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Effect of multiple cations in the feed solution on the performance of forward osmosis

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ABSTRACT

In this study, different combinations of feed stream such as 0.2, 0.3 and 0.4 M of $CaCl_2$ were, respectively, added with 1.0, 0.9 and 0.8 M of NaCl while maintaining the draw solution concentration at either 2.0 M of NaCl or $CaCl_2$ in order to compare likely changes to the flux generated when the feed stream contained NaCl only. The results obtained showed that more constituents in feed stream generated lesser flux. Increase in $CaCl_2$ concentration in feed stream resulted in more severe dilutive internal concentration polarisation (DICP) and hence, reduction in the performance ratio. The temperature and distribution of aggregated particle size also played a significant role in the overall performance of forward osmosis process. Further analysis showed that there is a relationship between the normalised driving force and flux behaviour which is governed by the effect of DICP. Additionally, the reflection coefficient was not unity as less than 2% traces of salt was found to permeate alongside with water towards the draw solution side.

Keywords: Dilutive internal concentration polarisation (DICP); Forward osmosis; Reflection coefficient; Salt aggregate; Water cluster; Water flux

1. Introduction

In the recent past, forward osmosis (FO) has gained attention and subsequently being utilised in applications such as concentration of liquid foods, treatment of wastewater and recovery of chemical from waste concentrate as in concentrating the centrate from anaerobic digesters, generation of electricity and reclamation of wastewater in space. Utilising FO in a reverse osmosis (RO) desalination process is discussed elsewhere [1]. Membranes used in FO applications are similar to the ones used in RO applications. Thus, the membrane would consist of an active layer and support layer which separate the feed and the draw streams (or solutions). When the active layer is placed to face the feed stream (or solutions), the operating mode is termed as "forward osmosis" or FO mode. Similarly, when the active layer is placed to face the draw solution, the operating mode is termed as "pressure retarded osmosis" or PRO mode. Since the membranes used are semi-permeable, water will move from the feed stream to the draw stream in both operating modes but at different flux. Both modes will create

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concentration polarisation on the external surfaces of the membrane [2]. The outer surface of the membrane facing the feed stream will create a concentrative external concentration polarisation (CECP), while the other outer surface of the membrane facing the draw stream will create a dilutive external concentration polarisation (DECP). However, the concentration polarisation created at the interface of the active and the support layer will be dilutive in FO mode (and called as dilutive internal concentration polarisation (DICP) and concentrative in the PRO mode (and called as concentrative internal concentration polarisation).

Operating under PRO mode generally produces higher flux as the net osmotic pressure difference between the surfaces of the active layer facing the feed and draw solutions is higher. Previous studies indicate that the effect of DECP on the flux is minimal [3] but non-linear trend was attributed to DICP [4]; deionised water was used as feed solution to eliminate the effects of CECP on the flux in those studies. Further, draw solutions with different solutes affected the DICP and subsequently the flux differently. For example, solutes with larger molecular weight (MW) could not diffuse as quickly as solutes with lower MW through the porous support layer [3]. This again reduces the net osmotic pressure difference between the surfaces of the active layer facing the feed and draw solutions and therefore the flux. Similarly, higher concentration of feed solution resulted in less flux at a given bulk pressure differential (i.e. osmotic pressure difference between the bulk feed and draw solutions) [5]. Normalised bulk pressure differential is considered as normalised driving force (NDF).

The effect of concentration of draw solutions was evaluated using a term called performance ratio (which is defined as the ratio between the experimental and the theoretical water flux) [5]. As the concentration of draw solution is increased the flux is increased. Therefore, the degree of dilution in the porous support is increased; i.e. the severity of DICP is increased. This will lead to reduction in the performance ratio and diminishing increase in flux at higher concentrations of draw solution. This reflected on the relationship between the NDF and the flux. At lower NDF, the flux increases sharply with the increase in NDF. However, at higher NDF, increase in flux diminishes as the NDF increases. Further, increase in flux increased the rejection of salt present in the feed stream. In one study, increasing the cross-flow of the feed (pre-treatment sludge of seawater RO process) and draw solutions (NaCl and $MgCl_2$) from 0.25 to 1.0 m/s did not change the flux significantly [6]. In another study, modelling of bidirectional solute permeation revealed that under FO mode, the model could predict fluxes of individual ions from the draw solution to the feed solution accurately [7]. Further, ion flux from the feed side to the draw side was inversely proportional to the reverse salt diffusion from the draw side to the feed side [8].

