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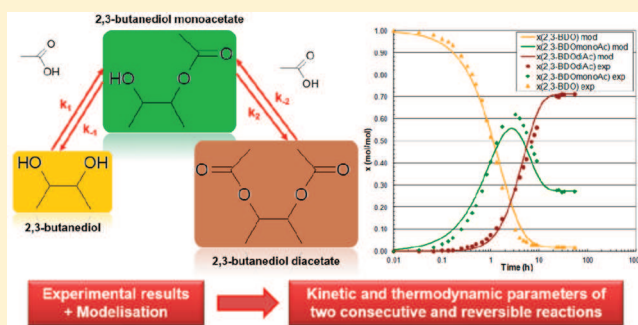
# Kinetics Modeling of the Heterogeneously Catalyzed Esterification of 2,3-Butanediol with Acetic Acid

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**ABSTRACT:** Esterification of 2,3-butanediol using a homogeneous catalyst was studied in 1945 under the Synthetic Rubber Program. The aim of this paper is to show that this reaction can be carried out with a heterogeneous catalyst, which presents many advantages such as the possibility of separation and recycling. The kinetic behavior of heterogeneous esterification of 2,3-butanediol with acetic acid over an ion-exchange resin Amberlyst 36 was investigated in a batch reactor. The experiments were conducted with different amounts of catalyst (from 1.1% to 4.4%, relatively to the initial molar quantity of 2,3-butanediol), with molar ratios of reactants (acetic acid to 2,3-butanediol) varying from 2 to 12, and at temperatures from 50 to 110 °C. Our experimental system was able to acquire kinetic data, even during the first minutes of the reaction. A simple model based on reliable hypotheses was built and the experimental data were used to determine all the kinetic and thermodynamic constants of the reaction. A single set of parameters is able to represent correctly the evolution of all different species present during the esterification reaction in function of time.



## 1. INTRODUCTION

Due to the lack of petroleum worldwide, alternative sources of energy are worth being developed.<sup>1</sup> Among renewable energies such as sunlight, wind, rain, tides, waves, geothermal heat, and biomass, the latter is particularly studied to replace fossil fuels.<sup>2,3</sup> Several feedstocks derived from biomass can be used: sugars, vegetable oils, lignocellulosic biomass, or algae. Fermentation processes of glucose can lead to various alcohols such as ethanol<sup>4</sup> or 2,3-butanediol (2,3-BDO).<sup>5</sup> These alcohols can also be transformed into other value-added products<sup>6,7</sup> such as 1,3-butadiene (1,3-BDE) which is mainly used in the production of synthetic rubber. Indeed, 1,3-BDE is currently produced by three petrochemical processes:<sup>8</sup> mainly by steam cracking of hydrocarbons (as a coproduct of ethylene manufacturing), and to a lesser extent by catalytic dehydrogenation of *n*-butane and *n*-butene (Houndry process), and oxidative dehydrogenation of *n*-butene (Oxo-D or O-X-D process).

In previous works, 2,3-BDO was used as a raw material to obtain 1,3-BDE. As the direct dehydration of 2,3-BDO leads to methylethylketone (MEK), which is thermodynamically stable, an intermediate product has to be obtained. Thus, a diester of 2,3-BDO, synthesized by an esterification process, can lead to 1,3-BDE with really good yields (about 90%) by pyrolysis without any catalyst. The esterification using a homogeneous catalyst was studied in 1945 under the Synthetic Rubber Program (SRP).<sup>9–16</sup> In this work, the esterification reaction between 2,3-BDO and acetic acid (AA) is discussed using a heterogeneous catalyst.

Esterification reactions are balanced reactions. In this case, as 2,3-BDO has two alcohol functions, the esterification reaction proceeds in two steps. A first step involves one mole of 2,3-BDO and one mole of AA to yield one mole of 2,3-BDO-monoacetate (2,3-BDOmonoAc) and one mole of water. The second step consists in esterifying the alcohol function of the residual monoester with a second mole of AA to give one mole of 2,3-BDO-diacetate (2,3-BDOdiAc) and a second mole of water (Figure 1).

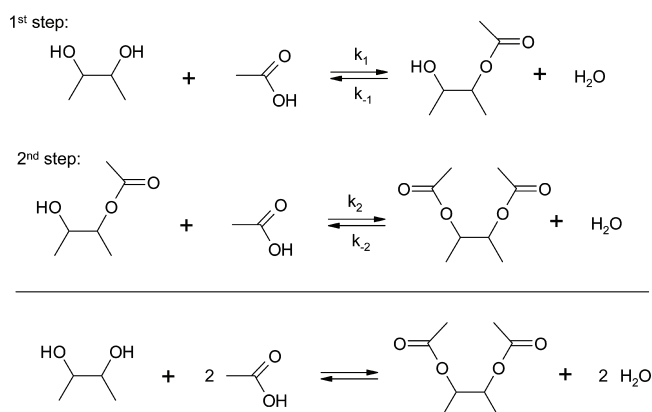
Rate constants  $k_i$  can be defined as the rate constants of forward reactions (formation of esters) and rate constants  $k_{-i}$  as the rate constants of reverse reactions (hydrolysis of esters). The thermodynamic constants of these reactions ( $K_i$ ) can be written as the ratio between the forward rate constants and the reverse rate constants:

$$K_i = \prod_j [j]^{v_j} = \frac{k_i}{k_{-i}} \quad (1)$$

where  $[j]$  is the concentration of species  $j$  (mol·L<sup>-1</sup>) and  $v_j$  is the stoichiometric coefficient of species  $j$ .

Thus, thermodynamic constants can be defined as follows:

$$K_1 = \frac{[2,3BDOmonoAc] \times [H_2O]}{[2,3BDO] \times [AA]} = \frac{k_1}{k_{-1}} \quad (2)$$



**Figure 1.** Two steps of the esterification reaction of 2,3-BDO with AA and the global reaction.

$$K_2 = \frac{[2,3\text{BDOdiAc}] \times [\text{H}_2\text{O}]}{[2,3\text{BDOmonoAc}] \times [\text{AA}]} = \frac{k_2}{k_{-2}} \quad (3)$$

$$K_3 = \frac{[2,3\text{BDOdiAc}] \times [\text{H}_2\text{O}]^2}{[2,3\text{BDO}] \times [\text{AA}]^2} = K_1 \times K_2 \quad (4)$$

The reaction was first studied in the SRP in 1945. Two homogeneous acid catalysts were tested: sulfuric acid  $\text{H}_2\text{SO}_4$  (from 1% to 1.5%) and para-toluenesulfonic acid APTS (3%).<sup>15</sup> Sulfuric acid was used for the pilot plant process. The esterification reaction of 2,3-BDO was thus conducted in a batch reactor with  $\text{H}_2\text{SO}_4$ , using two various AA/2,3-BDO molar ratios and six different temperatures. To monitor the reaction, only the titration of AA as a function of time was achieved. Hence, it was not sufficient to establish a kinetic model. Nevertheless, thermodynamic constants have been determined and it appears that the reactions are balanced. The second step of the double esterification, that is, the esterification of 2,3-BDOmonoAc, is even less favorable ( $0.1 < K_2 < 0.2$ ) than the first step of the reaction, that is, the esterification of 2,3-BDO ( $0.8 < K_1 < 2.3$ ).<sup>15</sup>

This esterification reaction of 2,3-BDO was also recently studied<sup>17</sup> using a mixture of formic acid and acetic acid with a homogeneous catalyst (sulfuric acid), leading to good yields in diesters of 70% and 85%, respectively. Nevertheless, a kinetic model was not determined in this study either.

