

Modelling of mass transfer of volatile organic compounds in polymer dispersions

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Abstract

Polymers may contain low molecular organic components due to incomplete conversion, contaminated raw materials and/or undesirable side reactions. Aqueous polymer solutions, e.g. dispersion paints, adhesives or refining media in the paper industry, are usually applied to large surfaces. During this operation, low molecular weight components are emitted into the ambient air if not removed before. While existing removal processes operate fairly well, the mass transfer steps are still poorly understood and therefore there are no designing data which can be claimed to be reliable. Here a mechanical mathematical model is presented which accounts for the crucial mass transfer steps occurring in a stationary continuous, well mixed stripping apparatus. Phase equilibria and attainable monomer removal have been determined experimentally in an aerosol jet loop reactor. The results indicate that an efficient stripping process essentially depends on distribution coefficients, hydrodynamic properties and operating conditions while diffusion inside the latices is negligible. This is true for operating temperatures higher than the polymer glass temperature. These results are in contradiction to statements of some other authors who consider diffusion inside the latex particle as the limiting step. © 1997 Elsevier Science S.A.

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1. Introduction

When no additional treatment is done, polymer materials as well as polymer agents contain non-polymer, volatile organic components which may arise from

- incomplete polymerisation of the monomers
- raw materials containing non-polymerisable components
- secondary reactions occurring during the synthesis

These volatile organic compounds have to be removed from the polymers for several reasons.

- Low molecular weight contents in polymers deteriorate the materials' properties (e.g. fluidity, thermal stability).
- In order to comply with legislative standards, volatile organic compounds have to be removed from dispersions, especially when applied to large surfaces (e.g. in surface refining in the paper and leather industries as well as on coating).

The design of technical process units for the removal of volatile residual compounds has to be optimised with respect to energy consumption and investment costs. For this reason,

understanding the mass transfer behaviour between the gas phase and the aqueous polymer dispersion is quite fundamental.

1.1. Technical approaches

Odor problems led to early investigations on the removal of residual monomers from latex [8]. The first patents concerning the removal of monomers (styrene, acrylacidic ester) from bead polymers using steam date from 1930 [5]. All fundamental types of technical deodorization units have been developed and patented by 1970 [6,9,12,13,15,16].

The batch stripper usually consists of a tank or a stirring device containing the dispersion, with an inert gas (nitrogen, steam) fed into the reactor. Depending on working conditions the unit can be operated under low pressure and possibly be combined with a defoamer.

The single-stage vacuum stripper consists of a mixing device where the dispersion is brought into contact with the stripping gas, with defoaming units downstream. The multi-stage vacuum stripper can be operated either as a cross-flow or a counter-current device, i.e. steam will be fed to each stage or in the opposite direction, respectively. In the contin-

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uous counter-current stripping column the dispersion is fed from the column head, passing through the different stages. The stripping medium is removed at the column head.

1.2. Scientific approaches

These stripping processes have been treated first in 1970 from a scientific point of view. The removal of volatile organic compounds usually is described by an exponential decay

$$\frac{c}{c_0} \approx e^{-\lambda\tau} \quad (1)$$

where τ is the reaction time. The exponent λ is interpreted differently by many authors.

In 1972 Bolotnikov and Belen'kii [1] investigated the batch distillation of styrene-copolymer latices containing α -methylstyrene and styrene using steam. They considered the process to be limited by diffusion processes, with λ being the ratio of diffusion coefficients and gas residence time, τ_G .

$$\lambda \approx \frac{D}{\nu\tau_G} \quad (2)$$

Matveev et al. [10] described the blistering in highly viscous polymer solutions during the stripping process and recommended stirring and pressure changes to improve desorption.

Chan et al. [2] investigated the batch stripping of vinylchloride and defined three mass transport mechanisms:

- direct evaporation from the polymer particles into gas phase
- Fick diffusion from the polymer particles into water
- Fick diffusion from water phase into gas phase

The validity of the model is proved by measurements of both distribution and mass transfer coefficients.

Duda [3] stated that removal of residual volatile compounds from polymers is limited by the diffusion coefficients, which decrease drastically at low solvent concentrations. He calculated the diffusion coefficients using the Flory–Huggins interaction theory and the free-volume theory for binary diffusion.

Walther et al. [17] developed a model for the removal of low molecular compounds from PVC as a function of temperature, pressure, time, gas flow rate, particle size and diffusion pathway distribution. However, the exponent λ depends on the diffusion time of the monomers inside the polymers only.

$$\lambda \approx \frac{D}{r_L^2} \quad (3)$$

Omi et al. [14] performed stripping experiments on styrene-butadiene and styrene dispersions with low pressure steam. They modelled the decrease of styrene concentration by means of infinite series, where the same relation for λ as described by Walther et al. is obtained due to the rapid convergence of the series.

