

## ALKYLATION OF BENZENE WITH 1-DODECENE BY MACRORETICULAR RESIN CATALYSTS

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(Received 15 November 1984 • accepted 13 December 1984)

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**Abstract** — The alkylation of benzene with 1-dodecene was performed in a batch reactor by two types of macroreticular ion exchange resin catalysts, i.e., Amberlyst 15 and Amberlyst XN-1010. The external mass transfer resistance and the macropore diffusion resistance could well be neglected since the stirring speed and the resin particle size had little effect on the reaction rate. The experimental data on the initial reaction rates have been correlated fairly well with the Rideal kinetics, from which the reaction rate constant, the distribution coefficient and the adsorption equilibrium constant were estimated. The activation energy of alkylation was about 7 Kcal/g mole. It is believed that the isomerization occurs prior to the final attachment of the phenyl group to the alkyl chain. This was explained by the isomer distribution of phenyldodecane, which was not influenced very much by the reaction time, the temperature, and the feed composition.

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### INTRODUCTION

Alkyl benzene is an important raw material for the synthesis of the detergents. Especially the linear alkyl benzene (LAB) is through sulfonation (LAS) used for the biodegradable soft detergent. The number of carbon in the alkyl group varies from 10 to 16, but the average is about 12. Dodecyl benzene has several tens of thousands of isomers due to the branched structure of dedecyl (or tetrapropyl) group while phenyldodecane, which is a LAB, has five isomers.

Olson [1] reported that five isomers of the 2-, 3-, 4-, 5-, and 6- phenyldodecane can be synthesized from 1-dodecene and benzene by using  $\text{AlCl}_3$ , HF and  $\text{H}_2\text{SO}_4$  as catalysts with different product distributions. Swisher et al [2] suggest that the five isomers be separated due to their characteristic retention time and that the isomerization be due to the rearrangement of carbonium ions. Alul and McEwan [3,4] reported from their experiments on the reaction of 1- and 6- dodecene that the isomer distribution is affected by the acid strength, the acid types and the location of double bond in the olefins. The isomer distribution is important because LAS from 5- and 6- phenyldodecane have a better physi-

cal property in the foam stability and surface activity than those from 1-, 2-, 3-, or 4- phenyldodecane.

In the industrial process, the alkylation has been carried out by the acid catalysts such as HF or  $\text{AlCl}_3$ , which is very corrosive and unstable. Many efforts therefore have been made to apply the solid catalysts. Phosphoric acid coated on kieselguhr is being used for the cumene manufacture from propylene and benzene. Sebulsky and Henke [5] reported that a good yield of phenyldodecane can be obtained by using silitungstic acid ( $\text{H}_2\text{SiW}_{12}\text{O}_{40}$ ) supported on silica gel. Some metal ions exchanged on the clay [6-8] are also known to show a very good activity.

On the other hand, ion exchange resins can also be used as catalysts for the reactions usually catalyzed by mineral acids or bases. Macroreticular resins are especially useful for nonpolar reactants while gelular resins require polar reactants or swelling agent. Compared to its homogeneous counterparts, the resin catalysts have two major advantages; it can easily be separated from the reaction mixture, and it can drastically reduce the corrosion.

The present study is to analyze the mechanism of the alkylation of benzene with 1-dodecene over two different macroreticular resin catalysts. Also the effects of

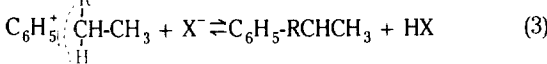
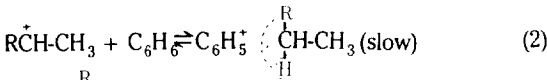
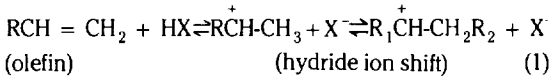
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the reaction conditions on the products distribution are to be investigated.

