

Analysis of the differences in $k_L a$ values determined by different variants of the dynamic method in stirred tanks

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An investigation on some variants of the well established *oxygen dynamic technique* is carried out, with the aim of setting up a reliable measurement technique to be employed for $k_L a$ measurements. In particular, comparison is made between $k_L a$ values determined in presence or in absence of inert gases such as nitrogen. The relevant experimentation is carried out with a standard gas-liquid stirred vessel. Results show that the gas-liquid mass transfer coefficient values obtained either in presence or in absence of dissolved nitrogen are significantly different. Possible reasons behind this discrepancy and the reliability of most of the available literature information are discussed.

1. Introduction

The design, scale-up and optimization of industrial processes conducted in multiphase agitated reactors require, among others, precise knowledge of the hydrodynamics, mass and heat transfer parameters and reaction kinetics. The dynamic oxygen-electrode method has been widely used for $k_L a$ measurements (Van't Riet, 1979; Linek et al., 1987). With this method, the oxygen concentration in the gas fed to the vessel is suddenly changed and the change of oxygen concentration as a function of time is followed using a dissolved oxygen probe.

The gas side mass transfer resistance is usually much smaller than the liquid side, and can therefore be neglected. For a perfectly mixed liquid phase, Eqn. 1 is obtained:

$$V_L \frac{dC_L}{dt} = \sum_{i=1}^{N_b} k_{L,i} a_{bi} (C_{L,i}^* - C_L) \quad (1)$$

where N_b is the total number of bubbles, a_{bi} is bubble surface and $C_{L,i}^*$ is the equilibrium oxygen concentration for each bubble. If k_L , and C_L^* are identical for all bubbles at any time throughout the process, equation (1) can be integrated to give:

$$\ln \left(\frac{C_L^* - C_L}{C_L^* - C_0} \right) = -k_L a (t - t_0) \quad (2)$$

It follows from equation (2) that, if the above hypothesis are reasonably abode by, plots of $\ln(C_L^* - C_L)$ versus t will result into straight lines with a slope equal to $(-k_L a)$.

Certain difficulties are encountered when using this method. As a matter of fact, Eqns. 1 and 2 strictly hold only when both the liquid and gas phases are perfectly mixed. In all other cases precise information on the gas and liquid behaviour is required in order to properly assess the mass transfer parameter.

It is worth noting that the only case in which there is no need to resort to models for the behaviour of the gas phase, is when a pure gas is absorbed in a completely degassed liquid (Linek *et al.*, 1987). In this case in fact there can be no question about the uniformity of gas concentration in the bubbles and the k_La value obtained using equation (1) does certainly coincide with the real value. The present authors are aware of only one example of application and comparison of this method in the open literature, namely that reported by Linek *et al.* (1987). They compared the k_La values obtained by the traditional dynamic method in a standard stirred reactor with the values obtained by the above variant. Notably, in the latter case the resulting k_La values were found to be larger, by about 20% for coalescing systems and up to 50% for non-coalescing systems, than those obtained by the former technique.

In this work, the mass transfer performance of a conventional stirred vessels is investigated. In particular, comparison is made between k_La values determined by the dynamic method, performed in two different variants: (i) pure oxygen absorption in an air-saturated liquid phase and (ii) pure oxygen absorption in a completely de-aerated liquid phase.

2. Experimental

The experimental apparatus consisted of a "standard" stirred reactor with ID = 190 mm, H = 300 mm. A "Rushton turbine" (six flat blade disk mounted) of 65 mm dia. was mounted on the 17 mm dia. shaft, leaving a clearance of T/3 from vessel bottom. The vessel was equipped with 4 vertical baffles 3 mm thick and 19 mm wide, deployed along vessel walls at 90° from each other. The vessel was filled with deionized water up to an height of 190 mm (H=T). The reactor was equipped by a stainless steel top to allow reactor evacuation. A Venturi vacuum pump was used to evacuate the vessel down to 0.1 atm. Oxygen concentration was measured by means of an electrode sensor (WTW CellOx 325) and control unit (WTW Oxi 340i). The electrode time constant was experimentally measured to be about 3.0 s thus a value significantly smaller than the expected time dynamics for oxygen absorption, so that neglecting the probe time dynamics should have negligible effects on the resulting k_La values (Van't Riet, 1979). The mechanical power dissipated by the impeller at various agitation speeds was measured by a "static-frictionless" turntable (Grisafi *et al.* 1998).

