

KINETICS OF ESTERIFICATION OF TEREPHTHALIC ACID WITH ETHYLENE GLYCOL

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Kinetics of the esterification of terephthalic acid with ethylene glycol was studied at the boiling point of the reaction mixture under elevated pressure, with and without addition of cobalt and manganese acetates as catalyst. Data on the time dependence of the composition of the reaction mixture were obtained and interpreted by a mathematical model describing overall process kinetics. The model includes volume changes of the liquid phase of the reaction mixture caused by dissolution of the solid phase and by evaporation of water produced in the course of the reaction. The process description involves formation of various oligomers with $n \leq 4$ by esterification and polyesterification reactions.

Polyethylene terephthalate is the fundamental component of polyester fibres. Its production by direct esterification of terephthalic acid with ethylene glycol is a relatively new process and there is still a lack of chemical engineering data for process description and design. The preparation of polyethylene terephthalate by direct esterification involves reactions which have received attention of several investigators¹⁻¹⁰. Previous kinetic studies, except those by Krumpolc and Málek^{8,9}, were based merely on simplified reaction models. The polyesterification was mostly followed solely by the determination of the carboxyl group or formed water. On the basis of data on the carboxyl group conversion in systems with equimolar amount of reaction components in the presence or absence of another acid as catalyst, the reaction was found to be of order 2 or 2.5 with respect to terephthalic acid. Krumpolc and Málek⁸ investigated the kinetics of formation of various reaction products including oligomers with $n \leq 3$ at initial molar ratios of ethylene glycol to terephthalic acid greater than 10 and with zinc oxide as catalyst. The reaction was carried out at boiling temperature of ethylene glycol at atmospheric pressure. Two different sets of reaction constants were estimated, one for the homogeneous and the other one for the heterogeneous region.

The aim of this work was to develop a mathematical model describing the course of esterification and polyesterification in the region of low ratios ethylene glycol to terephthalic acid and to estimate the effect of the reaction component ratio, of the cobalt-manganese catalyst and of an additive, recommended as inhibitor of diethylene glycol formation. The operating temperature 240°C and elevated pressure were chosen to simulate the technological conditions.

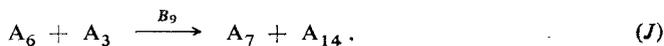
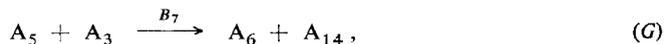
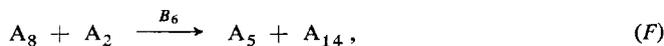
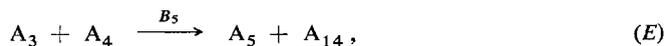
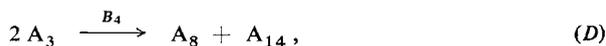
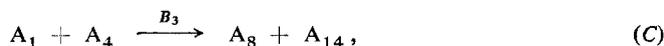
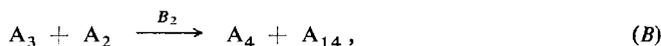
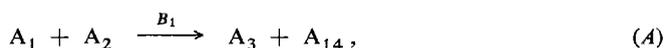
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THEORETICAL

The process of polyesterification of terephthalic acid with ethylene glycol involves a complex set of parallel, consecutive and reversible reactions. By continuous removal of water, produced by the reaction of the carboxyl and hydroxyl groups, the reversibility of all esterification reactions can be avoided. The limited solubility of the acid in ethylene glycol causes a complication in the description of the overall kinetics.

From the general point of view, two basic types of reactions should be considered for the kinetic description of the system, *i.e.* *a*) esterification reaction between the carboxyl and hydroxyl groups with the formation of an ester group and water and *b*) condensation reaction between two ester molecules leading to a higher oligomer and ethylene glycol. As both the entering reaction components are bifunctional, all of the reaction products formed by mechanism *a*) and *b*) are bifunctional too. Because the functional groups of the products can further react mutually, a variety of components can be theoretically expected in the reaction mixture. However, only the components, which are listed in Table I, were found in the reaction mixtures in significant concentrations. Oligomers of the type $\text{HO}(\text{C}_2\text{H}_4\text{OCOC}_6\text{H}_4\text{COO})_n \cdot \text{C}_2\text{H}_4\text{OH}$ with $n \ll 4$, acidic oligomers with $n \ll 3$, as well as diacidic and cyclic oligomers were not considered, because their concentration in the reaction mixture was very low and their identity was not unambiguously proved.

