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Kinetics and phase equilibria of competing aldolization and elimination in a three-phase reactor

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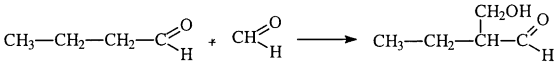
Abstract

Butyraldehyde was aldolized with formaldehyde over a weakly basic anion-exchange resin catalyst in aqueous solvent in a batch reactor operating at atmospheric pressure and at temperatures 50–70°C. The reaction mixture was a liquid–liquid–solid system, an emulsion, the phase equilibria of which were studied through chemical analysis of the organic and aqueous phase as well as of the mixed emulsion. Simplified rate equations were derived starting from molecular reaction mechanisms on the catalyst surface. A liquid–liquid reactor model for the fitting of the experimental results was developed on the basis of the rate equations and the phase equilibria. The model described very well the experimental data.

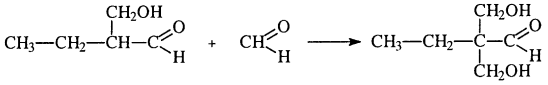
Keywords: Aldolization; Three-phase reactor; Phase equilibria

1. Introduction

Most chemical systems where a solid heterogeneous catalyst is present consist of a gas phase or a liquid phase or both of gas and liquid phases. In the present work we consider a system where two immiscible liquid phases are in contact with a solid catalyst. Crossed aldolization of butyraldehyde and formaldehyde takes place in two subsequent steps (reactions (1) and (2)), with the replacement of all α-hydrogens by hydroxymethyl groups. The reaction is carried out over a weakly basic anion exchange resin catalyst.

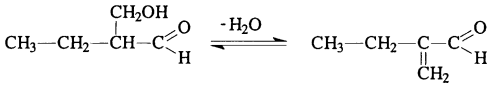


(A) (B) (1)



(2)

The product of reaction (1) is a rapidly reacting intermediate, thus steps (1) and (2) can be lumped together to give a single overall reaction. Elimination of water always appears as a parallel reaction in the process. In fact, the α-hydroxymethyl-substituted aldehyde appearing as intermediate (reaction (1)) undergoes reversible dehydration, leading to the corresponding unsaturated aldehyde, ethylacrolein (reaction (3)).



(3)

The above reaction is de facto a reversible process and it is possible to influence the product distribution

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Nomenclature

A	liquid–liquid interfacial area
c	concentration (mol/kg)
D	distribution coefficient
k	rate constant
K	adsorption equilibrium constant
m	mass
n	amount of substance
N	interfacial flux
r	component generation rate
R	reaction rate
R^2	degree of explanation
t	reaction time
Y	ratio of amount of substance ($Y_i = n_i/n_{0A}$)

Greek symbols

α	mass fraction of aqueous phase
θ	surface coverage
φ	ratio ($\varphi = m_{cat}/m$)

Subscripts and superscripts

a	aqueous phase
cat	catalyst
e	emulsion
i	component index
o	organic phase
0	initial concentration or amount of substance

Abbreviations

A	butyraldehyde
A1 . . . C2	reaction intermediates
B	formaldehyde
D	aldol 2
OH	base catalyst
X	ethylacrolein

by changing the reaction conditions, such as the ratio between the reactants and the solvent composition. When water is used as a solvent, the reaction takes place in an emulsion, since butyraldehyde-rich and formaldehyde-rich phases are formed. The aim of the present work is to investigate the mass transfer effects, the product distribution, the phase equilibria and the detailed reaction kinetics in the liquid–liquid–solid system.

2. Experimental

The aldolization was carried out in a jacketed, batchwise operating, stirred glass reactor under atmospheric pressure. The experiments were performed at constant temperature for 5 h. The catalyst was a commercial weakly basic anion-exchange resin with crosslinked acrylic gel structure matrix and tertiary amines as functional groups. The mean particle diameter was 760–960 μm. In order to investigate the effect of the catalyst particle size on the product distribution, the catalyst was crushed and sieved and the fraction between 250 and 500 μm was employed. Samples of the reaction mixture were withdrawn during the experiment and analyzed by high performance liquid chromatography (HPLC). The experimental details are described in previous papers [1,2].

