

Kinetic of liquid-phase reactions catalyzed by acidic resins: the formation of peracetic acid for vegetable oil epoxidation

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Abstract

A heterogeneous kinetic model which takes into account the complete physicochemical interaction of reactive species in a polar liquid phase with an ion-exchange resin acting both as selective sorbent and heterogeneous catalyst has been employed to analyze the peracetic acid synthesis from acetic acid and hydrogen peroxide in an aqueous solution. Model parameters were estimated using uncoupled data from phase equilibria, polymer sorption, chemical equilibrium and reaction kinetics. Activities rather than molar concentrations in the polymer phase and specific (dry weight of catalyst basis) rather than volume-based expressions were found to give the best constitutive equations for the heterogeneous reaction rate. © 2000 Elsevier Science B.V. All rights reserved.

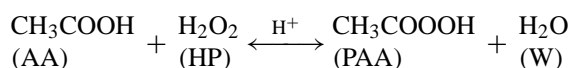
Keywords: Vegetable oil epoxidation; Heterogeneous models; Acidic resins

1. Introduction

The epoxidation of unsaturated triglycerides with percarboxylic acids is a common practice for obtaining low cost plasticisers of good performance from natural and renewable sources such as vegetable oils. Cost constrictions dictate the use of inexpensive peracetic acid (PAA) as the active reagent, while safety concerns demand an in situ preparation of the reagent, to avoid the handling of a pre-formed concentrated peracid. The in situ process involves a heterogeneous system, as epoxidation reaction occurs in the organic phase whereas the formation of PAA takes place

in an aqueous medium. The latter step is slow and controls the overall reaction rate; then, high conversions are generally achieved after several hours of reaction.

Traditionally, homogeneous acidic catalysts (e.g. sulfuric acid) have been used to facilitate the formation of peracetic acid by reacting acetic acid (AA) and hydrogen peroxide (HP):



Hydrogen peroxide (an oxygen source) reacts with acetic acid (an oxygen carrier) in the aqueous phase in the presence of the acidic catalyst (solvated protons) to give peracetic acid (PAA). The latter, in turn, transfers to the organic phase and quickly attacks the double bonds of the unsaturated vegetable oil (VO) to form the oxirane ring in the homogeneous epoxidation

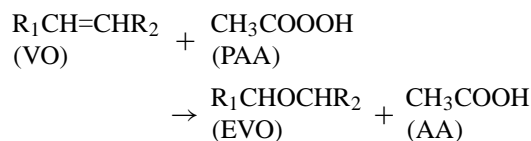
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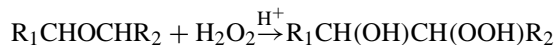
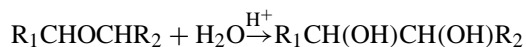
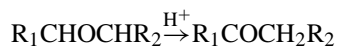
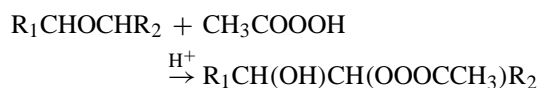
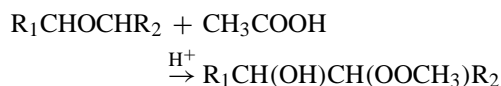
reaction:



The co-produced AA returns to the aqueous phase to close the sequence and re-start the production cycle.

Mass and heat transfer limitations may impose severe process constraints (epoxidations are highly exothermic) or may lead to undesirable side reactions. So, numerous workers have studied the epoxidation reaction pathway and a qualitative picture of it was agreed upon in the past decades [1–3]. The rate-limiting step of the in situ process is the formation of PAA in the aqueous phase. However, quantitative determination of the kinetic parameters was lacking, and only for two-phase epoxidations using homogeneous mineral acids more rigorous kinetic models had begun to emerge in the recent past [4,5].

