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Shorter Communications

Absorption of hydrogen sulfide in aqueous solutions of iodine—a critical review

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INTRODUCTION

The purpose of this communication is to highlight the inadequacy of the interpretations provided by Mehra and Sharma (1988) with respect to their experimental results and to provide alternative, albeit speculative, explanations.

Mehra and Sharma (1988) studied the absorption of hydrogen sulphide in aqueous solutions of iodides containing dissolved iodine followed by instantaneous reaction of hydrogen sulphide with iodine. They observed the interesting effect that in batch experiments the rate of absorption exceeded the rates that are expected in the instantaneous reaction regime. According to Mehra and Sharma (1988), this effect seems to be due to the influence of precipitating sulphur on the mass transfer of hydrogen sulphide. A two-parameter model has been developed by these authors to correlate the experimental data.

According to Mehra and Sharma (1988), the absorption rate of hydrogen sulphide into the liquid is given by

$$J_A = \frac{\sqrt{(1-\varepsilon_o + m_A\varepsilon_{\mathrm{eff}})}\,k_L C^i_A}{\mathrm{erf}\,(\eta/\sqrt{\mathbb{D}'_A})} \tag{1}$$

in which η is obtained from

$$\frac{\bar{C}_B}{\nu_B C^i_A}\sqrt{\frac{\mathbb{D}_A}{\mathbb{D}_B}}\left(\frac{1-\varepsilon_o}{1-\varepsilon_o+m_A\varepsilon_{\mathrm{eff}}}\right)^{1/2} \times \mathrm{erf}\,(\eta/\sqrt{\mathbb{D}'_A})e^{\eta^2/\mathbb{D}'_A} = \mathrm{erfc}\,(\eta/\sqrt{\mathbb{D}'_B})e^{\eta^2/\mathbb{D}'_B} \tag{2}$$

$\mathbb{D}'_A = \mathbb{D}_A/(1-\varepsilon_o+m_A\varepsilon_{\mathrm{eff}})$, $\mathbb{D}'_B = \mathbb{D}_B/(1-\varepsilon_o)$.

The sulphur that is produced during the reaction is assumed to consist of two kinds: (1) a fraction $\varepsilon_{\mathrm{eff}}$ of active sulphur, consisting of very small sulphur particles, that is capable of adsorbing an amount of $m_A\varepsilon_{\mathrm{eff}}$ of hydrogen sulphide; and (2) inactive sulphur that does not (significantly) adsorb hydrogen sulphide (due to large particle sizes). Active sulphur can be deactivated by collisions between active sulphur particles or by collisions of active with inactive sulphur particles.

The balance for the generation of the total amount of sulphur present in solution is

$$\frac{d\varepsilon_o}{dt} = \frac{J_A a M_w}{\rho_s} \tag{3}$$

and the balance for generation and deactivation of active sulphur

$$\frac{d\varepsilon_{\mathrm{eff}}}{dt} = \frac{J_A a M_w}{\rho_s} - k_2\varepsilon_{\mathrm{eff}}\varepsilon_o \tag{4}$$

with initial conditions $\varepsilon_o, \varepsilon_{\mathrm{eff}} = 0$ at $t = 0$.

Sensitive, but *a priori* unknown parameters in this model are the distribution coefficient m_A and the deactivation constant k_2. As we show below, the theoretically maximal value of m_A is orders of magnitude lower than derived by Mehra and Sharma (1988). This implies that their explanation of the effects observed cannot be correct. Alternative explanations are presented in this contribution.

CORRECTED RELATION FOR THE DISTRIBUTION COEFFICIENT

On close inspection of the two-parameter model of Mehra and Sharma (1988) the defining equation for the maximum theoretical value of the distribution coefficient appears to be incorrect. The equation derived by these authors, which is dimensionally inconsistent, is

$$m_A = \frac{24 \times 10^3 M_w}{N_{\mathrm{Av}}\pi d_m^2 d_p C^i_A} \tag{5}$$

with C^i_A expressed in mol/liter, d_m and d_p in meters, and m_A and N_{Av} are dimensionless. This equation of Mehra and Sharma (1988) predicts maximum theoretical values that are a factor 10^8 too high! Below, we derive a new relationship for the maximum theoretical value of the distribution coefficient, still based on the assumptions of Mehra and Sharma (1988).

