

# Diffusion of Cyclic Hydrocarbons in Benzene-Swollen, Divinylbenzene-Crosslinked Polystyrene Beads

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## Synopsis

Diffusion of cyclic hydrocarbons within benzene-swollen, polystyrene-divinylbenzene gel-type beads were studied at 25°C. Solute concentrations less than  $6.3 \times 10^{-2}M$  and volume fractions of polymer less than 0.6 were used. Diffusion coefficients were calculated assuming Fick's law diffusion, and were found to depend upon the volume fraction of polymer. The dependence suggests that the swollen polymer network acts as a physical obstruction to diffusion. Studies indicated that the solute-solvent interactions affecting diffusion were the same in the solvent-swollen polymer as in the pure benzene solvent.

## INTRODUCTION

Recently, there has been an interest in the attachment of homogeneous transition metal catalysts to insoluble polymer supports. Polymer-bound complexes exhibit catalytic properties similar to their homogeneous analogs. An important advantage of these polymer-supported catalysts over their homogeneous analogs is the ability to separate them from the liquid phase reaction mixture by filtration.

It has been shown<sup>1-4</sup> that intraparticle diffusional limitations can decrease the reaction rate. A Thiele-type model<sup>5</sup> describing mass transfer and reaction in a swollen polymer catalyst bead should allow prediction of the apparent rate. The intrinsic reaction rate constant and the effective diffusion coefficient of the substrate are required for a Thiele analysis.

Hydrogenation of cyclohexene is known to occur at mild conditions over  $(PPh_3)_3ClRh(I)$  bound to crosslinked polystyrene.<sup>1</sup> This catalyst system is being used to investigate intraparticle mass transfer limitations in polymer-bound catalysts. The initial phase of this investigation involves measuring the intrinsic reaction rate constant and the effective diffusion coefficient. This paper describes the diffusion of cyclic hydrocarbon solutes in benzene-swollen polystyrene crosslinked with divinylbenzene (DVB).

Diffusion of solute molecules in a solvent-swollen, crosslinked polymer has been related to diffusion in the pure solvent by Paul<sup>6,7</sup> and Meares.<sup>8,9</sup> Paul has shown that the diffusion coefficient in the polymer depends on the volume fraction of polymer, volume polymer/total swollen volume, and the properties of the swelling solvent. In general, the diffusion coefficient of the solute in the polymer decreases as the volume fraction of polymer increases. The polymer is considered to act as a physical obstruction to diffusion for polymer volume fractions less than 0.8.<sup>6</sup> A normalized diffusion coefficient is obtained by dividing the polymer-phase diffusion coefficient by the diffusion coefficient in the pure solvent. Plots of the normalized diffusion coefficient vs. the volume fraction

of polymer display a common shape.<sup>6</sup> Each polymer/solvent pair investigated by Paul led to a separate characteristic curve. A characteristic curve for polystyrene—(DVB)/benzene is presented using cyclohexene, cyclohexane, and cyclooctene as solutes.

## EXPERIMENTAL

The diffusion experiments were performed with the apparatus illustrated in Figure 1. A 50-mL round-bottom flask was used to contain the solvent-swollen polystyrene beads. The stopcock attachment minimized liquid evaporation and maintained a constant internal pressure of 1 atm. A rubber septum attached to the sidearm was used as an injection port and for the withdrawal of samples for GC analysis. A magnetic stirbar was used to stir the contents uniformly. The flask was maintained at 25°C by the constant temperature oil bath.

A gas chromatograph equipped with a flame ionization detector (FID) was used to analyze liquid samples. A 6 m × 2.16 mm ID column of 20% Carbowax 20 M on Chromosorb P-AW 60/80 mesh was used to separate the solute and solvent. The column was maintained at 130°C. Liquid phase mole fractions were calculated by comparing the peak height fractions to the peak height fractions of standard mixtures.

All reagents were reagent grade and were used as supplied without further purification. The benzene solvent used to prepare all calibration standards and for all diffusion experiments was spectro grade.

