Supporting Information

Oxidation of Ce(III) to Ce(IV) by ozone in nitric acid medium using a static mixer: Mathematical modeling and experimental validation

Sukhdeep Singh[1*], Tessy Vincent[1], Ashok N. Bhaskarwar[2], Trushit Makwana[1]

[1]Process Development Division, Nuclear Recycle Group, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085, India

[2]Department of Chemical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi, 110016, India

[*]Corresponding author: Sukhdeep Singh, Email: sukhdeep@barc.gov.in,

Phone: +91-22-25591431, Fax: +91-22-25505185

1 Pre-calculated value of mass transfer enhancement factor E for assumption (d)

Mass transfer enhancement factor E can be implicitly expressed[a] by the following eqs S1-S3.

$$E = \frac{\phi\sqrt{\dfrac{E_\infty - E}{E_\infty - 1}}}{\tanh\left(\phi\sqrt{\dfrac{E_\infty - E}{E_\infty - 1}}\right)} \tag{S1}$$

$$E_\infty = \left(1 + \frac{D_B C_B}{v_B D_A C_{AS}}\right) \tag{S2}$$

$$\phi = \frac{\sqrt{\left(\dfrac{2}{m+1}\right) k_{m,n} C_{AS}^{n-1} C_B^m D_A}}{k_L} \tag{S3}$$

For the calculation of mass transfer enhancement factor for an infinitely fast reaction E_∞, diffusivity D_B of B, i.e. of Ce(III), in aqueous solution was estimated from the well-known Stokes-Einstein equation (eq S4), by taking a hydrated radius[b] r_B of 261 pm, as shown below,

$$D_B = \frac{k_B T}{6\pi\mu_L r_B} \tag{S4}$$

where k_B is the Boltzmann constant equal to 1.38×10^{-23} J/K.

Diffusivity D_A of ozone in water was computed from eq 27, and solubility C_{AS} from eqs 5-7. Value of v_B, the stoichiometric coefficient of B in Ce(III) oxidation reaction, was 2.

For estimating the Hatta number ϕ, in view of eq 10, the original rate constant $k_{m,n}$ of eq S3 for a (m, n)[th] order reaction, was substituted here as the product of rate constant k and nitric acid concentration term i.e. $C_C^{0.54}$ in eq S5. This was because, eq 10 involved three species (A, B and C), but eq S3 for Hatta number calculation had only two species i.e. A and B. Therefore, term containing nitric acid concentration was coupled along with the rate constant k, considering its relatively abundance with respect to Ce(III) and insignificant change in magnitude over time during the reaction.

$$k_{m,n} = kC_C^p \tag{S5}$$

Liquid film mass transfer coefficient k_L can be estimated from eq S6, on dividing the volumetric mass transfer coefficient $k_L a$ (eq 18) by the specific interfacial area a.

$$k_L = \frac{k_L a}{a} \tag{S6}$$

Specific interfacial area a is expressed as a function of gas and liquid superficial velocities, and for a 'Lightnin' type of static mixer is given by eq S7[c].

$$a = 2990 u_L^{0.01} u_G^{0.9} \tag{S7}$$

Such an empirical correlation for a Sulzer SMX type of mixer was not available from literature, so the one that for a 'Lightnin' type was adapted for the approximation of k_L.

Using all the eqs S2-S7, mass transfer enhancement factor E can be calculated from the implicit eq S1, numerically. Under one of the best experimental conditions (C_B = 0.1 M, C_C = 4 M, G_0 = 29± 1.5 g/m^3 (NTP), Q_G = 5 L/min, Q_L = 11 L/min and T_C = 35.7 °C), the value of E was calculated to be **1.0504** only, which justifies the assumption (d) in the manuscript.

2   Calculation of ozone partial pressure from analyzer reading at NTP

Ozone analyser displays the gas concentration G_0 in g/m^3 at normal conditions of 0°C and 1 atm (NTP), but in the model we need this concentration in terms of partial pressure p_A (atm) at actual temperature and pressure (1 atm only) of the process, in order to calculate the ozone solubility using eq 6.

For this we have derived eq 7 directly correlating the analyser reading G_0 and ozone partial pressure p_A; starting from the ideal gas equation (eq S8), as shown below.

$$p_A V = n_A RT \tag{S8}$$

Putting moles of ozone in terms of mass and molecular mass and rearranging, we got eq S9.

$$p_A = \left(\frac{m_A}{V}\right)\frac{RT}{M_A} \Leftrightarrow G_A \frac{RT}{M_A} \tag{S9}$$

Now expressing G_A in terms of G_0 after having correction for process temperature T and pressure P, as per ideal gas equation (with $P = P_0$), we have eq S10.

$$\frac{P_0 V_0}{T_0} = \frac{PV}{T} \Leftrightarrow \frac{P_0 V_0}{m_A T_0} = \frac{PV}{m_A T} \Leftrightarrow \frac{P_0}{G_0 T_0} = \frac{P}{G_A T} \Rightarrow G_A = G_0 \left(\frac{T_0}{T} \right) \tag{S10}$$

Substituting G_A in eq S9 by G_A in eq S10, we arrive at eq S11.

$$p_A = G_0 \frac{RT_0}{M_A} \tag{S11}$$

Putting known values in eq S11, and dividing by 101325 to get p_A in atm

$$p_A = G_0 \left(\frac{8.314 \times 273.15}{48 \times 101325} \right) \tag{S12}$$

We got our final equation (eq S13 or eq 7) as below.

$$p_A = 4.6693 \times 10^{-4} G_0 \tag{S13}$$

Note: Symbols which have not been defined here, may please be looked into the nomenclature of manuscript.

References

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