Hydration of Propylene Oxide Using Ion-Exchange Resin Catalyst in a Slurry Reactor

Kinetics of hydration of propylene oxide using an ion-exchange resin catalyst in a slurry reactor was studied. The kinetics of homogeneous, uncatalyzed reaction was studied separately and used to obtain heterogeneous reaction kinetics. The homogeneous reaction was found to be 0.43 order with respect to propylene oxide concentration. The heterogeneous reaction was found to have intraparticle diffusional resistance under certain conditions. The intrinsic kinetic parameters and effective diffusivity were obtained from these data. The heterogeneous reaction was found to be 0.55 order with respect to propylene oxide concentration. The activation energies obtained for homogeneous and heterogeneous reactions were 51.5 and 53.4 kJ/mol, respectively. A theoretical model incorporating all the mass transfer resistances has been proposed.

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SCOPE

Most of the commercial processes for the manufacture of propylene glycol are via hydration of propylene oxide. This reaction can be carried out in the liquid phase with or without a catalyst. Generally soluble acid or ion-exchange resins are suitable catalysts for this reaction. The heterogeneous ion-exchange catalysts have some advantages over the soluble acid catalysts: (i) the separation of products is easier without contamination; (ii) corrosion of the equipment is minimized; and (iii) the catalyst can be regenerated and used repeatedly. Polyanski and Potudina (1963) have studied the hydration of propylene oxide using ion-exchange resins as catalysts. However, no intrinsic kinetics has been reported in the literature, thus providing incentive for this study. This system also provides an interesting example of a three-phase slurry reaction in which the reaction occurs both homogeneously in the liquid phase and heterogeneously at the catalyst surface. Theoretical models incorporating mass transfer effects for such systems have also been developed in this work. Such a study would be useful in the analysis of experimental data on this type of systems and design of reactors.

CONCLUSIONS AND SIGNIFICANCE

Hydration of propylene oxide to propylene glycol was studied using ion-exchange resin catalyst. This catalyst was found to be selective for the formation of monopropylene glycol. The homogeneous (uncatalyzed) and the heterogeneous reactions were studied separately. The contribution of homogeneous reaction was significant (about 25%) at lower catalyst loadings, (8.3 kg/m^3), while at higher loadings (50.0 kg/m^3) the homogeneous reaction rates were about 5% of the observed rates.

The homogeneous reaction, when studied separately was found to be kinetically controlled. The order of homogeneous reaction was found to be 0.43 with respect to propylene oxide concentration and activation energy was 51.5 kJ/mol.

The heterogeneous reaction kinetics was also studied and the order with respect to propylene oxide was found to be 0.55 with an activation energy of 53.4 kJ/mol. The intraparticle diffusional resistance was found to be important, and the values of effective diffusivity were determined from these data. These indicate a tortuosity factor of three for the catalyst used.

A theoretical model incorporating homogeneous and heterogeneous reactions and all the mass transfer resistances has been developed. An equation for an overall effectiveness factor for general order reaction has been derived. Based on this model the mixing pattern in the gas phase does not influence the semibatch reactor performance.

The main reactions involved in the hydration of propylene oxide to propylene glycols are:

$$\underset{(propylene\ oxide)(PO)}{C_3H_6O} + H_2O \rightarrow \underset{(monopropylene\ glycol)(MPC)}{CH_3OH\ CHOHC\ H_2} \qquad \text{(i)}$$

$$CH_3OHCHOHCH_2 + C_3H_6O \rightarrow \underset{(dipropylene\ glycol)(DPG)}{C_6H_{14}O_3} \qquad \text{(ii)}$$

The desired product is monopropylene glycol, though dipropylene glycol also has some applications. A summary of literature on hydration of propylene oxide is presented in Table 1. The following sections discuss the theoretical model and experimental results on this reaction using ion-exchange resin catalyst.

GENERAL THEORY OF HOMOGENEOUS-HETEROGENEOUS SLURRY REACTORS

Chaudhari and Ramachandran (1980) have described an approach for modelling of homogeneous–heterogeneous slurry reactions for first-order reactions. In this work an analysis for general power law kinetics has been presented, as the system, hydration

TABLE 1. LITERATURE ON HYDRATION OF PROPYLENE OXIDE

Investigator	Catalyst	Reactor Type	Reaction Conditions Temp. K	Reaction Conditions Pres. atm.	Yield of MPG %
McAteer (1951)	Aluminium Fluoride	Fixed Bed	530	1	90.0
Robeson and Webb (1952)	Aqueous Acid Medium	—	423 (pH = 4.7) 398 (pH = 5.3) 423 (pH = 6.2)	170 170 170	88.5 91.8 87.3
Ferrero et al. (1954)	Oxalic Acid	—	—	—	—
Long and Pritchard (1956)	Inorganic Acids and Bases	—	—	—	—
Pritchard and Long (1956)	Perchloric Acid	—	273	—	—
Freidlin and Sharf (1958)	K_3PO_4	Fixed Bed	505	1	50-7
Tokuno et al. (1962)	Cation and Anion Exchange Resin (PO Dissolved in 0.02% H_2SO_4)	Fixed Bed	323	—	—
Polyanski and Potudina (1963)	Ion-Exchange Resins	—	—	—	—
Myszkowski et al. (1966)	Noncatalytic	Tubular Pipe Autoclave	463-473	10-15	90.0
Levin and Shapiro (1970)	Tetrealkylammonium Halides, Halides of Alkyl Amine and Alkali Metal Halides	—	353-493	20-180	—
Izumi and Yutani (1973)	Calcium Apatite	Fixed Bed	523	—	59.6
Popova et al. (1974)	SO_2 Dissolved in Water	—	—	—	81-83
Cipriani et al. (1976)	Triethyl Amine	—	383	—	97.5
Lebedev et al. (1976a)	Carbonates and Bicarbonates	—	323-363	—	—
Lebedev et al. (1976b)	Carbonates and Bicarbonates	—	—	—	84-90
Carra et al. (1979)	Inorganic Bases	—	301-349	1	—