The gel-type polystyrene beads were supplied by Dow Chemical Co., Midland, Mich., and were sieved to -18 + 20 mesh. The beads had a dry solid density of 1.08 g/cm<sup>3</sup> and were used as supplied.

The polymer swelling ratio  $q$  (swollen vol/dry bead vol) for each crosslink density was measured by placing a weighed quantity of beads in a 25-mL graduated cylinder. The total dry volume was noted. Benzene was added such that

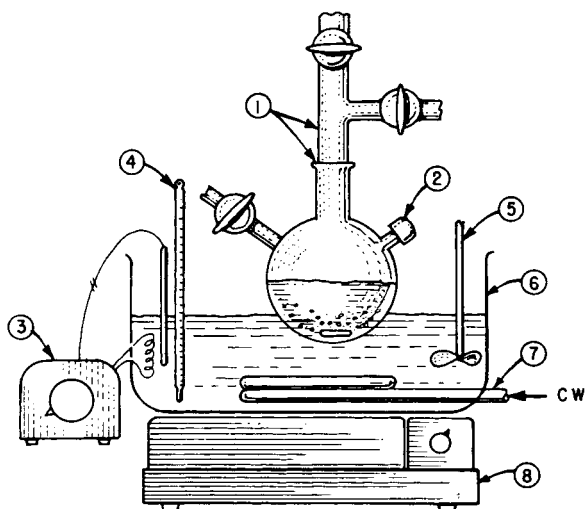


Fig. 1. Experimental apparatus: (1) Diffusion cell; (2) injection/GC sampling port; (3) constant temperature controller; (4) bath thermometer; (5) bath stirrer; (6) constant temperature bath (oil-filled); (7) bath cooling coil; (8) magnetic stirrer (for diffusion cell).

an excess was present after complete swelling. The beads were allowed to swell to their equilibrium volume at 25°C. The polymer swelling ratio was calculated assuming the swollen bed void fraction was the same as the dry bed void fraction (0.44). For the three different DVB crosslink densities tested, the polymer swelling ratios were calculated to be 3.44, 3.11, and 1.71.

For the diffusion experiments, the flask was charged with a mass of polymer beads, the mass dependent on the polymer swelling ratio. The mass of beads used were such that the change in bulk phase mole fraction of solute was constant, approximately  $1 \times 10^{-3}$ . [This mole fraction change corresponds to a change from an initial bulk phase solute concentration of  $6.3 \times 10^{-2}M$  to  $5.2 \times 10^{-2}M$  (nominal values) after the system had attained equilibrium.] Masses of 2.214, 2.567, and 7.609 g were used for polymer swelling ratios of 3.44, 3.11, and 1.71, respectively. Benzene (23.0 mL) was introduced into the flask and the beads were allowed to swell for a minimum of 24 h.

The flask was placed in the constant temperature bath and allowed to reach a temperature of 25.0°C. A 0.5-mL syringe was filled with the volume of solute required to produce an initial bulk phase mole fraction of approximately  $5.6 \times 10^{-3}$  ( $6.3 \times 10^{-2}M$ ). A 0.5- $\mu$ l GC syringe was placed in the injection/sampling port. The solute was injected into the flask and a stopwatch started. The first bulk phase sample was taken after 16 s. Five additional bulk phase samples were taken at intervals of approximately 20 s with the corresponding sample time noted for each. The samples were sequentially injected into the GC. A final set of three samples was taken after all diffusion had ceased in order to determine the equilibrium mole fraction of solute in the bulk phase.

### MATHEMATICAL MODEL

The process of solute diffusing into solvent-swollen crosslinked gel-type polymer beads from a bulk solution of limited volume was modeled assuming Fick's law diffusion. The swollen beads are assumed spherical, of uniform size, and initially free of solute. The bulk phase solution is well mixed, and the concentration of solute at the bead surface is equal to the bulk phase concentration at all times. The total amount of solute in the bulk phase and in the beads remains constant throughout the experiment. Since the solutions are dilute, the polymer swelling ratio in the presence of the solute can be assumed constant as diffusion proceeds, and equal to the polymer swelling ratio determined using pure benzene. Therefore, the bulk phase volume remains constant.

