Mass-Transfer Coefficients for Monobasic Potassium Phosphate in Aqueous Solutions

J. G. Chung and George Thodos[1]
Northwestern University, Evanston, Ill. 60201

Mass-transfer coefficients for the transport of monobasic potassium orthophosphate (KH_2PO_4) through a stagnant film of water were established by use of a differential bed of Celite spheres originally saturated with the phosphate solution. The orthophosphate was leached from the surface of the spheres. Extrapolation of the resulting effluent concentration-time profiles to zero time permitted calculation of mass-transfer coefficients. Three sizes of spheres (d_p = 0.145, 0.329, and 0.376 in.) were used with water flow rates over the range $1.3 < Re < 40$. The ratio of mass-transfer coefficient to superficial mass velocity k_l/L, when plotted against the modified Reynolds number Re, produced a single relationship for the three sizes of spheres, which is consistent in behavior with the j vs. Re correlation available for the flow of fluids through packed beds.

Over the last 30 years, considerable experimental information associated with mass-transfer studies has been reported in the literature. The primary objective of these studies centered toward the procurement of experimental data needed for the establishment of mass-transfer correlations specific to gas–solid systems. An initial attempt to involve mass transfer across liquid films was reported in 1949 by Hobson and Thodos (*5*). These investigators utilized an initial rate approach to establish rates of mass transfer for the elution with water of methyl ethyl ketone and isobutyl alcohol from the surface of Celite spheres saturated with these organic compounds. The information derived from their studies pointed to the existence of a mass-transfer factor correlation common to both gas and liquid systems.

Gaffney and Drew (*4*) investigated for liquid systems the effect of the Schmidt number ranging from 150 to 1300. McCune and Wilhelm (*6*) dissolved in water 2-naphthol from the surface of modified spheres to obtain liquid film data in the range, $40 < Re < 5000$. Additional experimental information with liquid film studies has been reported by Dryden et al. (*2*), Evans and Gerald (*3*), Wilson and Geankoplis (*8*), and Williamson et al. (*7*).

Current interest in the utilization of solid adsorbents for the removal of phosphates in the tertiary treatment of waste water requires that information become available for the transport of phosphates across liquid water–solid interfaces. Information of this specific type is nonexistent, and it becomes highly speculative to obtain from available correlations whose development has been based exclusively on data derived from systems involving organic constituents that are not ionic in nature. Furthermore, most existing correlations require that the Schmidt group be available, and the lack of diffusion coefficient data for such inorganic constituents through liquid water limits the establishment of this group.

Experimental

The present investigation centered on the establishment of experimental data involving the transport of orthophosphate through aqueous liquid stagnant films. The experimental approach is basically the same as that outlined by Hobson and Thodos (*5*). This approach involved, in the present study, a differential bed of porous Celite spheres saturated with a phosphate solution. Celite was selected as the carrier since an experiment was performed by contacting Celite spheres with phosphate solution for 40 days without any noticeable decrease in phosphate concentration of the solution. Therefore, phosphate solution occupies the pores of the Celite spheres without any physical bonding. The phosphate solution was prepared by dissolving monobasic potassium phosphate (KH_2PO_4) in distilled water. Two standard solutions were prepared: one containing 0.2866 g KH_2PO_4/l., the other 7.165 g KH_2PO_4/l. These two stock solutions were used to prepare from them other concentrations by diluting aliquot samples with distilled water.

The phosphate concentration of the solutions used to saturate the Celite spheres varied from 716.5 to 2866 mg KH_2PO_4/l. To determine the concentration of these solutions, the colorimetric analysis prescribed by the American Public Health Association (*1*) was used. This method consists of the reaction between ammonium molybdate, $(NH_4)_3MoO_3$, and potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$, in the presence of orthophosphate solution and sulfuric acid to produce the phosphomolybdate ion, $PO_4 \cdot 12MoO_3{}^{3-}$. The addition of ascorbic acid produces the intensely colored "molybdenum blue" which can be accounted for by spectrophotometric measurements at 700 mμ. These measurements were made with a Universal spectrophotometer (Coleman Model 14).