This study focuses on the performance of a FO process that contains a feed solution with two cations (Na^+ and Ca^{2+}) for two different draw solutions (NaCl and $CaCl_2$). The proportion of cations added to the feed solution plays a crucial role to the severity of DICP and therefore the flux. Selection of $CaCl_2$ was based on its high osmotic pressure for a given concentration compared to many other inorganic draw solutions; further, moderate diffusion coefficient as well as lower cost led to this choice [9].

2. Materials and methods

A flat sheet cellulose triacetate membrane with a woven embedded backing support obtained from Hydration Technology Inc., USA and cross-flow membrane cell arrangement (Fig. 1) were used in this study. The system was operated under FO mode. The initial volumes of feed and draw solutions were kelp at 1 L. The cross-flow rate of feed and draw solutions was maintained at 1.5 L/min. The experiments were carried out at room temperature (20 ± 2˚C). All experimental runs were conducted for 3 h.

Analytical grade sodium chloride (NaCl) and calcium chloride ($CaCl_2$) solutions were used as draw solutions. Sodium chloride or combination of NaCl and $CaCl_2$ were used as feed solutions in order to study the following: (1) effect of feed (NaCl) concentration, (2) effect of concentration of draw solutions (NaCl and $CaCl_2$), (3) effect of multiple cations (Na^+ and Ca^{2+}) present in feed solution and (4) effect of ionic strength and aggregation of cations. OLI stream analyzer was used to compute the osmotic pressure and viscosity of feed and draw solutions [10]. NZ nanosizer by Malvern was used for particle counting. DP70, Olympus BX51M microscope and OlympusU-TV0.5XC-3 Camera made in Japan with maximum magnification of 2000 was used to capture the water clusters [11–16]. Filters used in the camera were U-AN360-3 and U-DICR.

3. Results and discussion

All the experimental conditions and corresponding osmotic pressures and fluxes are shown in Table 1(a) and (b). While Table 1(a) is containing data relevant to

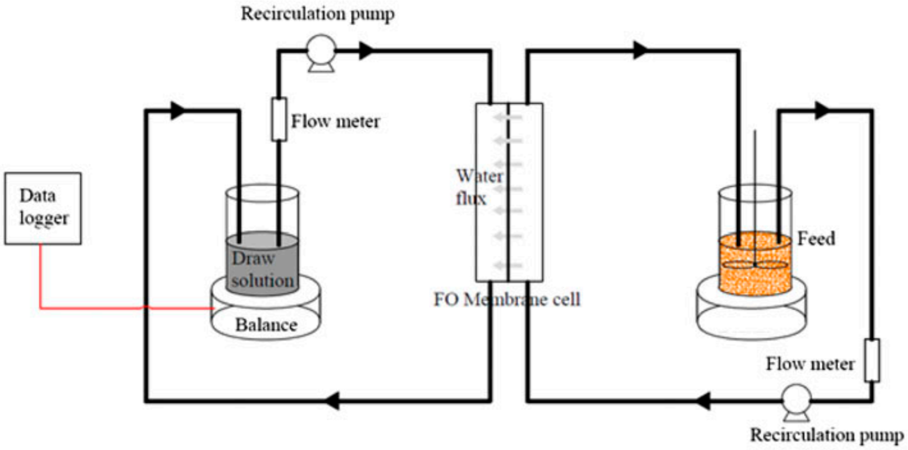

Fig. 1. FO experimental set-up.

Table 1
Relation ship among experimental fluxes, theoretical fluxes and bulk osmotic pressures of feed and draw solutions (a) 2.0 M $CaCl_2$ as draw solution (b) 2.0 M NaCl as draw solution
(a)

Experimental run	Concentration of feed solution, NaCl (M)	Concentration of draw solution $CaCl_2$ (M)	Bulk osmotic pressure, π_f of feed solution (bar)	Bulk osmotic pressure, π_D of draw solution (bar)	Experimental flux, $J_{w,ex}$ (L/m^2.h)	Theoretical flux, $J_{w,th}$ (L/m^2.h)
1	0.5	2.0	22.77	217.62	8.41	138.46
2	1.0	2.0	46.77	217.62	5.49	121.40
3	1.2	2.0	56.87	217.62	4.93	114.23
4	1.2	2.5	56.87	309.05	6.39	179.19
5	1.2	3.0	56.87	416.12	7.88	255.27
6	1.2	3.5	56.87	538.81	9.33	342.45
7	0.8 + 0.4C	2.0	78.02	217.62	4.23	99.20
8	0.9 + 0.3C	2.0	73.95	217.62	4.68	102.09
9	1.0 + 0.2C	2.0	69.26	217.62	4.88	105.42

