Esterification in Ionic Liquids

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In this paper we present a systematic study on the influence of different parameters on the phase equilibrium of esterification systems. As model systems esterifications of ethanol, 1-propanol and 1-butanol with acetic acid conducted in ionic liquids was studied. The ionic liquids used were 1-methylimidazolium hydrogen sulphate [HMIM][HSO$_4$], 1-ethyl-3-methylimidazolium hydrogen sulphate [EMIM][HSO$_4$] and 1-butyl-3-methylimidazolium hydrogen sulphate [BMIM][HSO$_4$]. Through the variation of the cation, alcohol and temperature in the range 30 to 50°C we obtained their influence on ternary and five compound systems containing reactants and products of these esterification reactions. This has been used to compare the product quality in a 10-stage cascade under equilibrium and non-equilibrium conditions.

1. Introduction

Ionic liquids (IL) are organic compounds having low melting points, usually below 100 °C (Welton, 1999). They are comprised of ions and have properties that make them interesting for extractive/reactive applications because of their low volatility. That means that IL can be recycled easily from a mixture with volatile compounds by distilling out the volatile compounds. There are no losses and environmental hazards due to the negligible partial pressure of the ionic liquids. A major drawback for broader application in the industry is due to e.g. the usually higher prices and nonsufficient experimental data for these chemicals.

As model systems for a systematic study we chose esterifications, since they are widely studied and there is already data on esterificatons in ionic liquids available (e.g. Fraga-Dubreuil, 2002, Gui, 2004, Ganeshpure, 2008, Li, 2008). The ionic liquids under consideration are 1-methylimidazolium hydrogen sulphate [HMIM][HSO$_4$], 1-ethyl-3-methylimidazolium hydrogen sulphate [EMIM][HSO$_4$] and 1-butyl-3-methylimidazolium hydrogen sulphate [BMIM][HSO$_4$] which contain an acidic anion. Such ionic liquids are often studied for esterification reactions since on the one side they can act as catalysts and on the other side they are immiscible with the ester products and allow thus biphasic operation.

In order to design a process using these ionic liquids, one has at first to know the phase equilibrium for the corresponding (sub-) systems. If one intends to use the ionic liquids, e.g. for a biphasic process, one has to know whether a system will be biphasic at the

desired conditions and to know in which phase are the reactants. Another question to be answered is: what is the expected effect of the ionic liquid on the reaction conversion. This information is unfortunately seldom available, though there have been many studies on IL in the last years. Since it is obviously not possible to obtain experimental data for all systems of interest, one possible solution is to study the relationships for the a test systems and to find some general valid trends. Having then data on some limited number of systems and knowing how different parameters like the alkyl chain length, cation, temperature and so on influence the phase equilibrium or the reaction conversion one can roughly estimate the behavior of a broad range of systems.

Data acquisition in the five component systems alcohol + acid + ester + water + IL can be done only when both phases are in chemical equilibrium, which is difficult with reacting systems. For this reason we started with investigating the behaviour of nonreactive ternary subsystems. Data for these systems containing ester + alcohol or acetic acid + IL are also useful in order to obtain the binary interaction parameters of a G^E-model like UNIQUAC. We varied several parameters, like alkyl chain length on the cation, alkyl chain on the alcohol/ester and temperature, and evaluated their influence on the phase equilibrium of ternary and five compound systems containing products and reactants of esterification reactions. It was also interesting to investigate whether there is an influence on the reaction (conversion) and to what extent.

2. Ternary Systems

The variation of the cation (Naydenov and Bart, 2007) influenced significantly the phase equilibrium of the ternary systems. An increase in the alkyl chain length reduces the size of the two phase region. Though all studied IL are practically immiscible with esters, the size of the two phase region varies with the cation and is very small for the BMIM systems, allowing biphasic operation only at very low alcohol/acid contents. The distribution of the reactants between the ester phase and ionic phase is dramatically influenced by the cation, e.g. both, only one or none of the reactants is better soluble in the IL phase when the cation is varied.

The study on the effect of the alkyl chain length on the ester and alcohol on the size of the binodal curve and the position of the tie lines is already published (Naydenov and Bart, 2009). The studied systems were [EMIM HSO4] + butylacetate + 1-butanol, [EMIM HSO4] + butylacetate + acetic acid, [EMIM HSO4] + propylacetate + 1-propanol, [EMIM HSO4] + propylacetate + acetic acid at 40°C. All systems are of type I at this temperature (one immiscible pair: EMIM and ester), however at room temperature butanol and EMIM are immiscible, too. With increasing the alkyl chain length on the ester and alcohol a decrease of the two-phase region is observed. This is explained with the increase of hydrophobicity of these chemicals. With increasing chaing length the alcohol becomes more soluble in the organic phase. For the acid + ester + [EMIM][HSO$_4$] systems the increase in the two phase region is not that pronounced and the tie lines are almost not influenced by the chain length of the ester.

