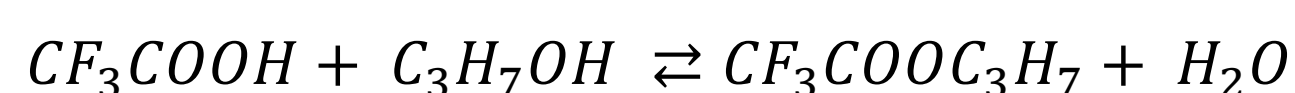


## Chemical Equilibrium and Kinetics in the Autocatalytic Reaction System 2,2,2-Trifluoroacetic Acid – Propan-1-ol – Water – Propyl 2,2,2-Trifluoroacetate

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## INTRODUCTION &amp; AIM

The esterification reaction of alcohols and acids is a fundamental method for synthesizing esters. Typical Fischer esterification reaction where one of the reactants is a weak acid requires the addition of an external catalyst to the system by reason of the slow reaction rate. The acid catalyst protonates the carbonyl oxygen of the carboxylic acid, which makes the carbonyl carbon more electrophilic and susceptible to attack by the alcohol nucleophile [1]. In contrast, systems that involve a strong acid as one of the reactants exhibit autocatalytic behavior. An example of such reaction is esterification between an alcohol and trifluoroacetic acid (TFA) [2].



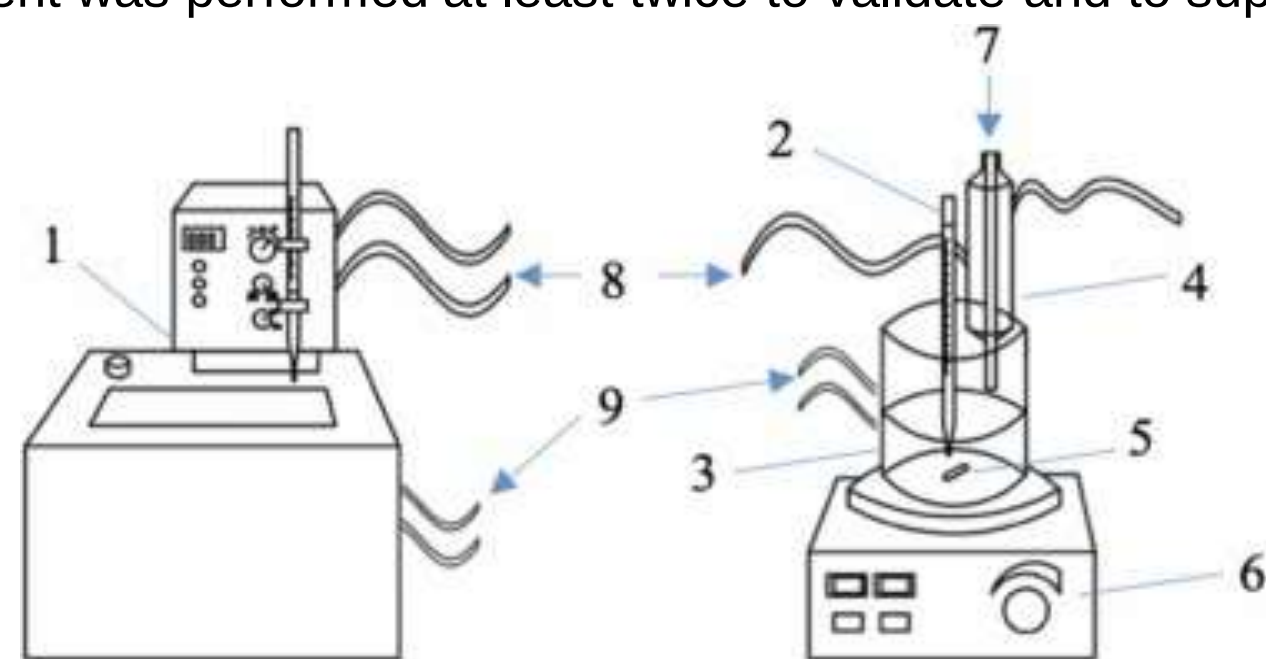
However, experimental data on equilibrium and kinetics of such autocatalytic systems remain limited and existing kinetic models are not universally applicable.

