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Chemical and Process Engineering 2020, 41 (4), 293–306
DOI: 10.24425/cpe.2020.136014

Kinetic investigations on esterification of maleic anhydride with butanols

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Kinetic studies of esterification reaction of maleic anhydride with butan-1-ol, 2-methylpropan-1-ol and butan-2-ol were carried out in a semibatch reactor, in the presence of four acidic catalysts: sulfuric acid, phosphotungstic acid, ion exchange resin Dowex 50WX8 and tetrabutyl zirconate. Phosphotungstic acid proved to be the most active catalyst. The temperature range was 383–413 K, the initial molar ratio of alcohol to acid ranged 2.2-5:1. The kinetic parameters were given. The kinetics appeared to be that of the second order with respect both to the acid and to the alcohol. The reaction carried out in the presence of tetrabutyl zirconate was very slow and depended only on acid concentration. The effect of temperature on the reaction rate follows the Arrhenius equation well.

Keywords: acidic catalysts, butyl alcohol, dibutyl maleate, esterification reaction, plasticizer

1. INTRODUCTION

The esterification reaction of maleic anhydride with butyl alcohol occurs in two stages (Fig. 1). In the first, rapid and practically going to the completion step, monoester monobutyl maleate is formed, which subsequently reacts with one molecule of butyl alcohol forming of diester – dibutyl maleate. This is a slow and reversible stage, therefore a catalyst is used. In industrial settings, the reaction is taken to completion by continuous removal of water from reaction system (Fischer et al., 2000; 2002; Liu et al., 2006a, 2006b; Nagasoe et al., 1999; Okabayashi et al., 2010; Reddy et al., 2005, Tuck et al., 2000).

Dibutyl maleate is widely used in industry, especially as a plasticizer for plastics. It can also be used for production of protective coatings, detergents, drugs, solvents such as tetrahydrofuran and γ-butyrolactone or butane-1,4-diol – an important intermediate in the polymer industry.

A review of the literature shows that while the synthesis of dibutyl maleate is well understood at a technological level, the kinetics of this reaction is still under investigation. In 1999–2005 a number of papers was published regarding the kinetics of the esterification reaction of maleic anhydride using higher molecular aliphatic alcohols – from C6 to C12. These studies were carried out with continuous removal of water from the reaction mixture (Grzesik et al., 1999, 2000; 2003; Kulawska et al., 2005a, 2005b). Only a few papers describing the kinetics of the esterification of maleic anhydride with low molecular weight C1-C4 alcohols were available in 20^{th} century. Sulfuric acid and its derivatives were used as catalysts (Alvarez and Alvarez, 1988; Dharwadkar and Hussain, 1977; Timofeev et al., 1985). Dharwadkar and Husain (1977) reported

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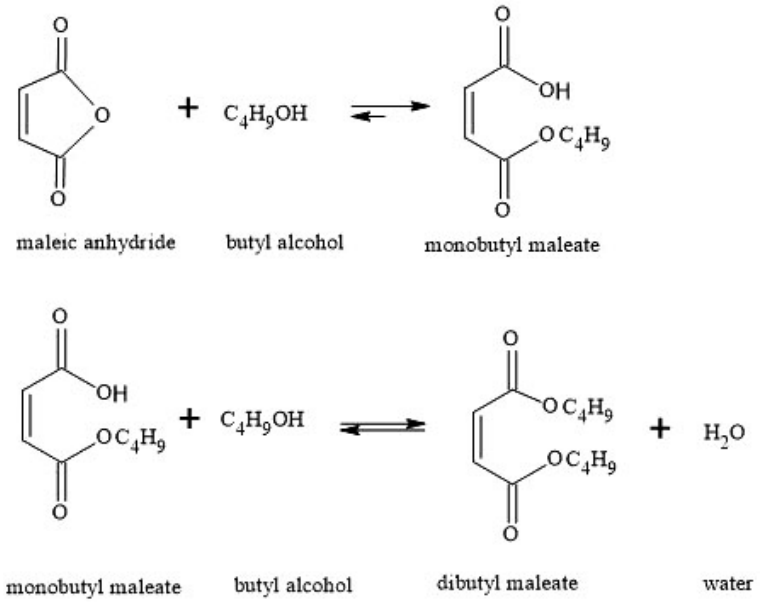

Fig. 1. Reaction scheme

the kinetics of the esterification of maleic anhydride with butan-1-ol in the presence of 4-methylbenzene-1-sulfonic acid. Timofeev et al. (1985) determined the kinetics of the non-catalytic reaction of monobutyl maleate with butan-1-ol to be that of a third order.

In the past few years, studies investigating the kinetics of the synthesis of C1-C4 alcohol maleates have focused on the use of non-toxic and eco-friendly heterogeneous catalysts. These kinetics studies were carried out in a batch reactor (Esfandmaz et al., 2018; Induri et al., 2010; Mulay and Rathod, 2017; Taysun et al., 2014; Yadav and Thathgar, 2002). Taysun et al. (2014) studied the esterification of maleic acid with butan-1-ol in the presence of Amberlyst-15 (dry and wet), Amberlyst 131H+ ion exchange resins and two deep eutectic solvents (DES). However, the tested range of reaction parameters was very limited and the conversion of maleic acid generally did not exceed 25% (Taysun et al., 2014). Mulay and Rathod (2017) applied Amberlyst-15 and Indion 225 catalysts in esterification reaction of maleic acid with butan-1-ol. The reaction carried out in the presence of Amberlyst-15 was determined as pseudo-first order and the high activation energy value of 299 kJ/mol was obtained.

The goal of the presented work was to carry out a wide range kinetic study of dibutyl maleate synthesis – using three butyl alcohol isomers and in the presence of four various acidic catalysts, in the conditions similar to industrial ones – with continuous removal of water from the reaction mixture. The esterification reactions of maleic anhydride with butan-1-ol, 2-methylpropan-1-ol and butan-2-ol in the presence of sulfuric acid, phosphotungstic acid, Dowex 50WX8 and tetrabutyl zirconate have been performed. Sulfuric acid is a highly effective and cheap catalyst, but it contributes to corrosion of the apparatus and production of large amounts of wastewater during catalyst neutralization. Phosphotungstic acid is a very active and selective esterification catalyst, less toxic than mineral acids (Alsalme et al., 2008; Dupont and Lefebre, 1996; Sepulveda et al., 2005). Dowex 50WX8 is a heterogeneous catalyst, which could readily be isolated from the reaction mixture and reused in the process many times after simply rinsing (Ali et al. 2007; 2009; Ju et al. 2011). Tetrabutyl zirconate is an easily available and nontoxic esterification catalyst used for long time in chemical production.

