

# Interaction between the reaction medium and an ion-exchange resin catalyst in the etherification of isoamylenes

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## Abstract

*tert*-Amyl methyl ether (2-methoxy-2-methylbutane, TAME) is synthesised in a liquid-phase reaction of methanol (MeOH) and isoamylenes (2-methyl-1-butene (2M1B), and 2-methyl-2-butene (2M2B)). The reaction rates of the formation of TAME were measured in a continuous stirred tank reactor (CSTR) at the temperature range between 323 and 353 K. The molar ratio of methanol to isoamylenes and the concentration of the reagents were varied in the feed. As the alcohol–isoamylenes mixture behaves non-ideality, the equilibrium constants and the kinetic analysis was performed in terms of activities using the Wilson method for activity coefficient estimation. In the first stage, the kinetic parameters of the published kinetic models were estimated with the experimental data. In order to describe the interaction of the reaction medium and the catalyst better, the solubility parameter was added to the kinetic models. The best fit was obtained with the model that included the solubility parameter and was based on the Eley–Rideal (ER) type mechanism. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Ion-exchange resin; Etherification; Kinetics; Solubility parameter; 2-Methoxy-2-methylbutane

## 1. Introduction

Tertiary ethers can serve as octane enhancing components in gasoline. So far, only methyl-*tert*-butyl ether (MTBE, 2-methoxy-2-methylpropane) has been widely used. However, recently the high water solubility of this ether has caused environmental problems, especially in California. As a substitute for MTBE, heavier tertiary ethers, e.g. *tert*-amyl methyl ether (TAME) and ethyl-*tert*-butyl ether (ETBE,

2-ethoxy-2-methylpropane) have already been used as octane boosters.

TAME is synthesised in a liquid-phase reaction of methanol (MeOH) and isoamylenes (2-methyl-1-butene (2M1B), and 2-methyl-2-butene (2M2B)). The kinetic behaviour of the reaction in the presence of an ion-exchange resin is complex to describe. The interaction between the sulphonic groups and the polar reaction medium has to be taken into consideration. Several kinetic models have been published for the synthesis of TAME. Few models are concentration [1,2], and some activity based [3–5]. Using models, which are written in terms of activities, one takes the non-ideality of the reaction mixture into account. Kiviranta-Pääkkönen et al. tested various kinetic models against batch reactor data for TAME synthesis [6]. The temperature was varied between 333 and 353 K and the MeOH/isoamylenes molar ratio

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between 0.2 and 2. Kiviranta-Pääkkönen concluded that the activity based models [4,5] predicted the experimental results better within a wider range of conditions than the concentration based.

Recently, Fite et al. [7] has studied the kinetics of MTBE synthesis. They compared the experimental results with calculated ones using the models from the literature. The experimental rate of reactions deviated from the calculated results, mainly in cases when the initial mol ratio of the reagents deviated clearly from 1. With excess MeOH the experimental reaction rates were lower than those calculated with the models. They concluded that the polarity of the whole reaction medium influences the activity of an ion-exchange resin. The kinetic model of the synthesis was improved by including a *solubility parameter* of the reaction medium in the model. The Hildebrandt solubility parameter was found to be the most suitable physical property to be connected to the kinetic equations. The empirical correction,  $1/\delta_M$ , was estimated at each temperature from the Hildebrandt solubility parameter of each compound by the expression

$$\delta_M = \sum_i \Phi_i \delta_i = \sum_i \Phi_i \sqrt{\frac{\Delta H_{\text{VAP},i} - RT}{V_i^L}} \quad (1)$$

where  $\Delta H_{\text{VAP},i}$  is the molar enthalpy of vaporisation,  $V_i^L$  the liquid molar volume and  $\Phi_i$  is the volume fraction for the pure component  $i$ . One should note that all the terms used in the calculation of  $\delta_M$  are measurable properties of the system or the compounds. Therefore, including this parameter into the kinetic equations, one does not increase the number of *estimated* parameters, and in that way improves the fit.

