In these calculations, we assumed the virial equation of state

$$Z^{V} = 1 + BP$$
, where $B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}$ (18)

for the vapor phase, and

$$v^L = x_1 v_1^L + x_2 v_2^L (19)$$

for the liquid phase. The P-x data were correlated with polynomials or spline fits as shown in Table 1.

In each of the four cases, convergence was sensitive to the value of pk (the convergence parameter) and to the nature of the P-x equation chosen to fit the data. However, after several trials, each case was satisfactorily solved. The results for the chloroform-ethanol system are shown in Figure 1.

ACKNOWLEDGMENT

Computational services were provided by the Department of Chemical Engineering at the University of Missouri-Rolla. Financial support for the research was provided by the Petroleum Research fund, administered by the American Chemical Society and by the Department of Chemical Engineering at the University of Missouri-Rolla.

NOTATION

 $a = \text{increment for } \alpha$

B = second virial coefficient

f = fugacity

F = function of α and x

P = pressure

pk = convergence parameter

v = specific volume

x = liquid mole fraction of component 1
 y = vapor mole fraction of component 1

Z = compressibility factor α = relative volatility

δ = binary interaction parameter

 ϕ = fugacity coefficient

Subscripts

i, j = component, grid point

Superscripts

L = liquid phase n = iteration V = vapor phase

LITERATURE CITED

Abbott, M. M., J. K. Floess, G. E. Walsh, and H. C. Van Ness, "Vapor-Liquid Equilibrium: Part IV, Reduction of P-X Data for Ternary Systems," AIChE J., 21, 72 (1975).

Abbott, M. M., and H. C. Van Ness, "Vapor-Liquid Equilibrium: Part III, Data Reduction with Precise Expression for GE," *ibid.*, 62 (1975).

Bruce, G. H., D. W. Peaceman, H. H. Rachford, and J. D. Rice, "Calculations of Unsteady-State Gas Flow Through Porous Media," *Trans. Am. Inst. Min. Met. Petrol. Engrs.*, 198, 79 (1953).

Ljunglin, J. J., and H. C. Van Ness, "Calculation of Vapor-Liquid Equilibria from Vapor Pressure Data," Chem. Eng. Sci., 17, 531 (1962).

Mixon, F. O., B. Gumowshi, and B. H. Carpenter, "Computation of Vapor-Liquid Equilibrium Data from Solution Vapor Pressure Measurements," Ind. Eng. Chem. Fundamentals, 4, 455 (1965).

Nagata, I. and T. Ohta, "Computation of Vapor-Liquid Equilibrium Data from Binary and Ternary Vapor Pressure and Boiling Point Measurements," Ind. Eng. Chem. Process. Design Develop., 13, 304 (1974).

Scatchard, G., and C. L. Raymond, "Vapor Liquid Equilibrium, II, Chloroform-Ethanol Mixtures at 35, 45, and 55°," J. Am. Chem. Soc., 60, 1278 (1938).

Van Ness, H. C., "On Integration of the Coexistence Equation for Binary Vapor-Liquid Equilibrium," AIChE J., 16, 18 (1970).

White, N., and F. Lawson, "The Integration of the Gibbs-Duhem Equation for a Binary Two Phase System at Constant Temperature," Chem. Eng. Sci., 25, 225 (1970).

Manuscript received November 23, 1976, and accepted January 14, 1977.

Light Transmission Through Bubble Swarms

M. J. LOCKETT

and

A. A. SAFEKOURDI

Department of Chemical Engineering
University of Manchester Institute
of Science and Technology
Manchester 1, England

The equation which applies is

$$\log_{10}\left(\frac{I_o}{I}\right) = \frac{Kal}{9.21} \tag{1}$$

Equation (1) holds when scattered light is not received by the detector, and K is approximately unity for particles having $d>100~\mu\mathrm{m}$.

