## Supporting Information

## The Molecular Origin for the Difficulty in Separation of

## 5-Hydroxymethylfurfural from Imidazolium Based Ionic Liquids

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Figure S1. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S2. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S3. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{HSO}_{4}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S4. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CF}_{3} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S5. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{OSO}_{3}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S6. O-H and C-H stretching for $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{NO}_{3}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S7. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CF}_{3} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL


Figure S8. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{N}(\mathrm{CN})_{2}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S9. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S10. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{OSO}_{3}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S11. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S12. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of $5-\mathrm{HMF}$ in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{HSO}_{4}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S13. $\mathrm{C}=\mathrm{O}$ and $\mathrm{C}=\mathrm{C}$ vibration of 5 - HMF in $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{NO}_{3}\right] / 5-\mathrm{HMF}$ mixtures as a function of mole fraction of the IL.


Figure S14. The variety of $\Delta \delta$ values for the protons of $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{COO}\right]$ as a function of mole fraction of 5-HMF in the IL/5-HMF mixtures.


Figure S15. The variety of $\Delta \delta$ values for the protons of [ $\left.\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{COO}\right]$ as a function of mole fraction of 5-HMF in the IL/5-HMF mixtures.


Figure S16. The variety of $\Delta \delta$ values for the protons of $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{HSO}_{4}\right]$ as a function of mole fraction of $5-\mathrm{HMF}$ in the IL/5-HMF mixtures.


Figure S17. The variety of $\Delta \delta$ values for the protons of $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CF}_{3} \mathrm{COO}\right]$ as a function of mole fraction of 5-HMF in the IL/5-HMF mixtures.


Figure S18. The variety of $\Delta \delta$ values for the protons of $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{NO}_{3}\right]$ as a function of mole fraction of $5-\mathrm{HMF}$ in the IL/5-HMF mixtures.


Figure S19. The variety of $\Delta \delta$ values for the protons of $\left[\mathrm{C}_{4} \mathrm{mim}\right]\left[\mathrm{CH}_{3} \mathrm{OSO}_{3}\right]$ as a function of mole fraction of $5-\mathrm{HMF}$ in the IL/5-HMF mixtures.

