

Communication

Sodium Tetraethylenepentamine Heptaacetate as Novel Draw Solute for Forward Osmosis—Synthesis, Application and Recovery

Qing Wu Long and Yan Wang *

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Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China; wubi86@126.com

* Correspondence: wangyan@hust.edu.cn; Tel.: +86-27-8779-3436; Fax: +86-27-8754-3632

Abstract: Osmotic energy, as a sustainable energy source with little environmental impact, has drawn much attention in both academia and industry in recent years. Osmotically driven membrane processes can harvest the osmotic energy and thus have great potential to produce sustainable clean water or electric energy. The draw solution, as an osmotic component, has been more and more explored by scientists in recent years in order to achieve a high osmotic pressure and suitable molecular size. In this work, a novel draw solute—sodium tetraethylenepentamine heptaacetate (STPH)—is synthesized and identified by nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) and Fourier transform infrared (FTIR). Its solution properties are optimized in terms of the solution pH and concentration, and related to the forward osmosis (FO) performance. A water flux of 28.57 LMH and a low solute flux of 0.45 g/MH can be generated with 0.5 g/mL STPH draw solution and de-ionized water (DI water) as the feed solution under pressure retarded osmosis (PRO) mode, which is superior to the FO performance with many other draw solutes reported. Further FO desalination test shows a stable water flux of 9.7 LMH with 0.3 g/mL STPH draw solution and 0.6 M NaCl feed solution. In addition, the draw solution recovery is also investigated.

Keywords: sodium tetraethylenepentamine heptaacetate (STPH); forward osmosis (FO); draw solution; membrane separation

1. Introduction

Nowadays, the growing global population is intensifying the demand for water and energy, which has led to the exploration of alternative water and energy resources for human beings. Emerging osmotically driven membrane processes, such as pressure retarded osmosis (PRO) and forward osmosis (FO), might provide sustainable solutions for the global need of clean energy [1,2]. Contrary to the pressure-driven membrane processes (e.g., reverse osmosis (RO), nanofiltration (NF), ultrafiltration), where intensive energy (pumping) are required to overcome the osmotic pressure of seawater, PRO and FO processes only require minimal external energy input for liquid circulation. The driving force for water to transport from the feed solution to the draw solution through a semi-permeable membrane is the osmotic pressure difference between two solutions of different chemical potential. It therefore possesses a high potential for desalination, wastewater treatment, power generation, and so on [3–5].

Nevertheless, existing practices have revealed that the FO performance was still limited by the availability of suitable semi-permeable membranes and draw solutions. In the past few years, growing efforts in both industry and academia have been devoted to developing high-performance

FO membranes with high permeation flux, high rejection, and low fouling tendency. However, much less attention has been devoted to seeking potential draw solutes, resulting in the delayed evolution of the FO process [6–8].

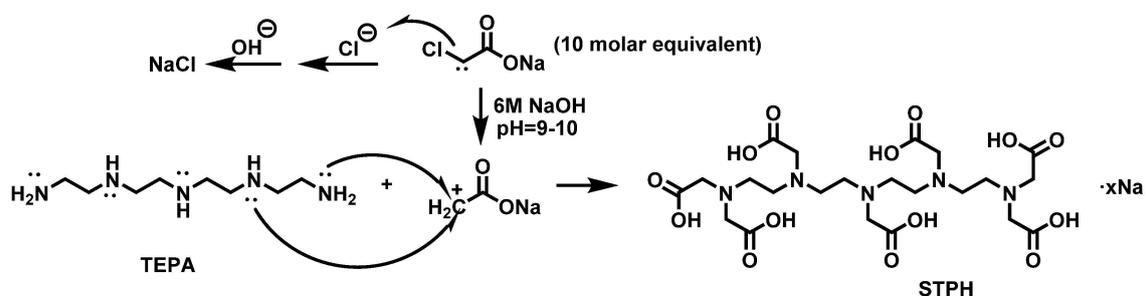
An ideal draw solute should be of a suitable molecular size, possess a high osmotic pressure and low solution viscosity, as well as easy recovery from the diluted solution [9,10]. In recent years, various novel draw solutes with enhanced properties have been reported based on different design strategies, including magnetic nanoparticles with enhanced surface hydrophilicity or expanded molecular size [11–13], and organic compounds with improved volatility [14,15] or physicochemical properties [16], *etc.* Previous works have reported polyacrylic acid salts (PAA-Na) with various molecular weights ranging from 1200 Da to 5000 Da [17], and Polyamidoamine with terminal carboxyl groups (PAMAM-COONa) [18] as novel draw solutes with good FO performance. Recently, we also demonstrated a novel ethylenediamine tetrapropionic sodium salts (EDTP) with multiple carboxyl groups [19]. The above studies all show that the introduction of carboxyl groups in the synthesized draw solute compounds can effectively improve their osmotic pressure and water solubility. In addition, the results also suggest that the reverse salt leakage decreases as the molecular weight increases. Therefore, a high-performance FO performance could be achieved to balance the water flux, salt leakage, and energy consumption, if the molecular weight and the solution property of draw solutes could be tuned properly.

In this work the compound sodium tetraethylenepentamine heptaacetate (STPH), a novel draw solute with a moderate molecular size and high osmotic pressure of the solution, is developed for FO applications. STPH with seven carboxyl groups incorporated in the chemical structure is synthesized by a one-step nucleophilic substitution reaction. Its physicochemical properties and FO performance of the resultant STPH draw solution are evaluated. The dewatering potential with STPH draw solution is assessed by a FO process using simulated seawater as the feed solution. The recovery of the diluted STPH solution after the FO test via two different processes is also explored.

