Sorption and Diffusion of Organic Vapors in Two Fluoroelastomers

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ABSTRACT: Immersion experiments with Aflas (I), poly(tetrafluoroethylene-co-propylene), and Fluorel (II) [poly(vinylidene fluoride-co-perfluoropropylene)], showed greater swelling of **I** in nonpolar liquids and much higher swelling of **II** in polar liquids: over 100% (wt/wt) in two ketones and a phosphate ester. Sorption isotherms determined for toluene and acetone at 25 and 35°C were fitted with the Flory-Rehner relation, employing a concentration-dependent solvent-polymer interaction parameter. The fitted K parameters indicated that the degree of crosslinking in II was lower than in I. However, the high swelling of II by polar solvents is attributed primarily to the polar nature of II resulting from the asymmetric $CF(CF_3)$ moiety. Diffusion coefficients determined from sorption kinetics, corrected for nonisothermal effects, and converted to solvent self-diffusion coefficients were fitted with the Fujita free-volume relation. The values were much higher for I than II with acetone and also slightly higher for I with toluene. The estimated zero-concentration values were 1.5 E-09 cm²/s for Aflas-acetone, 0.3 E-09 cm²/s for Fluorel-acetone, and even lower for toluene. The low diffusion coefficients, which contribute to the superior barrier performance of these elastomers, is due, in part, to the high glass transition temperatures of I and II, -7 and -21° C, respectively. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1525–1535, 1999

Key words: diffusion; organic vapors; fluoroelastomers; self-diffusion coefficient; interaction parameters; barrier properties

INTRODUCTION

Fluorel and Aflas are two fluoroelastomers designed to provide superior solvent resistance and, in the case of Fluorel, advantageous high-temperature properties. Fluorel is a family of copolymers consisting of vinylidene fluoride and hexafluoropropylene supplied by the 3M Co. (St. Paul, Minnesota). Aflas is a copolymer of propylene and tetrafluoroethylene supplied by Asahi Glass Co., Ltd. (Japan). For the

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strictly alternating copolymers, the fluorine content of Fluorel amounts to 71 wt %, and that of Aflas, to 53 wt %. The purpose of the present study was to examine the effect of the differences in chemical composition on the sorption and diffusion behavior of the two fluoroelastomers. The solubility of a small selection of liquids representing a range of polarities was determined under immersion conditions. In addition, the sorption isotherm and the concentration dependence of the diffusion coefficient were determined for toluene and acetone in the two fluoroelastomers. Toluene and acetone were chosen as representative nonpolar and polar solvents.

The analysis of the diffusion data for acetone in the Fluorel was complicated by the occurrence of a non-Fickian character in the sorption kinetics at the higher vapor activities, represented by "S"-

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Aflas		Fluorel		
Component	phr	Component	phr	
Aflas 150P	100	Fluorel 2174	80	
		Fluorel 2145	20	
Carbon black		Carbon black		
(N-990)	50	(N-990)	30	
Caranauba Wax	2	Caranauba Wax	3	
Diak #7	8	Maglite D	6	
Lupercol 101XL	9	Calcium hydroxide	2.5	

Table IIngredients of CompoundedFluoroelastomers

The rubber content is 59.2% in Aflas and 70.9% in Fluorel.

shaped curves of the fractional weight gain against the square root of time. Such effects are prominent in the sorption of water from the vapor state, due to nonisothermal conditions arising from the heat of condensation and heat of mixing of water. An analytical solution to nonisothermal diffusion was developed by Armstrong and Stannett¹ and applied to analyze some of their results for the sorption of water in wool fibers and cellulose films. However, it is only recently that similar non-Fickian effects in the sorption of organic vapors in polymer films have been attributed to nonisothermal diffusion conditions.² The direct observation of the temperature increase accompanying the sorption of acetone in Fluorel, determined as part of this study, was reported in a prior publication.³ The present report is concerned with an attempt to interpret the sorption and diffusion results as a key to understanding the differences in the properties of the two fluoroelastomer samples. To this end, characteristic parameters were developed by fitting the Flory-Rehner equation⁴ to the experimental sorption isotherms and by invoking the Fujita free-volume relation⁵ as the framework for correlating the dependence of the diffusion coefficient on the concentration.

