The effect of phase inversion during semibatch aromatic nitrations

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Abstract

The effect of phase inversion during semibatch aromatic nitrations is experimentally characterized and analysed. The influence of various parameters, i.e. interfacial area, effective heat-transfer coefficient and overall mass-transfer coefficient, is studied. The implications for optimizing nitrations are discussed from performance and safety points of view. The accumulation of unreacted nitric acid can be dangerous if accompanied by a phase inversion, owing to the fact that the rate may increase suddenly.

Keywords: Phase inversion; Liquid–liquid dispersion; Aromatic nitrations.

1. Introduction

Despite aromatic nitrations in mixed acid being one of the oldest and most common industrial reactions, there are still a considerable number of problems in predicting their behaviour in semibatch reactors. The interdependence of reaction and mass-transfer phenomena leads to a complex problem in characterizing and scaling-up these processes. Furthermore, nitrations involve high exothermicity and side reactions.

An important phenomenon is phase inversion, which may occur in such systems. When two immiscible liquids are agitated, a dispersion is formed by virtue of the continuous supply of energy by the stirrer. When the external supply of energy is stopped, the dispersion may remain stable or may disengage into two phases. In the first case, the dispersion is called an emulsion, while the term dispersion is normally applied to the second type.

After a transition period, a dynamic equilibrium between break-up and coalescence is attained, and a spectrum of drop sizes results. One of the phases becomes dispersed as droplets into the other, continuous phase. The type of dispersion depends on the volume fractions of the two liquids, their physical properties and the dynamic characteristics of the mixing process.

If more and more dispersed-phase material, as in the semibatch nitration process, is added to the stirred system, a point is eventually reached at which the addition of more dispersed phase causes an inversion: the continuous phase suddenly becomes the dispersed one and vice versa.

Notable for phase inversion is the ambivalent region [1], or the region where the nature of the dispersion depends on history. The phase inversion points differ according to whether the organic or the aqueous is dispersed. An appearance of hysteresis, termed the inside metastable area, characterizes the ambivalence region, see Fig. 1.

Inversion of phases is frequently accompanied either by a decrease or by an increase in the interfacial area. Fernandes and Sharma [2] reported a change of 32% in the interfacial area, for the system 2 M NaOH and 2 ethyl hexyl formate, depending on which phase was a continuous one. Luhning and Sawistowski [3] reported a stepwise change in drop size at phase inversion in all systems studied, and hence a change in interfacial area. In general, Clarke and Sawistowski [4] found for solute-free systems that the interfacial area increased on inversion from the organic/aqueous (o/w) to the aqueous/organic (w/o) configuration, and decreased on inversion in the opposite direction.

Guillinger et al. [5] found for phase inversion a step change in the viscosity of the dispersion, which produced a viscosity maximum at the inversion point for the system water–kerosene. Some studies of phase inversion have been made in batch as well as in continuous systems, with and without mass transfer. Investigators have tried to determine the dependence of phase inversion on physical properties and geometrical and process parameters of the system. Apparently contradictory observations have been reported by researchers. In a recent review, Ganguly et al. [6] concluded the phenomenon is still not well understood, and more research should be dedicated to it.

In the case of semibatch aromatic nitrations, a phase inversion might produce an unexpected step change in the heat generated by the reaction mass, if the conversion rate were mass-transfer-controlled. Therefore, the identification and limits of stability of the dispersed phase under different conditions of volume fraction, species concentration, temperature and stirrer speed are important for the operation of semibatch nitration plants. In this study the phase-inversion phenomenon was investigated to determine the main parameters which affect the dynamic behaviour of semibatch aromatic nitrations at inversion. Preliminary experiments to separate the effects of different factors were carried out, such as experimental determination by the chemical method, of the interfacial area during phase inversion with the similar system toluene with diisobutylene (DIB) and 77 wt.% sulphuric acid [7], and a continuous evaluation of the effective heat-transfer parameters for non-reactive heterogeneous mixtures of toluene and benzene and 70 wt.% sulphuric acid.

Some nitration experiments in which phase inversion took place are presented and analysed using previous experimental results. The contribution to the increase in conversion rate is studied in view of the previous experiments.

Fig. 1. Inversion characteristics for toluene (T)/water (W) system (see text for details on experimental data): (○) inversion from T/W to W/T; (*) inversion from W/T to T/W.

Fig. 2. Phase inversion point detection by change in reactor and jacket temperature (a), or by change in conductivity (b) for the system toluene–70 wt.% sulphuric acid and a stirrer speed of 8.33 s^{-1} . For (b) we have an arbitrary scale between 0 and 1.

2. Experimental phase-inversion detection

In phase-inversion studies, the experimental procedure is quite important. In discontinuous-type studies, two methods are used [6]:

- For batch studies, measured volumes of both phases are put into the vessel and mixing is started. The agitator speed is increased till inversion occurs. The experiment is repeated for different volume fractions of the two phases.
- In a semibatch study, a certain volume of one of the liquids is put into the vessel and subjected to stirring at a constant speed. The second liquid is added and dispersed while the first liquid remains continuous. At some hold-up the phase inversion occurs. Several techniques are commonly used for the detection of inversion, such as conductivity measurement or visual and photographic observations. Of these, the first method is the most popular.

