Kinetics of esterification of methacrylic acid with a mixture of methanol and water in the presence of sulfuric acid

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The basic kinetic data of the second consecutive reversible reaction taking place in esterification of methacrylamide sulfate with a mixture of methanol and water were measured. The rate constants, frequency factors, activation entropies, and activation energy for primary reaction ($E_1 = 52.8$ kJ mol^{-1}) and inverse reaction ($E_2 = 31.9$ kJ mol^{-1}) as well as reaction enthalpy ($\Delta H = E_1 - E_2 = 20.9$ kJ mol^{-1}) were calculated. Moreover, the dependence of the rate of conversion on excess water, methanol, and quantity of sulfuric acid was measured. The influence of the quantity of sulfuric acid manifests itself more significantly than the influence of temperature. An excess of water reduces the values of rate constants of the primary reaction as well as inverse reaction calculated on the assumption that these reactions are second-order reactions. An excess of methanol raises the value of formal equilibrium constant.

Были измерены основные кинетические параметры второй последовательной обратной реакции этерификации метакриламидсульфата смесью метанола с водой. Из их температурных зависимостей были рассчитаны константы скорости, частотные факторы, энтропия активации, энергии активации для прямой ($E_1 = 52,8$ кДж моль$^{-1}$) и обратной ($E_2 = 31,9$ кДж моль$^{-1}$) реакций, а также энтальпия реакции $\Delta H = E_1 - E_2 = 20,9$ кДж моль$^{-1}$. Далее была измерена зависимость скорости конверсии от избытка воды, метанола и количества серной кислоты. Влияние количества серной кислоты более значительно, чем влияние температуры. Избыток воды снижает скорость прямой и обратной реакций, рассматриваемых как реакции 2 порядка. Избыток метанола ведет к увеличению формальной константы равновесия.

The synthesis of the methyl ester of methacrylic acid (methyl methacrylate) has two important steps. It is the preparation of the amide of methacrylic acid (amidation) and its esterification giving rise to methyl methacrylate. The esterifica-

tion of methacrylamide sulfate itself is a complicated reaction involving two consecutive reactions which yield the required product, *i.e.* methyl methacrylate. The product of amidation — methacrylamide sulfate (MAAS) reacts with water in acid medium to give methacrylic acid (MAC) [1, 2] which is subsequently esterified by methanol in the presence of water and sulfuric acid to yield methyl methacrylate (MMA). Some side reactions of methanol taking place in the medium of sulfuric acid also accompany the esterification of MAAS.

The esterification of MAC with methanol (MeOH) in flow-through system in the presence of acid catex functioning as a catalyst has been described in literature [3]. The esterification of MAC with methanol catalyzed by sulfuric acid has been also reported [4]. However, the influence of water was not taken into account in that paper and the esterification was performed under conditions different from the conditions of complex esterification of MAAS with an aqueous solution of methanol. The aim of this study was to obtain basic kinetic data for the reaction of MAC with methanol in the presence of water and sulfuric acid under conditions resembling the conditions of complex esterification of MAAS.

Experimental

Chemicals

The following chemicals were used: Methacrylic acid (Merck), $\varrho^{20} = 1.015$ kg m^{-3}, m.p. 15—16 °C, b.p. 161—163 °C (101 kPa), $n_D^{20} = 1.4314$; methanol, anal. grade (Lachema, Brno); γ-butyrolactone, anal. grade (Fluka); hydroquinone (Lachema, Brno); 2,6-di-*tert*-butyl-4-methyl-1-hydroxy-benzene (ChZJD, Bratislava), and picric acid (Lachema, Brno).

Kinetics of esterification

The kinetic measurements were carried out in a jacketed glass reactor equipped with a temperature sensor, stirrer, and sampling cock at the bottom. The temperature in reactor was held constant by means of ultrathermostat within the range ± 1.5 °C. The number of revolutions of the stirrer was constant. γ-Butyrolactone (γ-BL) which did not react under reaction conditions was used as homogenizing solvent.