of propylene oxide, follows nonlinear kinetics. Only reaction i is assumed to occur which would be applicable for conditions under which dipropylene glycol formation is negligible. If the liquid is assumed to be completely backmixed and the gas phase moves in a plug flow, the rate of transport of A (propylene oxide) from the gas phase to the liquid bulk is given as (Chaudhari and Ramachandran, 1980):

$$R_A = M_A[A_{gi}/H - A_l] \tag{1}$$

The rate, R_A, is also equal to the rate of transport from the liquid bulk to the catalyst surface plus the amount of A reacting in the bulk liquid by noncatalytic heterogeneous reaction. Hence,

$$R_A = k_1 A_l^{n_1} + k_s a_p (A_l - A_s) \tag{2}$$

Also, the rate of reaction at the catalyst surface is given as:

$$k_s a_p (A_l - A_s) = \eta_c w k_2 A_s^{n_2} \tag{3}$$

where, η_c, the catalytic effectiveness factor is given as an approximation as (Bischoff, 1965):

$$\eta_c = \frac{1}{\phi}\left[\mathrm{Coth}(3\phi) - \frac{1}{3\phi}\right] \tag{4}$$

with

$$\phi = \frac{d_p}{6}\left[\frac{n_2+1}{2}\,\frac{\rho_p k_2 A_s^{(n_2-1)}}{D_e}\right]^{0.5} \tag{5}$$

Eliminating the unknown terms A_l and A_s in Eqs. 1 to 3, we obtain the following expression for the overall rate of reaction:

$$R_A = k_1\left[\frac{A_{gi}}{H} - \frac{R_A}{M_A}\right]^{n_1} + \eta_c w k_2 \left[\frac{A_{gi}}{H} - R_A\left(\frac{1}{M_A} + \frac{1}{k_s a_p}\right) + \frac{k_1}{k_s a_p}\left(\frac{A_{gi}}{H} - \frac{R_A}{M_A}\right)^{n_1}\right]^{n_2} \tag{6}$$

Equation 6 is implicit in R_A and a trial and error method has to be used to evaluate this quantity. When all the mass transfer resistances are negligible, the overall rate of reaction is given as:

$$R_A = k_1\left[\frac{A_{gi}}{H} - \frac{R_A V}{HQ}\right]^{n_1} + w k_2 \left[\frac{A_{gi}}{H} - \frac{R_A V}{HQ}\right]^{n_2} \tag{7}$$

The term $[A_{gi}/H - R_A V/HQ]$ can be shown to be equal to the dissolved concentration of A, corresponding to the outlet partial pressure by a simple material balance. Hence Eq. 7 can be written as:

$$R_A = k_1\left(\frac{A_{go}}{H}\right)^{n_1} + w k_2 \left(\frac{A_{go}}{H}\right)^{n_2} \tag{8}$$

This equation can be used to interpret the results in the absence of mass transfer effects.

The rate of reactions can be represented in terms of an overall effectiveness factor defined as (Ramachandran and Chaudhari, 1980):

$$\eta = \frac{R_A}{k_1\left(\frac{A_{gi}}{H}\right)^{n_1} + w k_2 \left(\frac{A_{gi}}{H}\right)^{n_2}} \tag{9}$$

Using the kinetic data (discussed in later sections) and conditions used for hydration of propylene oxide, the values of R_A and η were calculated using Eqs. 6 and 9 respectively for different values of w. Figure 1 shows a plot of η vs. w, for different temperatures. Some experimental values of η are also shown for 348 K, for comparison. With increase in w, the overall effectiveness factor, η, decreases. This is normally observed when gas-liquid mass transfer is the controlling resistance. However, in this particular case, the gas-liquid mass transfer resistance was found to be negligible (as shown later by experiments at different agitation speeds). Therefore, the drop in η at higher catalyst loadings can be ascribed to the

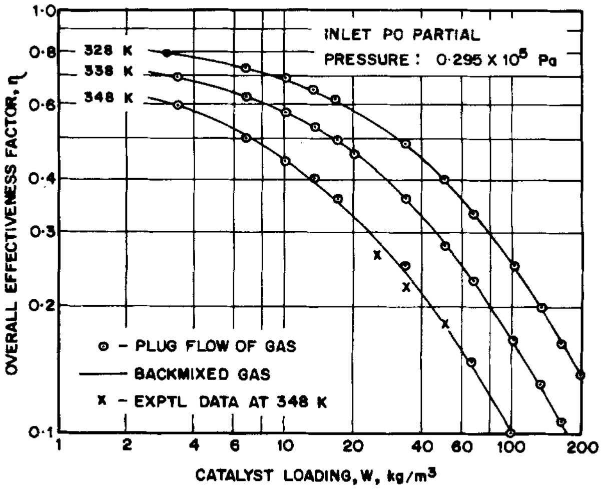


Figure 1. A plot of overall effectiveness factor vs. catalyst loading for propylene oxide hydration.