In order to study the influence of the temperature on the phase equilibrium we experimentally determined diagrams for the systems 1-butanol + butylacetate + [EMIM][HSO$_4$] and acetic acid + butylacetate + [EMIM][HSO$_4$] at 30 and 50°C and

compared them with data for 40°C. Though the temperature influences both the alcohol and acid binodal curves the change of the acetic acid systems is very small (Figure 1a). The points on the binodal curve differ by only 2-3wt.% for a temperature difference of 20°C and there is almost no change in the tie lines. In contrast to that the 1-butanol + butylacetate + [EMIM][HSO₄] system changes significantly with the temperature (Figure 1b). The size of the two phase region decreases significantly with the temperature, the slope of the tie lines changes near the top of the binodal curve. It seems that alcohol + alkylacetate + [EMIM][HSO₄] systems can be fine tuned by changing the operating temperature while the acid + alkylacetate + [EMIM][HSO₄] systems are negligibly influenced by this parameter. At lower temperature we have better separation of the phases and lower mutual solubility of ester and ionic liquid. This case would be preferred for extraction. At higher temperature we have a lot better miscibility of the alcohol with the ionic liquid, this is preferred for biphasic reactions conducted in the ionic liquid.
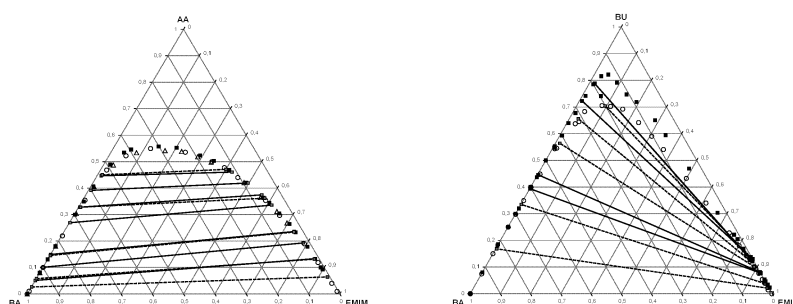

Figure 1. Effect of the temperature on the phase equilibrium for the systems acetic acid (AA) + 1-butylacetate (BA) + [EMIM][HSO₄] and 1-butanol (BU) + 1-butylacetate (BA) + [EMIM][HSO₄]. Data for 30°C (filled square, continuous line), 40°C (circle, dashed line) and 50°C (open triangle)

3. Five Component Systems

The goal of the study on the five component systems was firstly to compare the trends with the ones obtained for the three compound systems and to generalize the experimental information such that it could be extrapolated to other esterification systems not investigated yet. Secondly, to investigate the change in the equilibrium conversion with the IL and estimating their effect on the conversion for other esterification reactions. We studied all combinations of the three ionic liquids mentioned in the introduction with three reactions: the esterification of ethanol, 1-propanol and 1-butanol with acetic acid to the corresponding esters. The observed trends are similar to that for the ternary systems, e.g. smaller two phase region with increasing the alkyl chain length on the cation and better solubility of the reactants in the ionic phase. The reaction conversion was influenced somewhat by the ionic liquid: with [HMIM][HSO₄] we achieved the highest conversions for all reactions and with the [BMIM][HSO₄] the lowest. The difference in conversion for both IL is about 10%. We

assume that the solubility of the ester in the ionic phase is the main reason for this result. Indeed with the ionic liquid [HMIM][HSO$_4$] there is the lowest ester content and with [BMIM][HSO$_4$] the highest (often more than 20wt% in the ionic phase). More ester product is removed form the reactive ionic phase in the first case, thus contributing to the slight conversion increase compared to the results with the ionic liquid BMIM. When varying the esterification reaction (the alcohol) the trends are also similar to that for the three compound systems. In contrast to the ternary systems the effect of the temperature was not studied here.

4. Modeling and simulations

The available experimental data was used to estimate potential uses of the studied ionic liquids for a reactive extraction process. The idea is to use the products distribution in the biphasic system to hinder the back reaction and promote conversion beyond chemical equilibrium. For simulation purposes an equilibrium stage model, assuming both liquid-liquid phase equilibrium and chemical equilibrium with the reaction in the ionic (catalytic) phase, was implemented in Matlab$^{®}$. The liquid-liquid equilibrium can be approximated by constant distribution ratios or by a G^E-model like UNIQUAC to account for thermodynamic nonidealities. In a further step it was taken into account that the reaction equilibrium cannot be reached at the stages in a real process but only a fraction of it depending on the residence time. Kinetics investigation has been performed and enhancement is with increase of IL quantity or by admixture of sulfuric acid (example shown in Figure 2).
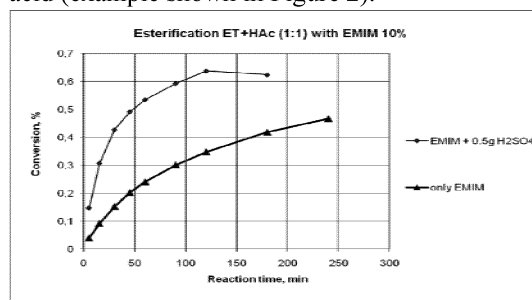

