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An ion-exchange membrane reactor for esterification of oleic acid and methanol: REMI

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Abstract

Full and complete esterification of oleic acid and methanol, catalyzed by cationic activation, is done quickly at room temperature in a new kind of reactor fitted with cation-exchange membranes, REMI. This type of reactor displays liquid phases and prevents the occurrence of the compensating ion of the proton, which catalyses the reaction, in the reaction medium. Some common inorganic (hydrochloric, phosphoric, sulphuric) and organic (acetic, methane sulfonic, paratoluene sulfonic) acids were used as catalysts. With such a reactor, ester is produced quickly at room temperature without mixing with the catalysing acid. No downstream processing is required. A dimensionless kinetic law is proposed for the present experiments and is suitable for all possible reaction mechanisms when cationic activation occurs with only one of the reactants.

1. Introduction

By esterification of a carboxylic acid R_1COOH with an alcohol R_2OH it is possible to obtain an ester R_1COOR_2 in homogeneous medium [1]. Currently, alcoholysis of fatty acids is performed in traditional well-mixed reactors [2]. As a consequence, hydrolysis of the ester by the water produced is possible. Finally, the concomitant reactions, esterification and hydrolysis, reach an equilibrium. At room temperature, the equilibrium state needs a long time to be attained. Using Le Châtelier's laws or with the help of catalysis, it is possible either to modify the equilibrium composition or to accelerate the overall kinetics of the reaction (1):

$$R_1COOH + R_2OH \rightleftharpoons R_1COOR_2 + H_2O \qquad (1)$$

Among the means suitable for the displacement of this equilibrium, it is possible to use a high content of one of the reactants, generally the alcohol [3], to eliminate one of the products, generally the water, (i) by modifying the equilibrium between phases, similar [4] or different [5], (ii) with a molecular sieve [6], (iii) with a desiccating compound [7], or (iv) with a membrane process, such as reverse osmosis [8] or pervaporation [9,10].

Among the means to increase the kinetics, it is possible to use homogeneous [11] or heterogeneous [12,13] catalysis, metallic [14] or enzymatic [15] catalysts, some being stereoselective [16]. When, catalysis is homogeneous, at the end of the reaction it is necessary to separate the catalysts from the mixture. A common way is to use distillation, even though high temperatures are disadvantageous [17]. When catalysis is heterogeneous, for example with ion-exchange resins

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[18], it is necessary to regenerate them from time to time, giving rise to polluting wastes [19].

Generally, increasing the temperature increases the reaction rates, but decreases the equilibrium constant [20]. Moreover, high temperature induces denaturation of organic compounds, formation of secondary products and parallel reactions. So, it is interesting to dispose a reactor allowing the formation of the ester at room temperature.

With the membrane reactor described in the following, the ester is produced without any mixture with the catalyst and any regeneration [21]. When ion-exchange membranes are correctly arranged and used it is possible to introduce only the catalysing species by diffusion or migration in the reacting volume. Then, if an ion-exchange membrane separates two liquids, only one of them contains the catalysing ionized compound and a layer of fixed counter-ions appears on each side of the membrane [22]. The concentration of the counter-ions in the charged layer is then obtained from Poisson's law [23].

In the present work, for the esterification of oleic acid and methanol with protons as catalyst, we used a cation-exchange membrane. So, a layer of protons appears on the surface of the membrane facing the mixture of alcohol and carboxylic acid and acts as catalyst. But, the anion associated to these protons in the catalysing acid remains on the other side of the membrane. So, at the end of the reaction with such a reactor exchanging membrane ions, REMI, it is not necessary to proceed with a down stream separation of the catalyst and no catalysing acid is lost.

2. Ion-exchange membrane reactor (REMI)

In our work, the esterification of oleic acid and methanol was performed at room temperature with a plate and frame stack previously described [24] fitted with cation-exchange membranes kindly supplied by Rhône-Poulenc (Fig. 1). In this laboratory stack, 4 cation-exchange membranes (cem) (7×6 cm^2 each) give 5 compartments (j′, b′, r, b″, j″) allowing changes of the surface area in contact with the reacting mixture, which generally circulates in the center compartment (r). In some cases an ion-exchange resin (Bayer K2411) is put in the compartments. The end plates (ep) are pressed by a screw press. The solutions are continuously recycled by means of a peristaltic pump (pp).