(b)

Experimental run	Concentration of feed solution, NaCl (M)	Concentration of draw solution NaCl (M)	Bulk osmotic pressure, π_f of feed solution (bar)	Bulk osmotic pressure, π_D of draw solution (bar)	Experimental flux, $J_{w,ex}$ (L/m^2.h)	Theoretical flux, $J_{w,th}$ (L/m^2.h)
10	0.5	2.0	22.77	100.40	5.86	55.16
11	1.0	2.0	46.77	100.40	3.37	38.11
12	1.2	2.0	56.87	100.40	3.01	30.93
13	1.2	2.5	56.87	130.20	4.49	52.11
14	1.2	3.0	56.87	161.95	6.66	74.66
15	1.2	3.5	56.87	195.62	7.02	98.59

Note: C represent $CaCl_2$, permeability coefficient $A = 2.0 \times 10^{-7}$ m/s bar. Experimental flux was calculated using Eq. (1) while actual flux was calculated using Eq. (2).

FO experiments which used NaCl as draw solute, Table 1(b) is consisting of data that are related to FO experiments in which $CaCl_2$ was used as draw solute. The theoretical and experimental fluxes were computed using Eqs. (1) and (2) respectively which are given below:

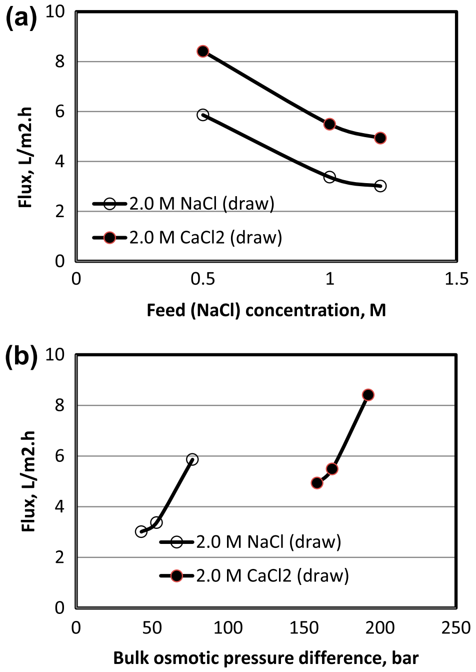

Fig. 2. (a) Effect of feed solute (NaCl) concentration on average flux when 2.0 M NaCl and 2.0 M $CaCl_2$ are used as draw solutes; (b) effect of bulk osmotic pressure difference on average flux when 2.0 M NaCl and 2.0 M $CaCl_2$ are used as draw solutes.

$$J_{w,th} = A \times \sigma \times (\pi_{ds} - \pi_{fs}) \tag{1}$$

where $J_{w,th}$ is the theoretical water flux, σ is the reflection coefficient, A is the membrane permeability coefficient which was found to be 2.0×10^{-7} m/s.bar and π_{fs} and π_{ds} are the bulk osmotic pressure of feed solution and draw solution, respectively. The value of σ was initially assumed to be unity which signifies complete rejection of solute but FO membranes typically have salt rejection in the region above 95% [5]. Reduction in feed volume in a given time interval will lead to increase in solute(s) concentration(s) in the feed side. This will lead to increase in conductivity and the increase can be computed theoretically. However, the actual increase in conductivity was found to be larger than the theoretical value which should be due to the movement of solute from the draw side to the feed side. This would help to calculate the rejection of draw solute. In this study an average of 98% draw solute rejection was computed from all experimental runs. Thus, σ is considered to be 0.98. The changes in the weight of the draw solution on the scale was recorded and used to determine the experimental water flux, $J_{w,ex}$ generated using Eq. (2):

$$J_{w,ex} = \frac{\text{Change in weight } (\Delta w)}{\text{Density of water } (\rho_w) \times \text{membrane surface area } (A) \times \text{time interval } (\Delta t)} \left(\frac{\text{L}}{\text{m}^2 \,.\, \text{h}}\right) \tag{2}$$