2. Results and Discussion

2.1. Draw Solution Synthesis and Structure Characterization

In this work, a direct one-step nucleophilic substitution reaction is performed to form STPH as shown in Scheme 1. Firstly, sodium 2-chloroacetate was converted to the corresponding chloride anion under alkaline conditions and the carbocation is formed. Then tetraethylenepentamine (TEPA) with its numerous basic amino groups immediately attacks the carbocation, resulting in an acetate linked to the raw amine. The target compound STPH can be formed after all amino groups are fully substituted by acetate groups. The reaction is conducted at 55–65 °C with added NaOH to trap the generated chloride anions. The resultant compound is characterized using nuclear magnetic resonance spectroscopy (¹H-NMR) and Fourier transform infrared (FTIR) spectroscopy.



Scheme 1. Reaction mechanism of sodium tetraethylenepentamine heptaacetate (STPH) synthesis.

Distinct evidence of complete amino group substitution in TEPA can be reflected by the signal absence in the $^1\text{H-NMR}$ spectrum. As shown in Figure 1, two new single peaks at 2.76 (peak a) and 3.22 ppm (peak b) of methylene groups are observed in the spectra of STPH, but are absent in that of TEPA due to its symmetrical chemical structure, suggesting that all amino groups in TEPA have been completely reacted. Besides, a similar result is also obtained with the FTIR spectra of unreacted TEPA and the resultant STPH. As shown in Figure 2, for unreacted TEPA, strong characteristic peaks of the corresponding amino groups (at 3361 cm^{-1} and 3296 cm^{-1}) and CH_2 groups (at 2945 cm^{-1} and 2844 cm^{-1}) are observed in the spectra of TEPA, but they disappear in that of STPH, indicating the successful linkage of the acetate groups to amino groups. The additional characteristic peaks for amine groups at 1573 cm^{-1} , 1473 cm^{-1} and 1315 cm^{-1} also indicate the same result. Appearance of other strong peaks at 1658 cm^{-1} and 1091 cm^{-1} in the spectra of STPH could be ascribed to the $\text{C}=\text{O}$ double bond and $\text{C}-\text{O}$ single bond in the carboxyl groups [20]. Thus, the above results show that STPH has been successfully synthesized.

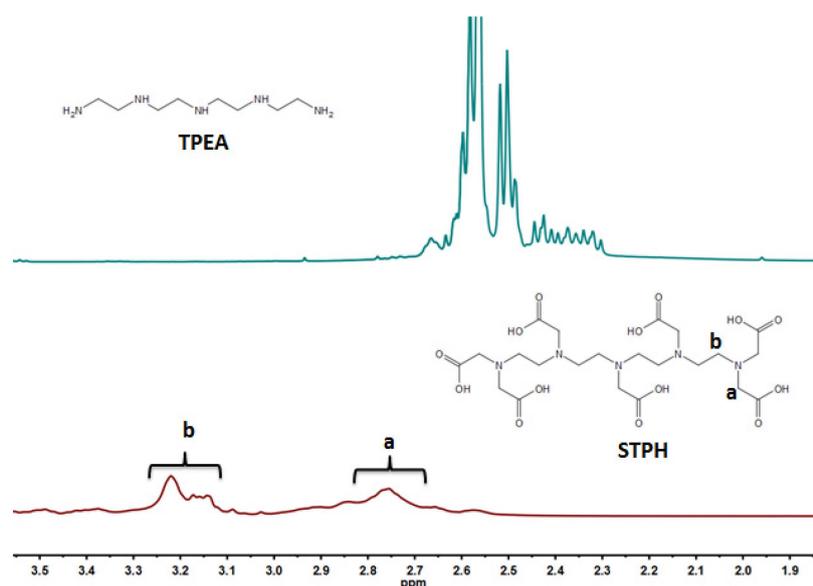


Figure 1. Nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) characterization of the compound STPH.

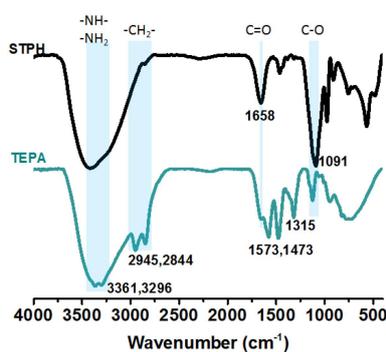


Figure 2. Fourier transform infrared (FTIR) spectroscopy characterization of the compound STPH.

2.2. pH Optimization of Sodium Tetraethylenepentamine Heptaacetate (STPH) Solution

To obtain a salt compound suitable as a FO draw solute, especially for organic salts, a simple pH optimization is often necessary. Our previous works [19] demonstrated that by the acid-base neutralization of EDTP draw solution using NaOH solution, an improved solute solubility and

compatibility with the FO membrane can be achieved. For solutions with a too high or low pH, the pH optimization must be carried out to avoid the severe membrane degradation and unpredictable salt leakage [21]. In this work, STPH solutions of various pH values (7–10) were studied.

