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Pervaporation Aided Esterification of Carboxylic Acids with Ethanol Catalyzed by *Porcine Pancreatic* Lipase

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The results of pervaporation-coupled esterification of various carboxylic acids with ethanol catalyzed by *Porcine pancreatic* lipase are reported. The effect of lipase and substrate concentrations has been studied and the advantage of pervaporation on the equilibrium conversion has been deduced. The kinetics of reaction were analyzed with a three-parameter model which coupled the effect of pervaporation. The intrinsic kinetic constants for all the reactions were estimated and correlated with the carbon number, an indicator of hydrophobicity of the acids. It was found that the rate constant increases with decrease in carbon number. The experimental concentration profiles were simulated from the model for all the reactions and the model prediction was found to be reasonably good. The water permeability was also correlated well with acid hydrophobicity. The pervaporation coupled reaction efficiency, as represented by the reaction time for equilibrium conversion, was found to bear a profound relation to membrane surface area per unit volume of the reaction mixture (A/V). The time for equilibrium conversion was found to decrease with an increase in A/V value, reaching a minimum and then increasing with a further increase of A/V. A probable explanation has been postulated for such an observation.

Keywords: Pervaporation; Lipase; Kinetics; Permeability; Hydrophobicity; Equilibrium

INTRODUCTION

Esterification of carboxylic acids represents a significant group of the reactions commonly found in the chemical industry. The equilibrium conversion of such reactions under otherwise identical conditions of substrate and catalyst concentration can be increased through use of an efficient *in situ* removal of inhibitory side product. Distillation is a commonly known technique for the removal of water, however azeotrope formation renders it prohibitive for the design of an efficient process (Keurentjes *et al*., 1994). In order to avoid this problem, membrane separation can be considered as a viable alternative. The use of membranes to separate water as the by-product in a reversible reaction is an effective method for preparing some esters. Various microporous membranes have been studied for separating gases from reaction product, including small molecules such as hydrogen (Jennings and Binning, 1960; Kita *et al*., 1987, 1988; Pearce, 1987). The use of dense membranes of polymeric materials for removal of water vapor generated by esterification and other reactions were separately studied by others (Kita *et al*., 1987, Okamoto *et al*., 1993, Ravindra *et al*., 2000). However, a systematic study of various carboxylic acids with ethanol has not been reported in the literature. The importance of pervaporation aided esterification reactions has been illustrated in a review published by the investigating group (Dutta and Barthakur, 1993).

In this paper, the *Porcine pancreas* lipase catalyzed esterification of various carboxylic acids with ethanol has been investigated using a Celgard 2400 hydrophilic membrane. An attempt has also been made to simulate the process via a suitable kinetic model that represents the combined effect of reaction and pervaporation.

THEORETICAL ASPECTS

Kinetics of the Reaction

Only a limited approach has been made so far to develop a kinetic model for pervaporation aided

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esterification reactions. The following two models are noteworthy:

Model I

Developed by Krupiczka and Kaszorz (1999), the model considers an intrinsic rate equation based on species activities as given by

$$r = k_f c_{cat}\left(a_{eth}a_a - \frac{a_w a_e}{K^a}\right) \quad (1)$$

where a_{et}, a_a, a_w and a_e are the appropriate activities and r, c_{cat}, k_f and K^a are the reaction rate, catalyst concentration, forward rate constant and equilibrium constant respectively and can be defined as,

$$K^a = \frac{a_w a_e}{a_{eth}a_a} \quad (2)$$

The molar rate of removal of water from the reaction mixture by pervaporation is assumed as the product of permeability coefficient and concentration of the liquid,

$$n_w = AP_w c_w \quad (3)$$

where A is the area of the membrane, n_w is the permeation flux and P_w is the permeability coefficient of water.

For pervaporation reaction coupling, we can define the water concentration profile starting with the water mass balance equation given as

$$\frac{d[Mc_w]}{dt} = -n_w + rM \quad (4)$$

where, M is total mass of reaction mixture in the reactor.

Now the total mass balance equation is,

$$\frac{d[M]}{dt} = -n_w M_w \quad (5)$$

where, M_w is the molar mass of water.

By introducing Eq. (4) into Eq. (3) and rearranging we have,

$$\frac{dc_w}{dt} = \frac{n_w}{M}(c_w M_w - 1) + r = \frac{AP_w c_w}{M}(c_w M_w - 1) + r \quad (6)$$

and by introducing Eq. (1) into Eq. (5), we get the water concentration profile as,

$$\frac{dc_w}{dt} = \frac{AP_w c_w}{M}(c_w M_w - 1) + k_f c_{cat}\left(a_{eth}a_a - \frac{a_w a_e}{K^a}\right) \quad (7)$$

The concentration profile of the acid can also be obtained by similar method and the following expression can be deduced:

$$\frac{dc_a}{dt} = \frac{AP_w c_w M_w}{M} c_a - k_f c_{cat}\left(a_{eth}a_a - \frac{a_w a_c}{K^a}\right) \quad (8)$$

Model II

This model was developed by David *et al*. (1991a,b) and considers differential mass balance of the species along with permeation flux across the membrane. The permeation flux of water is represent as

$$n_w = -D\frac{\delta c_w}{\delta x} \quad (9)$$

where x is the thickness of the membrane, D is the diffusion co-efficient of water in the membrane which is a function of local concentration of each component in the membrane. There is an almost linear relationship between permeation flux and water concentration in the case of the pervaporation of organic solvents containing a low amount of water and is written as,

$$n_w = Pc_w \quad (10)$$

The permeation flux is more generally written as a function of permeability Q, instead of the permeance.

$$n_w = \frac{Q}{e} c_w \quad (11)$$

where e is the homogeneous film through which pervaporation transport occurs.

In a very short time, dt, the number of moles of water produced by the reaction is N_{oalc} dX.

Since the number of moles of water produced and accumulated in the cell is N_{oalc}dY, the number of moles of water, dN_w, extracted during this length of time, dt may be calculated from this difference.

$$dN_w = N_{oalc}(dX - dY) \quad (12)$$

where $X = N_{est}/N_{oalc}$, $Y = N_w/N_{oalc}$ and N_{est} is the number of moles of ester produced at time t and N_w is the molar quantity of water in the reactor.Thus the pervaporation rate, n_w at a time t is given as,

$$n_w = \frac{N_{oalc}}{A}\left(\frac{dX}{dt} - \frac{dY}{dt}\right) \quad (13)$$

Combining this equation with Eq. (10),

$$Pc_w = \frac{N_{oalc}}{A}\left(\frac{dX}{dt} - \frac{dY}{dt}\right)$$

$$\text{or } P\frac{N_w}{V} = \frac{N_{oalc}}{A}\left(\frac{dX}{dt} - \frac{dY}{dt}\right) \quad (14)$$

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where V is the volume of the reacting mixture at time t.