Figure 2. Kinetics of the esterification oft ethanol with acetic acid at 60°C in [EMIM][HSO$_4$] with and without sulfuric acid added

Using the one stage module a counter-current multistage reactive extraction cascade was simulated. Depending on the distribution of the reactants between ester and IL there are several theoretical configurations that can lead to higher reaction conversion and/or product purity. For the esterification of ethanol with acetic acid in the ionic liquid [EMIM][HSO$_4$] the 10 stage cascade with side feeds,shownt in Figure 3 is favourable. The compositions of the organic phase and the ionic phase for a simulation are shown in Fig. 4 and 5 respectively. Since a high conversion (> 90 %) and relatively pure products are obtained, the proposed process has the potential for both low capital and energy costs.
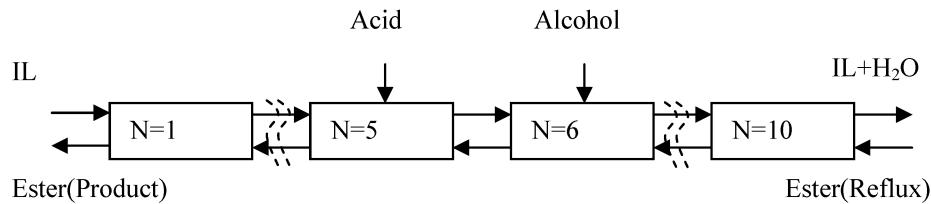
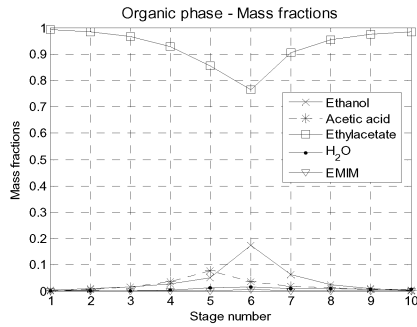Figure 3. Simulated counter-current reactive extraction process
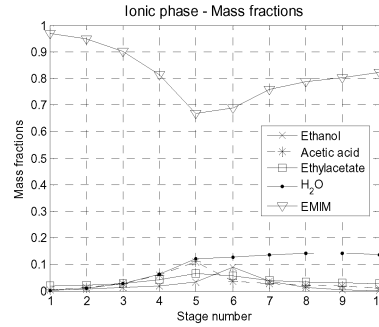

Figure 4. Mass fractions for
the organic phase

Figure 5. Mass fractions for
the ionic phase

The calculations assuming phase and chemical equilibrium give the theoretical maximum one could achieve at ideal conditions. To test whether the proposed method is possible at real conditions we did simulations for the same cascade and initial conditions like that presented in Figures 3 to 5 using the nonequilibrium model and thus assuming conversions at the reactive stages lower than the equilibrium conversions.
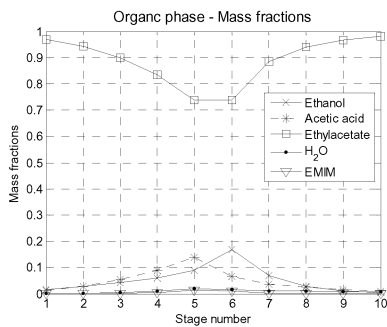

Figure 6. Mass fractions for
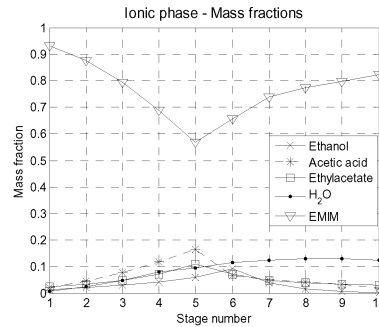the organic phase (nonequilibrium model)

Figure 7. Mass fractions for
the ionic phase (nonequilibrium model)

The simulations showed lower reaction conversion and somewhat lower product purities, compared to the equilibrium model, however, the concentration profiles and the mass flow profiles (Figures 6 and 7) are very similar. This indicates that under these

conditions a similar product quality can be achieved at the cost of additonal stages (Naydenov, 2009).

5. Conclusions

Through a systematic study, varying different parameters (cation on the ionic liquid, alkyl chain on the alcohol and temperature) we obtained their influence on the phase behavior of systems containing reactants and products of esterification reactions. Both nonreactive ternary and reactive five component systems were studied, and for the latter the influence of the ionic liquid on the conversion was also experimentally determined. The obtained information can be used to estimate the phase behavior of other esterification systems. This can be important for the selection of an appropriate ionic liquid for a given esterification reaction or developing a reactive separation process. Simulations with an equilibrium and non-equilibrium model using the experimental data gave the basis for a reactive extraction process with the potential for cost and energy savings compared to alternatives like e.g. reactive distillation.

References

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