Elastomer Solvent Interactions III-Effects of Methanol Mixtures on Fluorocarbon Elastomers

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Synopsis

Fluorocarbon elastomers exhibit high volume swell in methanol, but not in ethanol or other alcohols. Proton nuclear magnetic resonance (NMR) data indicate that neat methanol exists as a hydrogen-bonded tetramer with a solubility parameter close to that of the fluorocarbon elastomer, thus causing the high swell. The NMR and volume swell data show further correlations: Increased temperature or dilution of methanol with nonpolar solvents or water breaks down the hydrogen-bonded structure and reduces the volume swell. Mixtures of methanol and ethanol form mixed tetramer species. In this case the volume swell can be predicted by statistical theory which indicates that an all-methanol tetramer and a tetramer containing one ethanol molecule are the only swelling species. Similarly, a tetramer singly substituted with butanol is too bulky to swell the elastomer. Thus the molecular structure of methanol and its mixtures as determined by NMR provides an explanation for the swelling of fluorocarbon elastomers in these environments.

INTRODUCTION

The effects of blends of methanol, ethanol, and methyl t-butyl ether in gasoline on properties of commercial elastomers were studied in previous investigations.[1-3] The swelling behavior of elastomers in the above fuel additives and in the blends of the additives and gasolines was adequately explained in terms of the solubility parameter concept. The one exception was the unexpected high swelling of the fluorocarbon elastomer in methanol. In this report, we examine the behavior of the fluoroelastomer when exposed, at varying temperatures, to pure methanol and to mixtures of methanol with polar and nonpolar solvents. We also examine the correlation between the swelling behavior of the fluorocarbon elastomer and the structure of the methanol in solution as determined by NMR investigations of different methanol mixtures.

EXPERIMENTAL

The fluorocarbon elastomer used in this investigation was a copolymer of vinylidene fluoride and hexafluoropropylene (Viton A).[4] The polymer was crosslinked and reinforced with carbon black filler using the formulation shown in Table 1. The ingredients were mixed using a two-roll mill maintained at about 100°C. Standard ASTM slabs were then molded from the rubber at 163°C for 30 min and post cured for 24 h at 205°C. Samples for volume change and tensile measurements were obtained from the slabs. For most experiments the samples were used without further treatments.

TABLE I
Formulation of Fluorocarbon Elastomer

Ingredient	Concentration (phr)
Viton AHV (DuPont)	100
Maglite D, Magnesium Oxide	15
Hexamethylene diamine carbamate (Diak #1)	1.5
N990 Carbon Black	25

For some volume change measurements the samples were dried in a vacuum oven at 110°C for 72 h in order to ensure the absence of small amounts of water in the sample.

An anhydrous reagent-grade methanol was used without further purification. Two grades of ethanol, namely, a pure (U.S.I. Absolute, Reagent) grade and an anhydrous denatured grade were used. The water contents of the ethanol grades were measured by the Karl Fischer technique and found to be 0.15% (by volume) for the anhydrous grade and 0.03% for the pure grade. In some cases the water content of ethanol was also determined for samples in which the fluoroelastomer had been immersed for 72 h; the water contents of the ethanol before and after exposure to the fluoroelastomer were similar.

The gasoline used in this investigation was a standard fuel, Indolene HO-III, supplied by Amoco. It contained 65% by volume paraffin, 30% aromatics, and 5% olefins. All other chemicals were reagent grade and were used as received.

Volume change (swell) measurements of the fluorocarbon were conducted in triplicate. The samples were exposed to the fluids for 72 h at the specified temperatures. The measurements were conducted by the ASTM D471 procedure, except that weighing of the wet samples was carried out in closed bottles to prevent loss of the fuels by evaporation.

Nuclear magnetic resonance (NMR) measurements of methanol, ethanol, butanol, and their blends with the polar and nonpolar solvents were performed on a Varian HA-100D NMR spectrometer at ambient probe temperature (29°C) and in one case at a series of controlled temperatures using a variable temperature accessory on the NMR spectrometer. The solutions were prepared volumetrically and then transferred to 5-mm diameter NMR tubes. About 3% tetramethyl silane (TMS) was added to the NMR tube to provide an internal reference for field/frequency locking. Standard instrument operating conditions were used.[5]

RESULTS AND DISCUSSION

Fluorocarbon Elastomer and Pure Alcohols

Measurements of volume change of the fluorocarbon in water and C_1 to C_8 normal alcohols were performed and are shown in Table II. All measurements were conducted on samples exposed to the fluids for 72 hours at room temperature. The volume change of the fluorocarbon elastomer after exposure to water is −1%, indicating slight shrinkage. In the case of

TABLE II
Volume Change of Fluorocarbon Elastomer after Immersion for 72 h at Room Temperature
in Water and in Alcohols

Alcohol	% Volume change
Water	-1
Methanol	89
Ethanol	0.5
n-Propanol	0.7
n-Butanol	0.4
n-Pentanol	0.1
n-Hexanol	0.1
n-Heptanol	0.2
n-Octanol	0.3

all alcohols except methanol, a slight swell is observed ranging between 0.1 to 0.7%. However, for methanol a very large positive volume change of 89% is determined, showing that methanol is different in its interaction with the fluorocarbon elastomer than water or higher molecular weight alcohols.

The first attempt at explaining the data was to examine it in terms of the solubility parameter concept. The solubility parameter (δ) is a basic property of all materials. It is defined as the square root of the cohesive energy density or the energy of vaporization per unit volume:

$$\delta = (\text{CED})^{1/2} = \left[\frac{\Delta H - RT}{V_m} \right]^{1/2}$$

In the above equation CED is the cohesive energy density, ΔH is the enthalpy of vaporization, V_m is the molar volume, R is the gas constant, and T is the absolute temperature. Contributions to the total solubility parameter (δ) come from polar forces (δ_p), nonpolar or London dispersion forces (δ_d), and hydrogen bonding (δ_H). The total solubility parameter in terms of the contributions of these forces is:

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_H^2}$$

For solvent-polymer pairs the optimum solubility occurs when $\Delta H_{\text{mixing}} = 0$. ΔH_{mixing} is related to the solubility parameters of the solvent and the polymer as follows [6]:

$$\Delta H_{\text{mixing}} = V_m (\delta_o - \delta_p)^2 \phi_o \phi_p$$

δ_o and δ_p are the total solubility parameters of the solvent and the polymer, respectively, and ϕ_o and ϕ_p are the corresponding volume fractions. ΔH_{mixing} is zero at $\delta_p = \delta_o$.

In the case of cross-linked elastomers the polymer cannot be dissolved because of its three-dimensional network structure. Instead, swelling is observed. The degree of swelling has been found[7-9] to be a function of the

degree of crosslinking or the molecular weight between crosslinks M_c, and the polymer/solvent interaction parameter μ. Higher values of M_c or lower values of μ lead to increased swelling.[6] μ is related to the solubility parameter by the following relationship:

$$\mu = \mu_s + \frac{V_m}{RT}(\delta_o - \delta_p)^2$$

Hence, at constant degree of crosslinking the optimum swelling of the elastomer in a solvent occurs when $\delta_o = \delta_p$. In the above equation μ_s is a constant.

The solubility parameters of the fluorocarbon elastomer and of water and the alcohols are listed in Table III. The total solubility parameters (δ) and the polar (δ_p), the London dispersion (δ_d) and the hydrogen bonding components (δ_H) are listed in the table.[10-13] It is not obvious from this table why methanol swells the elastomer to a much greater degree than water or the higher molecular weight alcohols. In fact from the values of the solubility parameters, the swelling of the fluorocarbon elastomer in all alcohols including methanol is predicted to be low since the total solubility parameter δ has a much lower value in the case of the polymer as compared to the alcohols.

We examined the literature for other unusual behavior of methanol. In Figure 1 we show a plot of melting points and boiling points obtained from the literature[14] for water and C_1 to C_8 normal alcohols. Only water shows an abnormal behavior in the boiling point. Deviation in the melting point behavior is observed to a slight extent for ethanol and to a large extent for methanol and water.

In an effort to provide an explanation for the unusual behavior of methanol in swelling the fluorocarbon elastomer, the nuclear magnetic resonance spectra of methanol and its blends with CCl_4, gasoline, ethanol, butanol, and water were investigated in order to obtain information on molecular structure. This data is discussed in subsequent sections of the report.