Medrzycka [11] describes the degasification of hydrocarbons from oil in water emulsions via two different transport mechanisms.

- Hydrocarbons dissolved in water evaporate into the gas phase: λ is equivalent to the mass transfer coefficient.
- Emulsion droplets are in contact with the steam bubbles and hydrocarbons evaporate directly: λ is essentially determined by the hydrodynamics of the reactor.

According to the review by Englund [4] about the mechanism and process principles of deodorisation, the stripping rate is not limited by the diffusion inside latex particles but by the interfacial area between gas and dispersion. The concentration of volatile compounds decreases obeying first order kinetics.

While chemical process conditions for the removal of volatile organic compounds from dispersions are known-different working apparatus types have been optimised-only rudimentary knowledge and different, sometimes contradictory interpretations about the understanding of the mass transfer phenomena have been reported.

Therefore the purpose of this paper is the fundamental description of these mass transfer processes. Since indeed a continuous, entirely remixed aerosol jet loop reactor was available to perform our own experiments, the continuous deodorisation process has been modelled and confirmed. The obtained results are also valid for batch processes, which will be treated elsewhere.

2. Experimental

2.1. Reactor

The 0.7 m³ jet loop reactor—System Burdosa¹—consists of two concentric tubes. Steam saturated air is fed into the reactor via an ejector type nozzle. The diluted polymer dispersion is sprayed by air using a two-phase nozzle located in the upper part of the air jet nozzle. The air–liquid mixture reaches a reversing device at the end of the inner tube, and flows down to the reactor bottom. Part of the fluid is removed from the reactor via an annular gap between the inner and outer tubes, while the main stream is remixed with the inlet flow above the jet nozzle. The dispersion droplets impinge against the reactor walls so that an additional dispersion film is developed which contributes to the interfacial area. This deposit sufficiently prevents a discharge of the aerosol. The fluid is collected in the lower reversing system and can be removed via an adjustable valve. The dimensions of the reactor which is insulated to avoid heat loss are listed in Fig. 1. The employed binary nozzle, Caldyn type CSL, generates a narrow droplet size distribution with an average droplet diameter of 80 μm . Depending on the fluid and air flow rates, the interfacial area ranges from 10 to 30 m². These values have been determined by absorption measurements of CO₂ in aque-

¹ Burdosa, Giessen, Germany.

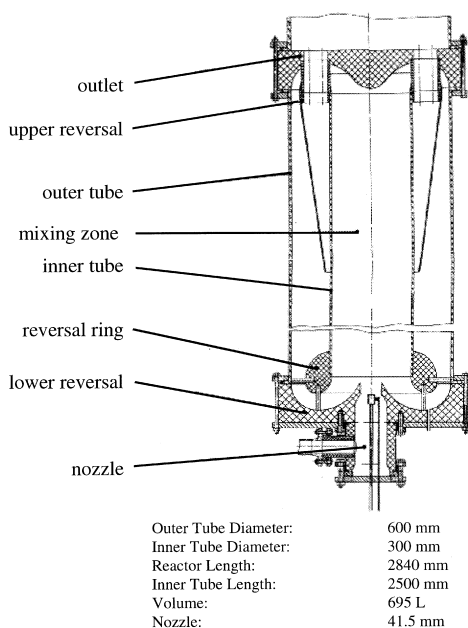


Fig. 1. Aerosol jet loop reactor System "Burdosa".

ous sodium hydroxide solution using the same drop size distribution. A 35 wt% aqueous butylacrylate-styrene-copolymer dispersion mixed with 1 wt% styrene has been used as a model system. The average latex diameter is 160 nm.

The air entering the reactor has been saturated with steam in order to prevent the liquid film from drying and solidifying. Simultaneously, the air fed into the reactor is adjusted to the desired temperature. With a circulation number of $n_U = 10$, the aerosol jet loop reactor is considered to be ideally mixed.

The operation conditions are:

- $\dot{V}_D = 20 \text{ L h}^{-1}$; $\dot{V}_G = 100\text{--}300 \text{ m}^3 \text{ h}^{-1}$;
- $\eta_L = 0.5$; $\rho_L = 1.04\text{--}1.08 \text{ kg L}^{-1}$;
- $c_D^f = 0.1 \text{ mol L}^{-1}$; $c_L^f = 0.3 \text{ mol L}^{-1}$.

2.2. System parameters

The assumptions which were made for the description of the macroscopic processes in an aerosol loop reactor are the following.

