

Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation

J. Lilja^a, D.Yu. Murzin^{a,*}, T. Salmi^a, J. Aumo^a, P. Mäki-Arvela^a, M. Sundell^b

^a Åbo Akademi, Process Chemistry Group, Laboratory of Industrial Chemistry, FIN-20500 Turku/Åbo, Finland

^b Smoptech Limited, Virusmäentie 65, FIN-20300 Turku/Åbo, Finland

Received 2 July 2001; accepted 22 October 2001

Abstract

Esterification of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol was studied in the presence of a fibrous polymer-supported sulphonic acid catalyst, Smopex-101. The reaction temperature in the experiments was 60 °C. Comparative experiments were carried out on an ion-exchange resin, Amberlyst 15 and with a homogeneous catalyst, liquid HCl. The effect of different molar ratios between the reactants (acid and alcohol) on the reaction rate was investigated. The rate constants were related to the substituent effects of the reacting molecules according to the Taft equation. The substituent effects of alcohols were found to follow the Taft relationship, which was not the case for the acids. The experimental results were modelled according to a simple second-order model and a more advanced adsorption-based model. The adsorption-based model, which includes the adsorption of carboxylic acid and water and is consistent with structure–activity relationship, was superior to the second-order model. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Esterification; Carboxylic acid; Fibrous polymer-supported sulphonic acid catalyst; Taft equation; Kinetic modelling

1. Introduction

The correlation between the structure of chemical compounds and their chemical reactivity is used to obtain information on both reaction mechanism and factors affecting the reactivity. Two kinds of equations of the form $\lg k = \rho\sigma$, in which σ is the characteristic for the polarity of the substituent, but is normally independent of the nature of the reaction and ρ the characteristic for the reaction and measures the susceptibility of the reaction to polar effects, are generally used: the Hammett equation, involving polar, resonance and steric effects in aromatic systems

and the Taft equation [1,2] involving polar and steric effects in aliphatic systems. Several authors have tried to establish that kind of relationships for different reactions, especially in homogeneous catalysis [1–4].

Application of Taft type equations to homogeneous esterification reactions usually holds, but for heterogeneous esterification reactions, it is not so evident. The complication in heterogeneous catalysis compared with homogeneous conditions arises from the complex nature of the heterogeneous processes, which include adsorption, desorption as well as several surface reaction steps [5–7]. However, application of such relationships to heterogeneously catalysed reactions is of particular interest, since it is possible to obtain information on the properties of both organic molecules and solids. Particularly analysis of kinetic and thermodynamic results can improve

* Corresponding author. Tel.: +358-2-215-4985;

fax: +358-2-215-4479.

E-mail address: dmurzin@abo.fi (D.Yu. Murzin).

the knowledge of the reaction mechanisms on solid catalysts as well as the nature of the active species.

Esters of carboxylic acids have practical importance, since millions of tons of polyesters are produced via the reaction of dicarboxylic acids with diols and a wide variety mono- and di-esters are used in the production of fine and speciality chemicals such as pharmaceuticals, pesticides and fragrances [8]. The esterification reaction is a liquid-phase process, where the limiting conversion of the reactants is determined by equilibrium. Typically esterification reactions are very slow; it requires several days to attain the equilibrium in the absence of catalyst. Therefore, the reaction is enhanced with an added catalyst. Mineral acids, such as H_2SO_4 , HCl and HI , and strong organic acids, such as HCOOH , can be utilised as homogeneous catalysts. The disadvantage with homogeneous catalysts is their miscibility with the reaction medium, which causes separation problems. Furthermore, at higher catalyst concentrations equipment corrosion can occur. Therefore, heterogeneous catalysts, such as ion-exchange materials containing sulphonic acid groups ($-\text{SO}_3$), are used in esterification reactions.

In this paper, we have studied esterification kinetics on a uniform polymer-supported ion-exchange catalyst with well-defined active sites. Comparative esterification experiments were carried out on a conventional cation-exchange resin, and with a homogeneous catalyst, liquid HCl . A family of carboxylic acids and alcohols was studied in order to reveal the structural relationships in kinetics.

2. Experimental

Esterification of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol was carried out in an isothermal glass reactor equipped with a heating jacket. The steering speed was 800 rpm and temperature was kept within 0.2°C . A reflux condenser was placed on top of the reactor in order to prevent the escape of volatile compounds. The acid and alcohol were preheated separately, and the reaction was commenced by pouring the preheated acid into the reactor. Samples were withdrawn and the amount of unreacted acid was analysed by titration with 0.1 M NaOH . The ratio between the molar mass of acid and the amount of active groups in

the catalyst was maintained constant (8.475×10^{-3}). Typically the amount of catalyst was between 1 and 5 g. The total liquid volume in the experiments was 130 dm^3 .

