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Diffusion and Chemical Reaction in Isobutylene Hydration Within Cation Exchange Resin

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The chemical reaction and diffusion rate parameters were determined for the hydration of liquid isobutylene to t-butanol with a cation exchange resin catalyst. High reaction rates were found to result from a high diffusivity of isobutylene within the resin catalyst. Both the high value for diffusivity and its negative temperature coefficient are consistent with the transport mechanism within the resin, being that of surface diffusion of isobutylene in an adsorbed state.

The hydration of isobutylene to *t*-butanol with cation exchange resin as catalyst is an alternative to the conventional hydration process, the hydrogen form ion exchange resin catalyst replacing the sulfuric acid normally used. The use of a resin catalyst gives rise to a three-phase system: an isobutylene-rich liquid phase, an aqueous liquid phase, and the solid catalyst. Phase equilibrium considerations indicate that one of the reactants, isobutylene, will be present only in very low concentrations in the hydrophilic resin phase. In spite of this the hydration rates are surprisingly high. Therefore the study was oriented toward obtaining an understanding of the mechanism of diffusion within the resin, since it appeared that this must be the key to the anomalously high reaction rates.

THEORETICAL MODEL

The theoretical model used contained the following assumptions.

1. Water is present in such large excess within the resin phase, relative to the isobutylene concentration, that the reaction should be independent of water concentration. Direct evidence for the validity of this assumption comes from the values of concentrations of isobutylene and water in the resin phase. The concentration of water in the resin was calculated from the data of Gregor et al. (*1*) and Pepper et al. (*2*). The concentration of isobutylene, measured as a part of this study (*3*), was found to be independent of butanol concentration over the existing concentration range. The equilibrium concentrations in fully swollen resin are:

Water	32.3 g.-moles/liter
Isobutylene	0.0172 g.-mole/liter

Furthermore, in the hydration of propylene with cation exchange resin catalyst, Kaiser et al. (*4*) also found the reaction rate to be independent of the concentration of water.

2. Reaction rate is first order with respect to isobutylene concentration. Lucas and Eberz (*5*) and Lashmet (*6*) have shown the reaction rates to be first order with respect to the olefin concentration.

3. Reaction is effectively irreversible for conditions of this study. The equilibrium constant for isobutylene hydration at 100°C. was determined by Smart et al. (*7*), who found, in terms of mole fractions, $K_x = 38$. For the range of reactant ratios used in this study, this equilibrium

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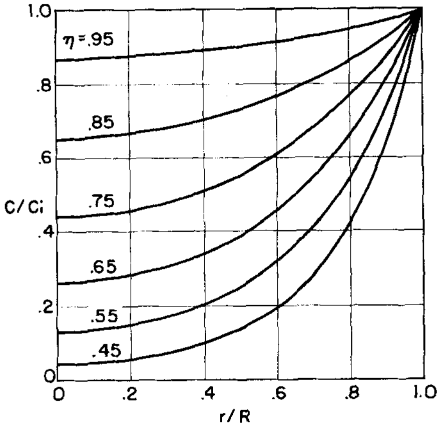

Fig. 1. Dimensionless concentration profiles.

constant corresponds to a minimum of 94% conversion of isobutylene, which is an order of magnitude higher than the conversions obtained in the present study. Measurement of reaction rate at different levels of conversion provided further confirmation for this assumption.

4. Resin particles are isothermal. The maximum temperature rise within the resin particles, from the method given by Damkohler (8), was calculated to be 0.0018°C.

5. Resin particles are perfectly spherical. A research grade of resin was used for the study. Furthermore, microscopic examination of the particles before and after use confirmed that the resin particles were perfectly spherical, were free from cracks, and that there was no breakage during the experiments.

6. Diffusivity of isobutylene is independent of its concentration. Little evidence was available to support this assumption. However, in one study Tayyabkhan (9) found that diffusion coefficients of glycerol and sodium chloride in cation exchange resin were independent of their respective concentrations. While this diffusivity may well be a function of concentration over appreciable ranges in concentration, the very low levels of isobutylene concentration within the resin in this study leave little possibility of concentration differences sufficient to affect the diffusion coefficient.