- the dispersion consists of two phases, latex (L) and water phase (W)
- latex particles are spheres (radial symmetry)
- no coalescence of the polymer pearls
- ideal macroscopic mixing of both, gas phase (G) and dispersion

The considered microscopic mass transport phenomena which were used for modelling this removal process are illustrated in Fig. 2, in detail they are:

- Fick diffusion of the monomer (M) inside the polymer phase
- validity of the two-film theory at the interfacial areas
- validity of a Nernst distribution law at the interfacial areas

The characteristic system parameters for mass transfer are the distribution coefficients H_G and H_L of styrene between

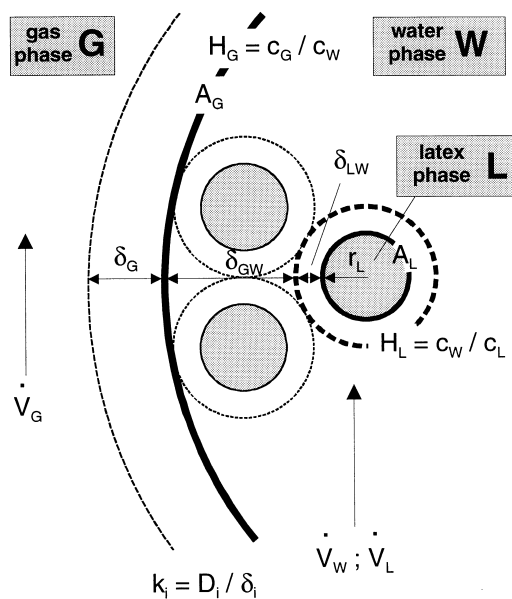


Fig. 2. Mass transfer mechanism.

the involved phases, as well as the transport resistances $1/k_i$. These are defined as

$$H_G = \frac{c_G}{c_W}; H_L = \frac{c_W}{c_L} \quad (4)$$

and according to the two-film theory

$$\frac{1}{k_i} = \frac{\delta_i}{D_i} \quad (5)$$

The distribution coefficient of styrene between the gas phase and the dispersion, H_D , is given by

$$H_D = \frac{c_G}{c_D} = \frac{c_G}{c_L \epsilon_L} \quad (6)$$

While H_D can be measured by headspace chromatography, it can also be interpreted as the product of the distribution coefficients H_G , H_L and the reciprocal value of the latex phase holdup ϵ_L .

$$H_D = H_G H_L \frac{1}{\epsilon_L} \quad (7)$$

Since H_G can be calculated from the concentration of styrene in the gas phase above pure styrene, c_G , and the solubility of pure styrene in water, c_W ,

$$H_G = \frac{c_G}{c_S} \frac{c_S}{c_W} = \frac{c_G}{c_W} \quad (8)$$

H_L can be estimated from the calculated H_G and the experimentally determined H_D . Fig. 3 shows the distribution coefficients as a function of temperature: $H_G = 0.1\text{--}0.8$, $H_L = 2 \times 10^{-3}\text{--}7 \times 10^{-3}$ at $T = 20\text{--}70^\circ\text{C}$. The calculated H_G values for styrene agree with the measured data of Yaws et al. [20]. The mass transfer coefficient between the gas phase and water, K_G , is given by

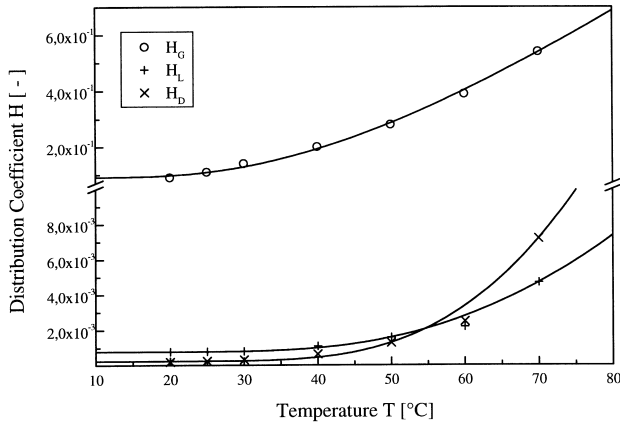


Fig. 3. Distribution coefficients H_G (water/humidified air), H_D (latex dispersion/humidified air) and H_L (water/latex particle) of styrene in dependence on the temperature.

$$\frac{1}{K_G} = \frac{1}{k_w} + \frac{1}{k_G H_G} \quad (9)$$

In order to estimate K_G , approximate diffusion coefficients of styrene and the boundary layer thicknesses need to be known. The following values have been chosen:

Gas: $D_G \approx 3 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ [7] $k_G \approx 3 \times 10^{-3} \text{ m s}^{-1}$.

The value of the gas film thickness has been estimated roughly; its order of magnitude shows that its contribution to mass transfer resistance cannot always be neglected.

Water: $D_W \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [19].

Gas-side liquid film (water phase): the average distance \bar{r} of the latex particles inside a dispersion drop to the drop center is

$$\bar{r} = \frac{\int_0^{r_T} (4\pi r^2) r \, dr}{\int_0^{r_T} 4\pi r^2 \, dr} = \frac{3}{4} r_T \quad (10)$$

The average diffusion length and thus the boundary layer thickness at the interface A_G then becomes

$$\delta_{GW} = r_T - \frac{3}{4} r_T = \frac{1}{4} r_T; \quad \delta_{GW} \approx 10^{-5} \text{ m} \quad (11)$$

thus $k_w \approx 10^{-4} \text{ m s}^{-1}$.