We were interested in the study of phase inversion during semibatch aromatic nitrations, and used conductivity measurement (Fig. 2(b)) and also a second method based on the change of reactor and jacket temperature due to the change of the overall heat transfer coefficient. For the second method we introduced a constant power of 23 W via an electrical resistance during the experiments; see Fig. 2(a) and Appendix 1 for a discussion on this method.

Phase inversion was studied in the RC1 reactor, whose characteristics are given in Table 1. Heterogeneous non-reactive mixtures of water/toluene or sulphuric acid of 70.0 wt.%/benzene or toluene were chosen to determine the phase inversion point. The aqueous phase was added to the organic phase, and phase inversion was detected by measuring the electrical conductivity. The experimental procedure was chosen to simulate the experimental conditions during nitrations. In a set of separate experiments, toluene was

Table 1

Characteristics of the equipment (four-bladed 45° inclined paddle impeller, vessel unbaffled)

Vessel	Diameter T (m)	Height H (mm)	Volume V (l)	Agitator type	Impeller diameter D_a (mm)	Impeller speed n_a (s ⁻¹)
Reactor RC1	115	200	2.0	FB45IP	59.0	6.6–13.3

added to water to check the occurrence of the hysteresis effect and the ambivalent region, see Fig. 1.

Tables 2 and 3 summarize the experimental results. For the system toluene–sulphuric acid, the experimental reproducibility was studied by repeating the same experiment. As can be seen in Table 3, the reproducibility of the experiments was usually within the range of $\epsilon = 0.02$ – 0.03 .

3. Modelling phase inversion: preparatory experiments and model validation

Phase inversion may affect semibatch nitrations by modifying:

- the internal heat transfer coefficient h_0 due to a change in physical and transport properties of the mixture,
- the conversion rate due to a change in the interfacial area a , and/or mass transfer coefficient k_L .

To characterize these effects separately, different experiments were carried out. The effective heat transfer parameter US was evaluated for non-reactive heterogeneous mixtures of toluene and benzene and 70 wt.% sulphuric acid. The interfacial area at phase inversion was measured by the chemical method with a similar system to that for aromatic nitrations; toluene and diisobutylene/77 wt.% sulphuric acid [7].

3.1. Effective heat-transfer parameters in liquid–liquid systems

The heat flow to the jacket is proportional to the temperature difference between the reaction mixture T_m and the jacket T_c :

$$q_{\text{removed}} = US(T_m - T_c)\Psi \quad (1)$$

Table 2

Volume fraction ϵ at phase inversion for the system toluene–water and water–toluene; $T = 308.2$ K

n_a (s ⁻¹)	$\epsilon_{\text{toluene}}$	$\epsilon_{\text{toluene}}$
6.67	0.41	—
8.33	0.40	0.55
10.0	0.39	—
11.67	0.38	0.54
13.33	—	0.51

where US depends on the fluid properties, operating conditions, and the geometry of the system. Ψ is a correction factor which takes into account the temperature variation of the heat transfer fluid between the inlet and outlet in the jacket. Experimentally, US is evaluated with calorimetric methods: heat-flow calorimetry has been demonstrated to be a useful technique [8].

We will check whether the mathematical model to predict the effective heat-transfer parameter, previously developed and tested for pure liquids [9], can be used for liquid–liquid dispersions. Furthermore, the effect of phase-inversion phenomena on this parameter is studied.

The effective heat transfer parameter can be divided into:

The overall heat-transfer coefficient. The overall heat-transfer coefficient is expressed as the inverse of the sum of the three main resistances of the film at the wall in the reaction mixture $1/h_0$, the wall thermal conductivity $1/h_w$ and on the film in heat-transfer fluid $1/h_1$:

$$U = \left(\frac{1}{h_0} + \frac{1}{h_w} + \frac{D_0}{D_1 h_1} \right)^{-1} \quad (2)$$

where D_0 and D_1 are the internal and external diameters of the reactor wall.

Correlations for the film-transfer coefficients are obtained from the Nusselt equation:

Table 3

Volume fraction ϵ at phase inversion for the systems toluene–70 wt.% sulphuric acid, $T = 308.2$ K and benzene–70 wt.% sulphuric acid, $T = 298.2$ K

n_a (s ⁻¹)	$\epsilon_{\text{toluene}}$	$\epsilon_{\text{benzene}}$
5.0	0.70	0.64
	0.72	
5.83	0.70	0.63
6.67	0.66	0.60
	0.65	
8.33	0.58	0.54
	0.58	
10.0	0.56	—
	0.52	
11.67	0.52	—
13.33	0.49	—

Fig. 3. Experimental (○) and simulated (line) effective heat transfer parameter for (a) 70 wt.% sulphuric acid solution and (b) benzene: $T = 308.2$ K, $n_a = 8.33 \text{ s}^{-1}$.

$$h_i = \theta_{1i} \frac{\dot{\lambda}}{D} \text{Re}^{\theta_{2i}} \text{Pr}^{\theta_{3i}} \text{Vi}^{\theta_{4i}} \quad (3)$$

The characteristic parameters (θ_{ji} terms) depend on the shape factors and fluid-dynamic regime, whereas the transport and physical properties of the reaction mixture and the heat-transfer fluid are taken up in the dimensionless numbers. Using the Nusselt equation, the external heat transfer coefficient can be expressed as

$$h_1 = \theta_{11} \frac{\dot{\lambda}_e}{D_t} \left(\frac{\rho_e D_t Q_e}{S_t \mu_e} \right)^{\theta_{21}} \left(\frac{\mu_e C p_e}{\dot{\lambda}_e} \right)^{\theta_{31}} \left(\frac{\mu_e}{\mu_{\text{at the wall}}} \right)^{\theta_{41}} \quad (4)$$

From more than 400 experiments it was found [9] that for the RC1 reaction calorimeter the characteristic parameters are $\theta_{11} = 1.11$, $\theta_{21} = 0.29$, $\theta_{31} = 0.33$ and $\theta_{41} = 0.14$.