Now, the rate of esterification can be written as

$$\frac{d[ester]}{dt} = k_1[alcohol][acid][cat] - k_{-1}[water][ester][cat] \quad (15)$$

where k_1 and k_{-1} is the forward and backward rate constant respectively.

The general kinetic equation for the reaction is unchanged except that the concentration in the reactor changes due to both the reaction and the pervaporation:

$$\frac{d[ester]}{dt} = k_1[alcohol][acid][cat] - \frac{k_1}{K_{eq}}[water][ester][cat] \quad (16)$$

where, K_{eq} is the equilibrium constant.

Using the degree of conversion instead of concentration, this equation is equivalent to,

$$\frac{dX}{dt} = k_1\frac{N_{oalc}}{V}[cat](1-X^2) - k_{-1}\frac{N_{oalc}}{V}[cat]X^2 \quad (17)$$

However, in the pervaporation, only water was extracted from the reacting media. In this condition, Eq. (17) can be rearranged to

$$\frac{dX}{dt} = k_1\frac{N_{oalc}}{V}[cat]\left[(R_o - X)(1-X) - \frac{XY}{K_{eq}}\right] \quad (18)$$

where k_1 and K_{eq} are the rate and equilibrium constants for the esterification without pervaporation ($m^6 mol^{-2}\ min^{-1}$), N_{oalc} is the initial molar quantity of alcohol (mole), R_o is the ratio of the initial molar quantity of alcohol to acid or acid to alcohol. When $N_{oalc} = N_{oac}$, Eq. (18) becomes,

$$\frac{dX}{dt} = k_1\frac{N_{oalc}}{V}[cat](1-X^2) - \frac{XY}{K_{eq}} \quad (19)$$

The above equation gives the production of ester. Now, the production of water is given as,

$$\frac{dY}{dt} = \frac{dX}{dt} - PY\frac{A}{V} \quad (20)$$

$$\text{Finally, } \frac{dX}{dt} - \frac{dY}{dt} = PY\frac{A}{V} \quad (21)$$

By plotting $\frac{dX}{dt} - \frac{dY}{dt}$ vs Y, straight lines of slopes proportional to permeance can be obtained.

During the reaction, the volume V changes due to *in situ* removal of water and transformation of reactants to products of different specific masses. By assuming the volume additivity of different components, the following relationship can be deduced:

$$\frac{V}{N_{oalc}} = \frac{M_{alc}}{\rho_{alc}} + R_o\frac{M_a}{\rho_a} + Y\frac{M_w}{\rho_w} + X\left(\frac{M_{est}}{\rho_{est}} - \frac{M_{alc}}{\rho_{alc}} - \frac{M_a}{\rho_a}\right) \quad (22)$$

where ρ_{alc}, ρ_{ac}, ρ_w, ρ_{est} are the specific masses of alcohol, acid, water and ester respectively and M_{alc}, M_{ac}, M_w, M_{est} are the molar weights of alcohol, acid, water and ester respectively.

MATERIALS AND METHODS

Porcine pancreatic lipase (with a specific activity 70 units per milligram protein) and ethanol were procured from SRL Ltd., Mumbai, India. Various carboxylic acids of 70% purity, esters and solvents were procured from CDH Ltd., New Delhi, India. Ethanol with 99.7% purity was procured from BDH Ltd., England. The pervaporation experiments were performed using a Celgard 2400 hydrophilic membrane procured from Hoechst Celanese, France.

A schematic diagram of pervaporation set up is shown in Fig. 1. The membrane was supported by a stainless steel (S.S.) screen embedded in a S.S. porous plate. Gaskets were placed on either side of the membrane, and the sandwich was kept between the glass column couplers and clamped together to give a vacuum tight arrangement. The effective area of the membrane in the PV cell was 0.159 m^2. The top half was used as the feed chamber and the bottom

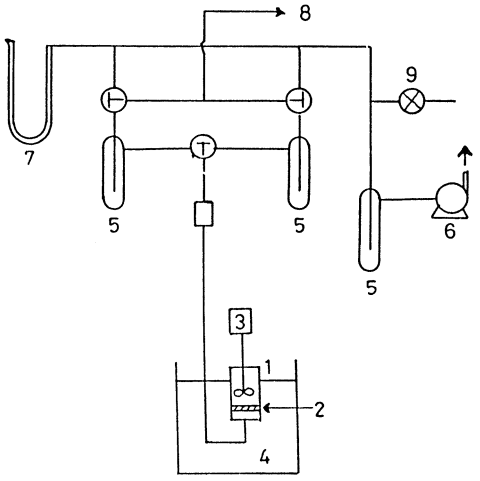

FIGURE 1 A schematic diagram of the experimental apparatus 1. reaction cell 2. pervaporation membrane 3. stirring motor 4. constant temperature 5. cold trap 6. vacuum pump 7. manometer 8. vent (N_2 gas) 9. by-pass stop cock.

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half worked as the permeate chamber. At the beginning of each run, a dry membrane was mounted in the cell. Feed was introduced in the upper chamber and vacuum was applied from the opposite side. The permeate pressure was measured with an Edwards Mcleod gauge. Each experiment was repeated twice, using fresh feed solution to check for reproducibility. The same volume of feed material was introduced in each run to avoid any experimental variation. Pure component feeds were used for all the experiments. A mixture of acid and alcohol with 20 mg/ml of lipase was introduced in the feed chamber maintaining the molar ratios of acid and alcohol at specified levels. The total amount of mixture was 20 ml and the molar ratios of acid and alcohol were 1:1, 1:2, 1:3 and 1:4.

In the feed chamber, the reaction mixture was stirred with a teflon stirrer at around 250 rpm. A gaseous mixture of ethanol and water generated by the esterification was refluxed and the inside of the membrane module was evacuated (13.3 Pa). The permeated gases mixture was collected with a liquid nitrogen trap and the composition of the permeate analyzed by gas chromatography. The amount of acid was titrated according to the testing method for acid value of fats and oils (JTS-K-3504) and that of the ester was determined by HPLC (Waters) equipped with U6K universal injector, 510 pumps, 746 Data Module and a μ-porasil column (300 mm × 3.9 mm ID) packed with μ-porasil particles of size 10 μm, 125Å. Elution was conducted with a hexane:isopropanol (80:20) mixture and the flow rate adjusted to 1.0 ml/min, under a pressure of 205 psi. Quantitative data were obtained with an integrator. Measurements of water vapor were carried out at 50°C according to the weighing method using a sorption apparatus equipped with a quartz spring (Crank, 1975). Ethanol concentrations were measured based on a calibration curve of ethanol concentration versus refractive index. All experiments were conducted at 0.01–0.05 mmHg in the permeate chamber. Experiments without pervaporation were carried out in a round bottom flask under conditions identical to those adopted in the pervaporation-coupled reactions.

