Draw solutions for Forward Osmosis process: Osmotic pressure of binary and ternary aqueous solutions of magnesium chloride, sodium chloride, sucrose and maltose

Malak Hamdan [a,*], Adel O. Sharif [a,b], Ghazi Derwish [a], Sami Al-Aibi [a], Ali Altaee [c]

[a] Centre for Osmosis Research and Applications, Chemical & Process Engineering Department, University of Surrey, Guildford GU2 7XH, United Kingdom
[b] Qatar Energy and Environment Research Institute, Qatar Foundation, Doha, Qatar
[c] Faculty of Engineering and Physical Science, University of the West of Scotland, Paisley PA1 2BE, United Kingdom

ABSTRACT

The objective of the present work is to investigate the behaviour of binary and ternary aqueous systems, which could be employed in the selection criteria for draw agents (DA) to be used in Forward Osmosis (FO) process applications. In this study the osmotic properties of the selected binary and ternary aqueous solutions of magnesium chloride ($MgCl_2$), sodium chloride (NaCl), sucrose and maltose are investigated. Osmotic pressures were calculated from water activities obtained from measured relative humidity of the solutions of concentrations in the range 0.5–6.0 mol kg^{-1} at 298.15 K. The osmotic behaviours of the ternary systems were compared with their binary counter parts; the results showed either positive or negative osmotic synergic effects. This could be used besides transport properties for considering the selection of favourable draw agents from those that exhibited positive synergy, i.e. the osmotic pressure of a ternary solution is greater than the sum of the pressures of the corresponding binary solutions. The results showed that the ternary aqueous solutions of $MgCl_2$ + NaCl showed significant positive synergy and therefore are possible suitable candidates as draw solutions, less so were the sugar–electrolyte systems.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Forward Osmosis (FO) process is the engineered application of the natural process osmosis as demonstrated by Sharif and Al-Mayahi (2011). Osmosis is one of the most fundamental phenomena found in chemical and biological systems which arise when two aqueous solutions at different concentrations are separated by a membrane permeable to water. It embodies the spontaneous transport of the solvent from the low-concentration solution across the solvent-selective permeable membrane into the higher-concentration solution. The generated chemical potential difference across the membrane gives rise to the osmotic pressure, π. The value of the osmotic pressure represents the minimum hydrostatic pressure that must be applied on the higher-concentration solution in order to stop solvent (Linares et al., 2014).

In the FO process, water moves from a feed solution of low osmotic pressure across a semi-permeable membrane to a draw solution (DS) of higher osmotic pressure (Anastasio and McCutcheon, 2013; Linares et al., 2014). The driving forces involved in FO are shown in Fig. 1; where C_s, C_d, a_s, a_d and μ_s, μ_d are the solute concentrations, water activities and water chemical potentials in the feed and draw solutes, S and D, respectively.

Beside desalination, osmosis processes are employed in a number of industries. In the food industry, osmosis has long been used as an alternative separation technology to thermal processing, where the impact on the nutritional and sensorial properties of the food product is found to be significantly more than in an osmosis membrane process (Jiao et al., 2004; Petrotos and Lazarides, 2001; Sant' Anna et al., 2012; Cath et al., 2006). In the pharmaceutical industry, there are among the known applications which involve osmosis: enrichment of the active pharmaceutical agent (e.g. lysozyme and proteins) and drug delivery systems (Cath et al., 2006; Herrlich et al., 2012; Zhao et al., 2012).

In the water purification industry, FO is becoming a viable desalination process, that has the potential to drastically reduce specific energy consumption (Zhao et al., 2012; McCutcheon et al., 2005; Yang et al., 2009; Miller and Evans, 2006; Sharif et al., 2009). In this process it is the ability of the draw solution to generate the relevant osmotic pressure level that is paramount (Cath et al., 2006;

---

* Corresponding author.
E-mail address: m.hamdan@surrey.ac.uk (M. Hamdan).

Zhao et al., 2012). Therefore investigating the behaviour of osmotic agents used in the draw solution is important in the design of an optimal such solution for the process.

The main purpose of this work is to investigate the osmotic pressure of binary and ternary systems as possible osmotic agents for the draw solution in Forward Osmosis. The osmotic pressures are obtained over a wide concentration range from water activities based on experimentally determined relative humidity, utilising known thermodynamic relations. Besides the typical electrolyte commonly used NaCl and $MgCl_2$, two sugar solutions were also investigated because of the applications of the FO process in the food and the biomedical industries (Sant'Anna et al., 2012).

1.1. Theoretical considerations

In the present work the determination of the water activity of an aqueous solution is based on the measurement of the relative humidity over the solution containing non-volatile electrolytes and organic solutes; these are related by Pitzer (1995) and Blandamer et al. (2005):

$$a_1 = \frac{P_1}{P_1^0} = \frac{RH}{100} \tag{1}$$

where a_1, is the water activity which is the ratio of the partial vapour pressure of water above a solution P_1, to that of the vapour above pure water P_1^0, at the same temperature, RH is relative humidity of the air above the solution with which it is in equilibrium. This study focuses on the osmotic behaviour of non-ideal concentrated solutions, here the van Laar equation (Granik et al., 2002) is used to obtain the osmotic pressure from the relative humidity calculated water activities, which is given by Eq. (2):

$$\pi = -\left(\frac{RT}{V_1^0}\right)\ell n\, a_1 \tag{2}$$

where π, osmotic pressure (atm); R, gas constant (8.314 J/mol K); T, thermodynamic temperature (K); a_1, water activity; and V_1^0, solvent molar volume (m^3/mol).