EXPERIMENTAL

Materials

The fluoroelastomer samples used in the present study were compounded, carbon black-reinforced elastomers prepared by Smithers, Inc. (Akron, Ohio), for the former Army Materials Technology Laboratory in the form of 6×6 -in. sheets of nominal 10-mil thickness. The recipes used in the formulation of the elastomers are given in Table I. The

densities of the pure Aflas and pure Fluorel gum rubbers are 1.550 and 1.880 g/cm³, respectively. The corresponding densities of the compounded rubbers are 1.638 for Aflas and 1.845 for Fluorel. Pure rubber densities were obtained from the manufacturers, and the densities of compounded rubbers, by the Army Materials Technology Laboratory. The glass transition temperatures, determined on these samples by DSC measurements,⁶ were -7° C for Aflas and -21° C for Fluorel.

Sorption Kinetics

The sorption experiments were made in a conventional thermostatted vacuum-sorption system using a quartz spring balance with a spring sensitivity of 10 mg/cm for the 10-mil thick sample. A ballast chamber of 10 L was used to minimize pressure drift during the run. Spring displacements in response to the weight change were read with a Gaertner cathetometer, with an accuracy of ± 0.001 mm. Measurements were conducted by the incremental sorption method in which the vapor pressure was increased in successive increments to map the sorption isotherm and the concentration dependence of the diffusion coefficient. Before conducting any sorption experiments, the samples were leached by immersion in liquid acetone to extract soluble processing aids. The samples reached constant weight within 1 day of immersion, but were leached for at least 48 h and then kept under a vacuum for several days until all of the acetone had been removed. The weight loss was 2.9% for the Fluorel and 5.1% for the Aflas samples.

RESULTS AND DISCUSSION

Liquid Immersion

An initial survey was conducted on the sorption uptake of the two fluoroelastomers in a set of liquids to characterize the effect of the elastomer chemical structure on the solubility behavior. The selection of liquid solvents was essentially random, except for polarity considerations, as the liquid immersion test was used for prescreening of the solvent for the vapor-sorption study. The results in Table II indicate that, overall, Aflas exhibits a more limited solvent swelling than that of Fluorel. However, Aflas exhibits greater swelling in the nonpolar solvents, such as cylclohexane and toluene. Fluorel displays only limited swelling in the nonpolar solvents but swells to a much

Organic Liquids	Aflas	Fluorel
Cyclohexane	5.0	0.0
Styrene	12.7	3.9
Toluene	18.5	8.74
Methyl ethyl ketone	23.3	108
Acetone	25.7	105
Tributyl phosphate	2.2	189
Ethyl alcohol	0.2	1.2

Table IISolubility of Organic Liquidsin Fluorel and Aflas

Solubility is weight percent based on the weight of compounded rubber in the compound.

greater extent in the polar solvents, with an uptake of over 100% in the ketones and phosphate ester. This solubility behavior indicates that Fluorel is a surprisingly polar polymer, despite its predominately fluorocarbon makeup, possibly due to the asymmetric disposition of fluorine in the $-[CF(-CF_3)]$ — moiety. The solubility behavior resembles that reported for Viton,^{7–9} which has a closely related chemical structure.

Sorption Isotherms

The sorption isotherm of acetone in Fluorel at 25°C is shown in Figure 1 and that of toluene in Aflas at 25°C is shown in Figure 2. The concentration is in grams of solvent per gram of compounded rubber, and the solvent activity is the vapor pressure relative to the saturation vapor pressure. In both figures, the weight uptake at unit activity is the value determined under immersion conditions. Sorption isotherms were also measured at 35°C with acetone. For Fluorel-acetone, the isotherms at 25 and 35°C were almost superimposable, indicating that the solvent-polymer mixing process is essentially athermal. For Aflas–acetone at 25 and 35°C, there was a small, consistent increase in the solubility at the higher temperature over most of the activity range. Since the diffusion results to be discussed in the next section are limited to 25°C, the 35°C isotherms are not shown, although the Flory-Rehner fitting parameters, discussed in the following section, are included in Table III for both the 25 and the 35°C data. Liquid solubilities were not determined for acetone or toluene at 35°C.

