Kinetic of esterification of diluted acetic acid with pure 2-ethyl-1-hexanol

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Abstract

The esterification of diluted acetic acid with pure 2-ethyl-1-hexanol is a purification process, involving a liquid–liquid–solid catalyst system, where streams of water containing small amount of acid are purified and the acetic acid is converted to a high commercial value ester at the same time. This process has been studied in a wide range of acetic acid (AA) concentration (6–15%, w/w). A maximum final conversion of 67% can be reached at 372 K.

A mathematical model is here proposed: this takes into account all the diffusional and reactive steps between the aqueous and organic phases and from the latter into the pores of the solid catalyst. The relative importance of the different steps is fully discussed.
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1. Introduction

The esterification reaction of acetic acid (AA) with various alcohols is a much investigated case. In the recent literature many papers are still devoted to the improvement of such a reaction especially from the catalytic point of view (both homogeneous and heterogeneous) [1–4]. The recovery of AA from much diluted streams is a very important industrial problem. Especially when the amount of water is large, the traditional separation methods cannot be used mainly for energetic reasons.

It was demonstrated [5] that extractive esterification is an interesting method to simultaneously purify water and product ester having a good commercial value. The new method proposed has the purposes to save the costs arising from the treatment of the wastewater and utilize the acetic acid otherwise eliminated in chemical synthesis. Diluted acetic acid (AA) streams (6–15%, w/w) were used in an extractive esterification with 2-ethyl-1-hexanol (AOH), exploiting the different solubilities of acetic acid and acetic ester in water. The performed reaction is a three-phase system with Amberlyst 15 as solid acid catalyst.

The experimental set-up was assessed using a special reactor in which the catalyst can be set in one of the two existing phases (aqueous (α) or organic (β)) or at the interphases between them [6]. This set-up has allowed demonstrating that the esterification takes place exclusively in the organic phase. Runs at concentrations of acetic acid (AA) in water (6–15%, w/w) have been performed and a simplified mathematical model has also been used to interpret the experimental results.

Notwithstanding the satisfactory results obtained using the two equation models [6], some drawbacks of this model are heavily involved: (i) the model does not consider the presence of the solid catalyst (its volume and porosity after swelling), which is really necessary to perform the esterification reaction; (ii) therefore the model does not consider both the diffusion/back-diffusion processes into the catalyst's pores; (iii) a simplified diffusion equation has been used for the migration of acetic acid (AA) from aqueous (α) to organic phase (β), without taking into account the activity coefficient of AA in α and β; (iv) in the simplified model two species are only considered (AA in α and ester in β phases, respectively), while AA and AOH in β phase are not considered. Such drawbacks do not allow a predictive use of the model to conditions different from those used to calibrate the parameters. In the present paper the same kinetic results have been interpreted by a complete model which removes the limitation of the simplified one.

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Nomenclature

AA	acetic acid
AOH	2-ethylhexanol
cat	catalyst
C	concentration (mol l^{-1})
Est	2-ethylhexanol acetate
f^{sw}	swelling factor in AOH (see Section 2)
F	value in the feed
k	kinetic constant (l min^{-1} mol^{-1})
K	mass transfer coefficient (min^{-1}) from α to β (αβ and similar indication in the superscript)
M	mass (g)
MW	molecular weight (g × mol^{-1})
n	number of moles
Por	porosity of the dry catalyst (3.44×10^{-4} l g^{-1}, Table 1 [6])
t	time (min)
V	volume (l)
W	water
Wt	weight of the catalyst (g)

Greek letters

α	aqueous phase
β	organic phase
γ	activity coefficient
ρ	density (g ml^{-1})

Fig. 1. Scheme of the used equipment (not in scale). The rotating basket, containing the catalyst, can be moved up and down.

In literature many papers are devoted to the kinetic models of catalytic esterification of acetic acid and alcohols over both homogeneous and heterogeneous catalysts [7–10], but in this case the used model is more complicated due to the coexistence of two liquid phases other than the solid phase (the catalyst).