Particle-side boundary layer (water phase): the ratio of latex phase volume V_L to the whole dispersion volume V_D is

$$\frac{V_L}{V_D} = \frac{1}{3} \quad (12)$$

This value is smaller than the ratio of V_L to the sum of the latex particle volume and the water boundary layer volume:

$$\frac{V_L}{V_D} = \frac{1}{3} \leq \frac{V_L}{V_L + V_{\text{Film}}} = \frac{N_L \frac{4}{3} \pi r_L^3}{N_L \frac{4}{3} \pi (r_L + \delta_{LW})^3} = \left(\frac{r_L}{r_L + \delta_{LW}} \right)^3 \quad (13)$$

Therefore, the ratio of the boundary layer thickness δ_{LW} to latex particle radius r_L is

$$\frac{\delta_{LW}}{r_L} \leq \sqrt[3]{3} - 1 \approx 0.44 \quad (14)$$

On the other hand, the diffusion coefficient of the transferred compound in water is at least 10^4 – 10^5 times larger than the one in latex. Therefore the ratio of diffusion times in the water-side liquid film and inside the latex particles becomes

$$\frac{t_L}{t_W} = \frac{D_W / \delta_{LW}^2}{D_L / r_L^2} \geq 10^4 \left(\frac{r_L}{\delta_{LW}} \right)^2 \geq 5 \times 10^4 \quad (15)$$

Thus, the mass transfer resistance in a layer around the latices can be neglected.

3. Modelling

As the continuous process is operated under isothermal and isobaric conditions the system is completely described by mass balance equations. The gas phase mass balance equation comprises terms for convection and mass transfer to the water phase, whereas the water phase equation additionally needs to account for mass transfer with the latices. Since the mass transport within the latex particles is proportional to the diffusion fluxes which occur at the surface of each particle. These particles have different residence times in the reactor, so that the macroscopic mass transfer between latex and water is a integral of the surface diffusion fluxes, multiplied by the residence time distribution of the particles $e(t)$. According to the assumed ideal mixing of the phases, the CSTR residence time distribution has been selected for $e(t)$ [18]:

$$e(t) = \frac{1}{\tau_L} e^{-t/\tau_L} \quad (16)$$

By using the phase ratio η , the specific interfacial area a , and the residence times τ ,

$$\eta_G = \frac{V_G}{V_W}; \quad \eta_L = \frac{V_L}{V_W} \quad (17)$$

$$a_G = \frac{A_G}{V_G}; \quad a_L = \frac{A_L}{V_L} = \frac{N_L 4\pi r_L^2}{N_L \frac{4}{3} \pi r_L^3} = \frac{3}{r_L} \quad (18)$$

$$\tau_G = \frac{V_G}{V_G}; \quad \tau_W = \frac{V_W}{V_W}; \quad \tau_L = \frac{V_L}{V_L} \quad (19)$$

and assuming that

$$\tau_W = \tau_L, \quad c_G^0 = 0, \quad c_W^0 = H_L c_L^0 \quad (20)$$

the stationary macroscopic balance equation for the gas phase is given by

$$0 = -\frac{1}{\tau_G} c_G - K_G a_G \left(\frac{c_G}{H_G} - \bar{c}_W \right), \quad \bar{c}_W = \int_0^{\infty} c_W(t) e(t) \, dt \quad (21)$$

For a drop at time $t > 0$, the mass balance in the water phase is

$$\frac{dc_w}{dt}(t) = \eta_G K_G a_G \left(\frac{c_G}{H_G} - \bar{c}_w(t) \right) - \eta_L a_L D_L \frac{\partial c_L}{\partial r}(t, r_L) \quad (22)$$

Multiplying (22) with $e(t)$ and integrating between $[0, \infty]$, the definition of \bar{c}_w and partial integration gives the macroscopic balance in the water phase as

$$0 = \frac{1}{\tau_L} (H_L c_L^0 - \bar{c}_w) + \eta_G K_G a_G \left(\frac{c_G}{H_G} - \bar{c}_w \right) - \eta_L a_L \int_0^\infty D_L \frac{\partial c_L}{\partial r}(t, r_L) e(t) dt \quad (23)$$

Assuming radial symmetry within the spherical latex particles, the microscopic diffusion equation is

$$\frac{\partial c_L}{\partial t}(t, r) = D_L \left(\frac{\partial^2 c_L}{\partial r^2}(r, t) + \frac{2}{r} \frac{\partial c_L}{\partial r}(t, r) \right); \quad 0 < r < r_L, t > 0 \quad (24)$$

with the boundary conditions:

$$\frac{\partial c_L}{\partial r}(t, 0) = 0; c_L(t, r_L) = c_w(t)/H_L; c_L(0, r) = c_L^0 \quad (25)$$