### KINETICS OF BENZENE ALKYLATION

Under the homogeneous acid catalysts, the benzene alkylation is known to proceed by a typical electrophilic substitution as follows:



The second stage of the attack by carbonium ion onto the benzene ring is a rate controlling step.

A similar mechanism can be inferred from the sulfonic acid ion exchange resin catalyst as shown in Fig. 1.

The carbonium ion is formed between the sulfonic acid group and 1-dodecene, and it attacks electrophilically the benzene ring. One can rewrite this mechanism as follows:

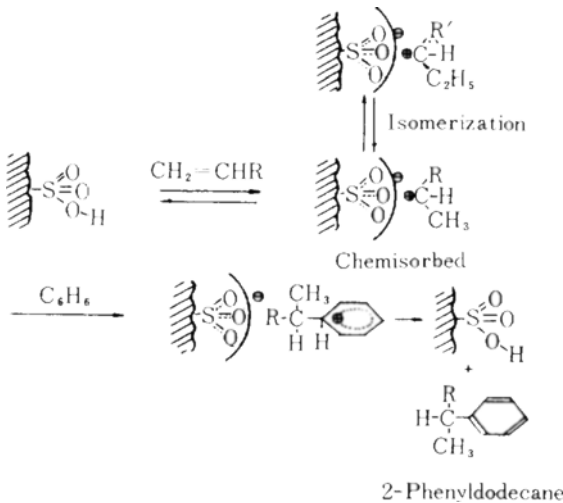
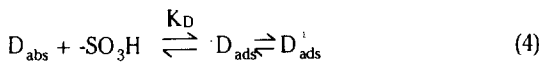


Fig. 1. Proposed reaction mechanism for alkylation of 1-dodecene ( $\text{CH}_2\text{CHR}$ ) and benzene ( $\text{C}_6\text{H}_6$ ) over sulfonic acid resin catalyst.

where the subscripted "abs" indicates the absorbed state and the "ads" the adsorbed state.

Therefore the reaction rate is determined by Eqs. (5)

$$r = k \theta_D \bar{C}_B \quad (6)$$

The adsorbed concentration of dodecene is given by Langmuir isotherm.

$$\theta_D = \frac{K_D \bar{C}_D}{1 + K_D \bar{C}_D} \quad (7)$$

And Eq. (6) becomes

$$r = \frac{k K_D \bar{C}_B \bar{C}_D}{1 + K_D \bar{C}_D} \quad (8)$$

The relation between the absorbed state and the bulk state in a binary system is usually expressed in terms of a distribution coefficient [9-10],

$$\frac{\bar{C}_B}{\bar{C}_D} = k_d \left( \frac{C_B}{C_D} \right) \quad (9)$$

One can derive the explicit expression for the absorbed concentration

$$\bar{C}_B = \frac{k_d Q_1 C_B}{Q_2 C_D + k_d C_B} \quad (10)$$

$$\bar{C}_D = \frac{Q_1 C_D}{Q_2 C_D + k_d C_B} \quad (11)$$

where  $Q_1 = d_B/M_B$  and  $Q_2 = \frac{M_d d_B}{M_B d_D}$ , and where  $M$  and  $d$  are the molecular weight and the density of each component respectively.

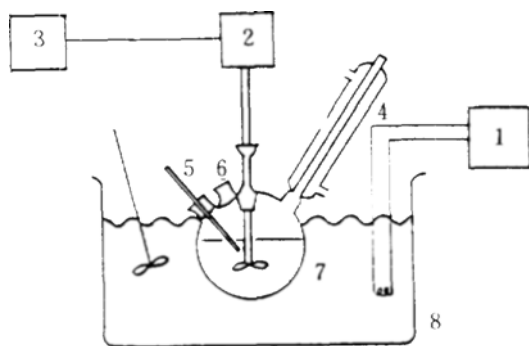
The overall reaction rate is given by

$$r = \frac{k k_d K_D Q_1^2 C_D C_B}{[k_d C_B + (Q_2 + k_d Q_1) C_D] (Q_2 C_D + k_d C_B)} \quad (12)$$

Table 1. Properties of ion exchange resins.