A mixture of water with H$_2$SO$_4$, γ-BL, inhibitors, and MAC were put into the thermostated reactor. Finally, MeOH was added and after 2 min stirring at higher revolutions the time started to be read. The samples were taken in regular time intervals. The values of equilibrium concentration were determined for $t = 180$ min. The reaction mixture was stabilized by a mixed inhibitor, *i.e.* hydro-

quinone and picric acid in mole ratio 1:1, used in the amount of 1.5 mass %, referred to MAC. The volume of reactor was calibrated. Its initial and final state was ascertained and the initial and final mass of reaction mixture was weighed. The arithmetic means of values were used for calculation and evaluation of kinetics. Samples were taken in certain time intervals and analyzed by gas chromatographic methods [2, 5] for the content of MAC and MeOH. The evaluation was performed according to known kinetic relationships [6, 7].

The investigated reaction may be described by the scheme

$$A_1 + A_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} B_1 + B_2 \tag{A}$$

where $A_1 = MAC$, $A_2 = MeOH$, $B_1 = MMA$, and $B_2 = H_2O$.

It results from the following differential equation

$$\frac{dx}{dt} = k_1(A_{01} - x)(A_{02} - x) - k_2(B_{01} + x)(B_{02} + x) \tag{1}$$

that the formal equilibrium constant is given by the expression

$$K = \frac{k_1}{k_2} = \frac{(B_{01} + \bar{x})(B_{02} + \bar{x})}{(A_{01} - \bar{x})(A_{02} - \bar{x})} \tag{2}$$

where k_1 and k_2 are formal rate constants of the primary and inverse reaction $(dm^3\ mol^{-1}\ min^{-1})$ because concentrations of reactants and products are different from their activities. A_{0i} and B_{0i} are initial concentrations of reactants and products in the time moment $t = 0$ (mol dm^{-3}), and x is decrease in concentration of reactants (conversion) (mol dm^{-3}) in the time moment t whereas $\bar{x}$ is decrease in concentration of reactants (conversion) (mol dm^{-3}) in the time moment when the equilibrium has been established.

Expression (2) can be rearranged into the form of quadratic equation for the roots of which the subsequent relations are valid

$$\bar{x} + \bar{x}' = \frac{1}{K-1}[K(A_{01} + A_{02}) + B_{01} + B_{02}] \tag{3}$$

$$\bar{x}\bar{x}' = \frac{KA_{01}A_{02} - B_{01}B_{02}}{K-1} \tag{4}$$

After rearranging by means of eqns (2—4) and integrating, eqn (1) assumes the form

$$Q = \ln\left[\left|\frac{\bar{x}}{\bar{x}'}\right| \cdot \left|\frac{\bar{x}' - x}{\bar{x} - x}\right|\right] = PMt \tag{5a}$$

where

$$P = \bar{x}' - \bar{x} \tag{5b}$$

and

$$M = k_1 - k_2 \qquad (5c)$$

The values of Q, P, and M were computed for each time moment. The product PM was determined from eqn ($5a$) adjusted by linear regression. The constants k_1 and k_2 were calculated from eqns (2) and ($5c$).

Results and discussion

The temperature dependence of the course of esterification was measured for temperatures $\Theta/°C$ 55, 58, 64, 85, 92, and 93. The last two values differ from each other in the temperature of heating medium in reactor. At the temperature of jacket of 100 °C, the temperature inside the reactor was 92 °C, while at the temperature of jacket of 120 °C the temperature of 93 °C was reached in the reactor. But the values of rate constants changed minimally.

