Diffusion in Slurries and in Non-Newtonian Fluids

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Diffusivities in slurries and in non-Newtonian solutions are predicted by means of an extension of the general Eyring rate theory. The fluid is considered as consisting of a number of discrete regions, each with its own contribution to the overall diffusion process. This model overcomes the unrealistic effects of fluid viscosity predicted by the conventional (empirical) equations. Whereas diffusivities predicted by means of prior art correlations were as much as 230 times lower than the experimental values in the systems, the maximum error in diffusivities predicted with the equations developed in this work was about 40%.

Experimental data are provided on two kinds of fluids: slurries and a polymer solution. Both were highly non-Newtonian (flow behavior indexes as low at 0.15). Benzoic acid and β-napthol were employed as the diffusing solutes. The principal limitation of the experimental data is that only aqueous systems were investigated.

Much further experimental work will be required to provide a truly adequate test of the theory and to evaluate the several unknown parameters in sufficient detail to enable highly accurate predictions. Additionally the model used suggests a possible mechanism for increasing diffusion rates in these systems which is worthy of exploration. It may also be applied to an analysis and prediction of diffusion rates in viscous Newtonian fluids, for which no adequate method is presently available.

In spite of the fact that many processes in which polymers or slurries are handled involve mass transfer, in addition to heat and momentum transfer, the latter problems have been studied almost to the exclusion of the former. For example changes in molecular alignment which occur under the influence of changes in shear rate have marked effects on momentum transfer rates. However no information is available to indicate whether or not changes in shear rate affect the diffusivities in a non-Newtonian liquid or slurry. [Harley (*9*) noted such changes in polymeric films]. It has been further suggested (*6*) that a number of operating industrial processes would be quite unattractive if, in fact, the diffusivities in these systems varied inversely with viscosity as predicted by most correlations for Newtonian fluids. Gerster (*7*) has recently commented on the similarly primitive state of the art for viscous Newtonian fluids. Tsvetkov and Klenin (*20*) have noted the absence of any viscosity effects in solutions of polybutyl-methacrylate in a variety of solvents. However the viscosities were determined at only one shear rate in each solvent (and not at the same shear rate in the various solvents). These limitations of their rheological data afford an opportunity for a masking of all but the grossest changes. Biancheria and Kagles (*1*) studied diffusion in very dilute polymer solutions, in this case under conditions of no bulk motion of the fluid. In no case was the decrease in diffusivity observed when the concentration of long organic molecules in solution was increased as large as the concomitant increase in viscosity. Only two other studies of diffusion in non-Newtonian systems are available. One develops a useful experimental technique for measurement of diffusivity as a function of shear rate (*3*). The other (*19*) develops a dimensional, empirical correlation which incorrectly predicts diffusivities in polymeric solutions which are as much as two and one half times greater than those in the pure solvent.

In light of the above status of the current literature the purposes of the present study were first to develop a theoretical approach for the prediction of diffusivities in viscous and non-Newtonian systems and secondly to obtain some quantitative data with which to check the theoretical prediction and to answer at least some of the questions raised above.

THEORY

The Eyring rate theory for mass and momentum transfer (*8, 16, 17*) was extended to include the problem of diffusion in slurries and in non-Newtonian fluids. In accordance with this approach, for the case of momentum transfer, the shearing stress is given by

$$\tau = \sum_{n=1}^{\nu} x_n \tau_n \qquad (1)$$

when there are ν kinds of flow units. The term x_n represents the fractional area occupied by the n^{th} type of flow unit and τ_n is the force per unit area acting on units of the n^{th} kind. This leads to the familiar non-Newtonian viscosity expression (*18*):

$$\mu = \sum_{n=1}^{\nu} \frac{x_n \beta_n}{\alpha_n} \frac{\sinh^{-1} \beta_n \dot{\gamma}}{\beta_n \dot{\gamma}} \qquad (2)$$

