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ORIGINAL PAPER

Solvent Effects on Fructose Dehydration to 5-Hydroxymethylfurfural in Biphasic Systems Saturated with Inorganic Salts

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Abstract Furan derivatives, such as 5-hydroxymethylfurfural (HMF), obtained from acid-catalyzed dehydration of carbohydrates, can serve as renewable chemical platforms for the production of fuels and chemical intermediates. Addition of an inorganic salt to concentrated aqueous solutions of fructose (30 wt% fructose on salt free basis) in biphasic systems containing an organic extracting phase improves HMF yields by increasing the partitioning of HMF into the extracting phase, as measured by the partition coefficient, *R*, equal to the concentration of HMF in the organic phase normalized by the concentration in the aqueous phase. We have studied the impact of solvent choice on HMF yield using primary and secondary alcohols, ketones, and cyclic ethers in the C_3–C_6 range as extracting solvents in biphasic systems saturated with NaCl. Biphasic systems containing C_4 solvents generated the highest HMF yields within each solvent class. Tetrahydrofuran demonstrated the best combination of high HMF selectivity (83%) and high extracting power ($R = 7.1$) at 423 K. The presence of NaCl provided the additional benefit of creating biphasic systems using solvents that are completely miscible with water in the absence of salt. We have also studied the impact of different salts on HMF yield in systems using 1-butanol as the extracting solvent. Na^+ and K^+ showed the best combination of extracting power and HMF selectivity of the monovalent and divalent chloride salts tested. Changing the anion of the salt from Cl^- to Br^- resulted in *R*-values and HMF selectivity values resembling the non-salt system, while changing to the SO_4^{2-} divalent species generated a high *R*-value (8.1), but a low HMF selectivity value (71%).

Keywords HMF · Solvent · Acid catalysis · Biphasic · Fructose

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1 Introduction

Major scientific interest exists in developing new technologies for the conversion of renewable resources into sustainable energy and chemical materials, due to environmental, political, and economic concerns associated with our dependence on petroleum. In addition to producing most transportation fuels, petroleum is also the feedstock used for the production of over 95% of all of the carbon-containing chemicals used in our society [1]. The backbone of the chemical industry is formed by a limited number of chemical building-blocks, including methanol, benzene, toluene, xylene, ethene, propene, and butadiene. Biomass, an abundant and carbon-neutral source that contains a broad class of compounds with different extents of functionality and molecular weights, has the potential to serve as a competitive renewable feedstock for the chemical industry. Specifically, molecules derived from biomass could serve not only to supply a portion of the petroleum-based building blocks, but also to establish a new set of chemicals with properties analogous to, or even superior to, those of current petrochemicals. The main challenge in establishing a biomass-based chemical platform is to develop novel methods to efficiently separate, refine, and transform biomass while maximizing feed conversion, minimizing waste, and successfully establishing economies of scale.

Furan derivatives, obtained by acid-catalyzed dehydration of sugars such as glucose, fructose, and xylose, have been identified as "key substances bridging carbohydrate chemistry and petroleum-based industrial chemistry" because of the wide range of chemical intermediates and end-products that they can produce [2]. Specifically, 5-hydroxymethylfurfural (HMF) could serve as a renewable precursor for the production of various high-volume plastics and biofuels [3, 4]. For example, thermally-stable and oxidation-resistant polyesters are produced by the combination of furanic diacid derivatives (obtained from the oxidation of HMF) and aromatic moieties [5, 6]. Similarly, furanic polyamides prepared using furan dicarboxylic acid and aromatic diamines show decomposition and glass temperature profiles analogous to those of Kevlar® [5]. It has been reported that furanic polyesters, polyamides, and polyurethanes demonstrate no difference in degradation when compared to the best aliphatic and aromatic counterparts [5].