As mentioned, secondary (acid-catalyzed) side reactions do appear. Invariably, they involve an opening of the oxirane ring and, consequently, lower yields of epoxidized vegetable oil [5]:



Heterogeneous catalysts such as functionalized microreticular ion-exchange resins (IER) can be advantageously used instead, since only the small carboxylic acid molecules can enter into their gel-like structure, while the bulky epoxidized triglyceride molecules cannot. The oxirane ring can thence be protected from the attack of the protons which are confined inside the gel matrix and, as a result, further ring decomposition is prevented. Also, catalyst recovery

and/or regeneration is much easier then. Several such strongly acidic sulfonic IER (e.g. Dowex 50; Amberlite IR 120, Chempro C20) have been reported to contribute to minimizing oxirane ring opening [6–9].

Three phases are present in the in situ processes catalyzed by IER: (1) a polymer phase, whose behavior (notably its swelling properties) is highly dependent on the physicochemical properties of the system, together with (2) an aqueous phase, immiscible with (3) the organic phase. A heterogeneous kinetic model of this three-phase system using IER has not been presented so far. We are presently developing a complete study of the epoxidation process, uncoupling the reaction and transport system into sub-systems of increasing complexity to allow a better quantification of the relevant process parameters.

This piece of work presents the modeling of one of these sub-systems whose understanding is crucial: the kinetics of formation of PAA in the heterogeneous aqueous phase-polymer (acidic catalyst) phase system. For this, the partition of each component between the two phases, as well as the swelling ratio (relative increase of the volume of the resin) are first quantified. Selective sorption/swelling leads to values of the relative compositions in the reaction locus (i.e. the polymer resin) and of the reactants' polymer-phase concentration which are different from those in the liquid phase. Both aspects are taken into account in the modeling. Then, the chemical equilibrium constant and kinetic parameters are estimated from the equilibrium and kinetics experimental data, respectively, using operating conditions typical of the industrial process. Lastly, the activation energy of the acid-catalyzed reaction is estimated from non-isothermal experimental data. The appropriateness of managing the kinetic equations in terms of activities, rather than concentrations, and mass of dry resin, rather than its volume, are discussed.

2. Experimental

2.1. Activation and conditioning of the ion-exchange resin

Rohm & Haas Amberlite IR-120 microreticular gel-type resin, DVB-styrene matrix, 8% cross-linking, d_p (dry)=215–775 μm (54.5% < 530 μm ; 75.3% <

600 μm ; 94.8% <670 μm), functionalized with sulfonic groups, was used throughout this work. As IER is commercially available in sodium form, hydrochloric acid (10% w/w) was used to fully activate it in successive ion-exchange steps (7 in total), with further washing (1:10 w/w) using distilled demineralized water until complete elimination of the residual salinity. Lastly, glacial acetic acid (purity: >99.7% w/w) was used to replace water inside the ion exchange resin.

The exchange capacity of the resin, as determined by titration using conventional volumetric techniques, was: $[\text{H}^+]^0 = 4.507 \text{ meq/g}$ (dry basis). The dry polymer density, as measured by pycnometry using *n*-heptane [10], was 1.437 kg/m^3 . A portion of the dry resin was crushed and sieved; successive washing and decantation in distilled demineralized water allowed the removal of undesired fines adhered to the crushed particles. Two fractions, <53 and >595 μm , were used to evaluate the possible impact of mass-transfer resistances on the process rate.

2.2. Determination of phase equilibrium partitioning of reactants between the aqueous and polymeric phases

Different dilutions of either acetic acid or hydrogen peroxide in water (40 g) were added to the dry resin (15 g). The system was kept at 333 K with occasional stirring until physicochemical equilibrium was achieved in about 4 h. The equilibrium composition of the liquid phase was measured by volumetric techniques (see below). A portion of the swollen resin was centrifuged at 2000 g for 5 min to eliminate any residual interstitial liquid [10]. The amount of sorbed liquid retained by the resin was found by weighting the centrifuged resin before and after drying in a stove at 378 K for 12 h [11].