Using Laplace transformation, Eqs. (21), (23)–(25) can be solved simultaneously. From Eqs. (24) and (25) the boundary value problem

$$s \hat{c}_L(s, r) - c_L^0 = D_L \left(\frac{\partial^2 \hat{c}_L}{\partial r^2}(s, r) + \frac{2}{r} \frac{\partial \hat{c}_L}{\partial r}(s, r) \right) \quad (26)$$

$$\frac{\partial \hat{c}_L}{\partial r}(s, 0) = 0; \hat{c}_L(s, r_L) = \frac{\hat{c}_w(s)}{H_L} \quad (27)$$

is obtained.

It can be solved using standard methods:

$$\hat{c}_L(s, r) = \frac{c_L^0}{s} + \left(\frac{s \hat{c}_w(s)}{H_L} - c_L^0 \right) \frac{1}{s} \frac{\tau_L}{\sinh \rho r_L} \frac{\sinh \rho r}{r} \quad (28)$$

where $\rho = \sqrt{s/D_L}$. Differentiation with respect to r yields the gradient at the lattices' surfaces

$$\begin{aligned} \frac{\partial \hat{c}_L}{\partial r}(s, r_L) &= (s \hat{c}_w(s) - H_L c_L^0) \\ &\times \frac{1}{s H_L \sinh \rho r_L} \left(\rho \frac{\cosh \rho r_L}{r_L} - \frac{\sinh \rho r_L}{r_L^2} \right) \\ &= (s \hat{c}_w(s) - H_L c_L^0) \frac{1}{s H_L r_L} (\rho r_L \coth \rho r_L - 1) \end{aligned} \quad (29)$$

From

$$z = \rho r_L = \sqrt{\frac{r_L^2}{D_L r_L}} = \sqrt{\frac{t_L}{\tau_L}} \quad (30)$$

where $t_L = r_L^2/D_L$ being the diffusion time in the latex particle, the macroscopic mass flux from latex to water becomes

$$\begin{aligned} R_L &= \eta_L a_L \int_0^\infty D_L \frac{\partial c_L}{\partial r}(t, r_L) e(t) dt \\ &= \eta_L a_L D_L \frac{\partial \hat{c}_L}{\partial r}(1/\tau_L, r_L) \frac{1}{\tau_L} \\ &= \eta_L a_L \frac{D_L}{H_L r_L} (z \coth z - 1) (\bar{c}_w - H_L c_L^0) \end{aligned} \quad (31)$$

since

$$\bar{c}_w = \int_0^\infty c_w(t) e(t) dt = \frac{1}{\tau_L} \hat{c}_w(1/\tau_L)$$

Accordingly, the average concentration \bar{c}_L in the latex is

$$\begin{aligned} \bar{c}_L &= \int_0^\infty e(t) \left(\int_0^{r_L} c_L(t, r) r^2 dr \right) dt / (r_L^3/3) \\ &= \frac{3}{\tau_L r_L^3} \int_0^{r_L} \hat{c}_L(1/\tau_L, r) r^2 dr \end{aligned} \quad (32)$$

i.e.

$$\bar{c}_L = c_L^0 + (\bar{c}_w - H_L c_L^0) (z \coth z - 1) 3 / (H_L z^2) \quad (33)$$

The driving concentration difference $\bar{c}_w - H_L \bar{c}_L$ then becomes

$$\bar{c}_w - H_L \bar{c}_L = (\bar{c}_w - H_L c_L^0) [1 - (z \coth z - 1) 3 / z^2] \quad (34)$$

so that R_L is defined as

$$\begin{aligned} R_L &= \eta_L a_L \frac{D_L}{H_L r_L} (z \coth z - 1) \\ &\times [1 - z \coth z - 1) 3 / z^2]^{-1} (\bar{c}_w - H_L \bar{c}_L) \end{aligned} \quad (35)$$

and Eq. (33) becomes

$$\begin{aligned} 0 &= \frac{1}{\tau_L} (c_L^0 - \bar{c}_L) + \frac{3}{t_L H_L} (z \coth z - 1) \\ &\times [1 - (z \coth z - 1) 3 / z^2]^{-1} (\bar{c}_w - H_L \bar{c}_L) \end{aligned} \quad (36)$$

Introducing the macroscopic mass transfer coefficient K_L between latex particles and water,

$$K_L = \frac{D_L}{H_L r_L} \frac{z \coth z - 1}{1 - 3(z \coth z - 1) / z^2} \quad (37)$$