The dependence of the synthesis rate of dibutyl maleate on temperature, reactant concentration, butyl alcohol isomer and catalyst type has been investigated. The form of the kinetic equations was determined by integral method with statistical evaluation of the calculation results. The relationship of temperature on the reaction rate was determined by the Arrhenius equation.

2. EXPERIMENTAL SECTION

2.1. Materials

Maleic anhydride, butan-1-ol, 2-methylpropan-1-ol, butan-2-ol (min. 99% purity), sulfuric acid (96%) were purchased from Avantor Performance Materials Poland. Phosphotungstic acid, Dowex 50WX8 and tetrabutyl zirconate (80% solution in butan-1-ol) were purchased from Sigma Aldrich.

2.2. Catalysts

Sulfuric acid, phosphotungstic acid and Dowex 50WX8 are Brønsted acids (protic acids). Sulfuric acid is a strong acid. Its disadvantage is its potential for generating some amounts of by-products, giving a color change and blushing of a product. Phosphotungstic acid, is a heteropolyacid with a complex Keggin structure and the chemical formula $H_3[P(W_3O_{10})_4]\cdot 6H_2O$. It is a superacid, completely dissociated in aqueous solution. Flexible structure, proton mobility, and easy absorption of polar molecules make the catalytic reactions in the presence of heteropolyacid occur both on the surface and inside of their crystalline structure. (Kozhevnikov, 1987; Kozhevnikov et al,. 2008; Shanmungam et al., 2004). The weakest among used protonic catalysts – Dowex 50WX8 is a sulfonated gel ion-exchange resin based on a copolymer of styrene and divinylbenzene with a cross-linking degree of 8%. The concentration of inbuilt sulfonic groups is 1.7 mlq·dm^{-3}. The maximum operating temperature of Dowex 50WX8 is approximately 393 K (Iovel and Lukevics, 1998; The Dow Chemical Company, 2002). Tetrabutyl zirconate is a Lewis acid. In comparison to protic acids, it minimizes side reactions and does not degrade the alcohol (DuPont.Tyzor, 2001; Johnson Mattey Catalysts, 2003).

2.3. Apparatus

The investigations were conducted in isothermal conditions, in a thermostatic glass reactor of 1 dm^3 capacity. The reactor was equipped with a thermometer, a sampling cock, an azeotropic head with a reflux condenser and a high-speed magnetic stirrer. The equipment enabled water to be removed instantaneously and completely from the reacting mixture; a sufficiently high flow of inert gas was used. The level of the nitrogen flow was determined experimentally by using progressively increasing nitrogen flow rates until further increase in the flow rate had no effect. The water was removed from reaction system in form of azeotropic mixture with butyl alcohol. An alcohol loss was filled by an addition of a suitable amount of pure butyl alcohol. The content of water was analytically determined by electrometric titration using the method of Karl Fischer. Under these conditions the reaction can be assumed to be irreversible.

2.4. Method and procedure

All experiments were conducted under atmospheric pressure. Because of a rapid progress of the first stage of the reaction, the subject of the kinetic studies was, in fact, a slow reaction of esterification of monobutyl maleate with butyl alcohol. The kinetic studies were carried out in the range of the initial molar ratios of butyl alcohol to the maleic anhydride from 2.2:1 to 5:1 and in the range of temperatures from 383 to 413 K. The reaction temperature range depended on the type of butyl alcohol used. Reactions with the higher boiling butyl alcohol isomers, butan-1-ol and 2-methylpropan-1-ol were carried out in the range from 383 to 413 K, while those with the most volatile isomer – butan-2-ol up to 403 K. The reactions with butan-2-ol have gone only over the most active catalysts – sulfuric acid and phosphotungstic acid. The concentration of a given catalyst was determined experimentally and it was kept constant in each experimental batch.

Each experiment was repeated under the same experimental conditions and the average value of the acid conversion was calculated.

Butyl alcohol was charged into the reactor and heated to the boiling point. Maleic anhydride was added and the mixture thoroughly stirred was heated to a desired reaction temperature. Then the catalyst was added and the first sample was withdrawn to determine the initial concentration of acid. The samples were collected at irregular intervals dependent on the rate of the examined reaction. The samples were cooled immediately and the acid value, corrected for the catalyst acidity, was measured.

3. RESULTS AND DISCUSSION

The reaction system could be considered as homogeneous and irreversible under these experimental conditions. A slight change of the reaction mixture volume as a result of water removal could be considered as negligible. The form of the kinetic equation was determined through the transformation and integration of the equation of batch reactor balance. Seven different reaction orders were tested (Table 1). The assumed form of the kinetic equation was verified by graphical method using the linear regression function. In the evaluation of the estimation results, the value of residual variation coefficient, determination coefficient and range of 95% confidence interval for regression coefficient were taken into account. The equation was considered to be correctly assumed if:

1) the degree of matching the experimental points to the tested kinetic model was high.
2) the determined values of the reaction rate constant k for a given esterification reaction carried out at the same temperature, but with different values of the initial molar ratio of the reactants, were so

Table 1. Tested kinetic equations of the esterification of monobutyl maleate with butanol