Fite et al. developed further the application of solubility factors into the kinetic rate equations of the synthesis of MTBE. They introduced a parameter with physicochemical meaning accounting for the interaction between the reaction medium and the resin catalyst [8]. The parameter is related to the swelling of resin backbone and to the accessibility of the active centres of a macroporous sulphonic resin. The interaction between the reaction medium and the resin was considered as a solution process. By analogy with the activity of a non-electrolyte in a solvent, the reaction medium–resin affinity can be quantify by means of

the following parameter [9]:

$$\Psi = \exp \left\{ \frac{\bar{V}_M \Phi_P^2}{RT} (\delta_M - \delta_P)^2 \right\} \quad (2)$$

where  $\bar{V}_M$  is the molar volume of the reaction medium,  $\Phi_P$  the volume fraction of the resin,  $\delta_M$  the solubility parameter of the reaction medium and  $\delta_P$  is the solubility parameter of the resin. The parameter  $\delta_P$  could be estimated by a contribution group method or could be adjusted.

The aim of this work was to study the interaction of the reaction medium and the resin swelling in the etherification of isoamylenes with MeOH. We studied the applicability of the solubility parameter for the kinetic model of the TAME synthesis in order to get an enhanced rate equation, which would be applicable in a wide concentration range.

## 2. Experimental

In the experiments, the effect of reaction temperature, the concentrations and molar ratio of the reagents on the formation rate of TAME was investigated.

### 2.1. Apparatus

The rate of reaction was measured in a continuous stirred tank reactor (CSTR) ( $V = 55.6$  ml, stainless steel), where the reaction mixture was magnetically stirred. The catalyst was placed in a metal gauze basket (60 mesh). The temperature was regulated by immersing the reactor in a thermally controlled water bath. The pressure was kept over 0.5 MPa in order to guarantee a liquid-phase operation at all temperatures. A liquid mass flow controller controlled the pulse-free flow rate (25–75 g/h) of the feed. The feed and the reactor effluent were analysed on-line with a gas chromatograph using an automated liquid sample valve.

### 2.2. Materials

A commercial, macroreticular strong cation-exchange resin Amberlyst 16W (Rohm & Haas) in  $\text{H}^+$  form was used as the catalyst. The amount of the catalyst varied between 0.2 and 1 g in various experiments. The ion-exchange capacity of the resin was 5 meq of

dry catalyst (in g). The catalyst was used unsieved having diameter between 0.35 and 1 mm. The catalyst was washed several times with water free MeOH at room temperature in ultrasound in order to remove water from the catalyst pores. After the experiments the used catalyst was removed from the reactor and it was dried in an oven overnight to constant weight. The rate of reaction was calculated on the basis of the amount of the *dried* catalyst.

MeOH was from Merck (>99.5 wt.%), the isomer mixture of 2M1B and 2M2B (technical grade) was from Fluka Chemie. Solvents were isopentane (IPEN) (>99 wt.%) from Fluka Chemie, cyclohexane (CHEX) and isooctane (IOCT) (>99.5 wt.%) both from Merck.

### 2.3. Analytical methods

A Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionisation detector (FID) was used for the analysis. The compounds were separated with a 60 m glass capillary column DB-1 (J & W Scientific). For quantitative analysis, the gas chromatograph was calibrated with an external standard.

The experiments were carried out at feed mol ratios of MeOH/isoamylenes 0.6, 1, 2 and 8 in the various concentrations of the reagents at temperatures 353 K (22 points), 343 K (6 points), 333 K (15 points) and at 323 K (3 points). Fig. 1 presents the output mol fractions of MeOH, the isoamylenes and the ether and the inert during the experiments. As an exam-

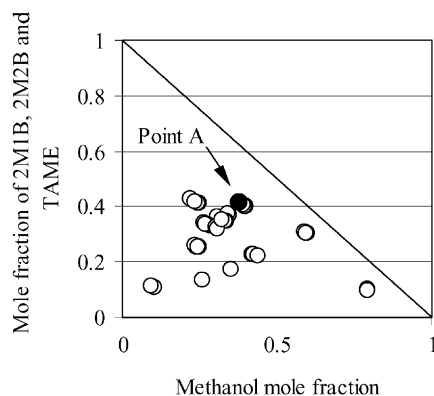


Fig. 1. . The sum of 2M1B, 2M2B and TAME in the reactor outlet as a function of MeOH mol fraction.

