

## Short Communication

## Thermodynamic prediction of the solvent effect on a transesterification reaction

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## HIGHLIGHTS

- Solvent effect on a reaction equilibrium can be predicted without using any reaction data.
- Interactions between reacting species and solvent were considered via a thermodynamic model.
- Solvent effect on reaction kinetics can be predicted in any solvent using only one kinetic experiment.
- Predictions are in excellent agreement with experimental data.

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## ABSTRACT

This work focuses on the thermodynamic prediction of solvent effects on the transesterification of butyl acetate with ethanol to butanol and ethyl acetate in the solvent heptane at 293.15 K and 303.15 K. Both, the reaction equilibrium and the reaction kinetics have been investigated experimentally by Schmidt et al. (1999). They found that the solvent heptane does not affect the reaction equilibrium but significantly influences the reaction kinetics. They described the solvent effect on the reaction kinetics by empirically correlating the experimentally-observed apparent rate constants with the dielectric constants of the different reaction mixtures.

In this work we re-evaluated the experimental data and now present a thermodynamic approach to consistently predict the solvent effect on both, the reaction equilibrium and the reaction kinetics. Accounting for the activity coefficients of the reactants/products obtained from the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) allowed for considering the interactions of the reactants/products among themselves and also with the solvent heptane. Accounting for those, it is shown that the solvent effect on the reaction equilibrium as well as on the reaction rate can even be predicted in very good agreement with the experimental data.

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## 1. Introduction

Solvents in which reactions are performed can significantly affect both, reaction equilibria and reaction kinetics. Therefore, to optimize yield, selectivity and reaction rate for a desired product, it is important to consider the solvent effect on a reaction.

Reichardt and Welton (2010) gave a comprehensive overview of studies on solvent effects on reactions. They presented both, experimental results and a modeling framework based on the Gibbs energy of solvation to correlate experimentally-observed apparent equilibrium constants and rate constants with the solvent polarity

scale  $E_T(30)$ . The drawback of these correlations is that they are derived empirically and moreover are specific for a given reaction. Therefore, they cannot be used for predicting solvent effects on other reactions than the ones from which they were derived.

In earlier works we already presented a thermodynamic approach that allows predicting solvent effects on reactions. This approach considers the interactions between the reacting species and the different solvents via activity coefficients (for the pure-liquid reference state) and fugacity coefficients (for the ideal-gas reference state). This could, in principle, be done using any appropriate thermodynamic model. In this work, we used PC-SAFT to determine the activity coefficients of the reacting species, as this was shown earlier to be superior compared to other models like UNIFAC, NRTL-SAC or COSMO-RS for that purpose (Riechert et al., 2015).

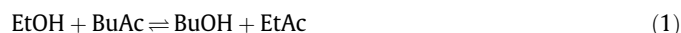
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For the esterification of acetic acid and of propionic acid with ethanol at different reactant ratios and in different solvents, this approach was applied to both, the reaction equilibrium (Riechert et al., 2015) and the reaction kinetics (Lemberg and Sadowski, 2017). This allowed determining solvent-independent equilibrium constants and rate constants and quantitatively predicting the solvent effects. The solvent effect on the reaction equilibrium was also successfully predicted for the hydroformylation of 1-dodecene in almost quantitative agreement with experimental data (Lemberg et al., 2017).

Besides this, very few studies exist that focus on the simultaneous thermodynamic description of the equilibrium and the kinetics of reactions. Pöpken et al. (2000) investigated the reaction equilibrium and the reaction kinetics for the esterification of acetic acid with methanol. They correlated both, equilibrium and kinetics simultaneously, while accounting for the activity coefficients of the reacting species via UNIQUAC. However, they did not focus on investigating or predicting any solvent effects.

In this work, we present a simultaneous thermodynamic prediction of the solvent effect on the reaction equilibrium and on the reaction kinetics for the transesterification of ethanol (EtOH) with butyl acetate (BuAc) to butanol (BuOH) and ethyl acetate (EtAc) in heptane (C7):



We refer to experimental data that were published in 1999 by Schmidt et al. (1999). They found that the solvent heptane does not affect the position of the reaction equilibrium but significantly influences the reaction kinetics. They modeled the solvent effect on the reaction kinetics with an approach similar to the one of Reichardt and Welton (2010) by empirically correlating the experimental data with the dielectric constants of the different reaction mixtures. In this work we now want to show how their empirical correlations can be replaced by a thermodynamic approach that allows to predict the solvent effect on both, the reaction equilibrium and the reaction kinetics.

## 2. Theory

### 2.1. Thermodynamic description of reaction equilibria and reaction kinetics

For an equilibrium reaction of type  $A + B \rightleftharpoons C + D$ , the reaction rate  $r$  is usually defined as

$$r = \frac{dc_C}{dt} = k_1 \cdot c_A \cdot c_B - k_{-1} \cdot c_C \cdot c_D \quad (2)$$

whereby  $c_i$  denotes the concentration of component  $i$  in mol/kg.  $k_1$  and  $k_{-1}$  are the rate constants of the forward and backward reaction, respectively. For reactions that are significantly affected by solvents,  $k_1$  and  $k_{-1}$  usually depend on the solvent. In the following, Eq. (2) is referred to as “common kinetic model”.