The efficient production of HMF requires the minimization of unwanted side reactions involving the reactant, the reaction intermediates, and the product (Fig. 1). Multiple reaction systems have been reported for the production of HMF using different solvents. Dehydration of fructose in pure water using solid and mineral acids is generally non-selective (HMF yields <20%) due to the degradation of HMF via rehydration reactions [7]. Conversely, high-boiling-point aprotic solvents, such as dimethylsulfoxide (DMSO), suppress unwanted side reactions and generate high yields of HMF (>90%); however, the separation of HMF from even trace amounts of these high-boiling point solvents is difficult and requires energy-intensive isolation procedures [8–12]. Biphasic systems, in which a water-immiscible organic solvent is added to extract continuously the HMF from the aqueous phase, offer an important advantage in that the product is separated from the reactant and reaction intermediates and is thereby protected against degradation reactions. However, most extracting solvents used show poor partitioning of HMF into the organic phase [13–19]. Recently, we developed a catalytic strategy for the production of HMF in high yields from concentrated fructose solutions in a biphasic reactor by increasing the partitioning of HMF into the organic phase [20]. The reactive aqueous phase in the biphasic reactor contains an acid catalyst and a sugar, and the extracting phase contains a partially miscible organic solvent (e.g., butanol, hexanol). Importantly, the addition of a salt (e.g., sodium chloride [NaCl]) to the aqueous phase improves the partitioning of HMF into the extracting phase by means of the "salting-out effect" and leads to increased HMF yields without the use of high-boiling-point solvents.

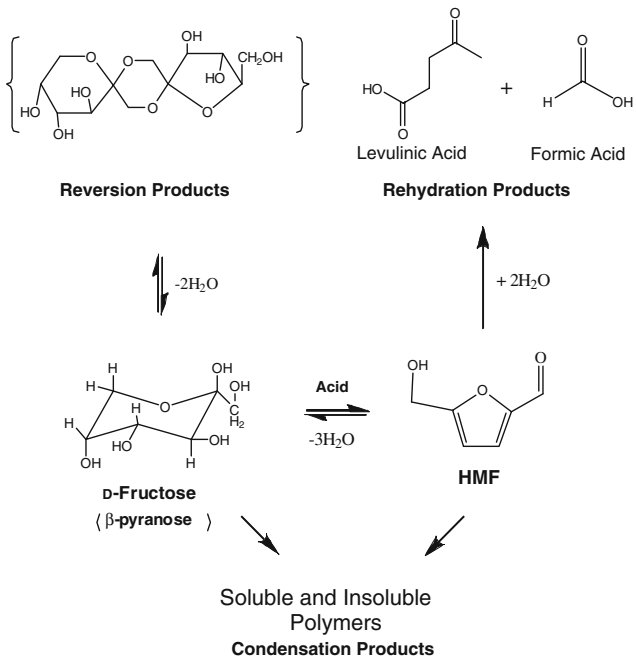

Fig. 1 Schematic representation of reaction pathways for acid-catalyzed dehydration of fructose

Several factors need to be considered in the proper selection of an HMF extracting solvent in a salt-containing biphasic system. First, the overall HMF processing scheme has to be evaluated in terms of the nature of the targeted end-product and the conditions of the subsequent HMF processing steps. For instance, in terms of the synthesis of HMF ethers (derived from the etherification reaction of HMF with alcohols) for fuel additive applications [21], the use of primary alcohols as solvents is ideal when considering the further processing of HMF. Similarly, in terms of the production of long-chain alkanes for use as biofuels (by way of aldol condensation) [4] extracting HMF with a ketone would turn the solvent into a reactant in the subsequent aldol condensation step. For processes involving hydrogenolysis followed by distillation (e.g., the production of the chemical intermediate 2,5-dimethylfuran) [20], the use of a saturated solvent with a low boiling point, such as tetrahydrofuran (THF, boiling point of 339 K and heat of vaporization of 30.3 kJ/mol at 339 K), is preferable to avoid solvent degradation and to minimize energy expenditure during distillation. In addition, solvents that can be directly produced from biomass promote sustainability and ease operational integration in the biorefinery. Currently, the main biomass-derived solvents are ethanol, isopropanol, n-butanol, and acetone, although new techniques are being developed continuously to synthesize new bio-solvents [22, 23]. Finally, other considerations for selection of the solvent include chemical stability and inertness towards components of the system, cost, and toxicity.