With these assumptions, the reaction rate-diffusion linked process may be described by the differential equation for a first-order, irreversible reaction in a spherical, isothermal particle:

$$D_e\left(\frac{d^2c}{dr^2}+\frac{2}{r}\cdot\frac{dc}{dr}\right)=kc \qquad (1)$$

Boundary conditions with Equation (1) are

B.C. I $c = c_i$ at $r = R$

B.C. II $dc/dr = 0$ at $r = 0$

The solution in terms of concentration is

$$\frac{c}{c_i}=\frac{R}{r}\cdot\frac{\sinh\left(r\sqrt{k/D_e}\right)}{\sinh\left(R\sqrt{k/D_e}\right)} \qquad (2)$$

Integration of Equation (2) gives the solution in terms of the reaction rate per particle θ:

$$\theta = 4\pi R c_i D_e \left\{R\sqrt{k/D_e}\coth\left(R\sqrt{k/D_e}\right)-1\right\} \qquad (3)$$

If the diffusion rate within the particle were very fast compared with the chemical reaction rate, there would be no concentration gradient within the catalyst particle, and the rate of reaction θ_i would be given by

$$\theta_i = \frac{4}{3}\pi R^3 k c_i \qquad (4)$$

The solution may be put in the form of the effectiveness factor $\eta = \theta/\theta_i$, originally proposed by Thiele (*10*) and Zeldowitsch (*11*), and extended by Wagner (*12*) to include the concept of effective diffusivity rather than pore diffusivity. The solution for the effectiveness factor η in terms of the Thiele number ϕ is

$$\eta = \frac{3}{\phi}\left(\coth\phi - \frac{1}{\phi}\right) \qquad (5)$$

where $\phi = R\sqrt{k/D_e}$

It is deceptively easy to have a case for which the assumption of an irreversible reaction is valid at the catalyst-fluid interface but is invalid toward the center of the catalyst spheres. This fact may be illustrated by reference to the generalized concentration profiles within a particle for a first-order irreversible reaction, given by Equation (2), which is plotted as Figure 1. It will be noted that for $\eta < 0.45$ the concentration at the center of the particle is very low relative to the concentration at the outer surface. At such low values of η, therefore, conditions at the center of the particle may be approaching chemical equilibrium, although overall the system may be far from equilibrium. This region of operation was therefore avoided in the present study.

EQUIPMENT AND PROCEDURE

The study was carried out in a stirred-tank reactor so that the mass transfer problem to the surface of the catalyst spheres could be eliminated. A schematic flow diagram of the equipment is shown in Figure 2. There were two gauging cylinders filled with distilled water. One of the gauging cylinders was connected to the bottom of a 20-liter isobutylene storage vessel, while the other gauging cylinder was connected to one side of a duplex pump. The isobutylene flow rate was measured by the rate of water which displaced isobutylene from the storage vessel to the duplex pump. To prevent flashing of isobutylene during the suction stroke of the pump, the storage vessel was kept at about 65 lb./sq.in.gauge pressure. The gauging cylinders could be refilled from a pressurized water storage vessel without disrupting a run. The pump used was a Milton-Roy reciprocating duplex pump for simultaneously pumping two separate liquid streams. The

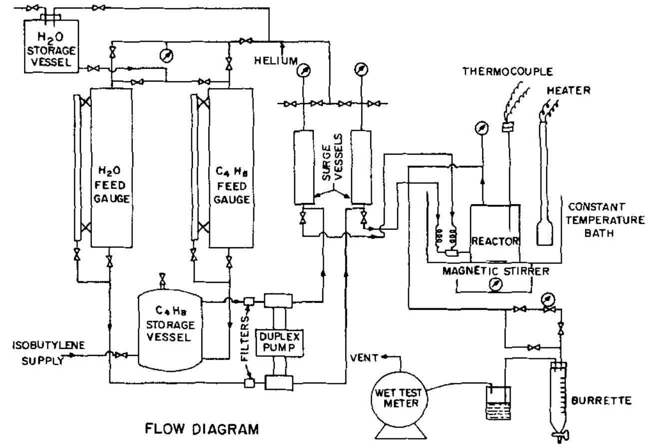

Fig. 2. Schematic flow diagram.

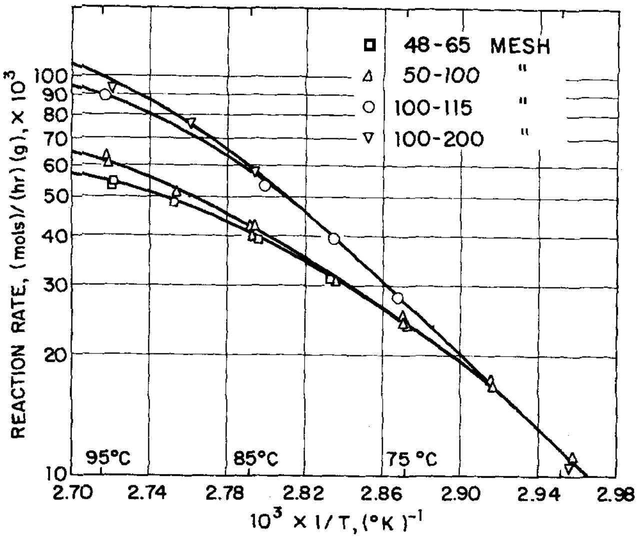

Fig. 3. Effect of temperature on reaction rate.

flow rate of each liquid could be independently and reproducibly controlled. Two helium loaded surge vessels were used to remove pulsations in liquid flow from the pump.