TABLE III
Solubility Parameters (cal/cc)$^{1/2}$ of the Fluorocarbon Elastomer and Some of the Alcohols Investigated[10-13]

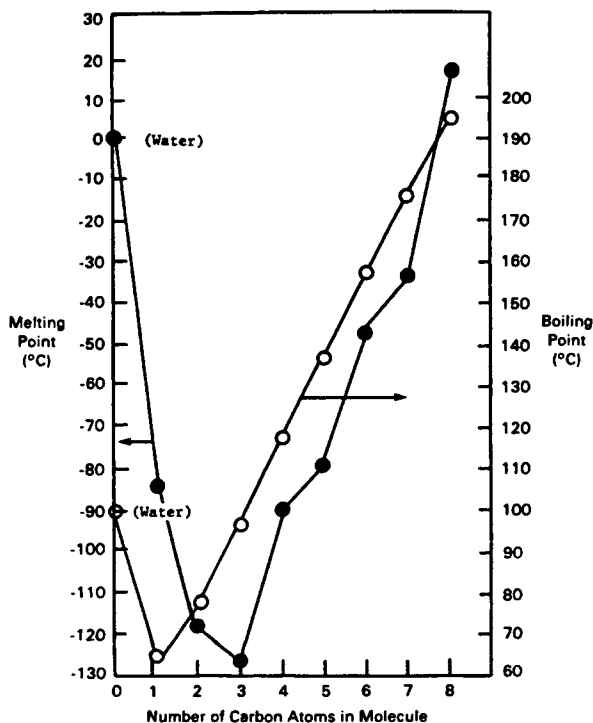|	Total solubility parameter, δ	Nonpolar solubility parameter δ_d	Polar solubility parameter, δ_p	Hydrogen-bonding solubility parameter, δ_H
Fluorocarbon elastomer	8.7	7.5	3.5	2.6
Water	23.5	6	15.3	16.7
Methanol	14.5	7.4	6.0	10.9
Ethanol	12.9	7.7	4.3	9.5
n-Propanol	12.0	7.8	3.3	8.5
n-Butanol	11.3	7.8	2.8	7.7
n-Pentanol	10.6	7.8	2.2	6.8
n-Heptanol	10.5	—	—	—
n-Octanol	10.3	8.3	1.6	5.8

Fig. 1. Melting points and boiling points of water and normal alcohols versus the number of carbon atoms in the molecule.

Fluorocarbon Elastomer and Mixtures of Alcohols with Nonpolar Solvents

For this investigation the two nonpolar solvents used were a standard gasoline, Indolene HO-III, and carbon tetrachloride. The effects of methanol/Indolene HO-III and ethanol/Indolene HO-III on the swell and mechanical properties of the fluorocarbon elastomer were measured at room temperature. The results are shown in Figure 2, and Table IV. As seen
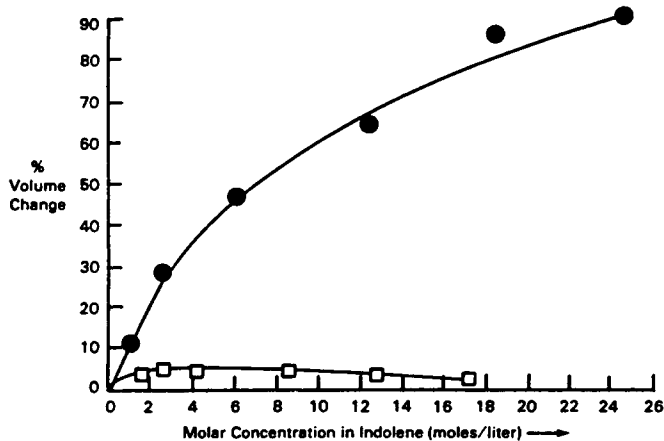
Fig. 2. Volume change of the fluorocarbon elastomer after 72 h exposure to (●) methanol/Indolene and (□) ethanol/Indolene mixtures versus molar concentration of alcohol.

TABLE IV
Effects of Methanol/Indolene and Ethanol/Indolene Mixtures on Properties of the Fluorocarbon Elastomer After Immersion for 72 h at Room Temperature

Alcohol	% Alcohol	Tensile strength, MPa	Elongation, %	Modulus at 100% elongation, MPa	Durometer shore A points	Volume change, %	Extractables, %
	Original properties	16.8	200	5.7	73	—	0
Methanol	0	15.8	232	5.3	76	0	0
	2	12.1	199	4.5	68	2	0
	5	11.7	219	4.0	63	11	0
	10	8.7	178	3.7	60	27	0
	25	5.3	127	3.9	59	46	0
	50	5.6	116	4.6	58	63	0
	75	4.8	96	—	57	85	0
	100	4.3	87	—	57	89	0
Ethanol	0	15.2	153	9.5	—	0	0
	5	12.7	153	6.3	—	3	0
	10	12.3	153	5.8	—	3	0
	15	12.7	150	7.0	—	4	0
	25	12.3	150	6.2	—	4	0
	50	13.0	158	6.3	—	4	0
	75	12.9	152	6.7	—	3	0
	100	14.6	160	7.1	—	2	0

from Figure 2 the volume swell of the elastomer in Indolene is close to zero. Addition of methanol to Indolene increases the swell, but not in direct proportion to the concentration of the methanol. High rates of increase are observed at low concentrations of methanol. A leveling off in the rate is observed in methanol-rich mixtures. The maximum swell of the elastomer (89%), occurs in pure methanol. In the case of ethanol/Indolene mixtures, only a slight swell (2 to 4%) of the elastomer is obtained in all mixtures over the entire concentration range (Fig. 2).

Tensile strength, elongation, and modulus values of the fluorocarbon elastomer were measured before and after exposure to varying concentrations of methanol/Indolene and ethanol/Indolene mixtures. The results are shown in Table IV. Exposure of the fluorocarbon polymer to both types of mixtures results in reduced tensile strength, elongation, and modulus values. The amount of reduction is quantitatively related to the degree of swelling of the elastomer as discussed in earlier reports.[2,3]

To investigate the structure of methanol we obtained NMR spectra of methanol in pure form and in solutions with CCl_4 and Indolene at various concentrations. The NMR spectrum of methanol in CCl_4 solvent is shown in Figure 3. The chemical shift or peak position of the OH changes systematically with dilution, whereas the CH_3 peak position remains constant. A downfield peak position (higher ppm value) means the methanol is highly hydrogen bonded while an upfield position indicates a lessening of hydrogen bond strength. At very high dilution (mole fraction $\chi_{alcohol}$, $<.01$) hydrogen-bonded structures break up into monomeric species.[15]

The methanol OH can exchange with other methanol OH's or with the OH's of other chemical species in the solution. If this exchange rate is very slow or nonexistent, the methanol OH will appear as a 4-peak spin multiplet due to coupling to the methanol CH_3 group. If the exchange rate is very fast, the methanol OH will appear as a sharp singlet. Intermediate rates
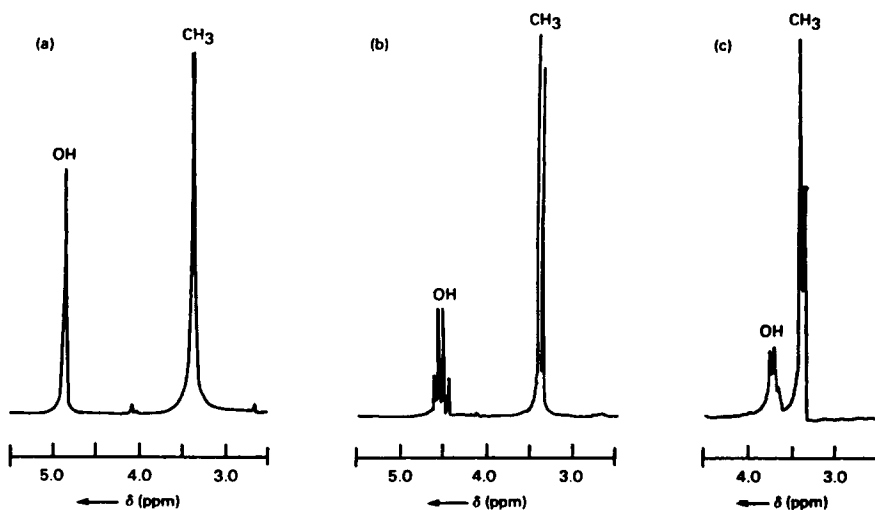