An attempt was made to fit the sorption isotherms with the Flory–Rehner equation⁴ with the solvent–polymer interaction parameter, χ , treated as being concentration-dependent:

$$\begin{aligned} \ln(a_1) &= \ln(1 - \varphi_2) + \varphi_2 + (\chi_0 + \chi_1 \varphi_2 + \chi_2 \varphi_2^2)\varphi_2^2 \\ &+ K \! \left(\varphi_2^{1/3} + \frac{\varphi_2}{2} \right) \end{aligned} \tag{1}$$

where K is defined as

$$K = \frac{V_S}{M_C V} \left(1 - \frac{2M_C}{M} \right) \tag{2}$$

and

$$\chi=\chi_0+\chi_1~arphi_1+\chi_2arphi_2^2+\cdots$$

Here, a_1 is the solvent activity; φ_2 , the volume fraction of the pure polymer; V_s , the molar volume of solvent; M_c , the molecular weight of the polymer between crosslinks; and M and V, the molecular weight and specific volume of the parent polymer, respectively. The volume fractions of the pure polymer (φ_1) and the solvent (φ_2) are calculated based on the weight of the solvent absorbed



Figure 1 Sorption isotherm for Fluorel-acetone at 25°C. Filled points are experimental data; the line is the sorption isotherm calculated from the fitted Flory-Rehner parameters.



Figure 2 Sorption isotherm for Aflas-tolulene at 25°C. Filled points are experimental data; the line is the sorption isotherm calculated from the fitted Flory-Rehner parameters.

and the densities of the solvent and the polymers. All additional components are ignored in the volume calculation such that $\varphi_1 + \varphi_2 = 1.0$.

A search for the best-fitting values of the χ parameters and K using an iterative leastsquares routine, without any restriction on the value of *K*, led to the results recorded in Table III. The sorption isotherms of both elastomers with toluene could be fitted by an equation with a value of χ that is concentration-independent, but the value of K is negative. The fit to the Fluorel– acetone data required the use of a concentrationdependent χ , following eq. (1), as well as a negative value of K. For Aflas–acetone, the value of Kis positive but varies widely between the two temperatures. The main purpose of the curve-fitting procedure was to calculate the thermodynamic correction factors from the slope of the sorption isotherm, for use in converting the experimental diffusion coefficients to solvent self-diffusion coefficients. Although the fitted values would serve this purpose, they are not capable of interpretation in terms of the solvent–polymer interactions.

As a result of these difficulties, a trial-anderror approach was adopted to fitting the values for χ and K, by calculating the activities which corresponded to the set of experimental solvent volume fractions. The fit to the isotherms was optimized at the higher concentrations, even if

Polymer-Solvent	T (°C)	Χo	χ1	χ_2	Κ	χ^{a}
		Computer F	lory–Rehner Fit			
Aflas-acetone	25	1.069	-1.767	-2.144	0.043	0.82
	35	-4.963	10.955	5.242	0.754	
Fluorel-acetone	25	1.596	-3.319	1.514	-0.034	0.59
	35	1.579	-3.146	1.268	-0.033	
Aflas-toluene	25	1.2			-0.2	0.8
Fluorel-toluene	25	1.4			-0.16	1.29
		Optimized F	'lory–Rehner Fit			
Aflas-acetone	25	1.33	-2.62	2.793	0.043	0.73
	35	0.378	0.772		0.043	
Fluorel-acetone	25	0.91	-2.37	1.286	0.016	0.44
	35	1.04	-2.29	1.060	0.016	
Aflas-toluene	25	0.79	-0.18	0.485	0.043	0.87
Fluorel-toluene	25	1.29	-0.225	0.225	0.016	1.29

Table III Parameters for the Flory-Rehner Equation

^a χ values in the last column are those at saturation from a liquid immersion condition.

this resulted in larger percentage errors at the lower concentrations, because the thermodynamic correction factors obtained from the slope of the sorption isotherm are larger at the higher concentrations. However, the resulting errors in the trial-and-error fit were no larger and were frequently smaller than those from the computer fit. This set of parameters is summarized in Table III for comparison with the previous computerderived results.