3.1. *Effect of feed solute (NaCl) concentration*

Experiments under FO modes were conducted with 0.5, 1.0 and 1.2 M NaCl concentrations in the feed solutions and 2.0 M NaCl or $CaCl_2$ concentrations in the draw solutions. As it can be seen in Fig. 2(a), the flux decreased with the increase in the concentration of feed solute. The average flux was higher when $CaCl_2$ was used as draw solution for a given concentration of feed solution. This is due to the presence of higher bulk osmotic pressure differential when $CaCl_2$ is used as draw solute (Fig. 2(b)). However, NaCl still has slightly higher diffusion coefficient compared to $CaCl_2$ at all equal molar concentrations when computed using the following formula [17].

$$D_0 = \frac{D_1 D_2 (z_1^2 C_1 + z_2^2 C_2)}{D_1 z_1^2 C_1 + D_2 z_2^2 C_2} \tag{3}$$

where D_0, D_1 and D_2 are the diffusion coefficients of the molecule and ions 1 and 2 forming the molecule, respectively; z_1 and z_2 are valencies of ions 1 and 2, respectively, and C_1 and C_2 are the ionic concentrations of ions 1 and 2, respectively. Therefore, if the curves in Fig. 2(b) are extrapolated carefully, it can be shown at a given bulk osmotic pressure differential, flux will be higher when NaCl is used as draw solute. This also can be seen in Fig. 3.

3.2. *Effect of concentration of draw solutes (NaCl and $CaCl_2$)*

Experiments under FO modes were conducted with 2.0, 2.5, 3.0 and 3.5 M NaCl or $CaCl_2$ concentrations in the draw solutions and 1.2 M NaCl concentration in the feed solutions. As it can be seen in Fig. 3(a), the average flux increased with the increase

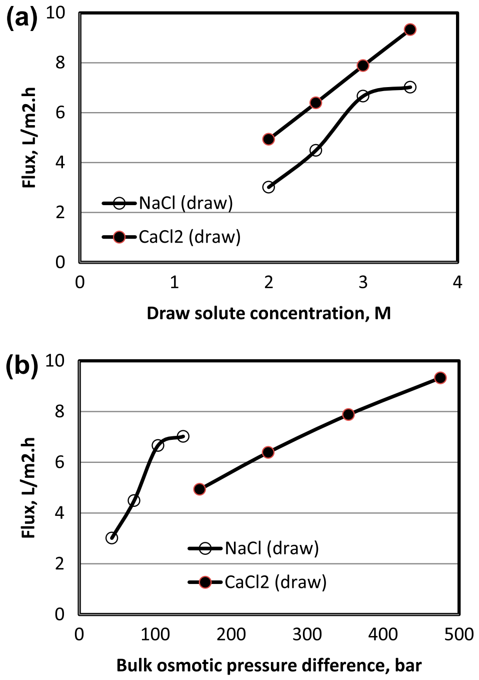

Fig. 3. (a) Effect of draw solutes (NaCl and $CaCl_2$) on average flux when 1.2 M NaCl is used as feed solute; (b) effect of bulk osmotic pressure difference on average flux when 1.2 M NaCl is used as feed solute.

in the concentration of the draw solute. Here again, higher fluxes were obtained when $CaCl_2$ is used as draw solute. However, when the bulk osmotic pressure differences were comparable, the flux was higher for NaCl draw solute as discussed in the previous section (Fig. 3(b)). Higher diffusion coefficient of NaCl helps to reduce the DICP in the support layer and increase the net osmotic pressure differential.

3.3. Effect of multiple cations (Na^+ and Ca^{2+}) present in feed solution

The flux and the osmotic pressure difference for results from experimental runs 12, 3, 7, 8 and 9 are shown in Fig. 4. It can be seen from Fig. 4(a) that the flux is high when $CaCl_2$ is used as draw solution. The presence of multiple cations tends to alter the bulk osmotic pressure difference as shown in Fig. 4(b).

As discussed previously, the performance ratio decreased with the increase in the bulk osmotic pressure difference between the draw and the feed solutions (Fig. 5(a)). This confirms the increase in the severity of DICP due to higher flux at higher concentrations of draw solutions. Fig. 5(b) also concludes that there is a steep increase in flux with the increase in NDF at lower NDF values.