Fig. 3.   Proton NMR spectra of methanol in CCl_4(a)$\chi_{methanol}$ $= 1.00$; (b) $\chi_{methanol}$ $= 0.375$; (c) $\chi_{methanol}$ $= 0.112$.
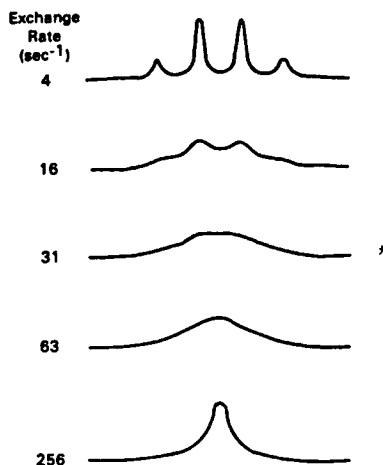
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Fig. 4. Collapse of the methanol hydroxyl four-peak spin multiplet as a function of exchange rate.

of exchange produce a broadened, and only partially resolved spin multiplet.[15] These effects are shown in Figure 4 and can also be seen in Figure 3. It is possible to calculate the absolute rate of exchange (units of exchanges per second) from such curves.[16]

Plots of the chemical shift of the methanol OH vs. methanol concentration in Indolene and CCl_4 are shown in Figure 5. The shapes of these curves somewhat resemble the volume swell curve obtained in Indolene (i.e., the rate of increase is high at low concentrations of methanol and tends to level off at higher concentrations of methanol) (Fig. 6). The four-line spin multiplet of the OH of the CH_3OH is observed at concentrations between $\chi_{methanol}$
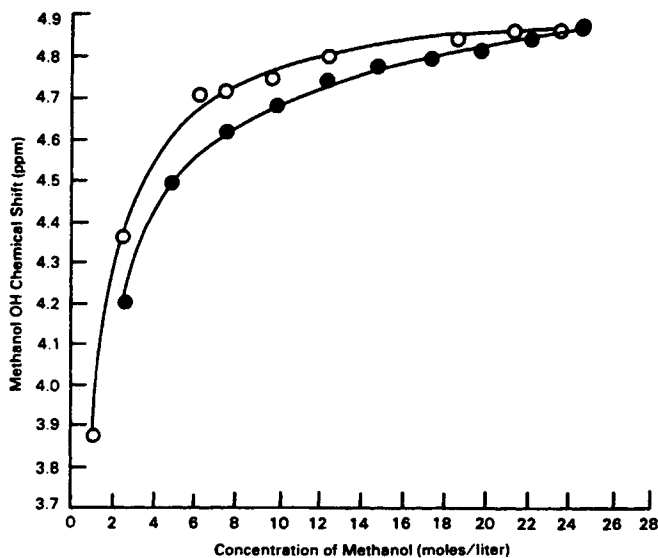
Fig. 5. NMR chemical shift of the methanol OH versus molar concentration of methanol in (○) Indolene and (●) carbon tetrachloride.
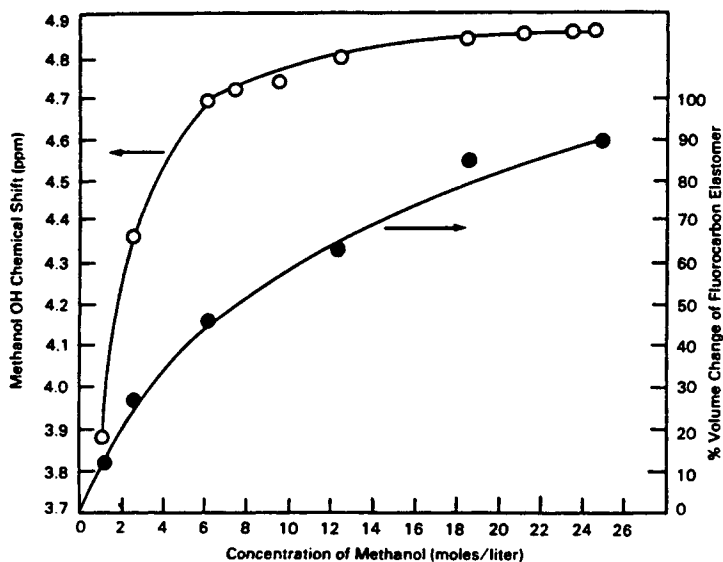
Fig. 6. Measured chemical shift (O) of the methanol OH for mixtures of methanol in Indolene and (●) volume change of fluorocarbon elastomer exposed to the same methanol mixtures.

$= 0.91$ and $\chi_{methanol} = 0.11$ in CCl_4 solution. This implies that the CH_3OH exists as a single hydrogen-bonded species throughout this concentration range. If other species existed, they would be observed as additional four-line spin multiplets; or as a single sharp line if the OH was time averaged by exchange. The only other explanation is that various oligomeric forms of CH_3OH are formed and all have the same chemical shift. This is very unlikely. The upfield shift of the spin multiplet with increasing dilution is explained as being caused by a weakening of the hydrogen bonds, perhaps due to increase in lengths caused by the diluent.[17] This is in contrast to the further dramatic upfield shift of the OH observed at very high dilution ($\chi_{methanol}$ from 0.1 to $\approx$ 0) which is known to be caused by the total breakup of hydrogen-bonded species into monomeric alcohol.[15]

By making measurements approximating "infinite dilution" conditions, Saunders and Hyne[18] calculate that the predominant hydrogen-bonded structure of methanol at concentrations of $\chi_{methanol} > 0.2$ in CCl_4 solutions is a cyclic tetramer, shown below:
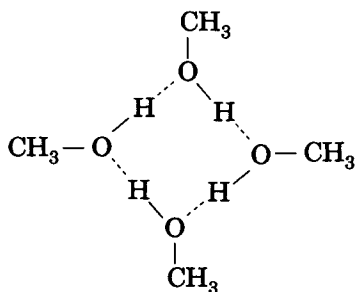
Other investigators have calculated that the predominant structure at and near $\sim 100\%$ methanol concentration is a hexamer,[19] or a long straight chain-associated hydrogen-bonded structure as suggested by infrared or Raman spectroscopy.[20,21]

Still other investigators have shown (by infrared measurements) that the predominant species for n-butanol and n-octanol is clearly tetramer.[22] Theoretical calculations for alcohol self-association via hydrogen bonding also predict the predominance of *cyclic* tetramer.[23]

In all these structures, the main species is:

$$ \cdots\,|\cdots \quad O-H \cdots\,|\cdots \quad O- $$
$$ \qquad\qquad\quad | $$
$$ \qquad\qquad CH_3 $$
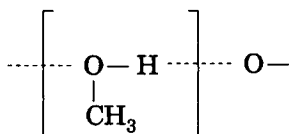
in which both the oxygen and the hydroxyl proton are involved in hydrogen bonds with methanol neighbors.

Using Small's method,[24] the solubility parameter of this species is calculated as follows.

$$ \delta = \frac{d\,\Sigma G}{M} $$

where d is the density of methanol and is equal to 0.7914 g/cm^3 at 20°C, M is the molecular weight, and G is the molar attraction constant for atoms and groups in the molecule. G is 214 for the CH$_3$ group, 70 for O (ether) and 80 for H. Hence, for bound methanol

$$ \delta = \frac{0.7914\,(214\,+\,70\,+\,80)}{32.04} = 9.0. $$

This value is very close to 8.7 which is the δ value of the fluorocarbon elastomer. This explains the high swell of the fluorocarbon elastomer in pure liquid methanol or in solutions containing high concentrations of methanol.

As mentioned earlier, the addition of nonpolar solvents such as Indolene or CCl$_4$ to methanol leads to lessening of the hydrogen bond strength as observed by lower values of the chemical shift (Fig. 5) and decreased effect on the swell of the fluorocarbon elastomer (Fig. 6). Both effects are accelerated in dilute solutions of methanol since at these concentrations the methanol approaches the concentration $\chi < 0.01$ where the hydrogen-bonded structure is broken up into monomeric species.

Using Small's method and assuming that ethanol undergoes the same type of association as methanol, the calculated solubility parameter of ethanol is found to be 8.5. This again is close to the solubility parameter of the fluorocarbon. The difference in the behavior of the two alcohols toward swelling the fluorocarbon elastomer (Fig. 2) is probably caused by

molecular volume differences. Strong evidence for this explanation is presented in the next section.