2. Experimental and results

All the chemicals used in the present paper are Fluka products: acetic acid, 2-ethyl-1-hexanol, and Amberlyst 15 (macroreticular-strongly acidic cation exchangers) with the following features: particle size: 16–50 mesh, hydrogen ion concentration: 4.7 mequiv. g^{-1} dry, surface area: 50 m^2 g^{-1}, porosity: 3.44×10^{-4} l g^{-1}, swelling from dry state to solvent saturated state in 2-ethylhexanol: 60%, in water: 40%.

Runs were performed at complete evaporation–condensation: due to such conditions, the temperature was maintained fixed in all the runs at 372 K (water incipient boiling temperature). All the evaporated species were condensed and then directly re-introduced into the reactor, avoiding the removal of any chemical during the reaction. All the tests were performed in a glass reactor provided with a mechanical stirrer at 100 rpm, a thermometer and a coil condenser (see Fig. 1) [6].

The reactor was also provided with two stainless steel perforated baskets ($h = 0.067$ m, diameter $= 0.032$ m) attached to the stirrer arm to confine the catalyst into one portion of the reac-
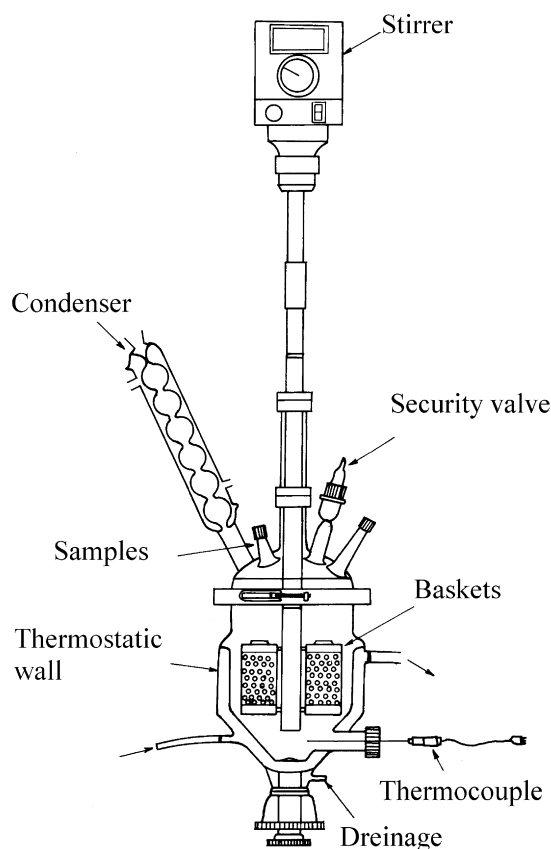
tor and then into a phase (aqueous or organic phase or between these two phases).

Operative conditions: 340 ml of bi-distilled water was contaminated with acetic acid (6–15 wt%, i.e. 1–2.5 M) and 160 ml of AOH was added. The reaction was performed at a constant temperature of 372 K. The catalyst (13 g) was added at room temperature: this particular amount allows having a packed bed inside the basket and any fluidization problems or excessive compression of the catalyst (that enlarges its volume due to the swelling process) are avoided [6].

The beginning of the kinetic run ($t = 0$) was assumed when the reaction mixture reaches the convenient temperature (372 K). In this case a small amount of ester was already present.

2.1. Analysis

In the reaction vessel, two phases were observed inside the reactor. The analyses of the upper organic phase (AA, 2-ethylhexyl acetate (Est) and AOH) were carried out by means of a gas chromatography-GC (ThermoQuest) equipped with a capillary SE52 column ($\varnothing = 5.3 \times 10^{-4}$ m, $L = 25$ m, $T = 423$ K).