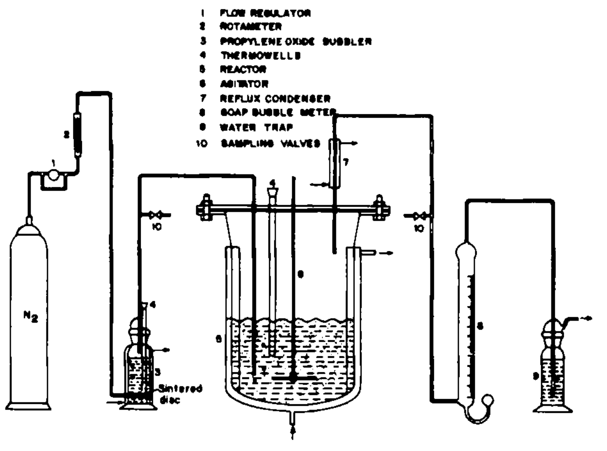


Figure 2. Schematic diagram of apparatus.

significant change in the gas-phase concentration of propylene oxide in the reactor (which results in lower effective concentration of dissolved propylene oxide). Under these conditions, the parameter M_A in Eq. 1 approximates to the term HQ/V and hence, the supply of propylene oxide becomes the controlling resistance and not $K_L a_B$.

Chaudhari and Ramachandran (1980) have shown that for both sparingly soluble gases and highly soluble gases, the effect of gas mixing is negligible. For the present system, as propylene oxide is highly soluble in water, the gas-phase mixing pattern is not likely to influence the reactor performance.

EXPERIMENTAL

In the present work, the hydration of propylene oxide was carried out in a slurry reactor in which propylene oxide was bubbled (with nitrogen as a diluent) in an aqueous suspension of ion-exchange resin. A schematic diagram of the experimental setup used is shown in Figure 2. The reactor used was an all-glass agitated reactor of 100 mm diameter and 200 mm height. An outer jacket was provided in the reactor through which water at constant temperature could be circulated. Temperature was maintained within ±0.1°C using a thermostat. A stainless-steel stirrer with six blades, turbine-type impeller (50 mm in width), and three baffles were provided in the reactor.

Propylene oxide was taken in a glass bubbler of 50 mm diameter and 200 mm height. This was also jacketed to circulate chilled water at a desired temperature. Nitrogen from a cylinder was bubbled through the propylene oxide. A uniform dispersion of nitrogen in propylene oxide bubbler was ensured by using a sintered glass disc distributor.

In a typical experiment, 0.6 L of distilled water and a known amount of dry catalyst (ion-exchange resin) were charged into the reactor. The operating L/D ratio in the reactor was almost equal to one. After the desired temperature was reached in the reactor and in the bubbler, the stirrer was switched on and a constant nitrogen flow was started through the bubbler. The propylene oxide-nitrogen mixture was then bubbled through the aqueous suspension of ion-exchange resin in the reactor. The agitator speed was 13.3 Hz. The minimum agitation speed required (Zweitering, 1958) to keep the catalyst particles in suspension, at the highest catalyst loading used (50 kg/m^3) was 6 Hz. The gas stream exiting the reactor, was vented through a reflux condenser. Liquid samples (about one mL) were taken out from the reactor through a sampling tube for analysis of dissolved propylene oxide, propylene glycol, and dipropylene glycol. The nitrogen-propylene oxide mixture entering and leaving the reactor were also analyzed to determine material balances. The samples were analyzed using gas-liquid chromatography. Two-meter columns were packed with 5% carbowax-1500 on chromosorb; and a thermal conductivity detector was used. The column and detector temperatures were 403 and 503 K, respectively. The carrier gas (hydrogen) flow rate was 7×10^{-7} m^3/s (42 mL/min).

Distilled propylene oxide and distilled water were used in all the runs. The pH of water used was 6.6. Ion-exchange resin used was Indion-225, supplied by Ms. Ion Exchange (India) Ltd. The resin is a strong acidic cross-linked polystyrene bead with SO_3^- as an active group ($\epsilon = 0.5$). Analytical grade propylene glycol and dipropylene glycol supplied by Ms. Fluka were used for preparing standard samples for analyses.

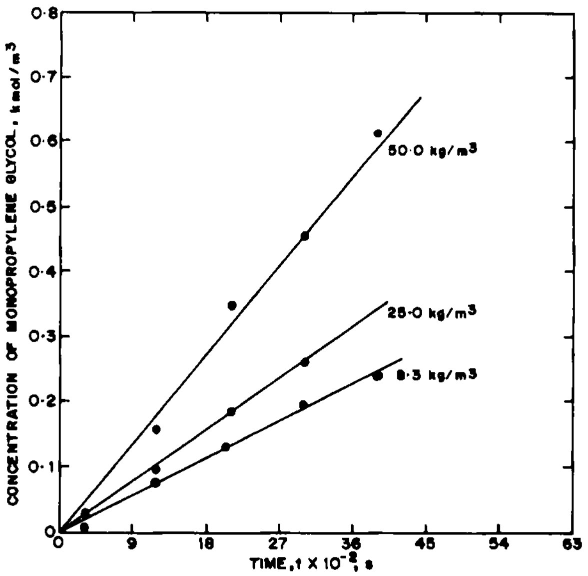


Figure 3. A plot of concentration of monopropylene glycol vs. time, for different catalyst loadings.

Calculation of Rates

Preliminary experiments indicated that the formation of dipropylene glycol was negligible during the initial period of the reaction (about 1 hour). Hence the rate of reaction of propylene oxide can be taken as equal to the rate of formation of monopropylene glycol. This was also confirmed by material balance. In each run the concentration of propylene glycol as a function of time was observed, and the reaction rates calculated from the slope of concentration vs. time plots. The activity of the catalyst was found to be constant over the initial period as noticed from the linear variation of product concentration with time (Figure 3). The homogeneous reaction was studied independently by carrying out some experiments in the absence of catalyst.