In the case of the internal heat-transfer coefficient, we have

$$h_0 = \theta_{10} \frac{\dot{\lambda}_m}{D_0} \left(\frac{D_a^2 \rho_m n_a}{\mu_m} \right)^{\theta_{20}} \left(\frac{\mu_m C p_m}{\dot{\lambda}_m} \right)^{\theta_{30}} \left(\frac{\mu_m}{\mu_{\text{at the wall}}} \right)^{\theta_{40}} \quad (5)$$

For a turbine impeller using five different fluids, Bourne et al. [8] found that $\theta_{10} = 0.42$, $\theta_{20} = 0.69$, $\theta_{30} = 0.33$ and $\theta_{40} = 0.14$ over range of $8 < \text{Re} < 4600$. Similar results were obtained in the reaction calorimeter [9].

Heat-transfer area. The heat-transfer area is the surface wetted by the reaction mixture; it can be calculated as a function of the reaction mixture volume and the stirring or vortex formation by

$$S = S_0 + \Delta S_v \quad (6)$$

where S_0 is the surface without agitation and ΔS_v is the surface increase due to the vortex. A correlation for ΔS_v was obtained by Zaldivar et al. [9].

3.2. Experimental validation for liquid–liquid systems

Two procedures were adopted to evaluate the effective heat-transfer parameter. The first consisted of periodically adding certain quantities to the reactor mass and evaluating US , see Appendix 1. The second con-

sisted of introducing a compound to the reactor at constant rate and a known amount of heat q_i ; US was determined following the procedure described in Appendix 1.

Pure compounds and homogeneous mixtures. The effective heat-transfer parameter for pure compounds and homogeneous mixtures was determined with the first procedure. Fig. 3 shows the experimental and calculated results for 70.0 wt.% sulphuric acid and benzene. The agreement is satisfactory, and the relative error lower than 10%.

Heterogeneous mixtures. The heterogeneous non-reactive mixtures of water–toluene, 70 wt.% sulphuric acid–toluene or benzene were chosen to study the overall heat transfer coefficient in liquid–liquid dispersions and the effect of phase-inversion phenomena. The two types of experiments described previously were carried out. The phase inversion point was measured by detecting the change in the conductivity measurement. Figs. 4 and 5 show the evaluated effective heat-transfer parameters using both procedures for benzene–70 wt.% sulphuric acid and toluene–70 wt.% sulphuric acid.

Fig. 4. Experimental effective heat transfer for the mixture benzene–70 wt.% sulphuric acid. The symbol ○ indicates periodical addition of aqueous sulphuric acid to 640 g of benzene and the evaluation of US ; $T = 308.2$ K. The lines indicate the experiments with a continuous evaluation of US , see Appendix 1.

Fig. 5. Experimental effective heat transfer for the mixture toluene–70 wt.% sulphuric acid. The symbols $\circ$ and $\times$ indicate the experiments with periodical addition of aqueous sulphuric acid to 631 g of toluene and evaluation of US ; $T = 308.2$ K. The lines indicate experiments with continuous evaluation of US .

As can be seen from experimental data, there is a change in the effective heat transfer parameter during phase inversion; also, the slope of US changes after phase inversion. Fig. 6 shows two similar experiments with different phase inversion points. Similar behaviour in the effective heat transfer parameter is observed when phase inversion occurs, and at the point where it occurs there is a change in the effective heat-transfer parameter. This delay time in phase inversion experiments was studied by Gilchrist et al. [10]; they found experimentally that it is sensitive to a wide range of parameters. In all the experiments carried out, going from organic to aqueous phase as the continuous phase, the effective heat-transfer parameter decreases at phase inversion point.

This change in US at phase inversion is caused by a change in the local internal heat transfer coefficient h_0 due mainly to the viscosity changes as observed experimentally by Guillinger et al. [5]. To calculate the viscosity of the mixture during phase inversion, different correlations (Appendix 2) were checked, and the best fit

Fig. 6. Experimental effective heat transfer for the mixture toluene–70 wt.% sulphuric acid in two similar experiments. The addition of aqueous sulphuric acid to 0.74 l of toluene was carried out at constant rate: $T = 308.2$ K, $n_a = 6.67$ s $^{-1}$.

Fig. 7. Experimental and simulated effective heat-transfer parameters for the system benzene–70 wt.% sulphuric acid.

was obtained with the correlation from Leviton and Leighton [11], which is an extension to Taylor's equation [12]; it has been employed previously by Kumar et al. [13]. Figs. 7 and 8 show the experimental and calculated effective heat-transfer parameters. It can be concluded that the classical approach, followed in this work for the prediction of the proportionality factor of Newton's law in jacketed agitated vessels, produces accurate results and can be extended to immiscible liquid systems by modifying only the transport properties.