3. Results and discussion

3.1. Selectivity aspects

The influence of temperature and formaldehyde-to-butyraldehyde molar ratio on the product distribution has been previously investigated by our group [1,2]. It turned out that the molar ratio between the aldehydes has a clear effect on the selectivity towards aldol, while the product distribution was not significantly influenced by the temperature. The product distribution as a function of the formaldehyde excess is presented in Fig. 1, which shows that the aldol-to-ethylacrolein ratio does not increase linearly as a function of the formaldehyde excess. This indicates the adsorption of formaldehyde on the solid catalyst, as discussed in a previous paper [1]. The results of the experiments carried out with different catalyst amounts in the reaction mixture (7, 14, 18, 28 and 42 g with a total liquid mass in the reactor of 120 g) are presented in Fig. 2, where the normalized concentration of aldol is plotted versus the normalized concentration of ethylacrolein. As it can be observed, the selectivity towards aldol increases as the catalyst mass increases. This effect can

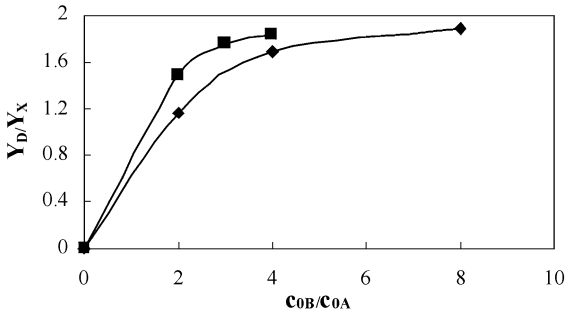


Fig. 1. Ratio between the concentrations of aldol (D) and ethylacrolein (X) versus ratio of the initial concentrations of formaldehyde (B) and butyraldehyde (A): (◆) methanolic solvent; (■) aqueous solvent ($Y_i = n_i/n_{0A}$, $T = 70°C$).

partially be explained by selective adsorption of ethylacrolein on the resin catalyst.

3.2. External and internal mass transfer effects

Aldolization experiments with different stirring rates (e.g. 800 and 200 rpm) were carried out. Neither the product distribution nor the reaction kinetics were significantly affected by the stirring rate.

The product distribution from the experiments carried out with different catalyst particle sizes are compared in Fig. 3, while the results of the aldolization experiment carried out with the catalyst with the smaller particle size are reported in Fig. 4. The particle size displayed a minor effect both on the product distribution and on the reaction kinetics. This result could be explained, since the reaction was carried out

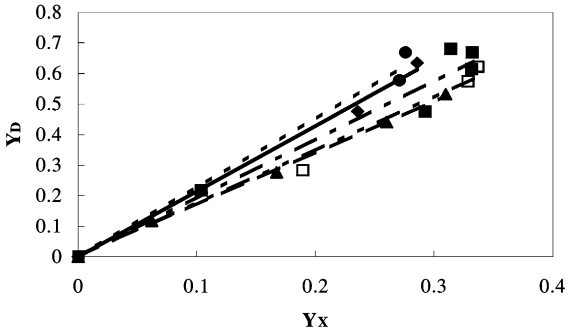


Fig. 2. Concentration of aldol (Y_D) versus concentration of ethylacrolein (Y_X) for different catalyst amounts: (●) 42 g; (◆) 28 g; (■) 18 g; (□) 14 g; (▲) 7 g ($Y = n_i/n_{0A}$). Conditions: formaldehyde-to-butyraldehyde molar ratio 4:1, $T = 60°C$.

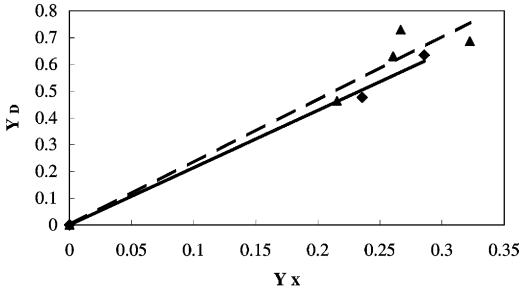


Fig. 3. Concentration of aldol (Y_D) versus concentration of ethylacrolein (Y_X) for different catalyst particle sizes ((◆) 760–960 μm; (▲) 250–500 μm).

in an aqueous environment and therefore the resin catalyst was swollen, which enlarged the pores and suppressed diffusional limitations.

3.3. Detailed two-phase kinetics

In two aldolization experiments carried out at 70°C and with formaldehyde-to-butyraldehyde molar ratios of 1.5:1 and 2:1, the samples withdrawn from the reaction were centrifuged and the organic and aqueous phases were separately analyzed by means of HPLC. The concentration profiles of butyraldehyde, aldol and ethylacrolein in the aqueous and organic phase as well as their average concentrations in the emulsion are reported in Figs. 5 and 6.