Eq. (36) and Eqs. (21) and (23) give the following set of algebraic equations

$$0 = \frac{1}{\tau_G} c_G - K_G a_G \left(\frac{c_G}{H_G} - \bar{c}_W \right) \quad (38)$$

$$0 = \frac{1}{\tau_W} (H_L c_L^0 - \bar{c}_W) + \eta_G K_G a_G \left(\frac{c_G}{H_G} - \bar{c}_W \right) - \eta_L K_L a_L (\bar{c}_W - H_L \bar{c}_L) \quad (39)$$

$$0 = \frac{1}{\tau_L} (c_L^0 - \bar{c}_L) + K_L a_L (\bar{c}_W - H_L \bar{c}_L) \quad (40)$$

since

$$\frac{3}{t_L H_L} = \frac{3}{r_L^2 H_L} = \frac{3}{r_L} \frac{D_L}{r_L H_L} = a_L \frac{D_L}{r_L H_L} \quad (41)$$

The problem can thus be reduced to a simple steady-state CSTR model for the three phases G, W and L, where $K_L a_L$ is explicitly given as

$$K_L a_L = \frac{D_L a_L}{H_L r_L} \varphi(z) = \frac{3}{H_L t_L} \varphi(z) \quad (42)$$

with

$$\varphi(z) = \frac{z \coth z - 1}{1 - 3(z \coth z - 1)/z^2} \quad (43)$$

Note that according to Eq. (41) the term $D_L a_L / (H_L r_L)$ is determined by the distribution coefficient H_L and the diffusion time t_L only. For the function $\varphi(z)$,

$$\varphi(z) \rightarrow 5 \text{ for } z \rightarrow 0 \quad (44)$$

and

$$\varphi(z) \approx \frac{z-1}{1-3(z-1)/z^2} \approx z-1 \approx z \text{ for } z \rightarrow \infty \quad (45)$$

are valid.

Therefore, two limiting cases can be considered for mass transfer.

(1) The diffusion time inside the latex particle is much smaller than the residence time of the droplet:

$$t_L \ll \tau_L: z \approx 0 \Rightarrow \varphi(z) \approx 5 \Rightarrow K_L a_L \approx \frac{5D_L}{H_L r_L} \frac{3}{r_L} a_L = \frac{15}{H_L t_L} \quad (46)$$

(2) The diffusion time inside the latex particle is much bigger than the residence time of the droplet:

$$t_L \gg \tau_L: z \rightarrow \infty \Rightarrow \varphi(z) \approx z \Rightarrow K_L a_L \approx \frac{D_L}{H_L r_L} a_L \sqrt{\frac{t_L}{\tau_L}} = \frac{3}{H_L \sqrt{t_L \tau_L}} \quad (47)$$

In the first case, only the system parameters H_L and t_L influence the mass transfer coefficient $K_L a_L$, whereas in the second case the operating parameter τ_L is also significant. By solving Eq. (38) for c_G , Eq. (48) is obtained.

$$c_G = \frac{K_G a_G}{\frac{1}{\tau_G} + \frac{K_G a_G}{H_G}} \bar{c}_W = \frac{\tau_G K_G a_G}{1 + \frac{\tau_G K_G a_G}{H_G}} \bar{c}_W \quad (48)$$

Eq. (40) gives

$$\bar{c}_L = \frac{\frac{1}{\tau_L} c_L^0 + K_L a_L \bar{c}_W}{\frac{1}{\tau_L} + K_L a_L H_L} = \frac{c_L^0 + \tau_L K_L a_L \bar{c}_W}{1 + \tau_L K_L a_L H_L} \quad (49)$$

Introducing these expressions into Eq. (39) and solving for \bar{c}_W yields

$$\bar{c}_W = H_L c_L^0 \frac{1 + \frac{\eta_L K_L a_L \tau_L}{1 + \tau_L K_L a_L H_L}}{1 + \frac{\eta_G K_G a_G \tau_L}{1 + \tau_G K_G a_G / H_G} + \frac{\eta_L K_L a_L \tau_L}{1 + \tau_L K_L a_L H_L}} \quad (50)$$

These relationships provide an expression for the relative average residual concentration of the dissolved organic compound,

$$\frac{\bar{c}_L}{c_L^0} = \frac{1}{1 + \tau_L K_L a_L H_L} \times \left(1 + \tau_L K_L a_L H_L \frac{1 + \frac{\eta_L K_L a_L \tau_L}{1 + \tau_L K_L a_L H_L}}{1 + \frac{\eta_G K_G a_G \tau_L}{1 + \tau_G K_G a_G / H_G} + \frac{\eta_L K_L a_L \tau_L}{1 + \tau_L K_L a_L H_L}} \right) \quad (51)$$

Applying the definitions of $K_L a_L$, τ_G and τ_L , the reciprocal value of the conversion becomes

$$\frac{1}{U} = 1 + \frac{z^2}{3\varphi(z)} + \left(\frac{1}{H_L K_G A_G} \frac{\dot{V}_L}{H_L H_G \dot{V}_G} + \frac{1}{H_L H_G \dot{V}_G} \right) \times \left[1 + \frac{H_L}{\eta_L} \left(1 + \frac{z^2}{3\varphi(z)} \right) \right] \quad (52)$$

If \bar{c}_L / c_L^0 is to be small, i.e. $U \approx 1$, then

$$\frac{z^2}{3\varphi(z)} \ll 1, \text{ i.e. } t_L \ll \tau_L \quad (53)$$

has to be satisfied.