Osmotic pressures of STPH solutions of different pH are shown in Figure 3a. It can be observed that for 0.1 g/mL STPH solution, the osmotic pressure increases significantly with the pH increase from 7 to 10, especially when the pH changes from 7 to 8. Besides, an osmotic pressure of 28 bar is obtained at pH 10, which is nearly 33.3% higher than that pH = 7 (21 bar). This phenomenon indicates that more carboxyl groups in STPH molecules are converted to carboxylate ions when the pH increases from 7 to 8, leading to more free ions generated in the aqueous solution. Similar results were also observed by Hau *et al.* [22] and in our previous work, where the pH plays an important role in the osmotic pressure, mainly because the solute components vary significantly with the pH change [19].

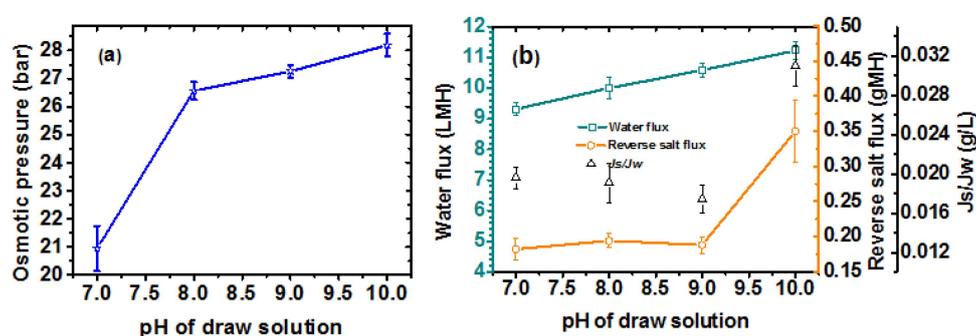


Figure 3. The effect of draw solution pH on (a) the osmotic pressure; (b) the forward osmosis (FO) performance. (0.1 g/mL STPH solution as the draw solution, the active layer of FO membrane facing the feed solution: PRO mode).

Figure 3b presents the water flux and the reverse salt flux with 0.1 g/mL STPH draw solution of different pHs (7–10) under PRO mode in FO process. The increasing trend of water flux with the increase in the solution pH is consistent with that of the osmotic pressure. As expected, the corresponding highest and lowest water flux of 11.22 and 9.31 LMH are observed at pH = 10 and 7, respectively. However, different from the change of the osmotic pressure, the trend of the water flux only exhibits a smooth and steady increase with pH increasing from 7 to 10. It is a common attribute that osmotic pressure is more sensitive to the component change of the draw solution, while the change of water flux could be retarded due to the combined effect of the solute diffusion coefficient, flow rate, diluted concentration polarization, *etc.* [23].

On the other hand, the increase in the draw solution pH also results in a change in the salt leakage. However, it is interesting to observe that the salt flux initially remains relatively constant when the solution pH is relatively low (7–9), then increases sharply when pH exceeds 9 (Figure 3b). Moreover, a highest salt leakage of about 0.35 ± 0.04 gMH is obtained for the STPH draw solution at pH = 10. This phenomenon should be caused by the fact that the STPH solution contains multiple negative groups which bond certain positive ions (Na^+) to maintain a charge balance. Once the STPH solution reaches a state of a better charge balance (at pH = 9), no excess Na^+ ions could escape from the mother solution of STPH, resulting in a much lower salt leakage in FO process. The J_s/J_w ratio is also shown in Figure 3b, where a lowest ratio of 0.017 L/g is achieved for the STPH draw solution at pH = 9, where the investment cost should be efficiently lower. In a word, the salt leakage can be reduced by pH optimization of the STPH draw solution, because of the expanded structure with multiple groups and high charge characteristics of the compound STPH [24].

2.3. Concentration Effect of STPH Solution

The concentration is an important factor for a draw solution since it directly affects its osmotic pressure and viscosity, and determines its FO performance and the relative investment cost. Generally, a draw solution with a high concentration will generate a high osmotic pressure and a high water flux, but this also causes a high viscosity and therefore a high energy consumption and a severe concentration polarization [19]. Therefore, the potential of the draw solution should be optimized by a concentration effect study.

Relative viscosities of STPH solutions of various concentrations (0.05–0.5 g/mL) (pH = 9) at 25 °C are shown in Figure 4. It can be seen that the viscosity increment is very small when the STPH concentration increases from 0.05 g/mL to 0.15 g/mL, and becomes more striking from 0.3 g/mL to 0.5 g/mL. It is also observed that the viscosity of the solution of 0.5 g/mL concentrations is about 5 and 10 times those of 0.3 g/mL and 0.15 g/mL, respectively, probably due to the restricted salt diffusion with the concentration increase. Similar trends were also found in previous works, where polyelectrolytes with large molecular weights can't expand fully at high-concentration due to the limited space [23]. However, the viscosity of STPH solution of a low concentration of 0.5 g/mL is lower than that of most other reported draw solutions [17,25–27], suggesting its great potential as a good draw solute candidate for FO applications.

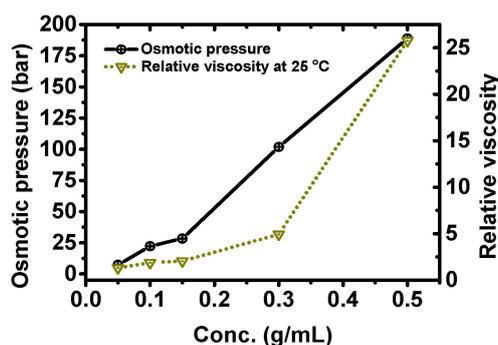


Figure 4. The osmotic pressure and relative viscosity of the STPH solution against de-ionized water (DI water) as a function of the concentration (pH = 9).

