GAS-LIQUID MASS TRANSFER IN STIRRED NON-NEWTONIAN CORN-STARCH DISPERSIONS

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Oxygen transfer in colloidal dispersions of 1 to 4 wt % corn starch in water was studied and the character-istic gas-liquid mass transfer coefficients in highly pseudoplastic conditions were obtained. The dispersions prepared were represented by flow behaviour indices between 0.64 and 0.90 and consistency indices between 0.002 and 0.2 Pa.s^n. Mass transfer coefficients from 0.004 to 0.03 s^{-1} were obtained corresponding to apparent viscosities between 1 and 40 mPa.s. An equation was proposed to fit most of the data favourably. The presence of an antifoam agent was also considered.

Introduction

Gas-liquid mass transfer in non-Newtonian starch media is an important example of gas absorption in pseudoplastic flow relevant to industrial starch degradation by amylolytic enzymes, suspension polymerization and food processing to name but a few. Recent analyses of the problem have been directed mainly towards bubble and fluidized bed reactors. Studies concerning agitated reactors have mainly been works from the past decade, as reported by Schügerl[17] and Joshi et al[2]. These authors have included the detailed but somewhat media-restricted studies of Perez and Sandall[15], Yagi and Yoshida[21], and Ranade and Ulbrecht[16], as well as those of Henzler[4], Höcker et al.[5] and Nishikawa et al.[11] Meanwhile, mass transfer has been studied in various cases of agitated power law liquids, examples being xanthan gum[8], starch and soybean flour[13,19]. However, no unified correlations have been proposed in these cases to include the entire range of flow behaviour parameters. Due to the complexities of gas absorption in non-Newtonian media, the correlations obtained by these studies were limited to just a few kinds of non-Newtonian fluids-named, Carbopol, CMC, PEO and PAA solutions. More information for other materials with complex rheology is required in order to obtain a more general correlation applicable to any system.

In the following, an attempt is made to extend the experimental analysis of gas-liquid mass transfer in stirred non-Newtonian fluids to also cover colloidal starch dispersions, their importance for practice usually being underrated.

1. Experimental

The experiments were run batch-wise with respect to the liquid in a 2.65 l glass reactor equipped with a Rushton six-blade turbine impeller (d = 50mm, d/T = 0.33, H/T = 1, h/T = 0.33, 4 baffles $T/10$). Gas was introduced into the reactor through a tube with an opening of ID 8mm positioned at the vessel bottom 25 mm below the impeller.

Water dispersions (2.65 l) containing 1-4 % non-soluble corn starch were prepared and used as the liquid phases. The swollen starch particles formed different grades of hydrogels which also contained traces of proteins. In some of the runs, 0.04-0.2 wt % antifoam agent (Karalin 102, Sanyo Chemical Industry Ltd.) was added to the dispersion to suppress foaming, especially at higher starch concentrations. In order to suppress eventual growth of microorganisms, 100 mg of Hg_2Cl_2 was added. The polymer additive as well as the traces of proteins in the starting material initiated experiments for testing their influence on the flow behaviour and surface tension of the system.

The flow curves of the liquid media were determined by a concentric cylinder rotary viscosimeter *Rheotest* (*MLW*, former East Germany) at shear rates of 1.5 to 1300 s^{-1} and were correlated by the power law equation of Ostwald de Waele, *i.e.* $\tau = K \cdot \dot{\gamma}^n$. The surface tension was measured by the Wilhelmy plate method[14] using a Krüss tensiometer.

The first test included an investigation of possible polymer weakening which could be the cause of time-variable flow behaviour. Starch dispersions behaved as pseudoplastic liquids but some thixotropy was also registered. The following analysis showed that this behaviour disappeared following a two-hour period of continuous mixing.

Flow characteristics of corn starch colloidal dispersions corresponding to different lengths of mixing periods were obtained, as illustrated in **Fig. 1**. As shown by the pattern of flow curves, in all cases a characteristic shift of the curve was registered between 1 and 2 hours of mixing, with no significant change afterwards, *i.e.* following additional mixing for 3 hours. This pattern was not

Fig. 1. Flow behaviour curves (τ vs $\dot\gamma$ of a colloidal starch dispersion following 1 hour (O), 2 h ($\square$), 3 h ($\triangle$), 4 h (+) and 5 h ($\times$) of mixing at 300 rpm