Properties	Amberlyst 15	Amberlyst XN-1010
Weight capacity of dry resin (meq./g)	4.50	3.30
% of surface-SO <sub>3</sub> H groups	4.39	52.78
Internal surface area (m <sup>2</sup> /g)	55	540
Porosity vol. (%)	36	50
Avg. pore diameter (Å)	265	51
Crosslinkage (%)	20-25	*

\* No data on crosslinkage of Amberlyst XN-1010 is available, but it may be higher than that of Amberlyst 15, comparing the other properties.



1. Temperature controller      5. Thermometer  
 2. Motor                            6. Sampling port  
 3. Speed controller            7. Reactor  
 4. Condenser                    8. Water bath

Fig. 2. Batch reactor system.

### EXPERIMENTAL SECTION

**Materials:** Ion exchange resins used as catalysts were Amberlyst 15 and Amberlyst XN-1010 provided by Rohm and Haas Company which were of the macroreticular types with sulfonic acid functional groups. Their physical properties such as pore size and internal surface area are different as shown in Table 1.

Benzene and 1-dodecene were of the pure reagent

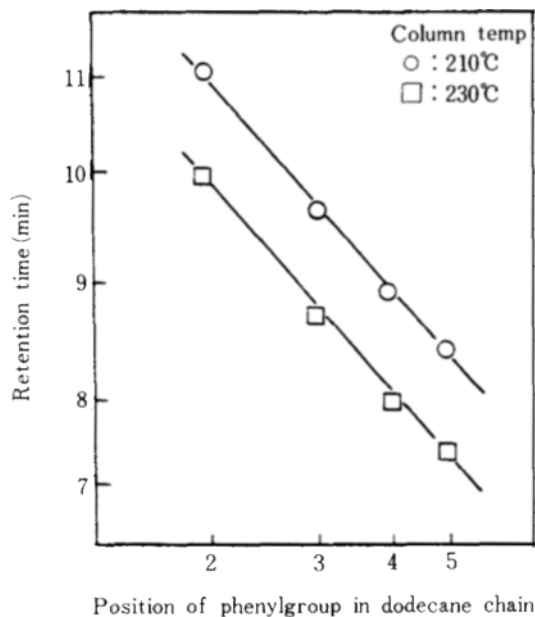


Fig. 3. Retention time of phenyldodecene.

Table 2. Effect of particle size and stirring speed on reaction rate (temperature: 40 °C, benzene/1-dodecene molar ratio: 10).

Resin	Particle size (mesh)	Stirring speed (rpm)	Reaction rate moles/eq.min)
XN-1010	28-32	2000	$1.47 \times 10^{-3}$
	28-32	2500	$1.51 \times 10^{-3}$
	28-32	3000	$1.50 \times 10^{-3}$
	16-24	2500	$1.48 \times 10^{-3}$
	32-50	2500	$1.51 \times 10^{-3}$
Amberlyst 15	28-32	2000	$5.24 \times 10^{-4}$
	28-32	2500	$5.26 \times 10^{-4}$
	28-32	3000	$5.27 \times 10^{-4}$
	16-24	2500	$5.25 \times 10^{-4}$
	32-50	2500	$5.25 \times 10^{-4}$

grades. Anhydrous aluminum chloride was used as catalyst for a reference reaction at 40°C.

Methanol, NaOH and H<sub>2</sub>SO<sub>4</sub> were used for the pretreatment of ion exchange resins, and Na<sub>2</sub>SO<sub>4</sub> was used for the determination of resin capacity.

**Reaction:** A batch reactor system with a four-neck flask was applied as shown in Fig. 2. Excess benzene was introduced to prevent any side reactions. The mole ratio of benzene and 1-dodecene was 10:1 except for the kinetic measurement. The reaction temperature was maintained at a desired value in a constant temperature bath. A vial of sample was taken every ten minutes to analyze the components with gas chromatography. A reference reaction with AlCl<sub>3</sub> as catalyst was carried out at 40°C, where water was added as a promoter.