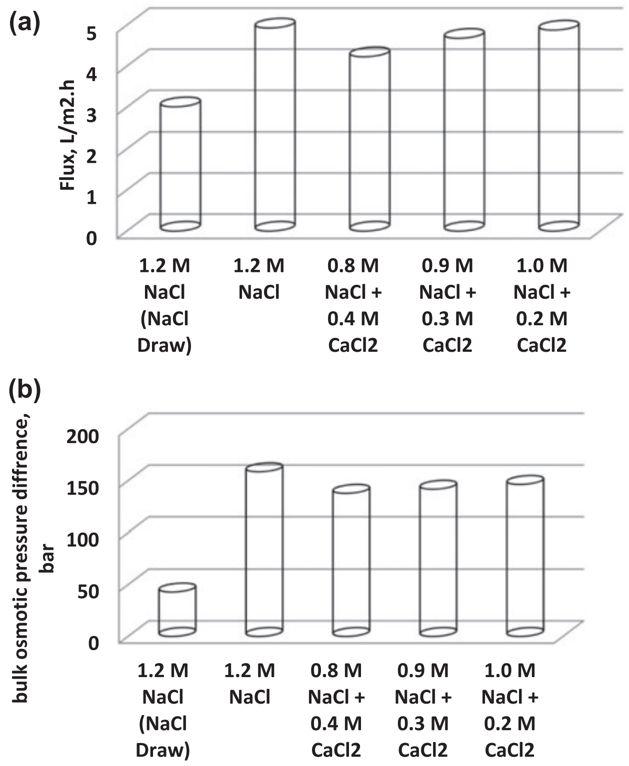

Fig. 4. (a) Effect of Na^+ and Ca^{2+} in the feed solution on average flux (the draw solution is 2 M $CaCl_2$ except for the one indicated in the *x*-axis title; results from experimental runs 12, 3, 7, 8 and 9 are shown on the *x*-axis from left to right); (b) effect of Na^+ and Ca^{2+} in the feed solution on Bulk osmotic pressure difference (the draw solution is 2 M $CaCl_2$ except for the one indicated in the *x*-axis title; results from experimental runs 12, 3, 7, 8 and 9 are shown on the *x*-axis from left to right).

3.4. Effect of ionic strength and aggregation of salts

High ionic strength of a draw solution can deswell a membrane which in turn can affect the flux and salt permeability [18]. Salt aggregation will also depend on the ionic strengths of feed and draw solutions which may affect the bulk osmotic pressure of those solutions. In this study, for the first time aggregation of NaCl and $CaCl_2$ molecules as well as water clusters present in FO process were identified through particle counting and microscopic observations. Although, we did not go into details of estimating the effect of salt aggregates on osmotic pressures under different experimental conditions the subsequent discussion will help to consider it in future studies. Fig. 6(a) shows the average particle sizes in the feed solutions with time during the FO process. Four different feed solutions were considered namely 1.2 M NaCl, 1.0 M NaCl + 0.2 M $CaCl_2$, 0.9 M NaCl +

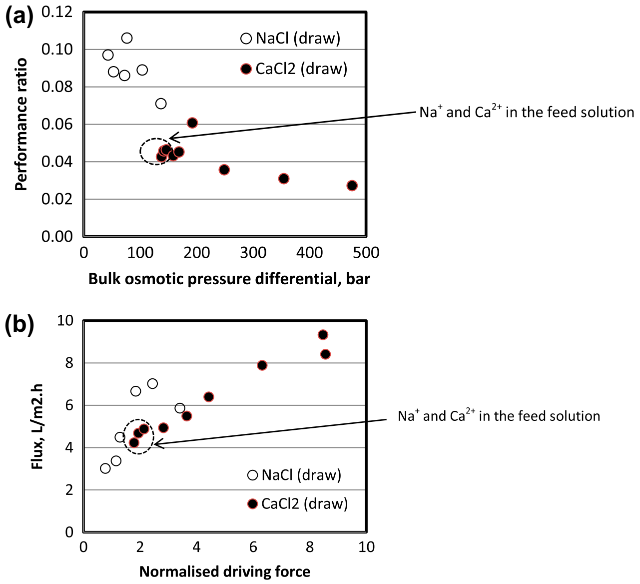

Fig. 5. (a) Performance ratio under all experimental conditions against bulk pressure differential; (b) flux under all experimental conditions against NDF.

0.3 M $CaCl_2$ and 0.8 M NaCl + 0.4 M $CaCl_2$. Fig. 6(b) shows the average particle sizes in the 2.0 M $CaCl_2$ draw solutions that were used in conjunction with those feed solutions.