Three sizes of Celite particles spherical in shape were used to prepare the necessary differential beds. These particles were 0.145, 0.329, and 0.376 in. in diameter, and the dry spheres were soaked overnight in a standard phosphate solution. Before preparing a differential bed with them, the excess solution was removed from their surfaces by rolling these soaked Celite particles on cheese cloth.

Each of the differential beds was accommodated in three different borosilicate glass tubes, each of which was provided with an inlet at the bottom. A thin Teflon ring, tightly fitted within each glass tube, provided a means for supporting a stainless-steel screen. This screen was fixed in position by another Teflon ring located above it and provided the space required for the differential bed reactor. The dimensions of the Teflon reactor rings were 0.745, 0.998, and 1.500 in. i.d. To obtain a representative effluent sample, the domed reactor section of Figure 1 accommodated the top of the differential bed. This section consisted of a Teflon ring which fixed in position a stainless-steel screen. The space immediately above this screen was filled with glass spheres to reduce the residence time of the effluent leaving the differential bed.

To maintain a constant head to the system, distilled water was pumped to a holding tank provided with an overflow port (Figure 2). The pumping was carried by a "Vibrostaltic" pump connected to the overflow and was recycled to the distilled water reservoir. This mode of oper-

---

[1] To whom correspondence should be addressed.

ation provided a constant liquid head to the system. The flow rate of distilled water leaving the bottom of the holding tank was regulated with a valve at the inlet of the rotameter located between the holding tank and the differential bed.

To minimize channeling and to approach packed-bed conditions, the Celite particles were at times dispersed in a matrix of plastic spheres of approximately the same dimensions. Samples leaving the reactor were collected and analyzed for phosphate content.

Interpretation of Data

Altogether 22 runs were made by use of each of the three Celite particle sizes of 0.145, 0.329, and 0.376 in. in diameter. A run was started by introducing at a constant rate, distilled water in the empty section of the reactor preceding the differential bed. The timing of a run was commenced when the water front contacted the bottom of the lower Teflon ring. When liquid effluent began to leave the unit, the time was again accounted for and represents the lag time used in extrapolating composition-time histograms. Thereafter, the time necessary to obtain approximately 30 cm^3 effluent samples was noted. This procedure usually produced five to six effluent samples which were later analyzed for phosphate content.

A typical effluent composition vs. time histogram is presented in Figure 3 for Run 30. A continuous relationship representing this histogram over its complete range permits the establishment of the instantaneous composition of the effluent leaving the sampling port at all times. Extrapolation of this relationship to the time when the effluent begins to leave the sampling port (ϑ = 15 sec) establishes the instantaneous composition of the effluent at that time. For this system, no axial dispersion contributions are present because the advancing front is represented by an air-liquid interphase. Therefore, for plug-flow conditions, the initial concentration of the effluent (ϑ = 15 sec) represents the concentration of the advancing liquid front leaving the differential bed at zero time. This concentration (c_0 = 6.25 ppm) now permits the calculation of the instantaneous rate of mass transfer and the driving force prevalent, at initial differential bed conditions of $\vartheta = 0$.

The initial phosphate concentration and the fact that at zero time, the concentration of phosphate on the surface of the solid is known, permit the establishment of not only a material balance, but also the proper initial driving force. This information was then used to calculate mass-transfer coefficients for the transport of monobasic potassium phosphate through the stagnant film of water surrounding the spheres. By use of the relationship:

$$r = k_l aV(c_s - c)_m \qquad (1)$$

In Equation 1 the product aV represents the surface area of the spheres; r, the rate of mass transfer, lb-mol KH_2PO_4/hr; and c, the concentration of phosphate, lb-mol KH_2PO_4/ft^3 of solution. By use of these dimensions for r, aV, and c, values for the mass-transfer coefficient k_l were calculated and are summarized in Table I along with other pertinent information associated with each run. The dependence of k_l on L, the superficial liquid mass velocity, is presented in Figure 4 for each of the three sizes of Celite spheres. The linear relationships of Figure 4 are parallel and have a slope of 0.32. Furthermore, the values of the liquid mass-transfer coefficient, for the transport of this phosphate, range from 0.0073 to 0.0385 lb-mol/hr ft^2 (lb-mol/ft^3). In similar studies reported in 1949 by Hobson and Thodos (5) for the transport of methyl ethyl ketone into water, mass-transfer coefficients