Fluorocarbon Elastomers and Mixtures of Methanol and Ethanol

Swell measurements of the fluorocarbon elastomers were conducted in methanol/ethanol mixtures. the results of this investigation are shown in Figure 7. In this mixed solvent system, high swell values for the fluorocarbon elastomers are observed in pure methanol and in mixtures containing up to 0.2 mole fraction of ethanol. A sharp drop in the swell values is observed for mixtures containing between 0.2 and 0.4 mole fraction of ethanol. At higher concentrations of ethanol the drop in swell continues but at a much reduced rate.

These phenomena can be best understood by examining the NMR spectra of the methanol/ethanol mixtures. Figure 8 is an example of these spectra. Over the concentration range $\chi_{methanol} = 0.93$ to $\chi_{methanol} = 0.33$, the 3-line spin multiplet of the ethanol hydroxyl and the 4-line spin multiplet of the methanol hydroxyl are observed simultaneously as discrete resonances in the same spectra. This unusual behavior means that the methanol and ethanol exist in only two chemically distinct sites. Saunders and Hyne[25] found that ethanol appears to have a hydrogen-bonded structure similar to that of methanol, that is, a cyclic tetramer. Hence we can assume that cyclic tetramers containing both ethanol and methanol in various molar ratios are likely to occur as shown in the structures below.
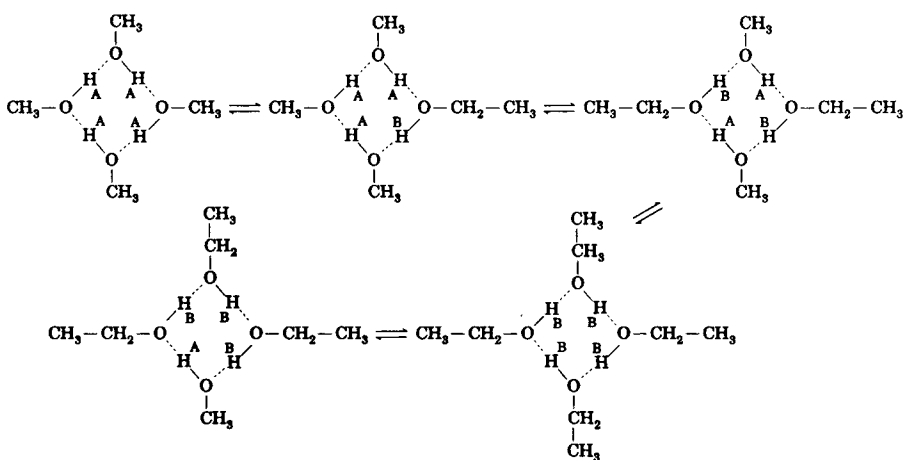
The "A" and "B" sites in each of the above mixed structures must be equivalent, that is, all the A's are equivalent and all the B's are equivalent.

The NMR spectra indicate that the ethanol and methanol interchange freely with one another and that the above "mixed" structures are indeed formed. This was determined in the following manner. The 4-line spin multiplet of the methanol hydroxyl and the 3-line spin multiplet of the ethanol hydroxyl are clearly observed at concentrations of $\chi_{methanol} = 0.5$. At concentrations of $\chi_{methanol} = 0.97$, the methanol hydroxyl collapses almost into
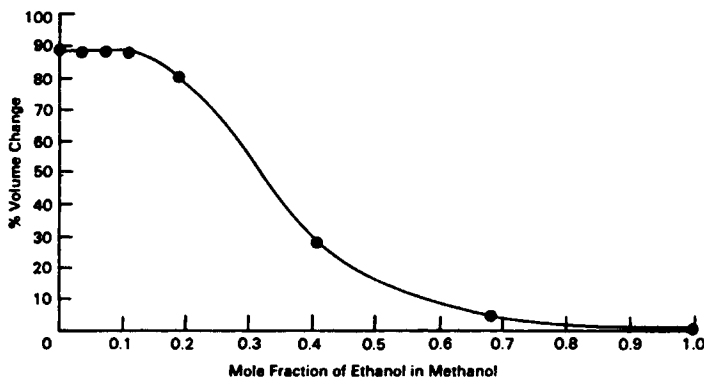
Fig. 7. Volume change of fluorocarbon elastomer after exposure to methanol/ethanol mixtures versus mole fraction of ethanol in the mixture.

a singlet as does the ethanol hydroxyl resonance. At concentrations near $\chi_{methanol} = 0.33$, both spin multiplets are increasingly clearly resolved. The interesting conclusion is that the methanol exchanges rapidly in the neat state and that the exchange rate decreases as it is diluted with ethanol. In contrast, the ethanol exchange rate slows down as its concentration in methanol increases. Much more importantly, we were able to use the shape of the methanol quartet and the ethanol triplet at each dilution ratio to calculate the actual exchange rates of these alcohols. The exchange can be either intra- or interspecies. The results are shown in Figure 9. The data points for both alcohols fall on the same curve. this strongly implies that the alcohols are freely interchanging with one another, that is, the mixed structures shown above are constantly forming, breaking up, and reforming.
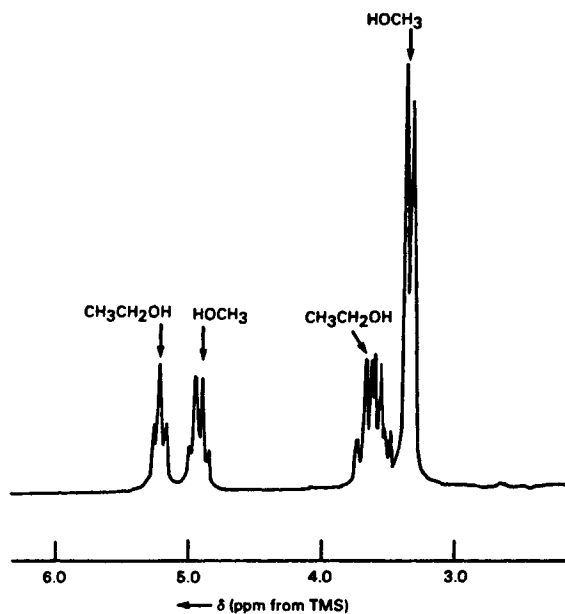

Fig. 8. Proton NMR spectrum of ethanol/methanol mixture ($\chi_{ethanol} = 0.458$).
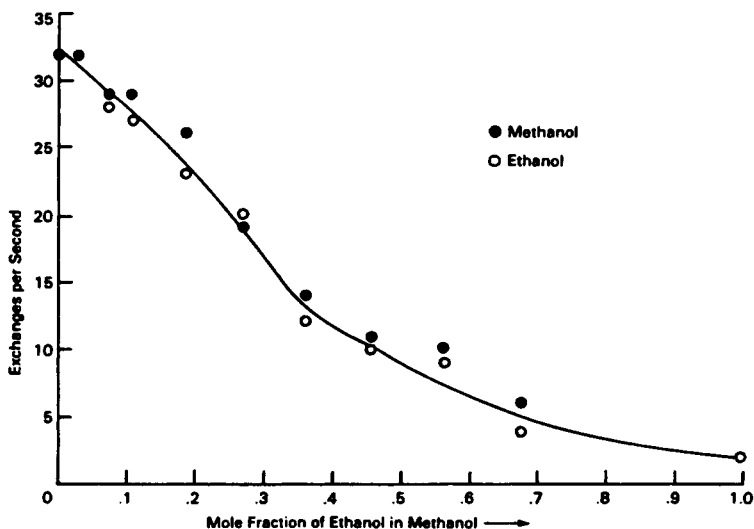
Fig. 9. Exchange rates of hydroxyl protons of methanol and ethanol versus mole fraction of ethanol in the mixture.