The stirred-tank reactor was an 18-8 stainless steel, flat-bottom, pressure vessel of 463 ml. capacity (3 in. diameter by 4 in. high) with 400-lb. flanges at the top. A ¼-in. stainless steel tube which served as outlet was inserted into the reactor through the center of the top mating blind flange. Just inside the reactor, three 316 stainless steel filter elements (Hoke 540 series, 40 to 55 μ) were connected to the outlet tube by means of an adapter. A thermocouple was also introduced into the reactor through the blind flange. The entire inside surface of the reactor was coated with Teflon with the exception of filter elements and adapter.

The entire reactor assembly could be put in a constant-temperature bath containing a polyalkylene glycol, Ucon 50-HB-280X (Union Carbide), heating fluid. The main advantage of Ucon fluid was its washability with water, so that the reactor could be easily cleaned when taken out of the bath.

The feed streams were separately preheated by passing them through 2-ft.-long, ⅛-in. I.D. tubes submerged in the constant-temperature bath in coiled form. The streams were allowed to mix just before entering the reactor. A piece of woven Teflon cloth, 25-μ pores, was fitted at the reactor inlet to prevent any resin from getting into the feed lines. Stirring in the reactor was obtained by using a magnetic stirrer. At the end of the bar magnet were inserted thin Teflon rings so that the bar actually rested only at those rings when placed on a flat surface. This arrangement completely eliminated breakage of particle due to the grinding action of the rotating bar. The stirrer and reactor were so positioned that the bar magnet was always at the center of the reactor.

The product left the reactor as a liquid through a helium loaded back-pressure regulator. The reactor pressure was maintained at about 30 lb./sq.in.gauge above saturation pressure of isobutylene. Downstream of the back-pressure regulator the unreacted isobutylene flashed at nearly atmospheric pressure, and the gas and liquid products separated at the inlet of the liquid product receiver. The liquid product collected in a 500-ml. burette as receiver, while the vapor flowed through an outlet at the top of the burette into a water bubbler, which removed butanol. The vapor then passed through a wet-test meter before being discharged to the atmosphere.

Standard operating procedures for steady state experiments were observed. In general, it took about 2 hr. to reach steady state conditions, as indicated by frequent refractive index determinations on liquid product. Steady state conditions were maintained for at least 1 hr. before proceeding to the next set of conditions. Resin was collected from the reactor for inspection and analysis at the end of each series of runs.

Materials

Pure grade isobutylene (99.2 mole %) was obtained from Phillips Petroleum Company. Fresh single-distilled water was used for all purposes. Tertiary butanol used was Eastman-Kodak, *highest purity grade No. 820.*

The cation exchange resin used was the hydrogen form of Dowex 50W, monosulfonated polystyrene crosslinked with 8% divinyl benzene, supplied by the Dow Chemical Company.

Moisture content of the resin was determined by heating small quantities of the resin at 100°C. under vacuum for 8 hr. The amount of resin used in experiments was always measured as anhydrous weight. The radius of particles used was based on the mean volume obtained by measuring one hundred swollen particle diameters on a projection microscope.

DATA ANALYSIS

In the stirred-tank reactor, the two liquid phases and the resin particles existed in a state of violent agitation. In such a system, it was expected that the concentration of isobutylene at all points on the surface of each resin particle would be independent of time. Under these conditions the isobutylene-water volumetric ratio would be expected to have no effect on the observed reaction rates.

In order to test this necessary condition, experimental runs were made with different water and isobutylene flow rates at four temperature levels. Results of this series of runs with various amounts of 50- to 100-mesh resin are summarized in Table 1. It is apparent from this table that the reaction rates were independent of the isobutylene-water volumetric ratio. The same data also show that the reaction rates were independent of the conversion level, which confirms the assumption noted earlier that the reaction is irreversible over our range of study. Finally, in Table 1, the agreement obtained between the various runs at the same temperature indicates that a satisfactory level of reproducibility was achieved for the overall experimental procedure.

Reaction rate data for twenty-seven runs, obtained with four resin size ranges, seven temperature levels, and various amounts of resin catalyst, are presented on Figure 3 in the form of an Arrhenius plot. Complete data in tabular form are available (*13*).