The dissolved concentration of propylene oxide (analyzed by GC) was found to be corresponding to the outlet partial pressure of propylene oxide in all the experiments. Hence the outlet partial pressure of propylene oxide was used in kinetic analysis. This is important to consider as the conversion of propylene oxide ranged from 2 to 81%.

RESULTS AND DISCUSSION

Solubility of Propylene Oxide in Water

For the interpretation of data on a gas-liquid-solid system, the solubility of the gaseous species in the liquid medium, must be known. This was determined experimentally for the present system. The concentration of dissolved propylene oxide in water corresponding to a given partial pressure was estimated by analysis of both liquid and gas samples. As will be shown later, under these conditions the mass transfer resistance was absent and hence the dissolved concentration of propylene oxide represented the solubility. The data obtained at different temperatures are presented in Table 2. These data were correlated by the following empirical equation.

TABLE 2. HENRY'S CONSTANT FOR PROPYLENE OXIDE-WATER SYSTEM

Temp. K	Henry's Const. from VLE Data $H' \times 10^{-4}$ Pa·m^3·kmol^{-1}	Henry's Const. (Experimental) $H' \times 10^{-4}$ Pa·m^3·kmol^{-1}
323	8.8345	8.2035
326	9.7423	10.7643
337	13.6744	15.6372
348	18.7647	17.4190

TABLE 3. EXPERIMENTAL DATA ON HOMOGENEOUS REACTION

Run No.	Reaction Temp. K	Partial Pres. of Propylene Oxide in Reactor Outlet $p_g \times 10^{-5}$ Pa	Homogeneous Reaction Rate $R \times 10^6$ kmol/m³/s
1	337	0.1988	8.885
2	348	0.1593	10.183
3	353	0.1334	12.767
4	359	0.0965	16.083
5	348	0.2060	12.267
6	348	0.2640	14.500
7	348	0.3854	17.833

$$\ln H' = 21.704 - 3347/T \tag{11}$$

where H' is the solubility coefficient defined as (p_g/A^*) and has the units Pa·m³·kmol⁻¹. The value of H' is also equal to

$$H' = \frac{\gamma_\infty P^*}{\rho_M} \tag{12}$$

where P^* is the vapor pressure of propylene oxide at a given temperature, γ_∞ is the activity coefficient of propylene oxide at infinite dilution and ρ_M is the molal density of the solution. H' is related to H as $H = H'/RT$. The vapor pressure data for propylene oxide above 40°C was reported by Bott and Sadler (1966) and was correlated as:

$$\log (P^*/133.2) = 7.658 - 1{,}472/T \tag{13}$$

Similarly the activity coefficient γ_∞ at infinite dilution is obtained from the VLE data reported by Wickert et al. (1952) and is equal to 29.073. Henry's constant calculated by this method agreed well with the experimental data within 10% (Table 2).

Homogeneous Reaction

To determine the kinetics of the homogeneous reaction of propylene oxide with water the rates were observed at different partial pressures of propylene oxide and temperatures (Table 3). Under the conditions used in this work, the agitation speed had no influence on the rate of reaction. Thus the reaction was assumed to be controlled by chemical kinetics. Also, as one of the reactants (water) was always in excess, the reaction can be assumed as pseudo n_1th order with respect to propylene oxide concentration. The rate of reaction can then be represented as (from Eq. 10 at $w = 0$):

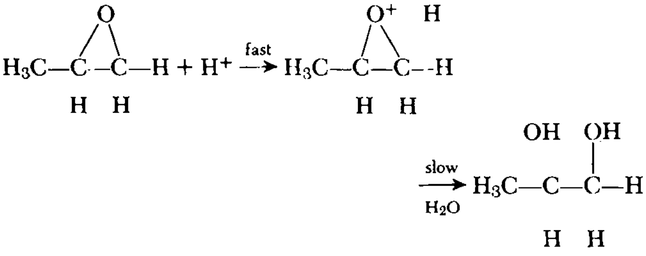
$$R_1 = k_1 \left(\frac{A_{go}}{H}\right)^{n_1} = \alpha_1 \exp\left(\frac{-E_1}{RT}\right)\left(\frac{A_{go}}{H}\right)^{n_1} \tag{14}$$

The effect of propylene oxide partial pressure on the rate of reaction is shown in Figure 4, which indicates a fractional order dependence. The values of α_1, n_1, and E_1, were obtained by a linear least-square analysis for the data. The values are:

$\alpha_1 = 1.792 \times 10^3\ (\mathrm{m^3/kmol})^{(n_1-1)} s^{-1}$
$E_1 = 5.148 \times 10^7$ J/kmol
$n_1 = 0.433$

The temperature dependence of the homogeneous reaction rate constant is shown in Figure 5, as a plot of $\ln k_1$ vs. $1/T$.

The fractional order with respect of propylene oxide deserves some comments. Gritter (1967) has proposed the following mechanism for acid catalyzed hydration of epoxides.