Turning now to the problem of mass transfer, Ree and Eyring (*17*) give the following expression for the diffusion coefficient in a Newtonian fluid:

$$D = \frac{k \;\, T}{\xi \lambda \mu} \frac{k'}{k''} \frac{d \ln a}{d \ln c} \qquad (3)$$

A diffusing species in the non-Newtonian fluid encounters several kinds of resistance to its motion, and Equation (3) would not be expected to be valid in the form given above. For example particles or polymer molecules in the suspension or solution would be expected to encompass small volumes having different resistances to motion of the diffusing species than would those portions of the fluid which consist of comparatively unaffected continuous phase or solvent. Under these conditions one may write, analogously to Equation (1), for the diffusivity in a non-Newtonian fluid

$$D_{NN} = \sum_{n=1}^{\nu} x_n D_n \qquad (4)^*$$

where the D_n represent the diffusivities in the different regions of the fluid, and the x_n represent the volume fraction (assumed equal to the area fraction) of the solution occupied by units or regions of the n^{th} kind.

The simplest application of Equation (4) would occur if the fluid were to consist of only two kinds of units, those largely associated with the solvent or the continuous phase of a solution or

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[*] It has recently been suggested (Duda, J. R., Private Communication) that the summation required by Equation (4) must be nonlinear and would lead to the analogue of the Maxwell equation for thermal or electrical conductivity for the special case $\nu = 2$. Over the range of x_{sp} values covered by the present data the differences between this approach and that used in the present paper would be negligible, but they may become important under other conditions.

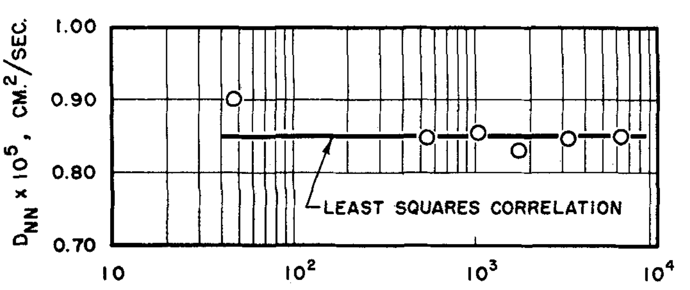

Fig. 1. Diffusivity of β-naphthol in a 1% aqueous carboxy methyl cellulose solution at 25°C. The diffusivity in pure water at this temperature is 1.14 × 10^{-5} sq. cm./sec. (*5,10*). The apparent viscosity of this solution varies between 29 and 310 centipoise over the range of shear rates covered. Complete rheological data are available (*5*).

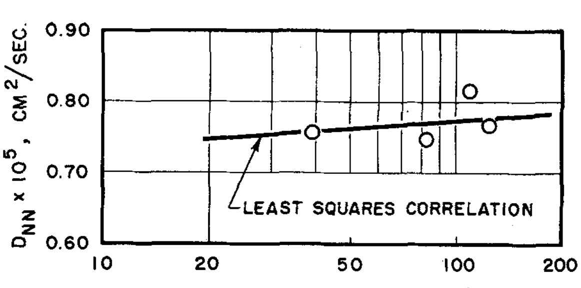

Fig. 2. Diffusivity of benzoic acid in a 20% kaolinite clay slurry at 20°C. The diffusivity in pure water at this temperature varies between 0.80 × 10^{-5} and 1.00 × 10^{-5}, depending upon concentration (*4,15*). The apparent viscosity of this slurry varies between 53 and 144 centipoise over the range of shear rates studied. Complete rheological data are available (*15*).