It is therefore necessary to implement a more complete reaction monitoring in order to build a model able to represent the evolution of the different compounds in the function of reaction time. Moreover, the aim of this paper is to show that the reaction of esterification of 2,3-BDO with AA can be carried out with Amberlyst 36, which presents many advantages of separation and recycling, compared to the several treatments involved with a homogeneous catalyst at the end of the reaction such as neutralization and filtration. Amberlyst 36 is a heterogeneous catalyst which is widely used for esterification. Indeed, it has been used to study the esterification of acetic acid with various alcohols (methanol,<sup>18</sup> pentanol,<sup>19</sup> and octanol<sup>20</sup>) and the esterification of methanol with various carboxylic acids (acetic acid<sup>18</sup> and propionic acid<sup>21</sup>). In addition, this heterogeneous catalyst has also been used to perform the esterification of ethylene glycol with acetic acid,<sup>22</sup> and similar performance with 2,3-BDO can be expected.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** As 2,3-BDO has two asymmetric carbons and a symmetry plan, three different stereoisomers can exist: an

enantiomeric pair which is composed of the (–) dextrogyre (also called RR) and the (+) levogyre (also called SS); and the meso form (RS form which is the same as the SR form). Pure isomers being very expensive, experiments were carried out with a mixture of diastereoisomers of 2,3-BDO (70% of RS and 30% of (RR+SS)) with a 99% purity from Sigma-Aldrich. On the counterpart, an analytical method was developed to quantify each diastereoisomer of the 2,3-BDO, the 2,3-BDOmonoAc, and the 2,3-BDOdiAc.

Glacial acetic acid was purchased from Sigma-Aldrich and its water content was determined before each reaction by Karl Fischer titration.

The heterogeneous catalyst is an ion exchanged resin, Amberlyst 36 produced by Rhom and Haas, with an acid sites concentration of  $5.4 \text{ mequiv}\cdot\text{g}^{-1}$  of wet resin, a harmonic mean size of 0.60–0.85 mm, a BET surface area of  $33 \text{ m}^2\cdot\text{g}^{-1}$ , an average pore diameter of 240 Å, and a total pore volume of  $0.2 \text{ cm}^3\cdot\text{g}^{-1}$ . Mercury porosimetry was measured on dry Amberlyst 36, and showed a porosity of 42%.

**2.2. Analysis Methods.** Mixtures were analyzed by gas chromatography (GC) using an Agilent Technologies apparatus (6890 N Network GC System) coupled to a flame ionization detector (FID) in order to determine 2,3-BDO, 2,3-BDOmonoAc, and 2,3-BDOdiAc amounts. With several different columns tested, one diastereoisomer of the 2,3-BDO and one diastereoisomer of the 2,3-BDOmonoAc were systematically coeluted. Only the capillary column (DB-WAX column, 10 m,  $50 \mu\text{m}$ ,  $0.1 \mu\text{m}$ ) from Agilent J&W GC Columns (JW 126-7013) allowed a complete separation of all components of the reaction media. The chromatograph was equipped with an automatic split injector and the injections ( $0.1 \mu\text{L}$ ) were performed with a split ratio of 4270 (split flow =  $500.0 \text{ mL}\cdot\text{min}^{-1}$  and total flow =  $502.3 \text{ mL}\cdot\text{min}^{-1}$ ). The carrier gas was helium and the column head pressure was adjusted to 100 psi. Injector temperature was  $250 \text{ }^\circ\text{C}$ . Initial temperature in the oven was  $60 \text{ }^\circ\text{C}$ . The temperature in the oven was ramped to  $110 \text{ }^\circ\text{C}$  at  $2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ , and then ramped to  $200 \text{ }^\circ\text{C}$  at  $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  and finally held 1 min at  $200 \text{ }^\circ\text{C}$ . The total running time was 35 min. The temperature of the detector (FID) was  $250 \text{ }^\circ\text{C}$ . Each sample was analyzed three times and the values of mass fractions ( $w_i$ ) given in this paper are the average of the three injections. The uncertainty is  $u(w_i) = 0.001$ , which corresponds to the maximum standard deviation calculated.

AA could also be quantified by GC-FID but results are less reliable. Indeed, an automatic titrator (751 GPD Titrino, Metrohm) was used to determine the quantity of AA in each sample. It was verified that no hydrolysis of 2,3-BDOdiAc occurred during the titration with sodium hydroxide (0.1 M), by using standard mixtures of AA and 2,3-BDOdiAc over the whole range of composition. The pH of the solution was measured throughout the titration thanks to the electrode, accuracy being more important with an electrode than an indicator. The end point corresponds to a sudden change in the measured pH, and then the equivalence point allows the determination of AA amount in the sample.

Moreover, the amount of water was determined using a coulometric Karl Fischer apparatus (831 KF Coulometer (KFC), Metrohm).

**2.3. Experimental Procedure.** The esterification reaction was carried out in a 30 mL-batch reactor with a double-jacket. Specific oil from a temperature-controlled bath flows inside the double-jacket to maintain the targeted reactor temperature. The reactor was equipped with a condenser also regulated at a temperature of  $-4 \text{ }^\circ\text{C}$ . All the reactions were led under

atmospheric pressure with magnetic stirring at 800 rpm, which avoids any mass transfer resistance due to external diffusion limitations.<sup>19,20</sup> Esterification reactions between 2,3-BDO and AA were carried out by using the following procedure: a mixture of the reactant with the highest quantity (generally AA) and the heterogeneous catalyst was introduced into the dry reactor, and the magnetic stirring was turned on at 800 rpm. The mixture was heated until the desired temperature was reached. At this point, the second reactant (generally 2,3-BDO) was added to the mixture of AA and catalyst. 2,3-BDO addition was considered as time zero of the reaction. Concerning the off-line analysis, homogeneous samples of 0.1 mL (without catalyst) were collected from the reactor at different reaction times in order to determine the kinetics of the reaction. These samples were immediately quenched in an ice-water batch and analyzed by GC-FID, automatic titrator (for AA content) and Karl Fischer apparatus (for water content).

Different conditions were applied for the batch esterification reactions. Several AA to 2,3-BDO molar ratios were tested ( $r = 2, 6, \text{ and } 12$ ). A series of experiments were also performed with different amounts of heterogeneous catalyst: 1.1, 2.2, and 4.4 mol % (referring to the initial 2,3-BDO amount). Finally, the temperature was ranged from 50 to 110 °C which is close to AA boiling point (50 °C, 70 °C, 90 °C, 110 °C).

**2.4. Numerical Study.** 2.4.1. *Modeling the Kinetics: Hypotheses and Resulting Equations.* Modeling experiments performed with a heterogeneous catalyst require to decouple different physical phenomena: reaction kinetics (catalyzed and uncatalyzed), mass-transfer, and adsorption.

Experiments were performed at high temperatures and high molar ratios of AA over 2,3-BDO, with and without catalyst. The uncatalyzed kinetics for both consecutive reactions appear to be 10 times slower than the catalyzed kinetics with 2.2%. It can be concluded that the uncatalyzed reaction kinetics can be neglected in the whole range of conditions tested.

Characteristic time for the diffusion through a porous catalyst can be roughly estimated with the following formula:

$$t_D = \frac{R^2}{D_m \frac{\epsilon_p}{\tau}} \quad (5)$$

where  $t_D$  is the diffusion characteristic time (s),  $R$  is the average radius of the particles (m),  $\epsilon_p$  is the porosity (-),  $\tau$  is the tortuosity (-), and  $D_m$  is the diffusion coefficient of 2,3-BDO ( $\text{m}^2 \cdot \text{s}^{-1}$ ) which can be estimated using the Wilke-Chang correlation,<sup>23</sup> knowing the viscosity of acetic acid and the density of 2,3-BDO<sup>24</sup> over the temperature range explored. Characteristic time for the diffusion is about 0.5 h at 50 °C, whereas approximately 100 h are necessary to reach the equilibrium. Moreover,  $t_D$  is about 0.3 h at 100 °C, whereas it takes 3 h to reach the equilibrium. Therefore, the mass transfer limitation due to internal diffusion limitation can be neglected.