This, in turn, implies that the relative amounts of the various "mixed" species present can be handled as a simple problem in statistics using the binomial distribution. If p is the probability that a single substitution (exchange) on a four-membered ring will be by a methanol molecule and $1 - p = q$ is the probability that the exchange will not be with a methanol molecule, then the probability that p will occur r times in n exchanges (4 times in 4 exchanges for our case) is given by

$$P(r) = \frac{n!}{r!(n-r)!} p^r q^{(n-r)} = \frac{(4)!}{(4)!\,(4-4)!} p^4 q^0 = p^4$$

or,

$$P(r) = p^4$$

where p, the probability of a single exchange being with methanol, is simply the mole fraction of methanol present. The expression $P(r) = p^4$ evaluated at each mole fraction of methanol in ethanol gives the percentage of four-membered rings containing only methanol at each mole fraction. Figure 10 is a plot of this function. We are next interested in the percentage of four-membered rings which contain one and only one ethanol substituent. This is given by

$$P(r) = \frac{n!}{r!(n-r)!} p^r q^{(n-r)} = \frac{(4)!}{(3)!(4-3)!} p^3 q^1 = \frac{4.3.2.1}{3.2.1.1.} = 4\,p^3 q$$

The expression $(P)r = 4p^3 q$ evaluated at each mole fraction of methanol gives the percentage of four-membered rings containing one and only one ethanol substituent at each mole fraction. Figure 10 contains a plot of this
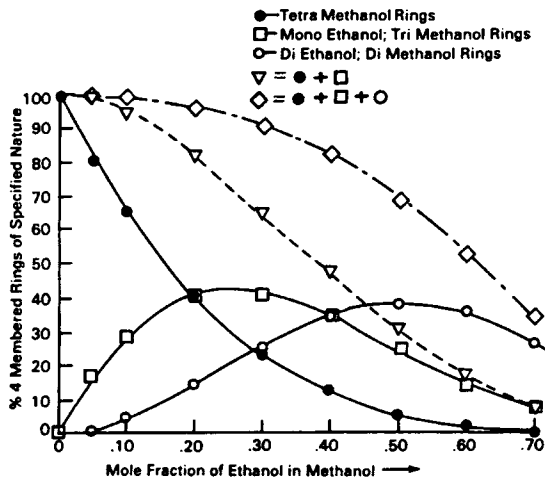
Fig. 10. Calculated percentages of four-membered rings of various types versus mole fraction of ethanol in methanol.

function. Notice that this plot peaks at $\chi_{methanol} = 0.25$. At higher concentrations of ethanol, double ethanol substitution becomes so probable that the percentage of rings containing only one ethanol substituent decreases.

The probability of double ethanol substitution was also evaluated in a manner completely analogous to that described above. A plot of this function is also shown in Figure 10. Notice that this plot peaks at $\chi_{methanol} = 0.50$. Also plotted in this figure are two sums. One plot is the sum of the percent *all methanol* and the percent *monoethanol-trimethanol* rings present at each mole fraction of ethanol in methanol. The other plot is the sum of the percentages of three types of rings; tetramethanol, monoethanol-trimethanol, and dimethanol-diethanol, present at each mole fraction of ethanol in methanol.

The first sum plot looks very much like the volume swell curve as seen in Figure 11. From this, we infer that the specific species capable of swelling the fluorocarbon elastomer are:
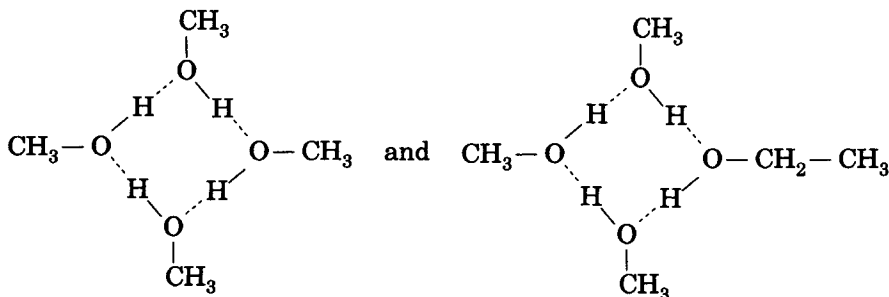
Apparently rings containing two or more ethanol molecules are large and hence become sterically unfavorable for swelling the fluorocarbon.
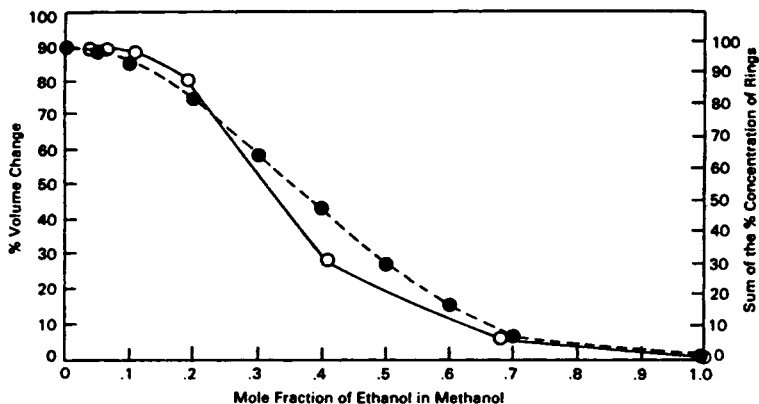
Fig. 11. Volume change of fluorocarbon (○) and calculated sum of rings consisting of 4 methanol molecules and rings consisting of 3 methanol molecules and 1 ethanol molecule (●) versus mole fraction of ethanol in methanol.

Fluorocarbon Elastomers and Mixtures of Methanol and Butanol

If we now consider the case of a mixture of methanol and n-butanol we would expect the monobutanol trimethanol cyclic tetramer (shown below) to no longer be a swelling species, because it is too bulky.

$$CH_3 O \cdots \begin{matrix} CH_3 \\ O \\ H \quad H \\ \\ H \quad H \\ O \\ CH_3 \end{matrix} \cdots O\, CH_2\, CH_2\, CH_2\, CH_3$$
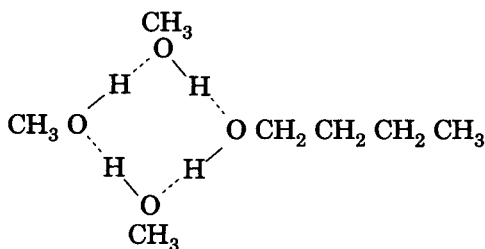
Therefore, the volume swell should be described by the *first term only* of the binomial expansion, i.e.,

$$\text{Volume swell} = k(\chi_{meOH} + \chi_{buOH})^4 = k[\chi_{meOH}^4 + \cdots]$$

Figure 12 is a plot of the experimental volume swell curve obtained for the fluorocarbon elastomer in the methanol/butanol mixtures along with a plot of the predicted χ_{meOH}^4 functional dependence. A fit is observed only at high χ_{meOH} values: $\chi_{meOH} \geq 0.92$ (i.e. $\chi_{buOH} < 0.08$). For smaller χ_{meOH} values, the volume swell curve falls off much faster than predicted.

Some clues as to why this occurs can be obtained from the NMR spectrum of a mixture of butanol and methanol. A typical spectrum ($\chi_{meOH} = 0.7$) is shown in Figure 13. The exchange rate of the OH proton of the methanol can be calculated from the half height-half width of this resonance peak (labeled "A"), and the exchange rate of the butanol OH proton can be
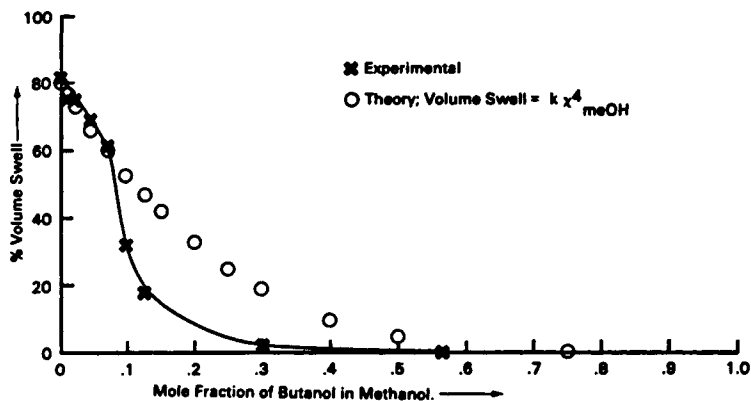
Fig. 12. Volume change of fluorocarbon elastomer (x) and χ^4_{meOH} (O) versus mole fraction of butanol in methanol.

calculated from the peak-to-valley ratio of the triplet (barely resolved) comprising this resonance (labeled "B"). This was done in the same manner as in the case of the ethanol/methanol blends. (Under conditions of slow exchange, the butanol OH resonance appears as a well resolved triplet and the methanol OH resonance appears as a well-resolved quartet.) In the present case we find that the methanol hydroxyl is exchanging over one-and-one-half times as fast as the butanol hydroxyl. This strongly suggests that there is restricted exchange of functional groups between the methanol and butanol hydrogen-bonded systems, probably because the butanol tetramer is energetically more stable.[22,23]