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RESULTS AND DISCUSSIONS

Effect of Pervaporation on Carboxylic Acid Concentration

The effect of acid concentration was studied at fixed lipase and alcohol concentrations. The time courses at four different acid concentrations, at and above stoichiometric concentrations of ethanol (which was maintained at 50 mM), for esterification of four carboxylic acids with and without pervaporation are shown in Figs. 2–5. In general, the conversion in pervaporation aided reactions under otherwise identical conditions is significantly higher than that obtained without pervaporation for all the carboxylic acids presumably due to a favorable shift in equilibrium through *in situ* removal of water. However, this may also be due to the progressive disappearance of both acid and alcohol molecules during the course of reactions. In the reaction system, water saturated solvent was used throughout, keeping the water activity close to unity thereby ensuring adequate enzyme activity. The pressure in the downsteam side of the membrane was maintained at nearly the vapor pressure, such that during the pervaporation process the water content in the liquid phase was adjusted to a level representing a water activity of unity. This indicates that there was a build up of water in the reactor, which resulted from faster production than removal by pervaporation. During the early course of reaction, pervaporation did not significantly affect the reaction rate due to the high ester production rate. It has been reported that the efficiency of water removal by a hydrophilic membrane changes with water content in contact with the membrane and, for a PVA based membrane in the range of low water content, the water pervaporation rate increases quasi linearly with the water content (Keurentjes *et al*., 1994).

In the middle range of conversion, the production of ester and water by esterification slows down because of the progressive disappearance of acid and alcohol from the medium while the membrane, through its contact with a mixture progressively richer in water, becomes more permeable to water. At a certain point, water is removed more rapidly by pervaporation than it is produced by esterification, and the water content in the medium goes through a maximum resulting in high equilibrium conversion as shown in Figs. 2–5. At high conversion, the reaction rate is lower but the removal of water decreases equally, as a result of which the conversion factor increases only marginally.

Effect of Lipase Concentration

An increase in the lipase concentration may be considered as an alternative way to accelerate ester production (David *et al*., 1991b). A few pervaporation-aided reactions were carried out with different lipase concentrations in order to assess its effect on the esterification rate. Fig. 6 shows the plot of initial reaction rate as a function of lipase concentrations at fixed substrate concentrations of 50 mM. A linear increase in the initial rate at the low range of lipase concentrations implies that the reaction is kinetically controlled in this range. When the concentration of the catalyst is increased, the water content in the reaction mixture increases due to the high reaction

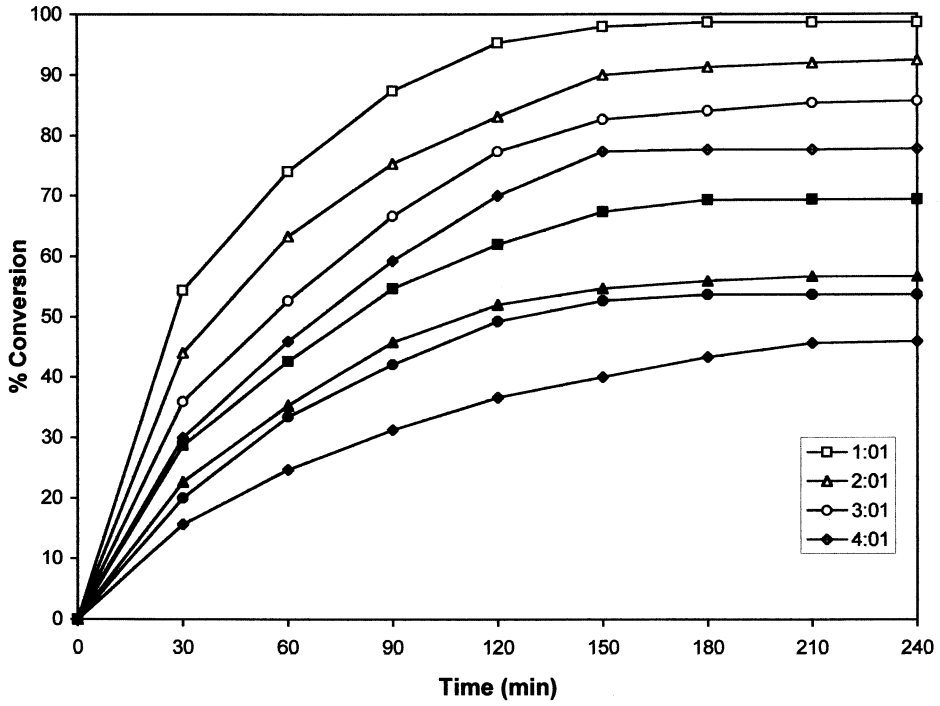

FIGURE 2 Time versus conversion profile of lauric acid and ethanol with varying acid alcohol mole ratio. Open symbols with pervaporation, closed symbols without pervaporation.

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rate, then it decreases faster during the course of the reaction due to permeation of water, an observation identical to that reported by David *et al*. (1991b) for esterification of 1-propanol and 2-propanol with propionic acid using peratoluenesulphonic acid as catalyst. At the beginning of the reaction, the rate of pervaporation is lower than the rate of esterification due to low water concentration. The increase in

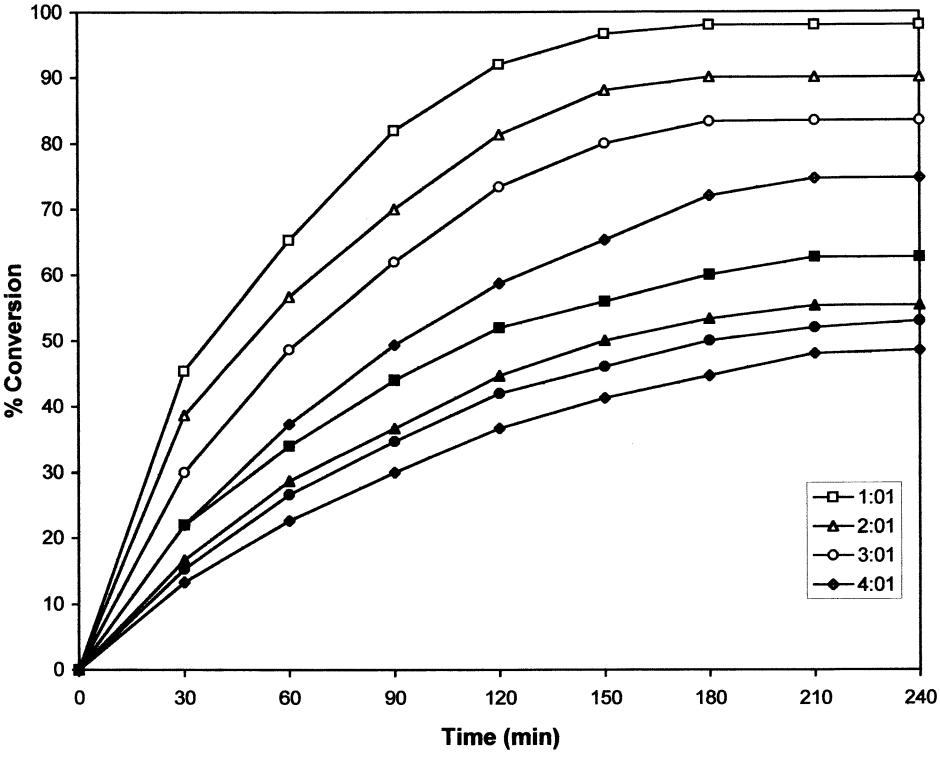

FIGURE 3 Time versus conversion profile of myristic acid and ethanol with varying acid alcohol mole ratio. Open symbols with pervaporation, closed symbols without pervaporation.

