



## Fractionation of aqueous sodium salts by liquid–liquid extraction in aqueous two phase systems



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### ABSTRACT

An important element in the work-up of brines is the separation of different ions present. Usually, energy consuming technologies, such as multi-stage evaporation, reverse osmosis, crystallization, and nanofiltration, are used to bring the composition of the brine to the required specification. Fractionation of salts by liquid–liquid extraction using thermo-responsive polymers is a novel concept. In the current study we have evaluated the fractional extraction of sodium chloride from brines containing sodium sulfate as well. Four different polymers (Dehypon<sup>®</sup> LS 54, PPG 425, Pluronic<sup>®</sup> L31 and Triton<sup>®</sup> X – 15) have been used. The quaternary systems of these polymers with water, sodium chloride and sodium sulfate have been obtained at 283.15 K and 298.15 K. From experiments at 298.15 K, it was concluded that the polymer Dehypon<sup>®</sup> LS 54 showed the most interesting combination of extracted sodium chloride yield and selectivity of sodium chloride over sodium sulfate. The polymer losses to the feed (brine) phase were limited. Collected extract phases were subjected to a temperature increase to 323.15 K, 333.15 K, 343.15 K, and 353.15 K in order to study the polymer recovery by temperature induced phase splitting. It was found that at higher temperature the miscibility gap increased strongly and limited amounts of polymer remained in the aqueous phase.

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### 1. Introduction

Sodium chloride in its ubiquitous presence in human society has been one of the most important minerals for a long time. This is e.g. reflected by the payment of Roman soldiers in the form of *salarium argentum*, salt money [1].

The main sources of salt are underground deposits, also known as rock salts, and oceans. The salinity of the oceans is around 3.5 wt%, which yields approximately 35 million tons of salt in each cubic kilometer of sea water. For obtaining salt from the rock salts either mechanical or solution mining is applied. In the latter case a saturated brine solution is produced. Consequently, in most cases water evaporation technology needs to be used for salt recovery [2–4]. Usually, the final salt product needs to be produced from brine containing several ions. In contrast very pure salts are

normally desired for different applications and brines with specific compositions are required for industrial use. Thus brine purification needs to be applied [5].

Major impurities in sodium chloride brines are calcium, magnesium and sulfate [6]. There are several technologies to bring the brine to the desired specifications, and many routes have been developed for the separation of the desired and undesired ions from brines. Precipitation and ion-exchange are often used for removal of calcium, magnesium and other metals. The separation of sulfates from chlorides is of industrial importance as well, e.g. in chlor-alkali production [7] and salt production [5]. Removal of sulfate is a multifarious procedure because of many available techniques and the fact that it can be implemented in many different stages of brine production [8]. Nanofiltration has been successfully introduced for the separation of sodium chloride from sodium sulfates, to replace other less environmental friendly technologies, since nanofiltration membranes show higher rejection for sulfates than for chlorides [9–11]. Nevertheless, there is a constant need to develop more economically attractive and environmentally clean technologies, as well as to improve and optimize existing technologies [12,13]. One of the promising technologies is fractional

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## Nomenclature

### Symbols and abbreviations

ATPS	aqueous two phase systems	$T$	temperature
cP	centipoise	$S/F$	solvent to feed
$D$	distribution coefficient $((g\ g^{-1})/(g\ g^{-1}))$	$w$	weight fraction for polymer free brines (–)
$D'$	distribution coefficient based on polymer free extractants and raffinates $((g\ g^{-1})/(g\ g^{-1}))$	$x$	fraction
EO	ethylene oxide (monomeric unit in PEG and block copolyethers)	$Y$	yield
$\Delta G$	Gibbs free energy	$[\ ]$	concentration
$h$	hydration number	<i>Superscript</i>	
HLB	hydrophilic–lipophilic balance	<i>cal</i>	calculated
IPS	induced phase separation	<i>Subscripts</i>	
K	Kelvin	<i>aq</i>	aqueous
LLE	liquid–liquid equilibrium	<i>bottom</i>	bottom of the two aqueous phases, the polymer lean raffinate phase
LLX	liquid–liquid extraction (g)	$F$	feed
$m$	mass	<i>feed</i>	initial salt concentration
mL	milliliter	$E$	extract
NaCl	sodium chloride	$P$	polymer
$Na_2SO_4$	sodium sulfate	$R$	raffinate
PO	propylene oxide (monomeric unit in PPG and block copolyethers)	$S$	salt
PEG	poly ethylene glycol	<i>top</i>	upper of the two aqueous phases, the polymer rich extract phase
PPG	poly propylene glycol	$W$	water
$R$	gas constant	$wt$	weight
rad/s	radium per second		
$s$	selectivity (–)		