suspension and those associated with the polymer molecules or suspended particles. It is evident that either kind of unit could overshadow the other in terms of relative importance. In the case of an ionic polymer chain and an ionized diffusing solute the contribution to diffusion which occurs along the chain might well exceed the diffusivity in the continuous phase. In this case one might expect pronounced effects of shear rate as the orientation of the ionic polymeric molecule is changed. In other systems one may deal with relatively *inert* polymer molecules or suspended particles which would simply block off a portion of the fluid. In this case one would expect the diffusivity through the regions made up of such units to be effectively equal to zero. For this type of system Equation (4) predicts

$$D_{NN} = x_{cp} \, D_{cp} \qquad (4a)$$

Equation (3) may be applied to predict D_{cp}, the diffusivity of the continuous phase portion of the non-Newtonian fluid. It must be emphasized that the properties of the continuous phase are not in general equal to those of pure solvent. Although it may be assumed to be Newtonian, it may contain some dispersed material which affects its behavior.

To carry the theoretical development further, consider a fluid prepared by the suspension of solids in a liquid or the addition of polymeric molecules to a solvent. The diffusivity of any given solute in the solvent itself is frequently readily predicted by means of existing correlations for Newtonian systems or by reference to data on related materials. Under these conditions the quantity of interest is simply the ratio of the diffusivity in the non-Newtonian or final fluid to that in the solvent itself. Applying Equation (3) to the calculation of the diffusivity in the solvent as well the continuous phase diffusivity term in Equation (4*a*) one obtains for this ratio

$$\frac{D_{NN}}{D} = \frac{x_{cp} D_{cp}}{D} = x_{cp} \frac{\xi}{\xi_{cp}} \frac{\lambda}{\lambda_{cp}} \frac{\mu}{\mu_{cp}} \frac{(k'/k'')_{cp}}{(k'/k'')} \frac{(d \ln a / d \ln c)_{cp}}{(d \ln a / d \ln c)} \qquad (5)$$

where the terms without the subscripts designate the quantity in the pure solvent.

The term k'' is the frequency factor for a site in the pure solvent, and k' is the corresponding rate constant in solvent having a finite concentration of the diffusing solute. While the ratio k'/k'' may not, in general, be considered equal to unity, it seems likely that any deviation from unity will be similar in the continuous phase of the non-Newtonian fluid and in the solvent. Thus the ratio $\frac{(k'/k'')_{cp}}{k'/k''}$ is assumed equal to unity. By means of a similar argument the derivative terms of Equation (5) are also dropped. Further the lattice parameter λ is usually taken equal to $(V/N)^{1/3}$ (*17*), and since the density of the continuous phase of the solution or slurry is not likely to differ from that of the solvent, the ratio of the λ terms also may be dropped. Thus for systems in which there is no positive contribution to the diffusion rate on the part of the suspended solids (or the dissolved polymer molecules) one may write with some generality

$$\frac{D_{NN}}{D} = x_{cp} \frac{\xi}{\xi_{cp}} \frac{\mu}{\mu_{cp}} \qquad (6)$$

With the possible exception of the case of inert (nonsolvated)solids suspended in a liquid the viscosity of the continuous phase portion of the non-Newtonian fluid μ_{cp} is not equal to μ, the viscosity of the pure solvent. However it will be equal to the viscosity of the most fluid "flow units" in the Eyring theory of viscosity, and this has been shown (*18*) to be equal to the limiting (Newtonian) viscosity reached by the non-Newtonian system at very high rates of shear. Data are available for a number of systems (*2, 11, 16*). When rheological data in the region of high shear rates are not available, it is still possible to estimate this quantity by fitting the Eyring-Powell-Ree type of viscosity expression, Equation (*2*), to the rheological data at lower shear rates. Methods for carrying out this operation have been discussed in some detail by Ree and Eyring (*17, 18*).

The ratio ξ/ξ_{cp} represents the final difficulty. Ree and Eyring (*17*) show that ξ is almost always between 5.5 and 8.0 and averages about 6.0 in nonpolar, organic fluids. The average is frequently unaffected by hydrogen bonding (*17*) but is strongly anomalous in aqueous systems, for which the best available average value is 15.5 and individual values may exceed 20 (*17*).