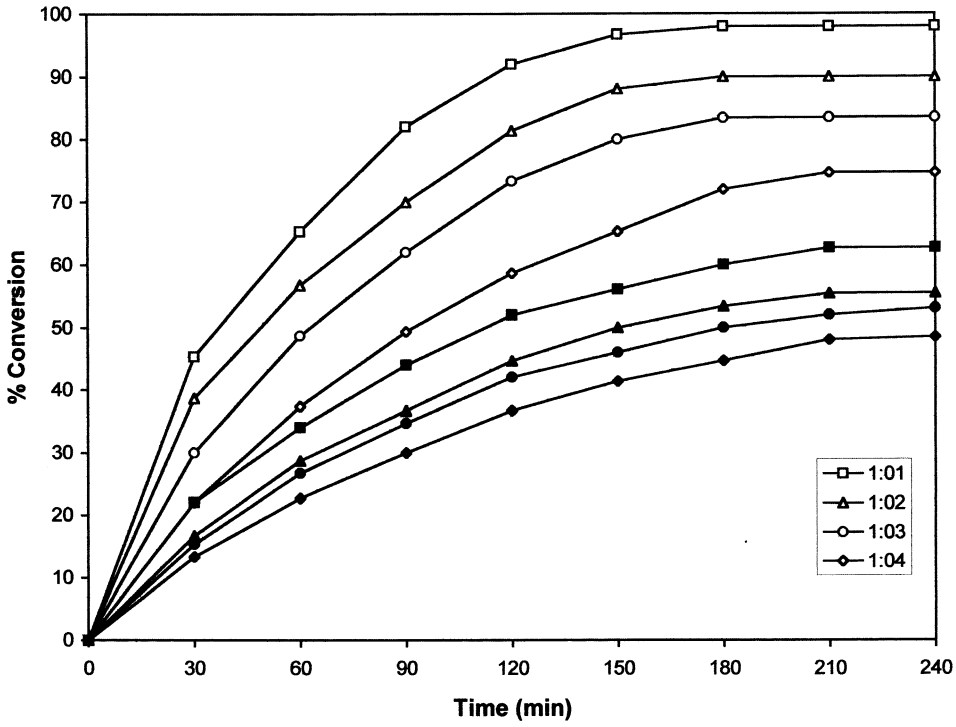

FIGURE 4 Time versus conversion profile of palmitic acid and ethanol with varying acid alcohol mole ratio. Open symbols with pervaporation, closed symbols without pervaporation.

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lipase concentration accelerates the production of ester with consequently higher water concentration, resulting in a higher rate of water removal so as to increase the equilibrium conversion.

Model Simulation and Kinetic Parameter Estimation

Eqs. (5), (7) and (8) of the first model and Eqs. (19), (20) and (22) from the second model were solved

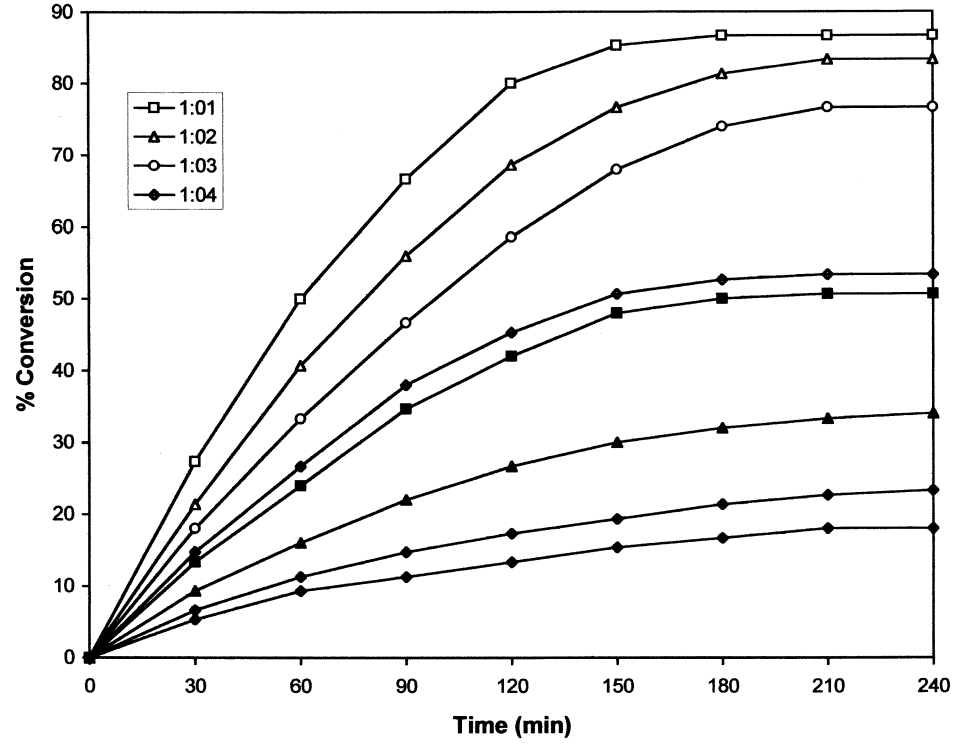

FIGURE 5 Time versus conversion profile of stearic acid and ethanol with varying acid alcohol mole ratio. Open symbols with pervaporation, closed symbols without pervaporation.