Table 1

Experimental conditions for one experimental point (Point A in Fig. 1)<sup>a</sup>

Component	Concentration (mol/l)	Rate (mmol/kg s)
MeOH	4.01	-55.0
2M1B	0.32	-5.2
2M2B	3.69	-50.5
TAME	0.42	55.9
IPEN	1.26	
CHEX	0.54	
IOCT	0.40	

<sup>a</sup> The output concentrations of MeOH, 2M1B, 2M2B, TAME, IPEN, CHEX, IOCT and the measured rates of reaction at temperature 353 K.

ple, Point A (MeOH mol fraction 0.37715) shown in Fig. 1, represents the experimental results presented in Table 1.

### 3. Results and discussion

In our recent study, Rihko-Struckmann et al. [10], we observed that the Wilson method can describe the compound activities very well in all ranges of MeOH mol fraction. Therefore, we here calculated the activity coefficients by the Wilson method using the binary parameters published in that paper. The experimental reaction equilibrium constants presented in Table 2 were calculated as well from the experimental results of Rihko-Struckmann et al. [10].

The stirrer speed in the reactor was 950 rpm during the experiments. As determined in our earlier study of the splitting of TAME [3], at this speed the external diffusion of the reagents from the liquid bulk to the catalyst surface was fast and the diffusion resistance

Table 2

The reaction equilibrium constants for the reactions of 2M1B, 2M2B and MeOH to TAME and for the isomerisation of the isoamylenes<sup>a</sup>

Reaction	Equilibrium constant
2M1B + MeOH → TAME	$K_1 = \exp(-9.11565 + 4275.087/T)$
2M2B + MeOH → TAME	$K_2 = \exp(-8.63090 + 3357.108/T)$
2M1B → 2M2B	$K_3 = K_1/K_2$

<sup>a</sup> Experimental data and the parameters for Wilson method activity coefficients are taken from Rihko-Struckmann et al. [10].

Table 3

Kinetic equations for the reactions of 2M1B to ether, 2M2B to ether and the isomerisation of 2M1B to 2M2B according to the mechanism proposed in Rihko et. al. [4], and Oost and Hoffmann [5]

Equations for ER type mechanism	Equations for LH type mechanism
$r_1 = \frac{k_1[a_M a_{1B} - (1/K_1)a_T]}{(K_T/K_M)a_T + a_M}$	$r_1 = k_1[(a_{1B}/a_M) - (1/K_1)(a_T/a_M^2)]$
$r_2 = \frac{k_3[a_M a_{2B} - (1/K_2)a_T]}{(K_T/K_M)a_T + a_M}$	$r_2 = k_3[(a_{2B}/a_M) - (1/K_2)(a_T/a_M^2)]$
$r_3 = k_5 a_{1B} [1 - (1/K_3)(a_{2B}/a_{1B})]$	$r_3 = k_5 (a_{1B}/a_M) [1 - (1/K_3)(a_{2B}/a_{1B})]$

could be neglected. The effect of internal diffusion was studied earlier as well. Some diffusion limitation was observed with the largest catalyst particles (>0.8 mm). However, because the percentage of fractions was very low (<1.5 wt.%), the diffusion resistance was assumed to be negligible and unsieved resin was used in the kinetic experiments.

### 3.1. Kinetic modelling

In the study, concerning published kinetic models for the etherification of isoamylenes with MeOH, Kiviranta-Pääkkönen et al. [6] found that the activity based models best describe the kinetic behaviour of the system. The model of Rihko et al. [4] and a model based on Langmuir–Hinshelwood (LH) mechanism presented originally by Oost and Hoffmann [5] both described well the data obtained from batch reactor experiments. Kiviranta-Pääkkönen et al. suggested some modifications for the model of Oost and Hoffmann, which are presented in detail in [6]. In the present study, the model by Rihko et al. [4] and the modified model from Kiviranta-Pääkkönen et al. were used as basic models and the effect of including of the solubility factors to these models were investigated.

The model of Rihko et al. [4] was based on the assumptions of Eley–Rideal (ER) type mechanisms. Only the alcohol and the ether was assumed to adsorb

to a considerable extent on the active sites of the catalyst. Oost and Hoffman [5] started their derivation from the LH approach assuming that the MeOH is the only component that is adsorbed and that there are no vacant site present on the catalyst surface since the reaction proceeds in the liquid-phase. On the contrary to the original paper of Oost and Hoffmann, Kiviranta-Pääkkönen et al. included in the rate equation the reaction equilibrium factor using the equilibrium constants from Table 2. Furthermore, Kiviranta-Pääkkönen et al. did not assume the isomerisation rate to be very fast compared to that of etherification rate and so the isomerisation equilibrium was not assumed.