In the present paper, we first show the effect of using different classes of extracting solvents (aliphatic alcohols,

ketones, and ethers in the C_3–C_6 range) on the dehydration reaction of fructose to produce HMF in a biphasic system containing saturated aqueous solutions of NaCl. Next, we show the effect of different salts on the dehydration reaction in biphasic systems using 1-butanol as the extracting solvent. The biphasic systems used in this work are rather complex, containing not only highly non-ideal mixtures of solvents in concentrated electrolyte solutions, but also using components with relatively unknown thermodynamic properties. Therefore, an experimental approach to identify and highlight the most appropriate solvents and inorganic salts is necessary.

2 Experimental

Aqueous- and organic-phase components, including fructose, all inorganic salts, all organic solvents, and the acid catalysts (HCl and H_2SO_4), were obtained from Sigma-Aldrich Corporation in reagent grade.

Batch catalytic experiments were carried out in 10 ml thick-walled glass reactors (Alltech) heated in a temperature-controlled oil bath placed on top of an Isotemp Digital stirring hotplate (Fisher Scientific). The reaction temperature of most experiments was set at 423 K. In a typical experiment, 1.5 g of an aqueous-phase solution composed of 30 wt% fructose (salt-free basis), adjusted to a pH of 0.6 using HCl, was combined with the amount of extracting solvent necessary to keep the ratio of volumes of both phases, V_{org}/V_{aq}, at 3.2. Prior to use, the extracting solvent was saturated with water and salt by pre-contacting it with an aqueous phase saturated with the corresponding salt. The reactor was placed in the oil bath and removed after 35 min. The reaction was stopped by cooling the reactor in an ice bath. Next, upon separation, the masses and densities of both phases were measured. Density values were measured by weighing out a specific volume (obtained by a micropipette) of each phase.

Sample analyses were performed by means of high performance liquid chromatography (HPLC) using a Waters 2695 system equipped with PDA 2996 UV (320 nm) and RI-2410 refractive index detectors. Fructose disappearance was monitored with an Aminex HPX-87H column (Biorad), using MilliQ water (pH = 2, H_2SO_4) as the mobile phase at a flow rate of 0.6 ml/min and a column temperature of 333 K. The concentration of HMF was quantified in the aqueous and organic phases with a Zorbax SB-C18 reverse phase column (Agilent), using a 2:8 v/v Methanol:Water (pH = 2, H_2SO_4) gradient at a flow rate of 0.7 ml/min and a column temperature of 308 K. Conversion, selectivity, and yield of reactant x and product y are defined as follows:

$$\text{Conversion} = \frac{\text{moles of } x \text{ reacted}}{\text{moles of } x \text{ initial}}$$

$$\text{Selectivity} = \frac{\text{moles of } y \text{ produced}}{\text{moles of } x \text{ reacted}}$$

$$\text{Yield} = \frac{\text{moles of } y \text{ produced}}{\text{moles of } x \text{ initial}}$$

Fructose conversion and HMF selectivity were calculated from the product of the aqueous and organic phase concentrations obtained in the HPLC and their corresponding volumes after reaction.

3 Results and Discussion

Saturating the aqueous phase of a biphasic system with an inorganic salt, such as NaCl, significantly alters the extraction equilibrium of HMF (Fig. 2). The partition coefficient R (defined as the ratio of the HMF concentrations in the organic and aqueous phases) increases in the presence of NaCl in comparison with non-salt systems. Importantly, the relative increase in the R-value is dependent on the nature of the solvent. For example, the 1-butanol system showed a two-fold increase in R from 1.6 to 3.2, whereas the 2-butanone system showed a three-fold increase from 1.8 to 5.4. The significant improvement in the value of R is attributed to the salting-out effect that NaCl induces on the extracting solvent, whereby the ions in solution alter the intermolecular forces between the liquids in equilibrium, resulting in an increased immisciblity envelope; therefore, the decreased mutual solubility of the aqueous and organic phases enhances the extraction of HMF from the aqueous phase [20, 24, 25]. It has been reported that the extent of the salting-out effect depends on the nature of the ionic interactions between all components of the system, and it depends on parameters such as concentration, temperature, and pressure [26]. Importantly, the salting-out effect has two other relevant attributes. First, it can be exploited to produce