The identification of phenyldodecene isomers was made from the linear correlation [2] in the semi-logarithmic plot of the retention time and the position of phenyl group in dodecane chain (see Fig. 3).

### RESULTS AND DISCUSSIONS

**Effects of Mass Transfer:** As shown in Table 2, the particle size and the stirring speed did not affect the reaction rate. One might safely neglect the effect of pore diffusion in the applied range of particle sizes. Also the external mass transfer resistance could be neglected if the stirring speed is above 2500 rpm. Therefore all the experiments, if not specified, were carried out at 2500 rpm and at a random combination of particle sizes.

**Effects of Reaction Temperature:** The logarithm of the initial reaction rate and the reciprocal of the reaction temperature are plotted in Fig. 4. This Arrhenius plot does not follow the straight line but shows some upward deviations at higher reaction temperatures. This seems

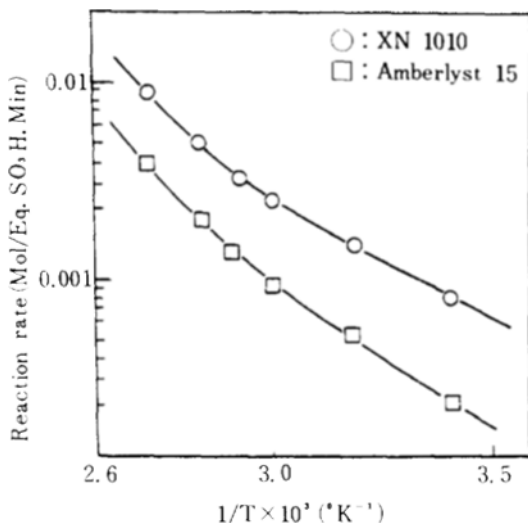


Fig. 4. Temperature dependence of reaction rate; benzene/1-dodecene mole ratio = 10.

to be due to the effects of parameters involved in the nonlinear rate expressions. The enhanced swellability with increased temperature of gelular microsphere can be more than enough to offset the reduced diffusivity [11]

**Reaction Kinetics:** The initial reaction rate with Amberlyst XN-1010 is larger than that with Amberlyst 15. This is expected because the fraction of surface sulfonic acid groups is more than ten times higher in Amberlyst XN-1010. If the reaction took place on the pore surface of gelular microsphere, the rate also should

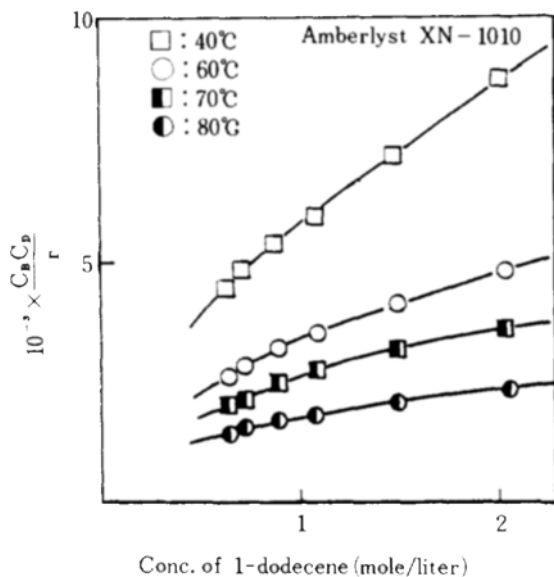


Fig. 5.  $C_B C_D / r$  vs.  $C_D$  for Amberlyst XN-1010.

