

# Hydroacid complexes: a new class of draw solutes to promote forward osmosis (FO) processes†

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**A new class of draw solutes from hydroacid complexes is presented. With hydroacid complexes as draw solutes in FO, superior performance is achieved in terms of high water fluxes and negligible reverse solute fluxes. The characteristics of expanded configurations, abundant hydrophilic groups and ionic species are essential for hydroacid complexes as competent draw solutes.**

Freshwater scarcity is a global issue with the rapid growth of population and economics. Nowadays the supply of potable water is increasingly relying on science and technology.<sup>1–7</sup> Reverse osmosis (RO) is the most widely used membrane technology in seawater desalination to produce clean water.<sup>1</sup> However, due to the high energy consumption in the RO process, forward osmosis (FO) has received much attention because of its unique characteristics of high water recovery, low operation pressure and minimal brine discharge.<sup>2–7</sup> It may potentially alleviate the stress of freshwater scarcity. Despite these advantages, however, the unavailability of cost-effective, easy recovery and high performance draw solutions is still a big obstacle to the advancement of FO.<sup>6,8</sup>

Given the importance of FO, the exploration of draw solutions has received great attention. Various draw solutes have been proposed over the past few decades.<sup>5–8</sup> Commercial compounds including mixed gases,<sup>9,10</sup> sugars,<sup>11,12</sup> inorganic and organic salts<sup>13–15</sup> have been extensively used in FO. Draw solutions from these compounds create reasonably high water fluxes but with significant reverse solute fluxes,<sup>15</sup> which not only contaminate the product water but also increase the replenishment cost of draw solutes. To overcome these drawbacks, synthetic draw solutes have been explored.<sup>16–21</sup> However, most of them have low osmotic pressures unless at high concentrations where concentration polarization may become a serious issue. To solve

this problem, a new class of draw solutes, hydroacid complexes, is explored in this study.

Coordination complex is a material consisting of metal(s) and ligand(s). The configuration of the metal center expands when it bonds to ligands. This feature may lead to a low reverse flux in FO and easy solute regeneration in posttreatment when complexes are used as draw solutes. Meanwhile, they can be designed freely according to the required functions by varying either the metals or ligands. Such characteristics make complexes appropriate candidates to be draw solutes. In this work, a series of cupric and ferric complexes with hydroxyl acids of citric acid (CA), malic acid (MA) and tartaric acid (TA) as ligands were synthesized according to a modified method.<sup>22</sup> Fig. 1 shows a representative structure of a ferric CA complex (Fe–CA), while structures of other complexes with their precursor ligands are illustrated in Table S1 (ESI†).

The coordination of the acids to the Cu<sup>2+</sup> or Fe<sup>3+</sup> metal core was confirmed by FTIR spectroscopy (the spectra of CA complexes are given in Fig. S1, ESI†). Characteristic absorptions at ~3400, 1608–1720 and 1396–1427 cm<sup>-1</sup> correspond to O–H, C=O and C–O groups, respectively,<sup>16</sup> indicating the presence of COOH. The band at ~570 cm<sup>-1</sup> corresponds to the characteristic absorption of the metal–oxygen bond.<sup>16</sup> All analytic results verify the successful coordination between hydroxyl ligands and metal centers.

The composition of the complexes was disclosed by TGA measurements (Fig. S2, ESI†). The thermal decomposition of CA and MA complexes takes place in two major stages: (i) dehydration of the hydrated complexes to form unhydrated intermediates (45–140 °C); (ii) decomposition of the unhydrated intermediates

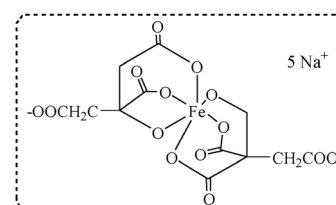


Fig. 1 Structure of Fe–CA.

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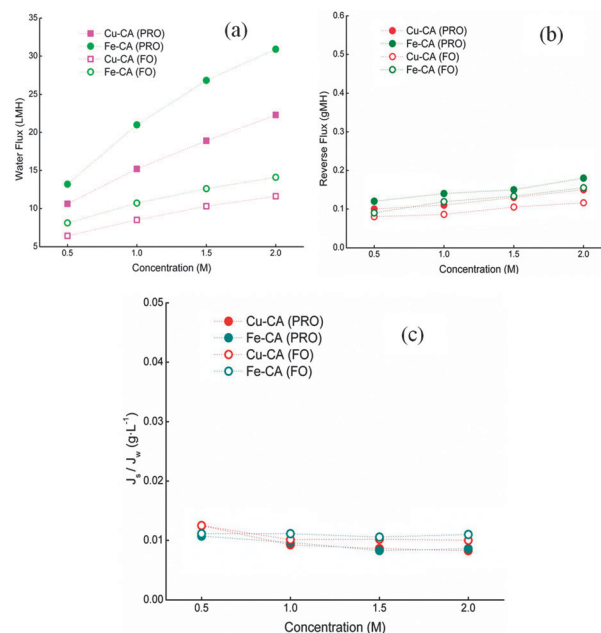
† Electronic supplementary information (ESI) available: Experimental (synthesis, characterization and relative viscosity of hydroacid complexes; FO set up and tests), structures and molecules, FTIR spectra, TGA spectra and weight losses. See DOI: 10.1039/c3cc43951h

