In this work an extended analysis of the influence of the cation alkyl side chain length of 1-alkyl-3-methylimidazolium chloride ionic liquids ([C\textsubscript{n}C\textsubscript{1}im]Cl, with \(n = 1\) to 14) in the formation of aqueous biphasic systems (ABS) was carried out. Aiming at gathering a broader picture on the formation of ionic-liquid-based ABS the substitution of the most acidic hydrogen in the imidazolium core by a methyl group was also evaluated. Ternary phase diagrams, tie-lines, and tie-line lengths for the several systems (ionic liquid + water + K\textsubscript{3}PO\textsubscript{4}) were determined at 298 K and atmospheric pressure. The increase of the cation alkyl chain length enhances the formation of aqueous biphasic systems if alkyl chain lengths up to hexyl are considered. On the other hand, the results for longer alkyl side chains show that the mechanisms that govern the ABS phase separation is indeed more complex and the capacity of the ionic liquid to self-aggregate also accounts for its liquid-liquid demixing ability: in the homologous series, the aptitude of each ionic liquid for phase separation as a function of the cation alkyl side chain length follows three isolated patterns. In general, it was found and will be shown that the entropic contributions play the most important role in liquid-liquid demixing whilst the influence of the self-aggregation of ionic liquids is secondary, yet significant.