Considering a spherical (solid) sulphur particle of diameter d_p, the number of adsorption sites occupying the surface of the particle is given by

$$N_1 = \frac{4d_p^2}{d_m^2} \tag{6}$$

which is obtained by dividing the surface area of the particle by the projected cross-sectional area of a sulphur atom of diameter d_m.

If each adsorption site maximally adsorbs only one molecule of hydrogen sulphide, the number of hydrogen sulphide molecules adsorbed on the surface area equals N_1. The maximum surface concentration of H_2S is

$$C^s_{A,\max} = \frac{N_1}{N_{\mathrm{Av}}}\frac{1}{\pi d_p^2} = \frac{4}{\pi d_m^2 N_{\mathrm{Av}}}. \tag{7}$$

Assuming a linear equilibrium exists between the surface concentration of H_2S and the dissolved liquid phase H_2S concentration, then

$$C^s_{A,\max} = K C^i_A. \tag{8}$$

On a volumetric basis the distribution coefficient is

$$m_A = \frac{6K}{d_p} = \frac{24\alpha}{\pi d_m^2 d_p C^i_A N_{\mathrm{Av}}} \quad (0 \leqslant \alpha \leqslant 1). \tag{9}$$

In this equation α is a correction factor that takes into account that the maximum surface concentration may occur only at a higher dissolved liquid phase H_2S concentration than C^i_A.

The maximum theoretical value of m_A is obtained by setting $\alpha = 1$ and $d_p = d_m$, i.e. all sulphur particles consist of one sulphur atom. Taking the highest value of

C_A^i (88.1 mol/m^3) in order to achieve $\alpha = 1$, m_A can be calculated to be 0.17×10^5. In order to explain their own experimental results, Mehra and Sharma (1988) had to use fitted values for m_A ranging from 0.3×10^5 to 31×10^5. It is clear therefore that the experimental results cannot be explained by mono-layer theory.

ALTERNATIVE EXPLANATIONS

Multi-layer adsorption

Bridging this discrepancy of maximum theoretical values of m_A and experimental values, one might assume multi-layer adsorption to occur. It can easily be shown that the total number of molecules adsorbed on a particle is given by

$$N_n = \sum_{i=1}^{n} 4\left[\frac{d_p}{d_m} + 2(i-1)\right]^2. \qquad (10)$$

For $n = 1$ (mono-layer) this equation reduces to eq. (6).

Substituting N_n for N_1 in eq. (7) gives, together with eqs (8) and (9):

$$m_A = \frac{24\alpha}{\pi d_p^3 C_A^i N_{Av}} \sum_{i=1}^{n} \left[\frac{d_p}{d_m} + 2(i-1)\right]^2. \qquad (11)$$

Again, maximum values are obtained by setting $\alpha = 1$ ($C_A^i = 88.1$ mol/m^3) and $d_p = d_m$. To explain the experimentally observed enhancement factors, a value of m_A as high as 31×10^5 is necessary. Assuming a multi-layer adsorption model, this asks for a sulphur atom to be capable of adsorbing at least five layers of H_2S molecules amounting to 160 molecules of H_2S per atom of S! Multi-layer adsorption therefore *alone* cannot provide an answer to the observed values of the enhancement of the H_2S absorption.