2.3. Reactor and experimental procedures

The rate of formation of PAA was studied in experimental runs conducted in a 1000 cm^3 closed cylindrical Pyrex reactor, furnished with a variable speed (0–1000 rpm) mechanical stirrer. The device had four teflon baffles to eliminate vorticity, an overhead reflux condenser and a fast-sampling device for collect-

ing representative liquid-resin samples of the reacting system. An internal cooling coil (OD: 1/4"; 316SS), combined with an external cylindrical heating mantle (400 W) linked to a PID temperature controller, ensured operating within $\pm 0.1 \text{ K}$.

In a typical experiment, glacial AA and pre-activated IER were added to the empty reactor and slowly heated to the reaction temperature under stirring. Simultaneously, the desired volume of a solution of HP (30% w/w) was also heated to that temperature, under reflux, and then added, at once, to the reactor (zero time of the reaction). Samples were periodically taken and immediately filtered to separate the resin and stop the reaction. Next, aliquots of the filtrates (1 cm^3) were diluted in ethanol (100 cm^3) and refrigerated for further analysis by GLC.

2.4. Analytical techniques

The concentration of AA and HP were measured by volumetric titration, using NaOH (0.1 N) and KMnO_4 (0.1 N), respectively. The contents of PAA acid in the reaction samples was determined by GLC after a previous derivatization with methyl *p*-tolyl sulphide; *n*-octadecane was used as internal standard [12]. A glass column ($500 \times 2 \text{ mm}$) packed with 3% FFAP on Chromosorb W AW DMCS (80–100 mesh) was employed.

3. Results and discussion

3.1. Intra- and extra-particle mass-transfer resistances

The absence of intra-particle mass-transfer resistances to any significant extent was experimentally corroborated using two widely differing particle sizes of the resin: >595 and <53 μm , under typical reaction conditions of the well-stirred mixture (375 rpm). Both runs gave identical results as is shown in Fig. 1. Also, the ratio of initial rates was close to unity even though particle diameters differed by more than 10-fold. Hence, extra-particle mass-transfer resistances are of no concern either and, thus, the commercial uncrushed IER beads were used to perform the kinetic study.

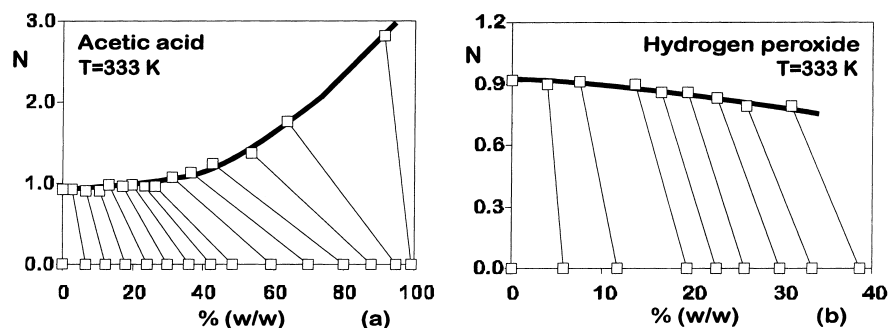


Fig. 1. Influence of particle size of the ion-exchange resin (Amberlite IR-120) on the reaction rate and final concentration of PAA at 333 K (reactants molar ratio: $\text{H}_2\text{O}_2/\text{HOAc}=1.1/0.5$). The full line corresponds to model predictions.

3.2. Kinetic model

As we have pointed out in Section 1, the selective sorption and swelling of the resin can have a strong influence on the observable reaction rate of this two-phase system, even though no change in the sequence of involved reaction steps (as compared to the homogeneous reaction) is to be expected for a strongly acidic material being the active catalyst. Then, a pseudohomogeneous kinetic model such as the following:

$$\frac{d}{dt}C_{\text{PAA}} = k_1 C_{\text{IER}} \left[C_{\text{HP}} C_{\text{AA}} - \frac{1}{K} C_{\text{PAA}} C_{\text{W}} \right] \quad (1)$$

which considers IER merely as a source of protons in the multicomponent liquid mixture would be certainly insufficient. In fact, for the set of experimental runs summarized in Table 2, every attempt we made to get satisfactory data fittings by means of a non-linear regression algorithm was unacceptable. So, a new model was developed to include explicitly the presence of the polymer phase.

