

UNCATALYZED HYDROLYSIS OF ISOBUTYRIC ANHYDRIDE: EFFECT OF PARTIAL MISCIBILITY OF REACTANTS ON KINETICS

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Summary

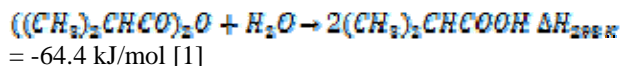
Un-catalyzed hydrolysis of isobutyric anhydride suffers from the mass transfer issues associated with the inherent partial miscibility of the participating reactants in a certain concentration-temperature space. Hence, activity-based models are used to describe the phase equilibrium behavior and the kinetics. In this work, the experimental and modeling approaches employed to study the kinetics in the single and two phase regions are presented. The effect of autocatalysis and the ratio of reactants within the organic and aqueous phases on the kinetic constants are studied. The contribution of the individual phases to the overall rate of the reaction is discussed.

Keywords

Multi-scale analysis, Reaction path analysis, kinetics, phase equilibrium, modeling

Introduction

Isobutyric anhydride (iBAn) is an important raw material for the synthesis of food chemicals, agrochemicals, coatings, pharmaceuticals, and flavor and fragrance chemicals. The kinetics of hydrolysis of iBAn is important for the safe handling and transportation of iBAn. The potential for an undetected water leak into the iBAn handling and storage vessels and the associated safety implications due to the exothermicity of uncatalyzed hydrolysis prompted the detailed investigation of this work. The hydrolysis reaction is represented by Eq.1:



There is not much information available in the literature on iBAn hydrolysis. Despite previous assertions that iBAn hydrolysis is slower than acetic anhydride hydrolysis, we have observed that the rates are similar (1). Also, depending on the ratio of iBAn and water, the reaction could be modeled as either a pseudo-first order, or a second order reaction. Though the extraction of the kinetic constant in the homogeneous/one phase region appears to be less challenging, the effect of solvent (acid) or the autocatalysis of the generated isobutyric acid on the hydrolysis of anhydride could affect the estimated kinetic parameter and this must be elucidated. Additional complexity is introduced into this system from the partial miscibility of water and iBAn within a certain range of temperature and concentration. Fig.1 shows the ternary diagram of iBAn-water-isobutyric acid system at 22 °C. In this two phase region, the mixing and the phase behavior

characteristics affect the rate of the reaction (2,3). This work investigates the hydrolysis kinetics in both the single and two phase regions.

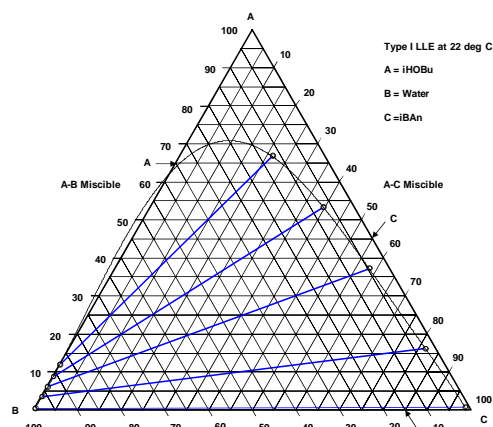


Figure 1: Liquid-Liquid Equilibrium (LLE) of iBAn-isobutyric acid-water at 22 °C

Experimentation and Analysis

In this work, a 2L Mettler-Toledo RC1 reactor was used to carry out the batch experiments. Multiple experiments were conducted covering a wide range of initial concentrations (equimolar initial concentration of the reactants as well as with excess water), three different temperatures and encompassing both the single and two

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phase regions of the ternary diagram. The experiments within single phase regions were usually carried out with some acid in the initial mixture. The reaction progress was monitored using an insitu-IR probe and by collecting samples periodically. The collected physical samples were analyzed using GC. Figures 2a and 2b show the simplistic representation of the kinetics using pseudo first order and second order reactions, respectively. The activation energy for this reaction is 52.3 ± 0.2 kJ/mol. We also found a dependence on the concentration of acid (auto-catalysis effect), which will be covered in the full paper.