The esterifications with different acids and alcohols were performed at 60°C with the initial molar ratio 1:1 between the acid and alcohol. A fibrous polymer-supported sulphonic acid catalyst, Smopex-101 (Smoptech), a conventional ion-exchange resin, Amberlyst 15 (Rohm and Haas, particle sizes $0.3\text{--}1.2\text{ mm}^2$, $4.9\text{ meq H}^+/\text{g}$) as well as liquid HCl (J.T. Baker, 37%) were used as catalysts. The effect of different initial molar ratios between the reactants on the reaction rate was studied on Smopex-101 at 60°C with acetic acid and ethanol (4:1, 2:1, 1:1, 1:2, 1:4) and propanoic acid and methanol (1:1, 2:3, 3:2).

The preparation procedure of Smopex-101 has been described in a previous paper of our group [9]. The capacity of Smopex-101 was $3.2\text{ mmol H}^+/\text{g}$, determined by acid–base titration. The polymer-supported fibre catalyst, Smopex-101, was investigated with a scanning electron microscope (SEM).

3. Results and discussion

3.1. Catalyst characterisation

An SEM image of the fibrous polymer-supported sulphonic acid catalyst, Smopex-101, is shown in Fig. 1, which reveals that the mean particle diameter of the Smopex-101 was about $10\text{ }\mu\text{m}$, while the average length was $4000\text{ }\mu\text{m}$.

3.2. The effect of different catalyst on reaction rate

The esterification of acetic acid with methanol was carried out at 60°C on different catalysts with the initial molar ratio of 1:1 between the reactants. As heterogeneous catalysts the fibrous polymer-supported sulphonic acid catalyst, Smopex-101, and the conventional cation-exchange resin, Amberlyst 15 were used, while liquid HCl was used as a homogeneous catalyst. The esterification catalysed by liquid HCl gave the highest reaction rate (Fig. 2). It can be noticed that the kinetic regularities with homogeneous and heterogeneous catalysts were similar (Fig. 2). Therefore, the irreversible second-order kinetics,

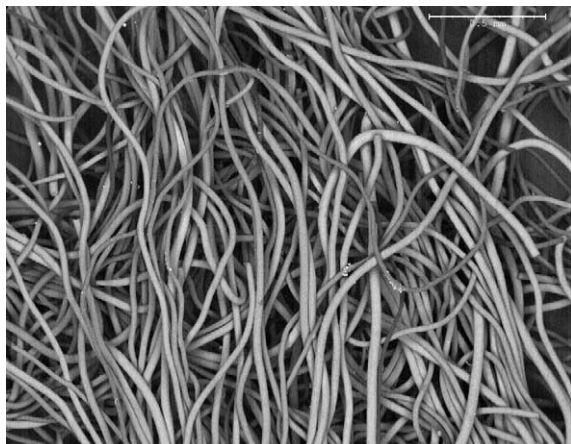


Fig. 1. SEM micrograph of the Smopex fibres. The fibre diameter = $10\ \mu\text{m}$, fibre length = $4000\ \mu\text{m}$.

which is usually applied for homogeneous catalysts [10–12] could in principle be assumed to be valid for heterogeneous catalysts. This second-order model for heterogeneous catalyst, ion-exchange resins, has been used also by other authors [13–15]. Chakrabarti and Sharma [16] state that the order of the chemical reaction on ion-exchange particles is the same as for homogeneous catalysis by dissolved electrolytes.

Difference in reaction rates observed for Smopex and Amberlyst should be either due intrinsic chemical

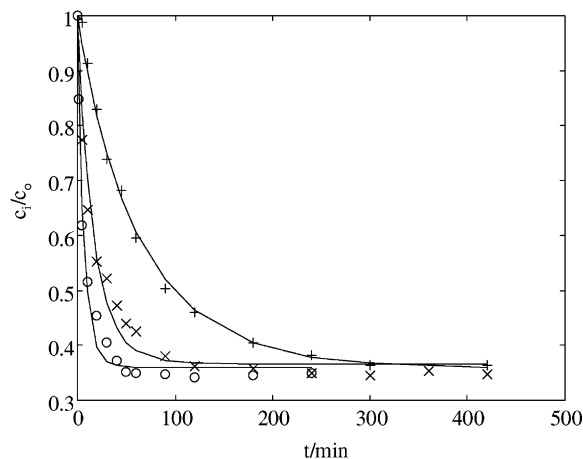


Fig. 2. Esterification of acetic acid with methanol on homogeneous and heterogeneous catalysts at 60°C with initial molar ratio 1:1 between the reactants: (O) liquid HCl; (x) Smopex-101; (+) Amberlyst 15.

difference between two catalysts or to diffusional limitations, as the sizes of catalysts are different.