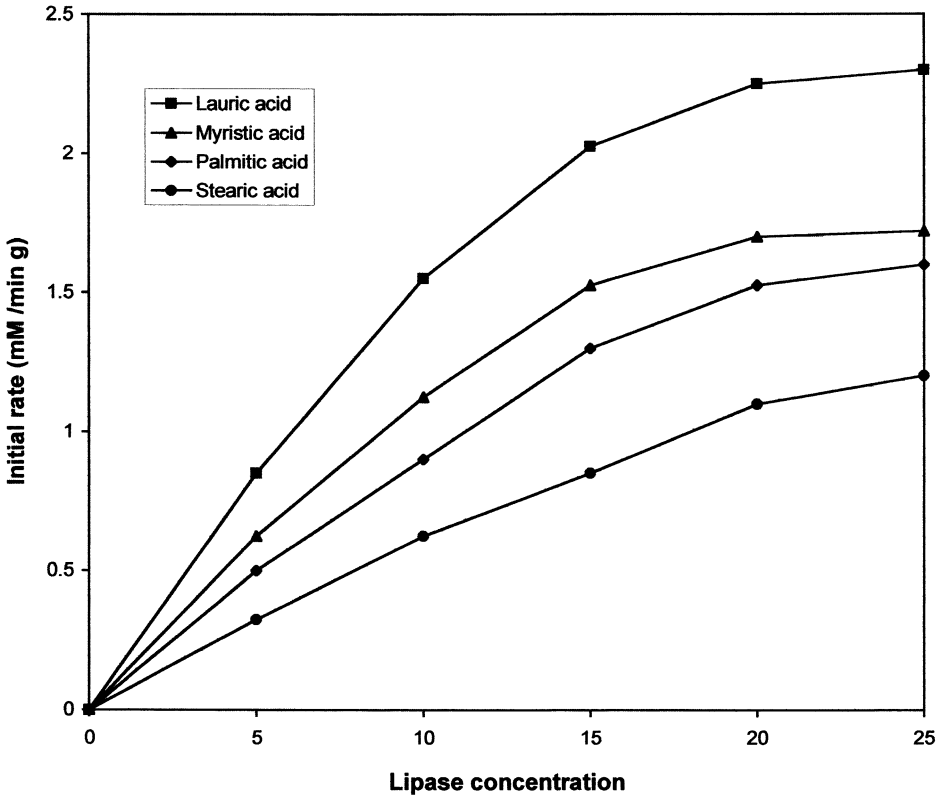

FIGURE 6 Lipase concentration as a function of initial rate.

numerically by the Runge-Kutta procedure using a Pentium PC to yield the concentrations of different species in the reactor at different times. The activity coefficients in the reaction mixture for model I were calculated by using the ASOG method (Walas, 1985) for four components. The input variables include the temperature, the required ASOG parameters and the measured amounts of acid, alcohol, ester and water.

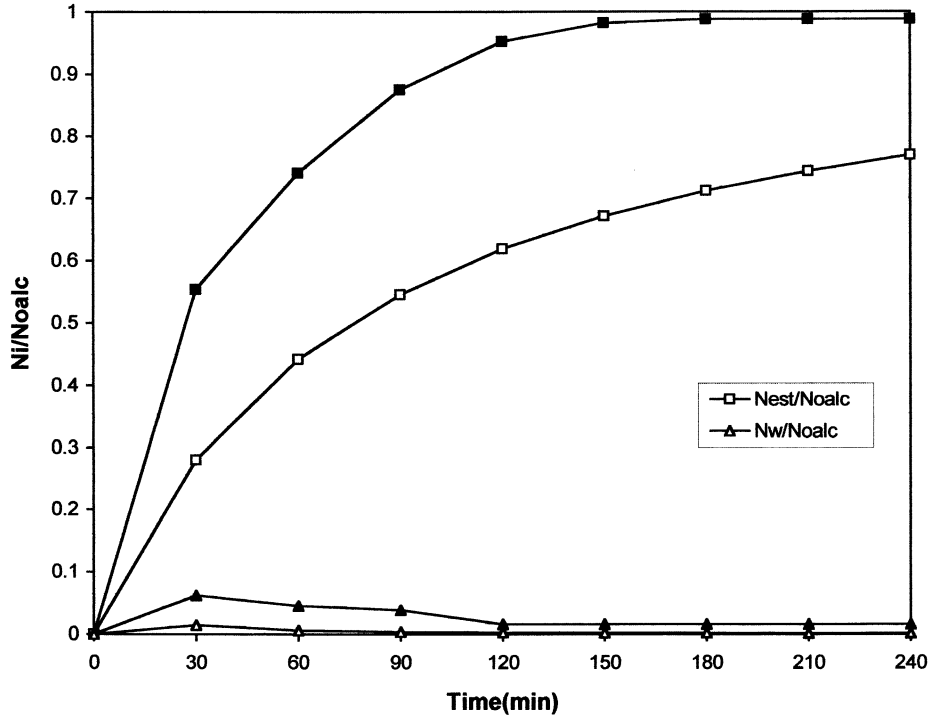

FIGURE 7 Comparison between experimental and theoretical curves of conversion versus time for the system lauric acid and ethanol, initial mole ratio, acid:alcohol = 1:1. Closed symbol experimental, open symbol theoretical.

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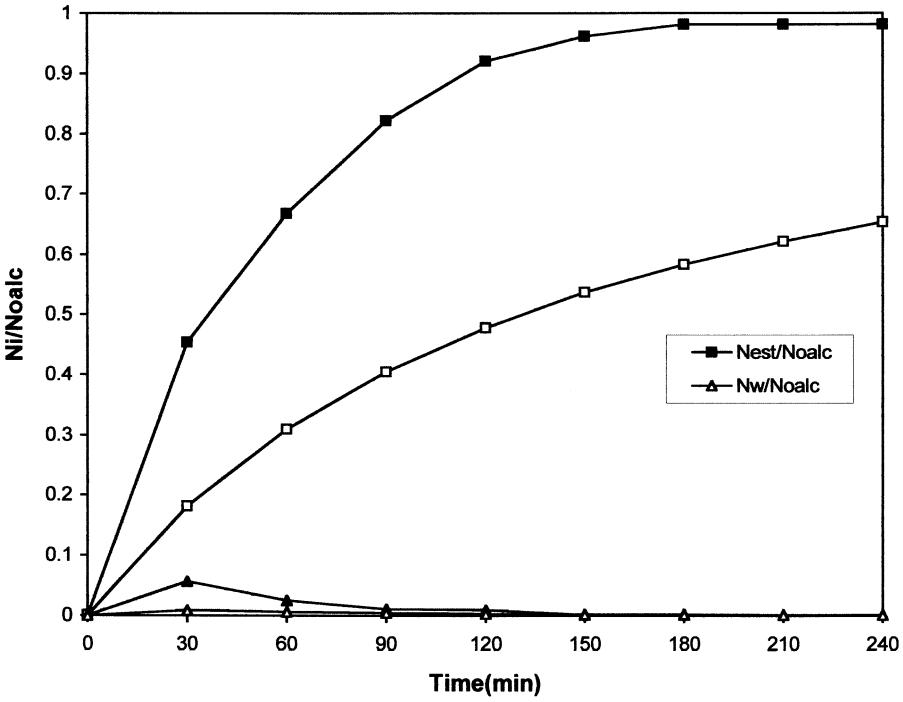

FIGURE 8 Comparison between experimental and theoretical curves of conversion versus time for the system myristic and ethanol, initial mole ratio, acid:alcohol = 1:1. Closed symbol experimental, open symbol theoretical.

