Liquid–liquid phase equilibria for ternary systems of several polyethers with NaCl and H_2O

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ARTICLE INFO

ABSTRACT

Liquid–liquid extraction using polymers followed by induced phase separation is a potential energy reducing technology for water–salt separation. Ternary equilibrium data have been determined and reported for the (block co)poly ethers–sodium chloride–water systems at two different temperatures at 298.15 K and 313.15 K and atmospheric pressure. The experimental data were correlated with the NRTL model, and the obtained binary interaction parameters to describe the ternary liquid–liquid systems at different temperatures are presented. The model predictions are in good agreement with the experimental data.

1. Introduction

In many different industrial fields, such as the production of chemicals, the desalination of sea water, and the produced water treatment in the oil and gas industry (e.g. in enhanced oil recovery and in fracking operations), the separation of water from aqueous salt solutions is a highly energy consuming process. For the various industrial processes, a wide range of feed concentrations enter the separation processes, while also the requirements with respect to final product range from high purity salt to high purity water. In most of the fields, the technologies used to concentrate salt solutions are water evaporation based processes [1–3]. Alternatively, reverse osmosis is used in a range of applications [4].

Liquid–liquid extraction (LLX) might be an alternative technology for water–salt separation [5,6], that can potentially save energy. The use of polymers in a LLX process to remove water from salt solutions has recently been reported by our team [7]. It was shown that low density (block co)polyethers gave the most interesting results. Many data has been published in literature on various polymer–water–salt ternary systems that form aqueous two phase systems (ATPS) [8] and several publications dealt with the mechanism behind the phase splitting [9–15]. 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 temperature. In temperature responsive systems, a phase separation may be induced with a mild temperature change due to an increasing miscibility gap. After extraction, the phases are allowed to settle and are collected separately. The separated extract and raffinate phases are then subjected to a temperature swing to induce phase separation in order to recover the polymer without evaporation of water. Such extraction plus induced phase separation processes (LLX + 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 a process concept for the proposed LLX + IPS process.

To make estimations on process economics possible, a conceptual process design requires basic data on the equilibrium in the ATPS and a thermodynamic model describing the phase behavior. A series of different (block co)poly ethers (Table 1) were investigated on their applicability in ATPS systems to concentrate aqueous NaCl-solutions over wide ranges of initial NaCl concentrations. Three polymers that exhibited interesting phase behavior at 298.15 K were also investigated at 313.15 K, and the NRTL-model was applied to correlate the data.

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Nomenclature

ATPS   aqueous two phase system
EO   ethylene oxide
F   feed (aqueous salt solution)
IPS   induced phase separation
LLX   liquid–liquid extraction
NRTL   non-random two liquid model
PEG   poly ethylene glycol (equivalent to EO)
PO   propylene oxide
pol   polymer
PPG   poly propylene glycol (equivalent to PO)
rRMSD   relative root mean square deviation
S   solvent (polymer)

Symbols
α non-randomness parameter in NRTL-model (–)
A parameter in NRTL-model (–)
B parameter in NRTL-model (K)
G interaction energy parameter in NRTL-model
τ interaction parameter in NRTL-model
x mol fraction (–)
w mass fraction (–)

Superscripts and subscripts
avg   average
cal   calculated
exp   experimental
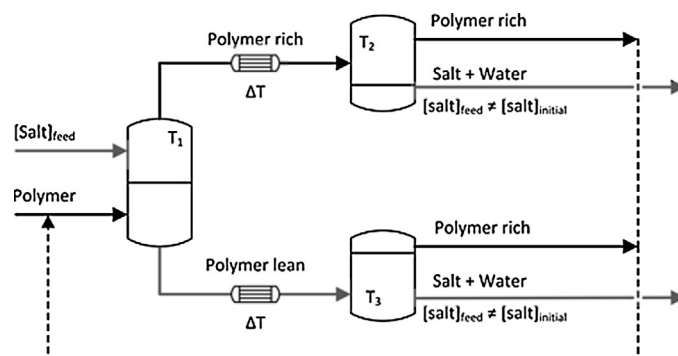in   initial (concentration in feed solution)

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

settle for 12 h. The phases were separated carefully and weighed. Aliquots of 2 mL were taken from both phases for analysis by Karl Fischer Titration to determine the water content and by atomic absorption spectrometry for the salt content. The polymer content in both phases was calculated.

2.3. Analytical techniques

The collected phases were weighed using a Mettler Toledo AX205 balance ($d = 0.01$). Karl Fischer Titrations were done using a 759 KFT Titrino Metrohm, standard deviation ±0.5%. Atomic absorption spectrometry was done using a Varian SpectrAA 110 spectrometer (standard deviation < 2%). Samples of 1 g were diluted into 500 mL water using a volumetric flask, and from that flask 5 mL was injected into the apparatus to determine the sodium content (mg Na^+/L) from which the salt concentration in g/L in the original sample was calculated.

2. Experimental

2.1. Chemicals

The following chemicals were purchased from Sigma Aldrich: nitric acid, sodium chloride (reagent grade, >99%), polypropylene glycol (425, 1000) and Pluronic® PEG–PPG–PEG L31. Dehypon®'s were kindly provided by Cognis–BASF. The water used was milli Q from MILLIPAK® Express 20 Millipore (0.22 μm). 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 S/F = 1 (mass based) for 2 h (equilibrium was reached within 1 h) with aqueous salt solutions (1 wt% < [NaCl]$_{initial}$ < 20 wt%) in 80 mL jacketed glass vessels that were temperature controlled by a water bath (T = 298.15 or T = 313.15) and stirred magnetically (>500 rpm). After 2 h the stirring was stopped, and the mixtures were allowed to

3. Theory

The most commonly used model for correlating equilibrium compositions in aqueous polymer systems is the NRTL (non-random two liquid) model [16]. This model was applied to describe the polymer–water–NaCl systems that were investigated in this work. The NRTL model was originally developed for molecular species [16], but it has been used to describe many different systems containing electrolytes as well, including systems containing polymers with electrolytes and systems containing ionic liquids [17–25]. This is a semi-empirical equation where the local composition contribution to the system Gibbs free energy is the physical foundation for the model. The molecular interactions are described by the local composition parameters A, B and α, which in practice are empirically found using experimental data. The equilibrium activities of all compounds (polymer = 1, water = 2, NaCl = 3) should be equal in both phases, the activity coefficients are described in

Table 1
Polymers that were studied and some selected properties. All polymers are in the liquid state at T = 298 K and p = 1.013 bar, and were used as supplied.

Polymer Number	Polymer	Structure	Molecular weight (Da)	Viscosity (cP) at 294 K
1	PPG 425	H[OCH(CH3)CH2]$_{7–8}$OH	425	80
2	PPG 1000	H[OCH(CH3)CH2]$_{17}$OH	1000	150
3	Pluronic® PEG–PPG–PEG L31 (10 wt% PEG)	H(EO)$_x$(PO)$_y$(EO)$_z$OH	1000–1100	175
4	Dehypon® LS-54	C$_{12–14}$alcoholate-(EO)$_5$-(PO)$_4$	638	47
5	Dehypon® LS-45	C$_{12–14}$alcoholate-(EO)$_4$-(PO)$_5$	652	44
6	Dehypon® LS-24	C$_{12–14}$alcoholate-(EO)$_2$-(PO)$_4$	506	34
7	Dehypon® 2574	Fatty alcohol alkoxylate mixture	n.a.	67
8	Dehypon® OCP 502	Oleyl cetyl alcohol propylene glycol ether	n.a.	27