The variation of MAC conversion with time is represented for individual temperatures in Fig. 1. The linearized forms of eqn ($5a$) are represented in Fig. 2.
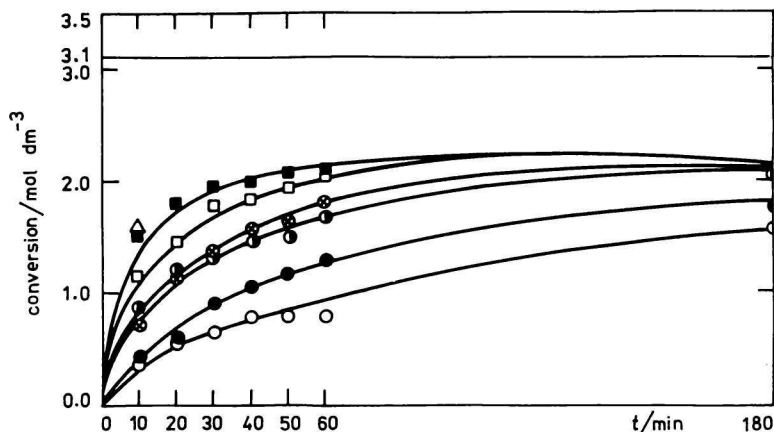

Fig. 1. Temporal dependence of MAC conversion at different temperatures.
○ 55 °C; ● 58 °C; ◐ 64 °C; ⊗ 75 °C; □ 85 °C; ■ 92 °C; △ 93 °C.

The values of rate constants as well as formal equilibrium constants are given for individual temperatures in Table 1.

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Table 1

Values of rate constants and formal equilibrium constant for
individual temperatures

| Temperature $\Theta/°C$ | K | $k_1 \cdot 10^3$ | $k_2 \cdot 10^4$ |
		$dm^3\ mol^{-1}\ min^{-1}$	$dm^3\ mol^{-1}\ min^{-1}$
55	4.51	1.62	3.63
58	6.30	2.85	4.53
64	10.14	4.82	4.75
75	10.21	5.43	5.32
85	10.85	10.75	9.91
92	11.39	15.00	13.15
93	10.48	14.50	13.84

The values of frequency factor and activation energy E_i of the primary as well as inverse reaction were determined by means of the linearized Arrhenius equation (Fig. 3)
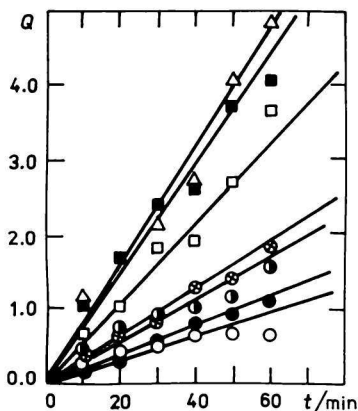

Fig. 2. Verification of kinetic equation (*5a*) for different temperatures.
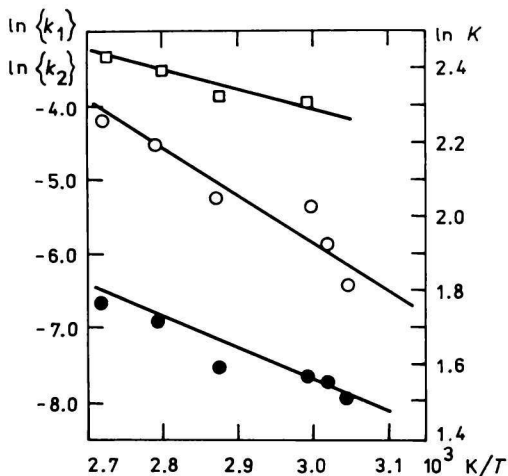○ 55°C; ● 58°C; ◑ 64°C; ⊗ 75°C; □ 85°C; ■ 92°C; △ 93°C.

Fig. 3. Variation of rate constants and formal equilibrium constant with temperature.
○ ln $\{k_1\} = -6.35 \times (10^3\ K/T) + 13.20$;
● ln $\{k_2\} = -3.83 \times (10^3\ K/T) + 3.75$;
□ ln $K = -2.52 \times (10^3\ K/T) + 9.45$.

$$\ln \{k_i\} = \left[-\frac{E_i}{R} \right] \cdot \frac{10^3}{T} + \ln \{k_{0i}\} \tag{6}$$

Symbol $\{k\}$ stands for numerical value of k. The values of k_1, k_2, and K obtained by means of eqn (6) are given in Table 2.