Figure 4 also shows the linear increasing trend of the osmotic pressure of STPH solution (pH = 9) with the increase in the solution concentration. The osmotic pressure increases from 7.34 bar at 0.05 g/mL to 188.8 bar at 0.5 g/mL, due to the increase of Na^+ ion number in the STPH solution at higher concentration. The osmotic pressure is superior to that of many other draw solutes at the same concentration, thus indicating that STPH possesses suitable features to be a desirable draw solute for FO applications.

2.4. Forward Osmosis (FO) Performance

The FO performance with STPH draw solutions with various concentrations is shown in Figure 5 using de-ionized water (DI water) as the feed solution under PRO mode at 25 °C. With the concentration increase of the draw solution, both the water flux and salt flux exhibit increasing trends from 0.05 g/mL to 0.5 g/mL, ascribed to the higher osmotic pressure. A high FO water flux of 28.57 LMH and a very low reverse salt flux of 0.45 gMH can be achieved using 0.5 g/mL STPH draw solution. The excellent FO performance with STPH draw solution could be assigned to the multiple carboxyl groups and relatively big molecular size of the STPH draw solutes, as well as the ion balance by simple pH optimization in the aqueous solution.

In addition, Figure 5 shows that the J_s/J_w ratio slightly drops initially with the draw solution concentration increase from 0.05 g/mL to 0.3 g/mL, and then slightly increases with the further

increase of the concentration to 0.5 g/mL test. Nevertheless, all J_s/J_w ratios remain below 0.024 g/L because of the high water flux and low salt flux, implying a possible low replenishment cost and the great potential of the STPH draw solution for FO applications.

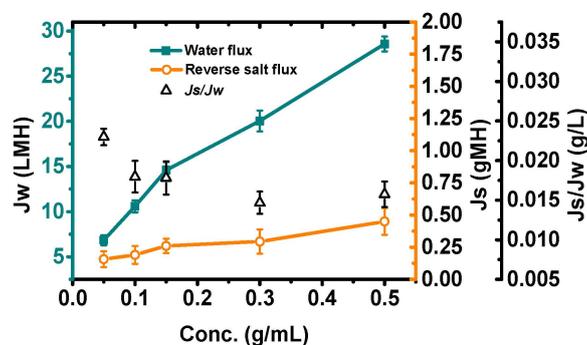


Figure 5. The FO performance with STPH draw solution of different concentrations (pH = 9, PRO mode, DI water as the feed solution).

With pH and concentration optimization, the FO test is further carried out with simulated seawater (0.6 M NaCl) as the feed solution and 0.3 g/mL STPH solution as the draw solution. As shown in Figure 6, a sharp flux decline occurs in the beginning of the test due to the growing concentration polarization phenomenon. After that, the water flux shows a steady decrease with the solution dilution. A relative high initial flux of 9.7 LMH is observed, suggesting that STPH is a good candidate for seawater desalination by a FO process.

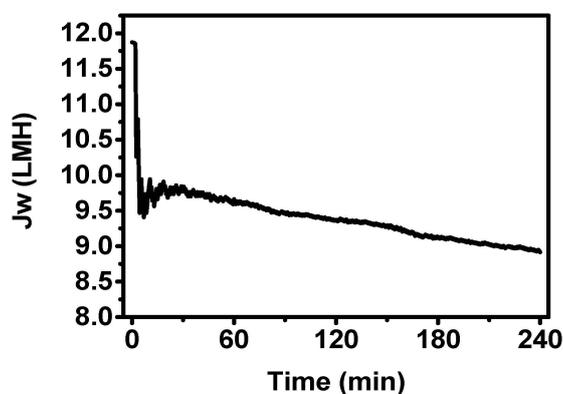


Figure 6. FO desalination with 0.3 g/mL STPH draw solution and simulated seawater (0.6M NaCl) as the feed solution.

This FO performance with the STPH draw solution was also benchmarked against most other reported draw solutes under comparable conditions, including dendrimers [18], hydroacid complexes [16,28], polyelectrolytes [29,30], responsive ionic liquid [31], and thermoresponsive copolymers [32,33]. Table 1 shows that the STPH draw solution exhibits superior FO performance to most of the other reported organic draw solutes. With 0.5 g/mL STPH draw solution (pH = 9), a high water flux of 28.57 LMH and a negligible salt flux of 0.45 gMH can be obtained because of its high osmotic pressure and low viscosity.

Table 1. Benchmarking of the forward osmosis (FO) performance using different draw solutions. Sodium tetraethylenepentamine heptaacetate: STPH; Polyamidoamine with terminal carboxyl groups: PAMAM-COONa; the active layer of the FO membrane facing the draw solution: PRO-mode.

Draw solution	Water flux (PRO-mode) (LMH)	Salt flux (PRO-mode) (gMH)	References
STPH, 0.5 g/mL	28.57 (TFC) ^a	0.45 (TFC)	This work
Polyacrylamide, 0.04 g/mL	4 (TFC)	~0.04 (TFC)	[29]
PAMAM-COONa (2.5G), 0.5 g/mL	29.7 (TFC)	8.86 (TFC)	[18]
Thermoresponsive copolymer, 0.5 g/mL	4 (TFC)	-	[32]
Responsive ionic liquid (P ₄₄₄₄ DMBS) ^b	4 (TFC) ^c	-	[31]
Ferric complex (Fe-OA), 0.39 g/mL	27.5 (TFC-PES ₁)	0.28 (TFC-PES ₁)	[16]
Ferric complex (Fe-CA), 2M	40.5 (TFC-PES) ^d	0.13 (TFC-PES)	[25]
Cobaltous complex (Co ₂ -CA), 2M	24.6 (TFC-PES)	0.13 (TFC-PES)	[25]
NaCl, 1M	36 (TFC)	-	[34]

^a Thin film composite membrane (TFC); ^b Tetrabutylphosphonium 2,4-dimethylbenzenesulfonate (P₄₄₄₄DMBS); ^c Feed solution: 0.6 NaCl; ^d Thin film composite membrane with polyether sulfone as substrate (TFC-PES).