The interaction between the resin and the reaction medium was investigated by including the reaction medium factors, the empirical,  $1/\delta_M$ , or the physico-chemical factor  $\Psi$ , for the models presented above. Table 3 presents the kinetic equations for the reactions of 2M1B to ether, 2M2B to ether and the isomerisation of 2M1B to 2M2B. In Table 4, the net rate of each main component in the etherification process — MeOH, 2M1B, 2M2B and TAME can be seen.

### 3.2. Parameter estimation

The parameters for the kinetic equations were estimated with the non-linear least-squares curve fitting

Table 4

The net rate of TAME ( $r_T$ ), MeOH ( $r_M$ ), 2M1B ( $r_{1B}$ ) and 2M2B ( $r_{2B}$ )

Basic kinetics	Factor $1/\delta_M$	Factor $\Psi$
$r_T = -r_M = r_1 + r_2$	$r_T = -r_M = (1/\delta_M)r_1 + (1/\delta_M)r_2$	$r_T = -r_M = \Psi r_1 + \Psi r_2$
$r_{1B} = -r_1 - r_3$	$r_{1B} = -(1/\delta_M)r_1 - (1/\delta_M)r_3$	$r_{1B} = -\Psi r_1 - \Psi r_3$
$r_{2B} = r_2 + r_3$	$r_{2B} = -(1/\delta_M)r_2 + (1/\delta_M)r_3$	$r_{2B} = -\Psi r_2 + \Psi r_3$

program KINFIT which uses an extensive data bank of the physical and chemical properties of the compounds [11]. The estimation was carried out minimising the weighted sum of residual squares (SRS) between the calculated ( $m_{\text{calc}}$ ) and experimental feed rates ( $m_{\text{exp}}$ ) of the compounds using a relative weight factor  $1/m_{\text{exp}}$  for each point. The Levenberg–Marquard method was used in the optimisation.

Prior to the estimation, the number of adjustable parameters was reduced by introducing some approximations. The ratio of adsorption coefficients ( $K_T/K_M = \exp(-3.5703 + 537.0/T)$ ) was based on the experimental rate data obtained by the splitting of TAME [3]. It was not possible to estimate accurately the reaction rate constant of the isomerisation of 2M1B to 2M2B with this experimental data. The ratio of 2M1B and 2M2B in the feed was very near to the thermodynamic equilibrium, causing minimal isomerisation of the isoamylenes and, therefore, the parameters for this reaction ( $k_5$  (353K) = 0.0688 mol/kg s,  $E_{\text{act}3} = 81600$  J/mol) was taken from our earlier batch reactor experiments where only one isoamylyene was present initially in the reaction mixture [4]. The particle porosity, which was used as  $\Phi_P$  in Eq. (2), was estimated to be 0.24 v/v accord-

ing to the product data sheet of Amberlyst 16 wet provided by the resin manufacturer Rohm & Haas.

The regression analysis was first carried out with the results of the experiments at 353 K. The results of the regression analysis are summarised in Table 5. The values of the parameters and their 95% confidence limits as well as the SRS are listed in the table. From the results of the regression analysis, it could be concluded that the model based on the ER type mechanism was more suitable to describe this experimental data than the model based on LH type mechanism. The weighted SRS was slightly higher for LH model than for model based ER type mechanism (see Fig. 2). With both tested kinetic models, the addition of the inverse of the empirical solubility factor  $\delta_M$ , decreased the SRS. The application of factor  $\Psi$  was not so successful for this set of data. Although with factor  $\Psi$ , the kinetic equation had one more parameter to adjust,  $\delta_P$ , the weighted SRS even increased slightly, if this factor was applied to the equations. The differences in the weighted SRS between the different models were not very large. This was to be expected, because in the earlier publication of Kiviranta-Pääkkönen et al. [6] both tested models were found to be good. The smallest SRS was obtained with the empirical factor,

Table 5  
Results of the regression analysis, the weighted SRS and values of the parameters at 353 K and 95% confidence limits

