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Liquid-liquid equilibria of ternary and quaternary systems involving 5-hydroxymethylfurfural, water, organic solvents, and salts at 313.15 K and atmospheric pressure

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ABSTRACT

HMF (5-hydroxymethylfurfural) is one of the bio renewable materials that can be used to produce a wide range of chemical products. In the HMF production process, yield and selectivity may be increased by liquid-liquid extraction of HMF using an organic solvent to prevent its degradation. Phase equilibrium data are required for rational design and optimal separation of HMF from the aqueous solution. In this study, liquid-liquid equilibrium (LLE) data of HMF, water, and methyl isobutyl ketone (MIBK) or 2-pentanol at 313.15 K (40 °C) and atmospheric pressure were measured and correlated using the NRTL and UNIQUAC models. The root mean square deviations (RMSD) of the NRTL and UNIQUAC models were 0.42% and 0.48% for the MIBK-HMF-water and 0.81% and 0.77% for the 2-pentanol-HMF-water system, respectively. The results indicated that higher distribution coefficients are achieved in the 2-pentanol-HMF-water system compared to the MIBK-HMF-water system. On the other hand, the separation ability of MIBK is better than that of 2-pentanol. In liquid-liquid extraction, not only a high distribution coefficient of HMF is important, but also a high separation factor is desirable to reduce the amount of co-extracted water. Therefore, in the present study the distribution coefficient of HMF from MIBK-HMF-water and the separation factor of the 2-pentanol-HMF-water system was improved by introducing a certain amount of salt into the aqueous solution. The salts examined in this study were based on the variety of cation (Na^+, K^+) and anion (Cl^-, SO_4^{2-}). The NRTL model was applied to correlate the LLE of organic solvent-HMF-water-salt systems, the results of which provided good agreement with the experimental data. The presence of salt can enhance the partitioning of HMF into the organic phase as well as the separation factor up to 2 times indicating the salting-out ability of the studied salts. The order of salting-out strength was $NaCl > Na_2SO_4 > KCl > K_2SO_4$ in which Cl^- and Na^+ demonstrated stronger salting-out ability than SO_4^{2-} and K^+.

1. Introduction

The development of biomass conversion into building blocks for the production of fuels and chemicals has been considered in various studies [1–6] to reduce the dependence on fossil resources. 5-hydroxymethylfurfural (HMF) is one of the promising platform chemicals, that can be obtained through hexose dehydration, and can be used for producing biofuels and a wide range of industrially important chemicals [6]. The main potential industrial application of HMF is the production of FDCA (2,5-Furandicarboxylic acid), a renewable material to replace the use of PTA (*para*-terephthalic acid) in the synthesis of PET (polyethylene terephthalate) used for production of synthetic fibers and plastic bottles [7].

A large number of studies provide improvements in understanding the mechanism and kinetics of the dehydration process for HMF production [6,8–16]. Researchers investigated the production of HMF in monophasic systems which resulted in low yields [6,8,9] due to the degradation of HMF and the formation of by-products. The use of biphasic systems involving organic solvents proved advantageous through higher yields. However the low separation factor and difficult separation of HMF from organic solvents made the HMF production economically infeasible. In the biphasic system, selection of the organic solvent plays a crucial role in order to improve the separation of HMF.

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Liquid-liquid extraction is one of the separation methods that can be applied in HMF production to enhance HMF yield and selectivity. The organic solvent is used to extract the HMF from its aqueous solution. In HMF production, the feed stream in the reactor unit contains fructose (carbohydrates), water, and catalyst as aqueous phase. In addition, the organic solvent is included in the reactor. The reaction takes place and HMF is extracted in the reactor into the organic phase which prevents the formation of side product. The aqueous phase from the bottom of the reactor which is still containing HMF enters the extraction unit. As we know that HMF can be more easily degraded at high temperature, as studied by Girisuta et al. [17]. They studied the decomposition of HMF in a temperature window of 98–181 °C which are in the range of reaction condition. Therefore, the extraction process is preferably carried out at a lower temperature than the reaction condition to optimally extract HMF. Furthermore, in order to consume less energy for cooling after the reaction, typically conducted at 80–250 °C [4–6], the temperature in the extraction unit should be higher than room temperature. Hence 40 °C (313.15 K) was selected in this study as a moderate operating temperature for the HMF extraction.

High boiling point organic solvents, such as DMSO (Dimethylsulfoxide), can give high yield and selectivity of HMF, but involve high cost and high energy consumption for separating HMF by distillation [6]. Therefore, more volatile polar compounds like alcohol and ketone have been considered as promising alternative solvents for HMF extraction [18–20]. In this study, the extraction solvents applied are methyl isobutyl ketone (MIBK) and 2-pentanol, that interact well with HMF molecule and have limited solubility in water. The extraction performance evaluation is based on values of two important parameter which is the separation factor and the distribution coefficient of HMF from the aqueous phase into the organic phase. Furthermore, the use of salt in the aqueous phase can enhance the partitioning of HMF into organic phase [18,19]. Hence, different salts composed of various cations and anions were studied, i.e. NaCl (Sodium Chloride), KCl (Potassium Chloride), Na_2SO_4 (Sodium Sulfate), and K_2SO_4 (Potassium Sulfate).