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It was assumed that the low concentration of the lipase does not influence the activities of the other components. As shown in Figs. 7–10, experimental points and theoretical curves obtained for the systems are in good agreement using Model II which does not have adjustable parameters. Thus, this kinetic model used with the experimentally determined values of the kinetic parameters gives a good representation of the phenomena involved in the combination of an esterification reactor with a pervaporation module.

The results of simulation for a 1:1 to 1:4 substrate molar ratio are shown in Figs. 7–10, wherein the experimental data are also shown. It is apparent from these figures that the agreement between experimental and predicted conversion profiles for

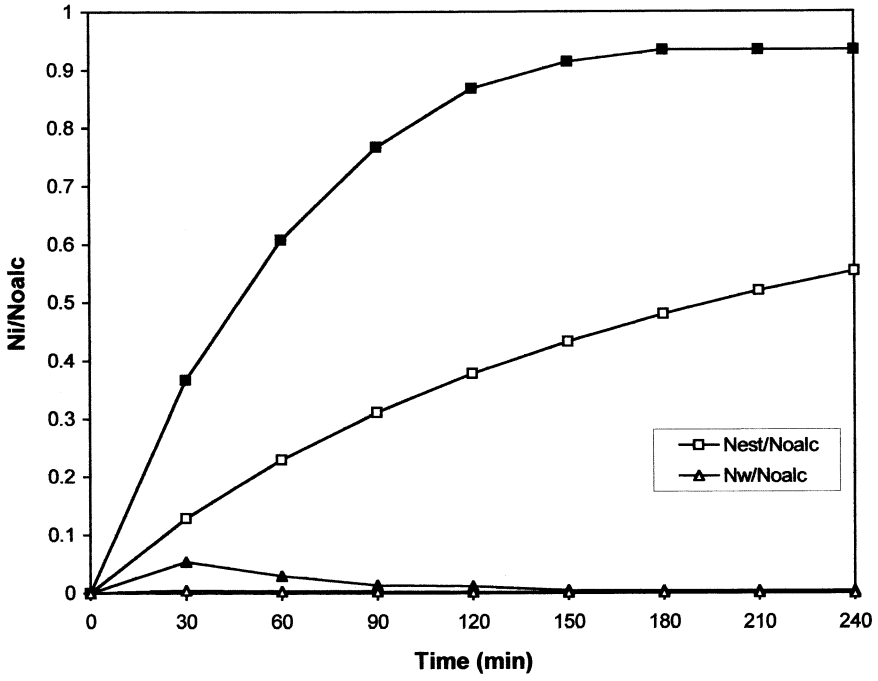

FIGURE 9 Comparison between experimental and theoretical curves of conversion versus time for the system palmitic acid and ethanol, initial mole ratio, acid:alcohol = 1:1. Closed symbol experimental, open symbol theoretical.

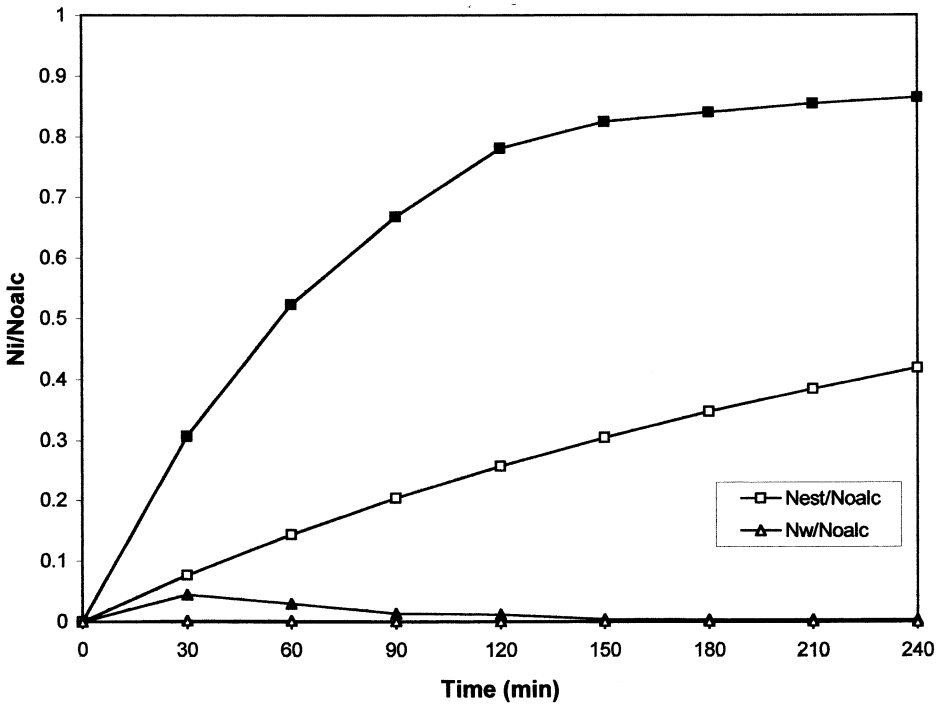

FIGURE 10 Comparison between experimental and theoretical curves of conversion versus time for the system stearic acid and ethanol, initial mole ratio, acid:alcohol = 1:1. Closed symbol experimental, open symbol theoretical.

all the carboxylic acids is quite reasonable. In these figures, the co-ordinates of the maxima in water content are of significant importance since, at these points, the rates of water production and water removal are equal and their relative positions indicate that the increase in the lipase concentration accelerates the pervaporation more than that achievable through an increase in the initial reactant molar ratio because of the acceleration of the esterification reaction without dilution.

Effect of Molecular Structure of Carboxylic Acid

The intrinsic kinetic and equilibrium parameters for the esterification of all the carboxylic acids are expected to correlate with their molecular structure. Accordingly, the value of rate constants (k_1) and equilibrium constants (K_{eq}) were plotted against carbon number of the carboxylic acids, as shown in Figs. 11 and 12, which indicate decreases of k_1 and K_{eq} with carboxylic acid carbon number implying

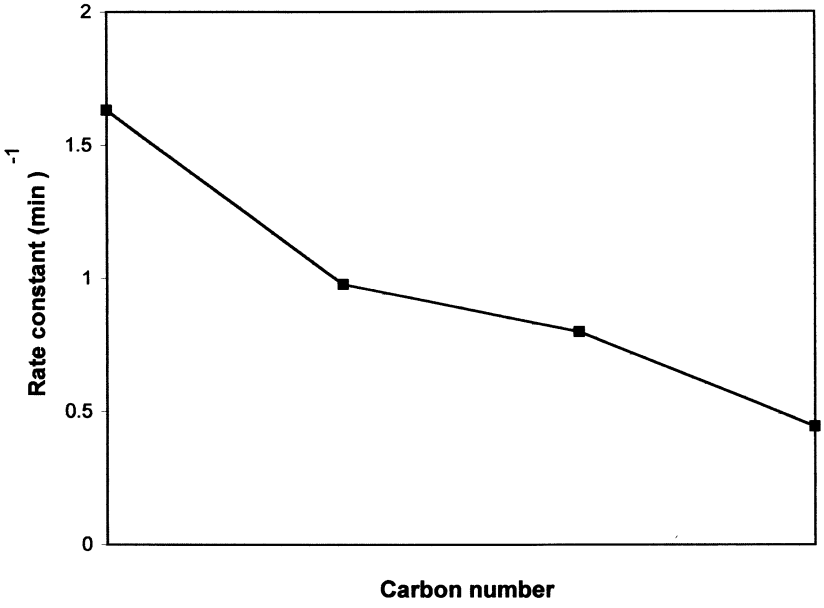

FIGURE 11 Rate constant as a function of carbon number.