Differential form		Integral form
$-\frac{dc_A}{dt} = k \cdot c_A$	$\frac{d\eta_A}{dt} = k \cdot (1-\eta_A)$	$k \cdot t = \ln(1-\eta_A)$
$-\frac{dc_A}{dt} = k \cdot c_A^2$	$\frac{d\eta_A}{dt} = k \cdot c_{A,0}\,(1-\eta_A)^2$	$k \cdot t = \frac{1}{c_{A,0}} \cdot \frac{\eta_A}{1-\eta_A}$
$-\frac{dc_A}{dt} = k \cdot c_A \cdot c_B$	$\frac{d\eta_A}{dt} = k \cdot c_{A,0}\,(1-\eta_A)\,(b_A-\eta_A)$ $b_A = \frac{c_{B,0}}{c_{A,0}}$	$k \cdot t = \frac{1}{c_{A,0}(b_A-1)} \ln \frac{b_A-\eta_A}{b_A(1-\eta_A)} \quad b_A \neq 1$
$-\frac{dc_A}{dt} = k \cdot c_A^{1,5}$	$\frac{d\eta_A}{dt} = k \cdot \sqrt{c_{A,0}} \cdot (1-\eta_A)^{1.5}$	$k \cdot t = \frac{2}{\sqrt{c}_{A,0}} \cdot \left(\frac{1}{\sqrt{(1-\eta_A)}} - 1\right)$
$-\frac{dc_A}{dt} = k \cdot c_A \cdot c_B^{0.5}$	$\frac{d\eta_A}{dt} = k \cdot \sqrt{c_{A,0}(b_A-\eta_A)} \cdot (1-\eta_A)$	$k \cdot t = \frac{1}{\sqrt{c_{A,0}(b_A-1)}} \cdot \ln\left(\frac{\sqrt{b_A-\eta_A}+\sqrt{b_A-1}}{\sqrt{b_A-\eta_A}-\sqrt{b_A-1}}\right)$
$-\frac{dc_A}{dt} = k \cdot c_A^{0.5} \cdot c_B$	$\frac{d\eta_A}{dt} = k \cdot \sqrt{c_{A,0}\,(1-\eta_A)} \cdot (b_A-\eta_A)$	$k \cdot t = \frac{-2}{\sqrt{c_{A,0}(b_A-1)}} \cdot \arctan\left(\frac{\sqrt{1-\eta_A}}{\sqrt{b_A-1}}\right)$
$-\frac{dc_A}{dt} = k \cdot c_A^{0.5} \cdot c_B^{0.5}$	$\frac{d\eta_A}{dt} = k \cdot \frac{1}{\sqrt{1-\eta_A} \cdot \sqrt{b_A-\eta_A}}$	$k \cdot t = -2\ln(\sqrt{1-\eta_A} + \sqrt{b_A-\eta_A}$

similar that the experimental points for all molar ratios could be treated as one set of data and plot one high-matching trendline for it.

3) for the reactions, the rate of which depended only on the concentration of monoester, the progress of the esterification reaction over time, at a constant temperature, at different values of the initial molar ratio of reactants should be similar.

The results of the best empirical data matching to kinetic model for tested reactions are presented in Tables 2–4 and Figs. 2–7. Determined residual variation coefficient values V_e for all experiments show that the differences between the predicted and the empirical values of dependent variable generally did not exceed 15%. The values of the determination coefficient R^2 above 0.96 indicate a strong linear relationship between the data. It can be concluded that the linear regression function is well fitted to the empirical data. The narrow ranges of the 95% confidence interval for the regression coefficient (usually much below 10% of the regression coefficient value) prove the precise determination of the reaction rate constant value.

Table 2. Linear regression function parameters for reactions described by the kinetic model: $r_A = k \cdot c_A^{1,5}$. Units of measure: k, S_k, 95% CI $[(\mathrm{dm^3 \cdot mol^{-1}})^{0.5} \cdot \mathrm{min^{-1}}]$; S_e $[(\mathrm{dm^3 \cdot mol^{-1}})^{0.5}]$

Catalyst	tetrabutyl zirconate					
Alcohol	butan-1-ol			2-methylpropan-1-ol		
Temperature	393 K	403 K	413 K	393 K	403 K	413 K
Molar ratio	2.5	2.2–3.0	2.5	2.5	2.2–3.0	2.5
$k \cdot 10^{-4}$	7.02	12.83	24.86	7.31	12.46	21.59
$S_k \cdot 10^{-4}$	0.14	0.33	0.38	0.18	0.39	0.55
$(95\% CI) \cdot 10^{-4}$	±0.30	±0.67	±0.84	±0.41	±0.79	±1.22
CI %	4.3%	5.2%	3.4%	5.6%	6.3%	5.6%
$S_e \cdot 10^{-4}$	150.88	429.90	231.46	156.95	657.19	316.79
V_e	6.2%	12.9%	5.1%	7.0%	16.5%	7.9%
R^2	0.995	0.978	0.997	0.995	0.966	0.994

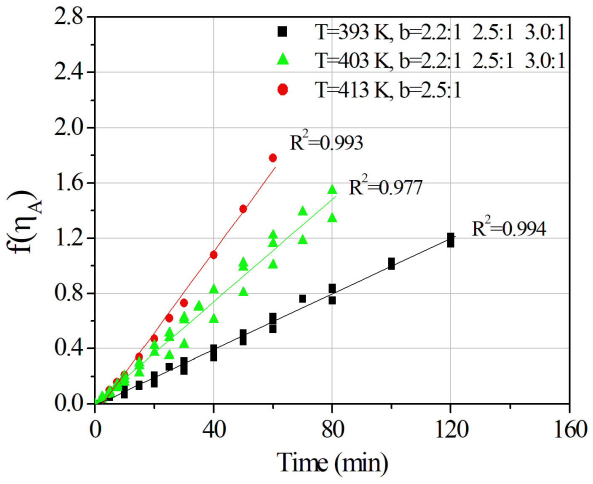

Fig. 2. Fit of experimental data to kinetic model ($r_A = kc_Ac_B^{0.5}$). Alcohol: 2-methylpropan-1-ol, catalyst: sulfuric acid

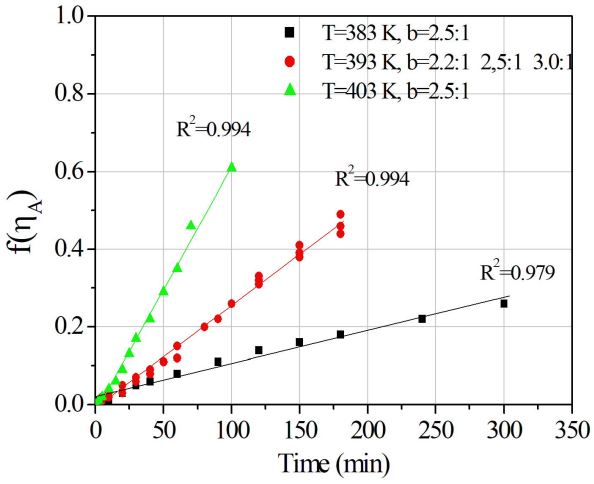

Fig. 3. Fit of experimental data to kinetic model ($r_A = kc_Ac_B$). Alcohol: butan-2-ol, catalyst: sulfuric acid

Table 3. Linear regression function parameters for reactions described by the kinetic model: $r_A = k \cdot c_A \cdot c_B^{0.5}$. Units of measure: k, S_k, *95% CI* $[(dm^3 \cdot mol^{-1})^{0.5} \cdot min^{-1}]$; S_e $[(dm^3 \cdot mol^{-1})^{0.5}]$