The above assumptions lead to the following conservation equation for radial diffusion of solute in a single bead:

$$\frac{\partial C_s(r,t)}{\partial t} = D_{ps} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_s(r,t)}{\partial r} \right) \right] \quad (1)$$

where  $D_{ps}$  is the diffusion coefficient of solute in the polymer and is assumed constant and  $C_s$  represents the solute concentration within the polymer bead. A material balance on the solute over the bulk phase gives,

$$\frac{dN_{s,\text{bulk}}}{dt} = -D_{ps} \left[ \frac{\partial C_s(r,t)}{\partial r} \right]_{r=R_p} (4\pi R_p^2)(n_{\text{beads}}) \quad (2)$$

where  $N_{s,\text{bulk}}$  is the total number of moles of solute in the bulk phase,  $R_p$  is the swollen bead radius, and  $n_{\text{beads}}$  is the total number of beads.

A normalized mole fraction of solute in the bulk phase,  $\psi$ , may be defined as

$$\psi(t) \equiv \left[ \frac{X_{s0} - X_s(t)}{X_{s0} - X_s^\infty} \right] \quad (3)$$

where  $X_{s0}$ ,  $X_s^\infty$ , and  $X_s(t)$  represent the bulk phase mole fraction of solute initially, at infinity, and at any time, respectively.

The solution to eqs. (1) and (2)<sup>10</sup> gives for the bulk phase

$$\psi(t) = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)}{(9 + 9\alpha + q_n^2\alpha^2)} \exp \left[ \frac{(-D_{ps})(q_n^2)t}{R_p^2} \right] \quad (4)$$

where the  $q_n$ 's are the nonzero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2}$$

and the parameter  $\alpha$  is given by

$$\alpha = \frac{V_{\text{bulk}}}{\left[ \left( \frac{4}{3} \pi R_p^3 \right) n_{\text{beads}} \right] (K)}$$

where  $K$  is the distribution factor of solute between the bulk phase solution and the solution within the swollen polymer at equilibrium. The distribution factor is defined as the ratio of the solute concentration in the swollen polymer bead to the solute concentration in the bulk solution.

## RESULTS

### Experimental

The normalized bulk phase mole fraction of cyclohexane is plotted vs. time for the three polymer swelling ratios in Figure 2. Cyclohexene and cyclooctene display similar curves. In all cases, the fastest rate of increase in  $\psi$  was observed for the polymer beads with the highest polymer swelling ratio. The lowest rate was observed for the lowest polymer swelling ratio beads.

### Calculation of Diffusion Coefficients

The diffusion coefficient  $D_{ps}$  for transport of solute molecules within the solvent-swollen polystyrene—DVB beads were determined by fitting eq. (4) to the  $\psi$  vs. time data with the diffusion coefficient as the only adjustable parameter. The diffusion coefficients for cyclohexene, cyclohexane, and cyclooctene are presented in Table I. Calculated values of  $\psi$  and the experimental data are presented in Figures 3–5 for cyclohexane.

The distribution factor  $K$  relating the equilibrium concentrations of solute between the bulk solution and the solvent-swollen polymer beads was calculated for each polymer swelling ratio and solute pair. All distribution factors were less than unity and varied from 0.300 to 0.673, indicating that the bulk phase concentration of solute was greater than that in the polymer at equilibrium. The distribution factors for each polymer swelling ratio/solute pair are also presented in Table I.