This restriction means that the latex particles must stay longer inside the reactor than the diffusion time if high conversion is required. In case that $t_L \ll \tau_L$ and also $H_L \ll \eta_L$ are valid (which corresponds to the good solubility of the transferred compound in the latex) Eq. (52) can be simplified to

$$U \approx \frac{1}{1 + \frac{1}{H_L K_G A_G} \frac{\dot{V}_L}{H_L H_G \dot{V}_G} + \frac{1}{H_L H_G \dot{V}_G}} \quad (54)$$

4. Results

According to the results obtained in Section 3, the removal function of styrene in the liquid phase by continuous steady operation is described by Eq. (51). Deodorization is determined by the distribution coefficients H_L and H_G , the specific interfacial areas a_L and a_G , the phase ratios η_L and η_G , the residence times τ_L and τ_G , as well as the mass transfer coefficients K_G and $K_L a_L$.

The latter has two different meanings depending on the ratio of the diffusion time t_L in the latex particle to the particle residence time, τ_L (determined at process conditions: $\tau_L = 60$ s). It has been shown that complete removal is possible only if the diffusion time of the organic compound in the latex is much smaller than the residence time of the latex particles in the reactor. For the studied system t_L is

$$t_L = \frac{r_L^2}{D_L} = \frac{64 \times 10^{-16}}{10^{-14}} = 0.64 \text{ s} \quad (55)$$

so that the restriction $t_L \ll \tau_L$ is satisfied for $\tau_L \geq 60$ s. The estimated value for D_L is valid at low concentrations of the volatile component. The diffusion coefficient increases at higher concentration [3], therefore the stipulation ($t_L \ll \tau_L$) remains valid in such regimes. Thus the conversion of the removed compound in the liquid phase can be simplified to

$$U \approx \frac{1}{1 + \frac{1}{H_L K_G} \frac{\dot{V}_L}{A_G} + \frac{1}{H_L H_G} \frac{\dot{V}_L}{\dot{V}_G}} = \frac{1}{1 + S_1 + S_2} \quad (56)$$

It should be added that an efficient process design requires operating conditions leading to negligible diffusion resistance.

In order to reach a value of $U > 0.9$, the variable terms in the denominator must become < 0.1 i.e.

$$\frac{\dot{V}_L}{H_L K_G A_G} < 0.05 \text{ and } \frac{\dot{V}_L}{H_L H_G \dot{V}_G} < 0.05 \quad (57)$$

This implies that the reactor should be operated at short residence times of the gas phase with respect to the latex phase, high distribution coefficients, i.e. high temperatures, and with a large interfacial area between gas and dispersion as related to the latex phase feed rate. This result is in contradiction to the statements of Walther et al. [17] and Omi et al. [14]. The conversion depends on the distribution coefficients H_G and H_L , as well as on the hydrodynamic parameters \dot{V}_L/\dot{V}_G and $\dot{V}_G/K_G A_G$ only. Fig. 4 shows the experimentally obtained dependence of styrene conversion on temperature for the operating conditions mentioned before, as well as the according values calculated from Eq. (54). The agreement between theory and experiment is good and verifies the estimation of K_G as described in Section 2.2.

From Fig. 5, showing the temperature dependent terms, it becomes obvious that for the relevant range of operating conditions, the conversion is limited by the interfacial area

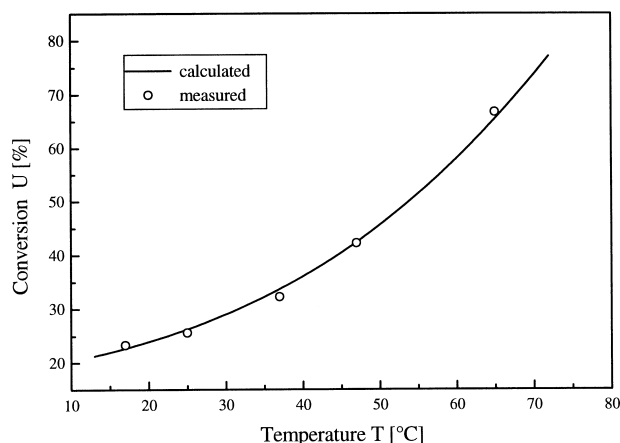


Fig. 4. Stripping conversion of dissolved organic compound in latex dispersion (calculation with $A_G = 12.5 \text{ m}^2$).