The methanol/ethanol system was an ideal one in that both the methanol and ethanol existed as cyclic tetramers in the neat state and in mixtures. The exchange rates of the hydroxyl protons of both species were measured
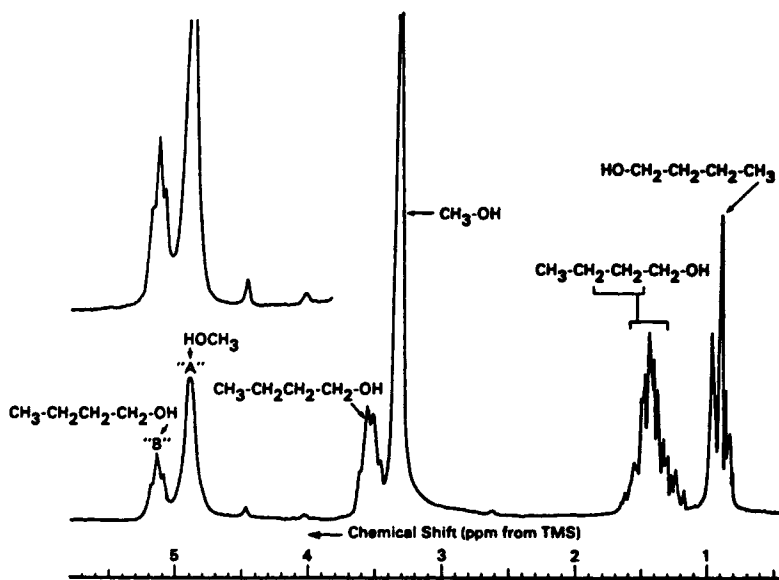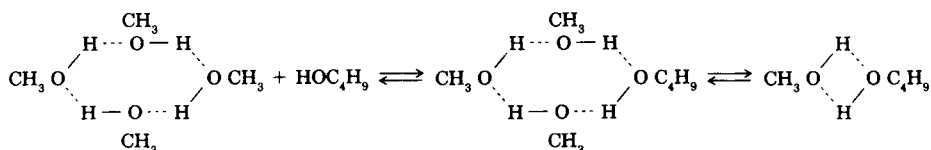

Fig. 13. Proton NMR spectrum of a methanol/butanol mixture ($\chi_{meOH} = 0.7$).
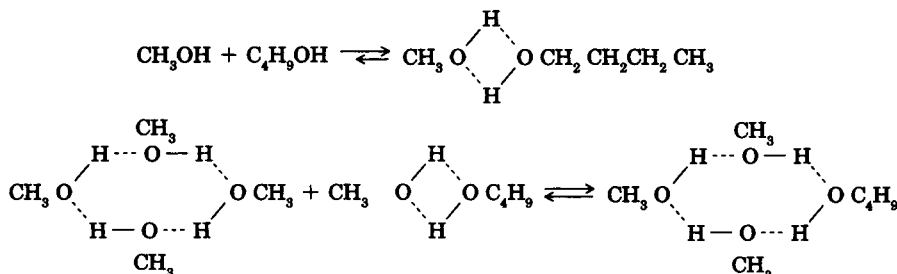
as equal over the entire χ value range. This implies free, random, and impartial exchange of functional groups in that system. This is not the case for the present system. The butanol, when present at high concentration, appears to "tie up" a portion of the methanol in structures which are not available for exchange with the rest of the methanol. The kinetics of such a process can be shown qualitatively as follows:

"Light" dilution with butanol (system behaves ideally).

$$
\begin{array}{c}
\quad\quad CH_3 \\
\quad H\cdots O-H \\
CH_3\,O \diagdown \qquad \diagup O\,CH_3 + HOC_4H_9 \rightleftharpoons \\
\quad H-O\cdots H \\
\quad\quad CH_3
\end{array}
\quad
\begin{array}{c}
\quad\quad CH_3 \\
\quad H\cdots O-H \\
CH_3\,O \diagdown \qquad \diagup O\,C_4H_9 \rightleftharpoons \\
\quad H-O\cdots H \\
\quad\quad CH_3
\end{array}
\quad
\begin{array}{c}
\quad\quad H \\
CH_3\,O \diagdown \quad \diagup O\,C_4H_9 \\
\quad\quad H
\end{array}
$$

"Heavy" dilution with butanol (system behaves nonideally).

$$
CH_3OH + C_4H_9OH \rightleftharpoons
\begin{array}{c}
\quad H \\
CH_3\,O \diagdown \quad \diagup O\,CH_2\,CH_2CH_2\,CH_3 \\
\quad H
\end{array}
$$

$$
\begin{array}{c}
\quad\quad CH_3 \\
\quad H\cdots O-H \\
CH_3\,O \diagdown \qquad \diagup O\,CH_3 + CH_3 \\
\quad H-O\cdots H \\
\quad\quad CH_3
\end{array}
\quad
\begin{array}{c}
\quad H \\
O \diagdown \quad \diagup O\,C_4H_9 \rightleftharpoons \\
\quad H
\end{array}
\quad
\begin{array}{c}
\quad\quad CH_3 \\
\quad H\cdots O-H \\
CH_3\,O \diagdown \qquad \diagup O\,C_4H_9 \\
\quad H-O\cdots H \\
\quad\quad CH_3
\end{array}
$$

The butanol/methanol adduct forms preferentially and when it exchanges with cyclic methanol tetramers it does so as a unit. If we assume that the added butanol complexes with a portion of methanol equal to the mole fraction of butanol we can express the volume swell as:

$$ \text{Volume swell} = k[\chi_{meOH} - \chi_{buOH}]^4 $$

A plot of this function is shown in Figure 14, again with the experimental volume swell curve. The fit in the region $\chi_{meOH} \leq 0.9$ (i.e., $\chi_{buOH} > 0.1$) is much better than that observed in Figure 12. Using the same constant k in both equations, the experimental volume swell curve can be described everywhere by:

$$ \text{Volume swell} = 82\,\chi_{meOH}^4 \text{ for } \chi_{meOH} \geq 0.92 $$

$$ \text{Volume swell} = 82[\chi_{meOH} - \chi_{buOH}]^4 \text{ for } \chi_{meOH} \leq 0.92 $$

A plot of these two functions is shown in Figure 15, again with the experimental volume swell curve. Good agreement between experimental and theoretical values is observed in the appropriate regions of χ.

By using a mathematical weighting function it is possible to smoothly join the above two equations and express the theoretical curve as a single
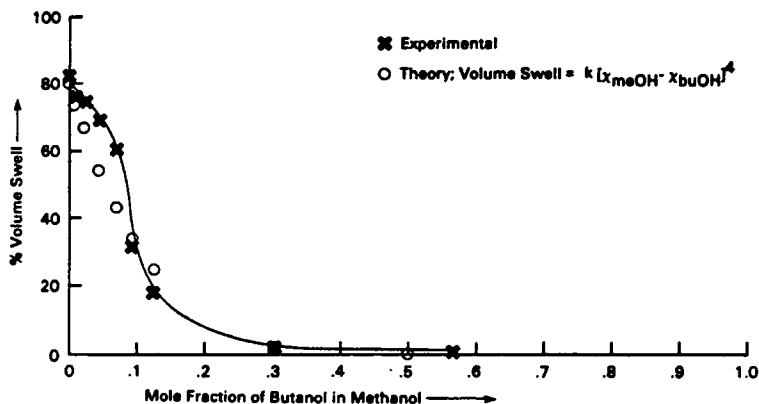
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Fig. 14. Volume change of fluorocarbon elastomer (x) and the function $k[\chi_{meOH} - \chi_{buOH}]^4$ versus mole fraction of butanol in methanol.

equation. Such a weighting function is $1 - e^{-10^4\,\chi_{buOH}^4}$ and the resulting single theoretical expression becomes:

$$\text{Volume swell} = 80[\,\chi_{meOH} - \chi_{buOH}\,(1 - e^{-10^4\,\chi_{buOH}^4})]^4$$

A small adjustment of k was required to give the best fit in the above equation. A plot of this function is shown in Figure 16 along with the experimental volume swell curve. Notice that the theoretical curve now has the correct shape at all χ values. The weighting function $1 - e^{-10^4\,\chi_{buOH}^4}$ is arbitrary and numerous other weighting functions could be found which produce the same result.