The mathematical model describing the overall kinetics of the process was based on the following set of reactions:



In deriving the kinetic equations following simplifying assumptions were made: a) all esterification reactions are considered as irreversible because of the efficient water removal from the reaction mixture under the experimental conditions; b) on the basis of the results of preliminary data evaluation and in agreement with previous findings⁸, only the reaction (*H*) as the most significant was selected from the variety of all possible condensation reactions; c) reactions leading to the formation of diethylene glycol and its esters were not taken into account as there was no possibility to distinguish these compounds from analogous compounds of ethylene glycol.

The reaction rates of the reactions (*A*) to (*J*) were related to the volume of the liquid phase as they proceed only in the liquid portion of the reaction mixture. The volume of the liquid phase of the reaction mixture changes in the course of the esterification process due to the dissolution of solid terephthalic acid, removal of the reaction water and losses of ethylene glycol with the aqueous distillate and has to be included as one of the variables in the process description.

With respect to the previously mentioned simplifications the description of the system concerns only the concentration changes of the eight key components $A_1 - A_8$. The concentration change of a component can be caused by any of the following three factors: formation of the component by a chemical reaction; input, either

TABLE I
List of Symbols and Chemical Formulas of Compounds

Compound	Symbol	Chemical formula
Terephthalic acid	A_1	$\text{HOOC}_6\text{H}_4\text{COOH}$
Ethylene glycol	A_2	$\text{HOC}_2\text{H}_4\text{OH}$
2-Hydroxyethyl hydrogen terephthalate	A_3	$\text{HOC}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COOH}$
Bis(2-hydroxyethyl) terephthalate	A_4	$\text{HOC}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COOC}_2\text{H}_4\text{OH}$
Dimer ^a	A_5	$\text{HO}(\text{C}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COO})_2\text{C}_2\text{H}_4\text{OH}$
Trimer ^a	A_6	$\text{HO}(\text{C}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COO})_3\text{C}_2\text{H}_4\text{OH}$
Tetramer ^{a,b}	A_7	$\text{HO}(\text{C}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COO})_4\text{C}_2\text{H}_4\text{OH}$
Acidic dimer ^a	A_8	$\text{HO}(\text{C}_2\text{H}_4\text{OOC}_6\text{H}_4\text{COO})_2\text{H}$
Diethylene glycol	A_{13}	$\text{HOC}_2\text{H}_4\text{OC}_2\text{H}_4\text{OH}$
Water	A_{14}	H_2O

^a Commonly used trivial names. ^b Pentamer and hexamer were found in some samples in negligible amounts. It was not possible to establish unambiguously the identity of the compounds, whose rather negligible peaks were observed in the chromatograms of some samples between the peaks of acidic dimer and bis(2-hydroxyethyl)terephthalate (probably diacidic or cyclic dimer) and between the peaks of trimer and dimer (probably acidic or cyclic trimer).

positive or negative, of the respective component into the liquid phase; volume change of the liquid phase.

Hence, the material balance of the eight key components can be expressed in the form of a vectorial differential equation (1):

$$d\mathbf{C}/dt = \mathbf{r} + \mathbf{r}' - (C/V)(dV/dt). \quad (1)$$

On the basis of previous studies^{2,3,6-8,11-15} the kinetics of the selected reactions can be assumed to be of second order. Under this assumption, the components of the vector \mathbf{r} can be expressed by a matrix equation (2):