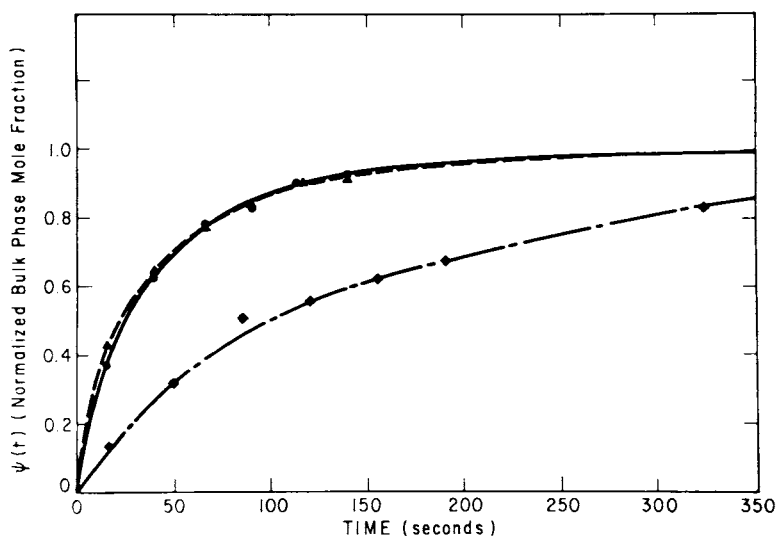


Fig. 2. Normalized experimental bulk phase mole fraction of cyclohexane vs. time. Solute: cyclohexane; solvent: benzene; PS bead data: size,  $-18 + 20$  mesh (dry); (●, —)  $q = 3.44$ ; (▲, - - -)  $q = 3.11$ ; (◆, — · —)  $q = 1.71$ .

The uncertainty in the calculated diffusion coefficients was determined by propagating the uncertainty in the measured quantity,  $X_s$ . The greatest observed standard deviation in  $X_s$  was  $\pm 0.03 \times 10^{-3}$  determined from the GC calibration standards. The uncertainty in  $X_s$  corresponds to a maximum relative uncertainty of 12% in the calculated diffusion coefficients.

The calculated curves corresponds well with the experimental data for the two highest polymer swelling ratio beads, as shown in Figures 3 and 4. The curve fit is slightly poorer for the low polymer swelling ratio beads, as shown in Figure 5. This poorer fit may be due to incomplete mixing caused by the large number of beads required to affect the  $1 \times 10^{-3}$  change in bulk phase mole fraction. Alternatively, the beads may have been in contact, hence decreasing the effective external area for solute diffusion.

TABLE I  
Diffusion Coefficients and Distribution Factors for Solutes within Benzene-Swollen,  
Polystyrene—DVB Beads

$q$	Solute	$K$	$D_{ps}$ ( $\text{cm}^2/\text{s} \times 10^6$ )
3.44	CHX <sup>a</sup>	0.624	5.89
	CHA <sup>b</sup>	0.606	5.32
	COE <sup>c</sup>	0.673	5.63
3.11	CHX	0.636	5.37
	CHA	0.604	5.24
	COE	0.652	4.60
1.71	CHX	0.341	0.82
	CHA	0.325	0.76
	COE	0.300	0.51

<sup>a</sup> Cyclohexene.

<sup>b</sup> Cyclohexane.

<sup>c</sup> Cyclooctene.