Two approaches can be followed to solve this hurdle. The first one focuses exclusively on the catalytic reaction pathway at the reaction locus, where two extreme situations are recognizable according to whether slightly dissociated sulphonic groups or free solvated protons are the catalytic agents [13–15]. The first case applies whenever the resin is imbedded into a slightly polar medium; the classic LHHW formalism can then be applied to model the reaction kinetics [16,17]. Here, the inclusion of adsorption parameters is both justifiable and flexible enough so as to fit up any observable changes in catalytic activity due to the presence

of polar components in minor amounts. If the resin operates into a strongly polar solvent such as water, the sulphonic groups are fully dissociated and the free solvated protons catalyze the reaction through ionic mechanisms of protonation. In many such situations, specially if just small amounts of resin are used, a pseudohomogenous model describing the reaction rate in terms of power-law kinetics suffices, as it does in homogeneous catalysis.

However, none of these models takes into account the selective sorption and swelling of the resin, which leads to values of the reactants' polymer-phase concentration and of the relative composition of both reactants and products in the polymer phase (i.e. the reaction locus) that are different from those in the liquid phase. A second approach is then needed, to explicitly differentiate the compositions of the aqueous and polymer phases whenever a significant amount of resin is used as a catalyst. For such purposes, the overall system can be considered as a two-phase system composed of a highly viscous multicomponent fluid phase containing $N+1$ species (with the swollen polymer as $(N+1)$ th species,) in physicochemical equilibrium with the N -component liquid phase, since the characteristic time for reaching phase-equilibrium conditions between them is usually of the order of a few minutes [18].

3.3. Activities of the species in the liquid phase

A predictive model is needed to compute the activity of the four species in the aqueous phase, rather than a correlative one, due to the scant information

available in the open literature about this reacting system. For these components, just a pair of binary data is available: water–hydrogen peroxide [19] and water–acetic acid [20]. Then, the UNIFAC group contribution method [21] is a suitable tool, as it does not involve any adjustable parameter. The central concept of the method rests on considering any mixture as a solution of functional groups interacting among themselves. Most of the extensions and refinement of the original concept have rested on finding new procedures for calculating the molecular interaction parameters between components, which initially came from vapor–liquid equilibrium data (UNIFAC VLE). Later, a new set of interaction parameters has been derived from the liquid–liquid equilibrium data (UNIFAC LLE) for making predictions related to these systems [22]. More recently, the dependence of the interaction parameters with temperature has also been included, in the Modified UNIFAC method [23].

We used each of these methods to predict the activities in the aqueous phase. The UNIFAC LLE method was found to give the closest fit when a comparison of model predictions with experimental data taken from the available vapor–liquid equilibria was made. It was then adopted for further use in our calculations.

3.4. Activities of the species in the polymer phase

The activity a_i^P of the i th species of a multicomponent polymeric solution can be evaluated in the framework of the extended Flory–Huggins model [25]:

$$\ln a_i^P = 1 + \ln v_i - \sum_{j=1}^{N+1} m_{ij} v_j + \sum_{j=1}^{N+1} \chi_{ij} v_j - \sum_{j=1}^{N+1} \sum_{k=1}^{N+1} m_{ik} v_j v_k \chi_{kj} + \eta V_i \left[\frac{5}{3} v_P^{1/3} - \frac{7}{6} v_P \right] \quad (2)$$

where N is the number of components excluding the polymer, which is the $(N+1)$ th species; v and v_P are the volume fractions of the i th species and of the polymer in the polymer phase, respectively; m_{ij} is the ratio of molar volumes of the i th and j th species ($m_{iP}=0$); V_i is the molar volume of i th species; η represents the number of moles of active elastic chains per unit volume and χ_{ij} represents the molecular interaction

between components i and j . The latter parameters are known to be temperature-dependent [24].

