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Diffusion of Organic Solvents into Spherical Cross-Linked Polystyrene Beads

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Diffusion of Organic Solvents into Spherical Cross-Linked Polystyrene Beads

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ABSTRACT

Organic solvents penetrating into a spherical cross-linked polystyrene bead advance over a sharp front and cause the bead to swell. The changing location of the advancing front and the increasing radius of the swelling bead were measured by microscopic techniques. The rate of solvent uptake by the copolymer beads was shown to be of the Fickian type. A mathematical model of the Fickian diffusion process, showing both the advancing front and the expanding sphere, was developed. Effective diffusivity coefficients for methylene chloride, trichloroethylene, tetrahydrofuran, and benzene were obtained by least-squares fitting of the calculated and the measured times necessary for complete swelling.

INTRODUCTION

Reports on the use of spherical cross-linked polystyrene beads for the preparation of ion exchangers have emphasized their unusual sensitivity to the composition of the reacting medium. In order to

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facilitate the diffusion of the reactants into the polymeric matrix [1], it has been found desirable to swell the beads with an inert solvent prior to any other chemical treatment.

In the present work the kinetics of the penetration of four different swelling solvents (methylene chloride, trichloroethylene, tetrahydrofuran, and benzene) into a spherical bead of 8% cross-linked polystyrene was studied. As the solvent molecules enter ever deeper into the polymer bead, swelling occurs, and a fairly sharp, advancing boundary separates the bead core from the swollen outer shell due to the discontinuity of the diffusion coefficient. In order to determine the numerical value of the diffusion coefficient of the solvent in the swollen shell, the nature of the diffusion process must first be determined—whether it is of the Fickian or any other type.

Experiments showed the solvent uptake as a function of time (in all four solvents) to be linearly dependent on $t^{1/2}$. Hence it can be concluded that the diffusion process is indeed Fickian and that a mathematical model using Fick's diffusion equation can be developed. The radii of the unswollen core and of the swelling shell of a single copolymer bead as functions of time in the four swelling solvents were tracked microscopically—experiments of a kind already carried out by Hartley [2] for cellulose acetate films and by Kwei [3] for epoxy resins. The data thus found were introduced into Fick's diffusion equation, the solution of which, under specified conditions, permitted the derivation of concentration profiles in a copolymer bead and the calculation of the effective diffusivity coefficient in the swollen region.

EXPERIMENTAL

Spherical beads of 8% styrene—m-divinylbenzene (400 to 500 μ diameter) were used in the microscopic measurements.

The penetration time of the solvents into a single copolymer bead was tracked with microscopic techniques developed by Freeman [4], a Zeiss standard WL microscope with a planochromat 2.5/0.08 objective, and ordinary light being used. The outer radius of the bead, R, and the radius of the unswollen core, y, were repeatedly measured during the swelling process (a schematic illustration of a partially swollen bead is given in Fig. 1). From these data the fractional weight gain during swelling—solvent absorbed vs time—was calculated, the results being shown in Fig. 2. All measurements were carried out at 25°C.

Calculations were made with an IBM 370 computer using the Continuous System Modelling Program III (CSMP III).

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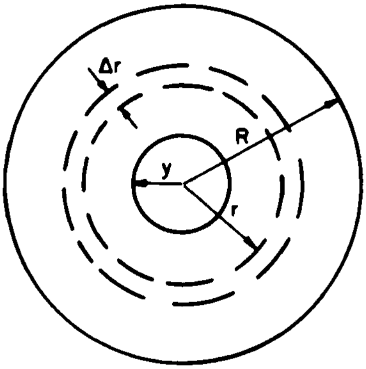

FIG. 1. Top view of a partially swollen bead, where R is the radius of the bead, y is the radius of the unswollen core, and r is the radius of the shell.