liquid–liquid extraction using thermo-responsive polymers as solvents in aqueous two phase systems (ATPS) [14,15]. These aqueous biphasic systems have also been reported for metal ion separations [16–21].

The process concept is depicted in Fig. 1 as a single stage batch process, since we have used this concept in our experimental study. However, multistage processing is an option as well. In the described concept a solution of two salts is contacted with a liquid polymer at temperature  $T_1$ . After phase separation of the extract and raffinate phases, a polymer rich (extract) and polymer lean (raffinate) phase are identified. The concept of the separation (fractionation) of the two salts is the difference between the distribution coefficients of the two salts ( $D_{salt1} > D_{salt2}$ ). This difference in distribution coefficients makes that salt 1 is extracted preferentially. Water is co-extracted with salt 1, thus creating ATPS systems. The separated extract ( $E$ ) and raffinate ( $R$ ) phases may be heated to recover the polymer by temperature induced phase splitting. After increasing the temperatures ( $T_2$  and  $T_3$ , respectively), in both extract and raffinate phase, the polymer is collected as the top phase after phase splitting has occurred. It should be noted that in this exploratory stage of the research, the focus will be primarily on single stage equilibrium contacting. However, conceptual processes utilizing multistage countercurrent contacting for optimized fractionation performance could be considered as well.

In previous studies, polymers used as solvents in liquid–liquid extraction processes were reported [22,23] to cause concentration of single salt NaCl and  $Na_2SO_4$  solutions. From those studies four polymers (see Table 1) have been identified that could possibly be used for separation of these two salts from aqueous (brine) solutions. The reason for their selection is that they form aqueous two phase systems (ATPS), are thermo-responsive, demonstrated different distribution coefficient ratios for chloride and sulfate sodium salts in single salt solutions, and in particular cases were demonstrated to show thermally induced phase separation for

the recovery of the polymers. Based on the distribution coefficients of chloride and sulfate reported in these papers [22,23], it may be expected that chloride will be collected preferentially in the top phase and sulfate in the bottom phase. The aim of the work presented here is to investigate the separation NaCl and  $Na_2SO_4$  experimentally in liquid–liquid equilibrium measurements at 283.15 K and 298.15 K, and for the best performing polymer apply phase splitting experiments to recover the polymer.

## 2. Experimental section

### 2.1. Chemicals

The following chemicals were purchased from Sigma Aldrich: nitric acid ( $\geq 90\%$ ), sodium chloride (reagent grade,  $>99\%$ ), sodium sulfate (reagent grade,  $>99\%$ ), polypropylene glycol (425), Triton X – 15 and Pluronic® PEG-PPG-PEG L31. Dehypon® LS 54 was kindly provided by Cognis – BASF. The water used was milli Q from MILLIPAK® Express 20 Millipore (0.22  $\mu m$ ). Buffer solution, pH 7.7 for high performance capillary electrophoresis was obtained from Fluka BioChemika. All polymers in this study are in the liquid state at room temperature and were used as supplied.

### 2.2. Experimental procedures

#### 2.2.1. Liquid–liquid equilibrium experiments

Equilibrium liquid–liquid extraction measurements were done with the investigated polymers by mixing the polymers in a solvent ( $S$ ) to feed ( $F$ ) ratio of  $1 < S/F < 5$  (mass based) for 2 h (it was previously experimentally determined that equilibrium was reached within 1 h). The feeds used were, aqueous salt solutions containing both NaCl and  $Na_2SO_4$  with mass fractions  $0.01 < x_{NaCl} < 0.10$  and constant  $x_{Na_2SO_4} = 0.0240$ . Feeds and solvents were supplied to

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