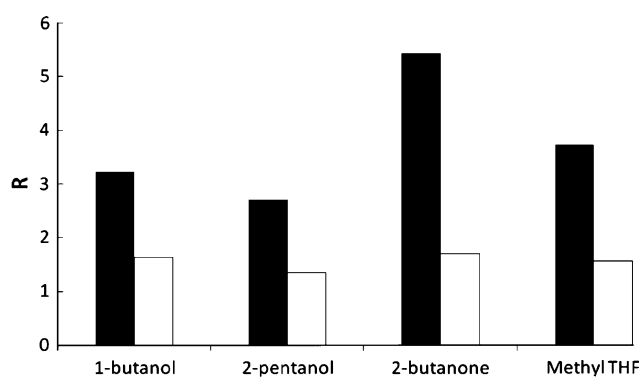

Fig. 2 Effect of NaCl on the partition coefficient R in representative biphasic systems. Black bars correspond to systems saturated with NaCl, while white bars represents systems without NaCl

biphasic systems with solvents that, in the absence of salt, are completely miscible with water; examples include 1-propanol, 2-propanol, acetone, and THF. Second, for partially miscible systems that exhibit an upper critical solubility temperature (UCST), defined as the temperature at which a mixture of partially soluble liquids becomes completely miscible, the presence of an inorganic salt increases this UCST, thereby allowing partially miscible solvent mixtures to remain biphasic even at higher temperatures. Thus, dehydration reactions carried out in water/1-butanol mixtures (UCST = 398.2 K) at temperatures above 398 K are monophasic in nature [26, 27]. Although it has been reported that lower fructose concentrations generate a higher HMF selectivity [28, 29], (and a biphasic system above its UCST is more dilute because the fructose is dissolved in the entire system volume rather than only in the aqueous phase), we observed that operating under biphasic conditions by using NaCl is more advantageous, generating a higher HMF selectivity than the non-salt monophasic 1-butanol system at 423 K (Table 1, runs 2 and 19).

A more efficient removal of HMF from the reactive aqueous phase translates into higher HMF yields due to the minimization of unwanted side reactions. Therefore, a higher *R*-value is usually correlated to higher HMF selectivity values. In Fig. 3, it can be seen that this trend holds for most organic solvents tested. However, in some cases, high *R*-value systems generated lower HMF selectivity values than expected. For example, we note that the 1-propanol and 2-propanol systems with *R*-values of 3.9 and 3.7 generated HMF selectivity values of 74 and 80%, respectively (Table 1, Runs 1 and 5), and these values are lower than some of their higher molecular weight analogs with lower *R*-values (e.g., Table 1, Runs 2 and 7: 1-butanol $R = 3.2$, 80% HMF selectivity; 2-pentanol $R = 2.7$, 82% HMF selectivity). A possible explanation for this behavior is that the partition coefficient is measured from the concentrations of HMF at room temperature rather than at the reaction temperature. Higher temperatures usually increase the mutual solubility of solvents, but the variation of the activity coefficient with temperature (i.e., the extent of the increase in the mutual solubility) is different for each solvent. Therefore, systems that experience a higher degree of mutual solubility at the reaction temperature (e.g., very hydrophilic solvents) exhibit lower *R*-values during the reaction, which translates into an increased rate of unwanted side reactions. Notably, very hydrophobic solvents that do not increase their water solubility even at high temperatures usually do not have a high affinity for HMF and will also have low *R*-values at the reaction temperature. As seen in Fig. 4, solvents containing four carbon atoms (C-4) generated the highest HMF selectivity values within each solvent class, thereby showing the highest affinity for HMF coupled with low water miscibility at the reaction temperature. 2-butanol showed the highest HMF selectivity value (85%) of all solvents studied at 423 K, although THF had the best combination of HMF selectivity (83%) and extracting power ($R = 7.1$).