On the basis of the separated analyses of the components in the aqueous phase (c_{ia}), in the organic phase (c_{io}) and in the mixed emulsion (c_{ie}), the mass fraction (α) of the aqueous phase was determined from the mass balance of any component:

$$c_{ia}\alpha m + c_{io}(1-\alpha)m = c_{ie}m \quad (4)$$

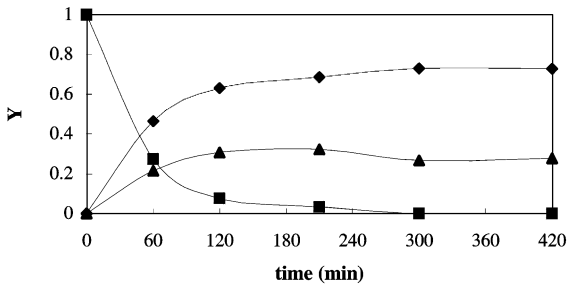


Fig. 4. Aldolization experiment: (◆) aldol; (■) butyraldehyde; (▲) ethylacrolein. Conditions: formaldehyde-to-butyraldehyde molar ratio 4:1, $T = 60°C$. Catalyst particle size, 250–500 μm.

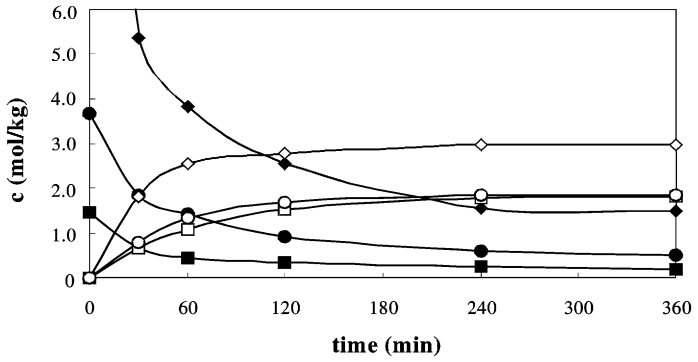


Fig. 5. Concentration profiles of aldol and butyraldehyde in the aqueous and organic phase and in the emulsion. Conditions: formaldehyde-to-butyraldehyde molar ratio 1.5:1, $T = 70°C$. (◆) c_{oA}; (■) c_{aA}; (●) c_{eA}; (◇) c_{oD}; (□) c_{aD}; (○) c_D.

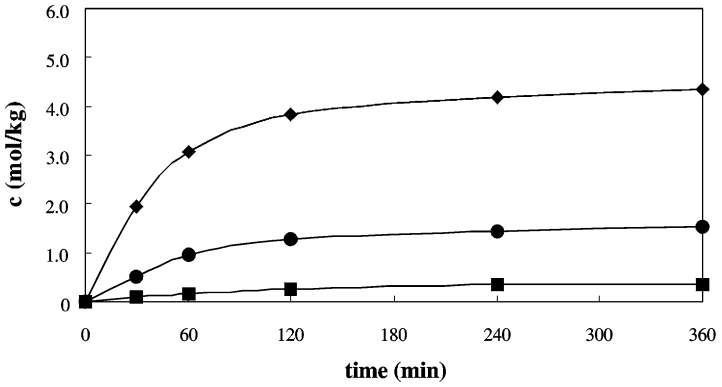
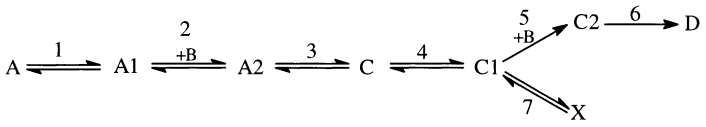


Fig. 6. Concentration profiles of ethylacrolein in the aqueous and organic phase and in the emulsion. Conditions: formaldehyde-to-butyraldehyde molar ratio 1.5:1, $T = 70°C$. (◆) c_o; (■) c_a; (●) c_e.

from which we get

$$\alpha = \frac{c_{ie} - c_{io}}{c_{ia} - c_{io}} \quad (5)$$

A complete reaction scheme for the aldolization of butyraldehyde with formaldehyde was presented in a previous paper [1]. Base-catalyzed aldolization is commenced by a nucleophilic attack of the base catalyst to the α-carbon atom of the aldehyde. A carbanion (A1 in Scheme 1) is formed, which reacts with formaldehyde giving aldol 1 (C); the catalyst is regenerated with a reaction with water. The mechanism for the formation of aldol 2 (D) is analogous. The carbanion formed from aldol 1 (C1) undergoes elimination which leads to the formation of unsaturated aldehyde and abstraction of water. Principally, the reaction scheme can be summarized to the following consecutive-parallel sequence with respect



