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Self-Diffusion of 1,3-Dimethyladamantane Dissolved in Hexafluorobenzene and in Polybutadiene

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ABSTRACT: We report self-diffusion measurements on both components of the systems 1,3-dimethyladamantane (1,3-DMA) dissolved in C_6F_6 and 1,3-DMA dissolved in polybutadiene. The concentration and temperature dependences of diffusion and the nonideal solution behavior follow free-volume models, permitting the deduction of free-volume and collision parameters for 1,3-DMA.

I. Introduction

The study of binary liquid solutions and solutions of liquids and rubbery polymers has been considerably furthered by measurements of transport properties, about which self-diffusion can yield detailed information.[1] Consequently, self-diffusion measurements of both components in a solution as functions of concentration and temperature can provide a detailed characterization of certain molecular attributes of one species if those of the other species are known. Self-diffusion in liquid or polymer systems is extremely sensitive to free-volume availability and to the dynamics of the collisions among molecules.[2] The parameters to be determined thus are those entering the free-volume theories suitably augmented by collision dynamic considerations.[3–5]

The molecule of interest in this work is 1,3-dimethyladamantane, not well-known until recently and to our knowledge not yet characterized in these terms. This molecule is relatively rigid and compact; its intermediate size makes it a suitable candidate to investigate the onset of dynamic anomalies that are known to be present in larger molecules such as 5α-cholestane and cholesta-3,5-diene[6] but that are absent in smaller molecules[4] and even in segmentally mobile n-paraffins.[7,8] In the process, an improved understanding of the diffusion process may be achieved.

The pulsed-gradient spin-echo method[9] is ideally suited for measuring self-diffusion in multicomponent systems at equilibrium concentration. The different components can be observed via NMR of mutually exclusive nuclides or by relying on differences in chemical shift. The samples may be reused indefinitely, making it convenient to measure the temperature dependence of diffusion and minimizing the consumption of expensive ingredients.

A preliminary report of this work has been given.[10]

II. Theory

It will be useful to collect here the theoretical expressions used in the analysis of the data. The fractional free volume f of a polymeric or other liquid of species i is given approximately by[11]

$$f_i = f_{g_i} + \Delta\alpha_i(T - T_{g_i}) \qquad (1)$$

This relation holds above the liquid's glass transition temperature T_g, where f reduces to $f_g = 0.025$. The free-volume expansivity $\Delta\alpha$ can be estimated from the difference in expansivity above and below T_g. In a binary mixture of liquids ($i = 1, 2$) the diffusion coefficients D_1 and D_2 depend on the weight fraction w_1 of the first species in a way described by Vrentas and Duda:[4,5]

$$\ln D_1 = \ln D_1^0 + B_1 w_1 S_1/(1 + w_1 f_2 S) \qquad (2)$$

$$\ln D_2 = \ln D_2^0 + B_2 w_1 S_2/(1 + w_1 f_2 S) \qquad (3)$$

where[6]

$$S = (\rho_2 f_1/\rho_1 - f_2)/f_2^2 \qquad (4)$$

$$S_1 = (\rho_2 M_1 f_1/\rho_1 M_2 - f_2)/f_2^2 \qquad (5)$$

$$S_2 = S_1 M_2/M_1 \qquad (6)$$

and

$$B_i = g\hat{V}_i^*/\hat{V}_2^0 \qquad (7)$$

Here ρ_i and M_i denote, respectively, the mass density and molecular or segmental mass of species i. The ratio M_1/M_2 in liquid systems may depart substantially from the molecular weight ratio when the species are dissimilar; in the general case, M_1/M_2 characterizes the collision dynamics

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of the diffusion process.[6] $\hat{V}_i^*$ and $\hat{V}_2^0$ ($\equiv 1/\rho_2$) represent, respectively, the specific critical hole volume of species i and the second (i.e., host) species' specific volume, and g is an overlap factor[4] ($0.5 \leq g \leq 1$). Equations 2 and 3 are intended to remove several restrictive assumptions in the earlier theory of Fujita and Doolittle,[12] which is properly applicable only to simple penetrants in polymers over a limited concentration range near $w_1 \simeq 0$. This older expression can be obtained from eq 2–7 by approximating $M_1 = M_2$ and $\rho_1 = \rho_2$ (hence $S_1 = S_2 = S$) and hence ignoring the distinction between weight fraction w_1 and volume fraction v_1.