Sulphur accumulation at the gas–liquid interface

Since multi-layer adsorption alone cannot explain the high values of m_A, another parameter must have an influence as well. On examination of eqs (1) and (2) it follows that an important contribution to absorption enhancement is due to the group $m_A \varepsilon_{eff}$. If m_A alone cannot explain the experimentally observed values, then ε_{eff} must be higher than expected. It indicates that ε_{eff} should be higher near the gas–liquid interface than in the bulk of the liquid. Experimental evidence supporting this hypothesis are: (1) the observation by Mehra and Sharma that careless purging operations lead to sulphur surface films, and (2) the separation by froth formation and flotation in iron chelate based sulphur removal processes (Blytas and Diaz, 1983; Klee, 1985). Another system in which such high concentrations near the gas–liquid interface are observed is the system investigated by Wimmers (1987) who measured the mass transfer of hydrogen from hydrogen bubbles surrounded by water containing palladium on carbon catalyst particles.

Following the method of Wimmers (1987), the concentration of sulphur particles near the gas–liquid interface can be related to the bulk concentration by a Freundlich isotherm. In eqs (1) and (2) ε_o should be replaced by $C\varepsilon_o^q$ and ε_{eff} by $C\varepsilon_{eff}^q$. C and q can be determined by independent experiments, as has been demonstrated by Wimmers (1987). In Fig. 1 several scenarios for H_2S adsorption and sulphur distribution are shown. For mono-layer adsorption ($n = 1$) m_A is assumed to have the maximum theoretical value, i.e. $m_A = 0.17 \times 10^{-5}$.

Computer simulations have been made with $C = 1$, 40 and 80 (q is arbitrarily set to 1). This means that the sulphur hold-up near the gas–liquid interface is allowed to accumulate 1, 40 or 80 times above the sulphur hold-up in the bulk of the liquid. The case of mono-layer adsorption and $C = 1$ represents the model of Mehra and Sharma (1988). From Fig. 1 it is clear that the model of these authors cannot explain the experimentally observed absorption rates. However, when increasing the sulphur hold-up near the gas–liquid interface well above the hold-up in the bulk of the liquid the fit improves rapidly. For double-layer adsorption ($n = 2$), again m_A is taken to have the maximum theoretical value, i.e. $m_A = 1.65 \times 10^{-5}$. Now computer simulations have been made taking $C = 2$ and 6 (q is arbitrarily set to 1). Since the value of m_A is now much higher, the hold-up of sulphur near the gas–liquid does not need to increase as high as in the case of mono-layer adsorption in order to improve the fit, as shown in Fig. 1. Figure 2 shows the corresponding curves of the hold-up of effective sulphur (ε_{eff}^q, with q arbitrarily set to 1) near the gas–liquid interface. The rise and decline of these curves is synchronous to the rise and decline of the corresponding absorption curves of Fig. 1. However, in case of mono-layer adsorption ($n = 1$), ε_{eff}^q rises to much higher values than in case of double-layer adsorption ($n = 2$).

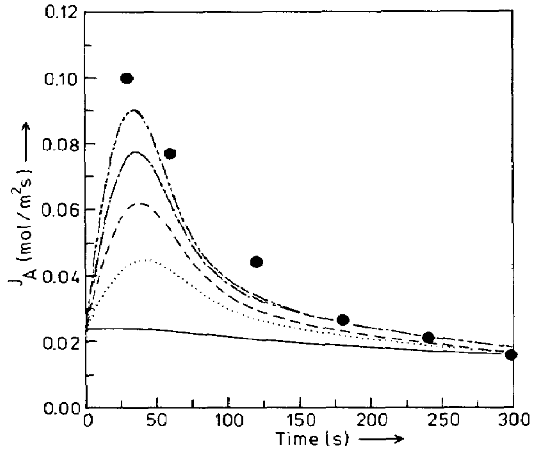

Fig. 1. Effect of sulphur hold-up near gas–liquid interface and multi-layer adsorption on absorption rate of hydrogen sulphide. Conditions: $\bar{C}_B = 700$ mol/m^3, $C_A^i = 76.7$ mol/m^3, $a = 47$ m^2/m^3, $k_L = 3.05 \times 10^{-5}$ m/s. (———) $n = 1$, $C = 1$ [model of Mehra and Sharma (1988)]; (– – – –) $n = 1$, $C = 40$; (— — —) $n = 1$, $C = 80$; (· · · ·) $n = 2$, $C = 2$; (— – ——) $n = 2$, $C = 6$; (●) experimental points of Mehra and Sharma (1988).