We do not believe the overall arguments used above are arbitrary; they correctly predict that the volume swell should go to zero at $\chi_{buOH} = 0.5$ which is what is observed experimentally. Also, no change in the normalization constant (the "80" numerical coefficient) is required as the equation
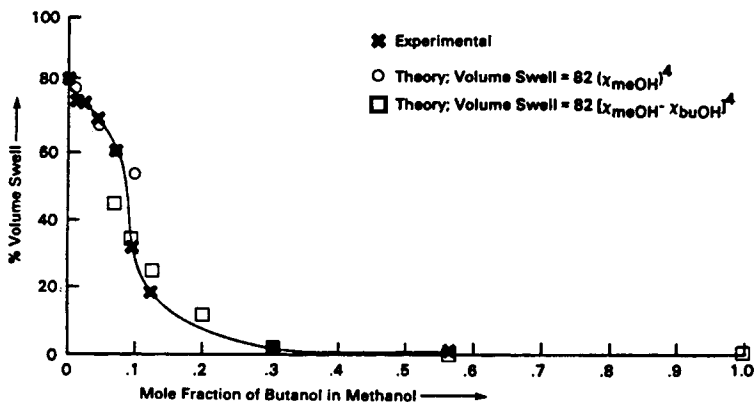

Fig. 15. Volume change of fluorocarbon elastomer (x) and the functions $82\chi_{meOH}^4$ and $82[\chi_{meOH} - \chi_{buOH}]^4$ versus mole fraction of butanol in methanol.
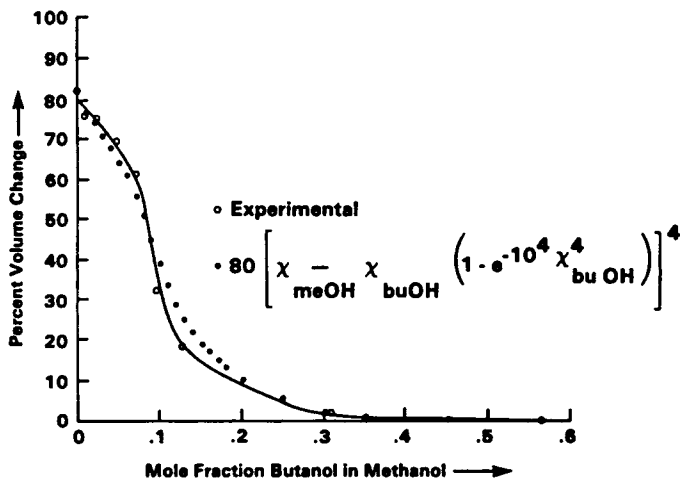
Fig. 16. Volume change of fluorocarbon elastomer and the function $80[\chi_{meOH} - \chi_{buOH}$ $(1-e^{-10^4} x^4 buOH)]^4$ versus mole fraction of butanol in methanol.

switches from one form to the other via the effect of the weighting function. The equation becomes undefined for $\chi_{meOH} = \chi_{buOH}$. Once methanol is sufficiently involved in the 1:1 adduct shown previously in this report the remaining cyclic methanol tetramer exchanges only with itself and with the adduct as a unit. The exchange with the adduct always produces a nonswelling species, and thus the volume swell falls off rapidly with increasing butanol content.

In summary, the butanol/methanol investigation shows that a tetramer containing one butanol and three methanol molecules is too bulky to swell the fluorocarbon elastomer. Empirically we found that the dependence of swell of the elastomer in methanol/butanol mixtures can be described by two terms: χ_{meOH}^4 at low concentrations of butanol and $(\chi_{meOH} - \chi_{buOH})^4$ at high concentrations of butanol. Theoretically the swell should be a function of χ^4 methanol for all concentrations. The observed deviation at high butanol concentration can be explained by the formation of a meOH/buOH adduct which exchanges with the meOH tetramer to always form a nonswelling species. NMR data gives evidence of such preferential processes for the two alcohols when both are present at a significant volume fraction.

Fluorocarbon Elastomers and Mixtures of Methanol with Water

The effects of methanol/water and ethanol/water mixtures on the degree of swell of the fluorocarbon elastomer are shown in Figure 17. The swell of the elastomer in ethanol/water mixtures is nearly zero at all concentration levels. However, the behavior of the fluorocarbon elastomer in methanol/water mixtures is quite different and surprising. As we have seen earlier a high degree of swell (89%) is observed for the elastomer when exposed to pure methanol. Addition of small amounts of water causes very fast reduction in the swell. Hence, the swell value of the fluorocarbon
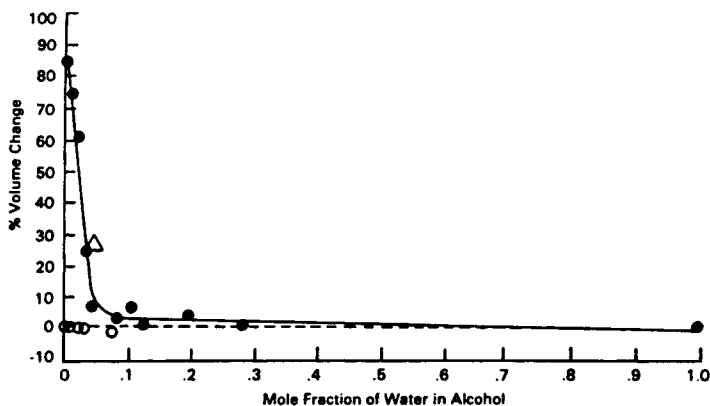
Fig. 17. Volume change of the fluorocarbon elastomer after exposure to water/alcohol mixtures versus volume fraction of water in the mixtures (●) methanol, (○) ethanol, (△) D_2O in methanol.

elastomer after exposure to methanol containing only 0.05 mole fraction of water is 9% (see Fig. 17). Further addition of water causes continued reduction of swell, but at a very slow rate. One of the swell measurement points shown in Figure 17 was obtained by adding 0.07 mole fraction of D_2O. The point falls on the curve for the water data.

NMR investigations of the effects of the addition of D_2O and H_2O to methanol were conducted. At very low D_2O additions ($\sim$0.2%) an H_2O band (*new*) appears in the spectrum. The D_2O used in these experiments was very pure ($\sim$99.99%) and the H_2O band observed cannot be due to the inadvertent addition of water. Hence the appearance of the H_2O bands implies that the following exchange has taken place:
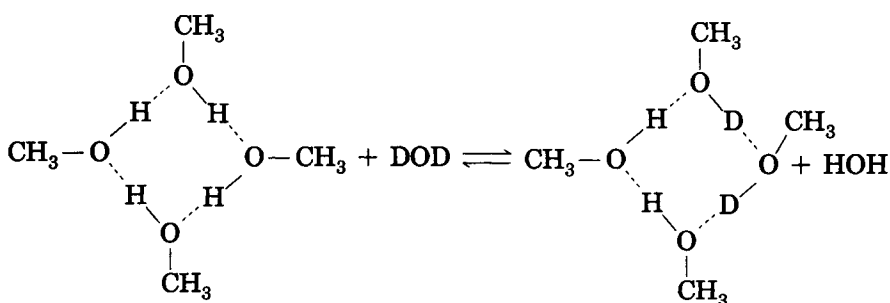
In other words, we add D_2O to the alcohol system and H_2O is produced by exchange.

Both H_2O and D_2O are very strongly hydrogen-bonding molecules. Hence, if present, they will form hydrogen bonds with methanol and alter the ring structure. A single water molecule apparently has the ability to complex with or render ineffective several methanol rings and cancel their ability

to swell the fluorocarbon elastomer. The resulting structures are of the following type:

$$
\begin{array}{l}
CH_3 \\
\end{array}
$$
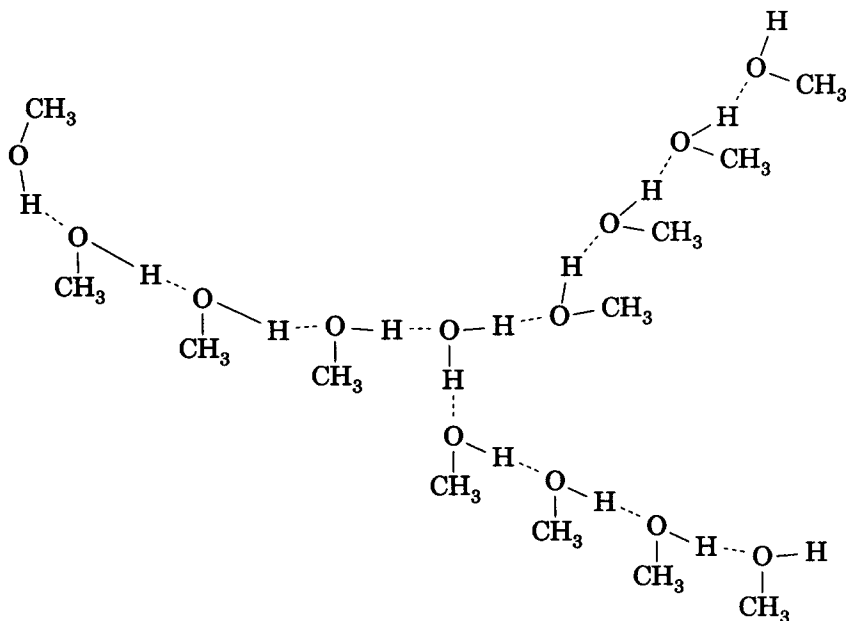
The formation of such a structure would explain the very rapid fall off in volume swell upon the addition of water. NMR cannot distinguish between this long-chain linear hydrogen-bonded structure and the cyclic tetramer, except that a new peak is observed for the linear structure which we attribute to the end groups.[26]