Solubility factor	Basis	SRS	Parameter	Value	At 95% confidence limits	
					Lower	Upper
	ER <sup>a</sup>	$4.78 \times 10^{-2}$	$k_1$ (mol/kg s)	0.1144	0.1114	0.1174
			$k_2$ (mol/kg s)	$6.50 \times 10^{-2}$	$6.27 \times 10^{-2}$	$6.74 \times 10^{-2}$
$1/\delta_M$	ER <sup>a</sup>	$4.18 \times 10^{-2}$	$k_1$ (mol Pa <sup>1/2</sup> /kg s)	$1.1259 \times 10^3$	$1.082 \times 10^3$	$1.170 \times 10^3$
			$k_2$ (mol Pa <sup>1/2</sup> /kg s)	$1.0429 \times 10^3$	$1.009 \times 10^3$	$1.077 \times 10^3$
$\Psi$	ER <sup>a</sup>	$4.98 \times 10^{-2}$	$k_1$ (mol/kg s)	0.1137	0.110	0.117
			$k_2$ (mol/kg s)	$6.44 \times 10^{-2}$	$6.16 \times 10^{-2}$	$6.72 \times 10^{-2}$
			$\delta_P$ (Pa <sup>1/2</sup> )	16457	12400	20500
	LH <sup>b</sup>	$6.87 \times 10^{-2}$	$k_1$ (mol/kg s)	0.0982	0.0954	0.1011
			$k_2$ (mol/kg s)	$4.99 \times 10^{-2}$	$4.76 \times 10^{-2}$	$5.21 \times 10^{-2}$
$1/\delta_M$	LH <sup>b</sup>	$6.09 \times 10^{-2}$	$k_1$ (mol Pa <sup>1/2</sup> /kg s)	$0.8775 \times 10^3$	$0.8365 \times 10^3$	$0.9185 \times 10^3$
			$k_2$ (mol Pa <sup>1/2</sup> /kg s)	$0.7982 \times 10^3$	$0.7665 \times 10^3$	$0.8300 \times 10^3$
$\Psi$	LH <sup>b</sup>	$7.63 \times 10^{-2}$	$k_1$ (mol/kg s)	$9.78 \times 10^{-2}$	$9.45 \times 10^{-2}$	$10.1 \times 10^{-2}$
			$k_2$ (mol/kg s)	$8.43 \times 10^{-2}$	$7.98 \times 10^{-2}$	$8.87 \times 10^{-2}$
			$\delta_P$ (Pa <sup>1/2</sup> )	16585	11800	21300

<sup>a</sup> ER type mechanism.

<sup>b</sup> LH type mechanism.

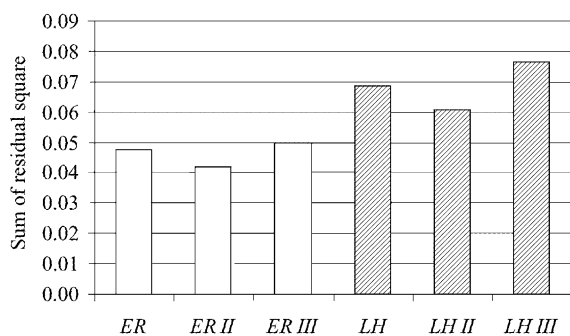


Fig. 2. The weighted SRS in the parameter estimation of experiments at 353 K for proposed kinetic equations: ER, ER with  $1/\delta_M$  (ER II), ER with  $\Psi$  (ER III), LH, LH with  $1/\delta_M$  (LH II) and LH with  $\Psi$  (LH III).

$1/\delta_M$ , applied in ER type mechanism. The adjustable parameters for the models were well identified with narrow confidence limits.