Catalyst	sulfuric acid					
Alcohol	butan-1-ol			2-methylpropan-1-ol		
Temperature	393 K	403 K	413 K	393 K	403 K	413 K
Molar ratio	2.5	2.2-5.0	2.5	2.2–3.0	2.2–3.0	2.5
$k \cdot 10^{-4}$	143.32	234.14	311.74	100.67	185.41	293.60
$S_k \cdot 10^{-4}$	4.42	3.91	16.44	1.24	4.52	7.89
$(95\%\ CI) \cdot 10^{-4}$	±9.86	±7.89	±36.18	±2.52	±9.14	±7.59
CI %	10.6%	3.4%	11.6%	2.5%	4.9%	6.0%
$S_e \cdot 10^{-4}$	476.04	443.34	742.32	290.56	682.10	510.73
V_e	9.9%	9.6%	14.9%	7.0%	12.9%	8.8%
R^2	0.991	0.988	0.970	0.994	0.977	0.993
Catalyst	phosphotungstic acid							
Alcohol	butan-1-ol				2-methylpropan-1-ol			
Temperature	383 K	393 K	403 K	413 K	383 K	393 K	403 K	413 K
Molar ratio	2.5	2.5	2.5–5.0	2.5	2.5	2.5	2.5–5.0	2.5
$k \cdot 10^{-4}$	45.04	115.73	441.86	710.05	39.36	103.35	357.06	694.80
$S_k \cdot 10^{-4}$	2.85	3.15	9.23	21.78	0.44	1.00	5.12	26.02
$(95\%\ CI) \cdot 10^{-4}$	±6.97	±6.50	±18.55	±49.26	±0.94	±2.05	±10.14	±57.26
CI %	15.5%	5.6%	4.2%	6.9%	2.4%	2.0%	2.8%	8.2%
$S_e \cdot 10^{-4}$	150.81	353.49	951.64	944.32	175.61	192.04	951.64	1134.62
V_e	13.0%	11.8%	13.8%	8.9%	3.9%	4.5%	14.5%	12.2%
R^2	0.977	0.983	0.979	0.992	0.998	0.998	0.976	0.985

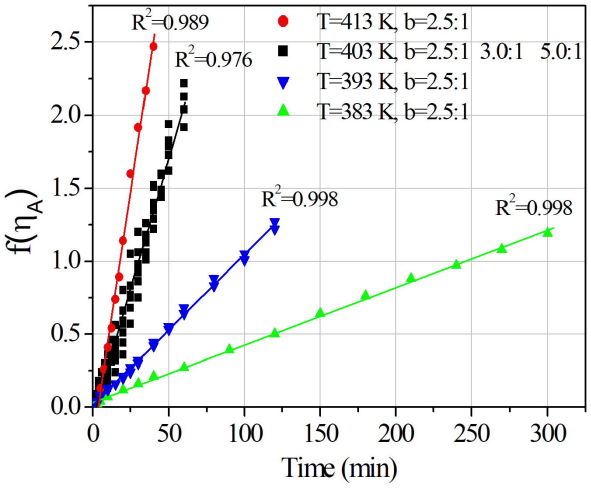

Fig. 4. Fit of experimental data to kinetic model ($r_A = kc_Ac_B^{0.5}$). Alcohol: 2-methylpropan-1-ol, catalyst: phosphotungstic acid

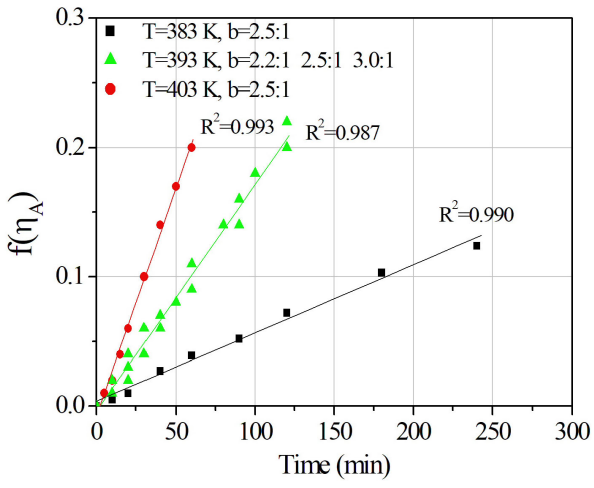

Fig. 5. Fit of experimental data to kinetic model ($r_A = kc_Ac_B$). Alcohol: butan-2-ol, catalyst: phosphotungstic acid

Table 4. Linear regression function parameters for reactions described by the kinetic model: $r_A = k \cdot c_A \cdot c_B$. Units of measure: k, S_k, 95% CI [dm^3·mol^{-1}· min^{-1}]; S_e [dm^3· mol^{-1}]

Catalyst	sulfuric acid			phosphotungstic acid		
Alcohol	butan-2-ol			butan-2-ol		
Temperature	383 K	393 K	403 K	383 K	393 K	403 K
Molar ratio	2.5	2.2–3.0	2.5	2.5	2.2–3.0	2.5
$k \cdot 10^{-4}$	8.48	26.29	62.94	5.34	17.54	35.48
$S_k \cdot 10^{-4}$	0.39	0.36	1.50	0.20	0.41	1.14
(95% CI) $\cdot 10^{-4}$	±0.88	±0.72	±3.31	±0.47	±0.84	±2.70
CI%	10.3%	2.8%	5.3%	8.8%	4.8%	7.6%
$S_e \cdot 10^{-4}$	126.48	122.73	156.38	46.06	79.17	67.16
V_e	11.5%	7.5%	8.3%	9.6%	9.9%	8.2%
R^2	0.979	0.994	0.994	0.990	0.987	0.993

Catalyst	Dowex 50WX8							
Alcohol	butan-1-ol				2-methylpropan-1-ol			
Temperature	383 K	393 K	403 K	413 K	383 K	393 K	403 K	413 K
Molar ratio	2.5	2.5	2.2–3.0	2.5	2.5	2.5	2.5–5.0	2.5
$k \cdot 10^{-4}$	3.92	10.54	57.18	109.79	3.87	12.49	56.46	78.61
$S_k \cdot 10^{-4}$	0.06	0.13	1.27	4.13	0.07	0.27	1.84	2.49
(95% CI) $\cdot 10^{-4}$	±0.13	±0.29	±2.55	±9.78	±0.16	±0.54	±3.82	±5.48
CI %	3.4%	2.8%	4.5%	8.9%	4.2%	4.3%	6.8%	7.0%
$S_e \cdot 10^{-4}$	67.81	64.34	841.71	158.18	88.77	201.93	363.78	268.64
V_e	5.4%	4.0%	12.2%	9.5%	6.1%	11.3%	14.9%	10.2%
R^2	0.997	0.998	0.975	0.990	0.996	0.985	0.977	0.989