Analysis of such data requires separation of the reaction rate and diffusion terms from the overall linked process. Recently the authors (*14*) have shown that the solution for general, first-order irreversible cases can be put in a form from which the reaction rate constant k, the diffusion coefficient D_e, the effectiveness factor η, and the Thiele number ϕ can be obtained directly, without recourse to the various curve-fitting procedures which have been used in the past. In the present study, all temperature levels were investigated with two particle sizes, thus

TABLE 1. EFFECT OF ISOBUTYLENE:WATER (B:W) VOLUMETRIC RATIO ON REACTION RATE

Run No.	Temp., °C	B:W vol. ratio	Conversion, %	Reaction rate 10^3 × moles/(hr.)(g.)
1	69.70	1.28	6.3	16.88
2	69.81	1.93	4.4	17.56
3	76.13	0.97	8.7	24.33
4	76.06	1.30	6.5	24.19
6	84.69	0.89	16.4	42.73
8	84.86	0.71	16.0	40.48
12	85.00	1.58	3.9	42.05
10	94.58	0.59	24.4	60.87
13	94.76	1.17	5.9	63.11

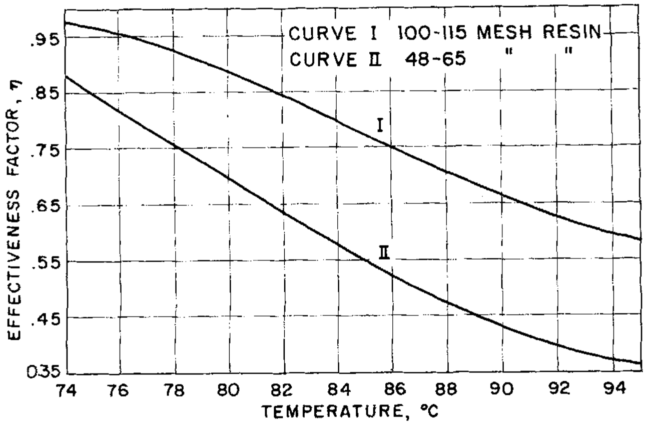

Fig. 4. Effect of temperature on effectiveness factor.

facilitating the determination of the reaction and diffusion parameters by this method. Since reaction rates per particle were required, the number of particles per gram of anhydrous resin and the appropriate particle radii were determined microscopically. Only the rate data for runs with resin of narrow size distribution range (screened in a semidried state) were used for calculation of diffusion and reaction rate constants. The results of these calculations, which yield the rate parameters as the groups c_iD_e and k/D_e, are given in Table 2. The effect of temperature on effectiveness factor is shown on Figure 4.

REACTION RATES

Knowledge of the observed reaction rate and the corresponding value of η made it possible to calculate the reaction rates for $\eta = 1.0$, which are plotted as a function of reciprocal temperature in Figure 5. While a major portion of this Arrhenius type of plot is a straight line, it begins to deviate from the straight line relationship as the temperature goes above 89°C. This behavior may be understood by considering the conditions within a particle. The effectiveness factor for 48- to 65-mesh particles at 89°C. is 0.45, and η decreases further as temperature is increased, as may be seen from Figure 4. For a value of $\eta = 0.45$, it may be calculated from Equations (2) and (5), as indicated on Figure 1, that the concentration of isobutylene at the center of the particle is only 4% of the surface concentration. For lower values of η, the isobutylene concentration at the center of the particle drops even lower. Thus, for $\eta < 0.45$, the concentrations in the vicinity of the center of the particles approach the condition of chemical equilibrium, thus invalidating the assumption of an irreversible reaction, even though the concentrations at the catalyst-liquid interface are far from equilibrium.

Since the ratio k/D_e was calculated with data from the narrow size distribution resin lots only, it was interesting to determine whether this general procedure could be used, with the calculated k/D_e values, to predict the results obtained with wide size distribution resin such as would be used commercially. The wide size distribution resins tested were 50 to 100 and 100 to 200 nominal mesh sizes. The diameters of one hundred particles of the 50- to 100-mesh size range were measured. Since the range of diameters was quite large for this size (largest:smallest diameter ratio being 4.3:1), the one hundred measured diameters were divided into five groups of twenty. The appropriate radii and weights of these groups were then calculated, and the values of ϕ, and thereby η, were predicted. Summation of the predicted reaction rates for each group gave the overall rate for one hundred particles, which in turn gave the reaction rate per gram of anhydrous resin. These predicted and experimental reaction rates for 50- to 100-mesh resin, shown in Figure 6, show excellent agreement. Agreement between predicted and experimental values of the reaction rates for the 100- to 200-mesh particles was not as good. The predicted values were always lower than the experimental values, with a maximum difference of 12% between the two. This difference can be attributed to the difficulty in measuring diameters of 100- to 200-mesh resin particles for which the diameter ratio, largest:smallest, was 13:1.