According to Eq. (2), 11 adjustable parameters would have to be determined for calculating the set of a_i^P of the four species in the polymer phase: η , and 10 molecular interaction parameters, four of them corresponding to interactions between the polymer and the other species (χ_{iP}) and six binary interaction parameters among the liquid phase components (χ_{ij}), since $\chi_{ij}=\chi_{ji}$ and $\chi_{ii}=0$ (see Ref. [18] for a full discussion on the subject).

The elasticity parameter and five of the binary interaction parameters were found independently (i.e. uncoupled), from the sorption equilibria of the water–acetic acid and water–hydrogen peroxide binary mixtures in contact with the resin. For this purpose, the activities of each pair of components in the aqueous phase were calculated using the UNIFAC LLE routine, which does not involve any adjustable parameter. Next, as in thermodynamic equilibrium

$$a_i^L = a_i^P \quad (3)$$

Eq. (2) was used for each binary mixture, using the Levenberg–Marquardt algorithm, to estimate the corresponding interaction parameters.

Fig. 2 shows representative sets of tie lines, in adsorbent-free mass coordinates ($N=g$ dry resin/ g adsorbate), obtained experimentally at 333 K. These data clearly indicate that water is more strongly sorbed than either acetic acid or hydrogen peroxide, and that the resin swelling is much higher in water than in acetic acid. It is also apparent that the polymer beads can expand even more (albeit slightly) with higher concentration of hydrogen peroxide.

Fig. 3 re-plots the experimental data (tie lines) shown in Fig. 2, as molar fractions in the polymer and liquid phases, for the water–acetic acid and water–hydrogen peroxide binary pairs, together with model predictions using the calculated parameters (the latter are included in Table 1). The agreement is satisfactory.

The experimental determination of the partition of PAA was not made owing to the obvious experimental difficulties and hazards involved in handling a highly concentrated peracid. Instead, the heuristic assumption was made that in the polymer phase the analogs—carboxylic acids (acetic and peracetic)—can be assumed to behave as identical molecules, as

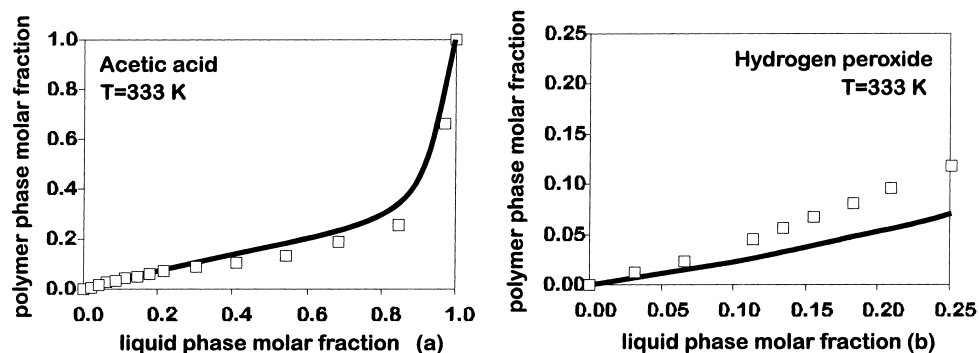


Fig. 2. Binary sorption and phase partition equilibria on Amberlite IR-120 of (a) water–acetic acid and (b) water–hydrogen peroxide binary mixtures, obtained experimentally at 333 K, in adsorbent-free mass coordinates (N =g dry resin/g adsorbate).

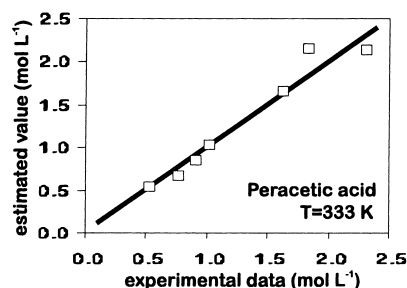


Fig. 3. Comparison of experimental data and model predictions for the water–acetic acid (a) and water–hydrogen (b) binary pairs shown in Fig. 2 (333 K).

far as their molecular interactions are concerned, and so $\chi_{AA-PAA}=0$. Likewise, an uncoupled estimation of the interaction parameters of the reactive binary pairs, PAA–water and acetic acid–hydrogen peroxide cannot be made, for obvious reasons. Nevertheless, under the previous hypothesis χ_{W-PAA} is identical to χ_{W-AA} . Lastly, the remaining interaction parameter can be estimated from chemical equilibrium data us-

ing asymptotic compositions (i.e. after long enough contact times) of the experimental runs. The procedure is described below, in Section 3.5.