Aggregated molecules of NaCl and $CaCl_2$ in the feed solutions and aggregated $CaCl_2$ molecules in the draw solutions can be observed from Fig. 6(a) and (b). Introduction of $CaCl_2$ tends to increase the average size of the aggregates in the feed solution and at the same time the dilution due to water flux decreases the aggregation of $CaCl_2$ in the draw solution.

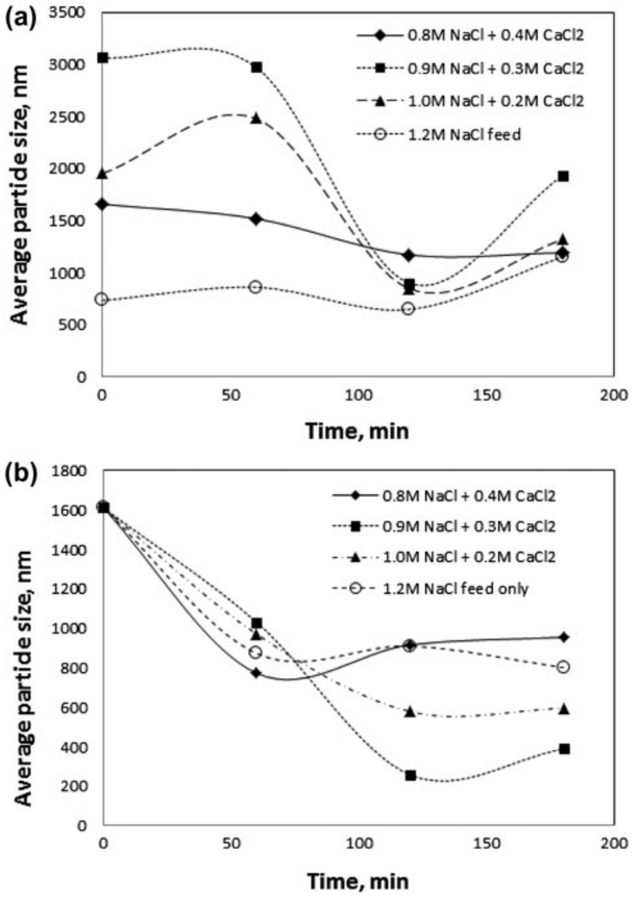

Fig. 6. (a) Average aggregate size in the feed solution during the FO process; (b) average aggregate size of $CaCl_2$ in the draw solution during the FO process.

When the feed solutions (1.0 M NaCl + 0.2 M $CaCl_2$; 0.9 M NaCl + 0.3 M $CaCl_2$ and 0.8 M NaCl + 0.4 M $CaCl_2$) were prepared, NaCl was the major constituent in those solutions and a single band was observed in the particle size analysis at several hundred nanometres with a maximum intensity of 75%. After 2 h of FO experiments, due to the recirculation of the feed as well as concentration (due to water flux from the feed to draw solution) the particle count produced three distinct bands, one around 1 nm (maximum intensity of 22%), another around several hundred nm (maximum intensity of 5%) and the third one around several thousand nm (maximum intensity of 11%). The band around 1 nm shows the true ionic or molecular constituents, and the band around several hundred nm indicates the aggregates of the NaCl and $CaCl_2$ molecules and the band around several thousand nm indicates the water clusters as there was no other impurities in the solution in that size range. After 3 h of experiment, the bands around several hundred nm and several thousand nm tend to merge to form a single band around several thousand nm. Fig. 7 shows the results obtained when the feed solution was comprised of 1.0 M NaCl and 0.2 M $CaCl_2$ with 2.0 M $CaCl_2$ as draw solution. This observation was consistent for all three feed solutions mentioned above. Similar outcomes for the particle counts of $CaCl_2$ draw solutions were also obtained in this study. Addition of salt into water showed the water clusters very clearly which were larger than the salt aggregates. A picture of NaCl dissolution in water is shown in Fig. 8 which shows that the salt aggregates are smaller than the water clusters. Existing literature provides numerous studies on water cluster [11–16]. Water molecules cluster in order to become stable through minimising the stabilisation energy and mathematical simulations indicate that around 30–48 molecules of water can cluster together [11,14]. These clusters could further agglomerate to give structures as shown in Fig. 8. Current mathematical models could not predict the water flux in FO processes accurately which might be