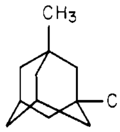
The magnitudes of D_1^0 and D_2^0 apply at $w_1 \rightarrow 0$, D_1^0 being the trace diffusion coefficient of species 1. The latter depends on the free-volume parameters of the host at the temperature of interest but also reflects intrinsic attributes of the trace molecule such as its size and mass and the energy needed to overcome intermolecular attraction. Its temperature dependence can be found from the expression of Williams, Landel, and Ferry[13] (WLF) as adapted to diffusion. In terms of the quantities defined above

$$\ln D_1^0(T) = \ln D_1^0(T_{g_2}) + \frac{B_1(T - T_{g_2})/f_{g_2}}{f_{g_2}/\Delta\alpha_2 + (T - T_{g_2})} \qquad (8)$$

The temperature and concentration dependence of self-diffusion of a penetrant species (1) in a polymer (2) is obtained by substituting eq 8 as well as eq 4–7 with eq 1 into eq 2. Since generally not all of the necessary parameters are known, they may be determined by adjusting them in a fit of the theory to the data.

III. Experimental Section

1,3-Dimethyladamantane, 1,3-DMA ($C_{12}H_{20}$, MW = 164.3, mp −26.5 °C, bp 201 °C, $\rho = 0.9011$ at 20 °C), is a relatively rigid molecule based on the highly symmetric adamantane molecule (tricyclo[3.3.1.1^{3,7}]decane), whose three rigid six-membered rings are in the chair form:



The 1,3-DMA was prepared by Sun Oil Co. as a research chemical and used as received.[14] Hexafluorobenzene (C_6F_6, MW = 186.2, $\rho = 1.65$ at 25 °C) was used as purchased from PCR, Inc. An un-cross-linked polybutadiene (45 NF, Firestone Tire and Rubber Co., $\rho \simeq 0.89$ at 25 °C) was cleaned of trace impurities by dissolving in tetrahydrofuran followed by reprecipitation with methanol and drying in vacuo.

Mixtures were prepared within the 7-mm-o.d. NMR sample tubes, which were sealed immediately after the last weighing to determine the concentration. Rubber-based solutions required moderate heating ($T \approx 60$ °C) for several hours (C_6F_6) or days (1,3-DMA).

Diffusion measurements were performed by using the pulsed-gradient spin-echo method;[9] our equipment and methods have been described in detail.[15–17] ^{1}H NMR was used for 1,3-DMA diffusion; in 1,3-DMA–rubber solutions the unattenuatable spin echo arising from the nondiffusing host was automatically subtracted by our data reduction program.[17] C_6F_6 diffusion was studied by ^{19}F echo attenuation. At no temperature or concentration in rubber-based systems was there any evidence of the diffusion of the rubber molecules, mainly because the highest 1,3-DMA concentration in the *cis*-polybutadiene (short of pure 1,3-DMA) was $w_1 = 0.85$.

Theoretical models were fitted to the data with a nonlinear least-squares computer program that could perform fits as functions of several independent variables or simultaneous fits of coupled models to several sets of data.[18] Preliminary analyses were conducted via an interactive terminal as described below.

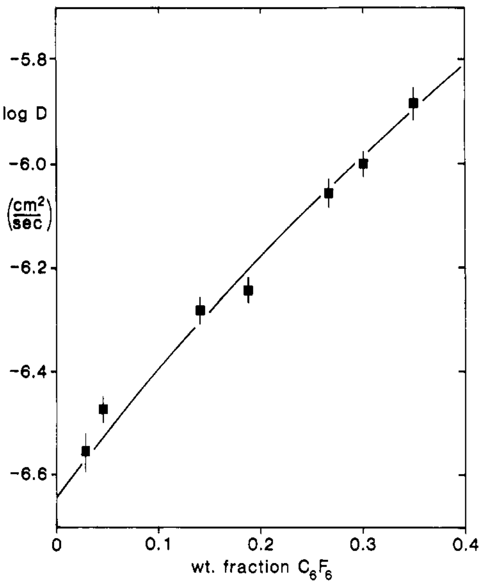


Figure 1. Concentration dependence of self-diffusion of C_6F_6 in *cis*-polybutadiene at 25 °C. Curve represents Fujita–Doolittle equation fitted to data.