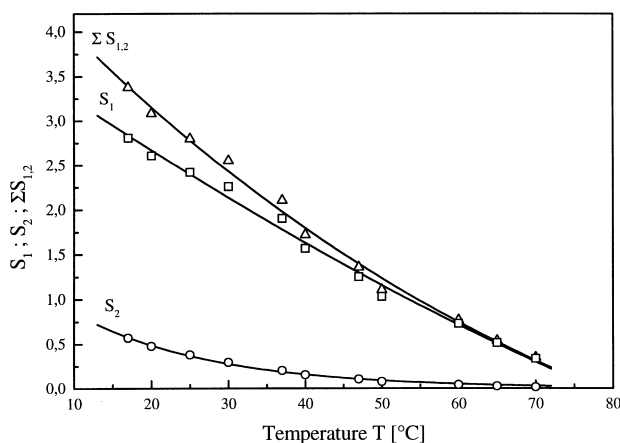


Fig. 5. S_1 , S_2 and $\Sigma S_{1,2}$ in Eq. (56) as a function of temperature.

as related to latex feed rate, i.e. A_G/\dot{V}_L . This parameter, however, can easily be manipulated by the reactor design.

In order to visualise the influence of τ_L/t_L on the achievable conversion, first the parameters of the system under consideration have to be determined. Special care has to be taken of the temperature dependence of the distribution coefficients.

Then a plot of Eq. (52) as a function of t_L with given τ_L reveals the range of maximal sensitivity. Fig. 6 shows the results of the calculation with the parameters given in Section 2 and with $\tau_L = 60$ s. The effect of the temperature is displayed by an equivalent variation of H_L . It is shown that diffusion inside the latex particle is negligible, provided the diffusion time is of smaller order than the residence time of the latex phase.

5. Summary

Volatile organic compounds contaminating aqueous polymer dispersions have to be removed to satisfy the product property constraints as well as environmental aspects. Strip-

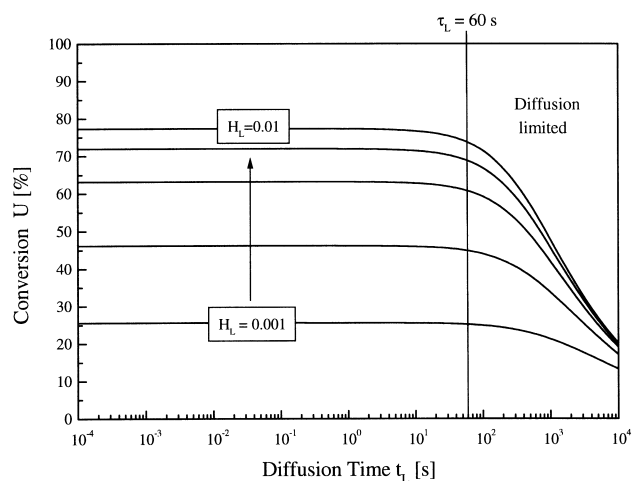


Fig. 6. Conversion U as a function of diffusion time t_L according to Eq. (52).

ping with an inert gas (i.e. nitrogen or steam) is suitable for this purpose. Mathematical modelling of the occurring mass transport processes reveals the relevant parameters:

- the distribution coefficients of the transferred components between the phases
- the interfacial area between the gas and the dispersion as related to the dispersion flow rate
- the ratio of the gas and the dispersion residence times

The diffusion resistance inside the latex particles can be neglected when the residence time of the dispersion τ_L is significantly larger than diffusion time t_L of the transferred compounds inside the latex. If the technical process equipment does not satisfy this condition, the removal rate becomes smaller and the ratio τ_L/t_L must be taken into account as a further parameter for the conversion computation. This result seems to be obvious, but has not been considered in the discussed literature.

6. Nomenclature

a	specific interfacial area (m^{-1})
A	interfacial area (m^2)
c	concentration (mol m^{-3})
d	diameter (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
e	distribution function (s^{-1})
H	distribution coefficient
k	mass transfer coefficient (m s^{-1})
K	mass transfer coefficient (m s^{-1})
N	number of particles
r	radius, coordinate (m)
R	mass flux ($\text{mol m}^{-3} \text{s}^{-1}$)
s	Laplace parameter (s^{-1})
t	time, diffusion time (s)
T	temperature ($^{\circ}\text{C}$)

U	conversion
V	volume (m^3)
\dot{V}	volumetric flow rate ($\text{m}^3 \text{h}^{-1}$)
z	time scale ratio
ϵ	phase holdup
λ	exponent (s^{-1})
η	phase ratio
ν	kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)
ρ	abbreviation (m^{-1})
φ	function
τ	residence time, process time (s)

Indices

D	dispersion
f	feed
G	gas
L	latex
M	monomer
T	droplet
W	water average value Laplace transform
0	inlet

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