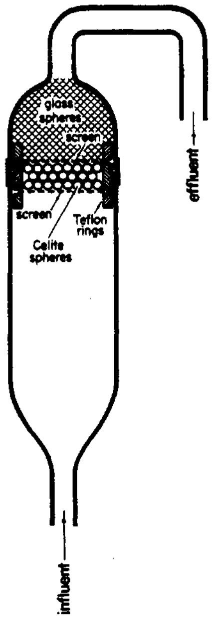

Figure 1. Schematic diagram of differential bed reactor

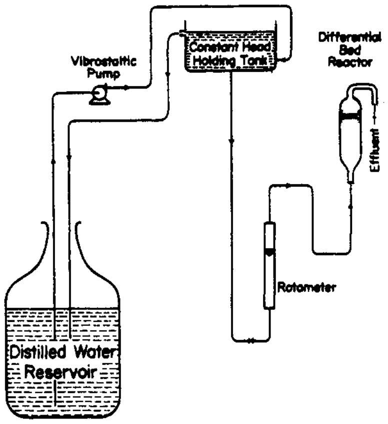

Figure 2. Schematic diagram of experimental unit

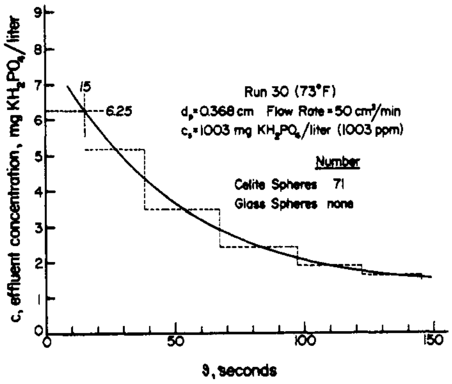

Figure 3. Effluent phosphate concentration-time relationship for Run 30

Table I. Mass-Transfer Data and Derived Quantities for Transport of Monobasic Potassium Phosphate into Water