### 3.3. Temperature dependence

The applicability of the models was tested as well for all the experimental data between 323 and 353 K. The parameters for the models presented above were fitted to Arrhenius type temperature dependence. The temperature dependence of  $1/\delta_M$  and  $\Psi$  was taken into consideration according to Eqs. (1) and (2). The parameters  $k_i$  consist a product of the true kinetic constant and the adsorption coefficients of the components. As a result, we will obtain the apparent activation energies for the reactions. In order to avoid strong correlation between the parameters, 353 K was selected as reference temperature and the kinetic parameters

at this temperature and the activation energies were estimated. The differences between the tested models were found to be similar over the whole temperature range studied as with the estimation for experiments at 353 K. The model based on ER type mechanism was more suitable than the one based on LH type mechanism having the SRS  $1.42 \times 10^{-2}$  and  $1.92 \times 10^{-2}$ , respectively. With the model based on ER mechanism including the empirical factor  $1/\delta_M$  we obtained the smallest sum of residual square ( $1.28 \times 10^{-2}$ ). The results of the regression analysis, the kinetic parameters at 353 K and the apparent activation energies for the reactions of  $r_1$  ( $E_{act1}$ ) and  $r_2$  ( $E_{act2}$ ) (the reactions, see Table 3) are presented in Table 6. The obtained values of activation energies for reaction  $r_1$  and  $r_2$  were rather low, 42 and 67 kJ/mol, respectively.

It is likely that the MeOH mol fraction in the system affects to the catalyst activity. The polar alcohol swells the catalyst polymer structure and solvates the proton. After the solvation more active centres will be accessible, but they will be less acidic. It was found that the experimental rates of reactions were typically lower in the excess of MeOH than ones calculated with the model. The empirical factor  $1/\delta_M$  was found to be a function of the MeOH mol fraction of the mixture, which is presented in Fig. 3. Including the factor  $1/\delta_M$  in the equations, the calculated rates decreased clearly in excess MeOH mol fractions, which improved the fit.

In Fig. 3, the factor  $\Psi$  is presented as a function of MeOH mol fraction as well. The factor  $\Psi$  decreased strongly as a function the MeOH mol fraction. Increasing the MeOH mol fraction from 0.1 to 0.8 the factor  $\Psi$  decreased approximately to the half of the initial value. If we want to consider the differences

Table 6

Results of the regression analysis, the apparent activation energies and the values of parameters at 353 K and 95% confidence limits

Parameter	Value	At 95% confidence limits	
		Lower	Upper
$E_{act1}$ (J/mol)	42390	38840	45930
$E_{act2}$ (J/mol)	66891	62323	71459
$k_1$ (mol Pa <sup>1/2</sup> /kg s, 353 K)	$1.1321 \times 10^3$	$1.0994 \times 10^3$	$1.1648 \times 10^3$
$k_2$ (mol Pa <sup>1/2</sup> /kg s, 353 K)	$1.0432 \times 10^3$	$1.0177 \times 10^3$	$1.0688 \times 10^3$
Number of observations	460		
Number of coefficients	4		
Residual d.f.	456		
Residual mean square root	$1.06 \times 10^{-2}$		
Residual mean square	$1.12 \times 10^{-4}$		
SRS	$5.10 \times 10^{-2}$		

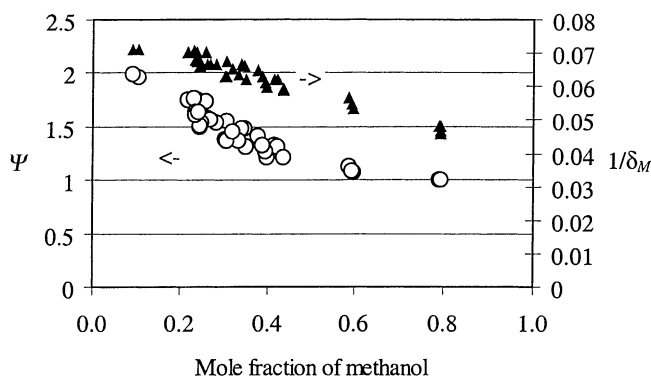


Fig. 3. The solubility factors  $\Psi$  and  $1/\delta_M$  as a function of MeOH mol fraction.

between the models, we have to compare the residuals of the models. The most important deviation between the basic ER type model and the one with empirical parameter  $1/\delta_M$  was under conditions where MeOH mol fraction was high. In the experiments, where the mol fraction of MeOH was between 0.415 and 0.791, the fit of the model including the solubility parameter was clearly better than without it.

#### 4. Conclusions

The applicability of solubility factor for the kinetics of TAME synthesis was studied. The kinetic equations based on the ER type mechanism was found to get better fit with the experimental data of TAME synthesis than one based on LH type kinetics. The model was further improved by including an empirical factor, the inverse of solubility factor into the kinetic equations of ER type mechanism.

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