REACTION RATE CONSTANT AND ACIDITY FUNCTION

The reaction rate constant has been plotted as a function of reciprocal absolute temperature in Figure 7. Taft (*15*) has shown that the logarithm of the reaction rate constant for the hydration of olefins in mineral acids is proportional to the Hammett acidity function. Therefore, for comparison of the catalytic action of ion exchange resins with that of mineral acids for the hydration of isobutylene, the acidity function H_o was chosen as the basis rather than acid concentration. Lucas and Eberz (5) have published values of the reaction rate constant for the hydration of dissolved isobutylene at 25°C. for various concentrations of nitric acid. Purlee et al. (*16*) have given the reaction rate constant for hydration of gaseous isobutylene with 0.973 M nitric acid. Since the distribution coefficient for isobutylene between vapor phase and nitric acid is also available in Purlee's paper, the reaction rate constant for dissolved isobutylene could be calculated. Values of H_o for nitric acid were taken from the paper of Paul and Long (*17*). Values of k for various acid con-

TABLE 2. CALCULATED RESULTS FROM THE REACTION RATE DATA

$1/T \times 10^3$, °K.$^{-1}$	Temp., °C.	ϕ_1	ϕ_2	η_1	η_2	$10^6 \times c_iD_e$	$10^{-4} \times k/D_e$
2.70	97.27	7.44	3.93	0.350	0.570	0.898	12.22
2.72	94.55	6.89	3.64	0.371	0.600	0.937	10.49
2.74	91.86	6.39	3.37	0.397	0.630	0.9505	9.01
2.76	89.22	5.50	2.91	0.448	0.680	1.047	6.67
2.78	86.61	4.57	2.41	0.522	0.750	1.204	4.61
2.80	84.04	3.79	2.00	0.585	0.802	1.387	3.17
2.82	81.51	3.20	1.69	0.648	0.848	1.558	2.26
2.84	79.01	2.56	1.35	0.728	0.900	1.920	1.44
2.86	76.55	2.01	1.06	0.800	0.940	2.470	0.889
2.88	74.12	1.53	0.81	0.870	0.960	3.429	0.516

Note: Subscripts 1 and 2 represent values calculated for 48 to 65- and 100 to 115-mesh resin, respectively. For these two sizes, R_1 = 0.0213 cm. and R_2 = 0.01125 cm.

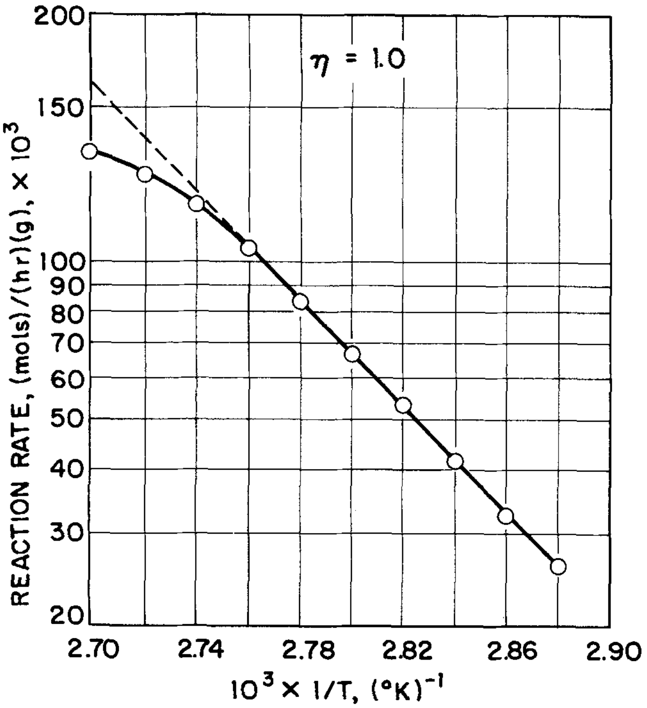

Fig. 5. Effect of temperature on reaction rate for $\eta = 1$.