2.1 k_La measurements

The volumetric mass transfer coefficient, k_La , was assessed by unsteady state experiments on the basis of pure oxygen absorption dynamics. In all runs the temperature inside the reactor was between 24 and 25 °C. This was obtained by adjusting the initial temperature and exploiting the circumstance that, due to the very slow temperature rise dynamics, the temperature increase during each single run was always less than 0.2 °C.

As previously stated, under the hypothesis of gas bubbles all made of pure oxygen and perfectly mixed liquid phase, the mass transfer coefficient k_La does simply coincide with the slope of the observed exponential decay (Eqn. 2). It is clear that there are several reasons for the real behaviour to detach from the above idealised model, namely the liquid phase is never perfectly mixed and gas bubbles may not be made of

pure oxygen. As a matter of fact, apart from the effectiveness of the air removal from the head space, if there initially is some dissolved nitrogen in the liquid phase, this is unavoidably transferred to the gas bubbles during the run, therefore diluting the oxygen there contained. For this reason two experimental procedures were compared (Scargiali et al. 2007).

Pure oxygen absorption in air saturated water (procedure “OAS”)

A typical “OAS” experimental run started from a condition of air-saturated liquid and no agitation conditions. Pure oxygen then started to be fed to the vessel sparger with a flow rate of about 6 l/min (1vvm). Data acquisition was started shortly after agitation. A transitory followed, in which the difference between the equilibrium concentration to pure oxygen and the time dependent oxygen concentration measured in the liquid phase decayed and eventually vanished.

Pure oxygen absorption in pre-evacuated water (procedure OApE)

This variant was devised in order to free the system from dissolved nitrogen, so avoiding the subsequent contamination of oxygen bubbles. To this end, the liquid inside the tank was almost completely degassed by repeated evacuation of the reactor headspace. In particular, pressure inside the reactor was typically brought down to about 0.1 bars while stirring at medium agitation speeds to fasten the degassing process. Vacuum and agitation were maintained for several minutes (typically 5 min) and then atmospheric pressure was restored by admitting pure oxygen to the reactor headspace. To make sure that practically all nitrogen initially dissolved in the liquid phase had been removed, a sequence of at least three evacuation cycles was carried out before beginning the experimental run. This last was then performed in the same way described in procedure “OAS”. After the first run, a single evacuation procedure was employed to partially desorb the oxygen dissolved in liquid phase and a new run could be started.

3. Results and discussion

A typical experimental oxygen concentration dynamics obtained by pure oxygen absorption in air saturated water (procedure OAS) is shown in Fig.2, where the dimensionless driving force for mass transfer is reported versus time in a semi-logarithmic plot. Data acquisition was started first and only after several seconds the agitator was started. As a consequence, time zero in the figure is meaningless. Nevertheless, as previously discussed, on the basis of the simplest concentrated parameter model (bubbles all made of pure oxygen, well mixed liquid phase) it was expected that, after some time, data points did align on a straight line with a slope equal to $-k_L a$. As it can be seen in Fig.2, this is actually the case and an estimation of the mass transfer parameter $k_L a$ (0.0396 s^{-1} in the particular case under examination) is obtained.

When the nitrogen-free procedure (OApE) was applied under the same operating conditions, the results reported in Fig. 3 were obtained. As it can be seen, once again (after some time) data points did align on a straight line, but the final slope obtained with OApE procedure (0.0548 s^{-1}) is significantly larger than that obtained with procedure “OAS” (0.0396 s^{-1}) at the same agitation speed.