The amount of water present in this organic phase was measured by means of a Karl-Fischer instrument. The presence of acidity in the aqueous phase (lower phase) was monitored by subsequent titration with NaOH 0.1 M using phenolphthalein as indicator.

Table 1
Acetic acid conversion as a function of the catalyst/acetic acid ratio at $T = 372$ K

AA in water (wt%)	Cat (g)	AA conversion% at $t = 2750$ min	CAT/AA (g mol^{-1})
6	13	67	32
9	13	61	22
12	13	59	17
15	13	56	14

To give solid basis to the kinetic model, some particular experimental determinations have been performed: the time ($t = 0$) of all the kinetic runs starts when the two liquid phases reach the reaction temperature (372 K). At $t = 0$ it is therefore necessary to determine the concentration of the two reagents (C_{AA}^{cat} and C_{AOH}^{cat}) inside the pores of the catalyst; obviously such concentrations cannot be zero, because during the heating from room temperature to the reaction one, the reagents have enough time to diffuse inside the catalyst pores. Such concentrations are calculated by molar balances (see Eqs. (6) and (7) of Section 3.1). Moreover, it has been experimentally verified that when the reaction temperature is reached, a part of the ester is already present in the organic phase. The partition coefficient of the ester between the organic and catalyst phase has been determined by a particular experimental procedure. In the first step, the partition coefficient of the ester between β and the catalyst pores is calculated as follows: $K_{Est}^{\beta cat} = \text{moles}_{Est}^{\beta}/\text{moles}_{Est}^{cat}$. The $\text{moles}_{Est}^{\beta}/\text{moles}_{Est}^{cat}$ ratio has been calculated performing three kinetics runs. After each run the catalyst surface has been rapidly wiped with an adsorbing paper, in order to eliminate the AOH layer on the surface of the catalytic particles. Then the sample has been transferred in a Soxlet apparatus where the ester present in the solid pores was extracted by AOH, and quantitatively measured by GC analysis, obtaining the "moles$_{Est}^{cat}$" value. In a similar way the "moles$_{Est}^{\beta}$" was calculated analyzing the organic phase by GC. The three obtained values of $K_{Est}^{\beta cat}$ are: 43.8; 38.1; 45.7; a mean value of 42.6 was assumed in the model. Obviously such procedure is based on the experimental evidence that traces of ester are found in β at $t = 0$ and assuming a rapid equilibration of ester between β and the catalyst. The influence of the ratio between the amount of the catalyst and the AA concentration has been studied too. In Table 1 such results are listed.

3. Kinetic model

3.1. Equations and molar balances

In Section 1 the aspects not considered in the simplified kinetic model [6] are qualitatively discussed. Now in a quantitative form such aspects will be taken in consideration, with reference to these steps (see Nomenclature):

(i) $AA^{\alpha} \rightarrow AA^{\beta}$: change of AA concentration in α due to its diffusion in β (Eq. (1)). In this equation the concentration of AA in α and β phases cannot be considered in equilibrium.

(ii) $AA^{\beta} \rightarrow AA^{cat}$: change of AA concentration in β due to a balance between the amount coming from α and that the one into the catalyst pores (Eq. (2)).

(iii) $AOH^{\beta} \rightarrow AOH^{cat}$: change of AOH concentration in β due to its diffusion into the catalyst pores (Eq. (3)).

(iv) $AA^{cat} + AOH^{cat} \rightarrow Est^{cat} + H_2O^{\alpha}$: change of the ester concentration into the pores of the catalyst due to the esterification reaction and the diffusion from the catalyst to β (Eq. (4)). In this equation the esterification reaction was considered irreversible due to the very fast migration of water in the aqueous phase. Besides, water has been considered in α phase due to its complete insolubility in the organic phase.

(v) $Est^{cat} \rightarrow Est^{\beta}$: change of ester in β due to its back-diffusion from the catalyst pores to β (Eq. (5)).