2.5. Draw Solution Recovery

2.5.1. Nanofiltration (NF) Recovery

For a continuous and stable FO system, the suitable draw solution recovery technology is a critical factor. A common recovery technology for the draw solution is the membrane-based technology due to its easy operation and low cost when compared to traditional methods. Among them, NF as a mature membrane technology is extensively studied for its high efficiency and relative low molecular weight cut-off (<1000 Da) [35].

In this work, the recovery of the diluted STPH solution after FO test is investigated using the NF process. The change of the water flux and the STPH rejection with the feed concentration in the regenerative NF process are shown in Figure 7. It can be seen that the water flux and the rejection both decrease with the increasing concentration of the treated STPH solution. A high rejection rate of about 90.7% against STPH can be achieved and remains quite constant with the change of the STPH solution concentration. The water flux decreases from 8.72 LMH to 4.94 LMH when the STPH concentration in the feed increases from 1 g/L to 20 g/L, due to its higher osmotic pressure at higher concentration and the severer concentration polarization in FO process. Moreover, a STPH solution with a higher concentration may cause more solutes to permeate through the NF membrane, leading to the rejection decline. This result, however, also indicates that the pressure-driven NF process is actually an energy-intensive process for the recovery of the concentrated draw solution. Exploration of other energy-efficient techniques should be devoted for the practical applications of draw solutes in FO process.

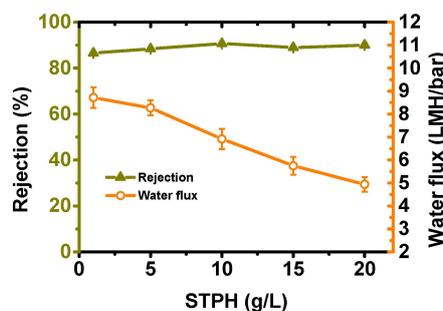


Figure 7. Recovery performance by nanofiltration (NF).

2.5.2. Recovery by Freezing Concentration (FC)

In nature, seawater can form sea-ice when the temperature decreases to its freezing point, and some dissolved salts (NaCl , MgCl_2) can therefore be excluded from ice crystals during this freezing process, resulting in a separation of brine and ice. This phenomenon is called freezing concentration (FC). The FC process could be used as a promising concentration and desalination technology because of its high separation efficiency, especially for the recovery of high-concentration draw solutions with existing high osmotic pressure. As well-known, the enthalpy of fusion of ice (latent heat of fusion: 333.5 kJ/kg) is six times lower than its enthalpy of vaporization (latent heat of vaporization of water: 2256.7 kJ/kg). This means that only 420 kJ/kg of energy is required to remove salt for the production of 1 kg of fresh water, which is six times lower than what multi-stage flash desalination requires [36,37].

In this work, the FC technology is also explored for the first time for draw solution concentration. Figure 8 shows the change of FO water flux and STPH concentration (STPH feed solution with an initial 0.3 g/mL concentration) during the draw solution recovery process for several FO-FC cycles. During each FO step, the water flux drops approximately 25.6% from the initial value of 20.35 LMH to 15.47 LMH after a 60-min test, while it increases from 15.47 LMH to 19.87 LMH after the concentration process by FC. It is observed that the water flux remains quite stable even after five cycles, demonstrating the high efficacy of FC for the recovery of the high concentration draw solution. Nevertheless, in real application, the actual energy involved still depends on the feed volume, operation temperature, and various other facility parameters, which may make them not so competitive as the NF process.

3. Experimental Section

3.1. Materials and Chemicals

TEPA (90%), sodium 2-chloroacetate (98%), NaOH (95%), concentrated hydrochloric acid (37%) were supplied by Sino-Pharm Chemical Reagent Co., Ltd. (Shanghai, China). All above compounds were used as received. All aqueous solutions were prepared using deionized water with a resistivity of $18.25 \text{ M}\Omega \cdot \text{cm}$, generated from an ultrapure water system (Wuhan Pin Guan Ultrapure Water LAB System Co., Ltd., Wuhan, China).

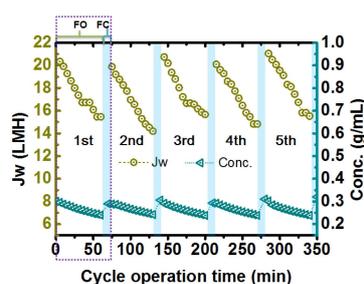


Figure 8. Recovery performance by freezing concentration (FC) process.