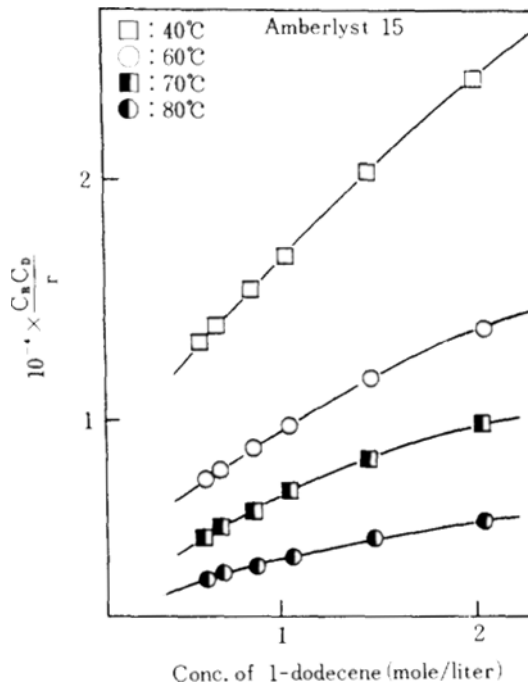


Fig. 6.  $C_B C_D / r$  vs.  $C_D$  for Amberlyst 15.

have been ten times larger. However the fact that the reaction rate is about five times larger indicates that only the surface functional groups may participate in the reaction with Amberlyst XN-1010 while some of internal sulfonic acid groups are utilized for reaction with Amberlyst 15.

The kinetics are not of simple second order reaction because the plots of  $r/C_A C_B$  depends upon  $C_D$ , the concentration of 1-dodecene as shown in Fig. 5 and Fig. 6. The solid lines show the satisfactory correlation of the data with Eq. (12).

For these correlations, nonlinear least squares method [12, 13] was used to predict the three parameters; the rate constant, the distribution coefficient, and the adsorption equilibrium constant (see Table 3). It is reasonable that the distribution coefficient is smaller than unity since 1-dodecene is more polar reactant than benzene.

Also Arrhenius plots were made from the rate constants in Fig. 7, and the activation energies are 7.09 and 7.37 Kcal/g-mol for Amberlyst XN-1010 and Amberlyst 15 respectively.

**Inhibition by water:** The effect of water addition was studied at 40°C and at the mole ratio (benzene/1-dodecene) of 10.

The reaction rate can be written by taking into account the inhibition by water, i.e.,

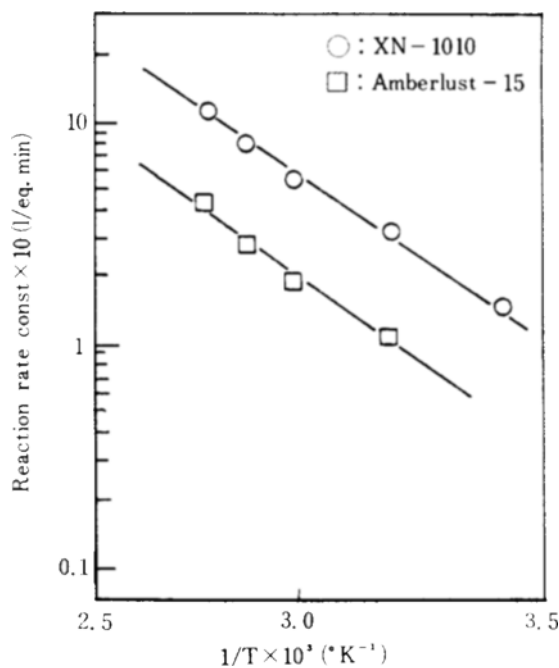
**Table 3. Estimation of the rate constant ( $k$ ), the equilibrium distribution coefficient ( $k_d$ ) and adsorption coefficient ( $k_b$ ).**

Resin	Temperature (%)	$k \times 10^3$ (l/eq. min)	$k_d$	$k_b$ (l/mol)
XN-1010	20	1.50	0.85	15.3
	40	3.18	0.86	14.8
	60	5.51	0.88	13.6
	70	8.23	0.92	13.2
	80	11.1	0.92	12.8
Amberlyst 15	40	1.11	0.90	18.5
	60	2.23	0.92	17.3
	70	2.89	0.93	16.2
	80	4.51	0.92	14.3

$$r = \frac{kK_d \bar{C}_B \bar{C}_D}{(1 + K_b \bar{C}_D + K_w C_w)} \quad (13)$$

where  $C_w$  is the water concentration and is assumed to be the same both inside and outside the resin.