The five mathematical equations deriving from the reported steps are the following:

$$-\frac{dC_{AA}^{\alpha}}{dt} = K_{AA}^{\alpha\beta}(\gamma_{AA}^{\alpha}C_{AA}^{\alpha} - \gamma_{AA}^{\beta}C_{AA}^{\beta}) \tag{1}$$

$$-\frac{dC_{AA}^{\beta}}{dt} = [K_{AA}^{\beta cat}(C_{AA}^{\beta} - C_{AA}^{cat})]$$
$$- [K_{AA}^{\alpha\beta}(\gamma_{AA}^{\alpha}C_{AA}^{\alpha} - \gamma_{AA}^{\beta}C_{AA}^{\beta})] \tag{2}$$

$$-\frac{dC_{AOH}^{\beta}}{dt} = K_{AOH}^{\beta cat}(C_{AOH}^{\beta} - C_{AOH}^{cat}) \tag{3}$$

$$\frac{dC_{Est}^{cat}}{dt} = [k^{cat}C_{AOH}^{cat}C_{AA}^{cat}] - K_{Est}^{cat\beta}(C_{Est}^{cat} - C_{Est}^{\beta}) \tag{4}$$

$$\frac{dC_{Est}^{\beta}}{dt} = K_{Est}^{cat\beta}(C_{Est}^{cat} - C_{Est}^{\beta}) \tag{5}$$

The evaluation of C_{AA}^{cat} was made considering the initial moles of AA and subtracting from these values the moles of AA in α and β and those of ester, the latter both in β and in the pores of the catalyst. Similarly C_{AOH}^{cat} was calculated by subtracting from the initial moles of AOH those in β and those of the Ester in β and in the catalyst pores.

$$C_{AA}^{cat} = \frac{n_{AA}^{cat}}{V^{cat}} = \frac{n_{AA}^{F} - C_{AA}^{\alpha}V^{\alpha} - C_{AA}^{\beta}V^{\beta} - C_{Est}^{\beta}V^{\beta} - C_{Est}^{cat}V^{cat}}{V^{cat}} \tag{6}$$

$$C_{AOH}^{cat} = \frac{n_{AOH}^{cat}}{V^{cat}} = \frac{n_{AOH}^{F} - C_{AOH}^{\beta}V^{\beta} - C_{Est}^{\beta}V^{\beta} - C_{Est}^{cat}V^{cat}}{V^{cat}} \tag{7}$$

In all the equations the catalyst volume V^{cat} was calculated taking into account the porosity of the swollen catalyst according the equation $V^{cat} = Wt^{cat} Por^{cat}/f^{sw}$ (for f^{sw} and Por^{cat} see Section 2).

Due to the strong polarity of water and, to a less extent, of AA and AOH, it should be considered that the force field around such molecules affects the diffusion process [11], hence the mass

transfer equations. In Eqs. (1) and (2) a correction to the concentrations of AA in the driving force, i.e. $C_{AA}^{\alpha} - C_{AA}^{\beta}$, was considered introducing the respective activity coefficients (γ_{AA}^{α} and γ_{AA}^{β}). Such coefficients take into account the interaction of AA with the solvent in the α and β phases. The calculations of γ_{AA}^{α} and γ_{AA}^{β} have been performed using NRTL equation and the suitable coefficients. In all other cases, no diffusion between the two different liquid phases occurs and therefore, the correction was not applied, for the sake of simplicity.

In Eqs. ((1)–(5)) it is assumed that neither ester nor AOH is soluble in the aqueous phase. The volumes of α and β phases, used in the molar balances (V^{α} and V^{β}, respectively) are not constant, i.e. $V^{\alpha} = V^{\alpha}(t)$, $V^{\beta} = V^{\beta}(t)$. In particular, $V^{\alpha}(t)$ was calculated by subtracting the volume of AA transferred to β from the initial value of $V^{\alpha F}$ and adding the volume of water formed by esterification reaction and transferred to α, being water quite not soluble in β.