Thus, the aim of the present study is to investigate the chemical equilibrium and kinetics of the esterification reaction of TFA and propan-1-ol (P-ol) without the introduction of an external catalyst.

## METHOD

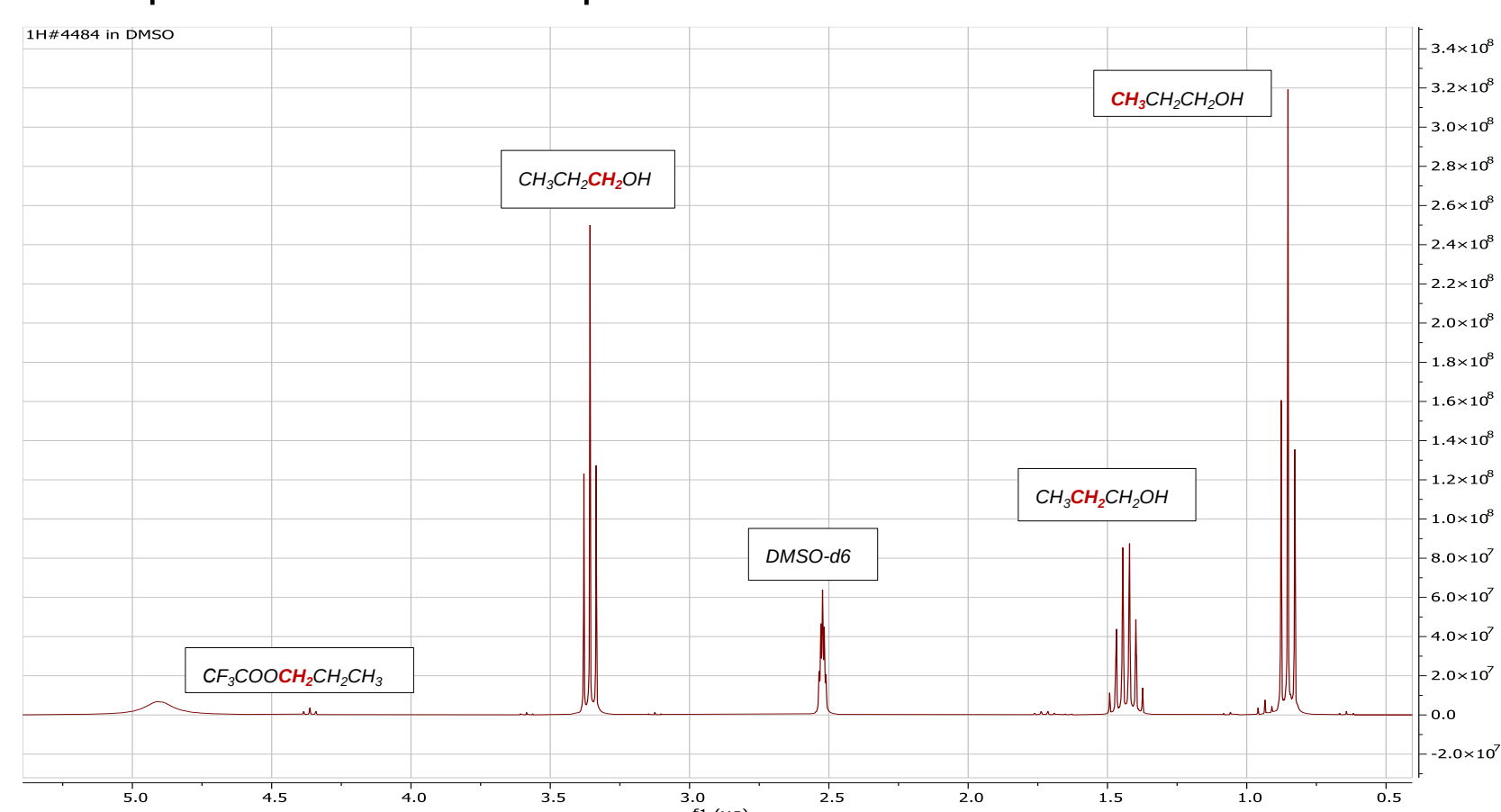
The chemical equilibrium of the esterification of TFA and P-ol was studied by continuous thermostating of samples at atmospheric pressure with known initial composition. For temperature range from 30 to 70 °C, parallel experiments were performed, and the equilibrium constant was taken as the average value.