As is shown in Table 1, the complete set of χ_{ij} interaction parameters indicates relatively low interaction between acetic acid, PAA and hydrogen peroxide, and moderate interactions of these with water and of the four liquid components with resin. The value obtained for the elasticity parameter was: $\eta=0.022 \text{ mol/cm}^3$, which is about one order of magnitude higher than the theoretical one. However, by imposing progressively lower values to this parameter there is worse agreement between model predictions and experimental data results, owing to the tight correlation among the parameters in Eq. (2). This problem has been discussed in a recent work on the kinetics of liquid-phase esterification of acetic acid with ethanol using Amberlyst 15, where about two orders of magnitude differences were encountered [18].

Despite these shortcomings of presently available phase partition equilibrium models, they allow one to reproduce rather satisfactorily the experimental data and seem sufficient to help in describing the kinetic behavior of these systems under reaction conditions.

Table 1

Estimated values of the interaction parameters of the extended Flory–Huggins model [Eq. (2)], at 333 K.

χ_{ij} i	j				
	AA	HP	Water	PAA	Resin
AA	0	−0.0088	0.3390	0	0.1592
HP	−0.0036	0	−1.9670	−0.0036	0.8809
Water	0.1039	−1.4886	0	0.1039	−0.6673
PAA	0	−0.0088	0.3390	0	0.1592

3.5. Chemical equilibrium

By solving the set of multicomponent sorption equilibrium equations, Eq. (3), together with the mass balances of each of the i th species:

$$n_i^L + n_i^P = n_i^0 + v_i \xi \quad (4)$$

Table 2
Initial loading and operating conditions of the batch experimental runs

Run	Temp (K)	AA (moles)	HP (moles)	Water (moles)	Resin mass (g)
1	333	1.329	2.734	11.470	7.447
2	333	1.345	3.480	15.205	8.667
3	333	2.783	2.734	11.94	5.226
4	333	5.497	2.734	11.947	4.820
5	333	10.945	2.734	11.947	5.616
6	333	0.768	2.734	11.947	11.993
7	333	0.574	2.734	11.947	21.375
8	323	1.329	2.734	11.947	7.447
9	343	1.329	2.734	11.947	7.447

and the condition of chemical equilibrium:

$$K = (a_{\text{PAA}}^P a_{\text{W}}^P / a_{\text{AA}}^P a_{\text{HP}}^P)_{\text{eq}} \quad (5)$$

it is possible to jointly estimate the interaction parameters for the reactive couple acetic acid–hydrogen peroxide and the equilibrium constant, K . Indeed, owing to a lack of reliable data, it was impossible to estimate K from ΔG^0 data, as the standard free energy of the formation of PAA is known within broad uncertainty limits. The calculated value of $\chi_{\text{HP-AA}}$ is given in Table 1. At 333 K the equilibrium constant was found to be $K=2.18$.

Values ranging from 0.7 to 5, which were found to be dependent both on the initial molar ratio of reactants and on the catalyst concentration, calculated from the equilibrium concentrations, have been reported by Rangarajan et al. [5]. With our approach, for the broad set of experimental conditions given in Table 2, a good fit of the data could be achieved using a single value of K , as is shown in Fig. 4.

The values of K at 323 and 343 K, obtained experimentally, were 1.911 and 2.778, respectively.

