After 1 h of mixing aqueous salt solutions (for the sodium salts 5 wt.% < [salt]_{initial} < 15 wt.%, for ferric chloride 10 wt.% < [salt]_{initial} < 30 wt.%) with the polymer of choice in a solvent to feed ratio of 0.25 (volume based for liquid polymers), and 0.2 g/4 mL for solid polymers at 500 rpm at 298.15 K and atmospheric pressure, the mixtures were allowed to settle for 2 h, after which it was determined whether a single phase system or an

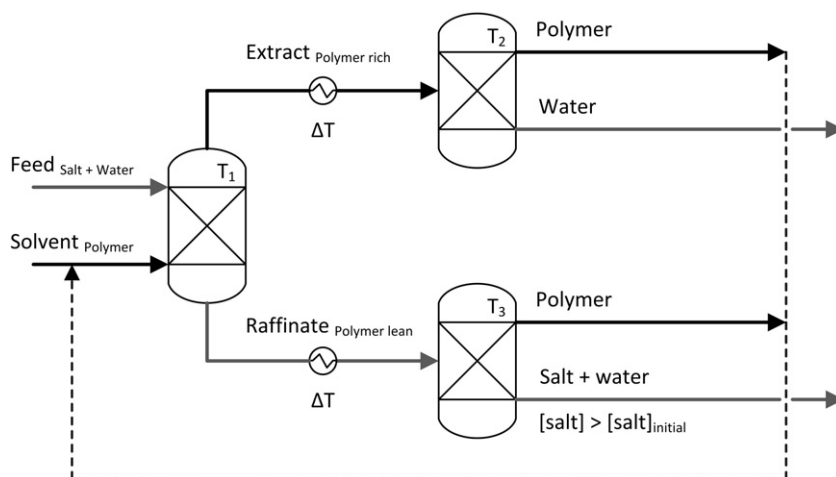


Fig. 1. Process concept for concentration of aqueous salt solutions through liquid–liquid extraction with polymers followed by thermally induced phase separation.

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