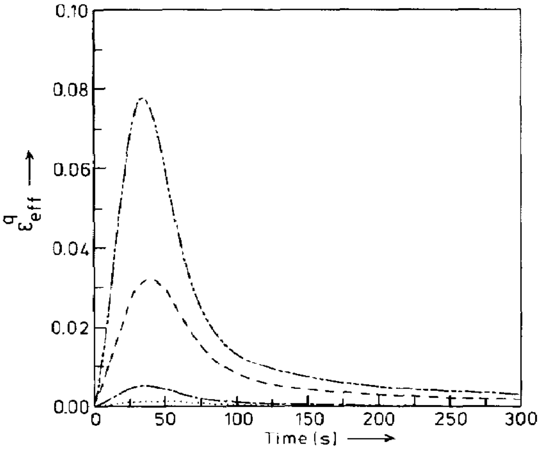

Fig. 2. Hold-up of effective sulphur near gas–liquid interface corresponding to absorption curves of Fig. 1. Conditions: $\bar{C}_B = 700$ mol/m^3, $C_A^i = 76.7$ mol/m^3, $a = 47$ m^2/m^3, $k_L = 3.05 \times 10^{-5}$ m/s. (———) $n = 1$, $C = 1$ [model of Mehra and Sharma (1988)]; (– – – –) $n = 1$, $C = 40$; (— — —) $n = 1$, $C = 80$; (· · · ·) $n = 2$, $C = 2$; (— – ——) $n = 2$, $C = 6$.

From Figs 1 and 2 it can be concluded that the simultaneous occurrence of both multi-layer adsorption and a relatively higher sulphur hold-up near the gas–liquid interface can explain the experimentally observed absorption rates of hydrogen sulphide into the liquid.

Effective diffusivities

If microphase hold-up in the diffusion layer reaches high values, another effect becomes important: the effect of the presence of the microphase on the effective diffusivity of a component in the (continuous) liquid phase. Jefferson *et al.* (1958) derived an expression for determining the effect of the presence of microparticles in a liquid on thermal conductivity, which approximated experimental data well. With increasing hold-up they found that the thermal conductivity changed markedly. This theory for thermal conductivity of dispersions can well be applied to diffusivity in the presence of microphases (Crank, 1975):

$$\frac{\mathbb{D}_{C,\,\mathrm{eff}}}{\mathbb{D}_C} = 1 + \frac{1.209(\gamma - 1)\varepsilon}{(1-\gamma)\varepsilon^{1/3} + 0.806\gamma} \tag{12}$$

where

$$\gamma = \frac{2\lambda}{\lambda - 1}\left(\frac{\lambda}{\lambda - 1}\ln\lambda - 1\right), \quad \lambda = \frac{m_A \mathbb{D}_D}{\mathbb{D}_C}. \tag{13}$$

The parameter λ is the ratio of the diffusivity through the microphase and the diffusivity through the continuous phase with a correction for differences in solubilities in the microphase and continuous phase expressed by the distribution coefficient m_A ($\mathbb{D}_D$ is a corrected surface diffusion coefficient in case of solids). This parameter shows the importance of adding a microphase in order to influence the effective diffusivity. If $\lambda > 1$, adding a microphase increases the effective diffusivity. For $\lambda = 1$, there is no difference between diffusion through the microphase or diffusion through the continuous phase; the addition of the microphase does not result in enhancement of diffusivity. If $\lambda < 1$, the effective diffusivity will decrease by adding a microphase. In Fig. 3 these cases are exemplified. In the experiments of Mehra and Sharma m_A probably has a value in the range of 100–10,000. If $\mathbb{D}_D$ ranges from $0.1\,\mathbb{D}_C$ to $10\,\mathbb{D}_C$ then λ ranges from 10 to 1000. Figure 3 shows that together with the hold-up of sulphur near the gas–liquid interface, one needs to take proper account of the *effective* diffusivity in the continuous phase as this correction can amount to a factor of 8.

