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Kinetic study on the catalytic esterification of acetic acid with isoamyl alcohol over Amberlite IR-120

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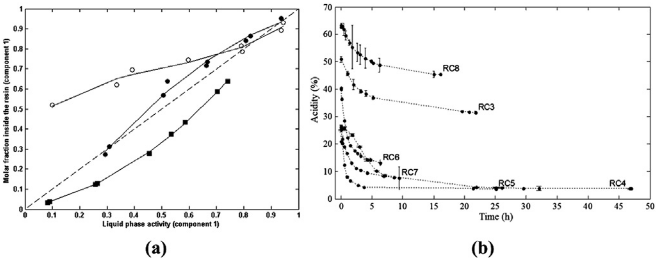
HIGHLIGHTS

- A kinetic model for the esterification of acetic acid and isoamyl alcohol in the presence of Amberlite IR-120 was fitted.
- Adsorption experiments, using pure and binary mixtures, were performed.
- Computational statistics estimated by a Markov Chain Monte Carlo technique were used.
- Twelve possible kinetic models were considered.
- A reaction rate model in terms of NRTL activity model is recommended.

GRAPHICAL ABSTRACT

Sorption (a) and kinetic (b) experimental results and simulation on the catalytic esterification of acetic acid with isoamyl alcohol over Amberlite IR-120.



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ABSTRACT

A kinetic model was fitted for the liquid phase esterification of acetic acid with isoamyl alcohol in the presence of the heterogeneous catalyst Amberlite IR-120. The experiments were performed in the temperature range of 322–362 K in a batch reactor. Sequential experimental design, based on the divergence criterion and tools from computational statistics such as the deviance information criterion estimated by a Markov Chain Monte Carlo technique, were used to discriminate among 12 possible kinetic models. Adsorption experiments using pure substances and binary mixtures were also performed. In statistical terms, two kinetic models appear as the most appropriate for this esterification reaction: a simple, easy-to-handle model that uses molar fractions and a second model based on the NRTL activity model, which is physically more realistic due to its congruence with the resin sorption phenomena.

1. Introduction

The increasing worldwide tendency of ethanol production by fermentation generates each year large amounts of fusel oil. Nearly 5 L of fusel oil are obtained for each 1000 L of produced ethanol. Fusel oil, mainly constituted of isoamyl alcohol, is commonly treated as a residue (Kuçuk and Ceylan, 1998). However, it could be used as a raw material and converted to more valuable products. Synthesis of isoamyl acetate by esterification of acetic acid with isoamyl alcohol is a promising option considering the multiple applications of isoamyl acetate in food, cosmetic and chemical industries (Aslam et al. 2010; Osorio-Viana et al., 2013a;

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Saha et al., 2005a). Nevertheless, the design of an esterification process in liquid phase requires a reliable rate of reaction expression that includes both the homogeneous reaction rate and the effect of a suitable solid catalyst.

As with other analogous reactions, this esterification is reversible and can be catalyzed using homogeneous mineral acids (Liu et al., 2006; Reid, 1948). The application of heterogeneous solid acid catalysts can overcome the drawbacks of the mineral acids such as: equipment corrosion, low selectivity, product contamination and recycle costs. Synthesis of isoamyl acetate by esterification of acetic acid with isoamyl alcohol in the liquid phase has been scarcely studied. Recently, Duque-Bernal et al., (2013) reported a rate of reaction expression for the esterification between acetic acid and isoamyl alcohol without the use of catalyst. They showed that there is an autocatalytic effect of acetic acid on the reaction rate which equilibrium constant (≈5.0) can be considered temperature independent and correlated a rate law expression using mole fractions as a concentration variable. Previously, Teo and Saha (2004) and Saha et al., (2005b) studied the kinetics of this heterogeneously catalyzed esterification using the ion exchange resin Purolite CT-175. To account the liquid phase non-ideality, UNIFAC model was used. The authors correlated a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model considering only the adsorption of isoamyl alcohol and water on the catalyst and the surface reaction as the rate limiting step. Other related studies, in which kinetic models were not shown, employed catalytic membranes of poly-vinyl alcohol containing sulfonic acid groups (Castanheiro et al., 2006), heteropolyacids like partially substituted Keggin salts (Pizzio and Blanco, 2003), immobilized lipase *Candida antartica* enzyme (Güvenç et al., 2007) and expandable graphite catalyst (Pang et al., 2008).

In this study, catalyst characterization and kinetic tests are discussed. A sequential experimental design has been used to correlate the parameters of several kinetic models for the isoamyl acetate synthesis reaction catalyzed by Amberlite IR-120 (an ion exchange resin). Experiments covered the temperature range of 322–362 K and 1/1, 1/2, 2/1, 1/3 alcohol/acid feed molar ratios in a batch reactor. Following a literature survey on models used for similar esterification reactions, a total of twelve kinetic models (four types of rate law with three computational forms for the liquid phase activity) were fitted and compared in statistical terms using a Bayesian approach. This involved the exploration of the *a posteriori* probability distribution of the model parameters using a Markov chain Monte Carlo technique (Duque-Bernal et al., 2013; Laine, 2008).