Scheme 1.

to the reacting aldehyde (A), where A is butyraldehyde, B formaldehyde, D and X denote aldol and ethylacrolein, respectively; A1, A2, C1 and C2 denote reaction intermediates described in [1]. Steps (5) and (7) are assumed to be rate-determining, while the other steps (1)–(4) are approximated to be rapid enough so that the quasi-equilibrium hypothesis can be applied. In addition, the proton transfer step (6) is rapid. Formaldehyde (B) is presumed to adsorb strongly on the catalyst surface; therefore, its concentration on the catalyst surface is described by the Langmuir's isotherm. The adsorption of the other components are discarded. Consequently, the velocities of the rate-determining steps are written as

$$R_5 = k''_5 c_{\mathrm{Aa}} \theta_{\mathrm{B}}^2 \tag{6}$$

$$R_7 = k''_7 c_{\mathrm{Aa}} \theta_{\mathrm{B}} - k''_{-7} c_{\mathrm{Xa}} \tag{7}$$

where θ_{B}, the surface coverage of formaldehyde, is given by

$$\theta_{\mathrm{B}} = \frac{K_{\mathrm{B}} c_{\mathrm{Ba}}}{1 + K_{\mathrm{B}} c_{\mathrm{Ba}}} \tag{8}$$

The generation rates of the components are obtained from the rates R_5 and R_7 by using the overall stoichiometry

$$r_{\mathrm{A}} = -R_5 - R_7 \tag{9a}$$

$$r_{\mathrm{B}} = -2R_5 - R_7 \tag{9b}$$

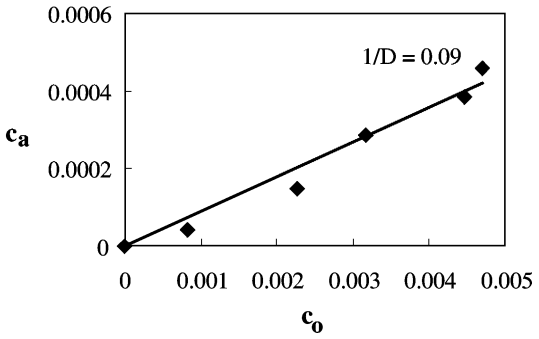


Fig. 8. Distribution plot for ethylacrolein. Conditions: formaldehyde-to-butyraldehyde molar ratio 2:1, $T = 70^{\circ}$C.

$$r_{\mathrm{D}} = R_5 \tag{9c}$$

$$r_{\mathrm{X}} = R_7 \tag{9d}$$

The reaction proceeds in the aqueous phase. The concentrations in the aqueous phase are used in the rate expression while the concentrations in the organic phase are related to the concentrations in the aqueous phase by the distribution coefficients

$$D_i = \frac{c_{i\mathrm{o}}}{c_{i\mathrm{a}}} \tag{10}$$

Examples of the distribution plots ($c_{i\,\mathrm{a}}$ versus $c_{i\,\mathrm{o}}$) are provided in Figs. 7 and 8.

The numerical values of the distribution coefficients and of α are reported in Table 1.

The mass balance equations for the components in aqueous and organic phases are written as follows:

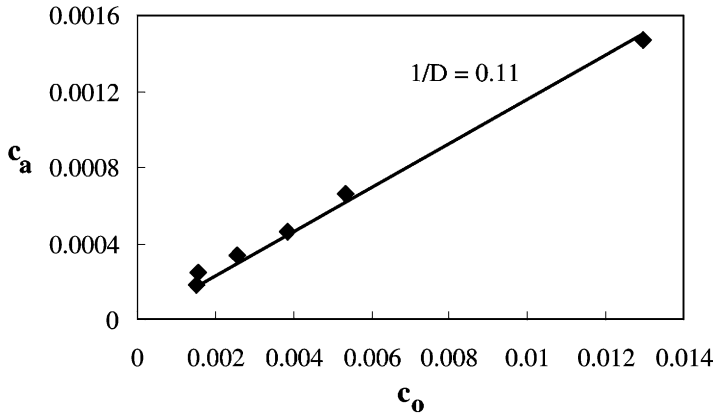


Fig. 7. Distribution plot for butyraldehyde. Conditions: formaldehyde-to-butyraldehyde molar ratio 1.5:1, $T = 70^{\circ}$C.