$$\begin{array}{l} r_1 \\ r_2 \\ r_3 \\ r_4 \\ r_5 \\ r_6 \\ r_7 \\ r_8 \end{array} = \begin{array}{cccccccccccc} -B_1 & 0 & -B_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -B_1 & -B_2 & 0 & 0 & 0 & -B_6 & 0 & -B_8 & KB_8 & 0 & 0 & 0 \\ B_1 & -B_2 & 0 & -2B_4 & -B_5 & 0 & -B_7 & 0 & 0 & -B_9 & 0 & 0 \\ 0 & B_2 & -B_3 & 0 & -B_5 & 0 & 0 & +2B_8 & -2KB_8 & 0 & -B_{10} & 0 \\ 0 & 0 & 0 & 0 & B_5 + B_6 & -B_7 & -B_8 & +KB_8 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & +B_7 & 0 & 0 & -B_9 + B_{10} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & B_9 & 0 & 0 \\ 0 & 0 & B_3 + B_4 & 0 & -B_6 & 0 & 0 & 0 & 0 & 0 & -B_{10} & 0 \end{array} \times \begin{array}{l} C_1 C_2 \\ C_2 C_3 \\ C_1 C_4 \\ C_3 C_3 \\ C_3 C_4 \\ C_2 C_8 \\ C_5 C_3 \\ C_2 C_5 \\ C_4 C_4 \\ C_3 C_6 \\ C_4 C_8 \end{array} \quad (2)$$

The rate of terephthalic acid dissolution can be described by mass transfer equation

$$r'_1 = (k\bar{A}/V)(C_1^+ - C_1). \quad (3)$$

The rate of ethylene glycol output from the system can be expressed by means of measured amounts of ethylene glycol in aqueous distillate

$$r'_2 = -dn_2/V dt. \quad (4)$$

Equation (5) is valid for all other key components of the system

$$r'_3 = r'_4 = r'_5 = r'_6 = r'_7 = r'_8 = 0. \quad (5)$$

On the basis of preliminary measurements of reaction mixture densities, it has been concluded that the change of reaction volume can be adequately described by the differential equation

$$dV/dt = (r'_2 M_2 / \rho_2 + r'_1 M_1 / \rho_1) V. \quad (6)$$

This equation takes into account the main factors affecting the volume change

in the course of the esterification including water removal. As soon as the solid phase disappears the system becomes homogeneous and $\bar{A} = 0$ and $r'_1 = 0$ (cf. Eq. (3)). The chosen experimental conditions did not allow to evaluate the time dependence of the interfacial area \bar{A} in Eq. (3) with sufficient accuracy. Therefore the relation (1) for component A_1 was not used in the heterogeneous region. Instead the values of terephthalic acid concentration in the heterogeneous region were interpolated from analytical data and afterwards applied for the calculation of the reaction rates r_1 and r_2 at this reaction stage. Eq. (1) was applied to the description of the concentration course of all reaction components in the homogeneous region. To differentiate exactly between the heterogeneous and homogeneous reaction stage it was necessary to determine with best accuracy the transition point, corresponding to the disappearance of the solid phase from the reaction mixture. This point was found from the time dependence of the amount n_1 of undissolved solid terephthalic acid, calculated by integration of the equation

$$-dn_1/dt = r_1 M_1 V. \quad (7)$$

The criterion for the transition point can be formulated as $n_1 \leq \varepsilon$, where ε is a sufficiently small value. The initial conditions for solving the set of ten differential equations (2), (6), (7) are given by the relations (8)–(10):

$$C_i(0) = C'_i(0), \quad i = 1, 2, \dots, 8, \quad (8)$$

$$V(0) = m_2/\varrho_2 + M_1 C'_1(0) V(0)/\varrho_1, \quad (9)$$

$$\begin{aligned} n_1(0) &= \\ &= m_1 - [C'_1(0) + C'_3(0) + C'_4(0) + 2C'_5(0) + 3C'_6(0) + 4C'_7(0) + 2C'_8(0)] M_1 V. \end{aligned} \quad (10)$$

Estimation of parameters $B_1 - B_{10}$ of these differential equations was based on an iteration procedure involving integration of the differential equations with guessed values of parameters, calculation of the deviation between calculated and measured concentrations, evaluation of the objective function and finally calculation of the corrections leading to new values of parameters. The concentrations of the individual components corresponding to time t_j were obtained by integration of the set of differential equations at corresponding initial conditions

$$C_j = f(B, C(0), t_j). \quad (11)$$

The deviations were calculated according to the relation

$$\delta_{ij} = (C'_{ij} - C_{ij}) W_i. \quad (12)$$

The objective function to be minimized

$$F(\mathbf{B}) = \sum_{i=1}^8 \sum_{j=1}^7 \delta_{ij}^2 \quad (13)$$

is a function of the parameters. The integration of the differential equations (1), (2), (6), (7) was performed by Runge-Kutta-Merson technique, search for the minimum of the function (13) by Marquardt's method. The minimum of the function (13) determines the optimum values of parameters.