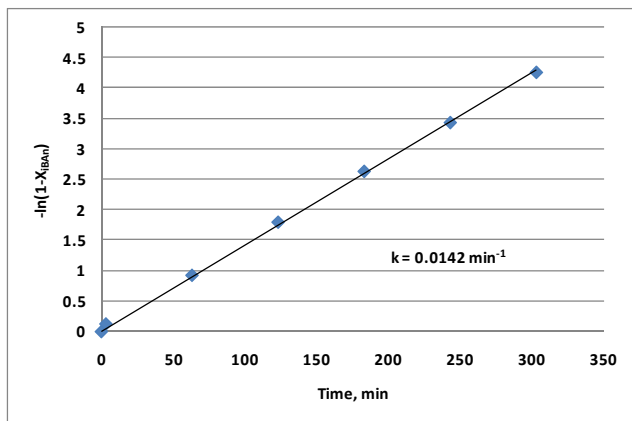


Figure 2a: Pseudo-first order (on anhydride) hydrolysis of iBAn at 50 °C with $C_{\text{water}} / C_{iBAn} = 5$

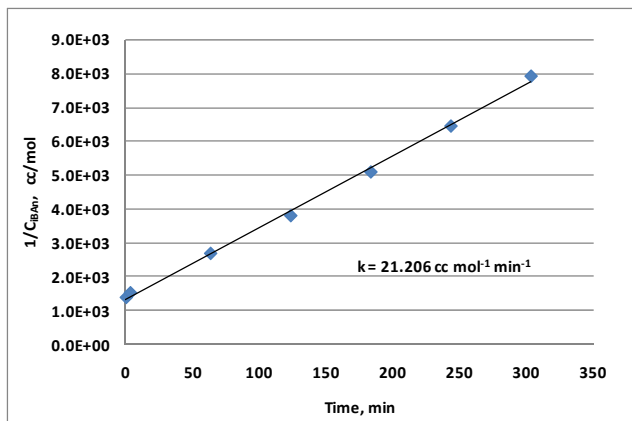


Figure 2b: Second order hydrolysis of iBAn at 70 °C with $C_{\text{water}} / C_{iBAn} = 1$

Partially Miscible Region

Activity based models should be used to describe the liquid-liquid phase equilibrium and reaction kinetics in the two phase region (2). A new model has been developed to extract the kinetics from the experiments carried out in the partially miscible region. Here the system volume (V) is modeled to consist of two phases/regions; organic and aqueous phases with respective volumes V_1 and V_2 . The reaction is allowed to take place in both the phases, with mass transfer and phase equilibrium occurring between

these two regions. It is assumed that there is negligible external mass transfer effect due to the high agitation rate used in this work. With this assumption, we relax the effect of dispersed phase droplet size distribution on kinetics; this could be taken up subsequently. The concentration in the modeled aqueous phase and organic phase, therefore, corresponds to average concentration across the reactor for the respective phases. From the previous study in the one phase region, it is observed that the kinetics of the hydrolysis is sufficiently slower, and hence, the phase equilibrium between the organic and aqueous phases is attained instantaneously as the reaction progresses. It is experimentally noted that with progress in time, the two phase mixture eventually becomes one phase (with acid generation) and further reactions will take place in the homogenous mixture. Accurate measurements of individual phase volumes, V_1 and V_2 and the concentrations of species in individual phases are required to predict the activity coefficient parameters, and thereby, the kinetic constants. The volume of individual phases during the kinetic experimentation is obtained by halting the agitation briefly during the progress of the reaction and measuring the individual volumes in the reactor. The activity coefficients could be simultaneously regressed from the experimental data or could be individually supplied from a different set of LLE experiments. The relative difficulty and the errors associated with the above two methods are discussed. This model will be used to extract the kinetics in two phase regions. The kinetics obtained in the two phase regions will be compared against that obtained in the single phase region. The contribution of the individual phases on the overall rate of the reaction will be reported.

References

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