COMMUNICATIONS TO THE EDITOR

Pressure Dependence of Liquid Phase Mass Transfer Coefficients

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In the design of gas absorbers, it is generally assumed that the liquid phase mass transfer coefficient, k_L, is independent of pressure. In connection with our biomedical engineering studies an interesting fact was observed: that is k_L for absorption of oxygen into water and aqueous solutions decreased with increasing pressure at moderate pressures.

EXPERIMENTAL PROCEDURE

The experimental apparatus used was a stainless steel autoclave 250 cc. in total volume. It was equipped with a propeller-type agitator, and the speed was adjusted by means of a magnetic drive mechanism. Oxygen supplied from a cylinder was absorbed into the liquid in the autoclave through the free interface. The pressure of oxygen in the autoclave was controlled with an accuracy of 1% by means of a precision reducing valve. By replacing the main body of the autoclave with a glass vessel of the same shape and size we were able to see that the free interface was practically flat for the agitator speeds studied. The electrode sheath inserted vertically into the autoclave acted as a baffle to prevent vortex formation. The area of the gas-liquid interface was 22 sq.cm.

The concentration, or the partial pressure of the oxygen in the liquid was determined by use of a homemade membrane electrode, comprised of a platinum cathode, silver-silver chloride anode, polyethylene or Teflon membrane, 0.1 m. potassium chloride solution saturated with silver chloride, and an acrylic resin sheath. A hole was drilled through the wall of the sheath at a point above the liquid level in the autoclave to equalize pressures in and outside the sheath. Calibration data indicated that, for a given solution, the potentiometer reading was a function of only the partial pressure of oxygen in equilibrium with the solution and was independent of the total pressure. Tests also showed that the response of the electrode to an instantaneous change of the partial pressure was a matter of several seconds.

In performing the experiment, 100 to 150 cc. of a liquid contained in the autoclave was first saturated with pure oxygen at atmospheric pressure. Then, without changing the agitator speed, the pressure of oxygen in the autoclave was instantly raised to a higher level and was kept precisely at this level. As absorption proceeded, the partial pressure of oxygen in the liquid increased. The potentiometer reading was recorded as a function of time. When the reading approached an asymptotic value, it was assumed that saturation had been reached. Such experiments were performed at various levels of the oxygen pressure, that is, the total pressure minus the vapor pressure of water.

DISCUSSION OF RESULTS

The liquid phase mass transfer coefficient k_L was obtained from the experimental data on the assumptions that the liquid phase was completely mixed, and the gas phase resistance was negligible. The Henry's law is known to hold for the systems and the pressure ranges studied.

$$V\ dc/dt = k_L\ A\ (c^* - c) \tag{1}$$

Substitution of the Henry's law relationship into Equation (1) gives

$$V\ dp^*/dt = k_L\ A\ (p - p^*) \tag{2}$$

Since equilibrium prevails at the beginning, the initial value of p^* is equal to p_o. Integration of Equation (2) gives

$$V\ \ln \frac{p - p_o}{p - p^*} = k_L\ A\ t \tag{3}$$

Thus, k_L can be evaluated from the slope of a plot of $\ln [(p - p_o)/(p - p^*)]$ against t for a given operating oxygen pressure p. Such plots from the experimental data

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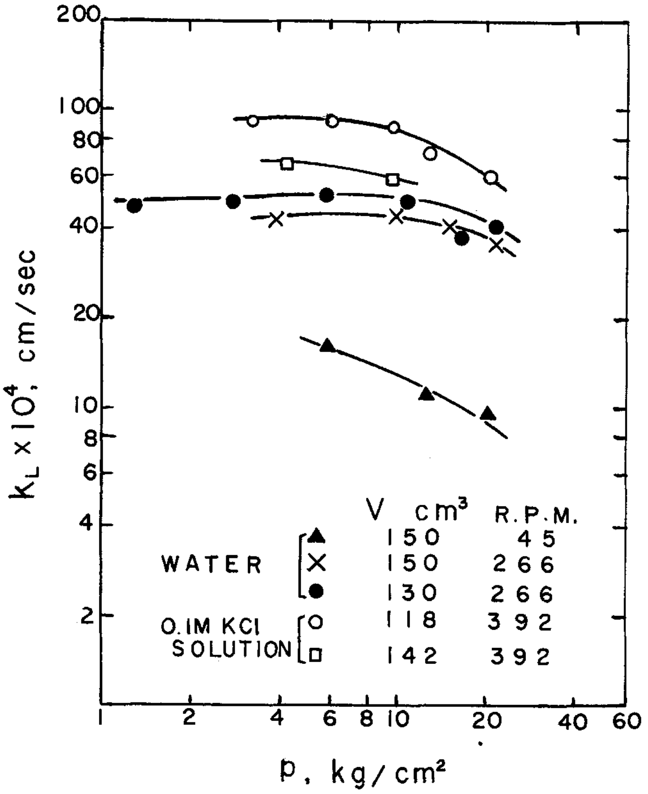