Thus in order to evaluate the real activity of competing catalysts, comparison of the intrinsic kinetics is necessary. As the effective diameters of the fibre catalyst and the conventional ion-exchange resins are very different, it is essential to reveal the role of internal mass transfer resistance inside the catalyst particles. This was with the aid of the normalised Thiele modulus. Calculations were done for the conditions when the reaction rate is highest, e.g. applying irreversible second-order kinetics. The effective diffusion coefficient is obtained from the molecular diffusion coefficient (Wilke–Chang equation) and the particle porosity-to-tortuosity ratio, which were set 0.25 for Smopex-101 and 0.4 for Amberlyst 15. Calculations showed that the effectiveness factor for Smopex-101 exceeds 0.95, therefore it can be concluded that the fibre catalyst, Smopex-101, operated practically under diffusion-free conditions. At the same time diffusional limitations appear for Amberlyst, since the effectiveness factor is less than 0.7. Correcting the ratio of intrinsic initial rates by taking into account the effectiveness factors, it was obtained that the corrected ratio becomes about 1.7 indicating that the differences in the esterification rates over Smopex-101 and Amberlyst 15 are not exclusively attributed to different diffusional properties, but also to different intrinsic kinetics. The observations thus suggest that Smopex-101 is the chemically more active catalyst.

3.3. Esterification of different acids with alcohols

Esterification of acetic acid with methanol, ethanol, 1-propanol, 2-propanol and butanol on the fibrous polymer-supported sulphonic acid catalyst (Smopex-101) was carried out at 60°C with the initial molar ratio of 1:1 between the reactants. As revealed by Fig. 3, the chain length and branching of the alcohol had a retarding effect on the reaction rate. This effect has been previously observed by several authors, who have studied heterogeneous catalysts in esterification [17–19].

Similar to acetic acid, esterification of propanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol was carried out at 60°C with an equimolar initial ratio between the reactants. The fibrous polymer-supported sulphonic acid catalyst

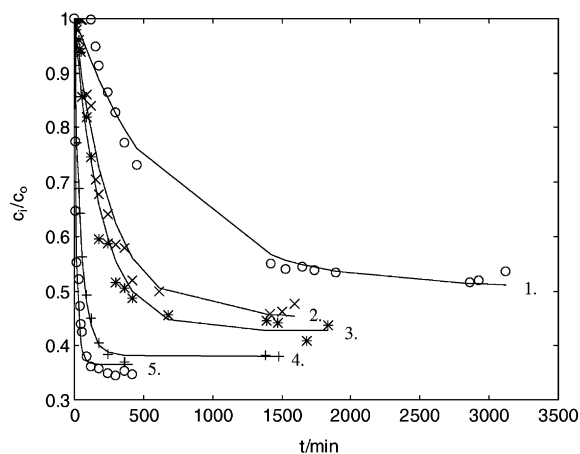


Fig. 3. Esterification of acetic acid with methanol (5), ethanol (4), 1-propanol (3), 2-propanol (1), and 1-butanol (2) at 60°C on Smopex-101 with the initial molar ratio 1:1 between the reactants.

(Smopex-101) was used in these experiments. The reaction rate was higher by shorter alcohol chain lengths, and branching of the alcohol chain retarded the reaction rate (Fig. 4).

The results from the esterification of pentanoic acid at 60°C with different alcohols on the fibrous polymer-supported sulphonic acid catalyst (Smopex-101) are presented in Fig. 5. Methanol, ethanol, 1-propanol, 2-propanol and butanol were used in equimolar amounts in these experiments. The reaction

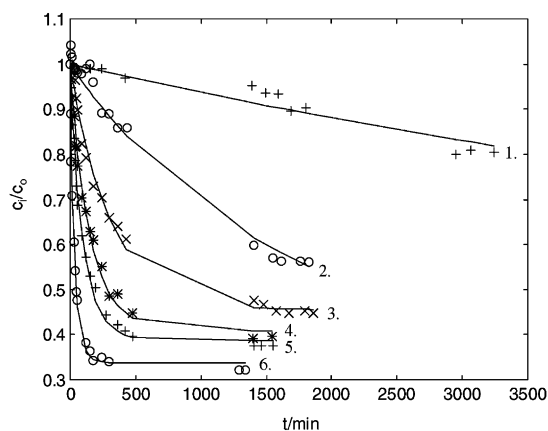


Fig. 4. Esterification of propanoic acid with methanol (6), ethanol (5), 1-propanol (4), 2-propanol (2), 1-butanol (3), and 2-butanol (1) at 60°C on Smopex-101 with the initial molar ratio 1:1 between the reactants.