The association between the solvent or continuous phase and the suspended or dissolved material in a non-Newtonian fluid would tend to skew the distribution of molecular velocities; the less energetic molecules would, in general, tend to be associated longer with the solvated dispersed material and the more energetic molecules would not. This suggests that there may be little association between these remaining energetic molecules in the continuous phase and the diffusing solute, that is that ξ_{cp} will usually be close to 6.0.

In summary Equation (6) will be assumed to correctly portray diffusivities in suspensions and in non-Newtonian fluids in which there is no peculiar association between the diffusing species and the dispersed solids or dissolved polymer. The ratio μ/μ_{cp} may be established by means of relatively simple and direct rheological measurements. In organic systems the ratio ξ/ξ_{cp} may have values as low as unity, but it may reach a value of 3.0 or even higher in aqueous systems. The volume fraction of the continuous phase x_{cp} may be directly estimated in nonsolvated systems and, in any case, represents a smaller range of uncertainty. Thus the primary purpose of experimental data would be to shed light on the correct choice of the ratio ξ/ξ_{cp}; once sets of values for this ratio have been established experimentally for non-Newtonian systems [similar to the ξ values already available for Newtonian fluids (*17*)] Equation (6) could be used to estimate diffusivities in these non-Newtonian systems with, hopefully, a very high degree of accuracy.

EXPERIMENTAL PROCEDURE

The following systems were investigated:

1. β-naphthol diffusing through a 1% aqueous solution of high viscosity sodium carboxymethylcellulose.
2. Benzoic acid diffusing through an aqueous 20% kaolinite clay slurry.
3. Benzoic acid diffusing through a 14.2% slurry of Attaclay X250 in water.

All three fluids were highly non-Newtonian under the shear rates employed, having flow behavior indexes as low as 0.15.

Because of the improbability of obtaining a uniform concentration of a viscous non-Newtonian fluid inside the void space of a conventional diaphragm diffusion cell, and because the effects of shear rate [or the absence of any, as predicted by Equation (6)] were to be investigated, the measurement of diffusivity was carried out in a flowing system. For this purpose smooth tubes of the diffusing solute were cast, and the non-Newtonian fluids were pumped through these tubes under conditions of laminar flow. At reasonably high flow rates (Graetz numbers) the concentration boundary layer is confined to a narrow region next to the tube wall, so that this technique may be made to approach the ideal of a perfectly constant and known shear rate as closely as desired. A nondissolving entrance region must be available so that the velocity profile has been well developed by the time the fluid reaches the soluble part of the tube wall. The rheological properties of the fluid were found to be unaffected by the addition of the diffusing solute except during an initial period at the beginning of some of the runs. Such initial points were, of course, discarded. For the data which are unaffected by such radial variations in physical properties the shear rate at the tube wall may readily be calculated by the Mooney-Rabinowitsch-Weissenberg relation (see reference *11*) provided there is no slip at the wall due to the presence of a thin layer of the solvent or continuous phase. Additionally the presence of such a low viscosity layer would, of course, invalidate any measured diffusion rates. Accordingly careful pressure drop measurements were made and compared with values calculated from the known rheological properties of the fluid. The close coincidence of these values proved the absence of any such low viscosity layer; the experimental and calculated values agreed within the experimental error of about 6% and exceeded the pressure drop of the continuous phase (water) by a factor of over 100. In addition the coincidence of rheological data obtained in tubes of widely different diameters checks the general tendency of these fluids to cling to the tube wall as a continuous medium rather than to slip.

TABLE 1. DIFFUSIVITY OF BENZOIC ACID IN A 14.2% ATTACLAY SLURRY AT 25°C.