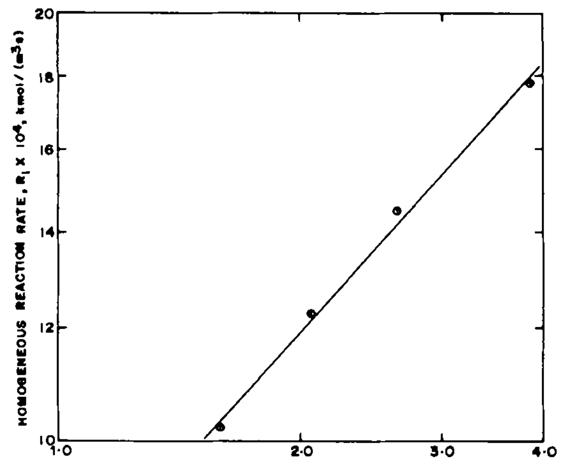


Figure 4. Effect of partial pressure of propylene oxide on homogeneous reaction rate.

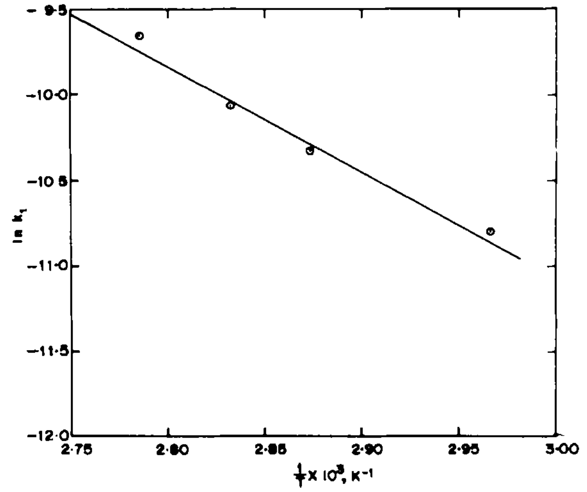


Figure 5. Effect of temperature on homogeneous reaction rate constant.

The rate equation based on this mechanism, assuming second step to be rate-controlling, is of the form

$$r_A = \frac{k_i'(\mathrm{H^+})(A_l)}{K_m + A_l} \tag{15}$$

which is similar to Michaelis–Menten kinetics for enzyme reactions. This type of rate models can also be approximated as a power law model with a fractional order with respect to the reactant A. The observed fractional order with respect to A in this work is therefore consistent with the above mechanism.

Overall Reaction Rates

The effects of different parameters on the overall rate of reaction (with catalyst) was studied, and the experimental data is presented in Table 4. The effect of catalyst loading is shown in Figure 6 for 348 K and an inlet propylene oxide partial pressure of 0.3040×10^5 Pa. This plot is approximately a straight line at lower catalyst loadings with a significant intercept which agrees well with the observed rate of homogeneous reaction in consistent with Eq. 7. The data at higher catalyst loadings deviate from the straight line because the effective partial pressure A_{go} also changes with catalyst loadings.

To determine the order of reaction for the heterogeneous reaction with respect to propylene oxide, a number of experiments were carried out at different inlet partial pressures of propylene oxide.

To ensure that the gas to liquid mass transfer resistance is neg-

TABLE 4. EXPERIMENTAL DATA ON OVERALL RATE OF REACTION

Run No.	Catalyst Loading kg/m^3	Reaction Temp. K	Partial Pres. of Propylene Oxide in Reactor Outlet $p_g \times 10^{-5}$ Pa	Overall Reaction Rate $R_A \times 10^5$ kmol/(m^3·s)	Net Heterogeneous Reaction Rate $R_2 \times 10^5$ kmol/(m^3·s)
11	33.3	323	0.5269	18.7000	18.0411
12	33.3	324	0.1327	9.6167	9.2375
13	33.3	329	0.1155	10.5330	10.0796
14	33.3	337	0.0947	11.3670	10.7969
15	33.3	353	0.0579	12.0400	11.1458
16	33.3	348	0.0989	15.0290	14.1025
17	33.3	348	0.2067	25.4170	24.1481
18	33.3	348	0.3506	40.9000	39.3086
19	8.3	348	0.1307	4.7510	3.7070
20	16.7	348	0.1067	7.8000	6.8441
21	25.0	348	0.0743	11.4560	10.6369
22	33.3	348	0.0635	12.5610	11.7951
23	50.0	348	0.0399	14.8320	14.2051

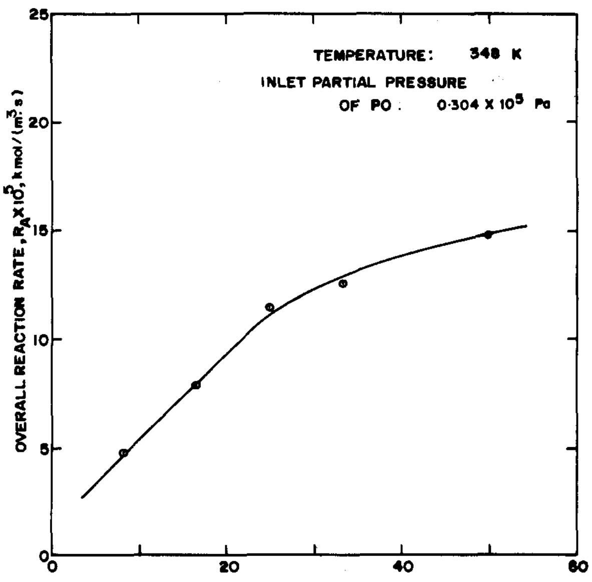


Figure 6. Effect of catalyst loading on the overall rate of reaction.