Experimental verification of the equation for gas-liquid systems has apparently been confined to low values of gas holdup, and reported holdups are less than 7% (Calderbank, 1958). This is probably because it is difficult to generate bubble swarms of well-defined properties at gas holdups much above 7%. Even for solid-liquid and liquid-liquid dispersions, however, Equation (1) has

Light transmission is a well-developed technique for determining particle size in dispersions (Rose and Lloyd, 1946; Boll and Sliepcevich, 1956; Dobbins and Jizmagian, 1966), and it has often been adopted for measurement of interfacial area in liquid-liquid and gas-liquid dispersions (Calderbank, 1958; Lee and Ssali, 1971; Trice and Rodger, 1956). The theory for the attenuation of the light beam has been given by a number of workers (Rose and Lloyd, 1946; Calderbank, 1958). Mclaughlin and Rushton (1973) have recently published a numerical confirmation of the theory for polydisperse systems, and the same result has been obtained more simply by Curl (1974).

A. A. Safekourdi is at Arya-Mehr University, P.O. Box 3406, Tehran,

apparently not been tested over a wide range of dispersed phase holdup. The theory leading to Equation (1) indicates that it should be independent of dispersed phase holdup, and it was one of the objectives of the work reported in the present communication to test this for gas-liquid systems.

For bubble swarms having a high gas holdup, the light reaching the detector by direct transmission is negligible compared with that which has undergone multiple scattering. In this case, we show that Equation (1) does not hold, and a linear relationship is demonstrated between interfacial area and the reciprocal of the received light.

Finally, in apparent contradiction to Equation (1), Abdel-aal et al. (1966) carried out experiments with bubbles in which they took care to exclude scattered light from the detector and they found a relationship of the form

$$a' = m\left(1 - \frac{I}{I_o}\right) \tag{2}$$

where m depended on the physical properties of the system. A further objective of this communication is to attempt to reconcile Abdel-aal's results with previous work.

EXPERIMENTAL PROCEDURE

The main feature of the equipment was an inverted glass rotameter tube of nominal diameter 76 mm into which bubbles were introduced at the base through a single formation tube. Water was allowed to flow down the tube, and its velocity was adjusted so that the bubbles were just prevented from rising. The water velocity profile was flattened before entry to the rotameter to overcome any tendency of the bubbles to rise preferentially at the wall. The apparatus and procedure have been fully described elsewhere (Kirkpatrick and Lockett, 1974; Lockett and Kirkpatrick, 1975).

The novelty of the technique was that swarms of uniform bubbles having gas holdups as high as 55% could be maintained. It is not possible to achieve these holdups by bubbling gases through stagnant liquids unless either the bubbles coalesce to form a proportion of large rapidly rising bubbles or unless a cellular foam is formed. Using the present technique, no bubble coalescence or foaming occurred (Kirkpatrick and Lockett, 1974).

A low air flow rate (100 mm³/s) was used in the formation tube (internal diameter 3.2 mm) so that the bubbles formed under surface tension controlled conditions, and consequently they were of uniform size. The bubble size was determined by collapsing the swarm containing a known number of bubbles (up to 1500) and collecting the air at the top of the apparatus. The average bubble diameter was corrected for hydrostatic head and was found to lie in the range 4.96 to 5.09 mm with an average diameter of 5.02 mm. At low gas holdups, bubble size could be checked from photographs, and it agreed closely with the above values. Gas holdup was determined by measuring the attenuation of a collimated beam of γ rays (Lockett and Kirkpatrick, 1975).

The light transmission system consisted of a 50 W bulb operated at 16 W, a plano-convex lens of focal length 175 mm placed between the light source and the column to produce a parallel incident beam, and a calibrated 20 mm diameter selenium photocell. The output from the photocell was smoothed and recorded on a chart recorder. The photocell was located 0.5 m from the glass column, and the light paths were enclosed in

matt black paper tubes to reduce the scattered light reaching the detector to a low level. It is not possible to completely exclude scattered light from the detector (Boll and Sliepcevich, 1956; Lothian and Chappel, 1951), and it is generally considered sufficient to ensure that the half angle subtended by the detector at the dispersion is less than about 1.4 deg. In this work the half angle was 1.15 deg.