Adsorption thermodynamics on a heterogeneous catalyst can be acquired measuring nonreactive isotherms, as it has been done by Tsai et al.<sup>18</sup> for the esterification of acetic acid and methanol in order to form methyl acetate and water with Amberlyst 36. With this system of four components, four nonreactive binary isotherms can be measured: water–acetic acid, water–methanol, acetic acid–methyl acetate and methanol–methyl acetate. Actually, measurement of only three nonreactive isotherms is necessary in order to get the relative adsorption selectivity of each component.

Since this is a more complex system with two consecutive reactions of esterification and five components involved, at least four nonreactive binary isotherms have to be determined. Unfortunately, the only nonreactive binary isotherms that can be measured are water–acetic acid, water–2,3-BDO, and acetic acid–2,3-BDOdiAc. Indeed, mixing 2,3-BDO and 2,3BDOdiAc over the catalyst produces 2,3-BDOmonoAc, water, and acetic acid. Moreover, if the 2,3-BDOmonoAc could be available or isolated, it would react with all the other components of the system, either by esterification/hydrolysis or transesterification/dismutation. Thus, only partial information on the adsorption selectivity can be experimentally obtained, and that is why a simple model not taking into account any adsorption phenomenon (pseudohomogeneous model) was used. To determine the apparent kinetic constants, a model representing the evolution of different species of the reaction is built with the following hypotheses:

- (i) 1st order for all compounds (other orders have been checked but only these results are presented in this paper)
- (ii) no mass transfer limitation, neither external nor internal
- (iii) no order for the heterogeneous catalyst: as its quantity is constant, it will be part of the apparent kinetic constant of the reactions
- (iv) balanced reactions: as the two esterification reactions are balanced, 2,3-BDO, 2,3-BDOmonoAc and 2,3-BDOdiAc are present at chemical equilibrium
- (v) no secondary reactions: this hypothesis was validated by GC-FID which did not show any byproducts
- (vi) the volume of the mixture is constant during the reaction: samples are neglected relative to the total volume and the medium density is constant during the reaction ( $d_{2,3\text{-BDO}} = 1,002$ ;  $d_{\text{AA}} = 1,082$ ;  $d_{2,3\text{-BDOdiAc}} = 1,035$  and  $d_{\text{water}} = 1$ )
- (vii) activity coefficient equal to 1 for all the species
- (viii) the model was solved using a first order discretization: concentration of component  $j$  can be written as follows

$$\left. \frac{d[j]}{dt} \right|_t \approx \frac{[j]_{t+\Delta t} - [j]_t}{\Delta t} \quad (6)$$

Thus, from the initial concentration values, it is possible to calculate the concentrations at time  $t = 0.1$  h. By recurrence, knowing the concentrations at time  $t$ , the concentrations at time  $t + \Delta t$  can be determined using the following formula:

$$[j]_{t+\Delta t} \approx [j]_t + \Delta t \times \left[ \left. \frac{d[j]}{dt} \right|_t \right] \quad (7)$$

Using all these hypotheses, the following equations of the model represent first order reaction kinetics for all the compounds:

$$\begin{aligned} \frac{d[2,3\text{BDO}]}{dt} &= -k_1[2,3\text{BDO}][\text{AA}] \\ &\quad + k_{-1}[2,3\text{BDOmonoAc}][\text{H}_2\text{O}] \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{d[2,3\text{BDOmonoAc}]}{dt} &= -k_1[2,3\text{BDO}][\text{AA}] + k_{-1}[2,3\text{BDOmonoAc}][\text{H}_2\text{O}] \\ &\quad - k_2[2,3\text{BDOmonoAc}][\text{AA}] \\ &\quad + k_{-2}[2,3\text{BDOdiAc}][\text{H}_2\text{O}] \end{aligned} \quad (9)$$

$$\frac{d[2,3\text{BDOdiAc}]}{dt} = k_2[2,3\text{BDOmonoAc}][\text{AA}] + k_{-2}[2,3\text{BDOdiAc}][\text{H}_2\text{O}] \quad (10)$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = k_1[2,3\text{BDO}][\text{AA}] + k_{-1}[2,3\text{BDOmonoAc}][\text{H}_2\text{O}] + k_2[2,3\text{BDOmonoAc}][\text{AA}] - k_{-2}[2,3\text{BDOdiAc}][\text{H}_2\text{O}] \quad (11)$$

$$\frac{d[\text{AA}]}{dt} = -k_1[2,3\text{BDO}][\text{AA}] + k_{-1}[2,3\text{BDOmonoAc}][\text{H}_2\text{O}] - k_2[2,3\text{BDOmonoAc}][\text{AA}] + k_{-2}[2,3\text{BDOdiAc}][\text{H}_2\text{O}] \quad (12)$$

The model was solved using a first order discretization. A 0.1 h step time was chosen as it presents satisfying accuracy and is a good compromise between calculation time and numerical errors.

**2.4.2. Determination of Kinetics and Thermodynamic Constants.** The parameters involved in the system are the four kinetic constants ( $k_1$ ,  $k_{-1}$ ,  $k_2$ , and  $k_{-2}$ ) and the two thermodynamic constants ( $K_1$  and  $K_2$ ). As these constants are related by two eqs (eq 2 and 3), only four parameters are adjustable so that the kinetics model best represents the experimental data obtained by GC-FID. We decided to vary two rate constants ( $k_1$  and  $k_2$ ) and the two thermodynamic constants ( $K_1$  and  $K_2$ ) in order to properly represent the evolution of the different compounds of the reaction system. The two thermodynamic constants are easily determined, as in all experiments thermodynamic equilibrium was reached. Thus, only two kinetic constants had to be determined by parameter identification. Criterion minimization was used for identifying these two kinetic parameters. The criterion is defined by the sum of the relative squared differences between the experimental measured data and the model output for each component of the reaction mixture (2,3-BDO, 2,3-BDOmonoAc, 2,3-BDOdiAc, AA, and  $\text{H}_2\text{O}$ ) at different reaction times:

$$\text{minimization criterion} = \sum_j \sum_i \left( \frac{C_j(i)_{\text{mod}} - C_j(i)_{\text{exp}}}{C_j(i)_{\text{exp}}} \right)^2 \quad (13)$$

where  $C_j(i)_{\text{mod}}$  is the calculated concentration of component  $j$  at reaction time  $i$ ,  $C_j(i)_{\text{exp}}$  is the experimental concentration (GC-FID data) of component  $j$  at reaction time  $i$  with  $j = 2,3\text{-BDO}$ ,  $2,3\text{-BDOmonoAc}$ ,  $2,3\text{-BDOdiAc}$ , AA, and  $\text{H}_2\text{O}$  and  $i = 1$  min, 3 min, ..., several hours. The Solver function of Microsoft Office Excel (2013 version) was used to minimize this criterion, working on the four kinetic constants as variables, which leads to the determination of these four constants. The criterion chosen in this work is based on the squared sums of relative variations and not on the squared sums of absolute variations because some concentrations such as those of 2,3-BDOdiAc at the beginning of the reaction or those of 2,3-BDO at the end of the reaction can be much lower than the other concentrations. Thus, by working with a criterion on relative variations, errors on all compounds are balanced, which is more representative of the system.

