



# Thermoresponsive cationic copolymer microgels as high performance draw agents in forward osmosis desalination



Yusak Hartanto<sup>a</sup>, Masoumeh Zargar<sup>a</sup>, Xiaolin Cui<sup>a</sup>, Yinghua Shen<sup>b</sup>, Bo Jin<sup>a,\*</sup>, Sheng Dai<sup>a,\*</sup>

<sup>a</sup> School of Chemical Engineering, The University of Adelaide, SA 5005, Australia

<sup>b</sup> College of Chemistry & Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

## ARTICLE INFO

### Article history:

Received 10 April 2016

Received in revised form

1 June 2016

Accepted 9 July 2016

Available online 16 July 2016

### Keywords:

N-isopropylacrylamide

Cationic microgels

Hansen solubility parameters

Forward osmosis

Desalination

## ABSTRACT

Thermoresponsive cationic copolymer microgels with aliphatic and aromatic cationic comonomers are synthesized and applied as the draw agents in forward osmosis (FO) desalination for the first time. The results show the FO desalination performance depends on the chemical structures and the dissociation constants ( $pK_a$ ) of the cationic comonomers. Cationic copolymer microgel containing 2-(diethylamino) ethyl methacrylate has the best overall performance with an initial water flux of 45.6 LMH and water recovery of 44.8%. This microgel also shows the shortest equilibrium swelling time which in turn reveals significant improvement in apparent flux of 5.5 LMH compared to other cationic and anionic copolymer microgels. Furthermore, Hansen solubility parameters are used to correlate the solvation behavior of these cationic microgels and their performance in forward osmosis desalination. Our results show Hansen solubility parameters and the dissociation constants of cationic comonomers can be used to estimate the performance of microgels in microgel-driven FO desalination systems.

© 2016 Published by Elsevier B.V.

## 1. Introduction

Forward osmosis (FO) is an emerging membrane-based separation process that has the potential to lower energy consumption in desalination process compared to reverse osmosis (RO) process due to the absence of highly applied hydraulic pressure [1]. However, low cost water recovery is the major problem associated with this technology [2]. In order to solve this issue, thermolytic solutes were proposed as the FO draw agents [3,4] due to their phase separation ability at mild temperature. The heating energy can be provided by low grade heat to reduce the overall energy cost. Although this strategy can reduce the energy cost of FO desalination, several drawbacks such as membrane stability [5], membrane scaling [6], final water quality [7] and reverse solute flux [8] still exist which hinder the practical application of these draw agents. In order to overcome the drawbacks of thermolytic solutes, various materials such as linear polymers [9–11], magnetic nanoparticles [12–14], synthetic organic solutes [5,15,16], ionic liquids [17,18] and switchable polarity solvents [19] were proposed as FO draw agents. Although reduced reverse solute flux can be achieved due to their large molecular sizes, these molecules always lead to severe concentration polarization that decreases the performance of these materials in water-drawing

process. Furthermore, pressure-driven membrane processes such as ultrafiltration, nanofiltration and reverse osmosis are still required at the water recovery process which might further increases the cost of process [2].

Thermoresponsive polymer hydrogels which are able to reversibly swell and deswell in respond to external temperature change have been recently proposed as effective FO draw agents [20–22]. The absence of reverse solute flux is one of the advantages of using hydrogels as FO draw agents [23]. However, the water flux generated from these hydrogels is much lower than other materials mentioned previously which could be caused by the poor contact between hydrogels and membranes [24,25]. Furthermore, poor liquid water recovery is another problem when bulk hydrogels are used as FO draw agents due to the formation of dense skin during hydrogel deswelling [26]. Although some strategies have been launched to improve the performance of these hydrogels in adsorbing water such as composite hydrogels [25,27–29], semi-interpenetrating network [21] and bifunctional layers formation [30], the water flux generated is still low compared to small molecules as draw materials.

Recently, thermoresponsive copolymer microgels of N-isopropylacrylamide and acrylic acid were proposed as the FO draw agents to overcome the problems associated with thermoresponsive bulk hydrogels [31,32]. Due to their small sizes and large surface areas, these microgels promote better contact with membranes, which results in significant improvement in water flux performance. Furthermore, the amount of acrylic acid plays an

\* Corresponding authors.

E-mail addresses: [bo.jin@adelaide.edu.au](mailto:bo.jin@adelaide.edu.au) (B. Jin), [s.dai@adelaide.edu.au](mailto:s.dai@adelaide.edu.au) (S. Dai).

important role on water flux and dewatering performance. Although there was improvement in water flux, the swelling kinetics of those microgels is still low which will impact the overall performance of the microgels. Therefore, improving the swelling kinetics of microgels is needed to achieve high apparent water flux.

A study investigating the FO performance of cationic polyelectrolytes of poly 2-(dimethylamino) ethyl methacrylate demonstrated that these polyelectrolytes were able to generate very high osmolality compared to weak acidic polyelectrolytes such as polyacrylic acid [9] in their protonated state [33]. In this paper, we prepared a series of thermoresponsive cationic copolymer microgels and applied them as FO draw agents for the first time. Our results show the FO performance of these cationic microgels depends on the chemical structures of cationic comonomers and their dissociation constants ( $pK_a$ ). Microgels with aliphatic cationic comonomers show higher water flux than those with aromatic cationic comonomers and the opposite behavior is observed in dewatering process. Copolymer microgel with 2-(diethylamino) ethyl methacrylate as a cationic comonomer shows the highest water flux and the fastest equilibrium swelling kinetics among other cationic copolymer microgels.