All the experiments were performed with the same amount of oleic acid (25 g), methanol (75

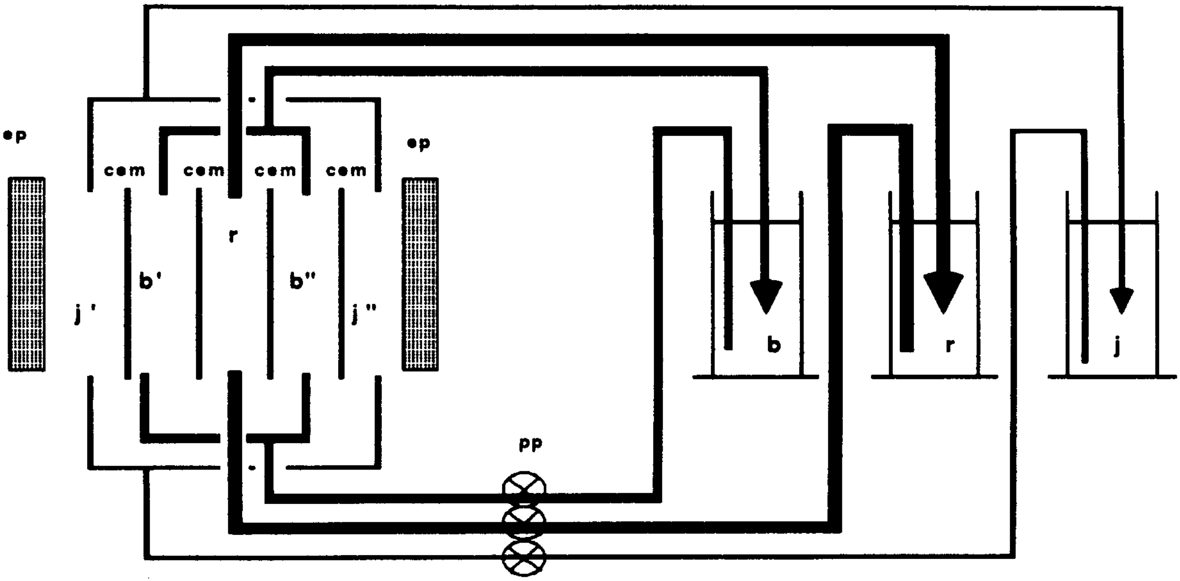

Fig. 1. Experimental fitting.

g) and catalysing acid (0.6 g) and, if used, of ion-exchange resin (3.9 g). Only the nature of the catalysing acid was varied.

3. Kinetic mechanisms and laws

3.1. Homogeneous mechanisms

Due to the industrial importance of the products resulting from esterification reactions between a fatty acid and an alcohol, it is useful to use a Lewis acid [25]. At temperatures lower than 50°C the catalytic effect is attributed to the formation of a protonated compound with one of the reagents. Then, the reaction occurs between this compound and the other reagent [26]. Initially it was suggested that alcohol was the protonated compound [27], but the use of oxygen isotopes shows that protons from the catalysing acid are fixed on the carboxylic acid molecules [28] and that the water molecules produced are created with the OH group of the carboxylic acid [29]. According to these results and taking into account the water content in the reacting volume due to the esterification reaction and to the hydration of the reagents or the catalysing acid XH, the reaction mechanism can be written as:

$$XH+H_2O \rightleftharpoons X^- + H_3O^+ \quad (2)$$

$$R_1COOH+H_3O^+ \rightleftharpoons R_1COOH_{2^+} + H_2O \quad (3)$$

$$R_1COOH_{2^+} + R_2OH \rightarrow R_1COOR_2 + H_3O^+ \quad (4)$$

Assuming that the limiting step is reaction (4) with a kinetic constant k_1, that the partial reaction order is 1 for every reacting species [30] and that the solution remains electrically neutral, the rate r of esterification is given by relationship (5) where K_A is the equilibrium constant for the protonation of the carboxylic acid, $h°$ the initial content of catalysing protons, C_A, C_B and C_W the concentrations of carboxylic acid, alcohol and water.

$$r=k_1 \cdot h° \cdot K_A \cdot C_A \cdot C_B(C_W + K_A \cdot C_A) \quad (5)$$

When the reaction is carried out with a large amount of alcohol, the relation is analogous to that in use for more than 3/4 of a century, but derived with the assumption of alcohol protonation [31,32] which has already been tabulated [33].

