Starch Particles in Enhancement of Iodine Extraction

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Rate enhancement by a homogeneous reaction in the absorbing (or extracting) phase in gas-liquid absorption (or liquid-liquid extraction) is well documented (Sherwood and Pigford, 1952; Danckwerts, 1970). The effect of reactive discrete particles on the interfacial transfer rate, however, has received hardly any attention even though such reaction systems do widely exist and are quite important in chemical industry. Examples are gas absorption in heterogeneous catalytic oxidation or hydrogenation in slurry reactors, and oxygen absorption in industrial fermentation processes involving suspensions of discrete bacterial cells in nutrient solutions. Recent interest in hydrocarbon fermentations provides additional examples of liquid-liquid interfacial mass transfer with bacterial cells at the interface and also in the aqueous phase (Humphrey and Erickson, 1970).

The lack of a strong interest up to now in the effect of reactive small particles on interfacial mass transfer is perhaps due to a general misconception in that the gas-liquid-particle or the liquid-liquid-particle transfer systems can be analyzed as having two noninteracting sequential steps, that is, gas-liquid followed by liquid-particle in absorption and liquid-liquid followed by liquid-particle transfer in extraction. This is apparently the approach adopted in the book by Satterfield (1970) and numerous other publications. Even though the sequential analysis is perhaps adequate on many occasions, Tsao (1968, 1969, 1970) pointed out that when the particles are small and reactive, they can penetrate into and reside at gas-liquid and liquid-liquid interfaces and thus enhance the rate of mass transfer. In some cases, when the small particles are surface active and tend to be selectively concentrated at interfaces, their effect on rate enhancement can be even more extraordinary. The theoretical analysis of this rate enhancement was discussed by Tsao and coworkers (Tsao, 1968, 1969, 1970, 1972a; Schierholz et al., 1971) and the related experimental evidence in gas absorption was reported in a number of recent publications (Tsao 1968, 1972; Freeman et al., 1971; Lee and Tsao, 1972). The present note will provide the experimental evidence of rate enhancement by small particles (starch granules) in a liquid-liquid extraction (CCl_4/H_2O) of iodine.

The reaction between iodine and starch which yields a blue colored complex has been one of the oldest known reactions and ever since its discovery in 1812 has intrigued carbohydrate chemists for many years. The reaction has caused many controversial discussions, and even today its exact reaction mechanism remains unknown (Rundle and French, 1943; Mould, 1954; Thoma and French, 1960, 1961).

Starch is derived exclusively from plant sources (Whistler and Paschall, 1965-1967). It is a mixture of two types of homopolymers of alpha-D-glucose. Starch in its native state exists in the form of granules ranging from 0.5 to 100 microns in size. By a heat or an alkali treatment in water, starch granules will absorb large quantities of water and form starch pastes which are usually quite viscous.

In analytical chemical procedures, usually dilute starch solutions are used to form the blue complex with iodine. The reaction apparently can also proceed between iodine and insoluble starch granules. However, the presence of iodide ions is necessary and the general belief is that I_3^- ions rather than elementary iodine molecules actually participate in the complexing reaction with starch.

In the present experiment, the rate of iodine transfer from a carbon tetrachloride solution to a potassium iodide aqueous solution was measured with starch granules suspended in the aqueous phase. Because of the density difference (CCl_4—1.6 g/ml and granular starch—1.5 g/ml) and the highly hydrophilic property of starch, no granules were in the organic phase. The rate of iodine transfer was determined by detecting the change in its concentration in the aqueous solution. The two liquid phases were agitated separately by a magnetic stirrer and a stirrer driven by a motor rotating in counter directions to prevent vortex formation. The center portion of the interface was filled with a solid disk to prevent the formation of liquid droplets and ripples which were found in the preliminary runs without the disk. The KI concentration is an important parameter in this experiment and was kept constant throughout. The total iodine in water phase (free iodine plus iodine in starch) was titrated by iodometry.

The experimental conditions were as follows:

Initial iodine in CCl_4 = 3.15 g/liter
Volume of aqueous KI = 350 ml
Volume of CCl_4 = 500 ml
KI concentration in water = 2 g/liter
Reactor: 1000 ml beaker of 10 cm I.D. and with a 5 cm disk
Temperature = 25°C
Extraction interphase area = 59 cm^2
Starch used: Granular potato starch from Mallinckrodt, dried at 70°C for 48 hours before use
Agitator speed: 200 rev./min. (top, counterclockwise), 120 rev./min. (bottom, clockwise)

The flux of interfacial mass transfer is often expressed, as in Equation (1), in terms of aqueous phase concentrations.