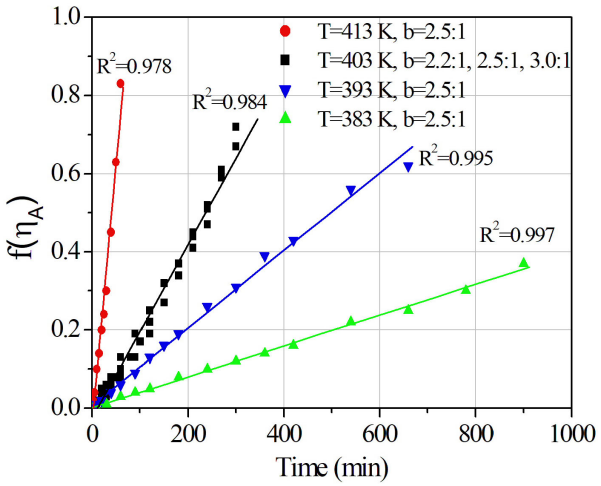

Fig. 6. Fit of experimental data to kinetic model ($r_A = kc_Ac_B$) Alcohol: butan-1-ol, catalyst: Dowex 50WX8

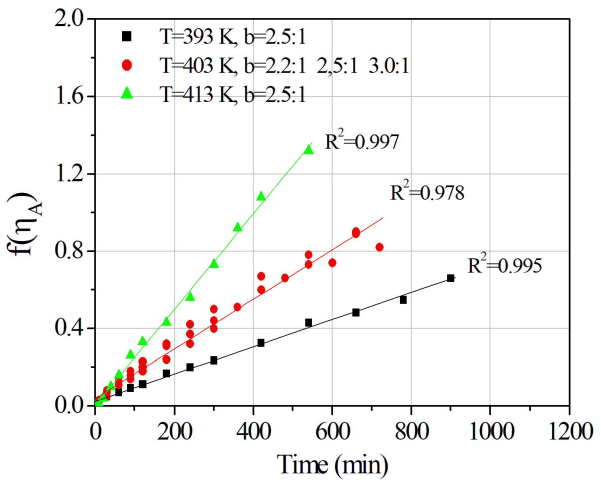

Fig. 7. Fit of experimental data to kinetic model ($r_A = kc_A^{1.5}$). Alcohol: butan-1-ol, catalyst: tetrabutyl zirconate

It was found that in similar reaction conditions primary butyl alcohols (butan-1-ol and 2-methylpropan-1-ol) revealed similar activity and they were much more active than the secondary isomer, butan-2-ol (Table 5, Fig. 8–10). This result is consistent with the generally accepted order of alcohol reactivity in esterification reactions. The greater steric hindrance, the slower course of the reaction (Morrison and Boyd, 1985).

Table 5. Determined reaction rates for esterification of monobutyl maleate with isomers of butyl alcohol at various reaction temperatures for $\eta_A = 0.60$ and $b = 2.5 : 1$

Catalyst	Alcohol	Catalyst concentration (mass%)	Determined reaction rate (mol·min^{-1}·dm^{-3}) × 10^{-3}			
			383 K	393 K	403 K	413 K
sulfuric acid	butan-1-ol	0.1	–	34.2	55.8	87.3
	2-methylpropan-1-ol	0.1	–	24.0	44.3	70.1
	butan-2-ol	0.35	3.5	11.0	26.3	–
phosphotungstic acid	butan-1-ol	0.5	10.8	27.6	105.6	169.6
	2-methylpropan-1-ol	0.5	9.4	24.7	85.3	166.0
	butan-2-ol	0.75	2.2	7.3	14.9	–
Dowex 50WX8	butan-1-ol	1.6	4,4	8.9	46.0	–
	2-methylpropan-1-ol	1.6	5.2	23.8	32.9	–
tetrabutyl zirconate	butan-1-ol	1.1	2.0	4.0	–	–
	2-methylpropan-1-ol	1.2	2.0	3.4	–	–

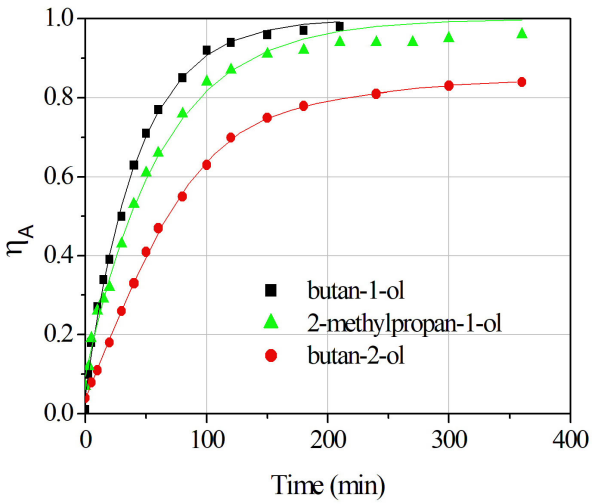

Fig. 8. Effect of butyl alcohol isomer. Catalyst: sulfuric acid, $T = 393$ K, $b = 2.5 : 1$

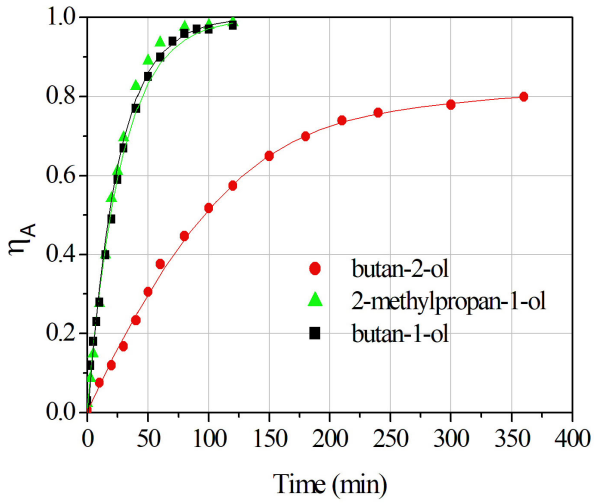

Fig. 9. Effect of butyl alcohol isomer. Catalyst: phosphotungstic acid, $T = 393$ K, $b = 2.5 : 1$