Table 2

Values determined by means of linearized eqn (6)

Parameter	K	k_1	k_2
$-E_i/R$ K	-2.5182	-6.3547	-3.8340
$\ln \{k_{0i}\}$	9.4495	13.2051	3.7478
$S_{\ln \{k_i\}}$	0.2340	0.2303	0.1658
$S_{\ln \{k_{0i}\}}$	2.4315	2.3903	1.7203
$S_{(-E_i/R\ K)}$	0.8361	0.8219	0.5915
E_i (kJ mol^{-1})$^{-1}$	20.9 ± 7.0	52.8 ± 6.8	31.9 ± 4.9
k_{0i} (dm^3 mol^{-1} min^{-1})$^{-1}$	12 702	543 128	42.428

S — standard deviation of the corresponding value.

The forms of eqn (6) for individual k_i are as follows

$$\{k_1\} = 5.43 \times 10^5 \exp \frac{(-52.8 \pm 6.8) \text{ kJ mol}^{-1}}{RT} \tag{7a}$$

$$\{k_2\} = 4.24 \times 10 \exp \frac{(-31.9 \pm 4.9) \text{ kJ mol}^{-1}}{RT} \tag{7b}$$

$$K = 1.27 \times 10^4 \exp \frac{(-20.9 \pm 7.0) \text{ kJ mol}^{-1}}{RT} \tag{7c}$$

A confrontation of kinetic parameters published in [4] with the values found by us is given in Table 3.

It is evident (Table 3) that the values corresponding to the primary reaction are in good agreement. Great differences appear in the values corresponding to inverse reaction and formal equilibrium constant. These differences are due to different concentrations of water in the reaction mixture at the start of reaction. The authors of paper [4] had no water in the reaction mixture in the time moment $t = 0$ owing to which the formation of MMA was favoured.

The activation entropies for individual reactions were calculated from the expression stated in paper [8]

$$\Delta S_{298}^{\star} = (19.159 \log k_{0i} - 253.43) \text{ J K}^{-1} \text{ mol}^{-1}$$

Table 3

Confrontation of the kinetic parameters presented in paper [4]
with the values found in this study

Ref. [4]	This paper
$E_1 = 53.6$ kJ mol^{-1}	$E_1 = 52.8$ kJ mol^{-1}
$E_2 = 2.1$ kJ mol^{-1}	$E_2 = 31.9$ kJ mol^{-1}
$\Delta H = 51.5$ kJ mol^{-1}	$\Delta H = 20.9$ kJ mol^{-1}
$k_{01} = 5.6 \times 10^5$ dm^3 mol^{-1} min^{-1}	$k_{01} = 5.43 \times 10^5$ dm^3 mol^{-1} min^{-1}
$k_{02} = 3.9 \times 10^3$ dm^3 mol^{-1} min^{-1}	$k_{02} = 4.24 \times 10^1$ dm^3 mol^{-1} min^{-1}
$K_0 = 1.4 \times 10^8$	$K_0 = 1.27 \times 10^4$

$K_0 = k_{01}/k_{02}$, $\quad \Delta H = E_1 - E_2$.

where k_{0i} has the dimension of rate constant (s^{-1}). We obtained

$$\Delta S_1^{\ddagger}(298 \text{ K}) = -177.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_2^{\ddagger}(298 \text{ K}) = -256.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{eq}^{\star}(298 \text{ K}) = -208.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

The numerical values of activation parameters do not significantly differ from the values commonly reported for the esterification of organic acids with alcohols catalyzed by acid catalysts.

Esterification of MAAS with aqueous solution of methanol is affected by free H_2SO_4. If the amidation is performed with a mixture of ACH and H_2SO_4 in mole ratio 1 : 1.5, 0.5 mole of H_2SO_4 (13.1 mass %) occurs in the reaction mixture at the beginning of esterification.
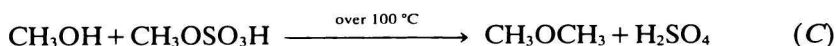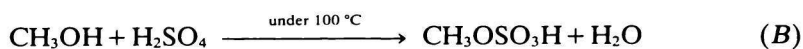
The aim of measurement was to ascertain the influence of H_2SO_4 concentration on one consecutive reaction, *i.e.* esterification of MAC with aqueous solution of methanol. The conditions of esterification were as follows: temperature 92 °C (in reactor), mole ratio MAC : H_2O = 1 : 4 (excess water), mole ratio ACH : MeOH = 1 : 1.66. The mass fraction of H_2SO_4 in the reaction mixture changed from 13.1 mass % (0.5 mole of H_2SO_4 in the reaction mixture) to 8.44, 5.79, and 1.51 mass % of H_2SO_4. Linearized relationships (*5a*) are represented in Fig. 4 which shows clearly that the formal equilibrium constant of esterification increases with concentration of H_2SO_4 in the reaction mixture (see also Table 4 which contains the rate constants and formal equilibrium constants for the values of mass fractions of H_2SO_4 used).