EXPERIMENTAL

Materials

Terephthalic acid, fiber-grade (Mobil Co., USA), corresponded to the standard requirements: *p*-aldehydobenzoic acid < 20 p.p.m.; benzoic acid < 50 p.p.m.; sum of phthalic and isophthalic acids < 500 p.p.m.; sum of heavy metals < 10 p.p.m.; sum of alkali metals < 30 p.p.m.; acidity number 674 ± 2 mg KOH/g; color test (triethylene glycol, 240°C, 30 min, purified nitrogen) less than 120 APHA units; ashes 0.005%; moisture 0.5%.

Ethylene glycol (Slovnaft) was characterized by following values: ρ_{20}^4 1.116 g/cm³; acidity 0.2 mval H⁺/kg; diethylene glycol 0.03%; distillation range 196.2–197.4°C; ash 0.0015%.

Both cobaltous and manganese acetates, used as catalysts, were prepared from the corresponding carbonates by dissolving in an excess of aqueous acetic acid and evaporating to dryness at room temperature. For Co(C₂H₃O₂)₂ · 4 H₂O calculated: 23.66% Co; found: 23.52% Co. For Mn(C₂H₃O₂)₂ · 4 H₂O calculated: 22.41% Mn; found: 22.51% Mn. Potassium chloride and all other reagents were of reagent grade purity.

Apparatus

The apparatus was designed as model equipment allowing the application of the obtained results to pilot plant design. To prevent corrosion, stainless steel was used for the construction of all inner parts. The design of the equipment allows the operation under pressure and continuous removal of water produced during the reaction, whereby ethylene glycol losses may be kept at minimum. The apparatus (Fig. 1) consisted of the following main parts: Esterification reactor (1) was a thermally insulated vessel of 3.7 liter capacity with conically shaped bottom. Reactants were introduced through an inlet (7) fitted with a sealed cover. Valve (2) at the bottom of the reactor allowed sampling of the reaction mixture. A wiremesh sieve (15) was inserted above the orifice (14) in order to separate solid phase and to permit sampling of pure liquid. Tube (19) connected the reaction vessel with a fractionation column. The reactor could be pressurized by nitrogen through the inlet (17). An efficient mixing was ensured by a screw and anchor type agitator driven by a hydromotor enabling continuous control of mixer revolutions in the range of 5–500 r.p.m. The clearance between the blades of the agitator (3) and the walls of the vessel was 0.5 mm. The reaction vessel was heated by two electrically heated coils (5) (2 kW each) inserted between the double wall aluminium block surrounding the whole vessel.

Fractionation column of 60 mm diameter (16) packed with wiremesh packing was equipped by an electrically heated jacket (0.5 kW). The head of the column was fitted with a partial con-

denser (10) with a controlled flow rate of thermostated cooling liquid (ethylene glycol). Temperature of vapours leaving the column was indicated by a thermometer (11). Vapours leaving the fractionation column were totally condensed in vertical water condenser (12). The condensate receiver (13) was equipped with an outlet valve for the condensate withdrawal. Temperature in the reactor, at the head of the fractionation column and in the heating block was measured by resistance thermometers (6, 8, 11, 4).

Procedure

The initial charge was kept at 1 500 g in all series of experiments. The ratios of reaction components (A_2/A_1) were 10, 7, 5, 3 resp., catalyst concentrations of 0.3 or 0.03 and 0.00% were used. Potassium chloride addition amounted to 0.3, 0.03 and 0.00%. All combinations of these variables were used. The reaction vessel was charged with the appropriate amount of terephthalic acid previously mixed with the chosen amount of potassium chloride and ethylene glycol. The mixture was stirred at 150 r.p.m. and heated until the temperature of 170°C was reached. At this instant, the catalyst was added. In order to elevate the boiling temperature of the reaction mixture to 240°C, the reactor system was pressurized by oxygen-free nitrogen to 0.3 MPa. At the same time, the temperature in the head of the fractionation column was adjusted so as to ensure efficient separation of water from the reaction mixture. The distillate contained $2.0 \pm 0.1\%$ of ethylene glycol. The boiling temperature of 240°C was kept constant with an accuracy of $\pm 5^\circ\text{C}$ by pressure control. The sampling of the reaction mixture was performed with the aid of a stainless steel sampling cylinder which was screwed on the orifice at the bottom of the reaction vessel and equipped with a drainage valve. The sampler was filled each time with approximately 10 ml of the filtered liquid phase of the reaction mixture, then cooled quickly by cold water and its contents stored for analysis. The first sample was taken when the temperature of the reaction mixture reached 240°C, further samples in 15 min intervals. At the sampling times the corresponding portions of the liquid condensate were collected for mass and density measurements.

