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Membrane distillation crystallization of concentrated salts—flux and crystal formation

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Abstract

Membrane distillation crystallization (MDC) can be used to process highly concentrated aqueous solutions. In MDC, membrane distillation (MD) is used to recover water and to generate the desired supersaturation in the crystallizer where product crystals can be precipitated. This paper discusses factors influencing flux at close to saturation and the formation of salt crystals. The flux behaviour was investigated using two aqueous salt solutions of sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) which have different solubility–temperature coefficients. For both salts it was observed that MD was operable at high concentrations at feed temperatures of 50 and 60 °C with fluxes up to 20 L m^{-2} h^{-1}. It was found that both concentration and temperature polarization influenced the performance of MD. When operated in batch concentration mode without the crystallizer the flux gradually declined due to vapour pressure suppression and concentration polarization, up to a critical degree of saturation. The flux data could be predicted by heat and mass transfer modeling or by a simple empirical relationship involving the overall vapour pressure driving force and the degree of saturation. Beyond the critical degree of saturation, rapid flux decline was observed due to crystal deposition and scale formation on the membrane which reduced the membrane permeability. The Na_2SO_4 solution was able to operate at slightly higher degrees of saturation, which may be because the negative solubility–temperature coefficient favours solubility in the polarization layer. In MDC the temperature and saturation level both in the MD and the crystallizer are critical operating parameters. Anhydrous sodium sulfate crystals can be produced by means of MDC with a relatively narrow crystal size distribution and average size of 60–80 μm.

Keywords: Membrane distillation crystallization; Concentration and temperature polarization; Flux decay; Crystal size distribution

1. Introduction

Membrane distillation crystallization (MDC) is an innovative process which can potentially be used for the recovery of valuable salts from effluents and the processing of brine from desalination operations. MDC is a combination of membrane distillation (MD) and a crystallizer in which pure water is produced as permeate from the MD process while the concentrated solutes can be recovered as solids from the crystallizer. MD is a membrane process that has yet to fulfill its early promise. However, it has benefits such as, lower operating pressures and use of modest temperatures, potentially complete retention of nonvolatile solutes and high purity of permeate water, so that its potential applications have been broadened in recent years [1]. Such applications include desalination using low grade heat, the concentration of aqueous solutions and fruit juices, acid recovery, removal of organic compounds in drinking water production and radioactive waste treatment [2–5].

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One particular virtue of MD is that it has an advantage over reverse osmosis (RO) as a concentration and water recovery process at high solute concentrations. When operating MD at high concentrations, viscosity and vapour pressure suppression are the factors influencing the flux [6,7]. However in MD, which is driven by thermally induced vapour pressure difference, the suppression of driving force caused by high concentrations is modest [6]. On the other hand, in the RO process, significantly elevated pressures are required to overcome the osmotic pressure in concentrate processing. In practice, MD can operate with reasonable fluxes at moderate temperatures with high solute concentrations. This attribute favours the combination of MD, rather than RO, to crystallization as a means of solids recovery. Wu and Drioli first reported that at sufficiently high concentration crystallization of solute may occur leading to the possibility of MDC [7]. Later, Wu et al. [8] performed pharmaceutical wastewater treatment for taurine production by means of MDC. They reported that the MD-crystallization phenomenon occurred after the flux had reduced to essentially zero. Gryta employed an integrated DCMD and crystallization process to concentrate sodium chloride solutions in both batch and continuous modes [9]. He illustrated that coupling of MD with salt crystallization could be used to produce 100 kg m^{-2} d^{-1} of NaCl. However his operating feed temperature was as high as 85 °C while the permeate temperature was 20 °C to achieve a flux of approximately 23 kg m^{-2} h^{-1}. From our observation this high bulk temperature difference may encourage membrane wetting. Tomaszewska [10] also performed MD to concentrate sulfuric acid solutions up to 40% in order to recover lanthane compounds. His experimental results showed the possibility of 25% lathane recovery from the precipitate obtained from the concentrated solution. Recently, Drioli and coworkers have demonstrated the production of NaCl crystals [11] using the MDC process at lower MD operating temperature of 29 °C while crystallization was carried out at 25 °C.

In common with the other membrane processes, membrane fouling is also possible in MD. At high concentration, solute from the feed solution can be deposited and grow as scale on the membrane surface resulting in flux decline and membrane wetting. The concept of MDC operation is based on the crystallizable nature of solutes which can be precipitated outside the MD module. The control of the crystallization process in MDC is important in order to minimize deposition and growth on the membrane and to maximize the crystal production and removal in the crystallizer. Thus, the development of the MDC process requires evaluation of MD performance at high salt concentrations and development of crystallizer control strategies.

In MD, the membrane surface temperature (T_w) is lower and the concentration (C_w) is higher than in the bulk solution due to temperature polarization (T_P) and concentration polarization (C_P), respectively. These polarization phenomena may play important roles in MDC as the solubility of the salt depends on the temperature. Chernyshov et al. [12] used mathematical models to calculate temperature and concentration distributions in an MD feed channel. Their calculations suggested that if the solubility of the salt decreases with temperature, maximum supersaturation could occur in the bulk of the flow rather than at the membrane surface. Thus for aqueous salt solutions with positive solubility–temperature coefficient (i.e. lower solubility at lower temperatures), such as for NaCl, the combined polarization effects could encourage crystal formation on the membrane due to the lower solubility near the membrane wall. This challenge can be minimized by use of low fluxes at low operating temperatures; for example, Drioli and coworkers [11] employed a flux of about 0.5 l m^{-2} h^{-1} for NaCl which is rather low for practical applications. On the other hand, for salts with a negative temperature coefficient (solubility decreases with temperature, for example, Na_2SO_4) the temperature polarization is more favorable, although higher temperature processing is not. However, to date there has been no systematic assessment of the limits to MD in terms of fouling by crystal deposition and growth.

In this study, we have applied MDC to both anhydrous sodium sulfate (Na_2SO_4) and sodium chloride (NaCl) since they represent commonly processed salts with negative solubility coefficients (Na_2SO_4) and positive coefficients (NaCl) [13,14]. Our aim has been to apply MD at the limit of solubility at conditions favouring relatively high fluxes (5–20 L m^{-2} h^{-1}) and examine factors affecting flux and fouling. We also report on operation in the MDC mode with crystal production in the crystallizer.

2. Theory

The mass flux J can be expressed by a well-known equation

$$J = C\,\Delta P \tag{1}$$

where ΔP is the vapour pressure difference across the membrane and C is membrane permeability which is approximately constant, usually varying only slightly with experimental conditions [14]. In terms of combined heat and mass transfer, flux can be written [15,16],

$$J = \frac{h_v}{\Delta H_v}\frac{h}{h_v + h_c + h}\Delta T_b \tag{2}$$

which can be rearranged as,

$$\frac{\Delta T_b}{J\,\Delta H_v} = \frac{1}{dP/dT}\frac{1}{C\,\Delta H_v}\left\{1 + \frac{k_m/\delta}{h}\right\} + \frac{1}{h} \tag{3}$$

By plotting experimental data, $\Delta T_b/J\,\Delta H_v$, against $1/(dP/dT)$, the membrane permeability, C, and the overall film heat transfer coefficient, h, can be determined. The concentration polarization coefficient (CPC) can be described by the film model,

$$\xi = \frac{c_w}{c_b} = \exp\left(\frac{J}{\rho K}\right) \tag{4}$$