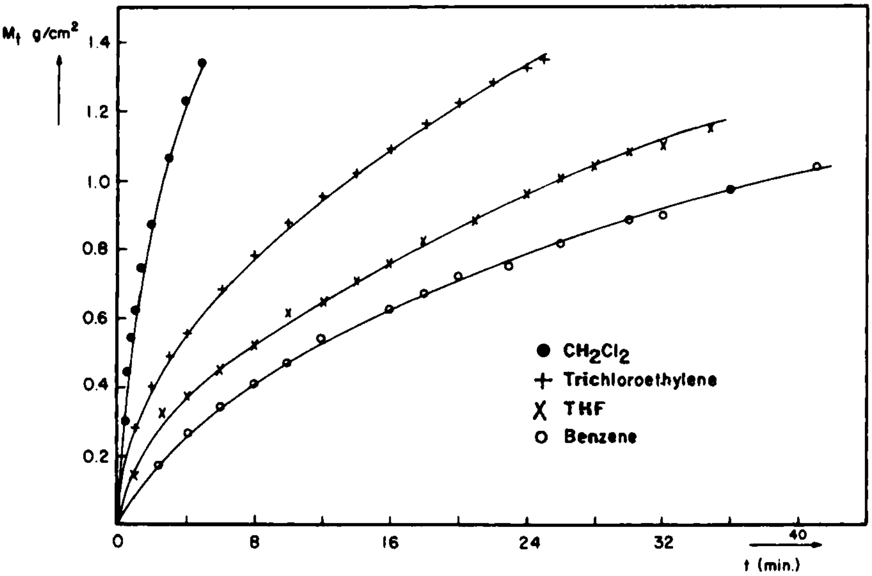

FIG. 2. Solvent uptake of single copolymer beads during swelling.

RESULTS AND DISCUSSIONS

In order to test whether the swelling process can be described by Fick's diffusion equation, the dependence between solvent uptake by the bead and time was examined. That dependence, as shown by Park [5], should be

$$M_t = D_p t^n$$

where M_t is the weight of absorbed solvent per unit area (g/cm^2), and D_p is the proportionality constant. If $n = 1/2$, the diffusion is Fickian.

Data taken from Fig. 2 were used to calculate M_t vs $t^{1/2}$ (Fig. 3) by computer, with function generation at all points. Figure 3 shows M_t to be a linear function of $t^{1/2}$ for all four solvents, so that Fickian diffusion through the swollen region can be assumed. In the following section a mathematical model, based on Fick's diffusion equation, will be developed, and solvent concentration patterns in a swelling bead will be established by computational methods. From these patterns, concentration-dependent diffusion coefficients can then be calculated.

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MATHEMATICAL MODEL OF DIFFUSION IN A SWELLING SPHERE

This mathematical model is based on the following assumptions: 1) The organic solvent penetrates a bead having spherical symmetry. 2) There is no chemical interaction between the solvent and the copolymer bead. 3) As soon as any amount of solvent has penetrated into the bead, the part of the bead so penetrated passes directly from the unswollen to the swollen state.

The concentration gradient established when a copolymer bead is immersed in an organic solvent is expressed by Fick's equation describing radial diffusion into a sphere:

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(Dr^2\frac{\partial c}{\partial r}\right) \qquad (1)$$

where c is the concentration of the solvent, t is the time, r is the distance of a particular shell from the center of the bead, and D is the diffusion coefficient of the solvent.

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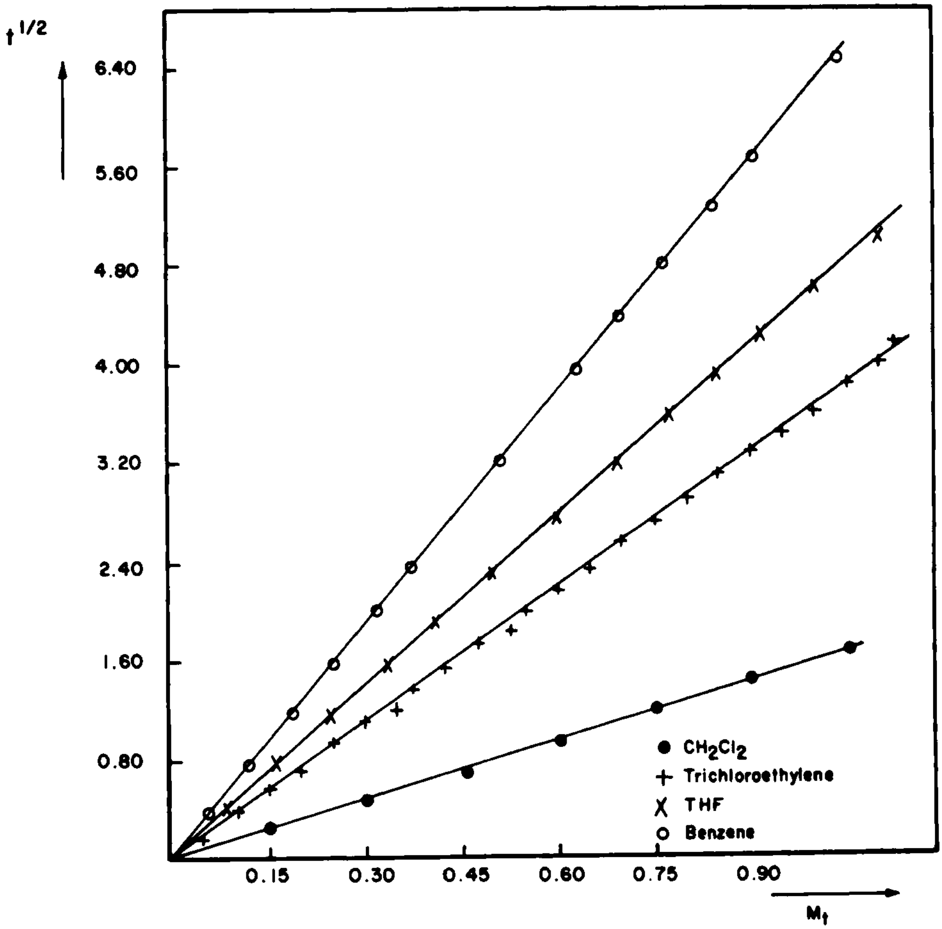