IV. Results and Interpretation

A. C_6F_6 in *cis*-Polybutadiene. In order to determine the free-volume fraction f of C_6F_6 at room temperature, we measured its diffusion as a function of its concentration in *cis*-polybutadiene. The results are shown in Figure 1.

Since the free-volume parameters of this rubber are known from Ferry's compilation[19] ($f_g \simeq 0.025$, $\Delta\alpha = 6.4 \times 10^{-4}$ K^{-1}, $T_g = 172$ K), fitting the Fujita–Doolittle equation to the data in Figure 1 with $B_1 = 1$ can provide an estimate of $f(C_6F_6)$. In applications of this kind the limitations of the Fujita–Doolittle equation are not severely tested; the more general equation (2) contains the ratio M_1/M_2, whose value cannot be determined from the data because of the smallness of the curvature. The two-parameter fit provides the intercept $\log D_1(25\ °C) = -6.640 \pm 0.020$ and $f(C_6F_6, 25\ °C) = 0.235 \pm 0.010$. The latter uncertainty includes a modest allowance for the effects of the approximations implied by the Fujita–Doolittle equation. The fitted theory is also shown in Figure 1. An identical procedure at 80 °C had yielded[8] $f(C_6F_6, 80\ °C) = 0.278 \pm 0.005$.

B. 1,3-DMA in *cis*-Polybutadiene. The diffusion of 1,3-DMA in *cis*-polybutadiene was measured over the full concentration range at each of four temperatures. The results are shown in Figure 2.

The logarithm of D(1,3-DMA) increases with temperature at a rate that decreases at higher temperatures. This behavior arises from the WLF equation[13] (eq 8) and persists at all concentrations. $\log D$ also increases with 1,3-DMA concentration as suggested by eq 2 with $S_1 > 0$. The concentration dependence is more pronounced at lower temperatures, where the denominator of S_1 is smallest (eq 5). The nearly linear concentration dependences suggest several observations.

First, the Fujita–Doolittle equation cannot reproduce these data, since, with $S_1 = S$ (eq 4 and 5), the higher the slope of $\log D$ vs. w_1, the greater must be the downward concavity of the curve. Even at 80 °C the curvature would be quite pronounced. But with eq 4 it is possible to have a finite slope without significant curvature; it is only necessary that $Sf_2 \ll 1$.

Secondly, this absence of curvature (hence $S \simeq 0$) persists over a 90 °C temperature range. Inspection of eq 4 and 1 suggests that, since $\rho_2 \simeq \rho_1$ in this case, f_1 and f_2

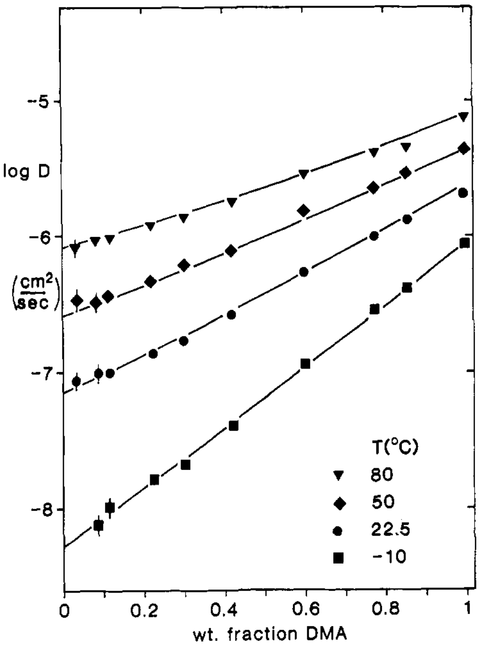


Figure 2. Diffusion of 1,3-DMA dissolved in *cis*-polybutadiene. Curves represent a single five-parameter fit of the theory of section II to all data. Results are given in Table I.

must be approximately equal over this range and hence that the T_g (as well as the $\Delta\alpha$) must be comparable. Together with the positive slopes ($S_1 > 0$) this implies $M_1/M_2 > 1$.