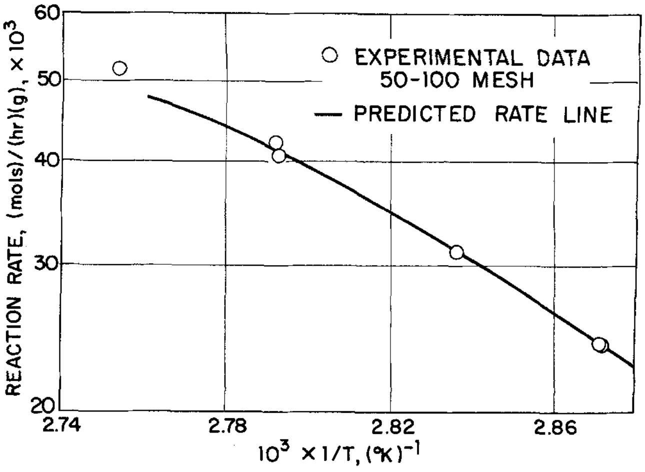

Fig. 6. Predicted and experimental reaction rates.

centrations thus obtained are plotted as a function of Hammett acidity function in Figure 8.

From the values of k obtained with ion exchange resin, as plotted in Figure 7, the value of k at 25°C. was calculated to be 4.53 hr.$^{-1}$. With this value of k used with Figure 8, the equivalent value of Hammett acidity function H_o of -0.50 was obtained for the ion exchange resin. This value of H_o corresponds to about 1.4 N sulfuric or nitric acids. Thus, the resin used in this study is comparable to 1.4 N sulfuric acid or the equivalent, when used as a catalyst for the hydration of isobutylene.

DIFFUSION COEFFICIENT

In order to determine the individual values of D_e and c_i from the calculated values of c_iD_e and k/D_e, one of the terms, k, c_i, or D_e, must be determined independently. The surface concentration of isobutylene, c_i, was measured experimentally (*3*), and the results led to a value of $c_i = 0.0172 \times 10^{-3}$ g.-moles of isobutylene/ml. of fully swollen resin. This value of c_i was found to be independent of both temperature and butanol concentration over the range of those variables in this study. From the measured value of c_i, values of k and D_e were calculated.

Calculated values of the effective diffusion coefficient D_e are plotted as a function of reciprocal temperature in Figure 9. Two particularly notable facts emerge: the diffusivity of isobutylene in the resin is quite high, and the diffusion coefficient decreases as the temperature is increased. That the diffusivities of isobutylene are high may be seen by observing that they are comparable to those for water as reported by Boyd and Soldano (*18*) and Srivastava and Douglas (*19*), despite the large difference in molecular size.

In order to understand this anomalous behavior, it is necessary to examine the condition in which isobutylene would exist within the resin. The sorption of isobutylene by water swollen ion exchange resin will be affected by two kinds of molecular interactions (*20*), namely, dispersion effects (London forces) between isobutylene molecules and the resin matrix, and orientation effects (dipole-dipole interactions) between water molecules within the resin. The result of both these interactions would be that the greater part of isobutylene absorbed by the resin will exist in an adsorbed state on the resin matrix chains. The most significant consequence of the existence of isobutylene primarily in an adsorbed state on the polymer chains would be that the diffusion of isobutylene molecules may occur by the mechanism of surface diffusion of adsorbed molecules along the matrix chains. Whether it is a weak physical or a strong chemical adsorption that occurs is not important, since it has been shown by Hwang and Kammermeyer (*21*) that "the surface flow does not depend upon the type of adsorption; instead it is governed by the activated state."

If the effect of temperature on diffusivity is put in the familiar exponential form, the exponent E_d, which would normally be the energy of activation for diffusion, must, of course, in the present case, be negative. In order to avoid confusion caused by nomenclature, it is preferable to define the exponent E_d simply as the temperature coefficient of effective diffusivity. What is more fundamental is not to confuse the temperature coefficient of effective diffusivity E_d with the energy of activation for true surface diffusion. The temperature coefficient (energy of activation) for diffusion in the adsorbed state, although small, is certainly positive. However, Barrer and Strachan (*22*) have shown that the total flux due to surface diffusion will always decrease as the temperature is increased. This conclusion may be appreciated by noting that the surface flow is proportional to the product of the diffusivity and the adsorption constant, that is, is proportional to D_sk_s. The temperature dependence of each of these terms may be given as $k_s = k_o \exp (\Delta E/RT)$, and $D_s = D_o \exp (-E/RT)$, where ΔE is the energy of adsorption and E is the energy of activation for diffusion. Since $\Delta E > E$, it is apparent that the surface flux must always decrease as temperature is increased. And since the effective diffusivity, by definition, is based on total flux, it will also decrease with increasing temperature. When it is realized that the temperature coefficient of effective diffusivity E_d includes not only the energy of activation for diffusion but also the effect of temperature on adsorption equilibrium and on the heat of sorption, the negative temperature coefficient no longer appears anomalous. For the purpose of analyzing the role of diffusion in heterogeneous catalysis, however, it is the effective diffusivity which is the essential variable.