3.3. Effect of phase inversion on the interfacial area: experimental study

The interfacial area per unit volume of dispersion can be calculated from

$$a = \frac{6\epsilon_d}{d_{32}} \quad (7)$$

where d_{32} is given by

$$d_{32} = Af(\epsilon_d)We^{-0.6}D_a \quad (8)$$

and $f(\epsilon_d)$ normally is a linear correlation

$$f(\epsilon_d) = 1 + B\epsilon_d \quad (9)$$

Fig. 8. Experimental and simulated effective heat-transfer parameters for the system toluene–70 wt.% sulphuric acid.

The constant B can vary between 2.0 and 9.0. The validity of such a correlation has been questioned for dispersions with a volume fraction higher than 0.3; see Brooks and Richmond [14], who recommended the correlation developed theoretically by Delichatsios and Probstein [15]. In this case the function of the dispersed phase volume fraction in Eq. (8) is

$$f(\epsilon_d) = \left(\frac{\ln(c_2 + c_3 \epsilon_d)}{\ln c_2} \right)^{-3/5} \quad (10)$$

where $c_2 = 0.011$ is a constant related to the cut-off velocity in the gaussian probability function, and c_3 is a constant proportional to the ratio of coalescence to break-up coefficients. c_3 allows for differences in collision efficiencies in different systems. The value of c_3 must be determined empirically and differs from system to system; it should be of the order of 1.0.

In the case of phase inversion, the volume fraction of the dispersed phase and the Weber number We will change, where

$$We = \frac{\rho_c n_a^2 D_a^3}{\sigma} \quad (11)$$

In the aromatic nitrations, if the acid phase becomes the continuous one, the density ρ_c will increase and, as a consequence, also We , which implies that d_{32} decreases and the interfacial area increases.

To study the change in interfacial area at phase inversion, a series of experiments were carried out using the system toluene + DIB and 77.0 wt.% H_2SO_4 . To check for phase inversion phenomena, conductivity measurements as well as on-line heat-transfer estimations were used. Phase inversion was observed in the experiment with $n_a = 6.67 \text{ s}^{-1}$ at 6950 s, which corresponds to an $\epsilon_d = 0.541$, just before the end of acid addition at 7200 s. This phenomenon is probably the cause of the significant difference observed between the values of the interfacial area calculated using the data from the semibatch period with acid addition and the batch period [16]. Phase inversion was not observed at higher agitation speeds, even if the dispersed-phase volumetric fraction was as high as 0.6.

To check the effect of phase inversion on the interfacial area, the parameters of Eq. (8) were fitted to the experimental data assuming either a linear dependence on the volume fraction or the dependence described by Delichatsios and Probstein [15]. The values of the fitted constants are respectively $A = 0.431$, $B = 2$ for the linear dependence and $A = 0.321$, $c_3 = 0.847$ for the correlation from Delichatsios and Probstein [15]. Fig. 9(a) shows the experimental and calculated values for the reactive extraction of diisobutylene with aqueous sulphuric acid (see Ref. [7] for experimental details), whereas in Fig. 9(b) the calculated values for the interfacial area are shown using the fitted curves. As can be seen in Fig. 9(a), there is no difference between the fit of

Fig. 9. (a) Concentrations of DIB in an RC1 reactor in semibatch and batch operation: $n_a = 6.67 \text{ s}^{-1}$. (b) Interfacial area calculated with linear and non-linear dependences on the volume fraction.

the linear dependence and the correlation of Delichatsios and Probstein [15], and both predict a similar increase in the interfacial area of approximately 69% and 75%, respectively. The reason for this high increase — Fernandes and Sharma [2] reported a change of 32% of the interfacial area in the system 2 M NaOH and 2 ethyl hexyl formate — is probably due to the high density difference between the organic and the aqueous phases of 843 against 1678 kg m^{-3} , which changes the Weber number from 410 to 817.

4. Conversion rates and phase-inversion phenomena

Benzene, toluene and chlorobenzene nitration under normal industrial conditions, typically 15 mol.% HNO_3 , 30 mol.% H_2SO_4 and 55 mol.% H_2O , occurs in a two-phase system and under stirring. It has been confirmed by various authors [17], that reaction is negligible in the organic phase and that the nitronium ion mechanism is applicable.

Furthermore, in the region of industrial interest, with a 70 to 80 wt.% sulphuric acid strength and 298 to 318 K, it was demonstrated that the nitration of benzene, toluene and chlorobenzene occurred in the fast regime [7].

In this case the rate of mass transfer is enhanced by the reaction, and the bulk of the reaction phase becomes less important, i.e. the concentration of the

aromatic component transferred into the acid phase becomes negligible even at short distances from the interface. The Hatta number is defined as

$$Ha = \frac{\sqrt{k_2 D_{ArH} C_{HNO_3}^{L2}}}{k_{L2}} \quad (12)$$

If $2 < Ha \ll (D_{HNO_3} C_{HNO_3}) / (D_{ArH} C_{ArH}^{i2})$, then the enhancement factor E equals Ha and the conversion rate becomes [18]

$$J_{ArH} a = a k_{L2} E C_{ArH}^{i2} = a \sqrt{k_2 D_{ArH} C_{HNO_3}^{L2}} C_{ArH}^{i2} \quad (13)$$

Hence, J_{ArH} no longer depends on the mass-transfer coefficient. In case of Ha not much smaller than $(D_{HNO_3} C_{HNO_3}) / (D_{ArH} C_{ArH}^{i2})$, diffusion limitation of HNO_3 occurs and the enhancement factor has to be calculated by iteration [1].