Analytical Methods

The total acidity of individual samples was estimated alkalimetrically¹⁰ in the medium of pyridine + methanol (1 : 1) against thymolphthalein with sodium methoxide. The total free and bound

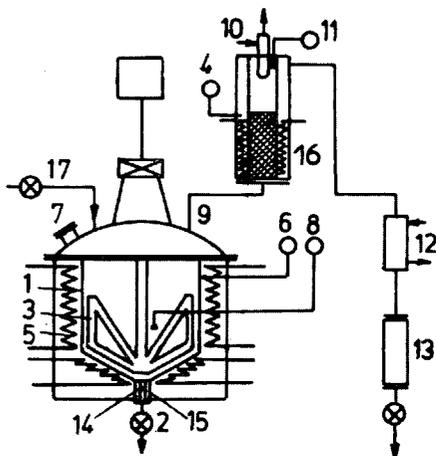


FIG. 1
Esterification Equipment

diethylene glycol was determined according to the previously described procedure¹⁶. Gel chromatography was used for the identification, separation and determination of the components A_1, A_3-A_8 (Table I) in the samples of the reaction mixture. A set of chromatographic columns was packed with styrendivynylbenzene copolymer beads, purified tetrahydrofuran with an addition of 0.1% acetic acid served as mobile phase. A differential UV-analyzer with a mercury-lamp (254 mm) as light source was used as a detector at the outlet of the last chromatographic column. The details of the chromatographic analysis will be described in a following paper¹⁷. As the gel chromatographic technique with the detector used did not allow to determine directly the concentration of ethylene glycol (A_2) its amount in the sample was estimated from the material balance assuming that the sample mass w_j was equal to the sum of masses of all chromatographically determined compounds and that of glycol according to

$$w_j = \sum_{i=1}^8 (w_{ij}) . \quad (11)$$

Test of the Evaluation Method

The arbitrarily chosen values of parameters B_1-B_9 given as exact values in Table II were used for the calculation of the concentration course of components A_1-A_8 according to the described model with given initial conditions. The time concentration dependences of individual components so calculated were then used as input data for the evaluation procedure together with the guess values of the parameters. Table II shows that the true values of parameters were found in 10 iteration cycles with 101 evaluations of the objective function.

TABLE II
Test of Evaluation Procedure

Quantity	Value			Exact values
	0 (guess)	5	10	
Iteration cycle				
Number of function evaluations	1	51	101	—
B_1	0.354	0.239	0.240	0.240
B_2	0.086	0.171	0.172	0.172
B_3	0.018	0.148	0.148	0.148
B_4	0.014	0.122	0.116	0.116
B_5	0.028	0.565	0.558	0.560
B_6	0.080	0.104	0.633	0.630
B_7	0.107	0.718	0.563	0.560
B_8	0.086	0.177	0.172	0.172
B_9	0.029	0.0493	0.0579	0.0580
Value of the objective function	$1.01 \cdot 10^{-1}$	$0.52 \cdot 10^{-5}$	$0.28 \cdot 10^{-7}$	—

RESULTS

Before the analytical data were used for further mathematical treatment their consistency and reliability were checked by material balance. For all samples the total amounts of terephthalic acid and ethylene glycol (both free and bound) were calculated and compared with the values derived from the initial batch composition. In most cases, the agreement between these values was better than 5%. This fact as well as the internal consistency of the data was considered as an evidence of a satisfactory reliability of analytical data.