As for $V^{\beta}(t)$ the values was calculated in a similar way by subtracting the volume of water formed and transferred to α and adding to the initial value of $V^{\beta F}$ the volume of AA transferred from α to β. Eqs. (8)–(11) are referred to such balances:

$$V^{\alpha}(t) = V^{\alpha F} - \left(C_{AA}^{\beta} V^{\beta} \frac{MW_{AA}}{\rho_{AA}} \times 10^{-3} \right)$$
$$+ \left(C_{Est}^{\beta} V^{\beta} \frac{MW_{W}}{\rho_{W}} \times 10^{-3} \right) \tag{8}$$

$$V^{\beta}(t) = V^{\beta F} - \left(C_{Est}^{\beta} V^{\beta} \frac{MW_{W}}{\rho_{W}} \times 10^{-3} \right)$$
$$+ \left((n_{AA}^{F} - C_{AA}^{\alpha} V^{\alpha}) \frac{MW_{AA}}{\rho_{AA}} \times 10^{-3} \right) \tag{9}$$

being:

$$V^{\alpha F} = \left[M_{W}^{F} \left(\frac{1}{\rho_{W}} \right) + M_{W}^{F} \left(\frac{1}{\rho_{AA}} \right) \right] \times 10^{-3} \tag{10}$$

$$V^{\beta F} = M_{AOH}^{F} \left(\frac{1}{\rho_{AOH}} \right) \times 10^{-3} \tag{11}$$

The objective function adopted and minimized in the mathematical calculation was the following:

$$\Delta\% = \frac{\sum_{r=1}^{N} \sum_{i=1}^{4} [|(C_{i,r})_{calc} - (C_{i,r})_{exp}|]}{\sum_{r=1}^{N} t_r} \times 100 \tag{12}$$

In the previous equation r is the index of the run number (max N), and i is the index of the species. The maximum value of i ($i = 4$) corresponds to the four substances included in the optimization procedure (AA^{α}, AA^{β}, AOH^{β}, and Est^{β}).

3.2. Evaluation of the parameters of Eqs. (1)–(5)

The integration of Eqs. (1)–(5) were performed by a fourth-order Runge-Kutta algorithm by giving the initial values of all the concentrations appearing in Eqs. (1)–(5), i.e. C_{AA}^{α}, C_{AA}^{β},

C_{AOH}^{β}, C_{Est}^{β}, C_{AA}^{cat}, and C_{Est}^{cat}. The first four concentrations were experimentally determined by sampling α and β phases at $t = 0$.

C_{AOH}^{cat} and C_{AA}^{cat} have been calculated from a molar balance using Eqs. (6) and (7) using the initial value of C_{Est}^{cat} as described in Section 2.

The aim of such calculations is to evaluate the parameters of Eqs. (1)–(5) both to fit the experimental results in all the range of AA concentrations (6–15%, w/w) and to give a good prediction changing the experimental conditions (water, AA, AOH, and catalyst amount).

The parameters to be evaluated are four mass transfer coefficients ($K_{AA}^{\alpha\beta}$, $K_{AA}^{\beta cat}$, $K_{AOH}^{\beta cat}$, and $K_{Est}^{cat\beta}$) and a kinetic constant (k^{cat}). The procedure used to calculate the above-mentioned parameters is a classical one consisting in a cyclic algorithm of numerical integration of the set of equations ((1)–(5)), followed by the minimization of the objective function which is the sum of square differences between the experimental and calculated values of C_{AA}^{α}, C_{AA}^{β}, C_{AOH}^{β}, and C_{Est}^{β}, for all the experimental runs. The Matlab program (6.0 Version) has been used applying an integration-optimization routine, which includes constraints for the parameters to be optimized.