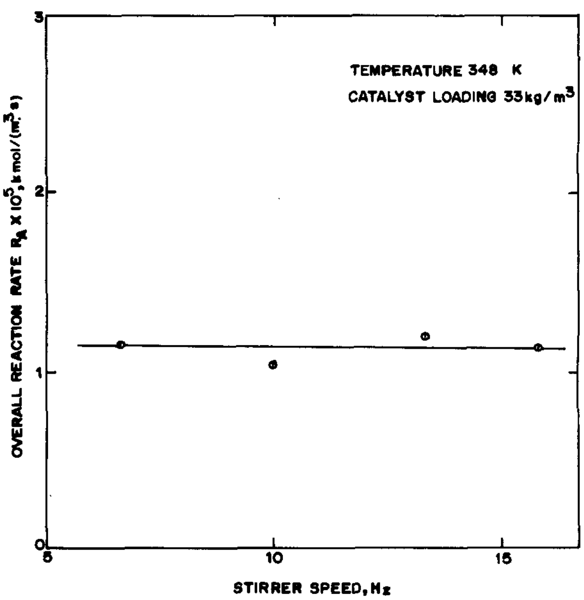


Figure 7. Effect of stirrer speed on the overall reaction rate.

ligible, a few experiments were carried out at different agitation speeds, keeping the other conditions constant. The effect of stirrer speed on the reaction rates is shown in Figure 7 for 348 K and a catalyst loading of 33 kg/m^3. From this figure it is seen that increases in agitation speed have no influence on the overall rate of reaction. This suggests that the gas to liquid mass transfer resistance is not important. This was also confirmed by comparing the observed rates with the maximum rate of gas-liquid mass transfer $(k_L a_B A_{go}/H)$. The ratio $[R_A/k_L a_B (A_{go}/H)]$ was found to be less than 0.03 for all the runs, thus suggesting the absence of gas-liquid mass transfer resistance. The value of $k_L a_B$ for these calculations was obtained from the correlation of Yagi and Yoshida (1975).

Similar calculations were performed to check the influence of liquid-solid mass transfer resistance. The value of k_s was obtained from the correlation of Sano et al. (1974). The factor $[R_A/k_s a_p(A_{go}/H)]$ for all the data was found to be less than 0.025, thus indicating that this resistance is unimportant.

To check the significance of intraparticle diffusion, the following criteria suggested by Satterfield (1970) can be used:

$$\phi_1 = \frac{R_o}{3}\left[\frac{n_2+1}{2}\,\frac{\rho_p R_2}{D_e w (A_{go}/H)^{n_2}}\right]^{0.5} < 0.2 \qquad (16)$$

for absence of intraparticle diffusional gradients. Here, R_2 is the rate of heterogeneous reaction obtained by subtracting the contribution of homogeneous reaction.

$$R_2 = R_A\ (\text{overall}) - k_1 (A_{go}/H)^{n_1} \qquad (17)$$

The values of ϕ_1 calculated assuming $n_2 = 0.55$ and $D_e = D\epsilon/\tau = 5.8442 \times 10^{-10}$, m^2/s (at 348 K), were in the range of 0.4 to 1.5, thus indicating that intraparticle gradients for propylene oxide concentration have to be considered.

Therefore, the rate of heterogeneous reaction can be represented as:

$$R_2 = \eta_c w k_2 (A_{go}/H)^{n_2} \qquad (18)$$

where η_c is given by Eqs. 4 and 5. In this equation there are three unknown parameters, k_2, n_2 and D_e. A trial and error method (search technique) was used to obtain these parameters for the data at 348 K. The value of D_e obtained was 5.8442×10^{-10} m^2/s. The molecular diffusivity D, calculated by Wilke-Chang (1955) equation, is 3.5065×10^{-9} m^2/s. This suggests a tortuosity factor value of three. The value of n_2 (0.55) obtained at 348 K was assumed to be valid at other temperatures also, and the values of k_2 was obtained by using Eq. 18. The D_e values required here were calculated from the molecular diffusivity (Wilke-Chang equation, 1955) and a tortuosity factor of three by the relationship $D\epsilon/\tau$. The results of k_2 and D_e at various temperatures are given in Table 5.

The temperature dependence of the heterogeneous reaction rate constant is shown in Figure 8 as a plot of $ln\ k_2$ vs. $1/T$. The acti-

TABLE 5. HETEROGENEOUS REACTION RATE CONSTANTS AND EFFECTIVE DIFFUSIVITIES

Temp. K	Heterogeneous Reaction Rate Constant $k_2 \times 10^6$ $\left(\frac{m^3}{kg}\right)\left(\frac{m^3}{kmol}\right)^{(n_2-1)} s^{-1}$	Effective Diffusivity $D_e \times 10^{10}$ m^2/s
323	7.9495	3.7509
324	9.8496	3.8252
329	13.1409	4.1324
337	19.9630	4.8666
348	40.5920	5.8442
353	43.0054	6.3172

vation energy determined from the slope of this plot, and the frequency factor were found to be

Activation Energy, $E_2 = 5.338 \times 10^7$ J/kmol
Frequency Factor, $\alpha_2 = 3.703 \times 10^3\ (m^3/kg)\ (m^3/kmol)^{n_2-1}\ s^{-1}$

The activation energies for both the homogeneous and heterogeneous reactions are nearly the same. This is not commonly observed and normally the activation energy for the catalyzed reaction is expected to be lower. However, in the present work it may be noted that though E values are nearly the same, the frequency factor (α) value observed for catalytic heterogeneous reaction is significantly higher than that for homogeneous reaction. This is consistent with some acid catalyzed reactions discussed by Bell (1941), where it is pointed out that the major cause of changes in the rate has been due to changes in frequency factor (α) rather than E. Bell also discusses the probable reasons for such an observation and points out that in such cases the mechanism of the reaction is quite complex. Similar observations for other reaction systems are reported by Ashmore (1963).