The mean values of kinetic parameters $B_1 - B_9$ evaluated by the described method are listed in Table III. The precision of the data obtained did not allow reliable discrimination of parameters B_3 and B_4 as well as B_7 and B_{10} because of mutual dependence. Therefore following simplifications were used: $B_3 = B_4$ and $B_7 = B_{10}$.

Preliminary evaluations of model parameters have shown that the reversibility of reaction (H) can not be neglected. The value of the equilibrium constant $K = 0.63$ was obtained as the best value of the results of all experimental runs. The comparison

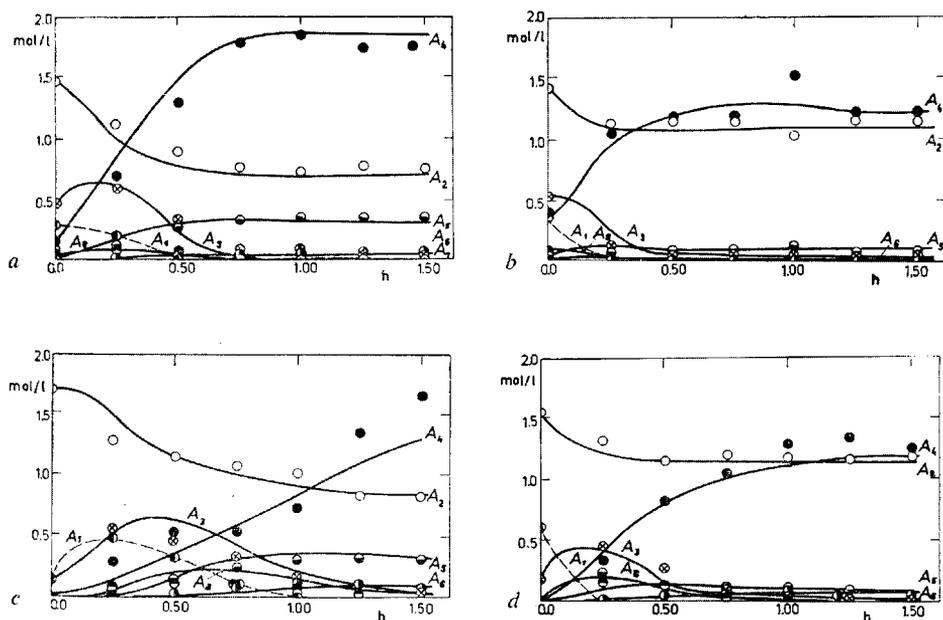


FIG. 2

Comparison of Measured and Calculated Concentration Courses

a, b 0.3% Catalyst, 0.3% KCl; *c, d* no catalyst, no KCl; *a, c* $A_2/A_1 = 5 : 1$; *b, d* $A_2/A_1 = 7 : 1$.

● A_1 ; ○ A_2 ; ⊗ A_3 ; ● A_4 ; ⊙ A_5 ; ⊙ A_6 ; ⊙ A_7 ; ⊙ A_8 . Concentration curve of A_2 plotted in 10 mol/l.

TABLE III
Parameter Values

Parameters $l \text{ mol}^{-1} \text{ h}^{-1}$	Series I ^a	Series II ^b
B_1	1.670	0.764
B_2	0.193	0.134
$B_4 (= B_3)$	2.28	2.52
B_5	3.03	1.26
B_6	1.39	0.35
$B_7 (= B_{10})$	0.57	0.71
B_8	1.52	0.19
KB_8	0.96	0.12
B_9	1.26	2.48
K^a		0.63

^a Catalyst concentration 0.3% based on the total batch weight; potassium chloride concentration 0.3% based on the total batch weight; ^b No catalyst, no potassium chloride were present.

of the measured and calculated concentration courses with parameter values given in Table III is shown in Fig. 2a–d. It can be seen that the derived mathematical model describes satisfactorily well the concentration course of all the components taken into account under given conditions. The same may be concluded from the comparison of found and calculated values of acidity of the reaction mixture (Fig. 3a,b).