3.3. Result of the calculations and discussion

Eq. (4) of the present model is of the quasi-homogeneous type (Q-H) used, in comparison with other models, by Lee et al. [7], in the study of esterification of AA with amyl alcohol on Amberlyst 15, using a two phases fixed-bed reactor.

Obviously a Langmuir–Hinshelwood (L–H) model, as modified by Gonzales and Fair [12], would reduce the objective function (Eq. (12) [7]), but with the disadvantage to introduce other three constants into the mathematical model, in addition to the five parameters to be optimized (i.e. two adsorption equilibrium constants on the catalyst for AA and AOH and the parameter α as defined in [12]). It is well known that in the optimization procedures of a model, the parameters are less significant the more they are.

The mathematical model previously discussed (Eqs. (1)–(5)) was used to interpret the experimental results concerning the concentration versus reaction time of acetic acid in aqueous and organic phase (C_{AA}^{α} and C_{AA}^{β}, respectively), 2-ethylhexanol (C_{AOH}^{β}), 2-ethylhexanol acetate (Est) in the organic and catalyst phases (C_{Est}^{β} and C_{Est}^{cat}, respectively). The parameters of the mathematical model were optimized for the runs in the following conditions: 6, 9, 12 and 15% of initial AA concentration and 13 g of catalyst for all runs (see Table 2).

On the basis of the averaged optimized parameters a comparison between calculated and experimental results was made for different runs. In Fig. 2 the results of such calculations versus the experimental results are shown for AA in the aqueous phase at different concentration of AA. In Fig. 3 an example of calculated and experimental values of all species (C_{AA}^{α}, C_{AA}^{β}, C_{AOH}^{β} and C_{Est}^{β}) are reported for the run using 15% AA.

It should be interesting to analyze which of the different steps illustrated at the beginning of Section 3.1 is more or less sig-

Table 2
Numerical values of diffusive and kinetics constants obtained from calculation by minimization of the objective function (12), being K mass transfer coefficients and k kinetic constants (see Nomenclature)

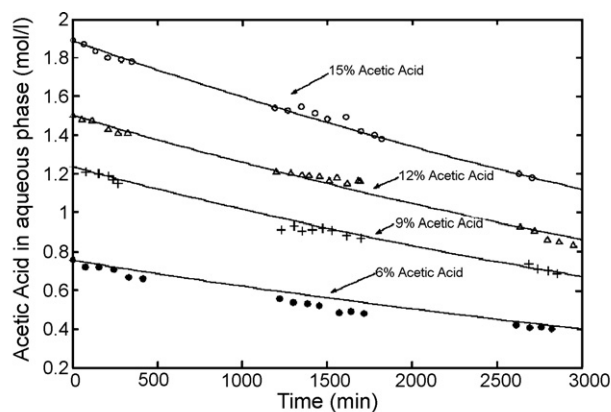| Run (%)	$K_{AA}^{\alpha\beta}$ (min^{-1})	k^{cat} ($\times 10^{-4}$ l mol^{-1} min^{-1})	$K_{AA}^{\beta cat}$ ($\times 10^{-3}$ min^{-1})	$K_{AOH}^{\beta cat}$ ($\times 10^{-4}$ min^{-1})	$K_{Est}^{cat\beta}$ ($\times 10^{-4}$ min^{-1})
15	8.09×10^{-5}	7.34	9.54	2.14	3.17
12	7.58×10^{-5}	6.91	9.67	1.90	2.83
9	1.53×10^{-4}	4.90	8.12	1.74	3.97
6	8.12×10^{-5}	6.04	9.45	1.55	7.69
Mean value	3.95×10^{-5}	6.46	9.27	1.94	4.07

Fig. 2. Predicted values (Eqs. (1)–(5)) of the acetic acid concentrations (solid line) vs. reaction time in the aqueous phase and comparison with the experimental results ($\bigcirc$, $\triangle$, +, $\bullet$ experimental results), T = 372 K.

