The Rate of Glycerol Absorption by Ion Exchange Resins

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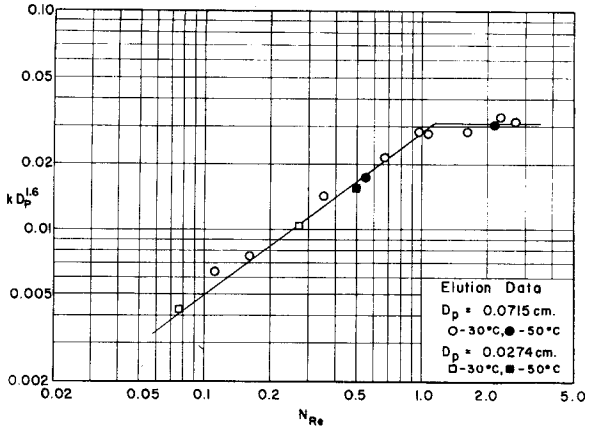

Fig. 1. Correlation of data from saturation experiments.

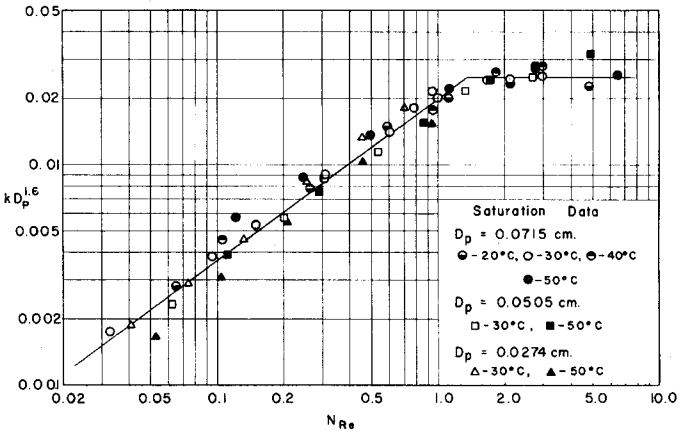

Fig. 2. Correlation of data from elution experiments.

Studies of the rate of absorption of glycerol from aqueous solutions by packed beds of ion exchange resin have recently been reported (*1*, *2*). In particular, Vassiliou and Dranoff (*2*) showed that the rate of absorption and desorption of glycerol in beds of amberlite IR-120 resin could be described by a linear rate equation containing an unknown mass transfer coefficient k. They studied the effect of Reynolds number on k in a limited number of experiments and also noted differences between k values for saturation and elution and an effect due to resin particle size. The present work was undertaken to obtain more complete and extensive data, including the effects of Reynolds number, temperature, and particle size on the transfer coefficient.

The detailed analysis of the transient operation of a packed bed during the saturation and/or elution cycle has been presented previously (*2*, *3*) and is therefore not repeated here. Suffice it to say that a linear rate equation of the form

$$\frac{\partial q}{\partial t} = k\,(K_a C - q) \qquad (1)$$

is combined with appropriate material balances and initial conditions to yield equations which predict the familiar breakthrough curves encountered in such operations. Comparison of these theoretical curves and those measured experimentally then makes possible the estimation of the appropriate k values.

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EXPERIMENTAL

The absorption of glycerol from dilute water solutions (approximately 6.5 wt. % glycerol) was carried out in a standard glass chromatographic col-

(*Continued from page 282*)

INFORMATION RETRIEVAL

Key Words: Heat Transfer-8,9, Liquid-Metal-5, Mercury-5, Sodium-5, Nack-5, Pipes-10, Annuli-10, Rod Bundles-10, Turbulent-8, Diffusivity-8, Eddy-8, Nusselt Number-7, Prandtl Number-6, Peclet Number-6, Reynolds Number-6, Eddy Transport-8, Internal Flow-8, Laminar-8, Convection-8.

Abstract: An equation is developed for evaluating the ratio of the eddy diffusivity of heat transfer to that for momentum transfer for use in estimating heat transfer coefficients for liquid-metals. This ratio is given as a function of two dimensionless groups: the Prandtl number and the ratio of eddy diffusivity of momentum transfer to kinematic viscosity. The equation gives eddy diffusivity ratios, which when incorporated in the usual semiempirical equations for estimating liquid-metal heat transfer coefficients, bring theoretical predictions and experimental results into good agreement for flow through pipes, annuli, and rod bundles.