1.2. Osmotic pressure and water activity

The osmotic pressure of solution is affected by adding a second solute that can influence the solute–solvent interaction. Solutes disturb the solvent structure. In the case of water as the solvent, the presence of solute affects the structure of liquid water. In pure liquid water, the molecules are heavily hydrogen bonded in an ordered structure. The presence of ions disturb such structures by creating strong electric fields, the water dipoles are then orderly arranged and strongly bound, thus affecting the freedom of water molecules and influence their hydrogen bond system (Finney, 2001; Hribar et al., 2002; Horne, 1969) .

In the case of non-ionic solutes, different structures may be produced depending on the nature of the solute molecules, polar or
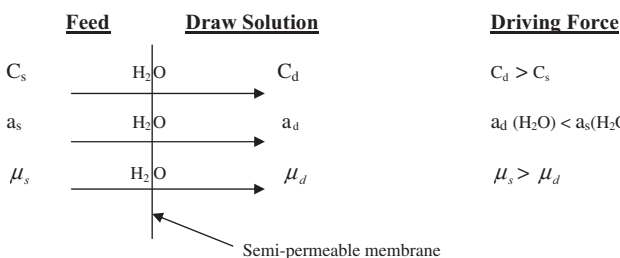

Fig. 2. Osmotic pressure of the binary systems, $MgCl_2$, NaCl, sucrose and maltose at 25 °C.

non-polar. In the former, dipole–dipole and dipole-induced dipole interactions are manifested producing structures affecting the free movement of water molecules, thus reducing the solution chemical potentials. Where the solute molecules can hydrogen-bond to water molecules, this will greatly disturb the structure of liquid water which influences strongly the hydrogen-bonded water structure, and could consequently decrease its chemical potential. In the case of non-polar solutes, the solute molecules maybe enclosed in micelle type structures, thus again disturbing the hydrogen-bonded structure of liquid water. On adding a second solute that can influence the solute–solvent interaction, the osmotic pressure of the resulting solution may be greatly affected. Depending on the nature of the second solute, the solute–solute and solute–solvent interactions, may lead to different osmotic behaviours (Gallo et al., 2014; Hribar et al., 2002; Yousef et al., 1998; Soper and Weckström, 2006; Collins et al., 2007).

The ternary system produced may show either non-additive or simple additive behaviour; in the latter the osmotic pressure of the solution is simply that of the sum of the osmotic pressures of the two corresponding solutions of either solutes.

2. Experimental

The apparatus used for the relative humidity measurements is the HygroLab 3 (Rotronic, UK). Its operation is based upon the changes in the dielectric properties of polymer sensor as a function of the prevailing relative humidity. The relative humidity is equivalent to the water activity, a_1. The instrument was calibrated by using Rotronic humidity standard solution (40% Lithium Chloride) as supplied by the manufacturer. The relative humidity values are then used to obtain the water activity as given by Eq. (1) above. A

Fig. 1. Schematic representation of the driving forces involved in FO in an ideal system where only water (H_2O) is transported across the membrane (i.e. 100% solute rejection by the membrane).
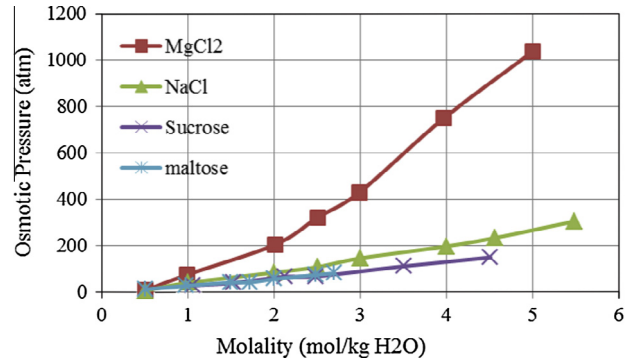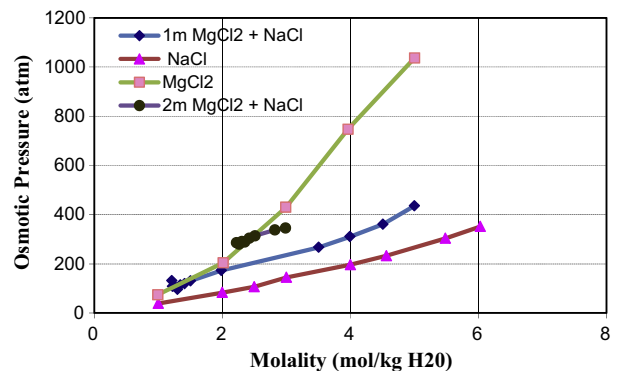

Fig. 3. Osmotic pressure of the binary compared with ternary solutions of variable NaCl with either 1 m $MgCl_2$ or 2 m $MgCl_2$ at 25 °C.