The ability to represent the experimental data is indicated by the examples of Figures 1 and 2. where the solid line represents the calculated isotherm. All the *K* values in the data set in Table III are positive, and for a given polymer, the K values are the same with acetone and toluene, as required by the definition in eq. (2). The values of the χ parameters are in good agreement for the athermal 25 and 35°C Fluorel-acetone data and similar to the results of the computer fit in Table III. There is still a large disagreement in the corresponding set of 25 and 35°C values for Aflasacetone, but the differences are not as large as the results of the computer fit. This difficulty is due to a problem in the 35°C vapor-sorption results, where the concentration at the highest vapor activity measured was too low to be consistent with the extrapolation to the liquid immersion value. A consistency check, involving the calculation of χ at saturation, using the sorbed concentrations determined under immersion conditions, leads to the values in the last column of Table III. These values of χ are consistent with the trend in the measured liquid solubilities. Finally, it is interesting to note that K for Aflas is almost three times greater than the value for Fluorel, despite the much higher density and, therefore, the lower specific volume of Fluorel. This indicates that the smaller solubilities measured for Aflas are due, in part, to the higher degree of crosslinking in this sample.

Diffusion Coefficients

The sorption kinetic data for acetone in both elastomers appeared to be affected by the nonisothermal sorption condition, which is caused by the heat released during the adsorption of acetone vapor onto the polymer surface. The heat would elevate the sample temperature when heat transfer to the surrounding is not fast. The elevated temperature will reduce the gas solubility in the polymer and thus slow the sorption process and lead to a lower apparent diffusion coefficient, *D*. In the case of desorption, the temperature will be lowered and the solubility increased. This will slow the devolatilization process and again leads to a lower D value. This nonisothermal effect becomes more pronounced as the acetone vapor activity increases (i.e., when a_1 reaches 0.6 in the case of Fluorel). In some experiments (i.e., a_1 > 0.9 for acetone sorption in Fluorel), the heat effect is too strong and the sorption appeared to be controlled by a gas-solid heat transfer at the initial stage, which is mainly because the diffusivity increases with the activity, leading to a faster heat accumulation on the solid polymer sample. This problem was discussed in a previously published article,³ and the model developed there was used in this work for the calculation of the diffusion coefficients in the nonisothermal affected sorption data. In the case of toluene sorption, the nonisothermal effect was much smaller and only a slight deviation from Fickian sorption was observed.

Comparisons of the experimental diffusion coefficients for Aflas and Fluorel as a function of the volume fraction concentration are shown for acetone in Figure 3 and for toluene in Figure 4. The volume fraction concentration was calculated at the adjusted weight fraction concentration, $C = C_i + 0.7(C_f - C_i)$, following the recommendation of Duda et al.¹⁰ for diffusion coefficients which are an exponentially increasing function of concentration. In contrast to the prior publication,³ the diffusion coefficients were not corrected for the increase of thickness on swelling at each equilibrium concentration, since the decrease in the sorption rate, which is proportional to the square of the increase in the thickness, is offset by the increase in the swollen area at equilibrium.

Only a portion of the Fluorel-acetone data, which extends to a volume fraction of almost 0.6, are shown in the comparison with the Aflas-acetone data in Figure 3, since the full data set are reproduced in Figure 5. The results for the Fluorel-acetone data appear to be reasonably smooth, except at the highest concentrations. Corrections to the measured diffusion coefficients for nonisothermal effects (i.e., the parameter R in ref. 3) ranged from a factor of 1.25 at a 15% acetone ($\varphi_1 = 0.26$) to 2.57 at 63% acetone (φ_1 = 0.5). The results obtained at higher temperatures, 35 and 43°C, which are not shown here, required somewhat higher nonisothermal corrections, due to the increase in the diffusion coefficients with temperature. The data for the other polymer-solvent pairs in Figures 3 and 4 cover a



Figure 3 Acetone diffusion coefficients, corrected for nonisothermal effects, versus concentration in Aflas, D(0) = 2.00 E-09, and Fluorel, D(0) = 0.40 E-09.

much smaller range than does the Fluorel-acetone data due to lower solubility. With Aflasacetone, nonisothermal corrections were required only for the two highest concentration points in Figure 3. Nonisothermal corrections were applied at the three highest concentration points with



Figure 4 Toulene diffusion coefficients, corrected for nonisothermal effects, versus concentration in Aflas, D(0) = 0.3 E-09, and Fluorel, D(0) = 0.15 E-09.