The effect of temperature on the dehydration reaction is shown in Fig. 5. An increase in reaction temperature from 423 to 453 K improved HMF selectivity for the 2-butanol system from 85 to 90% (Table 1, Runs 6 and 25). Similarly

Table 1 Dehydration results for 30 wt% fructose solutions in biphasic systems using different classes of solvents. Fructose weight percent calculated on a salt-free basis. Reaction conditions used were T = 423 K, $V_{org}/V_{aq} = 3.2$ with the aqueous phase adjusted to a pH = 0.6 using HCl, and a reaction time of 35 min (85 min for run 16 using THF)

Run	Solvent	Conversion (%)	Selectivity (%)	*R*
Primary alcohols				
1	1-propanol	68	74	3.9
2	1-butanol	73	80	3.2
3	1-pentanol	75	77	2.3
4	1-hexanol	78	72	1.5
Secondary alcohols				
5	2-propanol	39	80	3.7
6	2-butanol	67	85	3.7
7	2-pentanol	83	82	2.7
8	2-hexanol	74	73	1.8
Ketones				
9	Acetone	62	79	3.6
10	2-butanone	84	82	5.4
11	2-pentanone	97	71	3.4
12[a]	2-pentanone	73	76	3.2
14	2-hexanone	97	70	2.4
15[a]	2-hexanone	79	72	2.4
Cyclic ethers				
16	THF	53	83	7.1
17	THP	77	78	3.2
18	MTHF	87	76	3.7
Non-salt systems				
19[b]	1-butanol	93	69	1.6
20[b]	2-pentanol	89	74	1.3
21[b]	2-butanone	92	73	1.8
22[b]	THP	95	71	1.5
23[b]	MTHF	99	57	1.5
High temperature runs				
24[c]	1-butanol	67	82	3.0
25[c]	2-butanol	77	90	3.6
26[c]	THF	88	89	7.3

[a] Indicates runs with a reaction time of 20 min

[b] Indicates runs without the use of NaCl with otherwise same reaction conditions

[c] Indicates runs performed at a temperature of 453 K (433 K for run 26 using THF) and a reaction time of 8 min (50 min for run 26 using THF)

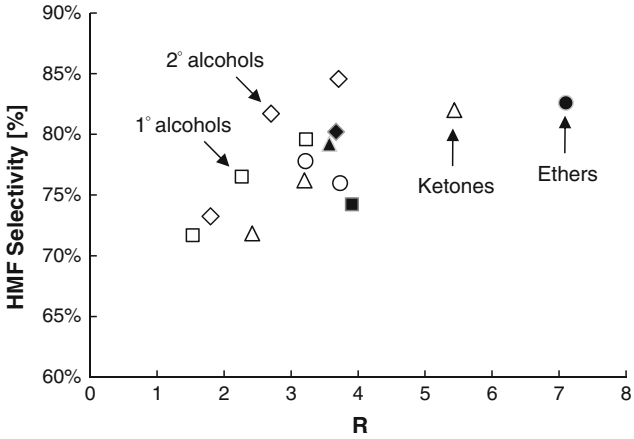

Fig. 3 Correlation of HMF selectivity, partition coefficient (R), and solvent type for dehydration reactions carried out in saturated solutions of NaCl. Legend for solvent types: ketones (△), ethers (○), secondary alcohols (◇), and primary alcohols (□). Open symbols correspond to solvents that are partially miscible with water and closed symbols correspond to the C-3 solvents and the C-4 ether (THF), which, in the absence of NaCl, are completely miscible with water at room temperature