Fig. 4a,b shows the time dependence of the relative amount of diethylene glycol (A_{13}) with respect to terephthalic acid (A_1) together with the corresponding carboxyl

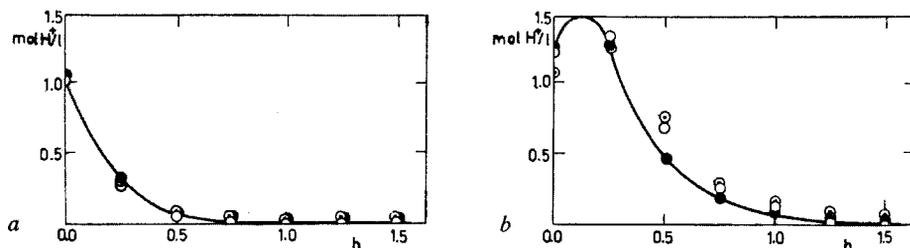


FIG. 3

Comparison of Measured and Calculated Acidity

a, b $A_2/A_1 = 5 : 1$; a 0.3% catalyst, 0.3% KCl; b no catalyst, no KCl. ● Calculated acidity, ○ measured by chromatography, ⊙ measured by alkalimetry.

conversion. Fig. 5a,b shows the dependence of the relative amount of diethylene glycol (A_{13}) with respect to terephthalic acid (A_1) on the carboxyl conversion.

DISCUSSION

The reliability of the analytical data is discussed in another work¹⁷. The standard deviation of the gel-chromatographic determination of the compounds A_1 , A_3 – A_8 was in the range 3–6% for samples taken in the homogeneous region of the reaction

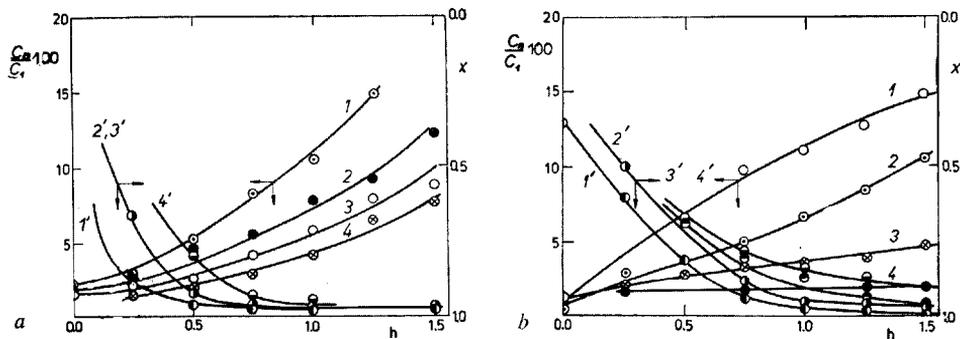


FIG. 4

Time Dependence of Diethylene Glycol Concentration and of Carboxyl Conversion (x) at Various Molar Ratios

a 0.3% Catalyst, 0.3% KCl; curve 1 $A_2/A_1 = 10:1$; 2 7:1; 3 5:1; 4 3:1; *b* no catalyst, curve 1 $A_2/A_1 = 10:1$, KCl; 2 10:1, no KCl; 3 3:1, KCl; 4 3:1, no KCl.

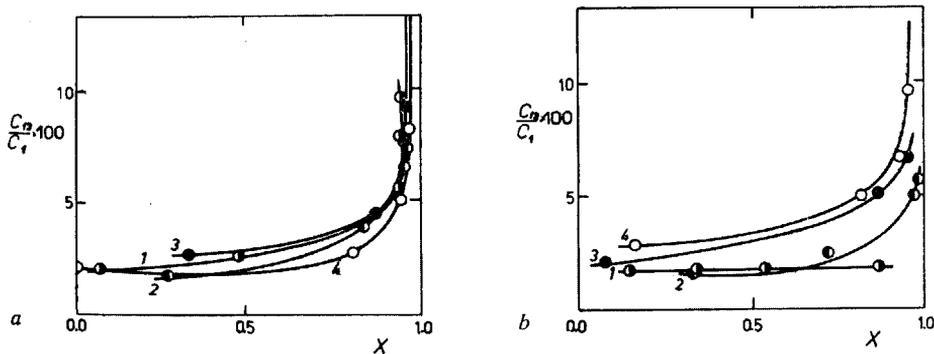


FIG. 5

Dependence of the Relative Amount of Diethylene Glycol on Carboxyl Conversion (x)

a 0.3% Catalyst, 0.3% KCl; *b* no catalyst, no KCl. Numbering of the curves see Fig. 4a.

process. This accuracy was slightly lower for samples taken in the heterogeneous region due to incomplete separation of undissolved terephthalic acid. The accuracy of the method for diethylene glycol determination was discussed in a previous report¹⁶.