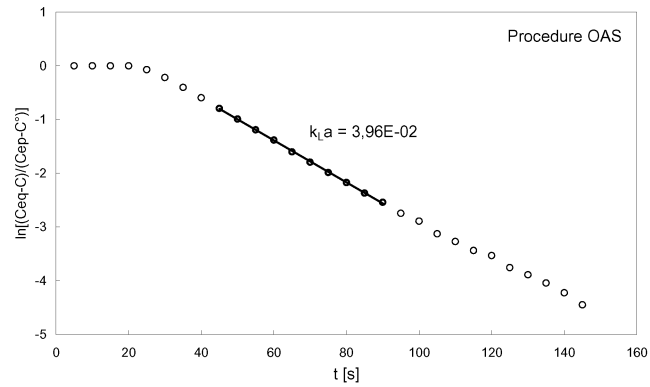


Fig.2: Typical oxygen concentration dynamics at $N=900$ rpm, $Qg=5.4$ lt/min. Procedure OAS (oxygen absorption in air saturated water)

The same behaviour was observed in all experiments carried out with procedure “OApE”, independently of agitation speed, as it can be appreciated in Fig. 4 where the k_{La} values obtained with procedure OAS are reported as solid symbols, while the values obtained with procedure OApE are reported as empty symbols. In this last case, experiments were repeated at least 3 times for each agitation speed, in order to appreciate technique reproducibility.

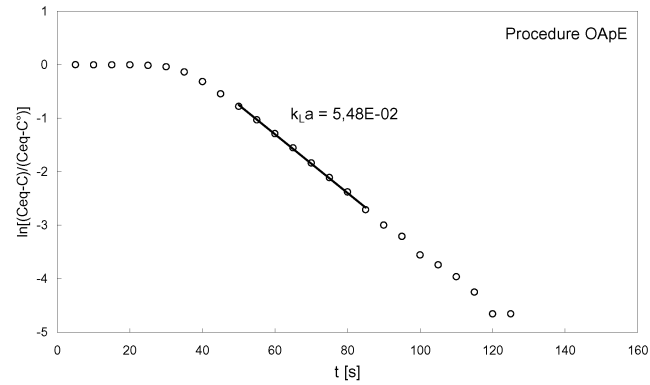


Fig. 3: Typical oxygen concentration dynamics at $N=900$ rpm, $Qg=5.4$ lt/min. Procedure OApE (oxygen absorption in pre-evacuated water)

It is worth stressing that procedure “OApE” is practically identical to procedure “OAS”, the only difference between the two being merely the initial presence of nitrogen in the liquid phase. The fact that values of k_{La} obtained with the former procedure are from 30 % to 50 % larger than those obtained with the latter is to be entirely attributed to measurement interference by dissolved nitrogen. This can quite easily be explained, as in the case of initially de-aerated liquid (procedure OApE) gas bubbles are all made of pure oxygen, apart from the liquid vapour pressure that is constant throughout the experiment. As a consequence, Oxygen equilibrium concentration in the liquid is

constant at any time and the driving force variation is only due to liquid bulk oxygen level variations.

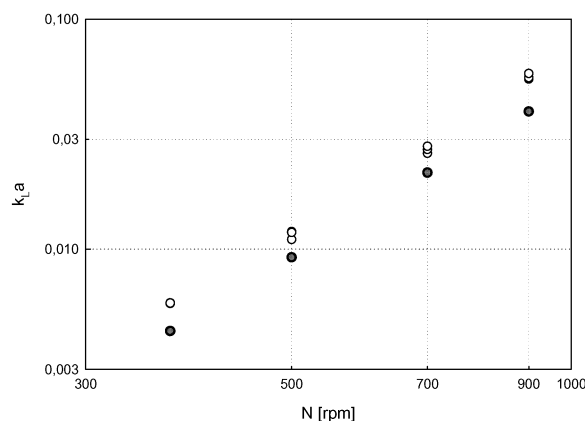


Fig. 4: Comparison between k_La values determined with the two variants of the dynamic oxygen absorption method at various agitation speeds. Solid circles: procedure OAS ; open circles: procedure OApE.