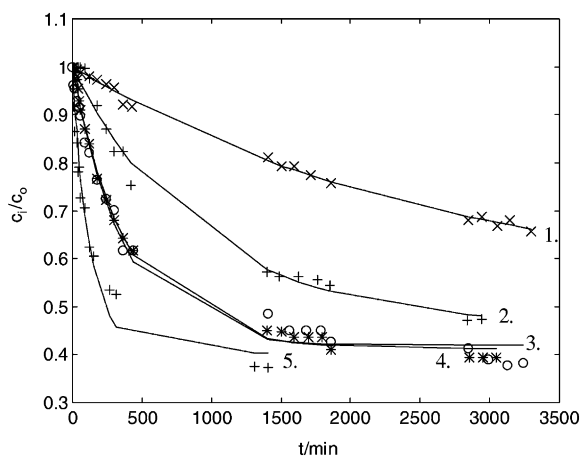


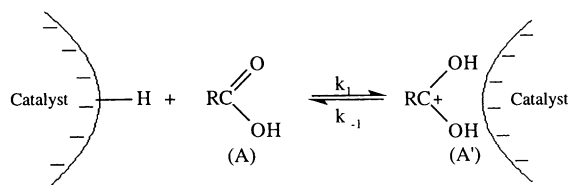
Fig. 5. Esterification of pentanoic acid with methanol (5), ethanol (3), 1-propanol (4), 2-propanol (1), and 1-butanol (2) at 60°C over Smopex-101 with initial molar ratio 1:1 between the reactants.

rate was retarded with increasing chain length and branching of the alcohol (Fig. 5). It should be also noticed (Figs. 3–5) that the reaction rate is retarded as the acid chain length grows, which has been observed by other researchers having been active in the esterification on ion-exchange resins [20,21].

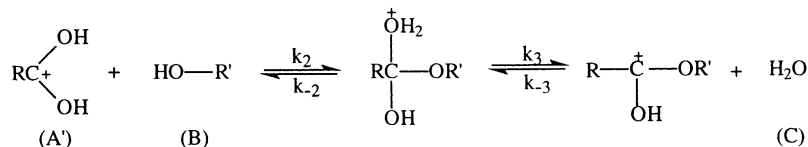
4. Mathematical model for esterification kinetics

4.1. Modelling based on second-order kinetics

The preliminary mathematical modelling of the observed esterification kinetics was based on second-order kinetics, which principally could be applied to both homogeneous and heterogeneous catalyst as discussed in Section 3.2. The reaction mechanism is presented below [22,23]. The sulphonic acid groups ($-\text{SO}_3$) on a heterogeneous catalyst or H^+ in a homogeneous catalyst (e.g. H_2SO_4 , HCl) initiate the esterification reaction by donating a proton to the carboxylic acid molecule:

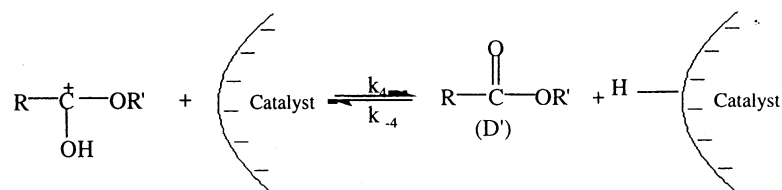


After the proton transfer, the carboxylic acid is accessible for a nucleophilic attack by the hydroxyl group from the alcohol (R'OH), and the reaction continues with water elimination:



On the other hand, for the overall reaction, the thermodynamic relations $K_c = K_1 K_2$ and $K_i = k_{+i}/k_{-i}$, $i = 1, 2$ are valid. After introducing the concentration-based overall equilibrium constant (K_c),

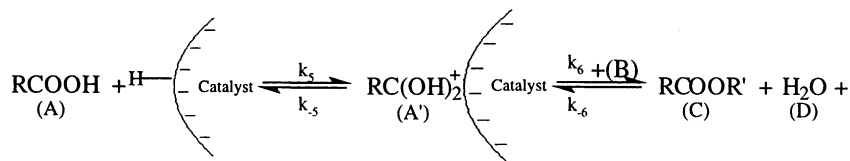
Finally, the catalyst is recovered:



The proton-donating step is usually assumed to be rapid, while the nucleophilic substitution is slow. Provided that the reaction steps following the nucleophilic substitution are rapid, the reaction mechanism is simplified as follows:

the rate of the RDS can be written as follows:

$$r = k_{+2} K_1 c_{\text{cat}} \left(c_A c_B - \frac{c_C c_D}{K_c} \right) \quad (4)$$



The rate-determining step (RDS) gives the overall rate equation for the reaction

$$r = (k_{+2} c_A' c_B - k_{-2} c_C c_D) c_{\text{cat}} \quad (1)$$

where k is the rate constant and c_i denotes concentration for component i .