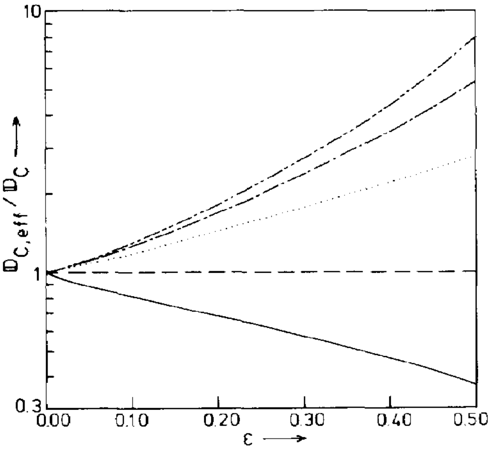

Fig. 3. Influence of hold-up of microphase on the effective diffusivity in the continuous phase: (— — — —) $\lambda = 1000$, (— – ——) $\lambda = 100$, (· · · ·) $\lambda = 10$, (- - - - -) $\lambda = 1$, (———) $\lambda = 0.1$.

Further extensions

Our concepts of multi-layer adsorption and increased sulphur accumulation at the interface are basically extensions of the Mehra and Sharma model. But even with these modifications the model still contains several (over)simplifications. Typical examples are the division of the precipitating sulphur into only two classes—active and non-active sulphur—and the quasi-steady-state assumption, which implies that bulk conditions do not change rapidly during contact time τ and that the sulphur being generated within a liquid element during this contact time does not affect absorption rate. This latter asssumption is violated at least for the very high enhancement factors observed experimentally. Only a detailed model incorporating population balances will show the applicability of the assumptions of Mehra and Sharma (1988). A mechanistic agglomeration model which takes care of the deactivation phenomena and the incorporation of the effective diffusivity along the lines of the effective diffusivity concept outlined above will allow us to abandon the Mehra and Sharma concept of active and inactive sulphur species.

CONCLUSIONS

We have presented arguments to support our contention that the sulphur hold-up near the gas–liquid interface must be substantially higher than the sulphur hold-up in the bulk of the liquid in order to explain the results of Mehra and Sharma. Other effects such as multi-layer adsorption and effective diffusion coefficients also have to be incorporated.

H. J. WUBS
A. A. C. M. BEENACKERS†
R. KRISHNA‡

Department of Chemical Engineering
University of Groningen
Nijenborgh 16
9747 *AG Groningen, Netherlands*

NOTATION

a	specific interfacial area, m^2/m^3 slurry
C	Freundlich constant
C_A^i	solubility of H_2S in liquid phase, mol/m^3
$\bar{C}_A$	bulk concentration of H_2S in liquid phase, mol/m^3
$\bar{C}_B$	bulk concentration of liquid phase reactant, mol/m^3
C_A^s	surface concentration of H_2S on sulphur, mol/m^2
$\mathbb{D}_A$	diffusivity of H_2S, m^2/s
$\mathbb{D}_B$	diffusivity of liquid phase reactant, m^2/s
$\mathbb{D}_C$	diffusivity in continuous phase, m^2/s
$\mathbb{D}_{C,\,\mathrm{eff}}$	effective diffusivity in continuous phase, m^2/s
$\mathbb{D}_D$	diffusivity in disperse phase, m^2/s
d_m	atomic diameter of sulphur, 0.206×10^{-9} m
d_p	diameter of sulphur particles, m
J_A	specific rate of absorption of A, mol/m^2 s
K	surface distribution coefficient, m
k_L	gas–liquid mass transfer coefficient, m/s
k_2	deactivation constant, s^{-1}
m_A	distribution coefficient, $\frac{\mathrm{mol\ H_2S/m^3\ sulphur}}{\mathrm{mol\ H_2S/m^3\ liquid}}$
M_w	molar mass of sulphur, kg/mol sulphur
n	number of adsorbed H_2S layers on particle
N_1	number of surface atoms per particle
N_{Av}	Avogadro's number, 6.022×10^{23} mol^{-1}
t	time, s

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† Author to whom correspondence should be addressed.