To our best knowledge, only few researchers have investigated the thermodynamics of HMF extraction [18–23]. Xiong et al. [20] have used the COSMO-SAC model [24] to predict the LLE systems containing HMF using primary alcohol as extraction solvent at 30 °C. The ePC-SAFT [25,26] was used to especially correlate the experimental LLE systems involving HMF using MIBK solvent in the presence of salt at 25 °C [19]. Dalmolin et al. [23] reported the LLE in systems containing HMF using alcohol as solvent at 25 °C and used the NRTL (Non-Random Two-Liquid) [27] as correlation model. There is still a great need for experimental equilibrium LLE data containing HMF in various aqueous-organic biphasic systems and their correlation with process conditions. Therefore, in the present study we investigated and provided LLE data for multi-component systems containing HMF using MIBK or 2-pentanol as extraction solvents at 40 °C (313.15 K) as a moderate operating temperature ensuring HMF stability selected in this work. Furthermore, the experimental ternary LLE data were correlated by the NRTL (Non-Random Two-Liquid) and UNIQUAC (Universal Quasi-Chemical) Thermodynamic models. Among all thermodynamic models, the NRTL [27] and UNIQUAC [28] activity coefficient models are good correlation models which are widely applied for describing phase equilibrium data in various systems [29–33]. They are direct models available in ASPEN Plus and much easier to use in process simulation. However, the thermodynamics study using these two well-known activity coefficient models, NRTL and UNIQUAC, is quite limited for correlating the LLE data of systems containing HMF and providing the binary interaction parameters [23]. Besides, the NRTL model can also be used to correlate LLE systems containing salts [34,35]. The NRTL model using de Haan and Niemann approach [34,35] provides a more simple calculation compared to the e-NRTL [36,37] and ePC-SAFT [25,26] models. Hence, in this study, we also measured LLE data for multi-component systems of HMF-water-organic solvent-salt at constant temperature (313.15 K) and correlated these data using the NRTL model. The LLE data provided in this work provide the basis for a rational design and optimal HMF extraction operation. The binary interaction parameters obtained are also needed for improving the operational efficiency of the HMF extraction process. Furthermore, this work can open a scope for the thermodynamics studies of HMF biphasic extraction systems.

2. Experimental section

2.1. Chemicals

All chemicals used in this study are described in Table 1. Methyl isobutyl ketone (MIBK) and 2-Pentanol were used as extraction solvent. Butylated hydroxyanisole (BHA) was used as antioxidant for HMF stability validation. Dimethylformamide (DMF) was used in HMF and organic solvent analyses as internal standard. Nitric acid (HNO_3) was used as diluent in salt analysis. The water used for the experiments was deionized ultrapure water with resistance of 18.2 MΩ cm.

2.2. HMF stability validation

The stability of HMF in the aqueous and organic phase was evaluated using BHA (Butylated hydroxyanisole) [38]. Sanborn et al. [38] indicated that the stability of HMF can be improved by adding 1000 ppm of BHA as antioxidant. Two samples with 10.07 wt% of HMF in water and two samples of 10.40 wt% of HMF in MIBK were prepared. For both mixtures 1000 ppm equivalent of BHA was added to one of the two samples. All samples were stirred and then placed in an oven set to 313.15 K. The concentration of HMF was analyzed by gas chromatography (GC) using the internal standard method at the start, after 1 day, 2 days, 5 days, 9 days, and finally after 15 days.

2.3. Tie line measurements

The LLE tie-lines were measured with a jacketed equilibrium cell at 313.15 K and atmospheric pressure. The water bath (Tamson-instruments TC 6 B, Holland) was used to circulate water and maintain the equilibrium cell at constant temperature with a standard uncertainty u(T) of 0.02 K. Aqueous feeds containing HMF-water and HMF-water-salts in different concentrations were prepared using a Mettler Toledo (MS 304 S/01, Switzerland) analytical balance with a precision of ±0.0001 g. In all tie-line experiments a mass ratio of 1:1 between organic solvent and aqueous feed solution was used with a varying HMF concentration and constant salt concentration in the feed. The mixture was stirred with a magnetic stirrer bar in the equilibrium cell for 1.5 h and allowed to settle for 20 h for low HMF concentration and at least 22 h for high HMF concentration at 313.15 K until the two liquid phases were completely separated. This equilibrium time was checked prior to the LLE experiment and it is adequate to reach equilibrium. Then, 1.2 g of sample was taken from each phase to determine the concentrations of HMF, organic solvent, water, and salt.

2.4. Analytical method

The samples from the equilibrium experiments were analyzed using a gas chromatography (Varian Technologies 430) system equipped with a flame ionization detector (FID). The concentrations