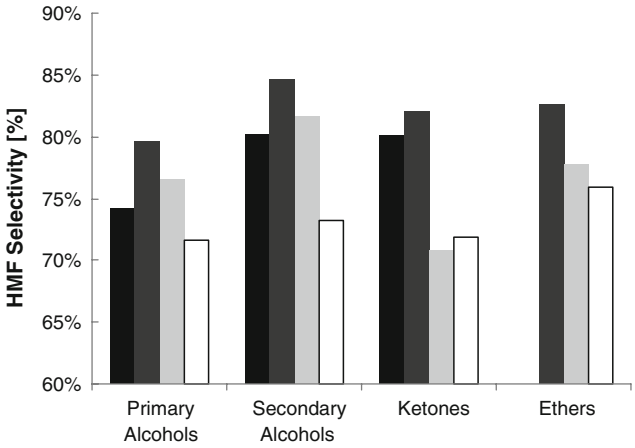

Fig. 4 HMF selectivity values for different classes of extracting solvents. Black bars correspond to three-carbon solvents (C-3), but no C-3 ethers were used in the experimental set; dark grey bars correspond to four-carbon solvents (C-4); light grey bars correspond to five-carbon solvents, and, for the ethers group, it corresponds to tetrahydropyran (THP); white bars correspond to six-carbon solvents (C-6), but for the ethers group, it corresponds to the C-5 methyltetrahydrofuran (MTHF)

an increase in temperature from 423 to 433 K increased HMF selectivity for the THF system from 83 to 89% (Table 1, Runs 16 and 26). These results demonstrating the benefit of performing the reactions at higher temperatures are in agreement with previously reported reaction kinetic studies on the fructose dehydration reaction, showing that the conversion of fructose to HMF has a higher activation energy (Ea = 143 kJ/mol) than the conversion of HMF or fructose into byproducts (Ea = 64 kJ/mol) [30]. Therefore, the optimal temperature for the formation of HMF reflects

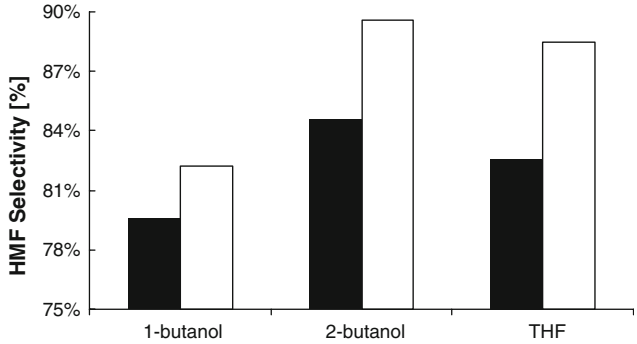

Fig. 5 Effect of temperature on HMF selectivity in representative biphasic systems. Black bars correspond to experiments performed at 423 K and white bars correspond to experiments performed at 453 K. For THF, the white bar corresponds to a reaction temperature of 433 K

a compromise between performing the reaction at high temperatures to take advantage of the high activation energy for reaction, and performing the reaction at sufficiently low temperatures to avoid solvent degradation reactions. For instance, we observed considerable solvent degradation in systems comprised of secondary alcohols at temperatures near 473 K and noticeable THF degradation at temperatures above 453 K.

The salting-out effect results from the interactions of all of the ionic species in solution with the non-electrolyte components in the biphasic system; it generally cannot be attributed to individual cationic or anionic contributions. The complex nature of these ionic interactions can be appreciated more clearly in Fig. 6 and Table 2, which show the effect of utilizing specific cations and anions in systems with 1-butanol as the extracting solvent. In cases where cations were varied and the anion was kept constant as Cl^-, we observed

