



Fig. 1. Comparison of experimental and predicted diffusivities for water as solute and as solvent.

then the mass action constant for the reaction must be large to account for the invariance of polymer to monomer ratio with water concentration, as suggested by the constancy of the factor 2.3. However if diffusion experiments were conducted in sufficiently dilute

water systems, then according to this explanation, the observed diffusion coefficients should approach those predicted by Equation (1).

It should be noted that the molar-volume ratio of four need not restrict the nature of the associated species to

that indicated by Equation (2). It is more likely that there exist polymers containing a variable number of single molecules, with an average chain length of four units. In this case the near-integer value of the molar-volume ratio is fortuitous.

#### NOTATION

- $D$  = diffusion coefficient, sq. cm. sec.  
 $M$  = molecular weight of solvent  
 $T$  = temperature, °K.  
 $V$  = molar volume of solute at its normal boiling point  
 $x$  = association parameter for the solvent  
 $\mu$  = viscosity of the solution, centipoises

#### LITERATURE CITED

1. Anderson, D. K., J. R. Hall, and A. L. Babb, *J. Phys. Chem.*, **62**, 404 (1958).
2. Glasstone, Samuel, K. J. Laidler, and Henry Eyring, "Theory of Rate Processes," McGraw-Hill, New York (1941).
3. Hufstelder, R. S., Sc.D. thesis, Colo. School of Mines, Boulder (1958).
4. Lemonde, H., *Ann. Phys.*, **9**, 539 (1938).
5. Lewis, J. B., *J. App. Chem. (London)*, **5**, 228 (1955).
6. Randall, M., B. Longtin, and H. Weber, *J. Phys. Chem.*, **45**, 343 (1941).
7. Scheibel, E. G., *Ind. Eng. Chem.*, **46**, 2007 (1954).
8. Sherwood, T. K., and R. C. Reid, "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
9. Thakar, N. S., and D. F. Othmer, *Ind. Eng. Chem.*, **45**, 589 (1953).
10. Wilke, C. R., and Pin Chang, *A.I.Ch.E. Journal*, **1**, 264 (1955).

## The Ratio of Fluids to Solid Temperature and/or Concentration in Fixed-Bed Processes

ADRIAAN KLINKENBERG

Bataafse Internationale Petroleum Maatschappij N. V.  
 (Royal Dutch/Shell Group), The Hague

The following is a comment on the communication by H. E. Hoelscher (1).

The temperature difference in a bed initially at zero temperature and heated by a gas at unit inlet temperature is given by

$$T_f - T_s = e^{-x-y} I_0(2\sqrt{xy})$$

where  $x$  and  $y$  are dimensionless place and time coordinates as defined by Hoelscher [see for instance (2), Equation (5)].

Or if use is made of a well-known expansion for the Bessel function  $I_0$  [see for instance (2), Equation (17)]

$$T_f - T_s = \frac{e^{-(\sqrt{y}-\sqrt{x})^2}}{2\pi^{1/2}(xy)^{1/4}} \left( 1 + \frac{1}{16\sqrt{xy}} + \frac{9}{512xy} + \dots \right)$$

This function is very near maximum for  $y = x$ , at the mid-point of breakthrough, when

$$T_f - T_s = \frac{1}{2\sqrt{\pi x}} \left( 1 + \frac{1}{16x} + \dots \right)$$

It is felt that the approach to the above problem via heat transfer theory (linear isotherms) is simpler than via

adsorption theory (Langmuir isotherms). A survey of the heat transfer literature for the step-function input has been given by Klinkenberg (2), while Klinkenberg and Harmens (3) have recently dealt with the generalized problems of arbitrary initial solid and gas temperatures.

#### LITERATURE CITED

1. Hoelscher, H. E., *A.I.Ch.E. Journal*, **5**, 410 (1959).
2. Klinkenberg, A., *Ind. Eng. Chem.*, **46**, 2285 (1954).
3. ———, and A. Harmens, *Chem. Eng. Sci.*, **11**, 260 (1960).