Table 1
Numerical values of D_i and α for aldolization experiments carried out at 70°C with formaldehyde-to-butyraldehyde molar ratio of 1.5:1 and 2:1

	α	D_A	D_X	D_D	D_B
n_{0B}:n_{0A} (1.5:1)	0.72	9.09	12.5	1.69	0.85
n_{0B}:n_{0A} (2:1)	0.80	8.33	11.1	1.82	0.75

$$\frac{dn_{ia}}{dt} = r_{ia}m_{cat} + N_i A \tag{11}$$

$$\frac{dn_{io}}{dt} = -N_i A \tag{12}$$

where N_i and A denote the interfacial flux and the interfacial area, respectively. The flux term is eliminated by adding the balances together. The sum $n_{ia} + n_{io}$ equals to $(c_{ia}\alpha + c_{io}(1-\alpha))m$, which de facto corresponds to the average concentration in the emulsion, i.e. $c_{ie}m$. Thus we obtain

$$\frac{dc_{ie}}{dt} = \varphi r_{ia} \tag{13}$$

Table 2
Results of the parameter estimation

Parameter	Estimated value	Estimated S.E.	Estimated relative S.E. (%)
$k''_{5,ref}$ (min^{-1})	0.246E+04	0.279E+03	11.3
$E_{a,5}$ (J/mol)	0.581E+05	0.124E+05	21.4
$k''_{7,ref}$ (min^{-1})	0.561E+01	0.102E+01	18.1
$E_{a,7}$ (J/mol)	0.700E+05	0.173E+05	24.8

where $\varphi = m_{cat}/m$, m_{cat} and m being the catalyst mass and the total mass. Provided that the interfacial mass transfer is rapid enough, the concentration in the organic phase can be solved from Eq. (10) and inserted in Eq. (4). Thus we obtain for the concentration in the emulsion

$$c_{ie} = (\alpha + (1-\alpha)D_i)c_{ia} \tag{14}$$

which is inserted in Eq. (13). The final form of the mass balance becomes

$$\frac{dc_{ia}}{dt} = (\alpha + (1-\alpha)D_i)^{-1}\varphi r_{ia} \tag{15}$$

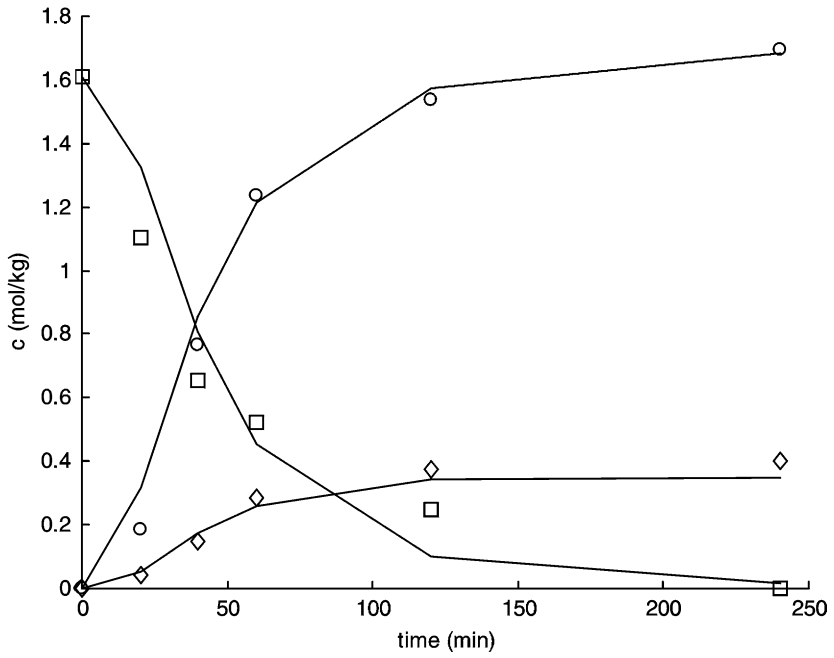


Fig. 9. Concentrations in the aqueous phase. The continuous lines represent model simulation. Conditions: formaldehyde-to-butyraldehyde molar ratio 2:1, $T = 70$°C. (□) Butyraldehyde; (○) aldol; (◇) ethylacrolein. Catalyst mass, 160 g.