For the rapid step, the quasi-equilibrium approximation gives:

$$K_1 = \frac{c_{A'}}{c_A c_{\text{cat}}} \quad (2)$$

where K_1 is the concentration-based equilibrium constant. The concentration of A' is solved from Eq. (2) and inserted into the rate equation (1):

$$r = (k_{+2} K_1 c_A c_B - k_{-2} c_C c_D) c_{\text{cat}} \quad (3)$$

A lumped rate constant $k' = k_{+2} K_1$ is introduced and the final form of the kinetic model becomes

$$r = k' c_{\text{cat}} \left(c_A c_B - \frac{c_C c_D}{K} \right) \quad (5)$$

where $K = K_c$.

The concentration of the carboxylic acid was measured by chemical analysis during the reaction. The overall stoichiometry gives the relations

$$c_B = c_A - (c_{0A} - c_{0B}) \quad (6)$$

$$c_C = c_D = c_{0A} - c_A \quad (7)$$

$$a = c_{0A} - c_{0B} \quad (8)$$

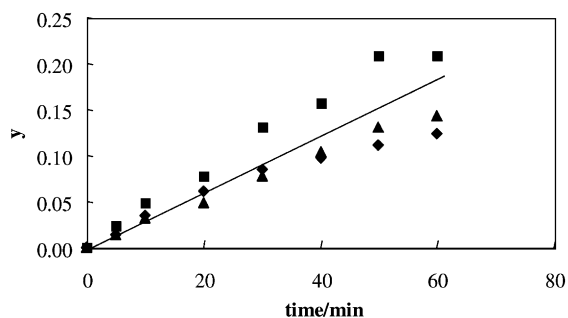


Fig. 6. The left-hand side of Eq. (11) versus time with different initial molar ratios between propanoic acid and methanol: (◆) 3:2; (▲) 1:1; (■) 2:3 at 60°C on Smopex-101.

After introducing these relations and the concentration of A into the rate equation, the mass balance of A can be written as

$$-\frac{dc_A}{dt} = k' c_{\text{cat}} \left[c_A (c_A - a) - \frac{(c_{0A} - c_A)^2}{K} \right] \rho_B \quad (9)$$

$$\rho_B = \frac{m_{\text{cat}}}{V_L} \quad (10)$$

where m_{cat} is the mass of the catalyst and V_L the volume of the liquid phase. At $t = 0$, $c_A = c_{0A}$.

In order to check the validity of the rate equation given by Eq. (1), separation of variables and analytical integration was applied. Eq. (9) can be integrated with the limits $[0, t]$ and $[c_{0A}, c_A]$ giving

$$\frac{1}{\sqrt{-A}} \ln \frac{[\sqrt{-A} + c_{0A} + c_{0B} - 2(c_{0A} - c_A)(c_{0A} - c_A)(1 - K^{-1})][\sqrt{-A} - c_{0A} - c_{0B}]}{[\sqrt{-A} - c_{0A} - c_{0B} + 2(c_{0A} - c_A)(1 - K^{-1})][\sqrt{-A} + c_{0A} + c_{0B}]} = k' \rho_B t \quad (11)$$

where $A = (c_{0A} + c_{0B})^2 - 4c_{0A}c_{0B}(1 - K^{-1})$.

A straight line should be obtained when plotting the left-hand side of Eq. (11) against the reaction time.

4.2. Check of rate expression

Test plots (Eq. (11)) from the esterification of propanoic acid with methanol for different molar ratios between acid and alcohol (3:2, 1:1 and 2:3) are presented in Fig. 6. Strong deviations from the second-order kinetics are observed, i.e. the simple second-order rate model is evidently not valid. The main reason might be that adsorption of the reactants and products influences the kinetics. Therefore, the

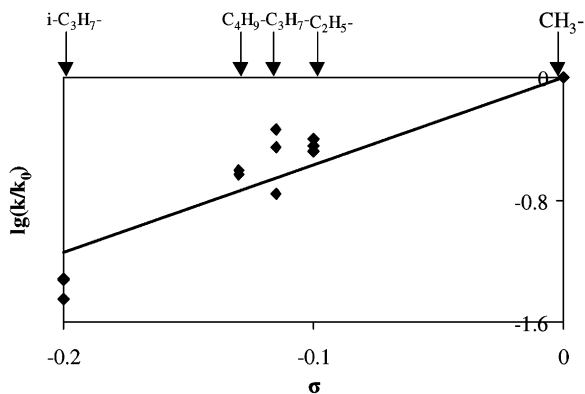


Fig. 7. Taft relationship of alkyl radicals in alcohols: (▲) acetic acid; (■) propanoic acid; (◆) pentanoic acid.

structure–activity relationship of Taft [1,2] was used to probe the influence of adsorption phenomena.