In the case of phase inversion, the interfacial area change plays an important role since the conversion rate is directly proportional to it. If $E = Ha$ holds, the conversion no longer depends on the mass-transfer coefficient. In view of the different nature of the mass transfer after inversion — from the continuous phase to the droplet or from the droplet to the continuous phase — it may be possible that the Ha number, which is inversely proportional to k_{L2} , changes and hence the nitration regime.

If the Hatta number decreases or k_{L2} increases, we may go to the slow regime, in which the rate of mass transfer is no longer enhanced by reaction, and the nitration proceeds in the bulk of reaction phase. Also it might be possible to reach the instantaneous regime, where no chemical limitations seem to exist. For an instantaneous reaction the conversion rate is so high that the reaction zone reduces to a plane in the boundary layer of the reaction phase.

5. Experimental study: model verification with reaction calorimetry

To study phase-inversion phenomena and their influence on the conversion rate, a series of toluene nitration experiments were carried out in the RC1 reaction calorimeter. This apparatus enables an accurate measurement of the heat removal from the reactor, which through a heat balance is used to determine the rate of heat generation in the reaction mass and hence the rate of conversion [19]. The precision of these calorimetric measurements [20] depends on the correct representation of all the secondary heat effects such as heat losses, stirring power supply, heat taken up by reactor wall and dilution heat [9]. In this particular case, the heat of dilution was evaluated using a model previously developed [21]. Also selectivity and yields were directly determined from concentration measurements by gas chromatography [22] and compared to the reaction rate

estimated from the calorimetric measurements [23]. Hence, two independent methods were employed to obtain experimental conversion rates.

To study the influence of phase inversion on the conversion rate, the previously developed model to calculate the effective heat transfer parameter was employed. Hence, the change of this parameter was taken into account to evaluate the conversion rates from experimental temperature profiles.

Fig. 10 shows experimental and simulated rate profiles vs. time for four different toluene nitration experiments, whereas in Fig. 11 the experimental and simulated conversions of toluene to *o*-MNT, *m*-MNT and *p*-MNT are shown. Phase inversion took place at 12600, 4260, 4900 and 4400 s or volume fractions 0.455, 0.424, 0.475 and 0.470, respectively. In all the experiments the initial continuous phase was the organic phase, and the stirrer speed was 6.67 s^{-1} . As can be observed, phase inversion increases the reaction rate suddenly, which is in accordance with the previously studied effects on the interfacial area. The simulated results gave increases in interfacial area of 42, 54, 40 and 45%, respectively. These increases are lower than those found using the system toluene(DIB)–77 wt.% H_2SO_4 which is coherent in view of the differences in the physical properties, mainly the density difference between the phases. The behaviour of the reaction rate during phase inversion not only depends on the increase of the interfacial area, but also on the nitric acid accumulated during the process; see Fig. 11 for the simulated concentration profiles of nitric acid.

Phase inversion was simulated as a one-step phenomenon, starting at a previously calculated moment in accordance with the experimental data. As can be seen, experimental phase inversion seems to be a slow process. This is in agreement with the findings of McClarey and Ali Mansoori [24], who showed that, for systems with large density differences between the phases, inversion took place over a range of volume fractions rather than at a single point.

From simulations it seems the increase in interfacial area is not the only parameter responsible for the increase in conversion rate. The best results, see Figs. 10 and 11, were obtained using the correlation of Kronig and Brink [25] for non-rigid droplets when the acid phase is the dispersed phase, whereas that of Calderbank [26] was best when phase inversion occurs and the acid phase becomes the continuous phase [7]. The simulations showed that, after the initial period, the reaction entered into the fast regime, with Ha numbers between 3 and 10, and k_{L2} between 10^{-6} and 10^{-5} m s^{-1} . As phase inversion occurs and mixed-acid phase becomes the continuous phase, the calculated value of k_{L2} decreases to values between 10^{-5} and 10^{-4} m s^{-1} and the system enters into the slow regime, in which the conversion rate can be expressed as

Fig. 10. Experimental and simulated conversion rates for some semibatch nitration experiments in which phase inversion took place. (a) $x = 78.9$ wt.%; feed time, 4 h; $T = 318.2$ K. (b) $x = 68.02$ wt.%; feed time, 2 h; $T = 308.2$ K. (c) $x = 66.1$ wt.%; feed time, 2 h; $T = 308.2$ K. (d) $x = 63.9$ wt.%; feed time, 2 h; $T = 308.2$ K.

$$R = ak_{L2}C_{ArH}^{i2} \quad (14)$$

which means $E \approx 1$. In this situation, the conversion rate depends on the overall mass-transfer coefficient, which produces an increase in the conversion rate even though the regime has changed from fast to slow. Experimental evidence is needed to confirm it.

The calculated effective heat-transfer parameters, using the correlations previously developed for heterogeneous liquid–liquid mixtures of aromatics and sulphuric acid solutions, are shown in Fig. 12: phase inversion under these circumstances seems to produce a relatively small change; the principal contribution to a US increase is the continuous addition of fresh mixed acid during the semibatch process, thus increasing the volume of the reactor and hence the heat-transfer surface; see the differences between the experiment with 4 h dosing time in Fig. 12a, and experiments with 2 h dosing time in Figs. 12(c) and 12(d).