SUMMARY

In the present work, intrinsic kinetics of hydration of propylene oxide using an ion-exchange resin catalyst has been studied. The kinetics of homogeneous reaction has been separately investigated and used further to analyze the overall rates of reaction for the homogeneous-heterogeneous reaction. The solubility of propylene oxide in water has been determined and a suitable correlation proposed. The effect of various parameters on the rate of reaction was investigated, and the rate data were fitted using a power law model. The homogeneous reaction was found to be 0.43 order with respect to propylene oxide while the heterogeneous reaction was found to be 0.55 order. The homogeneous reaction was found to be chemically controlled in the range of conditions investigated. The heterogeneous reaction was found to have intraparticle diffusional resistance under certain conditions and hence these data were used to evaluate simultaneously the intrinsic kinetic parameters and the effective diffusivity. A theoretical model for a homogeneous-heterogeneous reaction has been proposed and it has been shown that the predicted results agree well with the experimental data. This study provides a general approach to investigate multiphase (homogeneous-heterogeneous) reactions.

NOTATION

a_B = effective gas-liquid interfacial area per unit volume of slurry, m^2/m^3
a_p = external area of particles per unit volume of slurry, m^2/m^3

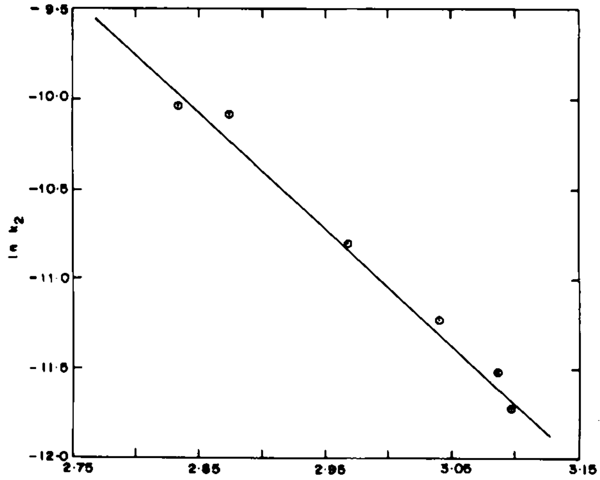


Figure 8. Effect of temperature on heterogeneous reaction rate constant.

A = concentration of species A at the conditions indicated in the subscript, $kmol/m^3$
d_p = average diameter of the catalyst particle, m
D = diffusion coefficient of the diffusing species in the liquid, m^2/s
D_e = effective diffusivity, m^2/s
H = Henry's law constant defined as, A_g/A
H' = Henry's law constant of solubility, $Pa/(kmol/m^3)$
k_1 = rate constant for homogeneous reaction, $(m^3/kmol)^{(n_1-1)}s^{-1}$
k_1' = rate constant in Eq. 15, s^{-1}
k_2 = rate constant for heterogeneous reaction, $m^3/kg\ (m^3/kmol)^{(n_2-1)}\ s^{-1}$
k_L = liquid film mass transfer coefficient, m/s
K_m = equilibrium constant in Eq. 15, $kmol/m^3$
k_s = liquid to catalyst particle mass transfer coefficient, m/s
K_L = overall gas to liquid mass transfer coefficient, m/s
L = total height of the slurry above the entrance of gas bubbles, m
M_A = parameter defined as $HQ/V\ [1 - \exp(-K_L\ a_B L/u_g H)]$
n_1,n_2 = order of homogeneous and heterogeneous reactions, respectively, with respect to propylene oxide
N = speed of agitation of slurry, Hz
p_g = partial pressure of A in the reactor, Pa
P^* = vapor pressure of A, Pa
Q = volumeteric flow rate of gas, m^3/s
R = gas constant, J/kmol/K
R_o = radius of the catalyst particle, m
R_1 = homogeneous reaction rate, $kmol/m^3/s$
R_2 = net heretogeneous reaction rate, $kmol/m^3/s$
R_A = overall rate of reaction of A, $kmol/m^3/s$
T = temperature, K
u_g = superficial velocity of gas in the reactor, m/s
V = total volume of the slurry, m^3
w = mass of the catalyst per unit volume of the slurry, kg/m^3

Greek Letters

α_1 = frequency factor for homogeneous reaction, $(m^3/kmol)^{(n_1-1)}s^{-1}$
α_2 = frequency factor for heterogeneous reaction, $m^3/kg\ (m^3/kmol)^{(n_2-1)}s^{-1}$
γ_∞ = activity coefficient at infinite dilution
η = overall effectiveness factor of a slurry reactor defined by Eq. 9
η_c = catalytic effectiveness factor
ϕ,ϕ_1 = Thiele parameter defined by Eqs. 5 and 16

ρ_p = density of the catalyst particle, kg/m^3
ρ_M = molar density of the solution, kmol/m^3
ϵ = catalyst particle porosity
τ = tortuosity factor of the catalyst

Subscripts

g = gas phase
gi = gas entering the reactor
go = gas leaving the reactor
l = liquid phase
s = external surface of the catalyst
$*$ = gas-liquid interphase

LITERATURE CITED

Ashmore, P G., *Catalysis and Inhibition of Chemical Reactions*, Butterworths, London, 17 (1963).

Bell, R. P., *Acid-Base Catalysis*, Oxford University Press, London, 175 (1941).

Bischoff, K. B., "Effectiveness Factors for General Reaction Rate Forms," *AIChE J.*, **11**, 351 (1965).

Bott, T. R., and H. N. Sadler, "Vapor Pressure of Propylene Oxide," *J. Chem. Eng. Data*, **11**, 25 (1966).