Run	Reactor, in.		t, °F	No. of spheres		aV, ft^2	Flow rate, cm^3/min	L, lb/hr ft^2	c, mg KH_2PO_4/l.		$\Delta c = (c_s - c)$, lb-mol KH_2PO_4/ft^3	r, lb-mol KH_2PO_4/hr	k_l $r/aV\Delta c$	k_l/L	Re, D_pL/μ
	Diam	Ht		Celite	Inert				Surface	Outlet					
$d_p = 0.145$ in.															
38	0.998	0.26	73.4	71	0	0.03251	10	243	1433	26	651 × 10^{-6}	0.254 × 10^{-6}	0.0120	4.928 × 10^{-5}	1.29
43	0.745	0.46	75.3	71	0	0.03251	8.2	357	2149	55	974	0.435	0.0137	3.842	1.95
41	0.745	0.46	77.1	71	0	0.03251	10	436	1433	33	650	0.320	0.0152	3.480	2.44
33	0.998	0.26	69.1	71	0	0.03251	25	608	1433	15	654	0.369	0.0174	2.857	3.06
44	0.745	0.46	73.4	71	0	0.03251	18.5	806	1433	22	652	0.397	0.0187	2.320	4.30
30	0.998	0.26	73.0	71	0	0.03251	50	1215	1003	6	459	0.304	0.0204	1.676	6.44
45	0.745	0.46	67.8	71	0	0.03251	39	1701	2866	27	1308	1.032	0.0243	1.426	8.42
35	0.998	0.26	67.3	71	0	0.03251	100	2431	716	3	328	0.297	0.0278	1.144	11.95
51	0.745	0.46	72.5	71	0	0.03251	78.3	3413	2866	17	1311	1.265	0.0297	0.870	17.99
47	0.745	0.46	73.0	71	0	0.03251	119	5187	2866	13	1312	1.459	0.0342	0.659	27.52
$d_p = 0.329$ in.															
56	0.998	0.63	73.0	14	0	0.03301	7	170	2866	46	1304	0.315	0.0073	4.302	2.05
42	0.998	0.63	74.6	14	0	0.03301	15	364	1003	8	458	0.120	0.0079	2.180	4.48
54	0.998	0.63	73.6	14	0	0.03301	33	802	2866	14	1311	0.464	0.0107	1.338	9.73
50	0.998	0.63	72.0	14	0	0.03301	70	1701	2866	9	1313	0.600	0.0138	0.814	20.21
49	0.998	0.63	69.4	14	0	0.03301	143	3475	2866	6	1313	0.777	0.0179	0.516	39.90
$d_p = 0.376$ in.															
61	1.500	0.42	76.5	15	15	0.04626	23.6	254	2866	16	1311	0.378	0.0062	2.457	3.65
58	1.500	0.42	76.2	15	15	0.04626	37.8	406	2866	11	1312	0.411	0.0068	1.665	5.83
57	1.500	0.42	75.2	15	15	0.04626	66	710	2866	9	1313	0.561	0.0092	1.301	10.05
52	1.500	0.85	76.0	30	0	0.09252	125	1344	2866	11	1312	1.367	0.0113	0.838	19.23
55	1.500	0.85	72.8	30	0	0.09252	125	1344	2866	11	1312	1.393	0.0115	0.854	18.46
62	1.500	0.42	76.5	15	15	0.04626	214	2300	2866	4	1314	0.835	0.0137	0.597	33.12
60	1.500	0.42	76.0	15	15	0.04626	216.6	2328	2866	4	1314	0.935	0.0154	0.661	33.31

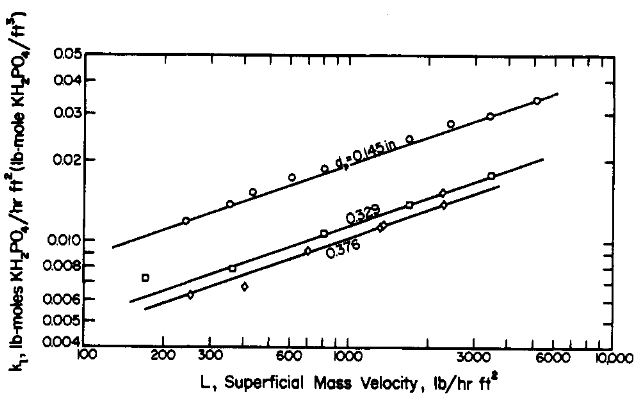

Figure 4. Relationships between k_l and L for each of the three sizes of Celite spheres

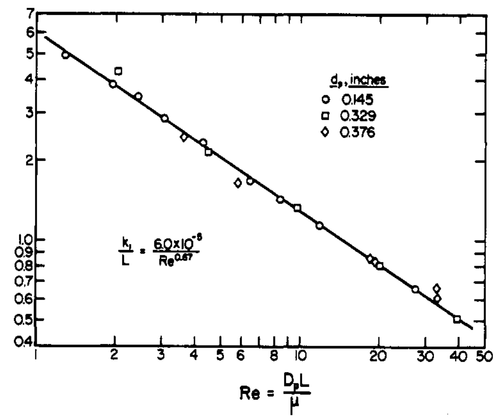

Figure 5. Relationship of k_l/L vs. Re resulting from experimental data of the three sizes of Celite spheres

are presented which range from 0.0849 to 0.149 lb-mol/hr ft² (lb-mol/ft³).