Fluid mix	Shear rate, sec.$^{-1}$	Fluid viscosity, centipoise	Diffusivity, sq. cm./sec.
I	1,480	11.	0.90×10^{-5}
I	6,200	7.0	1.21
I	9,100	5.7	0.96
II	3,260	63.	0.69
II	10,500	45.	0.60

Under these conditions the diffusivity may be calculated unambiguously from the measured total solution rate with the non-Newtonian equivalent of the familiar Graetz-Leveque solution for laminar heat transfer under conditions of constant wall temperature (*12, 13, 14*). Calculations based upon the experimentally determined diffusivities showed that the concentration difference between the fluid at the wall and that at any other radial position dropped to within 5% of its maximum value in a distance of 0.06 to 0.18 mm. from the wall of the tube, depending upon the conditions used. As these values are large as compared with the dimensions of the sodium carboxymethylcellulose molecules and clay particles, the diffusing species obviously penetrated well into the fluid stream, although not so far as to encounter fluid in which the shear rate was appreciably lower than in the fluid adjacent to the wall itself.

In the first two fluids the solution rates were obtained by mixing the fluid as it left the tube and titrating a sample of this mixed stream for the solute in question. In the third fluid this procedure was not found to be possible, and solution rates were obtained by periodically weighing the dissolving tube. This proved to be a far less accurate procedure; the data scatter considerably in this instance and may only be considered to be approximate. For the first two fluids, on the other hand, a given run at given conditions of shear rate was continued for from 2 to 4 hr., and between three and six samples were taken at periodic intervals (not including those discarded early in any given run). This procedure was adopted not only to prevent any erratic sampling errors but also to ensure the absence of any effects due to changes in fluid physical properties with time or to a concentration-dependent diffusion coefficient.

A statistical analysis of the data showed all such aberrations to be absent and the diffusivity to be independent of concentration in both systems. The several points obtained during each run were averaged and are reported as a single point in the present paper. The maximum deviation of any single determination from the average value reported here was usually less than 2 or 3% in the case of sodium carboxymethylcellulose solutions and less than 5% for the kaolinite slurry; the maximum deviation was above 10% in only one instance. Corrections for deviation of the fluid from the standard temperatures of either 20° or 25°C. were required in some of the early runs; this amounted to 6% in one instance and to 4% in another, but was otherwise negligibly small. Correlations which include effects of natural convection (*12*) indicate the lowest shear rate run made with the sodium carboxymethylcellulose solution may have incurred a 5% error for this reason hence this point was suitably corrected. No other corrections of any kind were applied, and problems such as reaction of the solute with the fluid or abrasion of the solute were shown to be absent. Thus the data reported for these systems are highly reproducible and well defined.

Complete details of the flow system, of the analytical and calculational procedures, as well as of the solubility data and descriptions of the techniques used to cast the smooth, long tubes necessary are available (*3, 5, 15*).

RESULTS

Figures 1 and 2 show the results for the sodium carboxymethylcellulose solution and the kaolinite clay slurry, respectively. The slope of the least-squares correlation of Figure 1 is 0.0003 and that of Figure 2 is 0.0035; both are statistically equal to zero at the 95% confidence level, showing the absence of any effect of shear rate on the diffusivity over the 3 to 130 fold ranges studied. Table 1 presents the results for two Attaclay slurries studied by means of the less accurate experimental technique. (While the clay concentration was the same in both runs, differences in mixing led to differences in the viscosity of the fluids.) In this case no rigorous interpretation of the data is possible, but it is interesting to note that they are in general agreement with Figure 2 even though the shear rates are higher by about 1 order of magnitude, extending the entire range of shear rates studied by a factor of nearly 2. Thus, a 220 fold range of shear rates is covered by the three sets of data.