The catalyst activity increased with the acid strength:

Tetrabutyl zirconate ≪ Dowex 50WX8 < sulfuric acid, phosphotungstic acid

The homogeneous protonic acids: sulfuric acid and phosphotungstic acid revealed the highest activity in the tested reactions (Table 5, Figs. 11–13). The slowest reaction rates were obtained for esterification carried

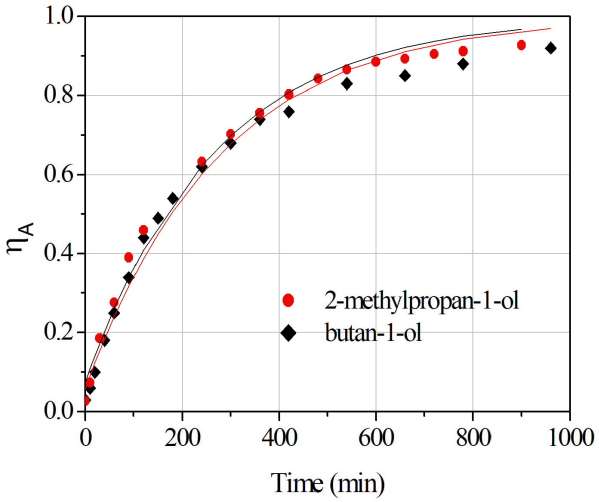

Fig. 10. Effect of butyl alcohol isomer. Catalyst: Dowex 50WX8, T = 393 K, b = 2.5 : 1

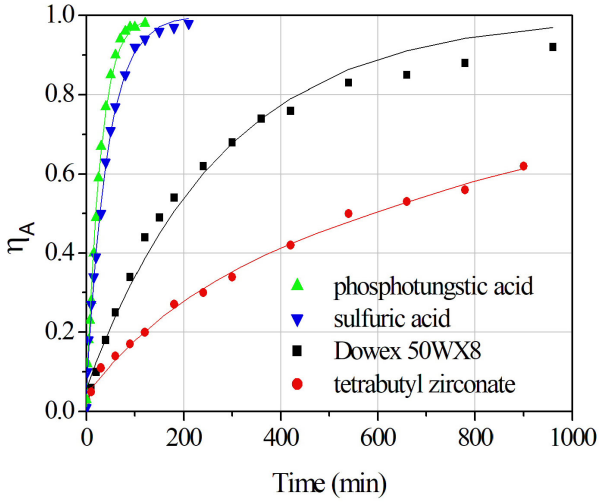

Fig. 11. Effect of different catalysts. Alcohol: butan-1-ol, T = 393 K, b = 2.5 : 1

out in the presence of tetrabutyl zirconate. This resulted from partial decomposition of tetrabutyl zirconate by water formed leading to dioxide zirconium formation. It could be seen as a turbidity of reaction mixture. The higher activity in dibutyl maleate synthesis was exhibited by heterogeneous catalyst Dowex 50WX8. It seems that some unexpected reaction rate values obtained for reaction with primary butyl alcohols in the presence of Dowex 50WX8 resin at temperatures higher than 393 K (Table 5) can be caused by the weak thermal stability of the catalyst over the temperature.

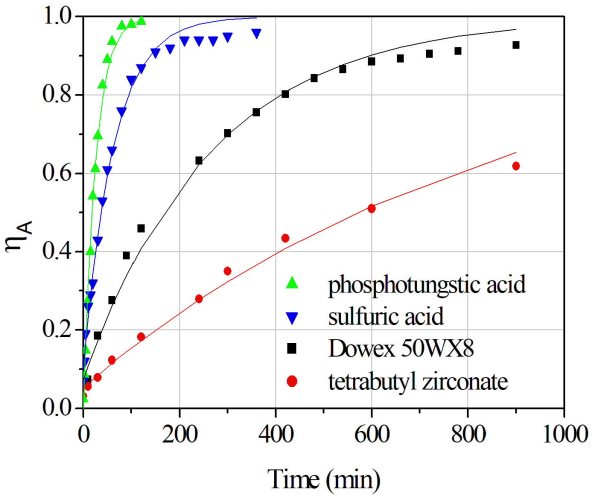

Fig. 12. Effect of different catalysts. Alcohol: 2-methylpropan-1-ol, T = 393 K, b = 2.5 : 1

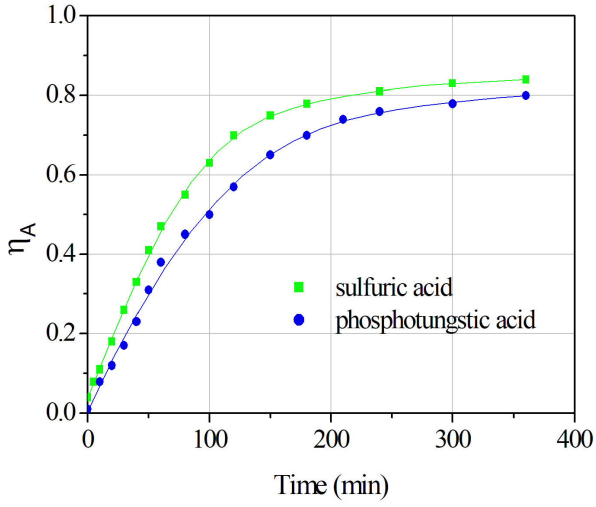

Fig. 13. Effect of different catalysts. Alcohol: butan-2-ol, T = 393 K, b = 2.5 : 1

The kinetic equation can be described by the general formula:

$$r_A = k \cdot c_A^{\alpha} c_B^{\beta} \tag{1}$$

The rate of most reactions was dependent on monoester and alcohol concentrations (Table 6, Figs. 14–16). Less sensitive to the alcohol concentration change were reactions carried out in the presence of the strong acidic catalysts – sulfuric acid and phosphotungstic acid. To a greater extent alcohol concentration affected the rate of reactions with less active isomer butan-2-ol or over less active catalyst such as Dowex 50WX8. The rate of the slowest esterification reactions in the presence of tetrabutyl zirconate was dependent only on the monoester concentration. These reactions were the most sensitive to the change of monoester

Table 6. Estimated kinetic parameters for esterification of maleic anhydride with butyl alcohols