Numerical values for the unknown parameters were obtained in the following way:

1. Reasonable values for $\Delta\alpha$ and T_g of 1,3-DMA were assumed (see above); f_g was set to 0.025 throughout. Trace diffusion coefficients were obtained by extrapolating D_1 to $w_1 = 0$.
2. The value of B_1 was obtained by comparing the ratio of the trace diffusion coefficients at +80 and −10 °C with the predictions of eq 8. The result is independent of $D_1{}^0(T_{g_2})$ since the free-volume parameters of the rubber are known.
3. With the correct B_1, the second term in eq 8 for a given temperature was subtracted from the corresponding measured log $D_1{}^0(T)$ to give $D_1{}^0(T_{g_2})$.
4. Given B_1, S_1 was determined from the difference in log D values at the extremes of the concentration range; the highest precision was obtained at the lowest temperatures. Equation 5 was solved for M_1/M_2 with the deduced S_1 and the known or assumed free-volume parameters that determine f_1 and f_2.
5. Steps 2–4 were repeated with different $\Delta\alpha$ and T_g for 1,3-DMA until the observed D(80 °C, $w_1 = 1$) was reproduced without introducing significant curvature into the concentration dependences.

Steps 2–4 were programed as a single calculation for an interactive computer terminal, so that each execution of step 5 showed the three parameters as well as tables of log $D(T,w_1)$. The best parameters were finally supplied as input guesses for a multidimensional curve-fitting batch program,[18] which further refined the parameters in a five-parameter fit of the complete expression $D(T,w_1)$ to all data of Figure 2. The results of the excellent fit are given in Table I, the fitted curves being included in Figure 2.

Table I
Fitted Parameters for 1,3-DMA

log D(trace 1,3-DMA in rubber, 172, K)	−22.8 ± 1
B_1(1,3-DMA in rubber)	1.16 ± 0.03
M(1,3-DMA)/M(segment)	1.46 ± 0.05
T_g(1,3-DMA), K	150 ± 5
$\Delta\alpha$(1,3-DMA), K^{-1}	$(5.1 \pm 0.6) \times 10^{-4}$

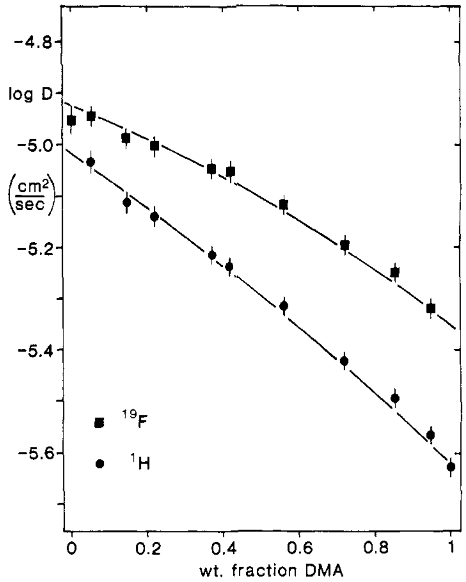


Figure 3. Diffusion of both components in the 1,3-DMA–C_6F_6 system at 25 °C. Curves represent a single four-parameter fit of eq 2 and 3 to all data. Results are included in Table II.