When one applies Equation (6), the ratio μ/μ_{cp} for the data of Figure 1 is taken as 0.89/3.0. The former value is simply the viscosity of water at 25°C., while μ_{cp} is obtained by fitting the Eyring-Powell-Ree viscosity equation to the rheological data (*5*). Values of ξ_{cp} and ξ are taken as 6.0 and 16 as being representative of nonassociating and highly associated systems (*17*) respectively, as discussed earlier. The effective volume fraction of the continuous phase x_{cp} should be taken appreciably lower than the before-mixing value of 0.99. If one arbitrarily assumes the solvation to double or triple the effective volume of a sodium carboxymethylcellulose molecule in solution, x_{cp} would be equal to 0.98 or 0.97. (While this may be in error, the uncertainty here is much less than in the choice of ξ.) With these values Equation (6) predicts the ratio D_{NN}/D to be equal to about 0.77, as compared with the experimental value of 0.85/1.14 or 0.75. In the case of the kaolinite slurry the partially rigid particles cannot imbibe nearly as much solvent as free sodium carboxymethylcellulose molecules, and a value of x_{cp} equal to approximately 0.85 appears reasonable. The ratio μ/μ_{cp} is found to be equal to 1.0/4.5 in this case (5). If one uses the same value of ξ/ξ_{cp} as above, the predicted ratio of diffusivities is 0.50 as compared with an experimental ratio of about 0.8. By increasing ξ from 16 to 23, as might be reasonable in view of the general trends exhibited for larger particles or molecules in the Eyring-Ree tabulation for Newtonian systems (*17*), the predicted and experimental diffusivity ratio are brought into agreement. No accurate experimental ratio is obtainable from the data of Table 1, but the agreement between the approximate experimental results and a prediction is about the same as for the kaolinite slurry.

As expected the question of whether or not there is agreement between the experimental and theoretical values rests upon choice of the ratio ξ/ξ_{cp}, about which there is necessarily great uncertainty at the present time. Unfortunately it is only within recent years that enough data have been accumulated on Newtonian systems to make rational choices possible in that simpler special case. Thus while it is clearly desirable to obtain further experimental data (especially for nonaqueous systems, for which the maximum range of the ratio ξ/ξ_{cp} is much smaller), it will likely be some time before accurate predictions by means of Equation (6) or improvements thereon will be possible. In the meanwhile it may be noted that the poorest choice of the ξ/ξ_{cp} ratio resulted in a prediction which was only 30 to 40% too low and which is therefore of sufficient accuracy to be of value under some circumstances. By contrast application of the usual correlations for Newtonian fluids would have resulted in predictions which were too low by a factor of between 6 and 130 for the slurries and between 25 and 230 in the case of the sodium carboxymethylcellulose solution. Thus while Equation (6) cannot yet be claimed to be of proven applicability, it is obviously a very significant improvement over the prior art.

The large errors in predictions with prior art correlations arise primarily because of the very small effect the viscosity of these systems is seen to have on the diffusion rate. As a crude approximation it would be better to estimate the diffusivity in a non-Newtonian fluid as being identical to that in the pure solvent than to adopt the inverse dependency on viscosity predicted by prior art equations. In general however such a procedure would not prove to be as accurate as the use of Equation (6).

CONCLUSION

Previously used mass transfer studies were extended to provide an experimental technique for the accurate measurement of a diffusion coefficient at a fixed shear rate, but at any shear rate level.

The Eyring rate theory has been applied to the problem of diffusion in non-Newtonian fluids and slurries. Whereas the usual correlations of diffusivities in Newtonian systems yield predictions which may be incorrect by as much as several hundred fold, in these systems the agreement between the present predictions and the experimental data was always better than within 40%. Much further experimental effort will be required to check the theory in detail and to provide the parameters necessary for highly accurate predictions.

A particularly interesting point for further work stems from comparison of Equations (4) and (4*a*); while the latter was derived from the earlier one by assuming that the portion of the fluid associated with the polymer molecule or suspended particle effectively blocked the diffusing species, a more interesting situation would be that in which the polymer molecule provided an easier path for diffusion than did the continuous phase. Molecular mechanisms for such diffusion along a polymer chain are possible and, if present, should enable appreciable increases in diffusivity above those obtainable in the pure solvent. In this case the fluid diffusivity may be expected to be shear rate dependent.