The rate constants of esterification of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol and butanol were related to the substituent effects [2] of the reacting molecules according to the Taft equation:

$$\lg \frac{k}{k_0} = \sigma \rho \quad (12)$$

where k is the rate constant, k_0 the rate constant for acetic acid, σ characterises the substituent ($\sigma = 0$, -0.1 , -0.12 , -0.13 and -0.20 for CH_3^- , C_2H_5^- ,

$n\text{-C}_3\text{H}_7^-$, $n\text{-C}_4\text{H}_9^-$ and $i\text{-C}_3\text{H}_7^-$, respectively) and ρ the characteristic for a particular reaction.

The substituent effects of different alcohols nicely follow the Taft equation, as illustrated by Fig. 7. This was not the case for the different acids as $\lg(k/k_0)$ was plotted against the substituent values in acids (Fig. 8). Thus, the Taft equation, which is applied with homogeneous catalysts to describe substituent effects for both acids and alcohols [24], seems to be valid in case of heterogeneous catalysts for alcohols only. This might be due to the differences in the reaction mechanisms on homogeneous and heterogeneous catalysts.

The bending of the test plots (Fig. 6) and consideration of the Taft equation called for the modification

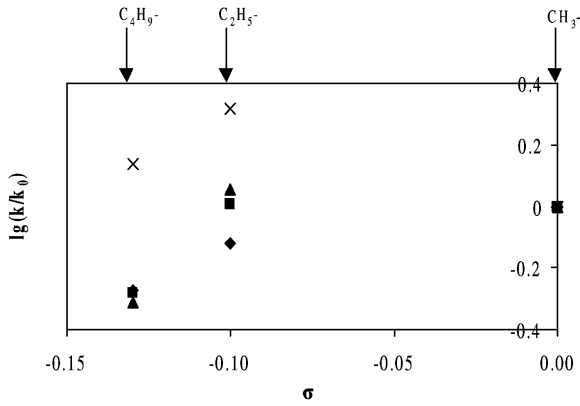


Fig. 8. Taft relationship of alkyl radicals in acids: (■) methanol; (▲) ethanol; (×) 1-propanol; (◆) 2-propanol.

of the second-order rate expression. More specifically, in case of heterogeneous catalysts, the adsorption of reactants and products should be taken into account.

If adsorption of all reactants and products is included in the kinetic model and the surface concentrations of the adsorbed species (θ) are expressed with Langmuir's adsorption isotherms, for instance

$$\theta_A = \frac{K_A c_A}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D} \quad (13)$$

$$\theta_B = \frac{K_B c_B}{1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D} \quad (14)$$

etc., the following rate equation is valid:

$$r = k_+ \theta_A \theta_B - k_- \theta_C \theta_D = \frac{k(c_A c_B - c_C c_D / K)}{(1 + K_A c_A + K_B c_B + K_C c_C + K_D c_D)^2} \quad (15)$$

where K_i is the adsorption coefficient for component i .

According to the Taft relationship, a dependence of $\lg(k/k_0)$ as a function of the substituent effect in alcohols was confirmed, indicating similarity between heterogeneous and homogeneous catalysis. This can be interpreted as a weak adsorption of alcohols, and consequently a weak adsorption of esters on the catalyst surface, too, leading to the following adsorption isotherms for an acid

$$\theta_A = \frac{K_A c_A}{1 + K_A c_A + K_D c_D} \quad (16)$$

and water

$$\theta_D = \frac{K_D c_D}{1 + K_A c_A + K_D c_D} \quad (17)$$

Therefore, the model (Eq. (15)) can be simplified including only the adsorption terms for the acids and water:

$$r = k_+ \theta_A c_B - k_- \theta_D c_C = \frac{k(c_A c_B - c_C c_D / K)}{1 + K_A c_A + K_D c_D} \quad (18)$$

For liquid-phase reactions, it is reasonable to assume that all the surface sites are covered by either reactants or products [25]. Hence, lumped constants, $K_A/k = \alpha$ and $K_D/k = \beta$, are introduced and the term $1/k$ is neglected in the denominator:

$$r = \frac{c_A c_B - c_C c_D / K}{\alpha c_A + \beta c_D} \quad (19)$$

After introducing the stoichiometric relations from Eqs. (6)–(8), the final model is obtained:

$$-\frac{dc_A}{dt} = c_{\text{cat}} \left[\frac{c_A(c_A - a) - (c_{0A} - c_A)^2 / K}{\alpha c_A + \beta(c_{0A} - c_A)} \right] \rho_B \quad (20)$$

The change of the liquid volume was included in the model, since the liquid volume was diminished during the reaction because of sampling:

$$V_L = V_{0L} - sV_S \quad (21)$$

where s denotes the number of samples and V_S the sample volume (ca. 0.5 ml).