In order to counteract the focusing effect of the curved glass tube wall, a clear plastic box, cross section 130×130 mm, was constructed around the glass column, and the space between it and the column was filled with water.

EXPERIMENTAL RESULTS

For spherical bubbles of uniform size, we have

$$a = \frac{6\epsilon}{d} \tag{3}$$

From the measured gas holdup and bubble diameter, the interfacial area was determined using Equation (3). The optical path length l through the two-phase dispersion on the axis of the beam was 0.072 m. The experimental results obtained in the present work are shown in Figure 1.

DISCUSSION

The results shown in Figure 1 clearly fall into two distinct parts. Equation (1) is valid with K=1.08 for al<26.5, where the light received by the detector after multiple scattering is negligible compared with directly transmitted light. As al varied from 0 to 26.5, gas holdup varied from 0 to 31%, so that Equation (1) is verified over a wide range of gas holdup.

For bubble swarms having al > 28, the directly transmitted light is negligible, and the light received by the detector arises from multiple scattering. Clark and Blackman (1948) have proposed a theory which predicts a linear relationship between the reciprocal of the light received and the interfacial area for the case where multiple scattering predominates. Figure 2 demonstrates that the present results are in reasonable agreement with such a prediction. There is, however, some considerable scatter at these very low light intensities. The line shown is fitted by least squares for al > 27. Other workers who have measured both multiply scattered and directly transmitted light have also found a similar relationship (Clark and Blackman, 1948; Langlois et al., 1954). However, these workers made no attempt to limit the amount of scattered light received by the detector, so that they

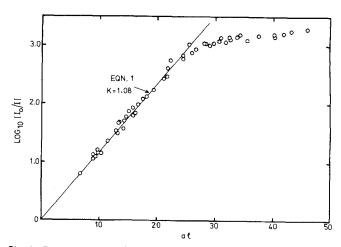


Fig. 1. Experimental results for light received by detector as a function of interfacial area.

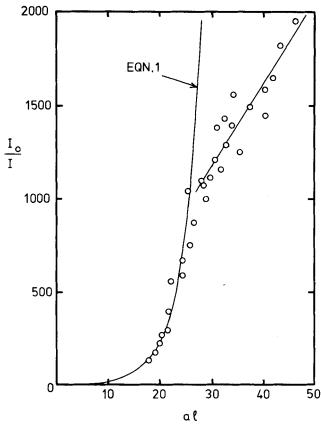


Fig. 2. Experimental results for light received by detector as a function of interfacial area showing linear relationship between $I_{
m o}/I$ and al at high interfacial areas.

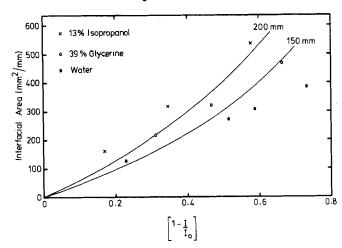


Fig. 3. Abdel-aal et al. results for interfacial area as a function of one minus intensity ratio ($I/I_{
m o}$). Curves are derived from Equation (1) for l = 150 and 200 mm.

found a linear relationship between I_o/I and a over the whole range of their results, and there was no region where Equation (1) applied.

It remains to consider Abdel-aal's (1966) results which led to Equation (2), even though multiply scattered light was excluded from the detector. Abdel-aal's data are reproduced in Figure 3. Also shown in Figure 3 is the relationship given by Equation (1) for optical path lengths l of 0.015 and 0.02 m. The optical path length was not recorded in the original work, and, as a stream of bubbles was used issuing from four closely grouped orifices, it is clear that I was not precisely defined. The interfacial area was altered by varying the air flow rate so that it is probable that l also varied during Abdel-aal's experiments. The estimated values of 0.015 and 0.02 m

are typical values of the diameter of the bubble swarm which were obtained by the present authors by blowing air through a single orifice at the flow rates used by Abdel-aal. In using Equation (1) in Figure 3, it is assumed that all the bubbles in Abdel-aal's experiments were contained within a cylindrical stream of diameter either 0.015 or 0.02 m.