## 2. Experimental section

### 2.1. Materials

N-Isopropylacrylamide (NP, >98%), purchased from Tokyo Chemical Industry, was purified by recrystallization using n-hexane and dried overnight at room temperature. N-N'-methylene-bisacrylamide (BIS, >98%), 2-(dimethylamino) ethyl methacrylate (DMAEMA, 98%), 2-(diethylamino) ethyl methacrylate (DEAEMA, 99%) and 4-vinylpyridine (VP, 95%) were purchased from Sigma-Aldrich. 1-vinylimidazole (VI, 99%) was purchased from VWR International. 2,2'-Azobis (2-methylpropionamide dihydrochloride (V-50) was purchased from Novachem, Australia. Sodium chloride was purchased from VWR. Cellulose triacetate forward osmosis (CTA-FO) membranes were purchased from Hydration Technologies Inc. (HTI, USA).

### 2.2. Synthesis of cationic thermoresponsive copolymer microgels

Different thermoresponsive cationic copolymer microgels were synthesized using surfactant-free semi-batch emulsion polymerization. In a typical experiment, 0.735 g of NP, 0.015 g of cationic comonomer, 0.0075 g of BIS and 75 mL of DI water were mixed in a 250 mL three-necked flask fitted with a condenser, a mechanical stirrer and gas inlet and outlet. The semi-batch feeding solution was prepared by dissolving 2.205 g of NP, 0.045 g of cationic comonomer and 0.0225 g of BIS in 45 mL of DI water. After degassing the solution for 45 min with nitrogen, the three-necked flask was immersed into a preheated oil bath at 70 °C under nitrogen protection and a 3 mL of V-50 aqueous solution (0.03 g) was injected to the flask to start the polymerization. The feeding solution was injected at a rate of 3 mL/hour using a syringe pump one hour after the batch solution turned cloudy. The polymerization was carried out overnight under continuous stirring and nitrogen protection. After cooling, the microgels were purified using membrane dialysis (MWCO 12–14 kDa) against DI water for several days to remove any unreacted compounds. Finally, the purified microgels were dried at 65 °C and grounded into fine powders. The nomenclature used in this study is MCG-Monomer I-Monomer II.

### 2.3. Characterization of thermos-responsive cationic microgels

#### 2.3.1. Dynamic light scattering and zeta potential measurements

The hydrodynamic diameters ( $d_h$ ) of the cationic microgels at different temperatures (20–50 °C) and their zeta potentials at pH ~6.8 and 20 °C were measured using a Zetasizer (Malvern, Nano-ZS). The swelling ratios (SR) of microgels are calculated using the following equation:

$$SR = \left( \frac{d_{h,To}}{d_{h,Ti}} \right)^3 \quad (1)$$

where SR is the swelling ratio of the microgel,  $d_{h, To}$  (nm) is the hydrodynamic diameter of the microgel at  $T_o$  °C (20 °C) and  $d_{h, Ti}$  (nm) is the hydrodynamic diameter of the microgels at  $T_i$  °C.

#### 2.3.2. Conductometric and potentiometric titration

The amounts of functional cationic comonomers in the microgels were determined using conductometric and potentiometric titration. Typically, the pH of a 100 mL MCG-NP-DMAEMA microgel dispersion (~1 mg/mL) was adjusted to 3 using concentrated hydrochloric acid. The solution was then back titrated using a 0.1 M NaOH solution. After each addition of NaOH, the conductivity and pH of the solution were measured using a pre-calibrated Aqua-CP/A pH and conductivity meter.

### 2.4. Forward osmosis desalination evaluation

#### 2.4.1. Water flux evaluation

100 mg dried microgel was loaded in a homemade FO membrane setup equipped with an on-line conductivity monitoring system [31]. The membrane configuration adopted in this experiment was the active layer facing draw solute (AL-DS). The active membrane area is 3.16 cm<sup>2</sup>. A conductivity probe (probe cell constant,  $k=1.0$ ) was immersed in the feed solution of 2000 ppm NaCl to continuously monitor the change in conductivity of the feed solution against time for two hours. The system was conditioned by immersing the membrane in the feed solution for 30 min before loading the microgels on the membrane. The conductivity data was converted into the concentration of sodium chloride in the feed solution through a calibration curve. The water flux is calculated using the concentration data based on the following equations:

$$V_t = \frac{C_i V_i}{C_t} \quad (2)$$

$$J_w = \frac{V_i - V_t}{A \Delta t} \quad (3)$$

where  $V_t$  (mL) is the volume of feed at time  $t$ ,  $V_i$  (mL) is the initial volume of feed,  $C_i$  (ppm) is the initial feed concentration,  $C_t$  (ppm) is the feed concentration at time  $t$ ,  $J_w$  (LMH) is the water flux,  $A$  (m<sup>2</sup>) is the effective membrane surface area and  $\Delta t$  (h) is the time interval where the conductivity of the feed solution changes.

#### 2.4.2. Water recovery

Water-saturated microgels were transferred to centrifuge tubes and weighed after two-hour water adsorption period. The microgels were then centrifuged at 40 °C and 10,000 rpm for 10 min to separate adsorbed water from the microgels. The recovered water was measured using gravimetric method. The water recovered from the deswelled microgels was calculated using the following equations:

Download English Version:

<https://daneshyari.com/en/article/632220>

Download Persian Version:

<https://daneshyari.com/article/632220>

[Daneshyari.com](https://daneshyari.com)