Diffusivities in viscous Newtonian fluids are not as low as predicted by prior art correlations. The present approach of subdividing the fluid into several kinds of flow units, each offering a different resistance to diffusion, may afford an opportunity for the calculation of diffusivities in these systems. In view of the known tendencies toward association of the molecules in these systems the presence of a variety of flow units in such Newtonian fluids is qualitatively reasonable.

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NOTATION

a = activity of the diffusing species
c = concentration of the diffusing species
d = tube diameter
D, D_{NN}, D_{cp} = diffusivity of a Newtonian fluid, a non-Newtonian fluid or a slurry, and in the continuous phase portion of a non-Newtonian fluid, respectively
k = Boltzmann's constant
k',k'' = frequency factors (relaxation frequencies) in the Eyring rate theory for a solvent containing a solute and the pure solvent, respectively
T = absolute temperature
V = mean fluid velocity
x_n = fractional area occupied by flow units or diffusion units of the n^{th} kind; for example x_{cp} denotes the fractional area occupied by the *continuous phase*

Greek Letters

α_n, β_n = dimensional groups of terms in the Eyring-Powell-Ree viscosity equation [see (*17*) for detailed definition]
$\dot{\gamma}$ = fluid shear rate; $\dot{\gamma} = \frac{3n' + 1}{4n'} 8V/D$ for well-developed laminar flow through a smooth, long tube, where

$$n' = \frac{d \log \tau_w}{d \log 8V/D}$$

λ = lattice parameter (distance a molecule advances during one jump)
μ = viscosity of the fluid
ν = number of kinds of flow or diffusion units
ξ = number of neighbors of the diffusing molecule which are sheared during its advancing a distance equal to one lattice parameter
τ, τ_n, τ_w = shearing stresses

Subscript

cp = properties or parameters of the continuous phase portion of the non-Newtonian fluid

LITERATURE CITED

1. Biancheria, A., and G. Kagles, *J. Am. Chem Soc.*, **79**, 5908 (1957).
2. Brodnyan, J. G., F. H. Gaskins, and W. Philippoff, *Trans. Soc. Rheology*, **1**, 109 (1957), and with E. G. Lendrat in *Trans. Soc. Rheology*, **2**, 285 (1958).
3. Burns, K. S., M.Ch.E. thesis, Univ. Delaware, Newark, Delaware (1960).

4. Chang, S. Y., S.M. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1949).
5. Clough, S. B., M.Ch.E. thesis, Univ. Delaware, Newark, Delaware (1961).
6. Emmert, R. E., Private Communication (1958).
7. Gerster, J. A., *Ind. Eng. Chem.*, **52**, 645 (1960).
8. Glasstone, Samuel, K. J. Laidler, and Henry Eyring, "The theory of Rate Processes," McGraw Hill, New York (1941).
9. Hartley, G. S., *Trans. Faraday Soc.*, **B42**, 6 (1956) and **45**, 820 (1949).
10. Linton, W. H., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1949). See also Linton, W. H., and T. K. Sherwood, *Chem. Eng. Progr.*, **46**, 258 (1950).
11. Metzner, A. B., in "Handbook of Fluid Dynamics," V. L. Streeter, ed., McGraw-Hill, New York (1961).
12. ———, and D. F. Gluck, *Chem. Eng. Sci.*, **12**, 185 (1960).
13. Metzner, A. B., R. D. Vaughn, and G. L. Houghton, *A.I.Ch.E. Journal*, **3**, 92 (1957).
14. Pigford, R. L., *Chem. Eng. Progr., Symposium Ser. No. 17*, **51**, 79 (1955).
15. Read, H. E., M.M.E. thesis, Univ. Delaware, Newark, Delaware (1961).
16. Ree, F. H., Taikyue Ree, and Henry Eyring, *Ind. Eng. Chem.*, **50**, 1036 (1958).
17. Ree, Taikyue, and Henry Eyring in "Rheology," Vol. 2, F. R. Eirich, ed., Academic Press, New York (1958).
18. ———, *J. Appl. Phys.*, **26**, 793, 800 (1955).
19. Saunders, A. R., Ph.D. thesis, Univ. Maryland, College Park, Maryland (1959).
20. Tsvetkov, V. N., and S. I. Klenin, *Tech. Phys. U.S.S.R.*, English Translation, 4, 1283 (1960).