Reference: Dwyer, O. E., **A.I.Ch.E. Journal, 9,** No.2, p. 261 (1963).

Key Words: Equation of State-8, Density-8, Argon-4, Gaseous and Liquid Substances-8, PVT Data-10.

Abstract: Available PVT data for argon were utilized to develop isochoric relationships between the normalized pressure and normalized temperature in the form of third-degree polynomials. The dependence of the coefficients of the polynomials on reduced density was established. These relationships permit the calculation of densities for argon and substances of similar nature (nitrogen, oxygen, carbon monoxide, and methane) for reduced temperatures less than 2.81° and reduced pressures up to 50 through a trial-and-error procedure. For argon, an average deviation of 1.29% and a maximum deviation of 3.66% resulted from a comparison between calculated and reported values.

Reference: Costolnick, John J., and George Thodos, **A.I.Ch.E. Journal, 9,** No. 2, p. 272 (1963).

ERRATUM

The article, "The Laminar-Turbulent Transition for Flow in Pipes, Concentric Annuli, and Parallel Plates," by Richard W. Hanks, which appeared on page 45 of the January, 1963, issue of the *A.I.Ch.E. Journal*, was omitted from the table of contents.

Abstracts and Key Words

Of the latest book in the Chemical Engineering Progress Symposium Series

APPLICATIONS OF PLASTIC MATERIALS IN AEROSPACE

Vol. 59, No. 40, 1963, $3.50 to members, $15.00 to nonmembers. Symposium Series books may be ordered from the Secretary's Office, the American Institute of Chemical Engineers, 345 East 47 Street, New York 17, New York.

Key Words: Reinforced Plastics-0, Structural Plastics-0, Heat Resistant Plastics-0, Glass-Reinforced Plastics-0, Asbestos-Reinforced Plastics-0, Low-Pressure Laminates-0, Filament Winding-0, Plastic Sandwich Construction-0, Ablation-0, Aerospace Applications-0, Mechanical Properties-0, Thermal Properties-0, Polyester Resin-0, Epoxy Resin-0, Phenolic Resin-0, Silicone Resin-0, Glass Fibers-0.

Abstract: Reinforced plastics are composite materials consisting of fibered reinforcements bonded together with a thermosetting resin. Reinforced plastics were developed just prior to World War II and found immediate use in aircraft construction. Presently, major emphasis in applying reinforced plastics to aerospace vehicles is placed on filament winding for pressure vessels and rocket cases and on ablation materials for thermal protection of re-entry vehicles.

Reference: Strauss, Eric L., Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 1 (1963).

Key Words: Epoxy Resins-1, Heat Shields-8, Ablation Materials-1, Ablation Mechanisms-7, Re-entry Vehicle Design-8, Thermal Properties-6, Charring Plastics-1, Plastics Mechanical Properties-6, Chemical Tailoring of Plastics-8, Physical Tailoring of Plastics-8, Cross-linking-6, Thermosetting Resins-1, Thermal Protection Systems-8, Transpiration-2, Transient Heat Conduction-1, Ablation Analysis-1, Avco Corporation-10, Re-entry Environment-5, IBM-704-10, Philco Model S-2000-10, Computers-10.

Abstract: The techniques are discussed for altering the physical and chemical nature of an acid cured epoxy resin system to make the resultant product useful as a heat shield material for either ballistic suborbital or manned superorbital re-entry vehicles. Ablation characteristics and thermal and mechanical property data are presented for several epoxy formulations. Examples of typical re-entry vehicle configurations as well as a weight comparison of several plastics are also presented.

Reference: Collins, James A., Omar K. Salmassy, and Lawrence E. McAllister, Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 9 (1963).

Key Words: Ablation-8, Polymer-9, Epoxy-9, Functionality-6, Lewis Acid-4, Pyrolysis-8, Pyrolytic Graphite-2, Silica Fibers-9, Silicon Carbide-2, Novolac-9, X-Ray Diffraction-10, Char-2, Fiber Glass-9, Plasma Arc-10.

Abstract: Recent physical, chemical, and thermal investigations have resulted in a better understanding of the ablative mechanism in unfilled and reinforced charring polymer systems. Ablative arc tests of cured epoxy resin systems indicated that a system functionality of 2.6 was required for the formation of stable ablative chars. In addition certain acids were found to induce stable ablative chars in noncharring epoxies. A mechanism of char-layer formation and removal has been postulated, wherein the polymer degradation products deposit pyrolytic graphite in the char layer during ablation. This graphite has been found to react with silica reinforcing fibers to form silicon carbide at the ablating surface.

