Thermal behaviour of different non-ionic surfactant concentration on the polymeric membrane

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Abstract. The principal objective of a study is indeed a well-functioning membrane such as high reject efficiency and high flow rate. In fact, too many studies are carried out on factors influencing the membrane, such as pressure intensity, polymer form, additive type, temperature influence during processing, and so on. Therefore, the study of thermal behaviour of surfactant concentration is vital to study the glass transition effect in good membrane production. Therefore, in this study, the main objective is to analyse the morphology structural effect of TX 100 surfactant on membrane by FTIR spectrum, and also to evaluate the thermal behaviour of different concentration of surfactant on membrane using DSC analysis. In order to study the thermal behaviour, membrane with 0, 1, 3 and 5 wt\% was prepared. The effects of TX 100 concentration on membrane and thermal analysis have been studied and discussed. Membrane without TX 100 has 30 °C of glass transition temperature (Tg) while membrane with 5 wt\% TX 100 has the highest Tg among the membranes. Therefore, the addition of surfactant to the membrane has an effect on Tg, thereby also impacting the porosity.

1. Introduction

To further increase the visual appeal, which is also an added value to the finished product, industries such as textiles, printing, paper, food and cosmetics use a number of dyes. However, as the pigment is poured into drains and flowing into large water bodies such as rivers or reservoirs, it often leads to environmental and health issues in the use of dyes. These impacts are not drastically seen, but because of constant waste absorption, they can have a long-term negative impact. Therefore, membrane separation is the most attractive solution to addressing these environmental issue, as well as providing low running costs [1]. Nanofiltration (NF) membrane is an interesting choice in the handling of dye wastewater since it has advantages such as low running and maintenance costs, high flux volume, ability to sustain high multivalent salt filtration, and high difference in osmotic pressure [2]-[4]. In addition, incorporating surfactant as an additive is an important strategy to synthesize high performance membranes in the separation process. Studies have shown that the uniform pore
distribution, suppressed macrovoids, high rejection efficiency and structure were established by surfactants [5].

The effect of the surfactant concentration on the system can affect the membrane's efficiency. It has been studied that the addition of surfactants would increase the permeation flux and NF membrane efficiency. In addition, various concentration of surfactants can give the membrane a different morphological structure [6].

In determining the thermal behaviour of surfactant compounds on the membrane, thermodynamic techniques are applied. Using thermal analysis, the physicochemical properties and stability of the surfactant may be calculated as a function of temperature. Differential Scanning Calorimetry (DSC) is an appropriate thermal analysis method used in the membrane industry to assess glass transition temperature, Tg and melting point, Tm of a sample. Additionally, membrane porosity also can be examined through Tg, which is a major factor for permeation flux [15].

The present work is undertaken, to analyse the morphology structural effect of surfactant on membrane by FTIR spectrum, to evaluate the thermal behaviour of different concentration of surfactant on membrane using DSC analysis.

2. Materials and Method

2.1. Materials
Polyethersulfone (PES), 1-Methyl-2-Pyrrolidone (NMP) and Polyethylene Glycol (PEG 600) was purchased from Merck and was used as polymer, solvent and additive, respectively in the preparation and production of membranes. The Triton X-100 (TX 100) used as a surfactant in this study was bought from Aldrich. Water was used in the phase inversion technique in the coagulant bath for membrane fabrication. Table 1 lists the physicochemical properties of the analyzed surfactant.

| Triton X-100 (TX 100) |
|-----------------------|
| Molecular formula     |
| C₁₄H₂₂O(C₂H₄O)ₙ      |
| Molecular weight      |
| ( g mol⁻¹ )           |
| 647                   |
| Molecular structure   |

2.2. Membrane Preparation

Referring to Table 2 for formulation, PES was inserted gradually until it dissolves into an NMP solution that is heated to a temperature of approximately 50 °C. After dissolving PES, PEG is added until it is well blended. At least 3 hours before stirring was over, TX 100 surfactant was applied. To extract air bubbles from the solution, the formulated solutions were held at room temperature without stirring at least for overnight [11].

| Membrane | PES (wt%) | NMP (wt%) | PEG (wt%) | TX 100 (wt%) |
|----------|-----------|-----------|-----------|--------------|
| M0       | 17        | 78        | 5         | 0            |
| MTX1     | 17        | 77        | 5         | 1            |
| MTX3     | 17        | 75        | 5         | 3            |
| MTX5     | 17        | 73        | 5         | 5            |
2.3. Membrane Fabrication
The phase inversion technique method for membrane fabrication is defined in Figure 1. Polymer solution will be poured onto a glass plate. With the casting knife set to 180 μm, the membrane was cast and the glass plate was immersed in a coagulation bath. The membrane is immersed in water for 24 hours, then in the ethanol solution for 24 hours and in the n-hexane solution for 3 hours. The membrane was then dried for 24 hours at room temperature for the final process [7].

![Figure 1. Phase inversion technique for membrane fabrication](image)

2.4. Characterisation

2.4.1. Fourier Transform Infrared Spectroscopy (FTIR) analysis
Using the FTIR Perkin-Elmer Spectrum RXI spectrometer, group functionality peaks were studied. The homogeneous solution was extensively blended with KBr powder and analyzed within the range of 4000 cm⁻¹. For each spectrum and history, 32 scans with a resolution of 1 cm⁻¹ were obtained.

2.4.2. Differential Scanning Calorimetry (DSC) analysis
Using a Metler Toledo DSC 822 with a rate of 10 °C min⁻¹, in the range of 0-100 °C with nitrogen flow, the DSC details were analyzed. During the heating phase, the glass transition temperature (Tg) of the membrane samples was measured by the heat flow against the temperature [11].

