ABSORPTION OF OXYGEN INTO SOLUTIONS OF POLYMERS

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Absorption of oxygen into water and aqueous solutions of poly(acrylamides) was studied in an absorber with a wetted sphere. The effects of changes in the liquid flow rate and the polymer concentration on the liquid side mass transfer coefficient were examined. The results are expressed by correlations between dimensionless criteria modified for non-Newtonian liquids whose flow curve can be described by the Ostwald–de Waele model.

The results of study of dissolution of oxygen in non-Newtonian liquids can be utilized, *e.g.*, in submersion aerobic cultivations, where oxygen dissolved in the nutrient solution is among essential components vital to the microorganism growth. Since nutrient solutions usually exhibit rheological behaviour of non-Newtonian liquids, aqueous solutions of polymers can be employed for their simulation.

Absorption of oxygen into a viscoelastic liquid in a stirred vessel has been studied by Yagi and Yoshida[1], who examined the dependence of the volumetric oxygen transfer coefficient on the stirrer velocity and on the polymer concentration in the solution. Absorption of oxygen into a pseudoplastic and a viscoelastic liquids in a multistage column has been investigated by Voigt, Hecht and Schügerl[2,3]. In the countercurrent flow of the fluids, the volumetric mass transfer coefficient was determined in dependence on the gas and liquid flow rates, on the properties of the liquid phase and also on the design parameters of the plates. Stejskal and Potůček[4] studied the possibility of using motionless mixers (Kenics type) as inserts in an air-lift tower reactor for intensifying the oxygen transfer into poly(acrylamide) solutions. In a contactor with rotating disks mounted on a horizontal shaft, Ravetkar and Kale[5] examined the absorption of oxygen and carbon dioxide into pseudoplastic solutions of poly(acrylamide) and carboxymethyl cellulose. The non-Newtonian properties of the liquid phase virtually did not affect the mass transfer coefficient. Absorption of oxygen into polymer solutions was also studied and the oxygen diffusion coefficient determined by Wasan and coworkers[6] in a column with wetted inner wall, and by Zandi and Turner[7] in an equipment with a laminar stream of the liquid phase.

In the present work, the absorption of oxygen into aqueous solutions of polyacrylamide is studied using an apparatus containing a wetted spherical body.

THEORETICAL

It can be found by qualitative treatment of the problem of absorption of a sparingly soluble gas into a Newtonian liquid in a column with a single vertical row of packing

elements[8-10] that the intensity of mass transfer, characterized by the liquid side mass transfer coefficient (k_L), depends on the diffusion coefficient of the gas in the liquid (D), the liquid velocity (u), and intrinsic properties of the liquid, *viz.* the dynamic viscosity (μ) and density (ϱ). The characteristic dimension of the packing particles d (for spherical particles, d is the particle diameter) also contributes. By dimensional analysis, these quantities can be combined into three dimensionless criteria, *viz.*

the Sherwood criterion,

$$\text{Sh} = k_L d/D \,, \tag{1}$$

the Reynolds criterion,

$$\text{Re} = du\varrho/\mu \,, \tag{2}$$

and the Schmidt criterion,

$$\text{Sc} = \mu/\varrho D \,. \tag{3}$$

Absorption of a sparingly soluble gas into a non-Newtonian liquid can be analyzed in the same terms as absorption into a Newtonian liquid except for the dynamic viscosity which no longer can be regarded as a constant. If the rheological behaviour of a non-Newtonian liquid can be described by a power relation between the shear stress τ and the shear rate γ,

$$\tau = k\gamma^n \,, \tag{4}$$

(the Ostwald–de Waele law), the consistency of the liquid phase is proportional to the consistency index k which, combined with the above five quantities k_L, D, u, ϱ, and d, can be employed for a qualitative treatment of the process. The dimensions of the six quantities can be set up from products of powers of the three basic dimensions: weight, length and time. Owing to this, three independent dimensionless arguments can be derived. This was so performed that the dimensionless criteria obtained corresponded in their physical meaning to those derived for Newtonian liquids.