to form metal oxides (250–350 °C).<sup>23,24</sup> The weight loss in the first stage corresponds to the departure of H<sub>2</sub>O molecules either coordinating to the metal cores or present in the complexes *via* H bonds. The weight loss in the second stage is primarily due to the decomposition of the unhydrated complexes to form metal oxides by losing H<sub>2</sub>O, CO or CO<sub>2</sub> molecules. Unlike CA and MA complexes, TA complexes do not contain water. Therefore, only one step of decomposition was observed in the range of 230–320 °C. For all complexes, the observed weight losses closely approximate the calculated ones (Table S2, ESI†).

Fig. S3 (ESI†) shows the relative viscosity ( $\eta_r$ ) of all complexes at different concentrations.  $\eta_r$  increases with an increase in the concentration. Comparing the respective cupric and ferric series,  $\eta_r$  only changes slightly when varying the ligands from CA to MA to TA. At the same concentration, the ferric complex with a more complicated molecular structure has a larger  $\eta_r$  than its cupric analogue. However, compared to polyacrylic acid sodium (PAA-Na) draw solutes,<sup>17</sup> all of these complexes exhibit insignificant  $\eta_r$ . This indicates that the adverse effect of draw solute viscosity on FO performance may be negligible when using these complexes as draw solutes. This hypothesis is verified by subsequent FO experimental results.

All complexes except Cu-TA are in anionic forms. Their sodium salts have good water solubility under neutral conditions and produce considerable osmotic pressures in water. Fig. S4 (ESI†) compares their osmotic pressures and shows that osmotic pressure increases with increasing solute concentration. The osmotic pressure of CA and its complexes follows the order of Fe-CA > Cu-CA > CA. In the studied complexes, Fe-CA has the highest osmotic pressure, which is determined by its structure. According to the van't Hoff equation,<sup>8</sup> the presence of more ionic species in an aqueous solution gives a higher osmotic pressure. Since the number of ionic species increases from a ligand precursor to its complexes and the ferric complexes have more ionic species than the cupric analogues, ferric complexes have higher osmotic pressures.

The configurations of these bulk complexes are either tetrahedral (Cu<sup>2+</sup> complexes) or octahedral (Fe<sup>3+</sup> complexes). The characteristics of their expanded structures along with low viscosity and high osmotic pressure make them good candidates to be draw solutes. Fig. 2 shows their FO performance using HTI membranes under both pressure retarded osmosis (PRO) (draw solution against the selective layer of membranes) and FO (draw solution against the support layer of membranes) modes. Water flux increases with increasing solute concentration, consistent with the change tendency of osmotic pressure (Fig. S4(a), ESI†). The water fluxes under the PRO mode consistently outperform those under the FO mode, as observed elsewhere.<sup>5–8,10,25</sup> The increment of reverse solute flux with the increase in solute concentration is very small. The highest reverse flux is below 0.2 g MH when the solute concentration is up to 2.0 M, which is one order of magnitude lower than that of NaCl draw solutions with comparable water fluxes under the same conditions.<sup>21</sup> The ratio of reverse solute flux ( $J_s$ ) to water flux ( $J_w$ ),  $J_s/J_w$ , is lower than 0.015 g L<sup>-1</sup>. This indicates that the complex loss in recovering water *via* FO is insignificant and the replenishment cost to maintain a constant concentration is negligible. Clearly, these

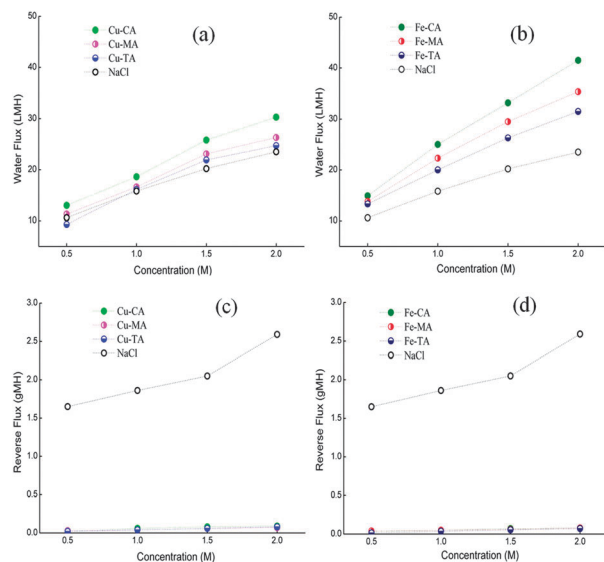


**Fig. 2** The performance comparison of Cu-CA and Fe-CA through HTI membranes: (a) water flux ( $J_w$ ); (b) reverse flux ( $J_s$ ); (c)  $J_s/J_w$ . DI water as the feed solution.