3.2. Synthesis of STPH

STPH was synthesized by a simple one-step nucleophilic substitution reaction as illustrated in Scheme 1. The detailed synthesis procedure was as follows: TEPA aqueous solution was prepared by dissolving TEPA (18.9 g , 0.1 mol) in DI water (250 mL), and then with the solution temperature was raised to $50 \text{ }^\circ\text{C}$, followed by the addition of aqueous solution of sodium 2-chloroacetate (100 mL , 116 g , 1 mol) over a period of 2 h. Afterwards, the temperature was raised to $70 \text{ }^\circ\text{C}$ for 5 h, while the pH was maintained at 9–10 by the addition of 6 M NaOH solution throughout the whole reaction. After that, the mixture was cooled to the room temperature and with pH adjusted to about 7 by 6 M hydrochloric acid solution. The resultant solution was further purified by dialysis to eliminate most

of the impurities, then dewatered on a Büchi R215 rotary evaporator to get a thick oily liquid, and further dehydrated in a vacuum oven for 6 h at 65 °C to give a yellow solid. The resulting product was abbreviated as STPH, and used directly for IR and ¹H-NMR characterization.

3.3. Structure Characterization of STPH

¹H-NMR was recorded on an on Bruker AVANCE III 400 MHz Instrument (Bruker, Karlsruhe, Germany) with D₂O used as deuterated solvent. FTIR spectra were obtained in the 4000–400 cm⁻¹ wavenumber range on a VERTEX-70 FTIR spectrometer (Bruker, Karlsruhe, Germany). The sample spectrum was recorded with the baseline corrected to remove the interfering signal of CO₂.

3.4. The Preparation and Characterization of STPH Draw Solution

STPH solution of 0.5 g/mL concentration (150 mL) was prepared by dissolving STPH solid (75 g as prepared in Section 3.2) in DI water at room temperature. The resultant solution was stirred at room temperature until all the solid was dissolved, and then diluted to get solutions of various concentrations (0.05 g/mL, 0.1 g/mL, 0.15 g/mL, and 0.3 g/mL). The osmotic pressure of the draw solution was tested based on the freezing point depression method, using a self-assembled system as described in our previous work [19].

3.5. FO Test

The FO test was conducted using a commercial bench-scale laboratory set-up (Suzhou Faith Hope Membrane Technology Co., Ltd., Suzhou, China) under PRO mode at 25 ± 1 °C [19]. Both feed and draw solutions with an initial volume of 150 mL were circulated co-currently by two peristaltic pumps, at the same flow rates of 0.3 L/min maintained by flowmeters. The TFC flat-sheet FO membrane was purchased from Hydration Technology Innovations (Albany, OR, USA) and assembled in a home-made rectangular polymethylmethacrylate (PMMA) cell with an active membrane area of 18.9 cm². Before use, it was immersed and rinsed with DI water for 30 min to remove the trapped glycerol completely. The FO experiment data was exported out to a computer with 30-second intervals by a digital balance (AND-EK4100i, Tokyo, Japan). At least three FO tests were performed to get the average data. The water flux and salt flux were calculated to evaluate the FO performance of the studied draw solute. The details are given in the Supplementary Information.

3.6. Draw Solution Recovery

3.6.1. Reconcentration by NF

The operational details for the NF recovery of the diluted STPH draw solution with a lab-scale NF system (Suzhou Faith Hope Membrane Technology Co., Ltd. Suzhou, China) were reported in our previous work [19]. The feed solutions studied here were STPH solutions ranging from 1 g/L to 20 g/L. A commercial flat-sheet NFX membrane from Snyder Filtration (California, CA, USA) with a MWCO of 150–300 Da with an effective membrane area of 17.35 cm² was employed. A stable pure water permeability of 10.79 LMH/bar can be detected under a hydraulic pressure of 3.5 bar. The calculation details on the water flux and rejection in NF process was given in the Supplementary information.

3.6.2. Reconcentration by FC

A lab-scale setup for FC was employed for the draw solution recovery. A schematic diagram is shown in Figure 9. It mainly consists of three parts, *i.e.*, a chiller, a stirrer, and a cylindrical crystallizer vessel [38]. The chiller filled with the cooling medium was firstly cooled down to 250 K, and then filled with 150 mL diluted STPH draw solution from a 250 mL crystallizer vessel. After 8 min the STPH solution was frozen, and the stirrer was started to fully mix the solution for 2 min, in order to reduce the concentration polarization near the ice front and accelerate the ice formation. The ice

crystal and entrained salt were then separated quickly by a Buchner funnel (diameter of 15 cm) and spray washing with cold water. After separation, the mother solution was then warmed to 25 °C by heat exchanger using the waste heat from the chiller, and recycled back to the draw solution tank. Each FO-FC experiment was cycled five times.

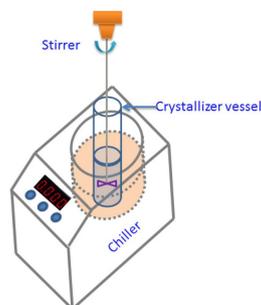


Figure 9. Lab-scale setup for FC [39].