In addition to the Sherwood criterion (1), a modified Reynolds criterion was derived for non-Newtonian liquids in the form

$$\text{Re}_m = d^n u^{2-n} \varrho/k \,, \tag{5}$$

which is the ratio of the inertia-to-friction forces. The intrinsic properties of non--Newtonian liquids can be expressed by the modified Schmidt criterion as

$$\text{Sc}_m = k d^{2(1-n)}/D^{2-n} \varrho \,. \tag{6}$$

The modified criteria were derived[11] for non-Newtonian liquids whose rheological behaviour can be described by the power relationship. It is clear that for the flow index n equal to unity the definition relations for the criteria became identical with those for Newtonian liquids, the dynamic viscosity being replaced by the consistency index k.

EXPERIMENTAL

The absorption experiments were performed in a model absorber containing a wetted spherical body. A glass sphere 8·5 cm in diameter was accomodated in a 15 cm long Plexiglass tube 10·5 cm inner diameter (Fig. 1). The liquid was recirculated through a desorption column where oxygen was displaced from the liquid by means of some inert gas (nitrogen, argon). The oxygen flow rate was constant, 50 cm^3 s^{-1}, the flow rate of the liquid was held at nine different values within the region of 50—260 cm^3 min^{-1}. Each measurement was repeated four times. The wetting liquid was either tap water or solutions of poly(acrylamides) in different concentrations. The temperature of the liquid was 20°C. The shear tensions at various shear rates were measured, for the polyacrylamide solutions, on a Rheotest II instrument. The shapes of the rheograms obtained obeyed the power relationship. The shear rates and the parameters of the power relationship, along with other properties of the liquid, are given in Table I.

For a characterization of the polymers produced by VEB Fettchemie Karl-Marx-Stadt, the mean molecular weights were also determined. The osmometrically obtained numerical centre of the molecular weights was 13 600 g mol^{-1} for Neuperm WF and 114 g mol^{-1} for Stipix; the mass centre determined viscometrically was 14 100 g mol^{-1} for Neuperm WF and 259 000 g . . mol^{-1} for Stipix.

The diffusivity of oxygen in the polymer solutions was determined experimentally on the same model equipment; details of the evaluation procedure have been reported[12]. The suitability of the method was tested on water; the oxygen diffusivity obtained, 1·96 . 10^{-9} m^2 s^{-1}, agrees well with published data.
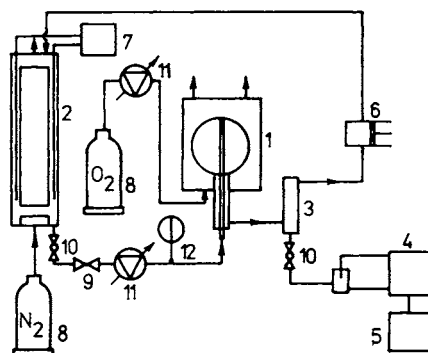

FIG. 1

Layout of the apparatus 1 absorber, 2 desorption column, 3 overflow and sampling device, 4 polarograph, 5 line recorder, 6 plunger pump, 7 thermostat, 8 pressure cylinder, 9 valve, 10 cock, 11 rotameter, 12 thermometer

The concentration of oxygen in the liquids was determined polarographically; a standard Pt––Ag-AgCl cell, as designed by Cherkasov based on Clark's principle[13], was used for the poly-(acrylamide) solutions.

RESULTS AND DISCUSSION

With regard to the fact that oxygen is slightly soluble in water and aqueous solutions of polymers, and moreover, the gaseous phase was only constituted by oxygen fed from a pressure cylinder, the overall mass transfer coefficient can be considered nearly identical with the liquid side mass transfer coefficient k_L. If both the equilibrium and balance dependences can be regarded as linear over the concentration region used, the driving force of the process can be expressed as the logarithmic centre of the driving forces at the absorber ends. The mass transfer coefficient then can be calculated from the relation

$$k_L = V\varrho(X_2 - X_1)/A(c^+ - c)_{lc} \tag{7}$$

(see the appended list of symbols). The regression coefficients for the dependence between the dimensionless quantities, which was treated in the form

$$Sh = b\,Re_m^{a_1}\,Sc_m^{a_2}\,, \tag{8}$$

were calculated on an EC 1033 computer.

