Measurement of mass transfer characteristics of gas/liquid reactors by sulphite system using on-line monitoring UV absorption

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ABSTRACT

The UV absorption at a wavelength of 255 nm is used for in-line monitoring of sulphite concentration. The method was originally used under conditions when calibration curve is pH-dependent. This dependence complicates the calibration and thus prevents wider application of the method for measurements of mass transfer characteristics of various absorption devices by the sulphite system. It is shown that the calibration curve is pH independent if the pH of solution is higher than 8. This simplifies the calibration and may promote broader application of this faster and more comfortable UV method in the engineering praxis. This is demonstrated on measurement of kinetic data of the reaction (measured in stirred cell), physical mass transfer coefficient $k_L a$ and interfacial area a (measured in mechanically agitated gas–liquid dispersion) using solution of 0.8 M Na_2SO_3 with various cobalt catalyst concentrations ranging from 5×10^{-7} to 2×10^{-3} M and pH in the range of 8–8.7. Effects of surface tension (Ocenol) and viscosity changing additives (CMC and Sokrat) on the calibration curve are also studied. The mass transfer characteristics measured by the UV method both in pure sulphite solution and with the additives agree with those obtained by the iodometric back-titration method. Comparison of the kinetic data with published ones has shown that the data for pure sulphite solution and one with addition of Ocenol are transferable from literature in the form of oxygen absorption rates N but the data of sulphite solution with CMC and Sokrat are not. "Instantaneous" absorption rates evaluated from the slope of UV responses confirmed that the interfacial area of dispersion measured by the chemical method decreases significantly due to bubble shrinkage at high cobalt catalyst concentrations used in the measurement. This phenomenon may play an important role whenever the results, measured at different absorption rates, are compared. This is demonstrated on the measurement of mass transfer coefficient from bubbles in dispersion.

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1. Introduction

Oxygen or air absorption into the sodium sulphite solution is one of the most frequently used model reaction systems for measurement of mass transfer characteristics in various absorption devices. The common method relies on determination of the sulphite concentration by iodometric back-titration. The main advantages of this technique [1,2] are non-aggressive, easy available and affordable reagents, high sensitivity of the reaction constant to catalyst concentration even at very small concentrations and low oxygen solubility which are the basis for small temperature and concentration changes of the reaction components in the measurement. This substantially reduces the effect of gas phase longitudinal mixing on a driving force of absorption in comparison with other frequently used reaction systems utilizing absorption of more soluble gases such as CO_2 or SO_2 into NaOH solution [3,4]. Major draw-

backs of the sulphite system are that it is very time-consuming and demanding on precision of the iodometric back-titration, and its difficult application for broader study of mass transfer, where changes of the physical properties of the solution are in question. Many of the common additives to change, e.g. viscosity (glycerol, PEG, etc.) influence the reaction kinetics as well as some natural impurities in the reagents itself. Thus it has not been recommended to adopt the kinetic constant of the reaction from the literature [1].

The titration is tedious and cannot be used for continuous monitoring of sulphite concentration which might substantially speed up experiments and data collecting. An UV spectroscopy method recently appeared [5] which is based on on-line monitoring of the change in UV absorption of sulphite solution during oxygen absorption at a wavelength of 260 nm. The authors [5] monitored the oxidation of 0.8 M sulphite solution in a stirred cell. Initial pH of the solution 7.6 dropped to 7.0 during the experiment due to conversion of sulphite to sulphate causing formation of bisulphite ion HSO_3^- which exists in equilibrium with $S_2O_5^{--}$ [6,7]. However, these anions have different absorbance from sulphite anion SO_3^{--}

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Nomenclature

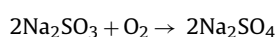|	
A	total interfacial area (m^2)
a	specific interfacial area referred to liquid volume (m^{-1})
a_0	specific interfacial area measured at sufficiently low absorption rate to prevent the decrease due to bubble shrinking (m^{-1})
c	concentration (M = kmol m^{-3})
c^*	equilibrium concentration with respect to partial pressure in gas (M = kmol m^{-3})
d_b	bubble diameter (m)
D	molecular diffusivity of oxygen (m^2 s^{-1})
E	activation energy (kJ/kmol)
f	agitator frequency (s^{-1})
k_L	physical mass transfer coefficient of oxygen (m s^{-1})
$k_L a$	physical volumetric mass transfer coefficient of oxygen (s^{-1})
k_n	nth-order reaction rate constant to oxygen (kmol$^{(n-1)}$ m$^{-3(n-1)}$ s^{-1})
N	oxygen absorption rate (kmol m^2 s^{-1})
[NA]	total oxygen absorption rate (kmol s^{-1})
p	partial pressure (Pa)
q	volumetric gas flow rate (m^3 s^{-1})
R	universal gas constant (kJ kmol^{-1} K^{-1})
r	adjustable parameter in the empirical relation (12)
S	slope of sulphite concentration time dependence from UV response (s^{-1})
s	empirical parameter in Eq. (12)
T	temperature (K)
t	time (s or min)
u	velocity at which bubbles move along their paths in the vessel (m s^{-1})
(UVA)	absorbance of sulphite solution
V_L	liquid volume in vessel (m^3)