An alternative (and thermodynamically correct) way of expressing the reaction rate  $r$  is represented by

$$r = \frac{dc_C}{dt} = k_1^* \cdot c_A \gamma_A \cdot c_B \gamma_B - k_{-1}^* \cdot c_C \gamma_C \cdot c_D \gamma_D \quad (3)$$

whereby  $\gamma_i$  denotes the activity coefficient of component  $i$ . The activity coefficients depend on the concentrations of all components present in the reaction mixture and account for all interactions among them, including interactions of the reacting agents with solvents. In this work, they were calculated using the thermodynamic model PC-SAFT. As long as the catalyst is not affected by the reacting species or solvents ( $\gamma_{cat.} = const.$ ),  $k_1^*$  and  $k_{-1}^*$  do not depend on the solvent and are therefore referred to in the following

as the intrinsic rate constants of the forward and backward reaction, respectively. In the following, Eq. (3) is referred to as “thermodynamic kinetic model”.

The reaction kinetics has to meet the thermodynamic reaction-equilibrium condition at infinite times where  $r = 0$ . Therefore, when using the common kinetic model, the ratio of the rate constants  $k_1$  and  $k_{-1}$  in Eq. (1) equals  $K_c$ , which is obtained from the equilibrium concentrations  $c_{i,eq.}$  of all reacting agents:

$$\frac{k_1}{k_{-1}} = \frac{c_{C,eq.} \cdot c_{D,eq.}}{c_{A,eq.} \cdot c_{B,eq.}} = K_c \quad (4)$$

Usually  $K_c$  is not a constant but depends on temperature and on the concentration of all components present in the reaction mixture as well as on the solvent. Therefore it is referred to as “apparent equilibrium constant” in the following.

When correctly accounting for the activity coefficients  $\gamma_i$  (Eq. (3)), the intrinsic rate constants  $k_1^*$  and  $k_{-1}^*$  are connected via the thermodynamic equilibrium constant  $K_a$  according to:

$$\frac{k_1^*}{k_{-1}^*} = \frac{c_{C,eq.} \cdot c_{D,eq.} \cdot \underbrace{\gamma_{C,eq.} \cdot \gamma_{D,eq.}}_{K_c}}{\underbrace{c_{A,eq.} \cdot c_{B,eq.}}_{K_c} \cdot \underbrace{\gamma_{A,eq.} \cdot \gamma_{B,eq.}}_{K_\gamma}} = K_a \quad (5)$$

In contrast to  $K_c$ ,  $K_a$  only depends on temperature and does neither depend on concentrations nor on the solvent used as reaction medium. In either way, whether using Eq. (2) or (3) for the modeling of reaction kinetics, only one kinetic parameter ( $k_1$  or  $k_{-1}$  and  $k_1^*$  or  $k_{-1}^*$ , respectively) has to be adjusted for the description of experimental reaction kinetics once the apparent equilibrium constant  $K_c$  (common kinetic model) or the thermodynamic equilibrium constant  $K_a$  (thermodynamic kinetic model) is known.

When considering a reaction at standard pressure ( $p^0 = 1.013$  bar), the thermodynamic equilibrium constant  $K_a$ , based on the activities  $a_i$  of the reacting agents, is connected to the thermodynamic equilibrium constant  $K_f$ , which is based on the fugacities  $f_i$  of the reacting agents, via:

$$K_a = \frac{K_f}{K_{\varphi_{oi}}} \quad (6)$$

Thereby  $K_{\varphi_{oi}}$  contains the pure-component fugacity coefficients  $\varphi_{oi}$  of every reacting agent according to:

$$K_{\varphi_{oi}} = \frac{\varphi_{0C} \cdot \varphi_{0D}}{\varphi_{0A} \cdot \varphi_{0B}} \quad (7)$$

Once  $K_a$  or  $K_f$  are known, the concentrations of reactants and products at reaction equilibrium  $c_{i,eq.}$  in any solvent can be predicted using the activity coefficients  $\gamma_i$  of these components in that particular solvent (Eq. (5)).

$K_f$  can be obtained from the standard Gibbs energy of reaction  $\Delta^R g^0$  at the ideal-gas standard state:

$$K_f(T, p^0) = e^{-\frac{\Delta^R g^0(T, p^0)}{RT}} \quad (8)$$

where  $R$  is the universal gas constant. The standard Gibbs energy of reaction  $\Delta^R g^0$  is accessible via the standard Gibbs energies of formation  $\Delta^F g_i^0$  of the reacting agents which usually can be found in the literature:

$$\Delta^R g^0(T, p^0) = \sum_i \nu_i \cdot \Delta^F g_i^0(T, p^0) \quad (9)$$

Thereby  $\nu_i$  denotes the stoichiometric coefficient of component  $i$  in the considered reaction.

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