Table 4

Variation of rate constants and formal equilibrium constant
with mass fraction of H_2SO_4

Mass fraction of H_2SO_4 in %	K	$k_1 \cdot 10^3$	$k_2 \cdot 10^4$
		$dm^3 \, mol^{-1} \, min^{-1}$	$dm^3 \, mol^{-1} \, min^{-1}$
13.10	11.39	15.00	13.15
8.44	8.38	6.34	7.57
5.79	7.50	3.92	5.23
1.51	2.35	1.20	5.10

However, the negative effects of H_2SO_4 in the complex reaction reported in [2, 9] as well as the possibility of side reactions interfere with the raise of H_2SO_4 concentration

$$CH_3OH + H_2SO_4 \xrightarrow{\text{under } 100\,°C} CH_3OSO_3H + H_2O \qquad (B)$$

$$CH_3OH + CH_3OSO_3H \xrightarrow{\text{over } 100\,°C} CH_3OCH_3 + H_2SO_4 \qquad (C)$$

Which of the reactions in system (B, C) prevails can be forecast mainly on the basis of reaction temperature.

It appeared that the influence of the amount of H_2SO_4 functioning as an accelerator of esterification was more significant than the influence of temperature. This phenomenon is the cause of the difficulties accompanying the evaluation of kinetics of the complex esterification of MAAS with aqueous solution of methanol. At temperatures under 100 °C the reaction of methanol with H_2SO_4 giving rise to methyl hydrosulfate prevails which results in consumption of H_2SO_4 in the system. Provided the temperature rise does not overreach 100 °C, the effect of H_2SO_4 decrease exceeds the effect of temperature increase [2]. That manifests itself in the evaluation of kinetics of the complex esterification of MAAS by apparent decrease in the values of rate constants k_1 and k_2 with increasing temperature.

In technical practice the esterification of MAAS is performed with a mixture of water and methanol. The content of water is an important factor. The measurements were carried out under the following constant conditions: temperature of heating medium was 100 °C (according to the quantity of water the temperature of reaction mixture in the reactor varied) at 13.1 mass % of H_2SO_4 and mole ratio MAC : MeOH = 1 : 1.66. Mole ratio MAC : H_2O was 1 : 10, 1 : 6, 1 : 4, and 1 : 2. Linearized relationships $(5a)$ are represented in Fig. 5. The values of constants k_1 and k_2 decrease with increasing content of water in the reaction mixture. The rate
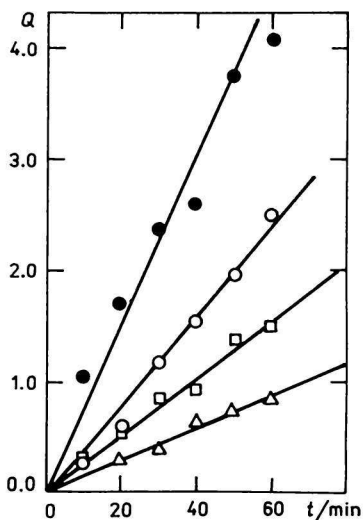
Fig. 4. Verification of kinetic equation (*5a*) for different mass fractions of H_2SO_4.
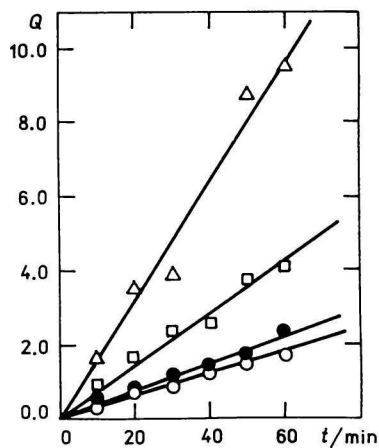● 13.10 mass % of H_2SO_4; ○ 8.44 mass % of H_2SO_4; □ 5.79 mass % of H_2SO_4; △ 1.50 mass % of H_2SO_4.