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Spontaneous Interfacial Cellular Convection Accompanying Mass Transfer: Ethylene Glycol-Acetic Acid-Ethyl Acetate

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Spontaneous interfacial cellular convection accompanying the extraction of acetic acid out of ethylene glycol with ethyl acetate was studied photographically with a Schlieren technique. A flat liquid-liquid interface at room temperature was photographed straight down with motion-picture and still cameras. The interface exhibited a dominant pattern of stationary and propagating polygonal cells, accompanied by stripes, cell cluster boundaries, and confined or unconfined ripples. The time-dependence of the average wave length (size) of the different patterns, their average speed of propagation, and their frequency was determined by means of an initial acetic acid concentration range of 0.1 to 10%, over a time span of 72 hr. The average wave lengths of cells, stripes, and ripples ranged from 0.02 to 0.14, 0.065 to 0.155, and from 0.03 to 0.10 cm., respectively. Cell and ripple velocities ranged from 0.27 to 1.33, and from 0.27 to 1.10 cm./min. respectively.

The relation between the observed interfacial cellular convection and the Sternling-Scriven theory of interfacial turbulence is discussed.

Mass transfer in liquid-liquid extraction, as described by the traditional two-film model, is a rather quiet and unexciting affair. Solute is visualized as transferring to and away from the interface by molecular or eddy diffusion. The interface as well as the interfacial regions of a mechanically unstirred ternary system are considered to be quiescent and motionless.

During the past decade a number of ternary systems have been discovered experimentally which challenge the universality of the two-film model. The interface in these systems is found to be disturbed during mass transfer by eruptions and spasms, while the nearby regions are agitated spontaneously. This phenomenon, known as *interfacial turbulence* (*17*), has more than an academic importance since it is invariably accompanied by mass transfer rates which may be several times higher than the theoretical ones as predicted by the two-film theory (*3, 7, 10, 18, 19, 21, 32*).

This study plans to explore the nature and form of the interfacial activity accompanying liquid-liquid extraction through a flat interface.

PREVIOUS EXPERIMENTAL OBSERVATIONS

Ward and Brooks (*38*) were the first to report the existence of spontaneous, highly localized, interfacial agitation accompanying mass transfer. Since then interfacial turbulence has been observed and studied in drops and flat interfaces both visually and photographically. Kroepelin and Neumann (*15*) photographed the flat, turbulent interface of the system ethyl acetate-acetic acid-water in profile using a Schlieren apparatus. The active interface of the system amyl alcohol-acetic acid-water was photographed by Brückner (*4*). Sherwood and Wei (*32*), while studying mass transfer with interfacial chemical reaction, noticed the occurrence of spontaneous turbulence in the phase boundary regions. Extending their observations to forty ternary and quaternary systems they found that interfacial turbulence was pronounced in the case of exothermic neutralizations. Some of Wei's experiments were repeated by Sternling and Scriven (*37*) who studied them cinematographically along with other surface-tension-driven flows.

Pendant droplets disturbed by rippling, pulsation, kicking, and eruptions were studied by Lewis and Pratt (*20*), Haydon (*11*), and Garner et al. (*8*). Haydon (*12*) investigated also the kicking of pendant drops both qualitatively and quantitatively and proposed a mechanism for it. Sigwart and Nassenstein (*33, 34*) made an extensive photographic study of eruptions in pendant droplets using a color Schlieren micro-

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