With Eqs. (10) and (11), the rate equation can be linearized for small amount of water in terms of  $C_w$  as follows



**Fig. 7. Arrhenius plot of reaction rate constant.**

**Table 4. Effect of time on product isomer distribution, wt % (temperature: 40°C, benzene/1-dodecene molar ratio: 10, stirring speed: 2500rpm).**

ISOMER	Time (min)			
	10	20	30	50
2-Phenyl dodecane	41	43	42	41
3-Phenyl dodecane	22	21	21	21
4-Phenyl dodecane	13	13	14	14
5&6-Phenyl dodecane	24	23	23	24

Amberlyst XN-1010

ISOMER	Time (min)			
	10	20	30	50
2-Phenyl dodecane	40	41	41	42
3-Phenyl dodecane	21	21	21	22
4-Phenyl dodecane	14	14	14	13
5 & 6-Phenyl dodecane	25	24	24	23

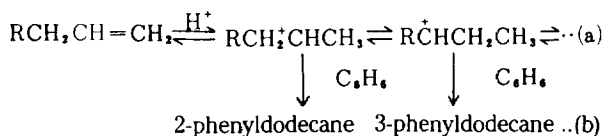
Amberlyst - 15

$$\frac{1}{r} = \frac{(Q_2 C_D + k_d C_B) K_w C_w}{k k_d K_D Q_1^2 C_D C_B} + \frac{(1 + \frac{K_D Q_1 C_D}{Q_2 C_D + k_d C_B})}{k k_d K_D Q_1^2 C_D C_B} \quad (14)$$

The validity of Eq. (14) can be evidenced by the straight line in Fig. 8. From the slope of the line, with the parameters given in Table 3, the values of  $K_w$  were estimated as 1529 and 395 l/mol for Amberlyst 15 and Amberlyst XN-1010 respectively. As compared to the value of  $K_D$ , this larger value of  $K_w$  indicates a high inhibition by water due to the strong adsorption.

**Distribution of Product Isomers:** The isomers of product were 2-, 3-, 4-, 5-, and 6- phenyl dodecane. The formation of 1-phenyl dodecane did not occur because the primary carbonium ion from the adsorbed 1-dodecene is rapidly converted to the secondary carbonium ion due to the hydride ion shift.

The isomer distribution was not affected by the contact time as shown in Table 4. An equilibrium among the isomers of carbonium ions seems to be established before the irreversible attack of the carbonium ion on the benzene ring as follows:



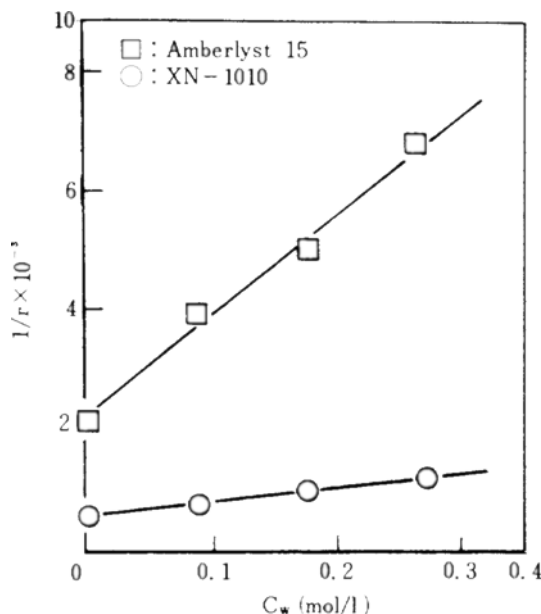


Fig. 8. Inhibition of water; determination of  $K_w$ .

Table 5. Comparison of ion exchange resins with other catalysts of various literatures in isomer distribution(1, 2, 5, 14).