Reith [8] derived the following relation for the oxygen absorption rate N accompanied by nth-order irreversible reaction:

$$N = (c_{O_2}^* - c_{O_2})\sqrt{\frac{2}{n+1}Dk_n c_{O_2}^{n-1} + k_L^2} \tag{1}$$

This equation may be used for interpretation of the results if the following conditions, discussed in detail in [1], are fulfilled:

- Concentration of sulphite must be sufficiently high to reach zero order of the reaction with respect to sulphite. It was shown conclusively that the assumption is safely fulfilled with all types of absorption equipment in common use if $c_{SO_3} > 0.45$ M.
- Reaction order n with respect to oxygen depends on the oxygen concentration at the interface. The results of thus performed measurements conform to the empirical rule that the reaction order is two if $c_{O_2}^* < 6 \times 10^{-4}$ M, and unity if $c_{O_2}^* > 7 \times 10^{-4}$ M. This concentration may be evaluated from the following empirical relation [1] using oxygen partial pressure in gas and sulphite concentration:

$$c_{O_2}^* = 5.832 \times 10^{-11} \exp\left\{\frac{1602.1}{T} - \frac{0.9407 c_{Na_2SO_3}}{1 + 0.1933 c_{Na_2SO_3}}\right\} p_{O_2} \tag{2}$$

According to this empirical rule, the reaction is of the first order for pure oxygen absorption into 0.5 M sulphite at 20 °C, of the second order for air absorption into 0.5 M sulphite and for air and oxygen absorption into 0.8 M sulphite at a temperature of 20 °C and higher.

- The reaction constant k_n depends strongly on cobalt catalyst concentration. Mistra and Srivastava [9] show that the true lower limit of validity of the linear relationship between the rate constant and the catalyst concentration c_{CoSO_4} is below 10^{-7} M. The upper limit of validity of the relationship is given by the concentration at which the catalyst begins to precipitate from the solution.

Kinetics of the reaction is usually measured in stirred cells under the conditions, when the absorption is accompanied with moderately fast reaction which enhances the reaction term in the relation (1) so that the physical mass transfer coefficient k_L is negligible compared to the reaction term and oxygen concentration in the liquid bulk $c_{O_2} = 0$. In dispersions, these conditions are usually fulfilled [1,2] if $c_{CoSO_4} > 3 \times 10^{-5}$ M, $c_{Na_2SO_3} > 0.45$ M and pH > 7.8. Under these conditions, the oxygen absorption rate does not depend on agitation intensity of liquid phase and the following relation applies:

$$N = c_{O_2}^*\sqrt{\frac{2}{n+1}Dk_n c_{O_2}^{n-1}} \tag{3}$$

Linek et al. [2] applied the relation on their own data of oxygen absorption in 0.8 M sulphite solution and obtained the following equation by regression of experimental data:

$$N = 4.469 \times 10^{-5} c_{CoSO_4}^{0.496}(pH - 6.459)\exp\left\{\frac{E}{R}\left(\frac{1}{T} - \frac{1}{303.15}\right)\right\}$$

$$\times \left(\frac{p_{O_2}}{9.5058 \times 10^4}\right)^{3/2} \tag{4a}$$

The activation energy $E = 19$ kJ/mol is pH independent and includes activation energy for solubility and molecular diffusivity of oxygen and for the second-order rate constant k_2. The equation applies also to a sulphite solution with 3 ppm Ocenol. A similar relations were derived [2] for sulphite solution with 0.2 wt.% CMC and

at a longer wavelength ($\lambda > 220$ nm, [7]) and also, the absorbance due to $S_2O_5^{--}$ is proportional to $(HSO_3^-)^2$ and thus makes the calibration curve pH-dependent in the range of pH used by Lewis and Roberts [5], i.e., pH from 7 to 7.6. The pH-dependence complicates the calibration and thus seriously impedes extensive utilization of this promising measuring technique for a continuous monitoring of sulphite concentration in experimentations.

The work aims to find the conditions when the calibration curve is not pH-dependent. Under these conditions, the spectrometric method is applied to the measurement of the following engineering mass transfer characteristics: oxidation kinetics of pure sulphite solution and sulphite solution with surface tension or viscosity changing additives, volumetric mass transfer coefficients and interfacial area in mechanically agitated dispersion. The results are compared with those obtained by classic titration and with the kinetic literature data aiming to test transferability of the sulphite oxidation kinetics from literature.

2. Theory

2.1. Reaction kinetics

Oxidation of sulphite by dissolved oxygen proceeds according to the following overall reaction scheme:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$