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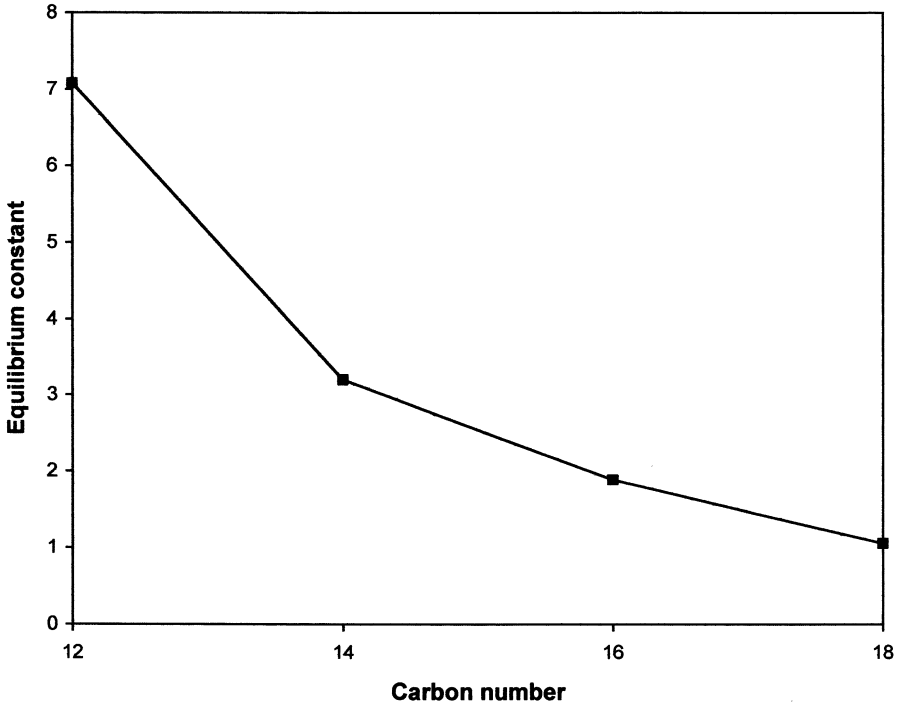

FIGURE 12 Equilibrium constant as a function of carbon number.

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that the rate constant and equilibrium constant for the reaction are lower for more hydrophobic carboxylic acids. From Table I, it is apparent that, as the molar ratio of alcohol and acid increases, the value of k_1 and K_{eq} decreases for each carboxylic acid.

The membrane permeance was estimated according to the model Eq. (14) and the values are given in Table II. The permeability coefficient of water in reactions with different carboxylic acids appears to be different, although for the same acid with different acid: alcohol molar ratios the value of membrane permeance are almost same. Hence, this seems to be affected by the hydrophobicity of the substrate molecule but not concentration of the reactants and products. Fig. 13 shows that the membrane permeance increases with increase in carbon number. The increase in membrane permeance for carboxylic acid with higher carbon number may be attributed to hydrophobic interaction with the membrane as well as a viscous dissipation effect likely to be caused by the acids of higher carbon number. However, values of the permeability co-efficient were reported to be the same in the cases of quaternary mixtures and binary system (David *et al*., 1991b). As shown in Fig. 13, the membrane permeance increases with increase in carbon number of the carboxylic acids, implying that hydrophobicity of an acid substrate plays a

TABLE I Estimated values of kinetic and equilibrium constant

Acid	Acid alcohol molar ratio	k_f	K_{eq}
Lauric acid	1:1	1.6297	7.0819
	1:2	1.3334	0.8750
	1:3	1.0371	0.4594
	1:4	0.4445	0.2745
Myristic acid	1:1	0.9778	3.1980
	1:2	0.8889	0.8101
	1:3	0.8000	0.4594
	1:4	0.5778	0.2501
Palmitic acid	1:1	0.8000	1.8840
	1:2	0.6222	0.4714
	1:3	0.0444	0.1298
	1:4	0.3556	0.0488
Stearic acid	1:1	0.4445	1.0545
	1:2	0.3556	0.1407
	1:3	0.2667	0.0298
	1:4	0.1778	0.0131

TABLE II Permeability of water in various reaction systems

Acid	Acid alcohol molar ratio	Membrane permeance (m min^{-1})
Lauric acid	1:1	0.4551
	1:2	0.4551
	1:3	0.4555
	1:4	0.4552
Myristic acid	1.1	0.7682
	1:2	0.7682
	1:3	0.7683
	1:4	0.7682
Palmitic acid	1:1	0.9521
	1:2	0.9522
	1:3	0.9523
	1:4	0.9521
Stearic acid	1:1	1.0310
	1:2	1.0311
	1:3	1.0311
	1:4	1.0311

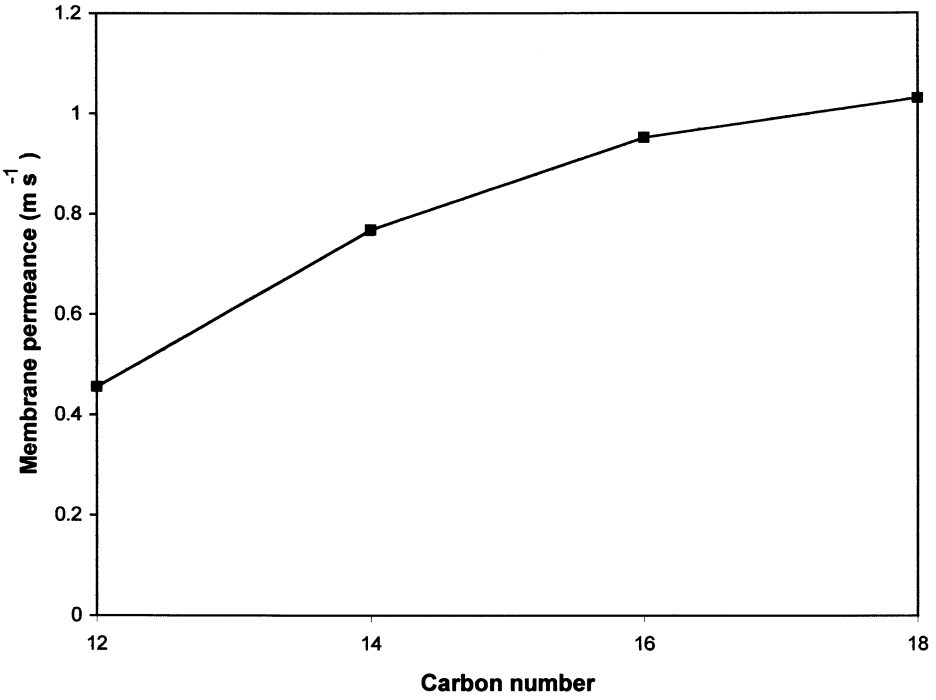

FIGURE 13 Membrane permeance as a function of carbon number.