Effect of Temperature on the Degree of Swell of Fluorocarbon Elastomer in Pure Methanol

The volume swell of the fluorocarbon elastomer in methanol was measured at 10 different temperatures ranging between $-40°C$ and $+60°C$. As seen in Figure 18 and Table V, the swell at $-40°C$ ($233°K$) has a very high value of 172%. At higher temperatures the swell decreases systematically reaching a value of only 16% at $60°C$ ($333°K$) as seen in Table V. A plot of natural logarithms of swell values versus $1/T$ is shown in Figure 19. The change in natural logarithms of swell versus $1/T$ is linear in the temperature range of $-40°C (1/T = 4.29)$ to $30°C (1/T = 3.3)$. A sharp drop in ln (swell) is observed at temperatures above $30°C$. The slope of the line in Figure 19 at temperatures of -40 to $30°C$ is 840. Hence, the enthalpy of swelling in this range of temperature is -1.7 kcal/mole. Above $30°C$ the enthalpy of swelling calculated from the slope of the best line fit is -17.9 kcal/mole. Obviously, above $30°C$ a drastic change has occurred to alter the mechanism of swelling of the fluorocarbon in methanol.
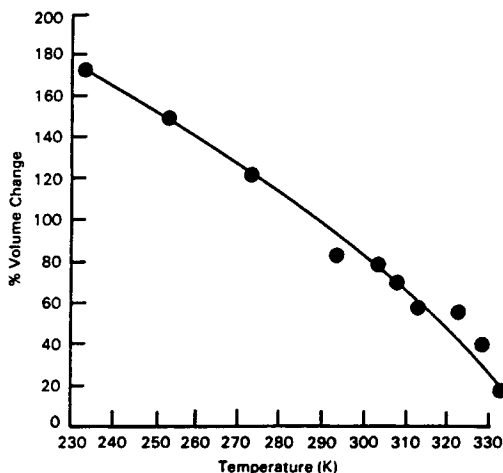
Fig. 18.   Volume change of fluorocarbon elastomer after exposure to methanol at various temperatures.

NMR data of the pure methanol, obtained between 10°C and 50°C, shows a temperature dependence similar to that observed for the swelling of the fluorocarbon elastomer in this solvent. For example, the relative OH exchange rate, which is known to increase with temperature, shows a break point (Fig. 20) roughly coinciding with the break point observed for the volume swell versus temperature curve (Fig. 19). Also, the·chemical shift of the OH group is known to decrease in a linear manner with temperature.

It is generally accepted in NMR spectrosiopy[27] that chemical shift effects caused by dilution and by temperature changes are completely analogous insofar as the change in chemical shift is the result of changes in hydrogen bonding. For example, the methanol cyclic tetramer is known to break up into monomeric species at very high dilution in CCl_4 solvent. High temperatures have the same effect (i.e., the methanol exists as monomeric species). Thus, the similar effect of dilution and temperature in changing the methanol hydroxyl chemical shift should be observed as a similar equiv-

TABLE V
Volume Change of Fluorocarbon Elastomer after Exposure to Methanol
at Various Temperatures

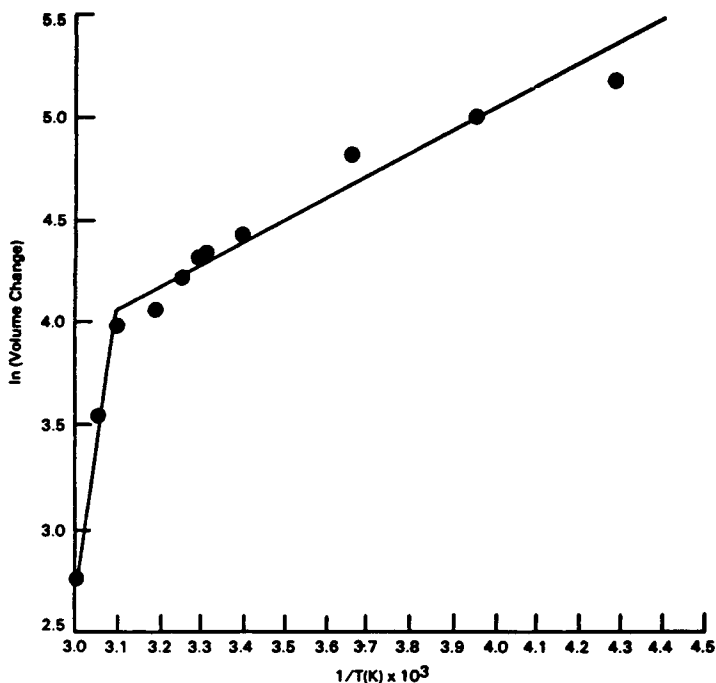| Temperature °C	% Volume change
−40	172
−20	149
0	121
21	84
30	76
35	68
40	58
50	54
55	39
60	16

Fig. 19. ℓn (volume change) of fluorocarbon elastomer in pure methanol versus $1/T \cdot T$ is the temperature (K) at which swell experiments were conducted.

alency when the volume swell is measured as a function of methanol dilution or as a function of temperature in pure methanol.

Support for this hypothesis is found in the qualitative comparison of Figures 2 and 18. They show that the swell of the fluorocarbon elastomer in methanol/indolene mixtures has a slow rate of decrease at high methanol concentrations and an accelerating rate at low methanol concentrations. Similarly, a slow rate of swell decrease is observed at low temperature with an accelerating rate at higher temperatures. In other words, the curves are qualitatively similar.
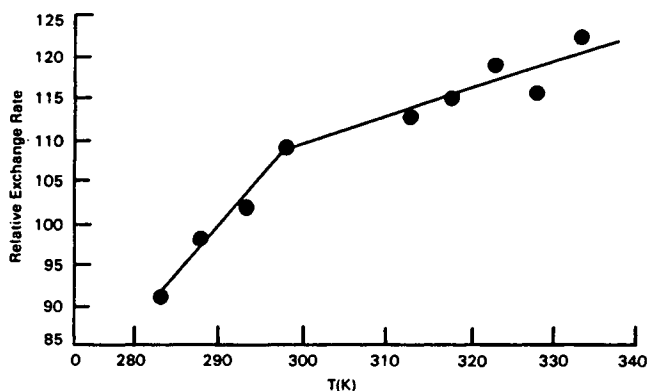

Fig. 20. Relative exchange rate of methanol hydroxyl proton versus temperature.

CONCLUSIONS

1. Methanol in pure form exists as a hydrogen-bonded tetramer with a solubility parameter close to that of the fluorocarbon elastomer. Hence high swell of the elastomer is observed in pure methanol.

2. Addition of small amounts of water leads to clustering of methanol and the breakdown of the tetramer cyclic structure, and hence a sharp decrease in swell.

3. Increasing the temperature or diluting the methanol with nonpolar solvents leads to a gradual weakening of the hydrogen-bonded structure and a gradual decrease in the swell.

4. Ethanol in methanol leads to the formation of mixed tetramer species. Only an all methanol tetramer and a tetramer containing *one ethanol* are effective in swelling the elastomer.

5. A tetramer containing one butanol and three methanol molecules is too bulky to swell the fluorocarbon elastomer.

6. The molecular structure of methanol determined from the NMR data provides an explanation for the swell of the fluorocarbon elastomer in methanol and its mixtures.

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