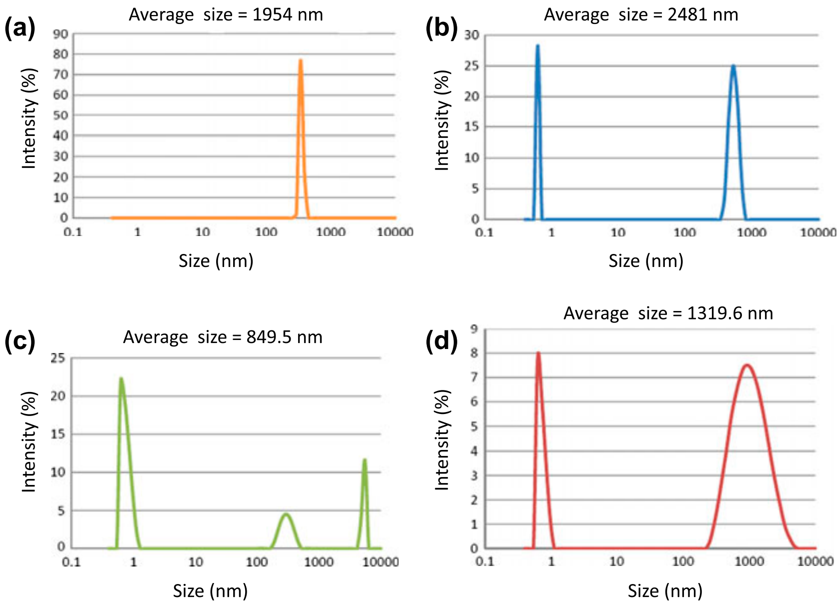

Fig. 7. Particle size analysis of 1.0 M NaCl and 0.2 M $CaCl_2$ feed solution (a) before the FO experiment; (b) after 1 h of FO experiment; (c) after 2 h of FO experiment; (d) after 3 h of FO experiment. Draw solution was comprised of 2.0 M $CaCl_2$.

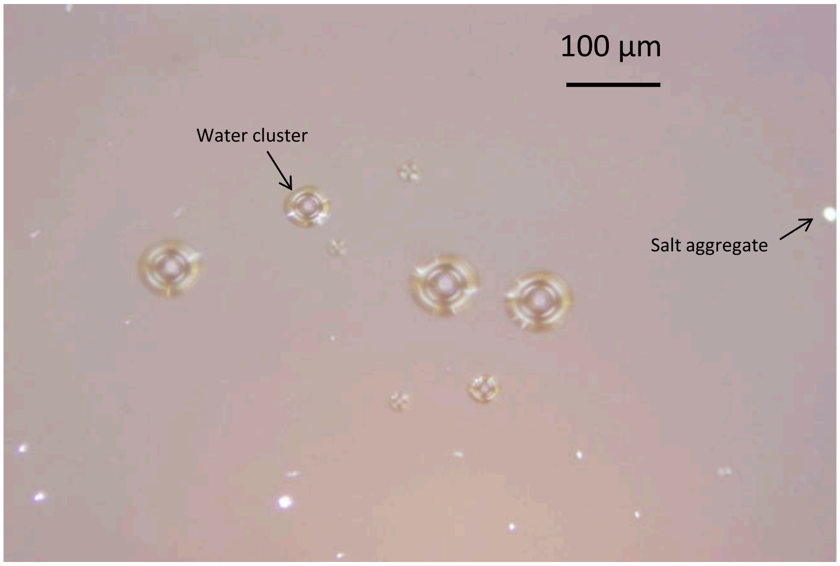

Fig. 8. Dissolution of NaCl salt into water revealing water clusters.

partially due to the effect of salt aggregates as well as water clusters on the flux. This needs further investigation and the outcomes of this study could be utilised to form a basis for such investigation.

4. Conclusions

FO experiments were conducted using either NaCl or $CaCl_2$ as draw solutions. Feed solutions were made with various concentrations of NaCl as well as the mixture of NaCl and $CaCl_2$. Effect of draw solutions on flux were evaluated using NaCl feed solutions; it was found that for a given bulk osmotic pressure difference, lower MW draw solute provided less DICP. This in turn produced higher flux. Higher concentrations of feed solute decreased the bulk osmotic pressure difference and subsequently reduced the flux. Mixed salts in the feed also reduced the bulk osmotic pressure difference. Aggregation of salt in the feed and the draw solutions were evident which should have played a role in the flux that needs further investigation.

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