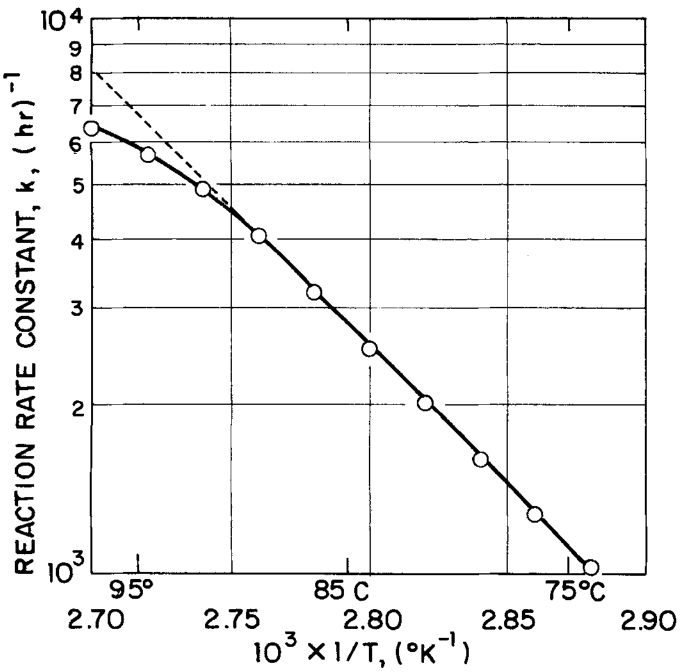

Fig. 7. Effect of temperature on reaction rate constant.

The results of this study appear to provide the most definite experimental evidence yet available for the occurrence of surface diffusion and the associated negative temperature coefficient for effective diffusivity in heterogeneous catalysis. As long ago as 1951, Wheeler (*23*) noted that, although there had not yet been any reaction rate data for which it was necessary to invoke surface diffusion to explain the rate of diffusion in catalysts, such reactions would no doubt be found. In 1962, Miller and Kirk (*24*) suggested the possibility that surface diffusion may have been occurring in their alcohol dehydration studies. Krusuk and Smith (*25*) in 1965 reevaluated the effect of surface diffusion for certain cases and reported that, based on their analysis of the data of Miller and Kirk, no definite conclusion concerning the presence of surface diffusion could be reached.

There are, however, a number of publications which deal with the measurement of surface diffusion and permeability of gases through porous and microporous solids, such as sintered glass and carbon plugs. For example, Gilliland (*26*) noted that the permeabilities of hydrocarbons through microporous media were many times larger than the values predicted from the correlation for nonadsorbed gases, and were sometimes forty to sixty times larger than bulk liquid permeabilities. He also noted that such permeabilities decreased rapidly as the temperature was increased. Hwang and Kammermeyer (*21*) and Carmen and Malherbe (*27*) also report a negative temperature coefficient for permeability of various gases through microporous media.

Thus the two principal findings with respect to the effective diffusivity of isobutylene in ion cation exchange resin, that is, the high values and the negative temperature coefficient, are both seen to be consistent with the phenomenon of surface diffusion, which in turn would be a consequence of the existence of isobutylene in an adsorbed state on the resin matrix. These observations and inferences are also consistent with the results of investigations for nonreactive systems and with the possibility for adsorption of isobutylene molecules on the resin matrix. From an overall point of view, this conclusion explains the surprisingly high rate of reaction for a heterogeneous system in which the key reactant is present only at a very low level concentration within the catalyst.

ENERGY OF ACTIVATION

In heterogeneous catalysis, the true energy of activation of the chemical reaction E_o may be determined from an analytic relationship between the diffusion parameters and the energies of activation of the chemical reaction, of diffusion, of the overall rate process. Weisz and Prater (*28*) gave such a relationship in the form

$$\frac{E}{E_o} = 1 + \frac{1}{2}\,\frac{d\,(\ln \eta)}{d\,(\ln \phi)} \tag{6}$$

Recently Gupta and Douglas (*14*) have derived the more general relation

$$E_o = \frac{2E + E_d\psi}{2 + \psi} \tag{7}$$

which does not omit, as did Weisz and Prater, the temperature coefficient of effective diffusivity E_d. The true energy of activation may also be determined directly from the temperature dependence of θ_i, given for the present case by Figure 5.

When the following set of values at 80°C. are used with Equation (7)

$$E_d = -20.95 \text{ kcal./g.-mole}$$

and for 48- to 65-mesh resin

$$E = 12.4 \text{ kcal./g.-mole}$$
$$\eta = 0.70$$
$$\psi = -0.51$$

the value calculated for E_o is 23.8 kcal./g.-mole. The fact that the value given by the Weisz and Prater equation for E_o is only 16.6 kcal./g.-mole emphasizes the importance of including the temperature dependence of diffusivity.