3. Result and discussion

3.1. Functional Group Analysis
FTIR has been used to analyse the functional group of TX 100 surfactant membrane. Functional group analysis is very important to identify and determine the organic compound in the membrane sheet. From Figure 2, the IR spectrum showed membrane containing 0, 1, 3, and 5 wt% of TX 100 surfactant exhibited a strong band at 1113.5 cm⁻¹ and 837.63 cm⁻¹ which corresponding to C-O-C band and C-H band from disubstituted benzene, respectively. Compared to the IR spectrum with no surfactant, there is no detection of peak in region of C-O-C band and C-H band. Thus, it can be concluded that data from IR spectrum showed the existence of TX 100 surfactant in the membrane. The peak intensity of each band was parallel increase with surfactant concentration which was observable from Figure 3. It can be seen that the peak intensity of C-O-C band and C-H band was increased when the concentration of TX 100 surfactant increased. As can be seen, the peak signify the concentration of each prepared membrane sample.
Figure 2. FTIR spectral changes of a membrane containing 0, 1, 3, and 5 wt% of TX 100 surfactant

Figure 3. Effect of TX 100 concentration on peak intensity

3.2. Thermal analysis
Glass transition temperature, \( T_g \) is commonly used for the understanding of membrane structure using a thermal inspection on a membrane. A higher \( T_g \) implies that the membrane, thus, has a looser structure and vice versa, has more free volume fraction [15]. From Figure 4, it is important to note that if higher surfactant concentration are applied, the endothermic peak changes to a higher temperature area. Obviously, the \( T_g \) is 60 °C for MTX5, which has the highest TX 100 concentration (5 wt%). All the membranes experience significant large endothermic peaks. The variations in the endothermic heat flow may be due to differences in the concentration of the surfactant TX 100. It is also evident that higher \( T_g \) means higher porosity of the membrane, which can contribute to greater membrane flux permeation. In Figure 5, it is shown that the membrane shows a \( T_g \) of 30 °C without TX 100. Meanwhile, \( T_g \) for 1, 3 and 5 wt% of TX 100 was 42, 53 and 60 °C, respectively. In conclusion the increase of TX 100 in membrane system have significant effect on glass transition temperature.

**Figure 4.** Thermal analysis containing 0, 1, 3, and 5 wt% of TX 100 surfactant

**Figure 5.** Effect of TX 100 concentration on glass transition temperature, \( T_g \)
4. Conclusion
Several membranes were prepared using the phase inverting technology for thermal behavior evaluation using DSC analysis with different surfactant concentrations of TX 100. It is considered to be a crucial factor to alter thermal activity through the presence of TX 100 surfactant with various concentrations. TX 100 surfactant can be observed to play an important role in modifying the thermal properties of the formed membranes, in particular the glass transition temperature (Tg). The TX 100 concentration and Tg appear to have a positive linear relationship. Higher Tg membrane may have variations in higher porosity, so the higher permeability flow may have a high effect. These results concluded that the TX 100 surfactant membrane has a high potential to produce high flux membrane in the wastewater industry.

5. References
[1] Lopes C N, Petrus J C C, and Riella H G 2005 Desalination, vol. 172, no. 1 pp. 77–83.
[2] Van Der Bruggen B, Curcio E, and Drioli E 2004 J. Environ. Manage. pp. 267–274.
[3] Ahmad A L, Harris W A and Ooi B S, 2002 J. Teknol., vol. 36, no. 1, pp. 31–44.
[4] Taylor P, Rashidi H R, Sulaiman N M N, Hashim N A, Hassan C R C, and Ramli M R 2015 Desalin. Water Treat. no. January, pp. 37–41.
[5] Chang H, Chen S, Lin D and Cheng L 2014 J. Memb. Sci., vol. 466, pp. 302–312.
[6] Amirilargani M, E. Saljoughi, and Mohammadi T 2009 Desalination, vol. 249, no. 2, pp. 837–842.
[7] Hassan A R, Rozali S, Hannan N, Safari M, and Besar B H 2018 Environ. Eng. Res., vol. 23, no. 3, pp. 0–2.
[8] Bezerra M A, Santelli R E, Oliveira E P, Villar L S and Escaleira L A 2008 Talanta, vol. 76, no. 5, pp. 965–977.
[9] Ghaemi N et al., 2015 J. Hazard. Mater., vol. 298, pp. 111–121.
[10] Hassan A R and Mohd Ali N S 2016 Malaysian J. Anal. Sci., vol. 20, no. 3, pp. 510–516.
[11] Sarah Husnaini Zainal M H M I, Abdul Rahman Hassan 2016 Malaysian J. Anal. Sci., vol. 20, no. 6, pp. 1524–1529.
[12] Saedi S, Madaeni S S, Shamsabadi A A and Mottaghi F 2012 Sep. Purif. Technol., vol. 99, pp. 104–119.
[13] Chaturvedi B K, Ghoshb A K, Ramachandhranb V, Trivedi M K, Hantab M S, and Misrab M 2001 vol. 133.
[14] Hassan A R, S S Sharifuddin, M H M Isa, and Yusra A F I, 2017 J. Fundam. Appl. Sci.
[15] Arthanareeswaran G, Thanikaivelan P, Srinivasan K, Mohan D, Rajendran M 2004 European Polymer Journal, 40(9), 2153–2159. https://doi.org/10.1016/j.eurpolymj.2004.04.024

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