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significant role in the pervaporation coupled reaction.

There is an almost linear relationship between the permeation flux (as estimated by Model II) and water concentration in the case of pervaporation of organic solvents containing low amounts of water. The values of the permeation flux for different carboxylic acid are different but not effected by the acid:alcohol molar ratios.

Effect of Membrane Area

It may be expected that the efficiency of the process is strongly related to the ratio of membrane area to the volume of the mixture (A/V). In a batch membrane reactor, one way to remove water more rapidly is to increase the ratio of the membrane area to solution volume. The variation in the A/V ratio will allow changes in parameter values directly affecting the esterification kinetics. In order to asses the A/V effect, the time for equilibrium conversion for a specific acid under the otherwise identical conditions of Fig. 9 has been plotted against A/V as shown in Fig. 14. At low A/V value, the water removal rate is too low resulting in low reaction times. Thus time decreases with an increase of A/V, up to a critical value above which the time increases again. The increase in the ratio of A/V leads to a faster conversion of acids through water removal, and an increase in the areas implies less accumulation of water in the reactor. This lower accumulation favors increased forward reaction because it reduces ester hydrolysis. The observed increase in time to equilibrium with further increase of A/V above the critical value is difficult to explain, but may be attributed to the simultaneous removal of ethanol adversely affecting the equilibrium shift. A similar effect of A/V has also been reported for esterification of tartaric acid with ethanol (Keurentjes *et al*., 1994). Shorter reaction time with increased membrane area is possible if the initial ethanol content of the batch is increased, or ethanol is added in a fed batch mode during the reaction. Thus, for practical application of pervaporation, it is possible to shift the reaction equilibrium towards synthesis by selecting an appropriate A/V value on the basis of economic considerations.

CONCLUSIONS

In the pervaporation aided esterification reactions studied, the equilibrium composition can be shifted significantly towards ester formation by *in situ* removal of water. The kinetic parameters, as well as equilibrium constants, have been determined using a computer program. The value of the rate constant and K_{eq} increases with decreasing carbon number of the carboxylic acids. The water permeability was also well correlated with acid hydrophobicity. The efficiency of the process is strongly related to the ratio of the membrane area to the volume (A/V) of the mixture. When the A/V value is low the water removal is too low, and when this value is too high too much ethanol is removed. The overall kinetics of the reaction can be modeled by combining the equations for the reaction kinetics

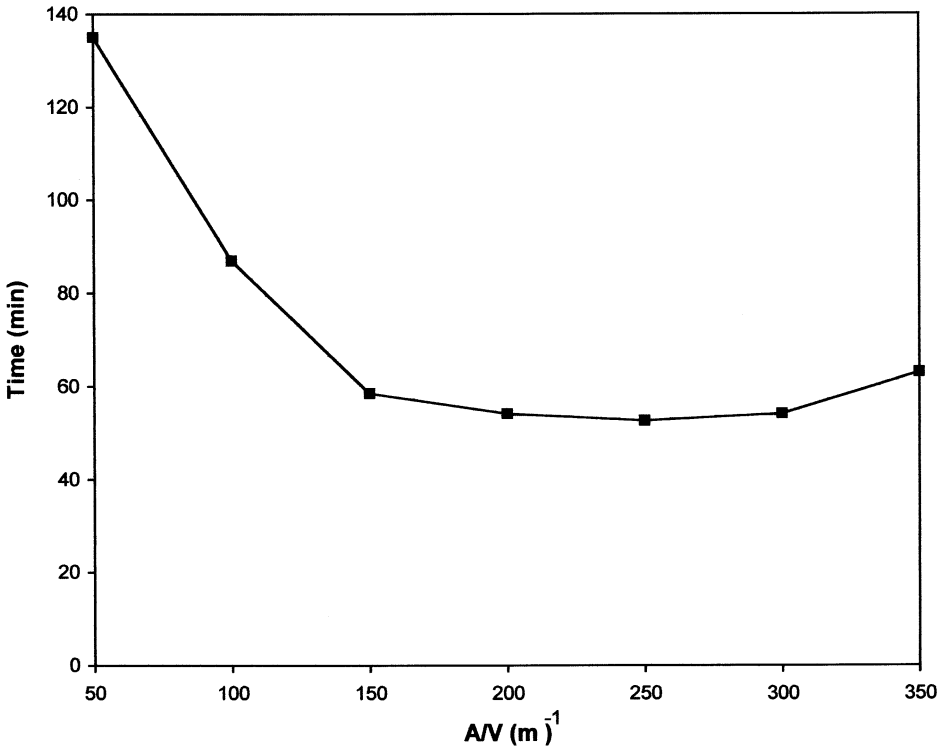

FIGURE 14 A/V as a function of reaction time.

and the permeation kinetics of water removal by pervaporation. The concentration-based model provides a better prediction of concentration profile.

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Appendix A

Nomenclature

a	activities of the components (mM/g)
A	membrane area (m^2)
c_I	concentration of the components (mM)
D	diffusion co-efficient of water in the membrane (m^2 min^{-1})
k_f	forward rate constant, (g^2/mM^2 min)
K^a	activity based equilibrium constant
K^c	concentration based equilibrium constant
m	specific mass of species (g m^{-3})
M	mass (g)
M	molar weights of species (g)
M_w	water molar mass (g/mM)
n	Permeate flux (mM/g min^{-2})
N_o	initial molar amount of species (mole)
P	permeance (m/min)
P_w	permeability co-efficient (g/m^2 min)
r	reaction rate (mM/g min)
t	time (min)

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V	volume of the reacting mixture at time t (m^3)
x	thickness of the membrane (min)
$X = \frac{N_e}{N_{oalc}}$	conversion degree
$Y = \frac{N_w}{N_{oalc}}$	ratio of the molar amount of water in the reactor at time t to the initial amount of alcohol

Subscripts

a	acid
cat	catalyst (lipase)
e	ester
eth	ethanol
i	component
w	water

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