Fig. 5. Verification of kinetic equation (*5a*) for different mole ratios MAC : H_2O.
○ 1 : 10; ● 1 : 6; □ 1 : 4; △ 1 : 2.

of esterification intensely increases with decreasing content of water. This fact is not due merely to a change of reaction temperature which amounts to 3—4 °C at most (Table 5).

The formal equilibrium constant shows a maximum for the values of mole ratio MAC : H_2O of about 1 : 6 or 1 : 4. The numerical values of constants k_1 and k_2 decrease with increasing excess of water.

Table 5

Formal equilibrium constant and rate constants measured as a function of mole ratio MAC : H_2O

MAC : H_2O	K	$k_1 \cdot 10^3$	$k_2 \cdot 10^4$	Temperature in reactor
		$dm^3\ mol^{-1}\ min^{-1}$	$dm^3\ mol^{-1}\ min^{-1}$	$\Theta/°C$
1 : 10	9.82	4.58	4.66	91.0
1 : 6	13.89	7.35	5.29	91.0
1 : 4	11.39	15.00	13.15	92.0
1 : 2	9.60	29.28	30.49	94.0

An excess of methanol like water significantly influences the esterification of MAC with methanol. As it is a reversible reaction, an excess of water hinders the formation of MMA, while an excess of methanol enhances the equilibrium shift in favour of MMA.

The influence of excess methanol was investigated for the temperature of heating medium of 100 °C (temperature in reactor varied according to the excess of MeOH in the reaction mixture), mole ratio MAC:H_2O = 1:4, and mass fraction of H_2SO_4 equal to 13.1 %. The excess of MeOH varied in ratios MAC:MeOH = 1:5, 1:3, 1:1.66, and 1:1. Linearized relationships (5a) are represented in Fig. 6. Table 6 contains the rate and equilibrium constants for individual mole ratios.
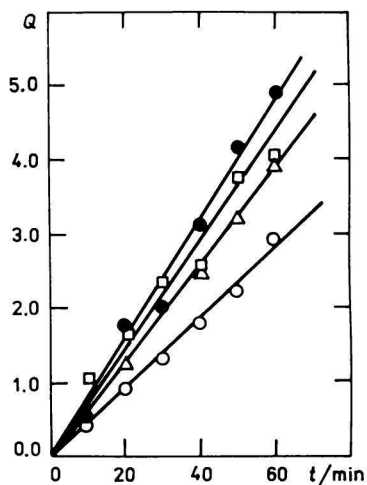

Fig. 6. Verification of kinetic equation (5a) for different mole ratios MAC:MeOH.
○ 1:5; ● 1:3; □ 1:1.66; △ 1:1.

Table 6

Formal equilibrium constant and rate constants measured as a function of mole ratio MAC:MeOH

MAC:MeOH	K	$k_1 \cdot 10^3$	$k_2 \cdot 10^4$	Temperature in reactor
		$dm^3\ mol^{-1}\ min^{-1}$	$dm^3\ mol^{-1}\ min^{-1}$	$\Theta/°C$
1:5	97.52	5.62	0.58	83.0
1:3	14.20	11.50	8.10	87.0
1:1.66	11.39	15.00	13.15	92.0
1:1	8.33	12.55	15.07	95.0

The formal equilibrium constant K increases with the excess of methanol. The rate constant of primary reaction k_1 decreases, whereas the rate constant of inverse reaction k_2 decreases more rapidly. This decrease is related with a decrease in reaction temperature ($-\Delta t = 12$ °C).

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