### 3. RESULTS AND DISCUSSION

**3.1. Preliminary Experiment.** First of all, we carried out an esterification reaction with a commercial 2,3-BDO (70% of RS

compound and 30% of RR+SS compounds) in order to determine the kinetics of the different stereoisomers. We observed that the kinetics of esterification of (RS)-2,3-BDO and (RR+SS)-2,3-BDO were nearly the same. Indeed, the difference of kinetics between the two stereoisomers is in the same order of magnitude as the uncertainty of analyses. Therefore, in the rest of this paper, the amount of 2,3-BDO will represent the sum of the amount of (RS)-2,3-BDO and (RR+SS)-2,3-BDO. In the same way, the amount of 2,3-BDOmonoAc (respectively 2,3-BDOdiAc) will be the sum of (RS)-2,3-BDOmonoAc (respectively (RS)-2,3-BDOdiAc) and (RR+SS)-2,3-BDOmonoAc (respectively (RR+SS)-2,3-BDOdiAc):

$$n_{2,3\text{-BDO}} = n_{2,3\text{-BDO}}^{\text{RR+SS}} + n_{2,3\text{-BDO}}^{\text{RS=SR}} \quad (14)$$

$$n_{2,3\text{-BDOmonoAc}} = n_{2,3\text{-BDOmonoAc}}^{\text{RR+SS}} + n_{2,3\text{-BDOmonoAc}}^{\text{RS=SR}} \quad (15)$$

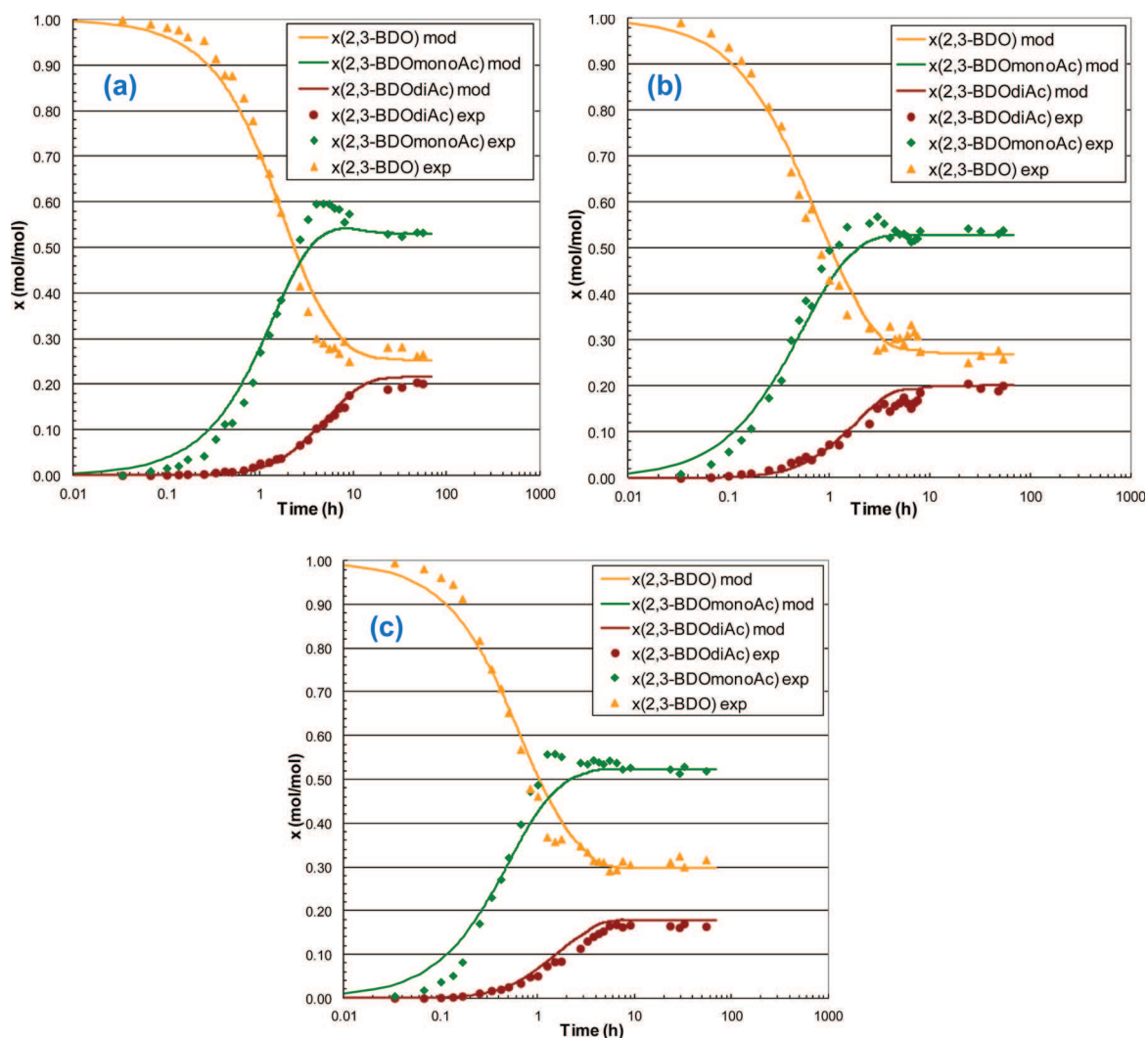
$$n_{2,3\text{-BDOdiAc}} = n_{2,3\text{-BDOdiAc}}^{\text{RR+SS}} + n_{2,3\text{-BDOdiAc}}^{\text{RS=SR}} \quad (16)$$

**3.2. Influence of Catalyst Amount.** In this section, the feasibility of the esterification reaction of 2,3-BDO with AA using Amberlyst 36 was shown. This catalyst is stored with a significant water content (given by the supplier as 50–60 wt %). It was dried (72 h in an oven at 120 °C) to determine precisely its water content, which is of 55.52 wt %. In the experiments we carried out, the wet form of the catalyst was used in order to have a constant value for the water content. This value was taken into account in our calculations to determine the initial amount of water, and is always consistent with the water concentration measured by Karl Fischer in the first aliquot taken, where almost no reaction had occurred. Indeed, the dry catalyst immediately hydrates in contact with air, which makes uncertain the water content when it is introduced into the reactor.

We conducted experiments with three different amounts of catalyst: 1.1%, 2.2%, and 4.4%, expressed relatively to the initial molar amount of 2,3-BDO. The other two parameters were set to 110 °C for the temperature and 2 for the initial AA/2,3-BDO molar ratio (stoichiometric ratio). Figure 2 shows the evolution of molar fractions of 2,3-BDO, 2,3-BDOmonoAc, and 2,3-BDOdiAc for the experiments conducted with 1.1%, 2.2%, and 4.4% of heterogeneous catalyst (at  $T = 110$  °C and an initial molar ratio  $n_{\text{AA}}/n_{2,3\text{-BDO}} = 2$ ). Experimental data are compared with the kinetic model.

The three experiments converge toward a similar thermodynamic equilibrium. The slight differences in thermodynamic equilibrium can be explained by the initial amount of water in each experiment which is a bit different because of the different water contents due to the catalyst amount:  $w_{\text{H}_2\text{O}} = 1.23\%$ ,  $2.37\%$ , and  $4.51\%$  for experiments with respectively 1.1%, 2.2%, and 4.4% of catalyst. The amount of catalyst does not influence the thermodynamics of the reaction but influences the kinetics of the reaction.

It may be noted that the proportion of 2,3-BDO decreases monotonically: 2,3-BDO is consumed by the esterification reaction with AA. As a result, the proportion of 2,3-BDOdiAc, the reaction product, increases monotonically with time until it reaches the thermodynamic equilibrium. Besides, we note that the proportion of 2,3-BDOmonoAc passes through a maximum before decreasing slightly, which means that the esterification reaction of the diol into monoester is faster than the esterification reaction of the monoester into the diester, which causes an accumulation of monoester. For the three experiments, the kinetic



**Figure 2.** Comparison of the kinetic model (continued lines) and experimental data (singular points) for the esterification of 2,3-BDO with AA with 1.1% (a), 2.2% (b), and 4.4% (c) of catalyst ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $T = 110$  °C).

model generally fits with the experimental data representing the evolution of all the compounds in function of time.