$$Q = E\,K_w(m'C_o - C_w) \tag{1}$$

with

$$\frac{1}{K_w} = \frac{1}{k_w} + \frac{m'}{k_o} \tag{2}$$

Since the value of m' determined in the present study was only 0.1 or less, the third term in Equation (2) can be

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neglected. Furthermore, C_w was found to be nearly zero in all extraction runs. Thus, Equation (1) is simplified to the following:

$$Q = E\, k_w\, C^* \qquad (3)$$

where C^* is the aqueous side interface iodine concentration which is assumed in equilibrium with the bulk iodine concentration in the organic phase. Experimental extraction runs were conducted to determine iodine transfer rate when different amounts of granular starch were added in the aqueous phase with all other conditions held constant (see Figure 1). With k_w in Equation (3) determined in a physical extraction run (iodine extraction with no starch granules added), and assuming C^* unchanged by varying amounts of starch present, the enhancement factor E due to starch addition was determined and given in Figure 2. From the results, it seems obvious that the presence of the iodine-absorbing starch granules has enhanced the rate of iodine transfer from the organic phase to the aqueous phase.

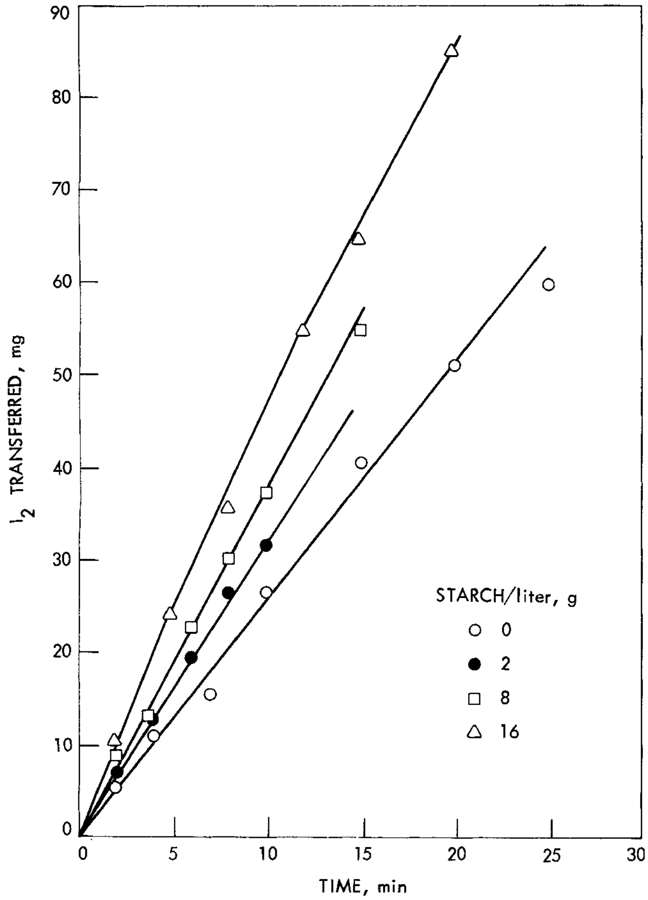

Fig. 1. Transfer of iodine from CCl_4 to aqueous KI at various starch levels in aqueous KI.

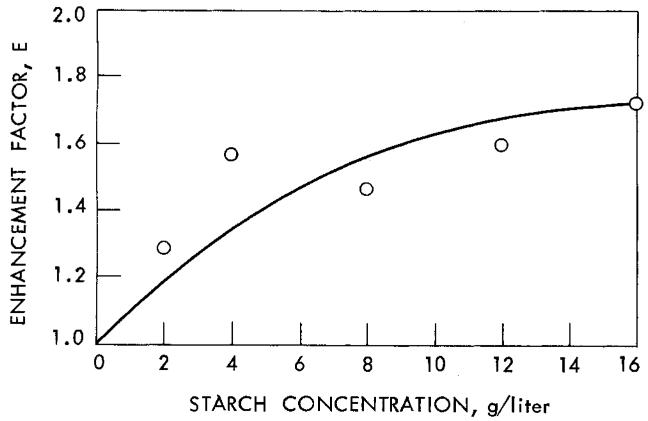

Fig. 2. Starch enhancement of iodine transfer.

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NOTATION

C_o = iodine concentration in organic phase
C_w = iodine concentration in aqueous solution
C^* = saturated iodine concentration in aqueous solution (in equilibrium with the organic phase)
E = enhancement factor
K_w = overall mass transfer coefficient based upon the concentration in the aqueous phase
k_o = mass transfer coefficient of the organic phase for the liquid-liquid interface
k_w = mass transfer coefficient of the aqueous phase for the liquid-liquid interface
m' = distribution coefficient of iodine in the aqueous phase and the organic phase
Q = mass transfer flux in liquid-liquid extraction

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