The rate of absorption of oxygen into liquids was characterized by its transfer coefficient. This quantity was found to increase with increasing flow rate (Figs 2 and 3). It was observed visually that increasing water flow rate was accompanied by increasing instability of the liquid film, appearing first in rippling of the film surface in the area of the lower hemisphere, which later extended to the entire area of the

TABLE I

Properties of aqueous solutions of poly(acrylamide) at 20°C

c mass %	ϱ kg m^{-3}	$k\,.\,10^3$ kg m^{-1} s^{n-2}	n	γ s^{-1}	c^+/c_w^+	$D\,.\,10^9$ m^2 s^{-1}
			Neuperm WF			
1·0	1 000·2	3·2	0·967	218·7 — 1 312	0·938	3·94
2·5	1 002·4	8·7	0·924	121·5 — 1 312	0·923	4·55
5·0	1 006·1	30·3	0·880	48·6 — 1 312	0·892	6·09
			Stipix			
0·25	999·5	3·3	0·969	218·7 — 1 312	0·894	5·73
0·50	1 001·0	9·5	0·901	121·5 — 1 312	0·827	5·17
0·75	1 002·2	21·0	0·838	48·6 — 1 312	0·758	4·45

sphere surface. The increasing convection component of the diffusion was apparently associated with the increase in the mass transfer coefficient occurring when the water flow rate was raised. Still, for a given water flow rate the oxygen transfer coefficient was about one-half as compared with that observed in a column with vertical row of spherical particles[14,15] where, moreover, mixing of the liquid took place as it passed between the particles.

The aqueous solutions of poly(acrylamide) exhibited non-Newtonian behaviour and, as the data in Table I indicate, they can be classed among pseudoplastic liquids. The solubility of oxygen in these solutions was lower than in water and decreased with increasing polymer concentration for both poly(acrylamide) types (Table I). The lowering in the solubility of oxygen in the solutions used was more pronounced than as reported by Wasan and coworkers[6], who, however, employed poly(acrylamide) of different types.

Similarly as with water, the oxygen transfer coefficient increases with increasing liquid flow rate also in the poly(acrylamide) solutions (Figs 2 and 3). For a given flow rate of the liquid, the transfer coefficient decreases with increasing concentration of the polymer both for Neuperm and for Stipix, in agreement with the data of refs[1-4,14,15].
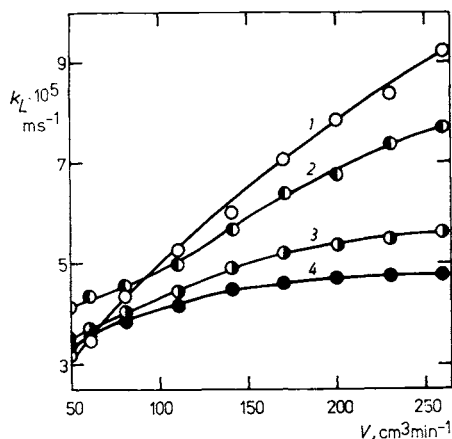

FIG. 2

Dependence of the oxygen transfer coefficient on the liquid flow rate for aqueous solutions of Neuperm poly(acrylamide). Neuperm concentration (mass%): *1* 0 (water), *2* 1, *3* 2·5, *4* 5
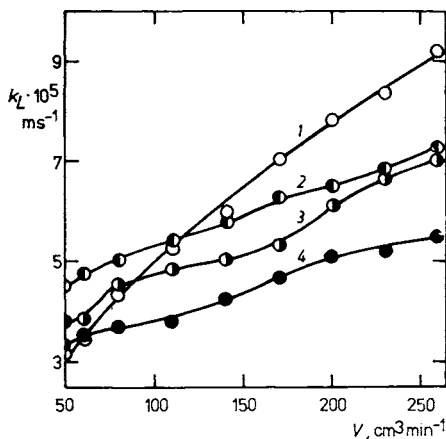
FIG. 3