The differential equation (19) was solved numerically with the backward difference method using the software Odessa [26]. The differential equation solver operated under a parameter estimation routine, which minimised the following objective function, the residual sum of squares:

$$Q = \sum_t (c_A(t) - \hat{c}_A(t))^2 \quad (22)$$

where c_A and \hat{c}_A denote the experimental and the predicted (Eqs. (9) and (20)) concentrations. A hybrid simplex–Levenberg–Marquardt algorithm was used in the minimisation of the objective function. The numerical algorithms were included in the program package MODEST [26].

Table 1
Estimated equilibrium, adsorption constants and degrees of explanation

Acid	Alcohol	K	Error (%)	α	Error (%)	β	Error (%)	β/α	R^2 (%)
Acetic ^a	Ethanol	2.83	7.3	87.55	5.7	149.21	7.5	1.70	99.51
Propanoic	Methanol	4.11	5.7	50.69	6.6	102.35	9.8	2.02	99.66
Propanoic	Ethanol	2.69	4.7	157.83	6.3	297.15	6.2	1.88	99.72
Propanoic	1-Propanol	2.38	8.1	188.52	7.9	433.58	15.1	2.30	99.54
Propanoic	Butanol	1.49	8.2	357.05	15.7	584.23	22.9	1.64	99.04

^a Experiments were done at varying molar ratios of acid to alcohol (4:1, 2:1, 1:1, 1:2, 1:4).

4.3. Kinetic results based on the improved model

As examples of the use of the improved model, which includes adsorption of reactants and products two different cases are presented in the sequel. Esterification of acetic acid with ethanol (Fig. 9) on Smopex-101 at varying initial molar ratios of the acid and alcohol (4:1, 2:1, 1:1, 1:2, 1:4), and esterification of propanoic acid with methanol, ethanol, 1-propanol and butanol on Smopex-101 with the initial molar ratio 1:1 (Fig. 10). Data on esterification of acetic acid with ethanol at varying molar ratios were modelled together, whereas modelling of propanoic acid with different alcohols were done separately. The estimated equilibrium and adsorption constants are presented in Table 1 along with the degrees of explanation.

The degrees of explanation is defined as follows:

$$R^2 = 1 - \frac{\sum (c_{i, \text{exp}} - c_{i, \text{model}})^2}{\sum (c_{i, \text{exp}} - c_{i, \text{mean}})^2} \quad (23)$$

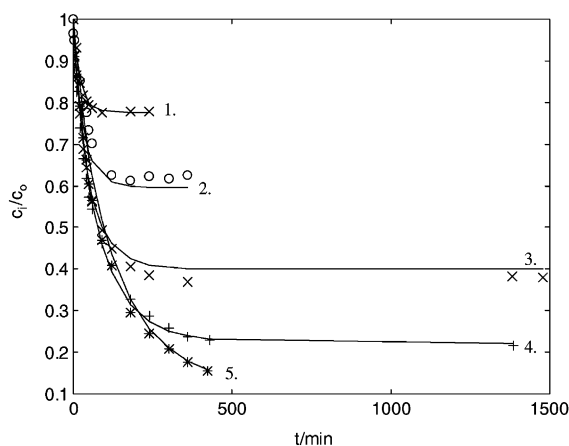


Fig. 9. Esterification of acetic acid with ethanol at 60 °C on Smopex-101 at varying initial molar ratios between acetic acid and ethanol: (1) 4:1; (2) 2:1; (3) 1:1; (4) 1:2; (5) 1:4.

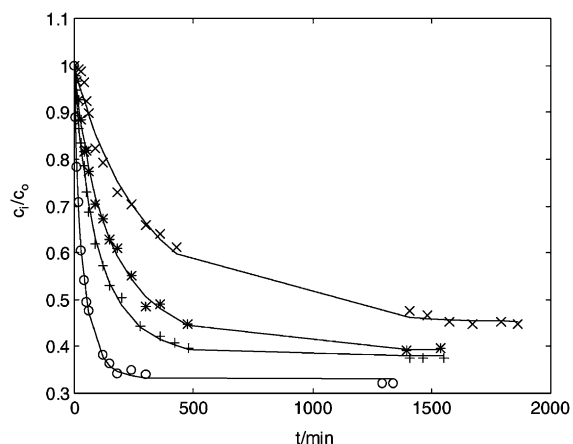


Fig. 10. Esterification of propanoic acid with methanol (○), ethanol (+), 1-propanol (*) and butanol (×) on Smopex-101 at 60 °C with initial molar ratio 1:1 between the reactants.

where $c_{i, \text{exp}}$ is the experimentally determined concentration of component i , $c_{i, \text{model}}$ the concentration of the component i predicted by the model and $c_{i, \text{mean}}$ the mean value of the concentration of component i .