FIG. 3. Weight gain of swelling beads vs $t^{1/2}$.

At relatively low solvent concentrations, D may depend linearly on the concentration [8]:

$$D = D_0(1 + \alpha c) \tag{2}$$

where α is a constant depending on the fractional pore volume of the medium, and D_0 is the effective diffusivity coefficient through the swollen region of the bead.

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The diffusion coefficient characteristic of the unswollen bead increases by three orders of magnitude in the swollen region, which in many respects has the properties of a liquid [6].

A solution to the combined mathematical expressions (1) and (2) can be found provided a frame of reference is attached to the moving boundary. A simplified form of Fick's equation is obtained by introducing a new variable, as defined by Crank [7]:

$$s = \frac{\int_0^c D\,dc}{\int_0^1 D\,dc} \tag{3}$$

Equation (1) will then take the form

$$\frac{\partial s}{\partial t} = D\left(\frac{\partial^2 s}{\partial r^2} + \frac{2}{r}\frac{\partial s}{\partial r}\right) \tag{4}$$

which is solved numerically by applying the Crank-Nicholson finite difference method [7]. The general equation for that method is

$$\frac{\partial s}{\partial t} = \frac{D}{m(\Delta r_m)^2}\left\{(m + 1)s_{m+1} - 2ms_m + (m - 1)s_{m-1}\right\} \tag{5}$$

where m is an integer, and Δr_m is the thickness of the m-th shell, which is dependent on the swelling ratio.

In order to enable the finite difference method to be used, the sphere is divided into 20 shells of thickness Δr. At the beginning the concentration of solvent inside the bead is zero. During the solvent penetration process, the concentration at the surface remains constant ($c = 1$), and there is no gradient across the center of the bead. This is expressed in the initial and the boundary conditions:

$c = 0;\ s = 0;\ t = 0;\quad 0 < r < R$

$c = 1;\ s = 1;\ t > 0;\quad r > R$

$\partial r/\partial r = 0;\ \partial s/\partial r = 0;\ r = 0$

Calculations of Eq. (5) were made with the aid of simulation models for the continuously changing systems represented by the differential equation, using the CSMP computer program. The calculation was stopped as soon as the sharp advancing front disappeared. At that moment the bead was fully swollen, and the solution immediately reached a steady state, which in this case is one of uniform concentration. Problems of this type have previously been solved by the relaxation method [7].

In the present case Fick's equation was solved numerically, and solvent concentration patterns were obtained as functions of radial position, as illustrated in Table 1 for the case of trichloroethylene.

Estimated values of D_0 were introduced into the simulation program using the method of false position until the time to reach the steady state was equal to the experimentally determined time. In the case of trichloroethylene (Table 1), the final time required for full swelling to be reached was 25 min. At that time, $c_m = 0.988$ and $D_0 = 1.3 \times 10^{-7}$ cm^2/sec.

The concentration distribution patterns of Table 1 were print-plotted on a computer document as illustrated in Fig. 4. The horizontal lines represent the concentration profile of the solvent at a given instant, while the vertical lines are descriptive of the changes in the concentration distribution with time. In Fig. 4 the boundary is clearly discernible and constitutes a quantitative interpretation of the pattern seen under the microscope. This pattern is very similar to the fringe patterns of the swollen part of the bead observed under the microscope with polarized light [9]. In a partially swollen bead the unreacted core induces strains in the swollen shell which in turn cause an optical anisotropy.