nificant. Due to the different units of the constants reported in Table 2, a procedure was adopted by increasing the numerical values of such parameter by an order of magnitude, and then analyzing the change of the objective function (Eq. (12)). Such results are reported in Table 3. In these calculations only one parameter was changed each time being the others kept constant. A control of Table 3 brings to conclude that the diffusion of AA from the organic phase into the catalyst pore is not a rate-limiting step. In fact the increase of $K_{AA}^{\beta cat}$ con-
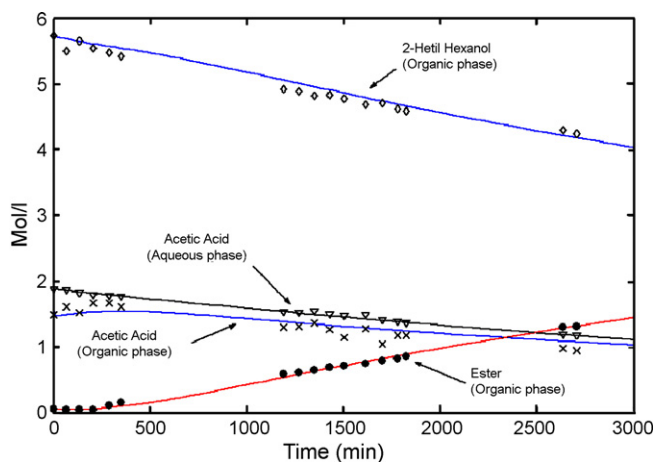

Fig. 3. Predicted values (Eqs. (1)–(5)) of the concentrations of the different components in the organic phase (solid line) and comparison with the experimental results (*, ×, ▽, ◇). AA 15 wt%; cat 13 g, T = 372 K.

Table 3
Variation of the objective function (Eq. (12)) obtained increasing one constant per time

Constants increased of one order of magnitude	Runs (%, w/w of AA)			
	6	9	12	15
None	3.1	3.3	2.1	1.2
$K_{AA}^{\alpha\beta}$	9.6	10.6	8.2	12.2
k_{cin}^{cat}	5.5	9.3	10.5	12.6
$K_{AA}^{\beta cat}$	3.5	3.8	2.4	1.5
$K_{AOH}^{\beta cat}$	5.6	8.1	9.7	15.5
$K_{Est}^{cat\beta}$	6.1	4.1	2.8	2.7

stant of an order of magnitude does not change significantly the values of the objective function for all the percentage of AA (6–15%). Also the diffusion of the ester from the catalyst to organic phase ($K_{Est}^{cat\beta}$ constant) seems to be a less important limiting step, mainly for AA concentration of 9, 12 and 15%. All the other constants bring to higher variations of the objective function.

4. Conclusions

The advantageous process of the extractive esterification used to eliminate AA from aqueous solution obtaining a useful product, can be mathematically interpreted taking into consideration experimental data with different AA concentrations (Figs. 2 and 3). The conversion of AA into water is quite a linear function (correlation coefficient = 0.987) of the ratio between the amount of catalyst and the initial acetic acid concentration (CAT/AA) as Table 1 shows. From these data it is possible to extrapolate an AA conversion of 90% using a ratio CAT/AA = 71 g_{cat} mol$_{AA}^{-1}$. The mechanism of the liquid–liquid–solid esterification reaction (Eqs. (1)–(5)) works well allowing a fair prediction of runs at different CAT/AA ratio and a more than satisfactory interpretation of the experimental results both for AA and all the other components in both phases.

Two diffusional steps (i.e. AA$^\beta$ → AA^{cat} and Est^{cat} → Est$^\beta$) are less rate limiting with respect to the other three evidenced steps (i.e. AA$^\alpha$ → AA$^\beta$; AOH$^\beta$ → AOH^{cat}; AA^{cat} + AOH^{cat} → Est^{cat} + H$_2$O$^\alpha$).

Acknowledgements

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