Because of the nearly linear concentration dependence of log D_1 over a wide temperature range, it is particularly obvious that the diffusional activation energy E varies in the same manner. The limiting values are $E = 10.2 \pm 0.3$ kcal/mol at $w_1 = 0$ and $E = 4.6 \pm 0.2$ kcal/mol at $w_1 = 1$. These are averages calculated from D_1 ratios between +80 and −10 °C. This factor-of-two decrease stands in contrast to the 50% increase in the activation energy of 5α-cholestane with concentration[6] in the same rubber at 80 °C. Similarly, the positive slopes in Figure 2 describe 1,3-DMA as a normal diluent rather than the "antiplasticizer" cholestane, for which the corresponding slope was negative.[6]

C. 1,3-DMA in C_6F_6. Diffusion measurements of both components of the system 1,3-DMA–C_6F_6 were performed at room temperature across the full range of concentration. The results are shown in Figure 3.

The diffusion of both components becomes less rapid as the 1,3-DMA concentration increases. This effect is somewhat more severe for the 1,3-DMA molecules. This nonideality[20] has been shown to be expressible[6] in terms of the quantity[4]

$$\xi = \frac{\hat{V}_1{}^*M_1}{\hat{V}_2{}^*M_2} = \frac{B_1S_1}{B_2S_2} = \frac{B_1M_1}{B_2M_2} \qquad (9)$$

expressed in the notation of eq 2–7. Nonideality in this hydrodynamic sense is signaled by the deviation of ξ from unity, ξ being measured as the ratio of the slopes of log D vs. w_1 for the two species, taken at the same w_1. In our case, the ratio is independent of w_1 and averages to $\xi = 1.46 \pm 0.02$.

Inspection of eq 2–7 shows that a knowledge of f_1, f_2, ρ_1, and ρ_2 at one temperature determines S and hence the curvature of log D_1 and log D_2 vs. w_1 in Figure 3. But the unknown B_1, B_2, and M_1/M_2 cannot be independently determined from the two other relevant measurements, the slopes of the concentration dependences near $w_1 = 0$. The quantity B_1 does, however, also enter eq 8. It is easily shown that measurements of the trace diffusion coefficients

Table II
Parameters for 1,3-DMA in C_6F_6

log D(trace 1,3-DMA in C_6F_6, 29.5 K)	-26.0 ± 1^a
B_1(1,3-DMA in C_6F_6)	1.35 ± 0.20^a
log D(trace 1,3-DMA in C_6F_6, 25 °C)	-5.020 ± 0.020^b
log D(pure C_6F_6, 25 °C)	-4.930 ± 0.020^c
M(1,3-DMA)/M(C_6F_6)	$1.04 \pm 0.03^{b,c}$
B_2(C_6F_6 in 1,3-DMA)	$0.96 \pm 0.15^{b,c}$
ξ(1,3-DMA/C_6F_6)	1.46 ± 0.02^d

[a] Derived from temperature dependence of D(1,3-DMA). [b] Derived from fit to D(1,3-DMA) vs. w_1. [c] Derived from fit to $D(C_6F_6)$ vs. w_1. [d] Calculated from fitted parameters via eq 9.

at two temperatures can determine B_1 (as well as $D_1(T_{g_2})$), provided the free-volume parameters of the host species (C_6F_6) are known. Assuming $f(C_6F_6)$ to have the temperature dependence of eq 1 with $f_g \simeq 0.025$, our determinations of $f(C_6F_6)$ at 25 and 80 °C (see section IV.A) suffice to determine $T_g = 29.5 \pm 8$ K and $\Delta\alpha = (7.82 \pm 0.06) \times 10^{-4}$ K^{-1}. The trace diffusion coefficients at 25 and 80 °C were obtained from measurements at $w_1 = 0.046$ and 0.146 by extrapolating to $w_1 = 0$.

Application of eq 8 to these values yields B_1(1,3-DMA in C_6F_6) = 1.35 ± 0.20 and log D_1^0(1,3-DMA in C_6F_6, 29 K) = −26 ± 1. Using this determination of B_1 in a four-parameter combined fit of eq 2 and 3 to the corresponding data in Figure 3 produced very good agreement with experiment. The fitted curves are shown in Figure 3, and the parameter values are listed in Table II. The free-volume fractions f_1 and f_2 at 25 °C needed in the fit were evaluated from eq 1, given $\Delta\alpha$ and T_g for 1,3-DMA (see Table I) and for C_6F_6 (see previous paragraph).