3.6. Kinetic equation

From Eq. (4) it is straightforward to recognize that in the well-mixed isothermal batch reactor the time rate of change of the observable degree of advancement of the reaction (ξ) is sufficient to fully describe the reaction process whenever equilibrium conditions between the bulk liquid and the polymer phase hold. Also, because the catalyzed reaction proceeds only inside the polymer phase:

$$\frac{d}{dt}\xi = W^P R^P \quad (6)$$

where W^P indicates mass of dry resin placed in the system (an invariable property) and R^P is the specific reaction rate (dry weight basis). Another choice, which is to write Eq. (6) in terms of a volumetric reaction rate, leads to awkward rate ‘constants’, as the volume of the polymer phase continuously changes during the reaction owing to the swelling properties of the resin.

In addition, as the system is highly non-ideal, the kinetic equation describing the reaction rate has to be written in terms of activities [26], accounting for the

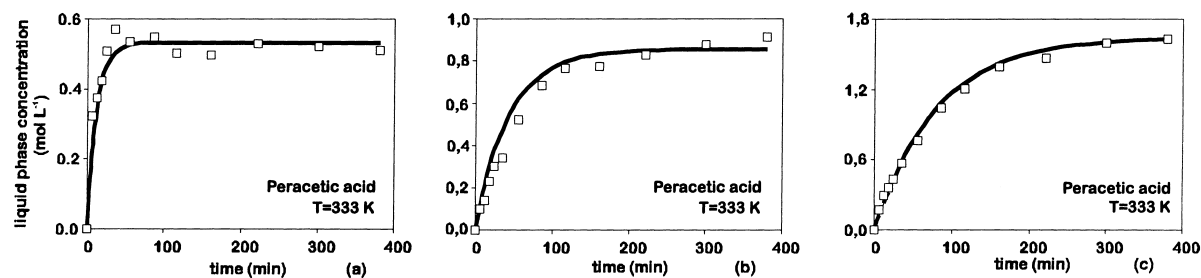


Fig. 4. Experimental and calculated concentrations of PAA in liquid phase at equilibrium conditions (333 K).

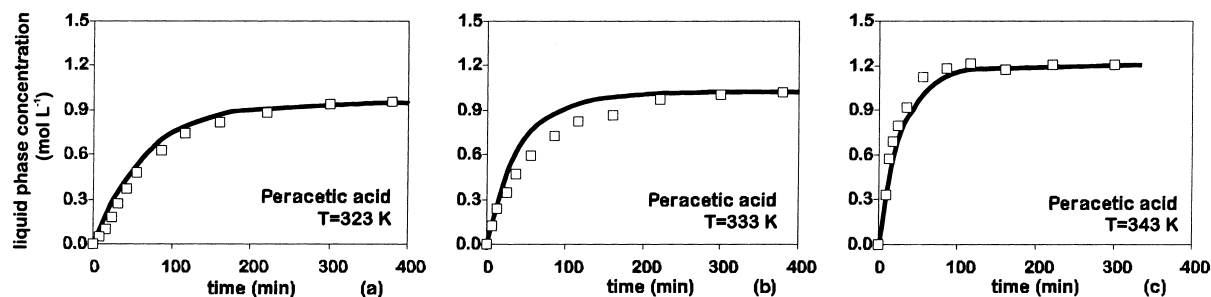


Fig. 5. Concentration of PAA in the liquid phase as a function of time for various values of the initial composition of the reacting mixture: (a) Run 7; (b) Run 6; (c) Run 3. Full lines represent model predictions.

chemical equilibrium as well (Eq. (5)). The simplest expression which satisfies these requirements is the following:

$$R^P = k a_{AA}^P a_{HP}^P [1 - K^{-1} a_{PAA}^P a_W^P / a_{AA}^P a_{HP}^P] \quad (7)$$

where k [$\text{mol s}^{-1} (\text{g dry resin})^{-1}$] = $k^0 [\text{H}^+]^0$. Its value was estimated by means of the Marquardt–Levenberg algorithm, solving for Eqs. (2), (3), (5)–(7) and using the experimental data from the runs indicated in Table 2, all of them obtained in the absence of mass-transfer limitations. The previous calculation of the interaction parameters and of the chemical equilibrium constants at each temperature allowed the uncoupled estimation of k . The values of the interaction parameters at 323 and 343 K were obtained from those at 333 K using the well-tested derivation of Flory [24]: $\chi(T)T = \chi(T')T'$.