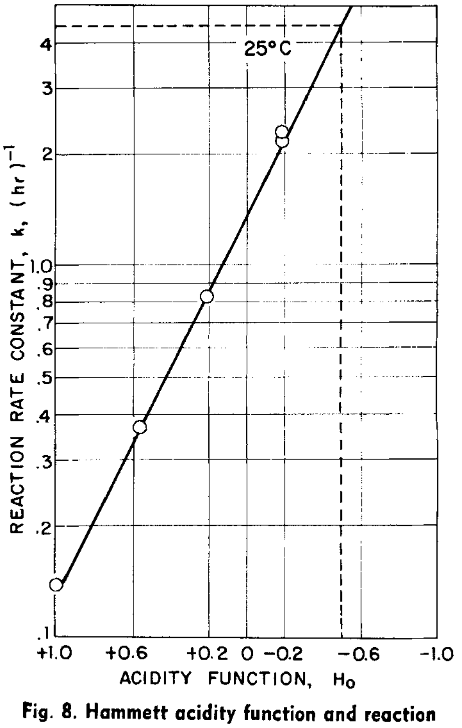

Fig. 8. Hammett acidity function and reaction rate constant.

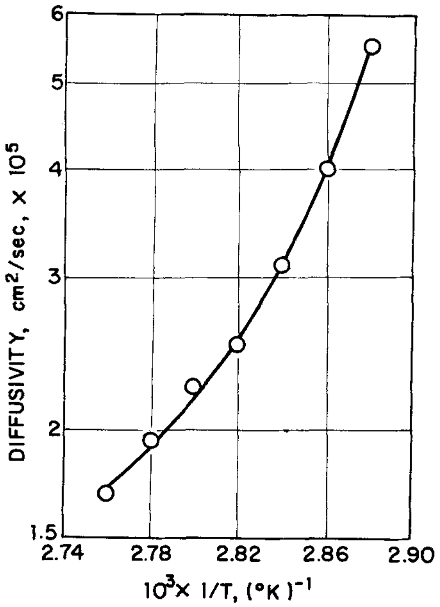

Fig. 9. Effect of temperature on effective diffusivity of isobutylene.

The values of the energy of activation for the hydration of isobutylene as calculated from the present study with cation exchange resin and those reported by Lucas and Eberz (*5*) and Purlee et al. (*16*) for reaction in aqueous acid solutions are in good agreement.

	Energy of activation, kcal./g.mole
From Equation (7)	23.8
From Figure 5	22.7
Purlee et al.	21.1
Lucas and Eberz	23.4

CONCLUSIONS

For the hydration of isobutylene with a cation exchange resin catalyst, a model in terms of first-order, irreversible kinetics and an effective diffusivity for isobutylene was found to be satisfactory for any particle size and temperature for which the effectiveness factor $\eta > 0.45$.

The equivalent Hammett acidity function for the cation exchange resin was found to be —0.50, indicating that the catalytic activity of the resin is comparable to that of 1.4 *N* sulfuric acid.

The energy of activation of the hydration reaction in the ion exchange resin agrees with the values reported for the reaction conducted in aqueous mineral acids.

The values of the effective diffusivity for isobutylene are relatively high, and they decrease with increasing temperature. The findings are consistent with the mechanism of transport of isobutylene through the resin being that of surface diffusion of isobutylene molecules which are adsorbed on the polymer matrix of the resin.

NOTATION

c = concentration of isobutylene within the resin, moles/ml.
c_i = concentration of isobutylene at the surface of the particle, moles/ml.
D_e = effective diffusivity (effective diffusion coefficient), sq.cm./hr.
D_s = surface diffusivity
E = apparent energy of activation, cal./mole.
= energy of activation for diffusion
E_d = temperature coefficient of effective diffusivity, cal./mole
E_o = true energy of activation for chemical reaction, cal./mole
ΔE = energy of adsorption
H_o = Hammett acidity function
k = reaction rate constant, hr.$^{-1}$
k_s = Henry's law adsorption constant
r = radial distance from the center of the particle, cm.
R = radius of the particle, cm.
T = absolute temperature, °K.

Greek Letters

η = effectiveness factor
θ = reaction rate per particle, moles/hr.
θ_i = reaction rate, moles/hr., for $\eta = 1.0$
ϕ = Thiele number, $R\sqrt{k/D_e}$
ψ = effective diffusivity function, $d(\ln \eta)/d(\ln \phi)$

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