4. Conclusions

In this work, a new draw solute, STPH, is developed and investigated for its osmotic potential in FO process. The STPH compound is successfully synthesized through a one-step substitution reaction and characterized by ¹H-NMR and IR. The ion balance in aqueous STPH solution can be regulated effectively by pH and concentration optimization, in order to improve its osmotic pressure and therefore the water flux, as well as to lower the salt flux. A water flux of 28.57 LMH and a relatively low salt flux (0.45 gMH) are obtained using DI water as the feed solution, which is superior to most of other reported draw solutes. During the desalination process, a water flux of 9.7 LMH could be achieved with 0.3 g/mL STPH draw solution, indicating its great potential for seawater desalination applications. In addition, the recovery of STPH solution shows that NF can concentrate the diluted solution with high selectivity; while FC recovers the concentrated solution with high efficiency.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1073/8/11/12344/s1.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

FC	Freezing concentration
FO	Forward osmosis
FO mode	The active layer of FO membrane facing the feed solution
MWCO	Molecular weight cut off, Da
NF	Nanofiltration
NMR	Nuclear magnetic resonance spectroscopy
PRO	Pressure retarded osmosis
PRO mode	The active layer of the FO membrane facing the draw solution
RO	Reverse osmosis
Rs	Solute rejection, %

References

1. Klaysom, C.; Cath, T.Y.; Depuydt, T.; Vankelecom, I.F.J. Forward and pressure retarded osmosis: Potential solutions for global challenges in energy and water supply. *Chem. Soc. Rev.* **2013**, *42*, 6959–6989. [[CrossRef](#)] [[PubMed](#)]
2. Han, G.; Zhang, S.; Li, X.; Chung, T.-S. Progress in pressure retarded osmosis (PRO) membranes for osmotic power generation. *Prog. Polym. Sci.* **2015**, *51*, 1–27. [[CrossRef](#)]
3. Loeb, S. Production of energy from concentrated brines by pressure-retarded osmosis: I. Preliminary technical and economic correlations. *J. Membr. Sci.* **1976**, *1*, 49–63. [[CrossRef](#)]
4. Energy sources. Available online: http://www.statkraft.com/globalassets/old-contains-the-old-folder-structure/documents/jostedal-official-assessment-final-10-may-2013_tcm9-27383.pdf (accessed on 10 May 2013).
5. Achilli, A.; Childress, A.E. Pressure retarded osmosis: From the vision of Sidney Loeb to the first prototype installation—Review. *Desalination* **2010**, *261*, 205–211. [[CrossRef](#)]
6. Post, J.W.; Veerman, J.; Hamelers, H.V.M.; Euverink, G.J.W.; Metz, S.J.; Nymeijer, K.; Buisman, C.J.N. Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electro dialysis. *J. Membr. Sci.* **2007**, *288*, 218–230. [[CrossRef](#)]
7. Achilli, A.; Cath, T.Y.; Childress, A.E. Power generation with pressure retarded osmosis: An experimental and theoretical investigation. *J. Membr. Sci.* **2009**, *343*, 42–52. [[CrossRef](#)]
8. Kim, Y.C.; Elimelech, M. Potential of osmotic power generation by pressure retarded osmosis using seawater as feed solution: Analysis and experiments. *J. Membr. Sci.* **2013**, *429*, 330–337. [[CrossRef](#)]
9. Shaffer, D.L.; Werber, J.R.; Jaramillo, H.; Lin, S.; Elimelech, M. Forward osmosis: Where are we now? *Desalination* **2015**, *356*, 271–284. [[CrossRef](#)]
10. Chung, T.-S.; Zhang, S.; Wang, K.Y.; Su, J.; Ling, M.M. Forward osmosis processes: Yesterday, today and tomorrow. *Desalination* **2012**, *287*, 78–81. [[CrossRef](#)]
11. Zhou, A.; Luo, H.; Wang, Q.; Chen, L.; Zhang, T.C.; Tao, T. Magnetic thermoresponsive ionic nanogels as novel draw agents in forward osmosis. *RSC Adv.* **2015**, *5*, 15359–15365. [[CrossRef](#)]
12. Ling, M.M.; Wang, K.Y.; Chung, T.-S. Highly water-soluble magnetic nanoparticles as novel draw solutes in forward osmosis for water reuse. *Ind. Eng. Chem. Res.* **2010**, *49*, 5869–5876. [[CrossRef](#)]
13. Na, Y.; Yang, S.; Lee, S. Evaluation of citrate-coated magnetic nanoparticles as draw solute for forward osmosis. *Desalination* **2014**, *347*, 34–42. [[CrossRef](#)]
14. Boo, C.; Khalil, Y.F.; Elimelech, M. Performance evaluation of trimethylamine–carbon dioxide thermolytic draw solution for engineered osmosis. *J. Membr. Sci.* **2015**, *473*, 302–309. [[CrossRef](#)]
15. Orme, C.J.; Wilson, A.D. 1-Cyclohexylpiperidine as a thermolytic draw solute for osmotically driven membrane processes. *Desalination* **2015**, *371*, 126–133. [[CrossRef](#)]
16. Ge, Q.; Chung, T.-S. Oxalic acid complexes: Promising draw solutes for forward osmosis (FO) in protein enrichment. *Chem. Commun.* **2015**, *51*, 4854–4857. [[CrossRef](#)] [[PubMed](#)]
17. Ge, Q.; Su, J.; Amy, G.L.; Chung, T.-S. Exploration of polyelectrolytes as draw solutes in forward osmosis processes. *Water Res.* **2012**, *46*, 1318–1326. [[CrossRef](#)] [[PubMed](#)]
18. Zhao, D.; Chen, S.; Wang, P.; Zhao, Q.; Lu, X. A Dendrimer-Based Forward Osmosis Draw Solute for Seawater Desalination. *Ind. Eng. Chem. Res.* **2014**, *53*, 16170–16175. [[CrossRef](#)]
19. Long, Q.; Qi, G.; Wang, Y. Synthesis and application of ethylenediamine tetrapropionic salt as a novel draw solute for forward osmosis application. *AIChE J.* **2015**, *61*, 1309–1321. [[CrossRef](#)]
20. Shao, L.; Cheng, X.Q.; Liu, Y.; Quan, S.; Ma, J.; Zhao, S.Z.; Wang, K.Y. Newly developed nanofiltration (NF) composite membranes by interfacial polymerization for Safranin O and Aniline blue removal. *J. Membr. Sci.* **2013**, *430*, 96–105. [[CrossRef](#)]
21. Beaudry, E.; Herron, J.; Lampi, K. Forward osmosis pressurized device and process for generating potable water. *U.S. Patent* 6,849,184, 4 December 2007.
22. Hau, N.T.; Chen, S.-S.; Nguyen, N.C.; Huang, K.Z.; Ngo, H.H.; Guo, W. Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge. *J. Membr. Sci.* **2014**, *455*, 305–311. [[CrossRef](#)]
23. Ge, Q.; Wang, P.; Wan, C.; Chung, T.-S. Polyelectrolyte-Promoted Forward Osmosis-Membrane Distillation (FO-MD) Hybrid Process for Dye Wastewater Treatment. *Environ. Sci. Technol.* **2012**, *46*, 6236–6243. [[CrossRef](#)] [[PubMed](#)]