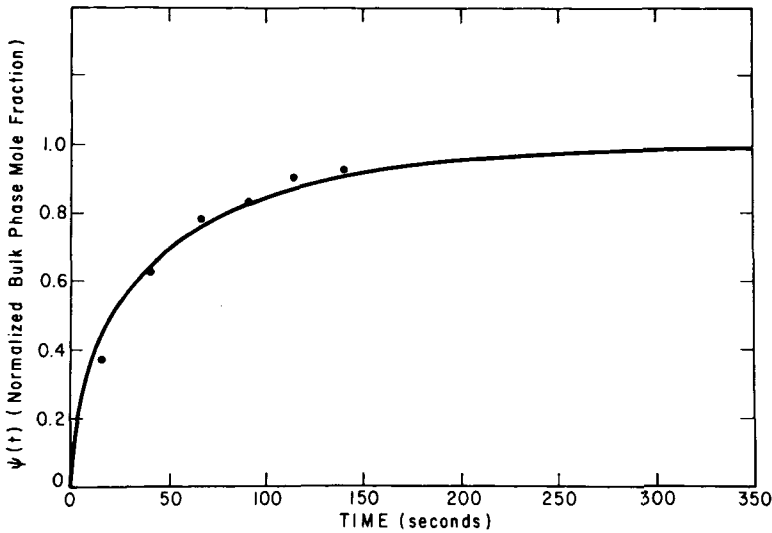


Fig. 3. Normalized bulk phase mole fraction of cyclohexane vs. time. Solute: cyclohexane; solvent: benzene; PS bead data:  $q = 3.44$ ; size,  $-18 + 20$  mesh (dry);  $D_{ps} = 5.32 \times 10^{-6}$  (cm<sup>2</sup>/s); (●) exptl point; (—) calcd points.

The assumption that the solute concentration at the polymer bead surface is the same as the surrounding bulk solution concentration was checked for the fastest mass transfer rate, cyclohexane diffusing into beads with a  $q$  of 3.44 at zero time. A mass transfer coefficient was estimated for forced convection from a surrounding liquid to a sphere<sup>11</sup> by assuming the stirred beads had a velocity relative to the liquid equal to the terminal velocity of the beads falling in pure solvent. The corresponding surface concentration of the bead was then calculated from the observed mass transfer rate. The analysis indicated that external mass transfer is unimportant relative to the intraparticle diffusion rate.

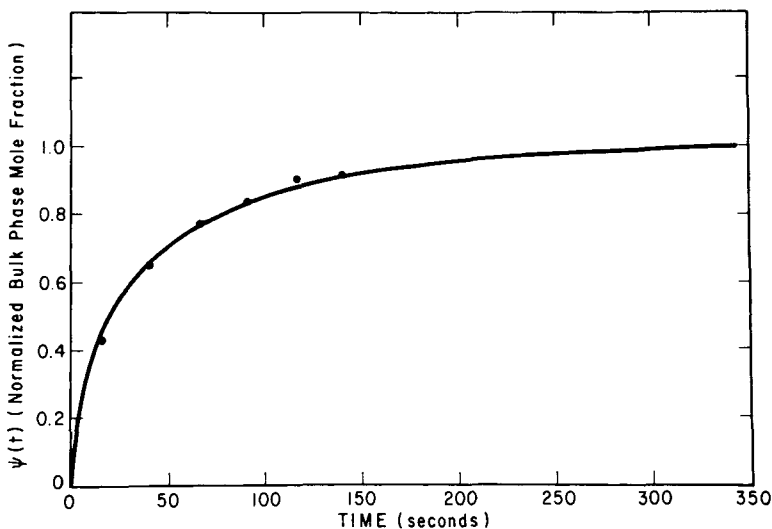


Fig. 4. Normalized bulk phase mole fraction of cyclohexane vs. time. Solute: cyclohexane; solvent: benzene; PS bead data:  $q = 3.11$ ; size,  $-18 + 20$  mesh (dry);  $D_{ps} = 5.24 \times 10^{-6}$  (cm<sup>2</sup>/s); (●) exptl point; (—) calcd points.