	Ace	Acetone		Toluene		
Polymer	Extrapolated Diffusion Coefficient	Free-volume Fit	Extrapolated Diffusion Coefficient	Free-volume Fit		
Aflas Fluorel	$\begin{array}{c} 2.0 \\ 0.4 \end{array}$	$\begin{array}{c} 1.5\\ 0.3\end{array}$	$\begin{array}{c} 0.3 \\ 0.15 \end{array}$	$\begin{array}{c} 0.28\\ 0.14\end{array}$		

Table IV Estimated Values of the Zero-concentration Self-diffusion Coefficient, $D_1(0)$, $(\rm cm^2/s) \times 10^9$

Aflas-toluene, in Figure 4, and no corrections were required with Fluorel-toluene.

In comparing the results for Aflas and Fluorel in Figure 3, it is clear that the diffusion coefficient of acetone is consistently much higher in Aflas than in Fluorel. The data for toluene in Figure 4 exhibit considerably greater scatter than for acetone, especially the Aflas-toluene data. Nonetheless, it is possible to reach a qualitative conclusion about the relative magnitude of the toluene diffusion coefficients for the two fluoroelastomers. Although the difference in the toluene diffusion coefficients is much smaller than with acetone, the toluene values are almost uniformly slightly higher for Aflas. To provide numerical estimates for comparison, the diffusion coefficients were extrapolated to an estimated intercept at zero concentration (Table IV). The acetone D(0) values are very low, somewhat greater for Aflas and less for Fluorel than $1.2 \text{ E-09 cm}^2/\text{s}$, the value reported for toluene in butyl rubber at 30°C (ref. 11) determined from the sorption kinetics. The toluene D(0) values are even lower than the set of acetone values and are almost an order of magnitude lower than the value for toluene in butyl rubber.

The zero-concentration diffusion coefficient should be equal to the solvent self-diffusion coefficient at zero concentration, $D_1(0)$, which is capable of interpretation in simple molecular terms. In an attempt to gain a more reliable measure of the $D_1(0)$ values, the Fujita free-volume relation was applied as a semiempirical curve-fitting routine. The diffusion coefficients determined in the sorption experiment are polymer mass-fixed values. These results were converted to mutual diffusion coefficients, D_{12} , assuming one-dimensional swelling, with the relation $D_{12} = D/\varphi^2$.^{12,13} Solvent self-diffusion coefficients were calculated by applying the thermodynamic correction factor $D_1 = (1/\varphi_2 d \ln \varphi_1/d \ln a_1)D_{12}$.¹⁴ The resulting values of the solvent self-diffusion coefficient, D_1 ,

were fitted to the Fujita free-volume relation⁵ in the form¹⁵:

$$D_1 = A \exp - \left(B \frac{1}{(\varphi_2 + G\varphi_1)} \right) \tag{4}$$

where G is defined as

$$G = \frac{\ln(D_1(0)/A)}{\ln(D_1(1)/A)}$$
(5)

From eq. (4) at zero concentration, $-B = \ln[D_1(0)/A]$. The definition of *G* assumes that the free-volume contribution of the solvent in the solvent–polymer mixture is equal to the free volume of the pure solvent. These procedures were described in detail in an earlier article.¹¹