To present the information of Figure 4 in a more generalized manner, the j-factor approach has been adopted for the analysis of the present data. Since the j-factor

$$j = \frac{k_l c_{lf}}{L/M} \left(\frac{\mu}{\rho D_l}\right)^{2/3}_{\text{film}} \tag{2}$$

is a function of the modified Reynolds number, D_pL/μ, it follows that the ratio k_l/L must be uniquely defined in terms of this parameter. Values of k_l/L have been plotted against D_pL/μ in Figure 5 for the three sizes of spheres to produce the single relationship presented in this figure. This relationship can be expressed in equation form as

$$\frac{k_l}{L} = \frac{6.0 \times 10^{-5}}{Re^{0.67}} \tag{3}$$

and covers the range included between Re = 1.3 and Re = 40. The slope of this relationship is consistent with the j vs. Re correlation obtained by Wilson and Geankoplis (*8*) for the water washability leaching studies of spherical particles of benzoic acid.

No attempt is made to establish j-factors for the runs of this study because of the lack of information associated with the diffusion coefficient for this phosphate system. This diffusion coefficient must be known with a good degree of accuracy to calculate for this system a reliable value for the Schmidt group. It would prove somewhat speculative at this time to back calculate such a value from existing j vs. Re relationships and particularly since this system involves the transport of molecules involving ionic bonds. Consequently, no attempt is made at this time to generalize the behavior of this system; this attempt should be made when completely independent information for the diffusion coefficient is made available. Therefore, the relationship of Figure 5 becomes specific to the transport of monobasic potassium phosphate through a stagnant film of water. When experimental liquid diffusivities for this system become available, then the information of Figure 5 can be translated to j-factor values. At that time, a comparison can be made between the j-factor plot resulting from the experimental values of this study and those of already existing correlations available in the literature (*5, 7, 8*).

Nomenclature

a = transfer area/unit volume, ft²/ft³
c = phosphate concentration in solution, lb-mol KH_2PO_4/ft³
c_0 = initial phosphate concentration leaving differential bed, lb-mol KH_2PO_4/ft³
c_{lf} = concentration of nontransferable component, lb-mol/ft³
c_s = phosphate concentration at solid surface, lb-mol KH_2PO_4/ft³
d_p = diameter of particle, in.
D_p = diameter of particle, ft
D_l = liquid-diffusion coefficient of system, ft²/hr
j = mass-transfer factor, dimensionless
k_l = mass-transfer coefficient for liquid film, lb-mol KH_2PO_4/hr ft² (lb-mol KH_2PO_4/ft³)
L = superficial mass velocity, lb/hr ft²
M = molecular weight of flowing liquid
r = rate of mass transfer, lb-mol KH_2PO_4/hr
Re = modified Reynolds number, D_pL/μ
V = reactor volume, ft³

Greek Letters

ϑ = time, sec
μ = absolute viscosity, lb/hr ft
ρ = density, lb/ft³

Literature Cited

(1) American Public Health Association, "Standard Methods for the Examination of Water and Wastewater," 12th ed., New York, N.Y., 1965.
(2) Dryden, C. E., Strand, D. A., Withrow, A. E., *Chem. Eng. Progr.*, **49**, 191 (1953).
(3) Evans, G. C., Gerald, C. F., *ibid.*, p 135.
(4) Gaffney, B. J., Drew, T. B., *Ind. Eng. Chem.*, **42**, 1120 (1950).
(5) Hobson, M., Thodos, G., *Chem. Eng. Progr.*, **45**, 517 (1949).
(6) McCune, L. K., Wilhelm, R. H., *Ind. Eng. Chem.*, **41**, 1124 (1949).
(7) Williamson, J. E., Bazaire, K. E., Geankoplis, C. J., *Ind. Eng. Chem. Fundam.*, **2**, 126 (1963).
(8) Wilson, E. J., Geankoplis, C. J., *ibid.*, **5**, 9 (1966).

Received for review July 19, 1972. Accepted March 19, 1973.