Reference: McAllister, Lawrence, J. Bolger, E. McCaffery, P. Roy, F. Ward, and A. C. Walker, Jr., Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 17 (1963).

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*For details on the use of these key words and the A.I.Ch.E. Information Retrieval Program, see *Chem. Eng. Progr.*, 57, No. 5, p. 55 (May, 1961), No. 6, p. 73 (June, 1961); 58, No. 7, p. 9 (July, 1962).

umn packed with ion exchange resin. The column, which was 36 in. long and 1 in. in inside diameter, was fitted with a concentric glass heating jacket for close temperature control. The packed bed, which had a height of 76 cm. in all experiments, was supported in the column by a sintered glass filter disk and was covered at the top by a fine stainless steel screen. The portions of the column above and below the resin bed were filled with 4-mm. glass beads. The bottom of the column was equipped with an Ultramax valve (*4*) that allowed fine control of the effluent rate. At the top of the column was a three-way stopcock which was used to direct fluid through the fixed bed or into a waste container.

The feed solutions were stored in 1-liter flasks located in a constant temperature water bath. Solution was pumped from these flasks through a rotameter and then to the column. The rotameter was used for estimation and control of the flow rates. All fluid lines were made of tygon tubing. The water in the constant temperature bath was also circulated through the concentric-tube heating jacket which, like all fluid lines, was insulated to minimize heat exchange with the surroundings. With this equipment it was possible to maintain the temperature of the feed solutions and the column contents constant to within one degree centigrade.

The resin used in this work was Dowex 50W-X8 in the hydrogen form. It was divided into three particle size ranges by dry screening through U. S. Standard screens. The mean particle size (and range) for each range was 0.0715 cm. (0.0590 → 0.0840), 0.0505 cm. (0.0420 → 0.0590) and 0.0274 cm. (0.0250 → 0.0297).

The resin bed was packed by the usual technique of allowing a slurry of particles to settle in the column when it was full of water. The resultant uniform bed had measured interparticle and intraparticle void fractions of 35 and 39.7%, respectively, based on the superficial bed volume. These values

TABLE 1. REPORTED VALUES OF K_d FOR AQUEOUS-GLYCEROL SOLUTIONS

Investigation	Glycerol concentrations, (wt. %)	Distribution constant, K_d
Vassiliou and Dranoff (2)	4.06	0.58
	7.05	0.60
	9.80	0.625
Shurts and White (5)	2.00	0.60
	7.00	0.63
This work (3)	6.5	0.63

were determined by the procedure reported previously (2, 3).

Effluent concentrations were determined with this system for both saturation and elution experiments. Analysis of solution composition was by refractive index measurement.

Additional details of equipment and procedure are presented elsewhere (3).

RESULTS AND DISCUSSION

Fifty-one saturation and fourteen elution runs were made at various conditions of flow rate, temperature, and particle size. (Elution data were not collected after every saturation experiment since early analysis indicated no unusual trends in these results.)

The breakthrough curves from several runs were analyzed to determine the equilibrium distribution coefficient K_d. The results indicated that K_d is not affected significantly by changes in temperature, flow rate, or particle size. Since K_d is an equilibrium parameter, it is to be expected that its value would not depend on flow rate or particle size. Although a temperature effect might be expected previous studies (1) have shown that this dependence is negligible over the range of temperatures considered here.

From the present results an arithmetic average value of 0.63 was chosen for use in subsequent calculations. This value is consistent with the data of Vassiliou (2) and Shurts and White (5) as shown in Table 1.
Note that these data indicate a slight concentration dependency which was assumed negligible for present purposes.

Mass transfer coefficients were calculated for each run after graphical matching of experimental and predicted breakthrough curves (3). Such matching was found to be quite satisfactory for all of the present data as was also noted by Vassiliou (2).

The effects of temperature, flow rate, and particle size upon the coefficient k were next considered. For a single particle size and temperature the value of k increased approximately with the 0.7 power of particle Reynolds number, as the latter was changed from 0.03 to about 1.0. Further increase in Reynolds number produced a rather sharp change after which k values appeared to be constant. The same kind of behavior was observed by Vassiliou, although the transition to constant k values was more gradual. Note that Reynolds numbers were based on average fluid properties corresponding to solutions of 3.2% glycerol.