Table 1. Rheological parameters of the studied dispersion

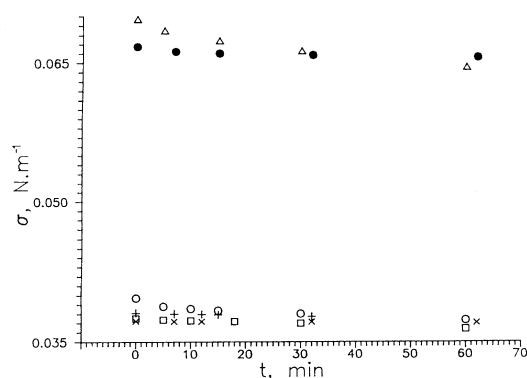| System starch / water with increasing degree of mycellial expansion		Concentration (%)	K [Pa. s^n]	n [–]
N-1	1	1	0.0023	0.9
	2*		0.0044	0.83
	3		0.0049	0.78
	4		0.0063	0.82
	5*		0.0132	0.65
	6*		0.0186	0.7
N-2	1	2	0.010	0.85
	2		0.043	0.67
	3		0.043	0.67
N-3	1	3	0.079	0.66
	2		0.083	0.66
N-4	1	4	0.16	0.64
	2		0.20	0.66

* Systems without antifoam agent.

Fig. 2. Surface tension vs. testing time for colloidal starch dispersions without ($\triangle$, ●) and with antifoam Karalin 1ml (O, +) and 5 ml ($\square$, $\times$)

affected by the presence of antifoam agent in the said concentrations. Therefore it was decided that a two-hour period of continuous mixing ensures purely pseudoplastic behaviour and all further measurements were carried out by mixing for two hours. Consequently, the values of the consistency index, K, and the flow behaviour index, n, were obtained for the studied systems as given in **Table 1**.

Surface tension profiles of several representative dispersions with and without antifoam agent of various concentrations are given in **Fig.2**. It is seen from the figure that the surface tension depends strongly on the presence of antifoam additive. However, regarding the antifoam additive concentration range 0.04-0.2 wt %, once the presence of antifoam agent was established, no significant variation over time of the surface tension of the individual system occurred. Based on these experiments, it was found that σ for the systems without antifoam additive varied in the range (66.1 $\mp$ 1.3). 10^{-3} N.m^{-1}, while σ by additive concentration of 0.04-0.2 wt % varied in the range (37.3 $\mp$ 0.7). 10^{-3} N.m^{-1}. These average values of the surface tension were used in subsequent calculations.

In all cases, the temperature was 26°C and the dispersion density was in the range 1000 $\mp$ 20 kg.m^{-3}.

Oxygen diffusivity was computed each time by using the equation $D/D_W = (\mu/\mu_w)^{-0.725}$ reported recently by Ju et al. [3]. No equation of this kind derived for non-Newtonian fluids has come to the authors' attention. On the other hand, D calculated from a similar equation, $D.\mu^{0.69}$ = const, recommended by Komiyama and Fuoss[7] for highly viscous (up to 100 mPa.s) mixtures was found to be within 7% of the value obtained by the first equation. However, Ju's equation was preferred since it referred to complex fermentation media with various additives.

Fluid viscosity at reactor conditions was evaluated by the equation $\mu = K \cdot \dot\gamma^{n-1}$ with an average shear rate, $\dot\gamma$, obtained from the formula, $\dot\gamma = 11.5$ N, supported by

Metzner et al. [9]. The validity of this equation for pseudoplastic fluids has been confirmed by Ducla et al.[1]

The mass transfer coefficient, $K_L a$, was determined by the dynamic response of a double-membrane oxygen electrode (Ingold) following unit step change in oxygen concentration while switching the gas from nitrogen to air. The electrode was mounted in the area of maximum mixing intensity which was 2 cm above and 2 cm apart from the impeller tip. Its response, taken as logarithm of the function $(R^*-R_L)/(R^*-R_o)$, was plotted against time and from its intercept and slope the time constants of the system were obtained based on the equation

$$(R^* - R_L)/(R^* - L_O) = [\tau_L/(\tau_L - \tau_E)] \cdot e^{-t/\tau_L}, \quad (1)$$

where $\tau_L = 1/K_L a$, and $\tau_E = 1/K_E$, is the electrode constant reciprocal value, and R_L, R_o, and R^* are the current and the initial probe responses and the response at equilibrium, respectively. The reliability of this method was tested in separate experiments with a glycerin-water system at 30 mPa.s by using the K_E-value 0.1 s^{-1} found for the same oxygen electrode previously[20].