Although the general trend of Abdel-aal's results follows the prediction of Equation (1), the results are clearly much better fitted by straight lines. The diameter of the bubble swarm would be expected to increase as interfacial area was increased by increasing the gas flow rate, so Abdel-aal's results show a greater change in the attenuation of the light beam with interfacial area than is predicted by Equation (1). It is difficult to make a proper comparison because of the lack of information about l. It is concluded that Abdel-aal's results and Equation (2) are specific to the particular apparatus which was used.

CONCLUSIONS

Equation (1) has been verified for gas bubbles in water over a wide range of gas holdup from 0 to 31%. When directly transmitted light is negligible compared with multiply scattered light, a linear relationship has been demonstrated between the reciprocal of the light received by the detector and interfacial area. Abdel-aal's results are apparently specific to his apparatus and are only roughly in agreement with Equation (1).

NOTATION

= interfacial area per unit volume of dispersion

a' = interfacial area per unit of column height (m)

d = bubble diameter (m)

Ι = intensity of light received by detector

= intensity of incident light I,

K = constant

= optical path length through the dispersion (m)

m

= gas holdup or volume of gas per unit volume of system

LITERATURE CITED

Abdel-aal, H. K., G. B. Stiles, and C. D. Holland, "Formation of Interfacial Area at High Rates of Gas Flow Through Sub-

merged Orifices," AIChE J., 12, 174 (1966).
Boll, R. H., and C. M. Sliepcevich, "Evaluation of Errors of Optical Origin Arising in the Size Analysis of a Dispersion by Light Transmission," J. Opt. Soc. Am., 46, 200 (1956).

Calderbank, P. H., "Physical Rate Processes in Industrial Fer-mentation, Part I: The Interfacial Area in Gas-Liquid Contacting with Mechanical Agitation," Trans. Inst. Chem. Engrs., 36, 443 (1958)

Clark, N. O., and M. Blackman, "The Transmission of Light Through Foam," Trans. Faraday Soc., 44, 7 (1948).

Curl, R. L., "Note on Light Transmission through a Polydisperse Dispersion," AIChE J., 20, 184 (1974).
Dobbins, R. A., and G. S. Jizmagian, "Optical Scattering Cross

Sections for Polydispersions of Dielectric Spheres," J. Opt. Soc. Am., **56**, 1345 (1966).

Kirkpatrick, R. D., and M. J. Lockett, "The Influence of Approach Velocity on Bubble Coalescence," Chem. Eng. Sci., 29, 2363 (1974).

Langlois, G. E., J. E. Gullberg, and T. Vermeulen, "Determination of Interfacial Area in Unstable Emulsions by Light Transmission," Rev. Sci. Instr., 25, 360 (1954). Lee, J. C., and G. W. K. Ssali, "Bubble Transport and Coales-

cence in a Vertical Pipe," Joint Meeting on Bubbles and

Foams, Sl-6.1, Verfahrenstechnische Gesellschaft im VDI-

Inst. Chem. Engrs., Nürnberg (1971).

Lockett, M. J., and R. D. Kirkpatrick, "Ideal Bubbly Flow and Actual Flow in Bubble Columns," Trans. Inst. Chem. Engrs.,

Lothian, G. F., and F. P. Chappel, "The Transmission of Light Through Suspensions," J. Appl. Chem., 1, 475 (1951).

Mclaughlin, C. M., and J. H. Rushton, "Interfacial Areas of Liquid-Liquid Dispersions from Light Transmission Measurements," AIChE J., 19, 817 (1973).

Rose, H. E., and H. B. Lloyd, "On the Measurement of the Size Characteristics of Powders by Photo-Extinction Methods I. Theoretical Considerations," J. Soc. Chem. Ind., 65, 52 (1946).

Trice, V. G., and W. A. Rodger, "Light Transmittance as a Measure of Interfacial Area in Liquid-Liquid Dispersions,' AIChE J., 2, 205 (1956).

Manuscript received September 16, 1976; revision received January 14, and accepted January 24, 1977.