The estimated values of the pre-exponential factor and activation energy of k are $(8.48 \pm 1.16) \times 10 \text{ mol s}^{-1} (\text{g dry resin})^{-1}$ and $48.4 \pm 0.47 \text{ kJ mol}^{-1}$, respectively, for a 95% confidence level. Given that the absence of mass transfer constraints was corroborated, this somewhat low E_{act} value, as compared with the one reported

in homogeneous systems, might be due to the steric constraints imposed on the acid-catalyzed bimolecular *rxns* of the reaction [3,4] by the microreticular resin rather than an incomplete degree of solvation [27].

Figs. 5 and 6 compare experimental results and model predictions which are fair. Additional fittings were made using empirical kinetic expressions for: (a) the specific reaction rate (dry weight basis) in terms of molar concentrations instead of activities of the reactants, and (b) the volumetric reaction rate in terms of activities of the components, factorized by the resin volume. In both such cases the new predictions were poorer than the one using the more sound Eq. (7), as the residual sum of squares were 58 and 238% higher, respectively.

4. Conclusions

A two-phase model has been proposed to describe the catalyzed reaction of the formation of PAA from acetic acid and hydrogen peroxide under a broad

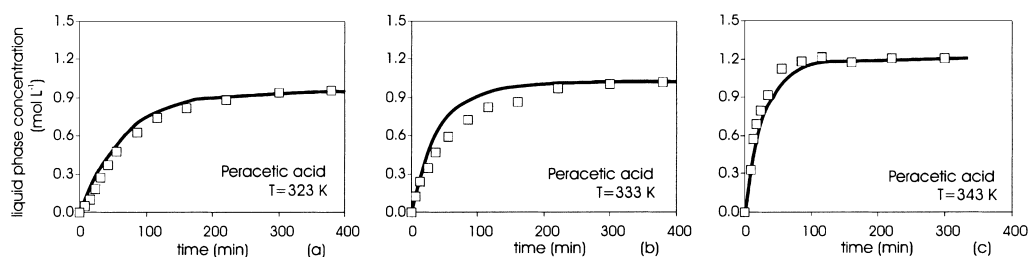


Fig. 6. Concentration of PAA in the liquid phase as a function of time for various values of the reaction temperature: (a) Run 8; (b) Run 1; (c) Run 9. Full lines represent model predictions.

range of conditions, using a sulphonated ion-exchange resin acting as both a sorbent and a heterogeneous catalyst. The developed model incorporates relevant aspects with regard to the different affinities of the reactive species toward the liquid and resin phases. The selective partitioning of each component between the two phases and the relative increase of the volume of the resin (i.e. its swelling ratio) with varying composition were corroborated, quantified and taken into account in kinetic modelling. These features, which have adequate literature support, had not been previously considered for this particular reactive system.

A progressive, uncoupled estimation of the model parameters was made using: (a) phase equilibrium/sorption data of unreactive pairs of components, to obtain the binary interaction parameters; (b) chemical equilibrium data, to estimate the thermodynamic equilibrium constant and binary interaction parameters of the reactive pairs, and (c) reaction rate data in absence of mass-transfer resistances to estimate the specific kinetic rate constant. Activities rather than molar concentrations and specific (dry weight of catalyst based) rather than volume-based reaction rates were used throughout the work.

For processing purposes the preferential partition of water inside the catalytic polymer phase (the reaction locus) is inconvenient because, being both a diluent and a reaction product, water lowers the rate of formation of PAA from the reversible reaction which is involved. Yet, the use of microreticular ion-exchange resins as heterogeneous catalysts for epoxidizing unsaturated triglycerides is desirable. Protons are then confined inside the polymer phase, which prevents their further attack on the oxirane ring and, so, higher oxirane indexes than those achievable in homogeneous catalytic processes can be realised.

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