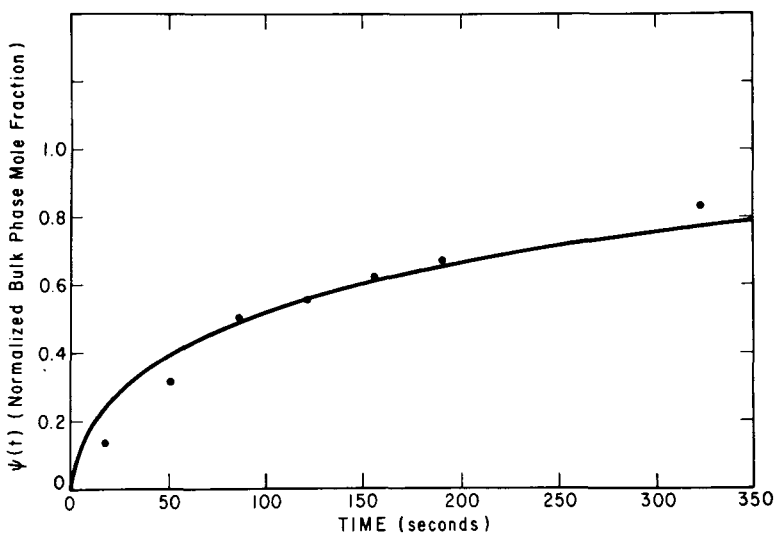


Fig. 5. Normalized bulk phase mole fraction of cyclohexane vs. time. Solute: cyclohexane; solvent: benzene; PS bead data:  $q = 1.71$ ; size,  $-18 + 20$  mesh (dry);  $D_{ps} = 0.76 \times 10^{-6}$  (cm<sup>2</sup>/s); (●) exptl point; (—) calcd points.

## DISCUSSION

Normalized diffusion coefficients for the three solutes were obtained by dividing the diffusion coefficient of the solute within the swollen polymer by the diffusion coefficient in pure benzene at infinite dilution. The diffusion coefficients at infinite dilution were calculated using the Scheibel correlation.<sup>12</sup> Molal volumes at the normal boiling point were calculated by the Schroeder method (12) for use in the Scheibel correlation.

A plot of the normalized diffusion coefficient vs. polymer volume fraction, reciprocal  $q$ , is presented in Figure 6. The shape of the curve is similar to those reported by Paul for other polymer/solvent systems.<sup>6</sup> This similarity in curve shape suggests that for polymer volume fractions less than 0.60, the benzene-swollen polystyrene—DVB network acts as physical obstruction to solute transport.

A separate study was conducted to investigate further the role of the polymer network on solute diffusion. Ratios of diffusion coefficients on the basis of solute molecular size were compared to similar ratios for the same solutes in benzene at infinite dilution. The experimentally determined diffusion coefficients within the polymer for the larger solute molecular sizes, cyclohexane and cyclooctene, were divided by the diffusion coefficient within the polymer for the smallest solute, cyclohexane, at each polymer swelling ratio. (Molecular sizes were compared on the basis of molal volumes at the normal boiling point.) Similar ratios were obtained for these solutes in benzene at infinite dilution. The results of these calculations are presented in Table II.

The average value of the ratio of the experimental diffusion coefficients within the three polymers tested was 0.94 for cyclohexane. The diffusion coefficient ratio in the pure benzene solvent was 0.96 for cyclohexane. The average value of the ratio for cyclooctene in the three polymers was 0.81, and the diffusion coefficient ratio in pure benzene was 0.78. The average ratios of the diffusion

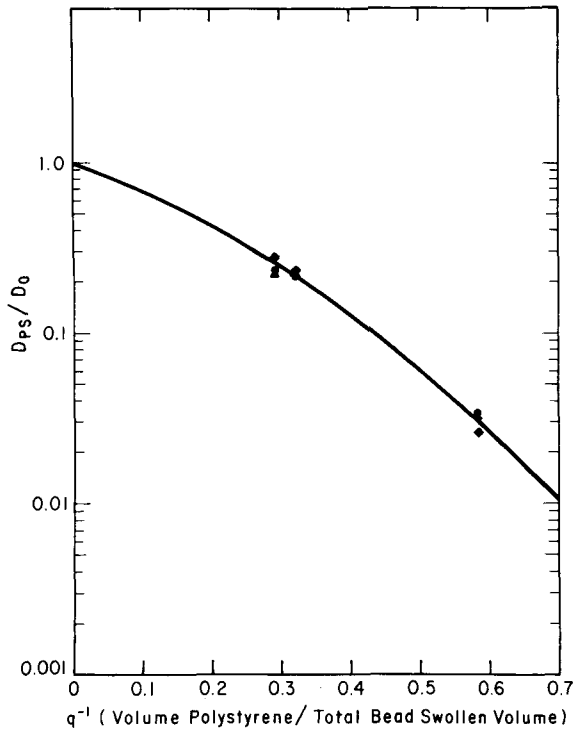


Fig. 6. Normalized diffusion coefficient vs. polymer volume fraction. Solute: (●) cyclohexene; (▲) cyclohexane; (◆) cyclooctene; solvent: benzene; temp = 25°C.