complexes are superior to the inorganic draw solutes such as MgCl<sub>2</sub>, NaCl, and NH<sub>4</sub>HCO<sub>3</sub> when comparing their losses in FO (0.015 vs. 0.57–2.48 g L<sup>-1</sup>)<sup>15</sup> with comparable water fluxes. In addition, the Fe-CA complex outperforms most draw solutes from synthetic materials developed recently such as imidazole derivatives,<sup>18</sup> nanoparticles,<sup>16,21</sup> organic salts,<sup>14</sup> and others,<sup>19,20</sup> in terms of higher water fluxes and negligible reverse fluxes.

The performance of cupric and ferric complexes were also evaluated using a self-made cellulose acetate (CA) hollow fiber membrane which has a smaller pore size and a thinner, dense selective layer than the HTI membrane.<sup>25</sup> For comparison, NaCl was included as a benchmark draw solute. Fig. 3 shows that water fluxes for all compounds increase with an increase in their concentration. Cupric and ferric complexes comprising CA have the highest water fluxes in their respective series. Meanwhile, the water fluxes of ferric complexes increase faster than those of cupric complexes upon varying the ligand from TA to MA to CA. In addition, ferric complexes produce much higher water fluxes than their cupric analogues due to the presence of more ionic species in the ferric molecules. Similar to the observation in HTI membranes, reverse solute fluxes for all complexes are negligible (Fig. 3(c) and (d)). These advantages demonstrate that an FO process using this type of complexes may provide solutions not only for water reuse but also for the separation of some special compounds such as protein enrichment where trace impurity due to reverse solute diffusion may denature the target products.<sup>26</sup>

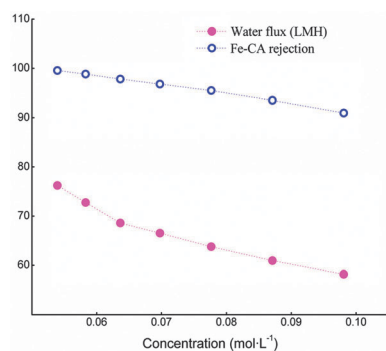
Compared to NaCl, cupric complexes produce comparable or slightly higher water fluxes. Ferric complexes, however, outperform NaCl greatly. All complexes exhibit superiority over NaCl in terms of reverse flux (Fig. 3(c) and (d)). These complexes also surpass the previous PAA-Na system<sup>17</sup> due to their much better FO performance under similar conditions. Moreover, unlike



**Fig. 3** Performance comparison *via* CA membranes: (a) water fluxes of Cu<sup>2+</sup> complexes and NaCl; (b) water fluxes of Fe<sup>3+</sup> complexes and NaCl; (c) reverse fluxes of Cu<sup>2+</sup> complexes and NaCl; (d) reverse fluxes of Fe<sup>3+</sup> complexes and NaCl. DI water as the feed solution under the PRO mode.

in the PAA-Na system, the increase of water flux in the current complex system is almost proportional to the complex concentration owing to the higher degree of dissociation. Interestingly, the FO performance *via* CA hollow fiber membranes (Fig. 3) is much better than that *via* HTI flat sheet membranes (Fig. 2) even though both have high water fluxes and low reverse fluxes. This is due to the tighter specifications of the CA membrane in view of the small pore size, thin dense layer and porous sublayer morphology.<sup>25</sup> Therefore, the performance of complex draw solutes would be further improved when a more ideal FO membrane is used.

In view of the best performance, 2.0 M Fe-CA was chosen to study seawater desalination *via* the CA membrane using 3.5 wt% NaCl as the feed. A water flux of 13.1 LMH was achieved under the PRO mode which is better than that of 9.98 LMH obtained using 2.0 M MgCl<sub>2</sub> draw solution under the same conditions.<sup>25</sup> Apparently, the characteristics of expanded



**Fig. 4** Water production and solute rejection in the recycling of Fe-CA.

structure, abundant hydrophilic groups and ionic species in aqueous solutions are crucial for draw solutes to exhibit good FO performance.

A pressure-driven nano-filtration process of 10 bar was used to produce water and regenerate the Fe-CA draw solute from its diluted solution after FO tests. Fig. 4 shows that water production and Fe-CA rejection decrease upon increasing the feed concentration. Concentration polarization may also contribute to the reduced water production. Nevertheless, a high rejection of more than 90% was achieved when the concentration increases from 0.05 to 0.10 mol L<sup>-1</sup>. To further improve the recycling efficiency, other types of membranes or other recycle processes, *e.g.* membrane distillation, will be explored.

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