But it is easy to show that such a relation is always obtained when any reagent or product is protonated. For example, when the ester produced with concentration C_E is also protonated, K_E being the equilibrium constant, and k_2 the kinetic constant, the denominator of the previous relation includes only one additional term:

$$r=k_2 \cdot h° \cdot K_A \cdot C_A \cdot C_B/(C_W + K_A \cdot C_A + K_E \cdot C_E) \quad (6)$$

3.2. Heterogeneous mechanisms

The method we suggest here, allows easy access of the carboxylic acid to the protons of the catalysing acid, as they are present on the surface of a cation-exchange membrane [22]. Then, the mechanism is quite the same as in the case of a homogeneous reaction, but the limiting step is the reaction between the alcohol and the protonated carboxylic acid bound to the anionic fixed charges of the membrane. However, part of the initial anionic fixed sites, of initial concentration $(\underline{h}°)$, are occupied by protonated water [34]. Then, the kinetic law, of constant k_6, is:

$$r=k_6 \cdot (\underline{h}°) \cdot K_{\underline{A}} \cdot C_A \cdot C_B/(1 + K_{\underline{A}} \cdot C_A + K_{\underline{W}} \cdot C_W) \quad (7)$$

$K_{\underline{A}}$ and $K_{\underline{W}}$ are the equilibrium constants for adsorption of carboxylic acid and water on the fixed anionic sites of the membrane.

3.3. Kinetic laws

In the expression of the previous kinetic rates (5),(6) and (7), it is interesting to introduce dimensionless variables. Using the conversion degree f of carboxylic acid A to ester E and the molecular amount e of alcohol B with regard to acid A:

$$f = C_E / C_A{}^{\circ} \tag{8}$$

$$e = C_B / C_A{}^{\circ} \tag{9}$$

the kinetic law for any esterification undergone with a limiting step occurring after an equilibrated protonation may be written as:

$$df/dt = k \cdot (1-f) \cdot (e-f)/(g+f) \tag{10}$$

k, g being constants and t the time. Assuming that f $(t=0) = 0$ and non-stoichiometric conditions, i.e. $e \neq 1$, integration of relation (10) gives:

$$k \cdot t = \{(1+g)/(1-e)\} \ln\{1/(1-f)\} - \{(e+g)/(1-e)\} \ln\{1-(f/e)\} \tag{11}$$

When, as in the following, the reaction occurs with a large amount of alcohol, i.e. when e is larger than 1, and, of course than f, this relationship reduces to:

$$k \cdot e \cdot t = \{(1+g)\} \ln\{1/(1-f)\} - f \tag{12}$$

where, for example, in the case of a homogeneous mechanism [35]:

$$k = k_1 \cdot h^{\circ} \cdot K_A / (1-K_A) \tag{13}$$

and

$$g = \{C^{\circ}_w + C^{\circ}_A \cdot K_A\} / \{C^{\circ}_A (1-K_A)\} \tag{14}$$

The expressions of k and g contain $(1-K_A)$ in the denominator, so the values of k and g must be negative as K_A is greater than unity since the protonation of the acid occurs.

4. Esterification: results and discussion

4.1. REMI with a catalysing acid and resin

Six catalysing acids, 3 organic and 3 inorganic, were tested. The mixture of oleic acid and methanol ($e = 26.3$) circulating in the center compartment (r) filled with the ion-exchange resin, the catalysing acid diluted in methanol circulated in the contiguous compartments (b) and (j). For a different initial content of catalysing protons h°, the conversion degree f was measured every two hours at room temperature. Then, for each experiment, the value of k in Eq. (12) was calculated, g being optimised to give the smallest standard deviation of k for all the measurements.