Kinetic measurements were carried out in a laboratory stirred reactor (Figure 1) under atmospheric pressure. Reaction mixtures were sampled at defined time intervals, and each experiment was performed at least twice to validate and to support data.



**Fig. 1.** Equipment for researching the kinetics of a chemical reaction. 1—thermostat, 2—mercury thermometer, 3—laboratory reactor with jacket, 4—condenser, 5—stirrer bar, 6—magnetic stirrer, 7—sample collection, 8—cooling medium, 9—heat-carrying medium.

Quantitative analysis of the samples was performed by NMR spectroscopy. The Bruker Avance II 300 MHz spectrometer (Bruker Corp., Billerica, MA, USA) was used to obtain both <sup>1</sup>H and <sup>19</sup>F spectra (Figure 2). The standard method to calculate the quantitative composition from NMR spectra was used.



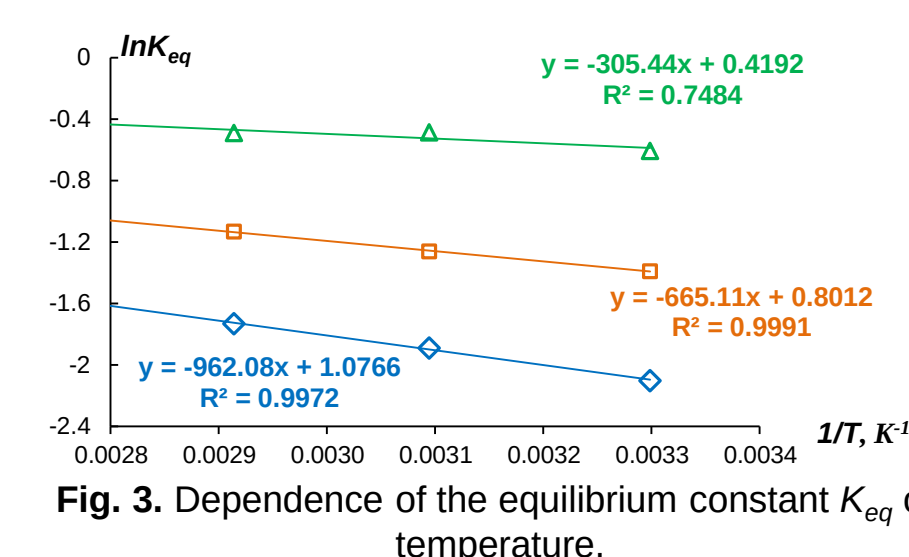
**Fig. 2.** <sup>1</sup>H NMR spectrum of the reaction mixture sample in d-DMSO.

## RESULTS &amp; DISCUSSION

In present study equilibrium constant ( $K_{eq}$ ) values were obtained over a wide range of conditions. The results showed that the reaction system with initial TFA concentrations of up to 0.3 mole fraction ( $x_{TFA}/x_{P-ol} \leq 3/7$ ) falls within the homogeneous area of chemically equilibrium compositions. For this homogeneous region the temperature dependence of the equilibrium constant (Figure 3) was determined. The Van't Hoff equation parameters (Table 1) indicates that the reaction is endothermic within the area.

**Tab. 1.** Van't Hoff equation parameters for the esterification reaction of TFA and P-ol.

| $x_{TFA}^0/x_{P-ol}^0$ | $\Delta_r H$ , J/mol | $\Delta_r S$ , J/mol·K | $K_{eq}$                                        |
|------------------------|----------------------|------------------------|-------------------------------------------------|
| 1/9                    | 7998.733             | 8.951                  | $= \exp\left(-\frac{962.08}{T} + 1.0766\right)$ |
| 2/8                    | 5529.725             | 6.661                  | $= \exp\left(-\frac{665.11}{T} + 0.8012\right)$ |
| 3/7                    | 2539.428             | 3.485                  | $= \exp\left(-\frac{305.44}{T} + 0.4192\right)$ |