A Method for the Study of Interphase Mass Transfer at Very Low Reynolds Numbers in Packed Beds

LAWRENCE T. NOVAK

Department of Chemical Engineering The Cleveland State University Cleveland, Ohio

The purpose of this note is to discuss a methodology for studying interphase mass transfer in packed beds at very low Reynolds numbers ($< 10^{-3}$). Reynolds numbers in this region usually occur in fluid-solid systems consisting of very small particles. Such systems are often referred to as porous media rather than packed beds. Another type of porous media or packed bed is a soil. It has been demonstrated by Novak (1976) that a Reynolds number of 10⁻³ would likely be an upper bound for gravity flow through soils. And so mass transfer at very low Reynolds numbers may be of importance in endeavors such as agricultural production and mineral extraction.

Very little data on interphase mass transfer exist in the very low Reynolds number region. However, a fair amount of experimental and theoretical work has been carried out in the low Reynolds number region (10^{-3} to 50). The major characteristic of that work has been the scatter in experimental data, the disagreement over the limiting value (if any) of the Sherwood number, and the lack of agreement on the form of the Sherwood number correlation. These characteristics have been discussed in an earlier paper (Novak, 1976).

The effect of solute diffusion has been incorporated into mass transfer models for nonadsorbable solutes (Miyauchi et al., 1976) and for adsorbable solutes (Shah et al., 1975; Novak et al., 1975) at low and very low Reynolds numbers. The model discussed below provides the foundation of a methodology for studying interphase mass transfer in packed beds at very low Reynolds numbers.

THEORY

When we deal with adsorbable solutes, the ideal system for studying the fluid film mass transfer phenomenon would consist of strictly nonporous solid particles which could reversibly adsorb a solute. Since porous solids may also be of interest, a model will be presented for the general case where the resistance to mass transfer occurs in both the fluid and the solid phases.

Two formulations are possible, depending on which driving force is used. The following solute material balances and the equilibrium relationships are given in dimensionless form with variables defined in the notation section:

Liquid phase driving force model (LPDF)

$$\frac{\partial Y}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 Y}{\partial \xi^2} - \frac{\partial Y}{\partial \xi} - \frac{St_L}{\epsilon} (Y - Y^{\circ})$$
 (1)

$$\frac{\partial X}{\partial \tau} = \frac{St_L}{N} \left(\frac{\rho_L}{\rho_p(1 - \epsilon)} \right) (Y - Y^{\circ}) \tag{2}$$

$$Y^{\circ} = \frac{X}{1 + A(1 - X)} \tag{3}$$

Solid phase driving force model (SPDF)

$$\frac{\partial Y}{\partial \tau} = \frac{1}{Pe} \frac{\partial^2 Y}{\partial \xi^2} - \frac{\partial Y}{\partial \xi} - \frac{St_s}{\epsilon} \left(\frac{\rho_p}{\rho_L}\right) N(X^* - X) \tag{4}$$

$$\frac{\partial X}{\partial \tau} = \frac{St_s}{1 - \epsilon} \quad (X^{\bullet} - X) \tag{5}$$

$$X^* = \frac{(1+A)Y}{1+AY} \tag{6}$$

Deviations from ideal plug flow are incorporated in the Peclet number term. At very low Reynolds numbers, the Peclet number would also be low (Pe < 1) for both gases and liquids. In this situation, the Peclet number would largely represent the effect of hindered solute diffusion in the fluid phase. This fact has been demonstrated by flow experiments using tracers (Miyauchi and Kikuchi, 1975).

The equilibrium relationships represented in Equations (3) and (6) are dimensionless forms of the Langmuir adsorption isotherm. For solutes that are very weakly adsorbed and/or present in very dilute concentrations, the dimensionless variable A would approach zero. This would result in a linear equilibrium relationship.

The Stanton numbers contain the overall mass transfer coefficients. By analogy with the two-film theory which has been applied to fluid-fluid interfacial mass transfer, the overall mass transfer coefficients can be related to the individual film coefficients.