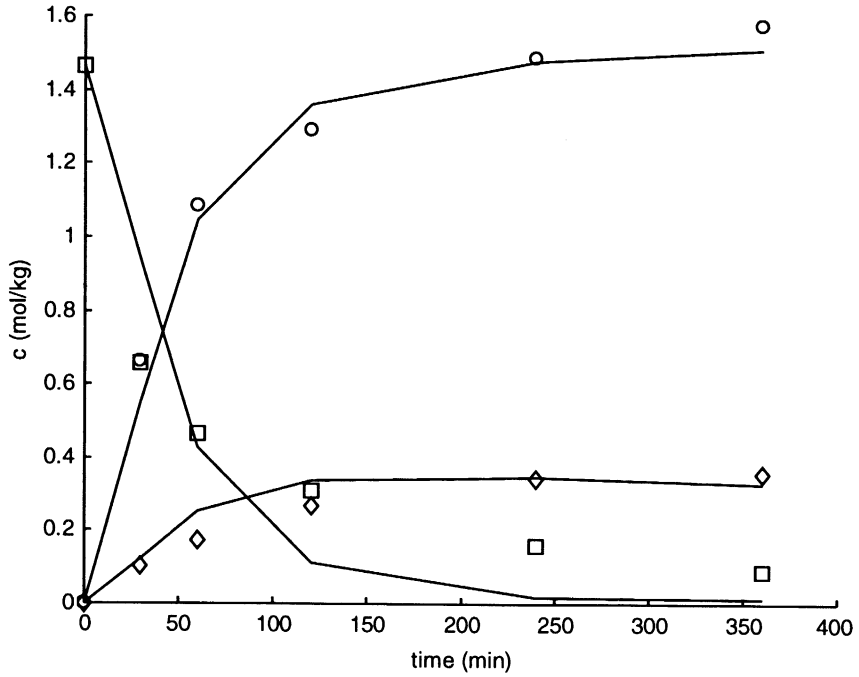


Fig. 10. Concentrations in the aqueous phase. The continuous lines represent model simulation. Conditions: formaldehyde-to-butyraldehyde molar ratio 1.5:1, $T = 70^{\circ}$C. (□) Butyraldehyde; (○) aldol; (◇) ethylacrolein. Catalyst mass, 160 g.

The kinetic parameters were estimated by solving the component mass balance equations (15) numerically for the different components and minimizing the objective function

$$Q = \sum (c_{i\mathrm{a}} - c_{i\mathrm{a\,exp}})^2 \tag{16}$$

where i = A, D and X; $c_{i\mathrm{a}}$ and $c_{i\mathrm{a\,exp}}$ denote the concentrations predicted by the model and recorded experimentally. The mass balance equations (15) were solved with the backward difference method and the objective function was minimized with a hybrid simplex-Levenberg–Marquardt algorithm implemented in the software Modest [3]. The mathematical regression of kinetic parameters was carried out on the runs performed at 70°C with formaldehyde-to-butyraldehyde molar ratios of 2:1 and 1.5:1, respectively.

The values of the kinetic parameters are listed in Table 2 and examples of parameter fitting results are provided in Figs. 9 and 10. The overall fit of the model was determined by the degree of explanation R^2 defined as

$$R^2 = 1 - \frac{\sum (c_{i\mathrm{a\,exp}} - c_{i\mathrm{a\,model}})^2}{\sum (c_{i\mathrm{a\,exp}} - c_{i\mathrm{a\,mean}})^2} \tag{17}$$

R^2 was 98.48%. In addition, Figs. 9 and 10 show that no systematic deviations of the model from the experimental data appeared. The minor deviations in the concentration of butyraldehyde at high conversions are due to inconsistencies in the analytical data. As shown in Table 2, the standard errors of the parameters were reasonably low.

4. Conclusions

The studies of the reaction system butyraldehyde–water–formaldehyde revealed that two liquid phases appear, an aqueous one and an organic one. The phase distribution coefficients were determined in the presence of the liquid phases and the solid aldolization

catalyst (Table 1). Rate equations were derived starting from a simplified reaction scheme, which accounts for aldolization and elimination. The rate equations and the phase equilibrium data were included in a batch reactor model for the liquid–liquid system (Eq. (15)). The kinetic parameters determined from the model were well-identified and gave a good description of the experimental behavior of the system (Figs. 9 and 10).

References

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