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The key parameters for selecting suitable ILs are the availability of VLE data and selectivity. Research studies on the extractive distillation of ethanol and water have involved a pool of various ILs, particularly imidazolium-based ones 8 28.

However, neither their comparison of performances in vapour-liquid laboratory experiments, process simulations, or pilot scale experiments produces a conclusive choice of IL as the best entrainer. Different papers are contradictory of one another in the selection of suitable IL, as they are judged using different solvent criteria. Using the available comparisons and results from literature, a fair choice of IL is made based on the overall analysis, with the following justifications. The first step in the selection is to ascertain the availability of VLE data of the ILs for ternary system involving ethanol and water. The respective VLE data of ILs that is available in literature is compiled by Figueroa et al. 29. Among all the possible choices of ILs for ethanol dehydration, the most frequently discussed cations for are Emim<sup>+</sup> and Bmim<sup>+</sup>, whereas the anions are BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, OAc<sup>-</sup>. The second step for IL screening is to compare the selectivities at infinite dilution between the ILs, which is reported by several papers 8 27 17.

ILs with higher selectivity will lead to a greater difference in volatility between the components in the feed, therefore increasing the separation. With a greater separation, the operation would require a lower entrainer mass and number of column stages, which reduces the operating and capital costs 14. As inferred by Ge et al. 17, the selectivity depends on both the cation and anion of the IL. The larger the cation size, the lower the difference

in relative volatility. By comparing the relative volatility between ethanol and water using Emim<sup>+</sup> and Bmim<sup>+</sup>, Ge et al.

found that the enhancement effect of Emim<sup>+</sup> was larger 17. This was further supported by a more recent study by Pereiro et al. 11, which investigated three cations, namely (in ascending order of chain length) Emim<sup>+</sup>, Bmim<sup>+</sup> and Hmim<sup>+</sup>, with Cl<sup>-</sup> as anion. The same result was found and attached in Figure 3, where the relative volatility decreased with size of cation at mole fractions of IL above 0.

03. Furthermore, when the molar fraction of IL increased, there was a greater enhancement in relative volatility. Figure 3: Relative volatility of chlorinated ILs with different cations at different IL molar fractions 11. Figure 4: Relative volatility of ILs 11.

As for anions, they have a greater impact on the relative volatility than cations 17 28. The relative volatility between ethanol and water was plotted against the different ILs studied by Pereiro et al. 11 in Figure 4. EmimCl had the highest selectivity among the ILs listed in the figure, followed by EmimOAc. This was also supported by other VLE study, by Ge et al. 17.

Both papers reported results of the relative volatility enhancement effect by the ILs to be in this descending order: Cl<sup>-</sup>, OAc<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, paired with cations Emim<sup>+</sup> or Bmim<sup>+</sup>. However, the viscosities of chlorinated ILs are high, and would have the mass transfer resistance, leading to the poor mass and heat transfer performance in separation units. This would also incur a high operating cost as more energy would be spent to overcome these

resistances in agitation and other operations 8. In addition to that, chlorinated ILs are also corrosive 28. Therefore, they are not chosen.

The IL with the second highest selectivity is EmimOAc, and is claimed to be a promising entrainer due to its lower viscosity compared to EmimCl 17.

However, several other papers have disputed its use because of its thermal instability 8 12. It has a low flash point of 164°C and is therefore infeasible to be recycled under high temperature conditions. Meindersma et al. 27 explained that the strong attachment of the acetate IL to water would cause the separation to be difficult during solvent recovery. The flash drum would need to operate at high vacuum conditions (0.

1 mPa in Meindersma et al.'s study) in order for the recovery to be feasible 27. This would incur a high energy demand, which leads to costly operation. Arlt et al. was the pioneer for the research of ILs in ethanol dehydration.

Their patent for BASF was published in 2004, concluding that it was feasible to break the azeotrope using EmimBF<sub>4</sub> as the entrainer. Since then, EmimBF<sub>4</sub> has become a popular choice to be used in multiple studies for the process design of the ethanol dehydration and comparison with other solvents 8 13. This is because EmimBF<sub>4</sub> has favourable characteristics over other ILs such as a high thermal stability (up to 450°C), high selectivity and is commercially available 24. Hence, EmimBF<sub>4</sub> is selected as the IL to be studied in this dissertation.