2. Experimental

2.1. Catalyst characterization

Table 1
Properties of ion exchange resin Amberlite IR-120 (Rohm and Haas) as reported by the manufacturer.

Physical form	Amber spherical beads
Matrix	Styrene divinylbenzene copolymer
Functional group	Sulfonic acid
Ionic form as shipped	H^+
Total exchange capacity	≥ 1.8 eq/L (H^+ form)
Moisture holding capacity	53–58% (H^+ form)
Shipping weight	800 g/L
Maximum reversible swelling	$Na^+ \rightarrow H^+ \leq 11\%$
Maximum operating temperature	135 °C

Table 1 presents the properties of the ion exchange resin Amberlite IR-120, as reported by Rohm and Haas. The resin was preconditioned previous to every reaction test. This procedure was based on successive washings with HCl and NaOH aqueous solutions as follows: (1) treatment with HCl solutions increasing the concentration stepwise: 0.5 M; 1 M; 2 M, followed by a continuous treatment with 3 M; then, washing with HCl solutions of stepwise decreasing concentrations: 2 M; 1 M and 0.5 M; (2) washing with deionized water; (3) stepwise treatment with NaOH solutions: 0.1 M; 0.5 M; 1 M; 0.5 M and 0.1 M; (4) washing again with deionized water; (5) stepwise treatment with HCl solutions: 0.5 M; 1 M; 2 M; 1 M and 0.5 M, (6) washing with water, (7) finally, a cation exchange was performed with 1 M HCl to obtain the resin in its H^+ form (Zagorodni, 2007). Next, the resin was dried in an oven at 70–75 °C and under vacuum pressure of 40–50 Torr for approximately 8 h, time at which a constant weight was obtained. To estimate the cation exchange capacity of the resin, standard titration using an automatic burette (Titrino Metrohm SM 702) was performed with an aqueous solution 0.1 M in NaOH supersaturated with NaCl (Helfferich, 1995).

Particle size distribution was measured using a screening sieving machine with 6 Tyler plates (1–0.15 mm screen size) and mechanical agitation for 20 min, using approx. 200 g of resin saturated with atmospheric moisture. The retained weight of resin in each sieve was measured.

When the resin is brought into contact with a liquid, some of the liquid is incorporated inside the resin. As this phenomenon also involves the solid bulk phase (absorption) and not only its surface (adsorption), here the term sorption is used to include both as suggested by the IUPAC recommendations (IUPAC, 2004). Resin swelling and sorption equilibria were estimated as proposed by Gregor et al. (1951). Dry resin density was measured with a 10 mL picnometer (class A) in which a given quantity of resin was brought into contact with heptane (Merck), a solvent which does not swell the resin due to its non-polarity (Gregor et al., 1951). Then, dry resin was brought into contact with each of the reaction substances during 24 h; then, the liquid–solid mixture was separated by centrifugation; the swollen resin density was determined as stated before, using the corresponding substance instead of heptane. For sorption experiments, three binary non-reactive mixtures were prepared (alcohol–acetate, acid–acetate and acid–water) at several initial concentrations. For each mixture a dry resin sample of 2 g was mixed, using a shaker, with a given mass of the solution in a 50 mL beaker at 20 °C for at least 24 h. Next, a sample of the liquid in equilibrium with the resin was measured by gas chromatography (Perkin-Elmer, FID detector) and automatic titration (Titrino Metrohm SM 702) with NaOH for the binary mixtures with acetic acid. For all tests, the following reactive grade chemicals were used without further purification: isoamyl alcohol (Merck, 98%), isoamyl acetate (Merck, 99%), acetic acid (Panreac, 99.7%), HPLC grade water (Thermo Scientific Barnsted Nanopure unit, resistivity at 25 °C: 18.0 MΩ cm).

Resin swelling at room temperature was estimated assuming additive volumes and using the experimental data for densities of: solvents (ρ_{liq}), dry resin (ρ_{dr}) and wet resin (ρ_H). It is reported in terms of the absorbance ratio (*RW*) and the swelling ratio (*RH*), which are defined as follows:

$$RW = \frac{1-(\rho_{liq}/\rho_{dr})}{1-(\rho_{liq}/\rho_{H})} \tag{1}$$

$$RH = RW\frac{\rho_{dr}}{\rho_{H}} \tag{2}$$

Using both the *RW* and the experimental binary sorption data, the mass fraction of component *A* inside the resin (w_A^S) in equilibrium with the liquid can be computed considering global and component material balances, according to Eq. (3), where *RS* stands for