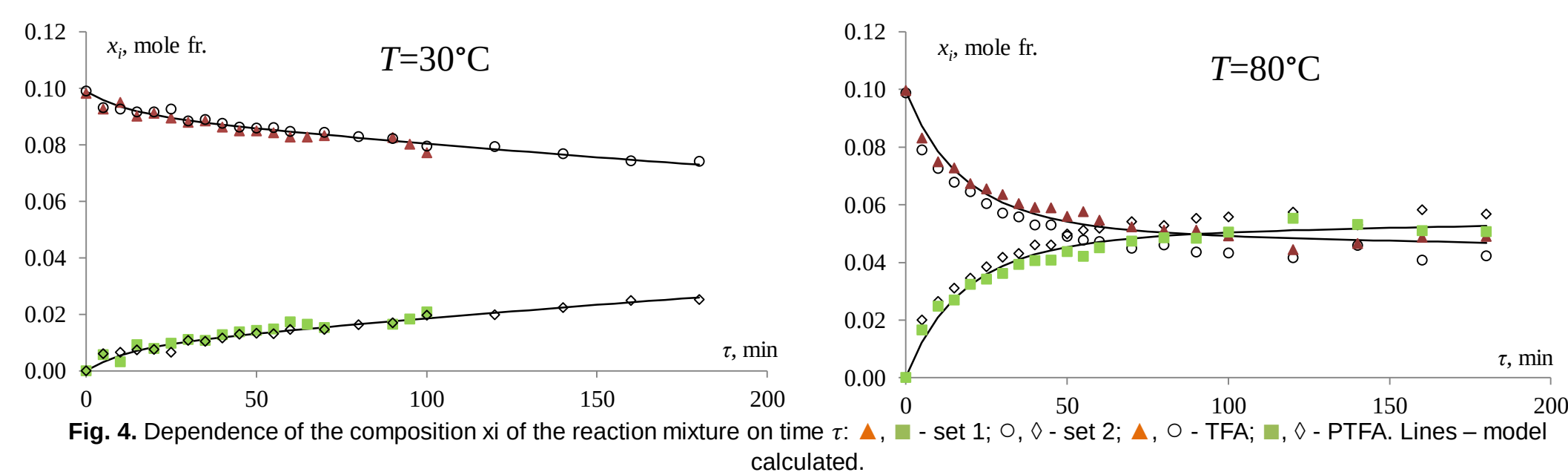
**Fig. 3.** Dependence of the equilibrium constant  $K_{eq}$  on temperature.

Kinetic data were obtained for the homogeneous area at an initial molar ratio of reactants of 1:9. At this stage of the study, none of the tested kinetic models were able to adequately describe the esterification kinetics of TFA and P-ol by reason of several limiting factors. Therefore, to correctly describe the experimental data, a mathematical model was proposed in which it is assumed that the reaction rate coefficient depends on the concentration of the acid.

Based on the kinetic equation of the reaction  $\frac{dx}{dt} = k_1 x_{CF_3COOH} x_{C_3H_7OH} - k_2 x_{CF_3COOC_3H_7} x_{H_2O}$  taking into account that  $K_{eq} = \frac{k_1}{k_2}$  the following equation was obtained

$$\frac{\left(x_{CF_3COOH} x_{C_3H_7OH} - \frac{x_{CF_3COOC_3H_7} x_{H_2O}}{K_{eq}}\right)^{-1} dx}{dt} = k_1 = a + bc \cdot \exp(-ct)$$

Coefficients a, b and c were calculated from experimental kinetic data. The experimental data and results of modeling with use of proposed equation are shown in Figure 4.



**Fig. 4.** Dependence of the composition  $\xi$  of the reaction mixture on time  $\tau$ :  $\Delta$ ,  $\square$  - set 1;  $\circ$ ,  $\diamond$  - set 2;  $\Delta$ ,  $\circ$  - TFA;  $\square$ ,  $\diamond$  - PTFA. Lines – model calculated.

## CONCLUSION

The chemical equilibrium and kinetics of the esterification reaction of TFA and P-ol were experimentally studied. A new model for describing the esterification kinetics, taking into account the change in the reaction rate coefficient during the process, is proposed and adequately describes the experimental data.

## FUTURE WORK / REFERENCES

In the future, it is planned to further develop the proposed model and test it on other autocatalytic reactions.

## References

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