It may be seen that the dynamic mass ratio M_1/M_2 is essentially unity, reasonably close to the molecular weight ratio of 0.88. The source of the nonideal ξ thus is the value of B_1, which exceeds B_2 by 30%.

V. Discussion and Conclusions

The relatively unknown 1,3-dimethyladamantane has been characterized in terms of its free-volume parameters and its diffusion kinetics and hydrodynamics in solutions. The results show that the relatively small free volume of 1,3-DMA arises mainly from its high glass transition temperature and that in solutions its effective hydrodynamic mass and critical volume are not anomalous. In this sense, 1,3-DMA is not a bulky molecule, in contrast with 5α-cholestane and cholesta-3,5-diene.[6]

Furthermore, it is clear that nonideality in solutions cannot be directly related to molecular size. For 1,3-DMA as well as 5α-cholestane[6] in solution with C_6F_6, ξ (see eq 9) has nearly the same value, $\xi \simeq 1.5$, whereas their molecular weights differ by a factor of more than 2 and their hydrodynamic behavior is dissimilar. However, in the case of 1,3-DMA in C_6F_6 the ratio of specific critical volumes $\hat{V}_1^*/\hat{V}_2^* = B_1/B_2$ is significantly smaller ($\approx$1.4) than the ratio of the specific occupied volumes $(1-f_1)\rho_2/(1-f_2)\rho_1 \approx 2.16$, whereas these figures were comparable in the cholestane–C_6F_6 solutions. This denotes that a 1,3-DMA molecule requires only two-thirds the relative critical hole volume (critical hole volume per volume of molecule) of that needed by C_6F_6 to perform a jump, whereas cholestane is approximately equal to C_6F_6 in this respect. Comparison of the shapes of the three molecules supports the conclusion that the 1,3-DMA molecule derives its greater efficiency in the use of hole free volume from its relative lack of surface features. Protrusions or concavities tend to require or create extra free volume, unavailable in the needed shape or inaccessible and hence not involved in diffusion.

This information is derived from concentration and temperature dependences of diffusivity. No use has so far been made of the differences in $D_1(w_1 = 0)$ and $D_2(w_1 = 0)$. Trace cholestane in C_6F_6 diffuses only about 62% as rapidly (at 80 °C) as the host molecules, an effect tentatively attributable to its greater molecular mass. But this explanation fails to describe trace 1,3-DMA in C_6F_6: the molecular weight of 1,3-DMA is slightly less than that of C_6F_6 whereas its trace diffusion coefficient (at 25 °C) is only 78% of that of C_6F_6. However, it has been suggested[4,21] that the trace diffusion coefficient depends directly on the size rather than the mass of the impurity molecule. The molar occupied volumes $V \simeq M(1-f)/\rho$ for C_6F_6, 1,3-DMA, and cholestane are in the ratio 1:1.9:4.3. Since single-species self-diffusion is trace diffusion with host and impurity identical, diffusion does indeed decrease with increasing molecular size, although at a slower rate, consistent with $D_1^0(V_1) \propto V_1^{-1/3}$. This quantity is inversely proportional to the diameter of the hole required for a jump of the impurity; this is generally not equal to the diameter of the hole created by a jump of one host molecule,[3] at least for sufficiently large impurities. The distinction between a mass dependence of D_1^0 and a volume dependence is not evident in the case of nearly constant densities. Diffusion of trace n-paraffins in C_6F_6 may be said to depend on either paraffin mass[22] or volume, since their density varies slowly with carbon number. But there the power law exponent is greater, $D_1^0(V) \propto M_1^{-0.7\pm0.1}$, almost certainly for collision dynamic reasons peculiar to long, flexible molecules.[22] However, at 80 °C trace diffusion of n-paraffins in C_6F_6, interpolated at a paraffin molecular weight equal to that of the host, is only 80% as rapid[22] as the self-diffusion of pure C_6F_6. This again suggests that volume considerations dominate mass dependence and is consistent with the negative one-third power dependence on V_1. To be sure, intrinsic diffusion rates are also affected by intermolecular attractive forces. Thus, in comparison of trace diffusivities of unlike molecules in a common solvent, differences in intermolecular attraction may obscure the simple dependence of D_1^0 on host free-volume fraction f_2 and the volume V_1 of the trace molecule.[4]