In the other case (procedure “OAS”) the initially dissolved nitrogen undergoes transport towards gas bubbles. As a consequence in the gas phase oxygen starts to be diluted, resulting in an oxygen interface concentration smaller than assumed in the simple model employed for results interpretation. This in turn leads to a reduction of mass transfer rates, which are mistakenly seen by the model as a reduction of k_La average values. It is clear that improving the interpretation model to account for these effects is not easy. As a matter of fact, different bubbles will experience different dilution levels depending on their size, residence time spent in the system. As a consequence, at any instant in the system there are many bubbles, with many different sizes and histories, each of which has a more or less diverse oxygen concentration, and taking proper account of this by data interpretation models is very complex if not impossible. From the above considerations, it can be concluded that the OApE procedure, being free from these disturbances and interpretation difficulties, is the only one that leads to fully reliable results.

The present results may be compared with the only literature data obtained in absence of initially dissolved nitrogen, namely those reported by Linek *et al.* (1987). In order to make results meaningful, the k_La data obtained in the two works are to be compared for given specific power inputs, as due to the difference of vessels size ($T=0.29$ m in the case of Linek’s vessel) stirrer speed would not be a suitable comparison basis. This is done in Fig. 5, where also the regression lines for the data obtained here and those obtained by Linek *et al.* (1987) are reported.

As it can be seen, Linek *et al.* 1987 correlation, based on experimental measurements obtained with a procedure very similar to procedure OApE, gives rise to results almost coincident with the present OApE data. At a closer look, the agreement is better at the lowest specific power dissipations, while at the highest specific power dissipations, Linek’s correlation underestimates somewhat the present OApE results.

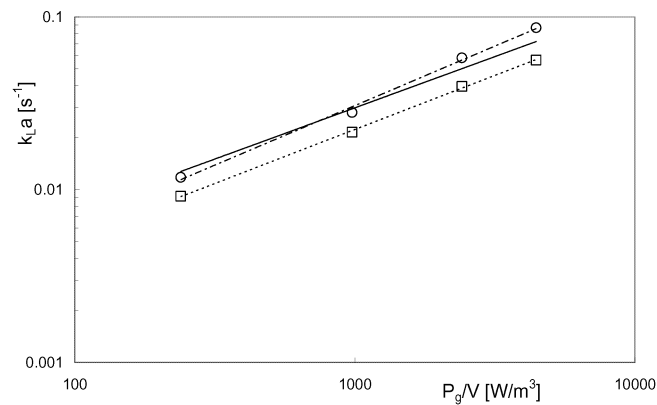


Fig. 2.14: Mass transfer coefficient vs specific power input. Circles: OApE procedure; dash dotted line: equation 2.7. Squares: OAS procedure; dotted line: eqn. 2.8; Solid line: Linek *et al.* (1987) correlation.

The reason behind this discrepancy may lie in the fact that Linek *et al.* (1987) used a topless vessel, therefore nitrogen was present in the gas above the free surface, and this may well have resulted into some nitrogen contamination of the liquid, especially at the highest agitation speeds, where surface aeration is likely to occur.

4. Conclusions

Gas-liquid mass transfer coefficients obtained in absence of species other than water and oxygen, are about 30 % - 50 % greater than those (less reliable) measured in the same hydrodynamic conditions but starting with an air-saturated liquid phase, i.e. in the presence of dissolved nitrogen. Results clearly show that it is extremely important to use correct methods of k_La measurement, able to produce physically consistent data, as only such data with clear physical interpretation can lead to successful design and scale-up of apparatuses.

References

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