6. Correlation of the phase-inversion point

The determination of the phase inversion point is complicated by the existence of an ambivalence region, in which what phase is dispersed depends on the method by which the dispersion was formed and the time delays that may occur in these systems. All agitated heterogeneous liquid–liquid systems exhibit this

hysteresis. For these reasons, only a few attempts have been made to quantify the parameters controlling phase inversion. Quinn and Sigloh [27] found that, for dispersions of organic liquids in water, the volume fraction of organic phase at phase inversion could be correlated by

$$\epsilon_{dPI} = \epsilon_{D0} + \frac{C'}{P} \quad (15)$$

where ϵ_{D0} and C' are constants. ϵ_{D0} is the asymptotic value of the volume fraction at which the stirrer speed no longer affects the phase inversion point, and the latter is only related to the physical properties of the dispersion. P is the power introduced by the stirrer; for the highly turbulent regime it can be expressed by

$$P = \phi \rho_m n_a^3 D_a^5 \quad (16)$$

where ϕ may be considered constant in the system studied, see Table 1; in our case, $\phi = 2.2$ [28]. Substituting Eq. (16) into Eq. (15) and rearranging gives

$$\epsilon_{dPI} = \epsilon_{D0} + \frac{C''}{\rho_m n_a^3} \quad (17)$$

Droplet size in a dispersion is determined by droplet break-up, droplet collision and droplet coalescence. Arashmid and Jeffreys [29] assumed phase inversion will occur when the coalescence frequency is equal to the collision frequency, i.e. every collision results in a coalescence. Hence, if T is the ratio between the coalescence and collision frequencies, phase inversion occurs

Fig. 11. Experimental and simulated conversion profiles of the reactants for the above-described semibatch nitrations in which phase inversion took place.

when $T = 1$. Using the expression deduced by Misek [30] for the collision frequency and the expression deduced by Howarth [31] for the coalescence frequency, Arashmid and Jeffreys arrived at the following expression

$$T = \frac{C'''}{\epsilon_d d_{32}^2 n_a^\alpha} \quad (18)$$

where C''' and α are constants that depend on the characteristics of the stirrer and the physical properties of the mixture. Experimental results agreed well with this equation, although incorrect forms for the collision frequency [5] and for the coalescence frequency [32] were used.

In both models the ambivalence region can be represented by adjusting the constants in Eqs. (17) and (18), depending on whether the initial dispersed phase is the organic or the aqueous. Fig. 13 shows the experimental and calculated results using Eq. (18) for the different systems studied. The constants C''' and α were obtained by non-linear regression over the experimental points in Tables 2 and 3, and are $C''' = 2.26 \times 10^{-4}$ and $\alpha = 2.7$ for the water–toluene system, $C''' = 1.42 \times 10^{-4}$ and $\alpha = 2.7$ for toluene–water, $C''' = 1.05 \times 10^{-3}$ and $\alpha = 3.3$ for toluene–70 wt.% sulphuric acid, and $C''' = 8.7 \times 10^{-4}$ and $\alpha = 3.3$ for benzene–70 wt.% sulphuric acid. As can be seen, the influence of stirrer speed, represented in the constant α , changes from one system to the other.

During semibatch aromatic nitrations, the compositions of organic and aqueous phases change as reaction proceeds. As can be seen from concentration data in Fig. 11, at the phase inversion point the composition of the reaction mixtures was different. Therefore, the correlations developed by previous authors cannot be used to predict the phase inversion point.

7. Conclusions

The accumulation of unreacted nitric acid in semibatch aromatic nitrations can be dangerous if accompanied by a phase inversion, owing to the fact that the rate may increase suddenly, since the reaction rate is usually mass-transfer-controlled under industrial operating conditions. The main parameter responsible for this increase in conversion rate is the interfacial area, which increases if the continuous phase changes to acid with the accompanying change in density of both phases.

The inside heat-transfer coefficient influences the heat removal rate. The change of this parameter is correlated to the change in physical and transport properties of the mixture during phase inversion. Here, the viscosity plays an important role.

The correlation developed by Arashmid and Jeffreys [29] can be used to predict the phase-inversion point in systems with constant composition. However, it is not possible to use it for reacting systems, in which phase

Fig. 12. Experimental and simulated effective heat-transfer parameters for the above-described semibatch nitrations in which phase inversion took place.

compositions change continuously, i.e. in semibatch aromatic nitrations. Unfortunately, the prediction of the phase-inversion point is difficult, since it depends on the stirrer speed, temperature, interfacial tension, etc. Moreover it exhibits hysteresis phenomena, and in some cases inversion takes place over a range of volume fractions rather than at a single point, i.e. it is not an instantaneous phenomenon. More attention will be dedicated to this aspect in future research.

The mathematical model derived can be used to predict the influence of phase inversion on the dynamic behaviour of a nitrator; the mass-transfer coefficient should be investigated further to clarify whether it changes during phase inversion.

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Appendix 1. Continuous determination of the effective heat-transfer parameter US

Different experimental and empirical methods have been proposed to evaluate the effective heat-transfer parameter US ; heat-flow calorimetry has been demonstrated to be a useful technique [8] and is widely used.