As Table 1 reveals the ratio β/α is approximately 2 for esterification of propanoic acid with different alcohols indicating that water is more strongly adsorbed on the catalyst surface than propanoic acid.

5. Conclusions

The esterification of various acids with alcohols can be successfully carried out on the fibrous polymer-supported sulphonic acid catalyst, Smopex-101. The increase of the alcohol chain length and branching of the alcohol chain had a retarding effect on the reaction rate. Similarly, the increase of the acid chain length retarded the reaction rate. The experimentally

recorded concentrations were modelled based on a simple second-order model and a model based on adsorption of acid and water on the catalyst. The frequently applied second-order model was not able to explain the experimental data properly. The esterification rate constants of different acids with alcohols were related to the substituent effects of the reacting molecules according to the Taft equation. The substituent effects of different alcohols followed the Taft relationship with exactly the same slope. This was not the case for the acids, which could be due to the differences in reaction mechanisms between homogeneous and heterogeneous catalysts: acids being first adsorbed on the catalyst surface and then reacting with alcohols from the liquid phase. The adsorption of water was found to be stronger than the adsorption of acid.

Acknowledgements

This work is part of the activities at the Åbo Akademi Process Chemistry Group within the Finnish Centre of Excellence Programme (2000–2005) by the Academy of Finland. Financial support from the Graduate School in Chemical Engineering (GSCE) is gratefully acknowledged.

References

- [1] R.W. Taft, *J. Am. Chem. Soc.* 74 (1951) 3120.
- [2] R.W. Taft, *J. Am. Chem. Soc.* 75 (1953) 4231.
- [3] J. Vojtko, *Z. Phys. Chem.* 271 (1990) 1227.
- [4] J. Vojtko, *Chem. Z.* 4 (1983) 467.
- [5] A. Finiels, P. Geneste, C. Moreau, *J. Mol. Catal. A* 107 (1996) 385.
- [6] D.Yu. Murzin, N.V. Kul'kova, *React. Kinet. Catal. Lett.* 63 (1998) 317.
- [7] D.Yu. Murzin, S. Smeds, T. Salmi, *React. Kinet. Catal. Lett.* 71 (2000) 47.
- [8] K. Weissermel, H.-J. Arpe, *Industrial Organic Chemistry*, 3rd Edition, VCH, New York, 1997, p. 289 (Chapter 11).
- [9] P. Mäki-Arvela, T. Salmi, M. Sundell, K. Ekman, R. Peltonen, J. Lehtonen, *Appl. Catal. A* 184 (1999) 25.
- [10] R. Rönneck, T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, E. Tirronen, *Chem. Eng. Sci.* 52 (1997) 3369.
- [11] C.E. Leyes, D.F. Othmer, *Ind. Eng. Chem.* 37 (1945) 965.
- [12] M. Petro, D. Mravex, J. Ilavský, *Chem. Z.* 37 (1983) 461.
- [13] R. Roy, S. Bhatia, *J. Chem. Technol. Biotechnol.* 37 (1987) 1.
- [14] P. Dakshinamurty, M.V.S. Ramarao, Ch.V. Ramachandramurty, *J. Chem. Technol. Biotechnol. A* 34 (1984) 257.
- [15] S.Y. Kekre, M. Gopala Rao, *Ind. Chem. Eng. N* 10 (1969) 115.
- [16] A. Chakrabarti, M.M. Sharma, *React. Polym.* 20 (1993) 1.
- [17] F. Zidan, M.F. El-Hadi, M.R. El-Nahas, *Pakistan J. Sci. Ind. Res.* 29 (1986) 397.
- [18] O.N. Karpov, I.I. Somova, *Khim. Technol.* 5 (1974) 61.
- [19] O.N. Karpov, R.M. Bystrova, *Zh. Prikl. Khim.* 40 (1967) 1399.
- [20] Y.A. Elewady, M.R. El-Nahas, M.N.H. Moussa, *Ind. J. Chem. A* 26 (1987) 63.
- [21] Y.A. Elewady, A.M. El Wakil, M.R. El-Nahas, M.N.H. Moussa, *J. Ind. Chem. Soc.* 61 (1984) 517.
- [22] B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 5th Edition, Addison-Wesley/Longman, Harlow, 1989, p. 696 (Chapter 5).
- [23] J. McMurry, *Organic Chemistry*, Brooks/Cole, Belmont, 1992, p. 804.
- [24] M.S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 204.
- [25] D.Yu. Murzin, N.V. Kul'kova, *Kinet. Catal.* 36 (1995) 70.
- [26] H. Haario, *MODEST—User's Guide*, Profmath Oy, Helsinki, 1994.