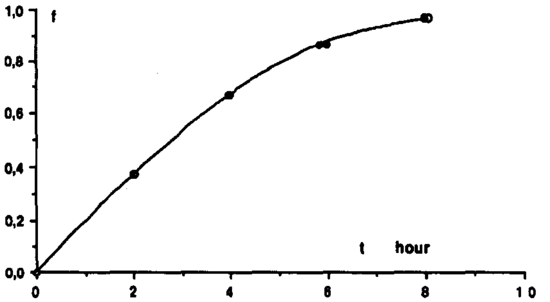

Fig. 2. Example of the application of law (12). ●, experimental point; ○, calculated value.

As a result, it is possible to compare the calculated and the experimental values of f. As shown in Fig. 2, they agree very well, indicating that the hypothesis made concerning the mechanism and relation (12) can accurately represent the real phenomena. The above calculations always give negative values for both constants k and g as postulated. From the 12 experimental values, it is possible to calculate, for each acid, the mean value of k/h° and g. The values are indicated in Table 1. They show that acetic and phosphoric acid must be discarded as they give values for g greater than -1. Consequently, the 4 remaining acids can be used as the values of k/h° are lower than -1, the best being sulphuric acid. Furthermore, this agreement shows that no secondary products are formed, corroborating the experimental observations.

4.2. REMI with resin and without catalysing acid

For comparison, tests were performed without catalysing acid, but with the resin filling the central compartment (r) or all the compartments (j, b, r): in both cases, the value of k/h° is higher than in the previous case, indicating that catalysis by protons from the catalysing acid is capital.

Table 1
Calculated values of k/h° and g for the six catalysing acids

Catalysing acid	$10^3 \cdot k/h^\circ$ ($m^3 \cdot min^{-1} \cdot kmol^{-1}$)	g (dimensionless)
Acetic	−13.692	−0.510
Sulphuric	−12.619	−1.297
Hydrochloric	−10.918	−2.996
Paratoluene sulfonic	−6.294	−1.447
Methane sulfonic	−2.636	−1.120
Phosphoric	−0.262	−0.320

4.3. REMI without resin and with a catalysing acid

Again for comparison, tests were performed without resin filling the central compartment (r) but with a catalysing acid. The values of k/h° were always higher than when resin filled the central compartment (r), corroborating the idea that protons from the catalysing acid are necessary and resin unnecessary.

4.4. Comparison with a traditional reactor

These results where compared to data obtained with a traditional perfectly mixed reactor working at room temperature. Fig. 3 shows such a comparison. It clearly appears that in this membrane reactor, REMI, esterification always occurred faster than in a tank reactor, even though its design is more sophisticated.

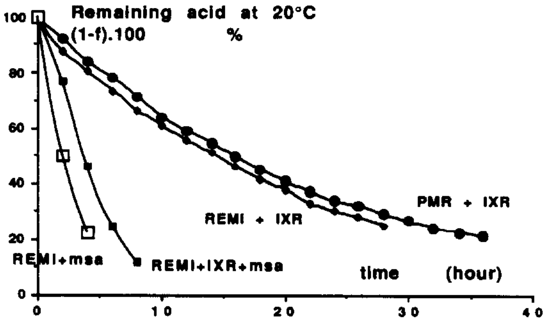

Fig. 3. Comparisons of esterifications of oleic acid and methanol at room temperature between a perfectly mixed reactor (PMR) and an ion-exchange membrane reactor (REMI), filled with an ion-exchange resin (IXR) or not and catalysed with methanesulfonic acid (msa) or not.

5. Conclusion

First of all, these experiments show that esterification is well performed with the ion-exchange membrane reactor 'REMI' described. However, unlike the membrane reactors used for chemical reactions, the present ion-exchange membrane reactor works on liquids [36,37]. Consequently, this ion-exchange membrane reactor allows exclusion of the counter ions of the catalysing protons in the reacting mixture thus obviating the need for their elimination with special downstream treatments. Moreover, this membrane reactor works at room temperature favouring reactor 'REMI' with a catalysing acid, but without an ion-exchange resin filling the compartments.

So, esterification is cheaper and cleaner than with traditional mixed reactors: this ion-exchange membrane reactors will contribute to a cleaner chemical industry.