The method consists in introducing a known amount of heat q_i in the reaction mass by means of an electrical resistance, and comparing the area under the curve of a plot of $(T_m - T_e)\Psi$ against time over the period of the calibration [33] while keeping the reactor temperature constant via the control system:

$$US = \frac{q_i}{(T_m - T_e)\Psi} \quad (A1)$$

The correction factor Ψ takes into account the temperature variation of the heat-transfer fluid through the jacket, and can be obtained by means of a local heat balance

$$Y = \left[\frac{1 - \exp\left(-\frac{US}{Q_e C_{p_e}}\right)}{\frac{US}{Q_e C_{p_e}}} \right] \quad (A2)$$

The effective heat-transfer parameter is determined at the start of the experiment, before chemical reaction starts, and at the end, when all the reagents have been consumed. Linearity between these two points is assumed for further evaluations. This simplification may produce important errors when the measured power is used to estimate kinetic parameters, for scale-up procedures, for implementation of temperature control strategies, etc. To solve this problem, different approaches can be used, among them the application of model-based estimation techniques [34], continuous calibration [35], etc.

Fig. 13. Experimental and calculated phase-inversion points for the systems water–toluene (+), toluene–water (×), toluene–70 wt.% sulphuric acid (○), benzene–70 wt.% sulphuric acid (*). For data, see Tables 2 and 3.

Here a continuous calibration method, based on a mathematical model previously developed and validated for the RC1 reaction calorimeter [9] was used to estimate US during phase-inversion studies using non-reactive mixtures. The formulation of the energy balance for the reactor contents enables us to determine time dependence of the temperature of the reactor mixture [23], assuming there is no heat of reaction:

$$\frac{dT_m}{dt} = \frac{1}{\Gamma_m} [q_E + US(T_m - T_c)\Psi + q_a + q_i + q_d] \quad (A3)$$

where the different thermal flows taken into account are q_E for mass addition, q_a for the agitation, q_i for the exchange with the surroundings, q_d for the input by the calibration heater; Γ_m is the thermal capacity of the reaction mixture and internal wetted devices in the reactor.

The continuous-calibration method consists of adding a well-known and constant amount of heat q_i to the mixture, by means of an electric heater, during the entire experiment. The term of heating/cooling by mass addition can be determined from the enthalpy difference between the feed stream and the reaction mixture as follows

$$q_E = - \sum_{j \in A_L} F_{E_j} \int_{T_m}^{T_{E_j}} C_{p_j} dT \quad (A4)$$

where F_{E_j} is the molar input flow of j and

$$F_{E_j} = \sum_{k \in A_L} Q_k C_{E_j} ; \quad k = 1, \dots, N_E \quad (A5)$$

where Q_k is the mass flow of the k th input stream, and C_{E_j} is the concentration of j in mol kg^{-1} .

The power supplied by stirring was previously evaluated by Zaldivar et al. [9] as

$$q_a = 2.2 \rho_m n_a^3 D_a^5 \quad (A6)$$

whereas the term of heat losses is proportional to the temperature difference between the mixture and the surroundings [33]:

$$q_i = 0.1(T_{\text{amb}} - T_m) \quad (A7)$$

The thermal capacity of the reaction mixture is calculated as the product of the number of moles and the specific heat of the species in the reactor, including the thermal capacity $\Gamma_b = 69 \text{ J K}^{-1}$ of the devices wetted by the mixture:

$$\Gamma_m = \sum_{j \in A_L} n_{m_j} C_{p_{L_j}} + \Gamma_b \quad (A8)$$

By registering the reactor, jacket, dosing and ambient temperatures plus the calibration heat introduced, it is possible after filtering the signal to estimate US continuously during the addition, and hence to check the influence of phase inversion.

Appendix 2. Physical and transport properties of liquid–liquid dispersions

Correlations for newtonian liquid–liquid mixtures and their effective viscosity, density, specific heat capacity, thermal conductivity, diffusivity and interfacial tension have been derived. The test for the adequacy of the methods used for calculating the average viscosity and density has been the relation between the Power number and the Reynolds number for single-phase data. In this relation, the average density and viscosity for dispersions are introduced. For newtonian liquids this is perfectly satisfactory.

Interfacial tension and diffusivity in multicomponent mixtures still cannot be predicted correctly, so experimental data and empirical correlations must be used [7,28]. The arithmetic, average density of a liquid–liquid mixture is calculated using the volume fraction of each phase [36]

$$\rho_m = \epsilon_d \rho_d + (1 - \epsilon_d) \rho_c \quad (A9)$$

The average specific heat capacity of the mixture can be calculated using the mass fraction of each phase