‡ Present address: Department of Chemical Engineering, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands.

Greek letters

α	correction factor for surface concentration
γ	constant defined in eq. (17)
ε	volumetric fraction of dispersed phase
ε_{eff}	volumetric fraction of active sulphur
ε_{eff}^{q}	volumetric fraction of active sulphur with Freundlich constant q
ε_o	volumetric fraction of total sulphur
η	proportionality constant for the motion of the reaction plane, $m/s^{1/2}$
λ	corrected diffusivity ratio
ν_B	stoichiometric constant
ρ_s	density of sulphur, kg/m^3

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Prediction of radial porosity distributions in randomly packed fixed beds of uniformly sized spheres in cylindrical containers

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INTRODUCTION

The use of randomly packed fixed beds of uniformly sized spheres with containing walls is common in many technical fields and applications. It is well known that the radial porosity distribution in such beds is affected by the surrounding walls. The first layer of spheres in contact with the wall tends to be well-ordered, with most of the spheres touching the wall. Subsequent layers are less and less ordered as one moves away from the container wall. In layers far removed from the container wall a randomized configuration is attained. The published experimental research of Roblee *et al.* (1958), Benenati and Brosilow (1962), Scott (1962), Ridgway and Tarbuck (1966), Thadani and Peebles (1966) and Pillai (1977) clearly shows that the radial porosity distribution for packed beds of spheres displays damped oscillations near the containing wall which die away into the packed bed. For large diameter aspect ratios, the radial oscillations are damped out at about four to five sphere diameters from the container wall. This fluctuation in the radial porosity gives rise to so-called wall effects in the flow of fluids and the transfer of heat and mass in randomly packed particle beds.

The wall effects are an important factor in the analysis and design of fixed packed bed equipment used in nuclear and chemical reactors, heat exchangers, and distillation columns. To more rigorously simulate the transfer processes in a packed bed, many investigators account for the radial porosity variation by the use of a simple smoothed exponential function which approaches an average bulk porosity. Hunt and Tien (1990) have shown that the inclusion of the variable porosity and the no-slip boundary condition dramatically alters the velocity and temperature profiles from those predicted by models using uniform or Darcian flow regions. They used an exponential function to closely approximate the porosity in the near-wall region. The exponential functions neglect the damped oscillations of the radial porosity which have been observed by Benenati and Brosilow (1962) and others. Vafai (1984) considers the oscillations to be secondary since the emphasis is on the decay of the porosity from the container wall, which has the primary effect. However, Bahnen and Stojanoff (1987) have determined that computations of the velocity field using a smoothed exponential porosity function of Vortmeyer and Schuster (1983) do not agree with their experimental results.

Predictions of the radial porosity distribution which include the damped oscillations have been reported by Govindarao *et al.* (1990), Govindarao and Ramrao (1988) and Govindarao and Froment (1986). They provide procedures for predicting the void fractions up to distances of five particle diameters from the wall. Theoretically, their expressions can be incorporated into flow, energy, and mass balance equations for the simulation of packed beds. However, the form of their correlations are such that they are not very convenient to use in analytical packed bed transport models. Cohen and Metzner (1981) and Martin (1978) have also published empirical models which include the damped oscillations. Their models consist of a set of equations that are piecewise continuous. Cohen and Metzner's (1981) model consists of three principal equations. The first equation is a parabola for the near-wall region. The near-wall region is assumed to extend a distance of one particle diameter away from the wall. The second equation is a damped cosine function for the transition or oscillation region. This region is assumed to extend to five particle diameters away from the wall. The third equation is a constant for the bulk region which extends beyond five particle diameters from the wall. Martin's (1978) model consists of two principal equations, a parabola and a damped cosine plus a constant. A model that consists only of one principal equation would be more convenient to use in analytical packed bed transport models than a set of equations.

The purpose of this investigation is to correlate the experi-