The calculated values of D_0 for the four solvents studied by this method are listed in Table 2.

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CONCLUDING REMARKS

The purpose of the kinetic measurements was to show how the change of radii of the partially swollen bead and of the unreacted core can be fitted into Fick's equation in order to yield concentration patterns from which concentration-dependent diffusion coefficient can be calculated. The fact that the swelling of the bead takes place simultaneously with the diffusion process must be taken into account when methods for this calculation are developed. It is thus a problem of diffusion between two moving boundaries, namely the radius of the expanding bead, R, and the radius of the unswollen core, y, both changing with time.

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TABLE 1 Concentration Profile of

Type	0.0	2.5000	5.0000	7.5000	10.000	12.500
0(1)	0.0	0.0	0.0	0.0	0.0	0.0
0(2)	0.0	0.0	0.0	0.0	0.0	0.0
0(3)	0.0	0.0	0.0	0.0	0.0	0.0
0(4)	0.0	0.0	0.0	0.0	0.0	0.0
0(5)	0.0	0.0	0.0	0.0	0.0	0.0
0(6)	0.0	0.0	0.0	0.0	0.0	0.0
0(7)	0.0	0.0	0.0	0.0	0.0	0.0
0(8)	0.0	0.0	0.0	0.0	0.0	0.0
0(9)	0.0	0.0	0.0	0.0	0.0	0.0
0(10)	0.0	0.0	0.0	0.0	0.0	2.47754E-03
0(11)	0.0	0.0	0.0	0.0	0.0	0.36849
0(12)	0.0	0.0	0.0	0.0	9.04685E-03	0.51368
0(13)	0.0	0.0	0.0	0.0	0.40807	0.61773
0(14)	0.0	0.0	0.0	2.12883E-02	0.56039	0.69902
0(15)	0.0	0.0	0.0	0.44544	0.66738	0.76516
0(16)	0.0	0.0	0.35151	0.81058	0.75034	0.82033
0(17)	0.0	0.0	0.55800	0.72810	0.81779	0.86715
0(18)	0.0	0.53897	0.70845	0.81537	0.87421	0.90741
0(19)	0.0	0.74267	0.82580	0.88780	0.92228	0.94238
0(20)	0.0	0.88707	0.92094	0.94835	0.96379	0.97300

Trichloroethylene in a Single Copolymer Bead

15.000	17.500	20.000	22.500	25.000
0.0	0.0	0.0	0.0	0.95355
0.0	0.0	0.0	7.89368E-04	0.95423
0.0	0.0	0.0	0.50227	0.95536
0.0	0.0	1.30921E-05	0.63207	0.95688
0.0	0.0	7.02027E-02	0.70907	0.95877
0.0	2.39083E-05	0.44601	0.76286	0.96097
0.0	8.82171E-02	0.58500	0.80352	0.96343
3.07416E-04	0.42188	0.67284	0.83566	0.96609
0.25245	0.56143	0.73560	0.86186	0.96890
0.44568	0.65380	0.78352	0.88368	0.97181
0.57024	0.72190	0.82172	0.90219	0.97476
0.66084	0.77505	0.85314	0.91810	0.97773
0.73076	0.81808	0.87953	0.93195	0.98065
0.78681	0.85384	0.90213	0.94412	0.98351
0.83298	0.88413	0.92172	0.95491	0.98628
0.87173	0.91018	0.93886	0.96453	0.98892
0.90487	0.93284	0.95404	0.97316	0.99147
0.93345	0.95274	0.96746	0.98092	0.99382
0.95846	0.97034	0.97954	0.98793	0.99606
0.98048	0.98600	0.99029	0.99427	0.99811

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       CONTOUR PRESENTATION OF CONCENTRATION PROFILE (TRICHLOROETHYLENE)
   CONTOUR PRESENTATION FOR C(1)                SCALE VALUES    'L' = 0.0
   '1'=1.000E-01   '2'=0.200   '3'=0.300     '4'=0.400      '5'=0.5000
   '6'=0.600       '7'=0.700'  '8'=0.800     '9'=0.900      'H'=1.00