Catalyst	Alcohol	Kinetic equation $r_A = k \cdot c_A^{\alpha} \cdot c_B^{\beta}$		Temperature range (K)	Pre-exponential factor $(dm^3 \cdot mol^{-1})^{(\alpha+\beta-1)} \cdot min^{-1}$	Activation energy $(kJ \cdot mol^{-1})$
		α	β			
sulfuric acid	butan-1-ol	1	0.5	393–413	3.59×10^6	63.2
	2-methylpropan-1-ol	1	0.5	393–413	4.17×10^7	72.3
	butan-2-ol	1	1	383–403	3.17×10^{14}	128.7
phosphotungstic acid	butan-1-ol	1	0.5	383–413	8.76×10^{14}	126.7
	2-methylpropan-1-ol	1	0.5	383–413	1.95×10^{15}	129.7
	butan-2-ol	1	1	383–403	2.33×10^{13}	121.8
Dowex 50WX8	butan-1-ol	1	1	383–413	4.72×10^{15}	140.3
	2-methylpropan-1-ol	1	1	383–413	4.17×10^{15}	139.2
tetrabutyl zirconate	butan-1-ol	1.5	0	393–413	1.48×10^8	85.2
	2-methylpropan-1-ol	1.5	0	393–413	3.73×10^6	73.1

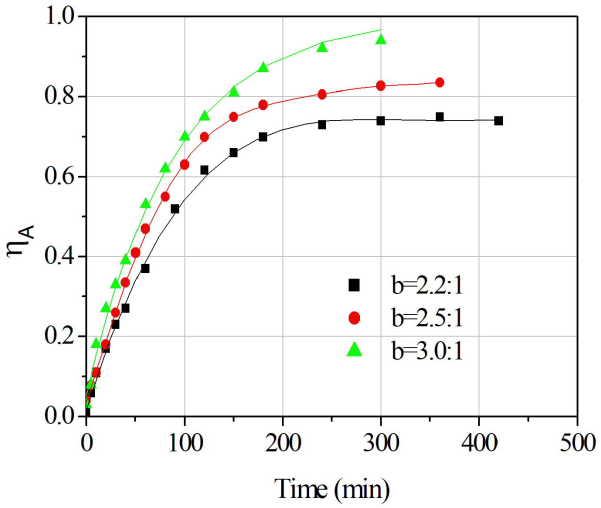

Fig. 14. Effect of molar ratio. Alcohol: butan-2-ol, catalyst: sulfuric acid, T = 403 K

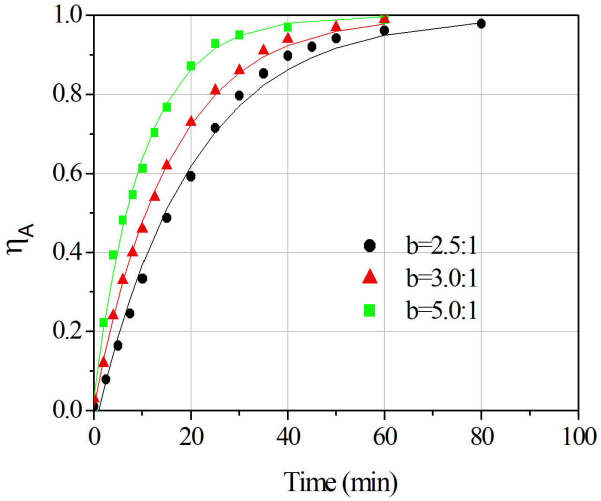

Fig. 15. Effect of molar ratio. Alcohol: 2-methylpropan-1-ol, catalyst: phosphotungstic acid, T = 403 K

concentration. It was the result of a "double" role of monoester, a substrate of the reaction and also, as a weak organic acid, a catalyst of the process (Grzesik et al., 2003).

The use of the low values of initial molar ratio of the alcohol to maleic anhydride made it possible to capture the effect of alcohol concentration change on the reaction rate. This is an empirical correlation, but consistent with commonly postulated kinetic model for these types of esterification reactions, described as a second order – first order with respect to acid and first order with respect to alcohol (March, 1992).

The determined activation energy values ranged from 63.2 to 140.3 $kJ \cdot mol^{-1}$ (Table 2), within the range obtained for most catalytic reactions: 40–240 $kJ \cdot mol^{-1}$ (Burghardt and Bartelmus, 2001). To the least degree the temperature affected reactions of primary butyl alcohols in the presence of sulfuric acid and tetrabutyl zirconate. The reactions carried out in the presence of tetrabutyl zirconate were so slow that

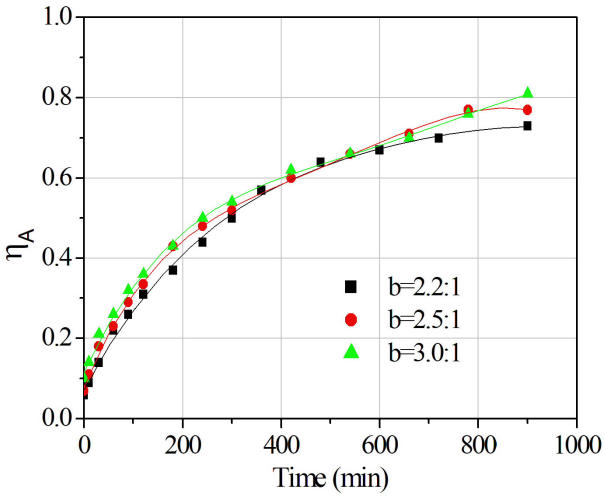

Fig. 16. Effect of molar ratio. Alcohol: butan-1-ol, catalyst: tetrabutyl zirconate, T = 403 K

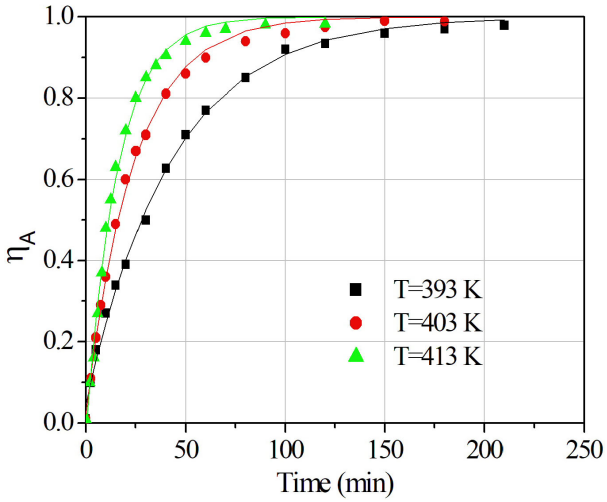

Fig. 17. Effect of temperature. Alcohol: butan-1-ol, catalyst: sulfuric acid, b = 2.5 : 1