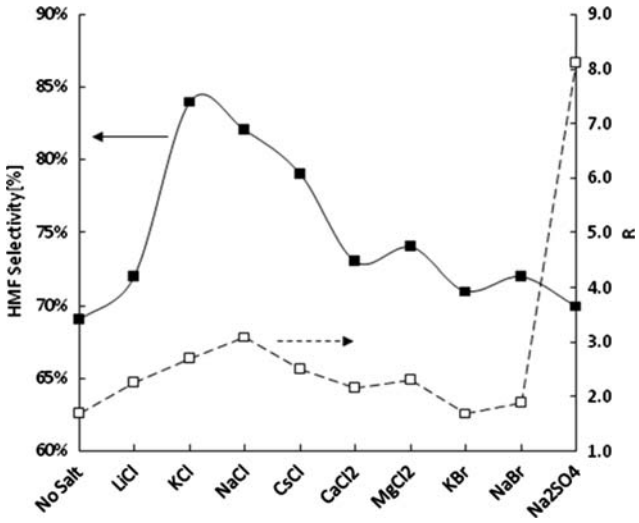

Fig. 6 HMF selectivity and *R*-values for different inorganic salts in biphasic systems using 1-butanol as the extracting solvent. The solid line corresponds to HMF selectivity values and the dotted line corresponds to *R*-values

Table 2 Dehydration results for 30 wt% fructose solutions using different salts to saturate the aqueous layer of biphasic systems using 1-butanol as the extracting solvent

Run	Salt	Conversion (%)	Selectivity (%)	*R*
27	No salt	77	69	1.7
28	LiCl	71	72	2.2
29	KCl	89	84	2.7
30	NaCl	87	82	3.1
31	CsCl	92	80	2.5
32	$CaCl_2$	77	73	2.2
33	$MgCl_2$	78	74	2.3
34	KBr	77	71	1.7
35	NaBr	90	73	1.9
36	Na_2SO_4	62	71	8.1

Fructose weight percent calculated on a salt free basis. Reaction conditions used were T = 453 K and $V_{org}/V_{aq} = 3.2$ with the aqueous phase adjusted to a pH = 0.6 using HCl (or H_2SO_4 for Run 36) and reaction times ranging from 8 to 15 min

that K^+ and Na^+ generated both the highest partition coefficients (2.7 and 3.1, respectively) and the highest HMF selectivity values (84 and 82%, respectively) among the monovalent and divalent cations tested. Indeed, Gorgenyi et al. [31] reported that the magnitude of the hydrated ionic radius is an important factor in the salting-out effect, with smaller hydrated ions, such as Na^+ and K^+, having a stronger influence on the salting-out effect than larger hydrated ions, such as Li^+. In addition, Tan and Aravith [25] showed that NaCl and KCl salts have similar effects on the distribution of acetic acid in water/1-butanol biphasic systems. However, when the anion is changed from Cl^- to Br^-, both Na^+ and K^+ ions have minimal influence on the *R*-value and generate HMF selectivity values similar to those of the system with no salt. Interestingly, we note that although Na_2SO_4 did not produce biphasic systems with C-3 alcohols, acetone, or THF, it was very effective at salting-out HMF in the 1-butanol system, generating a surprisingly high *R*-value of 8.1. Gorgenyi et al. [27] and Reber et al. [31] concur that for salts with double charged anions, the salting-out effect is significantly larger than for salts with single charged ions, especially for asymmetric divalent ions, such as SO_4^{2-}, with more polarizable electron clouds [27, 31]. Unfortunately, the HMF selectivity for the system using Na_2SO_4, a salt with a strong tendency to form hydrates and other complexes, is low (71%), implying that this salt may not be inert during the dehydration reaction in the 1-butanol system.