Carra, S., E. Santacesaria, M. Morbidelli, and L. Cavalli, "Synthesis of Propylene Oxide from Propylene Chlorohydrins. I: Kinetic Aspects of the Process," *Chem. Eng. Sci.*, **34**, 1123 (1979).

Chaudhari, R. V., and P. A. Ramachandran, "Three Phase Slurry Reactors," *AIChE J.*, **26**, 177 (1980).

Cipriani, G., C. Neri, and U. Romano, "Alkylene Glycols," *Ger. Offen.*, 2,615,595 (1976).

Ferrero, P., L. R. Flamme, and M. Fourez, "Propylene Chlorohydrin, Oxide and Their Derivatives," *Industrie Chim. belge*, **19**, 113 (1954).

Freidlin, L. Kh., and V. Z. Sharf, "Glycols," USSR, 114336 (1958).

Gritter, R. J., "Reactions of Cyclic Ethers," *The Chemistry of Functional Groups*, Interscience Publishers, New York, Ed., S. Patai (1967).

Izumi, Y., and K. Yutani, "Ethylene Glycol and Propylene Glycol," Tokuyama Soda Co. Ltd., *Japan Kokai*, **73**, 22,406 (1973).

Lebedev, N. N., V. F. Shvets, L. T. Kondrat'ev, and L. L. Romashkina, "Kinetics and Mechanism of Reactions of Hydrolysis of Oxides During Catalysis by Carbonates," *Kinetika i Kataliz*, **17**, 576 (1976a).

Lebedev, N. N., V. F. Shvets, L. L. Romashkina, and L. T. Kondrat'ev, "Selectivity of α-Oxide Hydrolysis Catalysed by Carbonates," *Kinetika i Kataliz*, **17**, 583 (1976b).

Levin, S. Z., and A. L. Shapiro, "Alkylene Glycols," All Union Scientific Res. Inst. of Petrochemical Processes, USSR 287,916 (1970).

Long, F. A., and J. G. Pritchard, "Hydrolysis of Substituted Ethylene Oxides in H_2O^{18} Solutions," *J. Am. Chem. Soc.*, **78**, 2663 (1956).

McAteer, J. H., "Vapor Phase Hydration," U.S. 2,547,766 (1951).

Myszkowski, J., A. Z. Zielinski, and U. Scislewska, "Influence of Some Parameters on the Pressure Hydration of Propylene Oxide to Propylene Glycol," *Prezm. Chem.*, **45**, 619 (1966).

Polyanski, N. G., and N. L. Potudina, "The Hydration of Propylene Oxide in the Presence of Cation Exchange Resins as Catalysts," *Neftekhimiya*, 3, 706 (1963).

Popova, E. G., Z. G. Lysenkova, V. P. Pakhomov, and L. I. Budanova, "Preparation of Propylene Glycol for use in Pharmaceutical Practice," *Khim. Farm. Zh.*, **8**, 28 (1974).

Pritchard, J. G., and F. A. Long, "Kinetics and Mechanism of the Acid Catalysed Hydrolysis of Substituted Ethylene Oxides," *J. Am. Chem. Soc.*, **78**, 2667 (1956).

Ramachandran, P. A., and R. V. Chaudhari, "Overall Effectiveness Factor of a Slurry Reactor for Non-Linear Kinetics," *Can. J. Chem. Eng.*, **58**, 412 (1980).

Robeson, M. O., and T. P. Webb, "Hydration of 1-2 Propylene Oxide to 1-2 Propanediol," Celanse Corp. of America, U.S. 2,623,909 (1952).

Sano, Y., N. Yamaguchi, and T. Adachi, "Mass Transfer Coefficients for Suspended Particles in Agitated Vessels and Bubble Columns," *J. Chem. Eng. Japan*, **7**, 255 (1974).

Satterfield, C. N., Mass Transfer in Heterogeneous Catalysis, MIT Press, Cambridge, MA (1970).

Tokuno, I., H. Yamamoto, and M. Yamaguchi, "Propylene Glycol from Propylene Oxide," Asahi Electrochemical Co., Ltd., Japan, 5904('62) (1958).

Wickert, J. N., W. S. Tamplin, and R. L. Shank, "Phase Equilibria in the System Propylene Oxide-Water," *Chem. Eng. Symp. Ser.*, **48**, 92 (1952).

Wilke, C. R., and P. Chang, "Correlation of Diffusion Coefficients in Dilute Solutions," *AIChE J.*, **1**, 264 (1955).

Yagi, H., and F. Yoshida, "Gas Absorption by Newtonian and Non-Newtonian Fluids in Sparged Agitated Vessels," *Ind. Eng. Chem. Proc. Des. Dev.*, **14**, 488 (1975).

Zweitering, T. N., "Suspending of Solid Particles in Liquid by Agitators," *Chem. Eng. Sci.*, **8**, 244 (1958).

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Theory on Colloidal Double-Layer Interactions

The potential energy between two interacting colloidal particles is derived by a knowledge of the energy of interaction of two parallel flat plates. The proposed method maps pairs of infinitesimal surface elements from the two interacting bodies to parallel plate-like elements. The results obtained from this theory are compared with the Derjaquin approximation for large κR and the Levine and Dube approximation for small κR.

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SCOPE

An understanding of the forces acting between interacting particles in a colloidal suspension is essential for the explanation of the macroscopic phenomena of colloidal stability and coagulation. Controlled colloidal phenomena may in turn be used for the reclaiming of precious materials from wastes, water pollution control, and the production of numerous industrial and consumer goods.

In many instances the most important interparticle forces are those which arise from the interaction of the electrical double

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