With the above definitions, the concentration dependence of the diffusion constant is constrained by the solvent self-diffusion constant at a unit volume fraction, equal to the self-diffusion coefficient of the pure solvent and the solvent self-diffusion coefficient at zero concentration, which should be equal to the value of the polymer mass-fixed diffusion coefficient extrapolated to zero concentration. If these quantities are known, then the concentration dependence of the diffusion coefficient can be fitted by varying A, as the single arbitrary parameter. The fit was optimized by using a spreadsheet which was organized so that changes in the above parameters caused an automatic change in the linked table of D_1 values and accompanying plot. For toluene, the solvent self-diffusion coefficient was taken as 2.25 E-05 cm²/s, equal to the value determined by NMR.¹⁶ The value for acetone was taken as 3.15 E-05 cm^2/s , based on the value for toluene adjusted by the ratio of the viscosity of toluene relative to acetone. Although the fit of the free-volume prediction is sensitive to the value of the solvent



Figure 5 Comparison of acetone diffusion coefficients and self-diffusion coefficients for Fluorel.

self-diffusion coefficient, the effect of a small change in the solvent self-diffusion coefficient can be compensated by changing the value of A.

The full set of unmodified diffusion coefficients for Fluorel-acetone are compared with the calculated solvent self-diffusion coefficients in Figure 5 to a limiting volume fraction concentration of 0.6. The two sets of values diverge at higher concentrations where the correction factors are larger. The free-volume fit to the data, represented by the continuous line, extends to the value of the acetone self-diffusion coefficient at unit solvent activity. The satisfactory agreement between the free-volume correlation and the experimental values provides increased confidence in the experimental data.

In the comparison of the Aflas-acetone and Fluorel-acetone solvent self-diffusion coefficients (Fig. 6), the Aflas-acetone values are uniformly higher than are the Fluorel-acetone results. The two sets of data can be fitted by nearly parallel free-volume curves with the $D_1(0)$ about five times higher for Aflas than for Fluorel (Table IV). Although the Aflas-toluene self-diffusion coefficients also appear to be generally higher than the Fluorel-toluene values (Fig. 7), the considerable scatter in the Aflas data allows a wide variation in the free-volume

fitted curve. In fact, it is not possible to fit the four highest concentration values for Aflas-toluene without further increasing the discrepancies in the lower concentration fit. The four high concentration values might be in error due to an overestimation of the nonisothermal correction to these data, but there is no systematic explanation for the uncertainty in the low concentration data. As a result, it is possible that the D_1 values for Aflas converge with those of Fluorel at zero concentration. However, it is unlikely that the Aflas $D_1(0)$ value would be any higher than that indicated in this figure. Thus, the ratio of the $D_1(0)$ values for Aflas and Fluorel is no greater than 2.0 (Table IV), compared to a ratio of 5 for acetone in the two fluoroelastomers.

The resulting values of the zero-concentration diffusion coefficient from the free-volume correlation are summarized in Table IV. These values are very close to the estimates based on the extrapolation of the original diffusion data. However, the present values are based on the best fit to all the available data within the constraints of the free-volume correlation, rather than an unconstrained extrapolation controlled largely by the lowest concentration values.



Figure 6 Acetone self-diffusion coefficient versus concentration, Aflas and Fluorel. Free-volume parameters: Aflas–acetone, $D_1(0) = 1.50 \text{ E-09}$, $D_1^* = 3.15 \text{ E-05}$, A = 1.40 E-04; Fluorel–acetone, $D_1(0) = 0.3 \text{ E-09}$, $D_1^* = 3.15 \text{ E-05}$, A = 2.8 E-04.

The contrasting $D_1(0)$ results for acetone and toluene raise the question of whether it is possible for two polymers to exhibit $D_1(0)$ values that are

very different for one solvent but nearly identical for a second solvent. An answer to this question can be found in the formulation of the free-volume



Figure 7 Toluene self-diffusion coefficient versus concentration, Aflas and Fluorel. Free-volume parameters: Aflas-toulene, $D_1(0) = 0.28 \text{ E-09}$, $D_1^* = 2.25 \text{ E-05}$, A = 1.4 E-04; Fluorel-toulene, $D_1(0) = 0.14 \text{ E-09}$, $D_1^* = 2.25 \text{ E-05}$, A = 6 E-04.

theory of Duda and Vrentas,¹⁷ which is based on well-defined molecular quantities. In the limit of zero solvent concentration, their relation can be written as

$$\ln D_1(0) - \ln D_0 = \gamma_2 V_2^* \frac{\xi}{f(T)}$$
(6)