Catalyst	HF	$AlCl_3$	$H_2SO_4$	$H_4SiW_{12}O_{40}$ supported on silica gel	Resin
Isomer					
2-Phenyldodecane	20	32	41	34	40
3-Phenyldodecane	17	22	20	28	21
4-Phenyldodecane	16	16	13	14	15
5&6-Phenyldodecane	47	30	26	24	24

Olson [1] reported that 2-phenyldodecane is predominant at the beginning of the reaction with  $AlCl_3$ , and decreasing until an equilibrium is reached. This indicates that the isomerization by the step (a) and the alkylation by the step (b) occur simultaneously and that the alkylation is irreversible. It was also confirmed that the isomer distribution is not affected by the reaction temperature, the reactant mole ratio and the stirring speed [15]. Only the nature of catalysts can affect the product distribution. The product distributions for various different catalysts are given in Table 5.

### CONCLUSION

1. A Rideal type of kinetics where the adsorbed 1-dodecene reacts with the adsorbed benzene gave a satisfactory correlation with experimental data. The activation energy for the present alkylation reaction was about 7 kcal/gmol.

2. Comparison of the initial reaction rates with two different ion exchange resin catalysts shows that the reaction occurs mainly on the surface functional groups for Amberlyst XN-1010 and some of the inner functional group participate in the alkylation with Amberlyst 15.
3. The isomer distribution is not affected by the reaction time or the feed composition but by the nature of catalysts. It is believed that an equilibrium among the isomers of carbonium ions is established before the irreversible alkylation occurs.

### NOMENCLATURE

- C : Concentration, mol/l  $\bar{C}$ : inside resin  
d : Density, g/l  
k : Reaction rate constant, l/eq. min.  
K : Adsorption coefficient, l/mol  
 $k_d$  : Equilibrium distribution coefficient defined by Eq.(9)  
M : Molecular weight, g/mol  
m : Moles of component  
 $Q_1$  : Constant defined by  $d_B/M_B$  for benzene  
 $Q_2$  : Constant defined by  $M_d d_B/M_B d_D$   
r : Reaction rate, moles/eq. of  $SO_3H$  min.  
 $\theta$  : Fraction of catalytic sites chemisorbed

### Subscript

- B : Benzene D : 1-dodecene  
W : Water P : Phenyldodecane

### REFERENCES

1. Olson, A.S.: *I. & EC.*, **52**, 833 (1963).
2. Swisher, R.D., Kaelble E.F. and Liu, S.K.: *J. Org. Chem.*, **26**, 4066 (1961).
3. Alul H.R. and McEwan, E.J.: *J. Org. Chem.*, **32**, 3365 (1967).
4. *Ibid*, **33**, 1522 (1968).
5. Sebulsky R.T. and Henke, A.M.: *I. & EC, Prod. Res. Dev.*, **10**, 272 (1971).
6. Stridde, G.E.: U.S. Patent 3, 929, 467 (1967).
7. Stridde, G.E.: U.S. patent 3, 965, 043 (1976).
8. Stridde, G.E.: Patent 4, 046, 821 (1977).
9. Helfferlich, F.: "Ion Exchange", McGraw Hill, New York, 1962.
10. Suh, S.S.: M.S. Thesis, KAIS, Seoul, 1980.
11. Ihm, S.K., Suh, S.S. and Oh, I.H.: *J. Chem. Eng. Japan*, **15**, (3), 206 (1982).
12. Marquardt, D.W.: *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
13. Kuester J.L. and Mize, J.H.: "Optimization Techniques with Fotran", McGraw Hill, New York, 1973.
14. Alul, H.R.: *I & EC Prod. Res. Dev.*, **7**, 11 (1968).
15. Park, H.S.: "Alkylation of Benzene with 1-Dodecene Catalyzed by Ion Exchange Resins", M.S. Thesis, Korea Advanced Inst. Sci. & Tech., Seoul, 1982.