Working gases were air and nitrogen. Referring to our previous experience and to reports in the literature[12, 16], no

Table 2. K_La-values with a two-fold decrease of interfacial surface tension

$\dot{\gamma}$ [1/s]	μ [mPa.s]	K_La^* [1/s] at σ=0.066 [N.m⁻¹]	K_La^* [1/s] at σ=0.037 [N.m⁻¹]	System code
	1.8	0.012		N12
	1.6		0.008	N14
152	4.0	0.015		N16
	4.5		0.013	N23
	1.8	0.018		N12
184	1.4		0.0165	N11
	1.6		0.015	N13

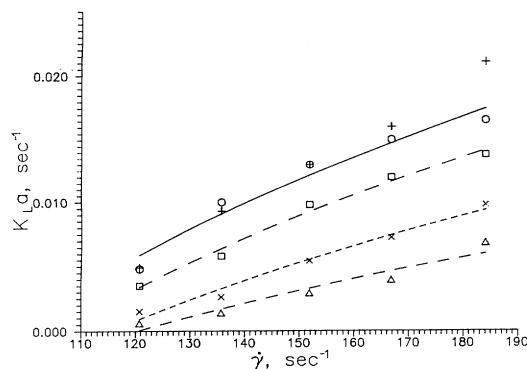* Average valued based on six measurements

Fig. 3. K_La vs. shear rate by oxygen transfer in corn starch colloidal dispersion of various consistency. System codes as in Table 1: N11 (○), N21 (+), N32 (□), N42(△), N41(×)

significant effect of gas velocity was expected in the agitator-dominated region of mass transfer (*i.e.* mixing intensity between 10 and 20 r.p.s.) and so it was kept constant at $1.6.10^{-3}$m/s.

2. Results and Discussion

Upon investigation of mass transfer in the range of impeller velocities (N) between 600 and 1100 rpm, K_La versus average shear rate values were obtained at different starch concentrations, *i.e.* apparent viscosity μ, as well as at different values of surface tension σ as given in **Fig. 3** and in **Table 2**.

As seen from these data, some reduction of K_La occurred by dispersion thickening (Fig. 3) as well as by lowering the surface tension σ (Table 2). The effect of σ was found to be significant only at low shear while at high shear rates this effect was found to abate. In general, the effect of σ was within a range which could be neglected. In our opinion, it is likely that σ affected K_La by influencing both the mass transfer in the boundary layer, K_L, and the amount of interfacial area, a. However, both parameters included in K_La changed in opposite directions (K_L increased in the presence of antifoam while it decreased due to enhanced bubble coalescence) with K_La remaining almost constant. Similar mass transfer performance was also observed in earlier[16, 6] studies.
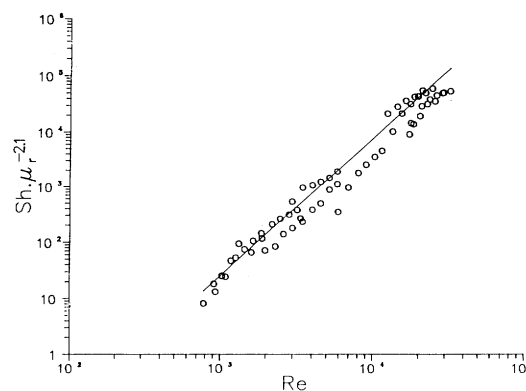
In contrast, the effect of consistency and thus of viscos-

Fig. 4. General correlation for K_La for oxygen transfer in non-Newtonian 1-4% starch colloidal dispersions

ity on K_La a was found to be more pronounced. Based on these data, impeller velocity and fluid apparent viscosity were found to be the two variables with substantial effect upon K_La in corn starch dispersions and K_La-values were obtained over wide range of these variables.

In order to generalize our observations, a correlation for K_La was tested to determine if it would fit the data by following a least squares procedure over a wide range of the studied variables. The starting point of this work was the empirical correlation for gas-liquid mass transfer in agitated vessels proposed by Sideman et al.[18]:

$$Sh = A \cdot Re^{n_1} \cdot \mu_r^{n_2} \cdot Sc^{n_3} \cdot G^{n_4} \qquad (2)$$

In this equation, *Sh*, *Re* and *Sc* are the continuous phase Sherwood, Reynolds, and Schmidt numbers, respectively, G is the dimensionless gas flow group and μ_r is the relative gas viscosity.