Dependence of the oxygen transfer coefficient on the liquid flow rate for aqueous solutions of Stipix poly(acrylamide). Stipix concentration (mass %): *1* 0 (water), *2* 0·25, *3* 0·5, *4* 0·75

Although according to refs[2-4,14,15] the mass transfer coefficient in solutions of polymers is lower than in water, in our case this was not true over the entire liquid flow rate region. With water, higher transfer coefficient values were only observed at flow rates of 110 cm^3 min^{-1} and higher, whereas at lower flow rates the mass transfer coefficient decreased to the extent that the values approached those for poly-(acrylamide) solutions and at 50–60 cm^3 min^{-1} they were even lower. Hence, change in the flow rate of the liquid affects the mass transfer coefficient more in the case of water than in the case of poly(acrylamide) solutions. Since the latter possess a higher consistency than the former, the liquid film on the sphere was more stable and the rippling only appeared at higher flow rates and their intensity was considerably lower than with water.

For the correlation (8), the regression coefficients were calculated over the regions of Re_m from 0·2 to 17·4 and Sc_m from 891 to 47 700. The correlations were obtained in the forms

$$Sh = 501·5 \, Re_m^{0.30} \, Sc_m^{0.04} \tag{9}$$

for Neuperm (correlation coefficient 0·985), and

$$Sh = 123·1 \, Re_m^{0.30} \, Sc_m^{0.19} \tag{10}$$

for Stipix (correlation coefficient 0·950).

Since in Eq. (9), the effect of the modified Schmidt number on the Sherwood number is little marked, the former was omitted from the treatment for Neuperm to obtain

$$Sh = 708·4 \, Re_m^{0.27} \tag{11}$$

with a correlation coefficient of 0·983.

The difference in the effect of the substance properties for the two poly(acrylamide) types may be due to the different distribution of macromolecules in them, with different chain lengths, as indicated by the measured mean numerical and mass molecular weights. The effect of the modified Reynolds number, on the other hand, is nearly the same for the two poly(acrylamides).

In refs[8-10] the correlation dependences between the Sherwood number and the Reynolds and Schmidt numbers defined by Eqs (2) and (3) were obtained for the absorption of carbon dioxide into water in a column with an array of disks on a vertical shaft. At lower water flow rates the Reynolds number exponent was from 0·33 to 0·47, the Schmidt number exponent, from 0·25 to 0·50. These values are higher than those obtained for the absorption of oxygen into solutions of poly(acrylamide).

Further study should be aimed at the extension of the data to other non-Newtonian liquids and at the explanation of the effect of the shear rate in the interface range on the intensity of mass transfer during the absorption.

SYMBOLS

A	interface area, m^2
a	regression coefficient
b	regression coefficient
c	oxygen concentration in liquid, $kg\ m^{-3}$
c^+	equilibrium oxygen concentration in liquid, $kg\ m^{-3}$
D	diffusion coefficient, $m^2\ s^{-1}$
d	diameter, m
k	consistency index, $kg\ m^{-1}\ s^{n-2}$
k_L	liquid side mass transfer coefficient, $m\ s^{-1}$
n	flow index
u	linear velocity of liquid, $m\ s^{-1}$
V	liquid flow rate, $m^3\ s^{-1}$ ($cm^3\ min^{-1}$)
X	relative mass fraction (kg oxygen/kg liquid)
γ	shear rate, s^{-1}
μ	dynamic viscosity of liquid, $kg\ m^{-1}\ s^{-1}$
ϱ	liquid density, $kg\ m^{-3}$
τ	shear stress, $kg\ m^{-1}\ s^{-2}$
Re	Reynolds criterion
Re_m	modified Reynolds criterion
Sc	Schmidt criterion
Sc_m	modified Schmidt criterion
Sh	Sherwood criterion

Subscripts:

lc	logarithmic centre
w	water
1	inlet
2	outlet

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