Thanks to the model, it is possible to extract the kinetic and thermodynamic constants of the reaction in function of the amount of catalyst (Table 1):

**Table 1. Kinetic and Thermodynamic Constants for Different Amounts of Catalyst ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $T = 110$  °C)**

	0%	1.1%	2.2%	4.4%
$k_1$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0108	0.0400	0.1000	0.1000
$k_{-1}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0064	0.0235	0.0588	0.0588
$k_2$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0030	0.0120	0.0400	0.0400
$k_{-2}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0091	0.0364	0.1212	0.1212
$K_1 = k_1/k_{-1}$	1.70	1.70	1.70	1.70
$K_2 = k_2/k_{-2}$	0.33	0.33	0.33	0.33

We also carried out an experiment without catalyst. As it was previously stated in this paragraph, the thermodynamic equilibrium is unchanged without catalyst but the reaction rate is the slowest in this experiment (about 100 h to reach equilibrium). Moreover, it may be noted that the kinetics of the reaction is lower with 1.1% of catalyst (about 10–20 h to reach equilibrium) than with 2.2% and 4.4% of catalyst

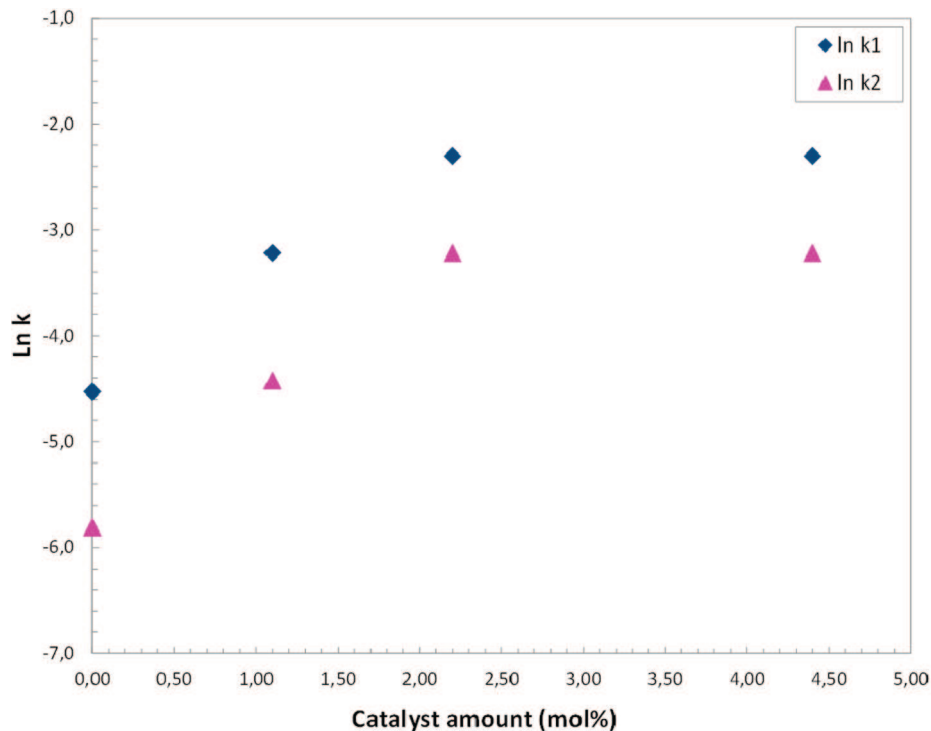
(approximately 5 h) for which kinetics are substantially the same within experimental errors.

Evolution of kinetic constants in function of the catalyst amount were also calculated. For example, Figure 3 shows the kinetics constants of the two forward esterification reactions ( $\ln k_1$  and  $\ln k_2$ ).

The catalyst amount only affects the kinetics of the reaction: kinetic constants are the same for 2.2% and 4.4% of catalyst, are lower for 1.1% of catalyst, and even lower without catalyst at all. A catalyst amount of 2.2% relatively to the initial molar quantity of 2,3-BDO seems to be the suitable amount for this esterification reaction.

**3.3. Influence of Temperature.** The evolution over time of the molar composition of the reaction mixture was also studied at various temperatures: 50 °C, 70 °C, 90 and 110 °C. The initial molar ratio AA/2,3-BDO was set at 2, whereas the amount of heterogeneous catalyst was set at 2.2% relative to the initial molar amount of 2,3-BDO. The initial water content (water originally contained in 2,3-BDO and AA) was measured by KFC before the start of the reaction and is equal to 2.4 wt %. Figure 4 represents the evolution over time of the composition of the medium during reactions carried out between 50 and 110 °C.

Regarding the kinetics, it can be noticed that this reaction is relatively slow, since the equilibrium is reached after several hours.



**Figure 3.** Comparison of kinetic constants during 2,3-BDO esterification with AA over different catalyst amounts ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $T = 110$  °C).

The classical influence of temperature is shown here: the higher is the temperature, the faster is the reaction. Indeed, it takes about 200 h to reach equilibrium with a temperature of 50 °C, whereas it takes approximately 10 h to reach the equilibrium at 110 °C. Moreover, we can notice that the thermodynamic equilibrium reached during these four reactions is quite similar to the following molar compositions: from about 25% to 28% of 2,3-BDO, from 52% to 56% of 2,3-BDOmonoAc, and from 16% to 20% of 2,3-BDOdiAc, whatever the temperature. It means that the temperature has a low influence on the thermodynamics of this system.

Although the model seems to be less representative for the experiment at 50 °C (the reaction may be too slow at this temperature and limitation of the hypothesis made for our model may be reached in these conditions: viscosity of 2,3-BDO may be too high at this temperature, which involves a slower internal diffusion), the corresponding kinetic and thermodynamic constants can be obtained thanks to the model (Table 2).

The thermodynamic constants determined can be compared with those obtained in 1945 for the esterification of 2,3-BDO with AA using a homogeneous catalyst<sup>15</sup> (Table 3).

The analytical technique available at that time was not able to determine the equilibrium proportion of 2,3-BDO, 2,3-BDOmonoAc, and 2,3-BDOdiAc. We can therefore not understand how the thermodynamic constants  $K_1$  and  $K_2$  were determined (Table 3). Nevertheless, some reactions were carried out using 2,3-BDOmonoAc. However, no information is given on how this product was obtained. It can be noticed that it is still not commercialized nowadays.

As a result, the different activation energies of the esterification reaction of 2,3-BDO with AA can be determined using the kinetic constants at different temperatures. Indeed, using the Arrhenius law (eq 17), pre-exponential factors  $A_i$  ( $L \cdot mol^{-1} \cdot h^{-1}$ ) and activation energies  $E_{a_i}$  ( $J \cdot mol^{-1}$ ) associated with forward and reverse reactions can be calculated:

$$k_i = A_i \exp\left(-\frac{E_{a_i}}{RT}\right) \quad (17)$$

where  $R$  is the gas constant ( $R = 8.314 J \cdot mol^{-1} \cdot K^{-1}$ ) and  $T$  is the temperature (K). This equation can also be written as