Again as found by Vassiliou (2), the k values for elution runs were considerably higher than corresponding values for saturation experiments. The only explanation for this difference presently available is that nonlinearities in the K_d concentration relationship may be responsible. Further experiments will be necessay before this may be confirmed.

A correlation of the data for various particle sizes and temperatures was then sought. It was found that as temperature was increased at constant flow rate, the value of k also increased. However the Reynolds number increased as well, owing to decreases in the viscosity of the liquid, with the result that the data for any particle size fell on essentially one curve. Furthermore decrease in particle size also produced an increase in k. Such increases were higher than might be accounted for simply in terms of the larger particle-solution interfacial area per unit volume of bed associated with the smaller particles.

It was found that the data could be best correlated by a plot of $kD_p^{1.60}$ against Reynolds number. Such plots are shown in Figure 1 for saturation data and Figure 2 for elution data. Simple equations were fitted to these data and the results are as follows:

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INFORMATION RETRIEVAL

Key Words: Ablation Mechanism-1, Nozzle, Uncooled-2, Thrust Chamber, Uncooled-3, Reinforced Phenolic Materials-4, Char-5, Space Environment-6, Combustion Products, Effect-7, Erosion-8, Vacuum-9, Radiation-10, Space Engines-11, Liquid Propellants-12, Solid Propellants-13, Resin-14, Reinforcement-15.

Abstract: This paper includes a discussion of the ablative mechanism, the internal environmental conditions acting on the materials, and the special problems in space applications for ablative nozzles and thrust chambers. Discussion is intended to cover the fields of solid and liquid propulsion. Included are mathematical solutions to some of the above problem areas.

Reference: Lyons, C. S., and D. D. Lawson, Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 33 (1963).

Key Words: Resin-10, Plastics-10, Fiberglass-Reinforced-Plastics-10, Stress Analysis-1, Isotropic Materials-1, Orthotropic Materials-1, Creep-9, Impact-9, Fatigue-9, Strain Analysis-1, Design-10, Immersion-5, Axes Rotation-1, Elastic Modulus-7, Plates-9, Buckling-8, Resisting Moment-8, Beams-8, Flexure-1, Secondary Elastic Modulus-7, Shear Stress-9, Normal Stress-9.

Abstract: Reinforced plastics have not been as widely accepted by structural designs as should be expected. The reasons for this are outlined through statements about mechanical properties, testing procedures, and design requirements. Using these characteristics as vehicles the authors suggest ways in which researchers in the Fiberglass-Reinforced-Plastics field can gain wider acceptance of these materials for engineering structures.

Reference: Antoni, Charles M., and John R. Verna, Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 51 (1963).

Key Words: Fire Research-8, General Survey-9, State-Of-The-Art-9, Research Need-9, Application-9, Hazards-9, Aerospace-0, Plastics-10, Reinforced Plastics-10, Structural Plastics-10, Combustion-6, Toxicity-7, Collapse-7, Extinguishment-7, Tests-10.

Abstract: The increased use of reinforced plastics in structural application, particularly in aerospace vehicles, has emphasized the importance of fire properties of these materials. Basic concepts of fire properties, terminology, and test methods are reviewed. The categories of combustion and spread, structural collapse, toxicity, and extinguishment are discussed. The past and present state-of-the-art is briefly reviewed, and the need for specific fire research on structural plastics is emphasized.

Reference: Aidun, A. R., and R. Ford Pray, III, Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 57 (1963).

Key Words: Plastic-1, Ablation-8, Pyrolysis-8, Char-2, Techniques-10, Properties-8, Heat Dissipation-8, Thermal Conductivity-8, Physical Properties-8, Mechanical Properties-8, Test-10, Heat Shield-1, Rocket Nozzle-1, Thermal Insulation-8, Photomicrography-10, Porosimetry-10, Thermogravimetric Analysis-10, Differential Thermal Analysis-10, Hardness-8, Emissivity-8, Thermal Diffusion-8, Phenolic-1, Silicone-1, Epoxy-1, Nylon-1, Silica Fibers-1, Glass Fibers-1, Asbestos-1.