$$C_{p_m} = \frac{M_c C_{p_c} + M_d C_{p_d}}{M_c + M_d} \quad (A10)$$

Table A1
Effective viscosity for liquid–liquid mixtures

Author	Correlation
Taylor [12]	$\mu_m = \mu_c \left[1 + 2.5\epsilon_d \left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c} \right) \right]$
Leviton and Leighton [11]	$\mu_m = \mu_c \exp \left[2.5 \left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c} \right) (\epsilon_d + \epsilon_d^{5/3} + \epsilon_d^{1/3}) \right]$
Vermeulen et al. [41]	$\mu_m = \frac{\mu_c}{1 - \epsilon_d} \left(1 + \frac{1.5\mu_d\epsilon_d}{\mu_d + \mu_c} \right)$
Laity and treybal [42]	$\mu_m = \frac{\mu_c}{1 - \epsilon_d} \left(1 + \frac{6.0\mu_d\epsilon_d}{\mu_d + \mu_c} \right)$
Vanderveen [43]	$\mu_m = \frac{\mu_c}{(1 - \epsilon_d)^{1.5}} \left(1 + \frac{\mu_d\epsilon_d}{\mu_d + \mu_c} \right)^{1.5}$
Barnea and Mizrahi [44]	$\mu_m = \mu_c B \left[\frac{\frac{2}{3}B + \left(\frac{\mu_d}{\mu_c} \right)}{B + \left(\frac{\mu_d}{\mu_c} \right)} \right] \text{ where } B = \exp \left[\frac{5\epsilon_d A}{3(1 - \epsilon_d)} \right] \text{ and } A = \left(\frac{\mu_d + 0.4\mu_c}{\mu_d + \mu_c} \right)$
Barnea and Mizrahi [45]	$\mu_m = \mu_c \exp \left[\frac{2.5\epsilon_d}{1 - \epsilon_d} \left(\frac{\mu_d^* + 0.4\mu_c}{\mu_d^* + \mu_c} \right) \right]$

Estimates of the thermal conductivity of liquid–liquid emulsions can be made using Tareef's correlation [37], which has been recommended by Choudhury et al. [38] for this type of system:

$$\lambda_m = \lambda_c \frac{2\lambda_c + \lambda_d - 2\epsilon_d(\lambda_c - \lambda_d)}{2\lambda_c + \lambda_d + \epsilon_d(\lambda_c - \lambda_d)} \quad (\text{A11})$$

The effective viscosity of a heterogeneous system μ_m is related to the viscosity of the continuous phase μ_c and is increased owing to the presence of the dispersed particles or droplets. At low concentrations, or $\epsilon_d \rightarrow 0$, they manifest themselves only by being impermeable for the continuous phase. This effect was derived by Einstein (see Rietema [39]) to be

$$\mu_m = \mu_c(1 + 2.5\epsilon_d) \quad (\text{A12})$$

Vand [40], taking into account the hydrodynamic interaction of the flow fields around the neighbouring particles, derived an expression for rigid, dispersed particles and low concentrations

$$\mu_m = \mu_c \exp \left[\frac{2.5\epsilon_d}{1 - 0.61\epsilon_d} \right] \quad (\text{A13})$$

When the dispersed particles are droplets or gas bubbles, one might expect the hydrodynamic interaction between the flow fields of neighbouring particles to be less strong. On the basis of experiments, different correlations based on the Einstein or Vand equations have appeared in literature (see Uhl and Gray [36] and Rietema [39] for a review), which are summarized in Table A1.

Barnea and Mizrahi [45] carried out an experimental study on the effective viscosity of relatively coarse and unstable liquid–liquid dispersions like water/silicone

oil, toluene/glycerine and tetradecane/ethylene glycol in a dispersion range limited to ϵ_d lower than 0.33, and they found the experimental results corroborated their correlation. Similar results could be obtained using the relation of Leviton and Leighton [11]. In fact, numerical comparison of both equations reveals a reasonable agreement in the range of ϵ_d between 0 and 0.5. Barnea and Mizrahi [45] use μ_d^* as an adjustable parameter representing the “effective” viscosity of the dispersed phase.

Appendix 3. Notation

a	interfacial area ($\text{m}^2 \text{m}^{-3}$)
A	constant (Eq. (9))
c_3	constant (Eq. (10))
C	concentration (kmol m^{-3})
C_p	specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
d_{32}	Sauter mean diameter of droplets (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
D_a	impeller diameter (m)
D_0	internal reactor diameter (m)
D_1	external reactor diameter (m)
E	enhancement factor
F	molar flow (mol s^{-1})
h	partial heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
Ha	Hatta number
J_A	molar flux ($\text{mol m}^2 \text{s}^{-1}$)
k_L	mass transfer coefficient (m s^{-1})
k_2	measured second-order rate constant ($\text{m}^3 \text{kmol}^{-1} \text{s}^{-1}$)
m	distribution coefficient
M	mass (kg)

n	molar hold-up
n_a	impeller speed (rev s^{-1})
q	thermal flow (W)
Q	volumetric flow ($\text{m}^3 \text{s}^{-1}$)
R	overall reaction rate ($\text{kmol m}^{-3} \text{s}^{-1}$)
S	heat transfer surface (m^2)
t	time (s)
T	temperature (K)
U	overall heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
US	effective heat transfer parameter (W K^{-1})
V	volume (m^3)
x	sulphuric acid strength

Greek letters

ϵ_d	dispersed phase volume fraction
γ	surface tension (N m^{-1})
λ	thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
μ	viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ρ	density (kg m^{-3})
σ	interfacial tension (N m^{-1})

Subscripts and superscripts

0, 1	internal and external sides
A	diisobutylene
a	acid phase
ArH	aromatic compound
B	sulphuric acid
c, d	continuous and dispersed phases
e	jacket
i1, i2	aqueous and organic interphase
L1, L2	aqueous and organic phase
m	reaction mixture
o	organic phase
PI	phase inversion
t	hydraulic
To	toluene
w	reactor wall

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