$$\ln k_i = \ln A_i - \frac{E_{a_i}}{R} \times \frac{1}{T} \quad (18)$$

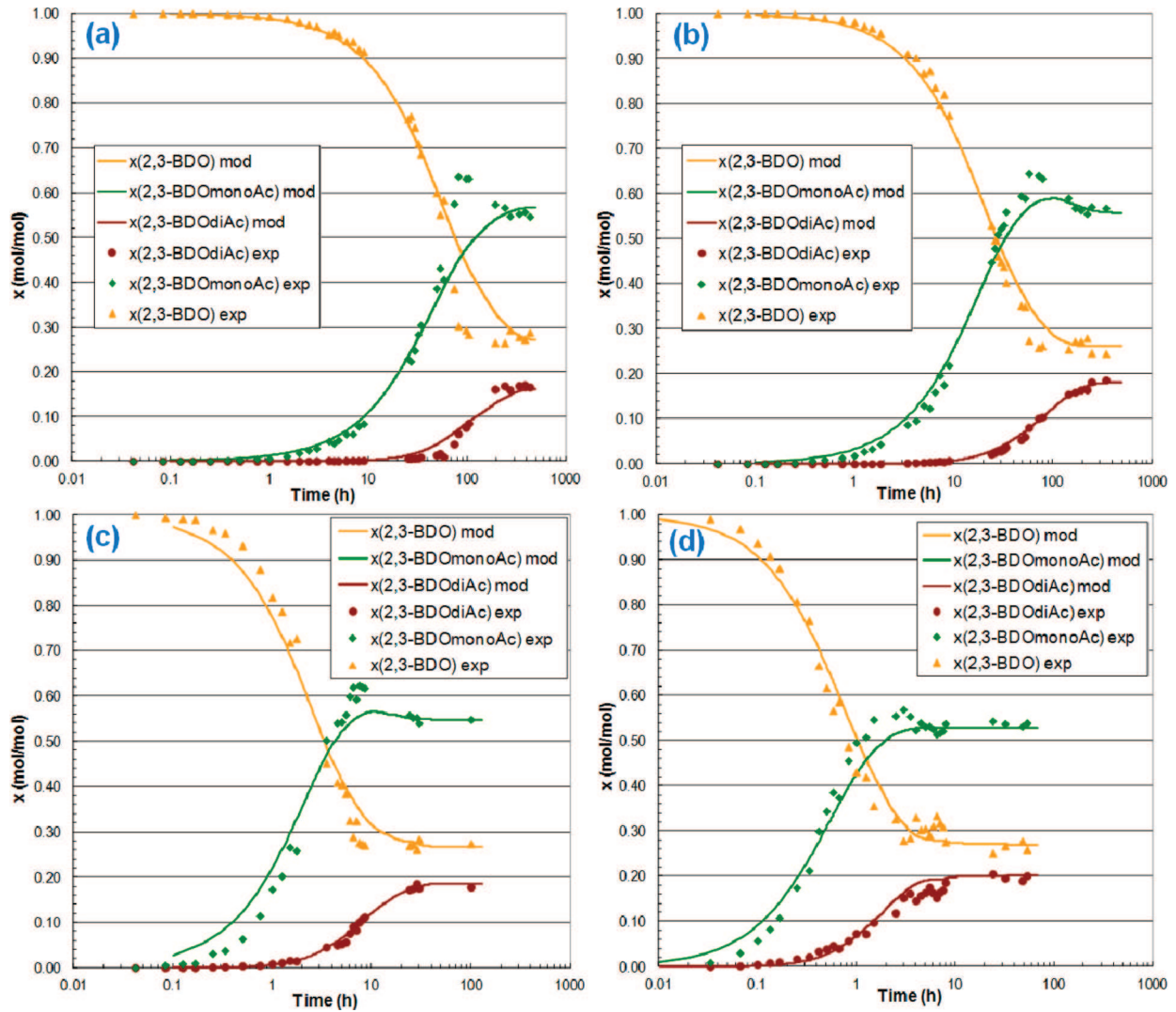
The relation  $\ln k_i = f\left(\frac{1}{T}\right)$  is linear, with a slope equal to  $-\frac{E_{a_i}}{R}$  and a y-intercept of  $\ln A_i$ .

As can be seen in Figure 5, the curves obtained are similar to straight lines with  $R^2$  correlation coefficients between 0.88 and 0.98. Using this representation, the activation energies can be determined. The results are summarized in Table 4.

These activation energies (about  $80 kJ \cdot mol^{-1}$ ) can be compared with those involved in the esterification of ethylene glycol with acetic acid catalyzed by Amberlyst 36<sup>22</sup> (about  $40 kJ \cdot mol^{-1}$ ). Although they are of the same order of magnitude, the difference can be explained by steric hindrance of the two methyl groups present in the 2,3-BDO compared to ethylene glycol which is a more accessible molecule.

The activation energies of the two successive esterification reactions of 2,3-BDO have the same order of magnitude (Table 4), which means that an increase of temperature does not favor the kinetics of a reaction regarding the other. Nevertheless, it can be noticed that the pre-exponential factors of the second esterification ( $A_2$  and  $A_{-2}$ ) are about four times smaller than those of the first esterification ( $A_1$  and  $A_{-1}$ ), which means that the esterification of 2,3-BDO to monoester is approximately four times faster than the esterification of monoester to diester. This difference in kinetics can explain the “roll-up” observed on the curves showing the evolution of the amount of monoester over time.





**Figure 4.** Comparison of the kinetic model (continued lines) and experimental data (singular points) for the esterification of 2,3-BDO with AA at 50 °C (a), 70 °C (b), 90 °C (c), and 110 °C (d) ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{catal}/n_{2,3-BDO} = 2.2\%$ ).

**Table 2. Kinetics and Thermodynamic Constants for Different Temperatures** ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{catal}/n_{2,3-BDO} = 2.2\%$ )

	50 °C	70 °C	90 °C	110 °C
$k_1$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0013	0.0035	0.0280	0.1000
$k_{-1}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0007	0.0018	0.0156	0.0588
$k_2$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0005	0.0006	0.0060	0.0400
$k_{-2}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0019	0.0021	0.0200	0.1212
$K_1 = k_1/k_{-1}$	2.00	1.90	1.80	1.70
$K_2 = k_2/k_{-2}$	0.27	0.29	0.30	0.33

**Table 3. Thermodynamic Constants at Different Temperatures**<sup>15</sup>

temp	$K_1$	$K_2$	$K_3 = K_1 \times K_2$
62 °C	0.856	0.115	0.098
64 °C	0.839	0.115	0.097
81 °C	1.106	0.123	0.136
85 °C	1.286	0.126	0.162
112 °C	2.106	0.132	0.278
120 °C	2.281	0.135	0.308

Furthermore, using the Van't Hoff law (eq 19), it is possible to calculate enthalpies  $\Delta H_i$  (J·mol<sup>-1</sup>) and entropies  $\Delta S_i$

(J·mol<sup>-1</sup>·K<sup>-1</sup>) of the two consecutive and reversible reactions and thus the overall enthalpy and entropy of the esterification reaction of 2,3-BDO with AA.

$$K_i = \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (19)$$

where

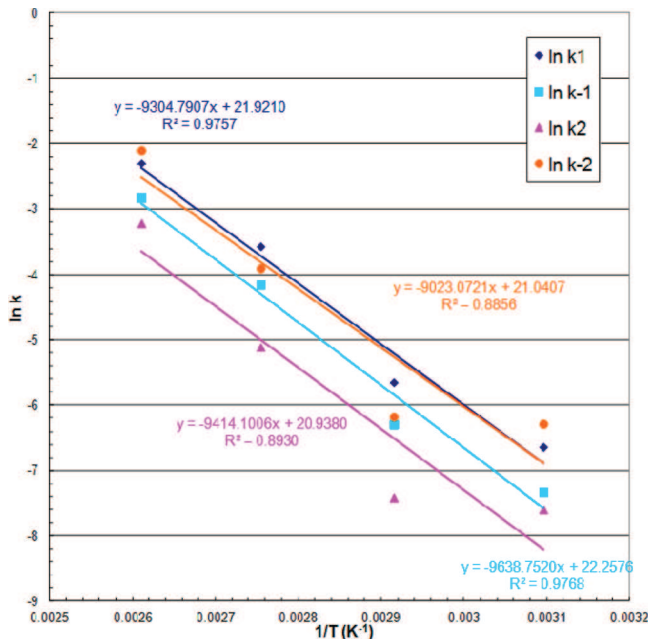
$$\Delta G_i = \Delta H_i - T \times \Delta S_i \quad (20)$$

is the Gibbs free energy of reaction  $i$  (J·mol<sup>-1</sup>). Combining these two equations, we can write

$$\ln K_i = -\frac{\Delta H_i}{R} \times \frac{1}{T} + \frac{\Delta S_i}{R} \quad (21)$$

The relation  $\ln K_i = f\left(\frac{1}{T}\right)$  is thus linear, with a slope equal to  $-\frac{\Delta H_i}{R}$  and a y-intercept of  $\frac{\Delta S_i}{R}$ .