References

[1] M. Berthelot and Péan de Saint Gilles, Ann. Chim. Phys., 65 (1862) 385–422.
[2] J. Villermaux, Génie de la réaction chimique, Lavoisier Edt, Paris, 1982.
[3] W. Ling and Ch. Geankoplis, Ind. Eng. Chem., 50 (1958) 939–942.
[4] M. Loury and M.T. Mellier, Oléagineux, 5 (1947) 254–259.
[5] M. Zaidan, S. Domenech and B. Gilot, Entropie, 129 (1986) 62–68.
[6] H. Harrison, W. Haynes, P. Arthur and E. Eisenbraun, Chem. Ind. (London), 45 (1968) 1568–1574.
[7] A. Arrieta, T. Garcia, J.M. Lago and C. Palomo, Synth. Commun., 13 (1983) 471–487.
[8] R. Audinos, A. Lalou, Z. Mouloungui and B. Gilot, Journ. Chevreul, Toulouse, 22–23 Nov. 1990.
[9] H. Kita and S. Sasaki, Chem. Lett., (1988) 2025–2028.
[10] P. Schaetzel, M. David, Q.T. Nguyen and J. Neel, Rects. Prog. Gen. Proc., 6 (21) (1992) 389–394.
[11] D. Othmer and S.A. Rao, Ind. Eng. Chem., 42 (1950) 1912–1919.
[12] M. Sardin and J. Villermaux, Nouv. J. Chim. 3 (4) (1979) 256–261.
[13] S. Shimizu and C. Hirai, Bull. Chem. Soc. Jpn., 59 (1986) 7–11.
[14] E. Nasr, Thesis Dr. Ing., INPT Toulouse, June 1983.
[15] M. Habulin and Z. Knez, J. Membrane Sci., 61 (1991) 315–324.
[16] G. Rios, F. Lambert and J. Jallageas, Entropie, 163 (1991) 31–36.

[17] D.B. Keyes, Ind. Eng. Chem., 24 (1932) 1096–1103.
[18] K.S. Markley, Fatty Acids, Interscience Publishers Inc., New York, 1961.
[19] P. Marchal, C. Masson, Z. Mouloungui, M. Delmas and A. Gaset, Rev. Fr. Corps Gras, 32 (1985) 429–432.
[20] B. Chemseddine, Thesis INPT, Toulouse, May 24, 1994.
[21] R. Audinos and B. Chemseddine, Eur. Pat. Fr. 93.04558.
[22] J. Koryta, Ions, Electrodes and Membranes, J. Wiley, Chichester, 1992.
[23] R. Patel and K.-C. Lang, IEC Fund. 16, (1977) 340–348.
[24] R. Audinos and S. Paci, Desalination, 67 (1987) 523–545.
[25] Ch. Leyes and D. Othmer, Ind. Eng. Chem., 37 (1945) 968–977.
[26] S. Datta, J. Day and C. Ingold, J. Chem. Soc., 61 (1939) 838–840.
[27] A. Williamson and C. Hinshelwood, Trans. Faraday Soc., 30 (1934) 1145–1149.
[28] C. Ingold, Structure and Mechanisms in Organic Chemistry, Cornell Univ., Ithaca, 1953.
[29] I. Roberts and H. Urey, J. Am. Chem. Soc., 60 (1938) 2391–2393.
[30] H. Smith, J. Am. Chem. Soc., 61 (1939) 254–260.
[31] H. Goldschmidt and O. Ubdy, Z. Physik. Chem., 60 (1913) 728–755.
[32] H. Goldschmidt and A. Thuesen, Z. Physik. Chem., 81 (1913) 30–67.
[33] NBS, Tables of Chemical Kinetics, US Dept of commerce, Washington, 1951.
[34] J. Germain, Catalyse hétérogène, Dunod, Paris, 1959.
[35] B. Chemseddine and R. Audinos, J. Chim. Phys., 91 (1994) 223–245.
[36] H. Hsieh, AIChE, 85 (1989) 53–57.
[37] L. Bernstein and C. Lund, J. Membrane Sci., 77 (1993) 155–164.