Fig. 1. Pressure dependence of k_L.

gave straight lines, indicating that k_L was constant throughout a single run.

Figure 1 shows the values of k_L which were obtained for absorption of oxygen into a water and 0.1 m. potassium chloride solution at 37.5°C. at three agitator speeds, plotted on logarithmic coordinates against the oxygen pressure. All these data indicate that at pressures above several atmospheres k_L decreases with increasing pressure.

What causes the effect of pressure on k_L is not obvious from the present experiments. The effect of pressure per se on liquid diffusivity is negligible at such moderate pressures used in the present work. Possibly the diffusivity of oxygen in the liquid phase varies with the oxygen concentration in the liquid, which in turn depends on the gas pressure. Another possibility is that the driving potential used in defining k_L may not be appropriate. However, it is more likely that pressure dependence of k_L is due to the change in the surface renewal rate, or in the degree of interfacial turbulence, which in turn could be accounted for by change in surface tension due to the gas pressure. The fact that the pressure effect is more pronounced at lower agitator speeds might support this supposition, see Figure 1. Although no data are available for the effect of pressure on the surface tension of the systems studied, data (*1*) on several gas-liquid systems indicate a variation of surface tension with gas pressure.

It might be mentioned that such pressure dependence of k_L was hardly observed in the physical absorption of oxygen into blood containing oxygen-saturated red blood cells, which was performed in the same vessel. In this case an antifoam agent was added to the blood, which probably changed the surface-tension characteristics of the system.

Such pressure dependence of k_L, as found in the present experiments, may be of practical significance. The aim here is to report the existence of such phenomena and not to clarify its mechanism. Further investigations, theoretical and experimental, are desired.

NOTATION

A = gas-liquid interfacial area, sq.cm.
c = concentration of oxygen in liquid, g.-moles/cc.
c^* = c in equilibrium with p, g.-moles/cc.
k_L = liquid phase mass transfer coefficient, cm./sec.
p = partial pressure of oxygen in gas phase, atm.
p^* = partial pressure of oxygen in equilibrium with c, atm.
t = time, sec.
V = liquid volume, cc.

Subscript

o = initial value

LITERATURE CITED

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Electrodialysis of Monocarboxylic Acid Salts

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In the applications of electrodialysis that have been summarized (*1*), most of the work has been directed toward desalinization and the renovation of municipal and industrial wastewaters for reuse. Little consideration has been given to the transport of organic ions across membranes, particularly short-chain organics whose dimensions would permit ready passage. Of particular interest in wastewater renovation are carboxylic acids, especially the short-chain acids such as formic, acetic, and propionic which are among the highest bio-oxidation products of most naturally occurring organic compounds before final conversion to carbon dioxide and water. In addition there is a need to define in general the behavior of organic compounds in an electrodialysis unit. Extensive theoretical and applied research has been carried out in the general area of membrane transport. Helfferich (*2*) has described transport by diffusion, convection, and electrical transference and has analyzed the effects of film control vs. membrane control. Coupling effects have been studied by Wills and Lightfoot (*3*), and new models of membrane transport have been developed by Kawabe, *et al.* (*4*). Some introductory work has been carried out on transport in a continuous-flow unit (*5*).

The objective of this investigation is to determine experimentally the electrodialytic transport through an

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