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Clathrate hydrate dissociation conditions for refrigerant + sucrose aqueous solution: Experimental measurement and thermodynamic modelling

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ABSTRACT

It has been shown in literature that gas hydrates can be used in sugar milling processes as a means of increasing the solids content in aqueous carbohydrate systems. In order to fully understand the practicalities of using gas hydrate technology in this regard, it is important to accurately know hydrate formation/dissociation conditions. The aim of this study is to obtain hydrate dissociation conditions of various refrigerant hydrates in the presence of sucrose aqueous solutions. The data will be used to design an aqueous solution separation process. The measurements were performed using the isochoric pressure search method with a newly developed high-pressure apparatus. New experimental gas hydrate systems measured include R134a + water + (12 or 15) weight percent sucrose, R410a + water + (12 or 15) weight percent sucrose, and R507 + water + (12 or 15) weight percent sucrose. Measurements were undertaken in the temperature range between (276.5 and 289.1) K and pressures ranging from (0.136–0.962) MPa. In addition, a sucrose sample supplied by the Sugar Milling Research Institute (SMRI) in Durban, South Africa was also investigated. The results show that the presence of sucrose exhibits an inhibition effect on hydrate formation. This is seen by the shift of the equilibrium phase boundary to either higher pressures or lower temperatures. Additionally, through measurements performed on the SMRI sample it can be seen that the presence of additional carbohydrates (glucose and fructose) in the system increases the effect of inhibition on hydrate formation. A thermodynamic model based on the van der Waals–Platteeuw solid solution theory was used to model the hydrate dissociation conditions. A good agreement between the experimental measurements and the model was observed.

1. Introduction

Gas hydrates (or clathrate hydrates) are a type of clathrate compound which falls under the class of a solid inclusion compound [1]. An inclusion compound consists of two species of molecules arranged in such a manner that one molecular species physically entraps the other. The water molecules, which form the entrapping framework by hydrogen bonds, is known as the ‘host’, whereas the entrapped molecular species (low molecular weight gases or liquids) is known as the ‘guest’ or ‘hydrate former’ [2]. Formers are found to stabilize the hydrate crystal, allowing it to exist at temperatures higher than that of pure water crystals [2,3]. Common hydrate formers (such as methane, ethane, and carbon dioxide) tend to form hydrates at high pressures (>1 MPa) and low temperatures (0–5 °C); therefore the use of refrigerants to form hydrates is attractive as formation may occur at near ambient conditions [4]. Gas hydrate formation presents a promising technology for separation [4–6], water desalination [4,7–9], gas storage and transportation [10–13], carbon dioxide capture and sequestration [14,15], refrigeration [16–20], natural gas recovery from natural hydrate formations [21–23], and separation of close boiling

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point compounds [24–26]. There exists a variety of aqueous solutions that can be separated via gas hydrate formation in an approach similar to, but more economical than conventional freeze technologies [3,27,28]. Currently, one of the major challenges within process engineering is the development of more economical and less energy intensive processes, in order for them to be more sustainable. One industry which is currently facing major challenges with regard to energy use and process economics is the South African sugar milling industry. This industry is experiencing diminished returns as a result of global sugar prices [29]. The South African sugar industry has the potential to be one of the largest suppliers of renewable energy into the national energy grid, and in doing so, not only increase the industry's profitability, but also assist in meeting government's renewable energy targets [30]. One such area of the sugar milling process where excess energy could be cultivated is the highly energy-intensive aqueous sucrose separation process. The majority of food industries, such as the South African sugar industry, are concerned with separations involving the removal of water. In most cases this separation is performed by either multiple-effect evaporation or freeze concentration [6,31,32]. According to Heist and Barron in 1983 [33], this is an ideal area of application for hydrate separation processes. It has been found that the energy consumption in the separation of aqueous solutions via evaporation can be reduced by 70–90% by using hydrate formation technologies [33]. The thermodynamic basis for this substantially lowered energy requirement is due to the fact that the latent heat of fusion is less than that of evaporation, and since the process operates at lower temperatures, the entropy of separation is also less than that compared to evaporation processes. It was found that the crystallizing temperatures of aqueous solutions could be raised by up to 30 °C by the use of refrigerant hydrate systems [33]. In addition to being less energy intensive, separation of aqueous solutions via gas hydrate formation also has many other advantages. Since this is a low temperature operation and it can be designed to be totally sealed, it is especially suitable for volatile or heat sensitive foods, such as sucrose. The low temperature operation also reduces microbiological activity, resulting in longer periods between equipment cleaning and thus better equipment utilization [3]. Lower temperatures also reduce corrosion effects; therefore less expensive materials of construction are required [27].