The evaluated values of the parameters can not be considered as true values of the corresponding reaction rate constants with regard to the limited extent of information obtained and the simplifications made. One of the factors affecting the estimates of parameters is the proper choice of initial conditions, *i.e.* of the initial concentration of all components (at time $t_j = 0$). In fact, the true values of these concentrations were not exactly known. They were determined with the same precision as the concentrations in subsequent samples and therefore they should have been optimized in the same way as other parameters. It was beyond the scope of this work to apply this more rigorous procedure. Such a procedure would increase the number of parameters and would not be justified with regard to other sources of errors. The mathematical model takes into consideration only a limited set of chemical reactions selected from a larger number of reactions actually occurring in the system. As a result of this simplification, the estimated parameter values include also the effect of the reactions which were not taken into account. This is probably significant for parameters related to higher oligomers ($n \gg 3$), as their concentration changes are affected not only by the considered reactions. With respect to the structure of the mathematical model, it can be expected that the sensitivity of an objective function to certain parameters is small and that the estimates of some parameters can be mutually dependent. Consequently, the determined values of parameters can be used for the design of the polyesterification process only taking the mentioned limitations into account, *i.e.* if the composition of the reaction mixture does not differ substantially from the conditions described in this study.

From the comparison of the change of product composition with time for different experimental conditions (Fig. 2a-d), it is clear that larger amounts of oligomers are formed in the case of uncatalyzed reaction. This is probably due to the fact that the catalyst enhances the degradation reaction, *i.e.* the glycolysis of the produced oligomers. This is in agreement with the values of the kinetic parameters B_8 as shown below for different catalyst concentration levels (Table IV). The value 0.63 of the equilibrium constant K of the reaction (H), found for the whole range

TABLE IV
Effect of Reaction Mixture Composition on Parameter B_8 ($l \text{ mol}^{-1} \text{ h}^{-1}$)

Catalyst, %	0.3	0.03	—	—
KCl, %	0.3	0.3	0.3	—
B_8	1.524	0.762	0.389	0.19

of experimental conditions, is lower by 16% than that found by Werner¹¹ (0.75, 223°C) and by 25% than that of Málek¹⁰ (0.85, 190°C). The formation of diethylene glycol was not included in our mathematical model. The change of its concentration with time (Fig. 4a,b) shows that its formation is favoured at higher A_2/A_1 ratios, while no retardation effect of KCl was observed. As it is seen from Fig. 5a,b, diethylene glycol is formed with an increasing rate after a certain acid conversion is reached. It can be concluded that the lower is the molar reactant ratio A_2/A_1 , the faster is the formation of oligomers and the lower is the final amount of diethylene glycol formed. The catalyst used has a pronounced effect in enhancing the formation of 2-hydroxyethyl hydrogen terephthalate and bis(2-hydroxyethyl) terephthalate and in facilitating the glycolysis of the oligomers formed.

LIST OF SYMBOLS

$A_1 - A_{14}$	compounds listed in Table I
\bar{A}	interfacial (solid-liquid) area
$B; \mathbf{B}$	kinetic parameter of the mathematical model; vector of kinetic parameters
$C; \mathbf{C}$	component concentration (calculated); vector of the calculated component concentration
C'	component concentration (measured)
C^+	solubility
k	mass transfer coefficient
K	equilibrium constant of reaction (H)
M	molecular mass
n_1	mass of solid terephthalic acid
n_2	mass of free and bound ethylene glycol
$r; \mathbf{r}$	rate of component formation by chemical reaction; vector of component formation rate
$r'; \mathbf{r}'$	rate of component transfer into the liquid phase; vector of component transfer rate into the liquid phase
t	reaction time
V	volume of the liquid phase
w	mass of a component in the analyzed sample
W_i	weight factor in Eq. (12)
δ	weighed deviation
ϱ	specific mass

Subscripts

i	component
j	sampling time
k	chemical reaction

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