24. Guo, C.X.; Zhao, D.; Zhao, Q.; Wang, P.; Lu, X. Na⁺-functionalized carbon quantum dots: A new draw solute in forward osmosis for seawater desalination. *Chem. Commun.* **2014**, *50*, 7318–7321. [[CrossRef](#)] [[PubMed](#)]
25. Ge, Q.; Fu, F.; Chung, T.-S. Ferric and cobaltous hydroacid complexes for forward osmosis (FO) processes. *Water Res.* **2014**, *58*, 230–238. [[CrossRef](#)] [[PubMed](#)]
26. Zhao, Q.; Chen, N.; Zhao, D.; Lu, X. Thermoresponsive Magnetic Nanoparticles for Seawater Desalination. *ACS Appl. Mater. Interfaces* **2013**, *5*, 11453–11461. [[CrossRef](#)] [[PubMed](#)]
27. Cai, Y.; Shen, W.; Wang, R.; Krantz, W.B.; Fane, A.G.; Hu, X. CO₂ switchable dual responsive polymers as draw solutes for forward osmosis desalination. *Chem. Commun.* **2013**, *49*, 8377–8379. [[CrossRef](#)] [[PubMed](#)]
28. Ge, Q.; Chung, T.-S. Hydroacid complexes: A new class of draw solutes to promote forward osmosis (FO) processes. *Chem. Commun.* **2013**, *49*, 8471–8473. [[CrossRef](#)] [[PubMed](#)]
29. Zhao, P.; Gao, B.; Xu, S.; Kong, J.; Ma, D.; Shon, H.K.; Yue, Q.; Liu, P. Polyelectrolyte-promoted forward osmosis process for dye wastewater treatment—Exploring the feasibility of using polyacrylamide as draw solute. *Chem. Eng. J.* **2015**, *264*, 32–38. [[CrossRef](#)]
30. Ou, R.; Wang, Y.; Wang, H.; Xu, T. Thermo-sensitive polyelectrolytes as draw solutions in forward osmosis process. *Desalination* **2013**, *318*, 48–55. [[CrossRef](#)]
31. Cai, Y.; Shen, W.; Wei, J.; Chong, T.H.; Wang, R.; Krantz, W.B.; Fane, A.G.; Hu, X. Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes. *Environ. Sci. Water Res. Technol.* **2015**, *1*, 341–347. [[CrossRef](#)]
32. Zhao, D.; Wang, P.; Zhao, Q.; Chen, N.; Lu, X. Thermoresponsive copolymer-based draw solution for seawater desalination in a combined process of forward osmosis and membrane distillation. *Desalination* **2014**, *348*, 26–32. [[CrossRef](#)]
33. Li, D.; Wang, H. Smart draw agents for emerging forward osmosis application. *J. Mater. Chem. A* **2013**, *1*, 14049–14060. [[CrossRef](#)]
34. The membrane technical data sheet. Available online: <http://www.htiwater.com/shop/research/form.php> (accessed on 12 Decemeber 2012).
35. Shao, L.; Cheng, X.; Wang, Z.; Ma, J.; Guo, Z. Tuning the performance of polypyrrole-based solvent-resistant composite nanofiltration membranes by optimizing polymerization conditions and incorporating graphene oxide. *J. Membr. Sci.* **2014**, *452*, 82–89. [[CrossRef](#)]
36. Fang, Y.; Bian, L.; Wang, X. Understanding membrane parameters of a forward osmosis membrane based on nonequilibrium thermodynamics. *J. Membr. Sci.* **2013**, *437*, 72–81. [[CrossRef](#)]
37. Khosa, M.A.; Shah, S.S.; Feng, X. Metal sericin complexation and ultrafiltration of heavy metals from aqueous solution. *Chem. Eng. J.* **2014**, *244*, 446–456. [[CrossRef](#)]
38. Fujioka, R.; Wang, L.P.; Dodbiba, G.; Fujita, T. Application of progressive freeze-concentration for desalination. *Desalination* **2013**, *319*, 33–37. [[CrossRef](#)]
39. Williams, P.M.; Ahmad, M.; Connolly, B.S.; Oatley-Radcliffe, D.L. Technology for freeze concentration in the desalination industry. *Desalination* **2015**, *356*, 314–327. [[CrossRef](#)]



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