According to our previous experiments, the effect of U_G on mass transfer was found to be insignificant as compared to the effect of linear mixing velocity, Nd, as was the effect of σ, with regard to the data in Table 2. Case D was assumed to be a power-law function of μ and both were dependent on the effective shear rate due to mixing. The effect of the Schmidt number was not studied separately. Consequently, the gas flow number G and the Sc number were excluded in the subsequent correlation.

Based on reference data valid for mass transfer in pseudoplastic fluids, the apparent viscosity of the colloidal dispersion was introduced instead of gas viscosity. Then, the following equation was obtained which has been employed previously with good results for purely pseudoplastic fluids of CMC and PAA solutions[16]:

$$Sh = A \cdot Re^{n_1} \cdot (\mu / \mu_w)^{n_2} \qquad (3)$$

On the basis of a total of 61 points for oxygen transfer in starch solutions, the following values for A, n_1 and n_2 were obtained:

$$A = 9.71.10^{-7}, n_1 = 2.47, n_2 = 2.10 \qquad (4)$$

Figure 4 contains the plot of this correlation in logarithmic coordinates. The average mean deviation of the data from this correlation was 18.4 % and the standard devia-

tion was 43.9 %. Bearing in mind the wide interval of flow behaviour and consistency indices covered by this equation, it was considered promising for further analysis. The following analysis of exponents in this equation confirms this statement.

By observing the previous data concerning dependencies of mass transfer on impeller revolutions in other systems, the exponent at N for dispersions of corn starch found in this work, i.e. 2.47, compared well with the values, 2.4-3.0, reported by Elsworth et al. for Newtonian fluids, as well as to the one of 2.4 reported by Hyman[18]. Similarly, the exponent of the viscosity term, -0.37, was very near to the exponents -0.4 and -0.5 found earlier for pseudoplastic CMC by Yagi and Yoshida[21] and Nishikawa et al.[11].

It is noteworthy that the observed values for n_1 and n_2 in this correlation ($n_1 = 2.47$, $n_2 = 2.10$) are somewhat higher than the values obtained by Ranade and Ulbrecht[16] which were 1.8 and 1.39, respectively. In our opinion, this is due to the stronger dependence of dissipated power on Reynolds number and viscosity in the range of Re just below the fully turbulent region valid in this paper. (The correlation in Ref.[16] represents the region Re > 20000). For the region Re < 10000, or more often 800 < Re < 5000, such effects have recently been observed for pseudoplastic fluids by Nienow et al.[10].

Conclusion

Gas-liquid mass transfer was studied experimentally in corn starch colloidal dispersions with strong non-Newtonian flow behaviour. Experiments with colloidal dispersions with and without antifoam agent showed that, though the interfacial surface tension changed markedly, it did not influence mass transfer significantly, especially at high shear rates. Impeller velocity and fluid apparent viscosity were found to be the variables with substantial effect upon K_La. K_La-values were obtained in a wide range of these variables corresponding to the transient region of Reynolds numbers. A modified and reduced form of Sideman's equation including these variables in dimensionless form, is shown to fit the experimental data favourably.

Acknowledgement

Nomenclature

d	= impeller diameter	[m]
D	= diffusivity	[m^{2}s^{-1}]
D_w	= diffusivity in pure water	[m^{2}s^{-1}]
h	= impeller clearance from bottom	[m]
H	= liquid height	[m]
n	= flow behaviour index	
N	= impeller rotation speed	[s^{-1}]
K	= consistency index	[Pa.s^m]
K_La	= volumetric mass transfer coefficient	[s^{-1}]
T	= tank diameter	[m]
U_G	= superficial gas velocity	[m·s^{-1}]
G	= gas flow number	[$\mu U_G \cdot \sigma^{-1}$]
Re	= Reynolds number	[d$^2.N\rho.\mu^{-1}$]
Sc	= Schmidt number	[$\mu\rho^{-1}.D^{-1}$]
Sh	= modified Sherwood number	[K$_L$a.d^2.D^{-1}]
$\dot{\gamma}$	= shear rate	[s^{-1}]
μ	= apparent viscosity of fluid	[Pa.s]
μ_G	= viscosity of gas	[Pa.s]
μ_W	= viscosity of water	[Pa.s]
μ_r	= relative viscosity	[$\mu.\mu_w^{-1}$] or [$\mu.\mu_G^{-1}$]
ρ	= fluid density	[kg.m^{-3}]
σ	= surface tension	[N.m^{-1}]
τ	= shear stress	[Pa]

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