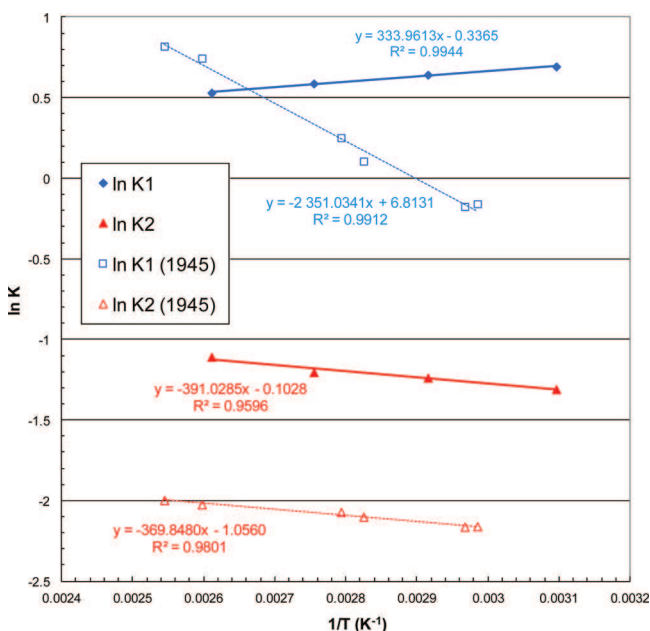
On Figure 6, we can see that the curves are significantly linear with correlation coefficients  $R^2$  of 0.9944 for  $K_1$  and 0.9596 for  $K_2$ . Using this representation, the enthalpy and entropy of reaction can be determined. The results are summarized in Table 5.



**Figure 5.** Determination of kinetics parameters ( $E_a$  and  $A_i$ ) of esterification of 2,3-BDO with AA ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ )

**Table 4.** Kinetic Parameters of the Esterification of 2,3-BDO with AA ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ )

	$E_a$ (kJ·mol <sup>-1</sup> )	$A_i$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )
reaction 1	77.4	$3.3 \times 10^9$
reaction -1	80.1	$6.3 \times 10^9$
reaction 2	78.3	$1.2 \times 10^9$
reaction -2	75.0	$1.4 \times 10^9$



**Figure 6.** Determination of thermodynamic parameters ( $\Delta H_i$  and  $\Delta S_i$ ) of esterification of 2,3-BDO with AA ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ ) and comparison with 1945 data.

The thermodynamic constants of the overall reaction  $\Delta H_3$  and  $\Delta S_3$  can be written as

$$\Delta H_3 = \Delta H_1 + \Delta H_2 \quad (22)$$

$$\Delta S_3 = \Delta S_1 + \Delta S_2 \quad (23)$$

Thus, we showed that the overall enthalpy  $\Delta H_3$  is almost zero ( $0.47 \text{ kJ}\cdot\text{mol}^{-1}$ ), which means that the reaction is athermal: the temperature change does not affect the thermodynamics of the reaction. However, working at a high temperature enables to reach thermodynamic equilibrium more quickly, which is preferable if an equipment is up to be designed.

To conclude, in the range of 50 to 110 °C, the highest temperature (110 °C) appears to be preferable to conduct the esterification reaction of 2,3-BDO with AA in the presence of a heterogeneous catalyst, considering various constraints. Indeed, temperature cannot be increased because of AA boiling point (118 °C) at atmospheric pressure, and also catalyst degradation (above 150 °C) or side reactions.

### 3.4. Influence of the Initial AA/2,3-BDO Molar Ratio.

One of the most important variables affecting the diester yield is the initial molar ratio between acetic acid and 2,3-butanediol. Regarding the stoichiometric coefficients of the reaction, the esterification of 2,3-BDO requires two moles of AA per mole of 2,3-BDO to form one mole of diester and two moles of water. However, as the esterification is a balanced reaction, a large excess of AA shifts the equilibrium to the forward reaction of diester formation.

In this part, we conducted three experiments with different initial molar ratios of AA/2,3-BDO ( $r$ ):  $r = 2$  (stoichiometric ratio),  $r = 6$  (3 equiv of AA compared to 2,3-BDO) and  $r = 12$  (6 equiv). The two other parameters were set: the amount of catalyst at 2.2% and the temperature at 110 °C.

Figure 7 represents the experiments with respectively 1 equiv of AA (a), 3 equiv of AA (b), and 6 equiv of AA (c).

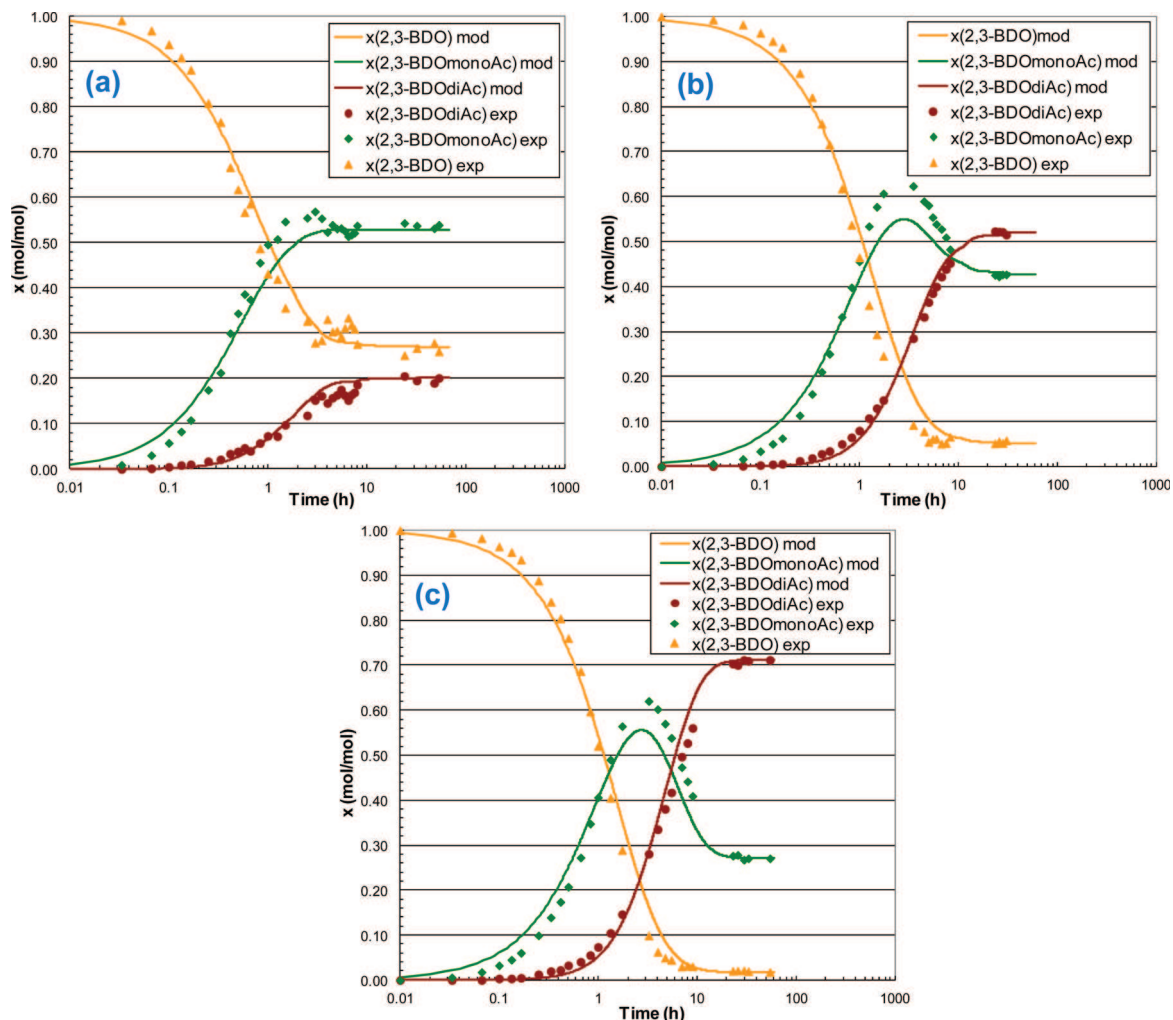
As it was expected, it is clear that the equilibrium is shifted to the forward reaction, that is, the product formation, when one of the reactants (here AA) is in excess. Indeed, an increase of the initial molar ratio AA/2,3-BDO leads to a better conversion of 2,3-BDO into monoester and diester. The resulting compositions of these three balanced reactions carried out with the same amount of catalyst (2.2%) and the same temperature (110 °C) are summarized in the following Table 6.