4 Conclusions

The presence of NaCl increases the partition coefficient of HMF in biphasic systems, thus increasing HMF selectivity by removing it more efficiently from the reactive aqueous solution. NaCl is also useful in creating biphasic systems with solvents that are otherwise completely miscible with water, as well as increasing the upper critical solubility temperature of certain partially soluble solvents. C_4 solvents generated the highest HMF yields among the C_3 to C_6 range aliphatic alcohols, ketones, and ethers studied, most likely due to the fact that these solvents posses the highest *R*-value at the reaction temperature. Overall, THF showed the best combination of HMF selectivity and extracting power. Although the *R*-value measured at room temperature may be different than the value of the HMF partition coefficient at reaction temperature, it still provides a good indication of the performance of the biphasic system and appears to be a useful tool in the solvent selection process. Studies of the effect of different salts using 1-butanol as the extracting solvent showed that K^+ and Na^+ generated the best combination of extracting power and high HMF selectivity from the monovalent and divalent chloride salts. However, when the anion was changed from Cl^- to Br^-, both the *R*-value and the HMF selectivity resembled the non-salt system, and when it was changed to SO_4^{2-}, the *R*-value increased considerably, but the HMF selectivity remained low. These results indicate that the combined effects of the cation and anion species must to be taken into account when selecting the most appropriate salt to improve the selectivity for HMF formation and the partition coefficient for HMF extraction.

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References

1. Christensen CH, Rass-Hansen J, Marsden CC, Taarning E, Egeblad K (2008) Chem Sus Chem 1:283
2. Bicker M, Kaiser D, Ott L, Vogel H (2005) J Supercrit Fluids 36:118
3. Werpy T, Petersen G (2004) Top Value Added Chemicals from Biomass: Vol 1—Results of Screening for Potential Candidates from Sugars and Synthesis Gas. Tech. Report No. Report No. NREL/TP-510-35523 (National Renewable Energy Laboratory)
4. Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) Science 308:1446
5. Gandini A, Belgacem MN (1997) Prog Polym Sci 22:1203
6. Chaabouni A et al (1999) Journal de la Societe Chimique de Tunisie 4:547
7. Rapp KM (1987) US Patent, *4,740,605*
8. Brown DW, Floyd AJ, Kinsman RG, Roshan-Ali Y (1982) J Chem Technol Biotechnol 32:920
9. Musau RM, Munavu RM (1987) Biomass 13:67
10. Nakamura Y, Morikawa S (1980) Bull Chem Soc Jpn 53:3705
11. Szmant HH, Chundury DD (1981) J Chem Technol and Biotechnol 31:135
12. van Dam HE, Kieboom APG, van Bekkum H (1986) Starch 38:95

13. Kuster BFM, van der Steen HJC (1977) Starch 29:99
14. Peniston QP (1956) U.S. Patent *2,750,394*
15. El Hajj T, MasRoua A, Martin JC, Descotes G (1987) Bulletin de la Societe Chimique de France 5:855
16. Rigal L, Gaset A, Gorrichon J-P (1981) Ind Eng Chem Prod Res Dev 20:719
17. Moreau C et al (1996) Appl Catal A Gen 145:211
18. Rivalier P, Duhamet J, Moreau C, Durand R (1995) Catal Today 24:165
19. Moreau C, Belgacem MN, Gandini A (2004) Top Catal 27:11
20. Roman-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA (2007) Nature 447:982
21. Gruter G, Maria JDF (2007) Avantis International, European Patent Office EP20060075564
22. Jain MK and Datta R (1991) US Patent Office 5063156
23. Krouwel PG, Groot WJ, Kossen NWF, van der Laan WFM (1983) Enzyme Microb Technol 5:46
24. Eisen EO, Joffe J (1966) J Chem Eng Data 11:480
25. Tan TC, Aravinth S (1999) Fluid Phase Equilib 163:243
26. Treybal RE (1963) Liquid Extraction, 2nd edn. McGraw Hill, New York
27. Reber LA, McNabb WW, Lucasse WW (1942) J Phys Chem 46:500
28. Kuster BFM, van der Baan HS (1977) Carbohydr Res 54:165
29. Kuster BFM (1990) Starch 42:314
30. Moreau C, Finiels A, Vanoye L (2006) J Mol Catal A Chem 253:165
31. Gorgenyi M, Dewulf J, Van Langenhove H, Heberger K (2006) Chemosphere 65:802