In a comparison of families of like molecules, the power law exponent m ($D_1^0(V_1) \sim V_1^m$) can vary from $-^1/_3$ (for simple molecules in liquids) to −1 (for simple or chain molecules in polymers[7,23]), intermediate values occurring for chain molecules in simple liquids.[22] Our results for 1,3-DMA in rubber (Table I) are included in this correlation.

1,3-DMA and cholestane differ in molecular mass as well as molecular volume by a factor of about 2, but both (ref. 6 and Table I) are characterized by an identical M_1/M(segment) $\simeq$ 1.4 in *cis*-polybutadiene. We suggest that this again illustrates the observation[8] that the jumping segment of a polymer molecule for collision dynamic purposes adjusts its size to the penetrating molecule, without necessarily equaling it in mass.

Finally, the evidence accumulating suggests that removing the fixed polymer molecular cages does not necessarily result in an enhancement of diffusivity of the solvent or diluent molecules. Enhancements by a factor of $^3/_2$ have suggested;[24] an effect of nearly this size was observed between 95% and 100% diluent concentration in the benzene–polyisobutylene system,[25] and a smaller enhancement was found in light extender oil by comparison with its diffusion in synthetic *cis*-polyisoprene.[15]

However, for at least the heavier paraffins,[7,8] 1,3-DMA (present work), and 5α-cholestane[6] in rubbers, the internal friction between these molecules is apparently high enough to replace the effects of the constraining polymer chains without noticeable transition. Because the mass of all diluent molecules is the same, this internal friction cannot originate in differential inertial confinement.[22] We tentatively suggest that larger diluent molecules may not find the polymer molecular segments to be effective constraints; collisions between large diluent molecules and segments may displace these segments as effectively as they would other diluent molecules. In that case no diffusivity enhancement at high diluent content is observed because the enhancement exists at all concentrations.

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Controlled Release of Fluoride Ions from Methacryloyl Fluoride–Methyl Methacrylate Copolymers. 2. Solution Hydrolysis and Release of Fluoride Ions

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ABSTRACT: The hydrolysis of acid fluoride groups in methacryloyl fluoride (MF)–methyl methacrylate (MMA) copolymers was carried out in dioxane/water solution. Four different MF–MMA copolymers with MF mole fractions of 0.225, 0.368, 0.494, and 0.663 were used. The influence of polymeric structure on the rate of reaction was examined, and the rate was found to be dependent on the content of MF units and increased with increasing mole fraction of the MF unit at temperatures of 60, 70, and 80 °C. From infrared analysis, it was found that at low conversion the intensity of an acid fluoride band decreased quickly, while that of the MMA ester band remained unchanged and a carboxylic acid band was absent. The pseudo-first-order rate constants were closely related to the number fraction of (MF–MF) dyads in the copolymers. On the basis of these findings, it is concluded that the hydrolysis occurred at the (MF–MF) configurations, followed by the anhydride formation.

This study is part of our ongoing effort to develop appropriate drug–polymer sustained-release systems for the prevention and prophylaxis of various dental problems. To a greater extent, these systems are based on drugs and other agents covalently bound to polymers, and the release of the agent is generally through a hydrolytic mechanism.

It is well-known that fluoride combats tooth decay by the interaction of fluoride ions with the tooth structure, by interfering with the growth and metabolism of acid-forming bacteria in plaque, or by inhibiting the formation of polysaccharides. Today, teeth are treated with fluoride using fluoridated drinking water, toothpaste, dentifrice, or mouthrinse to increase the resistance of teeth to decay. Some of the dental cements and cavity liners for the restoration of diseased teeth and some of the dental fissure sealants for the purpose of dental caries prevention contain fluoride compounds that are released upon use. The most widely used fluoride compounds added to the above dental

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