The reaction carried out with 6 equiv of AA regarding the 2,3-BDO amount ( $r = 12$ ) yields to a mixture containing 71.1% of diester, 27.1% of monoester, and 1.8% of unreacted diol. It can be noticed that the thermodynamic constants ( $K_1$  and  $K_2$ ) are slightly different: it may be due to activity coefficients which have not been taken into account in our model. Indeed, between  $r = 2$  and  $r = 12$ , the composition of the medium is very different and activity coefficients may thus have a low influence. Furthermore, regarding the kinetics of these three reactions (Table 7), kinetic constants decrease with increasing initial molar ratio AA/2,3-BDO. This is due to a dilution effect: AA concentration is certainly higher when the initial molar ratio AA/2,3-BDO is increased, but the other species (containing four atoms of carbon) concentrations are much lower. For example, initially, the product  $[AA]^*[2,3-BDO]$  is equal to  $49.6 \text{ mol}^2\cdot\text{L}^{-2}$  for  $r = 2$ , whereas this value is only  $33.6 \text{ mol}^2\cdot\text{L}^{-2}$  for  $r = 6$  and  $21.0 \text{ mol}^2\cdot\text{L}^{-2}$  for  $r = 12$ .

When the ratio  $r$  is increased, equilibrium are shifted toward the monoester and diester formation but the time to reach equilibrium is also increased. The dilution of the medium (because of a higher amount of AA) would thus involve higher cost on an industrial plant (cost of separation units). Therefore, a molar ratio AA/2,3-BDO of 2 may be used for this reaction of esterification.

**Table 5. Thermodynamic Parameters of the Esterification of 2,3-BDO with AA ( $n_{AA}/n_{2,3-BDO} = 2$ ,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ )**

	$\Delta H_i$ (kJ·mol <sup>-1</sup> ) (our work)	$\Delta S_i$ (J mol <sup>-1</sup> ·K <sup>-1</sup> ) (our work)	$\Delta H_i$ (kJ·mol <sup>-1</sup> ) (1945 data) <sup>15</sup>	$\Delta S_i$ (J mol <sup>-1</sup> ·K <sup>-1</sup> ) (1945 data) <sup>15</sup>
reaction 1	-2.777	-2.798	19.546	56.644
reaction 2	3.251	-0.855	3.075	-8.780
reaction 3	0.474	-3.652	22.621	47.865



**Figure 7.** Comparison of the kinetic model (continued lines) and experimental data (singular points) for the esterification of 2,3-BDO with AA at  $r = 2$  (a),  $r = 6$  (b), and  $r = 12$  (c) ( $T = 110$  °C,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ ).

**Table 6. Comparison of the Medium Compositions at Equilibrium and Thermodynamic Constants for the Three Different Experiment Varying the Initial Molar Ratio AA/2,3-BDO ( $n_{cata}/n_{2,3-BDO} = 2.2\%$ ,  $T = 110$ °C)**

at equilibrium	$x_{2,3-BDO}$	$x_{2,3-BDOmonoAc}$	$x_{2,3-BDOdiAc}$	$K_1$	$K_2$
$r = 2$	26.0%	53.9%	20.1%	1.7	0.33
$r = 6$	5.8%	42.7%	51.5%	2.5	0.37
$r = 12$	1.8%	27.1%	71.1%	2.6	0.44

**Table 7. Kinetic Constants for the Three Different Experiment Varying the Initial Molar Ratio AA/2,3-BDO ( $T = 110$  °C,  $n_{cata}/n_{2,3-BDO} = 2.2\%$ )**

	$r = 2$	$r = 6$	$r = 12$
$k_1$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.1000	0.0500	0.0400
$k_{-1}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0588	0.0200	0.0154
$k_2$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.0400	0.0200	0.0150
$k_{-2}$ (L·mol <sup>-1</sup> ·h <sup>-1</sup> )	0.1212	0.0541	0.0341

**3.5. Comparison of Homogeneous and Heterogeneous Catalysis.** As only AA composition in the medium was measured in 1945 (no data on the diol, monoester, and diester), kinetic constants could not be determined. However, times to reach thermodynamic equilibrium were obtained in 1945. At low temperatures, time to reach equilibrium with a homogeneous catalyst is thus lower than this time with a heterogeneous catalysis (Table 8).

**Table 8. Comparison of Times to Reach Equilibrium of the Esterification Reaction of 2,3-BDO with AA ( $r = 2$ ) with a Homogeneous Catalyst<sup>15</sup> or a Heterogeneous Catalyst (Our Work)**

	62 °C	81 °C	120 °C
homogeneous catalyst H <sub>2</sub> SO <sub>4</sub> 1.6% (1945) <sup>15</sup>	6 h	5 h	4 h
heterogeneous catalyst 2.2% (our work)	250 h	50 h	5 h

Nevertheless, under elevated temperatures (between 110 and 120 °C), times to reach thermodynamic equilibrium, either with a homogeneous or heterogeneous catalyst, are similar. As the working temperature would be 110 °C, using a heterogeneous catalyst should present great advantages such as possibility of easy separation compared to operations involved by a homogeneous catalyst.

#### 4. CONCLUSIONS

This study of the esterification of 2,3-BDO with acetic acid showed that the reaction can be carried out with a heterogeneous catalysis (Amberlyst 36). The main advantage of working with this type of catalyst is its implementation on a fixed bed or on trays of a reactive distillation column, which enables its recycling but also avoids separation operations of the catalyst at the end of the reaction, as it usually occurs with a homogeneous catalyst. Thus, a heterogeneous catalyst seems more attractive than a homogeneous catalyst because it is much easier to implement (no precipitation/filtration stage of the homogeneous catalyst) for equivalent performance. The influence of various parameters such as the amount of catalyst, the initial molar ratio of the two reactants AA/2,3-BDO and temperature was studied over a wide range of values. Favorable parameters were determined to be an initial molar ratio AA/2,3-BDO of 2, with 2.2% of heterogeneous catalyst at 110 °C. Thanks to the different analytical techniques (GC-FID, AA titration, KFC), it was possible to quantitatively determine the composition of the reaction mixture in the function of time. Thus, the mathematical model built is able to accurately represent the evolution of the compounds involved in the reaction and was used to determine kinetic and thermodynamic parameters which have not yet been published to our knowledge. Among the outlooks of this work, a coupling of reaction–separation could be implemented in order to shift the thermodynamic equilibrium and obtain a total conversion of 2,3-BDO into 2,3-BDOmonoAc and 2,3-BDOdiAc.

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##### Notes

The authors declare no competing financial interest.

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