                                       1  1  1  1  1  1  1  1  1  1  2
TIME        1  2  3  4  5  6  7  8  9  0  1  2  3  4  5  6  7  8  9  0
0.0         LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL
0.50000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 57
 1.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL2467
 1.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL2467
 2.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL  5  7 8
 2.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL2  67 8 9
 3.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 2  67 8 9
 3.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 3  6 7 8  9
 4.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL  5 67  8 99
 4.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 2 5 67  8 99
 5.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL  4  6 77 8  99
 5.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 3 56 77 8  99
 6.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 3  6 77 8  99
 6.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL1  345 6 7  8  99
 7.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 3 5 6 77 88  999
 7.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 3 5 6 7  88  99
 8.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL12  45 6  7  88  99
 8.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 34 5 6 77  88  999
 9.0000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL  23 5 6  7  88   99
 9.5000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL12 4 5 66 77  88  999
 10.000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 34 5 6  77  88   999
 10.500     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL  123 5 66 77  88   999
 11.000     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL1  4 5 66 77  888   999
 11.500     LLLLLLLLLLLLLLLLLLLLLLLLLLLLLLL 34 5 66 77  888   9999
 12.000     LLLLLLLLLLLLLLLLLLLLLLLLLLLL 1     5 6  77  888   999
 12.500     LLLLLLLLLLLLLLLLLLLLLLLLLLLL1  4 5 66  77  888   9999
 13.000     LLLLLLLLLLLLLLLLLLLLLLLLLLL  34 5 66  77  888   9999      H
 13.500     LLLLLLLLLLLLLLLLLLLLLLLLL  23  55 6  77   88    9999      H
 14.000     LLLLLLLLLLLLLLLLLLLLLLLLL  44 5 66  77  8888   99999      H
 14.500     LLLLLLLLLLLLLLLLLLLLLLLL  34 5 66  77  888    99999       H
 15.000     LLLLLLLLLLLLLLLLLLLLLL1  34 5  6  77   888    99999       H
 15.500     LLLLLLLLLLLLLLLLLLLLLL  4 55 66  77   888    99999        H
 16.000     LLLLLLLLLLLLLLLLLLLL   34 5 66  77   888    99999        HH
 16.500     LLLLLLLLLLLLLLLLLLL123 4 5 66  77   888     99999        HH
 17.000     LLLLLLLLLLLLLLLLLLL  4 5  6   777  888     99999         HH
 17.500     LLLLLLLLLLLLLLLL  1234 5 66  777  888     99999         HHH
 18.000     LLLLLLLLLLLLLLLL1  4 5  6   777  888     999999         HHH
 18.500     LLLLLLLLLLLLLLLL 34 5 66   77  8888     999999          HHH
 19.000     LLLLLLLLLLLLL 12   5 66   77  8888     999999          HHHH
 19.500     LLLLLLLLLLLLL  4 5 66   777  8888     999999           HHHH
 20.000     LLLLLLLLLLL  23 5 66   77  8888     9999999           HHHHH
 20.500     LLLLLLLLLL  4 5  6   777  8888     9999999            HHHHH
 21.000     LLLLLLLLL 23 5 6   777  888      99999999            HHHHHH
 21.500     LLLLLLL  4 5 66   77  8888     99999999             HHHHHHH
 22.000     LLLLL  2 5 6  77    8888     99999999              HHHHHHHH
 22.500     LLLL  5 6  777    8888    999999999               HHHHHHHHH
 23.000     L1    66 77  8888      999999999                 HHHHHHHHHH
 23.500     L2  77  888      9999999999                    HHHHHHHHHHHH
 24.000     L  77 88    9999999999                     HHHHHHHHHHHHHHHH
 24.500     99999999999999                          HHHHHHHHHHHHHHHHHHH
 25.000                                     HHHHHHHHHHHHHHHHHHHHHHHHHHH
```

FIGURE 4

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TABLE 2. Diffusion Coefficients for Organic Liquids in Cross-Linked Polystyrene at 25°C

Solvent	Swelling time (min)	D_0[a] (cm^2/sec)
Methylene chloride	5	5.0×10^{-7}
Trichloroethylene	25	1.3×10^{-7}
Tetrahydrofuran	35	1.0×10^{-7}
Benzene	50	5.7×10^{-8}

[a] Diffusivity coefficient through the swollen region.

The magnitude of the D_0 values obtained, and shown in Table 2, is similar to those encountered in the diffusion of organic vapors into polymers above the glass temperature (T_g). For Fickian diffusion this result should also be expected above the glassy state [6]. It is further seen from the data of Table 2 that only small, low polarity molecules can penetrate among the polymeric chains of the rigid copolymer with relative ease. This is the reason why small chlorinated hydrocarbons have been adopted as swelling agents for the preparation of ion exchange resins.

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