Prior to designing an economical and practical hydrate based process, for separation of the aqueous solutions consisting of sucrose, it is essential to be aware of their formation/dissociation conditions. In this study, the dissociation data of hydrates for the systems of CO_2 + water + 20 weight percent sucrose; R134a + water + (12 or 15) weight percent sucrose; R410a + water + (12 or 15) weight percent sucrose; and R507 + water + (12 or 15) weight percent sucrose were measured. Sucrose concentrations of 12 weight percent and 15 weight percent were investigated as these concentrations represent typical evaporator feed compositions in a South African sugar milling plant. A thermodynamic model based on the van der Waals–Platteeuw solid solution theory was used to model the hydrate dissociation conditions.

2. Literature review

Using gas hydrates in the separation and concentration of fruit juices, sugar aqueous solutions, and enzyme suspensions has been investigated by numerous researchers [1,2,5,27,28,34–44]. Previous studies on the separation of aqueous solutions by use of gas hydrate formation [1,5] reported the characteristics of methyl bromide, trichlorofluoromethane (R11) and 1,1-difluorethane (R152a) hydrates formed in a range of aqueous solutions containing carbohydrates, proteins and lipids, as well as for the concentration of apple, orange, and tomato juices. These chlorofluorocarbon (CFC) formers were chosen on the basis that they form hydrates which are stable under conditions of relatively high temperatures and low pressures [5]. In these studies, sucrose concentrations of 20 and 60 wt.% were investigated. It was reported that the hydrates formed easily in the 20 wt.% solutions; however hydrate formation in the 60 wt.% solutions was not possible. Even though the application of CFC hydrates in juice concentration has been shown to be quite promising, there is little promise for application as these refrigerants have been phased out due to environmental legislations. Gaarder and Englezos in 1995 used gas hydrates for the concentration of pulp mill effluents [36]. Werezak in 1969 [2] also examined the separation of aqueous solutions by gas hydrate formation in an attempt to establish a technology for the separation of temperature sensitive and/or viscous aqueous mixtures. The solutions used consisted of 25 wt.% coffee extract, sucrose, and sodium chloride. The hydrate formers used included ethyl oxide, trichlorofluoromethane, propylene oxide, sulphur dioxide and methyl chloride. Studies on the separation of aqueous solutions by gas hydrate formation went into a lull between 1990 and 2001. In 2001, the separation of aqueous coffee solutions by use of xenon gas hydrates was investigated by Purwanto et al. [37] and showed promising results. They investigated the effect of solution concentration and xenon pressure on the induction time and size distribution of gas hydrates [37]. The phase equilibrium behaviour of various formers in the presence of carbohydrate systems has rarely been investigated in the literature, however three such investigations were performed by Chun and Lee (1998, 1999) [28,38] and Carbone et al. (2012) [39]. Common hydrate formers, carbon dioxide and methane, as well as a refrigerant gas, chlorodifluoromethane (R22), were investigated in these studies in order to establish how the properties of the former affected hydrate formation, as well as the effect that sugar systems exerted on hydrate formation. Andersen and Thomsen in 2009 [40] investigated the possibility of using gas hydrates for the concentration of sugar juice. Even though the application of gas hydrates may not be economically feasible for concentration of sugar juice due to their shortcomings such as high formation pressure and large volume requirements, they show great advantage over traditional methods in the case of sensitive and high value products [40]. In order to develop an efficient process for the separation of coffee solutions using xenon hydrates, Purwanto et al., in 2014 [41] investigated the effect of steel screen size, stirring rate, temperature conditions, and dissolved xenon on coffee concentration. Li et al., in 2014 [42] proposed a new method for orange juice concentration using C_2H_4 hydrate formation and found that with an increase in the feed pressure, the rate of secondary nucleation increases. Recently in 2015 and 2014, Li et al. [43,44] investigated the effect of pressure, temperature, and juice volume on the dehydration ratio for the system of CO_2 hydrates in the presence of aqueous solutions of tomato and orange juice, and found that tomato juice does not have any effect on the CO_2 hydrate equilibrium conditions. The rate of CO_2 hydrate formation was however increased. In addition, with an increase in the feed pressure, the dehydration ratio increases [42,43]. In addition, they found hydrate formation technology as an effective method for orange juice concentrations [44]. Since no investigations into the effects of using fluorinated hydrate formers in the food industry have been conducted, it was decided to consider several criteria in order to determine a suitable commercial fluorinated hydrate former for the concentration of aqueous sucrose solutions. Commercially available fluorinated compounds were first screened against molecules allowable for use by the Montreal Protocol. Only those refrigerants that were not banned, or would not be banned in the near future, were considered for investigation. These refrigerants included R32, R125, R134a, R290,

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