Here, D_0 is the preexponential factor, V_2^* is the specific hole free volume of the polymer jumping unit, γ_2 is a correction factor for the overlap in the free volume available to more than one polymer jumping unit, and f(T) represents the temperature-dependent terms of the diffusion coefficient, which can be related to the WLF constants of the polymer. The parameter ξ is the ratio of the solvent molar volume at 0 K and the molar volume of the polymer jumping unit and is the only term on the r.h.s. of eq. (6) which involves a solvent-related parameter. According to eq. (6), if D_0 is independent of the nature of the solvent, the ratio of the zero-concentration self-diffusion coefficient of any given solvent in two polymers will be the same. Additionally, if D_0 is a solvent-independent parameter, the ratio of $D_1(0)$ for two different solvents will be the same for any polymer. However, D_0 can vary widely, even for seemingly similar solvents, as the data for polyisobutylene demonstrates: $D_0 = 4.47$ E-04 for benzene and 1.87 E-04 for toluene. Therefore, the simplifying correlations of $D_1(0)$ cannot be expected to apply a priori. There is no reason to assume that the ratio of $D_1(0)$ for two solvents will be the same in different polymers or that the ratio of $D_1(0)$ will be the same for two polymers with different solvents.

CONCLUSIONS

Although both are considered to be solvent-resistant fluoroelastomers, the properties of Aflas and Fluorel differ in significant aspects. Aflas is a copolymer of tetrafluoroethylene and propylene, whereas Fluorel is a copolymer of vinylidene fluoride and perfluoropropylene. Assuming a one-toone copolymer composition, the single difference in the repeat unit structure is the replacement of the CH(—CH₃) moiety in Aflas with the CF(—CF₃) moiety in Fluorel. The resulting greater aliphatic character of Aflas is evident in the higher uptake of the nonpolar solvents in Table II. The surprisingly polar nature of Fluorel, evident in the high ketone solubilities, is probably due to the asymmetric substitution of the $CF(-CF_3)$ moiety. However, it is interesting to note that the analysis of the sorption isotherms, in terms of the Flory–Rehner relation, also suggests that the degree of crosslinking is lower in Fluorel than in Aflas. To accommodate a value of K = 0.043, instead of 0.016, would require a reduction in the immersion solubility from 105 to 79%, which is well beyond the experimental error of about 5%. The use of the higher Kvalue would also increase the errors in the predicted Fluorel-toluene isotherm at the higher vapor activities and the immersion condition. Despite the indication of a lower degree of crosslinking, the higher solubility of polar liquids like ketones in Fluorel, nearly four times greater than that of Aflas, is essentially due to the more polar nature of Fluorel.

The diffusion coefficients in both Fluorel and Aflas appear to be unusually small at low concentrations, even in comparison with butyl rubber. However, the high glass transition temperature of the two fluoroelastomers, compared to butyl rubber and other common elastomers, may account for the difference. It is clear that the diffusion coefficients for acetone are much higher in Aflas than in Fluorel over the entire concentration range for which there are experimental data. The Aflas data are also consistently, if marginally, higher for toluene as well. The concentration dependence of the diffusion coefficient for acetone and toluene can be correlated with the Fujita free-volume relations, assuming reasonable values of the solvent self-diffusion coefficients for the pure liquids. These results led to a fivefold higher value of the zero-concentration acetone self-diffusion coefficient in Aflas compared to Fluorel but an increase of only one-half for toluene. Although the semiquantitative comparisons are beyond dispute, the exact values of the solvent self-diffusion coefficient are subject to considerable error. Despite the use of the free-volume relations, the reliability of the extrapolation to zero concentration is extremely sensitive to the consistency of the data at low concentrations. Nonetheless, it is clear from these results that the barrier properties of Fluorel are due, in part, to the low values of the diffusion coefficient. It is of interest to point out that these results conflict with the expectation that the diffusion coefficients in Aflas should be smaller than in Fluorel, since the glass transition temperature of Aflas is 14°C higher than that of Fluorel.

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