Abstract: The properties of ablative plastics governing their performance in re-entry and propulsion environments are separated into three major categories: thermal, chemical, and physical-mechanical. Laboratory procedures described include techniques for determining surface temperature and emissivity in hot gas streams, molecular weight and chemical identity of gaseous pyrolysis products, weight fractions of gaseous and residual solids from pyrolyzed plastics, heat of decomposition of plastics, apparent thermal diffusivity and thermal insulating characteristics, mechanical properties and cell structures, and other physical characteristics of residual chars from pyrolyzed plastics.

Reference: Schwartz, H. S., Chem. Eng. Progr. Symposium Ser. No. 40, 59, p. 64 (1963).

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For saturation:

$$kD_p^{1.60} = 0.0275N_{Re}^{0.74}, \quad N_{Re} \leq 1.35$$
$$kD_p^{1.6} = 0.0250, \quad N_{Re} \geq 1.35$$

For elution

$$kD_p^{1.60} = 0.0275N_{Re}^{0.74}, \quad N_{Re} \leq 1.15$$
$$kD_p^{1.60} = 0.031, \quad N_{Re} \geq 1.15$$

In these relationships the *units of k are* taken as $(\text{minutes})^{-1}$, and D_p is given in centimeters. The above equations will reproduce the experimental data of this investigation with an average absolute difference of 9.75% for saturation data and 5.57% for elution data.

Over the range of flow conditions studied here, it seems clear that the rate process is controlled by a combination of external or film diffusion of solute at low N_{Re} and internal or particle diffusion at N_{Re} greater than about 1.0. These conclusions are based upon the observed influence of changes in N_{Re} which are characteristic of such regimes of operation.

An attempt was made to separate these two mechanisms by assuming they act in series, much as was done by Baddour and Gilliland (*6*) with ion exchange data. The results were negative in that consistent values of system parameters could not be determined. This was in part due to the sharp, almost discontinuous change in the N_{Re} dependence mentioned above and shown in Figures 1 and 2. It thus appears that a somewhat more detailed model of the transfer process is required to explain the observed phenomena. Although the linear rate equation used here does lead to breakthrough curves of appropriate shape, the effective mass transfer coefficient k is obviously a complex parameter which demands further study.

It should be noted that the data of this study are in good agreement with those of Vassiliou. The Reynolds number dependence agrees exactly as does the value of k at high N_{Re}. At lower values however Vassiliou's data appear to be higher than those reported here. This may be due to poorer flow rate control in the earlier work or to use a different resin (Amberlite IR 120) with possibly different cross linkage.

In summary, it has been again shown that a simple linear rate model may be used to describe glycerol absorption in packed beds of ion exchange resin at low flow rates. The effects of temperature, flow rate, and particle size upon the one parameter of this model have been correlated empirically to yield working relations of moderate accuracy. The data indicate that the process is controlled by some combination of diffusion within and at the surface of the resin particles, although the exact mechanism of the rate process is not yet clearly understood.

NOTATION

C = solute concentrations in external solution, (wt.%)
C_o = input solute concentration
D_p = particle diameter, (cm.)
K_d = equilibrium distribution coefficient, (dimensionless)
k = mass transfer coefficient, (min.$^{-1}$)
L = solution flow rate, ml./(min.)(sq. cm.)
N_{Re} = particle Reynolds number, $\frac{D_p L \bar{\rho}}{\bar{\mu}}$
q = solute concentration in internal solution, (wt.%)
t = time, (min.)
$\bar{\rho}$ = average fluid density, (g./ml.)
$\bar{\mu}$ = average fluid viscosity, g./(cm.)(min.)

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2. Vassiliou, Basil, and J. S. Dranoff, *A.I.Ch.E. Journal*, 8, 248 (1962).
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6. Gilliland, E. R., and R. F. Baddour, *Ind. Eng. Chem.*, **45**, 330 (1953).

BOOKS

Absorption, Distillation and Cooling Towers, W. S. Norman, John Wiley and Sons, Incorporated, New York (1961). 477 pages. $11.50.

This book is devoted to the chemical engineering treatment of mass transport phenomena and, more particularly, to the mass transfer unit operations involving gas and liquid phases. Its principal value is as a knowledgebale, up-to-date, and extensive review of engineering research work in these areas.

The first three chapters deal with molecular transport properties and the development of the mass transfer coefficient. The fourth chapter treats the fundamental procedures for the analysis of performance of absorption and distillation towers, and the fifth chapter contains information on equilibrium relations and special distillation processes. The sixth through the thirteenth chapters must be considered the heart of the book. Found here are rather complete discussions on