coefficients in the polymer correspond closely to the ratios of the diffusion coefficients in benzene at infinite dilution. This observation suggests that the diffusion coefficients in the polymer decrease with increasing solute molecular size in nearly the same manner as the diffusion coefficients in the pure solvent decrease with increasing solute molecular size. This correspondence is expected if the solute-solvent interactions affecting diffusion are the same in the solvent-swollen polymer as in the pure solvent.

TABLE II  
Diffusion Coefficient Ratios on the Basis of Solute Molecular Size

$q$	Solute	$V_b^a$ (cm <sup>3</sup> /Gmol)	$[D_{ps}/D_{ps,CHX}]^b$	$[D_0/D_{0,CHX}]^c$
3.44	CHX	112	1.00	1.00
	CHA	119	0.90	0.96
	COE	154	0.96	0.78
3.11	CHX	112	1.00	1.00
	CHA	119	0.98	0.96
	COE	154	0.86	0.78
1.71	CHX	112	1.00	1.00
	CHA	119	0.93	0.96
	COE	154	0.62	0.78

<sup>a</sup> Solute molal volumes at the normal boiling point.

<sup>b</sup> Diffusion coefficients in benzene-swollen polystyrene—DVB.

<sup>c</sup> Diffusion coefficients in benzene at infinite dilution.



## CONCLUSIONS

A plot of the normalized diffusion coefficient vs. polymer volume fraction has been experimentally determined for the diffusion of cyclic hydrocarbons within benzene-swollen, polystyrene—DVB for polymer volume fractions less than 0.60. The curve shape suggests that the polystyrene—DVB network acts as a physical obstruction to solute diffusion over the range of polymer volume fractions investigated.

Diffusion coefficients for reaction species are needed to quantify intraparticle transport limitations within polymer-bound transition metal catalyst systems. If the presence of catalytic sites does not influence substrate transport within the solvent-swollen polymer catalyst bead, curves similar to Figure 6 can be used to predict the diffusion coefficients during reaction. The applicability of this approach is currently being tested for olefin hydrogenation over  $(\text{PPh}_3)_3\text{ClRh(I)}$  bound to polystyrene—DVB.

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## NOMENCLATURE

$C_s(r,t)$	solute concentration within solvent-swollen polymer bead (Gmol/cm <sup>3</sup> )
$D_{ps}$	diffusion coefficient of solute within solvent-swollen polymer bead (cm <sup>2</sup> /s)
$D_0$	diffusion coefficient of solute in solvent at infinite dilution (cm <sup>2</sup> /s)
$K$	distribution factor (dimensionless)
$n_{\text{beads}}$	total number of polymer beads in diffusion flask
$N_{s,\text{bulk}}$	total moles of solute in bulk phase (Gmol)
$q$	polymer swelling ratio (swollen vol/dry bead vol) (dimensionless)
$q_n$	eigenvalue [eq. (4)]
$r$	radial coordinate (cm)
$R_p$	swollen polymer bead radius (cm)
$t$	time (s)
$V_b$	molal volume at normal boiling point (cm <sup>3</sup> /Gmol)
$V_{\text{bulk}}$	total bulk phase volume (cm <sup>3</sup> )
$X_s$	bulk phase solute mole fraction
$X_{s0}$	initial bulk phase solute mole fraction
$X_s^\infty$	bulk phase mole fraction at time infinity
$\alpha$	parameter defined by eq. (4)
$\psi(t)$	normalized bulk phase mole fraction

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