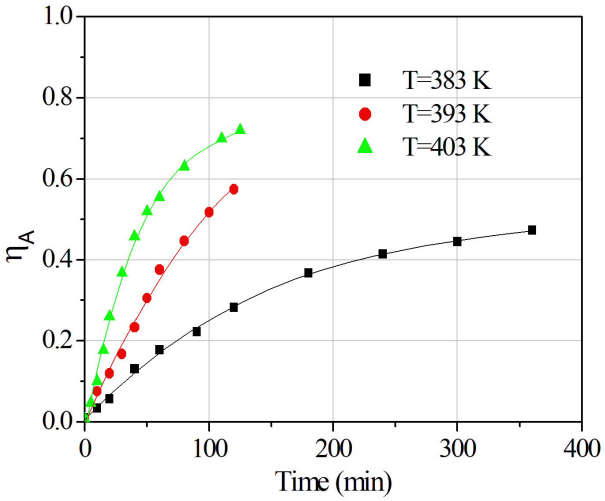

Fig. 18. Effect of temperature. Alcohol: butan-2-ol, catalyst: phosphotungstic acid, b = 2.5 : 1

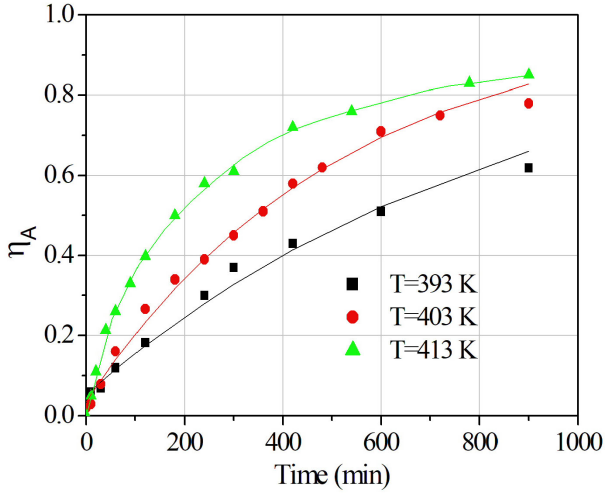

Fig. 19. Effect of temperature. Alcohol: 2-methylpropan-1-ol, catalyst: tetrabutyl zirconate, b = 2.5 : 1

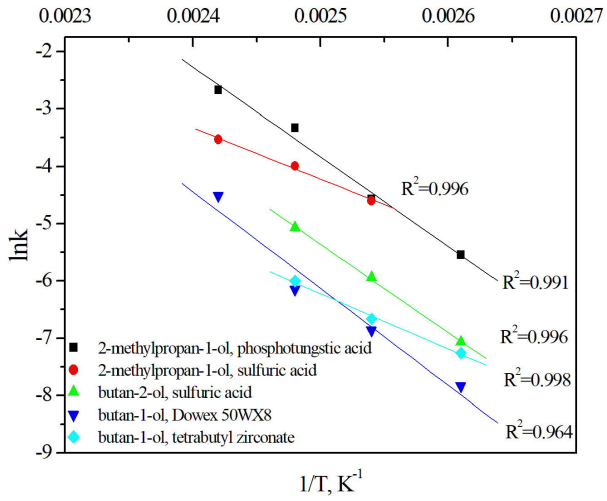

Fig. 20. Arrhenius plot for tested reactions, T = 383–413 K, b = 2.5 : 1

increase in temperature accelerated them only slightly. All reactions with butan-2-ol and with primary butyl alcohols performed in the presence of phosphotungstic acid and Dowex 50WX8 were sensitive to temperature change. In Figs. 17–20 the effect of the temperature on the reaction rate was presented.

4. SUMMARY

Kinetic investigations of the esterification of maleic anhydride with three isomers of butyl alcohol were performed to high conversion of acid at continuous removal of water from the reaction mixture. Kinetic models were presented. A good fit of empirical data to adopted models was confirmed by statistical analysis. It was found that the effect of the substrate concentration and the temperature on reaction rate depended on the catalyst used and was different for various isomers of butyl alcohol. The dependence of the reaction rate constant on the temperature follows well the Arrhenius equation. The application of a heterogeneous catalyst Dowex 50WX8 made the process much slower than classic homogeneous catalysts. Sulfuric acid harmful for environment could be replaced by heteropolyacid phosphotungstic acid that gave high yields in a short reaction time especially using both primary butyl alcohols.

The results of presented studies could be used to model this process in a greater scale.

SYMBOLS

b	initial molar ratio of butyl alcohol to maleic anhydride
b_A	initial molar ratio of butyl alcohol to monobutyl maleate, $b_A = b - 1$
c_A	molar concentration of monobutyl maleate (mol·dm^{-3})
c_B	molar concentration of butyl alcohol (mol·dm^{-3})
c_{cat}	catalyst concentration (mass%)
95% CI	the 95% confidence interval for regression coefficient in general population, $CI = t_\alpha \cdot S_k$, where: t_α – critical value of the Student's t – distribution for significance level $\alpha = 0.05$ and $n - 2$ degrees of freedom
CI%	the 95% confidence interval for regression coefficient related to regression coefficient value: $CI\% = (CI \cdot k^{-1}) \cdot 100\%$
E_a	activation energy (J·mol^{-1})
k_o	pre-exponential factor
k	reaction rate constant as a product of catalyst concentration and constant k', $k = k' \cdot c_{cat}$, regression coefficient
r	reaction rate (mol·min^{-1}·dm^{-3})
S_k	standard error of regression coefficient
S_e	standard error of the estimate, residual standard deviation
t	reaction time (min)
T	reaction temperature (K)
V_e	residual variation coefficient, $V_e = (S_e \cdot \overline{y}^{-1}) \cdot 100\%$, where $\overline{y}$ – arithmetic mean of the dependent variable values
η_A	conversion of monobutyl maleate
α	reaction order with respect to monobutyl maleate
β	reaction order with respect to butyl alcohol

Subscripts

A	monobutyl maleate
B	butyl alcohol

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Received 22 July 2020
Received in revised form 22 November 2020
Accepted 24 November 2020